



Is the exchangeable fraction determining the activity of mineral associated carbon?

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Sorption of organic molecules to mineral surfaces is assumed to be playing an important role for the long-term persistence of organic carbon (OC) in soils. Possibly due to the different mechanisms by which organic matter can be associated with minerals, not all carbon is equally strong bound to mineral surfaces. Therefore, it was observed that despite old average ages of mineral associated carbon, a portion is typically active. Assuming that active carbon has to be desorbed from mineral surfaces before mineralization, we hypothesize that (1) exchangeable OC will be younger than the residue, and that the portion of exchangeable carbon will (2) depend on the amount of pedogenic oxides and (3) decline with soil depth due to increasing ages of mineral associated OC with depth.

To test these hypotheses, we treated the heavy fraction ($d > 1.6 \text{ g cm}^{-3}$) of five different soils and from three soil depths (0-5 cm, 10-20 cm, 30-40 cm) with NaF as a strong anion exchanger. Carbon and radiocarbon (^{14}C) content were determined in both, extracts and residues. In order to test, if the extraction was able to remove all active carbon from mineral surfaces, and to get an idea about maximum ages of mineral associated carbon, we additionally treated the heavy fraction with heated (60°C) H_2O_2 , and analyzed OC and ^{14}C content in the residue. The NaF treatment removed on average $60 \pm 10\%$ of total carbon from mineral surfaces. Following our expectation, the age of removed carbon was younger, and the residue older than the bulk HF fraction across soils and soil depths with an average ^{14}C difference of 91% . There was, however, no detectable influence of soil mineralogy or soil depth on the portion of exchangeable OC. Exchangeable OC was rather correlated to total OC in mineral associated fractions across sites and depths and proportional to OC in the residue. Only at the agricultural site studied with overall smallest OC contents, exchangeable OC was 25% less than at the other sites, suggesting that mineral surfaces were potentially not saturated. Similar to OC, also ^{14}C contents of extracts and residues were positively correlated. Accordingly, also the ^{14}C content of the exchangeable carbon was not staying young with depth, but its age is increasing proportional to ^{14}C in the residue. Neither absolute ^{14}C contents nor differences between extracts or residues were related to type or amounts of pedogenic oxides. The H_2O_2 treatment removed on average $88 \pm 9\%$ of total carbon from mineral surfaces. While the ^{14}C content of the removed carbon was almost similar for both treatments, ^{14}C contents of the H_2O_2 residues were much smaller than for NaF (between 30 and 400%). Accordingly, the NaF treatment was able to separate a large, but not the total active fraction of OC across soil profiles and depths, suggesting that besides anion exchange also other mechanisms determine the activity of OC at mineral surfaces.