



Short-term effects of plant litter addition on mineral surface characteristics of young sandy soils



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ABSTRACT

Initial stages of soil development are characterized by structural changes of mineral surfaces over time. The specific surface area (SSA) is closely related to pedogenic properties and soil organic matter (SOM). Interactions between SOM and mineral surfaces induce quantitative and qualitative changes in SSA and corresponding soil properties. However, the knowledge about ranges, effects and mechanisms of organic coverage in the very initial phase of pedogenesis is very limited. Therefore, our objective was to study these processes in young sandy soils and the effects of plant litter addition. Soil samples taken from the constructed catchment “Chicken Creek” were used in a microcosm experiment over 80 weeks. The silt and clay fractions of samples (<63 μm) were analyzed before the experiment and after 40 and 80 weeks. The effects of litter addition and weathering on SSA were assessed using the BET-N₂ sorption approach. We found increases of SSA between 16.4% and 41.6% within the 80 week experimental period, but a relative reduction in SSA due to organic coverage of these new surfaces after plant litter addition. The removal of the soil organic matter (SOM) by mulling increased SSA (6.8–12.9%). The results for SSA corresponded to changes in surface specific parameters like cation exchange capacity (CEC), surface enthalpy and the fractional coverage of mineral surfaces by SOM. In conclusion, the results showed that the soils were clearly in a very initial state of soil development. However, the potential of these young sandy soils to adsorb nutrients and soil organic matter as one of the main important soil functions clearly increased within the relatively short experimental period and changes in SSA indicate relatively large increases in mineral surfaces within short time periods during the initial phase of soil development compared to long-term pedogenesis.

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1. Introduction

The initial stage of soil development is characterized to a high degree by structural changes. Soil development results in changes in chemical and physical properties as a function of soil age (White et al., 1996; Suarez and Wood, 1996; West et al., 2005). Chemical and physical functions of mineral soils, particularly of the fine-grained soil fractions depend largely on the amount of its specific surface area (SSA) (Lutenegger and Cerato, 2001). Studies have shown that SSA is closely linked to pedogenic properties, such as cation exchange capacity (Banin and Amiel, 1970; Evans, 1982), liquid limit (Farrar and Coleman, 1967), and swelling potential (Dasog et al., 1987). In addition to soil oxides (Borggaard, 1982), silt and clay minerals (soil fraction of <63 μm) are key indicators affecting the SSA (Keil and Hedges, 1993; Ransom et al., 1998; Hepper et al., 2006; Macht et al., 2011). As a result of differences in mineralogy and particle-size distribution, the SSA of soils shows large variations (Yukselen-Aksoy and Kaya, 2010). Besides mineral surfaces, the soil pore structure

is an important parameter for chemo-physical processes in soils (Filimonova et al., 2006).

Soil organic matter (SOM) influences both, SSA (Mayer, 1994) as well as pedogenic pore structures (Feller et al., 1992; Kaiser and Guggenberger, 2003). Direct proportionality between SSA and SOM has been shown by Mayer (1994). However, the understanding of processes and range of SOM coverage on soil mineral surfaces is still incomplete (Wagai et al., 2009), in particular in the initial stages of pedogenic development. As a result of interaction of organic matter with mineral surfaces changes occur in both chemical and physical properties (Mayer, 1999), reducing the sorption capacity of soils by covering with SOM. The significant increase of SSA after removal of SOM demonstrates that coverage of soil surfaces decreases SSA (Feller et al., 1992; Mayer and Xing, 2001; Wagai et al., 2009). Therefore, the abundance of mineral surfaces seems to be strongly related to SOM storage (Kahle et al., 2002). SSA analysis using N₂ sorption is based on the method by Brunauer, Emmet and Teller (BET; Brunauer et al., 1938). Specific surface area measurements using the BET approach are considered to access the external area of soil mineral surfaces and to generate low specific surfaces of SOM in a magnitude of 1 m²·g⁻¹ or less (Burford et al., 1964; Chiou et al., 1990; de Jonge and

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Mittelmeijer-Hazeleger, 1996; Mayer, 1999; Kaiser and Guggenberger, 2007). Therefore, the influence of SOM on mineral surfaces and pores could be demonstrated.

