Preservation of fire-derived carbon compounds and sorptive stabilisation promote the accumulation of organic matter in black soils of the Southern Alps

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Abstract

Cryptopodzols are black soils that occur under forests dominated by chestnut trees (*Castanea sativa*) in Southern Switzerland. Their soil organic carbon (SOC) stocks reach an average of 150 t C ha⁻¹ and are thus among the highest of European forest soils.

We investigated the processes leading to the accumulation and stabilisation of SOC in these soils by analysing three Cryptopodzols and one Cambisol for charred organic matter content (macrocharcoal and BPCA), the amounts of Fe and Al, and the colour and SOC content in bulk soil and density fractions. The results showed that charred organic matter produced by frequent fires in the area for at least 10,000 years is highly abundant in Cryptopodzols: the stocks of macrocharcoal and BPCA-C amount to up to 31 t ha⁻¹ and 17 t ha⁻¹, respectively. These high amounts of charred organic matter are responsible for the dark soil colour and high SOC concentrations that are, however, also closely related to Fe_p and Al_p concentrations. We concluded that the occurrence of charcoal across the whole profiles of Cryptopodzols seems to be the dominating factor, although both the formation of organo-metallic or organo-mineral complexes in the subsoil and the high abundance and stability of charred organic matter are responsible for the high SOC stocks in Cryptopodzols.

Keywords

soil organic matter, charcoal, BPCA, Fe/Al oxides, density separation

Introduction

Soils of Southern Switzerland are often characterised by a black colour throughout the profile down to the parent material (Blaser et al., 1997). These soils occur mainly under forests dominated by chestnut trees (*Castanea sativa*) at elevations below 1000 m asl. Their mean soil organic carbon (SOC) stocks of 150 t C ha⁻¹ are the highest in Switzerland (Perruchoud et al., 2000) and among the highest in European forest soils (Liski et al., 2002).

Blaser et al. (1997) classified these soils as Cryptopodzols. They have features of Podzols because pedogenic oxides were eluviated from the topsoil, but the typically bleached eluviation horizon is masked by a dark soil colour. Blaser et al. (1997) explained the high amounts of SOC and the dark colour with the presence of both tannin-rich chestnut litter and aluminium (Al) and iron (Fe) in the parent material. The very low bulk density ($< 1 \text{ g cm}^{-3}$) of Cryptopodzols and the humid climate of the Southern Alps promote the leaching of dissolved organic carbon, including tannins and other polyphenols, from the litter layer through the soil profile, where the organic matter readily forms organo-metallic complexes with Al and Fe oxides. These complexes stabilise SOC in the mineral soil matrix, and therefore are responsible for the high SOC contents and the dark soil colour (Blaser and Sposito, 1987; Blaser et al., 1997). The importance of organo-metallic complexes as stabilising agents is pronounced especially when allophanes and imogolites are present in the subsoils of Cryptopodzols (Zanelli et al., 2006).

Stabilisation processes of organic matter in soils are, nonetheless, still not well understood. Theoretical concepts of SOC stabilisation describe different mechanisms of protection: (1) recalcitrance of organic matter due to the primary or secondary molecular structure, (2) spatial inaccessibility, i.e. inclusion of organic matter into aggregates or micropores, which leads to a physical protection of organic matter from microorganisms and enzymes, and (3) sorption processes on minerals and interaction with metal ions that are known to play an important role in SOM preservation (Sollins et al., 1996; Baldock et al., 2004; von Lützow et al., 2006; Wiseman and Püttmann, 2006).

The knowledge about binding mechanisms between SOC and mineral surfaces that have been identified derived mainly from statistical correlations between soil mineralogy and the presence of soil organic matter (Kögel-Knabner et al., 2008). Stable

SOC in acidic temperate soils seems to be predominantly associated with Fe oxides and short-range order Al silicates, which provide large reactive surface areas (Eusterhues et al., 2005) with hydroxyl groups (Kögel-Knabner et al., 2008). The findings of Mikutta et al. (2006) and Wiseman and Püttmann (2005) suggested that amorphous or poorly crystalline phases are the main binding reagents. The separation of soils into density fractions showed that a large proportion of SOC in subsoils is associated with the heavy fraction due to complexation of SOC with mineral surfaces, and that the proportion increases with depth (Schulten and Leinweber, 2000). The mean residence time of SOC increases with increasing density, which indicates that the mineral-associated heavy fraction comprises stable SOC fractions (e.g., Sollins et al., 2006).

The black colour and the stabilisation of SOC in Cryptopodzols might also be related to the accumulation of charred organic matter. Fires have been a common feature of southern Alpine forests for at least 10,000 years (Tinner et al., 1999). Wildfires during the frequent dry periods and deliberate burning, used to promote the growth of chestnut trees in the region, has produced significant amounts of charred organic matter (Hajdas et al., 2007). Charcoal is considered to be highly resistant to decomposition due to its condensed aromatic structure and can, therefore, persist in soils or sediments over millennia (Bird and Cali, 1998; Skjemstad et al., 2004). The resistance of charcoal to biological or chemical decomposition is determined by the combustion conditions and depends on the elemental composition or chemical recalcitrance of the individual charcoal components (Krull et al., 2006). Recent studies, however, showed that charcoal particles or certain compounds of fire-derived organic matter, seem to be susceptible to surface oxidation and subsequent microbial decomposition (Cheng et al., 2006; Hockaday et al., 2007).

