We thank Reviewer #1 for his/her thorough report on our manuscript. His/her main concerns revolve around three aspects of the manuscript, namely i) potential time scale effects that could explain some of our observations, ii) the relevance of the weathering regime metrics we use in driving ecosystem dynamics and rock-derived nutrient cycling, and iii) our contention that biological uptake of rock-derived nutrient might induce a bias when catchment-scale weathering rates are estimated from river chemistry data. To address the concerns raised by reviewer 1, we plan to significantly rewrite some parts of the manuscript (in particular sections 4.4 and 4.7) during revision, and below we provide clues about how we want to proceed to do so.

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.

We are glad that the reviewer values our approach and appreciates the overall structure and writing of the manuscript. This version was already proof-read before submission by a native (US) English speaker, but before submission of the revised version we will ask again for proof-reading to another native speaker.

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 10^3 to 10^5 years and sediment gauging data integrating over some tens of years are used in the metrics of this manuscript.

The time scale issue is indeed a recurring problem in geochemical mass balance approaches. We actually see two questions embedded in this particular remark:

(1) The timescale over which erosion is "measured" differs between sediment gauging and cosmogenic nuclides. However, as explained in our manuscript, only a handful of Andean rivers display a significant (by more than a factor of 2) difference in erosion measured by the two methods, most likely due to a recent ($< 10^2$-10^3 yrs old) increase in erosion (Wittmann et al., 2011). However, we believe that this potential effect is taken into account in our analysis as when w^{Ba}_{fluxes} (the calculation of which relies on the knowledge of erosion rate) is plotted (figs. 8 and 9) both sediment gauging- and cosmogenic nuclide-derived values are shown. Taking one or the other does not affect our conclusions.

(2) Beyond their effect on erosion rates, time scale might affect other variables we use too, and thus explain some of the differences we observe between parameters. Indeed, the values of all parameters of the river mass budget equations (eqs. 11 and 12, and eqs. C1 to C6) are likely to depend on the timescale over which they are estimated. And in a way, part of our discussion in explaining the differences between the various river mass budget parameters is indeed about time scale effects. For example, when we propose that the export of particulate organic debris could account - at least partially - for the observed disequilibrium in the Ba river mass budget, we assume that such a component of the river flux would be missed because they could be preferentially exported during relatively rare events such as floods. This is typically a time scale issue. Same for the scenario we propose where this particulate organic carbon is currently accumulating in the soils of the basins

rather than being exported by rivers - would sampling of rivers last over much longer time scales, it would be very plausible that this organic carbon is exported by erosion and/or dissolution (because it cannot accumulate indefinitely), and the difference would disappear. Of course, there is a daunting number of time scale effects that could shift the values of individual variables of our approach, and result in the observed differences. Some of them have already been explored in previous studies (see *e.g.* Stallard et al., 1995; Gaillardet el al., 1995, 1997; Lemarchand et al. 2006; Bouchez et al., 2013). We do not see how we could cover all these possibilities in our manuscript. However, first during revision where relevant we will emphasize how our current interpretations relate to time scale issues. Second, we think the fact that the river mass budget of Li across the Amazon Basin rivers is equilibrated (see section 4.5 and fig. S5) suggests that these time scales issues are minor for the "inorganic" part of the rock-derived nutrient cycle (Dellinger et al., 2015). During revision, we will also emphasize how we think that Li isotopes indicate that some of the potential time scale issues do not affect our analysis.

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).

First, we would like to emphasize that within our mass balance framework, only the *net* formation of an isotopically-fractionated phase (*i.e.* its formation rate minus its destruction rate) is important for the isotope budget (lines 288 to 296 of our manuscript and Bouchez et al., 2013). In this scope, we believe that NEE = GPP - TER (ecosystem respiration) is a more sensible metric of net formation of organic matter to which we should compare our isotope-derived F^{Ba}_{bio} parameters.
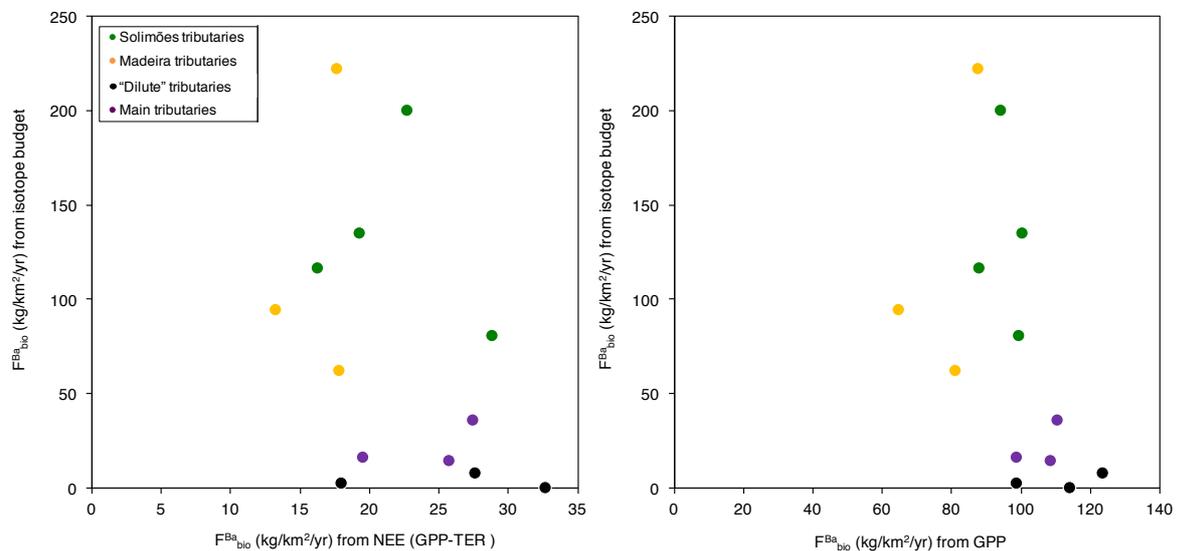

