

SOIL Discuss., author comment AC2
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Reply on RC2

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.,
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Thank you for your detailed and constructive comments and for supporting the publication of our paper. Please find below our detailed reply to each of your comment (that we reported as well) and the description of changes we made to the manuscript.

Specific comments:

Three major issues should be addressed in the revision of the paper:

Assignment of Hedley fractions to soil minerals. Recent research has shown that the assignment of different Hedley P fractions to specific mineral types is not straightforward, and in specific cases may be completely wrong. See: Gu & Margenot (2021) *Plant Soil* 459:13–17 (<https://doi.org/10.1007/s11104-020-04552-x>) and Klotzbücher et al. (2019), *J Plant Nutr Soil Sci* 182:570-577. <https://doi.org/10.1002/jpln.201800652>.

Considering this, the authors should be more careful in assigning their Hedley P fractions to specific mineral phases (e.g. "Al- and Fe-bound" phases). This is particularly the case because (i) no support of their statements by other analyses (e.g. P K-edge XANES), (ii) not even any information about the absence, presence, and (iii) no data on contents of different potentially P-sorbing Al- and Fe minerals have been provided in the paper.

REPLY: *Thank you for raising this point. Indeed, in this study, we had no independent evidence of the specific composition of the Hedley P pools. Accepting your suggestion, in the new manuscript version we have changed the P pools names and called them by the name of the extraction reagent (e.g. HCl-P). We did not change the names of the microbial and available P as the first represents a biological fraction and the resin P is usually considered a very good proxy for the available P. We changed the description of these pools in the materials and methods accordingly (lines 177-178):*

Originally: "NaOH-EDTA extractable P (bound to iron- (Fe) and aluminum- (Al) oxides and to organic P), and HCl extractable P (mineral P, mostly P bound to Ca in apatite)"

Changed to: "NaOH-EDTA extractable organic and inorganic P (NaOH-Po and NaOH-Pi, latter is supposed to contain P bound to oxo-hydroxides), and HCl extractable P (HCl-P, targeting mostly P bound to Ca)."

I understand that conduction of XANES analyses is probably out of reach for the authors of

the paper, but analytical determination of dithionite-citrate-bicarbonate Fe (Fed, estimating Fe present in well-crystallized Fe oxyhydroxides, like goethite) and of acidic oxalate-extractable Fe and Al (Feo, Alo, estimating the Al and Fe present in short-range order minerals and gibbsite) may help to support the assignment of the NaOH-extractable Hedley P fraction to Al and Fe minerals. To be on the safe side, of course, one has to refrain from attributing the Hedley fractions to particular minerals as a whole, and just focus on the different availability of the different fractions to plants and soil microorganisms. If I understand the key message of the paper correctly, this is the main aim of the paper, and attribution of the Hedley fractions to particular mineral phases is of secondary importance.

REPLY: *As you mentioned, the composition of Hedley fractions in terms of mineral phases, although interesting, is of secondary importance in our paper, as we focussed on biological availability of these pools as revealed by their isotopic composition. As replied above, we have changed the names of the Hedley pools throughout the manuscript in a way that is more "neutral".*

We have down-tuned in the interpretation of P pools data in the discussion, see for examples lines 489-490:

Originally: "However, at the youngest sites, this flux can be considered as negligible compared to other contributions, due to the relatively small concentration of the P bound to oxides."

Changed to: "However, at the youngest sites, this flux can be considered as negligible compared to other contributions, due to the relatively small concentration of the NaOH-Pi, which is supposed to target P bound to oxides."

And lines 526-527:

Originally: "50 years of soil development and contributed also to the phosphate sorbed on oxides"

Changed to: "50 years of soil development and contributed also to the phosphate sorbed onto secondary minerals, presumably Fe and Al oxides"

2) I strongly recommend analysis of some additional soil variables, provided that some sample material is still available. (1) Analysis of dithionite-citrate-bicarbonate Fe (Al) and acidic oxalate-extractable Fe and Al (as mentioned before) would help to clarify the assignment of the reported Hedley P fractions to mineral phases. Moreover, it is a generally important soil variable, and helps to characterize the different soils in the study of Frkova et al. with respect to their stage of pedogenesis. I assume that some Alo and Feo will be present particularly in the older soils of the chronosequence, even though the pH is >7.7 (which normally prevents silicate weathering). This may raise discussions about the sources of pedogenic oxides (see an earlier paper of mine on two glacier forefields in China (also Tibetan Plateau) and Switzerland (Damma): Prietzel et al. 2013, GCA 108:154-171; <https://doi.org/10.1016/j.gca.2013.01.029>). Alternatively, Alo and Feo also includes organically bound Fe and Al in addition to/independent of mineral-bound Fe and Al – However, this line of argument may disprove the statement made in the paper that the NaOH-extractable P is bound to Al and Fe minerals.

