



Labile soil organic carbon for assessing soil quality: influence of management practices and edaphic conditions

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ABSTRACT

Soil organic carbon (SOC) is a complex set of pools, and to understand its dynamics it is necessary to know which of these pools are sensitive to the edaphic and climatic conditions or the agricultural practices, or to both. The objectives of this study were to evaluate the relationships between permanganate oxidizable C (POX-C) and various soil organic carbon fractions in different land-uses and soil types, and to examine whether the POX-C fraction is sensitive to different agricultural management practices in soils under no-tillage. Three treatments were identified at four sites located in the Argentine Pampas region: two different agricultural scenarios in terms of crop rotation, fertilizers and use of agrochemicals (Good Agricultural Practices and Poor Agricultural Practices, GAP and PAP, respectively) and an undisturbed natural (NE) environment adjacent to the agricultural sites as the control treatment. The following organic fractions were quantified: SOC, coarse and fine particulate organic carbon (POC_c and POC_f, respectively), hot water and acid extractable organic carbon (HWC and HAC, respectively) and POX-C. Soil POC values ranged from 0.46 to 7.29 g kg⁻¹, HAC values ranged from 1.50 to 6.73 g kg⁻¹, HWC values ranged from 0.20 to 1.10 g kg⁻¹ and POX-C values ranged from 0.41 to 1.04 g kg⁻¹ soil, POC_c being the most variable fraction (CV = 72%) and POX-C the least (CV = 22%). Soil POC_c and POC_f at 0–10 cm, and POC_c at 10–20 cm were largely explained by management practices with a component of variance > 50%. The relationship between POX-C and SOC was generally stronger (R² = 0.76–0.92) than POX-C with other organic fractions and where depth and site factors have a greater influence on this relationship than management practices. Among the labile fractions, the most sensitive indicators of soil quality in agricultural soils were POC_f and HWC, which displayed the highest F-statistic values. Despite the dilute solution used (0.02 mol L⁻¹ KMnO₄) the POX-C demonstrated limited sensitivity to different agricultural practices. However, this methodology could be used to estimate SOC regarding site conditions and depths. The POC_f was the fraction most affected by agricultural practices, indicated by high relationships with both the soil physical attributes (macroporosity, bulk density, and density, volume and stability of aggregates) and the agronomic parameters (soybean and maize yields).

1. Introduction

Agricultural management practices, such as no-tillage, crop rotation and crop sequence intensification through the use of double-cropping and cover crops, increase soil organic carbon (SOC) sequestration through its effect on the rate of soil organic matter (SOM) decomposition, and on the increase in input of crop residues (Villamil et al., 2006; Caviglia et al., 2011). In the Pampas region, known as the main crop area in Argentina (Reussi Calvo et al., 2013), some farmers have simplified the production system through a single crop (full season soybean) or a wheat/soybean sequence (Viglizzo et al., 2011). These

practices have led to physical, chemical and biological soil degradation even under no-tillage (Duval et al., 2016). In response to a decline in soil quality, a group of farmers started to adopt and promote crop species rotation, cover crops, integrated pest, weed and disease management, nutrient restoration and a rational use of agrochemicals as an integral part of a no-tillage system. Together these practices are called “Good Agricultural Practices” (GAP) (AAPRESID, 2013).

The content and quality of SOC are key indicators of soil physical, chemical, and biological properties and processes (Fageria, 2012; Duval et al., 2013). Therefore, the knowledge of SOC dynamics in agricultural soils is very important. Nevertheless, short- and medium-term SOC

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changes in response to management practices are difficult to detect due to higher background levels and natural soil variability (Purakayastha et al., 2008). In contrast, the more active constituents of SOC fractions are often early indicators of management impacts on soil quality (Culman et al., 2013).

Many researchers have used different labile SOM fractions, such as particulate organic carbon (POC) (Galantini et al., 2014; Benbi et al., 2015), hot-water extractable carbon (HWC) (Ghani et al., 2003; Yousefi et al., 2008), hydrolyzable carbon with acid extractions (HAC) (Bongiovanni and Lobartini, 2006; Duval et al., 2013) and permanganate oxidizable carbon (POX-C) (Weil et al., 2003; Chen et al., 2016) as early indicators of soil quality changes due to management practices. These labile fractions are characterized by being an organic material in transition between fresh plant residues and stabilized organic matter, with a turnover time of < 10 years (Janzen et al., 1997; Benbi et al., 2012).

The sensitivity and dynamics of the labile SOM fractions have led to wide adoption of these methods in soil science as indicators of change in the soil ecosystem (Wander, 2004). Over the years, several of the chemical and physical fractionation methodologies have been developed to isolate and separate labile SOM fractions that allow better understanding of key processes, such as cycling and nutrient availability, soil aggregation and carbon sequestration (Six et al., 1998; Benbi et al., 2014). Aspects that should be taken into account when selecting a measurement method involve the laboratory equipment, analytical veracity, cost, environmental and safety concerns, easiness of use, and its comparability to standard reference methods, among others (Lettenens et al., 2007; Morrow et al., 2016). For example, the separation and quantification of POC is expensive due to the labor required and the combustion analyzer to quantify the total carbon (C) in the extracted fraction, although adaptations have been made to streamline the extraction process (Marriott and Wander, 2006). Another drawback is the great degree of variation in how researchers extract and define the organic fractions.

The HWC and HAC represent an active component in the global C cycle. The HWC contains simple compounds, such as microorganisms, soluble carbohydrates and other compounds that account for the labile SOM fraction (Ghani et al., 2003). The use of dilute hot sulfuric acid to determine HAC hydrolyzes the entire fraction of polysaccharides including cellulose and therefore reflects the total carbohydrate content of most soils (Cheshire, 1979). Both fractions respond to land-use changes in the short-term and have been used to detect the effects of different land management practices (Yousefi et al., 2008; Fernández-Romero et al., 2016) and so is useful to obtain information about soil quality (Ghani et al., 2003). However, there are several limitations to their determination as a measure of soil quality: the procedure requires expensive laboratory equipment (water bath, shaker, centrifuge, spectrophotometer), some reagents such as phenol used in these methods are highly toxic making them hazardous for routine use in the laboratory or field, and the results show poor repeatability and high sensitivity to operator technique (Islam and Weil, 1997). So these methodologies can make comparisons of labile fractions (POC, HWC, HAC) difficult across studies and may restrict the drawing of generalizations from a rich body of literature (Wander, 2004). An alternative to this problem is to quantify the amount of organic C oxidizable with potassium permanganate (KMnO_4) as a measure of SOC lability (Blair et al., 1995).

Potassium permanganate has many characteristics that are propitious for a routine method. The intense purple color of the KMnO_4 solution enables it to serve as its own indicator. Several studies have used different concentrations of permanganate ($0.02\text{--}0.33\text{ mol L}^{-1}\text{ KMnO}_4$) to measure soil labile C (Blair et al., 1995; Weil et al., 2003). However, it has been found that the more dilute concentrations were those that showed greater sensitivity to differentiate management practices (0.02 to $0.03\text{ mol L}^{-1}\text{ KMnO}_4$) (Weil et al., 2003; Vieira et al., 2007). Weil et al. (2003) have used $0.02\text{ mol L}^{-1}\text{ KMnO}_4$ to measure the SOC labile

fraction. This fraction, called permanganate oxidizable C (POX-C) is rapid, inexpensive and can be adapted for field use (Morrow et al., 2016). In turn, it has been demonstrated that POX-C is related to most indicators of soil microbial activity (Weil et al., 2003; Culman et al., 2010) and with the POC and SOC (Weil et al., 2003; Culman et al., 2012).

There are studies that consider POX-C as a useful parameter of soil labile C and a sensitive indicator of different uses (grasslands-agriculture, Blair et al. (1995)) and management practices (different types of residue incorporation, Chen et al. (2016)). However, there is a lack of information about the sensitivity of POX-C in reflecting changes in management relative to other SOC fraction measurements. Moreover, little is known about how these relationships might change due to geographic, climatic, and/or edaphic factors. Therefore, the objectives of this study were (i) to evaluate the relationships between POX-C and various soil organic C fractions (i.e. POC, HWC, HAC and SOC) over different land-uses and soil types, and (ii) to examine if the POX-C fraction is sensitive to different agricultural management practices in soils under no-tillage.

2. Materials and methods

2.1. Study sites

The study sites were located in the most agricultural area in the Argentine Pampas, at Bengolea (Córdoba, $33^{\circ}01'32.9''\text{ S}$; $63^{\circ}37'36.4''\text{ W}$), Monte Buey (Córdoba, $32^{\circ}58'17.0''\text{ S}$, $62^{\circ}27'02.4''\text{ W}$), Pergamino (Buenos Aires, $33^{\circ}56'42.6''\text{ S}$, $60^{\circ}33'35.6''\text{ W}$) and Viale (Entre Ríos, $31^{\circ}52'42.2''\text{ S}$, $59^{\circ}41'16.2''\text{ W}$) (Fig. 1). These four study sites, located across a West-East transect present differences in climate and soil conditions: In Bengolea and Monte Buey the climate is temperate semihumid with a mean annual temperature of 17°C ; in Pergamino and Viale the climate is temperate humid with a mean annual temperature of 16 and 18°C , respectively. Mean annual precipitation is 870 , 910 , 1000 and 1160 mm in Bengolea, Monte Buey, Pergamino and Viale, respectively. The granulometric composition also shows a variation along the transect, with increasing clay and decreasing sand content from Bengolea (West) to Viale (East) (Table 1).

