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Advances in the knowledge of how heating can affect aggregate stability in Mediterranean soils: a XDR and SEM-EDX approach

Patricia Jiménez-Pinilla [a,b,*], Jorge Mataix-Solera [a,b], Victoria Arcenegui [a,b], Rafael Delgado [c], Juan Manuel Martín-García [c], Elena Lozano [a,b], Lorena Martínez-Zavala [b], Antonio Jordán [b]

[a] GEA (Grupo de Edafología Ambiental) Environmental Soil Science Group, Departamento de Agroquímica y Medio Ambiente, Universidad Miguel Hernández, Avenida de la Universidad s/n, 03202 Elche, Alicante, Spain
[b] MED_Soil Research Group, Departamento de Cristalografía, Mineralogía y Química Agrícola, Facultad de Química, Universidad de Sevilla, C/Profesor García González, 1, 41012 Sevilla, Spain
[c] Departamento de Edafología y Química Agrícola, Facultad de Farmacia, Universidad de Granada, Campus Cartuja, 18071 Granada, Spain

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ABSTRACT

Aggregate stability (AS) is a key property in the soil system and it has been previously observed that its response to the fire can be very different with patterns that can show opposite trends depending on the principal cementing agents that control the aggregation between particles. In the case of some Mediterranean soils, previous studies observed an increase of AS. However it is not clear if this increase is real or apparent since fire could destroy a part of the aggregates and, therefore, what we are measuring is the AS that remains after fire. Soils from five different areas were heated in a muffle furnace at different temperatures (300, 500 and 700 °C) for 20 min. The weight of aggregate size fractions of 0.25–4 mm and <0.25 mm before and after heating treatments was quantified. The loss of weight by the combustion, the organic matter content and AS were also measured in all samples studied. A selection of aggregates of the three studied soils (control and heated at 700 °C) were also analysed by X-ray diffraction (XRD) and the surface soils were observed by scanning electron microscopy (SEM-EDX), in order to identify mineralogical and structural changes in the surface of aggregates due to heating. Results showed an initial decrease in the proportion of the macro-aggregates at 300 °C with regard to control (unheated) samples for all the soils analysed ($p < 0.05$). We presumed it is mainly due to the loss of SOM by combustion and subsequent disruption of some aggregates in lower sizes. However, this effect was not enhanced by heating the soils at 500 and 700 °C compared to 300 °C for any soil studied. Moreover, the heating treatments caused an increase in AS with heating temperature, despite no significant decrease for 0.25–4 mm aggregate fraction and the decrease of SOM produced by the combustion. Therefore, these results are not apparent as a consequence of the selection of the most resistant aggregates because of the destruction of other soil aggregates. X-Ray diffraction patterns and SEM-EDX analyses results in selected aggregates assisted us to explain the above-mentioned results of the increase of AS with heating temperature. The relative mineral abundances of the heated aggregates at 700 °C were slightly modified with regard to control. We observed some changes in the iron (hydr)oxides minerals, where the intensities had decreased and dehydroxylated to form maghemite. The presented results also show the disappearance of kaolinite for one of the soils. An increase of relative content of dolomite and calcite was also observed in the other two soils. In general, changes in compactness of soil micro-fabric units that have been produced as the consequence of the recrystallizations and micro-structural modifications observed by SEM-EDX in the surface of the soil aggregates after heating. These changes in cementing minerals may lead to a stabilization of the aggregate structure and hence an increase in the AS.

1. Introduction

Fire may cause important variations in the first centimetres of soil profile inducing chemical, physical and biological changes in soil properties (Certini, 2005). These changes, despite usually only affecting the topsoil centimetres, e.g.: 1–3 cm depth under field and under laboratory conditions with different semiarid soils (Aznar et al., 2013; Badía et al., 2014; Badía-Villas et al., 2014); can have important implications for the soil functioning of the system and therefore on the ecosystem (Mataix-Solera and Cerdà, 2009). Soil structure is one the most affected properties since it is controlled by many factors that fire can also affect (organic matter, water repellency, microbial populations, mineral changes, etc.; Mataix-Solera et al., 2010). Soil aggregate stability (AS) provides key information about the capacity of soil functions to define the soil quality (Chrenková et al., 2014; Brevik et al., 2015). It also has

* Corresponding author at: GEA (Grupo de Edafología Ambiental) Environmental Soil Science Group, Departamento de Agroquímica y Medio Ambiente, Universidad Miguel Hernández, Avenida de la Universidad s/n, 03202 Elche, Alicante, Spain.
E-mail address: pjimenez@umh.es (P. Jiménez-Pinilla).

