# Organic matter composition at intact biopore and crack surfaces of Luvisol B-horizons analyzed by FTIR spectroscopy and Pyrolysis-Field Ionization Mass Spectrometry

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In the B-horizons of Luvisols, surfaces of biopores and aggregates can be enriched in clay and organic matter (OM), relative to the bulk of the soil matrix. The OM composition of these coatings determines their bio-physico-chemical properties and is relevant for transport and transformation processes but is largely unknown at the molecular scale. The objective of this study was an extended characterization of the OM composition at intact biopore and aggregate surfaces. Specifically, we aimed to improve the interpretation of data obtained with Fourier transform infrared spectroscopy in diffuse reflectance mode (DRIFT) by combining the signals from DRIFT spectra with data from pyrolysis-field ionization mass spectrometry (Py-FIMS) as a more detailed molecular-scale analysis. 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 OM at earthworm burrow walls was characterized by a mix of chemically labile aliphatic C-rich and more stable lignin and alkylaromatic compounds whereas the OM of coated cracks and pinholes was dominated by relatively stable heterocylic N and nitriles, and high-molecular aromatic compounds (benzonitrile and naphthalene). This more recalcitrant OM likely originated from the combustion of biomass and, in case of the till-derived Luvisol, from diesel exhausts. The OM composition of pore walls reflected the differences between biopores (i.e. topsoil and plant residual, worm activity) and cracks (i.e. solutes and colloids, rapid percolation). The information of Py-FI mass spectra enabled the assignment of OM functional groups also from spectral regions of overlapping DRIFT signal intensities to specific OM compound classes. In particular, bands 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 such as heterocyclic N-compounds, benzonitrile and naphthalene. Based on such relations, the OM composition at intact soil structural surfaces relevant for sorption and wettability could be characterized in more detail even by using DRIFT spectroscopy.