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Comment on hess-2022-126

Anonymous Referee #1

Referee comment on "Seasonal variation and release of soluble reactive phosphorus in an agricultural upland headwater in central Germany" by Michael Rode et al., Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2022-126-RC1, 2022

I enjoyed reading " Seasonal variation and release of soluble reactive phosphorus in an agricultural upland headwater in central Germany" by Rode et al. The authors investigated potential delivery flow paths for P during various baseflow conditions: groundwater (GW) discharge, hyporheic exchange through stream sediments, and soil drainage. This case study is valuable for understanding how P in agricultural catchments is hydrologically delivered to streams and buffered along the way.

I think the manuscript needs at least moderate revision to make the story more effective and clearer. Additionally, I am not so convinced that the GW P delivered to the stream is "geogenic" nor that sediment porewaters are not adding any SRP to the stream -- these points needs more nuance.

Main criticisms

Inconsistencies in methods, results, and conclusions lead to discounting sediment porewaters:

- The radon data are used to support conclusions about GW gains within the stream but much remains unclear. What were the radon concentrations in the GW wells? How was the degassing actually determined? Further, if stream turbulence is the key component behind degassing (L198), then why is the degassing of Rn so much greater in the very slow flow of the summer campaign compared to the winter one?

- Given the issues noted here by the authors, it may help to consult the review by Raymond et al. 2012 to set an initial estimate of Rn degassing for this system based on basic stream hydrology information.

- My impression of the Rn data is that flow in the summer campaigns was so slow that the gas transfer velocity for Rn was perhaps dominated by gas diffusion. The authors seem to corroborate this point on L313-315.

- Further, the water level must have indeed been very shallow for the September 2020 event (L313). For this event, using the reported velocity of ~0.07 m/s, discharge of 0.51 L/s, assuming the smallest stream width of 0.33 m (derived from 10 m / 30 as mentioned on L174-175), and further assuming a simple rectangular stream channel, I calculate a stream depth of 2.2 cm! (Relaxing the assumptions above may yield an even shallower depth.)

- Given that the stream was moving this slow and the depth was this shallow, I really doubt that sediment porewaters have such apparently little connection to SRP in the water column. Note that the sampled sediment porewaters 7 cm deep (L225) are relevant, but it's likely the uppermost 1 to 2 cm of the sediment that dominate P exchange between sediments and the water column. I suspect that SRP in the porewaters may possibly be lower towards the top of the benthos due to the oxygen gradient (see Palmer-Felgate et al. 2010 for example) but this still may not completely stop a significant flux of SRP to the overlying water column. It's been observed elsewhere that SRP can increase in summer months and that it's likely tied to redox status of benthic sediments (Smolders et al. 2017 cited in text; L75-79) -- why might this argument not apply in this case study?

- Although it's possible that the more oxic sediments at the very surface should have a stronger sorption capacity than the deeper sediments, there's also the possibility of colloidal P -- generated from below -- bypassing the sorption sites and increasing the SRP signal (Gottselig et al. 2017). (I'm assuming filtered water samples [filter size not stated, 0.45 microns?], were still not small enough to prevent these colloids.) There seems to be enough Fe and DOC in the waters to support this.

- It is inappropriate to treat SRP or DP as conservative endmembers mixing in this system, as text on e.g., L331-335 suggest is the basis for arguing that sediment porewaters are insignificant. A more compelling argument is needed. (Further, the data cited on these lines is from 7 cm deep so the DP there may be even less relevant.)

Only geogenic P in GW?

- I find it surprising that GW P in this predominantly agricultural catchment (receiving regular P applications (L104)) is considered geogenic (paragraph starting L401). It seems that these soils have reasonably high P (L120-122). It is even stated on L125 that fluctuations in soil P "suggests a transport of soluble P compounds to deeper layers". [Note that this sentiment reverses later in the paper on L416-418.] So can we really assert here that there's no agricultural P reaching GW and, later on the flowpath, the stream?

- It seems that true natural reference points for GW SRP (i.e. with no history of agriculture) would be needed to support this -- is this available in the Wriedt et al. 2019 reference?

