Reviewer 1 comment:

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 13C NMR spectroscopy and CuO oxidation) fail to identify these aromatic compounds. I suggest to carefully check the literature for solid-state 13C 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 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 13C 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}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}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}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}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 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).

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 4, lines 2 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 form background. Here a more professional graphics approach is needed to improve the figure.

Authors: The figure has been revised.

Reviewer 2 comments

Reviewer: This paper focuses on the stability of aromatic litter components in the (mineral) soils and provides some interesting insights on the paradoxical evidence of persistence or lability of aromatic organic carbon (OC; including lignin) in the soil and dissolved organic matter (SOM and DOM). This research topic has received increasing attention in the past decades and this opinion paper is timely for synthesizing the mounting (controversial) evidence for/against the stability of aromatic OC in soils (although I feel that more literatures can be included). In addressing this issue, the authors have put a special emphasis on the analytical limitations of detecting and quantifying mineral-protected aromatic OC, which in my opinion is indeed a key bottleneck limiting our understanding on the fate of plant OC in the soils. I therefore wish that the authors may extend the discussions of future research strategies in the last part to provide some "practical" suggestions on potential research directions or tools to overcome the current analytical weaknesses. For instance, a key issue with the lignin CuO oxidation method is its unknown extract efficiency, which may vary for samples with different mineral matrix or SOM interactions. But this is rarely tested or stated in the papers because we are short-handed dealing with complex macromolecules such as lignin. There is hardly any pure natural macromolecular lignin standard for us to test the method. Can we circumvent this problem using pyrolysis GC/MS or isotopic labeling? Or a combination of different methods may provide further insights on the "hidden" lignin? Before any major analytical breakthrough is made, we must make full use of the current tools for soil lignin studies rather than abandon them, right?

Authors: Dear Dr. Feng, we thank you for the effort that has gone into evaluating our article. Your suggestions and comments led to a greatly improved manuscript. We agree that the part on future research strategies was too short and vague. The problems of quantifying total amounts of aromatics in soil may not be fully solvable with currently available analytical methods. However, strategies of combining different methods could help to gain improved estimates on how much aromatics might be `hidden` in soil. We added a more comprehensive discussion on the problem that not all of the aromatics can be extracted from soil (page 7, lines 27 ff.). In addition, the last part of the manuscript has been entirely revised and extended. It now presents a list of possible future research strategies that might help to step forward on solving the problems outlined in our article. The list includes open research questions as well as suggestions on methodological approaches.

Reviewer: I also agree with the authors that there is a big gap between the long-term fate of lignin and short-term laboratory experiment including sorption studies, in which "hot moments" of lignin transformation may not be captured. For instance, sorption experiments that observed selective binding of aromatics to minerals are typically void of microbial interactions due to the use of HgCl2 (and alike). In natural soils, aromatics that are presumed to sorb selectively to minerals may be preferentially degraded by microbial communities living at the mineral surfaces as well, hence leading to the paradox of "dissolved" and "solid phase line of evidence". Inclusion of both natural geochemical and microbial processes in laboratory or field experiments may be key to finding the missing piece of the soil lignin jigsaw puzzle". I believe this goes beyond mineral protection and analytical limitations.

Authors: We extended the discussion on current limits of process understanding (see chapter 4.2). One major aspect of the discussion is that the `fate` of sorbed material is hardly understood. We agree, the view that DOM leached from decomposing litter sorbs onto mineral surfaces and then contributes to stable SOM might be too simplistic. Further transformations, desorption, and transport of the sorbed OM might occur in soil. Possibly this depletes SOM in aromatics.

Reviewer: Last but not least, as indicated by the title, the discussion of this paper is focused on plant derived aromatics (lignin and tannin). But how important is black carbon in the overall distribution of aromatic signals in the soil and DOM? Can we distinguish the two? I think it may be useful to briefly differentiate and clarify the fate of lignin/tannin versus black carbon in the soil for the readers' benefit.

Authors: We decided to keep focused on plant litter-derived aromatics, but added a discussion on possible contribution of pyrogenic OM (page 8, lines 30 ff.). Current available literature on DOM mainly considers plant litter-derived aromatic compounds. Numerous studies addressed in the production of aromatics in forest floors during litter decomposition. Few studies are available on role of pyrogenic OM for DOM fluxes. Many studies on DOM use indicators for bulk aromatics (e.g., UV absobance). Hence, the unknown contribution of pyrogenic OM to DOM is an uncertainty in the interpretation of DOM flux data.

Reviewer: Other minor comments: Pg 3, L13: I'm not sure if this sentence is totally true forest floor is the result of greater litter inputs versus losses through mineralization and translocation via leaching and bioturbation, etc. For tropical forests with strong litter mineralization, forest floor can be thin or almost absent as well. Actually, I don't think it is necessary to mention the cause for forest floor formation here so this first sentence may be deleted.

Authors: We shortened the paragraph and deleted the discussion on bioturbation. We agree, it is a side aspect and not necessary to mention.

Reviewer: Pg 3, L15: decreases with depth.

Authors: Sentence has been removed.

