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Interactive comment on "Barium stable isotopes as a fingerprint of biological cycling in the Amazon River Basin" *by* Quentin Charbonnier et al.

Anonymous Referee #1

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Manuscript summary: In the manuscript entitled "Barium stable isotopes as a fingerprint of biological cycling in the Amazon River Basin" Quentin Charbonnier and co-authors measured barium stable isotopes on dissolved loads and suspended sediments of the Amazon River and its tributaries. They found that the dissolved load is isotopically different to parent silicate rock and attribute this difference to both the formation of secondary weathering products and Ba uptake by biota. Applying an isotope mass balance model, they find that Ba is strongly cycled through biota. Moreover, including rates of denudation the authors find a deficit in the Ba export, which they interpret to be of organic matter that is either exported in particulate form or accumulates in the study area. Finally, by correcting the river derived silicate weathering flux from the biological imprint they conclude that the CO2 consumption by chemical weathering

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is by about 20% underestimated.

Main Comments: This manuscript is well-organised and well-written. Given the presentation of in total 35 equations the authors have done a great job in writing, which allows the reader to easily follow the story. However, even though the English in general is fine the manuscript would benefit from proofreading by native speakers. Below in the line by line comments I waive from commenting on language issues. The presentation of the data and data quality is very good. The story is mostly scientifically sound. I have only three major concerns namely i) time scale issues and Ba uptake fluxes by biota ii) section 4.4, and iii) section 4.7.

Regarding i) even though I like the geochemical mass balance approach of how to estimate absolute fluxes in this manuscript I am missing a discussion on time scale issues to allow the reader to judge the applicability of the findings. This is because total denudation rates from cosmogenic nuclides integrating over 10ˆ3 to 10ˆ5 years and sediment gauging data integrating over some tens of years are used in the metrics of this manuscript. What is more, the authors estimate the Ba uptake flux of plants independent from direct measures by their mass balance approach. Principally, this is fine to me. But, given that GPP data is available I also would like to see a comparison of how their FˆBa_bio compares to a GPP-based Ba uptake flux by plants (e.g. using Ba concentrations in plants and GPP data).

Regarding ii) I am surprised about the trends shown for GPP vs. W/D and TER vs. W/D. Keeping in mind that my understand is that GPP is a proxy for total biomass production plus respiration (actually I think NPP would be a more appropriate metric for the purpose of this manuscript), TER is a proxy for nutrient recycling and W/D is a proxy for the weathering intensity I am surprised that both recycling and total biomass production increase with increasing weathering intensity. To my understanding increasing recycling requires energy and hence goes on the costs of biomass production unless there is a counterbalancing effect. This counterbalancing effect could be due to a gradient in MAP and/or MAT because biomass production primarily depends on energy,

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temperature, and water & nutrient availability. Thus, I recommend providing MAP and MAT in the study area section. On the other hand I am wondering that recycling increases with increasing W/D. Increasing W/D can either be understood as decrease in nutrient supply (because soils are heavily depleted, high W, leading to the need of recycling) or increase in nutrient supply (because soils are replenished by less weathered minerals, high E, no need for recycling). But recycling must not only be a nutrition strategy to cope with low nutrient supply through weathering or atmospheric deposition as recycling is also considered as the major nutrition mechanism (e.g. fast turnover of organic matter minimizes nutrient loss from the system). Importantly, there seems also to be a misunderstanding on the organic and geogenic pathway presented in Uhlig and von Blanckenburg 2019. This is, because both pathways operate simultaneously but in terms of fluxes (and on the short timescale) the organic pathway is way more important than the geogenic pathway which becomes essential on the centennial to millennial timescale. Given these complexities in ecosystem nutrition the authors are not putting their findings well in context of ecosystem nutrition. Thus, the authors somehow overinterpret their findings in section 4.4 because of the generalization made and because the field of ecosystem nutrition is widely ignored (e.g. lacking in the introduction). For this reason, I either recommend down tuning of the conclusion or discussing their relationships in the context of ecosystem nutrition (the latter would likely bias the focus of the manuscript). Moreover, that Ba is so strongly cycled through biota is surprising as to my knowledge Ba is neither essential to plants nor considered as a micronutrient or even as a plant beneficial element, following definitions by Marschner (2011) . Thus, the strong cycling of Ba through plants in the giant ecosystem of the Amazon may warrant more attention in the manuscript.

Regarding iii) I basically did not understand why the silicate weathering flux should be corrected for the imprint of the biosphere. This is because mineral nutrients, which were cycled through biota are mainly (apart from atmospheric inputs) of geogenic origin, hence released by chemical weathering then cycled through the biosphere and ultimately appear with some delay in the river. I may misunderstood section 4.7, thus

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please revise this section for more clarity.

In consideration of these main comments I suggest major revisions.

