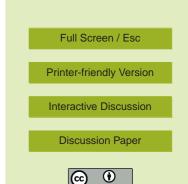**Biogeosciences
Discussions**

Interactive
Comment

Interactive comment on "Centennial black carbon turnover observed in a Russian steppe soil" *by* K. Hammes et al.

K. Hammes et al.

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Reviewer 3

1. Equation (1) defines turnover time as a solution to equation(s) described only as a one-pool donor controlled model'. Although I can guess, I am not sure quite what this means. I am always concerned when descriptions such as this are made, since researchers in different fields use conflicting terminology to define their mathematics. The underlying model (presumably a differential equation) should be published and terms defined in relation to the model. This would be extremely important if the turnover time calculation made sense as a major finding of this paper, but as I note elsewhere in this review, the assumptions underlying the calculation appear invalid given the and inconsistent with literature. However, I do make the suggestion of performing this calculation for each BPCA, and if this is under taken, then clarifying the

equations solved is most important.

We have expanded the Methods and Materials Section to explain the derivation of the model and the parameters that were used in the sensitivity analysis.

There seems to be a misunderstanding on the nature of the molecular markers (BPCA) used. BPCA are formed during analysis, those BPCA measured during analysis did not exist as BPCA in soil before. For more details see reply to Reviewer 2, point 20. Thus, calculating turnover times would not yield meaningful results. Still, one could measure 14C content of the individual BPCA, but this method does not (yet) exist and we do not have 14C values for the different BPCAs.

2. The statistical comparison in this work is not appropriate. The test appears to have been done on horizons, yet horizons are not independent samples. Therefore the assumptions of the statistical test are invalid. A rigorous comparison would require replicate soil profile BC stocks that are representative of the landscape. While it is ideal to have multiple samples from both the historic and contemporary period, I note that it would be reasonable to use contemporary samples to estimate the probability distribution around the single archived sample, and calculate a probability manually. I assume it is too late for the authors to complete this, but I note that such a calculation could be accomplished with perhaps 10 soil cores to 1 m, analyzed as single samples. This would not have been substantially more work than the data presented. Regarding statistics, if anything such as I suggest is under taken, the rational for using a one-tailed test (presumably that BC inputs ceased and therefore BC stocks could only decrease). Further, although complicated, it is possible to use horizon data rather than profile stocks, but when horizon data is utilized, the autocorrelation between horizons must be accounted for. Assuming no statistical approach can be taken, some data on the representativeness and apparent reproducibility of the contemporary soil profiles should be used to replace the statistical comparison at the beginning of the results and discussion, to inform readers of the value of the data.

The statistical test was done on pair-wise horizon samples, 10 horizons for each profile. The horizons of each core are not independent samples, but were compared pair-wise with one another of the same depth increment (corresponding horizons). We have made this more clear in the text.

The representativeness issue has been addressed in a paragraph and a table (see reviewer 2, nr. 1.2).

3. An fascinating aspect of this work is the apparent downward movement of BC in Figure 3. I strongly recommend more discussion of this interesting result. Several, seemingly testable hypotheses come to mind. In my own work, I have found clear evidence of downward transport, and modeled both the downward transport of colloids and DOM (Baisden et al., 2002; Baisden and Parfitt 2007). This includes California annual grasslands where fire is common, and was once probably more common, as well as New Zealand where fires were introduced by Polynesian and European settlers, and then ceased. The radiocarbon evidence for downward transport was remarkable in these soils with net leaching. In contrast, Torn et al (2002) found no similar radiocarbon evidence for downward in this Chernozem, and it is interesting to consider whether this is due to a lack of net leaching (as evidenced by carbonate accumulation) or the acid treatment used to remove carbonate. A key question is whether the BC appears to have moved as dissolved organic carbon (DOC) or as very fine colloids (with negative charge repelled by soil particles). It seems that a major opportunity for readers to examine or reject certain hypotheses is lost due to the failure to present the suit of BPCAs as a function of depth. In the supplementary material or figures, the results for each BPCA should be presented. Further, given the prominence of the authors in reviews of BC methods, it would really helpful to see carefully considered suggestions on the ability of the BPCA method to examine these transport related questions or whether another BC method may be more appropriate.

