

Carbon saturation in the silt and clay particles in soils with contrasting mineralogy

Saturación del carbono en las partículas de limo y arcilla en suelos con mineralogía contrastante

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SUMMARY

The silt and clay particles play a key role as stabilizing agents of soil organic carbon (SOC). Several lines of evidence indicate a theoretical maximum of C saturation in individual particles. In the present study, we hypothesized that a C fraction displaying linear accumulation relative to the SOC is not influenced by C saturation, while a fraction displaying an asymptotic relationship is regarded as saturated (Stewart *et al.*, 2008). The aim of the present study was to compare the amount of C in the silt and clay sized fractions in temperate and subtropical cropping soils across a range of textures with different mineralogy. Twenty-one and 18 soil samples containing 1:1 and 2:1 clay of temperate soil from Chile under monoculture of maize (*Zea mays* L.) for at least 30 years and 9 subtropical soils from Mexico under maize and bean (*Phaseolus vulgaris* L.) cropping for 9 years having mixed clay were collected at 0-0.1 m. The SOC of 2:1 soils was significantly higher (14 ± 0.5 g kg⁻¹ dry soil) than 1:1 soils (10 ± 0.7 g kg⁻¹). However, subtropical soils showed the highest values (59 ± 0.5 g kg⁻¹). A positive ($P < 0.01$) relationship was observed between the SOC and the C in the silt fraction (R^2 0.80-0.97, $P < 0.01$). In contrast, the clay fraction remained constant or showed asymptotic behavior. We conclude that the silt fraction, unlike clay, showed no evidence of C saturation, while clay accumulates C to a maximum. On average, the 2:1 clay was saturated at 1-2 g C kg⁻¹ and 1:1 at 1 g C kg⁻¹, and subtropical soils at 14 g C kg⁻¹.

Index words: *particle-size fractionation; ultrasonic dispersion; soil organic matter.*

RESUMEN

El limo y la arcilla juegan un papel clave en la estabilización del carbono orgánico del suelo (SOC) y son fracciones susceptibles de saturarse de C. En este trabajo se postula que si un reservorio de carbono (C) muestra una acumulación lineal del contenido de SOC, la fracción no está saturada con C, mientras que una fracción que muestre un plató o una relación asintótica se considera saturada (Stewart *et al.*, 2008). Se comparó el C en las fracciones del tamaño del limo y arcilla en suelos templados y subtropicales de cultivo que presentan un intervalo contrastante de texturas con diferentes mineralogías. Se muestrearon de 0-0.1 m, 21 muestras con arcillas del tipo 1:1 y 18 con arcillas del tipo 2:1 de suelos templados de Chile bajo monocultivo de maíz (*Zea mays* L.) por al menos 30 años y, 9 suelos subtropicales de México bajo rotación de maíz y frijol (*Phaseolus vulgaris* L.) por 9 años con arcillas mixtas. En promedio, el C en suelos con arcillas 2:1 fue significativamente superior (14 ± 0.5 g kg⁻¹) a los suelos con arcillas 1:1 (10 ± 0.7 g kg⁻¹). Sin embargo, los suelos subtropicales mostraron el valor más alto (59.0 ± 0.5). Hubo una relación positiva entre el SOC y el C en la fracción de limo (R^2 0.80-0.97; $P < 0.01$). En contraste, la fracción arcilla fue constante o mostró un comportamiento asintótico. Se concluyó que la fracción de limo, a diferencia de la arcilla, no mostró evidencia de saturación con C. La fracción de limo se considera parcialmente reactiva, mientras que la fracción de arcilla acumula C hasta un valor máximo. En promedio la arcilla se saturó con 1-2 g C kg⁻¹ para suelos 2:1, con 1 g C kg⁻¹ para suelos 1:1 y los suelos subtropicales se saturaron con 14 g C kg⁻¹.