For the black soils in Southern Switzerland, it is hypothesised that a combination of two main mechanisms have led to the development of dark soil colour and high SOC stocks: the accumulation of charred organic matter by frequent fires, and sorptive processes like the formation of organo-metallic associations. We investigated charred organic matter (charcoal and BPCA), as well as Fe and Al oxides in three Cryptopodzols of Southern Switzerland and compared the results with a Cambisol.

This study aimed at identifying the importance of the two processes, structural recalcitrance and interaction with minerals, for the stabilisation of SOC in the investigated Cryptopodzols. If structural recalcitrance was the mechanism that led to the

high SOC stocks in Cryptopodzols, then one would expect to observe a close relationship between SOC and BPCA or macrocharcoal concentrations. The interaction with metals would be expressed by a close relationship between SOC and Fe and Al compounds.

Materials and methods

Study sites

We investigated four soil profiles located in the Southern Alps of Switzerland (Ticino; Figure 1). The humid and moderate climate in the area is characterised by a mean annual temperature of 12°C (January, 1°C; July, 22°C; Eidgenössisches Department des Innern, 1992) and a mean annual precipitation of 1800 mm (Lugano, 273 m asl). Forest fires are common during the rather dry winter period. Spring and autumn are generally humid, whereas the summers are sunny but have sporadic thunderstorms. Below 1000 m asl the deciduous forests are dominated by chestnut trees (*Castanea sativa* Mill). Other important tree species are *Quercus petraea* (Matt.) Liebl. and *Quercus pubescens* Willd., *Alnus glutinosa* Gaertner, *Fraxinus excelsior* L., *Betula pendula* Roth., *Fagus silvatica* L. and *Tilia cordata* Mill. At higher elevations (> 1000 m asl) stands of *Abies alba* and *Picea abies* prevail, partly mixed with *Fagus silvatica* and *Sorbus aucuparia* (Brassel and Brändli, 1999).

We studied three Cryptopodzols and a Cambisol at different locations (Table 1). Two sites (Cryptopodzols; P1, Pian d'Arf and P3, Prebonella) are located in the Misox valley near Roveredo (Grisons). The third Cryptopodzol (P2) is situated near Pura (Ticino) in the area of Lago di Lugano. The Cryptopodzols developed on crystalline parent material (Gneiss). The fourth profile (P4), a Cambisol, is located close to the Italian border near Sagno and developed on siliceous Mesozoic sediments that contain some carbonates (Flysch).

Soil sampling and analyses

Soil samples of 1-2 kg were collected from each horizon. A high amount of material for analyses is required to obtain representative values for soils in Alpine environments. The error range due to soil variability can be kept below 10 % for organic C and N by using large bulk sample sizes (see Hitz et al., 2002). Soil bulk density (three replicates; error range < 10 %; see Hitz et al., 2002) was determined using soil cores and by

volume replacement in stony soils. Soil samples were dried at 40°C, soil aggregates were crushed and material > 2 mm (soil skeleton) was removed by sieving. Total C and N contents of fine-earth material were measured with an elemental analyzer (Elementar Vario EL). The analytical error range is ± 2.5 %. Measurements were controlled with a well-defined soil standard (S3, Kantonales Labor Zürich). Soil pH was determined in 0.01 M CaCl₂ by using a soil:solution ratio of 1:2.5. After a pre-treatment with H₂O₂ (3%), particle size distribution of the soils was determined by sieving the coarser particles (2000 – 32 μ m) and measurement of the smaller size-fraction (< 32 μ m) with an X-ray-sedimentometer (SediGraph 5100) according to Stoke's law (Gee and Bauder, 1986).

Macrocharcoals, i.e. carbonised fragments of wood that are visible by the naked eye (diameter > 2 mm) were separated from the soils by hand. The material was floated in water, the remnants were rinsed through a sieve and dried at 40°C. A selection of charcoal particles was radiocarbon dated after the wood species had been identified. The oldest charcoal (11180 $\pm$ 75 BP or 11270-10980 calBC; *Pinus* sp.) was found in Cryptopodzol Pura (P2) at the transition from B to C horizon. ¹⁴C AMS data and charcoal wood species were published in Hajdas et al. (2007).

Black carbon concentrations were determined in fine-earth using the benzene polycarboxylic acid (BPCA) marker method as described by Brodowski et al. (2005b). Results are given in the following as BPCA carbon (BPCA-C). The samples (three replicates) were first treated with trifluoroacetic acid (TFA) to remove polyvalent cations and then digested with HNO₃ at 170 °C for eight hours. After filtration the sum of BPCAs in each sample was analysed after derivatisation on a gas chromatograph equipped with a flame ionisation detector.

The dithionite-, pyrophosphate- and oxalate-extractable fractions were measured for the elements Fe and Al (McKeague et al., 1971). The extracts were centrifuged for 10 min at 4000 rpm and then filtered through a 0.45 μ m filter (S&S, filter type 030/20). Element concentrations were measured by atomic absorption spectroscopy (AAS).

The pyrophosphate extraction is often used to characterise the organically-bound Al fraction. There are, however, some limitations regarding this method (Kaiser and Zech, 1996). Kleber et al. (2004) presumed that the alkaline pyrophosphate extractant attacks not only organic fractions but, to a certain degree, also hydroxy-like Al in the interlayers of clay minerals or gibbsite. The dithionite reagent extracts various forms of

organic and inorganic Al and Fe: organic Al, noncrystalline and crystalline oxyhydroxides (e.g., Al substituted in ferrihydrite and goethite), some Al in hydroxy interlayers and allophanes (Wada, 1977; Shoji and Fujiwara, 1984; Borggaard, 1988; Dahlgren and Ugolini, 1991), organically-bound Fe, noncrystalline and crystalline Fe-oxyhydroxides and also Fe-bearing silicates, especially nontronite (Borggaard, 1988). The oxalate extraction dissolves organically-bound forms as well as weakly or non-crystallised forms.

