

Biogeosciences Discuss., author comment AC2  
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## Reply on RC2

Alessandro Montemagno et al.

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Author comment on "Dynamics of rare earth elements and associated major and trace elements during Douglas-fir (*Pseudotsuga menziesii*) and European beech (*Fagus sylvatica* L.) litter degradation" by Alessandro Montemagno et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2021-268-AC2>, 2022

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Dear Reviewer,

Many thanks, on behalf of all the authors, for accepting to revise our manuscript and for the clever suggestions you provide with such an evaluation.  
Please, find below the answers to your questions/comments in the same order as you submitted.

### *General comments*

- *The study aims to use the chemical signature of REE to better understand the decomposition rate of plant litter.*
- *I highly recommend normalizing the REE by the lower soil horizon or parent material or continental crust values. It is unusual to normalize by the dust since dust is typically a potential end member. All REE patterns should be reprocessed using a "true" regolith source. Dust can be transported from long distances, how can this be considered the sole parent material?*

It is not usual from a literature point of view, to normalize REE concentrations to dust. Nonetheless it must be said that the normalization by a specific material can usually be done according to given processes to be highlighted (for example Stille et al. 2009 - <https://doi.org/10.1016/j.chemgeo.2009.03.005> - who normalised soil leachates to soil solutions). As explained in lines 217-220, atmospheric deposition is an important input of cations and nutrients and we expected it to be also in terms of REE supply as previously suggested by Censi et al. (2017- <https://doi.org/10.1016/j.chemosphere.2016.11.085>). Therefore, this normalization is (also) a way to observe whether or not the atmospheric deposition has an impact on the REE composition (and thus on patterns) of leaves and litter. Indeed, if we obtained flat litter REE patterns when normalizing to the dust, we could have argued that most of the REE in the solid fraction of litter was delivered by the dust and not by the litter itself.

We remind also that the Weierbach regolith has multiple origins and it is composed of a Devonian slate substrate covered by 70-100 cm of Pleistocene Periglacial Slope aeolian deposit. This would also make difficult the choice of the regolith material to be used as standard for the normalization.

However, by normalising the dust REE concentrations by the PAAS (McLennan 1989 - <https://doi.org/10.1515/9781501509032-010>), it is possible to notice that the pattern obtained in this way has almost a flat shape characterised by a slight MREE enrichment (LaN/GdN=0.88 and GdN/YbN=1.16) and a slight Eu positive anomaly (Eu/Eu\*=1.12).

Consequently, changing the normalization to the PAAS would then produce almost identical patterns in the litter and in the leachates with the sole difference of an accentuation of the already shown europium anomaly and MREE enrichments.

#### *Abstract*

• *Write the abstract from the perspective of how the REE signatures inform the biogeochemical process involved on litter degradation. A more compelling story is the use of REE signatures as biogeochemical indicators of degradation steps. The abstract needs to be flipped from a different perspective. Let's say, I collect a sample from the O horizon and determine the REE signature, will this info reveal the stage of the organic matter decomposition. This is how reactive tracers are useful in future applications.*

We propose to improve the abstract according to the following comments.

• *Is there any difference on biogeochemical process under the two different type of litter? Are the REE signatures reflecting these differences? This was not mentioned in the abstract; however, since it is part of the tittle, I believe it should be relevant.*

We propose to add the following arguments to the final abstract:

- According to the REE dynamics, litters of the two tree species showed similar biogeochemical processes dominating these elements behaviour.
- Using REE, two main elements of distinction between the two species were highlighted:
  - Eu behaviour linked to the Ca during the leaves' senescence in the *Pseudotsuga menziesii*, linkage which was not found in the *Fagus sylvatica*;
  - Species-specific release of organic acids during the litter degradation which lead to differences in the MREE enrichment of the litter leachates.

*Lines 29-31: This type of statement needs to include the trend. What does a high or low ratio inform the degradation intensity?*

We agree. We also believe that the use of the Y/Ho ratios should be integrated in the statement of lines 29-31 (which refers only to the LaN/YbN ratios), in order to provide a more precise view on how these elements were used to gather information about the intensity of the degradation. We propose to modify the lines 29-31 as follow:

*"In particular, the degradation of the litter was characterised by a decrease in the Y/Ho ratio and an increase in the LaN/YbN ratio during the decay. The relationship between these ratios delivered information on the litter species-specific resistance to degradation, with Douglas-fir litter material showing a lower resistance."*

*Lines 31-33: The important implication here is how the white fungi activity influences organic matter degradation resulting in the Ce anomaly.*

We agree and, accordingly, we propose to reformulate as follow:

*"Finally, we showed the primary control effect that white fungi may have in the Ce enrichment of soil solutions, which appears to be associated with the dissolution and/or direct transport of Ce-enriched MnO<sub>2</sub> particles accumulated on the surface of the old litter due to the metabolic functioning of these microorganisms."*

*Lines 69-72: Add a reference citation.*

Regarding the fractionation of REE in plants: Liang *et al.* 2008 ([https://doi.org/10.1016/S1002-0721\(08\)60027-7](https://doi.org/10.1016/S1002-0721(08)60027-7)).