Reviewer: Pg 3, L20: 25-89% is a very high estimate does this only apply to soils with limited bioturbation and to subsoils? What about root input? Does this DOC flux include root exudates, which should be differentiated from that leaching from aboveground litter? As root biomass decreases with depths, it is natural that root-derived DOC decreases in mineral soils.

Authors: We present more details on the work cited in this paragraph. The estimates are for acidic forest soils with permanent forest floor. Hence, there is indeed limited bioturbation. The model calculations base on measured DOC fluxes, DOM sorption and mineralization. The role of roots as source of DOM is not clear. In general, there is little information available on that issue. We discuss it in the revised manuscript (page 5, lines 20 ff.).

Gone or just out of sight? The apparent disappearance of aromatic litter components in soils

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Abstract

Uncertainties concerning stabilization of organic compounds in soil limit our basic understanding on soil organic matter (SOM) formation and our ability to model and manage effects of global change on SOM stocks. One controversially debated aspect is the contribution of aromatic litter components, such as lignin and tannins, to stable SOM forms. In the present opinion paper, we summarize and discuss the inconsistencies and propose research options to clear them.

Lignin degradation takes place step-wise, starting with (i) depolymerisation, followed by (ii) transformation of the water-soluble depolymerization products. The long-term fate of the depolymerization products and other soluble aromatics, e.g., tannins, in the mineral soils is still a mystery. Research on dissolved organic matter (DOM) composition and fluxes indicates dissolved aromatics are important precursors of stable SOM attached to mineral surfaces and persist in soils for centuries to millennia. Evidence comes from flux analyses in soil profiles, biodegradation assays, and sorption experiments. In contrast, studies on composition of mineral-associated SOM indicate the prevalence of non-aromatic microbial-

derived compounds. Other studies suggest the turnover of lignin in soil can be faster than the turnover of bulk SOM. Mechanisms that can explain the apparent fast disappearance of lignin in mineral soils are, however, not yet identified.

The contradictions might be explained by analytical problems. Commonly used methods probably detect only a fraction of the aromatics stored in the mineral soil. Careful data interpretation, critical assessment of analytical limitations, and combined studies on DOM and solid-phase SOM could thus be ways to unveil the issues.

1 Introduction

Storage and quality of soil organic matter (SOM) determine many crucial soil properties and the cycles of carbon (C) and essential nutrients through ecosystems. The storage of SOM is determined by plant litter inputs and decomposition processes. Decomposition of SOM is a significant source of atmospheric CO_2, thus, a critical parameter in climate models (Schlesinger and Andrews, 2000). Decomposition rates are sensitive to global change factors such as temperature, precipitation, and land use. However, our ability to understand and predict such responses is limited by uncertainties about pathways of organic matter transformation in soil. In particular, the question as to why some SOM components persist in soil for centuries (denoted as `stable SOM` from here on) while others turn over quickly is still puzzling (Schmidt et al., 2011).

Recent research challenges traditional theories presuming that stable SOM results from neoformation of complex humic polymers in soil (`humification`). Stable SOM rather seems to be composed of relatively simple organic compounds that are protected against biodegradation, e.g., because they are tightly bound to mineral surfaces (Schmidt et al., 2011; Kleber et al., 2015). Herein, we hold to this view but argue that, despite extensive research in the last years, the chemistry and source of compounds incorporated into stable SOM is still largely uncertain. In particular, the importance of aromatic compounds ~~deriving~~ derivied from abundant plant litter components, such as lignin and tannins, is controversially debated (Figure 1). One line of evidence suggests that they are important contributors to stable SOM. It bases primarily on data from research on fluxes and behaviour of dissolved organic matter (DOM) in soil, hence, we will denote it as the `dissolved phase line of evidence`. A contrasting line of evidence ~~suggesting~~ suggests a quick degradation of aromatic compounds in soil derives primarily from analyses ~~soil bases derives primarily on from analyses~~ of the composition of solid SOM (~~-~~`solid phase line of evidence`). ~~-~~Herein, we sum up and confront the arguments of the two views, discuss potential reasons for the controversies (including limitations in analytical methods and process understanding) as well as their implications for our basic understanding on SOM formation.

2 Dissolved phase line of evidence

The view that plant-derived aromatics are a major source of stable SOM ~~bases~~ is based on the following two main arguments:

(1) DOM produced during litter decomposition and leached into mineral soil is a main source of stable SOM adsorbed on mineral surfaces.

(2) Aromatic DOM components produced during litter decomposition are resistant ~~against being mineralized~~to mineralization and preferentially sorb to mineral surfaces. Hence, they are preferentially stabilized in mineral soil.

