

Estimating soil organic carbon in Mollisols and its particle-size fractions by loss-on-ignition in the semiarid and semihumid Argentinean Pampas



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ABSTRACT

Recent interest in soil quality assessment underscores the need for an accurate measurement of soil organic carbon (OC) and its labile fraction, i.e. particulate OC. The loss-on-ignition (LOI) method has been proposed as a rapid, inexpensive and accurate method for estimating OC. The objectives of this study were i) to test the LOI method for soil organic matter (SOM) and particulate organic matter (POM), and ii) to evaluate the use of an adequate conversion factor (CF) for predicting OC from organic matter (OM) in soil and different particle-size fractions in several Mollisols of the Argentinean Pampas. Several agricultural fields (140) under no-tillage were sampled before crop sowing at 0–20 cm. SOM was physically separated by wet sieving, obtaining a coarse particle-size fraction (CPF, 105–2000 μm) and a medium particle-size fraction (MPF, 53–105 μm). Organic C and OM were determined by dry combustion (DC) and by LOI in whole soil (WS) and in both particle-size fractions. The values of OC (0.7–3.6 $\text{g } 100 \text{ g}^{-1}$) and OM (1.9–7.9 $\text{g } 100 \text{ g}^{-1}$) varied greatly between the soils. High and significant relationships ($P < 0.001$) were found between the different soil fractions determined by DC and LOI, with $\text{OM}_{(105-2000 \mu\text{m})}:\text{OC}_{(105-2000 \mu\text{m})}$ ($R^2 = 0.94$) $>$ $\text{OM}_{(\text{WS})}:\text{OC}_{(\text{WS})}$ ($R^2 = 0.88$) $>$ $\text{OM}_{(53-105 \mu\text{m})}:\text{OC}_{(53-105 \mu\text{m})}$ ($R^2 = 0.82$). These results indicated that the C content in each fraction was in the order of 45%, 50% and 41% for WS, CPF and MPF, respectively. The LOI method can predict OC in CPF (105–2000 μm) with reliable accuracy. The CF for predicting OC from OM was variable for each soil fraction considered: 2.23 for WS, 2.00 for CPF and 2.44 for MPF.

1. Introduction

Soil organic matter (SOM) plays a key role in several processes in the soil ecosystem, including soil structure formation, water retention, detoxification of anthropogenic chemicals, carbon (C) sequestration, nutrient cycling and energy supply to soil microorganisms (Galantini and Suñer, 2008; Galantini et al., 2016). The SOM comprises several fractions with different physical and chemical properties and consequently different degrees of stabilization by specific mechanisms with particular turnover rates (Duval et al., 2016). The labile SOM fraction - also called particulate organic matter (POM) - is a transitory pool characterized by materials easily decomposable by microbes, such as plant and animal residues (Cambardella et al., 2001; Martínez et al.,

2017a). The method for POM isolate, i.e. physical fractionation by particle-size, is simple, accurate and rapid (Cambardella et al., 2001). Furthermore, this method allows the isolation of fractions according to their decomposability (Duval et al., 2013), the 53–2000 μm fraction being more labile than the $< 53 \mu\text{m}$ particle-size fraction, known as the passive pool of SOM (Duval et al., 2016).

Over the last few decades, soil quality (SQ) definition and assessment techniques have become a major concern. Furthermore, scientific information is essential for finding appropriate indicators that can accurately assess SQ (Duval et al., 2013). In this sense, SOM and its C content, i.e. soil organic carbon (OC), as well as its labile organic fractions, i.e. particulate OC, are considered important SQ indicators (Reeves, 1997; Duval et al., 2013). For that reason, the recent interest in

Abbreviations: C, carbon; OC, organic carbon; OM, organic matter; DC, dry combustion; LOI, loss-on-ignition; NT, no-tillage; CF, conversion factor; SOM, soil organic matter; POM, particulate organic matter; WS, whole soil; CPF, coarse particle-size fraction; MPF, medium particle-size fraction; SQ, soil quality; WB, wet oxidation with potassium dichromate; SON, soil organic nitrogen; MAT, mean annual temperature; MAR, mean annual rainfall

