



## **Spatial distribution of clay-organic coatings and related physico-chemical properties at intact macropore surfaces**

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During preferential flow in structured soils, solute transport is largely determined by a complex network of macropores consisting of biopores, shrinkage cracks, and inter-aggregate spaces. Macropore surfaces can be coated by clay-organic material comprising increased contents of clay minerals, oxides and organic matter (OM), as compared to the matrix. These coatings may determine soil physico-chemical properties relevant for mass transport and organic carbon (OC) and nutrient turnover, such as surface wettability and sorption.

The main objective was to characterize the mm-to-cm scale, two-dimensional (2D) spatial distribution of OC and OM compounds in clay-organic coatings as well as of the corresponding cation exchange capacity (CEC), potential wettability, and surface roughness along intact macropore surfaces from structured subsoils. Soil samples were taken from Bt-horizons of Luvisols developed on loess and glacial till. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was used to analyze mid-infrared spectral properties of bulk soil, separated coating material, and intact macropore surfaces, the latter denoted as DRIFT mapping. Separated coating material was analyzed with respect to (i) OC content, using elemental isotope ratio mass spectrometry (EA-IRMS), (ii) OM compounds, using pyrolysis-field ionization mass spectrometry (Py-FIMS), (iii) CEC, using the BaCl method. The measurements each were related to DRIFT spectral data via partial least squares regression (PLSR). These relationships were used to predict maps of the spatial distribution of OC, OM compounds, and CEC for intact macropore surfaces by the help of DRIFT mapping spectra. The potential wettability (iv) of intact macropore surfaces was determined by water and ethanol drop penetration time (WDPT / EDPT) tests and the surface roughness (v) was characterized using confocal laser scanning microscopy (CLSM).

In contrast to the soil matrix and to earthworm burrow walls, the clay-organic coating material accumulated at cracks and in disconnected pores ("pinholes") showed increased contents of OC and of heterocyclic N-compounds, benzonitrile, and naphthalene. This relative enrichment suggested differences in the preferential OM transport between cracks and biopores and a stabilization of pyrogenic OM by clay minerals. Clay-organic coatings and fillings also showed highest CEC values (loess: 38 cmol kg<sup>-1</sup>, till: 29 cmol kg<sup>-1</sup>), in contrast to low CEC values of uncoated cracks and earthworm burrows (loess: 21 cmol kg<sup>-1</sup>, till: 14 cmol kg<sup>-1</sup>). Correspondingly, the CEC spatial distribution at intact macropore surfaces was found related to clay mineral and OM content. Thus, coating material can be strongly assumed to have quantitative effects on nutrient transport during preferential flow as well as on plant nutrient supply in macropores that may serve as preferential growth paths for plant roots. Under specific conditions, coatings were found to reduce the potential wettability and the roughness of macropore surfaces. The mm-to-cm-scale spatial heterogeneity of the clay-organic material along macropores of different types implies a more specific consideration of these surfaces when studying inter-domain mass transfer and OM turnover in structured soils.