Nevertheless, we acknowledge that the suggestion of the reviewer is a good one for the sake of the discussion. As shown in the attached figure, the uptake of Ba calculated from the isotope budget (eq. 8) is much larger than that based on GPP and NEE, for the Andean tributaries. By contrast, in the main and "dilute" tributaries, where the isotope-derived Ba uptake is lower the GPP-based Ba uptake is much larger. However, at this point we need to emphasize the poor constraints available on the Ba content of organic matter, which most likely entails significant uncertainty in this approach (let alone the uncertainty on NEE, which is calculated from a difference between two large fluxes, GPP and TER, each of those also being affected by significant uncertainty). An alternative to assess the broad reliability of our

analysis is to actually estimate the average Ba content of the organic matter formed ("net", *i.e.* remaining from GPP after plant and soil respiration as quantified by TER), through the combination of F^{Ba}_{bio} and NEE following: F^{Ba}_{bio} / (NEE x 1/[C]$_{org}$) = [Ba]$_{org}$.

By doing so, we find that a Ba content around 5 to 10 ppm is necessary in exported / accumulated organic matter for the Andean belt rivers – which remains an acceptable result regarding the Ba content of plants we can extract from our own compilation (18 ± 28 ppm; S.D). However, the calculated Ba content in exported organic matter drops between 1 to 0.1 ppm for the main and "dilute" tributaries, *i.e.* in the lowland areas of the Amazon. This is an interesting piece of result, as such lower predicted organic matter Ba content may come from a preferential release of Ba from litter during intense recycling. This idea is in agreement with the much higher f^{Ba}_{diss} (*e.g.* > 1 for the Rio Negro River) and stronger export of Ba by rivers than theoretically predicted for "dilute" rivers (see "Dilute tributaries" in fig. 8a). This is actually an interesting finding, and our suggestion for the revision is to include a short text (2-3 sentences) to explain this at the beginning of section 4.4, without adding the figures given above with the direct comparison between the isotope-derived F^{Ba}_{bio} and the GPP- or NEE-counterparts.

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.

First, and as explained in our manuscript, most of the ecological parameters used here are actually calculated based on GPP (Tramontana et al., 2016; Jung et al., 2017). As a result, TER and NPP strongly correlate with GPP (see figure below). Also, we specifically used in the manuscript GPP as a proxy for the size of the biomass, while TER is used as a proxy for remineralization. For these reasons, we plant on keeping the use of GPP and TER in that way.
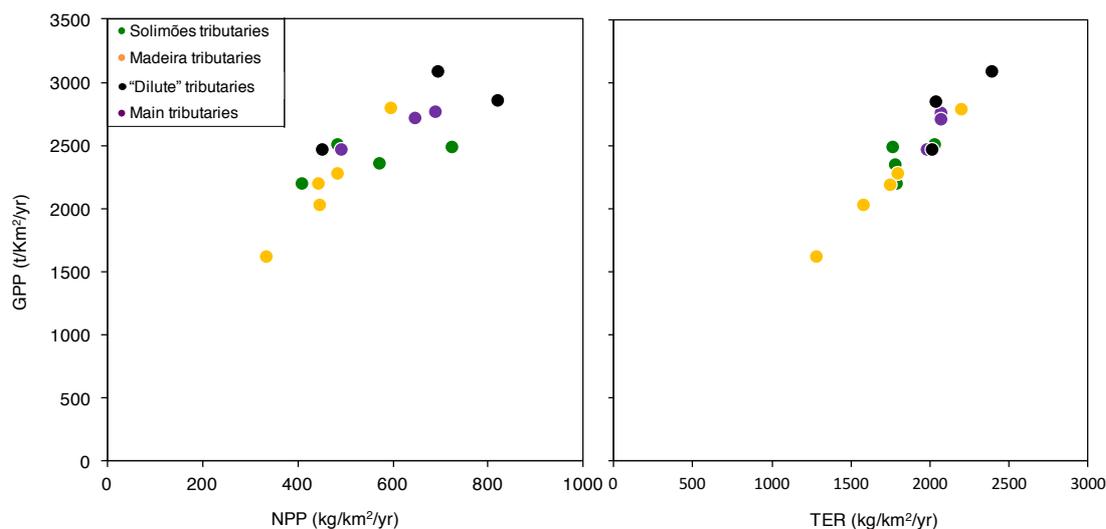
Second, regarding the "surprising" relation between W/D on the one hand and GPP and TER on the other hand, we gather that clarification is needed. In the Amazon Basin, W and D are positively related. Nonetheless, D increases (from the plain to the Andes) much quicker than W. Therefore, the W vs. D relation is that of a diminishing return, resulting in a negative relationship between W/D and D (see figure: this is because at high D a "kinetic limitation" is imposed on mineral dissolution - hence W - due to the short residence time of solids in the critical zone; see for example Ferrier and Kirchner 2008; Gabet and Mudd 2009; Dixon et al., 2012). Therefore, the positive relations between W/D and GPP or TER should not come as a surprise as the largest ecosystems of tropical forests in the Amazon Basin are found in the plains – where W/D is high.
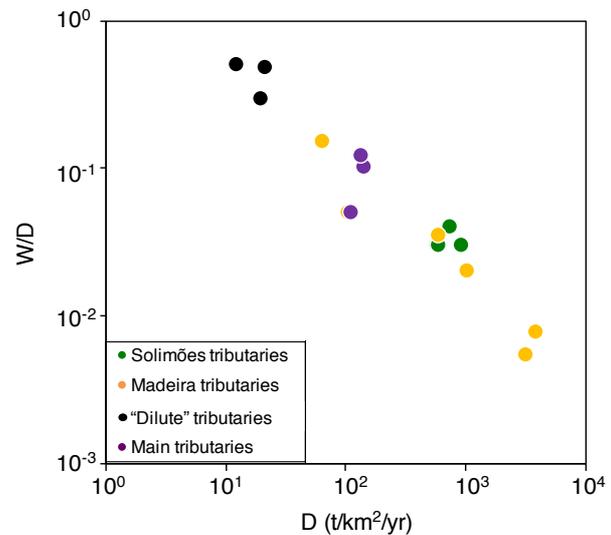
To my understanding increasing recycling requires energy and hence goes on the costs of biomass production unless there is a counterbalancing effect. This counterbalancing effect could be due to a gradient in MAP and/or MAT because biomass production primarily depends on energy, temperature, and water & nutrient availability. Thus, I recommend providing MAP and MAT in the study area section.

