Relative contribution of naturally-occurring carbonates and soil organic carbon to soil aggregation dynamics

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Abstract

Carbonates in the topsoil of many Mediaterranean soils interact with soil organic carbon (SOC) and aggregation dynamics, by decreasing organic matter mineralization and enhancing aggregate stability. The relative contribution of SOC and carbonates in two Mediterranean soils were studied. We hypothesized that SOC-carbonates interaction can alter aggregation hierarchy and that the relative role of these cementing agents can change depending on aggregate-size fractions. Topsoil (0-20 cm) of a carbonated (Typic Calcixerept) and a non-carbonated (Typic Haploxerept) soil were forced to pass a 250 µm sieve and incubated at 25 ºC for 63 days with the following treatments: carbonated (C) or non-carbonated (NC) soil with (ST) and without (NST) maize straw. Aggregates dynamics in the non-carbonated soil was controlled by organic matter, according to aggregation hierarchy (Six *et al.* 1998). Unlike the non-carbonated soil, we observed that carbonates had a major role in macroaggregate (>250 µm) formation at low SOC content in C.NST. Maize straw addition enhanced macroaggregates percentage in C.ST compared to C.NST. Microaggregates (50-250 µm) within macroaggregates percentage was similar in both treatments at day 21, but it was greater in C.ST than in C.NST thereafter. No effect of carbonates was observed in macroaggregates >2000 µm in the carbonate-rich soil. We concluded that carbonates presence in the carbonate-rich soil can interfere with SOC dynamics by modifying the aggregation hierarchy of soils as that described in the non-carbonated soil.

Key Words

Aggregate-size distribution, naturally-occurring carbonated soil, carbonates, soil organic carbon

Introduction

Soils of Mediterranean climate can have carbonates accumulation at some depth, as it happens in the Ebro Valley of Spain. Lithogenic or primary carbonates, originated from the calcareous parental material, are the main source for the formation of secondary or pedogenic carbonates in these soils. Evapotranspiration in arid and semi-arid soils enhances precipitation of secondary carbonates (Lal and Kimble 2000). Soil structure results from the arrangement of primary particles into micro- and macroaggregates, creating a pore space. The association of primary particles and aggregates is mediated by different cementing agents depending on soil conditions: organic matter, inorganic cations, carbonates, clay, and soil biota. Carbonates contribute to soil organic carbon (SOC) protection and aggregate formation and stabilization (Bronick and Lal 2005).SOC dynamics and aggregation dynamics are closely related when organic materials are the main binding agents of soil (Six *et al.* 2000). Carbonates can decrease SOC mineralization and enhance aggregation due to increased cationic bridging effect by Ca^{2+} and precipitation of secondary carbonates that forms coatings around primary particles and organic residues, acting as a stabilizing agent (Baldock and Skjemstad 2000; Lützow *et al.* 2006). Consequently, positive correlation of aggregate stability and SOC quality and quantity may change in carbonated soils (Bouajila and Gallali 2008).

In this work, we used a naturally-occurring carbonate-rich soil to study aggregation dynamic and contribution of SOC and carbonates to soil structure in medium-term incubations with maize straw addition. Many authors have studied the role of SOC and carbonates in aggregate formation and stability adding external sources of calcium to carbonate-free soils (Muneer and Oades 1989, Wuddivira and Camps-Roach, 2007), however few studies have used carbonated soils (Bouajila and Gallali 2008). We hypothesized that the relative role of carbonates and SOC in aggregation dynamics may change depending on aggregate-size fractions and that SOC-carbonates interaction can change aggregate hierarchy of the carbonated soil.

Methods

Site description and sampling

Surface soil (0-20 cm) was collected from a toposequence of the Oja River in La Rioja (Spain), with different carbonates content. The carbonate-rich soil in Rodezno (C) is a Typic Calcixerept (Soil Survey Staff 2006) with a loam texture (38% sand, 44% silt, and 18% clay), total organic carbon content of 8.8 g/kg, and carbonates content of 220 g/kg. The non-carbonated soil in Castañares (NC) is a Typic Haploxerept (Soil Survey Staff 2006) with a loam texture (47% sand, 38% silt, 15% clay) and total organic carbon content of 7.6 g/kg. The two soils have been conventionally cultivated with a rotation based on wheat (*Triticum aestivum* L.), pea (*Pisum sativa* L.), and sugar beet (*Beta vulgaris* L.) or potato (*Solanum tuberosum* L.) for the last 50 years. The climate in the area is sub-humid Mediterranean.

