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Interactive comment on "Physicochemical changes in pyrogenic organic matter (biochar) after 15 months field-aging" *by* A. Mukherjee et al.

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Authors: We thank the reviewers for your generous time in reviewing this manuscript. We have made many changes to the manuscript in response to your criticisms and suggestions (revised manuscript file with track changes provided here). In the below, we answer their comments point-by-point:

Reviewer 1 Comment #1: The authors present data on the impact of environmental weathering of biochar on the physicochemical properties. As the authors point out in the abstract this data is critical for the understanding of the both the mechanistic processes and the kinetics of the transformation. However, this manuscript contains a few shortcomings: 1. The design of the experiment includes a landscaping cloth cover – what was the mesh size? Would this impact the amount of water entering the column

with the contained biochar? What was the temperature difference between the column of biochar on the surface and those buried in the soil? There would have been different availability to water for each column – the pure biochar and the biochar+soil. This is critical since water is one of the compounds that easily and spontaneously reacts with charcoal. This could lead to serious differences between the biochar with and without soil, thereby confounding the results of the experiment.

Authors' response: The mesh size of the cloth is not definable as it is composed as it is a polypropylene random weave. It is markets as having excellent permeability so we expected no water impedance. We also do not expect that the temperature of the biochar-only and soil/biochar mixtures would have differed as they were both in the shade and in the same location, and, the biochar buckets were surrounded by a solid wood frame simulating the bucket of soil being surrounded by soil.

Reviewer 1 Comment #2: The presence of divalent cations are known catalysts for the abitoic reactions of charcoal. Yet these would not be present in the "biochar control"; yet this is not accounted for.

Authors' response: There are plenty of divalent cations in the biochar itself (listed in Supplemental Table S2 for both fresh and aged biochars). We do agree with the review that there are many ways in which the conditions of degradation of the biochar-alone and soil/biochar alone are not exactly the same, but this is unavoidable and is one of the caveats we make in the text.

Reviewer 1 Comment #3: If there was mass loss from the biochar with aging the comparison of solely the %C composition does not adequately account for the difference between the weathering profiles. There is no mention of sample preparation for this test.

Authors' response: This is correct, possible mass loss was not accounted for. However, in our previous experiments, using both column leaching and multiple batch desorption approaches, we found no significant mass loss from biochar (Mukherjee and Zimmer-

man, 2013).

Reviewer 1 Comment #4: In addition, the biochar + soil could have soil particles present in the pores of the material – Yet there was no discussion on this potential impact, both on the %O number determined (quartz) and the clay minerals and the biochar particle that was aged in soil.

Authors' response: It is just for this reason, i.e. the inseparability of biochar from soil OM and minerals, that chemical changes to biochar were not determined by doing chemical analyses on biochar particles picked out of the biochar/soil mixtures after incubation. This is way we had to use a mathematical mixing approach to determine these changes. And in fact, this is the most important novel feature of the research.

Reviewer 1 Comment #5: The authors solely analyzed two points – initial and final. They missed an opportunity to look at the temporal dynamic of the processes, which would have made a more significant contribution to the literature.

Authors' response: While this is true, time, funding and resources are always limiting factors. And which time points would one chose? There is will always be the possibility of meaning the period in which the most changes take place. We need to point out the fact that there is a scarcity of data of biochar field aging over any time frame. At least the paper makes a start and point out potential important processes for others to examine in greater detail.

Reviewer 1 Comment #6: Only two replicates – Samples were solely run in duplicate – no reason was given for this. This severely limits the strength of the statistical comparisons and there is no clear description given if only one piece of biochar was used for all the testing or how they collected a uniform sample from these artificial aged columns.

Authors' response: Authors agree to some extent with this criticism. We do wish that we had greater resources for conducting greater number of replicates. However, we can answer by pointing out that we were mainly concerned about 'trends' observed

among a range of biochar and types. That is, conclusions were generally based on consideration of a larger number of samples than just single biochar types. Also, this work represents a basis for making further scientific investigations with greater replications.

