Response to review by Susann Henkel.

Original colours in black, author responses are in blue

Review to “Technical Note: Uncovering the influence of methodological variations on the extractability of iron bound organic carbon” by Fisher et al.

Fisher et al. investigated how modifications of the frequently used citrate-dithionite buffer (CDB) extraction for iron-bound organic carbon influence the respective results. The CDB method is widely applied in soil and marine sciences to extract iron (Fe) and co-precipitated or adsorbed organic matter. Despite its common application, the method has some drawbacks that are, according to the authors, often neglected or at least not properly discussed. In this sense, this study reminds me of the recent publication by Hepburn et al. in Chem. Geol.: “The use of operationally-defined sequential Fe extraction methods for mineralogical applications: A cautionary tale from Mössbauer spectroscopy” and the study by Oonk et al. (2017, Chem. Geol.): “Fraction-specific controls on the trace element distribution in iron formations: Implications for trace metal stable isotope proxies“. As in these previous publications, Fisher et al. try to tackle the problem that wet chemical extractions lead to operationally defined fractions that are not entirely specific to distinct minerals. The authors set up experiments where they varied the strength of the chemical extract as well as the composition of the sample that‘s to be leached. They also tested whether a longer duration of the CDB treatment leads to higher Fe and Fe-OC yields. Studies like this are urgently needed to achieve comparability of datasets even though they unfortunately never result in a crystal clear recipe that is to be preferred for all kind of samples. However, this article will make researchers more aware of the shortcomings of the CDB method so that they are put into a better position to judge in which way they should apply it and discuss their data. The manuscript is for the most part well written and easy to understand. The figures and tables are adequate and the discussion is supported by the presented data.

We thank Dr Henkel for their review and agree that the overall importance of this study, and that of the similar studies outlined, is to increase the awareness of the factors which can influence the efficiency of these type of operationally defined chemical extractions.

What is missing a bit is a wider implication of the finding that CDB treatments do not lead to a full recovery of present reactive Fe in any of the tested samples. CDB is not only used for Fe-bound OC, but also for Fe-bound phosphate (see papers by Ruttenberg, Slomp, Kraal) and of course Fe-oxide extractions after Poulton and Canfield (2005), whereby dithionite was recently shown to also extract substantial amounts of magnetite (and clay). This might not be the exact topic of this article, but should at least be mentioned as I feel that it would increase the relevance of this article.

The CBD approach we apply here (per Lalonde et al. (2012)) differs from the method used for Fe-oxides by Poulton and Canfield (2005) both due to being operated at a higher pH and using a bicarbonate buffer rather than acetic acid. We currently cite Thompson et al. (2019) who compares the two different extractions on line 68 as a reference to this *“It should be noted, however, that lower pH extractions are known to be more efficient at extracting the targeted reactive Fe phases if the co-extracted organic compounds are not of interest (Thompson et al., 2019).”* We therefore did not seek to apply our results, showing incomplete recovery of reactive Fe in a pH 7 system, to suggest that this would similarly apply to the pH 4.8 extraction.

We thank Dr Henkel for the suggestion of including the Fe bound phosphate literature for the traditional SEDEX protocol, as this is a more comparable method (circumneutral pH). We accept the point that this could increase the relevance of the paper, so have, in the introduction made reference to these methods.

Line 45 onwards now includes: *"The circumneutral pH CBD extraction has also been used as part of the original SEDEX protocol for the extraction of Fe bound phosphate (Fe$_P$) (Ruttenberg, 1992;Kraal et al., 2012). Although thermodynamically different from the CBD extraction for OC-Fe$_R$ (8 hours at 25 °C vs 15 minutes at 80 °C), Slomp et al. (1996) showed no difference between the efficiency of this extraction and the shortened high temperature extraction of Mehra and Jackson (1958). While Ruttenberg (1992) and Thompson et al. (2019) report 90-100% of synthetic ferrihdyrite is extracted by the CBD method for Fe$_P$ it should be noted that the effective dithionite concentration used here is potentially more than twice as strong than that used for the OC-Fe$_R$ extraction by Lalonde et al., 2012, (1.125g dithionite for 0.5g sediment vs 0.25g dithionite for 0.25g sediment). However, it has recently been shown that CBD is less efficient at extracting crystalline hematite than previously thought, with only 18.4 ± 0.7% of Fe in a hematite sample recovered by Thompson et al. (2019). Further, this inefficiency has been similarly shown in the context of OC-Fe$_R$ extractions conducted at the lower dithionite strength with Adhikari and Yang (2015) reporting only 5-44% of OC was released from hematite-humic acid complexes upon Fe dissolution."*

The authors say that FeR extraction was incomplete for their synthesized sediment samples. I assume that it could potentially also be overestimated in some cases. (At least this is what I often observed and has been described in previous papers.) So my main recommendation would be to revise and complement the discussion accordingly and to expand the "framework" of the discussion a bit further in order to address more readers and demonstrate the real relevance of this nice experimental work. I will give some more recommendations in the following and recommend publication of this study after major revision.

