Referee Comments to HESS-2014-207: ”Iron oxidation kinetics and phosphate immobilization along the flow-path from groundwater into surface water”

Overall evaluation:

The manuscript deals with the important subject of cycling of P and Fe in a groundwater-surface system. It is clearly very relevant and original research, and I would recommend publication in HESS, though some “major revisions” remain to be carried out, regarding i) data analysis methodology and ii) manuscript structure, art work and text clarity and conciseness. This is elaborated under “general” and “specific” comments below, which I hope the authors will perceive as constructive; they are indeed meant to help improve the manuscript.

The manuscript more specifically deals with the attenuation and oxidation kinetics of groundwater iron (Fe) compared to the attenuation of phosphorous (P) along the flow path from groundwater to surface water in a low-land catchment (the Netherlands). The water samples are collected to represent i) groundwater residing in the aquifer near a ditch, ii) groundwater discharged directly as seepage into a specially constructed “reservoir” in the ditch or as drain water into separate containers, and iii) discharged groundwater mixed with drain water at two downstream surface water sampling points: the subcatchment and the catchment. The reservoir is cleverly designed to mimic, with respect to water level and residence time, the conditions of the ditch, while at the same time allowing a determination of the residence time, as well as to separate drain water from other water sources, the dominant being groundwater seepage, and minor components being overland and interflow. Also the seasonal variation of Fe and P along with pH of groundwater, reservoir water and drain water is presented. The observed iron oxidation rate in the reservoir is compared to predictions of Stumm and Lee (1961). The attenuation of P is then simulated using the same model, but with allowance of P to adsorb to the iron precipitate, according to the Dzombak and Morel (D&M) surface complexation model. A secondary modelling approach assumes, instead(?) of the D&M model, the formation of an ideal solid solution between amorphous Fe oxide and strengite.

General comments:

1. The model for Fe oxidation rate is applied with *average* pH (and temperature and pO_2) while the kinetics are in fact non-linearly dependent on pH (Eq. 1). For example, using Eq. 1, the amount of oxidized Fe over, say, two days at pH 7 would be much less than the amount of Fe oxidized during one day at pH 6 plus one day a pH 8, all other parameters fixed; the vast majority of the Fe in this example would be oxidized during the one day at pH 8. This makes direct comparison of models and observations (Fig. 6) somewhat difficult. To this one may add the non-linear isotherm for phosphate adsorption to iron oxides. The error thus introduced in the model prediction must be addressed thoroughly by the authors, and the manuscripts conclusions

reevaluated accordingly. This is my only major concern regarding the manuscript; everything below is minor. Some elaboration and suggestions on this regard follow here:

Because pH and pOH are log values, it would be more correct to use in Eq. 1 the average of $[OH^-]^2$ (average of ‘OH^- activity squared’) instead of a value arrived to via an average pH of pOH.

The sentence on p. 6651 l. 26-28 indicates that the reason for the simplification is the unknown Fe_i. However, temperature and pH *are* known so it is a pity to reduce *their* informative power just because Fe_i (and pO_2) is not known. For each data point in Fig. 6, it is actually possible to model a point for comparison, using the known pHs and temperatures of the preceding days during a “points” transit time. This manuscript would be very much improved, if the authors create a figure/figures with model predictions including all known information. The figure(s) could be showing the modeled values (CSTR with and without geochemical reactions) along one axis and the observed values along the other axis. The unknowns (Fe_i and pO_2) could be changed over a reasonable range to display in the new figure some sort of “confidence field”.

2. The authors need to adapt a clearly defined terminology for “surface water”, “groundwater”, “reservoir water” and “ditch water”. For instance, in p. 6650 l. 12 the term “surface water” apparently means “reservoir water”; in other places (e.g., Fig. 2) “surface water” refers specifically to water sampled at the “catchment” and “subcatchment” sampling points. In my opinion, the moment groundwater has entered the reservoir it is to be considered as “surface water”; albeit I do acknowledge the complication that tube drain water is not included in the reservoir.