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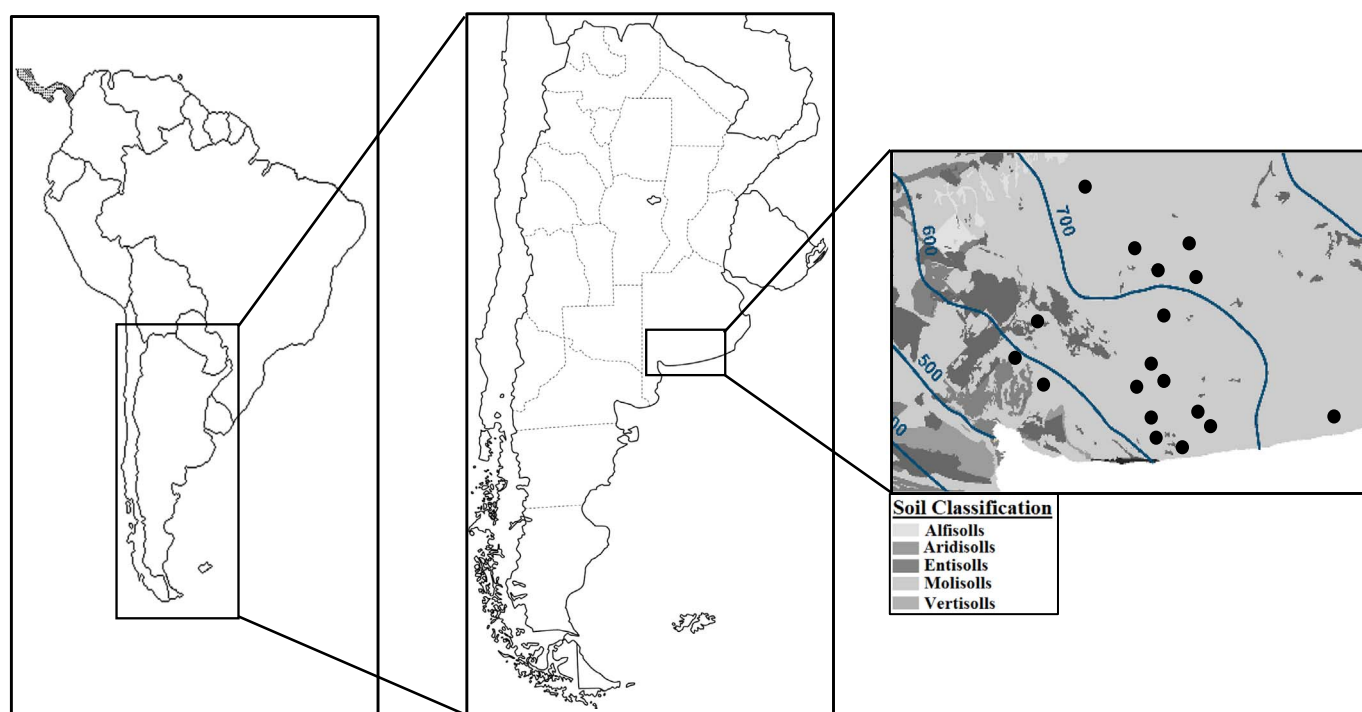


Fig. 1. Site location of the sampled fields in the southwest of the Argentine Pampas. The areas within the 500–700 and 700–800 mm isohyets were considered as semiarid and semihumid, respectively.

SQ assessment underscores the need for a rapid, inexpensive and accurate measurement of soil C.

Nowadays, several methods can determine C in soil and its fractions (Tabatabai, 1996; Eyherabide et al., 2014), the most widely used ones being the wet oxidation method with potassium dichromate (WB) (Walkley and Black, 1934) and the dry combustion (DC) method (Pribyl, 2010; Eyherabide et al., 2014; Martínez et al., 2017b). In particular, the WB method readily determines oxidizable C, but although it is fast and inexpensive, it uses large quantities of sulfuric acid and it generates toxic and carcinogenic products (Abella and Zimmer, 2007; Eyherabide et al., 2014). As well as using hazardous reagents, the final estimate of C requires a correction factor which is variable, because organic matter (OM) oxidation is incomplete and differs with the soil type (Nelson and Sommers, 1982). On the other hand, DC is an accurate and reliable method for determining organic C (Pribyl, 2010). It directly measures the total soil C without the need for a correction factor (Grewal et al., 1991; Périé and Ouimet, 2008). It has become the standard procedure for determining soil OC (Chatterjee et al., 2009; Pribyl, 2010; Eyherabide et al., 2014). The sample is mixed with a catalyst and heated in a stream of oxygen to approximately 1000 °C (Tabatabai, 1996). All C in the sample is oxidized to CO₂. The quantity of CO₂ released is measured by infrared absorption spectroscopy and converted to total C (Pribyl, 2010). This method is relatively expensive though, and it requires highly trained personnel and finely processed samples. Considering the importance of these techniques, it is desirable to test a fast and simple method to accurately determine OC and prevent any production of waste that might be toxic to the environment and human health (Martínez et al., 2017b).

