



Rapid assessment of soil organic matter: Soil color analysis and Fourier transform infrared spectroscopy



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ABSTRACT

Soil organic matter (SOM) content and composition may be affected by geographic region, land use (grassland vs. forest) and management intensity (intensive vs. extensive). To assess these effects SOM of 300 German soils was characterized using soil color analyses (L^* , a^* , b^* -values) and Fourier transform infrared (FTIR) spectroscopy. Soil lightness (L^* -value) was strongly negatively correlated with the soil organic carbon content and this relationship was stronger when the previously sieved soils were ground. Using the band at wavenumber 1634 cm^{-1} (as determined by FTIR) as a proxy for aromaticity of SOM the L^* -value was negatively correlated with aromaticity. Geographic region as well as land use affected L^* -, a^* - and b^* -values. FTIR results suggested that particularly amides and polysaccharides were affected by geographic region, while mainly polysaccharides were affected by land use. We conclude that soil color analysis can provide additional information on environmental circumstances/site effects which may affect SOM composition. A few only weak correlations of soil color/SOM composition parameters with management intensity indicate that either changes in SOM parameters were too small or that the applied management indices were not sensitive enough to management effects.

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1. Introduction

Soil organic matter (SOM) content is a main characteristic of soil as SOM plays an important role in soil fertility. SOM ensures nutrient availability, affects water holding capacity or maintains soil aeration (Allison, 1973; Tiessen et al., 1994; Reeves, 1997; Rumpel et al., 2015). Factors such as climate, topography, parent rock and related soil texture affect plant growth which in turn results in characteristic SOM contents and composition. The same factors also drive SOM stabilization in soils. Since these factors may vary by geographic region SOM content and composition may be regionally different (Dai and Huang, 2006). Plant biomass production and, thus, the amount, composition and decomposability of SOM are also affected by different land use (e.g. forest vs. grassland vs. cropland) (Post and Kwon, 2000; John et al., 2005; Helfrich et al., 2006). Management intensity (e.g. harvesting, grazing, fertilization) can influence SOM by differences in soil C input and nutrient availability which in turn not only affects vegetation or its chemical composition but may also favour different microbial communities which affect SOM turnover (e.g. Baumann et al., 2009). Since management effects can be difficult to detect (Vorony and Angers, 1995) large scale projects with a high number of replicates may help to detect even small effects. In

this context, soil color analysis is suggested to be a promising approach for a rapid and inexpensive analysis of soil properties such as soil organic carbon (SOC) content and iron oxides, which directly affect carbon stabilization because of their large specific surface areas they provide. Using optical instruments such as chroma meters, the color of soil can be determined objectively and precisely (Wutscher and Gregory McCollum, 1993) and can be expressed in the Commission International de l'Eclairage color (L^* a^* b^*) space system (CIELAB) (Torrent and Barrón, 1993). The L^* value ranges from 0 (black) to 100 (white), positive a^* and b^* values indicate the degree of redness and yellowness, respectively. Different colors in temperate climate soils can originate from e.g. humic substances and manganese (black), calcite CaCO_3 (white), ferrihydrite ($5\text{ Fe}_2\text{O}_3 \cdot 9\text{ H}_2\text{O}$) (reddish-brown), lepidocrocite ($\gamma\text{-FeOOH}$) (orange), and goethite ($\alpha\text{-FeOOH}$) (yellow) (Schwertmann, 1993; Kirillova et al., 2015; Schwertmann and Cornell, 1991).

The L^* -value has been shown to negatively correlate with the SOC content (Spielvogel et al., 2004; Eckmeier et al., 2007; Miralles et al., 2007). However, this relationship was non-linear suggesting that soil lightness was influenced by further parameters. Spielvogel et al. (2004) found linear relationships only after separating samples by CaCO_3 content, texture and carbon content (Histosols: carbon content $> 12\%$). Eckmeier et al. (2007), who investigated soils after slash-and-burn, explained their result of an exponential relationship by charcoal pieces covering mineral particles, and Miralles et al. (2007) reported variation in organic matter quality as a possible reason for a curvilinear

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relationship between soil lightness and SOC content which they found for soils differing in management history.

