

Reply on review of our manuscript HESS-2014-207 "Iron oxidation kinetics and phosphate immobilization along the flow-path from groundwater into surface water" by Søren Jessen

First of all, we would like to thank Søren Jessen for his effort for thoroughly reviewing our manuscript and his valuable comments which we will take in full consideration in improving our paper. Our replies to his comments are listed below. The Specific comments on which we do not reply were agreed upon anyway and will be processed in the revised manuscript.

General comment

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 at 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

It is true that we modeled the Fe oxidation rate with a non-transient pH value and that in the real world the pH might change during the Fe oxidation process, where it will be buffered by the alkalinity. As the kinetics are non-linearly dependent on pH this influences the Fe oxidation rate during the oxidation process. In this, we agree with the reviewer. For reasons described below, the objective of our model calculations was not to reconstruct the individual Fe measurements in the reservoirs but to compare the range and annually average trend of measured Fe concentrations with increasing transit time of the water within the reservoirs with model scenarios. Therefore, we performed three model scenarios representing a typical summer situation, a typical winter situation and an annually average situation with their accompanying pH values (resp. 6.2, 6.6 and 6.4) and other input parameters. The results are plotted together with observed concentrations against the transit time.

We agree with the reviewer that modeling of the individual Fe measurements followed by a comparison of measured data points and modeled data points would be the ultimate model goal. Ideally, physically-based distributed models are applied and all parameters are independently obtained in field application of transport models. In a previous study (Van der Grift & Griffioen, 2008) we argue that this can seldom be reached in field studies considering water quality. In fact, this can only be reached for systems that are rather homogeneous in their spatial characteristics, have a temporally constant input, and where a limited amount of processes is operational. If this is not the case, calibration of process parameters may be applied to improve the model performance. A problem with calibration is that non-unique calibration solutions may exist even for these relatively simple field systems or that there are no objective calibration criteria. Another kind of approach is based upon use of best available information using independently estimated or measured

parameters whether or not combined with a sensitivity analysis. We use this approach to model the Fe oxidation (and P immobilization) process as function of the reservoir transit time and compared the 'statistics' of the dataset with measured values with typical model scenarios. To our opinion the modeling exercise at our experimental field can best be carried out according to this approach for the following reasons: 1) the Fe_i and P_{O_2} spatial and temporal variable and not exactly known; 2) the pH value is known at time of sampling but is probably transient during Fe oxidation; 3) there is some uncertainty in the calculated transit time due to uncertainty in reservoir discharge and reservoir volume measurement. We are sure that it is possible to reconstruct the individual Fe measurement points by modeling with a good match between model predictions and observations by adjusting the Fe_i and P_{O_2} in a reasonable range (the Fe concentrations in the groundwater ranging between 0.2 and 45.5 mg.L⁻¹). However, we don't see added value of this kind of model calculations above our approach Using "best available information", that is even based on fundamental kinetic parameters

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.

Regarding the use of the average pH vs. the average of the $[OH^-]^2$: The reviewer is right that we used the average of measured pH values as input instead of the average of $[OH^-]^2$ as input for the model. PHREEQC is used to calculate the $[OH^-]^2$ from a given pH to deal with the temperature dependency of the dissociation constant of water and the ion strength. For representing a typical summer, winter and year average situation we prefer to use a typical pH value instead of an average $[OH^-]^2$. We as well calculated the average pH based on average $[H^+]$ from measured pH values. These values (6.17 for winter; 6.53 for summer and 6.31 for the year) slightly deviate from the values that we used in the manuscript (6.19 for winter, 6.60 for summer and 6.36 for the year). We will follow the reviewer's suggestion and plot the lines for average pH based on the average $[H^+]$. One may realise that the differences in Fe oxidation rates are minor.

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.

Strictly, the "reservoir water" is, as the reviewer suggests, surface water. To avoid confusion between the reservoirs, and the sampling locations at the sub-catchment and catchment outlet we prefer to use terms "reservoir water" for the reservoirs and "surface water" specifically for the sub-catchment outlet and the catchment outlet sampling points. Then it is indeed better to avoid the term surface water for other situations like p. 6650 l. 12. In these cases it is better to use the term ditch water. We will recheck the manuscript and revise when needed.

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 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".

We agree with the reviewer that this might be confusing. The scope of the manuscript is (bio)geochemical processes affecting Fe and P concentrations, and therefore P retention, during flow from groundwater into surface water and not something like P retention downstream a catchment due to sedimentation and resuspension of particulate P. We deliberately chose the words 'into surface water' in the title instead of 'to surface water' to point out that we consider the processes in the surface water as well. We will check if this is consequently done throughout the manuscript and revise when needed.

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.

We will follow this request.

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.

These sections describe as the reviewer points out 'implications' of our study that are not supported by data. To our opinion these implications are a valuable part of the discussions. We do support the suggestion of the reviewer and will rewrite this into a 'implications' section of the discussion

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.

We agree with the reviewer that the groundwater flow can be quite complex in this part of the field. Although it might be interesting, we do not aim to do a sophisticated study of the groundwater flow over the 20 m from the wells to the ditch. The groundwater flow in the field is approximately from northwest to southeast (see fig 5 in Rozemeijer et al., 2010). Therefore, we just state that it is conceivable that the difference in measured Fe concentrations between the reservoirs can be attributed to differences in Fe concentrations within the field and that the variation of Fe

concentrations between the different wells and the general flow direction within the field is consistent with the high Fe concentration in reservoirs 2 and 3. We will improve Fig. 1

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.*

The objective of discussing the data from our tube drain (especially drain 3 where the redox change occurs) is that the tube drains are an important route of groundwater flow into surface water and this topic lies within the scope of our study. We want to point out that the domain where a major part of the Fe oxidation takes place can shift in time from the soil to the surface water (after discharge to the ditch). For our field site this has, surprisingly, minor implications for P in drain water. Like the reservoir water, P concentrations of the tube drain water were always low, also during periods of high Fe concentrations. The dynamics of P in the drain water is consistent with that in the reservoir water.

Specific comments

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.*

Although our model calculation point to a rapid turnover of dissolved phosphate to a precipitated Fe(III)-phosphate type of solid during oxidation of Fe, we only collected a single Fe-oxide sample from a tube drain (p. 6653 l.20) This sample had the P/Fe ratio comparable with the groundwater. So, we agree with the reviewer that this conclusion is not thoroughly supported by measured data. Therefore we used the words '*seems an important geochemical mechanism*'. Moreover, we agree with the reviewer to distinguish in terminology between "particulate" and "precipitated" (specific comment 35.) and see this as a valuable comment. We will use *precipitated phosphate* instead of *particulated phosphate* in the revised manuscript.

References

Rozemeijer et al, 2010. Integrated modeling of groundwater-surface water interactions in a tile-drained agricultural field: The importance of directly measured flow route contributions. WRR 46.

Van der Grift, .B and J. Griffioen (2008) Modelling assessment of regional groundwater contamination due to historic smelter emissions of heavy metals. Journal of Contaminant Hydrology, (96) 48-68.

Van der Velde, Y., J.C. Rozemeijer, G.H. de Rooij, F.C. van Geer, H.P. Broers (2010) Field-scale measurements for separation of catchment discharge into flow route contributions Vadose Zone Journal 9 (1), 25-35.