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Comment on soil-2021-65

Zuzana Frkova et al.

Author comment on "Phosphorus dynamics during early soil development in a cold desert: insights from oxygen isotopes in phosphate" by Zuzana Frkova et al., SOIL Discuss.,
<https://doi.org/10.5194/soil-2021-65-AC1>, 2021

We would like to thank you very much for reviewing our manuscript, for positive feedback and for the helpful comments. We addressed them one by one below. Please note that the references to the manuscript line might not match with the final manuscript version as further modifications might be done.

- Title: I think this needs a slight re-word as it does not actually highlight which environment or the novelty/ breadth of the techniques used in this study

REPLY: Thank you for the suggestion. We modified the title as follows: "Phosphorus dynamics during early soil development in cold desert: insights from oxygen isotopes in phosphates"

- Figure 1: I think this figure could be re-worked, it would be really great to see a figure showing the sampling locations clearly, possibly with the old glacial limits as a visual representation of the speed of glacial retreat in the valley. At the moment this is very difficult to visualise from the large area map provided.

REPLY: We changed the figure according to your suggestions.

- Line 160: Five pools are mentioned here but only 4 described? Did you mean to include Po here?

REPLY: Yes, indeed the fifth pool is Po in the NaOH-EDTA extract. We modified the sentence accordingly to clarify that. Please, also note that in response to a remark from the second reviewer we changed the names of the mineral P (now HCl-P) and P bound to oxides (now NaOH-Pi) pools.

Originally: "NaOH-EDTA extractable P (bound to iron- (Fe) and aluminum- (Al) oxides and to organic P)"

Changed to: "NaOH-EDTA extractable organic and inorganic P (NaOH-Po and NaOH-Pi, latter is supposed to contain P bound to oxi-hydroxides)"

- 166: I think the working of this is a bit confusing. I read it as some sites only had values of X and Y where you mean some sites don't have values of X or Y. maybe just re phrase to make this clearer.

REPLY: We rephrased as follows:

Originally: "This was the case of microbial P in the samples from sites M1 and M2 and the P bound to oxides in the sample from site M2."

Changed to: "The $\delta^{18}O_P$ is missing for the microbial P pool at sites M1 and M2, and for the NaOH-Pi pool at site M2 (see Figure 2 and dataset in Frkova et al., 2021)"

- Line 175: I would be surprised with a $\delta^{2}H$ precision of 0.1... maybe 1.0?

REPLY: We agree, there was a mistake, now corrected. The precision is 1.0 ‰ for $\delta^{2}H$:

Originally: "Typical precisions are better than ± 0.1 ‰ for both $\delta^{18}O$ and $\delta^{2}H$, respectively".

Changed to: "Typical precisions are better than ± 0.1 ‰ for $\delta^{18}O$ and ± 1.0 ‰ $\delta^{2}H$, respectively".

- Line 179: Please add in the measurement precision here as with above.

REPLY: Sorry for this oversight. We added the following sentence:

We added the following sentence "Reproducibility of repeated measurements of internal standards was better than ± 0.06 ‰." (L 199-200)

- Line 183: do you have any Local meteoric water line data here, maybe from ongoing field campaigns?

REPLY: the Local Meteoric Water Line (LMWL) was constructed for Kashmir Valley (2013 – 2014) by Jeelani et al. 2017:

$$\delta^{2}H = 7.97 (+ 0.3) \times \delta^{18}O + 16.3 (+ 2.5) \quad (n = 229, R^2 = 0.97, p \leq 0.05).$$

The LMWL of the Kashmir Valley is comparable with the global meteoric water line (GMWL) $\delta^{2}H = 8 \times \delta^{18}O + 10$ and the deviation is related to the monsoonal influence.

However, glacier and snout melting, as well as soil water represent older climate conditions than 2013 and cannot be compared with the modern meteoric waters. We did not include a LMWL because modern atmospheric precipitation origin was beyond the scope of the paper.

- Lines 185-190: some info on sample weights and number of replicate analysis would be

good in here as well as the average standard error of sample replicate analysis. Additionally, this error information would be good to see on Figure 2.

REPLY: thank you for pointing out this out. We added the following sentences to the paragraph:

"Samples (250-400 μg) were run in duplicates whenever possible." (L207)

"...and average standard deviation of samples replicates analyses was 0.5‰" (L 211-212)

We did not add the error on Figure 2, because we only have the analytical error from sample replicates analysis at the mass spectrometer. Indeed, because of large soil quantity needed, we could run only one extraction per site. According to our experience with field samples, we have added a measure of the error of sample replicate extraction.

Addition: "We estimated the variability introduced by the extraction-purification procedure to be approximately $\pm 0.5\%$ according to our field samples datasets and we considered twice this value as a conservative threshold for significant differences (Pistocchi et al., 2017; Helfenstein et al., 2018; Tamburini et al., 2018)." (L173-175)

- How much of an issue is it for the rest of the interpretation that you only have P_o from the oldest site, and how valid is it to assume that P_o is the same across all of the other sites (Line 210)?

