Dear editor,

We are glad that you are considering our manuscript for publication after revision. Therefore, we implemented the answers already prepared and submitted for the two referees before in a now substantially revised version of the manuscript. Below you will find the referee comments and our answers again, as well as the marked-up version of the new manuscript.

Kind regards,
Marion Schrumpf
(on behalf of the authors)

We would like to thank the referee for taking the time to read and comment on our manuscript, which will help us improve its clarity in a revised version.

Answers to individual points raised follow below.

Referee 1

The manuscript reports on experiments characterizing mineral associate organic matter using a comparison of "extraction" by NaOH-NaF versus "oxidation" by H2O2. The treatments were coupled with 13C-NMR and 14C dating. The experiments are well designed according to current paradigms of SOM stabilization, but the manuscript requires substantial revision before it might be acceptable for publication.

A revised manuscript will be prepared based on the recommendations an suggestions provided by the two referees.

There are a large number of instances throughout the manuscript where diction and grammar are awkward or incorrect. The manuscript should be deeply reviewed by a native English writer to revise these subtleties.

As recommended, we will adopt the semantic changes suggested by the two referees, and the two native English speaking co-authors of the manuscript will double-check the overall language again for awkward wording and syntax flaws.

The end of the introduction should be restructured to move ln96-104 to the end of the section, where it will serve as a segue to the methods section. That is, I recommend an introduction with the structure: background, problem statement, hypotheses, ways to test them.

We will transfer the description of the methods used to test the hypotheses to the end of the introduction to obtain the structure recommended by the referee.

The hypotheses listed are not hypotheses sensu stricto because they are not testable in the strictest way. That is, they cannot be answer with a simple "yes" or "no". Several hypotheses have multiple conditions or clauses that should be broken into several subhypotheses. I am not necessarily a purist when it comes to these formulations, but when I know this, I typically replace the word "hypothesis", which can be reserved for strict statistical or logical uses, with the word "expectation". All this being said, I do recommend trying to break up the 5 bullets into expectations and outcomes. That is, it appears that some of these so-called hypotheses are actually expectations, which if are true, other conditions would also be true. Others are more contradictory, where if not true then... A clearer, more explicit and deliberate structure for all these expectation will result in better structured results and discussion sections.

We agree having several conditions in one hypothesis hampers simple yes/no answers to whether or not a hypothesis is supported by the data, as the answer could depend on the conditions.

We suggest rephrasing and simplifying the “hypothesis” in the following way:

Based on the literature review we expect that:

1. **extraction in NaF/NaOH releases a weaker bound fraction of total MOC, which is younger than the stronger bound, probably better stabilized residue fraction.**
2. **the proportion of NaF/NaOH-extractable MOC decreases with increasing contents of pedogenic oxides, which form strong bonds with OC.**
3. **the proportion of NaF/NaOH-extractable MOC declines from topsoils to subsoils due to declining OC loading of minerals.**
4. **MOC of soil samples with higher portions of extractable carbon should be younger than MOC with more extraction resistant OC.**
5. **the chemical composition of extractable MOC varies between study sites due to differences in vegetation composition, and thus litter chemistry.**
6. **the chemical composition of extractable MOC changes with soil depths due to declining contributions of plant and increasing contributions of microbial derived OC.**
7. **MOC should be less prone to desorption and accordingly of older ^{14}C age when organic molecules forming MOC have many carboxyl groups that enable strong bonds with minerals surfaces.**
8. **the strong oxidizing agent H_2O_2 removes more OC from MOC than NaF/NaOH.**
9. **oxidizable and non-oxidizable OC should both be older than the extractable and non-extractable OC fractions if the harsher oxidation treatment removes more, and thus presumably better stabilized OC from mineral surfaces, leaving OC residues of even older ^{14}C age behind.**

A few minor points in the methods section:
ln141: filters are normally described at least by their pore-size and sometimes their diameter, not their diameter only.

The diameter was 1.6 µm and this information will be added to the revised version.

ln161-162: The sentence on carbonates is unnecessary and likely the result of copy-paste text because ln158-159 already state that all soils were carbonate-free.

The referee is right that carbonate-free samples were chosen, and the sentence will be deleted in the revised version.

In some instances the order in which results are circuitous and confusing. Perhaps use the "hypotheses" or methods section as road maps for ordering the presentation of results.

We assume that mixing of ideas on the effects of NaF-NaOH and H_2O_2 was possibly confusing. Therefore we suggest to restructure the results section as follows: First, presentation of the extraction efficiency of NaF-NaOH, followed by the chemical composition of the extracts (NMR), and then of the ^{14}C data. Thereafter, presentation of the oxidation efficiency and ^{14}C contents of H_2O_2 treated samples. Finally, a comparison of results of the two treatments will be presented.

I like how the discussion section is structured. It places the results in a clear context. However, I’m not convinced that the results are "surprising", and I find the overall interpretation to be a little off the mark. I did not find it surprising that the proportions (vs."portions" which is incorrectly used throughout the manuscript) were consistent across most soils. This has been previously been observed for both H2O2 (eg, Plante 2014 EJSS) and acid hydrolysis (eg, Paul 2006 SSSAJ). This is one of the problems with chemical extractions: they rarely demonstrate the expected trends in inferred stability. A similar lack in expected trends has also been frequently observed in 14C dates.

The surprising result was not the lack of a trend in H_2O_2 oxidation but the uniform extractability in NaF-NaOH. While the two references mentioned by the referee (Plante et al. 2004?) indeed found similar proportions of soil OC removed by H_2O_2 treatment and acid hydrolyses, others did not. For example, Eusterhues et al. (2005 Organic Geochemistry) showed a strong depth dependence of H_2O_2- or $Na_2S_2O_8$-oxidizable proportions of bulk OC (between 5 and 58% of OC resisted oxidation with H_2O_2) and also Kleber et al (2005 EJSS) found a range of 28-87% for oxidation-resistant OC across different forest subsoils. After all, while studies on OC oxidation and hydrolysis were frequently done before and address rather the inherent chemical stability of soil OM, the focus of our study was on using OC extraction into NaF-NaOH as an indicator of the stability of the bonding between OC molecules and mineral surfaces (which is also why mineral associated and not bulk soil OC was studied). The controls on OC mobilization are therefore not necessarily the same and can be expected to be closer linked to mineral composition and OC loading of minerals, as indicated by previous results from the literature. The same applies to ^{14}C data. Therefore, the focus of the discussion was also on the NaF-NaOH results, while little emphasis was placed on the results of oxidation resistance since not specifically surprising.

We will replace “portion” by “proportion” in the revised version of the manuscript.

So, given that a substantial proportion of the results from this study did not meet expectations, I would strongly recommend reframing the manuscript. It might be much more compelling to more specifically spell out what the conceptual framework (paradigm) is that leads to the expectations outlined. The goal of the discussion would then be to describe where the problems are with either the assumptions etc. in the conceptual framework, or in the methods used to test them. The manuscript currently tries to address the former, but not necessarily the latter. Are NaOH-NaF and H2O2 appropriate tools for probing SOM stability? OR is our conception of SOM stability incorrect?

As the referee pointed out, we had a certain concept about MOC formation, its stability and potential drivers in mind when we started the experiment as outlined in the “expectations”. Many of them were not supported by the data, which can indeed be due to a combination of wrong methods used or because our conceptual understanding needs further refinement. In any case, changing the expectations a postori to make them meet the results is no reasonable way to achieve scientific progress. Instead, the discussion should be used to identify where our conceptual understanding is not in agreement with the results, derive hypotheses for the observed mismatch including potential limitations of the experimental approach, and eventually draw a modified version of the original concept and come up with ideas for further studies. Therefore one could also argue that it is useful if an expectation is not met, because it means that we can learn something from the study that we did not know before.

Nevertheless, one result of our study was that a large portion of MOC could be more homogenous in ^{14}C contents than expected, while only a very small portion has very old ages. Accordingly, different chemical fractionation schemes always remove OC from the same continuum, leaving increasingly old OC behind. Therefore, chemical extractions seem to be not able to isolate distinct homogenous fractions, and other approaches are needed to explain average ^{14}C values and age distributions of MOC as pointed out in the conclusions.

The match between expectations and results that I am referring to is well illustrated in the diction of the subheader in ln344. The use of the word "Missing" suggests it was expected a priori. A more objective and unbiased approach would be to refer to it is "lack of".

A negative statement in the headline will probably always hint at an unexpected result. Nevertheless, we will replace "missing" by "no", which is more neutral than "lack of", which, at least to our understanding, still indicates that something was expected to be there.

I also found it unsurprising that the chemistry of extracted OC was similar across samples and dominated by polar molecules (eg, alkyl). In essence, the experiment demonstrated the solubility of a polar fraction of OM in a highly polar solution. It would not be a reasonable expectation to see non-polar OM (eg, aryl) in such a polar solution, or vice-versa.

We agree that we were extracting the samples in a polar (aqueous) solution and that accordingly most of the extracted molecules are dissolvable in water – which is indeed not surprising given that they were probably transported and transferred to mineral surfaces via the aqueous soil solution. In general, alkyl-C and aromatic C (aryl-C) moieties would be non-polar, while carboxyl groups are polar. In that respect, we could state that it is rather surprising that the extracted fraction was dominated by alkyl-C. However, whether or not a molecule is soluble in water– similar to aryl-C- dependents on the type and number of functional groups attached. It is not possible to infer the solubility or polarity of extracted molecules from their NMR spectra, as these give only information on bond types of elements but not molecules. Therefore, we think that the use a polar NaF-NaOH extraction solution was not the reason for the observed results.

The tables and figures used to report the results are appropriate, though the figures are numerous.

While it is appropriate to report the 1:1 line in Fig7 (modeled vs. measured), I'm not sure why it is reported in Fig3. It seems to me the slope represents the proportion extractable. If I had to guess, the slope would be 0.58 (or its inverse). I'm not sure what it would mean to have the data fall on the 1:1 line in this case.

We agree that a visualization of the different efficiency of the two treatments in removing MOC does not need visualization with the 1:1 line. We will remove it.

I have become increasingly frustrated by the visual and qualitative interpretation of spectral data using a stack of "squiggly lines". While large differences might easily be apparent, smaller, more subtle differences, or large differences in smaller peaks may not be so apparent. Differences among spectra should be tested quantitatively/statistically, perhaps using a multivariate method such as PCA or NMDS.

We agree the simple visual interpretation of the NMR-data from figures is largely qualitative. Therefore the figures were complemented by proper quantification of the relative contribution of C species (see Methods) to total OC in Tables 2 and 3. Since the overall result is that differences were small, scaling them into a PCA or NMDS would possibly lead to an over-interpretation of small differences probably not relevant for explaining differences in desorption or ^{14}C ages, and thus for the topic of this study. Therefore, we do not think that adding multivariate statistics would add further information to our conceptual understanding of MOC stability.

We would like to thank the referee for taking the time to read and comment on our manuscript, which will help us improve the abstract and the overall manuscript.

Answers to individual points raised can be found below.

Referee 2

Overall, I thoroughly enjoyed this manuscript. However, I am concerned that much of the language in the discussion is speculative in nature.

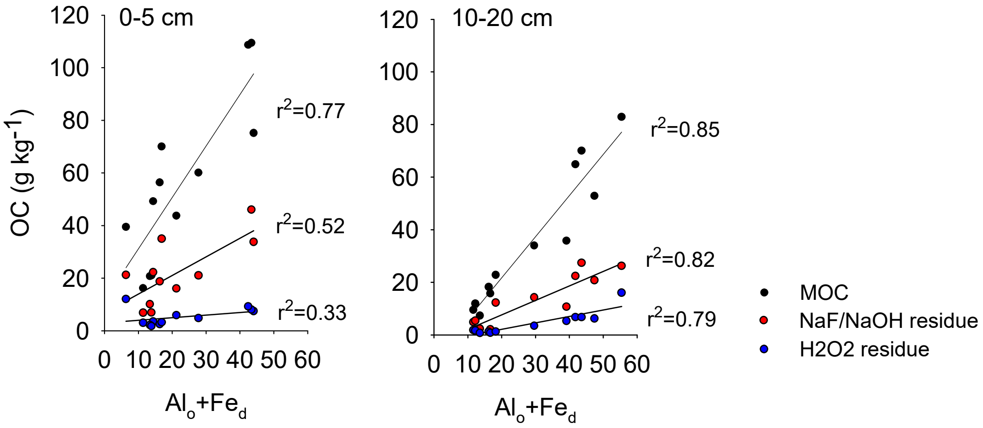
We agree with the referee that the discussion contains some speculation. The reason is that many results did not meet the expectations and that we therefore offer alternative hypotheses to explain them. We will make this point clearer and reduce the degree of speculation in the revised version.

I do not believe that reasonable speculation should not be allowed, as true statistical replication in soil studies is sometimes difficult to achieve due to measurement cost (NMR) or sample availability. But the number of statements basing interpretation of mechanism or process which are based on data from one sample or site seems very high in this manuscript.

We agree with the referee that more real replicates would help to underline the obtained results and others might prove us wrong in the future. However, for now we have to interpret the pattern that we see in the obtained result. With five study sites from different places in Europe and true replicates within the sites we are also not at the lower end of sample numbers being analysed in experimental studies considering topsoils and subsoils. The main result of our study is anyhow that the sites have more in common than we expected and so we focused the discussion rather on common patterns than on differences among individual sites. We agree that with only one sample being analysed for the NMR results of bulk MOC and MOC residues, the observed differences can only hint at potentially underlying mechanisms and mostly serve a basis for developing new hypothesis to be further tested in the future. The similarity of the spectra of extracted OC among sites and the uniform extractability suggest, however, that the idea of similar trends at other sites is not fully unrealistic. Nevertheless, we will reduce the degree of speculation and highlight the new hypotheses more clearly in the revised version. Besides the costs, also technical problems with low signal-to-noise ratios in C-poor and oxide-rich samples reduced the broader application of NMR for more samples in our study.

The authors could focus solely on interpretation of how extraction chemistry influences the portion and composition of extractable organic matter, and that would be sufficient. The comments linking NaF-extractable C with Al/Fe oxyhydroxides don't seem well supported by the data. Figure A2 illustrates a significant relationship between H2O2 residues and extractable Al/Fe. Why are there not similar plots for NaF residues?

Since we already showed in Schrumpf et al. (2013) that HF-OC was closely related to Al/Fe oxyhydroxides and NaF/NaOH extractable OC represented roughly 60% of the total HF-OC across sites, we thought it would not be necessary to show that plot. However, we are happily willing to add the graph shown below.



From the abstract it isn't clear from the abstract why these two particular extractants were chosen. This may be a major gap in my knowledge base, and if that is the case, please ignore. I have never previously seen an experiment that utilized a mixture of NaOH and NaF to evaluate SOM extractability/solubility. Is there a reference that can be associated with this method? If the abstract included an explanatory statement, it would be very helpful.

First of all, we thank the referee for the critical look at the abstract and are happy to extend the description and motivation of the methods further if the editor agrees that such an extension is not too detailed for an abstract and would make it overly lengthy.

We assume that the referee refers to the combination of NaF and NaOH as extractants since we thought that the reason for using NaF/NaOH and H_2O_2 was explained in the abstract. Both, NaOH alone and in combination with NaF have been used and published in the literature as extractants for OC before (see e.g. Möller et al. 2000 Aust. J. Soil Res., Kaiser et al. 2007 SSSAJ). The reasons for using NaOH were that it has the power to remove much of previously sorbed dissolved organic carbon from mineral surfaces, and because the high pH increases the deprotonation, and thus, the solubility of organic acids. Since NaF is more strongly competing for binding sites while less dispersive than $Na_4P_2O_7$, the combination of NaF-NaOH was used to study a potential maximal desorption. However, since it is not common to have references in the abstract, we would keep those in the main manuscript, but add the following sentence explaining the reason for using this extract in the abstract:
"The combination of NaF-NaOH was used because F^- is a strongly sorbing anion capable to replace anionic organic molecules from mineral surfaces and the high pH of the extract additionally supports desorption and solubility of MOC."

It sounds as if H2O2 is meant to represent oxidizable SOM, which the authors may be arguing is not very representative of the portion of SOM which is readily exchangeable under field conditions. In comparison, a NaOH and NaF solution presumably extracts SOM which is actually bound on the exchange surfaces of minerals. If this is indeed the case, it needs to be stated more explicitly in the abstract. Maybe something similar to the statement on lines 102-104 of the introduction.

Actually, we already wrote in lines 13-15 in the abstract: "Therefore, we determined the extractability of MOC into a mixture of 0.1 M NaOH and 0.4 M NaF as a measure for maximal potential desorbability, and compared it with maximal potential oxidation in heated H_2O_2." We believe that this sentence already demonstrates the main intention for using the two different treatments. It can be complemented by stating that they address different aspects of MOC stability: H_2O_2 addresses the chemical stability of the molecules, and NaF-NaOH the possible displacement and mobilization of the molecules from mineral surfaces by competing ions.

In the abstract, the language describing trends in radiocarbon data uses all the following terms: 14C, 14C content, MO14C, 14C-depleted, older, and age. It would improve the clarity of the results if the language was more consistent when describing this data.
Since depletion and enrichment are relative terms (depleted in comparison to what?), it seems necessary to include actual values with associated error terms when describing significant differences between extractions and residues.

Following the recommendation of the referee, we will add absolute ^{14}C values and error measures to the abstract and harmonize the language used to describe the results.

The abstract fails to mention that the soils were density fractionated prior to conducting the extractions.
To fulfil this request, we will change the sentence in lines 15ff. in the following way:
"We selected MOC samples (>1.6 g cm^3) obtained from density fractionation of samples from three soil depth increments (0-5 cm, 10-20 cm, 30-40 cm) of five typical soils of the mid-latitudes, differing in contents of clay and pedogenic oxides, and being under different land use."

It is unclear in the abstract how the experimental results could lead to the conclusion that MOC was dominated by OC interactions with pedogenic oxides. This seems like a complete non sequitur.

The conclusion on the role of pedogenic oxides in lines 36ff of the abstract is just repeating what was stated and introduced before. We would kindly like to draw the attention of the referee to lines 16 and lines 22-23 of the abstract. In line 16, we mentioned that sites were chosen to have some spread of pedogenic oxide contents. In lines 22-

23, we stated: “Total MOC amounts were linked to the content of pedogenic oxides across sites, independent of variations in total clay. The uniform MOC desorption could therefore be the result of pedogenic oxides dominating the overall response of MOC to extraction.” We can make this point more clear by adding that also MOC residues were correlated to pedogenic oxides. Therefore, one explanation for the uniform extractability of MOC is that MOC is dominated by interactions between OC and pedogenic oxides and that clay minerals were less important.

Throughout the manuscript, it would increase the clarity of the arguments and results if the language regarding radiocarbon analysis was cleaned up. I hate to argue semantics, but I believe the terms ‘stability’ and ‘lability’ are now often rejected by the community due to lack of specificity. Colleagues have been insisting on using the term ‘persistence’ as far as I know. I also believe ‘older’, ‘younger’, and ‘age’ are not appropriate for use in a manuscript, unless in reference to a ‘mean system age’.

We are not convinced that there is consensus in the community when it comes to terminology and on whether or when to use the term persistence instead of stability. The term “persistence” only became popular after its usage in the title of the Schmidt et al. (2011) paper and therefore stands maybe for replacing the old chemistry-based “stability” (=recalcitrance?)-paradigm by a new one. In that sense, using persistence in our manuscript might be appropriate but the term has not been clearly defined in the Schmidt et al. paper. We think it is reasonable to state that OC can become temporarily stabilized, e.g. by adsorption to mineral surfaces, and that it might be re-mobilized later on. Also, we think it makes more sense to directly refer to “stabilization processes” instead of “processes increasing the persistence of OC soils”. Both terms might have their justification and will re-check the manuscript for their correct use.
Regarding the ^{14}C results, we did not calculate any absolute ages, mean ages, age distributions or transit times of OC in samples, since this exercise requires models with specific assumptions. Irrespective of the reference system, it is correct to state that carbon in samples with smaller ^{14}C contents or more negative Δ^{14}C values than in other samples had been isolated from the atmosphere for a longer time and can accordingly be referred to as being older. We will add a respective sentence to the methods part to make clear what we mean when referring to younger or older carbon.