REPLY: *Thank you for this suggestion. Unfortunately, no soil material is left from the campaign of 2017. However, we are going to perform the suggested analyses on older samples (2011) taken in the proximity of our four sites and kept at -20°C. We will, therefore, fully respond to this remark once we have the data.*

Moreover, I recommend measuring inorganic carbon (carbonate) and the electric conductivity in the different soil samples. The climate conditions at the study sites, as well as the high pH in the investigated soils (7.7 – 8.7) both indicate the presence of carbonate and /or salt accumulation in the topsoil. Additionally, the good correlation between pH and total K in the different topsoils (see Table 1) suggests salt accumulation, which has a strong influence on weathering, soil P speciation, and probably also soil microbial communities and activity. The EC values are a good indicator for salt accumulation, and thus should be analyzed. I suspect that EC values are increased in the studied soils compared to ordinary soils under humid climate, and the investigated soils thus are probably affected by topsoil salt accumulation, which may be temporarily or continuously present at varying levels. If the investigated soils turn out to be affected by salt accumulation due to the arid-cool climate, the influence on weathering, soil P speciation, soil microbial communities, and activity should be addressed more deeply in the paper.

REPLY: *Thank you for the suggestion. Although we have not performed EC and carbonates analyses on our soil samples, we retrieved salinity and soil carbonate concentration data from previous sampling campaigns. The salinity was estimated according to the percentage of soil covered by salt efflorescence. We will also measure the EC on soil samples from the 2011 sampling (see above). Once complete, we will integrate these data in the discussion.*

3) In this respect I recommend reading a recent paper of mine dealing with P speciation changes in cold arid glacier forefield regions of Antarctica (Prietzl et al., 2019, GCA 246:339-362. <https://doi.org/10.1016/j.gca.2018.12.001> and the references therein. I have the impression that the environmental conditions in the paper of Frkova et al. and those reported in my 2019 study are quite similar in many (aridity, high UV influence) but not all (seasonality, day length) aspects.

REPLY: *Thank you for suggesting this reference. As you pointed out earlier, there are only few published data on P dynamics in cold-arid environment. We have integrated the reference in the introduction and in the discussion (L 84-85).*

Originally: "Direct forefield observations on the role of microorganisms in P cycling using O isotopes in phosphate are rare."

Changed to: "Direct forefield observations on the role of microorganisms in P cycling are rare especially under cold arid conditions (Prietzl et al., 2019)."

And L 422-425:

Addition: "However, these environments are sensibly more humid than the Chamser Kangri forefield. As reported by Prietzl et al., (2019) for polar cold arid soils, the weathering of primary P minerals like apatite is strongly retarded by the lack of water, which slows down soil acidification."

One minor issue that in a soil science paper I would like to see some soil type (WRB) description, maybe also horizon designations for the studied topsoil horizons.

REPLY: *According to Gupta and Arora (2017) the soils of the Ladakh region are mostly classified as Entisols (USDA classification). According to our field knowledge, they would fall in the order of Leptosols (WRB classification).*

Addition (line 126): "They can be classified as Leptosols according to the WRB (Anon, 2006)."

And lines 138-139:

Originally: "Soil samples were collected along the frontal (M1-3) and lateral (M4) moraines of the Chamser Kangri glacier chronosequence (5711, 5710, 5700 and 5598 m a.s.l., M1-M4 respectively)."

Changed to: "Soil samples were collected along the frontal (M1-3) and lateral (M4) moraines of the Chamser Kangri glacier chronosequence (5711, 5710, 5700 and 5598 m a.s.l., M1-M4 respectively) from the A1 horizon."