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Palabras clave: *fraccionamiento físico de partículas; dispersión por ultrasonido; materia orgánica del suelo.*

INTRODUCTION

Agricultural temperate and subtropical soils that have lost their soil organic carbon (SOC) might again accumulate a significant C stock (Paustian *et al.*, 1997, 2000; Lal, 2004; Smith, 2004). A new steady state can be achieved by increasing the C-input rates, improving soil fertility, conservation practices and zero tillage, converting cropping to grassland and improving agricultural practices as organic farming (Freibauer *et al.*, 2004). However, several lines of evidence indicate a maximal C pool (C-saturation) in the silt and clay fractions (Hassink, 1997; Six *et al.*, 2002), which might limit the stabilization capacity of bulk soil (Six *et al.*, 2002). C-saturation depends on the potential of silt and clay fractions to stabilize soil organic matter (SOM) from microbial mineralization (Baldock and Skjemstad, 2000). There are several mechanisms of SOM stabilization, including selective preservation by recalcitrant organic compounds, spatial inaccessibility within soil aggregates and SOM interaction with the mineral phase (Sollins *et al.*, 1996; von Lützow *et al.*, 2006). Mineral interaction is regarded as the most important mechanism. A direct relationship between SOC and the mass of silt and clay in tropical (Feller and Beare, 1997) and temperate soils (Quiroga *et al.*, 1996; Hassink, 1997; Carter *et al.*, 2003; Konen *et al.*, 2003; Galantini *et al.*, 2004; Müller and Höper, 2004; Arrouays *et al.*, 2006) has been demonstrated. Although these correlations have been improved by statistical treatments (Feng *et al.*, 2013), they are not widespread (Franzluebbers *et al.*, 1996; Scott *et al.*, 1996; Rühlmann, 1999).

On the other hand, despite the considerable evidence of textural control on SOM dynamics, the effect of mineralogy (2:1 and 1:1 clay) remains controversial. Soil samples rich in high-activity clay (2:1, smectites) do not retain more SOM than those dominated by low-activity clay (1:1, kaolinite) (Feller and Beare, 1997), including oxisols (Dalal and Mayer, 1986; Krull and Skjemstad, 2003). Wattel-Koekkoek *et al.* (2003) reported that the mean residence time of kaolinite-bound C in northern Mozambique did not differ significantly from that of smectite-bound C. Soil

organic C in kaolinitic soils in the tropics is similar to SOC in less-weathered soils of temperate climates (Sanchez and Logan, 1992). In contrast, Vertisols dominated by smectitic mineral clay contained greater amounts of organic matter than soils dominated by kaolinite, feldspars and quartz (Ngole and Ekosse, 2009). This is important because mineralogy can lead to C-saturation in the silt and clay fractions (Six *et al.*, 2002). The need for quantitative studies estimating the potential for C-sequestration and the role of soil texture and clay type on C-saturation is crucial (Curtin *et al.*, 2015).

It is very likely that soil C in silt and clay fractions can be in a steady-state (equilibrium) and, at the same time, be saturated with soil organic C. If the soil is under equilibrium, there is a potential for soil C sequestration, but when the maximum is achieved, further inputs of new organic matter cannot be stabilized in the fine particles of silt and clay. Based on the hypothesis that the C pool in the fine soil particles has an upper limit of soil C stabilization or C saturation, with respect to SOC levels (Stewart *et al.*, 2008), we used this approach to decide whether the C fraction is influenced by saturation. The C pool of a soil fraction displaying linear accumulation is interpreted as not being influenced by C saturation, while the opposite is true for a C pool exhibiting a plateau or asymptotic influence (Diekow *et al.*, 2005; Stewart *et al.*, 2008).

To test our hypothesis, we sampled 13 temperate soils in the central valley of Chile, which were compared with three subtropical soils sampled in three micro-basins of the southern region of Oaxaca, Mexico, by Matus *et al.* (2011). All soils were physically fractionated using the same method, ultrasonic dispersion and decantation. Ultrasonic procedures in soil without previous separation of particulate organic matter (POM) may contain a significant proportion of this material in the fine fraction (Amelung and Zech, 1999; Oorts *et al.*, 2005; Kaiser and Berhe, 2014). In the present study, soil particles were obtained using an optimized procedure. Consequently, we assumed a reduced redistribution of SOC in the fine fraction.