The soil lightness was expressed as L^* (CIE 1976 Standard Observer). The L^* values indicate the extinction of light on a scale from $L^* 0$ (absolute black) to $L^* 100$ (absolute white). The dried, homogenised but not ground soil samples were measured in triplicates using a spectrophotometer (Dr. Lange spectro-color) by observing the diffused reflected light under standardised observation conditions.

The density fractionation procedure was adapted from Christensen (1992) and Glaser et al. (2000). The following fractions were separated: $< 1.0 \text{ g cm}^{-3}$, $1.0\text{-}2.0 \text{ g cm}^{-3}$, $2.0\text{-}2.4 \text{ g cm}^{-3}$ and $> 2.4 \text{ g cm}^{-3}$. According to Glaser et al. (2000) and Sollins et al. (2006) the light fraction $< 1.0 \text{ g cm}^{-3}$ includes plant-derived polysaccharides, lignin, cutin, suberin and charcoal. The fraction $1.0\text{-}2.0 \text{ g cm}^{-3}$ contains, besides a high amount of organic carbon, also a mineral fraction ("organo-mineral" fraction). In fraction $1.0\text{-}2.0 \text{ g cm}^{-3}$ and especially in fraction $> 2.0 \text{ g cm}^{-3}$ aggregates and organo-mineral associations increasingly protect organic material from decay (Christensen, 1992; Egli et al., 2009). In fraction $2.0\text{-}2.4 \text{ g cm}^{-3}$ most soil organic matter should be adsorbed to metals and minerals, the mineral components generally prevail. Density fractions were separated according to Christensen (1992) using a sodium polytungstate density solution: (1) 20 g of soil was put into suspension in 1000 ml water and after 2 h the fraction $d \leq 0.998 \text{ g cm}^{-3}$, which was floating on the surface, was recovered by filtering; (2) the aggregates in 5 g soil ($d > 0.998 \text{ g cm}^{-3}$), suspended in 25 ml density solution ($d = 2 \text{ g cm}^{-3}$), were dispersed using ultrasonic (50 J ml^{-1}) and the fraction $d \leq 2 \text{ g cm}^{-3}$ was separated by filtering after centrifugation of the solution; (3) 25 ml density solution ($d = 2.4 \text{ g cm}^{-3}$) was added to the material left in the centrifuge beaker and after ultrasonic dispersion (50 J ml^{-1}) and centrifugation the fraction $d = 2\text{-}2.4 \text{ g cm}^{-3}$ was separated by filtering; (4) the material left in the centrifuge beaker is the fraction $d > 2.4 \text{ g cm}^{-3}$. The washed and dried samples were analysed for lightness, carbon and nitrogen as described

before. Only a few samples of the fraction $< 1 \text{ g cm}^{-3}$ could be analysed for soil colour due to the very small amounts of sample recovered.

Results

Bulk soil

All soils contain large amounts of skeleton material (particle size $> 2 \text{ mm}$), which is typical for soils of mountainous areas (Table 2). They have a sandy to silty-sandy texture, are deeply acidified and have a very low bulk density ($< 1 \text{ g cm}^{-3}$) in the top- and subsoil.

Soil organic carbon (SOC) concentrations were high in all soils, with similar values in the upper horizons (Table 3). The Cryptopodzols had particularly high SOC concentrations in the B horizons with values of up to 66 g C kg^{-1} (P2). The SOC concentrations decreased with depth with the exception of Cryptopodzol P1, where concentrations were relatively low between 15 to 50 cm depth, but higher in the deeper soil horizons.

The organic C stocks of the whole soil profiles (without C-horizon) were more than two to three times higher in the Cryptopodzols (241 to 339 t C ha^{-1}) than in the Cambisol (110 t C ha^{-1}). The high SOC concentration in Cryptopodzol P1 was also reflected by the high SOC stock in the subsoil horizon A1b (161 t C ha^{-1}).

All Cryptopodzol profiles were rich in charcoal fragments throughout the whole soil, in contrast to the Cambisol that contained only very few macrocharcoal particles. The largest stock of charcoal was found in Cryptopodzol P1 with $31 \text{ t charcoal ha}^{-1}$ (total profile), where horizon A1b contained a remarkably high amount of charcoal.

Charred organic carbon, determined using the molecular marker BPCA, was present in all profiles. BPCA carbon (BPCA-C) concentrations and stocks were smallest in the Cambisol. In the Cryptopodzols, concentrations reached more than $6.6 \text{ g BPCA-C kg}^{-1}$ (AE horizon, P2). Similar to the distribution of charcoal, BPCA-C concentrations were, in general, largest in the deeper A or B horizons. The proportion of BPCA-C to SOC was highest in Cryptopodzol P1, where it reached 13 % in the subsoil. The total stocks in the Cryptopodzols were large, they reached $17.2 \text{ t BPCA-C ha}^{-1}$ in Cryptopodzol P1, with the horizon A1b having the largest stock (6.1 t ha^{-1}).

The soil colour (Table 2) was darkest in Cryptopodzol P2 (min. $L^* = 26$) and lightest in the Cambisol (min. $L^* = 47$). The Cryptopodzols, with the exception of the

A-horizon of profile P1, were very dark throughout the soil profile, down to the deepest B-horizons.

