

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 Steeve Bonneville

First of all, we would like to thank Steeve Bonneville for his effort for reviewing our manuscript and his valuable comments which we will take in full consideration in improving our paper. Our replies to his addressed issues are described below.

- 1) *The preservation of the samples from oxidation.* We indeed did this in the field directly after filtration by acidification with  $\text{HNO}_3$ . We agree with the reviewer that Fe colloids will go through the 0.45  $\mu\text{m}$  filters and dissolve in the acid media. So, our measured Fe concentration may partly (for the drain water and reservoir water samples) or largely (for the surface water samples) be attributed to dissolved Fe(III) colloids. For the surface water samples taken at the sub-catchment outlet and catchment outlet we discussed this on p. 6651 l. 3-11. The Fe concentration of the surface water samples ranges around 1 mg/l. This value range that is commonly found in (oxygenated) surface water in the Netherlands. For example, Fe concentration in filtered samples in the FOREGS database for the Netherlands ranges between 0.014 and 0.787 mg/l (Salminen et al., 2005). The Fe concentrations of the anaerobic drain water and reservoir water during winter time exceed this value range by an order of magnitude or more. Combined with the observation of the decrease of 'dissolved' Fe concentrations in the continuum groundwater to sub-catchment/catchment outlet this leads us premise that a large majority of the measured Fe concentration in the drain water and reservoir water consist of Fe(II). We agree with the reviewer that this in not addressed properly in the manuscript and we will update the field procedure description and discuss the likeliness of dissolved Fe(III) colloids attributing to a small extent to the measured Fe concentrations in the drain water and reservoir water in the revised manuscript.
- 2) *Assume all the dissolved iron to be Fe(II):* This is in line with the previous issue and we will describe this better. The measured Fe concentration data in Fig. 6 may be (partial) dissolved Fe(III) colloid, especially the low concentration range below 1 mg/l. Therefore, our reported oxidation rate might indeed be overestimated slightly. This issue will be discussed in revised manuscript.

Following nitrate patterns from groundwater to surface water doesn't have much added value for our situation. The nitrate concentration in the (Fe-rich) groundwater that exfiltrate to the reservoirs, is very low. As a consequence the nitrate concentrations in the reservoirs are low as well. However, the nitrate concentration in the shallow groundwater can be fairly high (up to 100 mg/l in uppermost groundwater in some parts of the field). This groundwater is predominantly discharged to the ditch via the tube drains and does not end up in the reservoirs. At the sampling locations of the catchment outlet the nitrate concentrations ranges between 1 and 80 mg/l. This is mainly due to discharge of shallow groundwater via the tube drains (Rozemeijer, et al., 2010)

- 3)  *$p\text{CO}_2$  pressures of the groundwater:* these kind of values are common for groundwater in the Netherlands (Griffioen et al., 2013). Water with a  $\text{pH} = 6.4$  and  $\text{HCO}_3 = 140 \text{ mg/l}$  (which is very common as well) has a  $P_{\text{CO}_2}$  of 0.059 atm.

- 4) *Autocatalytic oxidation of Fe(II)*: we will pick this up. I'm interested in the opinion of the reviewer about the conclusion of Vollrath et al. (2012) that the original rate law of Stumm and Lee (1961) was already influenced by surface catalysis and, therefore, not strictly represent homogeneous Fe(II) oxidation. If this is true, and I'm correct, it does not matter for the oxidation rate if the reaction is homogeneous or autocatalytic.

#### References

Griffioen, J., Vermooten, S. & Janssen, G.J.A. (2013). Geochemical and palaeohydrological controls on the composition of shallow groundwater in the Netherlands. *Applied Geochem.* (39), 129-149. Doi: 10.1016/j.apgeochem.2013.10.005

Rozemeijer, J.C., Van Der Velde, Y., Van Geer, F.C., Bierkens, M.F.P., Broers, H.P. Direct measurements of the tile drain and groundwater flow route contributions to surface water contamination: From field-scale concentration patterns in groundwater to catchment-scale surface water quality (2010) *Environmental Pollution*, 158

Salminen, R, Batista, MJ, Bidovec et al (2005) *Geochemical Atlas of Europe. Part 1: background information, methodology and maps.* Geological Survey of Finland, Espoo