2.2. Treatments and experimental design

Three treatments were defined at each sampling location: (1) Good Agricultural Practices (GAP): Sustainable agriculture management under no-tillage, subject to intensive rotation with winter crops, such as wheat (*Triticum aestivum* L.), barley (*Hordeum vulgare* L.), and summer crops, such as soybean (*Glycine max* [L.] Merr.), maize (*Zea mays* L.) or sorghum (*Sorghum bicolor* L. Moench), and occasionally cover crops, such as vetch (*Vicia sativa* L.) and triticale (*X Triticosecal* Wittmack). Fertilizers were applied according to the crop nutrient needs, with minimal use of agrochemicals (herbicides, insecticides and fungicides) (Table 1); (2) Poor Agricultural Practices (PAP): unsustainable agriculture management under no-tillage subject to a minimal rotation or soybean monoculture, low nutrient application and high use of agrochemicals (Table 1); (3) Natural Environment (NE), soil without cultivation as a reference situation, with native vegetation, near to the cultivated plots (< 5 km), where an equilibrium between the different organic fractions had been achieved. Predominant species in the NE varied according to the sites.

The agricultural treatments had been managed under a no-tillage system for at least the last 5 years. The principal difference between the two agricultural managements was the predominance of soybean in the crop succession in the PAP, while GAP consisted of intensive maize–wheat–soybean rotations, including winter cover crops (Table 1). At each site, farmers' fields corresponding to these definitions were selected. Because of the difficulty in establishing strict replication of management practices in actual production fields, we have adopted the

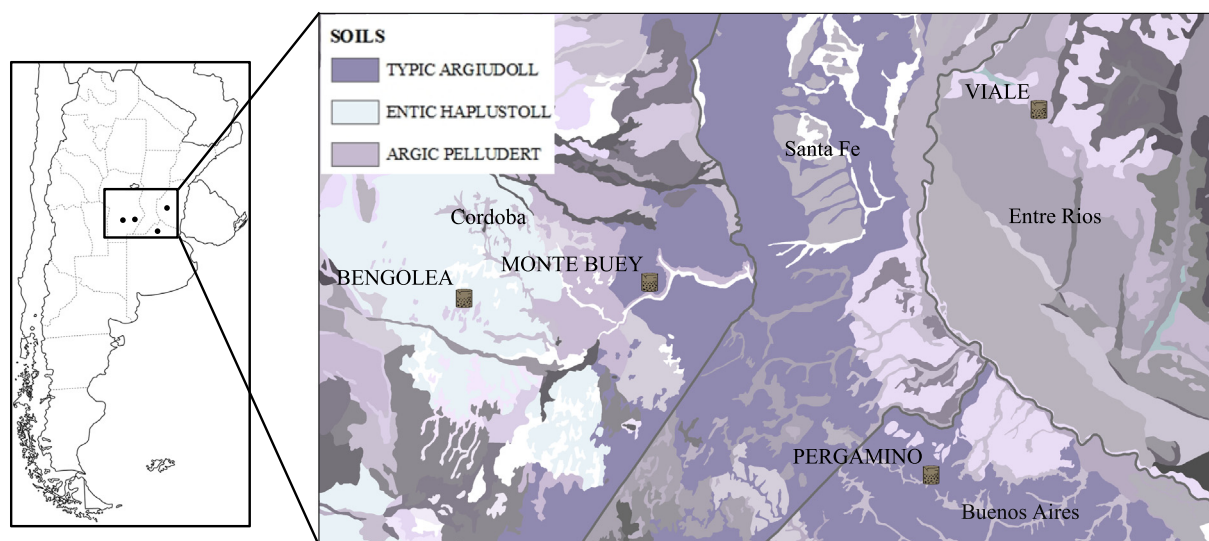


Fig. 1. Map of the Pampean Region with location of sampling sites.

criteria described by the program of Certification in Good Agricultural Practices of AAPRESID (<http://www.aapresid.org.ar/ac/buenas-practicas-agricolas>, AAPRESID (2013)) and the guidelines of Good Agricultural Practices developed by the Food and Agricultural Organization of the United Nations (www.fao.org/prods/GAP/index_en.htm). Table 1 summarizes the soil properties and information on the agricultural practices and crop yields of the different study sites.

Field measurements and soil sampling were carried out in February 2011 (summer). Three subsamples (as repetitions) were taken from the top 20 cm of soil at each location-treatment plot. Each subsample was a composite of three undisturbed soil samples randomly selected at 0–10 and 10–20 cm, using cores of 10 cm in height and 4.7 cm in diameter within an area of 50 m². The subsamples were separated by at least 50 m from each other, without following the drilling line in the field.

2.3. Soil analysis

2.3.1. Soil chemical properties

The soil samples were air-dried and passed through a 2000 µm sieve. The following chemical determinations were performed: soil organic carbon (SOC) by dry combustion (LECO, St. Joseph, MI), soil total nitrogen (Nt) using Kjeldahl (Bremner, 1996), extractable phosphorus (Pe) (Bray and Kurtz, 1945) and cation exchange capacity (CEC) were determined by the ammonium acetate 1 mol L⁻¹ method (Klute, 1986).

2.3.2. Labile SOM fractions

Labile soil organic fractions were measured by several SOC fractionation methods: soil fractionation by particle size was conducted using the method described by Duval et al. (2013). Briefly, 50 g of air-dried soil < 2000 µm was dispersed in 100 mL of distilled water and ten glass beads (5 mm diameter) were added to increase aggregate destruction. The samples were subjected to mechanical dispersion through

Table 1

Soil properties, management and crop yield in each agricultural management system and soil type.

Sites		Bengolea			Monte Buey			Pergamino			Viale		
		NE	GAP	PAP	NE	GAP	PAP	NE	GAP	PAP	NE	GAP	PAP
Management system													
Soil properties	Slope (%)	0.50	0.75	0.50	0.01	0.50	0.20	0.25	0.50	0.50	0.75	0.75	0.20
	Soil Taxonomy ^a	Entic Haplustoll			Typic Argiudoll			Typic Argiudoll			Argic Pelludert		
	Texture	Sandy loam			Silty loam			Silty loam			Silty clay loam		
	Sand	594	555	577	169	208	196	179	185	178	26	22	32
	Silt	284	306	293	570	578	578	621	587	605	609	519	588
	Clay	122	139	130	261	214	226	200	228	217	365	459	380
Agronomic-productive characteristics	History no-tillage (years)	–	13	5	–	28	10	–	6	5	–	13	9
	Soybean/maize ratio ^b	–	1.5	4	–	0.67	4	–	1.5	5	–	1.5	4
	% Wheat ^c	–	60	40	–	60	20	–	10	0	–	40	20
	% Winter cover crops ^d	–	20	0	–	40	0	–	0	0	–	20	0
	Fertilization N–P (kg ha ⁻¹ year ⁻¹) ^e	–	68–18	3–3	–	64–18	17–5	–	41–17	7–31	–	64–27	34–23
	Soybean yield (kg ha ⁻¹)	–	3067	2775	–	3167	2675	–	2933	2885	–	3000	1805
	Maize yield (kg ha ⁻¹)	–	10,500	2700	–	12,550	8000	–	9500	–	–	7030	3450
Carbon input (kg ha ⁻¹ year ⁻¹) ^f	–	5608	2765	–	6378	3548	–	4291	2486	–	4010	2845	

NE: Natural Environment; GAP: Good Agricultural Practices; PAP: Poor Agricultural Practices.

^a (Soil Survey Staff, 2010).

^b Number of soybean cycles to number of maize cycles over the last 5 years.

^c Percentage of winters that wheat was planted.

^d Percentage of winters that a cover crop (*Vicia* sp., *Melilotus alba* or *Lolium perenne*) was planted. Cover crops were chemically burned before summer crops were planted.

^e Calculated as kilograms of N and P (element) applied per hectare per year.

^f C input estimated (shoots + roots) as kilograms per hectare per year.

a rotary shaker (40 rpm) for 16 h. The soil suspension was poured through a pair of sieves of 53 μm and 105 μm of diameter mesh using a flow of water. All the material remaining on the sieves -defined as the particulate organic C- was washed into a dry dish, oven dried at 105 °C, weighed, ball-milled and analyzed for C by dry combustion (LECO, St. Joseph, MI). Three fractions were obtained: recently incorporated residues, which form the coarse particulate organic C (POC_c) fraction (105–2000 μm), fine particulate organic C (POC_f) fraction (53–105 μm) consisting of readily decomposable substances formed by microbial transformations of organic residues during the last 10 to 20 years, and biologically stable organic C (MOC) (< 53 μm) associated with the finer mineral fractions of the soil. The value of MOC was obtained by calculating the difference between SOC and POC_{c+f} (Duval et al., 2013).

Hot water and acid extractable organic C were determined employing two different procedures (Puget et al., 1999). The determination by HAC extraction was performed by acid hydrolysis as follows: 1 g of soil sample was treated with 10 mL of 0.5 mol L⁻¹ H₂SO₄, heated at 80 °C for 24 h. Secondly, for HWC determination, extraction was carried out as follows: 1 g of soil sample was suspended in 10 mL of distilled water and heated at 80 °C for 24 h, and hydrolysis was attained by adding H₂SO₄ to obtain a 0.5 mol L⁻¹ concentration as in the dilute acid hydrolysis procedure. After extraction, each suspension was centrifuged at 4000 rpm for 15 min (Puget et al., 1999). Extractable C contents were determined using the phenol-sulfuric acid spectrophotometric method with glucose as a standard curve (Dubois et al., 1956).

