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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 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 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, chemistry and source of compounds incorporated into stable SOM is still largely uncertain. In particular, the importance of aromatic compounds deriving 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 a quick degradation of aromatic compounds in soil bases primarily on 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 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 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 and preferentially sorb to mineral surfaces. Hence, they are preferentially stabilized in mineral soil.

2.1 Argument 1: DOM as source of stable SOM

The formation of permanent forest floors (i.e., moder or mor-type) on top of mineral soils is result of little or no bioturbation (e.g., Brussaard and Juma, 1996; Zech et al., 1996). With limited bioturbation, input of aboveground litter carbon to the mineral soil decreases. In turn, carbon leached from permanent forests floor into the mineral soil represents a large fraction (10-25%) of the annual litterfall carbon (data summarized in Guggenberger and Kaiser, 2003). Therefore, it appears reasonable to assume that in forests with permanent forest floors, DOM leaching is the major pathway of organic matter translocation from forest floor into the topsoil horizons. Estimates 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 base 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.

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, 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 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 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. 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 so far focused on DOM leached from aboveground litter. However, roots might also be a crucial source of stable SOM. 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 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 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.

3 Solid phase line of evidence

Many of the recent conceptual papers on SOM formation 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 also decreases with increasing density of soil fractions, hence, is 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 using ^{13}C nuclear magnetic resonance spectroscopy (^{13}C-NMR) typically finds high contents of alkyl and O/N alkyl C, suggesting that primarily microbial remains are stabilized at mineral surfaces (reviewed by Kögel-Knabner et al., 2008 and Miltner et al., 2012). Similar 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).

Lignin turnover times (i.e., transformation into CO_2 or non-lignin products) in temperate arable, grassland, and tropical forest soils have 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 lignin-type signatures within 1 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.

4 Reasons for the controversies?

The controversies in current literature might (partly) be explained by 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). 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). A major drawback of solid-state ^{13}C-NMR, the other widely applied technique, is its poor sensitivity for aromatics in soils (Simpson and Simpson, 2012). 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.

Another source of uncertainty, possibly explaining the controversies, is that the timescales of the different processes 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. In 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 long turnover times. Many factors possibly determining the long-term fate of sorbed organic matter are 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. Such processes may also exert crucial controls on the long-term storage of aromatics in soil.

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). 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 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? 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).