We fully agree with the review that MAP and MAT are important parameters for ecosystem nutrition that were pretty much not discussed in the first version of our manuscript. Therefore, we will include a discussion of the role of these parameters in the appropriate section and add the MAP and MAT of each basin in the table. We will also add panels to an existing figure to showcase the potential role of MAP and MAT, such as in the attached figure, where we note that F^{Ba}_{miss} displays a negative relation with both MAP and MAT. Hence, indeed lower MAP and MAT (in other words, a lesser source of energy required for
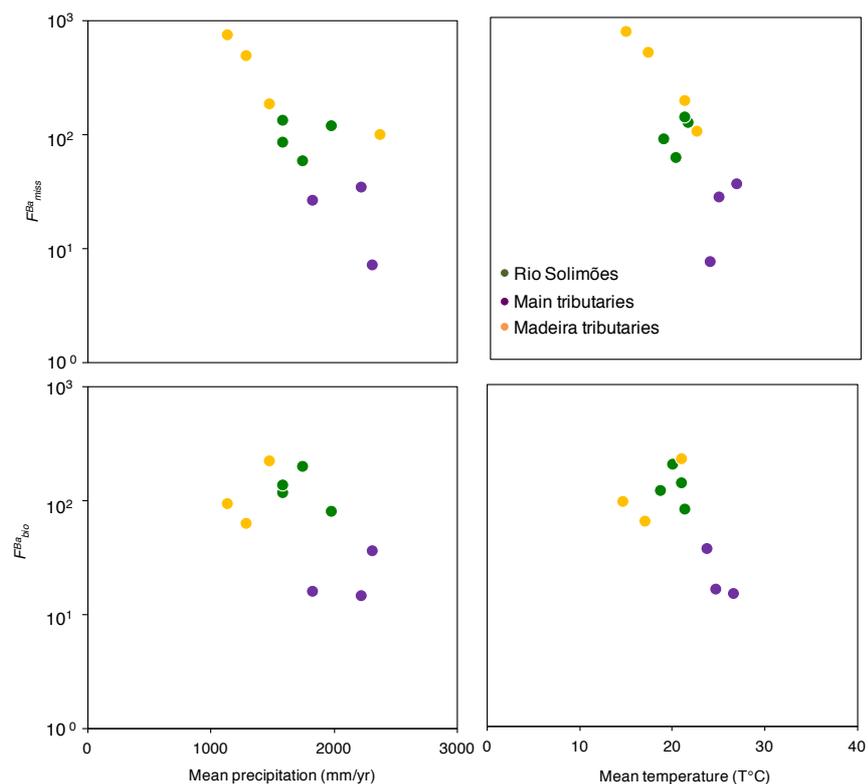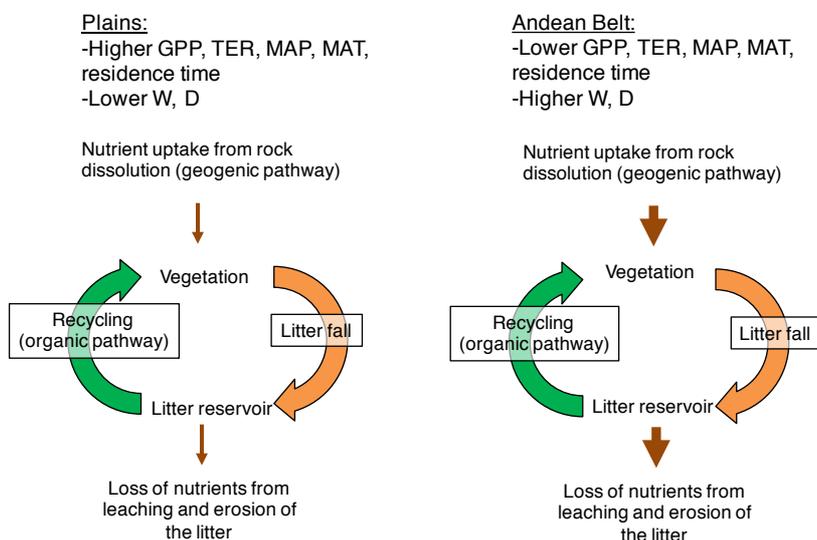
efficient organic matter remineralization) are associated with a larger missing flux of Ba. Therefore, water and temperature probably modulate the role of weathering regime on nutrient cycling, something that was not apparent in the previous version of the manuscript. We will significantly amend the text of section 4.4 to reflect this fact.