Reviewer 1 Comment #7: The SEM imagery: No indication how particles were selected or how many particles were used? Was there a difference with depth in the column? Or was this ignored?

Authors' response: Added to text: At least five particles were randomly selected and examined from each homogenized sample and attempts were made to present representative images. Thus, depth was not a factor.

Reviewer 1 Comment #8: Numerous statements in the manuscript (Starting just with the abstract! example P 732 line 12: likely via leaching; line 14-15: Role of OM-microbe-biochar interactions during aging; line 21 "soprbed SOM; line 20 "colonization by microbes"; etc.) which are not supported by data in the manuscript.

Authors' response: Because the data does not unequivocally prove these statements, we were always careful to couch the statements with such terms as "is suggested by" or "likely". For example, "likely via leaching" and "sorption of both microbially-produced and soil OM are likely processes that enhanced biochar aging". It is impossible for us to respond more specifically in defense of specific statements if these are not specified by the reviewer.

Reviewer 1 Comment #9: There are critical details missing in the methodology: Was the dry soil was re-wetted prior to the installation of the columns in the field? Why wasn't the microbial activity measured since this was a major emphasis of the experimental design? Were the soil +biochar columns also covered?

Authors' response: We do not think that any of these omissions are critical. To answer, no, the dry soil was not re-wetted before putting back the ground. Surely this would

have occurred sufficiently after a full year of rainfall. Many microbial aspects of these biochars in the environment were presented in another previous paper (Khodadad et al., 2011) and thus this study was mainly related to chemical aspects of biochar aging. Yes, soil+biochar columns were covered in the same way as the biochar-only as stated in the manuscript.

Reviewer 1 Comment #2: How were the columns homogenized? Was there an examination of the changes with depth in the column? This could have shed light on the fundamental mechanisms at work. . . Especially if the sampling was done with time.

Authors' response: The soil/biochar mixtures were homogenized by shaking manually for several minutes before incubation and all samples were homogenized after collection

Reviewer 1 Comment #10: There was no mention of the analyses of the leached precipitation in the columns; or the fact that the rainfall could have contributed DOC/DOM as a potential source for the differences as well. The use of solely the differences in the CN analyses is a very weak method for illustrating differences from aging, since you can have a loss of oxidized material in charcoal with no change in the bulk chemistry. Without true knowledge on the variance of the values in Table 1 the theoretical combination of the independent materials is not statistically justified.

Authors' response: We assumed rainfall did not have a significant contribution of C or other elements compared to the biochar and soil which are of exponentially higher concentrations. The objective was to find out if weathering would change surface and bulk chemistry of the studied materials over time, which is of course the important factor for soil fertility. The chemistry of leaching materials was already investigated on these biochars previously (Mukherjee et al., 2014; Mukherjee and Zimmerman, 2013). We disagree with the reviewer that the approach is a weak one. Strong conclusions can be made because similar trends were observed among the range of biochars and soils examined.

Reviewer 1 Comment #11: Calculation of oxygen by difference for grass materials is a source of significant error, due to the other elemental components: K, P, Ca, Si

Authors' response: C, N, H and O were calculated on a dry ash-free basis as is standard methodology for biochar analysis. So this should not a problem. We added this note to Supplemental Table S2 to clarify.

Reviewer 1 Comment #12: The SEM imagery: How were the authors sure that these circular objects were microbes? There was no staining or other techniques mentioned for this conclusion. There are numerous inorganic substances that also have this spherical shape, such as combined metal oxides (e.g., CoMn2O4) as well as calcium phosphate crystals also have this circular shape and similar size.

Authors' response: While it is true that spherical objects observed on the aged biochar surfaces were not confirmed to be microbes, they were of the same morphology and general appearance as those stated to be microbes in other studies that analyzed SEMs of biochars (such as those cited by the reviewer below). In addition, the fresh biochars were similar in inorganic element composition as the aged biochars but did not have any of the spherical objects that appeared on the surfaces of the aged biochars (Fig. 4).