The goal of this study was to elucidate whether or not the silt and clay fractions are saturated in the silt and clay fractions of temperate and subtropical soil from Chile and Mexico, respectively.

MATERIALS AND METHODS

Sampling Sites

Chile. A sampling area was selected along a longitudinal transect between 33° 30' and 35° 02' Latitude S and between 70° 45' and 71° 48' Longitude W in the Central Valley of Chile. The soil samples were taken on September 2006 over a total of 13 modal pedons series belonging to Alfisol, Entisol, Inceptisol, Mollisol and Vertisol orders (Soil Survey Staff, 1999). The soils formed under similar vegetation, parent material and climatic conditions (Hajek and Di Castri, 1975). Most soils originated from alluvial sediments subject to seasonal droughts and floods (CIREN, 2001). The selected soils were mostly under maize monoculture with conventional tillage in the farmer's field for more than 30 years (INE, 2007). The maize crop yield fluctuates between 12 and 15 Mg grain ha⁻¹ (15% moisture). Depending on the amount of crop residues, they are burned or incorporated by conventional plowing to the Ap horizon (0-0.20 m). Mean annual precipitation in this valley is 676 mm and mean annual temperature is 13.8 °C (Santibañez and Uribe, 1993).

Mexico. Matus *et al.* (2011) conducted a study in three representative micro-basins of the Southern region of Mexico in the state of Oaxaca, namely the Cuicateca, Mazateca, and Mixe microbasins, where a sustainable hillside management project was established (PMSL, 2004). These soils are characteristic of steep sites (> 30% slope), Ferrasol (FAO-ISRIC-SICS, 1998), where small farmers conduct agriculture. The sampling area is subjected to slash and burn agriculture following cultivation of maize and beans. Traditional farming (conventional cropping) in this area has low-inputs of nutrients. After 9 and occasionally up to 60 years of cultivation, farmers move into new areas where they clear secondary tree vegetation and establish new crop rotation. The mean annual precipitation in the Cuicateca micro-basin (2180 m) is 700 mm and mean annual temperature 19 °C. These conditions for the Mazateca (1689 m) are 2000 mm and 22 °C and for the Mixe (1422 m), 1500 mm and 22 °C.

Soil Sampling

At each sampling site, three soil pits were excavated 100 m apart on a line transect. Soil samples consisted of ~2 kg moist soil from the Ap horizon and they were

collected with a steel cylinder (0.05 m × 0.082 m diameter). Bulk density was also determined. In total, we took 39 soil samples in Chile and 9 samples in Mexico. The sampling areas and the scheme used in the present study followed the most common experimental design encompassing a single replicate per soil series when a large-scale experimental area is the only option and the knowledge is restricted to this particular area (Webster, 2007).

All soils were mixed and homogenized and coarse organic matter (leaves, wood, and roots), removed by hand. All soils were air dried and sieved through a 2 mm mesh.

Physical Fractionation

We followed the sonication and decantation procedure used by Matus *et al.* (2011) to obtain four particle size fractions [coarse sand (250-2000 µm), fine sand (53-250 µm), silt (2-53 µm) and clay (< 2 µm)]. All 48 soil samples, except Palquibudi, Piuchen and Hualañé, were physically fractionated in duplicate or triplicate. All samples were fully dispersed after the light fraction and floatable organic materials were removed (Matus *et al.*, 2011). The fractionation procedure is as follows. About 50 g of moist soils were suspended in half-liter capped plastic bottles containing 10 glass beads (5 mm diameter) and 180 mL water. The suspension was shaken for 16 h (40 cycles min⁻¹) and sieved through a 250-µm sieve. The material remaining on the sieve contained sand particles and visible fragments of organic debris (plant and animal structures). The material retained on the sieve was washed several times with tap water, then combined with < 250 µm fractions (fine sand, silt and clay) and re-suspended in 100 mL of water, and ultrasonically treated with 910 J mL⁻¹ (power output 37.3 W). The ultrasonic machine (Fisher Sonic Dismembrator, Model 300) was equipped with a titanium probe with flat tip (18.8 mm diameter and 56 mm length) operating at 20 kHz. The clay and silt fractions were separated after corrected settling time by gravity sedimentation, applying Stoke's law at room temperature until clear supernatant was obtained (15 decantation cycles). All fractions were oven-dried at 60 °C and weighed. The physical fractions of silt and clay (< 50 µm) did not show any visual evidence of plant and animal fragments that could have been transferred during the sonication and sedimentation procedure as observed under electron

