Author's responses

Interactive comment on "Vertical mobility of pyrogenic organic matter in soils: A column experiment" by Marcus Schiedung et al.

Anonymous Referee #1

Received and published: 31 August 2020

You find our final author responses written in blue.

General Comments

This manuscript provides information on the vertical mobility of pyrogenic organic matter in soils of contrasting nature. The study uses a column experiment where isotopically labelled char gets added to soils collected at different depths. The movement of both added PyOM and native soil is then traced through the soil column. The study is very relevant, well designed and impeccably executed. The MS is well written and provides a pleasant reading. It has been a few years since I did not enjoy reading a first submission as much as I have with this one. I have little doubt that this work will prove quite useful for researchers studying PyOM dynamics and ecosystem carbon cycling.

We are grateful and appreciate the positive feedbacks on our submitted manuscript.

There are just a few aspects where I would appreciate that the authors provide further critical discussion to make this contribution an even more useful one. These are as follows:

The PyOM used in this study derives from ryegrass. I can understand why such fastgrowing precursor biomass was used to produce PyOM in this labelled experiment. However, it is unavoidable to think that the resultant pyrogenic material will be of a highly contrasting physico-chemical nature compared to those derived from woody vegetation. Therefore, these distinct characteristics may greatly affect the mobility of the various PyOM produced. As such, I recommend the authors to include a paragraph in the discussion showcasing the potential limitations and applicability of the results obtained in this study. The results obtained here may be directly applicable in agronomic studies using grass-derived biochar. However, the mobility of PyOM in charcoal generated during wildfires affecting woody vegetation might be different from that observed in grass-derived PyOM.

We agree with the reviewer that this is an important aspect, which needs to be included to indicate the limitations of this experimental set-up. The ryegrass in our experiment is mainly used because it is much easier to produce with high label than wood. A lower label however, would constrain the tracing of the mobilized PyOM because of its quite low mobile fraction. In the present manuscript we already mentioned this limitation in line 302-303 by stating: "It needs to be noticed that we only included one type of PyOM (ryegrass derived and produced at 450°C) which constrains general assumptions".

However, we will follow the suggestion and highlight this important limitation again in the discussion and include it further in the conclusion. In general, grassland systems represent a major source of fire derived organic matter globally, so the use of grass material is still legitimate.

The existence of fluctuating levels of moisture in the soil is just natural. Please briefly include an statement about how soil drying and wetting events may cause the mobility of PyOM potentially diverge from your observed results obtained under saturated conditions.

We agree that unsaturated flow conditions are highly relevant for the mobility of PyOM under field conditions. Based on the findings from our experimental set-up, we cannot provide any statement how the mobility would be influenced under unsaturated conditions.

We found a quick interaction of the PyOM with the mineral phase even under saturated conditions in our experiment. Unsaturated conditions and unsaturated water flow could potentially increase the contact time of PyOM and the mineral phase and thus influencing the interaction with each other but it could also increase the preferential flow and thus increase the downward movement with less interaction with the mineral phase. This would also highly depend on the texture and aggregation of the soil. Therefore, this requires

more research and we stated in line 392-393 of the current manuscript: “This quick mineral interaction will control the long-term stability of PyOM in soils and requires more research under unsaturated and field conditions.”
We also discussed that our experimental approach has limitations that prevent a direct transfer to field conditions due to the continuous saturated flow conditions in our experiment and in line 408-409 of the current manuscript, we state: “In addition, we did not include unsaturated flow conditions which would resemble the mobility and retention under field conditions”.

I appreciate the addition of fresh PyOM in the subsoil to get deeper mechanistic understanding of the dynamics of PyOM in the soil. However, besides high erosion rates and subsequent deposition, it is just hard to envisage this happening in a real setting. Not that this is a problem, you might just want to make a brief mention of it.

We agree with the reviewer that the input of fresh PyOM in subsoils maybe not be common under field conditions. We stated this also in the beginning of our introduction in line 34-36 of the current manuscript: “Mass transport of PyOM mainly occurs during the first rain event after a fire, resulting in a translocation and re-deposition within the landscape and eventually in a PyOM burial at depositional sites (Abney et al., 2019; Cotrufo et al., 2016; Rumpel et al., 2015).” This burial may happen before the PyOM is significantly oxidized on its surfaces.
We further address this, when we discuss the dynamic of mobilized PyOM in section 4.2. by stating in line 323-323: “This may further cause an underestimation of the vertical PyOM transport from depositional landscape positions after redistribution following an initial lateral mass transport (Rumpel et al., 2015).” We will highlight again that depositional sites could represents location were PyOM may have entered subsoil regions and add a sentence in the discussion.

I am very satisfied with the methodology employed, as well as the results, tables, figures and derived conclusions. I congratulate the authors.

We highly appreciate the reviewers positive feedbacks.

Specific Comments
Introduction: This is a short but well accomplished introduction.

- Lines 55-57: The authors state that ‘the chemical composition, physical properties and the particle size control the mobility in soils and the interactions of PyOM with the soil mineral phase which further depend on other soil properties’. While this is true, it is important to also consider the preferential transport of fine PyOM derived from grass biomass reported elsewhere (e.g. Saiz et al, 2018). This is an important aspect considering the fine, and most likely, light nature of the PyOM used in this study, which undoubtedly will greatly affect its initial mobility after formation. (Reference: Saiz et al. 2018. Preferential Production and Transport of Grass-Derived Pyrogenic Carbon in NE-Australian Savanna Ecosystems. Frontiers in Earth Science 5, 115. doi:10.3389/feart.2017.00115)

We appreciate that the reviewer provided further literature to highlight this important aspect. We also agree that this needs to be clearly mentioned and we will improve the mentioned section. Saiz’s reference will be added to the manuscript.

Materials and Methods:
- Line 82: The values presented in Table 1 appear to have been produced by you. If that was the case, state the methodology used to obtain them.

All these values were measured by us. The methods, which were used for the bulk soil measurements, are given in section 2.4. To clarify this, we will refer to this section in the caption of table 1 and change to: “Table 1: Soil texture, total organic carbon (TOC), δ13C, pH, electrical conductivity (EC), oxalate extractable Fe(o) and Al(o) and density fractions (free particulate organic matter, fPOM and mineral associated organic matter, MAOM) for the topsoil (0-10 cm depth) and subsoil (40-60 cm) of the loamy and sandy soil (± 1 SE). See section 2.4 for the used methods.”

- Line 95-on: If possible, please provide more information about the PyOM produced (i.e. O/C, H/C, etc.). This will make your work more inter-comparable with other studies.

We are currently accessing the O/C and H/C ratios by additional CNHS O analysis and we will include these parameters in Table 2.

- Lines 98-103: These lines describe how PyOM was produced and, the oxidation treatment that some of those samples underwent. Please try to re-phrase these sentences as I got quite confused with the two oxidation instances that the text makes reference to.

We agree that the current description may not be clear and we will rephrase to the following: “Artificially altered PyOM was produced by chemical and heat accelerated oxidation presented by Cross and Sohi (2013); in brief, 1 g of C was oxidized with 0.1 mol of H_2O_2 at 80°C for two days. The samples were gently shaken five to seven times a day to ensure a homogeneous reaction.”

- Line 99: Table 2 shows what it seems to be a large variability between batches that have been treated in similar way. The authors may want to include some comment about it. But most importantly, if I understand well, the sandy soil gets added PyOM which is up to 10% higher in its C content compared to the PyOM that gets added to the loamy soil. Would this discrepancy not create an artifact in the behaviour of PyOM in both soils? Please critically discuss this aspect.

We noticed that a variability between the produced ryegrass batches exist. Such variation is hard to explain since the growing conditions were controlled and similar for all three batches. However, it is possible that the uptake of, for example, silica differs slightly between the batches which would result in variations of the C content. However, all the recovery calculations (total C and 13C) are based on the actual values presented in Table 2 and thus the variability is taken into account. We agree that this needs to be mentioned in the manuscript and we will include in section 2.2 the following: “It needs to be noticed that the three batches of ryegrass PyOM varied in C content and $\delta^{13}C$. To include this variation, all further calculations are based on the individual values (Table 2).”

- Line 143: Please state the nominal mesh of the glass fibre filter used.

Will be changed to: ”…filtered using a glass fiber filter (<0.7 µm).”

Results:

- Lines 205-207: Where can these data (statistics) be seen?

The data can be seen in figure 2. We choose the same scaling between the topsoils and subsoils as well as between the sandy and loamy soil to allow a direct comparison of the percolated PyOM. We will refer to Fig 2 again.

- Line 231: Please check the text: ‘..more to than the ..’

We will correct this sentence to: “Thus, PyOM addition significantly increased the nSOC leaching for the sandy topsoil the control without PyOM addition, from which 1.7 ± 0.1 % of the initial nSOC were leached ($p<0.01$)”

- Line 249-250: Please re-phrase this sentence.

We will rephrase the sentence to: “After the percolation, 89-96 % of the fresh and oxidized PyOM-C remained at its initial location in the PyOM layer in both soils.”

- Line 259: ‘The lowest sandy subsoil layer. . .’. Please check this text.

We will specify and rephrase to: “In 4.6-7.0 cm depth below the PyOM layer, the recoveries of oxidized ($p<0.05$) and fresh PyOM-C ($p<0.01$) were significantly higher in the sandy subsoils compared to the topsoil.

Discussion:

- Line 314-315: ‘The first flush contributed to the highest export of PyOM from the soil columns and the mobilized amounts decreased with the percolation for all soils’. This sentence is at the beginning of a discussion section. You need to contextualize the ‘flush’ term a bit better.

We specified the first flush as the first 1,000 l m^{-2} in the result section. We will specify it here again by adding: “The first flush, leached form the column with 1,000 l m^{-2}, …”

-Lines 318-319: In this experiment you had the opportunity to validate the statement about attributing the export of PyOM to mobile pyrogenic fractions directly produced during pyrolysis. Hadn’t you?

The production of large quantities of highly labelled PyOM is very challenging. Therefore, we do not have enough material left to determine water extractable fractions with a sufficient certainty.

Technical Comments
- Line 137: Typo in ‹form›.

We will correct and carefully check the manuscript again for similar typos

- Line 459: Typo in ‹form›.

Same as above

- Line 482: Typo in ‹desobed›.

Same as above

Interactive comment on “Vertical mobility of pyrogenic organic matter in soils: A column experiment” by Marcus Schiedung et al.

Anonymous Referee #2

Received and published: 5 October 2020

You find our final authors responses written in blue

General comments:
This paper is of high relevance, well written and provides interesting data which are certainly of interest for the readers of Biogeosciences. It is a follow-up of several previous publications, describing investigations about vertical transport in soil systems. Below, some of those publications which are not cited, but could contribute to the discussion of the present paper are mentioned. An important issue which has to be considered is the fact that there is no good distinguishing between Pyrochar (Biochar) and PyOM produced during vegetation fires. Of course both are pyrogenic organic matter, but biochar is produced under pyrolysis conditions. Such conditions may occur during peat smoldering or in subsoil fires but rarely occur during above ground fires. Although in both cases highly aromatic material is produced, there are chemical differences which may be mainly related to a more complete oxidation process during combustion in comparison to pyrolysis. This is also evidenced by the fact that combustion at 450◦C is in the most cases complete and no charred remains will accumulate. However, this does not decrease the value of the present paper, since pyrolysis-derived PyOM is still PyOM and this material is in soil since it is recommended to be used as soil amendment. Therefore, I recommend to correct the definition of PyOM in Line 30 and to include Pyrochar (biochar) into this definition to make it a bit more general. As a consequence, some aspects of Pyrochar may enter the introduction. Indeed, at some places the latter is already done, although I assume that this happened unintentionally, but still a clear differentiation is needed. Below you can find some additional comments. After following those suggestions, I think the paper can be published.

We thank the reviewer for the general positive feedbacks and for the useful suggestions for our manuscript. We agree that we need to include a better definition and differentiation between artificially pyrolyzed and natural PyOM which is a product from wildfires. Therefore, we will change the first sentence of the introduction to: ”Pyrogenic organic matter (PyOM) is a product of artificial (biochar) or wildfire induced incomplete combustion.”. We will also follow the suggestions below to state clearly that we used artificially pyrolyzed PyOM in our experiment and highlight the associated limitations.

Specific comments:

31: There are many indications that the age of PyOM is by far lower than 10 000 years (Santos et al., 2012)(Hockaday et al., 2006) . Since the “real” MRT of this material is still under discussion, it should not be stated here as a proven finding.

The first section of the introduction of the current manuscript provides an overview of the PyOM in the Earth system before it narrows down to the soil system. Therefore, the given residence time of >10,000, which is reported in the cited literature (e.g. Coppola et al 2018; Masiello and Druffel 1998), represents a residence time of PyOM in the Earth system. If we are not mistaken, the reviewer refers, with the suggested study from Santos et al. (2012), to the residence time in soils. We start to discuss the current knowledge of PyOM residence times in soils from the paragraph line 46-51 and following. Here we state that the MRT of PyOM is higher than the MRT of non-pyrogenic soil organic matter (line 47). However, we agree that this is still an open discussion and PyOM is also reported with lower MRT in soils. Thus, we will change line 47 as followed and include the suggested literature: “Pyrogenic organic matter is found with residence times in soils of several centuries to millennia, which is much more than the average age of SOC and is mainly attributed to its condense and aromatic composition and thus increased stability against degradation (Kuzyakov et al., 2014; Santos et al., 2012; Schmidt et al., 2011; Singh et al., 2012).”
The suggested literature, Hockaday et al. (2006), is already cited and included in our discussion (line 352-355). Since this publication is not reporting MRT, we think it is better not to cite it there, but, we agree that this study should be included in the introduction. We will add in line 66: “In addition, it is reported that PyOM found in fire effected watersheds underwent aging processes in soil prior to its export from the soils to the riverine system (Hockaday et al., 2006).”

