General Comments

The paper addresses an interesting and important topic and does help to advance geophysics in the field of hydrogeology. It demonstrates that the NMR method is applicable to characterize zones with iron oxides accumulations, being used in well characterization and hydraulics. The manuscript is well written, but especially ant the methods section to lengthy. It would be better to shorten it. The results are well presented. In the conclusion, I would recommend to stronger emphasize the difficulties one would expect to use NMR in the field, in contrast to the lab study presented.

Thank you for the positive feedback. Regarding the shortening we do not agree, please see our response below (response to P3 ff, chapter 2.2 and 2.3). The discussion on expected possible difficulties in the field will be extended in the Conclusions according to the reviewer's recommendation along with a similar recommendation of RC2:

Second, the relaxation analysis in this study is limited to T_1 data, the measurement of which in boreholes and on the surface is time-consuming and therefore often inefficient to date. Besides improving the performance of T_1 measurements, future research activities in the given context will also focus on T_2 relaxation measurements, which are often the preferred choice in practical applications. Considering the NMR relaxation theory, the findings of this study regarding the influence of the iron-coated pore surface on T_1 are expected to be valid for T_2 as well. However, the exact analysis of T_2 data regarding higher relaxation modes is crucial if measured in inhomogeneous $\boldsymbol{B_0}$, because the diffusion relaxation will mask the effect of the modes to some extent. This is expected to be the case for the measurement device used in this study but is also for borehole NMR (e.g. Sucre et al., 2011; Perlo et al., 2013). Moreover, data quality of field and borehole measurements is lowered compared to laboratory data by environmental electromagnetic noise. Future research in the framework of iron-coated soils and sediments will therefore focus on potential approaches to correct the influence of the diffusion relaxation rate caused by external field gradients and to identify and characterise the occurrence of relaxation modes in T_2 data under field conditions.

Specific comments and technical details

The introduction does not capture the current state of the art; most of the literature is outdated and new papers missing.

We do not fully agree with this general assessment. Regarding the literature with focus on the building processes for iron-oxides we will add some newer references. Regarding the NMR-related literature we think that the given references are state of the art with publishing dates up to 2017. However, we do not agree with the general idea that important findings can be "outdated" – only because the corresponding research was made decades ago. Given that these "older" research results are still relevant for our current work, we prefer to consider the corresponding publications directly and to appreciate in this way the work of the corresponding involved research pioneers.

In the methods section the textbook knowledge should be deleted.

We do not agree to avoid references to textbooks. What are these good for, if not for serving as source for comprehensive background information for the interested reader?

XRD data need to be added in the revision in order to proof mineralogy.

The synthesis procedures for ferrihydrite and goethite as applied in this study have been verified many times for decades (e.g. Cornell and Giovanoli, 1987; Janney et al., 2000), so we do not think that it is necessary to provide that proof another time. Moreover, the contents of Fe-minerals in our samples are far below 2 wt-%, so quantitative (and even qualitative) detection of the precipitates via XRD would be at least difficult, if not even impossible.

- *Cornell, R.M. and Giovanoli, R. (1987): Effect of manganese on the transformation of ferrihydrite into goethite and jacobsite in alkaline media. Clays and Clay Minerals 35 (1), 11-20.*
- *Janney, D. E., Cowley, J. M. & Buseck, P. R. (2000): Transmission Electron Microscopy of Synthetic 2- and 6-line Ferrihydrite. Clays and Clay Minerals 48(1), 111-119.*

P2, L1: do not repeat "vital". Please make clear more specific what is "vital" to you, avoid generalizing.

Agreed, in addition to the repetition of the word "vital" in these two sentences, they exhibit some redundancy, anyway. According to the reviewer's recommendation, we'll reformulate the passage including new literature:

They form some of the most important commercial iron ores worldwide but also play a vital role in soils and aquifers. As weathering products, iron oxides control the conditions for soil genesis and degradation (Stumm and Sulzberger, 1991; Kappler and Straub, 2005) and the mobility of nutrients, trace metals, and contaminants (Cornell and Schwertmann, 2003; Colombo et al., 2014; Cundy et al., 2014). Particularly in many tropic and subtropic soils, the building processes of iron-oxide exhibit high temporal dynamics and may change the environmental conditions within a few years, which makes it necessary to further develop measurement techniques to characterise and monitor the corresponding status of soils and aquifers.

New references:

- *Colombo, C., Palumbo, G., He, J.-Z., Pinton, R., Cesco, S.: Review on iron availability in soil: interaction of Fe minerals, plants, and microbes, J. Soils Sediments 14(3), 538–548, DOI 10.1007/s11368-013-0814-z, 2014.*
- *Cundy, A. B., Hopkinson, L. and Whitby, R. L. D.: Use of iron-based technologies in contaminated land and groundwater remediation: A review, Science of The Total Environment 400(1–3), 42-51, 2014.*
- *Kappler, A. and Straub, K. L.: Geomicrobiological Cycling of Iron, Reviews in Mineralogy & Geochemistry 59, 85-108, 2005.*
- *Stumm, W. and Sulzberger, B.: Cycling of iron in natural environments: Considerations based on laboratory studies of heterogeneous redox processes, Geochimica et Cosmochimica Acta 56, 3233-3257, 1991.*

You may want to include the role of iron in nutrient cycling and biology. Please also do not cite several times a textbook like Schwertmann and Cornell. Cite recent research literature.

We'll add additional references on that topic, please see the response on P2L1 above.