Weathering processes typically increase SSA of mineral soils and create a higher potential for SOM sorption (Kahle et al., 2004; Wu et al., 2009). However, most of these findings were derived from long-term chronosequence studies of relatively mature soils (Mavris et al., 2010; White et al., 1996; Wissing et al., 2014). In contrast, little is known about the rate of weathering processes, the interaction and mechanisms with organic matter during the very initial phases of soil development (Lützow et al., 2006). The constructed catchment ‘Chicken Creek’ in Eastern Germany (Gerwin et al., 2011) offers the opportunity to investigate these processes and to close the lack of knowledge about mineral surface characteristics at “time zero” of ecosystem development (Schaaf et al., 2011). Our objective was to study mineral surface related processes in these young sandy soils and the effects of organic matter (OM) addition in form of plant litter on soil mineral surface characteristics in a microcosm experiment. Release of dissolved soil organic matter by plant litter decomposition is important for soil weathering processes (Raulund-Rasmussen et al., 1998). We assumed that adsorbed SOM should be closely related to changes in SSA over time, even for the relatively short period of 80 weeks of the microcosm experiment.

We expected an increase in SSA over time due to weathering, but a relative reduction in SSA due to organic coverage of these new surfaces after plant litter addition. Our aim was to quantify these changes by the determination of SSA and surface specific parameters like cation exchange capacity (CEC), surface enthalpy and the fractional coverage of mineral surfaces by SOM.

2. Materials and methods

Soil samples were taken from a microcosm experiment including two different soil substrates from the constructed catchment “Chicken Creek” 30 km south of Cottbus (Brandenburg, Germany, +51° 37' 4.98", +14° 19' 33.94"; Gerwin et al., 2011; Schaaf et al., 2013), established in 2005. The microcosm experiment was carried out in an automated closed soil column system at constant temperature of 10 °C. In total, 48 microcosm columns (height: 30.0 cm; diameter: 14.4 cm) were filled to a height of about 20 cm at bulk densities of 1.4–1.5 g·cm⁻³ corresponding to field site data. Total soil weight of the columns ranged from 5.1 kg to 5.5 kg. The microcosms were irrigated at a rate of 6.6 mL, four times a day (in total 600 mm yr⁻¹) using artificial rain water at pH 5.5. The two soil substrates were classified as pure sand (PS) and loamy sand (LS) according to Boden (2005; Table 1). The mineral composition of the soil substrates (fraction

<63 µm) were similar, however, the ratio of silt to clay was much closer for LS than for PS (Table 1). Mineralogy of both soils was mainly composed of quartz (~40%), 2:1 clay minerals, such as illite and illite–smectite mixed-layer minerals (~40%), kaolinite (~5%), calcite (1–5%), K-feldspar (<5%) and plagioclase (<5%; Gerwin et al., 2011).

Plant litters from two plant species *Lotus corniculatus* L. (LOT) and *Calamagrostis epigejos* L. (CAL) were grown under greenhouse conditions (Table 1), details about the procedure are given in Esperschütz et al. (2012). The two plant species represent typical pioneer species found in early succession within the catchment (Gerwin et al., 2011). After harvesting, homogenized plant litter was dried at temperature of 60 °C and shredded (1–2 cm). 5 g of litter was added on top of each soil column. All treatment and substrate controls (0) were carried out in 8 replicates. 4 columns per treatment were harvested after 40 (40 W) and 80 weeks (80 W), respectively. More details of the microcosm experiment are described in Zönnchen et al. (2014).

Samples were taken after 40 and 80 weeks of the experiment from the upper soil layer (0–5 cm) of the soil columns. 100 g of air-dried samples was sieved using a universal shaker (Swip SM 25 DIGI; Edmund Bühler GmbH, Hechingen, Germany) with a mesh size of 63 µm at 4.5 Hz over a time period of > 1 h to remove the sand fraction. The samples contained no pedogenic aggregates. Agglomerates were formed during sample storage and the sieving procedure was gently pressed through the mesh. For further analyzes, only the silt and clay fraction (<63 µm) of soil samples was used. For all samples (source material (0 W), 40 W, 80 W) SSA_{BET} and adsorption enthalpy were measured. In addition, SOM, CEC and specific surface parameters were analyzed for the 80 W samples.