In hypothesis #5, it is unclear what the term ‘organic acids’ is referring to.

Hypthesis 5 will be reworded in the revised version following the recommendations of referee 1 and will now read: “MOC should be less prone to desorption and accordingly of older ^{14}C age, when organic molecules forming MOC have many carboxyl groups that enable strong bonds with minerals surfaces.”

In the figures, it would be helpful to readers if the soils were referred to according to their dominant physicochemical attribute rather than the site name. Hesse = loess/Cambisol; Laqueuille = grassland/Andisol: : : or something similar. That way the reader can immediately draw inferences based on differences in soil physicochemical characteristics.

We thank the referee for this suggestion and will complement the figure caption with a brief soil/site description.

Again in section 3.3, using site names gives little information, and forces the reader to continually check back to table 1 for context.

We agree and will provide the respective context in the revised version.

What was the pH of the NaF/NaOH solution (13-14, correct?), and what influence do the authors think this had on the amount and characteristics of the extracted C? Perhaps the effect of using such a strongly basic solution masked any influence of F on the amount of exchangeable C displaced on mineral surfaces.
The referee is right that besides F$^-$ also OH$^-$ anions from NaOH in the extraction solution will compete with and remove organic molecules from mineral surfaces. The higher pH will also lead to a deprotonation of organic acids.

Since both, NaF and NaOH affect desorption in the same way and direction (also NaF alone would lead to an increase in soil pH), their relative importance should be unimportant for the overall result.

Butnor et al., 2017 (doi: 10.1016/j.foreco.2017.01.014) is an additional reference that explores H2O2 residues and Fe oxyhydroxides.

We thank the referee for making us aware of that study. Using a combination of 20% H_2O_2 and 0.33 M HNO_3, Butnor et al. 2017 also found increasing oxidation resistance of OC with soil depths, and a relation between oxidation resistant OC and extractable Fe (Mehlich-3) and clay. We will add the reference to line 389 of the manuscript, where we are discussing the effect of pedogenic oxides for the oxidation resistance of OC.

It would offer additional insight if the authors cold measure _13C and _15N for the extracts and residues to see if there were significant differences in the degree of microbial processing. Perhaps it would be acceptable to use the 13C values from the AMS measurements? I know these aren't typically considered publishable due to possible fractionation effects, but it seems as though they could be used for intercomparison purposes if it can be assumed that all samples experienced similar degrees of fractionation during AMS measurement?

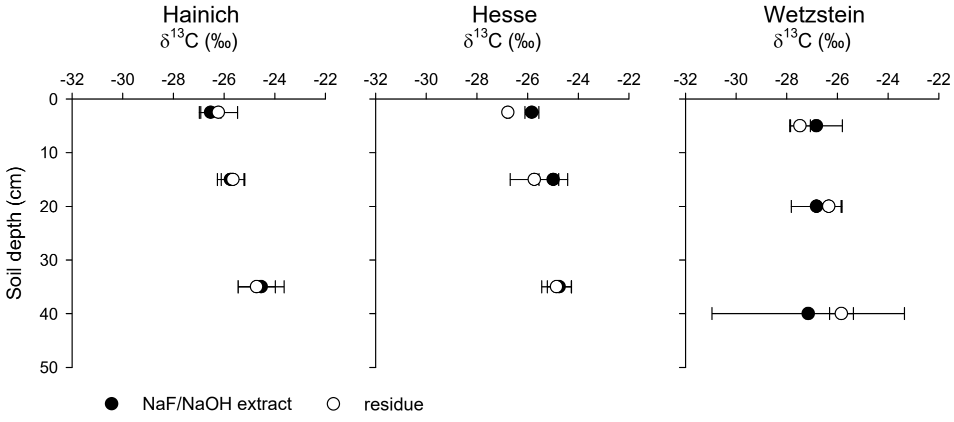
We thank the referee for this suggestion. We actually already tested the potential application of the OC-to-N ratio for a similar reason but did not obtain consistent, and thus, easily interpretable results, also because N concentrations in (subsoil) residues were sometimes very small. ^{15}N analyses cannot be added any more now because for many fractions the sample material was little and used up during analyses. The same applies for additional ^{13}C analyses. For the reason mentioned by the referee, we typically do not use the ^{13}C values of the AMS but will evaluate their application for the revised version and add them if appropriate. Unpublished results from a previous experiment showed that both, oxidation and NaOH extraction residues were depleted in ^{13}C (and ^{14}C) relative to the original sample, indicating that resistant OC was rather less microbial processed than the extracted or oxidized fractions.

Additional NMR data would also be interesting. Would it be possible to measure the H2O2 residuals?

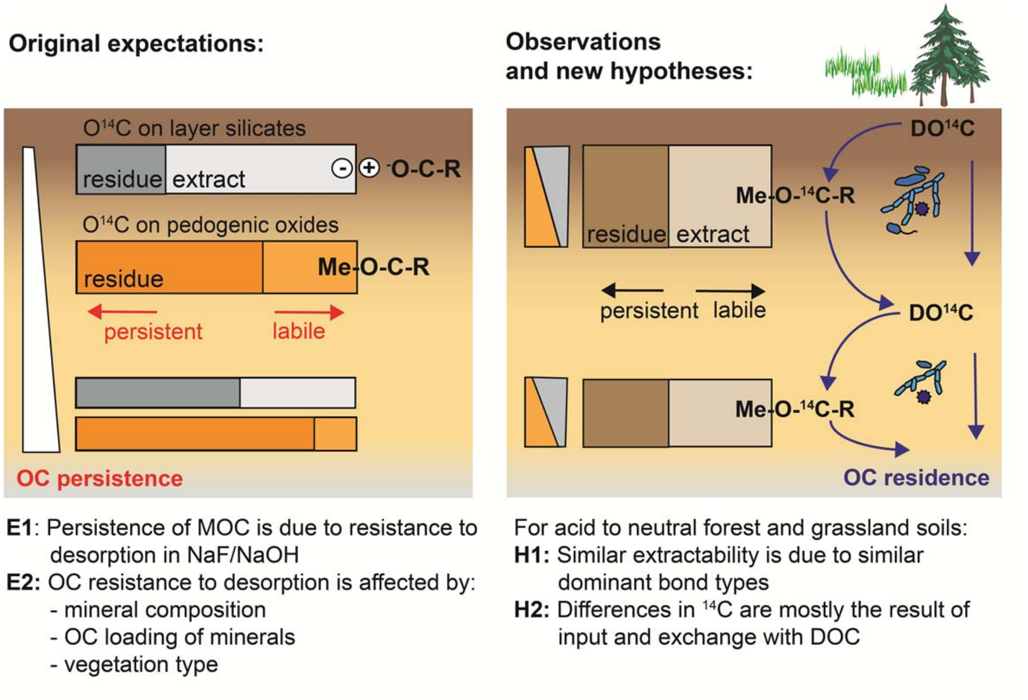
From a conceptual point of view we agree that it would be great to do that. Unfortunately, it is neither technically feasible nor reasonable. First, because of the small OC concentrations in the HF-residues, where the noise produced by the mineral background will impede the interpretation of the spectra even with long measurement times, and also because the H_2O_2 treatment probably also chemically altered the residues, so that it would be difficult to tell if the molecular structures observed now are no artefacts cause by the strong oxidation.

Supplement:

1) After receiving the ^{13}C data from the AMS of the ^{14}C-laboratory, we plotted them to test if further information can be gained on the origin of the extracted or residual OC from NaF-NaOH extractions as recommended by referee 2. However, as shown below for the tree forest sites (average of three samples per depth and standard deviation), extracts were neither consistently enriched nor depleted in ^{13}C, so that no general conclusion e.g. differences in the degree of microbial processing can be drawn. Given the larger uncertainties of AMS-based ^{13}C measurements, we would prefer not include them in the manuscript.



2) In order to enable a better distinction between the original expectations of the study regarding the role of desorption for OC persistence and 14C contents and the new hypothesis derived from the unexpected results, we suggest adding the following graphical summary to the conclusions of the revised version.



E1: Persistence of MOC is due to resistance to desorption in NaF/NaOH

E2: OC resistance to desorption is affected by:
- mineral composition
- OC loading of minerals
- vegetation type

For acid to neutral forest and grassland soils:

H1: Similar extractability is due to similar dominant bond types

H2: Differences in ^{14}C are mostly the result of input and exchange with DOC

Age distribution, extractability, and stability of mineral-bound organic carbon in central European soils

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Abstract. The largest share of total soil organic carbon (OC) is associated with minerals. ~~The portionproportions and~~However, the factors that determine the amount and turnover ~~of~~ of ~~stable~~ slower versus ~~and~~ faster cycling components of mineral-associated carbon (MOC) ~~as well as the determining factors across different soils and soil depths~~ are still ~~unknown~~poorly understood. Bioavailability of MOC is ~~supposedly~~ thought to be regulated by desorption, which can be facilitated by displacement and mobilization by competing ions. However, MOC ~~but instead, its~~ stability ~~was so far mostly~~is usually ~~tested~~ determined by exposure to chemical oxidation, which addresses the chemical stability of the organic compounds rather than the bonding strength of the OC-mineral bond ~~exposure to chemical oxidation~~. ~~Therefore, w~~We used a solution of ~~determined maximal potential desorbability the extractability ofof MOC by extracting OC using ainto a mixture of 0.1 M NaOH and 0.4 M NaF as a measure for maximal potential desorbability.~~ ~~The combination of NaF-~~NaOH, a strong agent for desorption due to high pH~~-~~, and NaF, ~~yiled~~adding F$^-$, a strongly sorbing anion that can replace anionic organic molecules on mineral surfaces, ~~was usedis a useful~~to measure the maximum potentially extractable MOC. ~~desorption agent due to the high pH of the solution, which supports desorption and solubility of MOC, and the presence of because F$^-$ is , a strongly sorbing anion capable tothat can replace anionic organic molecules fromon mineral surfaces and the high pH of the extract additionally supports desorption and solubility of MOC.~~ For comparison, we measured ~~also~~ maximal potential oxidation of MOC ~~was measured~~ using heated H_2O_2. ~~, and compared it with maximal potential oxidation in heated H_2O_2.~~ We selected MOC samples (>1.6 g cm^3) obtained from density fractionation of samples from three soil depth increments (0-5 cm, 10-20 cm, 30-40 cm) of five typical soils of the mid-latitudes, with a range of ~~differing in contents of~~ clay and pedogenic oxide~~s~~ contents, and ~~being~~ under different ecosystem types (one coniferous forest, two deciduous forests, one grassland, one cropland). ~~We selected samples of three soil depth increments (0-5 cm, 10-20 cm, 30-40 cm) of five typical soils of the mid-latitudes, differing contents of clay and pedogenic oxides, and being under different land use.~~ Extracts and residues were analyzed for OC and ^{14}C contents, and further chemically characterized by CPMAS-^{13}C-NMR. ~~We hypothesized NaF-NaOH extraction to remove less and younger MOC than H_2O_2 oxidation, and extractable MOC to be less and relatively older in subsoils and soils with high contents of pedogenic oxides.~~ We expected to remove less MOC by NaF/~~-~~NaOH extraction than

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by H_2O_2 oxidation, and for the NaF/~~-~~NaOH extracted OC to be relatively younger. We expected subsoils and soils with high contents of pedogenic oxides to have relatively less and relatively older extractable OC.

The results showed that ~~A~~a surprisingly ~~constant~~ consistent ~~portion~~proportion of 58±11% (standard deviation) of MOC was ~~extractable~~ extracted with Na~~OH NaF~~F/NaOH across soils, independent of depth~~s~~, mineral assemblage, or land use. NMR spectra revealed strong similarities of the extracted organic matter, with more than 80% of OC in the O/N alkyl and alkyl C region. Total MOC amounts were ~~linked to~~correlated with the content of pedogenic oxides across sites, independent of variations in total clay, and the same was true for OC in extraction residues. Thus, ~~. One explanation for~~ the uniform extractability of MOC ~~is therefore, that~~may be explained by dominant~~ MOC was dominated by~~ interactions between OC and pedogenic oxides across all study sites.

~~The uniform MOC desorption could therefore be the result of pedogenic oxides dominating the overall response of MOC to extraction.~~

While bulk MO^{14}C values suggested differences in OC turnover between sites, these were not linked to differences in MOC extractability. As expected, OC contents of residues had ~~smaller~~more negative Δ~~-~~^{14}C ~~contents~~ values than extracts (average difference between extracts and residues: 78±36‰), suggesting that non-extractable OC is older. ~~However,~~ Δ^{14}C values ~~^{14}C contents~~ of extracts and residues were strongly correlated and ~~proportion~~proportional to bulk MO^{14}C, but not dependent on mineralogy. Neither MOC extractability nor differences in Δ^{14}C values between extracts and residues changed with depth along soil profiles, where declining Δ^{14}C values might indicate slower OC turnover in deeper soils. Thus, the ^{14}C depth gradients in the studied soils were not explained by ~~Also along soil profiles, where increasing MOCdeclining Δ^{14}C values ages might indicate slower OC turnover with depth, neither MOC extractability nor differences in Δ^{14}C values^{14}C between extracts and residues changed. I~~increasing ~~bonding strength~~stability of organic-mineral associations with soil depth~~s did therefore not cause the ^{14}C depth gradients in the studied soils~~.

Although H_2O_2 removed 90±8% of the MOC, the Δ^{14}C values ~~^{14}C content~~ of ~~the OC~~ oxidized~~removed~~ OC w~~as~~ere similar to ~~that of the~~ those of OC extracted with NaF/~~-~~NaOH~~ extracted OC~~ (on average -50±110‰ for oxidized MOC and -51±122‰ for OC in NaF/~~-~~NaOH extracts). ~~, while o~~Oxidation residues were ~~, however,~~ much more ^{14}C-depleted than OC in NaF/~~-~~NaOH extraction residues (average of -345±227‰ for H_2O_2 and -130±121‰ for NaF/~~-~~NaOH residues). Different chemical oxidation treatments ~~apparently~~ removed OC ~~of~~ from the same continuum, leaving increasingly older residues behind the more OC is ~~being~~ removed. ~~Different from the~~In contrast to the NaF/~~-~~NaOH extractions, higher contents of pedogenic oxides ~~seemingly~~ slightly increased the oxidation-resistance of MOC, but this higher H_2O_2-resistance did not coincide with ~~older~~ more negative Δ^{14}C values of MOC or its oxidation residues.

Our results indicate that total MOC was dominated by OC interactions with pedogenic oxides rather than clay minerals, ~~so that no~~as we detected no difference in ~~MOC extraction in NaF/NaOH, and thus,~~ bond type or strength between clay-rich and clay-poor sites~~ was detectable~~. This suggests that site-specific differences in MO^{14}C and Δ^{14}C~~their~~ depth profiles~~declines~~ are ~~rather~~ driven by the accumulation and exchange rates of OC at mineral surfaces. ~~Accordingly, fFuture research on M^{14}OC~~

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~~should focus on soil and ecosystem properties driving dissolved organic matter formation, composition and transport along soil profiles, and the controls on pedogenic oxide stability and turnover.~~

1 Introduction

The persistence of organic matter (OM) in soil is ~~one~~ a key control of atmospheric CO_2 concentrations. Association of OM with ~~Binding to~~ minerals is considered an effective pathway of stabilizing otherwise degradable OM ~~against~~ from microbial mineralization (Schmidt et al., 2011; Lehmann and Kleber, 2015; Hemingway et al., 2019) and in many soils ~~most of the contained~~ the vast majority of organic carbon (OC) is bound to minerals (Kleber et al., 2015; Kögel-Knabner et al., 2008; Cotrufo et al., 2019). ~~Nevertheless,~~ Despite the abundance of mineral-bound OC (MOC), ~~–~~we ~~still~~ lack fundamental knowledge on the drivers of ~~the~~ stability and turnover of ~~of mineral-bound OC (MOC)~~MOC along soil profiles and across sites.

The formation of MOC involves sorption to reactive minerals such as phyllosilicate clays and pedogenic aluminum (Al) and iron (Fe) oxi-hydroxides (Schrumpf et al., 2013; Kögel-Knabner et al., 2008; Kaiser and Guggenberger, 2000; Khomo et al., 2017). Along with plant-derived decomposition products, microbial residues and metabolites are important precursors and sorbates for MOC formation (Avneri-Katz et al., 2017; Chenu and Stotzky, 2002; Cotrufo et al., 2015; Kalbitz et al., 2005; Kallenbach et al., 2016). Experimental studies ~~showed~~ have shown that sorption to minerals reduces OC mineralization (~~e.g.~~ Kalbitz et al., 2005; Jones and Edwards, 1998; Eusterhues et al., 2014; Porras et al., 2018). Radiocarbon (^{14}C) analyses confirmed the greater stability of MOC in soils, showing that average ~~it~~ MOC age is~~typically is of~~ older ~~average ages~~ than OC not bound to minerals (Schrumpf et al., 2013; Kögel-Knabner et al., 2008; Hemingway et al., 2019; Heckman et al., 2018). Several field and incubation studies suggested that ~~total amounts as well as stability of~~the total amount and stability of MOC ~~depend on the soil mineral composition, and~~ increases with the amount of pedogenic Al and Fe oxi-hydroxides (Bruun et al., 2010; Torn et al., 1997; Porras et al., 2017; Rasmussen et al., 2006). Other studies found ~~only~~ correlations between Al and Fe oxi-hydroxides and MOC concentrations but not with the ^{14}C content of MOC ~~and accordingly its~~or average age (Herold et al., 2014; Khomo et al., 2017; Schrumpf et al., 2013).

Studying MOC turnover and its drivers in soil is complicated because, similar to bulk soil OC, it is a mixture of younger and older carbon with a range of levels of stabilization ~~it is a mixture of young, less well stabilized, and older, presumably better stabilized, carbon~~ (Trumbore et al., 1989; Swanston et al., 2005; Schrumpf and Kaiser, 2015; Koarashi et al., 2012). Various chemical methods, ~~such as~~ including acid hydrolysis and chemical oxidation, ~~have~~ are ~~often~~ commonly ~~been applied~~used to distinguish faster and slower cycling fractions (~~e.g.~~ Mikutta et al., 2006; Jagadamma et al., 2010; Helfrich et al., 2007; Six et al., 2002; Paul et al., 2001; Eusterhues et al., 2003). ~~They all~~All methods separate~~d~~ bulk soil OC or MOC into younger and older fractions but differ~~ed~~ in the extent of OC removal and the ^{14}C contents of obtained residues. The oxidants H_2O_2 or $Na_2S_2O_8$ were more effective in removing OC from samples than NaOCl, and their residues were older (Jagadamma et al., 2010; Helfrich et al., 2007). With increasing presence of Al and Fe oxi-hydroxides in soils, larger amounts of OC resisted

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chemical oxidation, suggesting that binding to those minerals provides some protection against oxidative attack (Mikutta et al., 2006; Kleber et al., 2005; Eusterhues et al., 2005). However, there are indications that such chemically defined fractions are ~~possibly~~ not causally related to MOC bioavailability or persistence in soils (Poirier et al., 2003; Mikutta and Kaiser, 2011; Helfrich et al., 2007; Jagadamma et al., 2010; Paul et al., 2008).