Again, we seem to have failed to explain the nature of the molecular markers (BPCA) used to non-organic geochemists (below we copied our reply to Reviewer 2, point

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20). Probably there were two sources of confusion with the use of BPCA as molecular markers. First, the molecular markers (BPCA) are formed during analysis, those BPCA measured during analysis did not exist as BPCA in soil before. The BPCA are formed during acid digestion of soil when the aromatic fire-derived compounds are "cut in pieces" by the HNO3 and the aromatic rings substituted with carboxylic groups. An aromatic ring on the edge of a black carbon structure will form a "three substitution", i.e. B3CA. Rings in the center of the structure, are six times substituted and forms the B6CA. They are more protected against degradation than the rings on the outside. The highly condensed aromatic (and recalcitrant) core of black carbon structures produce relatively more B6CA molecules than those less condensed (and more decomposable) structures on the edge of the BC structure. Second, in Fig. 3 we show the relative contribution of B6Ca to the total of all BPCA. When the sum of all BPCA decrease but B6CA remain constant (as shown in Fig. 4) the relative contribution will increase. There was an upward movement of B6CA, rather a relative enrichment compared to the less functionalized BC.

This has been made clearer in the manuscript.

The BPCA method was specifically developed to quantify BC in soil. The advantage of this method above others is that it not only gives quantitative data but also a qualitative assessment of the data. Further advantages and disadvantages of all commonly used BC methods are found in detail in Hammes et al., 2007.

Hammes, K., M.W.I. Schmidt, R.J. Smernik, L.A. Currie, (retired), W.P. Ball, T.H. Nguyen, P. Louchouarn, S. Houel, Ö. Gustafsson, M. Elmquist, G. Cornelissen, J.O. Skjemstad, C.A. Masiello, J. Song, P. Peng, S. Mitra, J.C. Dunn, P.G. Hatcher, W.C. Hockaday, D.M. Smith, C. Hartkopf-Fröder, A. Böhmer, B. Lüer, B.J. Huebert, W. Amelung, S. Brodowski, L. Huang, W. Zhang, P.M. Gschwend, D.X. Flores-Cervantes, C. Largeau, J.-N. Rouzaud, C. Rumpel, G. Guggenberger, K. Kaiser, A. Rodionov, F.J. Gonzalez-Vila, J.A. Gonzalez-Perez, J.M. de la Rosa, D.A.C. Manning, E. López-Capél, and L. Ding (2007), Comparison of black carbon quantification methods to mea-

sure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. Global Biogeochemical Cycles, 21, GB3016, doi:10.1029/2006GB002914.

4. In relation to transport, it is also worth noting that Rumpel and others found that BC appears to be preferentially eroded. The potential for water or wind erosion (or lack thereof) should be noted, as it also represents a loss that contributes to turnover and could be important when integrated over 100 years.

Indeed, the possibility of erosion should not be ignored in any paper about soil organic carbon. We have amended the abstract and text to mention that loss could have occurred through erosion, leaching, or decomposition. We also explain why it unlikely that erosion played a significant role because the area is very flat, extensive windbreaks were planted around 1900 over vast areas to curb wind erosion, and there was almost no change in the depth intervals of horizons between archive and modern sampling. This has been made clearer in the manuscript.

5. As currently presented the turnover time calculation is inappropriate and inconsistent with both the known behavior of black C (Lehmann 2007; references cited on p662 L26) and information presented in Figure 4. Lehmann (2007) has indicated that BC from differing sources vary in their recalcitrance and some BC is partially oxidized over decades following incorporation in soil. Indeed, Figure 4 shows that the less condensed BPCAs show considerable turnover (e.g. BP4CA.) A much more useful interpretation of this valuable data is that approximately 25% of the BC is lost over 100 years, while the remainder appears to have roughly millennial residence times. Such a sensible interpretation is essentially consistent with previous estimates and consistent with the IPCC assessment. While this interpretation is stated or implied, it is not emphasized as it should be, and becomes confused with the turnover time calculation which is emphasized.