Technical corrections

L29: Please specify soil depth or horizon, where 95% of total P is mineral P

REPLY: It is now specified at L29

L30: Can you specify the "primary phosphate minerals"?

REPLY: Done (L30)

L34: should read: "becomes" instead of "become"

REPLY: Done

L149-152: Please specify: Have the analyses been conducted on sieved or in ground samples?

REPLY: All the analyses have been conducted on sieved samples (<2mm), except for the 18Op in the parent material. For that we milled a sample of the parent material and then dissolved it in HCl (L199-200).

L151: K, Mg, and Ca are not micronutrients

REPLY: You are right. We corrected the mistake

L152: This is "pseudo-total" P rather than total P, because silicates are not completely dissolved by HNO₃/HClO₄ digestion and the P bound in silicates thus is probably underestimated.

REPLY: Thank you for pointing this out. We modified the sentence as follows (L 162-164):

Originally: "total P and other major elements were analyzed by ICP-OES after sequential digestion by HNO₃ and HClO₄ (Kopacek et al., 2001)."

Changed to: "total P and other major elements were analyzed by ICP-OES after digestion by HNO₃ and HClO₄, although total P might be underestimated because of incomplete dissolution of silicates during the digestion (Kopacek et al., 2001)."

L160: How can NaOH-extractable P be bound to organic P? Please reword sentence in bracket

REPLY: The sentence was rephrased (L177-178):

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)"

L257: The estimation of bulk density should be described in more detail

REPLY: The equation has been added and the reference changed, the current reference is accessible and reports the equation we used originally from Leonaviciute, 2000, which was not accessible (L166-167):

Originally: "was estimated using a pedotransfer function (Leonaviciute, 2000), corresponding to eluvial deposits considering both the soil texture and organic carbon content"

Changed to: "was estimated using a pedotransfer function ($BD = 1.70398 - 0.00313 \text{ Silt} + 0.00261 \text{ Clay} + 0.11245 \text{ Organic carbon}$, Abdelbaki, 2018), corresponding to eluvial deposits"

L259 "0.03 to 0.6" Please add unit also here

REPLY: Sorry for the oversight. The units have been added

L287: Can you estimate average evaporation and a water balance from the d-excee data? Would be nice

REPLY: we can try an approximation, but it will be rather qualitative. The climate is a cold desert and evaporation signal is very biased. We will fully respond later on to this comment.

L301: Please report mineral P content in addition to percentage

REPLY: done

L303/4: Please report percentages of total P in addition to P content data

REPLY: The information has been added

L321: should read: "Nutrient" instead of "Nutrients"

REPLY: Done

L325: should read: "total topsoil N concentration"

REPLY: Done

L348: Should read: "precipitation events" instead of "precipitations"

REPLY: Done

L377: Important: These environments are much more humid. See my specific comment #2

REPLY: We modified the whole paragraph (L420-424).

Originally: Unlike these studies, along the Chamser Kangri chronosequence the pH decreased only slightly, most likely because of less acidic inputs from rainfall and a slower colonization by vascular plants, which prevented the rapid dissolution of primary apatite (Lajtha and Schlesinger, 1988).

Changed to: However, these environments are sensibly more humid than the Chamser Kangri forefield. As reported by Prietzel et al., (2019) for polar cold arid soils, the weathering of primary P minerals like apatite is strongly retarded by the lack of water, which slows down soil acidification. Along our chronosequence, this effect together with the slow colonization by vascular plants prevented the rapid dissolution of primary apatite (Lajtha and Schlesinger, 1988).

L379: Maybe change to "which slowed down soil acidification, and prevented..."

REPLY: See above

L402: Should read: " Depleted d18Op values have been observed"

REPLY: Modified

L406: Replace " findings" by "soil features" or "soil properties"

REPLY: Done

L413: Contributions (of what?). Please specify

REPLY: We have changed the title of the section as follows: "Contributions of microbial P turnover and Po mineralization to the available P: short-term P dynamics"

L424: Should read: "in low-sorbing sandy soils" instead of "in a low-sorbing sandy soils"

REPLY: Modified

L430: Should read: "d18Op value" instead of "d18Op values"

REPLY: Modified

L467: Maybe add: (alpine environments) with humid climate

REPLY: Modified as suggested