48: Considering an atomic H/C ratio of 0.5, one cannot talk about highly condensed (Every second C is connected to a H)

We are sorry for the misunderstanding. We did not mention in our text a H/C ratio of 0.5 and we are not addressing any aspect directly related to specific degree of aromaticity or condensed structure here. We will remove the “highly” in line 47 to avoid confusion. We already included this change in our response to the previous comment. Furthermore, we will include the actual H/C and O/C ratios in Table 2 as it was recommended by reviewer 1. ~~We are currently measure the H and O content but first results indicate that the H/C ratios are rather ranging between 0.1-0.2, indicating a higher degree of condensation than mentioned by the reviewer.~~ We have updated table 2 with the O/C and H/C ratios measured as described in Section 2.4.

51: The article by Velasco-Molina et al. (2013) is very closely related to the subject of the present paper and may be included into the discussion.

We agree that the study from Velasco-Molina et al. (2013) is supporting the assumption that vertical transport in soils is determine the long-term fate of PyOM in soils. However, we cite a very recent review from Hobley (2019) which already includes the mentioned study. In order, to be consistent, we will remove the citation of Foereid et al. (2011) and Leifeld et al. (2007) because these are also discussed in the review from Hobley (2019).

52: Change to physical and chemical, because the term phyisco-chemical is normally related to physical aspects of chemistry (i.e. thermodynamics etc.), which is definitively not the case here.

Will be changed as recommended by the reviewer

53: As mentioned above, pyrolysis is a process in which heat is applied in an oxygen-free or depleted environment. This is not the case during above ground vegetation fires. Here the vegetation is mostly combusted and the residues accumulate due to incomplete combustion (as mentioned in the introduced definition). During combustion, condensation is unlikely. In addition, the open space during a vegetation fire will decrease the probability that two volatiles can “meet” for recondensation”. Only if volatilize move vertically in the soil, they may form a layer of recondensed OM. I guess the authors are referring to biochar, but this is not really clear. However, here one has to bear in mind that modern biochar production allows the removal of the syngas which prevents condensation reactions within the biochar.

We agree that condensation can be interpreted in different ways and we do not provide a clear definition here. To avoid confusion, we will change line 53 to: “Pyrolysis affects the chemical and physical properties of the feedstock organic matter which result in a high porosity and large surface areas depending on the fuel biomass, duration and production temperature (Hammes and Abiven, 2013; Lehmann et al., 2015; Preston and Schmidt, 2006).”. Further, we will include an additional reference which we missed in the current manuscript but supports the given statement: Lehmann, J., Abiven, S., Kleber, M., Pan, G., Singh, B. P., Sohi, S. P., & Zimmerman, A. R. (2015). Persistence of biochar in soil. In J. Lehmann & S. D. Joseph (Eds.), Biochar for Environmental Management (Issue January, pp. 235–282). Routledge. https://doi.org/10.4324/9780203762264-17

59: High aromaticity is not necessarily equal to high molecular weight and it is also not clear why high molecular weight should cause strong sorption to soil minerals. At least a reference is needed where the interested reader could get to know the included mechanisms.

We are sorry for the misunderstanding. We did not want to say that high aromaticity is equal to a high molecular weight here. We state that PyOM is rich in aromatic compounds and thus will most probably have a higher sorption affinity to the mineral surface. This is discussed in the discussion section (line 450). We agree that this statement requires further references and we will include here: Kaiser, K., & Guggenberger, G. (2000). The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. Organic Geochemistry, 31(7–8), 711–725. The authors identified that the sorption of organic matter is depending on its chemical structure and compounds containing aromatic structures (such as lignin) have a higher sorption affinity than less aromatic compounds.

98: As mentioned above, material which is pyrolyzed is not necessarily the same as material that was partially combusted. In our laboratory we have seen that material that is pyrolyzed at low temperatures (< 500°C) contains more alkyl C then the same residues combusted at 350°C (with higher temperatures complete combustion occurs). This has to be considered in the discussion. Thus, in the present work, biochar was tested rather than charcoal that is produced during a vegetation fire.

We agree that partially combusted and artificially pyrolyzed PyOM differ in several properties. Actually, we already included this in our current discussion line 336:" Artificially produced PyOM is mostly more stable than naturally produced PyOM, which challenges the use of one type as a proxy for the other (Santín et al., 2017).". We agree that this needs to be addressed again in the mentioned section. Therefore, we will change this to: "The ryegrass was oven dried at 40°C and pyrolyzed at 450°C for 4 h under N_2 atmosphere (Hammes et al., 2006). Three independent growing batches of the initial ryegrass were pyrolyzed separately which were used in our experiment as a proxy for PyOM (Table 2)."

216: Most pH-meters are not exact enough to "trust" in the second post-coma digit. Thus, in the most cases it doesn‘t make sense to consider this digit (change to 0.2 and latter to 0.3-0.5)

Will be changed as recommended

293: The sentence Hilscher and Knicker. . . is not clear: what means "exported from the soil"?

Hilscher and Knicker (2011) reported that 0.4% of initially applied PyOM were found in the outflow of soil columns (8cm length) in a one-year incubation experiment. We will clarify this here and change to: "Hilscher and Knicker (2011) reported that 2.3 % of added PyOM migrated to 5 cm depth and 0.4 % were leached from soil columns (8 cm length) and found in the column outflow in a one-year incubation experiment."

301: The cited reference Hilscher et al. showed that PyOM from rye grass can be biochemically degraded. So why should this not be possible for the comparable material used in the present study? In the study by Velasco-Molina et al (mentioned above), the PyOM in the deeper soil horizons of a fire-prone region was highly oxidized and it was suggested that this oxidation facilitated the vertical transport. A comparable scenario may have happened here.

We agree that biochemical degradation and the associated oxidation of PyOM is an important factor controlling the vertical PyOM mobility in soils. This was also clearly shown with our experiment and the higher mobility and reactivity of the oxidized PyOM. In fact, we designed the experiment according to the existing information in the literature which reported higher mobility of aged and oxidized PyOM. In order to include aged PyOM, we used the accelerated aging as described by Cross and Sohi (2013). Due to the comparable short duration of our experiment (five days of percolation - line 119-121), we can assume that an additional biochemical degradation of the PyOM is negligible.

306: I have some problems to follow the argument. How can physical fragmentation break the bonds of an aromatic network? I think this would only work chemically. In addition, I have some problems to understand how such chemical breakdown of covalent bonds could work in soils, since such reactions need activation energy and rarely occur without catalysts or heat. What is the mechanisms behind the formation of colloids from PyOM? The authors did some Infrared on the starting material. A second analysis of the aged PyOM may deliver some more details and support the given hypothesis.

The physical fractionation discussed here and also discussed in the cited references (Hobley, 2019; Pignatello et al., 2015) takes place on a larger scale than mentioned by the reviewer. In the above references, it is reported that centimetric to millimetric PyOM particles will breakdown into smaller particles (sub millimetric) due to physical breakdown with time. This is a process happening rather on the scale of cm to µm than at the molecular scale.
The formation of colloids and PyOM particles aggregation is controlled by the surface interaction of the PyOM. According the cited literature in line 308 (Castan et al., 2019; Sigmund et al., 2018), the aggregation is controlled by van der Waals attraction and electrostatic repulsion.
The mid-infrared spectra of the fresh and oxidized PyOM showed an increase in functional groups with oxidation (Section 2.2 and Fig. 1). As mentioned above, further degradation should be negligible due to the short duration of the experiment, so we did not measure the mid-infrared spectrum of the PyOM after the experiment.

318: Again: Be careful with the term pyrolysis. This term is correct for the present paper, but does not describe the situation during natural vegetation fires described by Santos et al., or Rumpel et al., and as far as I understood, the material produced by Hilscher et al.. I also wonder about the mechanism about the production of mobile PyOM during combustion. I assume, the mobile phase would be composed of smaller molecules located within the aromatic network of PyOM which are washed out by water. But considering the hydrophobic nature of PyOM, I wonder how water can enter the porous system of the char to do its job and how the mobile material (which should also be hydrophobic due to its aromatic nature) gets dissolved in water. I wonder if a kind of preferential flow is more likely to explain the observed vertical translocation

We agree that the term pyrolysis is correct for the PyOM used in our experiment. Our experiment did not allow to specifically investigate the mechanism of the PyOM mobilization by the percolating water because we determined the mobile fraction as a sum of dissolved and particulate PyOM. Our breakthrough curve analysis, however, indicate the absence of preferential flow (See also supplement material) and that the application of PyOM did not change the hydraulic properties of the soil column compared to the controls.
Santos et al. (2017) concluded with their field observations that also natural PyOM may contain easily mobilized fractions which are mobilized with the first flush after the fire. However, the quantification of this initial pulse of PyOM flux was up to now mostly missing in the literature. We were able to capture this first pulse of mobilized PyOM in our experiment, which contributed to up to 84% of the total mobilized PyOM.

336: Do the authors have a proof of the statement that artificially produced PyOM is more stable than naturally produced PyOM? From a chemical viewpoint it does not make a lot of sense since the chemistry during combustion depends on the temperature and the chemistry of feedstock, irrespective of being created in the lab or in nature. Thus, PyOM of grass produced in the lab should show the same biochemical stability as material produced in nature, if it was subjected to the same temperature. However, again under natural conditions, PyOM is unlikely to have been produced at 450_C because at that temperature most of the organic matter had been volatilized. Thus, the differentiation between artificial and natural PyOM should be according to pyrolyzed and combusted charcoal. Nevertheless, I am not aware of degradation studies proofing the higher stability of “lab-made PyOM” (produced at the same temperature). If they exist, they should be referenced.

The cited study by Santín et al (2017) provides an extensive and direct chemical comparison of natural and artificially pyrolyzed PyOM produced at similar temperatures and similar feedstock (e.g. degree of aromaticity, H:C, O:C, recalcitrance index). The authors identified that slow-pyrolysis compared to the fast combustion during wildfires resulted in a higher stability of the artificial PyOM. Therefore, the authors concluded that the use of PyOM from pyrolysis as a proxy for natural PyOM may be limited. In order to be more specific, we will change the mentioned line 336-337 to: “Artificially produced PyOM is reported to have a higher stability than PyOM naturally produced during wildfires, which challenges the use of one type as a proxy for the other (Santín et al., 2017).”

345-360:I think the results given here, are in good agreement with the study of Velasco-Molina et. al. (2013), showing that PyOM dominates the deeper horizons of a soil in a fireprone region and that this PyOM is highly carboxylated.

We thank the reviewer for providing the additional literature which we will integrate to support our findings with field observations described by Velasco-Molina et al. (2013)

365-370: A conceptual model describing this mechanism very nicely has been published in (Knicker, 2011). It may be worth to be considered in the discussion, because it already describes a considerable part of the explanations given here. There is a further very recent publication by (Miller et al., 2020), which may supportive in the discussion of the present paper.

We thank the reviewer for further literature to strengthen our discussion and to include the existing conceptual model described by Knicker (2011).

Conclusion and implementation: This part is rather a summary than a conclusion. I am missing the description of the implication the obtained results may have for our understanding of PyOM in soils. Does the mobility of PyOM affect the aquifer? Is there an environmental threat? What may happen based on the findings of the present paper?

We think that a discussion of direct effects on aquifers and environmental threats would be too speculative with our small scale experiment. This would require more research under field conditions and on larger scale. Therefore, we will emphasis this by adding the following: “Further research is needed to understand the fate of PyOM under unsaturated and field conditions and larger scales such as pedon and catena. We identified that the vertical PyOM mobility is highly depending on soil properties and the degree of PyOM oxidation (age) which increases not only its mobility, but also reactivity in soils and influences its effect on nSOC. This will influence its dynamics in the vadose zone and between the terrestrial and aquatic systems.”

Suggested literature:

Hockaday, W.C., Grannas, A.M., Kim, S., Hatcher, P.G., 2006. Direct molecular evidence for the degradation and mobility of black carbon in soils from ultrahigh- resolution mass spectral analysis of dissolved organic matter from a fire-impacted forest soil. Org. Geochem. 37, 501–510.