scanning microscope (data not shown). On average, the amount of soil material recovered among all particle size fractions after dispersion and fractionation ranged between 93% and 111%. The slope of the regression analysis (e.g., $R^2 = 0.76$, $P < 0.01$) between the soil mass recovered for coarse sand, fine sand, silt and clay by physical fractionation and using pipette method showed no significant differences.

Carbon Analysis

Chilean soils and their physical fractions were analyzed for organic C in duplicates using acid dichromate oxidation by the Walkley and Black method (Matus *et al.*, 2009). The Mexican soil samples for the C concentration in the bulk soil and physical fractions were determined using an automatic C analyzer (TOC, Shimadzu 5000 SSM). The C concentration (g C kg^{-1} fraction) in each separate particle size was multiplied by the corresponding dry mass of the particle size to obtain the expression g C kg^{-1} soil for each fraction. Several studies have addressed the uncertainties of SOC determination by wet or dry combustion. However, no significant differences have been found (e.g., Arrouays *et al.*, 2001; Matus *et al.*, 2009). Therefore, we assumed that the SOC determined by the TOC method in subtropical soils were comparable with those obtained by wet combustion in temperate soils, particularly when the correction factor is used (Matus *et al.*, 2009).

X-ray Diffraction

Soil mineralogy of Mexican soils was obtained from PMSL (2004), while no records were found for Chilean soils. Identification of clay ($< 2 \mu\text{m}$) minerals of Colchagua, Macarena, Nilahue, Peteroa and San Vicente soils were conducted by X-ray diffraction (Shimadzu 5A, diffractometer) as exemplary soils to support early reports of similar genetic horizons sampled by Besoain *et al.* (1984) (see Table 1). Briefly, dry soil samples were prepared by removing the soil organic matter by strong oxidation with 30% H_2O_2 at 50 °C. Clay fraction ($< 2 \mu\text{m}$) was separated following the above indicated procedure and thereafter saturated with Mg (MgCl_2 1M) to improve the intensity of the reflections at Cu-K α radiation (40 kV and 20 mA).

Statistical Analysis

A Gaussian distribution of all variables was tested using a skewness test value of 0.5 (Webster and Oliver, 2001). The relationships between the C in the bulk soils and the C associated with fine particle-size fractions versus the silt and clay content of soils were examined by ordinary least square regression. The assumption of linearity and homoscedasticity of the predicted values was assessed. A paired t-test was used to compare the mean values. All regressions, t-test and ANOVAs were computed using JMP 3.2.2. (SAS Institute, Cary, NC, and U.S.A.) for $P < 0.05$.

RESULTS

Soil Characteristics

The sampled temperate soils presented different clay mineralogy (2:1 and 1:1) which were compared with the result presented by Besoain *et al.* (1984) (Table 1).

The clay content of the soils ranged from 55 ± 24 to $566 \pm 13 \text{ g kg}^{-1}$ soil in Chilean temperate soils, while these values in Mexican soils ranged from 150 ± 6 to $320 \pm 6 \text{ g kg}^{-1}$ (Table 1). The average of clay mass for 2:1 in Chilean soils was $249 \pm 22 \text{ g kg}^{-1}$ and for 1:1 soils $174 \pm 42 \text{ g kg}^{-1}$, while the mixed clay in Mexican soils averaged $213 \pm 53 \text{ g kg}^{-1}$. In general, the coarse sand fraction was always lower than the fine sand fraction, with the exception of Mixe soil. For Chilean soils, coarse sand ranged 56 ± 11 - $197 \pm 10 \text{ g kg}^{-1}$ for 2:1 and 46 ± 35 - $421 \pm 16 \text{ g kg}^{-1}$ for 1:1 soils; while in Mexican soils it ranged between 25 ± 5 and $146 \pm 6 \text{ g kg}^{-1}$.