Reviewer 1 Comment #13: Recent work has also casts some doubt on the "microbial habitat" theory for biochar additions (Quilliam et al., 2013; Criscuoli et al., 2014; et al., 2014). The authors need to purge or reword all the microbial findings to hypotheses since the claims are unsupported.

Authors' response: We agree with the reviewer that the "microbial habitat" theory has been challenged to some extent. The Jaafar et al., 2014 paper found that hyphae and microbe colonization of the surface of biochar particles were readily observed but with little occurrence of hyphae penetration into biochar pores, although the experiment was only 56 days so not really comparable. Quilliam et al., 2013 reported that microbial colonization of 3-year field-aged biochar took place, but was very sparse. Similar

observations were made by Criscuoli et al., 2014. However, our findings differ from these previous ones in a number of important ways: 1) We observe these 'sparse' microbes on biochar surfaces incubated 'alone', i.e. not with soil, 2) In incubations of soil mixed with biochar, the coatings of microbes and OM are much more pervasive that observed in these other studies, perhaps because of the subtropical environment in which our experiments were conducted. The text was changed to emphasize this point (that microbes were not likely as involved in the biochar-only aging).

Reviewer 1 Comment #14: Overall, the manuscript does present data that could be of interest. However, without the statistical foundation of a properly designed experiment (3-6 reps); there is very little that can be confidentially transferred from this study. Regrettably, the manuscript lacks the innovative nature – since at the end of the manuscript there is very little new insights into the transformations or knowledge of the temporal scale of these biochar transformations.

Authors' response: Authors would like to thank the reviewer for his/her generous time of expenditure on reviewing the manuscript. However, we strongly disagree with the conclusions of the reviewer. Most conclusions were based upon duplicate analyses of samples from duplicated treatments. While this is not optimal, there are plenty of excellent and well-cited studies that have used this level of replication. We were unable to carry out greater replication given our resources available and we chose to look at more treatment types (soil and biochar types) rather than more replicates of fewer treatments. You can fault us for making this choice, but I think it, as a result, provides some insight that no previous study has, i.e. great variations in aging among soil and bichar types. Thus, we also disagree that the study was not innovative. There have been few studies that used controlled field-incubations of biochar, none that simultaneously looked at multiple soil and biochar types, none that simultaneously incubated biochar alone and biochar-soil mixtures and none that used the additive approach to quantify interactive effects. You may think we were unsuccessful in obtaining significantly statistical results but you cannot say the approach was not innovative. And at

the very least, this paper deserves publication for that. But we also disagree that that the results do not provide new insight. You yourself pointed out one of them, i.e. previous studies did not see microbial colonization of biochar surfaces whereas we did. We also see a number of clear chemical shifts during aging that have not been observed previously such as the development of AEC (among all treatments – 8 samples), and increases in substituted aromatic funtional groups (all 4 samples examined).

References Khodadad, C. L. M., Zimmerman, A. R., Green, S. J., Uthandi, S., and Foster, J. S.: Taxa-specific changes in soil microbial community composition induced by pyrogenic carbon amendments, Soil Biol. Biochem., 43, 385-392, 2011. Mukherjee, A., Lal, R., and Zimmerman, A. R.: Impacts of biochar and other amendments on soil-carbon and nitrogen stability: A laboratory column study, Soil Science Society of America Journal, Accepted, 2014. 2014. Mukherjee, A. and Zimmerman, A. R.: Organic carbon and nutrient release from a range of laboratory-produced biochars and biochar–soil mixtures, Geoderma, 193–194, 122-130, 2013.

Please also note the supplement to this comment:
http://www.solid-earth-discuss.net/6/C313/2014/sed-6-C313-2014-supplement.pdf

Interactive comment on Solid Earth Discuss., 6, 731, 2014.