2.1 Argument 1: DOM as source of stable SOM

Leaching of DOM is a major pathway for organic matter translocation from forest floor into the topsoil horizons. ~~Dissolved OM represents only a small fraction of total SOM. However, it is continuously produced and transported within profiles. In forest soils with permanent forest floor horizons, much of the translocation of organic matter from the forest floor into mineral topsoils is due to DOM leaching, while bioturbation plays either a minor role or no role at all. For such systems, it has been estimated that 10-25% of the total C input to the forest floor via litter fall is leached into mineral soils in the form of dissolved organic C (DOC) (Guggenberger and Kaiser, 2003).~~ Estimates for acidic forest soils with permanent forest floor ~~based on quantifying DOC fluxes~~ suggest that 25-89% of the SOM stored in mineral soils derives from DOM (Neff and Asner, 2001; Michalzik et al., 2003; Kalbitz and Kaiser, 2008)~~. They~~ , based on the typical observation of decreasing DOC fluxes with depth of the mineral soil (a large compilation of data from studies on forest and grassland soils is presented by Neff and Asner, 2001). Two processes can explain the decrease: mineralization and sorption.

Sorption of DOM to mineral surfaces likely is a major process forming stable SOM in many soils. Evidence for its importance comes from findings that the turnover and storage of SOM in mineral soil horizons is often related to the contents of reactive secondary minerals (e.g., Fe hydrous oxides, short-range ordered Al hydroxides). Such relationships have been found across a wide range of soil types (Kramer et al., 2012; Kleber et al., 2015). Also, higher radiocarbon age of SOM in heavy (i.e., mineral) fractions compared to light density (i.e. organic) fractions indicates that sorption stabilizes organic compounds (e.g., Marschner et al., 2008, Kleber et al., 2015). Density fractionation procedures indicate that the total soil C associated with minerals in any given location can vary from 30% to 90% (see data compiled in Kleber et al., 2015). The relevance of sorptive stabilization depends on soil properties. Low soil pH enhances the formation of reactive secondary minerals and favors the formation of strong bonds between organic matter and the mineral surface (Kleber et al., 2015). Most studies cited herein (for both lines of evidence) examined acidic soils under temperate forests, in which sorptive stabilization clearly should play an important role.

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2.2 Argument 2: Preferential stabilization of aromatic DOM components

Lignin, a macromolecule composed of phenyl propane units, is a major plant cell wall component (Kögel-Knabner, 2002). Typically, lignin concentrations negatively correlate with litter decomposition rates. They are the predominant control on litter decomposition within biomes worldwide (Cornwell *et al.*, 2008), indicating that the lignin macromolecule is among the most persistent litter constituents. Nevertheless, results of recent studies suggest significant chemical alteration and losses of lignin already within the first months of litter decomposition (e.g., Preston et al., 2009; Klotzbücher et al., 2011). 'Degradation' of lignin has to be considered a step-wise process: (i) the first step is the depolymerization of the macromolecule, releasing (mainly aromatic) water-soluble depolymerisation products of varying molecular weight; (ii) these products can then be further transformed, and low-molecular weight compounds are eventually taken up by microorganisms to produce biomass or CO_2. Hence, losses of lignin-derived C during litter decomposition can occur due to leaching of water-soluble products of an incomplete degradation or as CO_2. Laboratory incubation tests on water-extractable organic matter from various forest floor materials suggest that aromatic components are more resistant to mineralization than non-aromatic components (Kalbitz et al., 2003 a,b; Hansson et al., 2010). This suggests that leaching is an important factor in loss of lignin-derived matter during litter decomposition. ~~In line~~Consistent with this conceptual model, the typically high UV absorptivity of DOM leached from forest floors is indicative of a large contribution of aromatic components (e.g., Kalbitz and Kaiser, 2008).

Another factor for the export of aromatic DOM from forest floors is leaching of tannins. Tannins are water-soluble polyphenols of a molecular weight ranging from 500 to 3000 Daltons. Tannins rapidly leach from fresh litter; most studies ~~report of~~suggest losses of ~80% within the first year of litter decomposition (Kraus et al., 2003).

It has been commonly found that the contribution of components likely ~~deriving~~ derived from lignin and tannins to DOM decreases with depth of the mineral soil (summarized in Table 1), i.e., the decrease in fluxes of these compounds with depth is more pronounced than the decrease of bulk DOM. One explanation might be intensive biodegradation of aromatics in mineral soil. However, this would contradict results of the DOM biodegradation studies ~~mentioned above~~previously discussed. Hence, a more likely explanation is sorption to mineral surfaces. Laboratory sorption experiments support this view; a typical observation is that lignin-derived aromatic DOM components are preferentially sorbed by minerals and soils (e.g., Kaiser et al., 1996; Chorover and Amistadi, 2001; Hunt et al., 2007), and for some soils it has been shown they displace previously bound organic components from mineral surfaces (e.g., Kaiser et al., 1996). The degree of preferential sorption may depend on the composition of the soil mineral assemblage. Chorover and Amistadi (2001) observed that high molecular weight aromatic components preferentially sorbed onto goethite, while for montmorillonite no preference for aromatic moieties was observed. A likely reason for the preferential sorption is the large content of carboxyl groups linked to the aromatic rings, which bind to metals at mineral surfaces via ligand exchange reactions.

2.3. Roots as source of stabilized aromatic SOM?

We have so far focused on DOM leached from aboveground litter. However, roots might also be a crucial source of stable SOM. The contribution of root and aboveground litter as major source of SOM has been debated in numerous studies, but the available information allows no definite conclusions yet (see discussion in Lajtha et al., 2014). Presumably, the relative importance of the two types of organic matter input for SOM storage in topsoils differs between ecosystems (Crow et al., 2009) and the importance of root-derived matter increases with soil profile depth (Rumpel et al., 2015).

