Larger contribution of non-protonated aromatics for organic matter in subsoil than topsoil horizons in Brazilian Ferralsols

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Several processes are involved in soil organic matter (SOM) formation and turnover across the soil profile. Interestingly, while deep soil C appears to turn over very slowly, it remains unclear whether this trend is related to the molecular chemistry of SOM retained therein or its interaction with the mineral matrix. Besides, the extent to which the molecular chemistry of SOM is related to the chemistry, amount, and frequency of C inputs in topsoil and subsoil horizons remains unclear. We addressed these questions by collecting soil samples from three deep Ferralsols (a Gibbsic, a Ferritic, and a Haplic Ferralsol) across the Brazilian Cerrado to include samples with distinct texture classes and mineralogical combinations. Interestingly, the vegetation of the Brazilian Cerrado is characterized by different proportions of trees and grasses, implying different depth of rooting. Moreover, the Cerrado biome is subjected to frequent fire events, which could affect the input rate and the chemistry of C added to the soils. At each site, samples were taken from topsoil (0–10 cm) and subsoil horizons (60–100 cm) and incubated with a double-labeled (13C and 15N) eucalypt litter for 12 months under laboratory conditions. After the incubation, the samples were submitted to physical fractionationation to isolate SOM within the particle-size fractions (PSF) greater and smaller than 53 µm. Subsequently, we quantified the total C and N remaining in these PSF. Subsamples of the clay+silt fraction (<53 µm) were treated with a 10% HF solution to concentrate SOM. The molecular composition of SOM within the HF-insoluble fraction was assessed by 13C/15N Nuclear Magnetic Resonance (NMR) spectroscopy by applying a multi/cross-polarization (multi/CP) pulse sequence, yielding a quantitative solid-state magic-angle spinning (MAS) 13C/15N NMR. After the incubation, litter-C was retained at approximate proportions in both PSF evaluated, while a larger fraction of the litter-N was concentrated within the clay+silt fraction. Based on the multi-CP MAS NMR results, carbohydrates (65–110 ppm) accounted for most of the total C forms identified in the HF-insoluble fraction, regardless of soil type, soil depth, and plant litter addition. In topsoil, differences in the molecular chemistry of SOM between samples treated with plant litter and the controls were small. Otherwise, plant litter inputs to subsoil led to major changes in the chemistry of SOM, with a substantial reduction in the proportion of non-protonated aromatics and the aromaticity degree of SOM. Although observed in the topsoil, this effect was much less pronounced for the three Ferralsols evaluated. In addition, following eucalypt litter addition the molecular composition of SOM in topsoil and subsoil tended
to converge, becoming enriched in alkyl-C (0–46 ppm), carboxylic and/or amide groups (160–190 ppm for $^{13}$C and 120 ppm for $^{15}$N-NMR). Our results suggest that in topsoil, SOM molecular chemistry is consistent with a continuous supply of fresh plant litter. Otherwise, the deep burial of plant litter appears to be less relevant for SOM formation in subsoil horizons, where the accumulation of charred/pyrogenic materials are significant.