For Chilean soils, SOC ranged between 7.4 ± 0.6 and $18 \pm 0.2 \text{ g kg}^{-1}$, and 1:1 showed the lowest average C content ($9.6 \pm 0.7 \text{ g kg}^{-1}$) compared with 2:1 soil ($13.8 \pm 0.4 \text{ g kg}^{-1}$). In general, the agricultural plots of Oaxaca under conventional cropping showed the greatest accumulation of C. The soil C content in cropped soils ranged from $24 \pm 0.3 \text{ g kg}^{-1}$ to $120 \pm 0.08 \text{ g kg}^{-1}$. Soil samples taken from the Mixe micro-basin showed the highest C content, while the samples from Cuicateca plots, the lowest (Table 1). On average, SOC in Mexican soils was more than four times higher than that in Chilean temperate soils (Table 2).

Bulk density ranged from 0.61 ± 0.04 to $1.44 \pm 0.01 \text{ kg m}^{-3}$, and the highest values were generally found in temperate soils with lower SOC.

Soil Fractions

The C in the clay fraction of Mexican soils was significantly higher (nine times) than the SOC accumulated in the clay fraction of temperate soils. However, C of 2:1 clay was twofold (2 g C kg^{-1} soil) than the amount in 1:1 clay soil. Similar results are shown for the silt fraction, although the silt content in both sites were comparable (Table 2).

X-ray Diffraction Results from Chilean Soils

X-ray diffraction analyses of clay fraction from five representative soils from Chile were consistent with those of similar modal top soils reported by Besoain *et al.* (1984) (Table 1) All soils showed evidence of

dominant phases of smectite (2:1), vermiculite (2:1), illite (2.1), chlorite (2:1) and kaolinite (1:1) and some amorphous silicate as reported earlier by Besoain *et al.* (1984). Results indicate that Peteroa and Nilahue soils had very clear reflections at 0.73 nm and 0.36 nm associated with the presence of kaolinite minerals. Both samples maintained the same *d*-spacing after ethylene-glycol solvation and heating at 490°C supporting the presence of kaolinite as the dominant clay mineral. The diffraction patterns for San Vicente, Colchagua and Macarena showed the basal reflections associated with smectitic clay. These reflections were moved to a 1.02 nm associated with mica structure when soils were treated and heated. All clay treatments confirmed the presence of smectite as the dominant clay in San Vicente, Colchagua and Macarena soils and minor presence of illite in Colchagua that was not evident in San Vicente and Macarena soils. The clay types for Mexican soils were obtained from PMSL (2004) and are shown in Table 1.

Table 1. Average of soil characteristics of soil sampled at 0-0.1 m[†].

