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Interactive comment on “Reduction of ferrihydrite with adsorbed and coprecipitated organic matter: microbial reduction by *Geobacter bremensis* vs. abiotic reduction by Na-dithionite” by K. Eusterhues et al.

Anonymous Referee #2

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General comments Interactions of hydrous Fe oxides and organic matter have been recognised as important controls on numerous processes in soils and aquatic environments. One major research focus during the last two decades was on stabilisation and accumulation of organic matter upon association with poorly crystalline mineral phases, such as ferrihydrites. In turn, work done during the 1980s und 1990s also showed that the surfaces of organic–mineral associations differ strongly from those of pure minerals, which causes different sorption and colloidal properties. Ferrihydrites tends to form in environments with organic-rich solutions. Some of these environments

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are also characterised by changes in redox conditions. Consequently, associated organic matter may not only be stabilised but could also become involved in the reductive dissolution and transformation into other minerals of ferrihydrite. Astonishingly, few studies addressed that topic so far. The presented, therefore, deserves attention and careful consideration. In general, the manuscript is well organised and the presentation of results and the discussion meet high scientific standards. Conclusions and implications are justified by the results. The overall experimental design is also well done; however, there could be a serious methodological flaw, which I hope the authors can address (see below). Considering the overall quality of the work and given that the authors can address the mentioned issue, I think the presented study would be an excellent contribution to the field.

Specific comments: Major concern: My major concern is the method used for preparation of ferrihydrite. Producing ferrihydrite from FeCl_3 requires careful control of pH to avoid undesired formation of akageneite as a side product. A standard method to produce pure ferrihydrite uses $\text{Fe}(\text{NO}_3)_3$, as done in the present study. Was that a good idea? I doubt. I am no specialist; I just have basic understanding of redox processes. However, a brief literature screening revealed *Geobacter bremesis* is Fe(II) oxidising and nitrate reducing species but can also oxidise organic compounds using either Fe(III) and nitrate as terminal electron acceptors. Could it be that some of the results relate to different contents of nitrate in the different organic–mineral associates? Could it be that the co-precipitated samples tended to larger contents of nitrate than those formed by sorption? Nitrate-richer systems would tend to less strong Fe(III) reduction, right? Also, could the presence of nitrate explain the re-oxidation of Fe beyond day 17 of the microbial incubation? The IR spectra clearly indicate the presence of nitrate in the organic–mineral associates but did the authors attempt to determine the contents? Did they monitor the nitrate concentrations in the incubation solutions? Finally, did the authors monitor the redox potential during the incubation? That could give indications of the possible role of nitrate in the different systems. In short, can the authors rule out, estimate, or at least rate possible effects of residual nitrate? I feel that

this could be crucial for the judging the study.

Minor concerns: The study also addresses possible mineral transformation during incubation. The topic, however, has not been addressed in the introduction, and so, is poorly justified. I recommend introducing the topic in greater detail. The forest floor material used is a mixture of Of and Oh (consider using Oe and Oa instead; these terms are more common in English). Why not one single horizon? The most logic setup would have been using only the Oh (Oa) horizon, which is the horizon immediately overlying the mineral soil. Could it be that the composition differed from previous studies due to different portions of the two horizons? And why was sample dried but not extracted fresh? Air-dried samples tend to give water-soluble organic matter of a composition rather different from that in fresh samples. Could it be, an extract for a fresh Oh (Oa) horizon would have given more electron shuttling compounds? Is possible to add a short explanation for using *Geobacter bremesis*? Sorption and co-precipitation experiments were carried out a pH 5 but incubation experiments at pH 7. Why? The higher pH in the incubations may favour desorption, depending on the loading of organic matter. The released organic matter may have become an additional carbon source and may have been involved in complexation of Fe ions. I am a bit wondering; the authors cared for phosphate as a potential desorbing anion but not for pH. Also, the incubation media contained HCO_3^- , which interacts with ferrihydrite as well and may also favour desorption of organic matter. Determination of Fe^{2+} was done using the phenanthroline assay, which fails in detecting small Fe^{2+} concentrations and is not always truly reliable. Did the authors consider using the ferrozine assay? The text, especially the introduction, contains long and complicated sentences, which can be shorted without loss of information by omission of repetitive phrases and the use of a more active voice.