~~contribution of root and aboveground litter as major source of „A recent study suggests that particularly in greater profile depth, mineral-associated SOM might derive to a large part from root litter decomposition (Rumpel et al., 2015).~~

This raises ~~the question~~issue of whether results from aboveground litter decomposition would also apply to root litter decomposition~~?~~. Data by Crow et al. (2009) suggest that lignin concentrations of roots are in the range of those of leaf and needle litter. ~~Hanssen~~ Hansson et al. (2010) showed that DOM production during root decomposition occurs in patterns that are similar to those of needle decomposition. Particularly during later decomposition stages, root-derived DOM is enriched in aromatics resistant to mineralization. Hence, available information suggests that root decomposition is just another important source of soluble aromatics in mineral soils. However, to the best of our knowledge, studies to quantify the contribution of root-derived aromatics to DOM fluxes in the field have yet to be conducted.

3 Solid phase line of evidence

Many of the recent conceptual papers on SOM formation are built on the assumption that lignin-derived aromatics disappear quickly in soil, while SOM in mineral soils is dominated by non-aromatic and microbial-derived compounds ~~-~~(Grandy and Neff, 2008; Schmidt et al., 2011; Dungait et al., 2012; Miltner et al., 2012; Cotrufo et al., 2013; Castellano et al., 2015). Empirical support is provided by studies characterizing the chemical structure of solid SOM using a variety of analytical methods. In the following, we sum up the most widely cited work.

Numerous studies on a wide variety of soil types used the cupric oxide (CuO) method to analyse the distribution of lignin-derived phenols in profiles. Most of them reported ~~of~~ decreasing phenol contribution to SOM from forest floor to A horizons and with depth of the mineral soil (reviewed in Thevenot et al., 2010). ~~It~~ Measured phenols also decreases with increasing density of soil fractions, hence, ~~is~~ are relatively small component in heavy (i.e., mineral-associated) and old soil fractions (e.g., Sollins et al., 2009; Kögel-Knabner et al., 2008; Cerli et al., 2012). Similar results are reported by studies using pyrolysis-gas chromatography/mass spectrometry (see e.g., data and references provided by Grandy and Neff, 2008 and by Buurman et al., 2007) and tetramethylammonium hydroxide (TMAH) thermochemolysis (Mason et al., 2012).

Analysis of ~~heavy soil fractions~~heavy and clay-sized soil fractions using cross polarization and magic angle spinning (CPMAS) ^{13}C nuclear magnetic resonance spectroscopy (^{13}C-NMR) typically finds high ~~contents~~ peak intensities of alkyl and O/N alkyl C (mostly assigned to polysaccharides and proteins) and low peak intensities of aryl C (mostly assigned to lignin and tannins)~~, suggesting that primarily microbial remains are stabilized at mineral surfaces~~ (see ~~reviewed by~~ reviews by Kögel-Knabner et al., 2008 and Miltner et al., 2012). In a comprehensive study on Ah horizons from 8 European forest sites, O/N alkyl C contributed up to 41-49% of total peak intensity in the <2-µm fraction, and the peak intensities were on average 10% higher than the those reported for bulk soil; the intensities of aryl C in the <2-µm fraction contributed 13-15% of total peak intensities, and they were on average 24% lower than values found for bulk soil (Schöning et al., 2005). Consistent with findings, the heavy soil fraction is characterized by low C/N values close to those of microbial tissues (Kögel-Knabner et al., 2008). Studies using near-edge X-ray absorption fine structure (NEXAFS) spectra supported the conclusions drawn from ^{13}C-NMR analysis of a significant contribution of microbial-derived compounds to SOM at mineral surfaces (Lehmann et al., 2007; Kleber et al., 2011). ~~Iup to - This is i with findings showing theatclose to thosesSimilar conclusions were drawn from near-edge X-ray absorption fine structure (NEXAFS) spectra (Lehmann et al., 2007; Kleber et al., 2011). In line, the heavy soil fraction typically is characterized by low C/N values indicative of microbial tissue (Kögel-Knabner et al., 2008).~~

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Lignin turnover ~~times~~ (i.e., transformation into CO_2 or non-lignin products) in temperate arable, grassland, and tropical forest soils ~~have~~ has been estimated using a combination of isotopic labeling and compound-specific isotope analysis of lignin-derived aromatics applying the CuO method. Most of the studies using this approach suggest that the turnover of lignin-derived aromatics is faster than the turnover of bulk SOM (Dignac et al., 2005; Heim and Schmidt, 2007; Heim et al., 2010). A modelling study based on the data by Dignac et al. (2005) suggested that about 90% of the lignin is mineralized as CO_2 or transformed into compounds ~~no more showing~~devoid of lignin-type signatures within ~~1~~ one year (Rasse et al., 2006). However, a study by Hofmann et al. (2009) suggests that after 18 years, approximately two-thirds of the initial lignin phenols remained in an arable soil. The authors concluded that lignin was preferentially preserved in the soil. It should be noted all of these land-use successional studies only determined turnover times in the top 10-30cm of the soil horizon and may not accurately represent lignin dynamics in the deeper soil.