Text: Line by line detailed comments:

L.4 delete “measured” as it is clear that the data was measured

L.14 please specify through what Ba is cycling exactly (e.g. biota, secondary minerals)

L.16 see comment L.14

L.21 To my understanding “minor nutrient” is not a well-defined term for nutrients. Nutrients are either called “essential” elements for plant growth or grouped into the categories “macronutrient”, “micronutrient” and “plant beneficial element”. Following Marschner (2011) Ba belongs to none of these groups.

L.24 for completeness it would be nice to also tell the reader the “yet reported value”

L.32 “making up our water quality” is out of place as the manuscript is not about water quality

L.48 The reference Napieralski et al. 2019 maybe useful here, but I do not think it is the most appropriate one for the general information made here.

L.59 The role Ba plays in plants should be briefly introduced. I also do not think that the Viers et al. 2005 reference is the most appropriate one.

L.88 should read “drainage area”

L.90 Mean annual temperature (MAT) and mean annual precipitation (MAP) should be provided as they may be important for section 4.4

L.96 Providing data on erosion rates (e.g. ranges) would help the reader to assess how high or low the rates really are.

L.105 see comment L.96

L.117 Please remove “are from . . . repository” as it is not important to tell where samples are stored

L.122 It reads that cation concentrations were measured by ion chromatography. Please revise if incorrect.

L.140 Please provide the typical sample weight used for digestion.

L.145 Which matrix elements were eluted with 2.5 M HCl and how many mL of 2.5 M HCl and 6M HCl were used?

L.146 What is meant by “carried out sequentially twice”? Needs rewording

L.152 “(up to 300 ng)” can be removed as this information is included in the range 250-300 ng L.153 “coupled to” should be replace by “using”

L.154 I am wondering why so many cups were used. Please explain why each of the measured isotopes were needed for data evaluation. The ones which are measured but not used for data evaluation must not be mentioned.

L.163 I am wondering why the delta 138Ba was calculated from delta 137Ba and not from the measured isotope ratios 138Ba/134Ba (as is done for delta 137Ba by using measured 137Ba/134Ba).

L.175 To allow the reader to evaluate how the data on reference materials measured in this study compare to literature values please also provide the previously published delta values.

L.253 To conclude that Ba behaves like a nutrient solely from the correlation of K/Na and Ba/Na is not very reasonable. Provided that stream water integrates over all critical zone processes this correlation could have several reasons. Importantly, K is much more soluble when rainwater passes through the canopy (throughfall) than other mineral nutrients. Thus, I am wondering whether Ba is also as mobile as K from the canopy (apparently not as the authors find that Ba is exported in particulate organic form or

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accumulates in the Amazon biomass).

L.272 I am wondering whether the term “model” is appropriate here as later in the manuscript (e.g. L.342) the authors call it “mass balance approach” which I think is the more appropriate term. L.330-335 Given that D is E+W this section would benefit from saying when E (or W) is high or low.

L.340 Please split the sentence into two sentences. The first should be on Ba, the second on Li. Also please say that Li has to date not been shown to fractionate during plant uptake.

L.343 I do not really see “correlations” in figure 5. Thus, either revise the wording or show a figure that illustrates correlations.

L.346 Another explanation could be that Ba is in principle less soluble than other elements (as stated earlier in the manuscript).

L.348 To me fˆBa_bio is not “fairly constant”. It simply does not show a trend but the fˆBa_bio data is too different to say that they are constant.

L.349 see comment L.343

L.351 Please use another word for “automatic”. I do not understand what the authors want to say.

L.355 typo, should read “eq. (10)”

L.357 Please remove “that we convert in . . .” as this conversion is trivial.

L.384 “rock supply rate” means “regolith production”? Please clarify.

L.399 Beginning from here I got confused and I think one of the reasons is that the authors should be more precise when presenting low or high W/D ratios. This means the reader needs to know that high or low W/D ratios are due to high or low W or E (D= W+E). This differentiation is quite important in order to understand why both

GPP and TER have a positive relation to W/D. As explained in the main comments it is somehow surprising that GPP (nutrient uptake) and TER (nutrient recycling) increase with increasing W/D.

L.410 To my understand TER does not say anything about the size of biota, if any, GPP would do so. Please revise.

L.413 As briefly explained in the main comments there seems to be a misunderstanding on the organic and geogenic pathway presented in Uhlig and von Blanckenburg 2019.

L.422 “made available through denudation” Please specify whether E or W in denudation is meant here, as both can have different effects on plant nutrition.

L.424 Please specify which elements are close to Ba in terms of their nutritional role.

L.426ff I doubt that larger pools of bio-available Ba “enhance” Ba uptake. First, the bio-available pool must be continuously replaced over time and second given that Ba is not a nutrient with high bio-available Ba pools more Ba might be taken up but uptake not enhanced. Hence, please revise the wording. I am also wondering why Ba should first be incorporated and then taken up from secondary weathering products. My understanding is that is less energetic to plants to take up dissolved nutrients. As Ba, which was incorporated into secondary products was already dissolved, I would assume plants should have utilised Ba before its incorporation into secondary products.

