Geoderma 288 (2017) 120–129

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Physical protection of organic matter in minesoils assessed by low-temperature ashing (LTA)

Luigi P. D'Acqui [a],*, Alessandra Bonetti [a], Roberto Pini [b], Giacomo Certini [c]

[a] *Istituto per lo Studio degli Ecosistemi, CNR, via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy*
[b] *Istituto per lo Studio degli Ecosistmi, CNR, via Moruzzi 1, 56124 Pisa, Italy*
[c] *Dipartimento di Scienze delle Produzioni Agroalimentari e dell'Ambiente, Università di Firenze, Piazzale delle Cascine 28, 50144 Firenze, Italy*

ARTICLE INFO

Article history:
Received 17 May 2016
Received in revised form 4 November 2016
Accepted 5 November 2016
Available online xxxx

Keywords:
Soil structure
Carbon sequestration
Physical protection
Aggregate stability
Minesoils
Low-temperature ashing (LTA)

ABSTRACT

Physical stabilization of soil organic matter (SOM) was assessed by a novel combination of methods in minesoils of Central Italy, cultivated or afforested with different species by 30 years. We studied this stabilization in: 1) a managed (thinned and mowed) English oak (*Quercus robur L.*) plantation; 2) a similarly managed 1:1 mixed plantation of Italian alder (*Alnus cordata Loisel.*) and English oak; 3) an unmanaged portion of the mixed plantation; 4) a yearly tilled and manured cropland; 5) an adjacent forest growing on a natural soil, which served as a term of reference. We focused on water-stable soil aggregates, in which SOM is physically protected from decay. Aggregates of 0.5 to 1.0 mm in diameter were subjected to Low-Temperature Ashing (LTA) by oxygen plasma, a technique able to progressively remove SOM with minimal or no damage to mineral constituents and soil fabric. All minesoils had behaved as C sinks, although to a different extent depending on land use, with cropland storing around half soil C than the afforested areas. Carbon enrichment improved soil structure promoting the formation of large and water-stable soil aggregates. The C contained in the core of these aggregates, measured here as the one able to resist 48 h of LTA treatment and confidently assumed as the C fraction best protected from decay, ranged from 43 to 70% of total C, depending on land use and horizon. The strict relationships found between the amount of "protected" SOM and the median diameter (d50) of water-stable soil aggregates ($R^2 = 0.88$), on the one hand, and the larger class of pores in water-stable soil macroaggregates ($R^2 = 0.99$), on the other hand, demonstrated the crucial role of this SOM pool in soil structure formation. This study showed the potential of LTA used in combination with laser diffraction analysis, FTIR-PAS spectroscopy, and mercury intrusion porosimetry to distinguish C stocks benefiting from different physical protection in aggregates and to assess their role in soil structure formation. Such a methodological approach could be highly useful to understand the mechanisms by which soils at the first stages of pedogenesis, such as reclaimed minesoils, sequester C and to reveal how much tillage and other types of soil disturbances expose the protected C to decay.

1. Introduction

Soil is the largest terrestrial reservoir of organic carbon (C) and small changes in soil organic matter (SOM) stocks may have significant impacts on CO_2 concentration in the atmosphere (Stockmann et al., 2013). Understanding the mechanisms that control stabilization and release of SOM is crucial for implementing strategies to increase C sequestration in soil and consequently mitigate climate change. Under suitable environmental conditions, soils at the first stages of pedogenesis are tremendous sinks of CO_2, because they comprise almost exclusively minerals and tend to quickly enrich in organic matter (Certini et al., 2002). Mine spoil banks are a source of soil parent materials able to uptake much CO_2 in the form of SOM (Ussiri and Lal, 2005; Rhoades et al., 2001). Reclamation of minesoils has thus great potential to mitigate climate change. The rate and mechanisms by which such young anthropogenic soils store C is still largely unknown, but it is clear that soil use and management is a crucial driving factor (Chatterjee et al., 2009; Ussiri and Lal, 2013). In particular, afforestation appears to be highly efficient in terms of soil C sequestration and stabilization (Chiti et al., 2011; Nave et al., 2013), although a general understanding of the extent of the effect of tree species and forest management across site types has not yet been reached (Jandl et al., 2007).