General comments:

There should not be a period after a title. (You wrote e.g. "Abstract.") Titles aren't sentences.

Removed for all titles and subheadings.

The manuscript should be checked for a consistent use of the expressions "concentration" and "content". I recommend reading Tolhurst et al. (2005, Estuarine, Coastal and Shelf Science): "Content versus concentration: Effects of units on measuring the biogeochemical properties of soft sediments". Furthermore, please check the order of references in the text. The cited publications should be ordered according to their year of publication.

Use of "content" and "concentration" have been checked, a number of changes have been made to the use of "concentration", primarily to change this to content when referring to solids (e.g. the content of OC-Fe in a sediment sample). In text citations are formatted according to the journal policy.

Scientific remarks: Line 86-88: "Wagai and Mayer (2007) performed a 16 hour extraction (substituting citrate with weak HCL acid rinses to avoid use of organic compounds), and Patzner et al. (2020) extended to 6 hours." "HCl" instead "HCL". And just a comment: I'm a bit puzzled by this statement regarding citrate. Citrate is added so that Fe-complexes are formed and Fe is kept in solution. I should probably read the paper by Wagai and Mayer, but acid rinses seem critical to me when it comes to comparability of datasets (which is obviously why you investigated it).

Corrected HCL to HCl. Wagai and Mayer use weak acid rinses instead of citrate to try and create an organic free extraction (since the method seeks to measure organic carbon). They say “In our fully inorganic dithionite extraction, we eliminated the citrate to allow measurement of liberated OC, which we compensated by a weak acid rinse of residues following dithionite extraction to redissolve Fe precipitated as acid-volatile sulfides and associated OC.”

We have added the section about redissolving Fe to clarify this in our text. This now reads *“Patzner et al. (2020) extended the CBD extraction to 6 hours and Wagai and Mayer (2007) performed a 16 hour inorganic extraction. In this method citrate, used to complex Fe, was substituted with a weak HCl rinse to redissolve precipitated Fe and avoid the interference of citrate (an organic compound) in OC quantification.”*

Lines 278-281: While 30-40% OC-FeR content is above the average for marine sediments, many samples exist in the 20-30% range. Indeed, the average value for marine sediment OC-FeR composition given by Lalonde et al. (2012) is greater than 20% with individual marine sediments recorded as exceeding 30% OC-FeR (e.g. Equatorial Pacific 0°N, 34.79% (Barber et al., 2017)).” I am, to be honest, a bit confused by these numbers. 20-30% of Fe-OC really seems high to me. I never had such high amounts of reactive Fe. Fe plus bound OC is surely higher than reactive Fe alone, but with dithionite you typically reduce all kinds of Fe oxides including ferrihydrite, lepidocrocite, hematite and goethite as well as (unfortunately) some magnetite. (At least with the Poulton and Canfield method published in 2005.) Nevertheless, by applying this method I never ended up with more than 3 wt% extracted Fe in the sediment out of usually around 6 wt% total Fe including all silicate Fe and sulfides. Please double-check your numbers!

These are two different things, in the manuscript we are discussing OC-Fe$_R$ here (i.e. the proportion of organic carbon bound to reactive iron as a fraction of total organic carbon). This is different to the Fe-OC relationship that the reviewer mentions (the proportion of the iron pool bound to organic carbon), we agree that 20-30% Fe-OC would be incredibly high and this is not something we are claiming to represent. Reference to absolute amounts of Fe in sediment are referred to by wt% throughout the manuscript.

As mentioned above, the usual CDB extraction includes crystalline phases like goethite and hematite that might not be so relevant for OC. I am missing a statement concerning how the (maybe in your case unintended?) leaching of more crystalline phases potentially skews the FeR : OC relationship. The typical amount of highly reactive Fe (amorphous phases) in shelf sediments is, I would say, less than 1 wt% (so by far lower than what you were testing for). So I would therefore be a bit hesitant to transfer the results of your experimental data to real marine sediments and it’s good that you included tests with Antarctic sediments in this study.

