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## Reply on RC1

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-AC1>, 2021

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Dear Dr. Pourret,

first of all I would like to thank you, on behalf of all the authors, for the time spent on reviewing our manuscript and for the useful insights you took care to share with us.

In the same order of your questions/comments, please find below our corresponding answers:

- *Analytical section (sample analysis) is very short, details should be added especially regarding QA/QC; isobaric interferences may occur, it must be checked and clearly stated.*

The concentrations of major cations and trace elements in all samples were analysed via Inductively Coupled Plasma - Mass Spectrometry (Agilent 7900). The measured isotopes were chosen with no isobaric interferences, and the polyatomic interferences were minimized by using the collision cell in Helium mode. Calibration standards and Quality Controls (QCs) were prepared with certified solutions (Chem-lab, Belgium and Merck, Belgium). QCs at low, medium and high levels of concentration of the calibration range were analysed each after ten samples to control the validity of the measurement. The limits of quantification (LoQ) for the different analysed elements are reported in Tables SI-3 and SI-4. Also, mineralization blanks were prepared following the same steps as for the samples to ensure the quality of the procedure.

- *In the discussion section, it would be useful to check how microorganisms, siderophores,... may have a role on redox behavior of Ce. It is stated in the M&M section that biotic communities were preserved.*

It is true that microorganisms may affect the redox behaviour of Ce through specific mechanisms. Unfortunately, we did not investigate the composition of the biotic communities in our samples but, among the microorganisms that have been found to have a potential role in the REE mobilization and behaviour, we proposed the ones fitting the best our data in order to develop the conceptual model. Initially we did not think about the role of siderophores in such a system and we thank you for the useful suggestion. Nonetheless, some considerations can be made regarding these specific compounds and their potential role in our experiment. The release of siderophores may occur both from fungi and bacteria to help the Iron assimilation, by the way we cannot imagine these compounds to play an important role in the redox behaviour of Ce in our system. Indeed,

the release of siderophores is more a condition-specific mechanism (it occurs in iron-deficiency conditions – Chennappa et al. 2019 <https://www.sciencedirect.com/science/article/pii/B9780444641915000195>) rather than timeframe-specific (e.g. during specific periods of litter degradation). Thus, we would expect siderophores to be released to enhance the Iron assimilation especially during the first stages of the degradation where the Fe concentrations are much lower when compared to the oldest fractions. Therefore, it is precisely in those early stages of decay where one would expect a greater participation of the siderophores in the geochemical behavior of Cerium. Kraemer et al. (2017 - <https://www.sciencedirect.com/science/article/abs/pii/S0016703716305336>) demonstrated that siderophores are able to scavenge Ce by oxidizing it to Ce (IV) forming stable complexes and leading to the development of positive cerium anomalies in solution, anomalies that are not shown in the leachates of the younger litter fractions where, as mentioned before, we would expect them according to the Fe-deficiency. It is important, therefore, to remember that the Ce enrichment occurs only in the leachates of the oldest litter fractions, which suggest that the process acting in these circumstances is timeframe-specific and occurs during the latest stage of the degradation. Other important aspects to take into account are the much higher concentrations of manganese in the leachates when compared to iron (Table SI-4) and the different behaviour (in terms of % of yields) that this latter shows between the leachates of the two tree species, while Ce instead shows the same dynamics in terms of anomaly development.

*- In the same part, authors consider Mn oxides, what about Fe oxides?*

The competitive scavenging of Ce operated by Fe and Mn oxides is a quite controversial argument. By the way, Bau and Koschinsky (2009 - [https://www.jstage.jst.go.jp/article/geochemj/43/1/43\\_1.0005/\\_article](https://www.jstage.jst.go.jp/article/geochemj/43/1/43_1.0005/_article)) demonstrated, through a sequential leaching experiment carried on ground Fe-Mn crust samples, that (in marine environment) also Fe oxides are able to scavenge Ce from the water column with a lesser extent when compared to Mn oxides as demonstrated by the higher positive Ce/Ce\* found in the Mn oxides fraction. Despite the fact that they found similar Ce/Ce\* anomalies in the two oxides, we have to mention that the Mn/Fe ratios in our leachates ( $33.6 \leq \text{Mn/Fe} \leq 276.5$ ) are much higher than the ones of the total concentrations in the samples treated by the above-mentioned authors ( $1.57 \leq \text{Mn/Fe} \leq 1.65$ ). This suggests that Mn is acting as protagonist in the Ce oxidation in our system rather than Fe. Of course our experiment is not a marine environment replica, but it is also true that our is the first attempt to explain not only Ce behaviour but more in general the REE dynamics during the litter degradation and this makes difficult to find suitable literature to compare our results with.