Permanganate oxidizable C was determined according to Weil et al. (2003). Briefly, 2.5 g of air-dried soil were weighed into 50 mL polypropylene centrifuge tubes. To each tube, 20 mL of 0.02 mol L⁻¹ KMnO₄ stock solution (prepared in 0.1 mol L⁻¹ CaCl) was added. The suspensions were shaken horizontally for exactly 2 min at 240 rpm. Tubes were removed from the shaker and allowed to settle for exactly 10 min. Shaking times and settling times are very important with this method, so batches of 15 samples or less were run. After 10 min, 500 μL of the supernatant were transferred into a second 50 mL polypropylene centrifuge tubes and mixed with 49.5 mL of deionized water and measured at 560 nm with a T60 U UV-visible spectrophotometer (PG Instruments).

The C fraction that was not oxidized by permanganate is defined as non-labile (Blair et al., 1995). In the current study, we have maintained this definition for consistency for both the POC and POX-C measurements, and the non-labile fractions were calculated as SOC-POC_{c+f} and SOC-POX-C, respectively. These recalcitrant fractions were defined as MOC and POX-C_{NL}.

2.3.3. Soil physical properties

The soil physical properties determined included the bulk density, BD (Mg m⁻³), soil macroporosity, $P_{>30\mu\text{m}}$ (m³ m⁻³), soil mesoporosity, $P_{30-0.2\mu\text{m}}$ (m³ m⁻³), soil microporosity, $P_{<0.2\mu\text{m}}$ (m³ m⁻³), total porosity, TP (m³ m⁻³), penetration resistance, PR (kPa), aggregate density, AggD (g cm⁻³), aggregate specific volume, AggV (%) and the aggregate stability, AS (mm). These parameters are often used as indicators (or potential indicators) of the soil physical quality in humid, medium-fine-textured agricultural soils (Reynolds et al., 2007). The BD was determined by the core method (Blake and Hartge, 1986) using 181 cm³ (4.8 cm diameter by 10 cm long) volume cores. The soil water retention curve was measured in undisturbed soil samples at matrix suction of 10, 33 and 15.000 kPa using pressure plate extractor (Soil Moisture Equipment Co., Santa Barbara, California) (Klute, 1986). The pore sizes corresponding to the pressures established were estimated using the capillary rise formula (Hassink et al., 1993). Thus, the volume of $P_{>30\mu\text{m}}$, $P_{30-0.2\mu\text{m}}$ and $P_{<0.2\mu\text{m}}$ were determined (Kay and Vanden Bygaart, 2002). Soil PR was determined using a static digital penetrometer (Fieldsout SC-900®) with 30° tip angle. Aggregate density (AD) and Aggregate specific volume (AV) were measured in 3–5 mm diameter aggregates with kerosene as non-polar liquid with the

methodology described by Stengel (1979). Aggregate stability index (AS) was determined according to the three pretreatments proposed by Le Bissonnais method (Le Bissonnais, 1996) (AS1—fast wetting-; AS2—stir wetting-; AS3—slow wetting-).

2.4. Statistical analyses

Analysis of variance (ANOVA) was applied for the statistical analysis of the results. The experimental design was a two-way factorial mixed model ANOVA including the fixed effect of the management system (sustainable or unsustainable agricultural practice, or undisturbed soil) and the four sites were considered as a random sample of possible sites with different climate and soil conditions (Table 1). When main treatment effects occurred, the least significant difference (LSD, $P < 0.05$) was used to compare the effects of the treatments in the soil organic fractions that were separately determined for the three soil depths of 0–10, 10–20, and 0–20 cm. Also, four separate ANOVA for each site, using POX-C, POC, HWC, HAC or SOC as a response variable. F-statistics from the model output were used to assess the relative magnitude of the effect of that factor on the C fraction, i.e. how sensitive that soil C fraction was to the agricultural practice.

A variance components analysis was used to determine the variance proportions attributable to treatments and sites in soil properties as a proxy to discriminate the dynamics and inherent behavior of each soil organic fractions. Multiple regressions (MR) were performed using SOC and their labile fractions for predicting the main crop yield (dependent variables) by means of the stepwise model with a maximum P -value of 0.05 for input and output. The MR model was used to determine the best combination of soil organic fractions that maximize the prediction of crop yield (grain of soybean or maize). Pearson's correlation was used to assess the relationships between the different analyses across all sites and treatments, and significant correlations were also identified at a P value of 0.05. All data were analyzed using Infostat statistical software (Di Rienzo et al., 2013).

3. Results and discussion

3.1. Soil organic carbon fractions

Different sites and treatments had significant effects on the SOC (Table 2). The concentration of SOC displayed large variations across site-treatment combinations, and at 0–20 cm soil depth it ranged from 9.4 to 36.4 g kg⁻¹ (Table 3). There was a strong site effect on SOC, with the lowest values in Bengolea (12.3 g kg⁻¹ soil) and the highest in Viale (26.5 g kg⁻¹ soil), following the texture gradient between sites (Table 1).

Labile SOM fractions were generally affected by different sites and treatments (Table 2). There was a wide range of labile SOM fraction values measured (Table 3). Soil POC values ranged from 0.46 to 7.29 g kg⁻¹, HAC values ranged from 1.50 to 6.73 g kg⁻¹, HWC values ranged from 0.20 to 1.10 g kg⁻¹ and POX-C values ranged from 0.41 to 1.04 g kg⁻¹ soil, POC_c being the most variable fraction (CV = 72%) and POX-C the least (CV = 22%). The fractionation methods used in this study differed notably regarding the SOC fraction quantified as labile fraction (Table 3). This result suggests that the different methods quantify different SOM fractions, including the C compounds less, or not readily, available to the soil microorganisms (Benbi et al., 2015). The labile SOM fractions that constituted only a small portion of the SOC were HWC and POX-C. These fractions include approximately 1.9 to 3.1% and 3.0 to 6.0% of SOC for HWC and POX-C, respectively (Table 3). These results are in agreement with previous studies of Ćirić et al. (2016) and Culman et al. (2012), who observed similar proportions for HWC (2–5%) and POX-C (1–4%), respectively. The physical fractionation method indicated the higher amounts of labile carbon (Table 3). The proportion of labile carbon in SOC increased from 9.6–14.6% in the coarse particulate fraction (2000–105 μm) to

Table 2

Two-way ANOVA of the effect of different treatment and sites on total SOC and labile SOC fractions (a), and the contribution of geographic position (site) and land management (treatment) to variance (b) of different carbon pools.

Organic fractions	Depth (cm)	(a) Source			(b) Variance component (%)			Residual
		Site (S)	Treatment (T)	S*T	S	T	S*T	
SOC	0–10	***	***	ns	45.0	24.1	8.3	22.6
POC _c		ns	***	ns	2.7	54.6	2.3	40.4
POC _f		***	***	ns	16.9	63.6	6.5	13.0
HAC		***	***	*	80.0	8.6	5.2	6.2
HWC		***	***	***	30.9	36.2	19.7	13.2
POX-C	10–20	***	***	*	73.6	16.9	3.3	6.2
SOC		***	**	ns	56.0	15.3	0.0	28.7
POC _c		***	***	***	12.7	60.3	17.0	10.0
POC _f		***	***	***	38.1	31.6	18.3	12.0
HAC		***	**	ns	74.7	6.5	1.3	17.5
HWC	0–20	***	***	***	38.9	25.4	25.1	10.6
POX-C		***	ns	ns	51.2	2.6	0.0	46.2
SOC		***	***	ns	45.0	24.2	8.3	22.5
POC _c		ns	***	ns	0.80	62.2	0.0	37.0
POC _f		***	***	ns	21.6	56.1	6.5	15.8
HAC	0–20	***	***	ns	82.4	9.2	0.7	7.7
HWC		***	***	***	35.4	31.7	20.7	12.2
POX-C		***	***	ns	61.9	21.7	0.9	15.5

SOC: soil organic carbon; POC_c and POC_f: particulate organic carbon coarse and fine, respectively; HAC: hydrolyzable carbon with acid extractions; HWC: hot water extractable carbon; POX-C: permanganate oxidizable carbon.

6.6–24.8% in fine particulate fraction (105–53 μm).

In order to obtain a proxy for discriminating between the dynamic and inherent nature of each SOC fraction, we used a variance components analysis to determine the contribution of site and management to the total variation (Table 2). The results indicated that at 0–10 cm, a higher percentage of the variance of two labile SOM fractions (POC_c and POC_f) was largely explained by management practices (> 50%), and to a lesser extent by climate and soil conditions (site) (Table 2). At the 10–20 cm depth only POC_c was largely explained by management practices. Therefore these fractions could be considered the most sensitive for detecting changes in SOC that are due to changes in land-use management. These findings were generally consistent with the previous studies of Yousefi et al. (2008) and da Silva Oliveira et al. (2017), who found significant changes due to land-use change managements.

Both SOC and labile SOM fractions (HAC and POX-C) were highly influenced by climate and soil conditions, reflected in their high variance components (> 45%), and hence classified as inherent soil properties (Table 2). The permanganate oxidizes lignin efficiently, although it has little effect on several SOM components that are widely recognized as easily degradable by soil microorganisms (Suárez-Abelenda et al., 2014). Nevertheless these organic pools were also influenced by treatments, showing higher values in NE than PAP fields at the four sites as discussed later (Table 5).