Samples were collected in different points at each soil and mixed to get a composite sample. The incubation protocol was adapted from Denef *et al.* (2001). After collection, field-moist soils (10-12% w/w) were gently forced to pass through a 250 µm sieve to reduce macroaggregates and recover only microaggregates (<250 µm) and sand, silt and clay primary particles. The 250-1000 µm sized sand and particulate organic matter fractions were kept and remixed with the 250 µm sieved soil. The following treatments and their combinations were studied with 3 replicates: (i) carbonated soil (C) or non-carbonated soil (NC) and (ii) with (ST) or without (NST) maize straw. In total, 60 soil cores were incubated at 25 ºC for 63 days. Soil subsamples, equivalent of 91 g dry soil, were placed in aluminium cylinders (diameter = 6.7 cm, height = 2.15 cm) closed at the bottom by a nylon mesh of 53 µm. They were carefully packed to obtain a bulk density of 1.2 Mg/ha. The soil cores were suspended in a sealed 1 l glass jar with 20 ml of deionized water in a beaker at the base to minimize desiccation. The added maize straw was only stems and leaves (C/N = 60) ground to the size of 200-500 µm (Cosentino *et al.* 2006). Soil subsamples were mixed with 353.89 mg of straw to obtain 1.75 mg C/g soil in each core. The soil cores were incubated at field capacity. The cores with maize straw were wetted up to field capacity with NH_4NO_3 solution to keep the sample C/N ratio around 10 and minimize N limitation during straw decomposition. In the same way, the cores without straw were wetted with deionized water.

Aggregate-size distribution measurements

Aggregate-size distribution was analysed at days 21, 42 and 63 according to Six *et al.* (2002). Soil cores were wet sieved following the method of Elliott (1986) to obtain large macroaggregate (>2000 µm), macroaggregate (250-2000 µm), microaggregate (50-250 µm) and silt plus clay (<50 µm) fractions. Approximately half of the soil core was submerged in deionized water on top of a 2000 µm sieve for 5 min before sieving. Each soil subsample was manually sieved by moving the sieve up and down 3 cm, 50 times in 2 min. The material passing through 2000 µm sieve was poured onto the next µm sieve and sieving was repeated. Fractions recovered in each sieve (2000, 250, and 50 µm) were oven-dried at 50 ºC.

The macroaggregate fraction (>250 µm) was used to isolate microaggregates within macroaggregates (Six *et al.* 2002). Macroaggegates were immersed in deionized water on top of a 250 µm sieve and shaken with 50 glass beads (diameter = 4 mm). A regulated continuous water flow through the sieve allow to flush all material <250 µm onto a 50-µm sieve, separated from the horizontal shaker, 125 rev/min). After all macroaggregartes are disrupted, only coarse sand and POM remained on the 250 µm sieve. Material remaining on 50 µm sieve was wet sieved to obtain water stable microaggregates. The two fractions were also oven-dried at 50 ºC. A subsample of microaggregates within macroaggregates and free microaggregates were used to separate sand between 50-250 µm. The percentage of soil mass in each aggregate-size fraction was determined (soil mass in the fraction/total soil mass in the subsample) after sand corrections for comparison among treatments and soils.

Data were analysed using ANOVA (univariate linear model). Treatment means were compared using significant differences ($P<0.05$), and post hoc analysis was performed by Duncan test ($P<0.05$). All statistical analyses were performed using SPSS 16.0software (SPSS Inc. 2008, Chicago IL).

Results

In the non-carbonated soil, fresh organic matter addition (i.e. maize straw) enhanced Magg formation, according to the aggregation hierarchy described by Six *et al.* (1998). Organic residues increased soil microbial activity, resulting in a greater production of organic binding agents, and macroaggregates percentage increased in NC.ST compared to NC.ST (Fig 1). As organic matter is decomposed, organic binding agents are gradually degraded and macroaggregates percentage decreased in NC.ST. After macroaggregates dispersion, microaggregates amount per macroaggregates mass unit was also greater in NC.ST than in NC.NST due to fresh organic matter addition (Table 1).

Table 1. Percentage of soil mass in large macroaggregate (LMagg, >2000 µm), macroaggegate (Magg, >250 µm), and microaggregate within macroaggregate (mMagg, 50-250 µm) fractions. Studied treatments: carbonated (C) or non-carbonated (NC) soil with (ST) and without (ST) maize straw. Values in the same column followed by different letters are significantly different at P<0.05 according to ANOVA.