4 Reasons for the controversies~~?~~

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4.1. Analytical limitations

The controversies in current literature might (partly) be ~~explained by~~due to difficulties in the analyses of aromatic matter in soils. Studies on DOM typically use bulk methods for inferring aromatic content, including UV absorbance and fluorescence spectroscopy. Limitations of this research include lack of identification of the source of aromatic compounds~~ (lignin vs. non-lignin sources, such as tannins) ~~, and poor quantification of the fluxes. Also data on contribution of aromatic components to solid SOM are semi-quantitative or qualitative.

Commonly applied methods such as CuO oxidation, pyrolysis or TMAH thermochemolysis focus on few defined lignin-derived monomers to estimate the overall contribution of lignin. These estimates, however, can largely differ depending on the method applied (Klotzbücher et al., 2011). As outlined by Amelung et al. (2008), compound-specific isotope analysis of lignin-derived compounds with the CuO method presumably overestimates the turnover rates of lignin as only part of the lignin-derived aromatics can be extracted from soil (incomplete extraction might also be a problem in all analyses of biomarkers, for which turnover times typically are estimated to be faster than turnover rates of bulk SOM). Firstly, CuO oxidation (as well as conventional pyrolysis or TMAH thermochemolysis) does not completely depolymerize lignin (Johannson et al., 1986; Goňi and Hedges, 1992; Filley et al., 2000). Secondly, lignin-derived aromatics bound to mineral surfaces are only partly assessed by the CuO method (Hernes et al., 2013). Thirdly, lignin-derived aromatics might be altered in a way that they escape the `analytical window` and cannot be ascribed to a lignin source anymore. For instance, the CuO method yields a number of aromatic monomers of unknown origin besides the lignin-derived monomers (Cerli et al., 2008). These compounds are typically not quantified, and thus, not considered in estimates of the SOM composition. Hence, monomer yield is a commonly used but uncertain measure of lignin concentration in soil. Our knowledge about how much lignin is `hidden` (Hernes et al., 2013) in soil is still insufficient.

~~ overall e,,,Furthermore, it has been shown that lignin-derived aromatics bound to mineral surfaces are only partly assessed by the CuO method (Hernes et al., 2013). ,,thus, not~~

~~considered in estimates of the,~~ The uncertainties related to quantification of SOM compositions with solid-state CPMAS ^{13}C-NMR have been intensively discussed in the literature (see Knicker, 2011). Mineral soil samples are commonly pretreated with hydrofluoric acid in order to remove paramagnetic minerals that disturb the analysis. The treatment can result in significant losses of SOM, and one might lose important information on SOM adsorbed onto minerals (e.g., SOM losses of 10-30% in topsoil samples and up to 90% in subsoil; Eusterhues et al., 2003). Further uncertainties arise from signal overlapping and a low sensitivity for aromatic C in soils (e.g., Skjemstad et al., 1996; Mao et al., 2000; Simpson and Simpson, 2012). It has been shown that the technique underestimates lignin vs. cellulose in ligno-cellulose isolated from wheat (Gauthier et al., 2002). By applying Bloch decay, another type of ^{13}C-NMR technique, one can overcome the problem of the reduced sensitivity for aromatic-C. The technique has been applied in studies on pyrogenic organic matter, for which CPMAS ^{13}C-NMR should be even less sensitive than for lignin as it is more condensed (Golchin et al., 1997; Simpson and Hatcher, 2004; Knicker et al., 2005). Bloch decay is, however, not routinely applied in SOM research as it is extremely time-consuming experiment and the required instrument time is frequently not available (Simpson and Hatcher, 2004).

~~,,,,n,,,,extremely ,~~ Pyrogenic organic matter is an important source of aromatic compounds in many soils. Despite extensive research efforts, rates and pathways of pyrogenic organic matter decomposition are still not well established (Schmidt et al., 2011; Kuzyakov et al., 2014). Analyses of benzenecarboxylic acids as molecular markers suggest that aromatic compounds derived from pyrogenic organic matter are translocated within soil profiles and bind to mineral surfaces (Haumaier, 2010). The quantitative contribution of pyrogenic organic matter to DOM in soil is, however, still poorly studied (Smebye et al., 2016). Bulk analyses of aromatic matter used in most research on DOM fluxes cannot distinguish if the compounds derive from plant litter or from pyrogenic organic matter. This limits our understanding of the processes controlling turnover of aromatics. If a significant part of aromatic DOM in mineral soil derives from pyrogenic organic matter, the `loss` of plant litter-derived aromatics in mineral soil would be even more pronounced. Problems distinguishing sources of aromatic compounds can also occur in analysis of solid-phase SOM with CPMAS ^{13}C-NMR analysis (Simpson and Hatcher, 2004).