The extractable Al and Fe concentrations (dithionite, oxalate and pyrophosphate; Table 4) were in a similar range in all Cryptopodzols, while the amounts were lower in the Cambisol. Noticeable is the increase in Al and Fe in the lower A-horizons of Cryptopodzol P1. The pyrophosphate-extractable Fe and Al contents in the topsoil of Cryptopodzol P2 exceeded the oxalate extractable fraction. Fe_p and Al_p contents often even equaled the dithionite-extractable contents in the topsoil.

Density fractions

Density fractionation (Figure 2) revealed that the carbon in the topsoil horizons of the Cryptopodzols was mainly present in the lighter fractions ($< 2.0 \text{ g cm}^{-3}$) with a maximum of 94 % in the A horizon of P2. The proportion of SOC in the lightest fraction ($< 1.0 \text{ g cm}^{-3}$) varied among the profiles. While the contribution of SOC in this fraction was very small in Cryptopodzol P1, about half of SOC was present in the lightest fraction in the A horizon of P2. In contrast, the density fractions in the Cambisol showed an irregular distribution with depth, with surprisingly high proportions of SOC in the fraction $< 1.0 \text{ g cm}^{-3}$ even in the C horizon. More than 40 % of total SOC was still present in the fractions $< 2.0 \text{ g cm}^{-3}$ of the humic B-horizons of the Cryptopodzols, although the proportion of mineral-associated carbon (fractions $> 2.0 \text{ g cm}^{-3}$) increased with depth. The C/N ratios (Table 5) do not show clear trends within and between the profiles, they were slightly higher in the fractions $< 2.0 \text{ g cm}^{-3}$ than in the heavy fraction. The average lightness values increased from $L^* = 27$ for all samples of the fraction $< 2.0 \text{ g cm}^{-3}$, which is very dark, to $L^* = 67$ in the heavy fractions.

Discussion

The SOC stocks of the investigated soils reached values of up to 340 t C ha^{-1} , which is typical for forest soils of Southern Switzerland (Perruchoud et al., 2000), but much higher than the average soil C stocks of 120 t C ha^{-1} in Swiss forest soils (Bolliger et al., 2008). They even reached values of Russian Chernozems under grassland which have particularly high carbon stocks ($280\text{--}340 \text{ t C ha}^{-1}$; Torn et al., 2002). Models of SOC stocks using litter inputs from published data, decomposition rates and climatic data had failed to predict the extraordinary high SOC stocks in Southern Switzerland

(Perruchoud et al., 1999), suggesting that SOC accumulation is not caused by high input of litter but by stabilisation mechanisms in the soil. SOM stabilisation in soils is still controversially discussed. As an example, Krull et al. (2006) considered molecular recalcitrance as the main trigger of long-term SOM stabilisation. Others concluded that, except for charred organic matter, there is hardly any analytical evidence for intrinsic molecular recalcitrance being a major stabilisation factor in soils, and that aliphatic compounds, polysaccharides and proteinaceous moieties were found in relatively old SOM fractions (Gleixner et al., 2002; Knicker, 2004; Marschner et al., 2008).

Is SOM stabilised by organo-metallic complexes?

Organo-mineral interactions are generally thought to be the main mechanism for SOM stabilisation in Podzols and other acidic soils (Lundström et al., 2000a, 2000b; Nierop et al., 2002; Kleber et al., 2005). Blaser et al. (1997) concluded that mainly organo-metallic complexes are responsible for the stabilisation of SOM and the high SOC stocks in Cryptopodzols.

Cryptopodzolic soils usually occur under chestnut (*Castanea sativa*) stands. Decomposing chestnut wood and leaves release tannins and other polyphenols (Luster et al., 1996). Polyphenols are incorporated into the soil as compounds of dissolved organic matter (DOM), where they bind with Al, Fe and other trace metals that derive from the parent material (Blaser and Sposito, 1987; Brunner and Blaser, 1989). The Cryptopodzols of Southern Switzerland contain more sesquioxides than Cambisols of the Swiss Plateau (Zimmermann et al., 2006). Zanelli et al. (2006) found that Cryptopodzols display early stages of podzolisation, and that they contain imogolites and allophanes in the subsoil that are capable of forming strong organo-mineral complexes. Organo-metallic complexes are typical for Andosols, which have characteristics similar to the Cryptopodzols. They are very dark, rich in charred organic matter and poorly crystalline Al and Fe-oxides (Al_o , Fe_o). Low alkyl C values and the presence of allophanes suggested that aluminium-organic complexes protect SOM from microbial breakdown (Baldock et al., 1992; Golchin et al., 1997a, 1997b).

The contents of Fe and Al oxides of all three Cryptopodzols increased from the A to Bhs horizons (Table 4) which is indicative for the podzolization in these profiles. As shown in Figure 3, the SOC concentrations in all soils were more closely related to the pyrophosphate-extractable and therefore organically bound iron ($R^2 = 0.645$, $p < 0.001$)