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).

Our answer to this comment echoes the answer given above about the relation between D and W/D, and we think that part of the misunderstanding might lies in a confusion between weathering intensity (W/D) and flux (W). High-W/D settings (typically featuring deep, heavily depleted soils such as those found in the Amazon lowlands) are characterized by low W (and low D, so low E too). So the reviewer is right saying that increasing W/D corresponds to a decrease in nutrient supply from weathering indeed (but this corresponds to low W, actually), but increase in nutrient supply (from weathering, not from recycling of organic matter) is necessarily associated to low W/D.

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.

We recognize that in the first version of our manuscript there was a bit of a "leap in interpretation" regarding the concept of "geogenic" *vs.* "organic" pathways of Uhlig and von Blanckenburg (2019) that was not doing justice to the original ideas developed by these authors. Uhlig and von Blanckenburg (2019) consider that the "slow" geogenic pathway (nutrient supply by weathering) could result in the compensation for the small, but continuous "leak" of organic matter (and associated nutrients).

Plains:
-Higher GPP, TER, MAP, MAT, residence time
-Lower W, D

Nutrient uptake from rock dissolution (geogenic pathway)

Vegetation

Recycling (organic pathway)

Litter fall

Litter reservoir

Loss of nutrients from leaching and erosion of the litter

Andean Belt:
-Lower GPP, TER, MAP, MAT, residence time
-Higher W, D

Nutrient uptake from rock dissolution (geogenic pathway)

Vegetation

Recycling (organic pathway)

Litter fall

Litter reservoir

Loss of nutrients from leaching and erosion of the litter

In this context, what we think our data and analysis show is that the size of this geogenic pathway (compared to the organic pathway) shifts with the weathering regime as indexed by W/D – and, as pointed out by the reviewer in a previous comment, with MAP and MAT too. As explained in the attached figure, we interpret our data as reflecting a more "subdued" geogenic pathway

in the Amazon plains (corresponding to regions drained by the "dilute" and "main" tributaries in our manuscript), because of low erosion rates (and associated slow litter loss), or high MAP and MAT allowing for efficient nutrient recycling from litter. By contrast, in the Andean belt, high erosion rates and lower MAP and MAT decrease the efficiency of recycling and thus increase the loss of nutrients, thus require a higher uptake from rock dissolution (see figure). To solve the concern raised by the review, the discussion in section 4.4 will be changed to remove any apparent opposition between the "geogenic" and "organic" nutrient pathways.

In addition, we also acknowledge the lack of contextualization with references to previous studies in ecosystem nutrition in the first version of our manuscript. To solve this problem, we will improve our discussion and in particular add relevant references in the discussion in section 4.4 on the ecosystem nutrition (*eg.* Chadwick et al., 1999; Elser et al., 2007; Selva et al., 2007; Cleveland et al.,2011; 2013; Augusto et al., 2017).

Thus, the authors somehow over interpret 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).

We agree with the reviewer, and will consequently tune down our conclusions in this part of the manuscript and will amend the text to clearly show that these interpretations should be seen as hypotheses that should be further tested in future studies.

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.

