Citation Classic

The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter: Fourteen years on

Ingrid Kögel-Knabner [a, b, *]

[a] Chair of Soil Science, Technical University of Munich, Emil-Ramann-Straße 2, 85354 Freising-Weihenstephan, Germany
[b] Institute for Advanced Study, Technical University of Munich, Lichtenbergstraße 2a, 85748 Garching, Germany

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ABSTRACT

My 2002 SBB paper, *The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter*, brought together knowledge on the chemical composition of the diverse inputs to soil organic matter. Both plant and microbial residues were examined with the analysis of their composition using a combination of different techniques. From this, the limitations of conventional proximate analysis methods were identified and the great potential of recent techniques, in particular solid-state ^{13}C NMR spectroscopy and molecular level analysis, for the overall characterization of the input materials were discussed. The paper emphasised the importance of differentiating between organic matter from plants (above-ground litter, root litter and rhizodeposition), microbial residues and extracellular polymers and their breakdown products as well as the need for quantitative measurements of the amounts of these materials entering soils. In the last 14 years much new knowledge has been generated regarding these inputs and their alteration during decomposition, yet we still lack quantitative data for the amounts, composition and transformations of the many different forms of organic matter entering the soil. This is particularly the case regarding the inputs to the subsoil *via* root litter and rhizodeposition and the significance of microbial residues and extracellular polymers and their turnover.

1. Introduction

When I started to write my paper there were several reviews available that described the chemical composition of plant residues from a geochemical (De Leeuw and Largeau, 1993) and wood science (Fengel and Wegener, 1984) perspective but which also had relevance for soils. Yet, there was much less information on the amount of plant material entering soils and the volume of below-ground litter. I was convinced that understanding the formation, properties and turnover of soil organic matter (SOM) required a close examination of the inputs of organic matter from different sources. I sought to combine and evaluate the knowledge on carbon input to SOM formation with respect to three questions: (i) how much organic carbon enters the soil; (ii) where does it enter the soil; and (iii) what is the composition of the organic matter input?

For this, I considered it relevant to integrate not only the knowledge on chemical composition, as available from plant and wood sciences, but also to provide examples of state-of-the-art techniques for investigating litter input and SOM composition in soils and soil fractions. The aim of the paper was to summarise and combine our knowledge of litter input to soils and its molecular-level composition using ^{13}C NMR spectroscopic analysis of different plant and microbial residues. I hoped that this would provide a basis for studies on the changes occurring during residue decay and SOM formation. The molecular-level information on composition was based on the techniques that were considered state-of-the-art at the time, i.e. analytical pyrolysis and various chemolytic procedures combined with gas-chromatography-mass spectrometry. The techniques were chosen because they can be applied to bulk litter materials and also soils, circumventing the need to extract organic matter with NaOH or other solvents. A major intention was to steer the research focus from above-ground litter to belowground organic matter (root materials, rhizodeposition) and to the importance of microbial residues as inputs for SOM formation (Fig. 1). In the years following the publication of this *Soil Biology & Biochemistry* paper, a number of advances have been

* Chair of Soil Science, Technical University of Munich, Emil-Ramann-Straße 2, 85354 Freising-Weihenstephan, Germany.
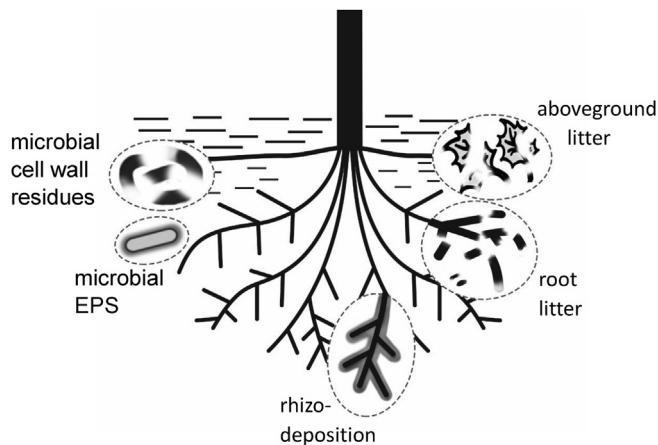E-mail address: koegel@wzw.tum.de.

Fig. 1. The input of OM to soils from above-ground litter, belowground litter consisting of roots and associated mycorrhiza, rhizodeposition, microbial extracellular polymeric substances (EPS) and microbial residues (necromass).

made concerning all these aspects of organic matter input to soils.