3.2. Relationship between permanganate-oxidizable carbon with labile organic fractions

Permanganate oxidizable C was significantly related to all labile

Table 3

Descriptive statistics for soil organic carbon and their labile fractions by individual sites at 0–20 cm depth.

Carbon fraction	Statistical measure	Bengolea	Monte Buey	Pergamino	Viale	Mean
SOC	Min-Max	9.4–16.6	15.7–33.9	12.3–23.4	17.0–36.4	9.4–36.4
	Mean	12.3	21.7	16.7	26.5	19.3
	%CV	18	29	29	27	39
POC _c	Min; Max	0.67–3.72	0.95–7.29	0.46–5.19	1.40–5.05	0.46–7.29
	Mean	1.79	2.26	1.75	2.55	2.09
	%CV	53	91	93	52	72
POC _f	POC _c /SOC (%)	14.6	10.4	10.5	9.6	10.8
	Min; Max	1.94–4.36	1.93–5.27	1.38–4.00	1.07–2.94	1.07–5.27
	Mean	3.05	2.84	2.33	1.76	2.49
HAC	%CV	28	39	44	40	41
	POC _f /SOC (%)	24.8	13.1	14	6.6	12.9
	Min; Max	1.56–2.69	2.37–4.11	1.50–3.75	4.32–6.73	1.50–6.73
HWC	Mean	1.96	2.99	2.57	5.47	3.25
	%CV	19	21	28	15	46
	HAC/SOC (%)	15.9	13.8	15.4	20.6	16.8
POX-C	Min; Max	0.20–0.34	0.34–1.10	0.20–0.69	0.36–0.76	0.20–1.10
	Mean	0.26	0.68	0.43	0.49	0.46
	%CV	18	46	45	31	52
POX-C	HWC/SOC (%)	2.1	3.1	2.6	1.9	2.4
	Min; Max	0.63–0.81	0.76–1.04	0.41–0.70	0.62–0.96	0.41–1.04
	Mean	0.74	0.88	0.55	0.79	0.74
	%CV	8	11	21	16	22
POX-C	POX-C/SOC (%)	6.0	4.1	3.3	3.0	3.8

SOC, soil organic carbon; POC_c, particulate organic carbon coarse; POC_f, particulate organic carbon fine; HAC, hydrolyzable carbon with acid extractions; HWC, hot water extractable carbon; POX-C, permanganate oxidizable carbon.

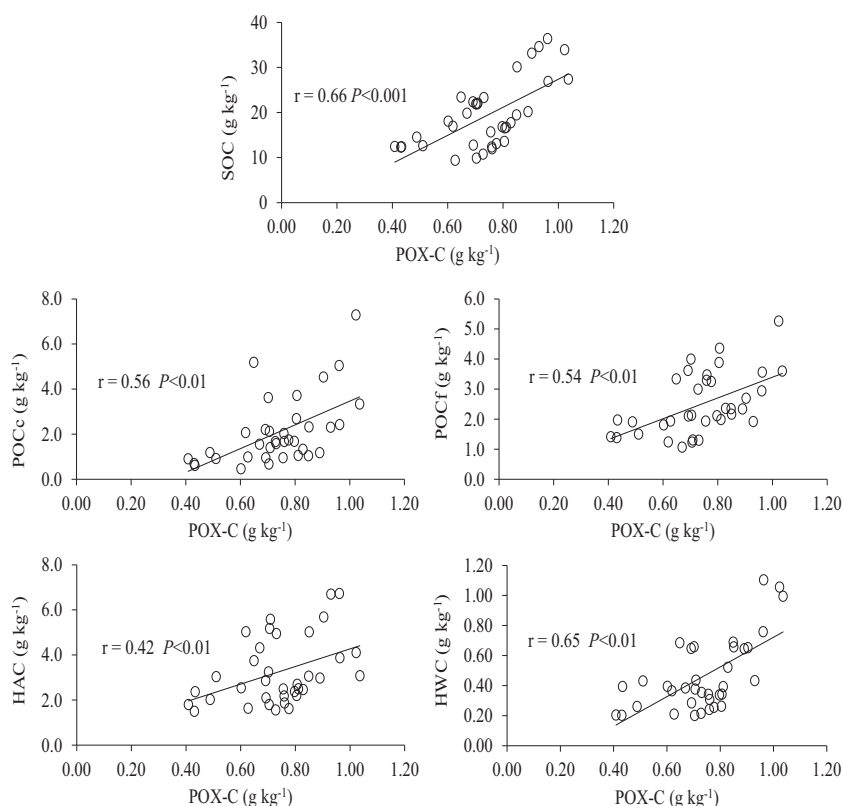


Fig. 2. Relationship between permanganate oxidizable C (POX-C) and soil carbon fractions: soil organic carbon (SOC), coarse and fine particulate organic carbon (POC_c and POC_f , respectively), hot-water extractable carbon (HWC) and hydrolyzable carbon with acid extractions (HAC) at 0–20 cm depth.

SOM fractions when data were from all the site-treatment combinations at 0–20 cm depth (Fig. 2). POX-C explained 0.31, 0.29, 0.18, 0.42 and 0.44 of the variation in POC_c , POC_f , HAC, HWC and SOC, respectively. Similarly, other authors also found poor correlations between POX-C and the labile SOM fractions and concluded that the different measurements responded differently to management (Culman et al., 2013; Morrow et al., 2016). However, when relationships between POX-C and the other labile SOM fractions were analyzed by each site, the relationships greatly improved, indicating that both edaphic and environmental factors from multiple sites contributed to unexplained variation in the data.

The relationship between POX-C and SOC was generally stronger than POX-C with other labile SOM fractions in nearly every site. This suggests that POX-C reflects a more processed, degraded fraction of soil C in agreement with the results observed by Culman et al. (2012), who observed close relationships of the POX-C with soil organic fractions of smaller sizes and heavy organic fractions. The ratio between labile fractions and SOC usually decreased with depth (Yang et al., 2009). The regression analysis showed that POX-C was more closely related to SOC at 0–10 and 10–20 cm depth, which confirms previous reports (Culman et al., 2012; Plaza-Bonilla et al., 2014). However, considering the relationships of POX-C and SOC by individual sites and depths, these relationships greatly improved, with a high coefficient of determination ($R^2 = 0.76–0.92$) (Fig. 3). These results suggest that depth and site factors have a greater influence on this relationship than management practices. Therefore, the development of these tests for farmers' use will have to pay close attention to the sampling depth in order to standardize measurements across sites (Franzuebbers, 2016). This result suggests the usefulness of the permanganate method which also eliminates the potential hazards related to the use of the dichromate in classical methods for SOC determination (Walkley and Black, 1947; Martínez et al., 2017a). Culman et al. (2012) also suggest that POX-C can also serve as a rapid and field-adaptable method to estimate the SOC

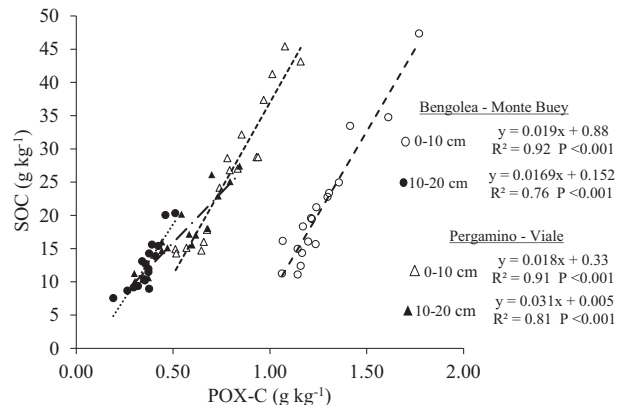


Fig. 3. Relationship between total soil organic carbon (SOC) and permanganate oxidizable carbon (POX-C) by each site and depth.

content.

3.3. Sensitivity of the organic fraction to management practices

Cultivation had a significant effect on the SOC and labile fraction concentrations at all sites ($P < 0.05$), but significant differences between agricultural practices were only observed in the labile fractions (POC_f , HAC, HWC and POX-C) (Table 4). Concentrations of all the labile SOM fractions were mostly higher in NE than in agricultural soils, indicating that cultivation produced decreases in the labile fractions at both soil depths. Generally, soils subjected to PAP had significantly lower POC_c , POC_f , HAC, HWC and POX-C values than the same soils under NE ($P < 0.05$) at both depths, whereas significant differences between agricultural practices were only found for POC_f in Bengolea and Pergamino, for HAC and HWC in Monte Buey and Pergamino, and

Table 4
Effects of different land use systems on soil carbon fractions (g kg⁻¹ of soil) at 0–10 and 10–20 cm depth.