The residence time of SOM is as important as its amount, and it is dictated by the interactions established with the mineral surfaces (Sollins et al., 1996; von Lützow et al., 2006) as well as by SOM composition (Kögel-Knabner, 2002). The SOM occluded in aggregates benefits from a physical protection that can increase SOM residence time (Six et al., 2002). Soil structure is thus a key factor of C

---

* Corresponding author.
E-mail address: dacqui@ise.cnr.it (L.P. D'Acqui).

http://dx.doi.org/10.1016/j.geoderma.2016.11.009
0016-7061/

sequestration (O'Brien and Jastrow, 2013). Imaging techniques (transmission electron microscopy, X-ray microtomography) on intact soil or thin sections are often used to assess physical protection (Chenu and Plante, 2006; Peth et al., 2008; Papadopoulos et al., 2009; Werth et al., 2010) but SOM identification can be difficult. A relatively recent promising approach to disentangle the role of physical protection to SOM is based on Low-Temperature Ashing (LTA) by oxygen plasma, which enables a controlled removal of SOM from the surface of soil samples inwards without damage of the inorganic constituents and disturbance of aggregate fabric (Sullivan and Koppi, 1987; De Kimpe and Schnitzer, 1990, D'Acqui et al., 1998 and 1999). The SOM in the peripheral regions of aggregates is in fact easily accessible to free electrons, excited atoms and molecules of plasma, since the rate of diffusion of plasma is ultimately controlled by soil porosity. Coupling elemental analysis and Photoacoustic Fourier transform IR spectroscopy before and after LTA treatments of different duration was proved to be a successful approach to gain insight into the nature of SOM removed from the aggregates (D'Acqui et al., 1998 and 1999; Pucci et al., 2008). Based on the assumptions that LTA mimics natural oxidative processes and does not depend on the intrinsic nature of organics, it is plausible to consider the residual C from the LTA treatment in the inner side of aggregates as physically protected.

The present study aims at addressing current questions on mechanisms of SOM protection and soil structure formation dynamics in reclaimed minesoils by using a novel combination of methods. In particular, by an LTA-based experiment we studied the physical protection for SOM in water-stable soil aggregates from afforested and cultivated minesoils. The quantity and quality of the SOM progressively removed inwards was investigated by elemental analysis and infrared photoacoustic spectroscopy (PAS), respectively. Pore size distribution (PSD) and aggregate stability to water before and after LTA treatment were determined by mercury intrusion and laser diffraction analyses, respectively. A naturally developed soil of an adjacent oak forest and the almost unaltered parent material collected at various meters of depth in the spoil banks were used as terms of reference.

2. Materials and methods

2.1. Site description

The study area is the coalmine district of Santa Barbara (43° 35′ 29″ N, 11° 29′ 17″E), Tuscany, Central Italy. The area has mean annual temperature of 13.1 °C and mean annual precipitation of 925.7 mm. In the 20th century, lignite extraction for energetic purposes caused removal of large amounts of superimposed silt–clay lacustrine sediments and their allocation in neighbouring areas. The spoil banks so formed reached even 60–70 m in height (Milillo et al., 1998). In the 1980′s, once the mining ceased, one of these spoil banks – confidently homogeneous in composition – was afforested using several indigenous species or cultivated for cereal production. The site selected for this study, Vincesimo, included five land uses: 1) managed (thinned and mowed) English oak (*Quercus robur L.*) plantation (hereafter indicated as Qr); 2) managed 1:1 mixed plantation of Italian alder (*Alnus cordata Loisel.*) and English oak (Al/Qr); 3) unmanaged portion of the mixed plantation (Al/QrNM); 4) a yearly tilled and manured cropland (Crop); 5) forest growing on a natural soil not affected by any mining activity (Nat). The forest plantations and the cropland were 30 years old. The forest on natural soil had experienced alder depletion due to both human interventions and the expected oak's prevalence. The soils of the forest plantations and the cropland, which are flat, did not show any evidence of erosion, while the steeper natural forest soil, which is representative of forest soils bordering minesoils, clearly underwent some runoff-induced loss. Further information and data on the study site can be found in Chiti et al. (2007).