1.1. Blending structural information with analytical techniques

A major intent when writing my paper was to compare the information on the many different structural components of SOM with that obtained using a technique that provides information on the presence of the many structural groups in the input materials. This analytical technique is solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. I sought to gather the information available from plant materials, specifically leaves, needles and roots from both gymnosperm and angiosperm litter as well as grasses. NMR spectroscopy also provided a description of the many changes occurring during the decomposition of plant litter in soils. My paper may have triggered many scientists to use this technique to help answer their specific questions. Major progress came from Baldock et al. (2004) and Nelson and Baldock (2005) who were able to bring the information on the molecular structures of plant components together with the data from solid-state ^{13}C NMR spectroscopy in the so-called mixing model. This was one of the first studies that showed that the composition of SOM can be explained using the chemical structures from mixtures of common biomolecules. They concluded that their soil and sediment samples had humic materials with a composition that could be approximated by mixtures of those common biologically derived molecules or that humic structures were not present in significant amounts.

The limitations of classical proximate analyses were revealed from an understanding of the complexity of the plant residue composition. Proximate analysis refers to the analysis of so-called Klason lignin (i.e. the residue remaining after hydrolysis with sulphuric acid) which is only suitable for wood and not for the more complex and varied compositions of roots and leaf litter. The same applies for the Van Soest procedure (Van Soest, 1963) which had been developed to analyse the nutritional value of forage but which is not suitable to isolate or quantify lignin in leaf or root litter. There was evidence that the fraction that could not be acid-hydrolysed (the so-called acid-unhydrolisable residue) contained other compounds in substantial amounts in addition to lignin (Johansson et al., 1986). These issues had been elaborated by Preston et al. (1997) who showed that proximate analyses have limited use for identifying the chemical compounds that control and arise from litter decomposition, and that many other biopolymers should be considered in degradation studies. Although more advanced

techniques have been adopted in many studies, proximate analyses are still widely used and even suggested as the basis for global modelling efforts (Garcia-Palacios et al., 2015). Recently, Preston and Trofymow (2015) analysed different forest litters with solid-state ^{13}C NMR spectroscopy and proximate analyses and argued that it is *"time for the scientific community to limit the use of the term 'lignin' to chemically meaningful contexts"*. McKee et al. (2016) also concluded from a methods comparison that wet chemical fractionation using the acid-unhydrolysable residue did not accurately reflect the initial litter structures, particularly lignin. They warned against the sole use of wet chemical methods and strongly encouraged coupling them with spectroscopic methods. In my original paper I also emphasized that the commonly used analytical techniques, i.e. chemolytic methods, analytical pyrolysis and solid state ^{13}C NMR spectroscopy, have different levels of resolution and vary in their ability to provide compositional information. Thus, it is advisable to use several techniques in a complementary way. This is now an often practised approach for the analysis of agricultural as well as forest soils (e.g., Pisani et al., 2016).

Nonetheless, we still do not have a detailed and accurate molecular description of the more stable SOM components. As it is, the mean residence times measured for the different molecularly identified compounds in SOM are lower than that of the bulk SOM (Amelung et al., 2008; Schmidt et al., 2011), which confirms that the composition of stable SOM is not identified at the molecular level. But there is more and more evidence that stable materials may have been 'slightly' transformed and are missed by our narrow analytical window - even though they may not be substantially different in their composition to those that have been identified from plant or microbial sources. Kelleher and Simpson (2006) expanded the results obtained from the molecular mixing model of Nelson and Baldock (2005) using advanced 2D NMR techniques. They found that a high proportion of the operationally defined humic material in soils is a complex mixture of microbial and plant biopolymers and their degradation products and did not belong to a distinct chemical category. This also implies that additional stabilization mechanisms operate to protect organic matter from degradation and include aggregation, the formation of organo-mineral associations, and effects of hydrophobic properties (von Lützow et al., 2006, 2008).

2. Amount and quality of litter input

The organic matter that is added to a soil, either from above-ground litter or belowground inputs, is the energy (C) and nutrient-source (e.g. N, P) for soil microorganisms and is, therefore, decisive for microbially mediated C- and nutrient fluxes and determines the amount of organic matter sequestered in a soil (Wardle, 1992; Scholes et al., 1997). The quantity and quality of litter inputs and the source of the material (roots versus shoots) can have nonlinear effects on soil C fluxes and microbial decomposition (Fontaine et al., 2004a; Craine et al., 2007; Crow et al., 2009; Kirkby et al., 2014). It is often considered that labile carbon input may reduce the formation and persistence of SOM in the soil carbon sink as microbes acquire nutrients (e.g. N) from recalcitrant organic matter: this is termed the priming effect (Kuzyakov, 2010). Most studies have emphasised soil organic carbon (SOC) losses induced by priming but have not reported net SOC balances between primed C and the gain from added labile OC. Priming increases SOC decomposition (e.g., Fontaine et al., 2004a; Sayer et al., 2011), but a fraction of the added organic carbon remains in the soil and compensates for the SOC loss. These effects could thus lead not to a net C decrease but to an increase in soil (Fontaine et al., 2004b; Ohm et al., 2011). Qiao et al. (2014) reported an overcompensation of priming-induced C losses, specifically if continuous inputs of organic carbon were