Yes, CBD can leach goethite and hematite in addition to, e.g., ferrihydrite, and we refer to this in the now modified section in the introduction by including values for hematite leaching from the Thompson et al., 2019 study. Hematite can play a role in OC binding, so in the same section we refer to the study by Adhikari and Yang on OC release from hematite-humic acid complexes. The reviewer is correct that leaching of Fe phases not associated with OC can skew the OC-Fe$_R$ relationship and this is shown in the Barber et al., (2017) study. We have not previously discussed this in this manuscript as we only include ferrihydrite in our experimental system (in part to get around problems such as these), so leaching of other phases is not directly relevant for this study.

Lines 324-328: “We postulate that freeze drying-induced aggregation of sediment particles could result in reduced Fe extractability compared to non-dried samples since grain size is a known key factor in limiting determination of bioavailable Fe (Raiswell et al., 1994).” I’d actually argue the other way around. I am wondering about the potential differences between grinded and non-grinded natural samples. You typically freeze-dry samples to be able to grind them and make them more homogenous. I would assume that the freeze-drying itself might result in a transfer of Fe from a more reactive into a less reactive pool. But at the same time I would guess you reduce effects of grain size differences or clogging/shielding of grains (coatings) by grinding the samples. Ok. I see that you mention this in the following sentence. (Add a space before “The influence. . .”) As grinding is what’s typically done, I’m not convinced that the aggregation plays the dominant role. I’d rather think that the amorphous Fe compounds aren’t stable during the processing (freeze drying). Would be worth checking whether there is a transformation of ferrihydrite during and after drying...

We have previously shown that the complexes we produce are definitely still 2-line ferrihydrite by XRD of the freeze-dried precipitate in Fisher et al., (2020) so transformation was ruled out as a reason for the difference between Fe recovery from dried and non-dried precipitates. We acknowledge later in the manuscript that grinding is typically performed but to an undefined grain size (“finely ground” or similar), which can introduce error.

Line 329 “*McKeague and Day (1966) similarly report that finer grinding of sediment resulted in an increased extraction of Fe. These findings indicate that particle size is a critical parameter in determining the amount of Fe extracted, however, all methods fail to define what is meant by “finely ground”. This lack of definition introduces an error of reproducibility as particle size is certain to vary with different sample preparation methods and therefore two identical chemical treatments may vary in extraction effectiveness because of physical differences in the sediment sample.”*

We have added a sentence to confirm transformation of the Fe phase did not occur during drying.

“An alternate hypothesis to describe the reduced Fe recovery for dried sediment, i.e., that transformation of ferrihdyrite occurred during freeze drying, was ruled out by x-ray diffraction (XRD) characterisation of the freeze dried phase as 2-line ferrihydrite (Fisher et al., 2020).”

Line 335-336: “The alternate tested method of using wet samples has largely been avoided, with only a few studies (e.g. van Bodegom et al., 2003;Chen et al., 2020) reporting the use of a wet slurry sample in soils and none for sediments.” Suggestion: The alternative method of using wet samples has largely been avoided, with only a few exceptions in soil studies (e.g. van Bodegom et al., 2003; Chen et al., 2020). Your statement is not true when you don’t limit your view to the Fe-OC extraction by dithionite but also consider the many studies focussing on the Fe or P. The Poulton and Canfield (2005) method that includes a similar dithionite step is often applied to wet sediments. Check papers by Natascha Riedinger, Laura Wehrmann and Katja Laufer (2019, Reactivity of Iron Minerals in the Seabed Toward Microbial Reduction – A Comparison of Different Extraction Techniques). The same is true for Fe-P extractions with CDB (Kraal, e.g. 2017 GCA paper). One reason for people sticking to the freezedrying and grinding is that with lots of samples, that’s the only option. I’m thinking of IODP material (usually pretty hard mud rock) or black shales.

We thank Dr Henkel for highlighting these papers, we agree it would be suitable to include these as examples of wet sediment treatments. However, not all the suggested papers actually use wet sediment (e.g., the Kraal 2017 GCA paper explicitly uses freeze-dried "ground sediment of 50 and 100 mg for sequential extraction of Fe"). While Laufer et al., (2019), Wehrmann et al., (2014) and Riedinger et al., (2017) do use wet sediment, these studies all freeze sediment at -20°C which we later go on to discuss has the potential to introduce freeze-thaw aggregation.

We have now cited these studies alongside our use of Arctic freeze-thawed samples.

"Wet thawed samples have been used more widely in the sequential extraction of Fe (e.g. Laufer et al., 2020, Riedinger et al., 2017, Wehrmann et al., 2014), additionally the Arctic sediment sample used in our analysis was similarly subject to freeze-thawing. However, our freeze-thawed sample showed no difference in its recovery for Fe compared to the dried aliquot, indicating no significant effect of the thawing stage."