We have added a note to the discussion that we cannot rule out that 25% of the BC was

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lost rapidly and the rest of the soil BC has a slower turnover time. We also expanded the explanation of the method of estimating turnover time and discuss the caveats, including the fact that BC almost certainly exists in soil as a continuum of turnover times rather than in multiple pools a single pool. We agree completely that BC cycling should be estimated with as many pools as the data will support. In this study, we could not constrain a multi-pool model, but the one-pool model, admittedly not the final word on turnover time for BC, does allow us to advance our understanding of BC cycling in soils.

6. The turnover time calculation may have some value, but the limited sensitivity analysis is flawed by not evaluating the potential implications of the black carbon being a heterogeneous pool with two or more residence times. If the residence time calculation is published at all, this deficiency should be carefully dealt with. Since models need to be used but not believed any model-derived turnover time should be accompanied by a clear suggestion of why it has been derived and what its intended use is. For example, a sensible reason to obtain a turnover time is to be able to estimate how much BC is likely to be lost over a 10 year period. From the model proposed in this work, such an estimate can be made from the one-pool model but could be very wrong if in fact 25% of the C was lost in 30 years, and the remainder has a millennial residence time.

Good point. We added a note to the discussion that we cannot rule out that 25% of the BC was lost rapidly and the rest has a slower turnover time. Also, we agree completely that BC cycling should be estimated with as many pools as the data will support.

7. Since a main problem with the residence time calculation is that the individual BP-CAs appear to show different degradation rates, an interesting alternative would be to attempt to calculate the residence time of each of the BPCAs measured. Such a calculation would be welcome, and would overcome the problem of a calculation inconsistent with both data in the paper and the literature. Such a calculation would also provide much more realistic sensitivity. For example, it may well turn out that the calculated turnover times do not neatly relate to the degree of condensation, and this could

be interpreted uncertainty resulting from the methods, analysis, and natural processes and variability.

See our reply to point 1.

8. The authors should more carefully consider the value of this dataset for designing future studies. The ability to examine a 100 year-old monolith in comparison to well-matched contemporary samples is unique opportunity. Unfortunately, we have the problem of n=1 for the archived monolith. Other very old samples do exist. For example, I know of a variety of samples collected by Hilgard in California, but these may be difficult to relocate or resample under similar land cover. More hopefully, there are a great many samples archived in various countries that are on the order of about 50 years old which often have clearly preserved information and site details. I believe the data presented suggests that other researchers will find it well worth examining archived and contemporary samples spanning a period of 50 or perhaps even 20 years to determine how rapidly different forms of BC appear to be lost.

Yes, it would be great if this work inspires other authors to pursue similar studies.

9. Overall, this work should attempt to use the unique dataset to make salient comments that can be used in designing emissions trading systems (including a global post-2012 agreement) that are compatible with biochar. Several points seem important. First, it appears that some BC may be lost over timescales of 100 years (and perhaps less). Second, it appears that considerable BC may be transported downward, but not lost from the soil. Since the bulk of BC was transported below 30 cm, the 30 cm accounting depth currently used may be inappropriate. Finally, when this data is combined with other information in the literature, does it support or cast doubt on the suggestion that biochar used as a soil amendments may be a valuable C sequestration opportunity? Based on the data, I conclude that biochar remains a valuable sequestration option and would also ask whether this study contains information relevant to defining sampling intervals and analysis methods that would be appropriate for

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C monitoring.

Good point, but we believe that the study of biochar has advanced sufficiently in the last year or so that it can be discussed on its own accord, while considering natural burning systems apart, at least in this particular case. However, we could add one sentence mentioning the point of biochar sequestration.

10. I do not include a list of lengthy list of typographical/writing points but do note the following. In figure 4 it is not clear what is plotted. Interpretation in this review assumes the bars are the archived and contemporary soil inventories.

Figure 4 has been amended.

Interactive comment on Biogeosciences Discuss., 5, 661, 2008.

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