EGU21-13614
https://doi.org/10.5194/egusphere-egu21-13614
EGU General Assembly 2021

Organic matter in black sand soils related to alkyl carbon and organo-mineral structures at the microscale

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Agricultural sandy soils with high organic matter (OM) contents are generally unexpected under the current paradigm of organic matter formation and stabilization. These so-called black sand soils occur in North-Western Europe and have been related to historical heathland vegetation. The properties and mechanisms of the high OM sequestration in these soils are not clear as they exceed common observations of OM stored in coarse-textured soils. In this study, we analyzed a subset of samples with 'black sand' properties from the European soil database "Land Use/Cover Area frame statistical Survey" (LUCAS). Through particle size fractionation, we isolated the fine fraction <20 µm which contained, on average, 55 % of the total soil organic carbon (OC), in only 8 % of the corresponding soil mass. The fine fraction <20 µm contained 301 mg OC g^{-1} with a C:N ratio of 17.4 on average and was positively correlated with the bulk soil OC. The characterization of OM composition in the fine fractions by solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy revealed that the share of alkyl C increased with OC concentrations whereas O/N-alkyl C decreased. To analyze the distribution of OM at the microscale, we analyzed five samples from the <20 µm fraction containing a gradient of 245-378 mg OC g^{-1} with nanoscale secondary ion mass spectrometry (NanoSIMS) at a spatial resolution of 120 nm. These microscale measurements revealed fine mineral particle structures associated with heterogeneously distributed OM. Using image analysis, we found that the proportion of OM-dominated area (indicated by $^{12}C_2^-$ and $^{26}CN^-$) increased from 52 to 80 % on average with increasing OC concentration of the fine fractions. A majority of OM-dominated area was correlated with higher $^{42}AlO^-$ counts, which might suggest a preferential co-localization. In turn, the particle area which was dominated by minerals (indicated by $^{16}O^-$, $^{28}Si^-$, $^{42}AlO^-$ and $^{72}FeO^-$) contained less Al and more Si. This shows that the more alkylated and OM-rich fine fractions are related with distinct patterns of organo-mineral structures at the microscale.