

Assessment of lignin and (poly-)phenol transformations in oak (*Quercus robur*) dominated soils by ^{13}C -TMAH thermochemolysis

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Abstract

Two sandy soil profiles under oak forest were examined for their phenolic composition using ^{13}C labelled tetramethylammonium hydroxide (TMAH) thermochemolysis, the first application of this method to soils. Lignin, demethylated lignin, hydrolysable tannin, and other phenolic acids could be distinguished, and as such indications of the relative distribution of these sources among the soil horizons was determined. Some compounds extracted from soils using TMAH thermochemolysis, all of which are permethylated phenols, can have multiple structural and botanical sources, such as 3,4-dimethoxybenzoic acid methyl ester from vanillic acid or demethylated vanillic acid derived from lignin, or protocatechuic acid as the initial compound. Correcting the common lignin proxies for contributions of non-lignin phenols and altered lignin, it was found that A (yield of monomers upon thermochemolysis), F/P (ferulic acid/*p*-coumaric acid), Ac/Al (acid/aldehyde) ratios, and I (indicator of side chain shortening) were severely influenced by non-lignin phenols. By contrast, the S/G (syringyl/guaiacyl) and C/G (cinnamyl/guaiacyl) ratios remained rather similar. The proxies that changed the most were those that affect interpretations of lignin patterns in terms of source, alteration and preservation. From L to Ah horizons, a progressive lignin alteration was found for both soils, but the differences in litter input among plant materials (leaves, bark, branches, roots) also potentially affected the lignin patterns within and between both profiles. Therefore, important insights into the rapid changes in lignin chemistry between organic and mineral horizons were provided as this method permitted enhanced distinction between fresh source input and decomposition. Even with the corrections to lignin proxies, the soil lignin and polyphenol chemistry remained complex and highlights the limitations of using a few or only one lignin proxy in assessing soil organic matter dynamics.

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1. Introduction

Soil plays a regulating role in the decomposition and stabilization of microbial and plant organic matter as the intrinsic rates of decay of both small and large biopolymers are depressed by the interactions

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of organic matter within the soil microfabric and its chemical environment (Oades, 1989; Golchin et al., 1994; Baldock and Skjemstad, 2000). Many factors control the stabilization of organic matter in forest soils including surface chemistry and surface area of soil minerals, stage of forest growth, plant type, soil pH, and soil micro- and macroflora and fauna. The relative degradation or preservation rate of plant input is an active field of study and recent findings have clearly illustrated how biopolymers once considered as “refractory” in both the litter and soil layer show relatively little preservation potential in deeper soil horizons (Rumpel et al., 2002; Nierop and Verstraten, 2003).

After cellulose and hemicellulose, lignin and tannin are the most abundant plant biopolymers in nature and apart from one type of tannin, the phlorotannins that occur in marine algae, they are ubiquitous in vascular plants. In addition, relatively large amounts of *p*-coumaric acid and ferulic acid distinguish non-woody tissues from wood lignin (Hedges and Mann, 1979). Both acids are considered to be esterified to lignin, polysaccharides and cutin and have also been suggested to form a polyphenolic domain of suberin (Kolattukudy, 2001; Bernards, 2002). Tannins are less abundant than lignin, but may exceed lignin in soft tissues such as leaves and needles (Hernes and Hedges, 2004). Two types of terrestrial tannins are identified: condensed tannins, which occur in all ferns and gymnosperms and in about half the families (the woody members) of angiosperms, and hydrolysable tannins that are only encountered in some 15 of the 40 orders of the dicotyledons (Harborne, 1997).

The analytical means by which chemical alteration or decomposition of plant matter is assessed may certainly impact on the findings. For example, overestimating lignin concentration or misinterpreting proxy degradation or source parameters may be a common feature in the analysis of lignin using unlabeled tetramethylammonium hydroxide (TMAH) thermochemolysis because the procedure is incapable of determining if an aromatic methoxyl group produced analytically was originally present as a hydroxyl or a methoxyl functionality. This analytical insensitivity makes it impossible to quantify relative inputs of fresh lignin, demethylated lignin and (hydrolysable) polyphenols into soils. Using ^{13}C -TMAH thermochemolysis, Filley et al. (2006) demonstrated that syringyl-based lignin from different fresh oak tissues contain significant amounts of ‘demethylated’ lignin monomers, of which most are

derived from hydrolysable tannins and other phenolic acids such as protocatechuic acid and caffeic acid. As hydrolysable tannins only occur in dicots (Harborne, 1997), they are always accompanied by syringyl lignin and therefore distinguishing between tannin derivatives and lignin products is not possible using conventional (unlabeled) TMAH thermochemolysis. However, even fully demethylated syringic acid is also indistinguishable from gallic acid, the main building block of hydrolysable tannins, after methylation by ^{13}C -TMAH. This is particularly true for oaks that exhibit relatively high contents of hydrolysable tannins, which therefore not only interfere with the study of demethylation of syringyl lignin but may also allow a comparative study of the fate of ‘intact’ lignin and hydrolysable tannin in soils under oak.

Lignin transformations in soils have been studied extensively and are characterized by side-chain oxidation, demethylation and depolymerization, the first processes that lead to the complete decomposition of lignin (e.g. Enoki et al., 1988; Chefetz et al., 2000; Filley et al., 2002). Compared with the large body of literature dealing with lignin degradation in soils, however, there is much less known about the fate of (hydrolysable) tannins in soil. Studies have shown that the amounts of extractable condensed tannins decline rapidly after litter fall (e.g. Lorenz et al., 2000; Valachovic et al., 2004), and that no tannins could be extracted from mineral soils (Schofield et al., 1998).

The extent to which lignin and tannin-derived carbon is partitioned in soil and influences the biogeochemistry of its surroundings is controlled by many factors including its original chemical composition and their transformation products (e.g. Hedges and Oades, 1997; Valachovic et al., 2004). For example, the functional group distribution of SOM and dissolved organic matter (DOM) determines the ability to chelate and retain metals such as iron, aluminium, calcium and magnesium (e.g. Ares and Ziechmann, 1988; Nierop et al., 2002) and influences the binding capacity for cations and mineral surfaces, which affects the preservation potential of organic matter pools (Kaiser and Guggenberger, 2000). Tannins play a major role in nutrient dynamics, especially in that of nitrogen (Kraus et al., 2003) and have an integral control on the activity of soil bacteria and fungi (Field and Lettinga, 1992).

In this paper, we test the ^{13}C -TMAH thermochemolysis technique for the first time on soils by studying two oak dominated profiles, which differ

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