Knicker, H., 2011. Pyrogenic organic matter in soil: Its origin and occurrence, its chemistry and survival in soil environments. Quat. Int. 243. https://doi.org/10.1016/j.quaint.2011.02.037

Miller, A.Z., De la Rosa, J.M., Jiménez-Morillo, N.T., Pereira, M.F.C., Gonzalez-Perez, J.A., Knicker, H., Saiz-Jimenez, C., 2020. Impact of wildfires on subsurface volcanic environments: New insights into speleothem chemistry. Sci. Total Environ.698, 134321. https://doi.org/https://doi.org/10.1016/j.scitotenv.2019.134321

Santos, F., Torn, M.S., Bird, J.A., 2012. Biological degradation of pyrogenic organic matter in temperate forest soils. Soil Biol. Biochem. 51, 115–124. https://doi.org/http://dx.doi.org/10.1016/j.soilbio.2012.04.005

Velasco-Molina, M., Knicker, H., Macías, F., 2013. The potential of humic material in sombric-like horizons of two brazilian soil profiles as an efficient carbon sink within the global C cycle, Functions of Natural Organic Matter in Changing Environment. https://doi.org/10.1007/978-94-007-5634-2_78

Literature which will be added

Kaiser, K., & Guggenberger, G. (2000). The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. *Organic Geochemistry*, *31*(7–8), 711–725. https://doi.org/10.1016/S0146-6380(00)00046-2

Make-up manuscript

Vertical mobility of pyrogenic organic matter in soils: A column experiment

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Abstract Pyrogenic organic matter (PyOM) is a major and persistent component of soil organic matter but its mobility and cycling in soils is largely unknown. We conducted a column experiment with a topsoil and subsoil of a sand and a sandy loam to study the mobility of highly ^{13}C labelled ryegrass PyOM (>2.8 ~~-~~at%), applied as a layer on a 7 cm long soil column, under saturated conditions. Further, we used fresh and oxidized PyOM (accelerated aging with H_2O_2) to identify changes in its migration through the soil with aging and associated surface oxidation. Due to the isotopic signature, we were able to trace the PyOM carbon (PyOM-C) in the soil columns, including density fractions, its effect on native soil organic carbon (nSOC) and its total export in percolates sequentially sampled after 1,000-18,000 l m^{-2}. In total, 4-11 % of the added PyOM-C was mobilized and <1 % leached from the columns. The majority of PyOM-C was mobilized with the first flush of 1,000 l m^{-2} (51-84 % of exported PyOM-C), but its export was on-going for the sandy soil and the loamy subsoil. Oxidized PyOM showed a 2-7 times higher mobility than fresh PyOM. In addition, twofold higher quantities of oxidized PyOM-C were leached from the sandy soil compared to the loamy soil. Besides the higher mobility of oxidized PyOM, its retention in both soils increased due to an increased reactivity of the oxidized PyOM surfaces and enhanced the interaction with the soil mineral phase. Density fractionation of the upper 0-2.3 cm, below the PyOM application layer, revealed that up to 40 % of the migrated PyOM was associated to the mineral phase in the loamy soil, highlighting the importance of mineral interaction for the long-term fate of PyOM in soils. The nSOC export from the sandy soil significantly increased by 48-270 % with addition of PyOM compared to the control while no effect was found for the loamy soil after the whole percolation. Due to its high sorption affinity towards the soil mineral phase, PyOM can mobilize mineral-associated soil organic matter in coarse textured soils, where organo-mineral interactions are limited, while finer textured soils have the ability to re-adsorb the mobilized soil organic matter. Our results show, that the vertical mobility of PyOM in soils is limited to a small fraction. Aging (oxidation) increases this fraction but also increases the PyOM surface reactivity and thus its long-term retention in soils. Moreover, the migration of PyOM affects the cycling of nSOC in coarse soils and thus influences the carbon cycle of fire affected soils.

1 Introduction

Pyrogenic organic matter (PyOM) is a product of artificial (biochar) or wildfire induced incomplete combustion~~Pyrogenic organic matter (PyOM) is a product of incomplete combustion of vegetation biomass during wildfires~~. It is one of the oldest terrestrial organic carbon (C) pools with residence times on the order of 10,000 years and an annual global production from wildfires of 196-349 Tg C (Coppola et al., 2018; Jones et al., 2019; Masiello and Druffel, 1998). After a wildfire, around 12-27 % of the initially burned biomass can remain as PyOM on the site of burning (Santín et al., 2015). It can directly enter the soils or can be transported laterally via mass transport prior to incorporation. Mass transport of PyOM mainly occurs during the first rain event after a fire, resulting in a translocation and re-deposition within the landscape and eventually in a PyOM burial at depositional sites (Abney et al., 2019; Cotrufo et al., 2016; Rumpel et al., 2015). In addition to this natural wildfire derived PyOM, artificially produced biochar is used as agricultural soil amendment to improve soil properties and is recognized as a C sequestration strategy to mitigate climate change (Lehmann, 2007).

Between the continuum of terrestrial and aquatic ecosystems, PyOM is continuously exported from soils to rivers with less seasonality compared to non-fire-derived soil organic matter (Dittmar et al., 2012a; Hockaday et al., 2007; Wagner et al., 2018). Globally, dissolved PyOM contributes to 0.1-15 % of the total riverine and marine dissolved organic carbon (DOC) pool (Coppola and Druffel, 2016; Jones et al., 2020). Furthermore, the quantity of dissolved PyOM in rivers was found to be decoupled from the fire history of the watershed (Ding et al., 2013; Santos et al., 2017), which indicates that soils are an important intermediate storage for PyOM in the terrestrial system prior to its export to aquatic ecosystems (Abiven and Santín, 2019; Bird et al., 2015; Santín et al., 2016).

In soils, PyOM contributes globally to 14 % (0-60 %) of the total soil organic carbon (SOC) which makes it to one of the main components of organic matter (OM) in soils (Reisser et al., 2016). Pyrogenic organic matter is found with residence times in soils of several centuries to millennia, which is much more than the average age of SOC and is mainly attributed to its condense and aromatic composition and thus increased stability against degradation~~Pyrogenic organic matter is found with residence times of >1000 years, which is much more than the average age of SOC and is mainly attributed to its highly condense and aromatic composition and thus increased stability against degradation~~ (Kuzyakov et al., 2014; Santos et al., 2012; Schmidt et al., 2011; Singh et al., 2012). Within the soil profile, PyOM contents can increase with depth indicating that vertical transport determines its long-term fate in soils and terrestrial ecosystems (Hobley, 2019; Soucémarianadin et al., 2019).

Pyrogenic organic matter and non-fire-derived OM differ in biological (e.g. degradability) and ~~physico~~physical and -chemical interactions in soils (Bird et al., 2015; Pingree and DeLuca, 2017). Pyrolysis affects the chemical and physical properties of the feedstock organic matter which results in a high porosity and larger surface areas depending on the fuel biomass, duration and production temperature ~~Condensation reactions during pyrolysis result in a high porosity and large surface areas depending on the fuel biomass, duration and production temperature~~ (Hammes and Abiven, 2013; Lehmann et al., 2015; Preston and Schmidt, 2006). The feedstock is one of the major precursors and PyOM derived from grass, for example, is reported with smaller and lighter particles compared to wood derived PyOM (Saiz et al., 2018). The chemical composition, physical properties and the particle size control the mobility in soils and the interactions of PyOM with the soil mineral phase which further depend on soil properties such as texture, pH and Fe/Al-(hydr-)oxides content (Hobley, 2019; Pignatello et al., 2015). In addition, PyOM is interacting with non-fire-derived OM and influences its mobility by direct sorption and stabilization on PyOM surfaces (Jiang et al., 2019; Mukherjee and Zimmerman, 2013). However, due to its high molecular weight (rich in aromatic compounds), PyOM has a strong sorption affinity to the soil mineral phase (Kaiser and Guggenberger, 2000). This can result in a mobilization of non-fire-derived and less adsorbing OM that is already adsorbed on the soil mineral surfaces (Jiang et al., 2016; Oren and Chefetz, 2012; Zhang et al., 2017).

Biotic and abiotic oxidation alter the surface reactivity of PyOM by increasing the abundance of oxygen and hydrogen containing functional groups (e.g. carboxylic groups) and thus influencing its properties over time and with aging. Aging of PyOM is reported to enhance its water solubility and thus its mobility in soils with vertical percolation (Abiven et al., 2011; Wagner et al., 2017). However, only a small fraction of the total PyOM (<1 %) was found to be solubilized and transported in soils (Abiven et al., 2011; Maestrini et al., 2014; Major et al., 2010). In addition, it is reported that PyOM found in fire effected watersheds underwent aging processes in soil prior to its export from the soils to the riverine system (Hockaday et al., 2006). The quantities and drivers controlling the vertical PyOM mobility in dissolved or particulate form in soils, its effect on non-fire derived SOC during its migration and the influence of aging are not well understood so far. This is limiting our understanding of the fate of PyOM in the terrestrial C cycle.

In this study, we assessed the vertical PyOM mobility by conducting saturated soil column experiments (7 cm length) with flow interruption. To trace mobilized PyOM, we applied highly ^{13}C labelled (>2.8 at% in excess) ryegrass PyOM-carbon (PyOM-C) on a topsoil and subsoil of a sand and sandy loam and determined the effect of soil properties on the PyOM mobility. Moreover, we compared the vertical mobility of fresh and oxidized PyOM (accelerated aging with H_2O_2) to identify changes in its mobility with aging and associated surface oxidation. Using highly ^{13}C labelled ryegrass PyOM under these controlled conditions allowed us, on the one hand, to trace even small proportions of mobilized PyOM-C in soils and potentially exported to aquatic ecosystems, and on the other hand, to detect changes in the native soil organic carbon (nSOC) mobility. We ~~hypothesised~~hypothesized that, (i) PyOM is continuously exported from the soil but its rate decreases over time, (ii) a higher degree of oxidation (aging) increases the mobility of PyOM through soils, (iii) PyOM can be retained in soils during its migration and (iv) PyOM migration through the soil influences the nSOC mobility.

2 Materials and methods

2.1 Soils

Topsoils (0-10 cm) and subsoils (40-60 cm) of a sand and a sandy loam, hereafter sandy and loamy soil, were used to obtain a range of texture and SOC contents between 2.64-21.91 g C kg^{-1} (Table 1). The sandy soil was sampled from an entic podzol near Gifhorn (55°22’44.0’’N; 10°25’224.5’’), Germany, under pine forest (*Pinus sylvestris*). The loamy soil was sampled from a haplic luvisol east of Eiken (47°32’33.5’’N; 8°00’31.5’’E), Switzerland, under mixed forest dominated by beech (*Fagus sylvatica*). Both sites are similar in terms of mean annual temperature (sandy soil=8.8°C and loamy soil=10.0°C) and mean annual precipitation (sandy soil=620 mm and loamy soil=780 mm). All soil samples were dried at 40°C over night and sieved to <2 mm.

The pH was lower in the sandy topsoil (3.4 ± 0.1) compared to the loamy topsoil (5.3 ± 0.1) but similar in both subsoils with 4.1 ± 0.1 and 4.0 ± 0.1, respectively. Oxalate extractable amorphous Fe and Al (hydr)oxides (Fe(o) and Al(o)) contents were higher in the loamy soil compared to the sandy soil (Table 1). The soils further differed in the SOC distribution between free particulate organic matter (fPOM) and mineral associated organic matter (MAOM) obtained by density fractionation (see Sect. 2.4 for procedure). The MAOM fraction contained 82.8 ± 0.2 % and 85.7 ± 1.0 % of the SOC in the loamy topsoil and subsoil, respectively. The sandy topsoil contained 73.2 ± 0.6 % of the SOC as fPOM. In the sandy subsoil, the fPOM contributed to 41.1 ± 0.8 % of the SOC.

2.2 ^{13}C labelled pyrogenic organic matter

Highly ^{13}C labelled ryegrass (*Lolium Perenne* L.) was produced in the multi-isotope controlled environment facility at the University of Zurich (Studer et al., 2017). The ryegrass was oven dried at 40°C and pyrolyzed at 450°C for 4 h under N_2 atmosphere ~~The ryegrass was oven dried at 40°C and pyrolysed at 450°C for 4 h under N_2 atmosphere~~ (Hammes et al., 2006). Three independent growing batches of the initial ryegrass were pyrolyzed separately which were used in our experiment as a proxy for PyOM (Table 2).~~Three independent growing batches of the initial ryegrass were charred separately (Table 2)~~. Artificially altered PyOM was produced by chemical and heat accelerated oxidation presented by Cross and Sohi (2013); in brief, 1 g of C was oxidized with 0.1 mol of H_2O_2 at 80°C for two days. The samples were gently shaken five to seven times a day to ensure a homogeneous reaction.~~Artificially altered PyOM was produced by chemical and heat accelerated oxidation presented by Cross and Sohi (2013); in brief, 0.1 mol of H_2O_2 were added to 1 g of C and oxidized for two days at 80°C while the samples were gently shaken five to seven times a day to ensure a homogeneous oxidation~~. The samples were dried at 105°C over night. The oxidation was conducted in glass test tubes (20 cm length and 2.5 cm diameter) with 1 g of PyOM using a 5 % H_2O_2 solution. These test tubes ensured a continuous exposure of PyOM to the oxidant. The oxidized PyOM from five test tubes was homogenized and stored in a desiccator.

Mid-infrared spectra at wave lengths from 4000-400 cm^{-1} were recorded (average of 64 scans per sample at 4 cm^{-1} resolution) by using diffuse reflectance infrared Fourier-transformed (DRIFT) spectroscopy (TENSOR 27 spectrophotometer, Bruker, Fällanden, Switzerland). Figure 1 shows the differences in the spectra of oxidized and fresh PyOM for the three PyOM batches, indicating an overall increase of O- and H-containing functional groups after the PyOM oxidation (increases of absorbance at A, C, E and G; Chatterjee et al., 2012; Keiluweit et al., 2010; Wood, 1988), loss of aliphatic compounds (decrease of absorbance at B and H; Chatterjee et al., 2012; Keiluweit et al., 2010), a shift in aromaticity (increase at C and decrease at D) and decarbonation (decreases at D and H; Rechberger et al., 2017), see Fig S2 for all spectra.