Lines 370-373: "As we observed incomplete Fe extraction (Fig. 1) for all our samples, a range of CBD extraction times were trialled to understand whether increasing the length of a reaction would increase Fe liberated, as seen for other chemical Fe extractions; oxalate, for example, is known to continue to extract Fe beyond a standard 1 hour treatment (McKeague and Day, 1966)." Okay, but it does not make too much sense to compare the CDB method to the oxalate method, because the oxalate extraction works differently. The extraction is actually catalyzed by dissolved Fe2+. So the longer the extraction continues, the more Fe2+ is in solution and the stronger gets the extraction (well described in Oonk et al., 2017, Chem Geol. and references therein).

This is a fair point, we have removed the reference to oxalate and changed this to reflect the OC-Fe dithionite based studies with variable time and linked this to the Fe-P methods previously added.

"As we observed incomplete Fe extraction (Fig. 1) for all our samples, a range of CBD extraction times were trialled to understand whether increasing the length of a reaction would increase Fe liberated, as seen in some iterations of the CBD method for OC-Fe_R (e.g. Patzner et al., 2020, Wagai and Mayer, 2007) as well as those for Fe_P (Ruttenberg, 1992) ."

Line 415-417: "We suggest that if future studies were to increase Na dithionite addition in the CBD method this should be followed by a similar increase in trisodium citrate to ensure the entire reduced Fe pool is complexed, preventing precipitation of Fe before quantification." I ran some tests with citrate myself with Fe contents that are comparable to natural occurrences and found that it's usually not limiting. The citrate concentration can in fact be reduced compared to original protocols (I tested the Poulton and Canfield method) as long as you work under strictly anoxic conditions (Henkel et al. 2016, Chem. Geol.). Might be a good alternative.

We have added this as an alternative earlier in the discussion where we first mention increasing citrate. Line 303 now includes: *"Alternatively, Henkel et al. (2016) found that a reduced concentration of dithionite is sufficient to fully complex the reduced Fe pool when the extraction is performed under anoxic conditions, which may remove the need to further increase the addition of citrate as an organic reagent."*

More specific technical remarks (sentence structure, typos etc.):

Line 16: I suggest to use "synthesized sample" instead of "sediment".

Changed to synthetic sample

Line 36: Delete “important” before “for water retention” as it is an unnecessary repetition.

Deleted

Line 99: “. . .rapid decomposition of dithionite in aqueous form suggesting, a quick loss of reduction potential. . .” Incorrect comma placement.

Comma removed

Line 118-119: “To achieve this, we mixed the precipitate with a marine sediment ‘carrier’ material as described by Fisher et al. (2020), using the same original carrier sample and similarly treated to liberate OC and inorganic carbon.” Weird sentence structure. In order to make it easier for the reader I suggest to include one or two sentences to what the carrier material is. I guess the original FeR contents are known? It’s fine to refer to the previous publication, but the reader shouldn’t be "forced" to look it up.

Replaced with: “To achieve this we spiked the precipitate into a marine sediment sample from the Barents Sea (water depth 141 m; sediment core depth, 33.5 cm; station B6, E40; cruise JR16006). This sample was ashed (650 °C, 12 hrs) to remove OC and fumigated with HCl vapour to remove inorganic carbon. The resulting carrier material was siliciclastic in nature with a Fe content of 16.33 mg/g.”

Line 126: Replace “A” by “The”.

Corrected

Lines 164-166: “Initial concentrations of Fe in synthetic samples were obtained by digesting ~2 mg of dried sample in 1 mL 12N HCl at room temperature followed by a 10-fold dilution with 1% HCl solution. Further dilutions were made as necessary, dependent on Fe content, using MilliQ water to produce a subsample within the detectable window (1–10 ppm Fe).” I’m not quite sure about the fraction that is intended to be dissolved here. Bulk Fe? I guess it’s okay in case that the synthetic sample does not contain Fe-bearing silicates. As mentioned above it would be good to add what was used as "carrier" for the Fe oxide-OC spikes.

Details on spike content has been added with the previous comment. The digest here is to determine the initial Fe content (i.e., the ferrihydrite we add), 12N HCl is more than sufficient to dissolve the spiked ferrihydrite and any reactive Fe in the synthetic sample.

Add “of the extract “after "10-fold dilution”.

Corrected

Section 2.6 about ICP-OES analyses: Generally (for future), I would recommend using an internal standard for correction of different ionic strengths.

Atomic absorption spectroscopy (AAS) was used for the analysis of Fe rather than ICP-OES in this study.

