

## ***Interactive comment on “Iron oxidation kinetics and phosphate immobilization along the flow-path from groundwater into surface water” by B. van der Grift et al.***

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This is an interesting study dealing with the important issue of groundwater geochemistry. In particular, this field study aims to elucidate the influence of Fe(II) oxidation on the immobilization of dissolved phosphorus in surface waters during exfiltration of anaerobic groundwater. Understanding the process controlling the mobility of P is of great interest for the readers of HESS as excess P in surface water is a primary cause of large scale eutrophication. Having collected a multiple year-long dataset of the geochemistry of their experimental catchment, the authors demonstrate using a simple modelling approach that Fe(II) oxidation, and consequently the P dynamic s

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are strongly impacted by the water temperature and water discharge of their drains (strong seasonality). During winter due to low temperature and larger discharge, Fe(II) oxidation take place in the surface waters while in summer warmer temperature a low discharge, inducing longer residence time favors oxidation in the reservoir. The authors back their interpretations with different modelling scenari corresponding to the different season and process involved Fe(II) oxidation in the immobilization of P (i.e. surface complexation vs. co-precipitation), the latter being favored. Having said that, the authors should address some issues. First of all, it would have been good to indicate how the water samples were preserved from oxidation by O<sub>2</sub> after collection in the field: are the water samples being acidified for instance – this is not indicated in the manuscript? If not, this is a problem as there is likely oxidation and precipitation of Fe oxides in the tube. This can decrease the dissolved Fe<sup>2+</sup> and their calculation of O<sub>2</sub>-oxidation rate. If there is indeed acidification right after after sampling , the 0.45 μm filtration is a bit lacking, to my point of view, Fe colloids which are likely present in the drain water are going through and to be later dissolved in the acidic media. The conditions of the sampling and some concerns about potential drawbacks of the sampling methods used here should be added to the manuscript. Another point, it seems that authors assume all the dissolved iron to be Fe(II) which is problematic. Some Fe(III) can be complexed by humic acids, for instance, and therefore the reported oxidation rate would probably slightly overestimated here. Similarly, it would have been judicious to follow nitrate patterns (I guess it could be fairly high in this environment), as nitrate reduction coupled to Fe(II) oxidation mediated by bacteria can be a significant pathway of Fe(III) colloids formation and P immobilization (?). It would have been interesting to see these points raised during the discussion about Fe(II) oxidation. I am not an expert in CO<sub>2</sub> in groundwater but I am puzzled the value reported for the groundwater pCO<sub>2</sub>, 0.056 atm. This seems very high (tome at least). Is this the normal range of pCO<sub>2</sub> groundwater? Any chance of siderite – Fe(II)CO<sub>3</sub>- precipitation under those conditions? A last remark, concerning the Fe(II) autocatalytic oxidation onto Fe(III) oxyhydroxides surfaces. The authors claim it is not important because this processes occur at pH > 7 (their

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average pH is between 6.2 - 6.4) and cite a rather old paper (Sung and Morgan 1980). Since the 80's, there have been a lot of work done on this and a little bit bibliography would have reveal that Pedersen et al. (2005) 69: 3967 in *Geochimica Cosmochimica Acta* have shown that the Fe(II) can interact with Fe(III) oxyhydroxides surface and can be oxidized at pH 6.5. Similarly, the electron transfer between dissolved Fe(II) and structural Fe(III) can occur at the surface of Fe(III)-bearing clay mineral such as smectite (see Schaefer, M. V.; Gorski, C. A.; Scherer, M. M. Spectroscopic evidence for interfacial Fe(II)-Fe(III) electron transfer in a clay mineral. *Environ. Sci. & Technol.* 2011, 45, (2), 540-545)). So I suggest the authors to moderate their conclusions on Fe(II) oxidation, several chemical and microbial processes can occur which may oxidize Fe(II). Overall, this is a solid contribution which is generally well written (expect some typos here and there) and I would recommend for publication in HESS with major corrections.

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