- I take issue here because it is increasingly acknowledged that many of our agricultural catchments are dealing with P "legacies" which will take decades or longer to remediate even with drastic action. Wrongly attributing P sources can lead to even weaker action and longer times for surface waters to recover, if at all.

- The discussion on L415-417 seems to ignore that N and P behave very differently in their transport; seeing faster movement of nitrate than for P is not surprising and doesn't support the statement on L416-417. In fact, the Dupas et al. 2017 paper cited in text argues this very point (and is summed up in their Figure 7).

- I actually concur with what's said on L426-428: SRP is probably well buffered in the catchment but that means that those sorption sites may slowly leak P to the system, maintaining ecologically relevant SRP concentrations in the stream for a long time.

Other general comments:

Stream description:

- The catchment is described quite thoroughly, but what about the stream itself? Slope, width & depth at time of sampling, morphology type, substrate characteristics, light availability, etc. would be quite pertinent to this study.

- Illustrating on Figure 1 or adding a new subplot with focus on the stream itself to show locations of all the measurements (tracers, sediments, etc.) would be great context.

Data visualization:

- Suggest sticking to the red/blue for summer/winter throughout (e.g. avoid the change in Figure 7)

- Please try to fix the x-axes in the figures with stream distance (m) so that they're similar/more comparable across figures. The aspect ratio for Fig 6 is too wide. The changes in figure styles and dimensions when 'distance from upstream' is on the x-axis makes it more difficult to follow the story across figures.

- Consider combining Fig 2 and 3 to save space. Figure 4 could also be combined with 2 and 3 by showing the observed groundwater level for the study period overlaid upon the prior 10 year average -- just an idea.

- Double y axes in general:

- My preference is to avoid them if possible. It clouds the comparisons between seasons and visual points of data do not immediately map to values on the y-axis (until I re-read the caption to know which is which)
- In some cases, they're entirely unnecessary, such as in Figure 7. (Also, why not just plot both series on log10 ? Having double axes *and* different transformations is doubly confusing -- this applies to both radon figures.)
- If double axes have to be used, I think a simple but very helpful improvement would be to color-code the y-axes text/title with the same red/blue color scheme for the points.

- With all the data available in some of the figures, the summary stats in Tables 1 and 3 aren't necessary and can be removed to reduce clutter; just make references to the stats of interest within text.
- I'm not sure the 3rd subplot in Figure 6 (with net change in SRP flux) is necessary -- it's simple enough to examine the pattern in the actual SRP flux data in the bottom subplot, in my opinion.
- While the log-axes in other figures are more clearly denoted (e.g. Figure 8), it's not very obvious in Figure 9 -- making figure styles more consistent would help here.

Writing and writing style:

- I had forgotten all of Section 3 was results *and* discussion, as there wasn't too much discussion until much later. (The last few paragraphs felt like a sudden 'dump' of discussion.) Perhaps this paper is better suited to separate R & D sections?

- Please streamline the introduction to build its focus up to the study objectives. I think introducing the main sources in points (a) to (d) on L50-54 and elaborating each is a fair way to structure the intro, but it seems that structure was forgotten after the intro had covered point 'c' (sediments, L71-79); L80 onwards breaks with that structure leaving me wondering where the intro was headed. Further, if the intro is going to focus on "SRP mobilisation ... in various headwater compartments" (L50) as the first paragraph indicated, then lead sentences in paragraphs such as on L63 should more clearly follow that thread. I.e., 'SRP mobilisation' should be the common theme throughout and clearly connected.

- Avoid excessive passive voice throughout. E.g., L336-337 could be rewritten to avoid the "were found" and so make the sentence clearer: "At the outlet, concentrations Fe, DOC, dissolved P, and NH4 were greater in the sediment pore water than in the stream (Table 2),..."

- Proofreading for clearer English would improve the paper. E.g., I'd suggest revising the sentence on L273-274 to: "The spatial pattern of SRP flux largely followed the pattern observed for discharge." This keeps the emphasis on the main topic of this paragraph (SRP flux) rather than on 'spatial pattern of discharge' in the original sentence. Another example sentence that could be made clearer/more effective is L56-59.

- Please break up the paragraph on L401-439 (139 lines!). Further, consider incorporating the discussion with the broader literature done here more evenly throughout Section 3.