Line 171-173: “Extraction of Fe was calculated by subtracting the amount of Fe lost in the control experiment from Fe lost following extraction, then subtracting this from the initial Fe of each sample.” The formulation of this sentence seems more complicated than necessary and I don’t fully get it. How about: "The recoveries of the extractions were determined as extracted Fe compared to the initial Fe content." (I suppose you made sure that the carrier sediment that you spiked did not contain any Fe?)

Changed to: *"The recovery of Fe following sample extractions was calculated by subtracting the control corrected loss of Fe from the initial Fe content of the sample."*

There was a small amount of Fe in the carrier sediment, as now detailed in the spiking section of the methods. However, this only makes a minor contribution to the overall Fe pool once spiked and not all of this will be reactive. We have no indication that the baseline Fe content affected any of the results, even if this Fe content was to have an affect it would be the same effect on all aliquots and iterations involving the sediment carrier.

Line 188: ". . .requires a 0.25 g addition relative to 0.25 g of dried sediment sample" Recommend to use "per" instead of "relative to".

Corrected

Lines 191-194: "All samples show incomplete reduction of Fe regardless of Na dithionite addition, with those samples containing the least Fe proving extractable for the greatest proportion of Fe." Unnecessarily complicated formulation. How about: "highest recovery of Fe in samples with low OC-Fe contents".

Changed

Line 199-201: "From this, we can deduce the maximal %Fe in sediment extractable by 0.25 g Na dithionite lies between a 20 and 30% OC-FeR mix, equivalent to 7-10 wt% Fe content in the sediment." I would slightly reformulate the last part of the sentence to not imply that this is total Fe you're talking about. And wouldn't it make sense (for practical reasons) to translate your "20 and 30% OC-FeR mix" into an absolute amount of Fe (e.g. in mmol or mg) that can be liberated?

Added: *"Therefore, assuming a 0.25g sample size, the absolute amount of Fe extracted would be between 17.5 and 25 mg. "*

Also changed wt% Fe to wt% Fe_R to clarify this is reactive not total Fe.

Lines 203-205: This is about LECO data, right? I wonder whether you could avoid confusion by just calling it "extracted OC" or OCFeR. Calling this fraction OC-FeR is a bit confusing as I would intuitively translate it as "OC-bound reactive Fe". But you mean "reactive Fe-bound OC". As for the Fe I assume that your carrier did not contain any further OC?

This is about measuring OC, the LECO data, yes. OC-Fe_R is the fraction of organic carbon bound to reactive iron, not reactive iron bound to OC so the reviewer translation is correct. And yes, the carrier is OC free, this has been clarified in response to a previous comment in the methods.

Line 255-256: "For the four synthetic samples we subjected to dithionite reduction, these differed in composition (7-24 wt% Fe, 20-50% initial OC-FeR content)." Didn't you also have a batch with 100% OC-FeR??? (See Table 2.)

The greater than 50% OC-Fe_R values are only used for the wet vs dry comparison as that is a more mechanistic relationship. In this section (4.1), we are discussing the concentration of Na dithionite used to extract OC-Fe_R from samples so the concentrations are closer to what may be found in a natural sediment.

Lines 256-257: "The concentration of Fe in these samples results in an effective dithionite to (wt) Fe reduction reaction ratio of 1:0.07-0.24." Replace "concentration of Fe" by "Fe contents", "results" by "resulted" and replace "effective dithionite to (wt) Fe reduction reaction ratio" by "effective dithionite to Fe mass ratio".

Changed

Line 261-262: "This has the potential to drive wt% Fe higher in small samples of sediment such as those treated by the method (0.25 g)." Recommend to replace "treated by the method (0.25 g)" by "typically used for the CDB extraction".

Changed

Lines 266-269: "Maximal extraction here is defined as the point from which further addition of Na dithionite does not increase the extraction of Fe beyond the amount of Fe extracted under the previous dithionite addition mass ± error. For example, the 20% OC-FeR sample subject to 0.25 g dithionite is removable for 88.79% ± 3.55 of FeTotal while 0.375 g addition extracts 90.94% ± 3.64; . . ." What is meant by "is removable for"??? Unnecessarily complicated formulation. Use "yields" or "liberates". Delete "beyond the amount of Fe extracted under the previous dithionite addition mass ± error" and add a "further" before "increase". How this is meant is getting clear through your example.

Changed

Line 276: Missing space before 2.69.