~~,,with, et al.,~~

4.2. Limits in process understanding

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~~Possible limitations of other methods in detecting mineral-bound organic matter have not yet been tested systematically. Hence, a part of the aromatics stored in mineral soils might be 'hidden', i.e., cannot be detected by conventional analytics of solid-phase SOM (Hernes et al., 2013). Consequently, turnover times of plant-derived aromatics might be underestimated.~~

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Another source of uncertainty~~, possibly explaining the controversies,~~ in quantifying the role of aromatics in SOM stabilization is that the timescales of the different processes affecting aromatic compounds vary considerably. Solubilization, leaching, and sorption of lignin-derived compounds might occur in a few days. In contrast, the composition of SOM as well as the mineral assemblage in soils is the result of years to centuries of biogeochemical processing. Possibly, one cannot simply extrapolate from patterns observed in 'short-term' DOM dynamics to explain 'long-term'-SOM formation.

For instance, i~~I~~n their comprehensive review on organo-mineral interactions, Kleber et al.~~,~~ (2015) question the view that strong bonds between organic matter and mineral surfaces really guarantee slow turnover rates and hence long turnover times. Many factors ~~possibly determining~~ that potentially determine the long-term fate of sorbed organic matter are still not well understood. They include~~, for instance,~~ exchange reactions between sorbed organic matter and new organic matter inputs or the impact of mineral weathering activity of roots on stability of sorbed organic matter. As proposed in Kaiser and Kalbitz (2012), the commonly observed increasing ^{14}C age of DOM with profile depth might be explained by temporal sorptive immobilization, followed by microbial processing and re-release of altered compounds into soil solution. ~~-~~Keiluweit et al. (2015) showed that root exudation of oxalic acid promotes the release of SOM sorbed onto mineral surfaces into soil solution through dissolution of mineral phases. Taken together, the view that DOM leached from litter decomposition sorbs onto mineral surfaces and then contributes to stable SOM might be too simple. Processing of sorbed material may exert a significant effect on SOM dynamics. This possibly prevents ~~This possibly~~the long-term storage of plant-derived aromatics in soil and explains the controversies outlined herein.

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Besides oxalic acid, many other organic compounds are released from living roots (the so-called `rhizodeposition`). Estimates suggest that rhizo-deposition constitutes a loss term of 17% (on average) of the net C assimilated by plants (Nguyen, 2003). It comprises low-molecular weight compounds (organic acids, simple sugars, amino sugars, phenolics) as well as high-molecular compounds (exoenzymes, root cells) (Wichern et al., 2008). Most of the compounds are degraded quickly, but a smaller portion might contribute to stable SOM (Nguyen, 2003; Pausch et al., 2013). The rhizosphere is considered a `hot-spot` in soil, where microbial processes are accelerated as they are not C-limited (Kuzyakov and Blagodatskaya, 2015). Possibly, root activity not only fosters production, but also stabilization of microbial-derived compounds in soil. To date, root activity effects on DOM dynamics and stabilization of plant-derived aromatics at mineral surfaces are poorly studied. This is partly because traditional analyses are focused on mixed soil samples, while the rhizosphere may only comprise a small volume of bulk soil, and fluxes of DOM are averaged for a soil surface (Kuzyakov and Blagodatskaya, 2015).

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Recent investigation at the submicrometer scale using Nano Secondary Ion Mass Spectrometry (NanoSIMS) or NEXAFS in combination with scanning transmission X-ray microscopy suggest that SOM associated with clay-sized minerals exists in small patches of varying chemical composition (Lehmann et al., 2008; Remusat et al., 2012; Vogel et al., 2014). Distinct patches of predominantly aromatic C can be differentiated from patches dominated by aliphatic C (Lehmann et al., 2008). Knowledge about processes controlling the submicrometer-scale distribution of SOM on mineral surfaces is still limited. Some of the patches are cell wall structures of microorganisms, which may contribute to stable SOM as they are composed of insoluble polymers and possibly sorb to the mineral surface (Miltner et al., 2012). Hence, stable sorbed organic matter might not only be derived from low-molecular weight compounds. On the other hand, it needs to be considered that microbial-derived compounds are continuously synthesized at the mineral surface. The microorganisms might use some of the older C (^{14}C age) for synthesis of relatively labile compounds. The age of the C atoms is, thus, decoupled from the stability of the organic matter, and microbial-derived compounds may `mimic` a similar or even higher stability than the plant-derived compounds (Gleixner, 2013). Hence, concentrations or ^{14}C age of microbial-derived compounds at mineral surfaces do not per se allow for conclusions on their contribution to stable SOM.

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5 Implications and future research strategies

The contradictions outlined herein limit our basic understanding on SOM formation, and our ability to model and manage effects of global change on SOM stocks.

For instance, elevated atmospheric CO_2 levels can induce increasing concentrations of aromatic components in plant litter (Cotrufo et al., 1994; Tuchman et al., 2002), and this raises the question whether this causes enhanced or decreasing storage of SOM in mineral soils. If aromatic matter is quickly degraded, and mineral-associated SOM primarily derives from microbial sources (as suggested by the solid SOM line of evidence), a `microbial filter` would control the built-up of stable SOM, which may then be determined by the microbial substrate use efficiency (i.e., the amount of organic C used by the microbial community to build biomass vs. the amount that is mineralized). As such, Cotrufo et al. (2013)~~, thus,~~ hypothesized that ~~rather~~ input of labile substrates fosters the build-up of stable SOM. Available data on effects of litter quality and SOM formation are, however, inconsistent (Castellano et al., 2015), and we believe that understanding on these effects is in part limited by uncertainties about the incorporation of aromatics into stable SOM.

