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Morphological analysis of soil particles at multiple length-scale reveals nutrient stocks of Amazonian Anthrosols

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ABSTRACT

We have imaged the particles of Brazilian soils at multiple length scales, from a few microns to millimeters, and soil particle size distributions were calculated with unmatched precision. The analysis included the Amazonian soil "Terra Mulata de Índio" (TMI), an anthropogenic soil (Anthrosol) with sustained fertility and a large amount of stabilized organic matter. Firstly, the soils were imaged ex situ, without any chemical processing, with sequential electron scanning of the pelletized soil samples, covering a total area of 8 × 8 mm. Secondly, it was performed a computational analysis of the large-field X-ray images assembled from hundreds of adjacent elemental maps, thus resulting in high-definition images (4800 × 4800 pixels). This analytical approach provides a large sampling with the identification of > 10,000 particles over the scanned area. The particles identified consisted of Al, C, Ca, Cr, F, Fe, Mg, Mn, Na, O, P, S, Si and Ti. A significantly larger concentration of C-, Ca- and P-based particles, of up to 100 μm^2 of cross-section area, was found in TMI samples in comparison with oxisol and ultisol soils. While the mean distance between neighboring C, Ca and P particles in TMI was of 40–70 μm, the value was of hundreds of microns in oxisol and ultisol. Furthermore, mapping of micrometric carbon particles by Raman spectroscopy indicated that they have a graphitic structure with a large amount of defects, partially associated with particle oxidation, although a well-preserved sp^2 graphitic structure is also present. From a technological perspective, improved soil amendments, such as biochar, can be rationally designed from the "fingerprint" described here for soil particles of Amazonian Anthrosols (i.e., morphological and structural characteristics), which can result in an increase in fertility and the optimization of carbon sequestration in the future.

1. Introduction

The structure of soil is comprised of a hierarchical organization of inorganic and organic matter in levels, that range from the sub-nanometer to the macroscopic scale (Gimknez et al., 1997; Jastrow, 1996). Inorganic matter (i.e., minerals) is present in the ionized state and/or organized in clusters and particles (nano to macroscale) (Hughes et al., 1994; Kahle et al., 2002). On the other hand, organic matter includes all carbon-based molecules, molecular-assemblies and particles, including plant and animal residues, and the biomass of living microorganisms and other fauna (Lal, 2007; Rinnan and Rinnan, 2007). Fertility is manifested from the fine-tuning of the abovementioned compositional and structural aspects, and represents a complex and emergent property of soil (Chaparro et al., 2012). Consequently, soil fertility is a crucial aspect in crop yields and food security.

More specifically, the definition of soil fertility is related to its capacity for providing the needs for the growth and development of plants, including aspects of productivity, reproduction and the quality of the resulting crops (Abbott and Murphy, 2007; Atkinson et al., 2010). A modern and complete determination of soil fertility involves the

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assessment of biological, chemical and physical aspects, and the consequent multiple and complex interactions/relations between these three aspects. For the physico-chemical characterization of soils, there are well-established protocols for the identification and quantification of soil ions and molecules by analytical chemistry protocols, such as extraction and fractionation (Huo et al., 1998; Qian et al., 1996; Wang et al., 2017; Xinde et al., 2000); chromatographic and spectroscopic methods (Hernandez-Soriano et al., 2016; Jáuregui et al., 1998; Malley et al., 1999; Pascaud et al., 2017; Udelhoven et al., 2003). However, both the particle (inorganic and organic) fractions present in the soil are difficult to identify, classify and characterize in soil samples, especially ex situ, without sample preparation/processing. The largely used granulometric methods involving gradual sieving provide some insights into soil particle sizes (De Souza et al., 2016; Li et al., 2016; van Reeuwijk, 2002; Villaverde et al., 2009; Yin et al., 2016), but they do not allow for the measurement of precise particle size distribution (PSD) functions for soil particles. A precise determination of PSDs is of particular importance for feeding mathematical models of flow and transport processes that occur in soil, thus allowing the determination of soil water retention and other hydraulic properties (Arya and Paris, 1981; Gupta and Larson, 1979; Mohammadi and Vanclooster, 2014).

Alternatively, light-scattering (LS) techniques of soil dispersion in liquid media can essentially determine PSDs (e.g., dynamic LS). Unfortunately, this technique has limited precision for polydisperse samples, such as soil, thus resulting in the characterization of only small particles of soil, at the micron range and below (Kretzschmar et al., 1998; Nguyen et al., 2017, 2013). In addition, to attain the soil dispersion in liquid media for LS analysis, it is necessary to use strong acids, oxidizing agents and/or salts (Kretzschmar et al., 1998; Ngolejeme and Ekosse, 2015; Nguyen et al., 2017, 2013; van Reeuwijk, 2002). Conversely, modern electron microscopy approaches are suitable for revealing, in great detail, soil particle morphology, as well as their elemental composition, by means of X-ray energy-dispersive spectroscopy (EDS) coupled to the microscope. However, these approaches are limited by the low sampling of particles imaged at high magnifications, in the case of both scanning and transmission electron microscopy (SEM and TEM, respectively) (Archanjo et al., 2014; Gilkes, 1994; Yang et al., 2016). In order to negate this issue, new microscopy approaches must image soil particles in a large sampling and at multiple length scales to determine particle compositions and reveal their morphologies from micrometers to centimeters. As recently shown by our group, this can be currently achieved by large-field (LF) X-ray imaging in combination with image analysis algorithms (Noronha et al., 2017; N.C. Oliveira et al., 2015; Sousa et al., 2017). Thus, by applying this approach for soil samples, one can unveil direct or indirect fertility aspects, especially those related to the sustainability of fertility, i.e., the "storage" of elements, such as carbon, phosphorus, nitrogen and calcium, which are present as particles (Kern and Kämpf, 1989). On this basis, with regards to the biology, physics and chemistry influencing soil fertility, LF imaging can unveil several aspects of the latter two with great precision.