Nagano and Nakashima (1989) reported that the a^* - and b^* -values of differently weathered Japanese granitic rock powders increased with increasing degree of rock weathering; the b^* -value was found to parabolically increase with increasing goethite content (Nagano and Nakashima, 1989). Scheinost and Schwertmann (1995) showed a non-linear relationship between dithionite-extractable iron (Fe_d) and the b^* -value. They concluded that both, Fe_d and the b^* -value are estimates of the goethite content, if goethite is the predominant Fe oxide in the soil (Scheinost and Schwertmann, 1995). Oxalate-extractable iron (Fe_{ox}) and the b^* -value were correlated by Moritsuka et al. (2014) using a wide range of Japanese agricultural soils. However, they could not find a general relationship on national soil scale; only on field scale, for paddy soils or Andosols a positive relationship was reported (Moritsuka et al., 2014).

Transmission Fourier transform infrared (FTIR) spectroscopy is a relatively quick and low-cost method to characterize SOM composition. Absorption bands are characteristic for specific functional groups, thus, allowing absorbance intensities in the mid-infrared region ($4000\text{--}400\text{ cm}^{-1}$) to be used as fingerprint of SOM composition (Raphael, 2011). Nature and relative content of the functional groups determine the chemical reactivity, sorptivity or hydrophobicity of SOM (e.g. Ellerbrock and Gerke, 2013). These characteristics of SOM may be influenced by land use and management practice. Using FTIR spectroscopy, Ellerbrock et al. (1999) as well as Gerzabek et al. (2006) showed effects of different management and land use on SOM composition. In arable soils, Ellerbrock et al. (1999) demonstrated higher C=O intensities after fertilization with cattle manure + NPK compared with straw + NPK fertilization and explained this by differences in composition of the added organic matter. Gerzabek et al. (2006) reported higher C=O intensities in grassland than in arable soil.

In the present study, we examine a total of 300 mineral soils from 150 forest and 150 grassland plots distributed over three German study regions to evaluate the suitability of soil color analysis and FTIR spectroscopy as rapid and inexpensive analyses of SOM content and composition. We investigate whether the methods can be used to study small temporal changes in SOC contents over a 3 year-period. We further proof whether geographical region, land use type and management practice are reflected in soil color and spectroscopic properties.

2. Materials and methods

2.1. Sampling sites and land use intensity

Soil samples were derived from the three study regions of the German Biodiversity Exploratories the UNESCO Biosphere Reserves Schorfheide-Chorin (SCH; NE Germany) and Schwäbische Alb (ALB; SW Germany) as well as the National Park Hainich-Dün and its surroundings (HAI; Central Germany) (Fischer et al., 2010). In each of the study regions 50 grassland and 50 forest plots were established in 2006. The main tree species of the forest plots in SCH were: pine, beech and oak (22, 21, 7 plots, respectively), in HAI: beech and spruce (46, 4 plots, respectively), and in ALB: beech and spruce (38, 12 plots, respectively) (Fischer et al., 2010). As a measure of management intensity, a land use intensity (LUI) index for each grassland plot was calculated by Blüthgen et al. (2012) taking into account the amount of fertilizer, frequency of mowing and grazing intensity per year, normalized for each region. Schall and Ammer (2013) calculated a silvicultural management intensity (SMI) indicator for each forest plot, taking into account tree species, stand age and aboveground living and dead wood biomass. Both management intensity indices increase with more intense management.