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an important role in avoiding erosion and degradation and in the ability to transfer liquids and gases, which are important features for the ecosystem health (Tisdall and Oades, 1982). AS is largely controlled by organic and inorganic soil components, such as, the quantity and quality of organic matter (Oades, 1993), and the clay content and its mineralogy (Singer, 1994).

There is a discrepancy in the previous literature regarding the effect of heat on AS. On one hand, soils in which organic matter is the main stabilizing agent are very prone to the degradation produced by high heating temperatures (Campo et al., 2014), producing the destabilization of aggregates (Giovannini, 1994; García-Corona, et al., 2004; Cerdà et al., 2009). On the other hand, soils in which inorganic compounds like iron and aluminium oxides and also carbonates (Andreu et al., 2001; Cerdà et al., 2009; Ketterings et al., 2000) are the main soil stabilizing agents, heating can also cause increases in soil aggregation (Campo et al., 2014). Other minerals like Kaolinite have been shown to decompose at temperatures between 500 and 700 °C (Richardson, 1972). Badía and Martí, (2003a) and Zavala et al. (2010) found a decrease of AS due to the destruction of soil organic matter (SOM) during burning under laboratory and field conditions, respectively. However, an AS increase could occur despite the decrease in SOM. Guerrero et al. (2001) and Arcenegui et al. (2008) explained that in some cases, increased AS after burning could be induced by other factors, such as changes in soil mineralogy (recrystallization of Fe and Al oxyhydroxides), after the soil has been exposed to moderate to high temperatures. Gibbsite may be completely destroyed by heating at 200 °C (Rooksby, 1972), and goethite is altered to hematite at ≈300 °C (Cornell and Schwertmann, 1996) for example. It is presumably known that all soils will not have an equal response to the heat impact and the mineralogical changes. Mataix-Solera et al. (2011) stated in a revision of state-of-the-art about this topic that AS may either increase or decrease depending on soil properties and temperature peaks reached during burning, and also on the heating residence time (Cerdà and Mataix-Solera, 2009), but from their review manuscript they conclude that in some cases with regard to the observed AS increase it is not sure whether this is real or apparent since fire and destruction of some aggregates can lead to a selection of the most resistant, which are those subjected to the AS analyses.

Important amounts of SOM are lost when temperatures in soils reach around 300 °C (Ulery and Graham, 1993; Iglesias et al., 1997; Ketterings et al., 2000), producing the consequent destabilization of the aggregates (Giovannini, 1994; García-Corona et al., 2004; Cerdà et al., 2009). Also, regarding the heating effects on soil properties, the most important changes occur at different temperatures thresholds (Giovannini, 1997; Doerr et al., 2000; Certini, 2005; Mataix-Solera et al., 2011). These changes were summarized by Campo et al. (2014) as: 25–100 °C: soil dehydration; 170–220 °C: hydrophobicity increasing and dehydration of the gel forms; 220–460 °C: combustion of SOM, re-aggregation of particles into sand-sized particles and hydrophobicity disappearance; 550–700 °C: loss of OH^- groups of clays; 700–900 °C: carbonate decomposition. The consideration that the internal reorganization and recrystallization of these inorganic compounds contribute to increase the resistance of the soil aggregates, particularly in concomitance with the combustion of the SOM, suggests that during the heating process, the soil undergoes "a kind of laterization" (Giovannini, 1997) with its consequent evolution. Despite the interest in how heating can affect soil structure, very few studies (e.g., Arocena and Opio, 2003) were addressed by SEM-EDX and related specific techniques.