Site	Treat.	Depth (cm)	SOC			Labile fractions			POC _c			POC _f			HAC			HWC			POX-C		
			Mean (± SD)	CV%		Mean (± SD)	CV%		Mean (± SD)	CV%		Mean (± SD)	CV%		Mean (± SD)	CV%		Mean (± SD)	CV%		Mean (± SD)	CV%	
Bengolea	NE	0–10	17.1 (± 3.64)	21	4.16 a (± 1.48)	36	4.61 a (± 0.66)	14	2.68 (± 0.43)	16	0.34 (± 0.09)	27	1.22 a (± 0.04)	3									
	GAP		14.5 (± 1.88)	13	2.93 ab (± 0.15)	5	4.19 a (± 0.35)	8	2.07 (± 0.17)	8	0.34 (± 0.06)	19	1.17 ab (± 0.03)	3									
	10–20	PAP	12.8 (± 2.87)	22	1.44 b (± 0.35)	24	2.46 b (± 0.16)	6	2.19 (± 0.43)	20	0.28 (± 0.07)	25	1.09 b (± 0.04)	4									
		NE	11.3 a (± 0.80)	7	1.46 a (± 0.24)	17	3.08 a (± 0.18)	15	2.03 a (± 0.18)	9	0.23 (± 0.02)	8	0.37 a (± 0.01)	3									
		GAP	9.4 b (± 0.67)	7	0.46 b (± 0.08)	17	2.30 b (± 0.27)	12	1.30 b (± 0.15)	12	0.18 (± 0.04)	19	0.34 ab (± 0.04)	12									
		PAP	8.5 b (± 0.92)	11	0.30 b (± 0.01)	4	1.65 b (± 0.16)	10	1.50 b (± 0.12)	8	0.19 (± 0.03)	14	0.26 b (± 0.06)	25									
Monte Buey	NE	0–10	38.5 a (± 7.68)	20	8.06 (± 5.14)	64	6.03 a (± 1.58)	26	4.53 a (± 0.54)	12	1.33 a (± 0.10)	8	1.60 a (± 0.18)	11									
	PAP		23.7 b (± 1.31)	5	2.21 (± 0.32)	15	3.68 b (± 0.20)	5	3.56 b (± 0.42)	12	0.79 b (± 0.09)	11	1.32 b (± 0.03)	2									
	10–20	NE	19.1 b (± 0.68)	4	2.35 (± 0.75)	32	2.59 b (± 0.18)	7	2.71 c (± 0.15)	5	0.40 c (± 0.04)	9	1.20 b (± 0.03)	2									
		PAP	20.3 a (± 0.23)	1	0.64 a (± 0.10)	15	2.26 a (± 0.40)	18	2.84 (± 0.54)	19	0.77 a (± 0.05)	7	0.42 (± 0.12)	30									
		GAP	14.6 b (± 1.64)	11	0.16 b (± 0.03)	21	1.01 b (± 0.21)	20	2.11 (± 0.23)	11	0.45 b (± 0.09)	19	0.39 (± 0.03)	8									
		PAP	13.7 b (± 0.60)	4	0.11 b (± 0.07)	64	1.44 b (± 0.07)	5	2.20 (± 0.08)	4	0.32 c (± 0.03)	8	0.38 (± 0.03)	9									
Pergamino	NE	0–10	29.9 a (± 1.96)	7	6.19 a (± 2.56)	41	5.32 a (± 0.25)	5	4.19 a (± 0.55)	13	0.94 a (± 0.03)	4	0.91 a (± 0.05)	5									
	GAP		15.3 b (± 0.67)	4	1.14 b (± 0.43)	38	1.99 b (± 0.42)	21	3.16 b (± 0.59)	19	0.51 b (± 0.05)	10	0.63 b (± 0.05)	8									
	10–20	PAP	15.7 b (± 1.90)	12	1.74 b (± 0.51)	29	2.19 b (± 0.54)	25	2.09 c (± 0.38)	18	0.27 c (± 0.04)	17	0.57 b (0.09)	16									
		NE	15.3 (± 0.67)	4	1.14 a (± 0.43)	38	1.99 a (± 0.42)	21	2.38 a (± 0.34)	14	0.39 a (± 0.03)	6	0.45 (± 0.02)	4									
		GAP	13.5 (± 5.80)	43	0.18 b (± 0.04)	23	1.53 a (± 0.10)	7	2.14 a (± 0.13)	6	0.31 b (± 0.02)	6	0.40 (± 0.13)	31									
		PAP	10.6 (± 0.63)	6	0.11 b (± 0.03)	22	0.95 b (± 0.06)	6	1.46 b (± 0.15)	10	0.18 c (± 0.02)	13	0.32 (± 0.02)	8									
Viale	NE	0–10	35.8 (± 13.4)	37	6.99 a (± 2.98)	43	3.44 a (± 0.95)	49	6.18 (± 0.89)	14	0.85 (± 0.33)	38	1.05 a (± 0.03)	3									
	GAP		35.7 (± 8.17)	23	3.48 ab (± 0.99)	28	2.54 ab (± 0.81)	32	6.13 (± 0.07)	1	0.72 (± 0.21)	29	0.99 a (± 0.16)	17									
	10–20	PAP	26.5 (± 2.24)	8	3.00 b (± 0.60)	20	1.44 b (± 0.22)	15	5.93 (± 0.49)	8	0.50 (± 0.03)	5	0.77 b (± 0.03)	4									
		NE	22 (± 7.46)	34	0.78 a (± 0.20)	26	1.14 a (± 0.15)	13	5.45 (± 1.17)	21	0.33 (± 0.08)	24	0.61 (± 0.37)	61									
		GAP	22.1 (± 5.56)	21	0.54 ab (± 0.07)	12	1.06 ab (± 0.07)	7	5.41 (± 1.66)	31	0.30 (± 0.05)	17	0.67 (± 0.08)	12									
		PAP	16.9 (± 1.25)	7	0.51 b (± 0.04)	8	0.96 b (± 0.02)	2	3.70 (± 1.10)	30	0.25 (± 0.01)	3	0.63 (± 0.04)	7									

Within individual sites and depths, mean values with different letters are significantly different ($P < 0.05$); SD: standard deviation of mean; CV: coefficient of variation (%).

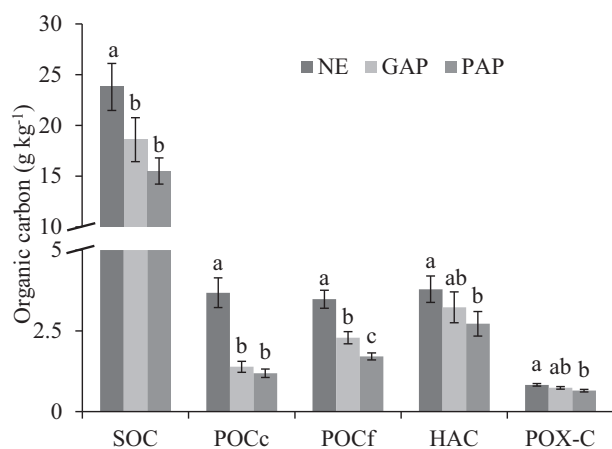


Fig. 4. Effects of different land-use systems on soil carbon fractions (g kg^{-1} of soil) at 0–20 cm depth. Vertical bars indicate standard deviation.

for POX-C in Viale (Table 4).

SOC and labile fractions, except HWC, showed similar effects of the treatment by climate and soil conditions (site) (not a significant interaction) at 0–20 cm depth, therefore, these fractions were analyzed as a whole (average dates) (Fig. 4). The weighted means for the 0–20 cm depth indicated 28 and 54% higher SOC in NE soils as compared to GAP and PAP soils, respectively (Fig. 4). It has been suggested that POX-C would be a suitable index of labile soil C, that is sensitive to soil management practices (Haynes, 2005; Culman et al., 2012). In our study, the highest values of POX-C were observed in the NE soils (0.83 g kg^{-1} soil) followed by GAP (0.74 g kg^{-1} soil), and PAP (0.65 g kg^{-1} soil) without any differences ($P > 0.05$) between agricultural management systems (Fig. 4). Similarly, Mandal et al. (2011) stated lower amounts of POX-C in cultivated soils than in the uncultivated land-use system. However, the other labile SOM fractions displayed more marked differences between the treatments (Fig. 4). Weighted mean values of POC_c and POC_f also followed similar trend at the 0–20 cm depth. The concentration of POC_c was from 62% to 68% lower under agricultural management in comparison with the NE soils, and 34–51% lower for POC_f concentration. In general, these fractions depend strongly on the C input to the soil (Vieira et al., 2007); an aspect which is certainly associated with shifts in the labile SOM fractions regarding the land-use changes at these sites (Table 1).

In the same way, HAC and HWC work as valuable indicators of anthropogenic impacts on soil, keeping in mind the differences between soils under native vegetation and agricultural conditions (Ćirić et al., 2016). Our results showed that the HAC concentration was from 15% to 28% lower under agricultural management in comparison to the NE soils (Fig. 4). In particular, the HWC concentration in agricultural soils was 13, 53, 52 and 25% lower than NE soils for Bengolea, Monte Buey, Pergamino and Viale, respectively.

The GAP system is still only practiced by a minority of farmers nowadays, even though it is considered to be more sustainable by the association of the no-tillage system in Argentina (Albertengo et al., 2011). Accordingly, in this study the GAP sites were previously managed as PAP for at least 15 years, according to the detailed management information provided by the farmers. Therefore the overall weighted mean revealed that POC_f was the only labile SOM fraction that detected any significant differences between the different types of agricultural management (GAP vs. PAP) in the short- and medium-term (Fig. 4). This result indicates greater differences in POC than in POX-C between the two land-uses, emphasizing that POX-C as a less sensitive indicator of SOC quality than the other labile SOM fractions. Also, this evidence suggests that GAP in areas that were previously used as PAP may enhance the quantity and quality of SOM in sites under this condition.