Specific surface area of soil samples was determined using a gas sorption approach. The method of Brunauer, Emmett and Teller (BET; Brunauer et al., 1938) using nitrogen adsorption is the most widespread method (Echeverría et al., 1999). The SSA was calculated by the multi-point BET nitrogen adsorption method at 0.05 > p/p₀ < 0.3 using an Autosorb A-1 (Quantachrome Instruments, Florida, USA). The BET Eq. (1) is defined by the number of molecules n at the partial pressure (p/p₀), expressed by the equilibrium vapor pressure in relation to the saturated vapor pressure of N₂ (Sing, 1985):

$$\frac{p/p_0}{n(p/p_0)} = \frac{(C_{BET}-1)}{n_m C_{BET}} p/p_0 + \frac{1}{n_m C_{BET}} \quad (1)$$

where the constant C_{BET} is related to the adsorption enthalpy and n_m corresponds to the monolayer capacity.

To obtain surface data by using N₂-BET, adsorbed gases of mineral surfaces, which would block the binding sites of the N₂ molecules, have to be removed (Sing, 1985). According to DIN ISO 9277 (2003), irreversible changes in SSA due to OM transformation may occur at high temperatures during the degassing process. Therefore a temperature of <40 °C was chosen as reported in studies of Feller et al. (1992) and Filimonova et al. (2006).

In addition to the surface measurements, specific surface parameters by a fractal analysis and sorption enthalpy were determined. For the sorption enthalpy the C_{BET} constant was used (Eq. (2)). The C_{BET} constant is related to the adsorption energy in the first adsorbed layer and consequently considered as a value which is indicating the range adsorbent–adsorbate interactions.

$$C_{BET} = \left(\frac{s}{i}\right) + 1 \quad (2)$$

where s is the slope and i the y-axis intercept at zero partial pressure of the BET plot. For determining C_{BET}, only the mid-range of N₂ partial pressures (0.1 > p/p₀ < 0.22) has been proposed to be the linear part of the BET isotherm (Mayer, 1999). To describe the roughness of surfaces by fractal dimension (D_s) the method after Neimark & Kiselev (Neimark et al., 1993) has been applied using gas sorption isotherms.

Table 1

Characteristic parameters of the two soil substrates (LS: loamy sand, PS: pure sand) and two plant litter types (CAL: *Calamagrostis epigejos*, LOT: *Lotus corniculatus*) used in the microcosms (Zönnchen et al., 2014; CEC: cation exchange capacity, N: total nitrogen, C_{tot}: total carbon, C_{org}: organic carbon; (sand: 63–2000 µm; silt: 2–63 µm; clay: <2 µm; mean values and standard deviation n = 4).

	Substrates		Plant litter	
	LS	PS	CAL	LOT
Sand [%]	87.8 ± 0.4	96.8 ± 0.1	–	–
Silt [%]	6.9 ± 0.3	2.5 ± 0.0	–	–
Clay [%]	5.3 ± 0.1	0.7 ± 0.2	–	–
CaCO ₃ [%]	0.4 ± 0.02	2.3 ± 0.04	–	–
pH [–]	8.2 ± 0.1	8.6 ± 0.1	–	–
CEC [cmol _c /kg]	5.8 ± 5.8	6.2 ± 0.5	–	–
C _{tot} [g·kg ⁻¹]	1.4 ± 0.0	3.2 ± 0.0	433.4 ± 0.4	422.0 ± 0.5
C _{org} [%]	0.09 ± 0.01	0.05 ± 0.01	–	–
N [%]	<0.01 ± 0.0	<0.01 ± 0.0	10.9 ± 0.0	35.3 ± 0.1
C/N ratio	–	–	39.4	12.1

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