General comments:
This is an interesting paper and addresses the importance of iron oxides on NMR signals, in this case focusing on T1 relaxation. And authors also probed into the relationship between surface relaxitivity $\rho 1$ and iron content. The structure and organization of this manuscript is good, and the presentation of the data is also satisfactory. The authors covered a lot of topical areas: impact of paramagnetic materials, novel NMR relaxation analysis, and so on. I feel a bit lost about the focus and the main findings of this paper. There are couple of other issues and suggestions

Thank you for the positive feedback. Regarding the main objectives of this study, we'll add a clarifying passage in the introduction section (See also the comment of RC1 on P3L15):

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.*

1. Pore size distribution estimation from particle size distribution is not reliable. The NMR mode analysis is based on the assumption of narrow (single) pore, I feel it is difficult to be convinced for this particular experiments as iron oxide precipitation would generate much smaller pores. This is a crucial point as the authors use reff information intensively, including calculating the diffusion regime. The updated reff could significantly alter the results and interpretation. Additionally, surface area analysis (i.e., BET) could help authors answer few ambiguous observations, e.g., the difference in surface relaxitivity between goethite and ferrihydrite.

We agree that estimates of pore size distribution (PSD) from grain size distribution (GSD) are of less plausibility. However, in soil physics it is common practice to use pedotransfer functions to estimate cumulative pore size distributions (=water retention functions) from texture information (e.g. Cornelis et al., 2001; Schaab et al., 2001). Consequently, the general judgement "not reliable" does not hold. Although not relevant for the paper, we want to refer to these publications:

- *Cornelis, W.M., Ronsys, J., van Meirvenne, M., Hartmann, R. (2001): Evaluation of pedotransfer functions for predicting the soil moisture retention curve. Soil Sci. Soc. Am. J. 65, 638-648.* => ***227 citations***
- *Schaap, M.G., Leij, F.J., van Genuchten, M.Th. (2001): Rosetta: a computer program for estimating soil hydraulic parameters with hierarchical pedotransfer functions. J. Hydrol. 251, 163-176.* => ***1459 citations***

Moreover, we do not estimate pore size distributions but a single effective pore size in this study. Estimating effective hydraulic quantities from grain size distributions is a

very reliable and proven concept. Consequently, many geologists have used those approaches for decades. Beginning with pure empirics by Hazen (1892) and followed by many others continuously fine-tuning the basic idea (see e.g. Vukovic and Soro, 1992; Boadu 2000; Chapuis and Aubertin, 2003; Glover and Walker, 2009; and the references therein), the reliability of estimating hydraulically effective measures from grain size distributions has been proven many times. Besides the traditional empirical approach of Hazen (1892), we decided to apply in addition a modern approach with physical background: the approach of Carrier (2003) who includes also the content of the smallest particles in the grain size distribution yielding a more reliable estimate of the effective radius. We think another proof that the principle idea works is beyond the scope of this paper. We just make use of a proven concept to test our results.

- *Boadu (2000): Hydraulic Conductivity of Soils from Grain-Size Distributions: New Models. Journal of Geotechnical and Geoenvironmental Engeneering 126 (8).*
- *Chapuis, Robert & Aubertin, Michel. (2003). Predicting the coefficient of permeability of soils using the Kozeny-Carman equation. Département des génies civil, géologique et des mines, Ecole Polytechnique de Montréal, Montreal, 2003.*
- *P. W. Glover and E. Walker (2009): Grain-size to effective pore-size transformation derived from electrokinetic theory GEOPHYSICS, 74(1), E17-E29. doi.org/10.1190/1.3033217.*
- *Vuković, Milan & Soro, Andjelko (1992). Determination of hydraulic conductivity of porous media from grain-size composition. Water Resources Publications, Littleton, Colo*

We also agree that iron oxide precipitation can lead to small particles. These particles and possibly their intrinsic porosity can be hydraulically relevant if they accumulate and clog the pore throats between the quartz grains. As explained in the Material section, our sample preparation was made with the focus on coating and an iron oxide distribution inside the sample holders as homogeneous as possible. Consequently, the iron oxide coats the surface of the very most samples, whereas additional small particles hardly occur. To support this statement, we'll add the grain size distribution curves as supplement to depict visually the minor amount of iron oxide particles against the predominating quartz grains (please see Fig.X below). As already described along with Fig.7a in the manuscript, only for the samples with iron oxide content > 1 g/kg, the effective hydraulic cross-section, i.e. the effective pore radius, starts to decrease. Even for these three samples, as for the others, the volume fraction of the pore space between few iron oxide particles can be assumed to be negligible. Please remember that our iron contents do not exceed 0.6 % by weight. So, we are convinced that our assumption of narrow pore size distributions holds for all investigated samples.

