

## ***Interactive comment on “Gone or just out of sight? The apparent disappearance of aromatic litter components in soils” by T. Klotzbücher et al.***

**T. Klotzbücher et al.**

thimo.klotzbuecher@googlemail.com

Received and published: 6 April 2016

Reviewer: I generally acknowledge that the authors try to pinpoint and discuss the apparent discrepancies between the fact that large amounts of aromatic compounds are entering the soil in dissolved phase and the fact that they are not found any more sorbed to the solid phase. The authors attribute this to the problems of analyzing lignin and claim that two methods (although completely independent and different in their analytical procedures, i.e. solid-state  $^{13}\text{C}$  NMR spectroscopy and CuO oxidation) fail to identify these aromatic compounds. I suggest to carefully check the literature for solid-state  $^{13}\text{C}$  NMR work that shows significant contributions of aromatic compounds (although mostly attributed to charred OM, see work by Knicker and coworkers, Skjemstad and coworkers). The authors need to explain why the technique fails to work for lignin-derived aromatic compounds, but does work well for other aromatic (and even

Printer-friendly version

Discussion paper



more condensed) structures produced from fire impact.

Authors: We thank the reviewer for the critical and constructive comments. The comments greatly helped to increase the quality of the manuscript. We extended the discussion on limitations of analytical methods and refer to the  $^{13}\text{C}$  NMR work suggested by the reviewer (see page 8 lines 14 ff.). We agree that this part of the discussion needs to be more precise. The low sensitivity for aromatic compounds is a problem related to CPMAS  $^{13}\text{C}$ -NMR spectroscopy. The Bloch decay technique does not have these limitations, and thus, is more sensitive. This technique is frequently used in studies that specifically address questions on pyrolytic OM. It is, however, not routinely applied in SOM research, probably as longer instrument times are required. The dominance of O/N alkyl C in CPMAS  $^{13}\text{C}$ -NMR of SOM is commonly used as one argument supporting the view that SOM is dominated by microbial-derived compounds. It fits to a number of other observations, and thus we do not doubt that microbial-derived compounds are important contributors to SOM. However, it is seldom discussed that aromatic C might be underestimated by CPMAS  $^{13}\text{C}$ -NMR. Another uncertainty of NMR is related to sample pre-treatment, i.e., mineral soil samples are commonly de-mineralized with hydrofluoric acid in order to remove paramagnetic minerals that disturb the analysis. The treatment can result in significant losses of SOM. In particular, compounds directly bound to the mineral may be preferentially lost. So, we keep to the argument that the interpretation of CPMAS  $^{13}\text{C}$ -NMR literature might add to an underestimation of the turnover rates of plant litter-derived aromatics in soil.

Reviewer: The problem that all compounds entering the soil after some decades leave the analytical window for and cannot be identified any more as specific plant or microbial derived compounds has been described and discussed previously and is not specific for aromatic compounds (see detailed discussion of the problem in Hedges et al. (2000)). It is also illustrated by the fact that all molecularly identified organic compounds in soil are younger than the mean age of SOM or their turnover is faster than that of bulk SOM (see Amelung et al., *Adv in Agronomy*, 2008 and later Schmidt et

Printer-friendly version

Discussion paper



al., Nature, 2011). Thus I suggest to refer in more detail to these discussions. It is necessary that the authors reflect on these already published discussions. Generally, the paper is too simplistic in its reducing the story to aromatic compounds.

Authors: We would like to keep focused on plant-derived aromatics, because the contradictions between research on DOM fluxes and research on solid-phase SOM composition are particularly evident for this compounds class. Nevertheless, this is an important comment by the reviewer. Also turnover times of other non-aromatic biomarker compounds might be underestimated because an unknown portion is not extractable (Amelung et al. 2008). We refer to aspects discussed in Amelung et al. (2008) in the revised manuscript (page 7, lines 30 ff.). The discussion now includes a more detailed discussion on possible reasons why only part of the aromatics can be extracted from soil by the CuO method and pyrolysis techniques.

Reviewer: The authors provide only a selected view on the pathways how organic matter enters the soils. The decomposition of roots is mentioned (although recent references on root biomarkers in soils are missing). However, the input of OM by rhizodeposition is completely ignored. Similarly, the authors consider only sorption of low molecular weight compounds to the solid phase as a mechanism for stabilization of OM in soils. Here again, recent concepts are ignored, e.g. the association of microbial cell wall envelope fragments (see work by Miltner and coworkers).

Authors: We added the suggested aspects to the revised manuscript. The discussion on the possible role of root input as source of SOM was extended (page 5, lines 17 ff.). The possible role of rhizodeposition in SOM turnover is discussed on page 10, lines 4 ff. We also discuss the view of Miltner et al. that some of the organic matter 'patches' on clay particles are composed of cell wall structures of microorganisms (page 10, lines 24 ff.). The addition of these aspects greatly improved our discussion about whether limits in process understanding might be the reason for the controversies outlined in the manuscript (chapter 4.2).

Printer-friendly version

Discussion paper



Reviewer: It is necessary to point out that the view of the authors is mainly restricted to acid forest soils, whereas there is also stabilization in neutral pH forest and arable soils where the interaction of acidic compounds with Fe(hydr)oxide surfaces is of minor importance (Kleber et al., 2015).

Authors: This aspect is pointed out in chapter 2.1 on the 'dissolved phase line of evidence' (page 3, lines 30 ff.).

Reviewer: Even if one agrees with all the problems raised, the authors do not provide novel solutions. Solution one is that "careful data interpretation, including critical assessment of experimental and analytical limitations, must become standard". This is a prerequisite of any scientific work and does not tackle the specific problem. The second solution is to use "combined studies on DOM and SOM". Here I agree and I encourage the authors to start such investigations. Authors: The last part of the manuscript has been revised completely. We summarize key research questions that are still open and provide more distinct suggestions about future strategies (including experimental and modeling work).

Reviewer: The figure is just terrible; colors are almost not distinguishable from background. Here a more professional graphics approach is needed to improve the figure.

Authors: The figure has been revised.

---

Interactive comment on SOIL Discuss., doi:10.5194/soil-2015-79, 2016.

Printer-friendly version

Discussion paper