The three batches of ryegrass PyOM varied in C content, δ^{13}C, O:C, H:C ratios and DRIFT spectra (particularly batch 3). This can be attributed to growing differences even under similar and controlled conditions. To take into account the variability, all calculations are based on the individual C and δ^{13}C values (Table 2).

2.3 Soil column set up and percolation

Columns of 11 cm length and 2.5 cm diameter were loaded with 49.0-57.5 g of soil to reach a bulk density of 1.4 ± 0.1 g cm^{-3}. The columns were loaded (from bottom to top) with 1.5 cm of decarbonized and combusted quartz sand, 7 cm soil, 1 cm of a soil-PyOM mixture and 1 cm quartz sand. The soil-PyOM mixture contained 0.5 g of PyOM and 4.5 g of soil for each column, which is equivalent to 11 t PyOM ha^{-1} input on the soil surface. Control columns without addition of PyOM were packed with 8 cm of soil. For each soil, four replicates with addition of fresh and oxidized PyOM and controls were used. The columns were packed dry and saturated from the bottom using a 0.01 M $CaCl_2$ solution with a flow of 0.1-0.2 ml min^{-1}. The percolation was conducted with 0.01 M $CaCl_2$ from the top using Mariott's bottles for a constant pressure head and an adjusted flow of 2 ml min^{-1}. In total, 8,640 ml (on average 590 ± 7 soil pore volumes) were percolated through each column over five days. Subsamples of 200 ml were sequentially sampled after a percolation of 480, 1,440, 3,840, 6,240 and 8,640 ml. This is equivalent to 1,000, 3,000, 8,000, 13,000 and 18,000 l m^{-2}. The percolation was stopped for 3-5 h (flow interruption) during the sampling, but the columns were continuously saturated. The experiment was conducted at room temperature and the columns were protected from light to avoid photo-degradation. The percolated samples were not filtered to reduce the risk of sample cross-contamination or losses. Therefore, the percolates contained the total mobile fraction of PyOM and nSOC including colloidal and dissolved forms.

2.4 Soils and percolate sample preparation and analyses

Amorphous Fe(o) and Al(o) were extracted by oxalate extraction according to McKeague et al. (1971) and measured using atomic absorption spectroscopy (ContrAA 700, Analytik Jena, Jena, Germany). Soil texture was determined after oxidizing the organic material with H_2O_2, after which samples were wet sieved <63 mm and the silt/clay fraction further quantified by a Sedimat 4-12 (UGT, Müncheberg, Germany).

At each sequential sampling time, the pH and EC of the percolates was measured (914 pH/Conductometer, Metrohm, Herisau, Switzerland). The pH and EC of bulk soils was measured using a soil-solution ratio of 1:2.5 in a 0.01 M $CaCl_2$ solution after shaking and settling for one hour.

The percolate samples were stored at 4°C for a maximum of three weeks. If longer storage was required, the samples were stored frozen. All liquid samples were freeze dried and weighed prior to further analysis.

The soil columns were sampled after drainage ~~form~~ from the bottom to the top to avoid any cross-contamination with labelled material from soil-PyOM layer. Three soil layers of 2.3 cm below the soil-PyOM layer were sampled and dried at 40°C over night, corresponding to 0-2.3, 2.3-4.6 and 4.6-7.0 cm depth layers.

Density fractionation was conducted with 5 g of the first 0-2.3 cm below the soil-PyOM layer and bulk soil samples. A sodium polygunstate (SPT) solution adjusted to a density of 1.8 g cm^{-3}, as recommended by Lavallee et al. (2019), was used to separate the fPOM after shaking and settling for one hour. The floating fPOM was decanted after centrifugation (30 min at 4000 rpm) and vacuum filtered using a glass fiber filter (<0.7 µm). The fPOM on the filter was rinsed with deionized water to remove SPT. The remaining heavier MAOM was rinsed with deionized water and centrifuged for three times to remove SPT. No further fractions were acquired and the commonly used ultrasonification, to separate occluded particulate organic matter, was avoided to reduce the risk of physical breakdown of PyOM particles and potential shift between density fractions. All samples were dried at 40°C over night.

Soil and density fraction samples were milled for further measurement. If the sample mass of the fPOM fraction was too little, the samples were ground manually with a mortar and pestle to reduce a potential loss of sample material. The freeze-dried percolate samples were homogenized by manual grinding. Bulk soil and bulk PyOM samples were dried at 40°C over night and milled. The total C and δ^{13}C, relative to the international Vienna Pee Dee Belemnite (VPDB) standard, of all solid samples were measured using a dry combustion module cavity ring-down spectroscopy system (Picarro, Santa Clara, USA). Since our soils were carbonate free (pH<6), the total organic C (TOC) was equal to the measured total C. To obtain O:C and H:C ratios of the PyOM, C and H were measured by dry combustion and O by high-temperature pyrolysis (TruSpec Macro Analyzer, Leco, Saint Joseph, USA).

2.5 Hydraulic properties of soil columns

Following the percolation experiment, breakthrough curves (BTC) were conducted in order to evaluate similar hydraulic properties and flow conditions. Afterwards the soils were sampled as described above (section 2.4). The BTC were performed using a NaCl (1 g l^{-1}) solution as an inert tracer. The tracer solution was added for 25 minutes with a constant pressure head allowing an average flow of 1 ml min^{-1}. Afterwards, the percolation was continued with 0.01 M $CaCl_2$ for further 47 minutes. The EC of the percolated solution was measured in 12 fractions each sampled after six minutes (see Fig. S2 for all BTCs). The percolated volume was added to the last percolate fraction.

The convective velocity v [cm min^{-1}] and the diffusion coefficient D [cm^2 min^{-1}] were estimated by using STANMOD (Version 2.08.1130; Šimůnek *et al.*, 2003) to solve the deterministic equilibrium convection-diffusion equation. Due to high flow rates under saturated conditions, it can be assumed that diffusion of the tracer within the soil was negligible and the dispersivity λ [cm] was calculated as the quotient of the D and v (Vanderborght and Vereecken, 2007). No significant differences of dispersivity were found between the columns of the same soil: 0.29 ± 0.04 cm for the loamy topsoil, 0.19± 0.04 cm for the loamy subsoil, 0.13 ± 0.01 cm for the sandy topsoil and 0.14 ± 0.02 cm for the sandy subsoil (see Table S1 for all values). Therefore, the packing and the addition of the soil-PyOM layer did not lead to any significant trend for changes in the hydraulic properties of the columns and thus hydraulic parameter were excluded as further explanatory variables in this experiment.

2.6 Calculations and statistics

The recovery of ^{13}C derived from the labelled PyOM was calculated with the atomic ^{13}C fractions following the recommendations presented by Coplen (2011). The measured δ^{13}C values were used to calculate the isotope-amount ratios $R(^{13}C/^{12}C)_{sample}$ of each sample, using an isotope-amount ration of 0.01118 for the VPDB standard. The atomic fraction of each sample $x(^{13}C)_{sample}$ was calculated following Eq. (1):

$$x(^{13}C)_{sample} = \frac{R(^{13}C/^{12}C)_{sample}}{1-R(^{13}C/^{12}C)_{sample}} \tag{1}$$

The excess isotope-amount fraction of each sample $xE(^{13}C)_{sample}$ was calculated following Eq. (2):

$$xE(^{13}C)_{sample} = x(^{13}C)_{sample} - x(^{13}C)_{control} \tag{2}$$

where $x(^{13}C)_{control}$ is the atomic ^{13}C fraction of the corresponding soil. Here, the mean of the control columns was used to calculate the excess isotope-amount fraction of the individual soil column depth after the percolation. The mean atomic ^{13}C fraction of all controls of the first percolate (1,000 l m^{-2}) was used to calculate the excess isotope-amount fraction of percolates from soil columns with addition of PyOM. The first percolates were observed to provide the most stable values for the atomic ^{13}C fraction of the control due to higher C contents compared to later percolates with less total C. The recovery of ^{13}C in [mg] was calculated following Eq. (3):

$$m_{recovery_{13C}} = \frac{xE(^{13}C)_{sample}}{xE(^{13}C)_{soil-PyOM}} \times m_{sample} \tag{3}$$

where $xE(^{13}C)_{soil-PyOM}$ is the excess isotope-amount fraction of the corresponding soil-PyOM mixture and m_{sample} is the total mass of C measured in the sample in [mg]. This recovery calculation allowed to distinguish between three separate C pools: (1) TOC, (2) the labelled PyOM-C and (3) nSOC. On average, the total recovery of TOC in the soil and percolates was 91.6 ± 1.0 % and 91.4 ± 2.7 % % of added PyOM-C. The recoveries were normalized to 100 % for further comparison.

Significant differences in PyOM-C between fresh and oxidized PyOM treatments were tested with a t-test. To test significant differences of nSOC in soils and percolates between controls and treatments with addition of PyOM, analysis of variance (ANOVA) was applied and p-values were computed with the post-hoc Tukey's 'Honest Significance Difference' of means method on a 95 % family-wise confidence level. The statistical analyses were performed using R version 4.0.0 (R Core Team, 2020). The standard error (error of the mean) of four replicates is presented for all data and error propagation was applied for cumulative nSOC and PyOM-C fluxes. Due to a potential sample contamination after the experiment, one control replicate of the sandy subsoil was excluded from the analysis. One replicate of the loamy subsoil with addition of oxidized PyOM was excluded from further analysis due to an unsteady flow during the percolation.

3 Results

3.1 Mobility of fresh and oxidized PyOM-C

The percolation and export of oxidized PyOM-C from the columns was higher compared to fresh PyOM-C for all soils over the whole percolations (Fig. 2). After a total percolation of 18,000 l m^{-2}, 0.70 ± 0.15 % of oxidized and 0.24 ± 0.03 % of fresh PyOM-C percolated from the sandy topsoil ($p<0.01$). From the sandy subsoil, 0.64 ± 0.08 % of oxidized and 0.26 ± 0.07 % of fresh PyOM-C were leached ($p<0.01$). The loamy topsoil showed a percolation of 0.40 ± 0.25 % of oxidized and 0.18 ± 0.03 % of fresh PyOM ($p=0.16$). Significantly more oxidized PyOM-C leached from the loamy subsoil, with 0.40 ± 0.06 % of oxidized PyOM-C compared to 0.17 ± 0.04 % of fresh PyOM-C ($p<0.01$). The total amount of percolated oxidized and fresh PyOM-C did not differ significantly between topsoil and subsoil for the loamy or the sandy soil. Between the two soils, the export of oxidized PyOM-C was significantly increased ($p<0.01$) for the sandy topsoil and subsoil compared to the loamy soil while the export of fresh PyOM-C was not significantly different ($p=0.38$; Fig. 2).

The first flush of 1,000 l m^{-2} caused the highest export of PyOM-C from the soil columns (Table S2) and contributed to 80.4-84.3 % of total percolated PyOM-C from the sandy soil, and to 50.6-79.8 % of the total percolated PyOM-C from the loamy soil (Fig. 2). The first flush of PyOM-C was similar between the sandy topsoil and subsoil (2,862.9-1,114.7 µg PyOM-C l^{-1}) and on-going over the whole percolation time. For the loamy topsoil, the first flush indicated higher PyOM-C concentrations (596.4-1,411.4 µg PyOM-C l^{-1}) compared to the subsoil (347.5-724.2 µg PyOM-C l^{-1}), but the concentrations decreased to non-detectable levels for the last percolation stage of 18,000 l m^{2} from the loamy topsoil and were on-going for the subsoil.

3.2 pH and electrical conductivity of percolates

The initial pH of the percolates increased with addition of PyOM for all soils (Table S2, Fig. S3). As an average of all percolates, the pH increased significantly by 0.2~~17~~ ± 0.1~~02~~ units in the percolates of the sandy topsoil. This effect was larger in the sandy subsoils with a significant increase by 0.3~~1~~-0.5~~46~~ units. For the loamy topsoil, the first flush (1,000 l m^{-2}) showed significantly increased pH values by 0.5~~46~~-0.8~~76~~ units with addition of PyOM, but thereafter approached the pH of the percolates from the control. Changes in pH were less dominant in the loamy subsoil but the pH increased continuously over the whole percolation.

The EC increased significantly with addition of PyOM ($p<0.01$) in the first percolates compared to the control for all soils (Table S2, Fig. S4). With further percolation, the EC equilibrated to the background value of the percolate solution (2.20 mS cm^{-1} of 0.01 M $CaCl_2$) for all soils with and without addition of PyOM.

3.3 Percolated nSOC

The addition of PyOM significantly increased the total percolated nSOC from the sandy topsoil and subsoil compared to the control, but did not change the total nSOC export from the loamy soil (Fig. 3). The addition of fresh PyOM significantly increased the total nSOC percolation compared to the oxidized PyOM in the sandy topsoil and subsoil ($p=0.01$). In total, 3.5 ± 0.6 % (0.73 ± 0.05 g nSOC kg^{-1} soil) of total initial nSOC leached with fresh PyOM and 2.5 ± 0.2 % (0.53 ± 0.02 g nSOCC kg^{-1} soil) of total nSOC with addition of oxidized PyOM from the sandy topsoil. Thus, PyOM addition significantly increased the nSOC leaching for the sandy topsoil compared to the control without PyOM addition, from which 1.7 ± 0.1 % of the initial nSOC were leached ($p<0.01$). ~~This was significantly more to than the control with an export of 1.7 ± 0.1 % of the total initial nSOC (p<0.01).~~ From the sandy subsoil, 4.9 ± 0.4 % of the total nSOC percolated from the control while significantly more nSOC percolated with fresh (9.9 ± 1.1 %; 0.26 ± 0.01 g nSOCC kg^{-1} soil) and oxidized (7.8 ± 0.5 %; 0.21 ± 0.01 g nSOCC kg^{-1} soil) PyOM ($p<0.01$).