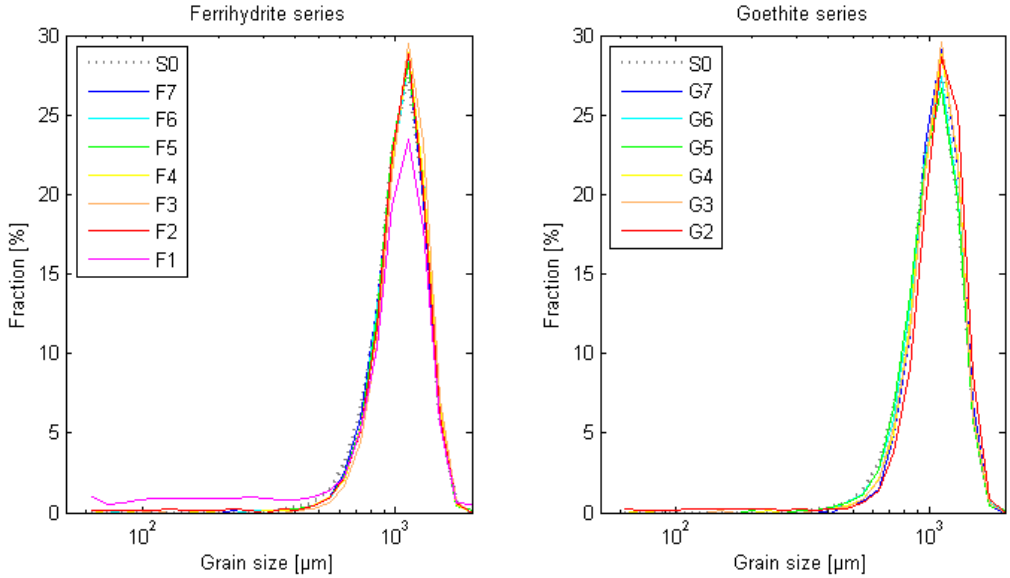


Fig.X: Grain size distributions of sample set A.

We also agree that the BET method is very capable to analyse the surface of iron oxide minerals (see e.g. Houben and Kaufhold, 2011) and it was actually our idea as well to measure it along with this study. However, the surface area of the samples was smaller than the accuracy limit of the device and, unfortunately, the results are of no use for us to quantify the difference between the ferrihydrite and goethite coatings in this case. We can provide the results as supplement by demand. During revision, a note will be added in the section Method and material with comments on our BET measurements:

A part of each sample was also prepared for the determination of the specific surface using the BET method (Brunauer et al., 1938). However, the corresponding results fell below the accuracy limit of the device and are not reliable. Obviously, the contents of iron oxide in the investigated samples are too small and the surface is still dominated by the quartz grains.

2. Can the authors discuss on the choice of coarse grain size particles? Also discuss what if the particles are fine.

For small pores the fast diffusion regimes holds, for which a calibration is necessary to quantify pore-size related information. This case is treated in many publications and corresponding references are already given in the manuscript. Our choice on coarse sand and gravel was due to the fact that there are many open questions on the estimation of hydraulic properties for these materials.

We'll add a passage in the introduction section to clarify the focus of this study (please see the reply on the general comments of RC1). The principle difference between large and fine pores regarding NMR relaxation theory is already discussed in section 2.2. In section 2.3 we'll add a sentence to emphasise once more the conditions for fine material.

If calibration data is given, empirical approaches are available to provide hydraulic conductivity estimates from NMR relaxation data under fast diffusion conditions (Kenyon, 1997; Coates et al., 1999; Knight et al., 2016). As explained above, these conditions appear if the pore sizes and/or the surface relaxivity of the investigated material are small enough.