	Incubation day		
	21	42	63
LMagg (>2000 µm)			
C.NST	0.23 ± 0.08 b	0.16 ± 0.07 b	0.15 ± 0.02 b
C.ST	7.53 ± 0.26 a	11.92 ± 1.64 a	6.77 ± 1.28 a
Magg (>250 µm)			
NC.NST	1.28 ± 0.08 c	1.46 ± 0.16 c	1.12 ± 0.16 c
NC.ST	3.93 ± 0.64 b	2.41 ± 0.20 bc	2.43 ± 0.30 b
C.NST	4.35 ± 0.55 b	3.05 ± 0.23 b	2.74 ± 0.13 b
C.ST	8.88 ± 0.97 a	8.64 ± 0.59 a	9.74 ± 0.52 a
mMagg (50-250 µm)			
NC.NST	0.96 ± 0.33 c	1.1 ± 0.48 c	1.11 ± 0.04 c
NC.ST	4.95 ± 0.84 b	2.72 ± 0.73 c	3.68 ± 0.59 c
C.NST	32.89 ± 0.05 a	29.64 ± 0.40 b	30.46 ± 1.97 b
C.ST	29.86 ± 1.93 a	38.17 ± 1.19 a	39.24 ± 1.02 a

LMagg and Magg percentage in expressed as aggregates amount per soil sample mass unit. The percentage of mMagg is expressed as microaggregates amount per macroaggregates mass unit.

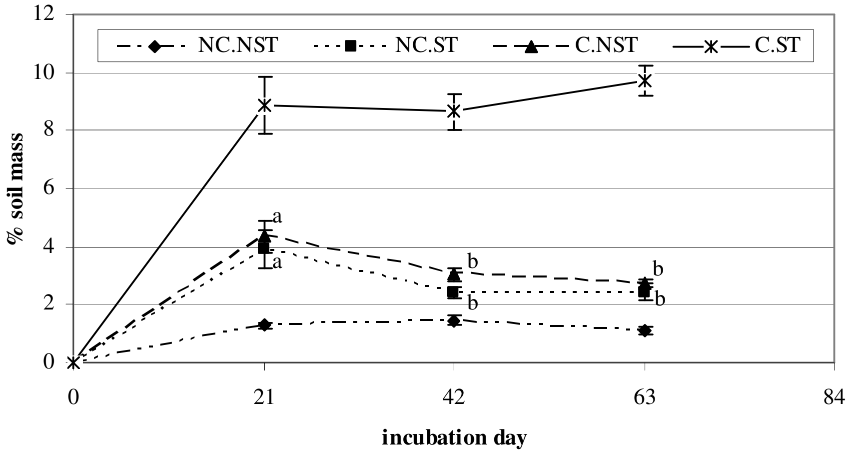

Figure 1. Percentage of soil mass in macroaggregate (>250 µm) fraction at incubation days 21, 42, and 63. Studied treatments: carbonated (C) or non-carbonated (NC) soil with (ST) and without (ST) maize straw. In each treatment, values followed by different letters are significantly different at P<0.05 according to ANOVA.

Comparing to the non-carbonated soil, two major differences were observed in the aggregation dynamics of the carbonate-rich soil. First, greater macroaggregates percentage in C.NST than in NC.NST (Table 1) indicates the role of carbonates in macroaggregation. Carbonates mediated in aggregation most likely due to cationic bridging effect of Ca^{2+} (mineral-mineral and mineral-organic matter linkages) and precipitation of secondary carbonates coatings (Clough and Skjemstad 2000; Baldock and Skjemstad 2000). Second, macroaggregates percentage was also greater in C.ST than in NC.ST. In addition, unlike the NC.ST, macroaggregates amount remained almost constant in C.ST during this short incubation (Figure 1). These results suggest that there is an interaction between fresh organic matter and carbonates that increased macroaggregates water stability. Shang ant Tiessen (2003) proposed that carbonates precipitation (i.e. coatings) may play a major role in the stability of more labile organic matter, resulting in an enhanced stability of aggregates.