Again, we agree with the reviewer that this aspect was not well discussed in the first version of our manuscript. According to the definitions of Marschner (2011) we will remove the term "micro nutrient" for Ba from the manuscript. Although the biological role(s) of Ba are still far from being elucidated – apart from the apparent toxicity of high Ba amounts for plants (*e.g.* Lamb et al., 2013, and reference therein) – previous studies have shown that its chemical similarity with other rock-derived nutrients enables its uptake by plants. Indeed, Bullen and Bailey (2005) have demonstrated the significant biological uptake of Ba and attributed it to its similar ionic radius compared to other alkali-earth elements (Ca, Sr), as well as likely K. A more recent study has shown that Ba uptake scales with that of Ca even if the exact role of Ba in plants has not been identified (Myrvang et al., 2016). Finally, significant uptake and recycling of Ba by the vegetation have been shown to exist by Bullen and Chadwick (2016) using the Ba isotope composition. Therefore, despite the poor constraints on the specific role of Ba in plants, existing knowledge argues in favor of a "nutrient-like behavior" for Ba. This is the term we plan to use in the revised version of the manuscript, and we will slightly extend the justifications in the introduction as to why Ba can be, to some extent, used as a tracer of other rock-derived nutrients. However, we also acknowledge that the behavior of Ba during uptake and recycling by plants is likely to differ to some extent from that of major rock-derived nutrients such as Ca, Mg, K or P (these different major nutrients already differing in their behavior during cycling by ecosystems). To reflect the potential decoupling between the cycling of Ba and that of other rock-derived nutrients, we will clearly state in the introduction that using Ba as a tracer of other rock-derived nutrients should be understood as a "working hypothesis" of the manuscript. We will also tune down, where relevant in the discussion, the

generalization we make from the quantification of the Ba cycle only, to the other major rock-derived nutrients.

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 please revise this section for more clarity.

Estimates of catchment-scale CO_2 consumption by silicate weathering from river dissolved chemistry rely on the assumption that each milli-equivalent of the major cations released by silicate weathering (Na^+, Mg^+, Ca^{2+}, K^+) has found its way to the river, and more particularly to the sampling point. Our study shows that after the release from silicate rocks, some rock-derived nutrients can be taken up by the biota to a significant extent and "go missing" in the rivers. In other words, each milli-equivalent of Mg^+, Ca^{2+}, or K^+ that ends up in the biota or dead organic matter on land, and *remains* there (and thus does not "appear with some delay in the river", as suggested by the reviewer) is absent when the "accounts are made" using river data. Importantly, this effect is important only if the nutrients remain in the (living or dead) organic reservoir, meaning that they are not returned to the river through litter remineralization. As discussed in our manuscript, for nutrients to remain in the organic reservoir, two possibilities exist: (1) if particulate organic matter is eroded fast enough such that remineralization is incomplete, (2) a transient accumulation of nutrients in the organic matter reservoir on land is certainly possible over some time scale (see our reply to the first reviewer comment above), that is difficult to determine. In any case, our discussion in section 4.7 suggests that the common assumption that river solute fluxes constitute a reliable proxy for catchment-scale weathering rates is basically wrong. As a result, the fact that elements in rivers are missing allows us to try to quantify and correct for this lost. The reviewer comment indicates that this was not clearly explained, and we thus will clarify section 4.7 during revision.

Text: Line by line detailed comments:

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

We will delete "measured" in the sentence.

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

The sentence will be reworded and we will point out that Ba is cycled through biota.

 L.16 see comment L.14

We will add "biological" in this sentence: "... allow us to discuss the role of erosion rates on the biological cycling of rock-derived nutrients".

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.

According to Marchner (2011), we will delete the "nutrient" term for Ba. Instead, we will switch to qualify Ba as having a "nutrient-like behavior", as explained above.

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

We will add the estimated value of CO_2 consumption through silicate weathering from Gaillardet et al. (1997).

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

We will delete this part of the sentence.

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

We will change this reference.

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.

As explained above, we will change the term "minor nutrient" to "showing a nutrient-like behavior", in order to avoid confusion. We will also add references demonstrating the uptake of Ba by the vegetation.

L.88 should read "drainage area"

We will add "area".

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

We will add information about the MAT and MAP of each basin in this section and discuss the role of this parameters in discussion section 4.4 as well (see our answer to the main concern ii) above).

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

We will add the range of erosion rates for each geographical unit of the Amazon Basin, based on the numbers reported by Wittmann et al. (2011).

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

We will remove this.

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

This is correct.

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

The quantity of solid samples requires is only a few mg. Nonetheless, we usually digest much higher quantities in order to perform several other isotope analyses. We will clarify this in the text.

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?

We consider that almost all of the matrix elements (Na, K, Mg, Ca and to a lesser extent Al, Fe and Ti for solid samples) are eluted with this step. We will add this information. We will also provide the number of mL used for each elution step.

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

The protocol of separation was applied twice (that is in series, not in parallel) to ensure a total purification of Ba. We will reword this sentence for clarity.

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"

We will remove this information and replace "coupled to" 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.

Collecting all isotope during measurements allows us to ensure that all isotope ratios follow mass-dependent fractionation and in particular that there is no isobaric interference affecting our measurements (see answer below).

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).

Small amounts of Ce and La remaining in the Ba eluates (for solid samples) can produce isobaric interferences on ^{138}Ba, thereby biasing the $^{138}Ba/^{134}Ba$ ratios. Thus we measured the $^{137}Ba/^{134}Ba$ ratios and convert them to $^{138}Ba/^{134}Ba$, assuming mass-dependent fractionation (which was checked using the relationship between $^{137}Ba/^{135}Ba$ vs. $^{137}Ba/^{134}Ba$, as explained in our Fig. S2).

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.

We will provide these 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 accumulates in the Amazon biomass).

