



Novel insights into the influence of calcium on SOC dynamics: the indirect effects of CaCO₃ on SOC cycling in a Swiss subalpine grassland.

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Research into soil organic carbon (SOC) dynamics has typically focused on Fe and Al dominated soils, while the influence of Ca on SOC accumulation and stabilisation mechanisms still requires further investigation (Rowley et al., 2018). The aim of this study was to evaluate the role of Ca on SOC dynamics at the Nant valley alpage, Switzerland, by comparing three soil profiles with CaCO₃ (Cambic Phaeozems) and three without (Eutric Cambisols). Our hypothesis was that occlusion would play a relatively more important role in the stabilisation of SOC in soils with CaCO₃ due to the promotion of flocculation and aggregation by exchangeable Ca. We further expected that the $\delta^{13}\text{C}$ values of bulk organic matter would be lower in CaCO₃-bearing soils due to the physical prevention of microbial recycling and ¹³C fractionation.

We thus separated 4 density fractions from the samples, a free light fraction (<1.6 g cm⁻¹; LF), two occluded light fractions separated by 10 and 200 j.ml⁻¹ sonication (O¹⁰LF and O²⁰⁰LF, respectively) and a heavy fraction (HF). Following decarbonation, organic carbon content and the $\delta^{13}\text{C}$ values of the various density fractionated SOC pools was measured. SOC (%) was approximately twice as high in profiles containing CaCO₃ as profiles without. Occluded SOC was an order of magnitude more abundant in the CaCO₃-rich sites than at the other sites but remained a very small pool overall, never accounting for more than 10% of total SOC. $\delta^{13}\text{C}$ profiles displayed the typical enrichment in ¹³C with depth, but the SOC was clearly more depleted in ¹³C in the profiles with CaCO₃ than those without. However, occlusion played a minimal role in explaining the differences in the $\delta^{13}\text{C}$ values, which instead reflected closely the signature of the HF.

The differences between the LF and HF at the sites were of particular interest. The $\delta^{13}\text{C}$ composition of fractions from profiles without CaCO₃ became more enriched from LF to HF signatures. This is widely reported within the literature and is thought to arise from the selective stabilisation of microbial byproducts by Fe and Al oxides. However, contrary to previous results, SOC composition of the HF in soils with CaCO₃ had a ¹³C-depleted signature that was similar to that of the LF. This drove the differences in the $\delta^{13}\text{C}$ profiles of the sites and suggests that, in Ca-rich systems, SOC is rapidly incorporated into the HF without undergoing extensive ¹³C fractionation. Therefore, fresh plant compounds could be more likely to form organo-mineral associations in the presence of Ca than in its absence. Thus, contrary to expectation in soil science, the stable C isotope composition of organo-mineral stabilised SOC (HF) in CaCO₃-rich profiles is similar to the LF composition. Further research is needed to investigate these systems and the oxidation state of C stabilised in the HF at the sites.

References

Rowley, M.C., Grand, S., Verrecchia, É.P., 2018. Calcium-mediated stabilisation of soil organic carbon. *Biogeochemistry* 137(1), 27-49.