investigated, but also from single inputs. They conclude from their experiments and previous studies that raising labile organic C input to soils by higher plant productivity will increase the SOC content even though priming accelerates decomposition of native SOC. It seems that the 50-year old conclusion of Jenkinson (1966) "*all of the published work on the priming action has shown that soil incubated with plant material contains more carbon at the end of a period of incubation than the same soil incubated by itself*" is still valid.

New concepts demonstrate how microbially mediated C and nutrient fluxes are regulated by stoichiometric imbalances between terrestrial decomposer communities and their input resources (Mooshammer et al., 2014). Such imbalances may reduce the amount of organic matter newly formed in stable SOM pools (Kirkby et al., 2014) as a certain amount of N seems to be necessary to form the N-rich stable SOM. Carbon and N mineralization are closely coupled processes during the decay of plant residues on or in the soil although Bimüller et al. (2014) suggest that they are decoupled in the mineral-associated fractions of the soil where the interactions of both C and N containing components strongly modulate mineralization dynamics.

Recent research has also focussed on a more detailed understanding of the effects of changes in the amount of root or litter residue entering to a soil. The Detritus Input and Removal Treatments (DIRT) experiment in Harvard Forest, a temperate system, showed clear effects of increasing or reducing litter inputs to forest soils (Pisani et al., 2016). Doubling aboveground litter inputs in the N-limited forest ecosystem decreased soil carbon content, increased the degradation of labile SOM, and enhanced the sequestration of aliphatic compounds. The exclusion of belowground inputs and the decrease in root-derived components enhanced the degradation of leaf cutin, a component of aboveground litter that is considered to be relatively recalcitrant to decomposition (Angst et al., 2016a). As similar studies in other climatic conditions showed different effects (Fekete et al., 2014) it is clear that we have not yet understood the complex relationships between above- and belowground inputs and SOM formation and turnover. It is likely that the source, quantity and quality of plant litter inputs will have a direct influence on the molecular-level composition of SOM and that this relationship will be ecosystem-dependent (Manzoni et al., 2010; Pisani et al., 2016). In the course of soil formation, organic matter and mineral particles are clustered and glued together into aggregates of various sizes which build a complex soil micro- and macro-structure. Our mechanistic understanding of how the site specific properties (e.g. soil mineralogy, molecular characteristics of organic matter input, structure of the microbial community) contribute to soil structure is still limited (Vogel et al., 2014). The greatest challenge now is to integrate the knowledge and information on the stoichiometry and chemistry of different input resources with the properties of site specific environments and the mechanisms of microbial response. These reactions will include changes in microbial substrate and energy use efficiencies, regulation of microbial extracellular enzyme production, and shifts in the microbial community structure related to components' specific element demands and the dynamic soil environment.

For all modelling endeavours and projections for changes in SOM under a changing climate, carbon input and its transformation is one of the decisive parameters (Gottschalk et al., 2012). Estimates are often obtained from just an inverse application of the model used or from modelled net primary productivity (NPP) which assumes that C inputs are proportional to NPP; this assumption is not valid for agricultural soils (Wiesmeier et al., 2015). We still have a dearth of applicable data for the amount of organic matter input on a regional or agrosystem-specific level.

3. Sources of organic matter input to soils

Our understanding of organic carbon dynamics in soils is still largely limited to the surface 20—30 cm (Rumpel and Kögel-Knabner, 2011; Campbell and Paustian, 2015) but there is increasing evidence that a significant proportion of the organic matter input is from belowground sources. This arises not only from dead roots but also the many different organic C and N containing materials released from living roots as rhizodeposition. These include sloughed-off cells, mucilage, and low molecular mass and polymeric exudates released from intact root cells (Fig. 1). Both aboveground and belowground litter quality and quantity are now recognized as major determinants of soil organic matter composition and turnover. The SOC depth profile in the subsoil (B and C horizons) is strongly controlled by root distribution (Ota et al., 2013; Spielvogel et al., 2014). But our understanding of subsoil SOC dynamics suffers from the lack in quantitative information on the amount of different C compounds entering soils from the various below-ground plant, animal and microbial sources and their turnover characteristics. This, in turn, limits the modelling of organic carbon dynamics in soils. As pointed out by Campbell and Paustian (2015) this ignorance is mainly due to logistic challenges in investigation of subsoil C inputs and processes and needs greater efforts to develop new approaches to solving this problem.