The issue is also related to the question ~~on~~ of links between chemical structure of organic matter and its persistence. It is oftentimes assumed that structural properties of plant-derived matter do not determine stable SOM formation. This argument is based on data suggesting that specific compound classes (lignin, cellulose, alkanes, proteins etc.) turn over faster than bulk SOM (Schmidt et al., 2011). However, conclusions of DOM research imply that structure plays a role for the behavior of organic compounds in soil, and eventually their contribution to stable SOM: soluble aromatics may resist oxidation by microbes as they yield less energy than other structures; furthermore, they bind to mineral surfaces due to carboxyl groups attached to the rings.

How could we resolve the controversies? Based on our literature analysis we propose the following research strategies:

- More studies addressing links between microbial processes, composition/fluxes of DOM, and composition~~,~~of solid-phase SOM are needed. The study by Kramer et al. (2012) is a first attempt to relate the fluxes of aromatics to solid-phase SOM properties. In particular, the presumed microbial processing of sorbed material, causing desorption~~,~~ and subsequent mineralization or further transport in the soil profile is poorly studied. Eventually, these processes might cause loss of aromatic compounds. A related question is how root activity affects de-/sorption processes?
- Computer simulations could help to unravel the complex interrelationships between DOM fluxes and solid-phase SOM composition. Recently developed models integrate

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- Our knowledge is limited by the constraints in analysis of aromatics in soil. Quantification of total amounts and source of aromatics in soil are still problematic. Even if the problems cannot be fully solved with the currently available techniques, there might be strategies to obtain improved estimates. The work of Hernes et al. (2013) provides a first hint about how much lignin might be not accessible to CuO oxidation analyses. The authors evaluated the extraction efficiency for lignin-derived aromatics bound to different minerals. The size of the non-extractable fraction depended strongly on the mineral. Almost all of the aromatics bound to ferrihydrite were extractable, but for kaolinite the non-extractable fraction made >40%. But how about extractability in soil under field conditions? Possibly, a combination of tracking of C isotopes, DOM flux/ composition assessment, and analysis of solid-phase SOM composition could provide better estimates on the hidden aromatics in soil.

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~~We currently see two options to tackle the main problem, which is that each of the analytical tools available offers only one perspective on aromatic matter in mineral soils. Firstly, careful data interpretation, including critical assessment of experimental and analytical limitations, must become standard. This includes extensive testing of new and complicated analytical tools to ascertain the real meaning of results. For instance, the suitability of ^{13}C NMR methods and the CuO method to study aromatic compounds attached to minerals is still not fully certain. Also, more attention should be paid to possible effects of sample preparation (e.g., losses of mineral-associated organic matter due to sample demineralization used in NMR methods; Eusterhues et al., 2003; Hernes et al., 2013). Secondly, combined studies on DOM and SOM will help to bridge the gap between the opposing views obtained from studying either DOM or SOM. The study by Kramer et al. (2012) is one of the very few trying to offer a comprehensive mechanistic view to organic matter in soils so far.~~

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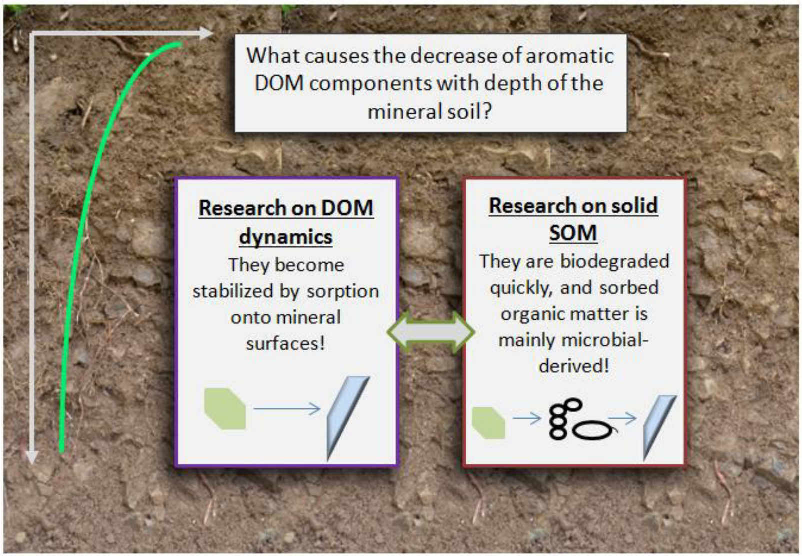
Table 1. Evidence from field studies suggesting that aromatic soluble (products of lignin depolymerization or tannins) disappear quickly once entering mineral soils.