3. Related to the above: The authors should be more clear about the scope. I see some difference in studying the P retention *in surface water* as compared to *during exfiltration* to surface water or *along the flow path from groundwater to surface water* (the latter in my view is also solely before the groundwater enters the ditch). An example is the first sentence of the abstract (p. 6638), but other examples are p. 6640 l. 25 and p. 6641 l. 3-4. With the sampling points used, the authors are both capable of making conclusions about Fe and P retention *along the flow path from groundwater to surface water*, and about Fe and P retention *at increasing flow distances (or “reaction times”) downstream the in the catchment*. The differences should be made clear and could be utilized more actively in the interpretation.

   The title could be changed to comply with the above changes, e.g. to something along the lines of “ Iron oxidation kinetics and phosphate immobilization *during exfiltration of anaerobic groundwater and in surface water*”.

4. Could the authors please provide in the manuscript more detail of the models used, including the solid solution model. It is for instance unclear if the solid solution model used in combination with the surface model, as might be perceived from p. 6654 l. 26-29.

5. The sections 4.5 and 4.6 contain mainly literature review on subjects where the authors have presented little if any data from the present study to compare with. I suggest the two sections to be either omitted (to make room for other improvements) or rewritten and combined (together with parts of section 4.4) into a shorter “implications” section.

6. When it comes to flow direction, quite a lot of deviation from the general flow direction can happen over the 20 m distance from the groundwater wells and to the ditch/reservoirs. Therefore, the hydrogeology and hydrology, including groundwater head distribution, needs to be better described in the text and Fig. 1 needs some improvement. Especially since some effort is done discussing which well represents groundwater arriving to which reservoir (cf. p. 6646 l. 4-5). For example, Van der Velde et al. (2010)’s similar figure is much better. On the other hand, if some discussion on the relation between groundwater well observations and individual reservoir concentrations is omitted, then a thorough description of hydrology/hydrogeology may not be needed.

7. Quite a lot of speculation of what is going on in tube drain 3 is presented, without substantial supporting data (e.g., p. 6650 l. 6-9). I suggest this speculation be reduced to increase focus on the very many other interesting subjects of the study.

Specific comments:

8. p. 6638 l. 2: *r* missing in *through*.
9. p. 6638 l. 24-27: Please clarify whether the term *particulate phosphate* as used here covers still mobile or immobilized phosphate. As I recall, no original data for mobile particulate P is presented in the manuscript, so perhaps conclusions on this regard should be left out from the abstract.
10. p. 6639 l. 12: Please clarify if they infer a difference the term *particulate bound phosphate* and the term *particulate phosphate* used in the abstract. If the same thing is meant, I suggest using the same term for clarity.
11. p. 6640 l. 1: Could the authors please consider not introducing the term *iron oxidation process*. In my opinion it will not help improve clarity in the text. The term *oxidative precipitation of Fe(II)* (used shortly below in l. 14) describe the same thing and is better in my view.
12. p. 6640 l. 7-9: Could the authors please provide a reference for the statement to be valid specifically for *lowland catchments*?

