

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

### **Anonymous Referee #2**

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With apologies for my late review. With interest I have read this manuscript, in which the authors explore P retention/precipitation mechanisms in New Zealand streams with contrasting underlying geology (alluvium, bedrock, sediment). The authors combine geochemical modelling based on analysis of dissolved chemistry of stream waters with chemical sediment analysis (Fe, P fractionation) to infer the likelihood of mineral precipitation and to determine P species in the sediments. The authors find that sorption onto Fe minerals (presumably Fe (oxyhydr)oxides) play an important role in P retention in sediments that consist mostly of recalcitrant Fe and P phases. The paper is generally well-written.

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I do find it difficult to fully appreciate the storyline in the paper. The introduction goes into some detail regarding eutrophication and P attenuation and the potential role of sediments. Then, quite suddenly it is mentioned that "therefore" (why?) the New Zealand streams in the Canterbury region have been investigated, because they "cover[] a variety of geologies, land use, and stream characteristics". Because of the heavy emphasis on eutrophication and attenuation in the paper, it would be good if these topic are touched upon in relation to the research area. At the moment, the two seem disconnected.

My second main points regards the balance between data and modelling. I like geochemical modelling as much as the next biogeochemist, and I think it is a very useful tool to explore the likelihood of certain precipitation mechanisms, and the validity of experimental findings. Here, I wonder about a few aspects of the approach. The authors use geochemical modelling with the stream data as input to investigate potential precipitation reactions in the stream bed material, with special emphasis on Fe(-P) and Ca(-P). The results and interpretation for Fe are, as the authors themselves mention, unreliable and probably related to measuring colloidal Fe-P phases that pass the 0.45  $\mu\text{m}$  filters (L327-335). Then, the authors also use stream chemistry to assess the likelihood of Ca-P precipitation. I wonder whether the overlying water is representative for the chemistry of the interstitial water, where mineral formation would occur? In many aquatic systems, there are large chemical differences between interstitial water and overlying water, resulting in large differences in saturation state with respect to relevant minerals. Given the emphasis on the role of hyporheic exchange, I wondered how this would work here. Is this also of relevance for the investigated stream sediments, or do the authors have good reasons to assume stream water is representative for all water in the system?

The authors use an extraction protocol (NaOH, BD, HCl) that is not very suitable to investigate authigenic Ca-P phases in the sediment. The HCl extraction removes large amounts of P that was supposedly associated with recalcitrant, geological apatite. I find

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the investigation of the possibility of Ca-P formation in the stream beds rather poorly developed with geochemical modelling of stream water and not interstitial water, and chemical extractions insuitable to explore authigenic Ca-P formation. The uncertainty around apatite exists throughout the paper. In the abstract, the authors mention that apatite does not occur in those streams. Then, in L304 it is mentioned that Ca-P formation is a best a secondary mechanism for P removal. Those are quite contrasting statements, and illustrate for me the unclear and unsatisfactory way in which Ca-P precipitation is deal with in the paper.

The main finding of the paper then appears to be that Fe (oxyhydr)oxides play an important role in P retention in these streams, and that reactive Fe abundance is a function of geology of the stream bed. In L362 and further, the authors then introduce literature from the field of Fe(II) oxidation and the resulting formation of a range of P-bearing Fe species (citation of the work of Senn et al. 2015), which seems quite out of context in this story as Fe redox cycling seems not to be a part of it. If it is, then the hyporeic zone is a very different geochemical zone altogether and using the stream water to explore mineral formaion makes little sense... To me, this is all a bit symptomatic of how bits and pieces of geochemistry are used in hypothetical and sometimes inappropriate ways, while there is relativey little robust data (solid-phase Fe and P fractionation, geochemical modelling of the stream water) to really pinpoint the processes governing P cycling and retention in the stream beds. The fact that poorly crystalline Fe (oxyhydr)oxides are important in P retention is very well-established, and therefore I have my doubts whether the findings in this contribution provide enough novel insight. The authors mention that this is the first time that the extraction potocol of Jan et al. (2015) is used, but that novelty is of limited relevance to me, especially as I do not think much understanding on P burial in the stream beds is gleaned from it.

Lastly, nothing is really done with the findings. As mentioned, in the introduction it does not become clear what relevance the understanding of P retention mechanisms in the investigated streams has, and in the discussion and conclusion it does

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not become apparent what the implications of the findings are. The findings fit with well-established concepts of Fe-controlled P mobility, but there is no link to the situation/future/management of the investigated streams.

Overall, this reviewer is left wondering whether the identification of a well-established P retention mechanism in New Zealand streams, while the finer details of P burial are obscured because of limited data and dependence on uncertain geochemical modelling, warrants publication in BG. Especially as neither the context for studying this area, nor the implications of the findings, are very well-developed.

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