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Solid-state 13C NMR experiments reveal effects of aggregate size on the chemical composition of particulate organic matter in grazed steppe soils

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Grazing is one of the most important factors that may reduce soil organic matter (SOM) stocks and subsequently deteriorate aggregate stability in grassland topsoils. Land use management and grazing reduction are assumed to increase the input of OM, improve the soil aggregation and change species composition of vegetation (changes depth of OM input). Many studies have evaluated the impact of grazing cessation on SOM quantity. But until today little is known about the impact of grazing cessation on the chemical quality of SOM in density fractions, aggregate size classes and different horizons. The central aim of this study was to analyse the quality of SOM fractions in differently sized aggregates and horizons as affected by increased inputs of organic matter due to grazing exclusion.

We applied a combined aggregate size, density and particle size fractionation procedure to sandy steppe topsoils with different organic matter inputs due to different grazing intensities (continuously grazed = Cg, winter grazing = Wg, ungrazed since 1999 = Ug99, ungrazed since 1979 = Ug79). Three different particulate organic matter (POM; free POM, in aggregate occluded POM and small in aggregate occluded POM) and seven mineral-associated organic matter fractions were separated for each of three aggregate size classes (coarse = 2000-6300μm, medium = 630-2000μm and fine = $<$630μm), three horizons (Ah1, Ah2, Ah3) and the four differently grazed plots. Chemical composition of POM was analysed using solid-state ^{13}C NMR spectroscopy (Bruker DSX 200 NMR spectrometer) and the cross-polarisation magic angle spinning technique at a spinning speed of 6.8 kHz. Depending on the C contents of the samples between 2,000 and 250,000 scans were accumulated.

Higher inputs of organic matter led to higher amounts of OC in coarse aggregate size classes (ASC) and especially in particulate organic matter (POM) fractions. We found no grazing-induced changes of soil organic matter quantity in fine ASC and mineral fractions. These differences were amplified in topsoils and decreased with sampling depths. Chemical composition of POM was comparable between differently grazed plots. We found a general increase in the degrees of decomposition from fPOM to oPOM to oPOM$_{small}$, with decreasing ASC and with increasing sampling depth. These differences were amplified for the alkyl C and the O-alkyl C. Contribution of alkyl C and O-alkyl C both generally decreased with depth while carboxyl C and aryl C increased. O-alkyl C in oPOM$_{small}$ was clearly higher in Ah3 of ungrazed plots compared to grazed plots.

To summarise, POM is decomposed hierarchically with ASC in steppe soils pointing towards aggregate hierarchy. POM decomposition is similar in different depths of steppe soils as we found no evidence for changing decomposition processes due to higher OM inputs following grazing cessation. Ungrazed plots had higher O-alkyl C and alkyl C contributions in deeper soil layers due to higher OM inputs through root litter and exudates (vegetation change to deeper-rooting species). Solid-state ^{13}C NMR spectroscopy showed chemical composition of POM in steppe soils to be primarily affected by aggregate size while grazing cessation and sampling depth were of minor importance.