Considering the perspectives presented for the LF imaging, we used here this approach in an attempt to assess the remarkable fertility capacities of Amazonian soil "Terra Mulata de Índio" (TMI), by imaging the soil particles ex-situ. It is known that this anthropogenic soil (i.e., Anthrosol) presents a sustained fertility in determined rims and is characterized by a high concentration of stable organic matter, phosphorus, calcium and contains the presence of potsherds (Hastik et al., 2013; Taube et al., 2013). However, there is no precise information on the PSDs of Amazonian Anthrosols. Furthermore, the composition and morphological characteristics of TMI were compared to oxisol and ultisol, which were collected from different regions of Brazil. A sequential scanning of the subjacent areas of the pelletized soil samples (with no chemical processing) was performed over the whole specimens (10 mm diameter disks). Computational analyses of the LF images further revealed, at multiple length scales (micrometers to millimeters), the soil particle compositions, morphologies and PSDs. In addition, a comparative-quantitative analysis of all detected elements (e.g., calcium, potassium and magnesium) in all samples could be performed with great precision due to the LF scanning. Therefore, a fingerprint of the nutrients and other elements/compounds present in soils of high and sustained fertility, such as TMI, could be obtained. Raman spectroscopy was also carried out to complement the above information in terms of structural information of the soils. The knowledge provided by this work is crucial to determine the suitable morphological and structural characteristics of possible soil amendments, such as biochar (Archanjo et al., 2014; Atkinson et al., 2010; Hernandez-Soriano et al., 2016; Meyer et al., 2011; Yang et al., 2016), which can improve soil fertility as well as carbon sequestration in the future.

2. Materials and methods

2.1. Soil sample collection and preparation

Soil samples representative of oxisol from Maringá (Paraná State; 23°23′16.63″S and 51°59′29.37″W), ultisol from São Jose do Rio Preto (São Paulo State; 20°48′19.79″S and 49°19′43.51″W) and TMI from the Amazon (Amazonas State) were sampled from three different places in Brazil, as shown in Fig. 1. Soil samples from the Amazon (SISBio authorization by Chico Mendes Institute for Biodiversity Conservation, Ministry of the Environment, No. 50042-2) were collected in an area of native forest (named TMI-1; 3°04′05.17″S and 58°34′11.68″W) and in an open area with only undergrowth (named TMI-2; 3°04′05.45″S and 58°33′51.11″W). Oxisol and ultisol were classified according to the Soil Survey Staff (2014), and are equivalent to "Latossolo" and "Argissolo", respectively, in the Brazilian System of Soil Science (EMBRAPA - Brazilian Agricultural Research Corporation, 2013).

Soil samples from each studied area were collected at a 0.00–0.30 m depth. After the soil was air-dried, it was sieved with a 10-mesh (2 mm) sieve to remove only large plant residues, stones and potsherds. Finally, 0.5 g soil samples (triplicate) were pelletized into disks of 10 mm in diameter and further introduced in the SEM chamber without sample preparation.

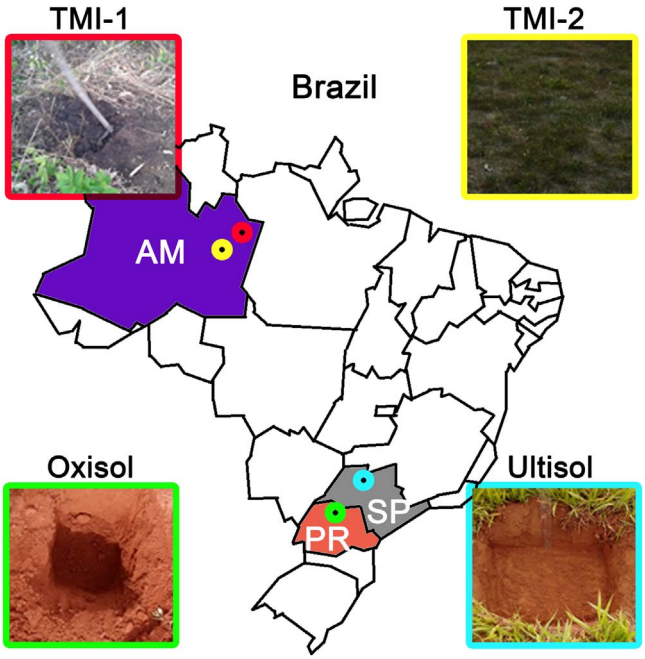

Fig. 1. Collection sites of Brazilian soils: ultisol (São José do Rio Preto, São Paulo State), oxisol (Maringá, Paraná State) and Amazonian dark earth TMI (Itacoatiara, Amazonas State). TMI soils were collected in an area of native forest (TMI-1) and in an open area with only undergrowth (TMI-2).