We agree with the reviewer that this correlation is no proof of the "nutrient-like" behavior of Ba, but believe it is an interesting additional indication (and a novel one compared to those already pointed out in previous studies, see our reply to main comment ii) above). Indeed, in the critical zone K is affected by both secondary, soil-forming phase (clays, oxides) formation and biological cycling as well. The fact that river dissolved Ba/Na* and K/Na* ratios display a positive relation simply suggests that Ba is affected by the same processes. However, combined with other observations, a specific role of biological uptake in driving this relationship can be inferred. For example, river dissolved Ba/Na* and K/Na* ratios are lowest in the Andean tributaries, where the role of secondary phase formation is limited (as inferred by Li isotopes; Dellinger et al., 2015), leaving biological uptake a very likely explanation for the low river dissolved abundance of these two elements. On the other end of the spectrum, the high river dissolved Ba/Na* and K/Na* ratios found for rivers draining the shields and lowlands suggest than the leaching of organic matter can be a source of Ba and K - instead of a sink - as these rivers display a higher Ba abundance than expected, and this, albeit a smaller extent of secondary phase formation (see Dellinger et al., 2015). We will make sure during revision that this is made clear.

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.

As suggested by the reviewer, we will change the term "model" to "mass balance approach", as model seems the more appropriate terms. However, we still believe that generally speaking the conceptual tool built here falls under the class of "models".

L.330-335 Given that D is E+W this section would benefit from saying when E (or W) is high or low.

Also, we will clarify which one of E or W increases with D (as explained in our replies to the reviewer's main comments above).

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.

We will split the sentence into two different parts and will add the relevant reference mentioning that Li is not taken up by the biota.

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

The relation actually exists, but is difficult to appreciate because data are presented as a bar chart. Nonetheless, we will change the term "correlations" to "positive relations" instead.

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

The term "soluble" as classically used in geochemistry (unlike in chemistry) has a mostly empirical meaning, simply reflecting the high proportion of a given element that is found in the dissolved load (of *e.g.* a river) compared to the total load. Therefore, a "low Ba solubility" is not incompatible (and actually is rather in line) with "processes" being significant drivers of the Ba cycle. However, we will remove this term from the discussion to avoid confusion.

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.

We agree that the more accurate wording should be "does not show any trend". In the next version, we will reword the sentences in that way.

L.349 see comment L.343

As answered above (please see L.343 comment), the relation is hard to appreciate because of their representation in a bar chart. Again, we will change "correlations" to "trends".

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

As the three parameters plotted in fig. 5 sum to 1, any change in one of them affects to some extent the other ones (in other words, the "closure constraint" induces a negative covariance between the pairs of "f-terms"). We will use "spurious" instead.

L.355 typo, should read "eq. (10)"

We will correct this mistake.

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

Following the reviewer's comment, we will remove this part of the sentence.

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

In soil-mantled landscapes, "rock supply rate" indeed refers to "regolith production". However, river material reflects the export of dissolved and solid material not only from landscape covered by proper regolith and soil, but also from bare bedrock (*e.g.* landslide scars). This is why we think that "rock supply rate" is a more adequate term in the context of our river-based study.

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.

As explained above in our replies to the reviewer's main comments (1) many previous studies have explored the relationships between W, D, and W/D (as already discussed at the beginning of the section 4.3 of the first version of our manuscript), and (2) we think that positive relations between W/D and both GPP and TER are consistent with the spectrum of weathering regimes and ecosystems in the Amazon, ranging from the Andes to the Amazonian rain forest plain. Nonetheless, we will reword this part of the manuscript in order to improve clarity.

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

We will rephrase this sentence for clarity.

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.

We answer to this comment above in our replies to the reviewer's main comments.

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.

As explained above, W and D increase in conjunction. It is thus difficult to disentangle the relative role of these two fluxes in "feeding" vegetation. However, we will clarify the sentence through *e.g.* "made available through sustained rock supply and subsequent weathering".

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

As answered to the main comment ii) regarding the possible role of Ba in plants, we will remove any part that would lead the reader to think that Ba is a "nutrient" and qualify Ba as having with a "nutrient-like" behavior, as suggested by the literature.

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.

The reviewer has clearly identified two weaknesses in this potential interpretation. We agree that this scenario constitutes an unsupported interpretation for the observed relationships, and does not add much to the manuscript. Thus we will remove it from the manuscript.

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

Although counter-intuitive, a longer water residence time below steeper slopes is the correct interpretation proposed in Torres et al. (2015) based on the isotopes of the water molecule. Indeed, following these authors deep, clay-rich soils in the plains might prevent water infiltration allowing for the rapid transfer of water to the streams during / after precipitation events. By contrast, in mountainous areas the presence of fractured and jointed rocks

(because of faulting due to tectonic activity) at shallow depths below ground allows for the formation of large rock-hosted aquifers, which in turn results in longer water residence time.

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

To us this basically means that the metric has no additive properties. We will remove this term for clarity and specify what we exactly mean by that.

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.

This is a fair comment, and we will provide uncertainties for each of the parameters plotted in fig. 8, not only $w^{Ba}_{isotopes}$. We already discuss time scale issues in our replies to the reviewer's main comment i) above.