To assess the ability of labile SOM fractions, tests for predicting

agronomic performance, the relationships with the crop yield (grain of soybean or maize) and soil C fractions (POC_f, POC_c, HAC, HWC, POX-C and SOC) at 0–20 cm depth were performed through multiple regressions. The results showed that the labile SOM fractions that best predicted maize yield were POC_f, HAC and HWC (Adj. $R^2 = 0.64$, $P < 0.01$), while for soybean yield they were POC_f and HAC (Adj. $R^2 = 0.43$, $P < 0.01$). These results indicate that both of these labile SOM fractions are capable of predicting the agronomic performance, and therefore they may be considered as reliable measurements of productivity and soil quality.

Another important aspect that should be taken into account when selecting a measurement is the veracity-method. This attribute could be categorized by basing it on the CV values from results of analysis (Table 4). In this sense, labile SOM fractions with CV values of $< 15\%$ were assigned as high precision, those between 15 and 35% were assigned as medium precision, and soil properties with CV values of $> 35\%$ were assigned as low precision (Pennock et al., 2007). Considering these criteria, SOC, POC_f, HAC, HWC and POX-C all scored as high to medium with a couple of exceptions, whereas POC_c scored as medium to low (Table 4). In this last case, the low precision is due to the fact that POC_c depends principally on recent residue input as was discussed above.

Labile soil carbon fractions, such as POC, HAC and HWC, are important indicators of changes in soil ecosystems brought about by management practices (Haynes, 2005; Benbi et al., 2015; Ćirić et al., 2016). In this study we hypothesized that POX-C may be a useful indicator of agricultural management changes, in a similar way as POC, HAC and HWC. So we defined the sensitivity of each carbon fraction as the F-statistic, where greater sensitivity of a fraction relative to other fractions is reflected by a larger F-statistic (Culman et al., 2012) (Table 5). The F-statistic analysis showed that all labile SOM fractions were more sensitive than SOC in agricultural soils (GAP vs. PAP). Therefore, POC, HAC, HWC and POX-C showed the highest sensitivity to the management practice changes. On the other hand, the most sensitive indicators of soil quality in agricultural soils were POC_f and HWC, which is in agreement with those reported by other studies (Duval et al., 2014; Ćirić et al., 2016).

The data presented in Tables 4 and 5 and Fig. 4 do not support partially our hypothesized framework where POX-C is a sensitive indicator to different land-use changes as discussed above. Our results confirmed that despite the dilute $0.02 \text{ mol L}^{-1} \text{ KMnO}_4$ solution used in

Table 5

Sensitivity of SOC and labile SOC fractions to detect significant differences between agricultural practices through F-statistics. F-statistics in bold indicate the method that demonstrated comparatively greater sensitivity in each site.

Sites	SOC	POC _c	POC _f	HAC	HWC	POX-C
F-statistics 0–10 cm						
Bengolea	0.7	47.1***	61.1***	0.21	1.22	6.22*
Monte Buey	36.3***	0.09	51.4***	11.1**	48.7***	26.3***
Pergamino	0.1	2.4	0.26	7.0**	38.8***	0.88
Viale	3.6	0.5	6.1*	0.54	3.3	5.0*
F-statistics 10–20 cm						
Bengolea	1.9	12.5**	12.5**	3.2	0.03	3.7
Monte Buey	0.7	1.3	11.3**	0.4	6.8**	0.3
Pergamino	0.8	6.2*	76.5***	36.3***	54.7***	1.4
Viale	3.6	0.5	5.1*	2.2	3.3	0.6
F-statistics 0–20 cm						
Bengolea	1.0	64.1***	65***	1.0	0.54	8.4**
Monte Buey	11.0**	0.03	35.7***	4.0	24.2***	7.6**
Pergamino	0.4	1.8	0.75	12.2**	65.8***	1.8
Viale	3.6	0.5	5.1*	3.0	3.3	3.6

SOC: soil organic carbon; POC_c and POC_f: particulate organic carbon coarse and fine, respectively; HAC: hydrolyzable carbon with acid extractions; HWC: hot-water extractable carbon; POX-C: permanganate oxidizable carbon. *, ** and *** significant differences at 0.1, 0.05 and 0.01 probability levels, respectively.

this study for determining POX-C (Weil et al., 2003), and the high precision ($CV < 15$), this labile fraction showed limited sensitivity to different agricultural practices and therefore may not be a reliable measure of labile C. However, the results showed that this methodology was both feasible and useful for estimating SOC in regards to the site conditions and depths, as reported by Culman et al. (2012). The POC represents the youngest and most biologically active SOM, such as particles of fresh or partially decomposed plant residues and microbial tissues (Skjemstad et al., 2006). As a result, different studies have demonstrated the greater sensitivity of the POC fractions to management practices as compared to other indicators, such as SOC, microbial biomass and POX-C (Banger et al., 2010; Yang et al., 2012). Alvarez and Alvarez (2016) showed through a meta-analysis in the Pampas Region that, regarding other organic fractions, changes in particulate-C (POC) were significantly greater than changes in organic-C induced by tillage or rotation. The C fraction by physical method also exhibited a notably higher sensitivity compared to SOC and other labile C methodologies in conversion from grassland to sugarcane (da Silva Oliveira et al., 2017). Moreover, the labile fractions by physical methods i.e. POC determination, depends strongly on the C input to the soil by crop residues (Vieira et al., 2007). This aspect is certainly associated with the shifts in the labile SOM fractions regarding the land-use change, where GAP generates a high C input to the soil (Table 1) as a consequence of the combination of crop rotation, winter cover crops and fertilization input.

Both physical fractionation (POC) and chemical oxidation (HAC and HWC) were highly sensitive to the agricultural management system (GAP vs. PAP) evaluated in this trial (Table 4). However, no single pool alone could be used as a sensitive indicator of land-use induced changes in SOC. In other words, no single method determining labile SOC fraction satisfied all aspects for gauging the efficacy of soil quality tools (Morrow et al., 2016).

3.4. Labile organic fractions and their relation to physical and chemical attributes

SOC and their labile fractions directly influence soil physical, chemical and biological attributes as well as the self-organization capacity of soils (Blair et al., 1995). In addition, labile SOM fractions are associated with nutrient mineralization and can make an important contribution to nutrient availability and cycling (Martínez et al., 2017b) and biomass production. Table 6 shows correlations between the labile SOM fractions and some physical and chemical properties of the soil for

the evaluation of soil quality. Results showed that humified organic matter (SOC, MOC and POX-C_{NL}) has a significantly positive correlation with textural porosity (TP and $P < 0.2 \text{ mm}$) ($r = 0.62$ to 0.81) and, labile organic carbon (mainly POC) has a significant correlation ($r = 0.43$ to 0.84) with structural porosity ($P > 30 \mu\text{m}$ and AS). In general, POC, HAC and HWC showed a higher correlation with the soil chemical and physical attributes than POX-C.

The amount of crop residues maintained on the soil surface has a great effect on soil structure aggregation, especially due to its effect on macro-aggregates (Huang et al., 2010). García et al. (2013) observed that POC was more strongly related to the physical properties than the other labile SOM fractions, when evaluating different crop rotations under no-tillage. These results are consistent with our findings, where the POC had more pronounced effects on the physical attributes (Table 6). For example, both POC_c and POC_f had the strongest positive relationship with macropores ($P > 30 \mu\text{m}$) and aggregate stability (AS), and significant negative relationships were found with bulk density (BD). Since most of the discussed attributes are referred to as soil physical quality indicators (Reynolds et al., 2007), it seems reasonable, therefore, to confirm that POC as a reliable indirect indicator for assessing the capacity of management systems promoting soil physical quality. Therefore, GAP can increase the POC fraction and significantly improve the soil physical quality. Vieira et al. (2007) suggested that the use of POC through the C management index, was a sensitive method for assessing the management systems' capacity to promote soil quality, due to its close correlation with soil physical, chemical, and biological attributes ($r = 0.88$).

Although the C content in HWC and POX-C is small (Table 3), these labile SOM fractions had a very close relationship with chemical properties associated with nutrient cycling (Nt, Pe and CEC). This suggests that the magnitude of SOM fractions emphasized that the oxidizable fractions (i.e., HWC and POX-C) are quantitatively essential to the mechanisms driving nutrient availability and cycling, providing energy for soil microorganisms (Benbi et al., 2015). On the other hand, the POC fractions are quantitatively essential for soil structural development. In this sense, Kraemer et al. (2017) observed that different morphological variables (visual evaluation of soil structure -VESS- and the number of faces) were related to labile carbon fractions (POC_c and POC_f).

Table 6

Pearson's correlations between labile and non-labile SOC fractions and soil chemical and physical parameters at 0–10 cm depth ($n = 36$).

