

## Persistence of soil organic matter and soil structure

<sup>1</sup>W. E. H. BLUM, <sup>1,2</sup>G. J. LAIR and <sup>1</sup>J. SCHIEFER

<sup>1</sup>Institute of Soil Research, University of Natural Resources and Life Sciences (BOKU), Vienna

<sup>2</sup>Institute of Ecology, University of Innsbruck

### Introduction

The persistence of soil organic matter (SOM) can be defined as resistance against biological decomposition, expressed as residence time in soils. Under this aspect, two types of SOM can be distinguished: biogenic organic matter derived from organic feedstock through biological decomposition (metabolisation, mineralisation) processes, and pyrogenic organic matter, produced through thermochemical fractionation in the absence of oxygen at high temperatures.

SCHMIDT *et al.* (2011) published the mean residence time of bulk SOM distinguishing between SOM derived from plant material, that of microbial origin and from different biological sources on one side, and pyrogenic (fire-derived) organic matter (biochar) on the other.

From these data it became clear that the mean residence time of biogenic SOM is on average less than 50 years, often less than 20 years, whereas the pyrogenic organic matter shows a considerably higher residence time.

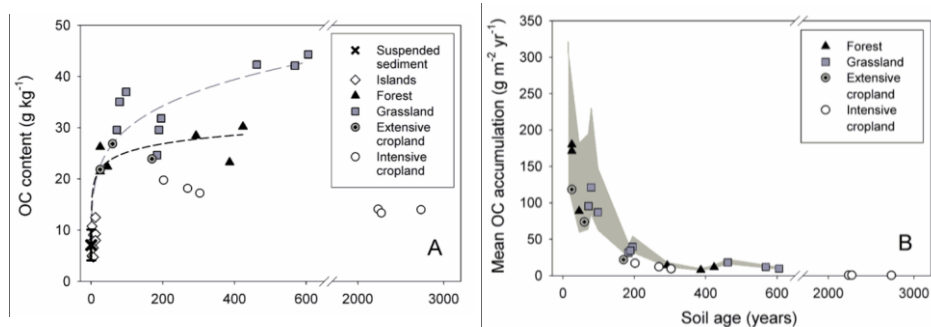


Fig. 1

Organic carbon accumulation in topsoils (0–20 cm) affected by different land uses (A) and rates of SOM accumulation (B) in the investigated topsoils (ZEHETNER *et al.*, 2009)

*Correspondence to:* WINFRIED E. H. BLUM, Institute of Soil Research, University of Natural Resources and Life Sciences (BOKU), Peter-Jordan-Str. 82. 1190 Vienna. Austria.  
E-mail: winfried.blum@boku.ac.at

Looking into the radiocarbon-dated SOM in various soil size fractions or physical-chemical humus fractions reveals that some SOM may reach a thousand to several thousand years of age.

A previous study by ZEHETNER et al. (2009) showed an increase in organic carbon (OC) in g/kg bulk soil with the soil age (yr) and the mean accumulation of OC in  $\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  in the bulk soils under different land uses (Fig. 1). These data indicate that the accumulation of OC during soil formation occurs very rapidly during the first 50–100 years but decreases quickly in the following years. Therefore, the question arises what is the reason for fast accumulation and the difference in persistence of SOM and how this phenomenon can be explained. In the following, only the persistence of biogenically derived SOM will be discussed.

## Material and methods

### *Research area and soils*

Within the EU-research project “Soil Transformations in European Catchments” (SoilTrEC, Grant No. 244118), focusing on Critical Zone research, this question was followed up, concentrating specifically on the clay-sized soil fractions (here called “micro-aggregates”) of a Chernozem chronosequence with different land uses (forest, pasture, agricultural cropland), ranging in age from a few years to more than eight thousand years. This Chernozem chronosequence developed on Danube sediments in the Marchfeld area, east of Vienna (see Fig. 2).