Between the loamy and sandy topsoil~~s~~, the total relative nSOC percolation did not differ significantly for the controls ($p=0.71$) and with addition of oxidized PyOM ($p=0.86$). But the addition of fresh PyOM resulted in a higher nSOC percolation in the sandy topsoil compared to the loamy topsoil ($p=0.01$). For the subsoils, the total nSOC percolation was significantly higher in sandy subsoil compared to the loamy subsoil with fresh PyOM (<0.01) and oxidized PyOM ($p<0.01$) but not for the controls ($p=0.28$).

The first flush (1,000 l m^{-2}) showed the highest nSOC concentrations in the percolates (Table S2). From the sandy topsoil, 45.54 ± 7.69 mg nSOC l^{-1} ($p<0.01$) with fresh and 28.16 ± 2.09 mg nSOC l^{-1} ($p=0.05$) were leached with addition of oxidized PyOM, whereas significantly less nSOC was leached from the control (12.12 ± 0.24 mg nSOC l^{-1}). The nSOC concentrations in the percolates were lower for the sandy subsoil (13.31-3.28 mg nSOC l^{-1}) compared to the topsoil, but higher for the last percolate indicating an on-going nSOC mobilization. The nSOC percolated from the loamy topsoil in the first flush was 9.65 ± 1.07 mg nSOC l^{-1} for the control and significantly increased to 21.14 ± 1.96 mg l^{-1} ($p=0.01$) and 15.89 ± 2.08 mg l^{-1} ($p=0.16$) with addition of fresh and oxidized PyOM, respectively. The loamy subsoil showed lower leached nSOC concentrations in the percolates with 7.86 ± 0.49 mg nSOC l^{-1} compared to the topsoil with addition of fresh (12.23 ± 1.55 mg nSOC l^{-1}; $p=0.07$) and with oxidized PyOM (10.92 ± 0.79 mg nSOC l^{-1}; $p=0.07$).

3.4 Changes in fresh and oxidized PyOM-C and nSOC in soil columns

After the percolation, 89-96 % of the fresh and oxidized PyOM-C remained at its initial location in the PyOM layer in both topsoils and subsoils. ~~The soil-PyOM layers contained on average of all soils 90-96 % of the total initially added fresh and 89-96 % of the total initially added oxidized PyOM-C after the percolation.~~ The first 0-2.3 cm below the soil-PyOM layer contained the largest proportions of mobilized PyOM with no differences between oxidized and fresh PyOM (Fig. 4). The recovered PyOM-C from this layer ranged between 3.5-9.7 % (0.84-1.50 g PyOM-C kg^{-1} soil) and 3.6-10.1 % (0.52-1.06 g PyOM-C kg^{-1} soil) of added PyOM-C in the sandy and loamy soil, respectively. With greater soil depth, the recoveries decreased to <1 %. In the soil layers at 2.3-4.6 cm and 4.6-7.0 cm below the soil-PyOM layer, only 0.01-0.13 % and 0.05-0.17 % of added fresh and oxidized PyOM-C were recovered, respectively. The recovery of oxidized PyOM-C in these layers was mostly significantly higher compared to the fresh PyOM-C (Fig. 4).

Between topsoil and subsoil, the first layer below the soil-PyOM layer (0-2.3 cm) showed no significant differences in the recovery of PyOM-C for both, sandy and loamy soil. The sandy subsoil indicated higher recoveries of oxidized PyOM-C ($p=0.12$) compared to the topsoil in 2.3-4.6 cm depth but not for fresh PyOM-C ($p=0.68$). In 4.6-7.0 cm depth below the PyOM layer, the recoveries of oxidized ($p<0.05$) and fresh PyOM-C ($p<0.01$) were significantly higher in the sandy subsoils compared to the topsoil.~~The lowest sandy subsoil layer, however, showed significant higher recoveries of oxidized (p<0.05) and fresh PyOM-C (p<0.01) compared to the topsoil.~~ The loamy subsoil showed significantly higher fresh ($p=0.05$) and oxidized PyOM-C ($p<0.01$) recoveries in 2.3-4.6 cm depth compared to the topsoil. For the deeper layer (4.6-7.0 cm), the recovery of oxidized ($p<0.05$) and fresh PyOM-C ($p<0.01$) were also higher in the subsoil than in the topsoil. The relative recovery of PyOM-C did not differ significantly between the loamy and sandy soils for the same depths.

The total nSOC loss from the soil columns significantly increased with PyOM for the sandy soil, but not for the loamy soil (Fig. 5). The nSOC contents decreased by 1.8 ± 0.2 % (3.9 ± 2.6 g nSOC kg^{-1} soil) with fresh PyOM and by 0.8 ± 0.1 % (1.8± 1.3 g nSOC kg^{-1} soil) with addition of oxidized PyOM in the sandy topsoil ($p<0.01$). In the sandy subsoil, the PyOM resulted in 4.8 ± 0.5 % (0.4± 0.2 g nSOC kg^{-1} soil) and 2.6 ± 0.3 % (0.3± 0.2 g nSOC kg^{-1} soil) lower nSOC contents after percolation with fresh and oxidized PyOM, respectively ($p<0.01$). The losses of nSOC were significantly larger with fresh PyOM than with oxidized PyOM in the sandy topsoil and subsoil ($p=0.01$).

3.5 Density fractionation of 0-2.3 cm below soil-PyOM layer

The density fractionation of the first 0-2.3 cm below the soil-PyOM layer revealed that large proportions of the PyOM-C remained in the light fPOM fraction in the sandy soil (Fig. 6). In the sandy topsoil, 93.3± 0.9 % of the PyOM-C was found in the fPOM fraction. The same fraction contributed to 86.3 ± 1.7 % of the total PyOM-C in the first sandy subsoil depth below the soil-PyOM layer (0-2.3 cm). In the loamy soil, 40.2 ± 1.8 % of the PyOM-C was associated with the MAOM fraction in the topsoil and subsoil, given as an average of fresh and oxidized PyOM. In general, the proportions of PyOM-C found in the two fractions did not differ significantly between the fresh and oxidized PyOM and between the loamy topsoil and subsoil. The sandy subsoil indicated significantly more oxidized PyOM-C in the MAOM fraction compared to the topsoil ($p=0.05$).

4 Discussion

4.1 Mobility of PyOM

At the end of the experiment, 3.8-10.8 % of the added PyOM moved vertically from its initial location. This includes PyOM recovered in seven centimeters of soil below the soil-PyOM application layer and exported PyOM in the percolates (Fig. 7). Large parts of the mobilized PyOM were translocated to the first 0-2.3 cm below the soil-PyOM layer (3.5-10.1 % of added PyOM-C; Fig. 4). The total recovery of PyOM in this layer did not differ significantly between the sandy and loamy soil. This indicates a potential accumulation close to the transition of the soil-PyOM layer and the upper 0-2.3 cm regardless of the soil texture. The PyOM-C recovered in deeper soil depth of 2.3-7.0 cm and in the percolates was most likely derived from dissolved and colloidal PyOM. Dissolved and colloidal PyOM is reported to be a major mobile fraction in soils (Wagner et al., 2017, 2018).

Abiven et al. (2011) reported that 0.31-0.42 wt% of PyOM were mobilized in a batch experiment without any soil addition as dissolved (<0.45 µm) and colloidal (0.45-5 µm) forms. In field incubation experiments (one to two years), a small proportion of 0.041-0.004 % of initially added PyOM was reported to be mobilized vertically to >15 cm depth in dissolved forms (Maestrini et al., 2014; Major et al., 2010). Hilscher and Knicker~~,~~ (2011) reported that 2.3 % of added PyOM migrated to 5 cm depth and 0.4 % were leached from soil columns (8 cm length) and found in the column outflow in a one-year incubation experiment.~~reported that 2.3 % of added PyOM migrated to 5 cm depth and 0.4 % were exported from the soil (>8 cm depth) in a one-year incubation experiment~~. We identified that 0.17-0.70 % of the added PyOM-C were exported from the soil columns (>7 cm; Fig. 2). This is in accordance to the relatively limited mobility of PyOM observed under experimental and field conditions compared to non-pyrolyzed OM.

Don and Kalbitz (2005) reported that fresh and 12 month in-situ incubated litter from a variety of temperate forest trees (e.g. sycamore maple, mountain ash, beech, spruce and pine litter) can release 0.3-6.5 % of water extractable DOC. Liebmann et al. (2020) applied highly ^{13}C labeled beech litter on the surface of a temperate forest floor and reported that after 22 months, 11.2 % of the applied litter migrated within a depth of 0-140 cm, but 87 % of this mobilized litter fraction was found in the upper 5 cm, indicating a minor importance of aboveground litter DOC input in deeper soils. However, ~~the~~ mobilized PyOM is most likely less controlled by microbial decomposition due to the high stability of PyOM (Kuzyakov et al., 2014; Singh et al., 2012), allowing a potential deeper migration. It needs to be noticed that we only included one type of PyOM (ryegrass derived and produced at 450°C) which constrains general assumptions since the chemical and physical properties of PyOM, such as particle size, are highly depending on the feedstock and production conditions (Lehmann et al., 2015; Saiz et al., 2018).

Under field conditions, pedoturbation (e.g. due to swelling and shrinking of clay rich soils) and bioturbation would potentially promote the vertical translocation of PyOM (Hobley, 2019; Rumpel et al., 2015). Physical fragmentation and break-down of PyOM during environmental aging reduces the particle size, which can increase the vertical mobility of PyOM due to decreasing friction of smaller particles during transport and the generation of colloids (Hobley, 2019; Pignatello et al., 2015; Spokas et al., 2014). These colloids tend to become more mobile with ageing, decreasing particle size, increasing pH, and in the presence of OM, whereas their mobility tends to decrease in the presence of clay minerals, hydrophobic contaminants, and high ionic strengths due to aggregation. (Castan et al., 2019; Sigmund et al., 2018). Fragmentation further increases the relative specific surface area of PyOM and may promote stabilization and thus its retention in soils due to increased physico-chemical interaction with the mineral phase (Singh et al., 2012; Xiao and Pignatello, 2015).

4.2 Dynamic of mobilized PyOM

The first flush, leached from the columns with 1,000 l m^{-2}, contributed to the highest export of PyOM from the soil columns and the mobilized amounts decreased with the percolation for all soils (Fig. 2 and Table S2). We hypothesized a continuous export of PyOM-C and decrease with time which can be confirmed with our experiment. Our results clearly indicate that the first flush is a major event of PyOM transport through soil and contributed to 80-84 % and 51-79 % of total exported PyOM from the sandy and loamy soil, respectively. This can be attributed to mobile PyOM fractions which are directly produced during the pyrolysis and easily mobilized with the initial flux (Hilscher et al., 2009). Therefore, the initial flux of PyOM may significantly contribute to its total export from soils and its transition to aquatic systems under field conditions. Most field experiments and observation miss the initial PyOM flux (lateral and vertical) with the first rain event after a fire, resulting in a potential underestimation of the dissolved transport rates of PyOM (Santos et al., 2017). This may further cause an underestimation of the vertical PyOM transport from depositional landscape positions after a redistribution following an initial lateral mass transport (Rumpel et al., 2015). The export of fresh PyOM with the first flush from the subsoils indicates that a large proportion can be mobilized before any aging associated oxidation occurs which can be of significance at depositional sites where relatively fresh PyOM can be buried.

The PyOM-C export was continuous for the sandy topsoil and subsoil indicating an on-going mobilization and migration through the coarse soil. Besides this large export of PyOM with the first flush, PyOM-C was not detectable in the last percolated fraction of the loamy topsoil. Therefore, large proportions of PyOM were able to migrate through the loamy topsoil with the first flush, but with decreasing PyOM-C concentration, the retention and most likely the sorption to the mineral phase and OM increased. In comparison, the loamy subsoil retained larger proportions of the PyOM mobilized with the first flush (flush of 51-58 % of the total exported PyOM) but continuously released the retained PyOM into the solution with further percolation.

The on-going PyOM export from soils in our experiment could potentially explain the steady, less seasonally affected and from fire history decoupled flux of soil derived PyOM to rivers as observed in the field (Bao et al., 2019; Dittmar et al., 2012a, 2012b; Santos et al., 2017; Wagner et al., 2018). In our experiment, the proportion of percolated PyOM-C of the total percolated C ranged between 2.4-17.2 % for the first flush and between 0.2-2.8 % for the last percolates, as an average of all soils (Table S2). Artificially produced PyOM is reported to have a higher stability than PyOM naturally produced during wildfires, which challenges the use of one type as a proxy for the other~~Artificially produced PyOM is mostly more stable than naturally produced PyOM, which challenges the use of one type as a proxy for the other~~ (Santín et al., 2017). The proportions observed here, however, are in line with globally reported dissolved black carbon proportions on total riverine (3-15 %) and marine (0.1-2.9 %) DOC (Coppola and Druffel, 2016; Jaffé et al., 2013; Jones et al., 2020; Wagner et al., 2018). However, we did not investigate degradation (biotic or abiotic) of mobilized PyOM and nSOC after the export from the soil, which would increase the proportion of PyOM-C on the total DOC.