REPLY: this is a good point. Published data on the $\delta^{18}\text{O}P$ of soil organic P and how it varies along biological and abiotic gradients are extremely rare. It is, therefore, difficult to assess the representativity of our extrapolation. We have added the following sentence to better acknowledge this issue:

"At younger sites only microbes contribute to P_o , while at site M3 and M4 also residues from vascular plants, which usually are enriched in the heavy O isotope (Tamburini et al., 2018; Pfahler et al., 2013) most likely represent a source of organic P. Therefore, at younger sites, the $\delta^{18}\text{O}P\text{-org}$ might be lower." (L234-237)

Additionally, we modified lines 493-496 in the discussion section:

Originally: As the $\delta^{18}\text{O}P_{\text{expected}}$ were lower compared to the measured $\delta^{18}\text{O}P$ of available P at sites M1 and M2, we conclude that the flux from P_o mineralization ($f\text{-}P_o$), which would carry a low $\delta^{18}\text{O}P$ value, was possibly overestimated.

Changed to: As the $\delta^{18}\text{O}P_{\text{expected}}$ were lower compared to the measured $\delta^{18}\text{O}P$ of available P at sites M1 and M2, we hypothesized either that the flux from P_o mineralization ($f\text{-}P_o$), which would carry a low $\delta^{18}\text{O}P$ value, was overestimated or that the $\delta^{18}\text{O}P\text{-org}$ was underestimated (see Eq. 2 and 3). Since $\delta^{18}\text{O}P\text{-org}$ was possibly overestimated at these young sites (see section 2.6), we concluded for the first option.

- Again, how representative are the full range of microbial P values going to be here. I don't question your rational in using the values from sites M3 and M4 but it would be good if you could comment on how representative you think these values are, especially as you are studying this site specifically as you expect and see major changes in soil and vegetation development leading clearly to different P pools becoming more or less important.

REPLY: as for the previous point, there are few data published on the isotopic composition of soil microbial P to allow us having an idea of the representativity of the values here. We acknowledge this issue adding the following sentence (L270-272).

"The used range (5.2‰) encompasses half of the natural occurring variation of $\delta^{18}\text{O}_\text{P}$ of soil microbial P from very different temperate and tropical ecosystems (+11.5 to +20.6‰, Tamburini et al., 2018)."

We additionally added a table in supplementary material (Table S3), to show how sensitive the estimations from the box model are to variations in the $\delta^{18}\text{O}_\text{P}$ of soil microbial P

- Table 2: Maybe I'm confused here and some of the data comes from long term averages but where are the fixed values in $\delta^{18}\text{O}_\text{w}$ and temp coming from? I think the Table caption needs to make this clear.

REPLY: Indeed, captions were not so clear. The table 2 was redesigned.

- Line 311: this is a little misleading, it sounds like oxide bound P is normally similar to the parent material, but actually from your 3 data points 2 diverge and only 1 is similar. This needs re-wording.

REPLY: Sorry for that. We rephrased as follows:

Originally: The $\delta^{18}\text{O}_\text{P}$ bound to Al- and Fe-oxides showed isotopic values similar to the parent material except for M3 and M4, where this pool carried a $\delta^{18}\text{O}_\text{P}$ of +15.40‰ and +6.05‰, respectively.

Changed to: Only the NaOH- Pi at site M1 showed isotopic values similar to the parent material, while at M3 and M4 this pool carried a $\delta^{18}\text{O}_\text{P}$ of +15.40‰ and +6.05‰, respectively.

- Figure 2: It would be good to see the theoretical equilibration value for the sites in a similar way to how you show PME or as a shaded bar. This will help visualise how distinct the values are from pyrophosphatase driven equilibrium. This would be good to visualise between sites, especially when in lines 355-370 you discuss this as a potential reason for lower microbial P values between M3 and M4.

REPLY: We changed the figure adding the equilibrium values calculated with measured soil water isotopes composition, representing the upper equilibrium limits, which allow visualising the differences between the sites.

- Line 370: significant suggests some statistical significance, if that's the case please quote if not just re-word. It would also be good to get a feeling of the analytical error you expect. i.e. error through chemistry as well as the MS, did you run duplicates at all through the $\delta^{18}\text{O}_\text{P}$ prep?

REPLY: thank you for pointing this out. It is now explained in the manuscript that because of the amount of soil required, we could not run replicates of the extraction-purification procedure (except sample splits, $n=2$, for the extraction step with labelled and unlabelled

HCl).

To have an idea of the analytical error expected, we used the standard deviation calculated on previous datasets from field samples (0.5‰). Although we cannot perform inferential statistics with only one field sample per site (although representative because pooled from at least ten sub-samples), we consider twice this standard deviation as a conservative estimation of a significant difference (Fay and Gerow, 2014) between samples and expected equilibrium values. (L190-193)

Minor comments:

REPLY: minor suggestions and comments were all implemented except the following one

- 139 cm⁻³ repeated?

REPLY: No, this is referred to the volumetric soil water content (cm/cm³)

References

Fay, D. S., & Gerow, K. (2013). A biologist's guide to statistical thinking and analysis. *WormBook: the online review of C. elegans biology*, 1-54.

Jeelani G, Deshpande R D, Shah R A & Hassan W (2017) Influence of southwest monsoons in the Kashmir Valley, western Himalayas, Isotopes in Environmental and Health Studies, 53:4, 400-412, DOI: 10.1080/10256016.2016.1273224