and aluminium ($R^2 = 0.502$, $p < 0.001$) than to BPCA-C concentrations ($R^2 = 0.346$, $p < 0.01$). SOC and oxalate-extractable iron ($R^2 = 0.275$, $p < 0.05$) correlated whereas the correlation with aluminium ($R^2 = 0.089$, $p > 0.05$) was not significant. Organically-bound iron seems to influence the soil colour (L^*) less ($R^2 = 0.384$, $p < 0.01$) than the SOC concentration ($R^2 = 0.662$, $p < 0.001$), as shown in Figures 3 and 4. The correlation of L^* with SOC could be described with a polynomial regression - indicating that a small increase in SOC rapidly darkens the soil until a certain level is reached. The correlation analysis supports the concept of SOM stabilisation by sesquioxides and metal-organic complexes (cf. correlation with Fe_p and Al_p , see also Zanelli et al., 2007). For individual profiles, the proportions of SOM in the medium and heavy density fractions increased with soil depth (Figure 2), which indicated an increasing contribution of organo-mineral complexes and of SOM coatings on mineral matter (Glaser et al., 2000). With an average of 45 % in the whole profile, a higher proportion of SOC was found in the light fractions of the Cryptopodzols than of the Cambisols (33 %). This strongly suggests that not only organo-mineral associations but also the resistance of particulate organic matter (charcoal) against decomposition contributed to the extraordinary high SOM stocks in the Cryptopodzols, especially when considering that charred organic matter could be also present in the medium and heavy density fractions (Glaser et al., 2000).

The stabilisation mechanisms, however, could not be easily assigned to organo-mineral interactions or chemical recalcitrance because one Cryptopodzol (P1) exhibited significant erosion and accumulation features (see Table 2). According to mineralogical investigations (X-ray diffraction, FTIR analyses; Nötzli, 2005), it is highly probable that less weathered material was deposited on top of a former soil at Cryptopodzol P1. The statistically based process analysis may have been partially influenced by this effect.

Charcoal as potentially recalcitrant carbon compound?

Some organic compounds like charcoal are considered to be of secondary recalcitrance, i.e. the chemistry of primary molecules has been altered by polycondensation or polymerisation (von Lützow et al., 2006). In soil carbon models, the charcoal fraction is therefore considered as an inert pool (Skjemstad et al., 2004), although it is known that charcoal could become more functionalised and degrades over time, which makes it susceptible to decomposition (Bird et al., 2002; Cheng et al., 2006; Cohen-Ofri et al.,

2006; Hockaday et al., 2006). The radiocarbon ages of charcoal particles found in our soils that reach up to 13,000 years BP (Hajdas et al., 2007), however, indicated that macrocharcoal was stable over millennia.

Charcoal and BPCA-C were found in all soils, with highest amounts in the Cryptopodzols. Cryptopodzol P1 contained the highest stocks of charcoal and BPCA-C. Taking into account that ca. 70 % of charcoal is carbon (Eckmeier et al., 2007b), the calculated macrocharcoal C stock in this profile would be 22 t C ha⁻¹. Mean BPCA and charcoal C stocks together were 39 t C ha⁻¹, which accounts for 12 % of total SOC stocks.

Although the distribution of charcoal and BPCA in the soils was similar, BPCA-C stocks correlated better with SOC stocks ($R^2 = 0.429$, $p < 0.01$) than with charcoal mass stocks ($R^2 = 0.211$, $p < 0.05$), probably because we determined macrocharcoal in the fraction > 2 mm and because it can be composed of variable amounts of carbon, depending on fire properties and wood type. Charcoal stocks, however, correlated well to the pattern of SOC stocks in all profiles ($R^2 = 0.541$, $p < 0.001$).

Data on BPCA-C stocks in other soils are rare. With stocks of 6 to 17 t BPCA-C ha⁻¹ the investigated Cryptopodzols are close to values of carbon-rich Chernozems from fire-prone ecosystems (Rodionov et al., 2010, note that BPCA-C was multiplied by a conversion factor of 2.27). Hammes et al. (2008) estimated BPCA-C stocks of 20 and 19 t C ha⁻¹ for two Russian Chernozem profiles, a German chernozem-like soil contained 10 t BPCA-C ha⁻¹ (Kleber et al., 2003).

Across all soils, BPCA-C concentrations did not explain the amount of SOC very well ($R^2 = 0.346$, $p < 0.01$). The contribution of BPCA-C to the total SOC in our soils reached a maximum of 12.5 % BPCA-C at 110-140 cm depth of profile P1. BPCA-data for other fire-affected soils is in most cases only available for topsoils. This data shows comparable proportions, e.g. in topsoils of German Chernozems and Phaeozems (54-65 g BPCA-C kg⁻¹ SOC; Brodowski et al., 2005b). Rodionov et al. (2006) measured BPCAs in whole soil profiles in the Russian steppe and also found a maximum in the subsoil, between 30 and 50 cm depth, which was related to leaching and particulate transport as well as to decreasing BPCA ratios by inputs of fresh organic matter from plant roots. Dai et al. (2005) measured BPCAs in a fire-prone mixed-grass savannah in depths of up to 20 cm and also observed an increase with depth (5-9 % BPCA-C at 0-10 cm, 7-13 % BPCA-C at 10-20 cm).

As shown in Figures 3 and 4, the soil colour (L^*) of all samples correlated significantly with the BPCA-C concentration ($R^2 = 0.625$, $p < 0.001$) and the SOC concentration ($R^2 = 0.662$, $p < 0.001$). The same trend is visible in the density fractions, where the light fractions ($< 2 \text{ g cm}^{-3}$) were darker than the heavier fractions ($> 2 \text{ g cm}^{-3}$), which could be a result of higher SOC concentrations ($R^2 = 0.619$, $p < 0.001$). These results are consistent with findings from Spielvogel et al. (2004) and Eckmeier et al. (2007a) who showed that soil colour is related to aromatic C concentrations. It is known from a variety of studies that the light fraction usually contains particulate charcoal (Skjemstad et al., 1996; Golchin et al., 1997a; Brodowski et al., 2005a; Sollins et al., 2006). Glaser et al. (2000) measured BPCA-C also in the medium and heavy fractions of Terra Preta soils, but the highest concentrations were found in the light fractions. They concluded that inert particulate black carbon is responsible for the high charred organic matter concentrations in Terra Preta soils.