*-In the discussion section, the part dealing with Eu anomaly need to consider all the relevant literature on the subject, check my latest article <https://doi.org/10.1007/s11104-021-05210-6...>*

We agree with your comment and we also believe that this literature should be implemented in our manuscript in order to give a broader overview on Eu behaviour in plants.

As you discussed, plenty of processes may result in the mobilization, sequestration and fractionation of REE in plants tissues. Among all these processes, the mobilization of Eu to the leaves from other tree's organs before the leaves' senescence is the one which may explain the (small) Eu enrichment we observe only in the new litter of Douglas-fir (Do OLn,  $\text{Eu/Eu}^* = 1.09$ ) which represent the newly deposited leaves just after the senescence. Indeed, If other processes (such the ones you mentioned) played an important role in the preferential Eu accumulation in our leaves samples, they would have occurred during all the living period and we would have observed an Eu enrichment

already in the fresh leaves, which instead does not occur ( $\text{Eu}/\text{Eu}^* = 0.93$  in Do FL). For what it may concern the Eu anomaly in the leachate, we proposed the Eu substitution of Ca in the Ca pectate to justify the positive  $\text{Eu}/\text{Eu}^*$  because this latter is occurring only in the leachate of the oldest Douglas-fir litter (Do OLv). Calcium pectate links cell walls giving rigidity to the whole structure. Such a strategic positioning between degradation resistant compounds (cell walls are composed of the most resistant molecules such as cellulose, hemicellulose and lignins), might make this molecule not easily accessible during the early stage of the degradation. This could give a clue on why we observe such an anomaly only in the latest stage of the degradation after that most of the "weak" tissues have been already degraded. Of course, the similarity between the ionic radii of Eu(III) and Ca might play a role on this substitution.

In the case of the other accumulation processes such as Eu binding to organelles and/or inner membranes, or binding with phosphates, we might expect these molecular associations to be among the first cell components to be degraded and/or released due to their chemical composition (organelles and membranes are mainly composed of lipids, proteins, glycolipids and glycoproteins) and position (both organelles and phosphate are present in the cytosol). Thus, in this case, we would have expected the Eu anomaly to appear already in the leachates of the younger litter fraction and fresh leaves. Furthermore, with an in-vitro experiment with Brassica napus cells, Moll et al. (2020 - <https://link.springer.com/article/10.1007/s11356-020-09525-2>) demonstrated that in plant's cell Eu is preferentially absorbed into cell walls as result of anti toxicity mechanisms. In case of the solely absorption operated by the cell walls, we have no reason to believe that such a mechanism would act preferentially on Eu rather than the other REE (into specific the two Eu neighbours). The enriched release of Eu during the last stage of degradation, instead, is suggesting that at least part of this Eu is fractionated or into slightly less degradation-resistant compounds (when compared to lignins where the other REE are supposed to be bound) or into specific not-easily-accessible positions which make its release into the environment not immediate at the beginning of the degradation. The late degradation of these afore-mentioned compartments would deliver additional Eu content during the degradation of the oldest litter fraction in addition to the Eu released together with the other REE, leading finally to the slight enrichment in the leachate of the Do OLv sample.

Finally, Eu/Ca ratios in the first 60 cm of soil and bedrock under the Douglas-fir stand ranged from 0.0005 to 0.0044 (Moragues-Quiroga et al., 2017 - <https://doi.org/10.1016/j.catena.2016.09.015>) which, according to Brioschi et al. (2013 - <https://link.springer.com/article/10.1007/s11104-012-1407-0>), for instance, indicate a Ca depletion in the regolith of our experimental site. The question on how such a Ca depletion could play a role on the Eu positive anomaly due to the fact that this latter is shown enriched in the leachates of the oldest litter fraction still remains. For what it may concern instead the slight enrichment in Eu occurring in the solid fraction, as previously mentioned, it is occurring in the Do OLn fraction (which was already on the ground) and not in the fresh leaves where instead the  $\text{Eu}/\text{Eu}^*$  is below 1. It is our opinion then, that the enrichment in the leaves is occurring just during the leaves senescence before the falling and not during their living period. But we agree on the fact that this question still needs to be studied and that our results cannot entirely answer to it.

#### *-Minor comments*

We agree with all the comments of this session and, accordingly, corrections will be applied to the final document. Figures' features have been already checked during the preliminary session for the article submission.

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

Alessandro Montemagno