Technical corrections Please avoid abbreviations; they are kind of jargon. Please consider a shorter title. Please consider replacing expressions such as “reactivity towards reduction” by “reduction”. p. 6041, l. 5–6: Consider changing the sentence into “Here,

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we investigated 2-line ferrihydrite, ferrihydrite with adsorbed organic matter, and ferrihydrite co-precipitated with organic matter for microbial and abiotic reduction of Fe(III).” p. 6041, l. 6–7: Consider dropping the sentence “As a surrogate ... forest floor”. It has little meaning. p. 6041, l. 18: Consider replacing “... when blocked by OM” by “... by attached organic matter”. p. 6041, l. 19: Consider dropping “... beside Fe(II) accumulation ...”. p. 6041, l. 19–20: Note, mineral-bound organic matter is not a mechanism but may be a factor. Consider replacing “... a further widespread mechanism to slow...” by “... a factor in slowing ...”. p. 6041, l. 24: Consider replacing “Because” by “Due to”. p. 6041, l. 25–26: Drop “it has been assumed that”. p. 6042, l. 1–4: Try to shorten; consider writing: Organic coverage may result in surfaces properties strongly different from those of the original oxides, with consequences for aggregation, mobility, and solubility. p. 6042, l. 5: Replace “frequently found” by “common”. p. 6042, l. 6: Replace “... which usually forms aggregates of only nanometer sized ...” by “... usually forming aggregates of nanometer-sized ...”. p. 6042, l. 13: Consider replacing “... so that coprecipitated Fhs are assumed to develop ...” by “... and so coprecipitated Fhs tend to ...”. p. 6042, l. 16: Consider replacing “widespread” by “common”. p. 6042, l. 17: Consider replacing “towards” by “to”. p. 6043, l. 7–8. Replace “reactivity” by “reduction” and omit “toward reduction”. p. 6043, l. 9: Omit “Fh reactivity towards”. p. 6043, l. 19: Replace “compounds” by “chemicals”. p. 6045, l. 21: Replace “checked” by “monitored”. p. 6046, l. 22: Consider replacing “analogue” by “analogues”. p. 6047, l. 9: Replace “Fe-minerals” by “Fe minerals”. p. 6047, l. 11: Replace “modelling” by “fitting”. p. 6047, l. 25 – p. 6048, l. 1: Consider replacing “but a lower content” by “and less”. p. 6049, l. 8: Replace “is” by “for”. p. 6049, l. 11: Consider replacing “Fe reduction kinetics observed during incubation ...” by “Incubation ...”. p. 6049, l. 16: Drop “toward reduction”. p. 6049, l. 17: Consider replacing “For example, in case of AFhA ...” by “In case of ...”. p. 6050, l. 1: Consider replacing “... was ruled out by XPS” by “... can be ruled out based on XPS results”. p. 6050, l. 20–24: Consider differences could be due to the type of organic matter in solution. p. 6051, l. 8: Consider replacing “engage” by “use”. p. 6051, l. 23–24: The idea of weaker bonds becoming

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increasingly involved with increasing surface coverage is no standard concept. Either give reference or explain better. p. 6051, l. 27: “reduce extracellular OM” – could it be that that should read “oxidise extracellular OM”? p. 6052, l. 1: Consider replacing “The often only partial ...” by “Partial ...”. p. 6052/6053: Is section 3.3 really necessary? Consider omission. p. 6053, l. 2: Replace “atoms” by “ions”. p. 6053, l. 3: How do the authors think that Fe ions might compete with OM? The two have opposing charges. p. 6054, l. 8–9: Give a reference to the citation in quotation marks. p. 6054, l. 13: The standard dithionite–citrate–bicarbonate method involves heating and pH 8.3, which might reduce the inhibitory effect of attached organic matter. p. 6054, l. 15: Consider replacing “the reactivity of Fh towards both”. p. 6054, l. 16: Consider replacing “Na-dithionite” by “Na dithionite of ferrihydrites”. p. 6054, l. 17: Consider omitting “which were”. p. 6055, l. 10: Consider replacing “display” by “have”. Figure 2: The caption of Figure 2A is not easy understandable; it obviously a sorption isotherm, with the equilibrium C concentration given on the x-axis. Please, amend accordingly.

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