The large stocks of charcoal fragments and the high radiocarbon ages of charcoal particles indicate that both the high fire frequency in Southern Switzerland (Tinner et al., 1999; Hajdas et al., 2007) and/or the slow degradation or even chemical recalcitrance of charcoal contributed substantially to the long-term C storage in these soils.

Is charred organic matter stabilised by organo-mineral complexes?

We found that not only SOC concentrations in general but also the BPCA-C concentrations correlated closely with Fe_p ($R^2 = 0.573$, $p < 0.001$) and Al_p ($R^2 = 0.737$, $p < 0.001$). Some SOC seemed to be stabilised by Fe-oxyhydroxides due to the correlation of SOC with Fe_o ($R^2 = 0.524$, $p > 0.05$). There is no significant correlation of BPCA-C with Fe_o and Al_o . This suggests the presence of solid metal-organic complexes in which BPCA-C is specifically involved.

Andosols in Japan have characteristics similar to the Cryptopodzols. They are very dark, have a high C content and are found in frequently burned grassland areas. Andosols are rich in charred organic matter and poorly crystalline Al and Fe oxides. Baldock et al. (1992) and Golchin et al. (1997a, 1997b) showed, among others, that aluminium-organic complexes in Andosols, favoured by the presence of allophanes, protect SOM from microbial breakdown.

Mineral compounds could be trapped physically within the fine pores of charcoal particles, or they could bind to the oxidized functional groups (carboxylic and phenolic functionalities) on the char surfaces (Glaser et al., 2002; Lehmann et al., 2005), especially of older charcoal particles (Cohen-Ofri et al., 2006). Brodowski et al. (2005a) investigated black carbon particles in different soil density fractions with SEM/EDX and found that despite being subject to ultrasonic treatment the particles stayed attached to minerals. They suggested that these interactions were facilitated by the relatively large surface areas of black carbon particles together with the occurrence of reactive deprotonated functional groups, and that the formation of organo-mineral complexes could lead to the formation of aggregates, which physically protect the charcoal from further decay. A similar mechanism must also be assumed for the investigated soils where organo-mineral complexes could contain a substantial amount of BPCA-C and protect it from biodegradation. In addition, we hypothesise that a significant part of the charred organic material, e.g. the very old charcoal, must degrade very slowly.

Conclusions

Our study on SOM stabilisation in C-rich soils in Southern Switzerland showed that: (i) charcoal, which has been present in the soils for 13,000 years, and BPCA-C can be detected in much higher concentrations and stocks in the Cryptopodzols than in the Cambisol; (ii) charred organic matter, measured as BPCA, intensifies the dark soil colour; (iii) the amount of SOC and BPCA-C correlated well with the concentrations of pyrophosphate-extractable, organically bound Al and Fe fractions in the soils; and (iv) SOC was mainly present in the light fraction of topsoils, but also in the medium and heavy fractions in the subsoil horizons. Our results suggest that organo-mineral, or organo-metallic complexation and the recalcitrance of charcoal particles are responsible for stabilising SOM. The presence of free particulate charcoal (not bound to the mineral phase) and its significant correlation to SOC is an evidence that not only sorption to mineral surfaces but also molecular recalcitrance is an important factor. BPCA-C, however, strongly interacts with metals that are organically-bound, and contributes through this mechanism to the stabilisation of SOM. However, the details of chemical interactions and the nature of the formed complexes still remain unclear. We conclude that fire-derived C contributes significantly to the black colour and to the high C stocks

in southern Switzerland. In addition, statistical evidence suggests that sorption processes stabilise plant and, also very likely, fire-derived SOC, mainly in the subsoil.

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Table 1 Characteristics of investigated sites.

Site	Altitude m asl	Exposure	Slope %	Dominating vegetation	Soil type	Geological substrate
Pian d'Arf P1	515	N	35	<i>Castanea sativa</i> , <i>Fagus silvatica</i> , <i>Picea abies</i>	Humic Umbrisol ²⁾ Cryptopodzol ¹⁾	Granite, orthogneiss
Pura P2	650	SW	22	<i>Castanea sativa</i> , <i>Fagus silvatica</i> , <i>Quercus sp.</i>	Humic Umbrisol ²⁾ Cryptopodzol ¹⁾	Granite, orthogneiss
Prebonella P3	950	E	56	<i>Castanea sativa</i> , <i>Picea abies</i>	Humic Umbrisol ²⁾ Cryptopodzol ¹⁾	Granite, orthogneiss
Sagno/ Brughee P4	730	SW	40	<i>Castanea sativa</i> , <i>Fraxinus</i> <i>excelsior</i> , <i>Fagus silvatica</i>	Dystic Cambisol ²⁾	Mesozoic sediments (Flysch)

¹⁾ Cryptopodzol according to Blaser et al. (1997); ²⁾ IUSS Working Group (2006).

Table 2 Physical properties, pH and colour (L*) of the investigated soils.