Soil [‡]	Lat/Lon [§]	Soil order [¶]	SOC [#]	Bulk density	Coarse sand ^{**}	Fine sand ^{**}	Silt ^{**}	Clay ^{**}	Clay min ^{**}
			g kg ⁻¹	kg m ⁻³	----- g kg ⁻¹ -----				
Chile 2:1 clay									
CUC	34°67' 71°29'	Mollisol	12.1±0.9	1.39±0.05	118±35	190±33	488±4	214±63	S, V
MAR	34°44' 71°02'	Inceptisol	10.9±0.5	1.43±0.01	161±16	274± 8	397±17	124± 5	S, Ch
MAO	33°41' 70°45'	Mollisol	12.3±0.8	1.44±0.01	145± 8	272±10	417± 0	134± 9	S
QHE	34°40' 71°22'	Vertisol	14.6±1.0	1.06±0.04	59± 9	81± 9	276±0	530±27	S
AGD	33°34' 71°08'	Mollisol	16.1±0.7	1.15±0.01	62± 3	116± 3	410±0	396±10	S
CLH	34°32' 71°24'	Vertisol	13.0±0.7	1.32±0.05	56±11	120±22	578±43	173±13	S, K, I
MPC	33°30' 70°48'	Mollisol	13.6±1.3	1.30±0.01	197±10	375±17	106±26	304± 0	S, V
SVT	34°25' 71°08'	Mollisol	18.0±0.2	1.30±0.02	61± 5	148±18	660±27	109± 9	S
Chile 1:1 clay									
HLE	34°58' 71°48'	Inceptisol	14.7±1.7	1.21±0.01	76±35	169±65	303±0	566±13	K, S, V
PIU	34°30' 71°33'	Alfisol	8.1±0.8	1.21±0.05	244±63	284± 2	424±28	55±24	K
NIL	34°23' 71°31'	Entisol	7.4±0.6	1.44±0.05	266±25	286±17	330±15	95±12	K, I
PQB	34°03' 71°32'	Mollisol	11.6±0.6	1.26±0.10	46± 4	132±16	556± 0	266±20	K, AS
PET	35°02' 71°42'	Mollisol	8.1±0.6	1.24±0.05	421±16	244±32	233±16	350±5	K, I
Mexico Mixed clay									
CUI	17°51' 96°51'	Ferrasol	23.5±0.3	1.15±0.06	146±6	195± 2	490±3	170±7	V, K
MAZ	18°09' 96°54'	Ferrasol	33.7±0.4	0.92±0.02	25±5	63± 2	590±2	320±6	V, S
MIX	17°01' 96°53'	Ferrasol	119.8±0.8	0.61±0.04	112±3	30± 1	710±12	150±6	V, S

[†] ±: standard error of the mean of six samples per soil series, except HLE, PIU and PQB where only three samples were considered. [‡] AGD = Agua del gato, CLH = Colchagua, CUC = Cunaco, HLE = Hualañé, MAO = Maipo, MPC = Mapocho, MAR = Macarena, NIL = Nilahue, PET = Peteroa, PIU = Piuchen, QHE = Quiahue, PQB = Palquibudi, SVT = San Vicente, CUI = Cuicateca, MAZ = Mazateca, Mix = Mixe. [§] Latitude and Longitude. [¶] Chilean soils classified by Soil Survey Staff (1999) and Mexican soils by (FAO-ISRIC-SICS, 1998). [#] Soil organic carbon. ^{**} Coarse sand = 250-2000 µm; Fine sand = 53-250 µm; Silt and clay = < 53 µm. ^{**} Clay mineralogy: Ch = Chlorite, K = Kaolinite, S = Smectite, V = Vermiculite, I=Illite, AS = Amorphous silicates (Besoain *et al.*, 1984).

Table 2. Average of soil properties by clay type (0-0.1 m).

	n	Weight		SOC [†] -g kg ⁻¹ soil	C	
		Clay	Silt		Clay	Silt
Chile 2:1	18	135 ± 9 [‡]	545 ± 32	13.7 ± 0.5	1.9 ± 0.09	7.5 ± 0.53
Chile 1:1	21	58 ± 7	456 ± 54	9.6 ± 0.7	1.0 ± 0.13	5.0 ± 0.67
Mexico mixed	9	213 ± 6	597 ± 6	59 ± 0.5	13.6 ± 0.7	34.7 ± 0.5

[†] SOC = Soil organic carbon. [‡] ± = Standard error of the mean.

Relationship of Soil Organic Carbon in the Bulk Soil, Silt and clay Fractions

We found a positive and significant ($P < 0.05$) relationship between SOC and the C in the silt fraction in both, 2:1 and 1:1 top Chilean soils (Figure 1). The slope of the linear regression for the silt fraction ranged from 0.62 to 0.86, but there was no relationship for the clay fraction (Figure 1). The same relationship for subtropical soils from Mexico showed similar trends (Figure 2). There was a significant relationship between SOC and C in the silt fraction. Although the values were concentrated at the two extremes, the slope was 0.70, similar to those values found in temperate soils. The clay fraction of Mexican soils exhibited asymptotic behavior.