4.3 Effect of oxidation on PyOM mobility and reactivity

The oxidation significantly increased the PyOM mobility and resulted in 2-7 times higher PyOM-C recoveries in the soil in 2.3-7.0 cm (Fig. 4) and 2-3 times higher losses through percolation (Fig. 2) compared to fresh PyOM (Fig. 7). This confirms our second hypothesis that oxidation (aging) is enhancing the mobility of PyOM. The similar quantities of fresh

PyOM-C found in the percolates from the sandy and loamy soil indicates that the mobility of fresh PyOM is most likely only partially influenced by soil texture and rather controlled by the total abundance of mobile compounds originated directly from the pyrolysis. For the oxidized PyOM, however, the exported quantities of PyOM-C revealed a nearly twofold higher mobility in the sandy soil than in the loamy soil. This indicates a higher mobility of PyOM with aging in coarse textured soils and a potentially higher retention of the oxidized PyOM in soils with a finer texture.

In a batch experiment, Abiven et al. (2011) reported an increase of water extractable PyOM fraction by 40-50 times after 10 years of natural aging compared to recent PyOM and a higher aromaticity of the solubilized aged PyOM. This, however, was estimated without any soil interaction of the mobile fraction. Hockaday et al. (2006) provided indirect evidence that PyOM in a fire-affected watershed is mainly derived from PyOM previously aged in soils and that it is undergoing a fractionation during its migration through the soil depending on its initial aromaticity. Velasco-Molina et al. (2013), identified that PyOM accumulated in tropical deep sombric horizons (>40 cm soil depth) and that this PyOM underwent oxidation process which increased its content of carboxylic groups. In a recent study, Braun et al. (2020) reported a decreasing aromaticity of water extractable PyOM extracted from agricultural soils compared to the bulk PyOM and no changes after three years aging under field conditions. Contrastingly, Wagner et al. (2017) reported an increased aromaticity of PyOM exported from soils with aging (>100 years) compared to fresh bulk PyOM. The authors, however, reported that the oxidation alone could not explain the reported higher mobility of PyOM with aging. This highlights that oxidation is not only increasing its mobility but also its reactivity in soil during aging and its transport.

The reactivity of PyOM in soils clearly increased with oxidation in our experiment and caused a higher retention of oxidized PyOM in 2.3-7.0 cm soil depth below the soil-PyOM layer in both soils (Fig. 4). This increased retention can be associated with enhanced interaction of the oxidized PyOM surfaces with the soil mineral phase and the native soil OM. Scanning electron microscopy showed a preferential interaction of partially oxidized PyOM and the soil mineral phase (Brodowski et al., 2005). The increased PyOM reactivity and mobility with oxidation can be attributed to the higher abundance of functional groups containing hydrogen and oxygen (e.g. carboxyl groups, Fig. 1) on the oxidized surface–(Knicker, 2011)~~(Fig. 1)~~. This oxidation consequently increased the polarity which enhances its water solubility and its interaction with the mineral phase (Cheng et al., 2008; Fang et al., 2014; Pignatello et al., 2015; Zhao and Zhou, 2019; Zimmerman, 2010).

Our results show that the long-term fate of PyOM in soils is highly controlled by its degree of oxidation and thus will change with aging. However, aging will not only increase the PyOM mobility and solubilization but also its reactivity and thus interaction with the soil mineral phase and OM and thus its long-term sequestration. Therefore, future studies should include the effect of aging for more than a few years under field conditions.

4.4 PyOM retention in soil

The majority of the mobilized PyOM was retained in the soil (92.8±1.0 %). This indicates the importance of PyOM retention in soils during its migration and thus confirms our third hypothesis. The density fractionation of the first soil layer (0-2.3 cm) below the soil-PyOM layer revealed that most of the translocated PyOM remained as fPOM with 85.6-94.5 % and

56.9-61.4 % in the sandy and loamy soil, respectively (Fig. 6). More than one third of the PyOM (40.2 ±1.8 %) in the loamy topsoil and subsoil, 0-2.3 cm below the soil-PyOM layer, however, was found to be association with the mineral phase. This is surprising considering the relatively short interaction time of PyOM and the soil mineral surface and soil aggregation in a saturated column experiment.

The soils in our experiment showed large differences in the contents of amorphous Fe(o) and Al(o) and in texture with 13-15 % clay and 22-23 % silt in the loamy soil compared to <12 % silt and clay combined in the sandy soil (Table 1). The aromatic compounds of the PyOM can directly interact with the edge functional groups of clay (Joseph et al., 2010; Lehmann et al., 2007; Pignatello et al., 2015). Brodowski et al. (2006) found up to 24 % of PyOM in forest soils to be occluded in aggregates and concluded that PyOM can act as a binding agent for the aggregate formation. In a field incubation experiment of ten months, Singh et al. (2014) recovered >25 % of the added PyOM in the occluded fraction in temperate forest soils and Vasilyeva et al. (2011) found up to 70 % of PyOM associated to the mineral fraction after 55 years of bare fallow in Chernozem. Here, the MAOM fractions contain both, PyOM which is in direct association with the mineral phase and occluded in aggregates. Our results show that the PyOM-mineral interaction and occlusions can occur very quickly in soils with reasonable clay and silt content and may be predominately controlled by the physical and chemical interaction rather than biological processes, since these were neglectable in our experiment given the short duration of five days. This ~~quick~~ rapid mineral interaction will control the long-term stability of PyOM in soils and requires more research under unsaturated and field conditions and also different PyOM feedstocks.~~.~~

The higher proportion of PyOM recovered as fPOM in the sandy soil indicate that the PyOM-mineral interaction was limited which is in agreement with the general higher proportion of TOC in fPOM fraction (41-73 %) and high sand contents (>88 %; Table 1). In coarse soils, Fe- and Al-(hydr)oxides are considered to interact and stabilize PyOM and SOC due to its great affinity to OM (Brodowski et al., 2005; Pignatello et al., 2015; Wiesmeier et al., 2019). Slightly more fresh PyOM ($p=0.24$) and significantly more oxidized PyOM ($p=0.05$) was recovered in the MAOM fraction in the sandy subsoil compared to the topsoil. This indicates that the sandy subsoil had a higher potential to retain PyOM due to increased mineral interaction compared to the topsoil.

Subsoils are unsaturated in OM due to little inputs, such as DOC from upper soil horizons, root derived and already microbially processed OM, but large mineral surfaces (Kaiser and Kalbitz, 2012; Lützow et al., 2006). Therefore, the probability of mobilized PyOM to interact with the mineral phase is higher in the subsoil, resulting in a higher retention compared to topsoils where OM is already occupying sorption sites on the mineral surfaces. The subsoils of the loamy soil contained significantly more PyOM at 2.3-7.0 cm depth below the soil-PyOM layer compared to the topsoil (Fig. 6 and 7). This was also the case for the last soil layer (4.6-7.0 cm) of the sandy subsoil and topsoil. Therefore, the loamy and sandy subsoils had a higher PyOM retention potential than topsoils, where the nSOC contents were five to ten times higher. It needs to be noticed, that the PyOM retained in this depth represented only <1 % of the added PyOM. In addition, we did not include unsaturated flow conditions which would resemble the mobility and retention under field conditions.

The higher retention of PyOM in the subsoils can explain its accumulation in greater soil depth which is found under field conditions (Brodowski et al., 2007; Soucémarianadin et al., 2019). We showed that PyOM can be continuously re-mobilized from subsoils by percolating water and thus can potentially be exported to deeper soil depth or to the groundwater which would finally result in the export from the terrestrial to the aquatic system such as rivers. Furthermore, it can be considered that large proportions of the mobilized PyOM will not be affected by microbial degradation to the same extent than non-pyrogenic SOC and DOC during the percolation through the soil (Don and Kalbitz, 2005; Kuzyakov et al., 2014; Tipping et al., 2012). This would result in increasing proportions of PyOM on the total subsoil OM.

4.5 Effects of PyOM on nSOC mobility

The addition of PyOM significantly enhanced the total nSOC export in the sandy topsoil and subsoil by 48-270 % which is equivalent to an additional loss of 0.07-0.37 g nSOC kg^{-1} soil (Fig. 3, Fig. 5 and Table S2). The nSOC export from the loamy soil was significantly increased compared to the control for the first flush (1,000 l m^{-2}) by 56-105 % (0.04-0.10 g C kg^{-1} soil), but negligible over the whole percolation. Therefore, our fourth hypothesis can be partially accepted and the effect of PyOM on nSOC mobility was clearly controlled by soil texture and properties of the soil and PyOM.

With PyOM, the pH of the percolates increased in all soils except of the loamy subsoil which can further enhance the nSOC mobility (Table S2, Fig. S3). Increases in pH can be associated to a liming effect due to carbonates which are formed during the pyrolysis (Smebye et al., 2016). The pH significantly controls the mobility of DOC (Kaiser and Guggenberger, 2000; Kalbitz et al., 2000) and an increase by 0.5 pH units was shown to enhance the DOC export by 50 % (Tipping and Woof, 1990). We found increases in pH by 0.~~17~~2-0.~~7~~8~~6~~ units (Table S2, Fig. S3). The liming effect lasted for the sandy soil over the whole percolation, which also showed a continuously higher export of nSOC with PyOM compared to the control. Therefore, the increasing pH in the sandy soil, with low initial pH values of 3.4-4.1, may have caused a re-mobilization of adsorbed nSOC derived DOC. The fresh PyOM had a significantly higher liming effect as indicated in the first flush of the sandy topsoil, and the loamy topsoil and subsoil, while the oxidized PyOM caused a higher EC in the first flush (Table S2, Fig. S4). This can be attributed to a decarbonatization of PyOM with oxidation, which was also observed with the MIR analysis (Fig. 1). Therefore, a liming effect of PyOM on the nSOC mobility will potentially decrease with aging but is substantial in coarse soils.

Barnes et al. (2014) reported that wood-derived PyOM (mesquite biochar, 400°C, 4 h) resulted in higher DOC fluxes from organic poor sandy soil in a soil column experiment (filled with soil-PyOM mixtures containing 10 % wt% PyOM), but attributed this increase to PyOM derived C and not soil-derived-C. The authors found no increase in DOC flux from organic- and clay-rich soil but identified an increase in the aromaticity of the DOC and the authors identified that leachable PyOM fractions were lost but soil-derived C was retained with PyOM. The authors concluded that the net increase in DOC export from soils with moderate amounts of clay, silt and OM is limited. Major et al. (2010) reported that wood-derived PyOM amendment (mango wood biochar, 400-600°C, 48 h) in a savanna soil (sandy clay loam) increased the flux of non-PyOM derived particulate organic carbon and DOC by 2.3-4.1 times after two years under field condition. However, the authors attributed these increases to a higher belowground net primary production and a corresponding increase in OM input with

PyOM. Jones et al. (2012) found no change in the DOC flux after PyOM (wood biochar, 450°C, 48 h) from a sandy clay loam in a three-year field trial. By tracing the highly labelled PyOM-C, our results confirm that PyOM may have a limited effect on the nSOC mobility in fine-textured loamy soils over the long-term since we could not identify significant differences in the cumulative nSOC loss from the soil columns with fresh and oxidized PyOM. However, the first flush of dissolved PyOM enhanced the loss of nSOC significantly in the loamy topsoil and subsoil. It is likely that this mobilized nSOC would be adsorbed again during its further transport through the loamy soil (>7 cm).

Dissolved organic matter mobility in sandy soils is mainly controlled by adsorption on Fe-/Al-(hydr)oxides. High molecular weight compounds with aromatic structures are reported to have a higher sorption affinity and can desorb less adsorptive compounds from soil mineral phases (Coward et al., 2019; Eusterhues et al., 2011; Kaiser and Kalbitz, 2012; Kalbitz et al., 2000). This is also shown by a fractionation of DOC migration through the soil (Oren and Chefetz, 2012) Recently, Zhang et al. (2020) identified a higher sorption affinity of dissolved organic matter derived from maize straw PyOM by hydrophobic partition, H-bonding and electrostatic interactions compared to non-pyrolyzed dissolved organic matter. Therefore, PyOM caused a re-mobilization of nSOC by desprobing it from complexes of the mineral phase and pre-existing OM. Due to a higher abundance of less oxidized highly aromatic compounds from fresh PyOM compared to oxidized PyOM, the desorption of nSOC was more dominant with fresh PyOM, while oxidized PyOM adsorbed mainly on free mineral surfaces due to its higher reactivity.

The mobilization effect of PyOM on nSOC was more pronounced in the sandy subsoil with 7.8-9.9 % of the initial nSOC exported compared to 2.5-3.5 % of initial nSOC exported ~~form~~ from the topsoil (Fig. 3). This supports the concept of continuous sorption, microbial processing and desorption during the vertical OM migration and thus an accumulation of microbially processed OM in subsoils as described by Kaiser and Kalbitz (2012) as the cascade concept. The binding of microbial processed OM to the mineral surfaces is weaker than for plant derived compounds (high in aliphatic, aromatic and carboxylic groups) and thus it is more easily mobilized by PyOM with a high sorption affinity towards the mineral surfaces. We found that even a small fraction of mobilized PyOM may cause a significant mobilization of potentially labile nSOC. Even if this effect decreased with oxidized PyOM, it indicates a long-term effect on nSOC mobility and influence of the C cycle of fire a~~e~~ffected soils.