Site/horizon	Depth	Bulk density	Sand	Silt	Clay	Skeleton	pH	Colour
	cm	$g\ cm^{-3}$	$g\ kg^{-1}$	$g\ kg^{-1}$	$g\ kg^{-1}$	$g\ kg^{-1}$	CaCl ₂	L*
<i>Cryptopodzol P1</i>								
A	0-15	0.39	643	303	54	123	3.8	40.3
AB	15-50	0.82	677	270	53	311	4.3	45.1
A1b	50-95	1.01	563	342	95	214	4.3	35.0
A2b	95-110	0.74	560	370	70	221	4.3	39.3
Bh _{sb}	110-140	0.83	570	380	50	219	4.5	41.4
B _b	140-200	0.90	537	407	56	293	4.9	52.4
BC _b	200-220	1.02	700	270	30	560	4.8	57.1
<i>Cryptopodzol P2</i>								
A	0-13	0.51	n.d.	n.d.	n.d.	19	3.5	27.5
AE	13-30	0.55	703	220	77	38	4.4	25.6
B _{hs} 1	30-40	0.61	n.d.	n.d.	n.d.	57	n.d.	30.4
B _{hs} 2	40-50	0.63	753	184	63	69	4.6	34.4
B	50-68	0.71	739	177	84	206	5.0	43.4
C	>68		720	222	58	n.d.	5.1	59.6
<i>Cryptopodzol P3</i>								
A	0-25	0.45	720	230	45	244	4.2	33.7
AB	25-35	0.51	680	270	50	130	4.3	33.6
B _h	35-55	0.62	670	300	40	107	4.5	34.1
B _{hs}	55-85	0.70	650	330	30	216	4.6	41.2
BC	85-110	0.59	810	170	10	220	4.7	42.1
C	>110	0.72	880	110	10	489	4.9	54.9
<i>Cambisol P4</i>								
A	0-10	0.65	n.d.	n.d.	n.d.	102	n.d.	47.3
BA	10-21	0.80	370	580	50	89	3.2	50.3
B _w	21-40	0.73	370	579	51	140	4.2	49.1
BC1	40-60	0.73	457	497	46	141	4.4	55.5
BC2	60-90	0.59	n.d.	n.d.	n.d.	445	n.d.	64.8
C	90-150	0.90	697	290	13	528	4.4	69.8

n.d. = not determined

Table 3 Carbon, nitrogen, BPCA-C and charcoal concentrations and stocks. The sum is given for the stocks in the whole profiles.

Site/ horizon	N <i>g kg⁻¹</i>	SOC <i>g kg⁻¹</i>	C/N	BPCA-C <i>g kg⁻¹</i>	BPCA-C/ SOC %	SOC stock <i>t ha⁻¹</i>	Charcoal stock <i>t ha⁻¹</i>	BPCA-C stock <i>t ha⁻¹</i>
<i>Cryptopodzol P1</i>								
A	3.9	73.1	19	1.1	1.5	37.2	0.1	0.5
AB	0.5	19.6	38	0.8	4.1	38.7	2.1	1.6
A1b	1.6	45.2	29	1.7	3.8	161.4	19.1	6.1
A2b	1.0	30.5	30	3.8	12.4	26.4	1.7	3.3
Bhsb	0.8	23.8	31	3.0	12.5	46.0	1.1	5.7
Bb	0.3	6.7	22	0.0	0.0	25.6	7.1	0.0
BCb	0.1	3.9	43	n.d.	n.d.	3.5	0.0	n.d.
Σ						338.8	31.2	17.2
<i>Cryptopodzol P2</i>								
A	6.9	119.1	17	5.7	4.8	77.7	1.3	3.7
AE	4.5	87.5	20	6.6	7.5	78.7	1.2	5.9
Bhs1	3.1	65.6	21	6.1	9.3	38.0	1.8	3.5
Bhs2	2.2	44.3	20	3.4	7.7	26.1	0.1	2.0
B	1.2	21.3	18	0.2	0.8	20.5	0.1	0.2
C	0.2	5.8	24	n.d.	n.d.	n.d.	n.d.	n.d.
Σ						241.0	4.5	15.3
<i>Cryptopodzol P3</i>								
A	5.8	93.7	16	1.2	1.2	80.1	0.2	1.0
AB	3.7	62.2	17	2.7	4.3	27.4	0.1	1.2
Bh	3.2	58.0	18	1.2	2.1	63.7	0.6	1.4
Bhs	1.4	29.9	21	0.8	2.7	48.9	0.7	1.3
BC	1.4	26.0	19	1.2	4.7	29.9	0.6	1.4
C	0.0	6.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Σ						250.0	2.2	6.3
<i>Cambisol P4</i>								
A	4.2	75.4	18	1.1	1.4	22.1	0.0	0.3
BA	1.6	27.0	17	0.6	2.2	21.7	0.0	0.5
Bw	1.6	26.9	17	0.3	1.2	32.2	0.1	0.4
BC1	0.7	15.5	23	0.3	2.1	19.5	0.0	0.4
BC2	0.6	7.5	14	n.d.	n.d.	7.4	0.0	n.d.
C	0.3	2.9	10	n.d.	n.d.	7.4	0.0	n.d.
Σ						110.3	0.1	1.6

n.d. = not determined

Table 4 Concentrations of dithionite (d), oxalate (o) and pyrophosphate (p) extractable Al and Fe.