Although macroaggregates percentage was greater in C.ST than in C.NST, similar microaggregates amount per macroaggregates mass unit was observed in both treatments at day 21. Microaggregates percentage was greater in C.ST than in C.NST thereafter (Table 1). In addition, microaggregates percentage was greater in C.NST and C.ST than in NC.NST and NC.ST. This indicates that carbonates rather than organic matter largely contribute to microaggregates fraction. The role of calcium in clay and organic matter flocculation into colloidal aggregates may be responsible of microaggregates formation and stabilization mechanisms (Muneer and Oades 1989). Moreover, fresh organic matter addition may improve this mechanism, increasing microaggregation.

When only large macroaggregate fraction (>2000 µm) was studied, no significant effect of carbonates was observed in C.NST (Table 1). Large macroaggregate formation in C.ST was due to organic matter addition only.

Conclusion

In the carbonated soil, both soil organic carbon and carbonates contribute to the aggregation dynamics. Carbonates controlled macroaggregates formation at low soil organic carbon content in C.NST; however, maize straw addition promotes fresh organic matter-carbonates interaction that enhanced macroaggregates formation and water stability in C.ST. Microaggregates formation was also largely related to carbonates aggregation mechanisms in C.NST and C.ST. We conclude that carbonates are the dominant binding agents of the naturally-occurring carbonated soil with low organic matter content. When fresh organic matter is added, interaction between carbonates and SOC affected aggregation dynamic of this soil. Aggregate hierarchy appeared to be altered when SOC is not the major stabilizing agent of soil. More research is needed to understand the relative role of SOC and carbonates on different aggregate-size fractions, in order to adapt the aggregate hierarchy model to carbonated soils. Research on this subject will also help to study mechanisms for organic carbon and inorganic carbon stabilization in soils.

References

Baldock JA, Skjemstad JO (2000) Role of the soil matrix and minerals in protecting natural organic materials against biological attack. *Organic Geochemistry* **31**, 697-710.

Bouajila A, Gallali T (2008). Soil organic carbon fractions and aggregate stability in carbonated and no carbonated soils in Tunisia. *Journal of Agronomy* **7**, 127-137.

Bronick CJ, Lal R (2005). Soil structure and management: a review. *Geoderma* **124**, 3-22.

Clough A, Skjemstad JO (2000) Physical and chemical protection of soil organic carbon in threeagricultural soils with different contents of calcium carbonate. *Australian Journal of Soil Research* **38**, 1005-1016.

Cosentino D, Chenu C, Le Bissonnais Y (2006). Aggregate stability and microbial community dynamics under drying-wetting cycles ina silt loam soil. *Soil Biology and Biochemistry* **38**, 2053-2062.

Denef K, Six J, Paustian K, Merckx R (2001) Importance of macroaggregate dynamics in controlling soil carbon stabilization: short-term effects of physical disturbance induced by dry-wet cycles. *Soil Biology and Biochemistry* **33**, 2145-2153.

Elliott ET (1986).Aggregate structure and carbon, nitrogen, and phosphorus in native and cultivated soils. *Soil Science Society of America Journal* **50**, 627-633.

Lal R, Kimble JM (2000) Pedogenic carbonates and the global C cycle. In 'Global Climate Change and Pedogenic Carbonates'. (Eds R Lal, JM Kimble, H Eswaran, BA Stewart) pp. 1-14. (CRC Press: Boca Raton, FL, USA).

Muneer M, Oades JM (1989) The role of Ca-organic interactions in soil aggregate stability. III. Mechanisms and Models. *Australian Journal of Soil Research* **27**, 411-423.

Shang C, Tiessen H (2003) Soil organic C sequestration and stabilization in karstic soils of Yucatan. *Biogeochemistry* **62**, 177-196.

Six J, Elliott ET, Paustian K, Doran JW (1998) Aggregation and soil organic matter accumulation in cultivated and native grassland soils. *Soil Science Society of America Journal* **63**, 1350-1358.

Six J, Elliott ET, Paustian K (2000) Soil macroaggregate turnover and microaggregate formation : a mechanism for C sequestration under no-tillage agriculture. *Soil Biology and Biochemistry* **32**, 2099-2103.

Six J, Callewaert P, Lenders S, De Gryze S, Morris SJ, Gregorich EG; Paul EA, Paustian K (2002) Measuring and Understanding Carbon Storge in Afforested Soils by Physical Fractionation. *Soil Science Society of America Journal* **66**, 1981-1987.

Wuddivira MN, Camps-Roach G (2007) Effects of organic matter and calcium on soil structural stability. *European Journal of Soil Science* **58**, 722-727.