

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

Anonymous Referee #2

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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 compar-

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ison 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.

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. 48: Considering an atomic H/C ratio of 0.5, one cannot talk about highly condensed (Every second C is connected to a H) 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. 52: Change to physical and chemical, because the term physico-chemical is normally related to physical aspects of chemistry (i.e. thermodynamics etc.), which is definitively not the case here. 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 volatiles 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. 59: High aromaticity is not necessarily equal to high molecular weight and it is also

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

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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 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. 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 fire-prone region and that this PyOM is highly carboxylated. 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. 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?

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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

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