3. In the study, only T1 relaxation has been studied (T2 was only used to calculate porosity). T2 relaxation is more important and it would be necessary to conduct T2 experiments and analysis. If both T1 and T2 measurements are obtained, more parameters like $\rho 1/\ \rho 2$ can be extracted to provide insights of NMR

monitoring of iron oxides. Why the authors didn't consider using low-field NMR core analyzer instead of one-side NMRMouse?

Agreed, T2 is important as it is certainly the method of choice in borehole practice. However, this is a scientific study on the principle relation of NMR relaxation and pore size. Using T1 measurements for the analysis we can ensure to exclude systematic bias by internal or external gradient fields in B0. These must always be considered when working with T2. Even if using a core analyser with perfect homogeneous B0 (perfect homogeneity is actually not possible), internal gradient fields might occur, especially if working with iron inside the investigated material. It is important at this state to quantify the pore surface related NMR effects first. The analysis of T2 with its specific problems and limitations is the second step, which will be part of our future research. We already have a discussion in the manuscript on the future role of T2 in practical application, see P15L26ff. This passage will be extended in the revision in consideration of RC2's comment No 3 along with similar recommendation of RC1 in his/her general comments:

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 lower 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.

A serious problem of the experiments in this study was the heterogeneity of the samples, as already explained in the manuscript at P7L30ff and depicted in Fig. 5 and in the supplement. Using the NMR Mouse instead of a core analyser, we could be sure to control and verify homogeneity of the iron oxide distribution. Using a core scanner, the entire sample is measured at once. We expected misinterpretation due to overlay of different relaxation regimes inside the sample caused by varying content of iron oxide particles over the sample. The reasoning for using the NMR Mouse instead of a common Core Analyser will be stressed with additional sentences at the beginning of section 3.4:

As decribed above in section 3.1, the stimulated precipitation yielded an obvious vertical gradient in iron oxide content. To identify the corresponding level of heterogeneity and to control and verify the homogeneity of the iron oxide distribution after the final mixing, an NMR device with vertical sensitivity, i.e. the ability to apply distinct measurements at different heights of the sample holder had to be applied. Using a common NMR Core analyser, the entire specimen is measured at once, which can lead to misinterpretation if different relaxation regimes overlap. Therefore, the experiments in this study were realised by a single-sided NMR apparatus (NMR Mouse, Magritek) with strong sensitivity to vertical changes inside the sample (Figure 2).

4. Similar to the first comment, the hydraulic conductivity should be measured in the lab to compare with NMR estimated value (from equation 12).

Direct measurements of hydraulic conductivity should certainly be preferred if possible. However, in this case those measurement would not have been reasonable:

a. The material had to be repacked, which leads to different porosity, packing density and hydraulic conductivity. We assessed those measurement to be of limited value compared to the estimation from the GSD.

b. We worried about material wash out in the corresponding flow experiments immediately after NMR, which would have disabled the entire reference analysis. This analysis (XRF, grain size, BET), on the other hand, was assessed to be more essential than flow experiments.
c. The portion that could have been reserved for flow experiments after subdividing the samples for the reference analysis was much too small to be a significant representative of the sample for determining hydraulic conductivity. In addition, experimental problems are expected regarding the small sample size in combination with coarse material. Due to high hydraulic conductivities and short flow distances, pressure loss in the material is very low and barely measureable. For reliable calculation of hydraulic conductivity, longer flow distances, i.e. larger sample sizes are essential. However, larger samples were not an option due to the requirements for the chemical treatment.

Finally, we chose the effective radius approach as our reference method here. Our future experiments will combine NMR and flow experiments. A note on that outlook will be given in the Conclusions:

Future studies will consider the existence of both different characteristic pore sizes and higher relaxation modes. In contrast to the experimental design used here, these studies must combine NMR and direct hydraulic measurements, because broad distributions of grains can systematically bias the results of simple hydraulic models based on texture (e.g. Boadu, 2000). Corresponding reference analysis regarding the pore size distribution might consist of imaging analysis or pressure-based water retention measurement.