Release of mineral-bonded OC, either by desorption or upon mineral dissolution under changing environmental conditions, can support or even be prerequisite for its microbial degradation (Keil et al., 1994; Mikutta et al., 2007). Desorption of OM, although ~~was~~ typically small under conditions similar to those during the formation of MOC ~~was typically small~~ (e.g. Gu et al., 1994), ~~but~~ increases~~d~~ in the presence of competing ions such as SO_4^{2-} or $H_2PO_4^-$~~,~~ and ~~was~~ is ~~largest when~~maximized ~~solution pH was raised~~ by increasing the alkalinity of solution (e.g. Kaiser and Zech, 1999; Kaiser and Guggenberger, 2007). While some studies observed an increased ~~that the~~ release of OC from minerals into alkaline solutions ~~increased~~ with greater ~~the~~ minerals~~'~~ OC loading (Kaiser and Guggenberger, 2007, Kaiser et al., 2007), others showed ~~larger~~ increased OC desorption ~~in subsoils~~ despite smaller OC concentrations (Kaiser and Zech, 1999; Mikutta et al., 2009). ~~Larger~~ Greater desorption and biodegradation of OM bonded to phyllosilicates than of OM bonded to Al and Fe oxi-hydroxides has been attributed to differences in bonding strength. The sorption between OM and phyllosilicates are largely a result of the weaker cation bridges and van der Waals bonds ~~[Cite]~~, while the sorption of OM to Al and Fe oxi-hydroxides involves surface complexation, which results in strong chemical bonds ~~The sorption of OM to Al and Fe oxi-hydroxides involves surface complexation, which results in strong chemical bonds, while the sorption between OM and phyllosilicates is largely due to weaker cation bridges and van der Waals bonds~~ (Singh et al., 2016; Mikutta et al., 2007). Thus, the ~~P~~presence and ~~amount~~ abundance of Al and Fe oxi-hydroxides ~~, therefore,~~ typically decreased both~~,~~ desorption~~,~~ and mineralization rates (Oren and Chefetz, 2012; Saidy et al., 2012; Singh et al., 2017). Unfortunately, OC desorption ~~was so far mostly~~has primarily been studied using model minerals in laboratory experiments, and observation times for desorption or mineralization were ~~short relative to~~much shorter than carbon residence times in soil.

Mikutta et al. (2010) analyzed the ^{14}C contents of MOC after removing all potentially desorbable OC by extracting soil with a combination of NaF and NaOH. This extraction ~~allows~~ enables ~~for studying~~the study of the potential displacement of complexed organic ~~functionalities~~functional groups by introducing ~~competing~~ OH^- and F^- anions to compete for and displace mineral-bound OC, and ~~the~~ by ~~rise~~ increasing the ~~in~~ pH (Kaiser et al., 2007). Consistently younger OM was extracted from MOC of topsoils, supporting the idea that desorbable OC turns over faster than more strongly bonded OC. Results for subsoils were more variable (Mikutta et al., 2010). Along with ^{14}C contents, the chemical composition of bulk soil OC extractable into alkaline solutions also changes with soil depth, with subsoils containing less lignin-derived aromatics but more O-alkyl C, possibly of microbial origin (Möller et al., 2000; Mikutta et al., 2009). Desorption of OC from MOC has, to our knowledge, ~~so far~~ not yet been studied systematically across soil types. ~~Assuming that~~If potential OC desorption ~~is closer to the mechanism behind~~better represents the mechanism of mineral protection of soil OC than the abovementioned oxidative or hydrolytic extractions, then further research must focus on factors controlling amount, age, and composition of

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desorbable OC in soils~~ deserve attention~~. Potential factors affecting MOC desorption include soil mineralogy, chemical composition of OM and thus vegetation type, and OM loading on minerals.

~~In order to test if maximum desorption is a suitable indicator for the labile portion~~proportion ~~of MOC, we took advantage of a former experiment, where MOC was isolated from soils by density fractionation (heavy fraction at a density cutoff of >1.6 g cm^{-3}, HF) for a range of sites across Europe (Schrumpf et al., 2013). We selected five sites to have a range of the amount and type of clays and pedogenic oxides as well as of land use, and, accordingly, amount and quality of litter input. Samples from three soil depths were extracted with a combination of NaOH and NaF, and analyzed for amount, composition, and ^{14}C contents of extracted OC. Results are compared to the amount and age of OC oxidizable by heated H_2O_2, which was shown to remove the largest and isolate the oldest part of MOC (Helfrich et al., 2007; Jagadamma et al., 2010). The desorption experiment is supposed to addresses mineral protection as stabilization mechanism, while the oxidation treatment should rather address the chemical recalcitrance of MOC.~~

Based on the literature review we expect that:

(10) extraction in NaF/NaOH releases a weaker bound fraction of total MOC, which is younger than the stronger bound residue fraction.
(11) MOC of soil samples with higher proportions of extractable carbon ~~should be~~is younger than MOC with more extraction resistant OC.
(12) the proproportion of NaF/NaOH-extractable MOC decreases with increasing contents of pedogenic oxides, which form strong bonds with OC.
(13) the chemical composition of extractable MOC varies between study sites due to differences in vegetation composition, and thus litter chemistry.
(14) the pro~~pro~~portion of NaF/NaOH-extractable MOC declines ~~from topsoils to subsoils~~with depth due to declining OC loading of minerals.
(15) the chemical composition of extractable MOC changes with~~ soil~~ depth~~s~~ due to declining contributions of plant and increasing contributions of microbial derived OC.
(16) MOC should be less prone to desorption and accordingly of older ^{14}C age when organic molecules forming MOC have many carboxyl groups that enable strong bonds with minerals surfaces.
(17) the strong oxidizing agent H_2O_2 removes more OC from MOC than NaF/NaOH.
(18) oxidizable and non-oxidizable OC should both be older than the extractable and non-extractable OC fractions if the harsher oxidation treatment removes more, and thus presumably better stabilized OC from mineral surfaces, leaving OC residues of even older ^{14}C age behind.

~~We hypothesize that:~~

~~(10) Extraction in NaF/NaOH releases a potentially desorbable, weaker bound fraction from total MOC, which is younger than the stronger bound, probably better stabilized residue fraction. Accordingly, total MOC should be younger with larger portion~~proportions ~~of total MOC being extractable.~~

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~~(11) The portion~~proportion ~~of total MOC extractable by NaF/NaOH decreases with increasing contents of pedogenic oxides, which form strong bonds with OM.~~

~~(12) The portion~~proportion ~~of young NaF/NaOH extractable MOC declines from topsoils to subsoils with declining OC loading and increasing stability and age of MOC.~~

~~(13) The strong oxidizing agent H_2O_2 removes more of the total MOC than NaF/NaOH. Assuming that OM becomes increasingly older the stronger it is bound to minerals, both oxidizable and non-oxidizable OC should be older than the extractable and non-extractable OC fractions.~~

~~(14) Extractability of mineral-bound OM with NaF/NaOH and oxidation of OC are related to the chemical composition of sorbed OC, and thus, vary with land use and soil depth. In particular, MOC should be less prone to desorption and oxidation, and accordingly older, where organic acids capable to from strong bonds with minerals prevail.~~

~~In order to~~To test if maximum desorption with NaF/NaOH ~~-~~is a suitable indicator for the labile proportion of MOC, we took advantage of a ~~former~~previous experiment~~, where~~ in which MOC was isolated from soils by density fractionation (heavy fraction at a density cutoff of >1.6 g cm^{-3}, HF) for a range of sites across Europe (Schrumpf et al., 2013). We selected five sites ~~to have a~~across ~~-~~ranges of ~~the amount~~clay content, ~~and~~ type of clay~~s~~ and pedogenic oxides, and ~~as well as of~~ land use, ~~an~~with associated differences in ~~d, accordingly,~~ amount and quality of litter input. Samples from three soil depths were extracted with a ~~combination~~mixture of NaF ~~NaOH~~ and NaOH~~, NaF~~, and the extracted OC was analyzed for amount, composition, and ^{14}C content~~s of extracted OC~~. ~~Results are~~We compared results from the extraction to the amount and age of OC oxidizable by heated H_2O_2, which was shown to remove the ~~largest~~most MOC and isolate the oldest ~~part of~~ MOC (Helfrich et al., 2007; Jagadamma et al., 2010). The in NaF/NaOH extraction experiment ~~is supposed to addresses~~seeks to elucidate mineral protection as a stabilization mechanism, while the oxidation treatment ~~should rather address~~ explores the chemical recalcitrance of MOC.

2 Materials and Methods

Composition and age structure of MOC were studied on heavy fraction (HF) material obtained at five of the sites presented by Schrumpf et al. (2013). The sites include two deciduous forests developed on loess at Hesse (France, ~~Cambisol~~Luvisol) and loess over limestone at Hainich (Germany, Cambisol). ~~The~~ Soils at the grassland site Laqueuille (France, Andosol) and the coniferous site Wetzstein (Germany, Podzol) are characterized by large contents of pedogenic oxides. The soil at the fifth site, a cropland at Gebesee (Germany, Chernozem), reveals a plow layer down to 30 cm, and large contributions of old OC throughout the profile (Schrumpf et al., 2013). The MOC fraction was separated using two-step sequential density flotation in sodium-polytungstate solution (1.6 g cm^{-3}). After removal of the unprotected free light fraction in a first flotation step, samples were sonicated (site-specific energy application) to disrupt aggregates and separate the occluded light fraction from the targeted MOC in the HF (for details see Schrumpf et al. (2013)). Concentrations of OC in MOC are shown in Figure 1 and ranged ~~in the uppermost layer~~ from 16.8 g kg^{-1} at Gebesee to 108 g kg^{-1} at Laqueuille in the uppermost layer, and from

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4.6 g kg^{-1} at Hesse to 44 g kg^{-1} at Laqueuille in the deepest studied layer. Selected bulk soil properties of respective samples were adopted ~~von~~ from Schrumpf et al. (2013) and are summarized in Table 1.

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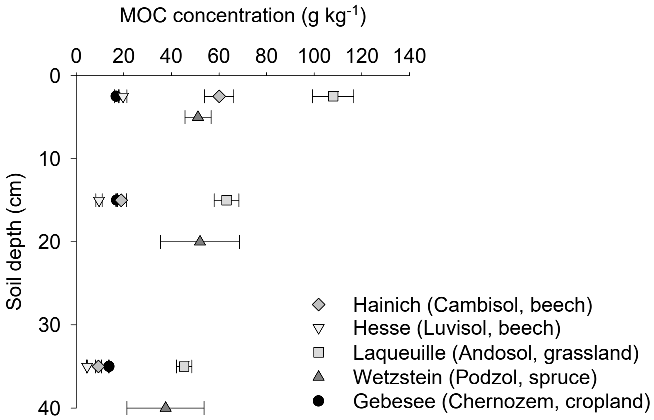

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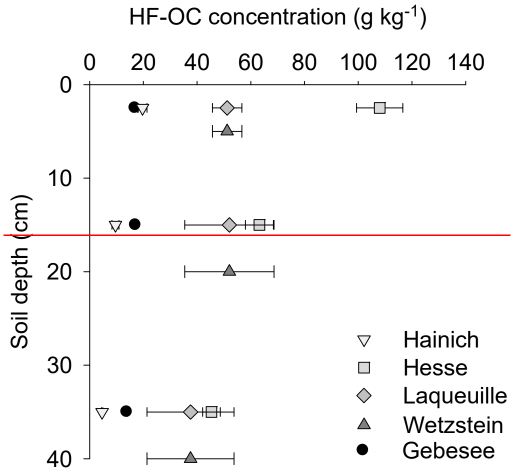

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Figure 1~~1~~: Figure 1: Original concentration of OC in mineral association (MOC, means and standard deviation) of the studied soil samples from 5 sites (data adopted from Schrumpf et al. 2013). Depth of symbols inidcate mid-points of integrated sampled depth intervals (Table 1).

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Table 1: Basic soil properties of the study sites (means of the three replicated samples analyzed for mineral associated carbon per soil depth with standard deviations in brackets). Values of selected cores are adopted from Schrumpf et al. 2013 (Ci: inorganic carbon, CN: OC-to-total nitrogen ratio, Feo: acid oxalate-extractable Fe, Alo: acid oxalate-extractable Al, Fed: dithionite-extractable Fe).

Site and soil depth	pH (H_2O)	OC	CN	Ci	Sand	Clay	Feo	Fed	Alo
		g kg^{-1}		g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}
Hainich (Cambisol, beech)									
0-5	6.1 (0.9)	73 (11)	13.0 (0.5)	0	22 (4)	546 (5)	3.0 (1.0)	14.0 (0.8)	1.9 (1.1)
10-20	6.7 (0.5)	27 (6)	10.7 (0.4)	0	28 (4)	514 (5)	2.0 (0.4)	15.3 (1.0)	1.8 (0.6)
30-40	7.4 (0.2)	11 (1)	9.0 (0.4)	0	23 (7)	731 (7)	n.d.	n.d.	n.d.
Hesse (Luvisol, beech)									
0-5	4.6 (0.7)	31 (6)	13.9 (0.6)	0	68	342	1.8 (0.3)	11.8 (1.3)	1.1 (0.2)
10-20	4.5 (0.3)	14 (4)	11.8 (0.5)	0	56 (12)	315 (11)	1.4 (0.5)	11.5 (1.1)	1.0 (0.1)
30-40	n.d.	6 (0)	8.3 (0.0)	0	55(3)	371 (22)	n.d.	n.d.	n.d.
Laqueuille (Andosol, grassland)									
0-5	5.3 (0.2)	126 (11)	11.1 (0.2)	0	186 (36)	263 (28)	12.7 (0.1)	24.0 (0.6)	19.3 (0.7)
10-20	5.6 (0.3)	66(7)	10.2 (0.2)	0	259 (58)	215 (8)	16.4 (3.0)	20.3 (0.9)	24.0 (2.6)
30-40	n.d.	50 (4)	10.7 (0.3)	0	236 (21)	225 (22)	15.8 (1.7)	20.6 (1.1)	27.6 (2.3)
Wetzstein (Podzol, spruce)									
0-10	3.5 (0.0)	76 (15)	24.6 (2.2)	0	264 (164)	250 (165)	9.2 (6.2)	17.0 (10.4)	1.5 (0.8)
10-30	3.8 (0.3)	60 (29)	22.0 (3.6)	0	219 (40)	344 (123)	24.9 (15.5)	37.0 (12.6)	4.4 (0.8)
30-50	4.2 (0.3)	45 (24)	19.1 (2.3)	0	221 (46)	364 (63)	17.4 (16.6)	27.4 (16.1)	7.8 (2.6)
Gebesee (Chernozem, cropland)									
0-5	6.8 (0.1)	26 (2)	11.3 (0.9)	0	28 (5)	345 (5)	1.4 (0.1)	6.9 (0.3)	1.3 (0.1)
10-20	7.0 (0.4)	22 (2)	10.5 (0.1)	0	26 (3)	336 (2)	1.4 (0.2)	6.9 (0.3)	1.4 (0.1)
30-40	n.d.	17 (1)	11.1 (0.2)	1.6 (0.9)	21 (1)	368 (1)	n.d.	n.d.	n.d.

We randomly selected three out of the original ten replicated soil cores per site and analyzed the soil layers 0-5 cm, 10-20 cm, and 30-40 cm (excluding ~~for~~ Wetzstein, where ~~it was~~ 0-10 cm, 10-30 cm and 30-50 layers were analyzed ~~and~~ from soil

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pits ~~instead of cores were analyzed~~instead of cores, see Schrumpf et al. 2013) for (1) extractable MOC and (2) oxidation-resistant MOC.

NaF-NaOH-~~E~~extractable MOC was determined as an indicator for maxial potential desportion by weighing 25 g of heavy fraction (~~HF~~MOC) material of each sample into 250-ml polypropylene centrifuge bottles and adding 125 ml of a 1:1 solution containing 0.8 M NaF and 0.2 M NaOH. Containers were then closed and agitated overnight (at least for 18 hours) in an end-over shaker. A few drops of magnesium chloride were added as flocculant to the solution, which was then centrifuged for 15 minutes at 4000 × g. Then supernatants were decanted into 1000-ml PE bottles and stored in the refrigerator. Another 125 ml of the extraction solution was added to settled soil material in the centrifuge tube, stirred and mixed well to repeat the extraction for a total of four times. Finally, the combined extract solution from each sample was passed through ~~90-mm~~ glass fiber filters with a pore size of 1.6 µm and stored in a 4° C ~~climate controlled~~ room until transfer into deionized water-rinsed, 75 cm long SERVAPOR 29-mm cellulose-acetate tubing~~s~~ for dialysis. The ~2/3 full tubes were placed into clean 10-l buckets filled with deionized water, which was frequently replaced until the electrical conductivity of the external solution was <2 µS. The content of the dialysis tubes was then freeze dried~~,~~ and analyzed for total C, N, and ^{14}C signatures (as described below). The extracted~~ion~~ residual soil containing the non-extractable OC was washed three times with deionized water to minimize remaining fluoride content before freeze drying and analyses of total C and N contents, and ^{14}C signature (as described below).

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Oxidation-resistant MOC was obtained ~~by~~ following a slightly modified procedure from Jagadamma et al. (2010). After letting 2 g of soil soak in 20 ml of Millipore DI water for ten minutes, 60 ml of 10% hydrogen peroxide (H_2O_2) was gradually added to the soil. After the frothing had subsided from the reaction of wet samples with 60 ml of H_2O_2 at room temperature, the samples were heated and stirred regularly in a 50°C water bath in order to catalyze the oxidation of organic matter. Because H_2O_2 decomposes with exposure to light and temperature, the samples were centrifuged, the supernatant decanted, and fresh H_2O_2 added to continue the oxidation. Each sample was oxidized for two periods of 24 hours and one period of 72 hours. After the final oxidation, samples were centrifuged at 3500 × g for at least 15 minutes, and then washed three times with 80 ml of deionized water. Magnesium chloride solution was added to enhance flocculation during centrifugation. After the final oxidation each sample was washed three times with DI water and afterwards freeze dried. The samples were then homogenized using a ceramic ball mill and measured for total carbon and nitrogen content by dry combustion with the Vario EL CN analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). All soils analyzed in this study were free of carbonate. Therefore, total carbon measurements are equivalent to total organic carbon in the soil.

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Radiocarbon contents of the samples were measured on graphitized samples at the ^{14}C laboratory in Jena, Germany (Steinhof et al., 2017). Soil samples were weighed into tin capsules and combusted in an elemental analyzer. ~~Samples containing carbonate were decalcified using 2 mol l^{-1} HCl solution prior to combustion.~~ The evolved CO_2 was transferred into a glass tube cooled by liquid nitrogen, and reduced to graphite at 600 °C under hydrogen gas atmosphere, using iron as catalyst. The graphite was analyzed by ^{14}C AMS (3MV Tandetron 4130 AMS ^{14}C system: High Voltage Engineering Europe, HVEE, The Netherlands). Samples with low OC concentrations from the H_2O_2 residues were combusted with CuO wire in quartz tubes

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and graphitized using a sealed zinc reduction method, then analyzed at the WM Keck Carbon Cycle AMS facility at UC Irvine (Xu et al., 2007).

Radiocarbon data are reported as Δ^{14}C in per~~-~~mille [‰], which is the relative difference in parts per thousand of the ~~activity~~ ^{14}C/^{12}C ratio of the sample with respect to an absolute standard (0.95 times the oxalic acid standard NBS SRM 4990C decay corrected to 1950), after normalization of the sample ^{14}C/^{12}C ~~-~~for mass dependent fractionation by normalizing to a δ^{13}C ~~-~~of -25‰. (~~-(fractionation correction) and correction for decay between 1950 and time of analysis (2015??? REFERENCE MISSING? Maybe use 14C book Chapter 2?~~). The average measurement precision of the Δ^{14}C values was 2.8‰.

