



Millimetre-scale spatial distribution of stable OM components at intact preferential flow path surfaces in the B-horizon of two Luvisols

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In structured soils, the interaction of percolating water and reactive solutes with the soil matrix is often restricted to surfaces of preferential flow paths. In the subsoil horizons of Luvisols, surfaces of biopores and aggregates can be enriched in clay and organic matter (OM). These coatings not only contribute to the OM stabilization in subsoil horizons but the OM composition of the coatings also determines the bio-physico-chemical surface properties which are relevant during rapid solute transport. Using a combined approach of Fourier transform infrared spectroscopy in diffuse reflectance mode (DRIFT) and pyrolysis-field ionization mass spectrometry (Py-FIMS), the OM composition of standardized (i.e. diluted and ground) samples separated from soil aggregate coatings was found to be enriched in chemically stable OM components. However, it remained unclear if these results could be verified for intact samples. The objective of this study was to analyse the mm-scale distribution of stable OM components at intact structural surfaces of two Luvisols based on DRIFT mapping and correlations between DRIFT spectra and Py-FI mass spectra. Samples were manually separated from the outermost surfaces of earthworm burrows, coated and uncoated cracks, root channels, and pinhole fillings of the B-horizons of Luvisols developed from loess and glacial till. The DRIFT spectra of these undiluted and particle-intact samples were interpreted by the help of Py-FIMS data to identify spectral regions representative of functional groups of chemically stable (i.e. recalcitrant) OM components. The DRIFT mapping technique was applied to determine OM functional group data (i.e. C=C and C=O signals) from stable OM components at the intact structural surface types in mm-scale transects and grids. The DRIFT signal intensities from C=O and C=C bonds in the infrared range of wave number 1688 ... 1565 cm⁻¹ were related to highly stable, chemically recalcitrant OM components, examined by Py-FIMS, such as heterocyclic N-compounds, benzonitrile and naphthalene. The signals were found to be relatively more intense at coated cracks and pinhole fillings compared to earthworm burrows and root channels, indicating surface type-specific differences in the OM composition. Within the surface types, higher signals were reported for the till-derived Luvisol compared to the loess-derived one, indicating site-specific differences in the levels of stable OM components. The results suggest that stable OM components of coatings of cracks and in pinhole fillings of Luvisol subsoil horizons result from specific relocation and accumulation processes. For subsoil horizons of the Luvisols, the spatial patterns of coatings and the mm-scale distribution of OM composition within coatings imply yet unknown effects on sorption processes during preferential flow.