Carbon flow from the roots is the starting point from which the rhizosphere (i.e. the soil zone influenced by roots) develops (Jones et al., 2009). Nonetheless, our SOM turnover models often ignore the contribution of belowground organic matter inputs, and specifically rhizodeposition. Estimates for the amount of root exudates are highly variable. Jones et al. (2004) stated that approximately 5—10% of the net fixed C is lost by root exudation. In contrast, Brüggemann et al. (2011) concluded that up to 40% of photosynthates are exuded by roots and are rapidly respired or invested in biomass by rhizosphere microorganisms. Other review studies indicate that roughly 40% of the net fixed C is allocated belowground to root growth and rhizodeposits (Jones et al., 2009). But this does not tell us how much of the C from decaying roots is entering the soil. The rate of C loss to the soil by root exudation as opposed to root turnover has rarely been compared in the same experiment (Jones et al., 2009). We need a major effort to initiate experiments designed to track and quantify C and N flow belowground.

This aspect of research is of particular importance as rhizodeposits are of a different composition compared to those plant tissues which contribute mainly structural polymers. Rhizodeposition is composed of mainly low molecular mass and readily metabolized organic compounds, such as organic acids, carbohydrates and amino acids with a high proportion of organic nitrogen (Jones et al., 2009). This also means that rhizodeposits are likely to be utilized by a different microbial community to that involved in the early stages of plant tissue degradation (Kuzyakov and Blagodatskaya, 2015). There is a substantial amount of work on rhizosphere microbial community composition as well as on the interactions between rhizodeposition and microbial processes (Berg and Smalla, 2009; Lagos et al., 2015). At the same time, there is almost no detailed analysis of the composition of SOM in the rhizosphere.

It has long been known that plant root exudates and mucilage contribute to soil aggregate formation and stability (Habib et al., 1990). Soil in the rhizosphere of European beech is more aggregated than the bulk soil and the aggregates have an organic composition different to that of the bulk SOM (Angst et al., 2016b). From these data it is to be expected that rhizodeposition has a strong effect, not only on microbial C processing but also on the stabilization of organic carbon in soils. More research is needed to discover if the specific rhizosphere inputs and their decomposition

have implications for soil organic matter formation and sequestration in the different SOM pools. As described by Oburger and Schmidt (2016), a number of new techniques are available to investigate the microbial interactions in the rhizosphere but their application to soil and its composition and processes is limited in most investigations. An extension of these plant-microbe interaction studies to plant-microbe-soil interaction studies in the rhizosphere is highly desirable.

When plant roots die, the rhizosphere soil surrounding the roots receive a change in input material dominated by polymeric structural plant components rather than low molecular mass rhizodeposits (Kuzyakov and Blagodatskaya, 2015). This root litter input enters not only the topsoil but also the subsoil. Thus, we need more detailed information how the assimilation of organic matter into microbial biomass is regulated in the subsoil with very different microbiological, chemical and physical characteristics to the topsoil (e.g., Müller et al., 2016). We also need more information with respect to subsoil microbial community composition and the composition of the long-term stabilized SOM.

Although in 2002 there were reports of the occurrence of charred organic matter or black carbon in soils (Haumaier and Zech, 1995; Skjemstad et al., 1996), I had not included this material in my 2002 review. During natural or human-induced fires (Schmidt et al., 1996; Knicker, 2011a; Santin and Doerr, 2016) the vegetation, litter and SOM undergo an incomplete combustion resulting in the formation of charred residues. These show different proportions of aromatic, partly condensed structures depending on the fire conditions. Charred residues from N-containing sources also contain heterocyclic aromatic N (Knicker, 2011b). The amount of charred residues as well as their turnover characteristics have important implications for the global C and N budget. The physicochemical characteristics of charred residues are quite variable, dependent on the organic precursor material and the conditions of formation. Whereas charred organic matter is considered highly stable due to these aromatic structures and the hydrophobic properties, it may be further stabilized by interactions with soil minerals and occlusion particularly within micro-aggregates (Brodowski et al., 2005, 2006). However, there is more and more evidence that a significant proportion undergoes transformation and mineralization on comparatively short timescales (Bird et al., 2015). Inspired by the fertility of ancient Terra preta do Indio (a fertile soil found in the Amazon basin), so-called biochar (charcoal that is produced by heating organic matter under oxygen-limited conditions) is now investigated as a soil amendment that may have multiple benefits for soils, depending on its production conditions and associated properties (Lehmann et al., 2015). Biochar is considered to increase nutrient and water retention in soils and can be helpful for remediation of contaminated soils (Abiven et al., 2014). There is increasing evidence for a long tradition of biochar addition to soils in different agricultural systems, e.g. paddy soils for rice cultivation (Lehndorff et al., 2014). Estimates of the mean residence time of biochar in soils vary from centuries to millennia and depend on the type and production conditions (Abiven et al., 2014). But it is clear that there is a lack of data obtained under realistic conditions, i.e. well-designed long-term field studies using biochar produced in commercial processes, and this limits our understanding of the potential of biochar to enhance crop production and mitigate the effects of climate change (Zhang et al., 2016). Finally, it has to be considered that soils in industrialized regions receive substantial amounts of black carbon input from industrial processes (Lehndorff et al., 2015). If such inputs occur they are likely to have major effects, not only on the composition of the SOM in these soils but also for estimating their ^{14}C content, as such components interfere with radiocarbon analyses (Flessa et al., 2008).