Soil attributes	Non-labile organic carbon			Labile organic carbon				
	SOC	MOC	POX-C _{NL}	POC _c	POC _f	HAC	HWC	POX-C
	Coefficient of correlation (r)							
TP	0.71***	0.75***	0.72***	0.49**	0.05	0.82***	0.38*	0.04
$P > 30 \mu\text{m}$	0.06	-0.14	0.05	0.38*	0.43**	-0.08	-0.06	0.32*
$P_{30-0.2 \mu\text{m}}$	-0.28	-0.38*	-0.28	-0.05	0.17	-0.48**	-0.23	-0.20
$P < 0.2 \mu\text{m}$	0.62***	0.81***	0.63***	0.17	-0.29	0.86***	0.41**	-0.11
BD	-0.68***	-0.53***	-0.67***	-0.70***	-0.55***	-0.53***	-0.43**	-0.52***
AD	0.63*	0.77**	0.63*	0.22	-0.64*	0.31	0.41	0.48
AV	-0.63*	-0.77**	-0.63*	-0.20	0.62*	-0.32	-0.40	-0.48
AS1	0.65*	0.51	0.65*	0.84***	0.55*	0.71**	0.76**	0.62*
AS2	0.35	0.23	0.34	0.37	0.60*	0.53*	0.54*	0.40
AS3	0.70**	0.57*	0.70**	0.78**	0.52*	0.80**	0.86***	0.72**
PR	-0.61*	-0.61*	-0.62*	-0.42	-0.04	-0.47	-0.52	-0.50
CEC	0.89***	0.96***	0.89***	0.52	-0.38	0.68*	0.72**	0.81**
Nt	0.99***	0.93***	0.99***	0.73***	0.47**	0.80***	0.85***	0.33*
Pe	0.41**	0.31	0.39*	0.36*	0.48**	0.13	0.67***	0.65***

*, ** and ***, significant at $P < 0.1$, $P < 0.05$ and $P < 0.01$, respectively. TP: total porosity; $P > 30 \mu\text{m}$: macroporosity; $P_{30-0.2 \mu\text{m}}$: mesoporosity; $P < 0.2 \mu\text{m}$: microporosity; BD: bulk density; AD: aggregate density; AV: aggregate volume; AS: aggregate stability; PR: penetration resistance; CEC: cation exchange capacity; Nt: soil total nitrogen; Pe: extractable phosphorus.

4. Conclusions

The soil management practices and soil conditions had significant effects of varying magnitude on SOC and its labile fractions. Both SOC and POX-C were highly influenced by climate and soil conditions, whereas POC, HAC and HWC displayed the greatest sensitivity for detecting changes in SOC due to changes in agricultural management practices. These findings suggest that the soil condition is the major factor that influences the SOC and POX-C fractions, whereas the land-use type is a major factor that influences POC, HAC and HWC.

Both POX-C and SOC were related but that the relationship was differentially influenced by depths and sites. Additionally, compared with SOC, the weak correlations between POX-C and the other labile SOM fractions suggest that the informational value of the parameter POX-C is restricted to SOM with a certain degree of processing and oxidation.

The methodology used to quantify labile SOM fractions is critical to infer about the different management practices effects on SOM. In this sense, both physical fractionation (POC_f) and chemical oxidation (HAC) were highly sensitive to the agricultural management system (GAP vs. PAP) evaluated in this trial, proving their ability as early indicators of soil quality, whereas with the large alterations due to land-use change (natural vs. agricultural soils), the SOM changes may be equally well expressed by the SOC. This suggests that no single labile SOC fraction assessed by different methods could be used as the most sensitive indicator of land-use induced changes on SOM.

POX-C displayed the smallest variation between land-uses and soil depths, which suggested that this fraction was less sensitive to land-uses and SOC changes in the short-term. However, considering the ease of measuring, it should be considered as an important component of soil quality assessment due to its strong relationship with SOC. The POX-C did not appear to be a sensitive indicator for assessing the quality of soil management systems despite its close correlation with physical, chemical, and biological soil attributes for assessing soil quality.

The POC_f was the fraction most affected by agricultural practices, and it showed high relationships with both the physical soil attributes (macroporosity, bulk density, and density, volume and stability of aggregates) and agronomic parameters (soybean and maize yields).

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References

AAPRESID, 2013. Program for Certification in Good Agricultural Practices. <http://www.aapresid.org.ar/ac/buenas-practicas-agricolas/2013/>, Accessed date: 10 April 2017.

Albertengo, J., Bianchini, A., Sylvestre Begnis, A., Lorenzatti, S., Fernandez Palma, G., Belloso, C., Peiretti, R., 2011. Sustainable Certified Agriculture: The Farmer's Production Alternative. World Congress on Conservation Agriculture (WCCA), Australia, pp. 1–3.

Alvarez, C.R., Alvarez, R., 2016. Are active organic matter fractions suitable indices of management effects on soil carbon? A meta-analysis of data from the Pampas. *Arch. Agron. Soil Sci.* 62 (11), 1592–1601.

Banger, K., Toor, G.S., Biswas, A., Sidhu, S.S., Sudhir, K., 2010. Soil organic carbon fractions after 16-years of applications of fertilizers and organic manure in a Typic Rhodalfs in semi-arid tropics. *Nutr. Cycl. Agroecosyst.* 86 (3), 391–399.

Benbi, D.K., Toor, A.S., Kumar, S., 2012. Management of organic amendments in rice wheat cropping system determines the pool where carbon is sequestered. *Plant Soil* 360, 145–162.

Benbi, D.K., Boparai, A.K., Brar, K., 2014. Decomposition of particulate organic matter is more sensitive to temperature than the mineral associated organic matter. *Soil Biol. Biochem.* 70, 183–192.

Benbi, D.K., Brar, K., Toor, A.S., Singh, P., 2015. Total and labile pools of soil organic carbon in cultivated and undisturbed soils in northern India. *Geoderma* 237–238, 149–158.

Blair, G.J., Lefroy, R.D., Lisle, L., 1995. Soil carbon fractions based on their degree of oxidation, and the development of a carbon management index for agricultural systems. *Aust. J. Agric. Res.* 46, 1459–1466.

Blake, G.R., Hartge, K.H., 1986. Bulk density. In: Klute, A. (Ed.), *Methods of Soil Analysis. Part 1. Agronomy*, 2nd ed. ASA and SSSA, Madison, WI, USA, pp. 363–375.

Bongiovanni, M.D., Lobartini, J.C., 2006. Particulate organic matter, carbohydrate, humic acid contents in soil macro- and microaggregates as affected by cultivation. *Geoderma* 136, 660–665.

Bray, R., Kurtz, L., 1945. Determination of total, organic and available forms of phosphorus in soil. *Soil Sci.* 59, 39–45.

Bremner, J.M., 1996. Nitrogen-total. In: Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnson, C.T., Sumner, M.E. (Eds.), *Methods of Soil Analysis. Part 3. Chemical Methods*. SSSA Book Series 5. Soil Sci. Soc. Am., Madison, WI, pp. 1085–1121.

Caviglia, O.P., Sadras, V.O., Andrade, F.H., 2011. Yield and quality of wheat and soybean in sole- and double-cropping. *Agron. J.* 103, 1081–1089.

Chen, S., Xu, C., Yan, J., Zhang, X., Zhang, X., Wang, D., 2016. The influence of the type of crop residue on soil organic carbon fractions: an 11-year field study of rice-based cropping systems in southeast China. *Agric. Ecosyst. Environ.* 223, 261–269.

Cheshire, M.V., 1979. Nature and Origin of Carbohydrates in Soils. Academic Press.

Čirić, V., Belić, M., Nešić, L., Šeremešić, S., Pejić, B., Bezdan, A., Manojlović, M., 2016. The sensitivity of water extractable soil organic carbon fractions to land use in three soil types. *Arch. Agron. Soil Sci.* 62 (12), 1654–1664.

Culman, S.W., DuPont, S.T., Glover, J.D., Buckley, D.H., Fick, G.W., Ferris, H., Crews, T.E., 2010. Long-term impacts of high-input annual cropping and unfertilized perennial grass production on soil properties and below ground food webs in Kansas, USA. *Agric. Ecosyst. Environ.* 137, 13–24.

Culman, S.W., Snapp, S.S., Freeman, M.A., Schipanski, M.E., Beniston, J., Lal, R., et al., 2012. Permanganate oxidizable carbon reflects a processed soil fraction that is sensitive to management. *Soil Sci. Soc. Am. J.* 76 (2), 494–504.

Culman, S.W., Snapp, S.S., Green, J.M., Gentry, L.E., 2013. Short-and long-term labile soil carbon and nitrogen dynamics reflect management and predict corn agronomic performance. *Agron. J.* 105 (2), 493–502.

Di Rienzo, J.Á., Casanoves, F., Balzarini, M.G., Gonzalez, L., Tablada, M., Robledo, C.W., 2013. InfoStat. Grupo InfoStat, FCA, Universidad Nacional de Córdoba, Argentina.

Dubois, M., Gilles, K., Hamilton, J., Rebers, P., Smith, R., 1956. Colorimetric method for determination of sugars and related substances. *Anal. Chem.* 28, 350–356.

Duval, M.E., Galantini, J.A., Iglesias, J.O., Canelo, S., Martínez, J.M., Wall, L., 2013. Analysis of organic fractions as indicators of soil quality under natural and cultivated systems. *Soil Tillage Res.* 131, 11–19.

Duval, M.E., de Sa Pereira, E., Iglesias, J.O., Galantini, J.A., 2014. Efecto de uso y manejo del suelo sobre las fracciones de carbono orgánico en un argiudol. *Ci. Suelo (Argentina)* 32 (1), 105–115.

Duval, M.E., Galantini, J.A., Martínez, J.M., López, F.M., Wall, L.G., 2016. Sensitivity of different soil quality indicators to assess sustainable land management: influence of site features and seasonality. *Soil Tillage Res.* 159, 9–22.

Fageria, N.K., 2012. Role of soil organic matter in maintaining sustainability of cropping systems. *Commun. Soil Sci. Plant Anal.* 43, 2063–2113.

