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Spatial distribution of heterocyclic organic matter compounds at macropore surfaces in Bt-horizons

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The illuvial Bt-horizon of Luvisols is characterized by coatings of clay and organic matter (OM) at the surfaces of cracks, biopores and inter-aggregate spaces. The OM composition of the coatings that originate from preferential transport of suspended matter in macropores determines the physico-chemical properties of the macropore surfaces. The analysis of the spatial distribution of specific OM components such as heterocyclic N-compounds (NCOMP) and benzonitrile and naphthalene (BN+NA) could enlighten the effect of macropore coatings on the transport of colloids and reactive solutes during preferential flow and on OM turnover processes in subsoils.
The objective was to characterize the mm-to-cm scale spatial distribution of NCOMP and BN+NA at intact macropore surfaces from the Bt-horizons of two Luvisols developed on loess and glacial till. In material manually separated from macropore surfaces the proportions of NCOMP and BN+NA were determined by pyrolysis-field ionization mass spectrometry (Py-FIMS). These OM compounds, likely originating from combustion residues, were found increased in crack coatings and pinhole fillings but decreased in biopore walls (worm burrows and root channels). The Py-FIMS data were correlated with signals from C=O and C=C groups and with signals from O-H groups of clay minerals as determined by Fourier transform infrared spectroscopy in diffuse reflectance mode (DRIFT). Intensive signals of C15 to C17 alkanes from long-chain alkenes as main components of diesel and diesel exhaust particulates substantiated the assumption that burning residues were prominent in the subsoil OM. The spatial distribution of NCOMP and BN+NA along the macropores was predicted by partial least squares regression (PLSR) using DRIFT mapping spectra from intact surfaces and was found closely related to the distribution of crack coatings and pinholes. The results emphasize the importance of clay coatings in the subsoil to OM sorption and stabilization. Differences between biopores and cracks suggest differences in the mass transport and OM turnover between these macropore types in Luvisols.