Specific comments:

1. Intro – The significance of studying iron oxide in saturated porous media is beyond the control of negative incrustations. I suggest authors consider making a broader argument of the importance of such study.

Agreed, we'll add a passage in the introduction to emphasise the importance also for soils and aquifers. See also the response on the comment of RC1 to P2L1.

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.

2. Intro – line 16 to 17 on page 2. The introduction of applying geophysical methods seems too sudden. The aim of this study would be better to placed after the introduction of NMR relaxometry. I think the effect of iron oxide (or paramagnetic materials in general) on NMR (surface relaxitivity) needs to further reviewed, and more references should be added here.

Agreed with both points, the passage will be reformulated to introduce the demand of geophysical methods in the given context (to be added after P2L15):

Geophysical field and borehole methods have the potential to comply with this demand. Geophysical methods such as electrical resistivity tomography, electromagnetics, and ground penetrating radar are sensitive to different phases and concentration of iron oxides in the pore space (e.g. van Dam et al., 2002; Atekwana and Slater, 2009; Abdel Aal et al., 2009). The same is also true for the method of nuclear magnetic resonance (NMR). The aim of this laboratory study is to assess the potential of NMR for identifying …

The history of systematic studies on paramagnetic effects on NMR will be added (to be added after P3L5):

Foley et al. (1996) demonstrated for instance that the amount of paramagnetic iron minerals is linearly correlated with the NMR relaxation rate for materials with otherwise identical pore space. Keating and Knight (2007, 2010) found that NMR relaxation is not only influenced by the amount but also by the specific kind of iron oxide mineral. Additional complexity might occur if paramagnetic and ferromagnetic particles accumulate inhomogeneously inside the pore space (Grunewald and Knight, 2011; Keating and Knight, 2012).

3. Basics of NMR – line 16-17 on page 5, I didn't follow how to simplify ξ_n to $(n + 1/2)_2\pi_2$. Can authors further explain (use formula if applicable)/

The quantitative meaning of this equation is not relevant for us, only its quality: the fact that the relaxation in the slow diffusion regime is independent from the surface relaxivity. As described and discussed in section 2.4 along with Fig.1 and in section 4.3 along with Fig.7b, we found proof that this pure analytical/mathematical statement holds in practice. Following the suggestion of RC1 not to overload the paper with mathematics that can be found elsewhere, we refer to the original paper (Brownstein and Tarr, 1979) for the mathematical details in this particular case.

4. Basics of NMR 2.4 – Do the authors assume single dominate pore size in analyzing the data? Can authors elucidate the applicability of Müller-Petke et al., (2015)'s conclusion in this study? For example, what characteristics of the samples used in this study to make this single pore size assumption valid?

A statement on the samples would be misplaced here in the theory section, i.e. before the material is introduced in the section material and methods. However, RC2 is right, the reasoning for the approach of Müller-Petke et al. (2015) appears too late. We'll reformulate the sentence on P5L29 ("In doing so,…") to

As demonstrated in the following section, the investigated sample material in this study allows the assumption of a single r_{eff} to describe the pore space. We accept the limitation on a single effective pore radius for the benefit…

In addition, we'll add a more detailed reasoning at the beginning of section 3.6:

The uniformity coefficient is defined by the ratio of the grain diameters corresponding to the 60- and 10-wt% percentile of the cumulative GSD. For all samples investigated in this study it is very low (i.e. < 5, see Tables 1 and 2), which indicates a narrow grain size and consequently narrow pore size distribution. Thus, the precondition to use the approach of Müller-Petke et al. (2015) (see Section 2.4) to fit and interpret the NMR data is fulfilled. The approximation algorithm,...

5. Basics of NMR 2.4 – Did you do similar intensity and ρr/D simulation and parameter search for T2 relaxation? Does the same conclusion hold?

Regarding the theory of NMR relaxation in porous media, no differences in the T_2,surf (Eq.4) term are expected. Regarding the data quality, on the other hand, one could expect advantages if using T2 for a similar approach because smaller relaxation times are better represented in the T2 data. These signals appear with higher amplitudes against the noise. However, reliable T2 simulation must consider T_2,Diff (Eq.4), which must be identified individually for a given device (=influence of external B0 gradient) and a given material (= influence of internal B0 gradient). This analysis and interpretation is far beyond the scope of this paper, but must be considered in future work on T2 in the given context. Corresponding notes on the outlook on possible NMR application are already given in the manuscript (P15L30), but will be extended in the revised version.