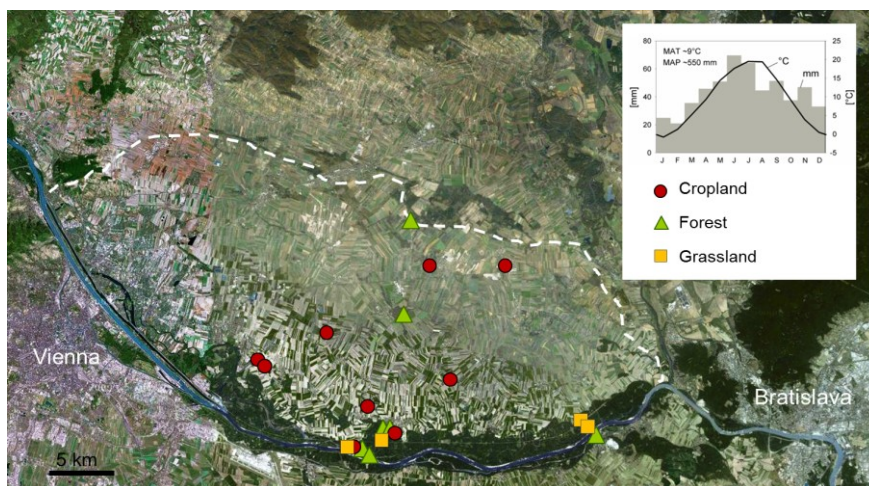
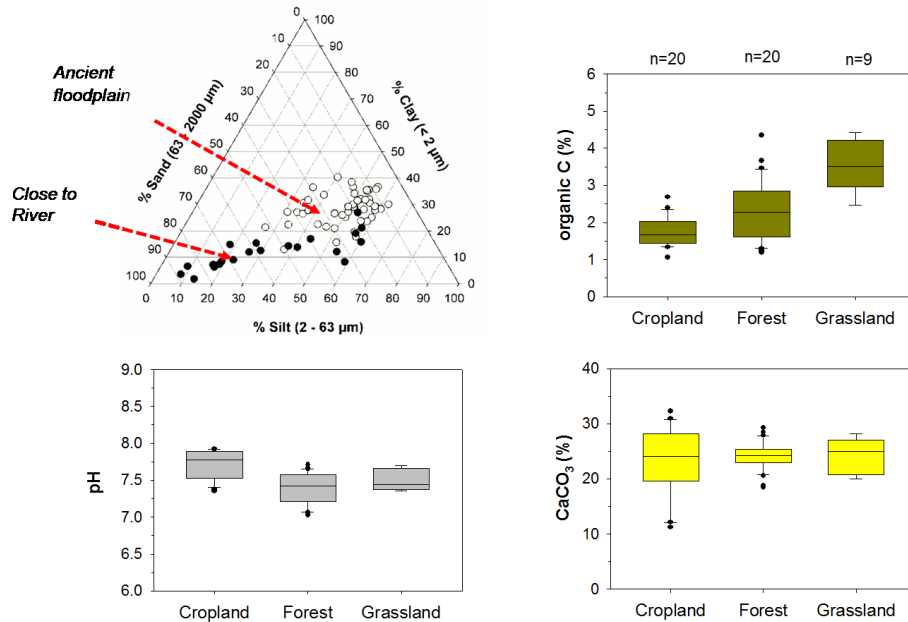


Fig. 2

Critical Zone Observatory (CZO) Marchfeld, located east of Vienna. The study area was bordered in the south by the River Danube, which created the former floodplain with fine sediments (indicated with white-dotted line) during the Holocene



*Fig. 3*  
Soil texture, pH(H<sub>2</sub>O), organic C and CaCO<sub>3</sub> content in topsoils (0–20 cm) under different land uses in the study area

Within this chronosequence, the age of the soils increases with increasing distance from the Danube River, ranging from the youngest soils on fresh sediments to Chernozems more than eight thousand years old (BANWART et al., 2012). The soil age was dated using <sup>137</sup>Cs, optically stimulated luminescence (OSL), the crystallinity of Fe-oxides (Feo/Fed) and archeological remnants (LAIR et al., 2009).

The texture, pH(H<sub>2</sub>O), organic C and CaCO<sub>3</sub> content of the top soils (0–20 cm) of the investigated chronosequence are shown in Fig. 3.

### Research concept and methods

In order to answer the question of SOM persistence, the aging of SOM with time was analysed in clay-sized “micro-aggregates” (< 2 µm) in the topsoils, based on the working hypothesis that the resistance of SOM to biological decomposition depends primarily on their capacity to bind at mineral surfaces.