4. Microbial residues as input to SOM formation

An intention of my 2002 paper was to highlight that microbial residues accumulate in soils and thus are an important contributor to the formation of SOM. The plant-derived organic matter is undergoing microbial processing and some of the resulting organic carbon is incorporated into microbial biomass. Thus, we always find a significant proportion of SOM that arises from microbial residues (or necromass, Miltner et al., 2012) as well as their exudates (enzymes, exopolysaccharides, lipids, glycoproteins) often referred to as microbial extracellular polymeric substances EPS (Chenu and Cosentino, 2011; Burns et al., 2013). Although this microbial residue contribution was suggested long ago by Waksman (1938), it has been often ignored and only plant residues considered as inputs to SOM formation. However, there is increasing and welcome research into bacterial and fungal necromass and its role in the formation of stable C and N in SOM (Ekblad et al., 2013; Cotrufo et al., 2013). There is growing consensus that microbial EPS and other microbial components dominate stable SOM pools (Kiem and Kögel-Knabner, 2003; Simpson et al., 2007; Liang and Balser, 2008) and the composition and degradation of these residues and exudates needs to be explored (Liu et al., 2013; Fernandez et al., 2016).

We still do not have as much information with regard to the composition of microbial cell walls (other than the few that have been studied in detail) as we have on plant-derived inputs. This is specifically the case for the vast majority of soil bacteria and fungi that have not been cultured, but that we know exist from their genetic signatures (Daniel, 2005). Similarly, we have very little information about the varied structures and contributions to SOM of the archaea, but have growing evidence that they are present in large numbers in soil and are involved in many processes (Timonen and Bombard, 2009; Angel et al., 2012). Archaea make up 1—15% of the prokaryotes in soils (Bates et al., 2011) with a greater abundance in wetland and paddy soils (Bannert et al., 2011). Archaea are, therefore, likely to make a significant (but previously unsuspected) contribution to SOM. Archaeal cells are different to bacteria in that their cell walls are not surrounded by a peptidoglycan murein layer but, instead, a crystalline protein layer that forms the sole cell wall structure (Meyer and Albers, 2014). In addition, archaeal membrane lipids are different from those found in the fungi and bacteria. The polar lipids of the archaea consist of isoprenoid chains, 20—40 carbons in length and usually saturated, which are attached *via* stable ether bonds to the glycerol carbons at the *sn*-2,3 positions. Polar head groups differ at the genus level of diversity and consist of mixtures of glyco groups (mainly disaccharides), and/or phospho groups primarily phosphoglycerol, phosphoserine, phosphoethanolamine or phosphoinositol, phosphocholine headgroups are rarely found (Meyer and Albers, 2014). The archaeal lipids can thus be used as biomarkers in soil and sediment samples (Bannert et al., 2011).

To fully understand the capacity for carbon storage and dynamics in soil, resulting from C flow through microbial biomass and then microbial residues and their re-utilisation, it is necessary to determine the microbial carbon use efficiency (the efficiency with which microorganisms convert available organic substrates into biosynthesized products) in more detail than is current (Geyer et al., 2016). Such investigations of this significant component of SOM become more and more relevant, as the importance of microbial residues and microbial recycling of organic carbon is now recognized as important to our understanding of SOM turnover and is increasingly incorporated in modelling efforts (Ahrens et al., 2015).

a lab with all the chemolytic techniques and freedom to explore. Pat Hatcher (now Old Dominion University, USA) opened his NMR spectroscopy lab to me and taught me to use the technique.

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