P2, L6: avoid self-citation if not necessary. There is nice literature from others. So far, the literature used is not sate of the art. New and important literature is missing completely in the introduction so far. Include this carefully in the revision.

We'll add additional references also at this place in addition to Houben et al. (2003):

- *Larroque, F. and Franceschi, M.: Impact of chemical clogging on de-watering well productivity: numerical assessment, Environmental Earth Science 64,119-131, 2011.*
- *Medina, D. A. B., van den Berg, G. A., van Breukelen, B. M., Juhasz-Holterman, M. and Stuyfzand, P. J.: Iron-hydroxide clogging of public supply wells receiving artificial recharge: near-well and in-well hydrological and hydrochemical observations, Hydrogeology Journal 21, 1393-1412, 2013.*

However, we do not agree to avoid self-citation, if the corresponding references is precise. This is the case here, so we'd like to keep Houben (2003) in.

P2, L13: Sorry, your literature is outdated. I will not comment this further. You need to include the current state of the art. Please invest carefully time to update your paper

We'll add additional references of younger age here:

- *Dippon, U., Pantke, C., Porsch, K., Larese-Casanova, P. and Kappler, A.: Potential Function of Added Minerals as Nucleation Sites and Effect of Humic Substances on Mineral Formation by the Nitrate-Reducing Fe(II)-Oxidizer Acidovorax sp. BoFeN1, Environmental Science and Technology 46, 6556-6565, 2012.*
- *Emerson, D., Fleming, E. J. and McBeth, J. M.: Iron-Oxidizing Bacteria: An Environmental and Genomic Perspective, Annual Review of Microbiology 64, 561-583, 2010.*
- *Geroni, J. N. and Sapsford, D. J.: Kinetics of iron (II) oxidation determined in the field; Applied Geochemistry 26, 1452-1457, 2011.*
- *Larese-Casanova, P., Kappler, A. and Haderlein, S. B.: Heterogeneous oxidation of Fe(II) on iron oxides in aqueous systems: Identification and controls of Fe(III) product formation, Geochimica et Cosmochimica Acta 91, 171-186, 2012.*

- *Pham, A. N. & Waite, T. D.: Oxygenation of Fe(II) in natural waters revisited: Kinetic modeling approaches, rate constant estimation and the importance of various reaction pathways, Geochimica et Cosmochimica Acta 72, 3616-3630, 2008.*

However, as already mentioned above: in our opinion there is no outdated literature, if the corresponding findings are still relevant and to-the-point. Proper acknowledgement to the pioneers of important research is just fair. Therefore, we'd like to keep the older papers in.

P3, L15: please make the goals of this paper after the setting you used clear to the reader
Agreed. RC2 gave a similar recommendation in her general comments. We'll add a passage at the end of the introduction section clarifying our goals:
In this study, we investigate the effects of paramagnetic iron oxide coatings for particularly coarse material. For large pores in the so-called slow diffusion regime, the otherwise linear relationship between relaxation time and pore size is disturbed because higher relaxation modes become relevant (Brownstein and Tarr, 1979; Müller-Petke et al., 2015). As a significant consequence, the common interpretation schemes to estimate pore size and hydraulic conductivity are not valid anymore. Past studies dealing with iron mineral coatings reported the occurrence of slow diffusion conditions during their NMR experiments (Keating and Knight, 2010; Grunewald and Knight, 2011). Our objective is to learn how to interpret NMR data also under these conditions and how to estimate hydraulic parameters from it. Therefore, the goals of this study are:

1. *to investigate the NMR relaxation behaviour as function of the content of paramagnetic iron oxide for large pores.*
2. *to correlate NMR relaxation parameters with hydraulically effective parameters.*
3. *to assess the model published by Müller-Petke et al. (2015) in the context of iron coated sediments, which is the first NMR interpretation approach that considers higher relaxation modes.*

P3 ff, chapter 2.2 and 2.3: please shorten this drastically. This is a research paper and not a student textbook or master thesis. Do not re-state things that can be read elsewhere. If you use formulae in the following, do so if needed for the paper.
It is true, the mathematics in the theory section is reproduction of given knowledge. However, it is not (yet) standard knowledge in geoscience! The basis of this theory was already manifested by Brownstein and Tarr (1979) in the seventies, but their focus was the application of NMR relaxometry in biological cells. Established textbooks on NMR with geophysical background treat the appearance of slow diffusion regimes as exotic behavior with negligible relevance for geomaterials, which might be true for sandstones, claystones, shales, and carbonates – potential host rocks for hydrocarbon resources. (Please remember that geophysical NMR applications were developed for oil exploration in the first place.)

Regarding the growing field of NMR research for aquifer and soil characterisation, we are convinced that pore spaces in the slow diffusion regime are much more relevant, which is proven by many recent experimental research activities (Grunewald and Knight, 2011; Keating and Knight, 2012; Müller-Petke et al., 2015). However, we lack of approaches to treat such behaviour when interpreting NMR relaxation data of soils and sediments. Our study is an important step towards bridging this gap and we feel that it is still necessary to summarise and emphasise the underlying theory.

In addition, the whole bunch of equations in chapter 2.2 and 2.3 is needed to understand and reproduce the data-fitting scheme that we apply and reproducibility is a necessity for scientific papers in the first place.

P7 and 8: you need to add XRD data to show you actually produced ferrihydride and not a mixture of other iron oxyhydroxides
XRD data was not acquired, because the iron contents were too low for a proper analysis. Please see our comments above.