

TURNOVER OF CUTIN AND SUBERIN IN A CROPLAND SOIL

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Plant residues and microorganisms are the main sources of organic matter in cropland soils. However the contrasting effects of humification and degradation processes turning the fresh plant material into stabilised soil organic matter (SOM) remain unclear. One major question concerns the contribution of aboveground versus belowground plant residues to SOM. To address this question, we analysed some biomarkers originating from biopolyesters which are specific for these tissues in non-woody plants. Indeed, cutin and suberin are supposed to be present respectively in the aboveground and the belowground tissues of higher plants. Cutin is an amorphous polyester usually constituted of carboxylic acids with an aliphatic chain length of 16 and 18 carbon atoms, bearing epoxy and hydroxy groups. Suberin is a structured polyester mostly composed of carboxylic acids, ω -hydroxy carboxylic acids and diacids. The particularity of the suberin is the large amount of monomers with a carbon chain length higher than 20 carbon atoms. The monomeric composition and the quantification of these macromolecules can be obtained through saponification and GC/MS analysis of the silylated derivatives.

In the present study we quantified these biopolyesters in several parts (leaves, stems and roots) of two plants, wheat and maize. These plants were chosen because of their different biosynthetic pathway (C3 and C4, respectively), hence different ^{13}C contents. Incorporation of these monomers in soil can therefore be followed by measuring the ^{13}C content of the same monomers in a soil on which a maize cropping replaced a wheat cropping. The chronosequence studied here is that of the Closeaux experimental field, onto which the change in cropping occurred up to 12 years ago.

Six classes of compounds were released upon saponification of the leaves, stems and roots of wheat and maize samples: carboxylic acids, alcohols, ω -hydroxy carboxylic acids, α -hydroxy carboxylic acids, diacids and mid chain hydroxylated compounds. As expected, mid chain (C_{16} and C_{18}) hydroxylated compounds dominated the monomers from leaves and stems. However differences in their distribution are noted between the two parts of the plant and also between wheat and maize. In wheat and maize roots, the ω -hydroxy carboxylic acids contributed for ca.50% of the total monomers with a significant contribution of the C_{20} to C_{28}

monomers, characteristic for suberin. Diacids from C₁₆ to C₂₂ were also released, but in lower amount than ω -hydroxy carboxylic acids (ca.18%). However diacids are characteristic for roots, since they were not detected in the other parts of the plants. In soils, the most abundant monomers released were the hexadecanoic acid (C₁₆), followed by the mixture of the 16,x-dihydroxy hexadecanoic acid isomers (Di-OH C₁₆), the octadecenoic acid, the ω -hydroxy docosanoic acid (ω C₂₂), the ω -hydroxy tetracosanoic acid (ω C₂₄), the octadecanoic acid (C₁₈) and the 9-hydroxy hexadecanedioic acid (9-OH DC₁₆). Carboxylic acids are not specific enough to be used to distinguish between the aboveground or the belowground sources. On the contrary, the Di-OH C₁₆ and 9-OH DC₁₆ monomers can be assigned to cutin polyester whereas the ω C₂₂ and the ω C₂₄ monomers are characteristic for root suberised tissues. Based only on the monomer concentrations in soils, the contribution of the two biopolymers into SOM can be assessed. However, to estimate their incorporation into SOM, the natural ¹³C labeling of the monomers is needed.

In wheat plant the $\delta^{13}\text{C}$ values ranged from -24‰ to -37‰ depending on the monomer. For maize, the $\delta^{13}\text{C}$ of the monomers ranged from -14‰ to -23‰. Carboxylic acids with C₁₆ and C₁₈ carbon atoms were enriched in ¹³C compared to mid chain carboxylic acids. However, no tendency in the ¹³C content was observed to distinguish between the monomers present in the three parts of the plant. In soils, an enrichment in ¹³C with years of maize cropping was observed due to maize incorporation. Nevertheless these changes depend on the considered monomer. For example, the $\delta^{13}\text{C}$ value of the carboxylic acid C₁₆ was -26‰ in soil under wheat and reached -23‰ after 12 years of maize cropping whereas no changes were detected in Di-OH C₁₆ $\delta^{13}\text{C}$ values. An increase of ¹³C was generally observed for other (mono/poly)-hydroxy carboxylic acids such as ω C₂₂, ω C₂₄ or 9-OH DC₁₆ monomers.

These results evidenced 1) the different behaviors of cutin and suberin in soils during the degradation and/or preservation processes; 2) a selective incorporation of some monomers for a same source of monomers (cutin or suberin) These contrasted behaviours of the monomers can be related to their chemical functions and their position into the polymeric structure.