Corrected

Line 276-278: "This finding demonstrates that the OC-FeR composition would not be correctly determined following the method of Lalonde et al. (2012) for these OC-FeR rich sediments, and the overall extent of OC-FeR in the marine sediment pool would be underestimated. You can delete the "pool". It kind of implies that you're talking of a specific fraction of the marine sediment, but here you mean the sediment itself (bulk). Why would you limit this to marine sediments? Couldn't you say this is a general outcome of your study no matter which sediment (fluvial or marine or soil) is used? (Now, again, it would be nice to know the composition of your carrier material.) I would write "amount" instead of "extent".

Changed from marine sediment to sample and extent to amount.

Line 290-291: "If the increased strength dithionite treatment increases dissolved Fe beyond the complexing capacity of citrate, then excess Fe likely precipitates out of solution before measurement." This can be avoided when performing the extraction under anoxic conditions (e.g. Henkel et al. 2016).

Added: "Alternatively, Henkel et al. (2016) found that a reduced concentration of dithionite is sufficient to fully complex the reduced Fe pool when the extraction is performed under anoxic conditions which may remove the need to further increase the addition of citrate as an organic reagent."

Line 293-295: "Measurement of OC-FeR extracted for the concentration of Na dithionite at which maximum Fe is extracted showed incomplete OC-FeR loss (Fig. 1)." I would replace "loss" by "liberation" or "recovery".

Changed to recovery

Line 294-295: "The similarity of OC-FeR and raw Fe extraction values indicates that OC and Fe are reductively released from the sediment in comparable proportions, as is expected due to the low molar OC:FeR ratio of the coprecipitate (~0.7:1) ." What is meant by "raw" values? Raw data is typically used in another sense.

Deleted raw

Lines 297-298: ". . .could benefit from using increased strength Na dithionite compared to the 0.1 M treatment currently used." Or shorter: "compared to the conventional 0.1 M treatment".

Changed

Line 308: Replace "have been" by "are".

Changed

Line 309: Replace "defined" by "assessed so far".

Changed

Line 346-347: However, the use of wet sediments is likely to be inappropriate for some analyses or sample sites. Yes! You should add one or two sentences to that. I believe it's for most cases not as if people using these methods are not aware of its shortcomings.

Added: "However, the use of wet sediments is likely to be inappropriate for some analyses or sample sites either due to practical considerations, such as the difficulty in transporting heavy wet sediments, or when there is a need to preserve the sediment profile, for example, protecting anoxic sediments from oxic biological transformations."

Line 354: You can delete the "method" after "storage". "Any storage" is enough.

Deleted

Line 366: ". . .slurry form. . ." Delete "form".

Deleted

Lines 373-375: "Additionally, as previously mentioned, some iterations of the CBD method have been repeated multiple times in succession to extract the full FeCBD pool, but it is unclear whether time or reagent concentration limit full extraction of this pool on the first treatment." By you or others? It's not getting clear here. "Iteration repeated multiple times in succession..." Here you say the same thing twice (or actually three times).

Changed: *"Additionally, in some examples of the CBD method the extraction stage is repeated multiple times for the same sample in order to extract the full* Fe_{CBD} *pool (e.g. Mehra and Jackson, 1958, Aguilera and Jackson, 1953), but it is unclear for these multiple stage treatments which parameter prevents full extraction of* Fe_{CBD} *on the first treatment."*

Line 379: ". . . concluding that an increase in chemical exposure time has no difference on Fe extractability." Replace "has no difference on" by "has not enhanced" or "has no effect on".

Changed

Line 381: "We would perhaps not expect any benefit from increasing the length of CBD treatment as dithionite, . . ." You don't seem to be very convinced by your data. Replace "would perhaps not" by "do not".

Changed

Line 382-383: “. . . with a rapid second order rate constant (K2) of 3.0 (g-molecule/L)-1 min-1 at 79.4 □C, . . .” The unit is written in an unnecessarily complicated way. I guess it should be L/(mol*min)? Please check!

This was originally taken from the, rather old, citation so can be updated. Gram molecules (g-molecule) are equivalent to moles so this has been simplified to 3.0 mol L^{-1} min $^{-1}$.

Lines 421-422: “Freeze drying induced aggregation appears to reduce Fe liberation in synthetic coprecipitates that were freeze dried relative to slurried, however, we were unable to replicate this increased extraction for natural samples.” Suggestion: Freeze-drying induced aggregation appears to reduce Fe liberation from synthetic coprecipitates. However, we were unable to confirm this reduced Fe extraction for a set of natural samples.