Loss-on-ignition (LOI) can estimate OM directly but it also seems to cause the most controversy. Given that all available methods for assessing SOM components include inherent limitations, it is important to consider the most applicable and accurate method for soil analysis (Rosell et al., 2001; De Vos et al., 2005). This precise, rapid and relatively inexpensive method (Abella and Zimmer, 2007) can determine the weight loss of the soil sample when exposed to high temperatures (250 to 850 °C) for periods ranging from 2 to 24 h (Davies, 1974;

Schulte and Hopkins, 1996; Martínez et al., 2017b). Davies (1974) reported that ignition of soil carbonates is avoided below 430 °C. Other authors (Schulte and Hopkins, 1996; Rosell et al., 2001) found that ignition temperatures higher than 500 °C could cause overestimation and lead to errors due to the loss of structural water from clay minerals, oxidation of ferrous ions and decomposition of hydrated salts and oxides. For this reason, the ignition temperature should be high enough to remove the maximum amount of OM but to minimize loss of other soil constituents (Schulte and Hopkins, 1996). Martínez et al. (2017b) concluded that the best conditions for improving OC prediction occurred at 550 °C for 2 or 4 h in several Mollisols of the same regions. Unfortunately, LOI estimates have to be calibrated against the most reliable C determination by DC for each soil type and region.

Estimating OC from OM determined by LOI is a simple and inexpensive procedure, but it requires the use of an adequate conversion factor (CF) (Pribyl, 2010). Historically, a CF of 1.724 is generally used for converting soil OM to estimates of soil OC (Van Bemmelen, 1890). It is based on the assumption that SOM contains 58% C (Tabatabai, 1996). However, the widespread use of CF for soil and its fractions could be erroneous. Galantini et al. (1994) found 58% C concentration in humidified SOM and up to 40–42% C in POM. The CF is not universally constant and is dependent on many factors, e.g. vegetation cover, OM composition and clay content (Wright et al., 2008; Pribyl, 2010). In addition, it has to be calibrated according to the soil properties and the environment. Moreover, the literature has not reported any studies using LOI in POM (Cambardella et al., 2001), and a different CF should be used according to the evaluated particle-size fraction because of the differences in the composition of SOM fractions. It is important to note that residue input from crops is limited in these regions and, considering that the proportion of POM changes with soil texture (Galantini et al., 2004), the CF may vary between soil types. However, little information is available in the literature about using CF in different soil fractions in soils. Our hypothesis is that LOI conditions may favor the estimation of the C contained in particulate fractions (higher than 53 μm) in comparison to the whole soil (WS), and the C composition in each fraction may differ according to the soil fraction

evaluated.

The objectives of this study were i) to test the LOI method for SOM and POM, and ii) to evaluate the use of an adequate CF for predicting OC from OM in soil and different particle-size fractions in several Mollisols of the Argentinean Pampas.

2. Material and methods

2.1. Experimental sites

During 2010, 2011 and 2012, one hundred and forty (140) agricultural fields under no-tillage (NT) were sampled from eighteen sites before crop sowing. The plots were located in the semiarid (500–700 mm isohyets) and semihumid regions (700–800 mm isohyets) in the southwest of Buenos Aires province, Argentina (Fig. 1).

The Pampas region in Argentina is known as one of the most important grain-producing areas in the world, the main crops being wheat (*Triticum aestivum* L.), maize (*Zea mays* L.) and soybean (*Glycine max* L. Merr) (Satorre and Slafer, 1999). Wheat is the basic crop in production systems across a wide region of the southwestern Pampas in Argentina (Martínez et al., 2016, 2017a). All sampled soils are Mollisols (Soil Survey Staff, 2010) that developed in aeolian sediments (loess), with a wide variability in depth, texture, soil OC content and fertility (Álvarez and Lavado, 1998). In semiarid and semihumid regions, the soils are characterized by a low SOM content, and their dynamics are affected more strongly by water availability (Galantini et al., 2016).