To gain the clay-sized aggregates from the topsoil (0–10 cm), a particle size fractionation method was chosen according to MONROZIER et al. (1991) and STEMMER et al. (1998). The bulk soil was treated with ultrasonication (55 Watt for 200 seconds) to disrupt the macro-aggregates without harming the micro-aggregates.

The suspension was centrifuged at 150 g (834 rpm) for 2 minutes. The supernatant was centrifuged again at 10 000 g (7 400 rpm) for 25 minutes. The residue (2µm–0.1µm) was freeze-dried for subsequent analysis.

The SOM characterisation for selected study sites was performed with Simultaneous Thermal Analysis (STA) and by solid state cross-polarisation magic angle spinning (CPMAS)  $^{13}\text{C}$  NMR spectroscopy.

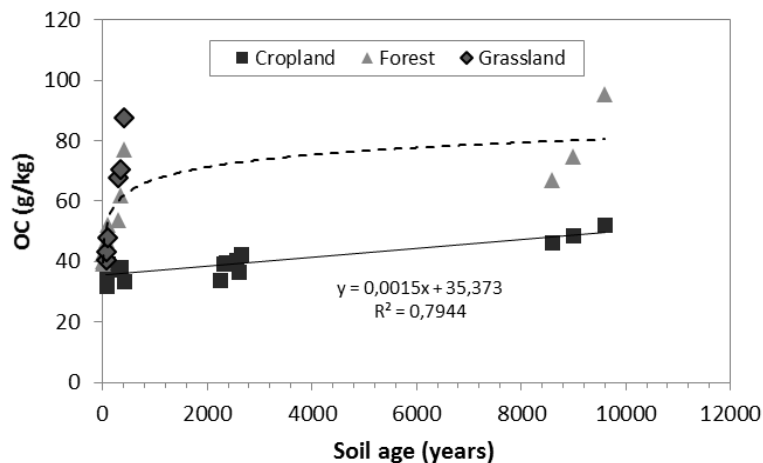
The STA heated up the soil samples to 600 °C and measured the constant weight loss. The weight loss in specific temperature ranges gives information about the quality of SOM in the soil samples: thermo-labile organic matter was gained between 190 and 390 °C, while thermo-stable organic matter was gained between 390 and 600 °C due to increased humification/polymerisation (DE LA ROSA et al., 2008).

The intensity of NMR signals is proportional to the concentration of the nuclei creating the signal (KNICKER & NANNY, 1997). These signals are separated into different chemical shift regions and assigned to organic groups: Carboxyl 220–160 ppm; Aryl 160–110 ppm; O-alkyl 110–45 ppm; Alkyl 45–0 ppm.

## Results and discussion

### *Development of OC in clay-sized micro-aggregates in the topsoils under different vegetation covers along the chronosequence*

Fig. 4 shows the accumulation of OC in clay-sized micro-aggregates over time.



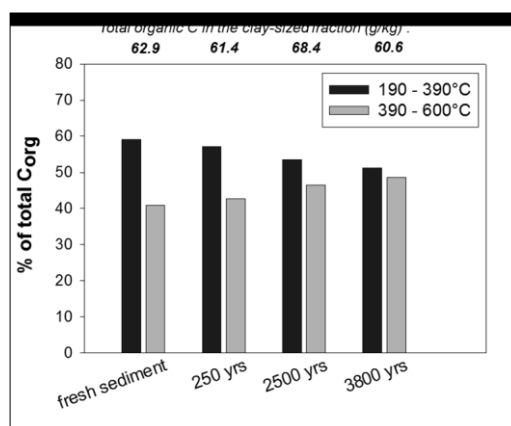
*Fig. 4*

Organic carbon contents in clay-sized “micro-aggregates” in topsoils of different age and land use. Forest “micro-aggregates” quickly reached an equilibrium level, whereas cropland “micro-aggregates” showed a steady increase with soil age

Especially under forests, an equilibrium can be argued towards an age of about eight thousand years, whereas under cropland a steadily increasing OC level can be observed for more than eight thousand years, with a measured increase of  $1.5 \text{ mg OC} \cdot \text{kg}^{-1} \text{ soil} \cdot \text{yr}^{-1}$ . However, studied croplands have been cultivated for a minimum of 120 years to a maximum of 800 years, which points to a co-evolution of SOM pools and new mineral surfaces during pedogenesis.