Site/ horizon	Al _d g kg ⁻¹	Al _o g kg ⁻¹	Al _p g kg ⁻¹	Fe _d g kg ⁻¹	Fe _o g kg ⁻¹	Fe _p g kg ⁻¹
<i>Cryptopodzol P1</i>						
A	6.5	6.0	6.0	9.0	4.6	4.6
AB	6.3	9.5	5.2	10.0	6.2	2.6
A1b	11.0	10.6	5.9	13.8	8.9	4.7
A2b	10.4	10.9	7.7	13.8	9.4	3.9
Bhsb	9.2	11.1	5.4	14.3	9.6	2.1
Bb	5.6	9.0	1.7	10.4	4.9	0.3
BCb	3.4	3.8	1.2	6.7	2.6	0.2
<i>Cryptopodzol P2</i>						
A	6.4	6.2	8.7	11.6	7.9	12.1
AE	14.6	10.4	14.1	12.3	5.8	9.5
Bhs1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bhs2	13.2	11.7	10.2	12.6	4.5	6.0
B	9.0	11.4	5.2	10.8	3.6	1.9
C	3.8	5.4	2.0	5.4	1.2	0.4
<i>Cryptopodzol P3</i>						
A	n.d.	8.5	6.2	11.9	7.0	4.2
AB	n.d.	9.4	6.6	13.4	7.9	4.8
Bh	n.d.	9.8	4.9	13.0	7.6	3.3
Bhs	n.d.	8.1	3.5	12.5	6.8	2.0
BC	n.d.	3.9	1.3	9.3	4.0	0.4
C	n.d.	4.0	0.9	5.9	2.1	0.2
<i>Cambisol P4</i>						
A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BA	2.4	1.5	2.2	5.8	2.8	4.2
Bw	3.2	2.1	3.4	6.1	3.5	5.8
BC1	3.9	2.5	3.1	5.7	2.8	3.8
BC2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
C	4.3	3.1	3.8	5.8	2.4	3.6

n.d. = not determined

Table 5 Carbon and nitrogen concentrations in the density fractions.

Site/ horizon	< 1 g kg ⁻¹			1 - 2 g kg ⁻¹			2 - 2.4 g kg ⁻¹			> 2.4 g kg ⁻¹		
	Corg g kg ⁻¹	N	C:N	Corg g kg ⁻¹	N	C:N	Corg g kg ⁻¹	N	C:N	Corg g kg ⁻¹	N	C:N
<i>Cryptopodzol P1</i>												
A	392.3	13.7	29	213.6	11.2	19	86.1	4.8	18	5.8	0.2	36
AB	357.3	7.7	47	285.2	7.0	41	67.9	2.9	24	2.9	0.0	
A1b	360.3	8.3	43	295.8	8.3	36	85.9	3.5	24	5.9	0.1	45
A2b	357.1	7.2	50	234.9	6.5	36	68.6	3.4	20	4.6	0.2	24
Bhsb	316.9	7.3	44	301.1	7.2	42	24.6	1.2	21	3.5	0.2	20
Bb	n.d.	n.d.	n.d.	300.8	7.3	41	34.7	2.0	18	3.1	0.1	25
BCb	n.d.	n.d.	n.d.	37.5	1.2	32	30.3	1.4	22	2.1	0.1	19
<i>Cryptopodzol P2</i>												
A	184.5	10.4	18	213.7	12.2	18	70.0	4.6	15	1.6	0.3	5
AE	227.7	8.7	26	218.9	10.7	20	71.1	4.1	17	6.2	0.0	
Bhs1	n.d.	n.d.	n.d.	217.2	10.8	20	80.3	5.1	16	6.7	0.2	28
Bhs2	298.1	8.6	35	201.9	8.8	23	59.8	3.7	16	6.2	0.9	7
B	273.1	8.5	32	188.6	7.7	24	48.6	3.5	14	5.1	0.3	16
C	n.d.	n.d.	n.d.	122.0	9.0	14	25.0	2.6	10	2.1	0.1	15
<i>Cryptopodzol P3</i>												
A	343.0	13.9	25	204.8	13.2	15	75.0	4.6	16	7.1	0.2	47
AB	279.3	11.2	25	219.5	10.9	20	97.6	6.2	16	7.2	0.2	34
Bh	332.8	9.5	35	216.0	9.8	22	75.2	4.8	16	6.1	0.3	23
Bhs	383.8	8.1	47	252.7	9.4	27	32.4	2.3	14	6.6	0.3	26
BC	212.5	9.0	24	243.0	7.5	32	45.5	3.0	15	5.4	0.2	26
C	228.0	5.9	39	n.d.	n.d.	n.d.	36.4	1.3	27	2.0	0.1	22
<i>Cambisol P4</i>												
A	228.0	11.3	20	227.6	12.1	19	99.1	7.1	14	5.2	0.6	10
BA	231.5	7.6	30	247.0	9.4	26	35.7	2.8	13	4.6	0.0	
Bw	274.2	9.6	28	243.0	9.9	24	43.9	3.6	12	4.4	0.2	28
BC1	274.9	7.9	35	275.5	7.6	36	35.8	2.9	13	4.6	0.3	16
BC2	346.3	8.9	39	n.d.	n.d.	n.d.	25.9	2.3	11	3.5	0.7	5
C	252.7	9.2	27	n.d.	n.d.	n.d.	7.3	1.9	4	1.6	0.1	15

n.d. = not determined

Figure 1 Map of Switzerland showing the investigation area in southern Switzerland and the location of the soil profiles (black dots): Cryptopodzol Roveredo (P1), Cryptopodzol Pura (P2), Cryptopodzol Prebonella (P3) and Cambisol Sagno/Brughee (P4).

Figure 2 The proportion of SOC in the lightest (black), light (dark grey), intermediate (grey) and heavy (white) density fractions, shown for Cryptopodzols P1 and P2 and Cambisol P4.

Figure 3 Relationships between soil colour (L*), soil organic carbon (SOC), BPCA carbon (BPCA-C), and pyrophosphate extractable Fe (Fe_p) and Al (Al_p).

Figure 4 Relationships between soil colour (L*) and soil organic carbon (SOC) in all bulk soil samples (A), and in the density fractions (B).