Reference	Study site/ soil type	Result
Qualls and Haines 1991	Oak-hickory forest in mountain region of North Carolina; soil types: Umbric Dystrochrept, Typic Hapludult, Typic Dystrochrept	Selective removal of hydrophobic acids as DOM percolates through the mineral soil.
Cronan 1985	Forests, North-Western USA; soil types: Dystrochrept, Haplorthod	Selective removal of hydrophobic acids as DOM percolates through the mineral soil.
Zech et al. 1994	Spruce forest in Bavaria, Germany; Soil types: Typic Dystrochrepts, Entic Haplorthods, Typic Haplorthods	Selective removal of lignin-derived phenols (determined with the CuO method) as DOM percolates through the mineral soil.
Gallet and Pellissier 1997	Bilberry-spruce forest in Alps, France; soil type: Humoferric Podzol	Selective removal of lignin-derived phenols (as well as of total phenols) as DOM percolates through the mineral soil.
Kaiser et al. 2004	Spruce forest in Bavaria, Germany; Soil type: Haplic Arenosol	Selective removal of lignin-derived phenols, hydrophobic compounds, and total aromatic C as DOM percolates through the mineral soil.
Dai et al. 1996	Spruce forest, Maine; Soil type: Aquic Haplothods	Selective removal of hydrophobic acids and aromatics (^{13}C-NMR data) as DOM percolates through the mineral soil.
Lajtha et al. 2005	Coniferous forest, Oregon, USA; soil type: Typic Hapludands	Selective removal of hydrophobic acids as DOM percolates through the mineral soil.
Sanderman et al. 2008	Mediterranean climate; forest and grassland soils; soil types: Haplustols and Haplohumults	Decrease in UV absorbance (a measure for content of aromatics) as DOM percolates through the mineral soil.
Hassouna et al. 2010	Mediterranean climate; maize field; soil type: fluvic hypercalcaric cambisol	Decrease in contents of aromatic compounds (UV absorbance, fluorescence specroscopy) in water-extractable organic matter with depth of the mineral soil.
Nakashini et al. 2012	Beech forest, Japan; soil: “brown forest soil”	Decrease in contents of hydrophobic acids in water-extractable organic matter with depth of the mineral soil.

Figure 1. Conflicting views on the fate of soluble aromatics once they enter the mineral soil (see text for references).



What causes the decrease of aromatic DOM components with depth of the mineral soil?

Research on DOM dynamics

They become stabilized by sorption onto mineral surfaces!

Research on solid SOM

They are biodegraded quickly, and sorbed organic matter is mainly microbial-derived!

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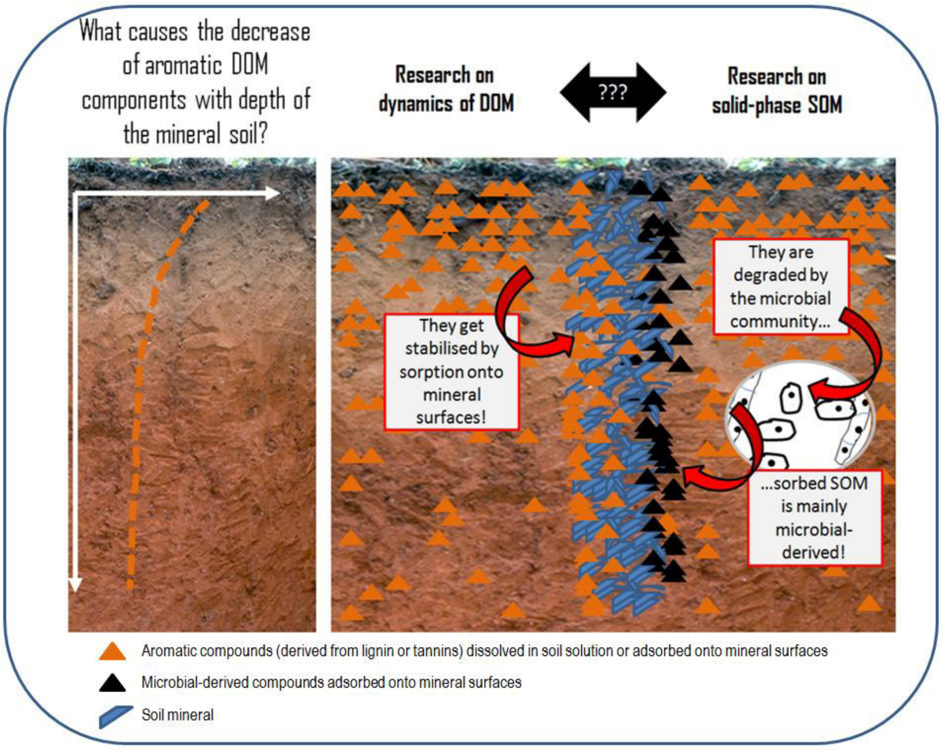
What causes the decrease of aromatic DOM components with depth of the mineral soil?
Research on dynamics of DOM
???
Research on solid-phase SOM
They get stabilised by sorption onto mineral surfaces!
They are degraded by the microbial community...
...sorbed SOM is mainly microbial-derived!
Aromatic compounds (derived from lignin or tannins) dissolved in soil solution or adsorbed onto mineral surfaces
Microbial-derived compounds adsorbed onto mineral surfaces
Soil mineral