2.2. Soil sampling

In 2011 and 2014, soil samples were taken at all 300 plots of the German Biodiversity Exploratories. On each of the 300 plots 14 soil samples were taken from the upper 10 cm of the soil using a 4.8 cm (diameter) auger sampler. In forests, the organic layer was removed with a metal frame ($15 \times 15\text{ cm}$) beforehand. A composite sample representative for each plot was prepared. The soil was sieved to pass 2 mm before air-drying (sieved soil). A representative portion of the air-dried sieved soil from 2011 was ground to $<0.5\text{ mm}$ (ground soil).

Soil color was determined on 600 sieved soils (2011, 2014) and 300 ground soils (2011). Fourier transform infrared (FTIR) spectroscopy was performed on 300 ground soils (2011).

Effects of region, land use and management on soil color were calculated for sieved soils from 2011. For changes in soil color over time, differences in soil color between sieved soils from 2011 and sieved soils from 2014 were determined. Grinding effects on soil color were analysed by comparing sieved soils and ground soils from 2011.

2.3. Soil color

Color of sieved soils was determined using a Konica Minolta chroma meter CR410 camera equipped with a light conducting tube of 2.5 cm (diameter). The light source of the chroma meter was a pulsed xenon lamp; the detector consisted of 6 silicon photocells. The used illuminant was C. The tube was placed vertically on the leveled soil and soil color was recorded in the CIELAB system (L^* , a^* , b^*). White calibration of the chroma meter was performed before soil analyses and after every 25 soil samples. The standard deviation of repeatedly measured L^* , a^* , b^* -values of sieved soil from grassland and forest of all three regional sites did not exceed 0.46, 0.04 and 0.28, respectively ($n = 10$ measurements of the same sample but different spots of the leveled soil).

2.4. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy was performed according to Ellerbrock and Gerke (2004). Briefly, one mg of ground soil ($<0.5\text{ mm}$) was mixed with 80 mg of KBr in an agate mortar. The mixture was dried in a desiccator before a pellet was formed by applying pressure of 6.8 t cm^{-2} (press: Graseby Specac, Britain). One pellet per sample was characterized using a BioRAD FTS 135 spectrometer (BioRad Corp. Hercules, CA, USA). The absorbance spectra of organic matter were collected in the wave number range of $4000\text{ to }400\text{ cm}^{-1}$ ($2500\text{--}25,000\text{ nm}$) with 16 scans per spectrum at 1 cm^{-1} resolution. After subtraction of the background (ambient air spectrum) the spectra were smoothed (boxcar moving average algorithm, factor 25), corrected for baseline shifts and apodized (Bessel) using the software WIN-IR Pro 3.4 (Digilab, Massachusetts, USA). Each spectrum was analysed for the following specific signal intensities of organic matter using band assignments compiled by Inbar et al. (1989), Ellerbrock and Gerke (2004) and Leue et al. (2015): band maxima at wavenumbers (WN) around 2925 and 2858 cm^{-1} (aliphatic C—H stretch), 1634 cm^{-1} (C=O vibrations in carboxylic acids/anions and amides, C=C stretch in aromatics), 1564 cm^{-1} (N—H and C—N vibrations in amides II), 1420 cm^{-1} (C=O vibrations of carboxylate ions, C=C in aromatics and C—N in amides), 1085 and 1033 cm^{-1} (C—O—C stretch in polysaccharides and Si—O—Si stretch in silicates and clay minerals). The intensity of each absorption band was measured as heights from the baseline. Only the intensities of the absorption bands at wave numbers 2925 and 2858 cm^{-1} were measured as the vertical distance from a local baseline plotted between tangential points to consider the effect of the underlying broad O—H band (e.g. Leue et al., 2015). For spectra comparison, absorption signal intensities (SI) were expressed as % of total signal intensity. Hydrophobicity of SOM was estimated from the ratio of the peaks at $WN(2925\text{ cm}^{-1} + 2858\text{ cm}^{-1}(\text{aliphatic C—H})) / 1634\text{ cm}^{-1}(\text{C=O, aromatics})$ (Ellerbrock et al., 2005). The ratio of the peaks at WN

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