~~For all measured samples wit~~Reported in this way, Δ^{14}C values close to zero indicate that most of the C in the sample is close to that of the standard, i.e. it was fixed from the preindustrial ~~atmsophere~~atmosphere (up to ~350 years prior to 1950). N~~h n~~egative Δ^{14}C values indicate lower ^{14}C/^{12}C than the standard and indicate ~~we assume~~ that ~~they~~most of the C in the sample had been isolated from the atmosphere long enough for detectable radioactive decay to deplete ^{14}C; samples with ~~and that OC in samples with more~~ negative Δ^{14}C values ~~than others was~~have been isolated longer ~~from the atmosphere and is accordingly on average older~~. Positive Δ^{14}C values ~~on the other hand~~ indicate enrichment with bomb-derived ^{14}C from nuclear weapon testing in the early 1960ies, which suggests that OC from these samples is younger and ~~has faster turnover than 300~~mostly fixed in the last century. ~~years. For samples collected in the year~~In 2004, ~~as in the present project study~~when samples in this study were collected, atmospheric Δ^{14}C values (about 70 ‰) were ~~already~~still declining from the peak bomb C in 1963 of about +900 ‰~~-~~. Thus, comparing oxidized or extracted C with the original MOM depends on its original Δ^{14}C values. ~~-~~For total MOM with negative Δ^{14}C values, we assume the extracted or oxidized C is 'younger' if it has Δ^{14}C values that are either less negative or positive. ~~-~~For total MOM that initially has positive Δ^{14}C values, we might expect 'older' C residues to have either higher Δ^{14}C values (closer to the bomb peak) or negative Δ^{14}C values; in both cases we expect 'younger' extracted Δ^{14}C values to have positive Δ^{14}C values. Our p~~For soil C pools with turnover times between 20 and 300 years, higher Δ^{14}C values however still indicate more bomb-C enrichment and thus faster turnover. Only for samples withFor samples with turnover times of less than 20 years, smaller Δ^{14}C values would indicate faster turnover and thus samples with younger carbon., but G given our p~~revious results based on temporal changes of Δ^{14}C values of MOC at the Hainich site ({Schrumpf, 2015 #26}), ~~it does not seemis not plausible that the largest sharemajority of~~indicate that total MOC in our soils will ~~turnover faster than~~have turnover times > ~~have turnover times of less than~~ 20 years. Therefore, ~~we~~if extracted/oxidized OC has ~~-interpret OC in samples with morerelatively negative~~ Δ^{14}C values that are higher than unextracted or residual MOM, ~~than others as being~~we refer to these as younger throughout the manuscript. ~~-older, and samples with more positive values compared to othersrelatively positive values as containing on average younger carbon throughout the manuscript.~~

To determine the amount of carbon in the residues from both extraction procedures, we multiplied the measured OC content in the recovered residues with its mass. The amount of carbon lost by the treatments was determined as difference between

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the original OC content of the HF sample and OC in the residues. The radiocarbon contents of the H_2O_2 residues were directly measured, and the ^{14}C fraction of the OC lost/extracted ($^{14}C_{extract}$) was determined by mass balance as follows:

$^{14}C_{HF} = (OC_{extract}/OC_{HF})\cdot {}^{14}C_{extract} + (OC_{residue}/OC_{HF})\cdot {}^{14}C_{residue}$

$^{14}C_{extract} = ({}^{14}C_{HF} - (OC_{residue}/OC_{HF})\cdot {}^{14}C_{residue)})/(OC_{extract}/OC_{HF})$

The same formula was used to determine the ^{14}C fraction of OC extracted by NaF/NaOH. Since OC extracted by NaF/NaOH extraction was also measured directly, the mass balance results allow for identifying potential bias in measured ^{14}C data caused by losses of extracted OC during dialyses.

Solid-state cross-polarization magic angle spinning ^{13}C-nuclear magnetic resonance (CPMAS ^{13}C-NMR) spectra of NaF/NaOH extracted, dialyzed, and freeze-dried OM were recorded on an Avance III spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany) at a resonance frequency of 100.5 MHz, with a proton spin-lock and decoupling frequency of 400 MHz. The proton nutation frequency was 80 kHz, corresponding to a π/2 pulse duration of 3.12 µs. The cross-polarization time was 500 µs. Samples were weighed into 4-mm zirconium oxide rotors that were spun at 10 kHz around an axis declined by the 'magic angle' of 54.74° against the static magnetic field; contact time was 1 ms and the recycle delay time was set to 0.4 s. Depending on the sample, between 4,000 and 35,000 scans were recorded. The spectra were processed with a line broadening of 100 Hz. Chemical shifts are given relative to the resonance of tetramethylsilane. After baseline correction, the intensities of spectral regions were corrected for different cross-polarization efficiencies in different spectral regions. To do so, ^1H $T_{1\rho}$ as well as T_{CH} were estimated selectively for the regions. Since OM samples with C contents >30% were ~~analysed~~analyzed, no treatment for removal of paramagnetic mineral phases was required and the obtained spectra were well resolved and showed no indications of paramagnetic interferences. In addition, we analyzed one bulk MOC sample low in pedogenic oxides without removal of paramagnetic phases. ~~Also~~ In all cases, ~~that~~ spectra ~~was~~ were reasonably well resolved and without indications of paramagnetic interferences.

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Resonance areas were calculated by electronic integration: alkyl region (0–50 ppm), mainly representing C atoms bonded to other C atoms (methyl, methylene, methine groups); O/N-alkyl region (50–110 ppm), mainly representing C bonded to O and N (carbohydrates, alcohols, and ethers) and including the methoxyl C (peak ~~centred~~centered around 56 ppm); aromatic region (110–160 ppm), representing C in aromatic systems and olefins, and (d) the carbonyl region (160–220 ppm), including carboxyl C (160–190 ppm). Further information on the assignment of ^{13}C-NMR regions are given by Wilson (1987) and Orem and Hatcher (1987).

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3 Results

3.1 Mineral-associated organic carbon ~~removed~~ extracted by NaF/NaOH ~~and H_2O_2~~

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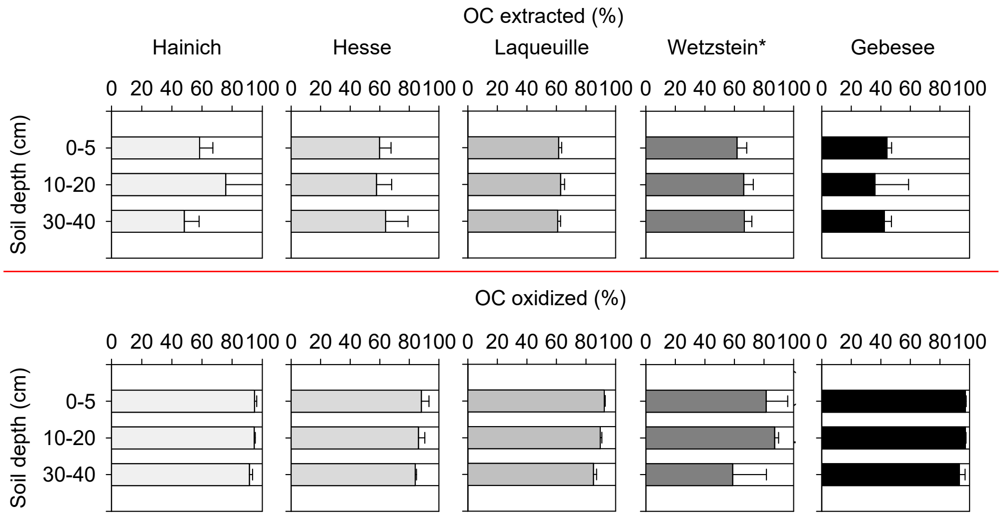
The NaF/NaOH extraction removed on average 58±11% of bulk MOC across sites and soil depths (Figure 2). Extraction efficiency was not explained by soil depth, as~~With average~~ average extraction removal values~~–~~ were ~~of~~ 57±7% in the uppermost, 60±15% in the intermediate, and 56±11% in the deepest analyzed soil layer~~, there was no trend in the extraction~~

~~efficiency with soil depth~~. Average ~~e~~Extraction efficiency was~~, however, on average somewhat~~ smaller at ~~site~~ the Gebesee site ~~than~~ compared to~~at at the~~ other~~s~~ sites (41±10% vs. 62±11% on average across depths). ~~As they represent similar portionproportions of bulk MOC, t~~The amounts of extracted and residual OC, which represent similar proportions of bulk MOC, were strongly correlated to bulk MOC concentrations across sites and soil depths (r=0.96, p<0.01; Figure 3, Figure A1). Neither contents of pedogenic oxides, OC loadings of minerals, nor soil pH affected the ~~portion~~proportion of extractable MOC~~ that was extractable~~. However, since bulk MOC concentration~~s~~ was positively related to contents of pedogenic oxides (Schrumpf et al. 2013), the same relationship applied to OC concentrations in extraction residues (Figure 4).



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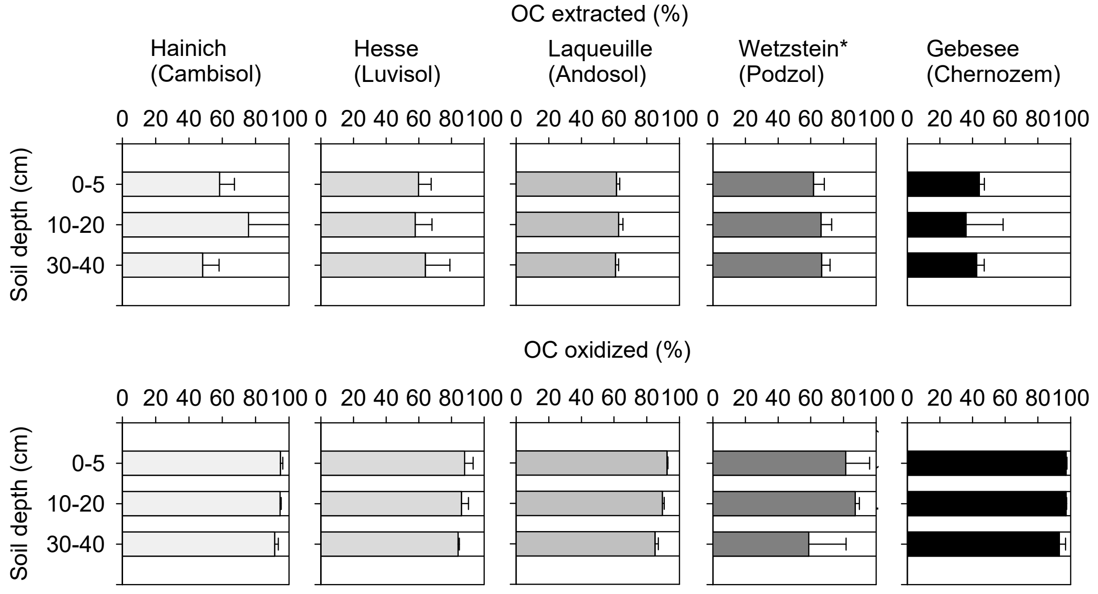

Figure 2: ~~Portion~~Proportion of OC extractable with NaF/NaOH or oxidized with heated H_2O_2 from the mineral associated OC fractions of soil samples from five different sites (Hainich, Hesse, Laqueuille, Wetzstein, Gebesee) and three soil depths (0-5 cm, 10-20 cm, 30-40 cm); for Wetzstein the studied soil depths were 0-10 cm, 10-30 cm, and 30-50 cm.

~~On average, only 11±6% of MOC resisted to treatment with heated H_2O_2, with 90±8% being removed in the uppermost, 90±6% in the intermediate, and 87±5% in deepest studied soil layer (Figure 2). Accordingly, an insignificantly smaller portionproportion of total OC was extracted in the subsoil than in the topsoil. The portionproportion of MOC resisting the H_2O_2 treatment differed between study sites. The largest portionproportion was found at the Wetzstein site (on average 19±4%), especially in the deepest layer, while smallest portionproportions of H_2O_2-resistant MOC occurred at Gebesee (5±3%). The absolute amount of H_2O_2-resistant OC was correlated with the bulk MOC concentration (r=0.76, p<0.01; Figure 3), however, the correlation was weaker than those found residual OC after NaF/NaOH extraction.~~

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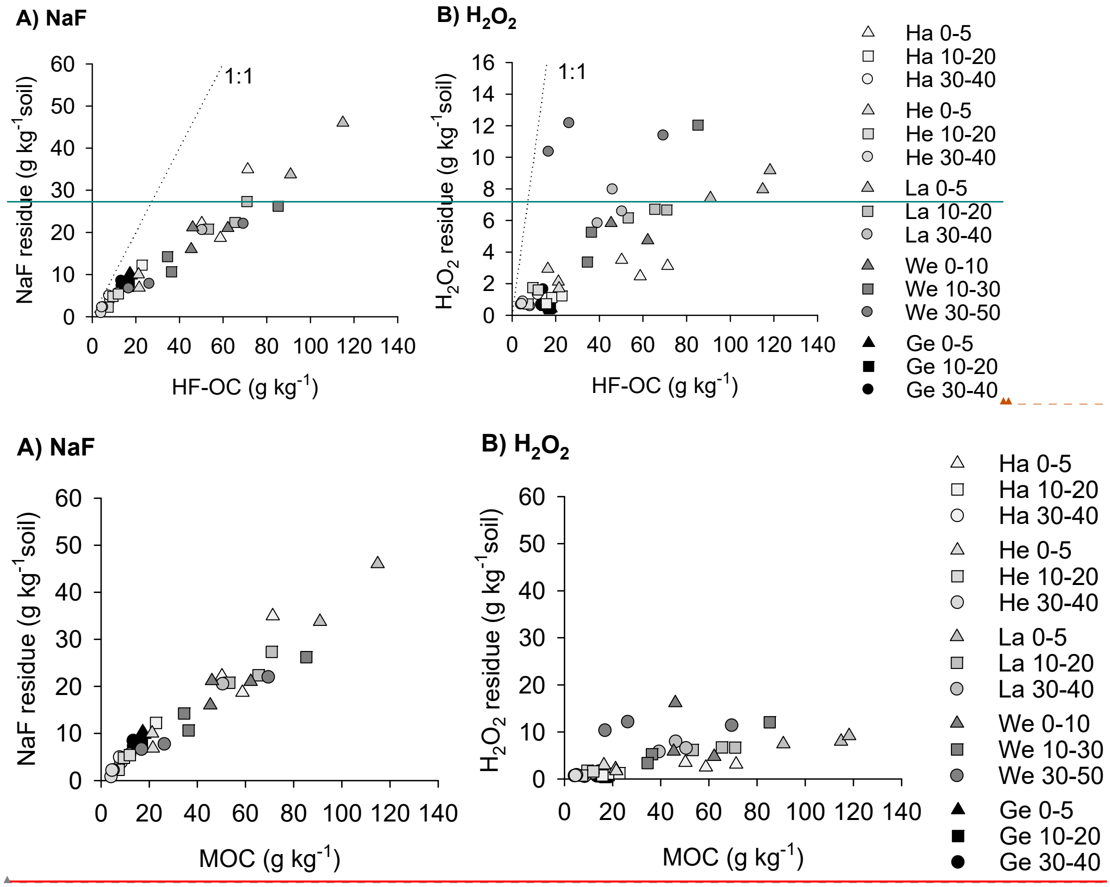

Figure 3: ~~Dependency of r~~Residual OC ~~from~~ depended on original concentrations of mineral associated OC for A) NaF/NaOH extraction (left) ~~or~~ and B) the H_2O_2 oxidation (right) for all study sites (Hainich (Ha), Hesse (He), Laqueuille (La), Wetzstein (We), Gebesee (Ge)).

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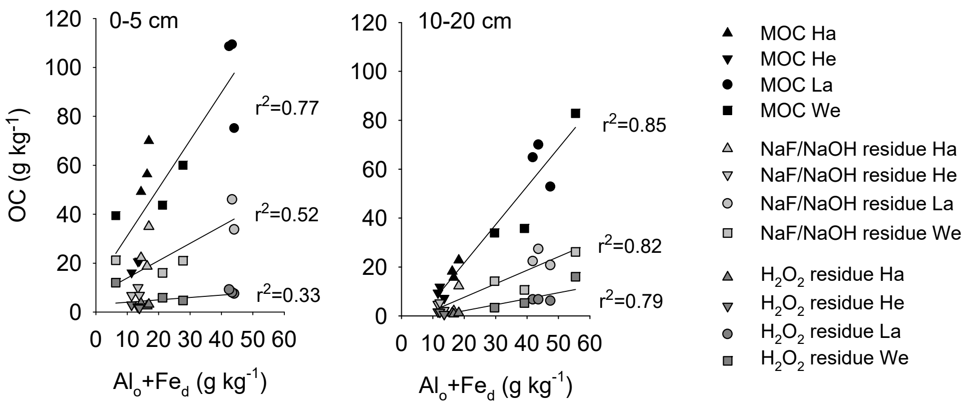

Figure 4: ~~Relation between OC concentrations in bulk MOC, NaF-NaOH extraction residues and oxidation residues and the contents of pedogenic oxides expressed as the sum of oxlate extractable Al and acid dithionite extractable Fe.~~ OC concentrations in each fraction (bulk MOC, NaF~~-~~/NaOH extraction residue, and oxidation residue) was related to the pedogenic oxide content of the sample, which is expressed as the sum of the acid oxalate~~-~~extractable Al and ~~acid~~ dithionite~~-~~extractable Fe.

3.1 Radiocarbon contents of NaF/NaOH extracts and residues

~~Results for directly~~Directly measured $\Delta^{14}C$ values ~~in~~of dialyzed NaF/NaOH extracts were ~~overall~~ comparable to calculated $\Delta^{14}C$ values in extracts ~~from~~using the mass balance approach (Figure 5), suggesting that there were no systematic losses of older or younger C during the extraction and subsequent dialysis procedure. The only exception were the results from ~~Only for~~ Gebesee, where the mass balance approach suggests that some young carbon was ~~probably~~ lost during dialys~~e~~is of the extracts.

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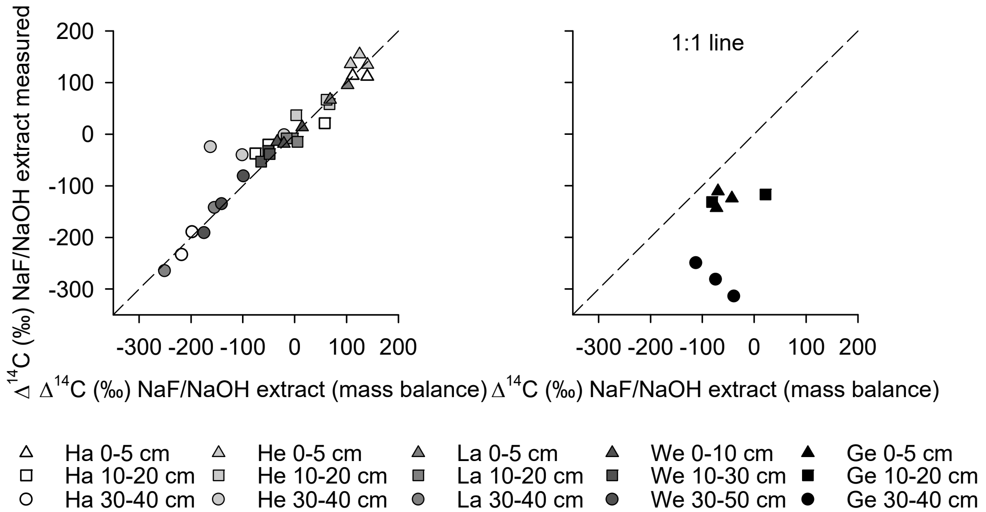

Figure 5: Comparison of ^{14}C contents of NaF/NaOH extracted OC obtained using a mass balance approach ~~and from~~with direct measurements of the extracts after dialyses (study sites: Hainich (Ha), Hesse (He), Laqueuille (La), ~~-~~and Wetzstein (We) on the left, Gebesee (Ge) on the right).