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.

We will add line 534 (and elsewhere, where relevant) the term "relative" when we talk about the missing flux, but note that f^{Ba}_{miss} was already named a "relative flux" (line 529).

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

As said above, we will add the term "relative" where f^{Ba}_{bio} is mentioned.

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

A discussion on the typical parameter timescales will be given (as discussed above in the replies to the main comment i)).

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?

Yes, this is exactly what we mean. Deep aquifers might exist in the subsurface of the Andes or of the Amazon plain (Hu et al., 2017; Frappart et al., 2019), resulting in a water and solute flow that is not accounted for by collecting water at our river sampling locations. We will clarify this.

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

This is true. We will add a term "[C]_org" term in the equation.

L.591 please add "particulate" to "organic carbon"

We will add "particulate" to the sentence.

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.

We will change the title of this section to avoid over-interpretation and over-generalization. We will also add panel letters to fig. 11.

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

We will add this citation.

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.

We agree, and will modify the text to account for the fact that no clear trend in visible in fig. 12. However, we note that this ratio is higher than 1 for many rivers, which is the most important finding in this section.

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

"[X]_bio" effectively corresponds to a concentration and not to a flux. We will fix this issue in the text.

L.702 better use "assess" instead of "appraise"

We will change "appraise" to "assess".

L.707 "atm" in "(Ba/Cl)_atm" should be replaced by "seawater" as according to the text it represents the seawater ratio?

Strictly speaking, the Ba/Cl ratio of atmospheric inputs can differ from that of seawater as dust dissolution (in rain droplets, or in soils after deposition) or biogenic components (Boström et al., 1989) might increase Ba over Cl in this contribution (although this is something we assume to be negligible here, or at least that such dust would be derived from within the considered catchment, such that its contribution could enter the "rock weathering" component, as classically made in river studies). Regarding particles with biogenic origin, their dissolution is taken into account in our isotope mass balance approach, as the latter considers the net difference between uptake and dissolution. Therefore, "atm" is a more generic term than "seawater" to characterize this contribution. As a consequence, we would like to keep using this term in the next version, but will clearly mention that we assume that (Ba/Cl)_atm is equal to the Ba/Cl of seawater.

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.

We will add this caption and remove the left-hand part of the altitude scale.

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

We will add the per mil sign.

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 FˆBa_bio only shows Ba and no other elements and as this information does not provide additional information that the axis label and legend itself.

As explained in one of our reply above, because the three relative proportions sum to 1 they are to some extent automatically anti-correlated. When scaled to dimensional fluxes using a common factor, they are likely to show some degree of correlation, as shown in fig. 6. In our case, the relative proportion f^{Ba}_{diss} decreases while f^{Ba}_{sec} increases with an increase of D. As these two parameters are changing to larger extent than f^{Ba}_{bio}, the latter does not really change with D. As a result, to further examine the spatial variability in Ba biological uptake, we need to turn it into a dimensional flux.

We will also change the layout of the figure according to the reviewer's comments.

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 FˆBa_bio in dependence of both pathways in this figure.

We will provide uncertainties on the Ba-based parameters, and change the layout of the figure according to the reviewer's comments. As answered in the replies to the reviewer's main comments, we will fix the apparent misunderstanding in the concepts around the "geogenic" and "organic" pathways, both in the text and in this figure.

Figure 8 In the figure caption it says "Uncertainties on wˆBa_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.

We will provide uncertainties on these parameters in the next version. The difference between negative and positive error bars stems from the fact that uncertainty here was calculated by Monte-Carlo simulations, which allows for non-symetric (in particular, non-normal) probability distribution of the calculated parameters (this is because the calculated parameters results from multiplicative operations between variables that are assumed to be normally distributed - multiplication between normally-distributed parameters does not result in normally-distributed parameters).

Figure 9 The arrows next to the x-axis and y-axis do not provide additional information and should be removed. Latest with this figure I would like to see a comparison of the F^{Ba}_{bio} with a

more direct estimate of the Ba uptake flux, e.g. based on GPP and Ba concentrations in plants.

We will remove the two arrows of the x and y-axis of Figure 9. Nonetheless, we don't think that providing F^{Ba}_{bio} based on GPP will add more information, as discussed in our replies to the reviewer's main comments. However, we plan to add a short piece of text discussing of how this comparison informs on the Ba content of the exported organic matter across the Amazon Basin, and this compares to independent estimates of the Ba content in biological material (as estimated from our own compilation), as explained above.

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.

We will name each panel to avoid confusion. Also, we will change the arrow size accordingly to size of the corresponding fluxes, and explain this in the caption.

Reference used:

Bouchez, J., Von Blanckenburg, F., & Schuessler, J. A. (2013). Modeling novel stable isotope ratios in the weathering zone. *American Journal of Science*, *313*(4), 267-308.

Boström, K., Boström, B., & Andersson, P. (1989). Natural and anthropogenic components in bulk precipitation at Blidö (Archipelago of Stockholm). *Water Resources Research*, *25*(6), 1291-1301.

Bullen, T. D., & Bailey, S. W. (2005). Identifying calcium sources at an acid deposition-impacted spruce forest: a strontium isotope, alkaline earth element multi-tracer approach. *Biogeochemistry, 74*(1), 63-99.