Changed

Lines 422-424: “While we speculate this may be due to the use of freeze thawed samples, which can introduce aggregation in itself, it is hard to see a practical implementation of this adjustment for marine sediments due to the difficulty in transport of pristine samples.” Replace “which” by “where freeze thawing”, otherwise your reference isn’t fully correct. (You’d refer to the samples and not the process of thawing.) And I believe you can delete the “in” before “itself”.

Changed

Line 425: Add “the” before “dry weight”.

Changed

Line 427: Period missing after “extraction”.

Changed

Figure 1: I have difficulties understanding your black and blue symbols. Shouldn't the percentage of extracted Fe be equivalent to the extracted OC-Fe? Or is the data behind the blue symbols the LECO-data? Do you really need the separate axis with the different scale??? It's just (at first glance) confusing that e.g. the blue diamond is so much further up the fitted curve. And the offset in "dithionite added" between blue and black symbols (equivalent to maybe 0.1 g) is odd, too.

The percentage of Fe would only be equivalent to OC-Fe if there was a 1:1 OC/Fe ratio. The blue symbols are the LECO data. Blue symbols were originally offset on dithionite concentration to make the symbols easier to distinguish but these can be put back to maintain accuracy. They do need separate axes as they are different measurements (one Fe, one C) regardless of the different scales.

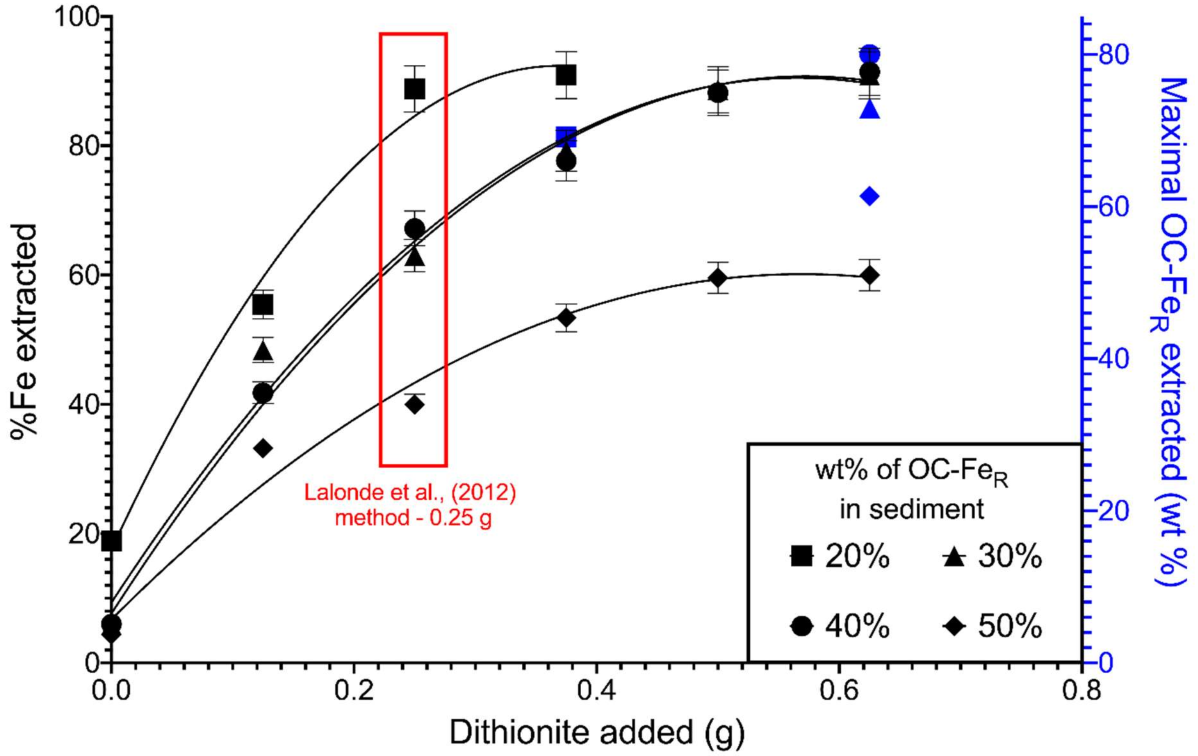

Figure 2: You don’t need 3 different patterns if you distinguish between the different OC contents by different colors (gray scales). So reduce the complexity of this graph by just using 3 colors for the three differing OC batches and filled vs. hatched bars for dry and wet. I would also (for clarity) change the figure a bit so that it doesn’t appear as if the OC-Fe to total sediment ratio was 5% for the lowermost wet batch 3 COOH mix and close to 30% for the lowermost dry batch 1 COOH mix. You know what I mean? Those extractions all belong to the 20% test, right? Figure caption: Colon after “Figure 2”.