Extracted fractions had consistently ~~larger~~higher ~~Otherwise,~~ $\Delta^{14}C$ values ~~were always larger in the extracted fractions~~ than ~~in the~~ extraction residues, and $\Delta^{14}C$ values decreased ~~at all sites~~ with ~~soil~~ depths at all sites (Figure 6). The $\Delta^{14}C$ values of the OC extracted from the uppermost layers increased in the order Gebesee (Chernozem) < Wetzstein (0-10 cm, Podzol) < Laqueuille (Andosol) < Hainich (Cambisol) < Hesse (Luvisol) from -126‰ to 142‰. The average difference in $\Delta^{14}C$ between extracted and residue OC was 79±36‰ across sites and increased in the order Gebesee (34±4‰) < Laqueuille (38±6‰) < Hainich (63±3‰) < Hesse (84±5‰) < Wetzstein (100±15‰). As indicated by the almost parallel shifts in $\Delta^{14}C$ values, there was no general trend for increasing or declining differences in ^{14}C contents with soil depth~~s~~ (Figure 6). Instead, $\Delta^{14}C$ values of extracts and extraction residues were highly correlated ($r^2=0.91$, $p<0.01$, supplementary Figure S2). However, $\Delta^{14}C$ values of bulk MOC, extractable or residual MOC were ~~, however,~~ all unrelated to total MOC or its extractability (results not shown).

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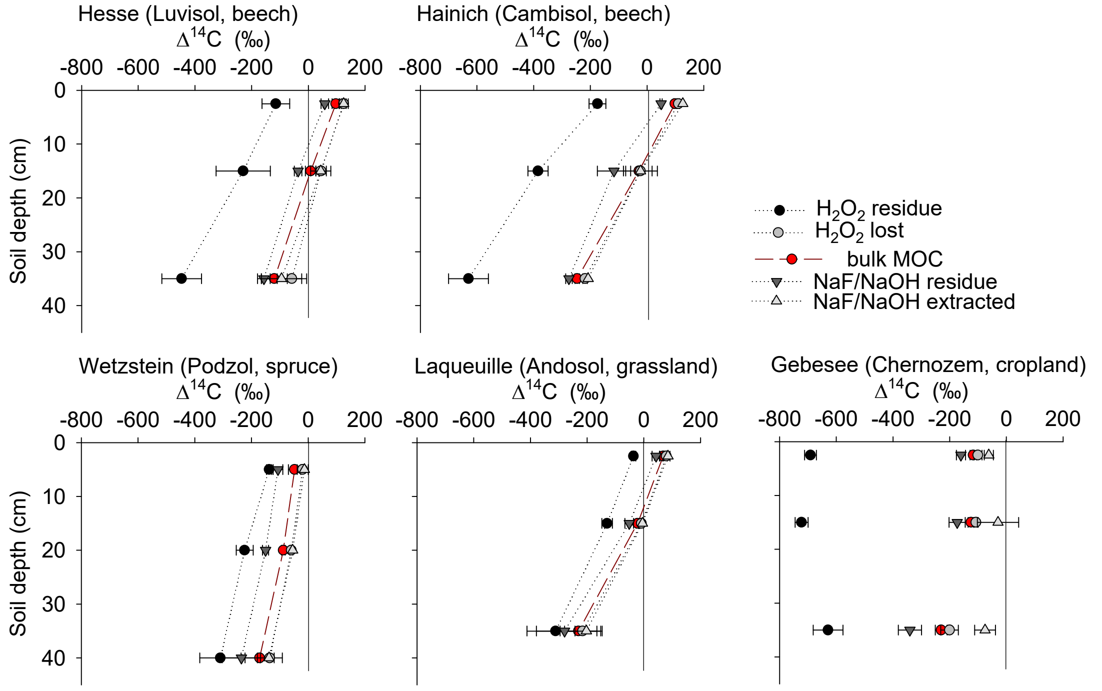

Figure 6: Depth profiles of radiocarbon ($\Delta^{14}C$) in bulk mineral associated OC (bulk MOC), as well as in OC removed from mineral surfaces using either NaF/NaOH or H_2O_2, and in the respective OC residues remaining on mineral surfaces.

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3.~~2~~3 NMR spectroscopy of NaF/-NaOH treated samples

The NMR spectra of extracted OM from soils of the sites Hainich, Hesse, and Laqueille were remarkably similar and dominated by signals in the O/N-alkyl C region (62-74% of total peak area across sites and depths) and the alkyl C region (18-25%), suggesting a strong contribution of carbohydrates and aliphatic compounds to the extracted OM (Figure 47, Table 2). All six spectra also reveal a distinct peak centered around 174 ppm, due to carboxyl C, which is in line with the fact that the alkaline extraction tends to ~~release ~~preferentially release acidic compounds (5-9%). All spectra show small signals in the aromatic regions centered around 150 ppm (phenols) and 130 ppm (non-substituted aromatic systems). All six spectra featured signals, some even well-resolved, around 56 ppm, indicating the presence of methoxyl C.

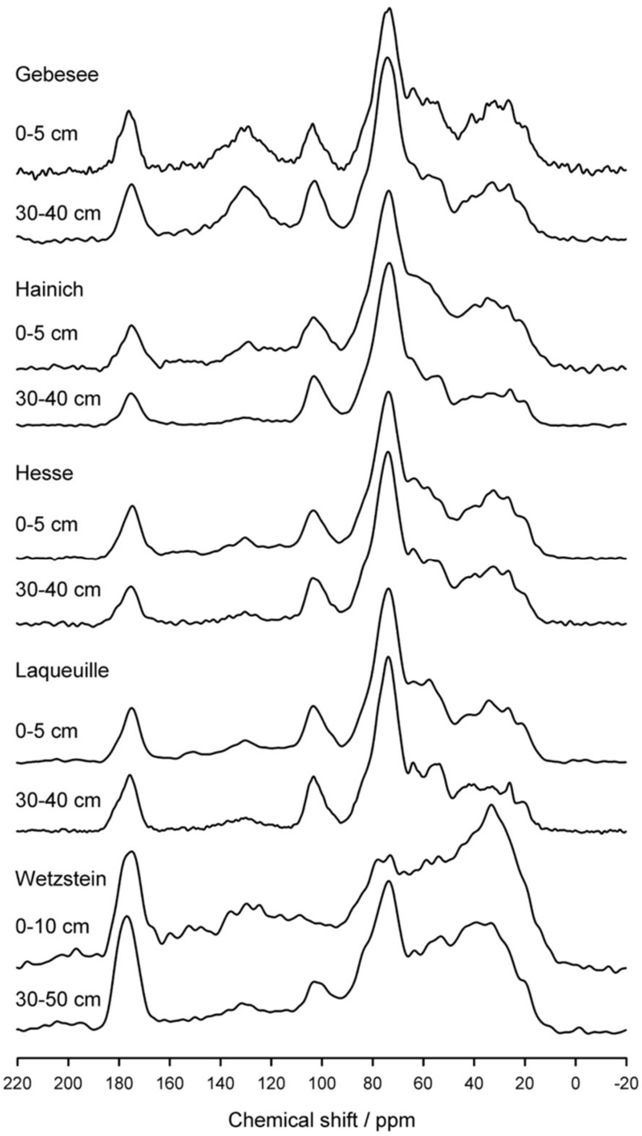

Figure 47: NMR spectra of OM extracted into NaF/NaOH from the mineral associated fraction of two soil depths from the five study sites Gebesee (Chernozem, cropland), Hainich (Cambisol, beech), Hesse (Luvisol, beech), Laqueuille (Andosol, grassland), and Wetzstein (Podzol, spruce).

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Table 2: Distribution of C species in organic matter extracted into ~~0.8 M NaF–0.2 M NaOH~~NaF/NaOH from heavy fractions of mineral topsoil (0–5 cm depth) and subsoil (30–40 or 30–50 cm depth) layers as revealed CPMAS-^{13}C-NMR.

Sample	Carbonyl/carboxyl C 220–160 ppm	Phenolic/aromatic C 110–160 ppm	O/N-alkyl C 45–110 ppm	Alkyl C –10–45 ppm
		%		
Hainich (Cambisol, beech)				
~~Hainich~~ 0–5 cm	6	8	63	24
~~Hainich~~ 30–40 cm	5	3	74	18
Hesse (Luvisol, beech)				
~~Hesse~~ 0–5 cm	8	6	62	24
~~Hesse~~ 30–40 cm	5	3	67	25
Laqueuille (And~~o~~isol, grassland)				
~~Laqueuille~~ 0–5 cm	9	8	62	21
~~Laqueuille~~ 30–40 cm	9	6	63	22
Wetzstein (Podzol, spruce)				
~~Wetzstein~~ 0–10 cm	14	17	35	34
~~Wetzstein~~ 30–50 cm	14	9	47	30
Gebesee (Chernozem, cropland)				
~~Gebesee~~ 0–5 cm	9	14	52	25
~~Gebesee~~ 30–40 cm	6	15	60	19

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The spectra obtained on OM extracted from the Chernozem-type soil at site Gebesee resembles those of the sites Hainich, Hesse, and Laqueille, except for that they indicate more non-substituted aromatic systems, which is ~~in accordance~~consistent with ~~findings on~~ the ~~occurrence~~ ~~occurence~~occurrence of pyrogenic OM in ~~such~~ this soil type~~soil~~. When comparing the spectra of OM from top- and subsoils, differences were surprisingly small at Hainich, Hesse, Laqueille, and Gebesee, with proportions of alkyl and aromatic C tending to decrease in favor of increased signals of O/C-alkyl C. The contribution of carbonyl C remained constant with soil depth.

The spectra obtained on extracted OM from the Podzol-type soil at Wetzstein showed the strongest deviation in spectral features. The signals due to carbonyl/carboxyl, aromatic, and alkyl C ~~are~~ were much more prominent than in all other spectra.

~~When comparing the spectra of OM from top- and subsoils, differences were surprisingly small at Hainich, Hesse, Laqueille, and Gebesee, with tendencies of decreasing proportions of alkyl and aromatic C tending to decrease in favourfavor, of increased signals of O/C-alkyl C. The contribution of signals of carbonyl C remained fairly constant with soil depth.~~ Also t~~T~~he change in composition with depth was much more evident for the Podzol site Wetzstein than the others. Here, aromatic and ~~especially~~ alkyl C decreased while O/C-alkyl increased, ~~probably~~ reflecting the strong re-distribution of OM along the profile during podzolization. The composition of the subsoil OM at Wetzstein approached that of the OM at the sites Hainich, Hesse, and Laqueille.

To understand how the extract differed from the bulk and residual fractions, we also analyzed ~~T~~the bulk MOM and the NaF/NaOH extraction residue of the Hainich 0-5 cm sample ~~were additionally analyzed~~. The signal-to-noise ratio of these spectra was l~~ess~~ower than ~~for~~ in the extracted OM due to the presence of paramagnetic minerals (Figure ~~5~~8). Nevertheless, the results reveal larger ~~portion~~proportions of carbonyl/carboxyl C and especially aromatic C but less O/N-alkyl C for the extraction residue than ~~for~~ in the extracted OM (Figure ~~5~~8, Table 3).

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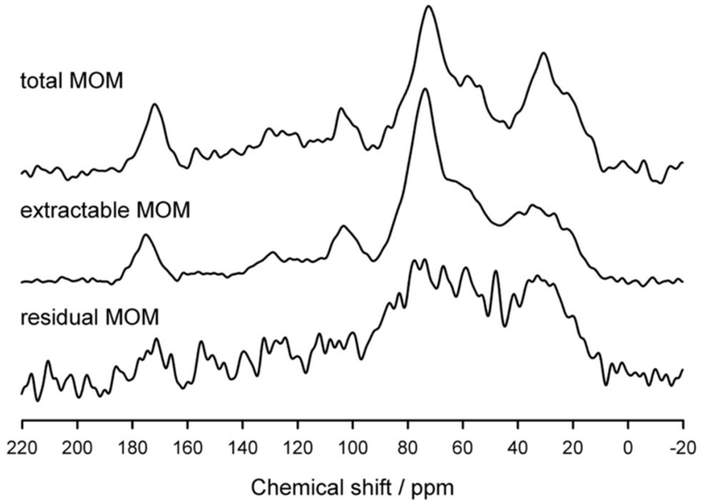

Figure ~~5~~8: NMR spectra of OM from the 0-5 cm layer of the site~~s~~ Hainich (Cambisol, beech). Top: total mineral associated OM (MOM), middle: MOM-fraction extracted into NaF/NaOH, bottom: residual OM after extraction of MOM into NaF/NaOH.

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Table 3: Distribution of C species in total, ~~0.8 M NaF 0.2 M~~ NaF/NaOH-extractable and residual organic matter of the heavy fraction of the mineral topsoil layer (0–5 cm depth) at ~~site~~ Hainich (Cambisol, beech) as revealed by CPMAS-^{13}C-NMR.

	Carbonyl/carboxyl C	Phenolic/aromatic C	O/N-alkyl C	Alkyl C
	220–160 ppm	110–160 ppm	45–110 ppm	–10–45 ppm
Sample	——————— % ———————			
Total OM	8	14	52	26
Extracted OM	6	8	63	24
Residual OM	9	15	50	26

~~The radiocarbon contents were always larger in the extracted or oxidized fractions than in the residues, and decreased (except for the H_2O_2 residues at Gebesee) at all sites with soil depths (Figure 6). Decrease in ^{14}C contents with soil depth was strongest for Hainich and Laqueuille, and least for Wetzstein and Gebesee. Figure 7 shows that results for directly measured ^{14}C in dialyzed NaF/NaOH extracts were overall comparable to calculated ^{14}C in extracts from the mass balance approach, suggesting that there were no systematic losses of older or younger C during the extraction and subsequent dialysis procedure. For Gebesee, the mass balance approach suggests that some young carbon was probably lost during dialyses of the extracts.~~

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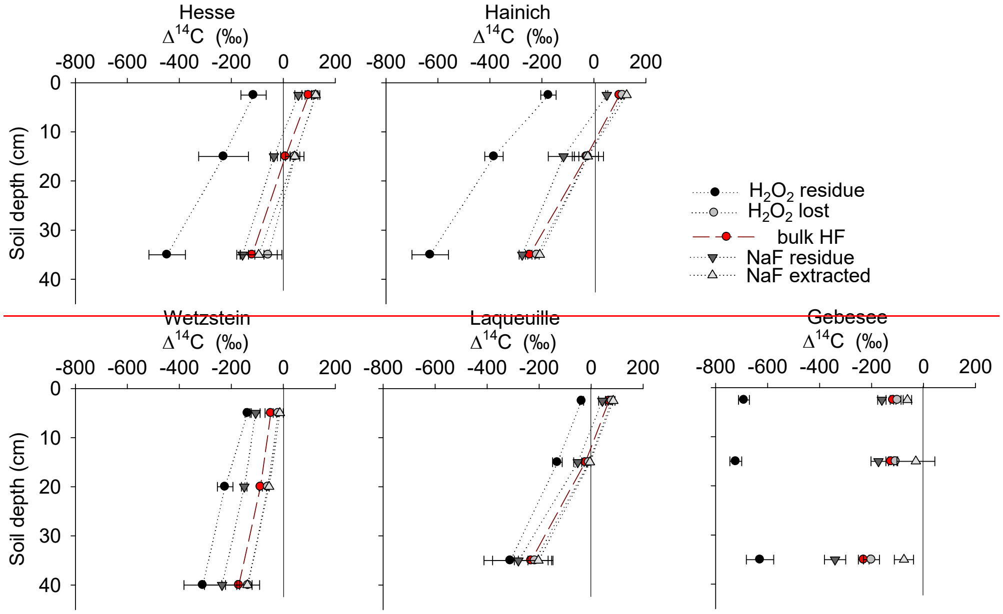

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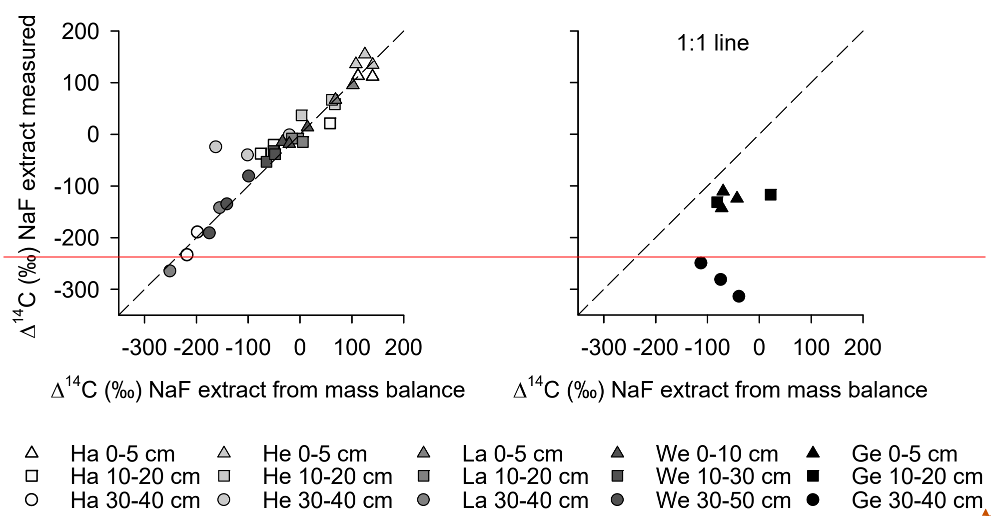
~~Figure 6: Depth profiles of radiocarbon ($\Delta^{14}C$) in bulk mineral associated OC (bulk HF), as well as in OC removed from mineral surfaces using either NaF/NaOH or H_2O_2, and in the respective OC residues remaining on mineral surfaces.~~

~~The ^{14}C contents of the OC extracted from the uppermost layers increased in the order Gebesee < Wetzstein (0-10 cm) < Laqueuille < Hainich < Hesse from -126‰ to 142‰. The average difference in ^{14}C between extracted and residue OC was 79±36‰ across sites and increased in the order Gebesee (34±4‰) < Laqueuille (38±6‰) < Hainich (63±3‰) < Hesse (84±5‰) < Wetzstein (100±15‰). As indicated by the almost parallel shifts in ^{14}C contents (Figure 6), there was no general trend for increasing or declining differences in ^{14}C contents with soil depths. Instead, ^{14}C contents in extracts and extraction residues were highly correlated (r^2=0.91, p<0.01, supplementary Figure S2). ^{14}C contents of bulk MOC, extractable or residual MOC were, however, all unrelated to total MOC or its extractability (results not shown).~~



~~Figure 7: Comparison of ^{14}C contents of NaF/NaOH extracted OC obtained using a mass balance approach and from direct measurements of the extracts after dialyses (study sites: Hainich (Ha), Hesse (He), Laqueuille (La), Wetzstein (We), Gebesee (Ge)).~~

3.~~3~~4 ~~Radiocarbon content of MOC~~ MOC oxidation in heated H_2O_2

On average, only 11±6% of MOC resisted ~~to~~ treatment with heated H_2O_2, with 90±8% ~~being~~of MOC ~~removed~~oxidized in the uppermost layer, 90±6% oxidized in the intermediate layer, and 87±5% oxidized in deepest studied soil layer (Figure 2). ~~oxidized~~The proportion of MOC resisting the H_2O_2 treatment differed between study sites. The largest proportion of H_2O_2-resistant MOC –was found at the Wetzstein site (Podzol, on average 19±4%), especially in the deepest layer, while the smallest proportions of H_2O_2-resistant MOC occurred at Gebesee (Chernozem, 5±3%). The absolute amount of H_2O_2-resistant OC was correlated with the bulk MOC concentration ($r=0.76$, $p<0.01$; Figure 3) but~~, however,~~ the correlation was weaker than the one found for residual OC after NaF/NaOH extraction and bulk MOC.