5 Conclusion and implementation

The vertical mobility of PyOM was limited to only a small fraction (<11 %) migrating through the soil columns. Large proportions of the mobilized PyOM were retained in the soil and accumulated mainly in particulate form close to the initial layer within the first 0-2.3 cm. Less than 1 % of the added PyOM migrated to greater depth and was exported from the soil (>7 cm). Furthermore, the majority of the exported PyOM was mobilized with the first flush. Oxidation and thus aging of PyOM, significantly increased its mobility and also its reactivity, resulting in an overall larger mobilization but also larger retention in the soil of oxidized PyOM compared to fresh PyOM. Both can be clearly ascribed to the oxidized PyOM surfaces with a higher abundance of oxygen and hydrogen containing functional groups. The migration of oxidized PyOM was further largely influenced by the soil texture resulting in a higher export from the sandy soil and higher retention in the loamy soil due to an increased association to the soil mineral phase.

Fresh and oxidized PyOM significantly increased the mobility of nSOC in the sandy soil and in the first flush of the loamy soil, but not over the whole experiment. This can be attributed to a higher sorption affinity of high molecular weight PyOM compounds to the mineral phase and thus a desorption of already sorbed and mineral associated nSOC, which will eventually be exposed to microbial degradation. The re-mobilization of nSOC was greater in the sandy subsoil compared to the topsoil, supporting the concept that subsoil OM is already microbially processed and its association to the mineral phase is weak (because of low availability of mineral surfaces): hence it can be easily desorbed by younger OM with a higher sorption affinity.

Further research is needed to understand the fate of PyOM under unsaturated and field conditions and larger scales such as pedon and catena and including PyOM from different feedstocks. We identified that the vertical PyOM mobility is highly depending on soil properties and the degree of PyOM oxidation (age) which increases not only its mobility, but also reactivity in soils and influences its effect on nSOC. This will influence the PyC and nSOC dynamics in the vadose zone and between the terrestrial and aquatic systems.~~Further research is needed to understand the fate of PyOM under unsaturated and field conditions. However, we identified that the vertical PyOM mobility is highly depending on soil properties and the degree of PyOM oxidation (age) which increases not only its mobility, but also reactivity in soils and influences its effect on nSOC.~~

Authors contribution

MS and SA designed the experiment. MS conducted the experiment, analyzed the data and wrote the manuscript. SA, SB, GS and KK provided input to the data discussion and the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgment

We thank Esmail Taghizadeh and Thomas Keller (University of Zurich) for support with analyses and technical assistance. We also thank Rahel Wanner (Zurich University of Applied Science) for CHN-O analyzes. This study was funded by the Swiss National Science Foundation (project no. 200021_178768)

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Table 1: Soil texture, total organic carbon (TOC), δ^{13}C, pH, electrical conductivity (EC), oxalate extractable Fe(o) and Al(o) and density fractions (free particulate organic matter, fPOM and mineral associated organic matter, MAOM) for the topsoil (0-10 cm depth) and subsoil (40-60 cm) of the loamy and sandy soil (± 1 SE). See section 2.4 for the used methods.

	Soil depth	**Texture[1]**			**TOC**	**δ^{13}C**	**pH ($CaCl_2$)**	**EC ($CaCl_2$)**	**Fe(o)**	**Al(o)**	**Density fractions**	
	[cm]		[%]		[g kg^{-1} soil]	[‰]	[-]	[mS cm^{-1}]	[g kg^{-1}]	[g kg^{-1}]	[% of total SOC]	
		Sand	Silt	Clay							fPOM	MAOM
Loamy soil	0-10	65	22	13	20.14 (0.67)	-29.1 (0.2)	5.3 (0.1)	2.33 (0.01)	1.85 (0.17)	1.30 (0.17)	17.2 (0.2)	82.8 (0.2)
	40-60	62	23	15	5.66 (0.18)	-28.9 (0.2)	4.0 (0.1)	2.35 (0.03)	2.12 (0.10)	1.99 (0.15)	14.3 (1.0)	85.7 (1.0)
Sandy soil	0-10	88	5	7	21.91 (0.01)	-28.8 (0.1)	3.4 (0.1)	2.45 (0.01)	1.01 (0.12)	0.43 (0.03)	73.2 (0.6)	26.9 (0.6)
	40-60	92	3	5	2.64 (0.08)	-30.1 (0.2)	4.1 (0.1)	2.34 (0.01)	0.93 (0.04)	0.83 (0.10)	41.1 (0.8)	58.9 (0.8)

[1]according to WRB texture classes

Table 2: Total C, ~~and~~ δ^{13}C, O:C and H:C ratios of PyOM used for the corresponding soil column experiment (± 1 SE). See section 2.4 for the used methods.

PyOM	**Soil**	**Type**	**Total C** [%]	**δ^{13}C** [‰]	**O:C** [-]	**H:C** [-]
1.	Loamy topsoil	Fresh	40.6 (0.8)	4135.7 (5.3)	0.51	0.71
		Oxidized	42.1 (1.5)	4201.7 (5.2)	0.50	0.75
2.	Loamy subsoil	Fresh	35.7 (1.2)	3471.6 (7.7)	0.55	0.72
		Oxidized	38.9 (2.1)	3457.5 (18.5)	0.54	0.72
3.	Sandy topsoil & subsoil	Fresh	48.5 (1.8)	2877.0 (5.7)	0.45	0.64
		Oxidized	49.4 (1.3)	2942.6 (3.2)	0.42	0.66

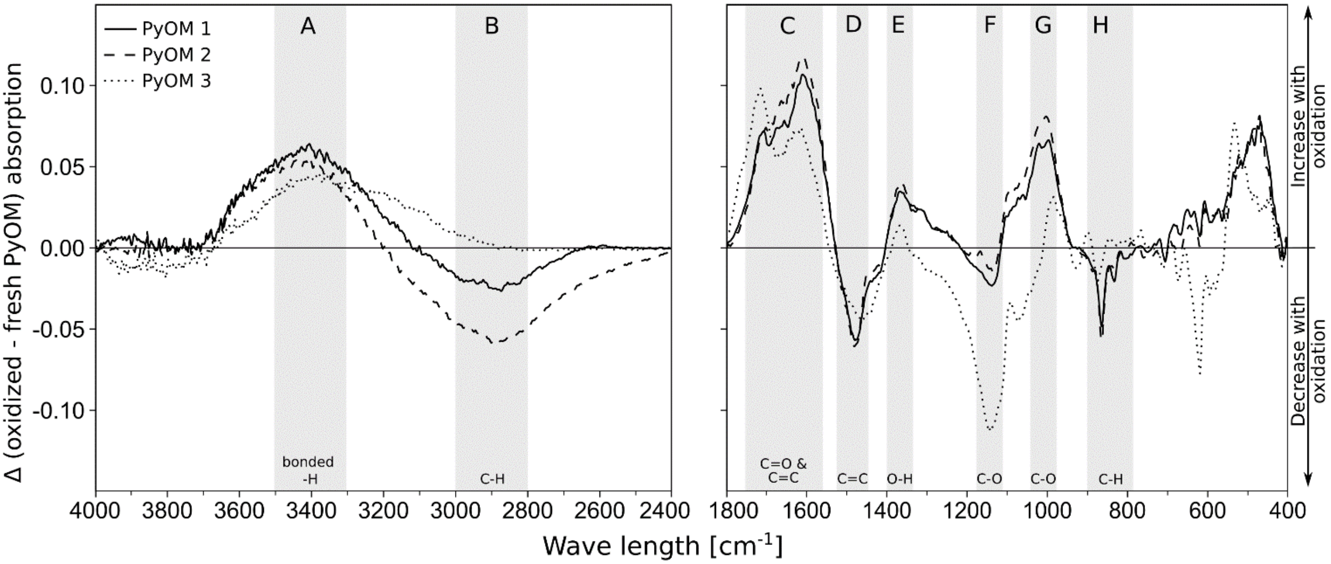


Figure 1: Difference of oxidized and fresh PyOM DRIFT spectra for PyOM 1 (loamy topsoil), PyOM 2 (loamy subsoil) and PyOM 3 (sandy soil). Areas A-H indicate the main changes after oxidation with the corresponding absorption bands indicating increases in A = 3500-3200 cm^{-1}, C-O bonds, hydroxyl groups and H_2O; C = 1730-1680 cm^{-1}, aromatic carbonyl/carboxyl C=O bonds and C=C bonds (1590-1560 cm^{-1} and 1620-1610 cm^{-1}); E = 1375 cm^{-1}, O-H bonds and G = 1060-1020 cm^{-1}, C-O bonds. Oxidation decreased the absorption at bands B = 2980-2820 cm^{-1}, aliphatic C-H bonds; D = 1500 cm^{-1} aromatic C=C bonds; F = 1280-1200 cm^{-1}, C-O and H-O bonds and H = 880 and 805 cm^{-1}, aliphatic C-H bonds. Decreases at 1480 cm^{-1} and 864 cm^{-1} can be assigned to a decarbonation with oxidation. See supplement (Fig. S1) for full spectra.

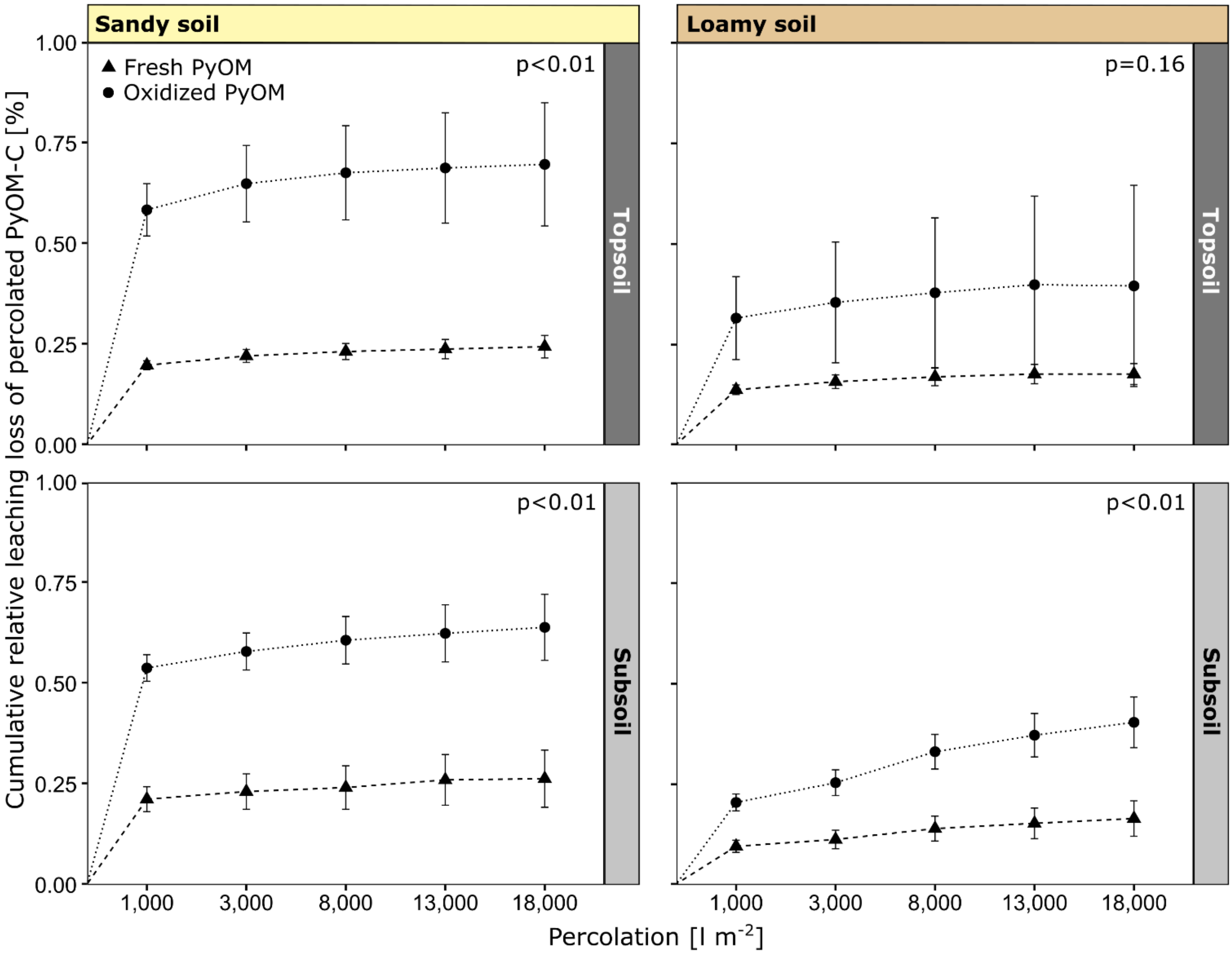
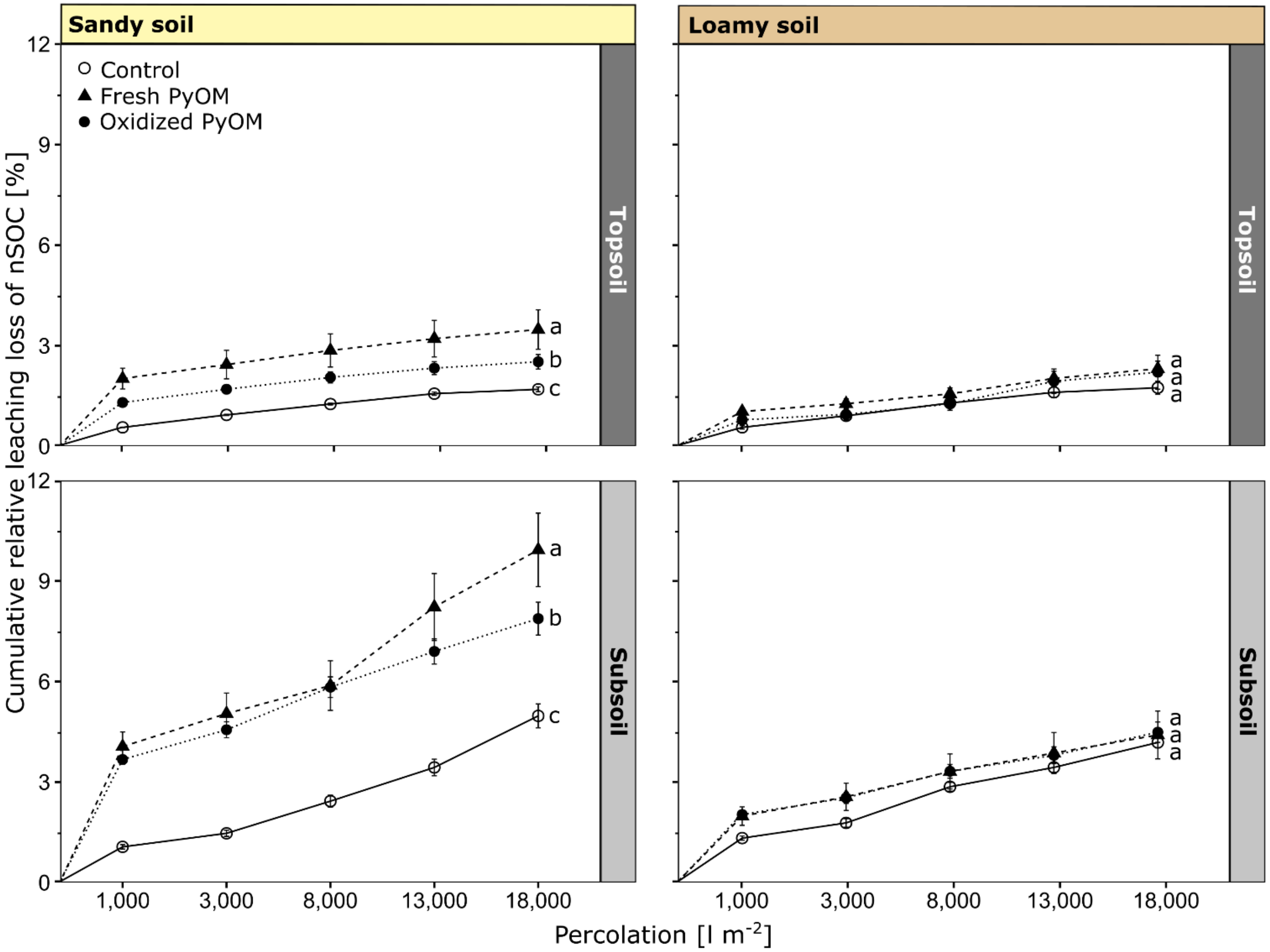