Specific comments

- L177-178: I'm confused by this sentence. What is the 'time lapse' issue here and why should that matter if you're moving upstream?

- Section 2.2.1: was there any potential for significant sub-daily variation in discharge or was it stable?

- L199-201: it is stated here that there are multiple ways to estimate the radon degassing from the stream -- which the authors described as a "crucial parameter" just above. So... how was this actually determined here in the present study?

- Section 2.2.2: was there any reason for not measuring Rn in the September 2019 campaign? Also, why were sampling locations different from the salt tracer points?

- L344-350: I don't have any expertise with radiocarbon dating but is it really the case that DOC in the stream is millennia old? Could there be more discussion with literature in this section? Additionally, there's no mention here about the stream metabolism involved. If there's enough light, much of the DOC is likely autochthonous for summer baseflow, especially considering the high nutrient availability.

- L354: Can more concrete evidence be given instead of stating "...probably transported by preferential flow paths."

- L402: where in the paper are the 'oxidised groundwater conditions' established? Could this be included in Table 2?

- L432: Please avoid the "source/sink" dichotomy for P and sediment sorption. It ignores the transient nature of sediment P and how, really, sorptive materials in catchments only *buffer* P.

Technical comments

- Please superscript all atomic mass numbers: e.g. ^{222}Rn and ^{14}C; fix subscripts too ("Psat" on L59, "NO3" on L69)

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L30: 'SRP losses' here is kind of ambiguous in terms of the direction of the flux.

- L31: 'SRP-fraction for dissolved P' is unclear.

- L59: 'soil P sorption saturation' on its own doesn't mean greater P mobility unless you refer to soils with *high* P sorption saturation (typically, the saturation is expressed as some sort of *degree*). Additionally, is "Psat" ever used again in this manuscript? If not, no need for a new acronym.

- L69: "NO3" should be defined.

- L75: don't use "molybdate reactive P" if 'SRP" is used everywhere else

- L89-90: suggest moving the list of pathways out of the parentheses as they're quite important

- L90: "locate" instead of "localise"?

- L92: the "gaining- and losing water fluxes" needs to be reworked, avoid the dangling hyphen if no hyphen is used for 'losing'

- L112-114: this sentence doesn't seem to state anything clearly -- what's the message here?

- L122: move the Kistner et al. 2013 reference up one sentence (to align with the "Previous research has..."). Also, no need to give a new acronym for DPS if that's not used again.

- L150: I think there's a zero instead of "O" in the "NO3" here.

- L150: The Dupas et al. 2017 reference here is out of place; save this for the discussion.

- L213-215: Were the probes calibrated on the day of measurement? Please cite a reference for the 'standard methods' for the P analyses and give some note of accuracy and/or method detection limit.

- L217: how was dissolved iron measured? detection limit?

- L268: 'proportion' not 'proportionate'

- L270: "neutral" is an odd term to use here, perhaps switch for "had little net change in discharge"

- L275: perhaps switch out 'gained' for 'contributed'?

- Figure 7: please also add to the caption or indicate on the figure what the dashed line means (L286). And shouldn't this apply to Figure 8 too? Also, please keep the time labels consistent with other plots (i.e. January 2019 and September 2020 instead of 'winter' / 'summer').

- L310, how reliable are the values given here for groundwater given the text on L296? Is some value representing uncertainty (e.g. confidence interval) possible here?

- Section 3.4: edit the title to include "in summer baseflow (September 2020)" as that's crucial context in this whole section.

- L336: make NH4+ more consistent throughout text (replace "NH4"); consider also including the valence for "NO3-"
- Table 2: why is the Fe in the outlet stream sample "n.d." (unsure whether this is "not determined" or "not detected")? Or was it below detection? If the below detection, what was the MDL?
- Table 2: please add pH, dissolved oxygen (or some indication of redox status), conductivity, and temperature here as that would be very helpful context (and seems to have been measured according to 2.2.3).
- L432: should this be 'House 2003'? This reference is missing
- References -- suggest checking all:
  - Kleinman et al. 2009; van Dael 2020 reference is duplicated
  - also some refs are CAPITALIZED
  - LLFG 2021 reference (L104) is missing

References cited

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