L.433 Please check whether water residence time in the critical zone is longer at steeper slopes. To me the opposite makes sense.

L.473 Please specify what is meant by an “intensive” metric.

L.478 To assess whether there is really a difference between wˆBa_fluxes and (Ba/Th)n uncertainties would be helpful which are missing in figure 8a. Also, provided that wˆBa_fluxes relies on Q and D (equation C6) integrating over much different timescales I am wondering whether the differences in figure 8a could also be explained by time scale issues.

L.534 fˆBa_miss is a relative flux and should be named as such to not confuse the reader as the reader is anyhow busy in differentiating when absolute and when relative fluxes are presented.

L.536 should read “with the relative amount” as fˆBa_bio is a relative flux.

L.543 Please let the reader know the time scale.

L.552ff I am surprised about the groundwater discussion as to my understanding rivers, particularly at baseflow, are mainly fed by groundwater. Or do the authors mean an over regional groundwater aquifer contributing to streamflow?

L.585 Either the C in the left-hand term (FˆC_miss) should be removed or *[C]_org added to the right-hand term in equation 15. Otherwise the equation is wrong.

L.586 see comment in L.585

L.591 please add “particulate” to “organic carbon”

L.609ff The section heading reads that it is valid for all mineral nutrients. Please add “Ba” in order to avoid a generalization which may not hold for other mineral nutrients. Figure 11 could be called 11a and 11b which would allow the authors to cross reference each scenario mentioned in section 4.6 directly to the scenarios shown in figure 11. Please see again major comments (ii) for revision.

L.615 “new” Ba is a formulation from Cleveland et al. (2013) (new P), thus please cite.

L.628 Please see major comments (iii). Moreover, I do not see a clear trend in figure 12, thus high or low R_sil+bio/sil should be treated with caution.

L.636 “the uptake flux of this element” is misleading because [X]_bio represents a concentration in equation 17.

L.702 better use “assess” instead of “appraise”

L.707 “atm” in “(Ba/Cl)_atm” should be replaced by “seawater” as according to the text

it represents the seawater ratio?

Figure 1 Axis caption “latitude, longitude” is missing. Also, the left-hand part of the altitude scale can actually be removed as information on the altitude is more relevant for the sample locations.

Figure 2 Please add the per mil sign next to delta 138Ba

Figure 6 I am wondering why “bio” and “sec” show trends for absolute fluxes when plotted against D or W/D in Figure 6 but not for relative fluxes in Figure 5. Provided that in this manuscript so many equations, ratios and ratio over ratios are presented please explain this difference. Regarding style, please frame the legend. Instead of using “+” in this and the other figures please write “increasing” or “decreasing” as the plus is confusing. Also, please remove the arrow and “Biological uptake of rock-derived nutrients” as Fˆ Ba_bio only shows Ba and no other elements and as this information does not provide additional information that the axis label and legend itself.

Figure 7 In order to better assess whether the trends in this figure are real I would like to see uncertainties. The arrows and text next to the y-axis of panel a and b can be removed as they do not provide additional information. In panel d, I believe there is a misunderstanding regarding the “organic” and “geogenic” nutrient pathway as in eroding systems both are present. The main pathway is the organic one (most important on time scale of up to a few years only) and the geogenic one is minor in terms of fluxes but most important on the centennial to millennial timescale. Thus, it makes no sense to put Fˆ Ba_bio in dependence of both pathways in this figure.

Figure 8 In the figure caption it says “Uncertainties on wˆ Ba_fluxes” but in panel 8a no uncertainties are shown. Is this correct or are the uncertainties smaller than symbol size. This needs clarification. Regarding uncertainties I also noticed that the error bars are differently long towards positive and negative directions. Please check.

Figure 9 The arrows next to the x-axis and y-axis do not provide additional information

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and should be removed. Latest with this figure I would like to see a comparison of the Fˆ Ba_bio with a more direct estimate of the Ba uptake flux, e.g. based on GPP and Ba concentrations in plants.

Figure 11 Please name both panels (e.g. “a” and “b”), which allows the authors to cross reference the figure more detailed in the main text (section 4.6). Also in the figure caption tell the meaning of the arrow sizes.

References mentioned in this review

Cleveland, C. C., B. Z. Houlton, W. K. Smith, A. R. Marklein, S. C. Reed, W. Parton, S. J. Del Grosso, and S. W. Running. 2013. “Patterns of New versus Recycled Primary Production in the Terrestrial Biosphere.” Proceedings of the National Academy of Sciences 110(31):12733–37. Marschner, P. 2011. Marschner’s Mineral Nutrition of Higher Plants.

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