The rainfall amount and frequency are irregular across all sites, the rainiest seasons being autumn (March–April) and spring (September–October). All soils had been under a NT system of continuous agriculture for 10–15 years. This system was characterized by the absence of tillage with over 30% residue covering the soil surface on all sites. In general, a herbicide (1–2 L ha⁻¹ of glyphosate) was applied for weed control and to start the chemical fallow. Data on annual mean temperature and rainfall were collected from the SMN (National Weather Service) weather stations.

Three georeferenced, homogeneous and uniform sampling areas of about 50m² were selected in each field of about 50 ha; they were representative of the plots to reduce spatial variability. Composite soils samples were taken (12 to 15 soil cylinders) from the 0–20 cm depth prior to crop sowing. The soil was air-dried, sieved and homogenized to 2 mm, and the retained plant residues were discarded. Then, they were analyzed for the following soil routine parameters: soil total nitrogen (SON) by the Kjeldahl method (Bremner, 1996) and pH on a 1:2.5 soil-water suspension. Soil granulometry was estimated by particle-size fractionation (Duval et al., 2013; Martínez et al., 2016), subtracting the percentage of OC from each fraction (higher and lower than 53 μm) and estimating the silt-plus-clay content in the fraction. Each soil sample was tested with hydrochloric acid to verify the presence of carbonates (Schoeneberger et al., 1998). However, no carbonates were found in any of the samples at the 0–20 cm soil depth. Table 1 shows the site and plot characteristics and the chemical and physical properties.

2.2. Physical fractionation of SOM by particle size

The SOM was physically separated by wet sieving (Cambardella and Elliott, 1992; Duval et al., 2013). Then, 50 g of previously air-dried and sieved soil was dispersed in 120-mL glass containers and mixed with 105 mL of distilled water. Ten glass beads (5 mm diameter) were added to increase aggregate destruction and reduce any potential problems created by sand (Cambardella and Elliott, 1992). After dispersion, the soil suspension was sieved through 2 connected sieves of 53 and 105 μm diameter. The sieves were moved back and forth and the soil retained on the top of the sieve was sprinkled with distilled water until the water in the bottom sieve was clear to the naked eye. Two fractions were obtained: i) a coarse particle-size fraction (CPF) (105–2000 μm) containing coarse POM and coarse and medium sands, and ii) a medium

particle-size fraction (MPF) (53–105 μm) containing the most transformed POM and fine and very fine sand. The fine particle-size fraction (< 53 μm) was discarded.

2.3. Determination of organic carbon by DC

Briefly, 0.5 g of WS and both particulate organic fractions (53–105 μm and 105–2000 μm) were weighed. The DC was measured on a Leco TruSpec automatic C analyzer (Leco Corporation, St Joseph, MI). The analyzer was calibrated with standards provided by the equipment manufacturer (Leco Corporation = 3.00 ± 0.24).

2.4. Determination of soil organic matter by LOI

Then, 5 g of soil sample was weighed into previously weighed 25 mL porcelain crucibles and they were placed in an oven at 105 °C for 24 h. In the case of the coarse and medium particle-size fractions, 2 g of sample was weighed. The samples were cooled in a desiccator and weighed. They were then placed in a muffle at 550 °C for 4 h and transferred to a desiccator; after cooling, the weight was recorded again. The temperature and calcination time were selected following the suggestions and applications of other authors (De Vos et al., 2005; Wright et al., 2008; Martínez et al., 2017b). The OM was estimated by the difference in weight Eq. (1) according to the model proposed by Schulte and Hopkins (1996):

$$OM(g\ 100g^{-1}) = \frac{DW - CW}{DW - W_c} * 100 \quad (1)$$

where,

OM: organic matter (g 100 g⁻¹).

DW: weight of the sample at 105 °C plus the crucible (g).

CW: weight of the calcinate sample plus the crucible (g).

Wc: weight of the porcelain crucible (g).