DISCUSSION

As expected, C in 2:1 soils was higher than that in 1:1 soil, indicating that the nature of clay type plays an

important role in SOC accumulation (Feller and Beare, 1997). Vertisols dominated by smectitic mineral clay have been reported to contain greater amounts of organic matter than soils dominated by kaolinite, feldspars and quartz (Ngole and Ekosse, 2009). However, subtropical Ferrasols, having a mixed clay type, showed higher SOM than temperate soils. This result reflects influence of management practices involving hand tilling and occasional plowing by animal traction with decades of maize and beans cultivation, leading to greater amount of C in subtropical soils (Matus *et al.*, 2011). In contrast, temperate soils have been arable for more than 30 years under conventional tillage with frequent plowing and burning.

In general, silt and clay fractions of subtropical soils exhibited more than 8 and 10 times more soil C than the same fractions of temperate soils. Our primary organo-mineral complexes are defined as the C bound to primary mineral particles, isolated after complete dispersion of soil (data not shown). Chenu and Plante (2006) reported that, in temperate silty soils, clay-

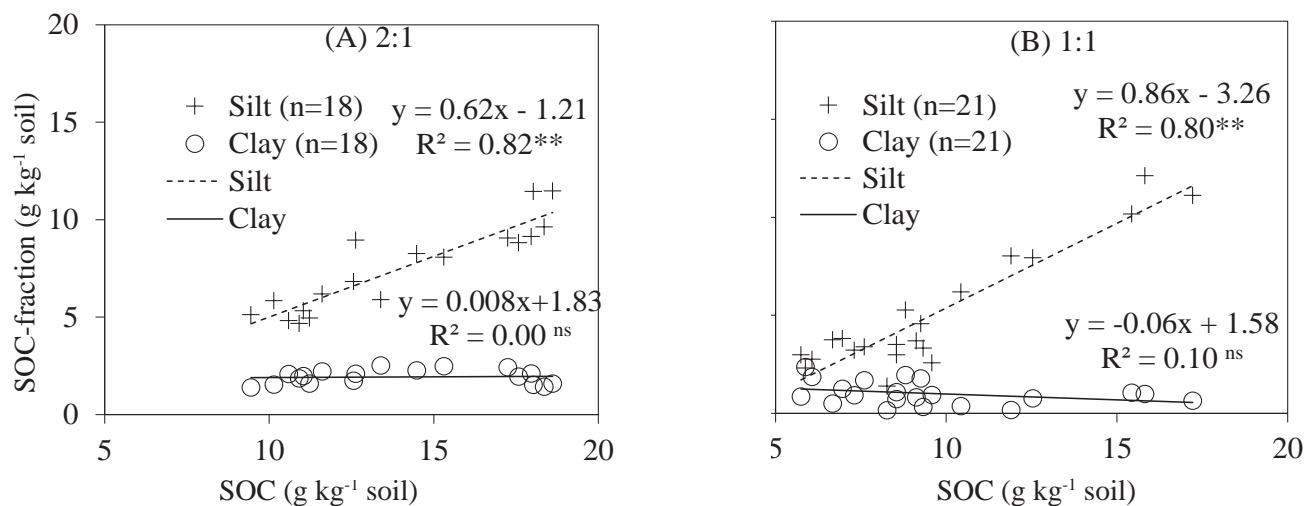


Figure 1. Relationship between soil organic C (SOC) and the C in the individual particles of silt and clay of temperate cropped soils with maize in Central Chile. * $P < 0.05$, ** $P < 0.01$.

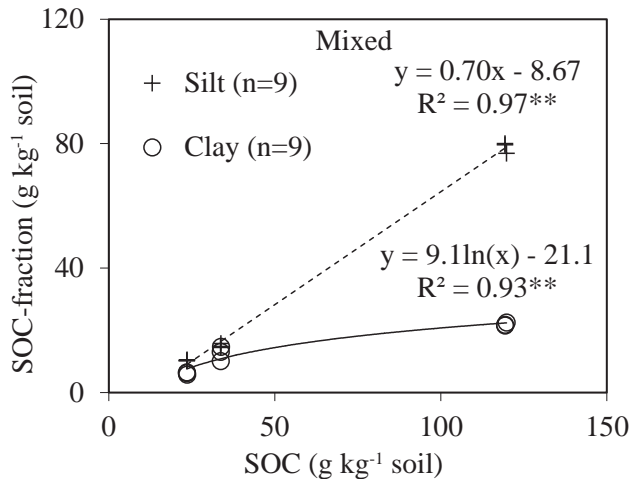


Figure 2. Relationship between soil organic C (SOC) and the C in the individual particles of silt and clay of subtropical cropped soils with maize in Oaxaca State, Mexico. * $P < 0.05$, ** $P < 0.01$.

