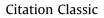
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The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter: Fourteen years on

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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 ¹³C 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 inputs to the subsoil *via* root litter and rhizodeposition and the significance of microbial residues and extracellular polymers and their subsoil *via* root litter and rhizodeposition and the significance of microbial residues and extracellular polymers.

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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 belowground 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

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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 molecularlevel composition using ¹³C 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







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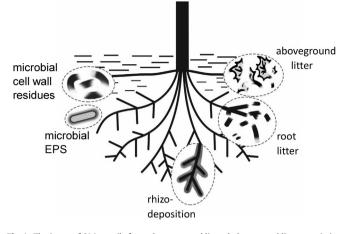


Fig. 1. The input of OM to soils from above-ground litter, belowground litter consisting of roots and associated mycorrhiza, rhizodeposition, microbial extracellular polymeric substances (EPS) and microbial residues (necromass).

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 ¹³C 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 ¹³C 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 solidstate ¹³C 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 ¹³C 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 organomineral 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 aboveground litter or belowground inputs, is the energy (C) and nutrientsource (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 Download English Version:

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