2.5. Statistical analysis

Descriptive statistics was applied to OC and OM in the WS and in both particulate organic fractions. Simple linear regressions were used to develop relationships between OC_(WS)-OM_(WS); OC_{(105–2000 μm)}}-OM_{(105–2000 μm)}} and OC_{(53–105 μm)}}-OM_{(53–105 μm)}}. In order to establish the OM-OC relationships for each soil fraction, regressions were made using the intercept in the prediction equations. De Vos et al. (2005) reported the importance of using the intercept in regressions, because it has a real value and it represents part of the variation. Pribyl (2010) also considered that it is necessary to include the intercept, unless the sample size is small, but this condition was not fulfilled in the present study. Grewal et al. (1991) suggested that the intercept makes it possible to study the interaction between the composition of the sample and the LOI conditions. A covariance analysis (ANCOVA) was performed to compare the equality of the regression slopes for each soil fraction. A cluster analysis was applied to identify different groups of soils, clustering all sampled soils (n = 140) of similar soil properties (silt-plus-clay; SON and pH). Cluster analysis was undertaken according to Ward's minimum variance method (Ward, 1963). The results are shown in a dendrogram where steps in the hierarchical clustering solution and values of the distances between clusters (Euclidean distance) are represented. This multivariate analysis was carried out on account of the wide edaphic differences in these Mollisols, allowing soils with similar characteristics to be grouped. Differences between the soil properties by groups of soils were analyzed using a *t*-test. Then, an ANCOVA was conducted to verify the regression slopes by different soil groups equally for each fraction evaluated. The statistical analysis was carried out with the Infostat software (Di Rienzo et al., 2013).

Table 1
Soil, climatic and general characteristics and chemical and physical soil properties (mean ± standard deviation) of the sites.

Location	Site	n ^a	Soil classification ^b	Previous crop (%)	MAT ^c	MAR ^d	SON	pH	silt plus clay (g kg ⁻¹)	
					(°C)	(mm)				(g kg ⁻¹)
1	33°21'S 62°08'W	García del Río	5	Haplustoll	Wheat (60); Barley (40)	14.9	658	1.15 ± 0.16	7.0 ± 0.6	383 ± 120
2	38°47'S 61°38'W	Las Oscuras	17	Typic Argiustoll	Wheat (60); Pea (40)	15.0	669	1.11 ± 0.23	6.0 ± 0.2	468 ± 124
3	38°19'S 61°44'W	Saldungaray	13	Typic Argiustoll	Wheat (75); Sunflower (25)	14.7	694	1.74 ± 0.46	7.1 ± 0.6	537 ± 63
4	38°55'S 61°36'W	Cnel. Rosales	9	Entic Haplustoll	Wheat (105)	14.9	664	0.87 ± 0.21	6.1 ± 0.2	272 ± 112
5	38°30'S 61°36'W	Cnel. Pringles	6	Typic Haplustoll	Wheat (75); Sorghum (25)	14.8	686	1.37 ± 0.26	6.5 ± 0.5	514 ± 87
6	38°36'S 61°44'W	Falcón	10	Typic Haplustoll	Wheat (50); Barley (50)	15.0	692	1.22 ± 0.57	6.2 ± 0.5	319 ± 178
7	38°37'S 62°00'W	Cabildo	7	Typic Haplustoll	Wheat (105)	14.5	560	1.48 ± 0.20	6.4 ± 0.3	208 ± 105
8	38°31'S 62°10'W	Bahía Blanca	4	Typic Haplustoll	Wheat (50); Barley (50)	14.5	550	1.27 ± 0.18	7.0 ± 0.5	424 ± 85
9	38°54'S 61°21'W	Monte Hermoso	7	Typic Argiustoll	Wheat (70); Barley (30)	14.8	683	1.19 ± 0.14	6.5 ± 0.6	384 ± 87
10	38°22'S 61°28'W	Cnel. Pringles	4	Typic Argiudoll	Barley (50); Wheat (25); Soybean (25)	14.8	695	1.61 ± 0.30	6.5 ± 0.3	613 ± 79
11	38°10'S 62°01'W	Tornquist	18	Typic Argiudoll	Sunflower (50); Wheat (40); Soybean (10)	14.5	740	1.36 ± 0.26	6.4 ± 0.2	507 ± 54
12	38°36'S 61°03'W	Cnel Dorrego	7	Typic Argiudoll	Barley (40); Wheat (60)	14.7	726	1.53 ± 0.25	6.5 ± 0.3	422 ± 60
13	37°58'S 62°09'W	Tornquist	8	Typic Argiudoll	Sunflower (50); Barley (30); Wheat (10); Oat (10)	14.3	756	1.51 ± 0.35	6.5 ± 0.1	533 ± 74
14	38°24'S 60°52'W	El Pérdido	7	Typic Argiudoll	Wheat (60); Barley (40)	14.7	726	1.09 ± 0.16	6.2 ± 0.3	369 ± 129
15	37°34'S 62°09'W	Pigue	9	Typic Argiudoll	Soybean (70); Wheat (20); Oat (10)	13.8	796	2.18 ± 0.41	6.4 ± 0.5	599 ± 77
16	38°06'S 62°07'W	Tornquist	6	Typic Argiudoll	Wheat (70); Sunflower (15); Maize (15)	14.5	741	1.66 ± 0.16	6.3 ± 0.4	581 ± 53
17	38°00'S 62°06'W	Tornquist	2	Typic Argiudoll	Sunflower (105)	14.4	753	1.77 ± 0.16	6.4 ± 0.1	596 ± 47
18	38°45'S 60°06'W	Tres Arroyos	1	Typic Argiudoll	Pea (105)	14.9	790	2.44 ± 0.01	5.6 ± 0.3	719 ± 44

^a n, number of sampled fields by site.