2.2. Soil sampling and soil aggregates preparation

Soil was sampled at three randomly selected points in each land use. Undisturbed soil samples were collected after litter removal from both the A1 horizon (or the 0–5 cm layer in cropland, where the uppermost pedogenic horizons were mixed by the tillage) and the underlying A2 horizon (5–15 cm layer in cropland). In laboratory, the samples were air-dried at room temperature to constant weight. Half sample was gently crushed by hand and aggregates of centimetric size were selected for pore size distribution (PSD). The rest was passed through 1.0 mm and 0.5 mm sieves to obtain calibrated aggregates. The other half sample was passed through a 2 mm sieve for soil characterization analysis.

From a 20 m long soil core extracted from the cropland we collected samples from 5, 10 and 20 m depths to assess some initial properties of the spoil banks, since these samples were assumed to be very slightly or not at all affected by pedogenic processes. The aggregates and the fraction <2 mm from the core samples were obtained by the same procedure as described above.

2.3. Soil characterization

All samples were analysed for particle-size distribution (hydrometer method, as described in Gee and Bauder, 1986), pH (by a potentiometer, in a 1:2.5 W/V distilled water suspension), total organic C and nitrogen (N) content (dry combustion by a Carlo Erba NA 1500 CHNS Analyzer, Milan, Italy) and soil inorganic C, as the difference between total C and the C measured by dry combustion in a sample treated with excess HCl, for carbonate removal (Santi et al., 2006). Coal-C was assumed as C that resisted the chemothermal oxidation at 375 °C (CTO-375 method in Gustafsson et al., 1997). Bulk densities were determined by core method (Blake and Hartage, 1986) collecting a specimen at each sampling point. Mineralogical investigation of the bulk soil was conducted by a X-ray Diffractometer Philips PW3830 working on randomly oriented powders with CoKα radiation, 0.02° step size, and 1 s step time each point over a 2θ range of 70° (5–75°).

2.4. Low-temperature ashing (LTA) technique

The LTA treatment was performed by the self-assembled equipment described in D'Acqui et al. (1999). The sample was allocated in the LTA reactor and evacuated to 45 Pa under an oxygen 20 mL min^{-1} flow rate. Oxygen plasma was produced applying a radiofrequency of 13.56 MHz by a power input of 100 W and a reflected power of 5 W. In these conditions the surface temperature was maintained below 80 °C. The size of the aggregates to submit to LTA treatment – 0.5 to 1.0 mm – was chosen on the basis of tests that showed the technical difficulty in these soils to guarantee complete oxidation of SOM in larger aggregates. Carbon was measured on three aliquots (~1 g) per sample exposed to different treatment times, *i.e.* 5 h, 24 h, and 48 h. No further C removal was noticed beyond 48 h, which was therefore selected as longest LTA exposition time.

2.5. Water aggregate stability

To evaluate the role of SOM on aggregate stability, untreated (0 h) and LTA-treated (5 h, 24 h and 48 h of exposition), both dry and pre-wetted by gently spraying deionised water, soil aggregates were immersed in distilled water and submitted to ultrasound (max. power 35 W). A laser granulometer analyzer Malvern Mastersizer 2000 was then used for determining the particle size distribution in the range of 0.02–2000 μm. Ultrasound was applied until the size distribution of dispersed particles was constant. The granulometer was equipped with a wet sample dispersion unit. The granulometric curve obtained just after immersion was compared with the curve obtained at the end of ultrasound treatment, to have