Figure 2: Cumulative leaching loss of percolated fresh and oxidized PyOM from sandy and loamy topsoil and subsoil. The p-values indicate the significance of differences between fresh and oxidized PyOM after a total percolation of 18,000 l m^{-2}. All values are shown with propagated SE.

1200



1205 **Figure 3: Cumulative leaching loss of native soil organic carbon (nSOC) from sandy and loamy topsoil and subsoil for controls and columns with addition of fresh and oxidized PyOM. The significant differences ($p<0.05$) of the total percolated nSOC after 18,000 l m^{-2} are indicated by letters. All values are shown with propagated SE.**

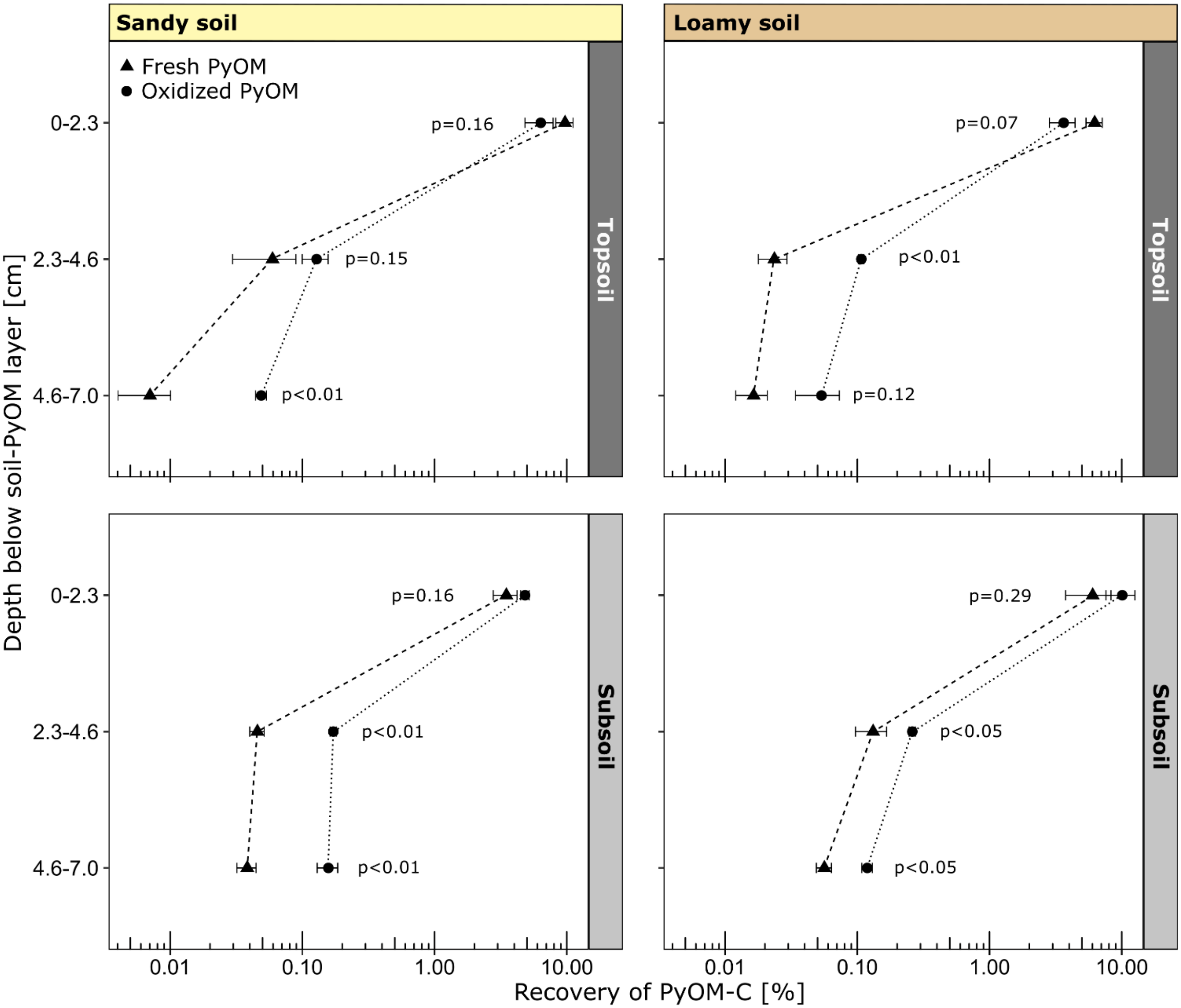


Figure 4: Recovery of PyOM-C in soil below the soil-PyOM layer of the sandy and loamy topsoil and subsoil (± 1 SE). The p-values indicate the significance of differences between fresh and oxidized PyOM at each depth.

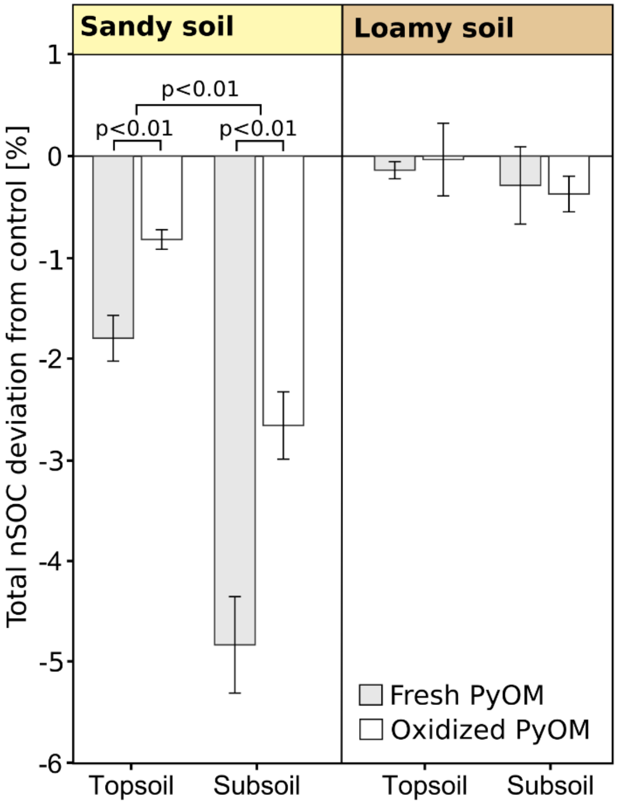


Figure 5: Relative deviations of native soil organic carbon (nSOC) to control of the total soils in soil columns (over all depth) after the percolation for sandy and loamy topsoil and subsoil with addition of fresh and oxidized PyOM (± 1 SE). Negative values indicate leaching losses. Significance of differences of fresh and oxidized PyOM and the significance of the deviation from the control is shown with p-values. No significant differences were found for the loamy soil.

1220

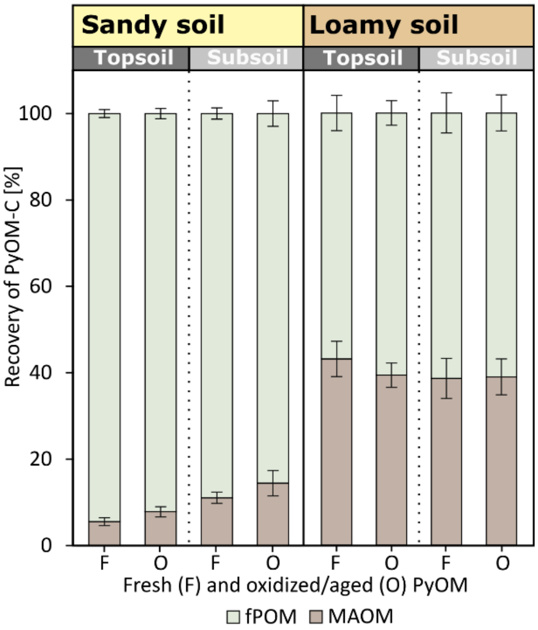


Figure 6: Relative recovery of fresh (F) and oxidized (O) PyOM-C in fPOM and MAOM fractions in the first layer below the soil-PyOM layer (0-2.3 cm) of sandy and loamy topsoil and subsoil (± 1 SE).

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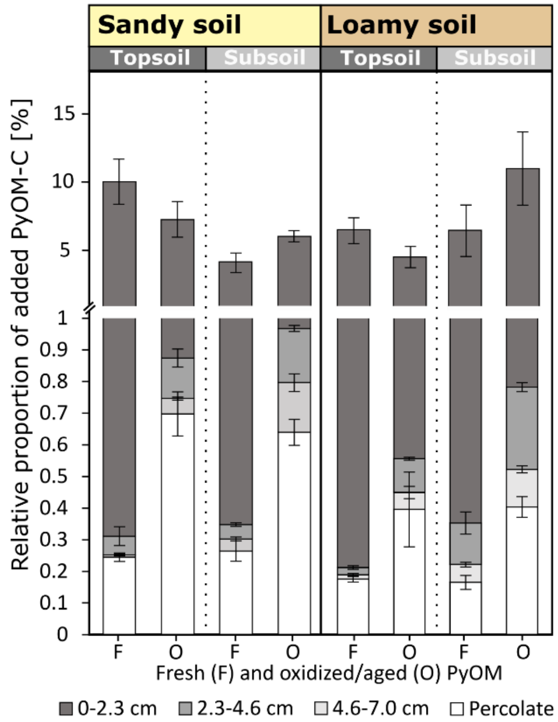

Figure 7: Total mobilized fresh (F) and oxidized (O) PyOM and its relative proportion in the percolates after total percolation and in the soil column in 0-2.3, 2.3-4.6 and 4.6-7.0 cm below the soil-PyOM application layer for the sandy and loamy topsoil and subsoil (± 1 SE). The significances are presented in Figure 2 and 4.