13. p. 6640 l. 13-19. The authors closely cite Spiteri et al (2006) to argue that Fe oxidation rate is controlled by pH more than by pO_2 and that a pH increase in mixed freshwater (pH 5.7) seawater (pH 7.9) resulted in a seven-fold Fe(II) oxidation rate increase. The citation is correct a little bit confusing: the seven fold increase reported by Spiteri et al. is the result of increase in pH of just 0.4-0.5 pH unit which take place at initial part of the pH gradient in Spiteri al.'s modelled cross section. An increase from pH 5.7 to 7.9 would increase the rate by about 50000-fold. I suggest the authors save space by just citing Spiteri et al. for the fact that pH is a more controlling factor than pO_2, and then just make reference to Eq. 1 to explain why (OH^- activity is squared, pO_2 is not).
14. p. 6641 l. 4-5: I suggest the authors delete the second *experimental*, because only the field set-up is experimental, not the catchment.
15. p. 6642 l. 10 (and elsewhere): *in-stream* could be replaced by *in-ditch* for improved clarity.
16. p. 6643 l. 9: Could the authors please elaborate on how the pH and *t*emperature (not *T*emperature) were carried out. For instance, if a flow cell was used...?
17. p. 6643 l. 21: I assume that *concentrations* should be replaced by, e.g. *oxidation kinetics.*
18. p. 6643 l. 22-23: The authors can omit *homogeneous* (cf. Vollrath et al., 2012) and *in laboratory systems* (because laboratory systems are very different from each other).
19. p. 6644 l. 8: If k in Eq. 2 is the same as K in Eq. 1, please consider using the same case (either k for both or K for both).
20. p. 6644 l. 20: …*an* ideal solid solution…
21. p. 6647 l. 8: *ditch water* or reservoir water?
22. p. 6647 l. 9-14: The author's discussion of the extent of oxygen saturation should be moved to the Discussion (since no data are available to back up these considerations) and merged with the part on p. 6652 l. 11-17. Also, the authors should provide references to support their statements. For instance, the present formulations does not seems to acknowledge that O_2 concentrations must be controlled by a balance between the rate of O_2 consuming processes such as Fe(II) oxidation, respiration, and organic matter degradation, and O_2 supply by diffusion and photosynthesis.
23. p. 6647 l. 12: …93% of *the* time period.
24. p. 6647 l. 21: Please rewrite; *reservoir volumes* appear twice.
25. p. 6648 l. 4: replace *felt dry* by *went dry*.
26. p. 6648 l. 23: I guess the authors mean the OH^- *activity* rather than *concentration*.
27. p.6648 l. 13: I suggest the authors use the phrase *consistent with* instead of *indicating*, because the observation mentioned does not indicate where the removal takes place. This might be partly alleviated by presenting the supporting data, namely Fig. 7, in the Results section.
28. p. 6649 l. 6: Please consider replacing *changes* by *increases* to improve clarity of the text. Also replace *of surface water* by *from surface water*.
29. p. 6649 l. 8-10: Please move to Results section.
30. p. 6649 l. 17: …degassing *of* groundwater with a pH *of* 6.16…

31. p. 6649 l. 17-21: Please comment on how this compares with Fig. 4?
32. p. 6649 l. 24 (and elsewhere, including Fig. 6a+6b+caption): Please make sure that to distinguish correctly between *mean transit time* and *transit time.*
33. p. 6649 l. 26: The authors may consider to replace *at moments on which* with *when.*
34. p. 6652 l. 18: The authors might consider moving the statements about *microbial Fe(II) oxidation* down to p. 6653 l. 4.
35. p. 6654 l. 5-6: The authors did not measure particulate P, so they cannot make conclusions regarding whether lost dissolved P is particulate (and hence quite mobile in my terminology) or adsorbed to immobile surfaces or precipitated.
36. p. 6654 l. 7: *depleted* means totally "totally gone" in my word book (but alright, English is not my native language; I don't think neither P nor Fe became *depleted*.
37. p. 6654 l. 9: …black and blu*e…*
38. p. 6654 l. 12: …of *a* solid solution…
39. p. 6654 l. 17, first word: replace *de* by *the*.
40. p. 6654 l. 20: …prec*i*pitation…
41. p. 6654 l. 23: Delete *the* after *The.*
42. p. 6655 l. 17-18: Please clarify whether the *reduction of the Fe(II) oxidation rate* and the *increased inflow* took place in winter or summer for ease of reading.
43. p. 6655 l. 21: I believe the figure reference should be to *Fig. 2c* and not *Fig. 3*, right?,
44. p. 6656 l. 1: Please clarify the scale under consideration: e.g., do the authors mean the *sediment-interface* of a grain or mineral.
45. p. 6656 l. 3-4: Please rephrase sentence.
46. p. 6656 l. 12-14: To me it is surprising that only three times as much P (units of e.g. mg/kg sediment?) was found in the "Fe oxide ring", compared to unaffected surrounding soil, if this zone is thought to be continuously P retarding. Could the authors please elaborate on how this makes sense?
47. p. 6656 l. 16-17: No data for the amount of Fe-oxides flocs created or their contribution to the suspended sediments is presented. If I am wrong, the authors are encouraged to make the data much more visible.
48. Fig. 4, caption: Please replace *groundwater* with *reservoir water*.
49. Fig. 5, caption: …*inside…* (not insight).
50. Fig. 6: Isn't it the *mean transit time* on the *x*-axes?