Residues of the H_2O_2 treatment ~~were much older~~had much ~~smalle~~lower $\Delta^{14}C$ values than residues of the NaF/NaOH extractions (Figure 6). The average $\Delta^{14}C$ values ~~^{14}C contents~~ of H_2O_2 residues ranged between -36±8‰ (Laqueuille) and -691±21‰ (Gebesee) in the uppermost, and between -310±73‰ (Wetzstein) and -630±70‰ (Hainich) in the deepest layer (Figure 6). The difference between $\Delta^{14}C$ values ~~^{14}C contents~~ of oxidized and residual OC in the uppermost layer increased in

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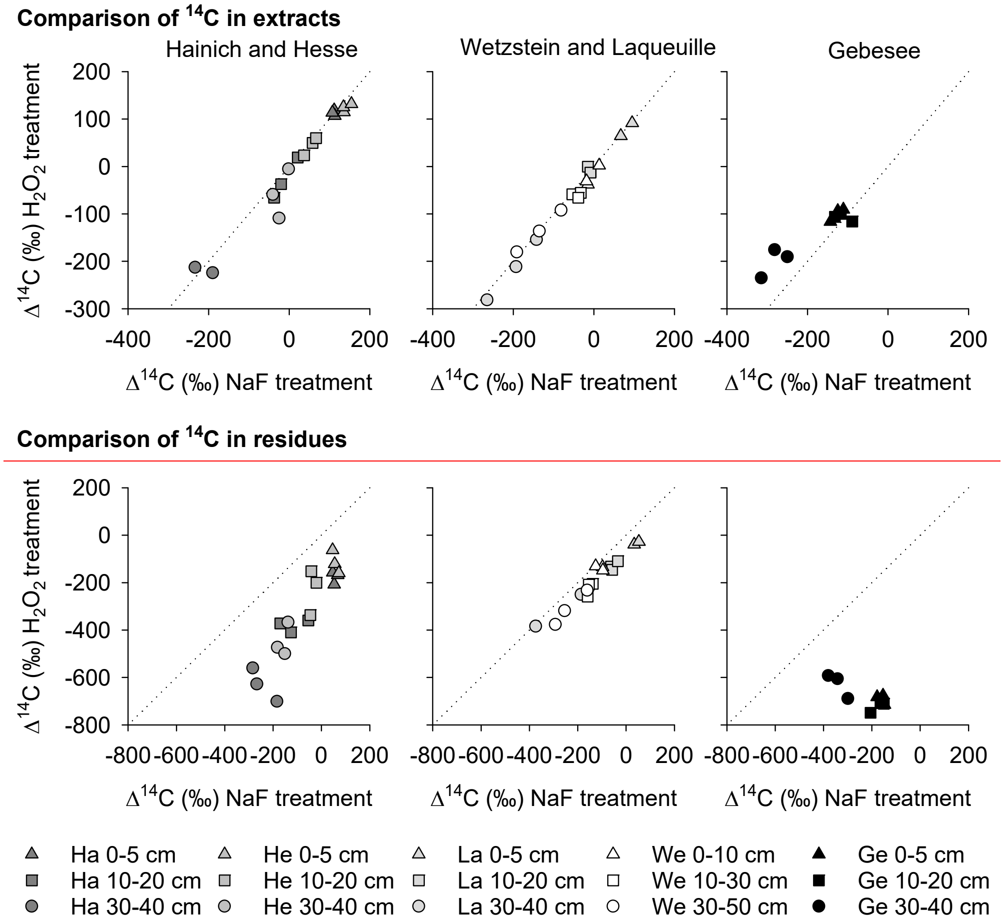
the order Laqueuille = Wetzstein (115‰) < Hesse (239‰) < Hainich (290‰) < Gebesee (591‰), and increased slightly with soil depth at Hesse, Hainich, and Wetzstein.

When comparing Δ^{14}C values ~~^{14}C contents~~ of OC removed by either NaF/NaOH or H_2O_2 treatments, we ~~found, surprisingly,~~were surprised to find ~~that there was basically~~ no ^{14}C-difference for most sites (Figure ~~8~~9), despite different ~~total~~ amounts of ~~total~~ OC being removed by the individual procedures. ~~As indicated by the~~The almost parallel shift in Δ^{14}C values ~~^{14}C contents~~ of H_2O_2 residues from NaF/NaOH residues in all soil profiles~~,~~ indicate that both were ~~typically~~ highly correlated within depth profiles (Figure ~~8~~9). For the sites rich in pedogenic oxides, Wetzstein and Laqueuille (Podzol and Andosol), ~~While~~ Δ^{14}C values ~~^{14}C~~ in NaF/NaOH residues ~~of the sites Wetzstein and Laqueuille~~ deviated from H_2O_2 residues by only 62±26~~‰,~~ ‰. In contrast the difference in extraction and oxidation residual Δ^{14}C values~~-~~ ~~but it was~~were 258±99‰ for the Luvisol and Cambisol sites Hesse and Hainich (Figure ~~8~~9). The only exception was again the Chernozem site (Gebesee), where OC extracted by NaF/NaOH was on average younger than OC removed by H_2O_2, and ^{14}C contents of the two residues ~~were not correlated and~~ differed on average by 456±135‰ and~~.~~ were not correlated.


Comparison of ^{14}C in extracts
Hainich and Hesse
Wetzstein and Laqueuille
Gebesee
$\Delta^{14}C$ (‰) H_2O_2 treatment
200
100
0
-100
-200
-300
-400
-200
0
200
$\Delta^{14}C$ (‰) NaF treatment
Comparison of ^{14}C in residues
$\Delta^{14}C$ (‰) H_2O_2 treatment
200
0
-200
-400
-600
-800
-800
-600
-400
-200
0
200
$\Delta^{14}C$ (‰) NaF treatment
▲ Ha 0-5 cm
■ Ha 10-20 cm
● Ha 30-40 cm
▲ He 0-5 cm
■ He 10-20 cm
● He 30-40 cm
△ La 0-5 cm
□ La 10-20 cm
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■ Ge 10-20 cm
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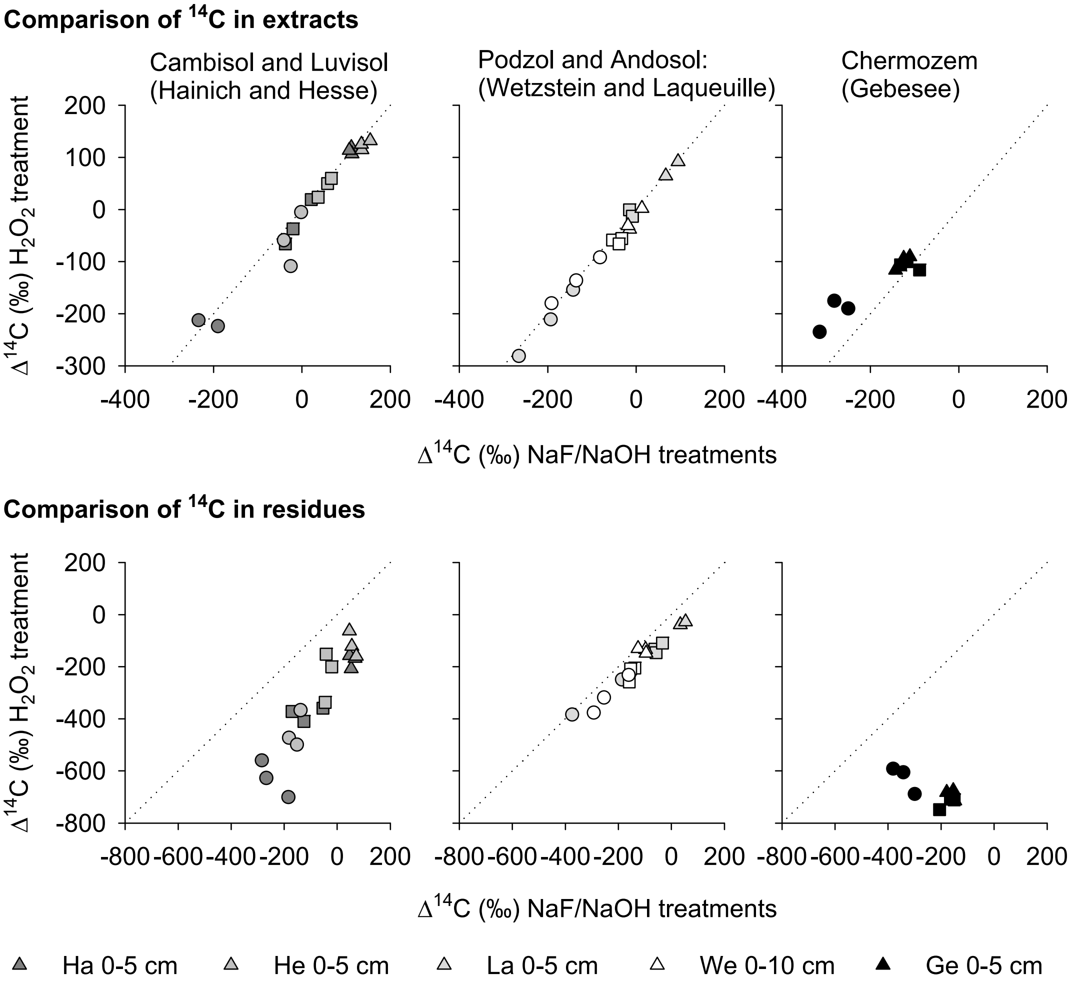

Figure ~~8~~9: Relationships between the radiocarbon content of OC removed from mineral surfaces by H_2O_2 and NaF/NaOH (upper graphs) and ~~between~~ the radiocarbon content of OC residues after treatment with H_2O_2 and NaF/NaOH (lower graphs) for the study sites Hainich (Ha), Hesse (He), Laqueuille (La), Wetzstein (We), and Gebesee (Ge).

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4 Discussion

4.1 Unexpected similarity of the NaF/NaOH-extractable ~~portion~~proportion ~~of total~~ MOC

Strong hysteresis, rendering part of adsorbed OC resistant to desorption, is a common phenomenon found in sorption-desorption experiments with OM (Gu et al., 1994; Oren and Chefetz, 2012). Given that desorption rates in~~to~~ ambient soil solutions are ~~small~~low, we ~~applied~~ consider NaF/NaOH extractability an indicator for maximum potential desorption~~ion,~~. Because the NaF/NaOH extraction ~~introduces~~offers~~, the~~ ideal desorption conditions of the ~~operating via the~~ combination of competing OH^- and F^- anions~~,~~ and alkaline conditions~~, as indicator for potential maximal desorption. Accordingly~~, the method targets OC bound to minerals by Coulombic forces and surface complexation. ~~However, , butt~~The OC desorbed likely also includes ~~likely includes~~ OC held by different ~~more weakly~~weaker forces, such as hydrogen bonds, cation bridges, or hydrophobic interactions.

We ~~hypothesized~~expected that the ~~portion~~proportion of extractable C would increase with OC loading of minerals and ~~accordingly~~ thus be higher in topsoils with larger MOC concentrations than in subsoil layers with smaller ~~ones~~concentrations. Since minerals have different characteristic dominant binding modes for OC at a given pH (Mikutta et al., 2007), we further assumed that extractability would depend on mineral composition and soil pH, with ~~smallest~~ the lowest desorption in acidic soils with larger ~~contents~~ amounts of pedogenic oxides (i.e. the Podzol or the Ando~~i~~sol site in our study). And finally, we expected that land use- and site-specific differences in OM quality would influence MOC extraction. Our results showed, however, that for ~~most~~ our four uncultivated test sites a surprisingly constant ~~portion~~proportion of on average 62±11% of the MOC was extracted by NaF/NaOH, irrespective of soil depth, study site, and original OC concentration. ~~Only at the site under arable management, Gebesee, the portion of extractable OC was smaller (41%).~~ Thus, despite the presumed variation in the chemical composition of litter input and the mineral assemblage between sites, actual interactions between soil OC and minerals ~~seem rather~~were uniform.

~~This could be due to the depletion in weakly bound MOC in response to reduced input and accelerated mineralization of OC caused by the constant soil mixing typical for agricultural sites (Plante et al., 2005; Helfrich et al., 2007). For less disturbed soils with natural vegetation our results suggest that despite the presumed variation in the chemical composition of OC and the mineral assemblage, actual interactions between them seem rather uniform.~~ ~~Experiments on model minerals suggested that desorption increases with increasing OC loading of minerals (Kaiser and Guggenberger, 2007). This would be in line with our observation of reduced desorption at the agricultural soil Gebesee, where OC loading of minerals is probably reduced relative to undisturbed soils by smaller inputs, increased mineralization, and soil mixing by plowing. Although the OC loading of minerals is smaller in subsoils, soil depth did not affect MOC extractability in this study. Also Mikutta et al. (2010) and Möller et al. (2000) observed no significant increase in NaF/NaOH extractability of OC with soil depth. One reason could be that DOC input to subsoils probably occurs mostly along specific flow paths (Bundt et al., 2001) so that exposed mineral surfaces in subsoils could be similarly loaded with OC as topsoils, resulting in similar desorption. Additionally, increasing pH with soil depth possibly reduces the sorption capacity of minerals in subsoils. In any case, an~~

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~~overall consequence of our findings is that a decline in potential desorption is not responsible for greater subsoil OC stability (Rumpel and Kögel-Knabner, 2011) and cannot explain the typically observed increase in carbon ages of MOC with soil depths.~~

Laboratory ~~Experiments~~ experiments ~~in the laboratory~~ showed similar proportions of extracted OC by NaF/NaOH ~~extractability of OC~~ from~~in NaF/NaOH from~~ two Fe-oxides, despite differences in the absolute amounts of OC sorbed by goethite and ferrihydrite (Kaiser et al., 2007). The amounts extracted ~~extractability~~ from these model MOC ~~was~~ werealso ~~unexpectedly~~ surprisingly similar to results of this study (around 65%, Kaiser et al., 2007).~~;~~ ~~and~~ ~~r~~Results from another experiment in which OC was extracted with NaOH from experimentally produced MOC on ~~goethite in another experiment~~goethite also extracted a similar fraction of MOC (57-60%, Kaiser and Guggenberger, 2007). ~~Nevertheless,~~ Thus, we expected to ~~see~~observe ~~a~~ ~~greater~~ more extractable MOC ~~extractability~~ at sites poor in Fe- and Al-oxides but rich in clay minerals (like for the Cambisol at Hainich with 50-70% clay), which we expected would have a larger ~~ith a hypothesized larger~~ share of ~~more~~ weakly bound OC on MOC. It is possible that some of the weakly bonded OC was already lost ~~during~~ in the preceding density fractionation with Na polytungstate solution (Schrumpf et al., 2013). However, ~~T~~the ~~missing relation between soil mineralogy and~~uniform extractability suggests that the extracted OC was ~~predominantly OC~~ bound to minerals by the same mechanism ~~was extracted~~, irrespective of mineral composition. This indicates that either the same dominant bond mechanism operates for different minerals, or that extracted OC originated predominantly from one mineral type. While ~~it is typically assumed that especially pedogenic oxides hold adsorbed~~ OC ~~by~~adsorbed by covalent bonds is usually associated with pedogenic oxides, covalent bonds have also been shown to bind OC on ~~these bonds seem also relvant e.g. for Pedogenic oxides as well as~~ the edges of clay minerals. ~~can hold adsorbed OC by covalent bonds~~ (e.g. Chen et al., 2017; Gu et al., 1994). In our study, ~~These bonds are formed between metal-coordinated hydroxyl groups exposed at surfaces of pedogenic oxides and clay mineral edges and carboxyl groups of OM. The lacking variation in extractability of MOC can thus reflect the dominant role of this type of sorptive interaction in the formation of mineral-organic associations under the acidic to neutral soil reactions of the study sites.~~ t~~T~~he linear relation between MOC and extraction residues with the sum of oxalate-extractable Al and dithionite-extractable Fe ~~in our study~~ indicates that pedogenic Al and Fe oxi-hydroxides were important for OC binding across the study sites (Figure 4, A2). ~~Apparently, even~~Even very high clay contents (>50%),~~,~~ such as at the Hainich site, ~~cannot~~ could not compensate for ~~smaller contents of~~lower pedogenic oxide content~~s~~, resulting in lower ~~for~~ MOC storage. The measured uniform extractability of MOC ~~could accordingly also~~ is therefore likely ~~be~~ an immediate result of the pedogenic oxides controlling MOC accumulation.

~~Despite its different chemical composition, desorption of MOC from the coniferous forest site Wetzstein did not differ from desorption of MOC from the other non-arable sites. This indicates that the overall molecular composition of OM matters less for sorption-desorption than the presence of functional groups capable to interact and form bonds with mineral surfaces. This is in agreement with the idea discussed above, that extracted MOC was predominantly from the same bond type, and rather driven by the presence of functional groups on both, minerals and OM, than by their type or composition.~~

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The ~~very~~ similar chemical composition of MOC extracted from the sites Hainich, Hesse, and Laqueille ~~hints also at~~further supports a uniform ~~ing~~m-echanism ~~processes within the mineral soilon~~dominating -association of organic C with minerals, ~~again with~~especially given ~~no a~~the lack of variation~~s with~~ with ~~differing contents of~~ pedogenic oxide~~s~~ content. One explanation could be that the type of sorptive interaction targeted by the NaF/NaOH extraction ~~used~~ selects for a specific composition of the extracted MOC. Alternatively, the similar MOC composition may reflect ~~the~~ uniform~~ing~~ microbial processing of the organic input (Liang et al., 2017). However, differing chemical composition at the sites Gebesee and Wetzstein suggest that ~~specific site~~site-specific properties and pedogenic properties can ~~nevertheless~~ indeed~~be~~ ~~imprinted~~ ~~in~~influence MOC composition. For the Chernozem at Gebesee, higher contents of non-substituted aromatic systems are ~~probably~~ likely due to a different vegetation history, where also fire played a role. Differences in OM composition between the sites Wetzstein and Laqueille were ~~somewhat~~ surprising, since the pedo-environmental conditions (acidity and mineralogy) of OM accumulation in Podzol-type and ~~Andosol~~Ando~~i~~sol-type soil are often ~~often~~ considered similar (Aran et al., 2001; Young et al., 1980). The unique MOC composition in the podzol-type soil are likely due to the unique~~The decomposing~~ decomposition conditions at that site ~~at the Podzol-type soil~~ (conifer-dominated vegetation, pH, microbial community, ~~conifer-dominated vegetation,~~ soil climate), which subsequently uniquely influences the ~~probably affected the~~ dissolved organic carbon production and chemistry~~, and thus~~ at that site. ~~MOC formation and composition.~~

Experiments on model minerals suggested that desorption increases with increasing OC loading of minerals, i.e. when more OC is bound per mineral content of a sample (Kaiser and Guggenberger, 2007). This ~~would be in~~is ~~line~~ consistent with our observation of reduced NaF/NaOH extraction at the agricultural soil Gebesee, where OC loading of minerals is ~~probably~~ reduced relative to undisturbed soils ~~by~~due to ~~smaller~~ lower inputs, increased mineralization, and soil mixing by plowing (Plante et al., 2005; Helfrich et al., 2007). Although Figure 4 shows that for the same amount of pedogenic oxides, less OC was bound to MOM in subsoils~~lower~~, soil depth did not affect MOC extractability in this study. This result is supported by studies by ~~Also~~ Mikutta et al. (2010) and Möller et al. (2000), which observed no significant decrease in NaF/NaOH extractability of OC with soil depth. ~~Assuming that it requires similar OC loading,~~ O~~o~~ne explanation for the uniform extraction with soil depth could be that DOC input to subsoils occurs mostly along specific flow paths (Bundt et al., 2001), ~~so that~~enabling exposed mineral surfaces in subsoils ~~could be similarly loaded with OC~~to have similar OC loads as topsoils. Additionally, increas~~ing~~ing pH with soil depth ~~possibly reduces~~could reduce the sorption capacity of minerals in subsoils. Assuming that pH reduces the total number of available sorption sites at depth, the same proportion of available sorption sites could be occupied in subsoils than in topsoils, despite a smaller ratio of OC-to-pedogenic oxide contents. ~~In any case, an overall consequence of our findings~~ Whatever the mechanism, our findings confirm ~~is~~ that a decline in potential desorption is not responsible for greater subsoil OC stability (Rumpel and Kögel-Knabner, 2011) and cannot explain ~~the typically observed~~ increased ~~in~~ carbon ages of MOC with ~~soil~~ depths.