bound SOM was in fact nanometer- to micrometer-sized micro-aggregates in which SOM was encrusted by minerals or coated minerals. In their study, very small micro-aggregates were the major sites of SOM stabilization, both by adsorption and by entrapment of organic matter (Chenu and Plante, 2006). Caner *et al.* (2010) reported that temperate $< 0.04 \mu\text{m}$ fraction of Neo-Luvisol, rich in smectite, displayed lower SOC than a ferralic Cambisol with kaolinite as the dominant species; however, the $0.2\text{-}2 \mu\text{m}$ SOC fraction was higher for Neo-Luvisol. These supported the hypothesis that poorly crystallized kaolinite exhibits a large specific surface area allowing greater sorption of C than smectite clay. Thus, the low C in $< 2 \mu\text{m}$ fraction in temperate soils having 2:1 clay compared to subtropical Ferrasols (mixed clay) can be explained by the stabilization of C within the micro-aggregates (Caner *et al.*, 2010).

Soil Fraction and C Saturation

Based on the evidence that fine silt and clay fractions can become saturated with SOC, in the present study the approach of Stewart *et al.* (2008) was used to decide in which fractions C accumulation is influenced by saturation. A soil fraction exhibiting linear accumulation is interpreted as not being C saturated, while the opposite is true for asymptotic accumulation (Diekow *et al.*, 2005; Stewart *et al.*, 2008). Although the Mexican soils were located

at the extreme of the curve, the clay fraction reached a plateau along the SOC like temperate soils, while the soil C in the silt fraction increased proportionally, and this was interpreted as not influenced by C saturation. Our analyses are based on the fact that there is a hierarchical saturation level from primary to secondary soil structure (soil aggregates) (Six *et al.*, 2002; Kool *et al.*, 2007). Therefore, we expected clay particles to be saturated before silt particles. In the present study, differences in C in the clay and silt fractions of 1:1 and 2:1 soils suggest that SOC is controlled by organo-mineral interactions because the specific surface area and adsorptive capacity are clearly different among soil minerals (von Lützwow *et al.*, 2006; Wagai *et al.*, 2009). For the subtropical soils examined here, Matus *et al.* (2011) found that silt-associated C, unlike clay-associated C, increased linearly with SOC. This is because the silt-sized class includes a partially reactive C fraction (Diekow *et al.*, 2005; Virto *et al.*, 2008). The silt-sized particle class had a relatively high void volume, where the SOC is located and physically protected (Monreal and Kodama, 1997). Thus, the silt fraction allows a linear C fraction accumulation in similar proportions across the varied soil SOC level.

CONCLUSIONS

The results of the present study confirm early findings that individual particles such as clay fraction can achieve a maximum C accumulation or saturation. When this maximum is reached, further inputs of new organic matter cannot be physically protected in the clay fraction and organic compounds progressively accumulate in the silt fraction and as uncomplexed free materials, namely particulate (POM) or free organic matter in the sand-sized fraction (Matus *et al.*, 2008). In fact, the silt-sized fraction of Chilean temperate alluvial soils and subtropical Ferrasol from Mexico did not show evidence of C saturation. In contrast, the clay fraction from the two sampled sites exhibited C saturation. On average, the clay fraction of temperate soils was saturated at $1.9 \pm 0.1 \text{ g C kg}^{-1}$ in 2:1 soils and $1.0 \pm 0.1 \text{ g C kg}^{-1}$ in 1:1 soils, while in subtropical soils they were saturated at $13.6 \pm 0.7 \text{ g C kg}^{-1}$. C accumulation in the silt fraction was explained in terms of partial reactivity and habitat pore space for microbial growth. Thus, the silt fraction allows linear C accumulation in similar proportions across SOC levels.

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