Fernández-Romero, M.L., Clark, J.M., Collins, C.D., Parras-Alcántara, L., Lozano-García, B., 2016. Evaluation of optical techniques for characterising soil organic matter quality in agricultural soils. *Soil Tillage Res.* 155, 450–460.

Franzluebbers, A.J., 2016. Should soil testing services measure soil biological activity? *Agric. Environ. Lett.* 1 (1).

Galantini, J.A., Duval, M., Iglesias, J.O., Krüger, H., 2014. Continuous wheat in semiarid regions: long-term effects on stock and quality of soil organic carbon. *Soil Sci.* 179, 284–292.

García, R.A., Li, Y., Rosolem, C.A., 2013. Soil organic matter and physical attributes affected by crop rotation under no-till. *Soil Sci. Soc. Am. J.* 77 (5), 1724–1731.

Ghani, A., Dexter, M., Perrott, K.W., 2003. Hot-water extractable carbon in soils: a sensitive measurement for determining impacts of fertilization, grazing and cultivation. *Soil Biol. Biochem.* 35 (9), 1231–1243.

Hassink, J., Bouwman, L.A., Zwart, K.B., Bloem, J., Brussaard, L., 1993. Relationships between soil texture, physical protection of organic matter, soil biota, and C and N mineralization in grassland soils. *Geoderma* 57, 105–128.

Haynes, R.J., 2005. Labile organic matter fractions as central components of the quality of agricultural soils: an overview. *Adv. Agron.* 85, 221–268.

Huang, S., Peng, X., Huang, Q., Zhang, W., 2010. Soil aggregation and organic carbon fractions affected by long-term fertilization in a red soil of subtropical China. *Geoderma* 154, 364–369.

Islam, K.R., Weil, R.R., 1997. Stability of soil quality indices across seasons and regions. In: *Agronomy Abstracts*. Am. Soc. Agron., Madison, WI, pp. 215.

Janzen, H., Campbell, C., Ellert, B., Bremer, E., 1997. Soil organic matter dynamics and their relationship to soil quality. *Dev. Soil Sci.* 25, 277–292.

Kay, B.D., Vanden Bygaart, A.J., 2002. Conservation tillage and depth stratification of porosity and soil organic matter. *Soil Tillage Res.* 66, 107–118.

Klute, A., 1986. Water retention: laboratory methods. In: Klute, A. (Ed.), *Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods*. Agronomy Monograph No. 9, 2nd ed. ASA and SSSA, Madison, WI, pp. 635–660.

Kraemer, F.B., Soria, M.A., Castiglioni, M.G., Duval, M., Galantini, J., Morrás, H., 2017. Morpho-structural evaluation of various soils subjected to different use intensity

- under no-tillage. *Soil Tillage Res.* 169, 124–137.
- Le Bissonnais, Y., 1996. Aggregate stability and assessment of soil crustability and erodibility: I. Theory and methodology. *Eur. J. Soil Sci.* 47, 425–437.
- Letten, S., De Vos, B., Quataert, P., van Wesemael, B., Muys, B., van Orshoven, J., 2007. Variable carbon recovery of Walkley–Black analysis and implications for national soil organic carbon accounting. *Eur. J. Soil Sci.* 58, 1244–1253.
- Mandal, U.K., Yadav, S.K., Sharma, K.L., Ramesh, V., Venkanna, K., 2011. Estimating permanganate-oxidizable active carbon as quick indicator for assessing soil quality under different land use systems of rainfed Alfisols. *Indian J. Agric. Sci.* 81 (10), 927–931.
- Marriott, E.E., Wander, M.M., 2006. Total and labile soil organic matter inorganic and conventional farming systems. *Soil Sci. Soc. Am. J.* 70, 950–959.
- Martínez, J.M., Duval, M.E., López, F.M., Iglesias, J.O., Galantini, J.A., 2017a. Ajustes en la estimación de carbono orgánico por el método de calcinación en suelos Molisoles. *Ci. Suelo (Argentina)* 35 (1), 171–180.
- Martínez, J.M., Galantini, J.A., Duval, M.E., López, F.M., 2017b. Tillage effects on labile pools of soil organic nitrogen in a semi-humid climate of Argentina: a long-term field study. *Soil Tillage Res.* 169, 71–80.
- Morrow, J.G., Huggins, D.R., Carpenter-Boggs, L.A., Reganold, J.P., 2016. Evaluating measures to assess soil health in long-term agroecosystem trials. *Soil Sci. Soc. Am. J.* 80 (2), 450–462.
- Pennock, D., Yates, T., Braidek, J., 2007. Soil sampling designs. In: Carter, M.R., Gregorich, E.G. (Eds.), *Soil Sampling and Methods of Analysis*. CRC Press, Berlin, pp. 1–15 (Chapter 1).
- Plaza-Bonilla, D., Álvaro-Fuentes, J., Cantero-Martínez, C., 2014. Identifying soil organic carbon fractions sensitive to agricultural management practices. *Soil Tillage Res.* 139, 19–22.
- Puget, P., Angers, D.A., Chenu, C., 1999. Nature of carbohydrates associated with water-stable aggregates of two cultivated soils. *Soil Biol. Biochem.* 31, 55–63.
- Purakayastha, T.J., Rudrappa, L., Singh, D., Swarup, A., Bhadraray, S., 2008. Long-term impact of fertilizers on soil organic carbon pools and sequestration rates in maize-wheat-cowpea cropping system. *Geoderma* 144, 370–378.
- Reussi Calvo, N.I., Sainz Rozas, H., Echeverría, H., Berardo, A., 2013. Contribution of anaerobically incubated nitrogen to the diagnosis of nitrogen status in spring wheat. *Agron. J.* 105, 321–328.
- Reynolds, W.D., Drury, C.F., Yang, X.M., Fox, C.A., Tan, C.S., Zhang, T.Q., 2007. Land management effects on the near-surface physical quality of a clay loam soil. *Soil Tillage Res.* 96 (1), 316–330.
- da Silva Oliveira, D.M., Paustian, K., Cotrufo, M.F., Fiallos, A.R., Cerqueira, A.G., Cerri, C.E.P., 2017. Assessing labile organic carbon in soils undergoing land use change in Brazil: a comparison of approaches. *Ecol. Indic.* 72, 411–419.
- Six, J., Elliott, E.T., Paustian, K., Doran, J.W., 1998. Aggregation and soil organic matter accumulation in cultivated and native grassland soils. *Soil Sci. Soc. Am. J.* 62, 1367–1377.
- Skjemstad, J.O., Swift, R.S., McGowan, J.A., 2006. Comparison of the particulate organic carbon and permanganate oxidation methods for estimating labile soil organic carbon. *Soil Res.* 44 (3), 255–263.
- Soil Survey Staff, 2010. *Keys to Soil Taxonomy*, 11th ed. USDA-Natural Resources Conservation Service, Washington, DC.
- Stengel, P., 1979. Utilisation de l'analyse des systèmes de porosité pour la caractérisation de l'état physique du sol in situ. *Ann. Agric.* 30, 27–51.
- Suárez-Abelenda, M., Kaal, J., Camps-Arbestain, M., Knicker, H., Macías, F., 2014. Molecular characteristics of permanganate- and dichromate-oxidation-resistant soil organic matter from a black-C-rich colluvial soil. *Soil Res.* 52, 164–179.
- Vieira, F.C.B., Bayer, C., Zanatta, J.A., Dieckow, J., Mielniczuk, J., He, Z.L., 2007. Carbon management index based on physical fractionation of soil organic matter in an Acrisol under long-term no-till cropping systems. *Soil Tillage Res.* 96, 195–204.
- Viglizzo, E.F., Frank, F.C., Carreno, L.V., Jobbágy, E.G., Pereyra, H., Clatt, J., Pincén, D., Ricard, M.F., 2011. Ecological and environmental footprint of 50 years of agricultural expansion in Argentina. *Glob. Chang. Biol.* 17, 959–973.
- Villamil, M.B., Bollero, G.A., Darmody, R.G., Simmons, F.W., Bullock, D.G., 2006. No-till corn/soybean systems including winter cover crops: effects on soil properties. *Soil Sci. Soc. Am. J.* 70, 1936–1944.
- Walkley, A., Black, I.A., 1947. Determination of organic matter in the soil by chromic acid digestion. *Soil Sci.* 63, 251–264.
- Wander, M., 2004. Soil organic matter fractions and their relevance to soil function. In: Magdoff, F., Weil, R.R. (Eds.), *Soil Organic Matter in Sustainable Agriculture*. CRC Press, Boca Raton, FL, pp. 67–102.
- Weil, R.R., Islam, K.R., Stine, M.A., Gruver, J.B., Samson-Liebig, S.E., 2003. Estimating active carbon for soil quality assessment: a simplified method for laboratory and field use. *Am. J. Altern. Agric.* 18, 3–17.
- Yang, Y., Guo, J., Chen, G., Yin, Y.Y., Gao, R., Lin, C., 2009. Effects of forest conversion on soil labile organic carbon fractions and aggregate stability in subtropical China. *Plant Soil* 323, 153–162.
- Yang, X., Ren, W., Sun, B., Zhang, S., 2012. Effects of contrasting soil management regimes on total and labile soil organic carbon fractions in a loess soil in China. *Geoderma* 177, 49–56.
- Yousefi, M., Hajabbasi, M., Shariatmadari, H., 2008. Cropping system effects on carbohydrate content and water-stable aggregates in a calcareous soil of Central Iran. *Soil Tillage Res.* 101 (1), 57–61.