~~Experiments on model minerals suggested that desorption increases with increasing OC loading of minerals (Kaiser and Guggenberger, 2007). This would be in line with our observation of reduced desorption at the agricultural soil Gebesee,~~

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~~where OC loading of minerals is probably reduced relative to undisturbed soils by smaller inputs, increased mineralization, and soil mixing by plowing. Although the OC loading of minerals is smaller in subsoils, soil depth did not affect MOC extractability in this study. Also Mikutta et al. (2010) and Möller et al. (2000) observed no significant increase in NaF/NaOH extractability of OC with soil depth. One reason could be that DOC input to subsoils probably occurs mostly along specific flow paths (Bundt et al., 2001) so that exposed mineral surfaces in subsoils could be similarly loaded with OC as topsoils, resulting in similar desorption. Additionally, increasing pH with soil depth possibly reduces the sorption capacity of minerals in subsoils. In any case, an overall consequence of our findings is that a decline in potential desorption is not responsible for greater subsoil OC stability (Rumpel and Kögel-Knabner, 2011) and cannot explain the typically observed increase in carbon ages of MOC with soil depths.~~

4.2 ~~No relationship between~~ ~~Missing relations~~ ~~between~~ MOC desorption and ~~and~~ ~~^{14}C-age~~Δ^{14}C values

Results of ~~the~~ ^{14}C analyses of NaF/NaOH extracts and residues confirmed our hypothesis of preferential extraction of younger carbon, with ~~smalle~~lower Δ^{14}C-values ~~than~~in residues compared to extracts or unextracted MOM~~. That result was consistent~~ across soil types and depths. ~~It suggests tha~~These findings indicate that desorption facilitates the exchange of old OC for new OC on mineral surfaces, ~~resulting in on average younger extractable than~~ while non-extractable OC~~, which~~ is less frequently exchanged. Using Na pyrophosphate as extractant, Heckman et al. (2018) also observed consistently younger OC in MOC extracts and older OC in extraction residues across different soils and soil depths. We expected Na pyrophosphate ~~has~~ would have a similar effect on MOC as NaF/NaOH due to ~~a~~ the comparable ~~raise~~ increase in pH and because both~~,~~ pyrophosphate and fluoride~~,~~ act as chelating agents~~, and thus,~~ to strongly compete with OC for binding sites on mineral surfaces.

~~One reason for the extraction resistance of s~~Some ~~OC on MOC~~MOC may be resistant to extraction due to multiple chemical bonds binding the OC ~~could be that it is more tightly bound to~~with greater strength to mineral surfaces ~~by multiple bonds~~ {Kaiser, 2007 #19}. ~~One question remaining is what characterizes the non-desorbable MOC fraction. While most aggregates were destroyed by the sonication treatment during density fractionation, potential contribution of stable microaggregates to OC protection against extraction cannot be excluded. Since desorption of OC with NaOH did not result in an increase in the micropore volume, and because non-desorbable OC had a higher apparent density, Kaiser and Guggenberger (2007) ascribed the MOC fraction not extractable into NaOH to OC tightly bound to mineral surfaces by multiple bonds, preferably at the edges of and across micropores.~~ Since multiple bonds require a higher number of~~-~~ involved functional groups~~ involved~~, OC of extraction residues of multiply bonded OC ~~should~~should be enriched in carboxylic groups. ~~This is supported by our~~Our NMR data support the resistance mechanism of multiple bonds, showing a higher share of carbonyl/carboxyl groups in non-extractable than in extractable MOC from the Hainich site. Phenolic and aromatic groups, which are also known to bind preferentially and strongly to mineral surfaces (Chorover and Amistadi, 2001; Kothawala et al., 2012; Avneri-Katz et al., 2017), were also enriched in the residues, while O/N-alkyl-C was depleted. Given this mechanism, we expect t~~T~~he non-

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desorbable ~~portion of~~ OC ~~could accordingly~~to be composed of aromatic and other compounds strongly bound to mineral surfaces by multiple functional groups, but this remains to be tested in future studies.

Our results did not confirm our original expectation, that the average age of MOC is inversely related to its extraction in NaF/NaOH, due to the strength of the stabilizing chemical bonds in non-desorbable MOC.

~~Our results did not confirm oWe further hypothesized that soils with more extractable have older average ages than, could however not be confirmedMOC should have on average younger ^{14}C ages. . Such a positive relation between extractable OC and ^{14}C was not observed for any soil depth or fraction across sites.~~ This ~~is possibly a~~may be a direct consequence of the ~~rather~~ small variation in OC extractability~~-~~ between samples and shows that extraction~~p~~ in NaF/~~-~~NaOH is not able to explain between-site variation in Δ^{14}C values. ~~Further, some laboratory studies showed that OC sorbed to goethite is less bioavailable than OC on clay minerals (e.g. Mikutta and Kaiser, 2011; Mikutta et al., 2007). This should lead to faster turnover of MOC in clay-rich sites relative to sites rich in oxides, and so we expected to find younger extractable MOC at clay-rich than at oxide-rich sites. By contrast, we also found no indication that clay-rich soils have generally younger carbon than soils rich in pedogenic oxides. Again, the assumptive dominant control of pedogenic oxides on total MOC contents across sites could have masked a potential effect of mineral composition on bioavailable MOC.~~

4.3 Comparison between NaF/NaOH extraction and H_2O_2 oxidation results

~~In accordance with our expectation~~As expected, residues of H_2O_2 treatments were older than residues of NaF/NaOH extractions. We further hypothesized that~~, as a result of~~ the heated H_2O_2 treatment would remov~~al of~~e a larger~~,~~ and ~~therefore~~ on average more ~~stabilized~~ stable fraction~~ with the heated H_2O_2 treatment~~, and therefore the oxidized OC ~~oxidized~~ would ~~also be on average older~~have an older mean age than the extracted OC. ~~DespiteBut while~~While H_2O_2 removed on average 89% of bulk HF-OC and NaF/NaOH removed only 62%, the ^{14}C ages of ~~eac~~MOC~~h~~ ~~both r~~removed ~~MOC~~ by oxidation were surprisingly ~~fractions had were~~ comparable to those extracted by NaF/NaOH~~-^{14}C ages~~. ~~Seemingly,~~ This result indicates that NaF/NaOH residues ~~still~~ contain oxidizable OC of similar or only slightly older age as the extracted material. ~~This result indicates that~~We found that both~~,~~ NaF/NaOH and H_2O_2~~,~~ mostly removed ~~mostly~~ OC from a ~~large~~ younger~~,~~ ^{14}C-~~richer~~ enriched pool, ~~leaving~~ resulting in increasingly old residual OC ~~OC behind, the~~as more OC is removed. ~~While unexpected,~~ Jagadamma et al. (2010) ~~silimarly~~similarly ~~, O~~observed that sequentially stronger oxidants removed C with ~~also observed~~ similar ^{14}C contents~~ of OC removed from bulk soil samples with different oxidation reactants~~, irrespective of the extent of OC removal. Applying a mass balance approach to the results of the ~~different~~ extraction procedures ~~applied~~ used by Helfrich et al. (2007) ~~shows~~ showed ~~that also for their~~similar soil~~s~~ ^{14}C contents of removed OC~~ were similar~~, irrespective of the

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extracted OC amounts. Accordingly, a large ~~portion~~proportion of MOC ~~could~~ is ~~be~~ more homogenous in ^{14}C contents than ~~expected~~previously thought, while ~~apparently~~ only a ~~rather~~ small ~~portion~~proportion ~~has~~ is very old ~~ages~~.

The Δ^{14}C difference between NaF/NaOH and oxidation residues was unexpectedly smaller for the two soils rich in pedogenic oxides (Laqueuille, Wetzstein) ~~than~~ compared to~~for~~ the Luvisol and the Cambisol ~~the other sites~~. The soils rich in pedogenic oxides ~~also~~ had slightly higher amounts of OC left in oxidation residues, suggesting that they protected a larger ~~portion~~proportion of OC against oxidation. ~~, but this OC was younger than in the soils from the other sites.~~ Eusterhues et al. (2005) similarly observed that more OC resisted H_2O_2 oxidation in subsoils rich in pedogenic oxides, and older residues in the Dystristic Cambisol than the Haplic Podzol studied. This study, in combination with our results, suggests that ~~Accordingly, h~~high contents of pedogenic oxides in soils ~~seem to~~ increase oxidation resistance of MOC but do ~~generally~~ not increase residue ages. Accordingly also oxidation is likely not the dominant mechanism for exchange of OC on these mineral surfaces. The ~~comparatively~~ relatively young oxidation residues at Wetzstein and Laqueuille in our study could be due to high DOC fluxes, and thus, overall faster OC replacement of all MOC components at the Podzol site Wetzstein, and the younger soil age of the ~~Andosol~~ Ando~~i~~sol soil at Laqueuille. It is further possible that at some of the sites, old oxidation-resistant OC was inherited from the parent material (e.g., the loess layer or limestone residues ~~in~~ at Hainich and Hesse) or a specific fire history (e.g., at the Chernozem site Gebesee, where only small, but very old amounts of OC were left after the H_2O_2 treatment).

4.4 Changes in OC turnover along soil profiles

The close correlations between Δ^{14}C ~~contents~~ values of NaF/NaOH extracts and residues along the soil profiles (see also Figure A4) result in a parallel decline in Δ^{14}C values~~^{14}C~~ of both fractions with soil depths. ~~Accordingly, n~~Not only was the same ~~portion~~proportion of OC ~~was~~ extract~~able~~ed across soil depths, but also the absolute differences between Δ^{14}C values ~~^{14}C contents~~ of extracts and residues remained constant. ~~In line~~The ~~with the~~ observed constant extractabilit~~y,~~y indicates that changes in Δ^{14}C ~~^{14}C depth~~ with depth~~profiles of MOC~~ are ~~therefore apparently~~ not driven by an ~~specific~~ increase in the stability of ~~either~~ residual or extractable OC. ~~Instead, the same extraction-sensitive bond type and strength was affected along soil profiles, independent of site-specific differences in absolute ^{14}C values or the slope of the depth decline in ^{14}C.~~ This suggests that (1) the distribution ~~of MOC between~~ fast and slower cycling MOC is constant with depth ~~with depth~~ and that (2) the ~~overall~~ shape of the ^{14}C distribution ~~within~~ of ~~a~~ MOC~~sample~~ (if we consider ~~MO~~^{14}C in MOC to be a continuum) remains constant with depth. This is supported by the observation that ~~also~~ residues of the H_2O_2 treatment, though on average much older, declined almost parallel to NaF/NaOH residues with soil depth. ~~Whatever~~ The factor that causes the ~~^{14}C~~ decline of Δ^{14}C values with soil depth~~, it~~ is ~~apparently~~ shifting the entire ^{14}C ~~age~~ distribution of ~~the~~ MOC. This, along with ~~hints, similar to~~ the uniform extractability, suggests~~at~~ that subsoil and topsoil MOC ~~being similarly~~are at comparable equilibriums with ~~its~~ their environment, and the reasons for overall ^{14}C declines with depth in soils are not due to changes in the character of mineral- organic matter stabilization mechanisms ~~than topsoil MOC.~~ .

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~~Differences in the overall depth decline of ^{14}C between sites could be due to differences in (D)OC transport rates along the soil profile or in root litter input. Kindler et al. (2011) measured overall much higher DOC leaching rates from topsoils at Wetzstein than at Laqueuille or Hainich, while leaching rates from Wetzstein subsoils were only slightly increased, suggesting that a large portion of this mobilized topsoil DOC at Wetzstein was adsorbed in the subsoil. This probably resulted in a rejuvenation of subsoil OC, and thus, the less steep depth decline of ^{14}C relative to the other two sites.~~

~~The small increase in the portion of oxidation-resistant OC at depth together with the slightly stronger decline in ^{14}C of oxidation residues with depth relative to bulk MOC, indicate that, different from desorption resistance, oxidation resistance, i.e., chemical recalcitrance, of a small portion of MOC becomes a bit more relevant to the formation of stable MOC with soil depth.~~ Previous studies showed that the oxidation resistant proportion of bulk soil samples ~~was~~ increas~~ing~~ed with soil depth {Butnor, 2017 #169;Eusterhues, 2005 #107}. While the MOC analyzed in this study~~For the MOC samples studied here,~~ showed only ~~this was only~~ a small and insignificant trend in oxidation resistance with depth~~.~~, we did observe ~~Since there was also~~ a ~~slightly~~ stronger ~~The small increase in the portion of oxidation-resistant OC at depth together with the slightly stronger~~ decline in Δ^{14}C values~~^{14}C~~ of oxidation residues with depth relative to bulk MOC. Thus,~~Accordingly, , indicate that, different from desorption resistance,~~ oxidation resistance (~~,~~ i.e., chemical recalcitrance), rather than desorption resistance is likely responsible ~~of a small portion of MOC might becomes a bit more relevant to~~ the formation of stable MOC with soil depth. ~~However, t~~The ~~observed increase in Δ^{14}C differences~~divergence of ~~between~~ oxidized and residual Δ^{14}C values ~~OC with smaller~~as more OC is oxidized occurred across sites ~~OC amounts left in H_2O_2 residues across sites~~ (Figure A3), suggest~~s~~ing ~~that there could also be~~ an overall trend ~~for~~of increasingly older OC ~~the~~ with smaller ~~the~~amounts of ~~OC amount left~~OC remaining on the minerals.

5 Synthesis and implications

5.1 Suitability of chemical fractionation schemes to study MOC stability

NaF/NaOH extraction and H_2O_2 oxidation results suggest that, rather than averaging over a wide distribution of ages, the ~~largest share~~majority of total MOC has very similar ^{14}C contents,~~, irrespective of the way it is removed,~~ ~~while and~~with only a small proportion (on average <12%) of total MOC ~~is~~being much older than the mean of the extracted or oxidized fractions. The ~~D~~different chemical fractionation schemes ~~apparently always~~ removed OC from the same pool, leaving increasingly old OC behind. ~~Also n~~Neither chemical oxidation nor NaF/NaOH extractability of MOC were related to ~~its~~the Δ^{14}C values of the

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removed OC. The combined application of several chemical fractionation schemes can therefore help ~~to~~ identify ^{14}C distributions of samples, but their value for explaining site-specific differences in Δ^{14}C values ~~seems overall~~ is limited.

5.2 Similarity of MOC extraction results across sites

The initial assumption of this study was that the stability of mineral-bound OC ~~should~~ would be related to desorption, and thus, vary between soils with different mineral composition and under different land use. ~~It turned out~~We found that OC extracted in NaF/NaOH was indeed consistently younger than bulk MOC, suggesting that desorbed OC was more frequently exchanged than the older residue. The ~~overall~~ chemical uniformity of extracted MOC ~~across~~for three sites (two beech forests and one grassland) ~~and depths~~ suggests a certain selection for specific OC molecules during MOC formation or that ~~.~~ ~~Alternatively,~~ microbial processing of OC on mineral surfaces homogenizes MOC composition relative to original OM differences from litter and vegetation types. However, the Podzol site and the Chernozem site ~~showed a certain deviating pattern~~deviated from the pattern of the other results, indicating that factors including decomposition conditions affecting DOC ~~amount and composition, or~~ or a~~a~~ specific fire history can affect the organic matter composition of MOC.

~~The extractability of~~Despite differences in mineral and chemical composition, extractability of MOC was~~, however nevertheless,~~ uniform across non-cultivated soils and depths for the acid to neutral central European soils studied~~, irrespective of mineral composition or chemical composition of extracted OC~~. Based on these results, ~~it seems that the formation of~~most extractable MOC is formed from ~~mostly due to~~ specific -interactive functional groups,~~,~~ ~~such as~~including metal-coordinated hydroxyl groups on the minerals and carboxyl groups of OM.~~, while the~~ The minerals or OM molecules that~~,~~ these groups are attached to~~,~~ are ~~rather~~ interchangeable. ~~However, as~~~~Because~~Since ~~T~~total MOC amounts were controlled by contents of pedogenic Al and Fe oxides across sites, ~~, irrespective of the clay content in the samples. Therefore,~~ ~~e~~extraction results may~~probably~~ mostly reflect ~~only~~ the response of oxides, which ~~then~~ would ~~conceal~~ overshadow potential mineral-specific differences in binding strengths observed ~~for~~ in pure minerals in the laboratory. ~~This~~ This ~~is~~ supports~~ing~~ the paradigm that oxides are more important than clay for OC storage in soil (Rasmussen et al., 2018) and could facilitate ~~easier simpler~~ modelling of MOC formation and turnover in the future.

5.3 Subsoil MOC stability

We observed ~~N~~no indication ~~for~~ of the presence of stronger, less desorbable bonds between OC and minerals in subsoils than topsoils ~~was observed~~, ~~and there was no preferential~~and declines in the ^{14}C content of extracts ~~or~~and extraction residues with depth paralleled each other. Consequently, ~~most~~ subsoil OC ~~would also~~was not ~~be~~ better protected against desorption, and thus, potential subsequent degradation than topsoil OC. Although older, subsoil MOC can be equally vulnerable to changes

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Formatiert: Kommentartext, Zeilenabstand: 1,5 Zeilen in soil environmental conditions like temperature. Reduced ~~desorption~~NaF/NaOH-extraction ~~observed~~ at the cropland site indicates that ~~it~~desorption m~~ight~~ay ~~not be totally~~be ~~unrelated~~explained in part by ~~to~~ OC -loading of minerals. A possible explanation for the missing depth gradient in MOC extraction is that subsoil MOC is typically ~~similarly~~ at a similar equilibrium with the local conditions as the topsoil. This could be the case if OC input to undisturbed subsoils occurs mostly in hotspots, for example via root inputs ~~and~~or along preferential flow paths, where OC ~~is binding~~binds to exposed mineral surfaces but bypass~~ing~~es surfaces located inside aggregates or away from such hot spots.

~~The overall chemical uniformity of extracted MOC across sites and depths suggests selection for specific OC molecules during MOC formation. Alternatively, microbial processing of OC on mineral surfaces homogenizes MOC composition relative to original OM differences from litter and vegetation types. Small differences in the amounts of e.g. aromatic compounds in extracted MOC with soil depth and between sites still indicate the contribution of strongly sorbing compounds to MOC formation. However, the formation of extractable MOC seems to be overall controlled by the presence of interactive functional groups, such as metal-coordinated hydroxyl groups on the minerals and carboxyl groups of OM, while the minerals or OM molecules, these groups are attached to, are rather interchangeable.~~

5.4 Alternative hypothesis for site- and depth-specific differences in ^{14}C

Despite the overall similarity in MOC composition and extractability across sites, Δ^{14}C values ~~^{14}C contents~~ of extracted MOC (and of extraction residues) were pro~~portionpro~~portional to Δ^{14}C values in bulk MOC~~,~~ and ~~thus,~~ exhibit~~ing~~ed site-specific differences. ~~. In contrast to total MOC storage, its ^{14}C content seems not controlled by sorbing minerals~~Since Δ^{14}C values ~~^{14}C contents~~ of bulk MOC and its fractions are ~~apparently~~ independent of OC resistance to desorption ~~-~~and soil mineralogy, site specific differences ~~are possibly rather~~are likely driven by ~~OC input~~other factors driving MOC accumulation and displacement, rather than intrinsic differences in bond stabilities. Assuming that MOC is the product of DOC entering and leaving mineral surfaces, Δ^{14}C values of MOC should be ~~senstitive~~sensitive to site-specific differences in fluxes, ~~compostion~~composition and Δ^{14}C values of DOC (Figure 10). These ~~would probably rather~~metrics should reflect differences in overall ecosystem properties and decomposition conditions ~~than soil mineralogy~~, including ~~like~~ litter chemistry, soil pH, microbial community composition or climate, rather than soil mineralogy. ~~This would imply that MO^{14}C should be sensitive to the ^{14}C content and amount of DOC entering or leaving MOC, and thus, ecosystem properties driving OM decomposition, DOC production and transport (such as litter or OM amount and chemistry, pH, microbial community, climate).~~

Differences in depth profiles of Δ^{14}C values would then be caused variations in OC input by roots and DOC transport. Under conditions of lower direct litter input, vertical OC transport e.g. ~~according to~~ the "cycling downwards" concept (Kaiser and Kalbitz, 2012) would ~~become more important for~~be shape the trends of Δ^{14}C values ~~in subsoils, thereby shaping the different depth profiles.~~ with depth. ~~-~~Alternatively, differences in the stability of pedogenic oxide minerals themselves are also shaped by soil environmental factors.