6. Page 6, repeated use of the word 'unambiguous', consider changing some of it to other words like 'nonunique'.

The word is used twice in section 2.4 (one appearance on P5 and one on P6) with more than 20 lines between the two. We do not feel the necessity to change the wording.

7. Basics of NMR 2.4 – Could the authors define what are apparent surface relaxitivity and apparent pore radius? Equivalent value or NMR estimated value? The last sentence of this section 'An important objective of this study is the comparison …' seems to be a bit lost in the context. If this is an important objective, I suggest the authors review the relationship between rapp NMR and reff.

Agreed, a reformulation of the sentence on P6L30 ("They suggested…") is necessary to clarify that these are NMR-estimated measures:

They introduced and defined the apparent surface relaxivity $\rho_{i,app}$ in combination with an apparent pore radius r_{app}^{NMR} to explain NMR relaxation of porous media with narrow pore size distribution. Following their suggestion, we define $\rho_{i,app}$ to include both the effect of an increasing ρ_i and the corresponding increase of pore surface roughness due to iron oxide coating, while r_{app}^{NMR} is considered to be the mean radius of the corresponding capillary. The hypothesis demands…

8. Material and methods – I suggest the authors use a flowchart to facilitate the explanation of the sample preparation and iron coating treatment. Why the authors didn't measure the reff using MICP or imaging analysis? The estimation of reff from particle size is not reliable. If the authors want to compare the reff with rapp NMR, a realistic estimation of reff from analytical characterization is necessary.

We agree that imaging analysis can yield r_eff estimates as well, given that a representative region of the sample is captured, i.e. enough pores are observed to verify the result by statistics. However, there is a conflict regarding the resolution especially if working with coarse material. To satisfy the requirement above, the investigated specimen must be large enough, which comes at the price of lowering the resolution. We expect that it is very difficult to balance resolution and representative sample size for the material in this study and we are sure to get into a serious discussion about the resolution problem, which would be beyond the scope of this paper. This study is focused on the effective quantities NMR can provide in the given context and as explained above we are convinced that the effective radii estimated from the GSD are qualified as reference data.

However, we accept the suggestion of RC2 and will include quantitative imaging analysis into our future research facing the challenge of finding a reliable trade-off between resolution and statistics. A note on imaging analysis will be added in the Conclusions (Please see reply to RC2's general comments No.4).

9. Material and methods – line 18 page 8. 'due to the high proportion of quartz, contents of siliceous iron are generally expected to be very low in fresh filter sand'. Does it mean the siliceous iron content is extremely low due to high purity of SiO2?

Yes, the most filter sands are usually very pure quartz. However, this sentence is irrelevant and will be deleted. Instead, we'll give an additional note on the actual quantification of the amount of siliceous iron in our samples a few lines later:

The difference for the samples of Set A indicates an amount of siliceous iron in the range of 0.5 to 0.7 g/kg.

10. Material and methods – 3.4 why B0 has a strong gradient in *z* direction? Inhomogeneities in permanent magnets? Could you elaborate on this? I'm curious to know.

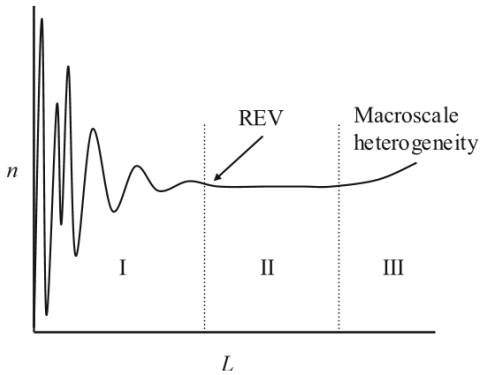
The magnetic field strength naturally decreases with increasing distance to the magnet, therefore the gradient cannot be avoided for the NMR-Mouse. For details please see the original paper(s). The sentence on P9L25 will be extended to clarify: *…to the B1 coil, the B0 field strength decreases with increasing distance to the magnets, which yields a strong B0 gradient …*

11. Results and discussion – 4.1 page 11 line 22 and line 30'the latter exhibits a relaxation time of less than 0.2 s', it didn't seems to be 0.2s to me from the figure. Why coarse material will contribute to uncertainties in porosity estimation?