The AS values in Mediterranean calcareous soils are usually high for long-term undisturbed or even natural forest soils (Mataix-Solera et al., 2002; Zornoza et al., 2007, 2008; Arcenegui et al., 2008). Mediterranean calcareous soils mostly belong (>90%) to the orders of Soil Taxonomy Entisol, Inceptisol, Vertisol and Alfisol (Torrent, 1995). Entisols and Inceptisols represent about 80% of Spanish surface (Gómez-Miguel and Badía-Villas, 2016). In our region for forest soils main orders are Entisol and Alfisol. Although there are a few previous studies which have included the soil type as a factor in experiments of fire effects on soils (Badía and Martí, 2003a, 2003b), it is not very common and therefore a novel additional part of this research.

The main objective of this study is to make advances on how different heating temperatures influence AS behaviour under laboratory conditions in some different soils of Mediterranean areas (southeast Spain). For this, a laboratory heating experiment was designed to study aggregation before and after heating treatments at different temperatures and in addition, to complete this study, some selected aggregates from three of the study sites considered as representatives have been analysed by X-ray diffraction (XRD) and the scanning electron microscopy (SEM-EDX) methods. The key aim of using these X-ray and electronic methods in this work was to establish the first contact with these techniques to identify potential mineralogical, micromorphological, and microanalytical changes, mainly related to mineral species and their relative abundance, fabric types (particle organization and voids), cements and other soil constituents, sensitivity to heat, produced by the impact of high temperatures and also, to study the relation of such effects with the apparent increasing stability of the remaining aggregates trying to confirm our hypothesis that the increase of AS due to heating is real and not apparent.

2. Material and methods

2.1. Soil samples used for laboratory experiments

Samples of five different sites were used for this study (Fig. 1). Three from Alicante, SE Spain, (S-1, Llíber; S-3, Gorga; and S-4, Sierra de la Grana), one from Valencia, E Spain, (S-2, Navalón) and one from Cádiz, S Spain, (S-5, Sierra del Algibe in Parque Natural de Los Alcornocales). Soils S-1 and S-5 were Alfisols (Soil Survey Staff, 2014) and S-2, S-3 and S-4 Entisols. Parent materials were (Table 1): Cretaceous limestone (S-1), Cretaceous calcarenite (S-2); Miocene marly limestone (S-3), Tertiary limestone (S-4) and Miocene sandstone (S-5). Soil samples were taken from 0–2.5 cm depth of topsoil mineral horizon and beneath vegetation influence mainly composed of: *Pinus halepensis* in the case of S-1, S-2, S-3 and S-4, and *Pinus pinaster* in the case of S-5. The mean annual rainfall for each soil sampling area is: 556 mm for Llíber; 405 mm for Sierra de la Grana; 495 mm for Gorga; 479 mm for Navalón; and 1440 mm for Sierra del Algibe.

2.2. Laboratory experiments

All soil samples were dried at room temperature (~25 °C) during a week. Triplicate soil samples were carefully dry-sieved to obtain 0.25–4 mm and <0.25 mm sieve fractions, recording the weights of both fractions, and discarding coarser material (>4 mm). Sieve fractions were mixed again and placed on porcelain containers to be heated in a preheated muffle furnace at 300, 500 and 700 °C during 20 min, simulating different heating scenarios (samples were stirred after 10 min heating to mix and homogenize the heating conditions). After each heating treatment, samples were sieved again through a 0.25-mm mesh and both fractions were separately weighted for control and for each heating temperature for the two fractions studied. Triplicate unheated samples were used as control. With this data we determined the percentage of mass lost by volatilization after heating (VL: volatilization loss), and the percentage of mass weight (MW) in each fraction to know if heating treatments produced a direct destruction of aggregates of fraction 0.25–4 mm and transferred to the <0.25 mm fraction.

Soil aggregate stability (AS) was measured in the 0.25–4 mm sieved fraction in control (unheated) and in 300, 500 and 700 °C heated samples ($n = 60$), and determined with the rainfall simulator method according to Roldán et al. (1994) and based on the method of Benito and Díaz-Fierros (1989). This method examines the proportion of macroaggregates that remained intact after a soil sample was subjected to artificial rainfall of a specific energy. Four grams of soil material (4–