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For example, at the Podzol site Wetzstein, the thick ~~humus~~organic layer (8-14 cm) overlying the topsoil could have contributed to old Δ^{14}C values of total and extractable MOC in the uppermost mineral layer relative to the other undisturbed sites via input of pre-aged DOC. Kindler et al. (2011) measured ~~overall~~ much higher DOC leaching rates from topsoils at Wetzstein than at Laqueuille or Hainich, ~~while~~ despite only slightly higher subsoil leaching rates ~~from Wetzstein subsoils were only slightly increased~~, suggesting that a large proportion of this mobilized topsoil DOC at Wetzstein was adsorbed in the subsoil. This ~~probably resulted in a~~likely rejuvenat~~ion~~ed ~~of~~ subsoil OC, and thus, the less steep depth decline of ^{14}C relative to the other two sites. Future research on the role of DOC formation, composition and Δ^{14}C values ~~values~~ for accumulation and exchange rates of OC on mineral surfaces along soil profiles under field conditions ~~might help to better understand the emergence~~will contribute to the understanding of the age distribution of MOC in soils.

~~Assuming that DOC is either the main direct source for new MOC or the carbon source of microbial residues sorbing to minerals, its concentration, composition, and flux in the soil solution could determine OC accumulation and exchange rates on minerals (Kaiser and Kalbitz, 2012; Sanderman et al., 2008). Similar to the chemical composition of the extractable MOC, also its age could be controlled by DOC production, and thus, the overall decomposition conditions and ecosystem properties. The idea is supported by the positive relation between the ^{14}C contents of NaF/NaOH extracts and ^{14}C contents of the light fractions in topsoils (Figure 9). Site-specific differences in MO^{14}C are, therefore, possibly dependent on local microbial activity and litter decay rates. MOC ages can further be modified by site- and soil depth-dependent differences in the ^{14}C content of DOC. The thick humus layer (8-14 cm) overlying the topsoil of the Podzol at Wetzstein could for example have contributed to the old extractable MOC in the uppermost mineral layer via input of pre-aged DOC.~~

~~Since difference in desorption cannot explain different MO^{14}C depth distributions, these are then probably rather due to variations in OC input by roots and DOC transport. Under conditions of much lower direct litter input, vertical OC transport according to the "cycling downwards" concept (Kaiser and Kalbitz, 2012) would become more important for ^{14}C in subsoils, thereby shaping the different depth profiles.The thick humus layer (8-14 cm) overlying the topsoil of the Podzol at Wetzstein could for example have contributed to the old extractable MOC in the uppermost mineral layer via input of pre-aged DOC.~~

~~but rather by the turnover, accumulation, and displacement rates of OC. This would imply that MO^{14}C should be sensitive to the ^{14}C content and amount of DOC entering or leaving MOC, and thus, ecosystem properties driving OM decomposition, DOC production and transport (such as litter or OM amount and chemistry, pH, microbial community, climate).~~

~~No indication for the presence of stronger, less desorbable bonds between OC and minerals in subsoils than topsoils was observed, and there was no preferential decline in the ^{14}C content of extracts or extraction residues with depth. Consequently, most subsoil OC would also not be better protected against desorption, and thus, potential subsequent degradation than topsoil OC. Reduced desorption observed at the cropland site indicates that it might not be totally unrelated to OC-loading of minerals. A possible explanation for the missing depth gradient in MOC extraction is that subsoil MOC is typically similarly at equilibrium with the local conditions as the topsoil. This could be the case if OC input to undisturbed subsoils occurs~~

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~~mostly in hotspots via root input and along preferential flow paths, where OC is binding to exposed mineral surfaces but bypassing surfaces located inside aggregates. Since difference in desorption cannot explain different MO^{14}C depth distributions, these are then probably rather due to variations in OC input by roots and DOC transport. Under conditions of much lower direct litter input, vertical OC transport according to the "cycling downwards" concept (Kaiser and Kalbitz, 2012) would become more important for ^{14}C in subsoils, thereby shaping the different depth profiles.~~

~~NaF/NaOH extraction and H_2O_2 oxidation both suggest that the largest part of total MOC has similar ^{14}C contents, irrespective of the way it is removed, while only a small portion (<20%) of total MOC is much older. Different chemical fractionation schemes apparently always remove OC from the same continuum, leaving increasingly old OC behind. Future research on the role of DOC and soil solution chemistry for accumulation and exchange rates of OC on mineral surfaces along soil profiles under field conditions might help to better understand the emergence of the age continuum of MOC.~~

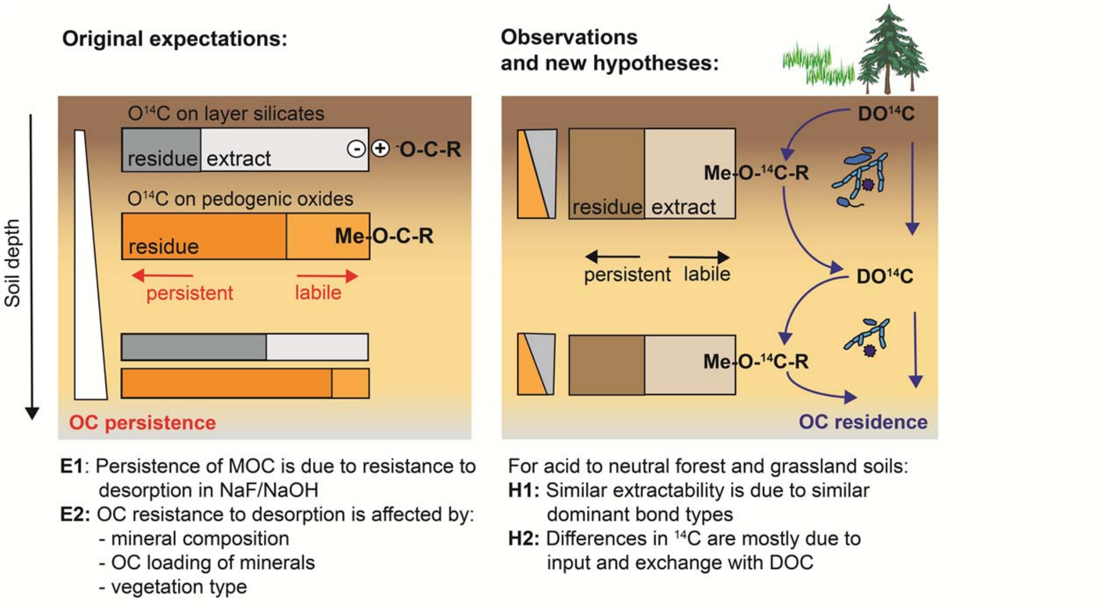

Figure 10: Graphical summary of (1) original expectations (left) where potential MOC desorption explains MOC persistance and varies with mineral composition and soil depth; (2) the observation of site-independent desorption (right), and alternative hypotheses explaining Δ^{14}C values of MOC across sites and with depth.

7 Appendices

Appendix A: Additional Figures.

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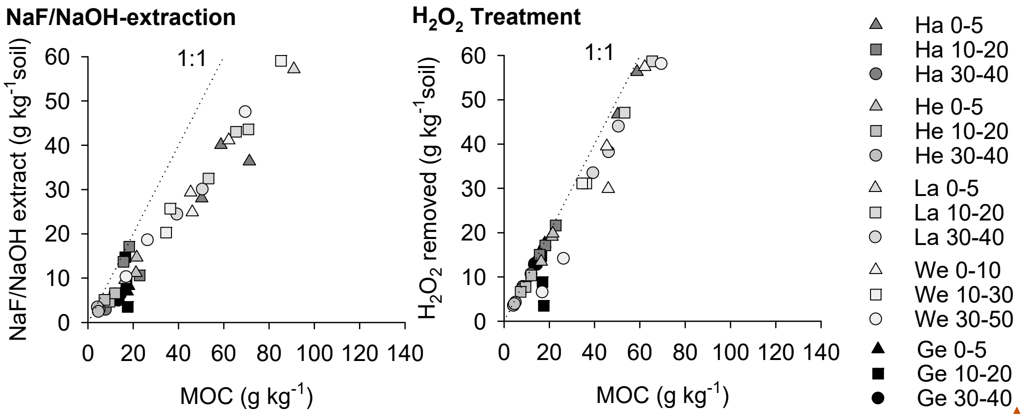

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Figure A1: Dependency of removed OC from original concentrations of mineral-associated OC for the NaF/NaOH extraction (left) or the H_2O_2 oxidation (right).

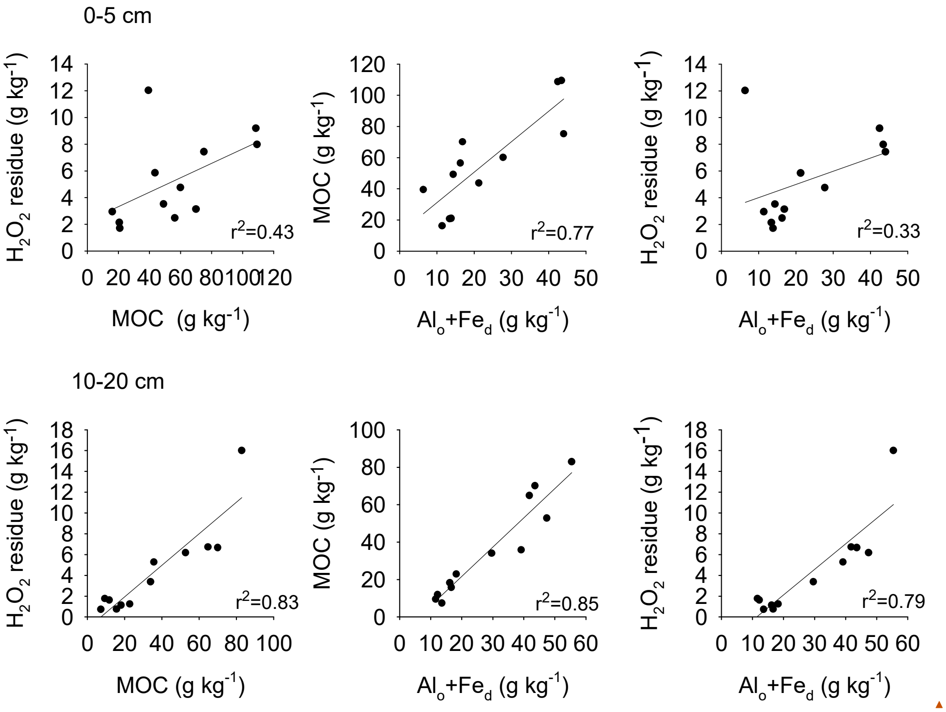

Figure A2: Relations between OC in mineral association (MOC), the amount of OC left from MOC after the H_2O_2 treatment (H_2O_2 residue) and the content of oxalate-extractable Al (Al_o) and dithionite-extractable Fe (Fe_d) for two soil depths (Al_o and Fe_d data were taken from Schrumpf et al. (2013)).

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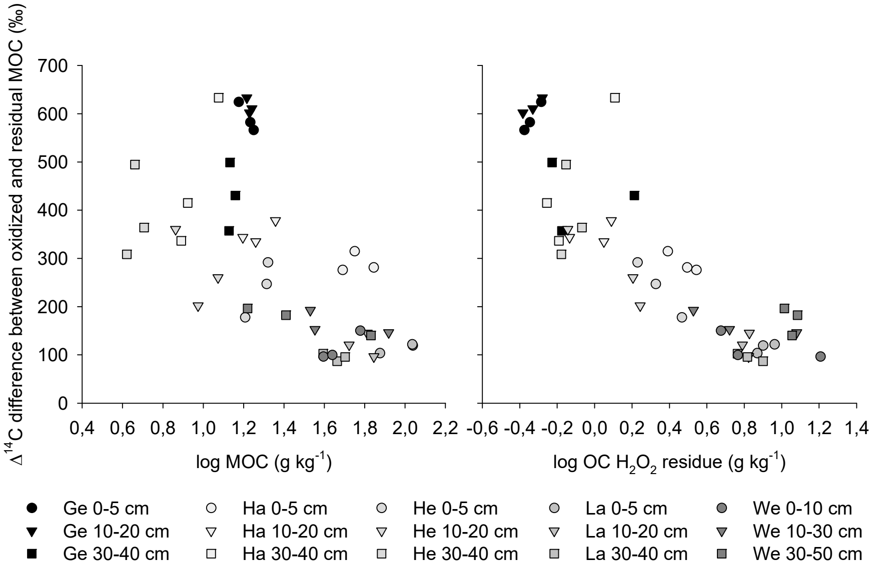

Figure A3: Decline in ^{14}C differences between oxidized and residual OC after H_2O_2 treatment with increasing OC amounts in total MOC and OC left in H_2O_2 residues across sites and depths.

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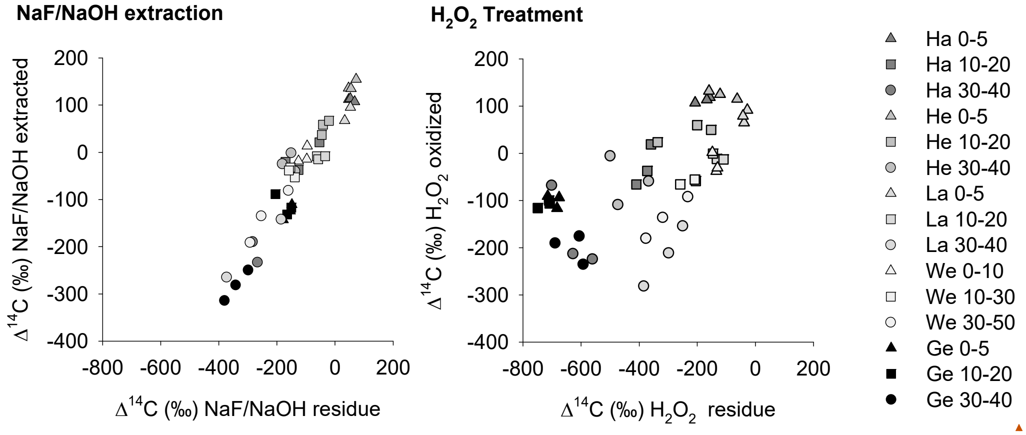

Figure A4: Correlation between ^{14}C contents of NaF/NaOH extracts and extraction residues of HF-OC (left) and between oxidized OC and residue OC following treatment of HF-OC with heated H_2O_2 (right).

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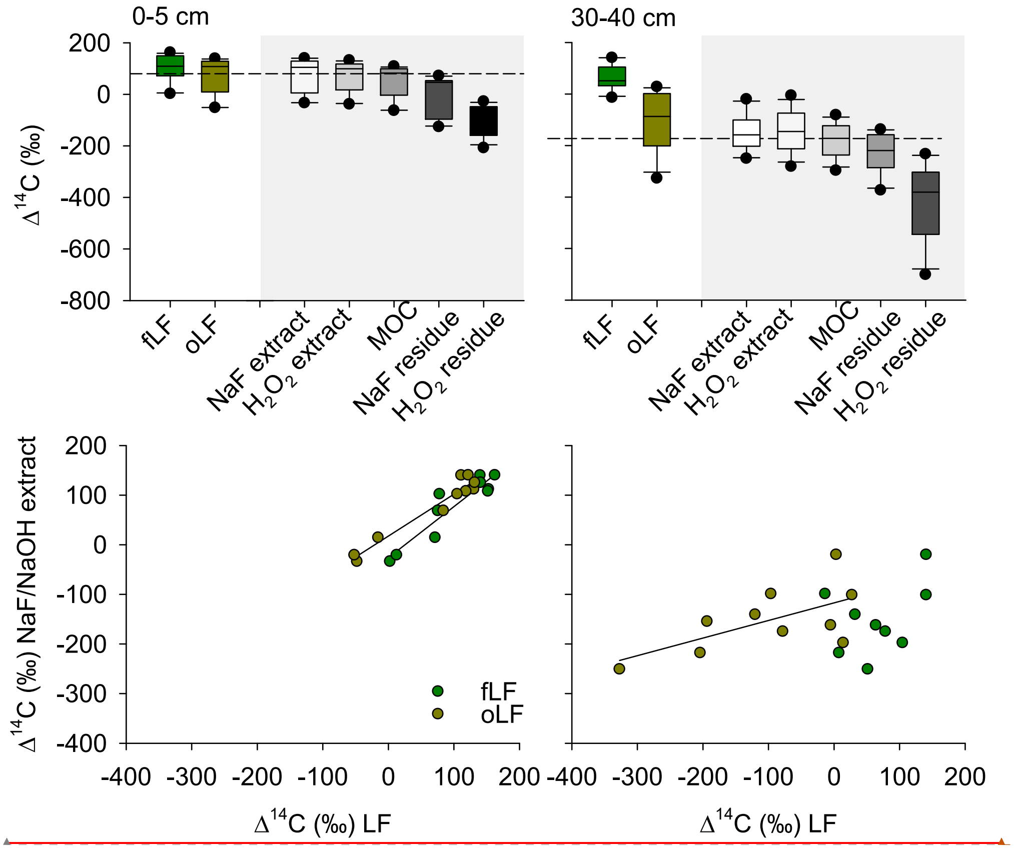

Figure A5: Top: box-plots giving an overview of ^{14}C contents in all OC fractions separated from bulk samples in 0-5 cm (left) and 30-40 cm (right) depth for the non-arable samples (dashed line denotes the median of the ^{14}C in bulk MOC). Bottom: relation between ^{14}C contents of OC in NaF/NaOH extracts of MOC and OC in the two light fractions in 0-5 cm (left) and 30-40 cm (right) depths for the non-arable samples. fLF: free light fraction, oLF: occluded light fraction, values adopted from Schrumpf et al. (2013).

8 Code availability: not applicable

9 Data availability: we intend to publish the data in the ISRAD database~~Pangaea data repository upon opening of the online discussion when the dataset can be linked to the publication as asked for in the uploading process. Since the assignment of a~~

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~~DOI takes more than 8 weeks in the current situation as indicated by the webpage, we decided to submit the manuscript and the data in parallel. If needed earlier, we can also submit the data as supplement to the manuscript.~~

10 Sample availability: all remaining material of original MOC samples and the obtained fractions is stored at the MPI-BGC and can be made available upon request**.**

11 Video supplement: none

12 Supplement link: not applicable unless primary data should be provided for review in the supplement

13 Team list: who should be mentioned in addition to people contributing as authors or added to the acknowledgement?

14 Author contributions

MS, KK, AM and ST designed the experiments and AM carried them out. GH conducted the NMR analyses. MS prepared the manuscript with contributions from all co-authors.

15 Competing interests: none

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16 Disclaimer ~~?~~

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17 not applicable

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