Bullen, T., & Chadwick, O. (2016). Ca, Sr and Ba stable isotopes reveal the fate of soil nutrients along a tropical climosequence in Hawaii. *Chemical Geology*, *422*, 25-45.

Chadwick, O. A., Derry, L. A., Vitousek, P. M., Huebert, B. J., & Hedin, L. O. (1999). Changing sources of nutrients during four million years of ecosystem development. *Nature*, *397*(6719), 491-497.

Cleveland, C. C., Townsend, A. R., Taylor, P., Alvarez-Clare, S., Bustamante, M. M., Chuyong, G., ... & Marklein, A. (2011). Relationships among net primary productivity, nutrients and climate in tropical rain forest: a pan-tropical analysis. *Ecology letters*, *14*(9), 939-947.

Cleveland, C. C., Houlton, B. Z., Smith, W. K., Marklein, A. R., Reed, S. C., Parton, W., ... & Running, S. W. (2013). Patterns of new versus recycled primary production in the terrestrial biosphere. *Proceedings of the National Academy of Sciences*, *110*(31), 12733-12737.

Dellinger, M., Bouchez, J., Gaillardet, J., & Faure, L. (2015). Testing the steady state assumption for the Earth's surface denudation using Li isotopes in the Amazon basin. *Procedia earth and planetary science.*, *13*, 162-168.

Dixon, J. L., Hartshorn, A. S., Heimsath, A. M., DiBiase, R. A., & Whipple, K. X. (2012). Chemical weathering response to tectonic forcing: A soils perspective from the San Gabriel Mountains, California. *Earth and Planetary Science Letters*, *323*, 40-49.

Elser, J. J., Bracken, M. E., Cleland, E. E., Gruner, D. S., Harpole, W. S., Hillebrand, H., ... & Smith, J. E. (2007). Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. *Ecology letters*, *10*(12), 1135-1142.

Ferrier, K. L., & Kirchner, J. W. (2008). Effects of physical erosion on chemical denudation rates: A numerical modeling study of soil-mantled hillslopes. *Earth and Planetary Science Letters*, *272*(3-4), 591-599.

Frappart, F., Papa, F., Güntner, A., Tomasella, J., Pfeffer, J., Ramillien, G., ... & Moreira, D. M. (2019). The spatio-temporal variability of groundwater storage in the Amazon River Basin. *Advances in water resources*, *124*, 41-52.

Gabet, E. J., & Mudd, S. M. (2009). A theoretical model coupling chemical weathering rates with denudation rates. *Geology*, *37*(2), 151-154.

Gaillardet, J., Dupré, B., & Allègre, C. J. (1995). A global geochemical mass budget applied to the Congo Basin rivers: erosion rates and continental crust composition. *Geochimica et Cosmochimica Acta*, *59*(17), 3469-3485.

Gaillardet, J., Dupre, B., Allegre, C. J., & Négrel, P. (1997). Chemical and physical denudation in the Amazon River Basin. *Chemical geology*, *142*(3-4), 141-173.

Hu, K., Awange, J. L., Forootan, E., Goncalves, R. M., & Fleming, K. (2017). Hydrogeological characterisation of groundwater over Brazil using remotely sensed and model products. *Science of the Total Environment*, *599*, 372-386.

Lamb, D. T., Matanitobua, V. P., Palanisami, T., Megharaj, M., & Naidu, R. (2013). Bioavailability of barium to plants and invertebrates in soils contaminated by barite. *Environmental science & technology*, *47*(9), 4670-4676.

Lemarchand, D., & Gaillardet, J. (2006). Transient features of the erosion of shales in the Mackenzie basin (Canada), evidences from boron isotopes. *Earth and Planetary Science Letters*, *245*(1-2), 174-189.

Myrvang, M. B., Hillersøy, M. H., Heim, M., Bleken, M. A., & Gjengedal, E. (2016). Uptake of macro nutrients, barium, and strontium by vegetation from mineral soils on carbonatite and pyroxenite bedrock at the Lillebukt Alkaline Complex on Stjernøy, Northern Norway. *Journal of Plant Nutrition and Soil Science*, *179*(6), 705-716.

Selva, E. C., Couto, E. G., Johnson, M. S., & Lehmann, J. (2007). Litterfall production and fluvial export in headwater catchments of the southern Amazon. *Journal of Tropical Ecology*, 329-335.

Stallard, R. F. (1995). Tectonic, environmental, and human aspects of weathering and erosion: a global review using a steady-state perspective. *Annual Review of Earth and Planetary Sciences*, *23*(1), 11-39.

Torres, M. A., West, A. J., & Clark, K. E. (2015). Geomorphic regime modulates hydrologic control of chemical weathering in the Andes–Amazon. *Geochimica et Cosmochimica Acta*, *166*, 105-128.

Wittmann, H., von Blanckenburg, F., Maurice, L., Guyot, J. L., Filizola, N., & Kubik, P. W. (2011). Sediment production and delivery in the Amazon River basin quantified by in situ–produced cosmogenic nuclides and recent river loads. *Bulletin*, *123*(5-6), 934-950.