Colours have been changed. The y axis represents the original mix of the sample (precipitate to sediment), they are not all the 20% extraction but the 20,40,60,80 and 100% extractions. So the y axis is what was added and the x is what was extracted, added groupings to the y to make it clearer that this is categorical and not continuous data.

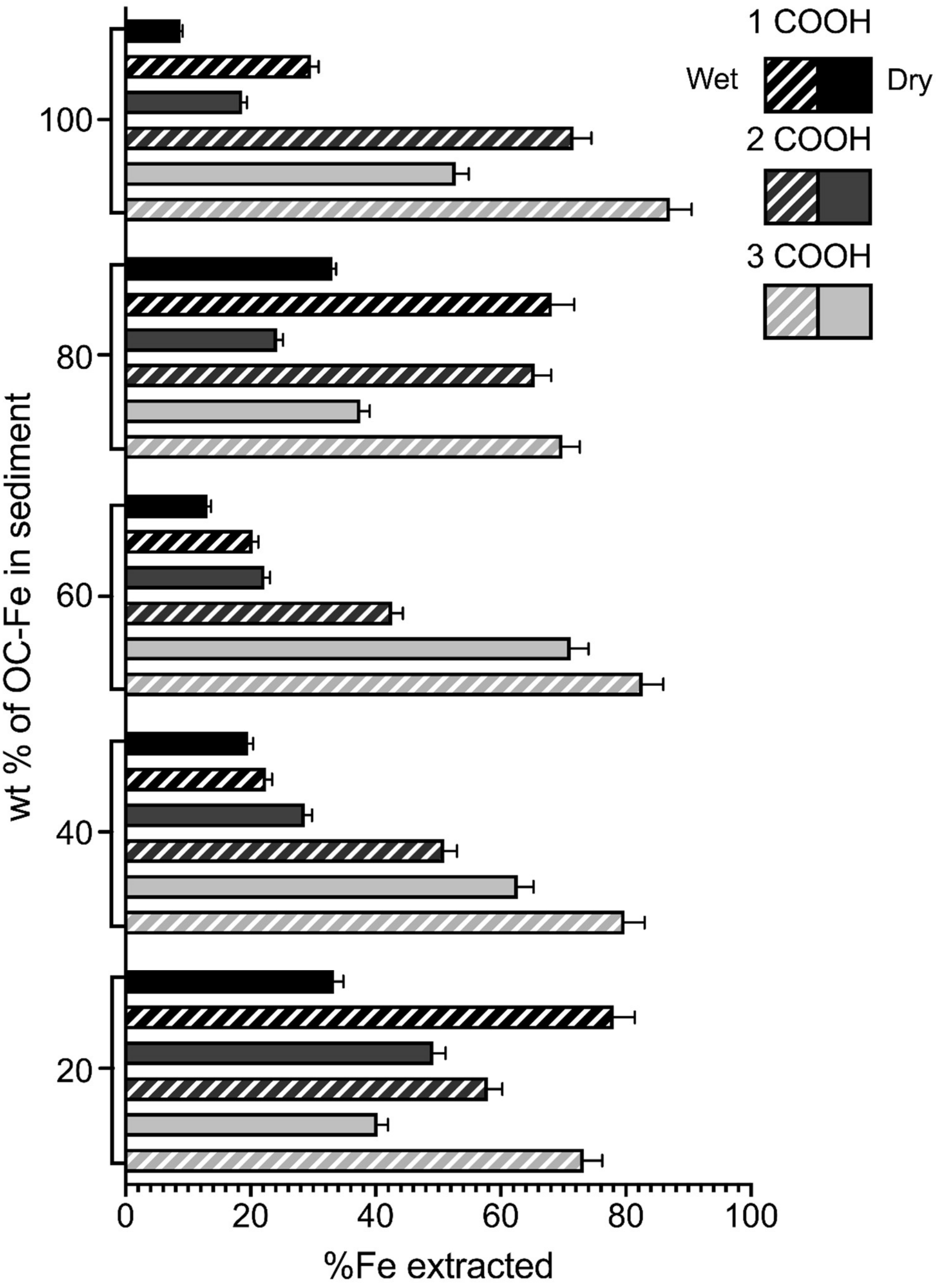

Figure 3: Colon after “Figure 3”.

Added

Table 1: Use format "left-aligned" in the first column.

Changed

Table 2: I find the expression "%OC-Fe:sediment" a bit confusing. I guess you mean % of OC-Fe coprecipitate to total sample". It’s inconsistent because when you write "Sediment (mg)" you mean the carrier only.

Changed to “%OC-Fe in sample”.