Based on this observation, all further analyses were concentrated on the cropland top soils. Grassland soils revealed high OC accumulation rates similar to those under forests. Unfortunately, no soil samples were available at older sites along the chronosequence.

#### *Stabilisation of the OC in the clay-sized fraction of cropland soil based on thermogravimetric analysis*



*Fig. 5*

Stabilisation of organic carbon in the clay-sized “micro-aggregates” of cropland soils ( $< 2 \mu\text{m}$ ) during soil formation (190–390 °C = thermo-labile organic matter; 390–600 °C = thermo-stable organic matter)

The results from STA analysis on selected sites in the CZO Marchfeld area showed a clear relationship between thermo-labile (190–390 °C) and thermo-stable OC (390–600 °C) changes with soil age, with a constant increase in the thermo-stable fraction with time (Fig. 5).

#### *Changes in the persistence of specific OC compounds as revealed by $^{13}\text{C}$ -NMR*

From Fig. 6 it became evident that organic compounds that are more resistant to biodegradation, such as Carboxyl-C and Aryl-C, representing mainly acids, amides and aromatic groups (e.g. lignin), increase with time, whereas more easily biodegradable compounds in the O-Alkyl C group (e.g. polysaccharides) and the Alkyl-C group, which includes lipids and hemicellulose, decrease.

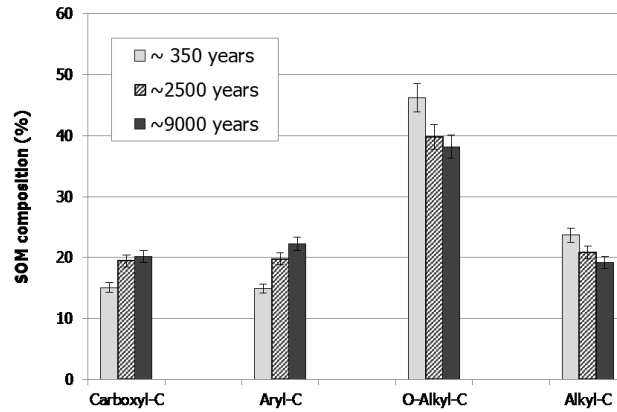


Fig. 6

<sup>13</sup>C-NMR characterisation of selected clay-sized “micro-aggregates” (< 2 µm) in topsoils (0–10 cm) under cropping in the CZO Marchfeld area

### Conclusions

The changes observed in the total content and in the biophysical and biochemical composition of OC in the clay-sized “micro-aggregates” in Chernozem topsoils revealed that the OC in the clay-sized fractions became increasingly more stable with time. This indicates that there are biophysical and biochemical mechanisms that increase the persistence and therefore the age of the OC in soils. This process may be related to changes in the volume and size of soil aggregates, and concomitantly, the volume and size of soil pores, which may influence the access of microbes to the OC over time.

### Summary

The persistence of SOM was investigated in a dated Chernozem chronosequence on Danube sediments east of Vienna, analysing changes in the total content, thermo-stability and biochemical composition of organic matter in the clay-sized “micro-aggregates” (< 2 µm) in cropland topsoils (0–10 cm) with soil age.

The results indicate some of the biophysical and biochemical processes behind the aging and increasing persistence of organic matter in soils. There is a fast accumulation of OC in the < 2 µm micro-aggregates in the first years of soil development under forest and grassland sites, which levels off after ~350 years. Cropland sites show a steady but not strong increase along the chronosequence.

Soil organic matter composition was analysed with Simultaneous Thermogravimetric Analysis (STA) and <sup>13</sup>C NMR and showed the expected changes with increasing soil age.

Both the thermo-labile SOM pool (i.e. mass loss between 190 and 380 °C) and the carboxyl and Alkyl-C pools showed a strong decrease, while the thermal-stable SOM pool (mass loss between 380 °C and 600 °C) and the Aryl-C pool increased with soil age in the < 2 µm micro-aggregates.

**Keywords:** soil chronosequence, SOM persistence, Chernozem, clay-sized fractions, biophysical and biochemical changes.

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