Reply on P11L22: The relaxation time marks the point on the T2 curve, where the initial signal amplitude E0 is decreased down to E0/e=E0/2.7183, which corresponds to 1.4715 for the data of the pure water in Fig. 4a. At this point, the time axis counts 0.2 s. No changes necessary.

Reply on P11L30: It is an issue of the reference volume (see e.g. Costanza-Robinson et al., 2011): with decreasing sample dimension (L in the figure below), the porosity estimate (n in the figure below) gets more and more inaccurate. The sentence at P11L30 will be reformulated in the manuscript to underline this effect for our experiments more clearly:

The reason for this is the relatively thin sensitive slide of 200 µm in combination with the investigated coarse material exhibiting mean r_{eff} values of 95 to 474 µm (see Table 1 and 2). The inaccuracy of the porosity estimates must be accepted as a natural consequence of the fact that some of the observed pores exceed the z-dimension of the probed reference volume (e.g. Costanza-Robinson et al., 2011).



Source: *Costanza-Robinson, M. S., B. D. Estabrook, and D. F. Fouhey (2011), Representative elementary volume estimation for porosity, moisture saturation, and air-water interfacial areas in unsaturated porous media: Data quality implications, Water Resour. Res., 47, W07513, doi:10.1029/2010WR009655.*

12. Results and discussion – 4.2 What is the scanning interval in your experiments? I thought you use 8 measurements at different depths for each sample, but the data points on figure 5 look much more than 8.

We used a scanning increment of 1 mm for all NMR measurements, which leads to more than eight measurements for the sample holders before homogenisation, which are larger than the sample holders after homogenisation. This will be clarified on P10L11:

For each sample, SR measurements at different heights were conducted using 1-mm steps in range of z = 3 to 15 mm before and z = 3 to 10 mm after homogenisation.

13. Results and discussion – 4.2 ‘This assumption is acceptable because the grain size distribution and consequently also the pore size distribution is narrow for the well-sorted materials studied here’ This statement is not convincing. I would expected a quite broad range (at least bimodal) of pore size distribution as much smaller iron oxide precipitation occurred. Especially authors also pointed out that rapp gets smaller when iron content increased. As I brought up before, the estimation of pore size distribution from grain size distribution is not convincing and the authors need to show evidence of pore size distribution from analytical measurements.

As explained above (see response on the general comments No.1), we …

a. do not share the opinion of RC2 regarding the estimation of hydraulically effective measures from the GSD
b. consider the pore space between the iron particles to be of less importance regarding their content of less than 1% by weight.

Thus, we hold to our interpretation scheme of using r_eff and the corresponding hydraulic conductivity estimates from GSD as reference values to verify the NMR results.

14. Results and discussion – 4.2 Did the authors calculate K using other models like SDR or Coates model? How did it compare to the K estimation using equation 12? Which equations you used to calculate K_{KC} and 2.20 K_{Hz}? Did you actually measure K in the lab for different samples? It is very necessary to do such measurements.First,

The reviewer is focusing on empirical standard models (SDR – Schlumberger-Doll-Research and Coates, 1999) that are normally used for interpreting NMR well logging data. However, these models do not apply here.

First, they work only in the fast diffusion regime, where a linear relationship of relaxation times and pore size is given and every pore is represented by a unique relaxation time. These conditions are excluded for the samples in this study.

Second, these models need a calibration on the surface relaxivity which is expected to change in every sample due to the individual amount of paramagnetic surface coating. That means, the application of these models demands an individual hydraulic-conductivity calibration for each sample, which makes the estimation of the hydraulic conductivity pointless.

Sentences will be added in section 2.3 (Special cases of relaxation) to clarify that these models are reliable only under fast diffusion conditions (see the reply on RC2’s general comment No.2).