Biogeosciences

Discussions

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Interactive comment on "Phosphorus attenuation in streams by water-column geochemistry and benthic sediment reactive iron" *by* Zachary P. Simpson et al.

Zachary P. Simpson et al.

zpsimpso@gmail.com

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We have taken the opportunity to further address the comments raised in referee #2's report, which are summarized as follows: 1.The fact that the geochemical modelling was done in the water and not in the sediment interstitial water where the geochemistry will be very different and the key P reactions are likely to be taking place. The reliability of the modelling is also further in question because of the presence of colloidal Fe-P phases that pass through the 0.45 micron filters. 2. The extraction scheme used does not identify Ca associated P which is highly relevant to the modelling 3. The key finding that P sorption is most closely associated with amorphous Fe is not really new

or insightful in this case.

In this process, we have refocused the paper via major revisions and so do not go into detailed changes to the text.

Broadly, we have more carefully treated the topic of Ca cycling in streams and have included new data (an estimate of authigenic Ca-P phases in sediments) to support our discussion, following concern raised in referee #2's report. We balance the themes of Ca and Fe cycling more carefully and make Fe cycling a more apparent theme. Most importantly, we more clearly identify the novel finding of our study: that despite being much more sorptive due to greater poorly crystalline Fe oxide content, streams with sediments with high P sorption capacity actually had greater (not less) DRP. Overall, we think this discussion has forced us to sharpen our points made in the paper and think the paper has greatly benefited as a result.

1. The fact that the geochemical modelling was done in the water and not in the sediment interstitial water where the geochemistry will be very different and the key P reactions are likely to be taking place. The reliability of the modelling is also further in question because of the presence of colloidal Fe-P phases that pass through the 0.45 micron filters.

We make effort to constrain our discussion to the quick hyporheic flow paths (very upper few cm of the benthic substrate). While deeper hyporheic waters – where geochemical and nutrient changes relative to the water column would be most pronounced – are generally important, they require more difficult sampling designs and would target much slower flow paths (i.e., low rates of exchange with the water column).

Having said that, we do note more clearly how previous research has shown, for example, calcite deposition/dissolution in streams: such mineral formation creates deposits on the upper benthic substrate (gravel, cobbles, leaves, etc.) but may be incorporated into interstitial sediments over time.

While the likely presence of Fe colloids which passed our conventional 0.45 micron filters does bias equilibria regarding Fe phases, this bias does not affect Ca or other mineral equilibria. As a check, we ran a sensitivity analysis (data not shown) where input Fe concentrations were cut in half before entered into PHREEQC: only Fe phase results changed (e.g., ferrihydrite SI's) while others (e.g., calcite, hydroxylapatite) remained unaffected.

Related to this point, we moved much of the discussion regarding geochemical equilibria out of the main text and into the supplementary material. This has helped to focus the results and outcomes of the study.

2. The extraction scheme used does not identify Ca associated P which is highly relevant to the modelling

We initially chose the Jan et al 2015 scheme because of our interest in Fe oxides and P sorption, while the focus of the study does lean more towards Fe now, we agreed that this point is relevant to the discussion around Ca-P cycling.

Hence, we took the opportunity to measure an authigenic Ca-P phase as suggested by referee #2. Using freeze dried sediments we had stored, we applied a modified SEDEX procedure to generate this P fraction (termed acetate-P, inline with how the other P fractions are termed according to their extractant). Additionally, we measured the following HCl-P step: the sum of acetate-P and this SEDEX HCl-P agreed very well with the original HCl-P data (see attached figure).

The acetate-P fraction is discussed in detail in the text. Notably, we think this fraction overestimated authigienic Ca-P, due to organic matter content (which has been observed by others cited in text). But, the fraction did appear to relate to P sorption capacity (along with Fe oxides), possibly related to carbonates (like calcite) providing some reactivity. Unfortunately, few methods exist currently to examine authigenic Ca-P phases in stream sediments.

3. The key finding that P sorption is most closely associated with amorphous Fe is not really new or insightful in this case.

We had not fully reasoned through our dataset which made this point the most important to address. Of course, it's thoroughly documented that poorly crystalline Fe oxides are strongly P sorptive and we do not wish to make this a key finding. Rather, we revised the manuscript to focus on the unexpected finding that, for streams with permeable sediments, greater ASC (P sorption capacity) did not translate into lower DRP concentrations but instead was associated with increases in DRP. We think this is a critical observation, which forces us to think more deeply about the (bio)geochemical cycling of Fe in streams. We have reframed our discussion regarding this key finding and think the story is clearer and more effective for it.

We thank referee #2 for these comments.

Fig. 1.