



## Thermal stability of soil organic matter fractions and their $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values after $\text{C}_3 - \text{C}_4$ vegetation change

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Carbon isotopic composition of soils subjected to  $\text{C}_3 - \text{C}_4$  vegetation change is suitable tool for estimation of C turnover in bulk soil and in soil organic matter (SOM) pools with fast and intermediate turnover rates. We hypothesized that biological availability of SOM pools is inversely proportional to thermal stability of SOM pools. Soil samples from field plot with 10.5-years cultivation of  $\text{C}_4$  plant *Miscanthus x giganteus* were analyzed by thermogravimetry coupled with differential scanning calorimetry (TG-DSC).

According to differential weight losses (TG) and energy release or consumption (DSC), five SOM pools with increasing thermal stability were distinguished (20-190 °C, 190-310 °C, 310-390 °C, 390-480 °C, 480-1000 °C) and their  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values were analyzed. The weight losses up to 190 °C were connected with water evaporation, since no significant C and N losses were measured and  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of the residual SOM remains unchanged. The maximum weight losses occurred between 190 and 310 °C as well as 310 and 390 °C. The pool decomposed between 190 and 310 °C contained 38% of  $C_{org}$  and had  $\delta^{13}\text{C}$  value of -18.8‰. The pool decomposed between 310 and 390 °C contained 54% of  $C_{org}$  with  $\delta^{13}\text{C}$  of -17.0‰. The  $\delta^{13}\text{C}$  values of these thermal labile fractions were slightly closer to the  $\delta^{13}\text{C}$  of the *Miscanthus* root and shoot tissues (-11.8 ‰) compared to the most thermally stable SOM pool decomposed between 480 and 1000 °C. The fraction decomposed above 480 °C held only 1% of  $C_{org}$  and showed  $\delta^{13}\text{C}$  (-19.5‰) closer to the original  $\text{C}_3$  soil (-26.5‰). The intermediate SOM pools decomposed between 390-480 °C contained 10% of the

$C_{org}$  and had no differences in  $\delta^{13}C$  (-17.0‰) compared to 190-310 °C and 310-390 °C pools.

The portion of the *Miscanthus*- $C_4$ -derived C in SOM was calculated considering identical isotopic fractionation by humification of  $C_3$  and  $C_4$  plant residues. During 10.5 years of *Miscanthus* cultivation the amount of new  $C_4$ -C in SOM of bulk soil reach 54%. However, the  $C_4$ -C contribution in 190-310 °C pool was 62% and decreased up to 9% in the pool decomposed above 480 °C.

Based on this  $C_4$ -C contribution and the period after vegetation change (10.5 years), the SOM turnover rates were calculated. The C turnover in the pools decomposed at lower temperatures was faster than that in the pools decomposed at high temperatures. The Mean Residence Time (MRT) of 190-310, 310-390 and 390-480 °C SOM pools were similar (11, 13 and 16 years, respectively) and the pool above 480 °C had MRT of 117 years. Therefore, we conclude that biological availability of thermal labile SOM pools (<480 °C) was higher, than that of the thermal stable pool decomposed above 480 °C and the last pool was chemically protected.

Contrasting to the  $\delta^{13}C$ , the  $\delta^{15}N$  values showed strong differences between SOM fractions suggesting that the N turnover in soil is different from the C turnover.