The references regarding REE as emerging pollutants are reported in lines 74-75 as the sentence in those lines is connected to the previous one. To make it more clear for the reader, we propose to put those references at the end of the sentence in the lines you suggested.

#### *Methods*

- *In Figure 1, the authors refer as humus material the fragmented litter. This is an incorrect definition of humus material. The thick brown or black substance that remains after most of the organic litter has decomposed is called humus. Humus material should be unrecognizable which is not the case in Figure 1. This material should be simply called partially fragmented litter not humus.*

We agree on this comment. Subsequently, the correction on the nomenclature of the fragmented litter will be applied to the final document.

- *Please justify why the digestion for the litter was different from the dust.*

We applied the HNO<sub>3</sub>/HF/HClO<sub>4</sub> acid mixture digestion using hot plate in order to totally dissolve the dust sample because this is the standard protocol used in our laboratory for this type of sample. Indeed, HF is needed for breaking the strong Si-O bonds of the silicate mineral phases that could contribute to atmospheric dust (Lequy *et al.*, 2012 in *Forest Ecology and Management*). Due to the number of samples and the related amount of litter material to be digested, we opted for a more convenient digestion of the organic-derived samples by using a microwave-assisted oven, which allows reaching higher temperature and pressure conditions (maximum temperature and pressure reached 212 °C and 24.2 bar respectively). The microwave-assisted oven technique does not allow the use HF in our laboratory and we decided to test different digestion methods (HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, Aqua Regia) to validate the most efficient one. Aqua Regia delivered solutions without any precipitates nor suspended particles as they resulted clear and transparent not only at the moment of the digestion but also long time after.

However, we agree that Aqua Regia is not a total digestion method, and this will be specified in the manuscript for clarification.

*What is the scientific rationale to use the local atmospheric deposition for normalization? Atmospheric dust should be treated as an end member. The dust can affect the REE signature. Is this normalization widely accepted in the literature? I highly recommend normalizing by the lower soil horizon or parent material or continental crust values. I question if the REE signatures are truly reflecting the decomposition of the litter or are biased by the dust normalization.*

Please, for this point, refers to the first comment.

*Line 180: Aqua Regia is not a total digestion method. Please clarify that this is a partial digestion.*

We agree and will clarify that aqua regia is not a total digestion method as you suggest.

*Section 2.3: Include information about the standards used in the calibration curve and the internal standard.*

The calibration standards were prepared with Chem-lab (Belgium) and Merck (Belgium) certified solutions, while the internal standards were prepared with Chem-lab (Belgium) rhenium and rhodium certified solutions.

*Section 2.4: Define the LREE, MREE, HREE*

The REE groups were already defined in lines 76-77

*Results*

*Line 335: Specify, results are for the solid matrices.*

It will be done.

*Line 336: significant different... was this tested statistically? If not, how do you know is significant different?*

We noticed that the use of the word "significant" was not appropriate in this manuscript. In this particular case, the intention was to draw attention to specific aspects of the REE pattern shapes to highlight the differences between the patterns of the two tree species. We propose to remove the word "significant" in this instance.

*Line 366/374: significant Eu/Ce positive anomalies... where are the statistics to support these statements?*

Also in this case, "significant" was not related to the use of statistics. Just an inappropriate use of the term, which was instead intended as "meaningful". Again, we propose to remove the word "significant".

*Discussion*

*It is confusing in some instances to follow if the discussion relates to the solid or leachates. Please make it clear across.*

We will proceed to specify whether the sentences refer to the solid fraction or to the leachates.

*Lines 425-433: This reads as results descriptions. There are no implications associated to these descriptions.*

We wanted to use those lines as an introduction to the next sentences of the manuscript. We suggest removing lines 426-433 and improving the associated discussion in the following text.

*Line 527: ... significant positive Ce anomalies... Where is the p-value?*

As above, we propose to remove the word "significant" in order to avoid these misunderstandings.

I would like to thank you again and to wish you all the best,

Alessandro Montemagno