^b Soil Survey Staff (2010).

^c MAT, mean annual temperature (°C).

^d MAR, mean annual rainfall (mm). Previous crop, in parenthesis % of the previous crop in the n plots per site. SON, soil organic nitrogen (g kg⁻¹). Previous crops: wheat; barley (*Hordeum vulgare* L.); sunflower (*Helianthus annuus* L.); oat (*Avena sativa* L.); pea (*Pisum sativum* L.); sorghum (*Sorghum spp.*).

3. Results

3.1. Organic carbon by DC and organic matter by LOI in a whole soil and in both particle-size fractions

The results of determinations of OC and OM by DC and LOI are detailed in Table 2. The values of soil OC (0.7–3.6 g 100 g⁻¹) and SOM (1.9–7.9 g 100 g⁻¹) showed a broad range of variability between soils. High coefficients of variation (CV) were found for OC_(105–2000 μm) and OM_(105–2000 μm), with values of 102 and 80%, respectively. These results indicate that composition of the CPF was the most variable one between fractions in these soils.

3.2. Relationships between determinations by DC and LOI and conversion factor

High and significant relationships (P < 0.001) were found between the different soil fractions determined by DC and LOI (Fig. 2), where OM_(105–2000 μm):OC_(105–2000 μm) > OM_(WS):OC_(WS) > OM_(53–105 μm):OC_(53–105 μm), with a R² of 0.94; 0.88 and 0.82, respectively. The regression slopes were 0.422; 0.499 and 0.385 for WS, MPF and CPF, respectively. The analysis of covariance—assuming equal slopes—showed high and significant differences (P < 0.001) between the slopes for each soil fraction. The OM_(105–2000 μm):OC_(105–2000 μm)

Table 2

Mean, standard deviation, range of values and coefficient of variation for OC and OM in a whole soil and in both particle-size fractions (n = 140).

	n	OC _(WS)	OC _(105–2000 μm)	OC _(53–105 μm)	OM _(WS)	OM _(105–2000 μm)	OM _(53–105 μm)
		(g 100 g ⁻¹)					
Mean	140	1.7	1.5	0.7	4.4	3.0	2.1
Maximum		3.6	7.1	2.1	7.9	11.5	3.7
Minimum		0.7	0.1	0.2	1.9	0.6	0.9
SD ^a		0.6	1.5	0.3	1.2	2.4	0.6
CV ^b		33	102	48	28	80	30

WS, whole soil; 105–2000 μm, coarse particle-size fraction (CPF); 53–105 μm, medium particle-size fraction (MPF).

^a SD, standard deviation.

^b CV, coefficient of variation.

regression slope differed statistically from the OM_(WS):OC_(WS) and OM_(53–105 μm):OC_(53–105 μm) slopes, without any significant differences in the slopes between the latter (P = 0.52).

Considering the inverse of the regression slope, different CF were obtained for soil and both particle-size fractions with values of 2.23; 2.00 and 2.44 for WS, CPF and MPF, respectively (Fig. 2). These results indicated that the C content in each of these fractions was 45% for WS, 50% for CPF and 41% for MPF.

3.3. Grouping soils by properties

The cluster analysis based on soil properties showed two main clusters (Fig. 3). Cluster A contained 71 field plots with a high proximity, and Cluster B included 69 field plots. Fig. 4 shows the differences between the edaphic properties considered for cluster analysis. High and significant differences (P < 0.01) in the silt-plus-clay content, and significant differences (P < 0.05) in SON and pH were found by grouping clusters, with higher values of silt-plus-clay and SON in Cluster A soils (Fig. 4). The ANCOVA analysis that was conducted to compare the equality of slopes by groups for each soil fraction only showed significant differences (P = 0.023) in WS (Fig. 5), whereas none were found between the slopes in either particle-size fraction (P > 0.10). When analyzing the linear regressions by soil group in WS, a higher R² (> 0.74) was observed in both soil groups, but with a

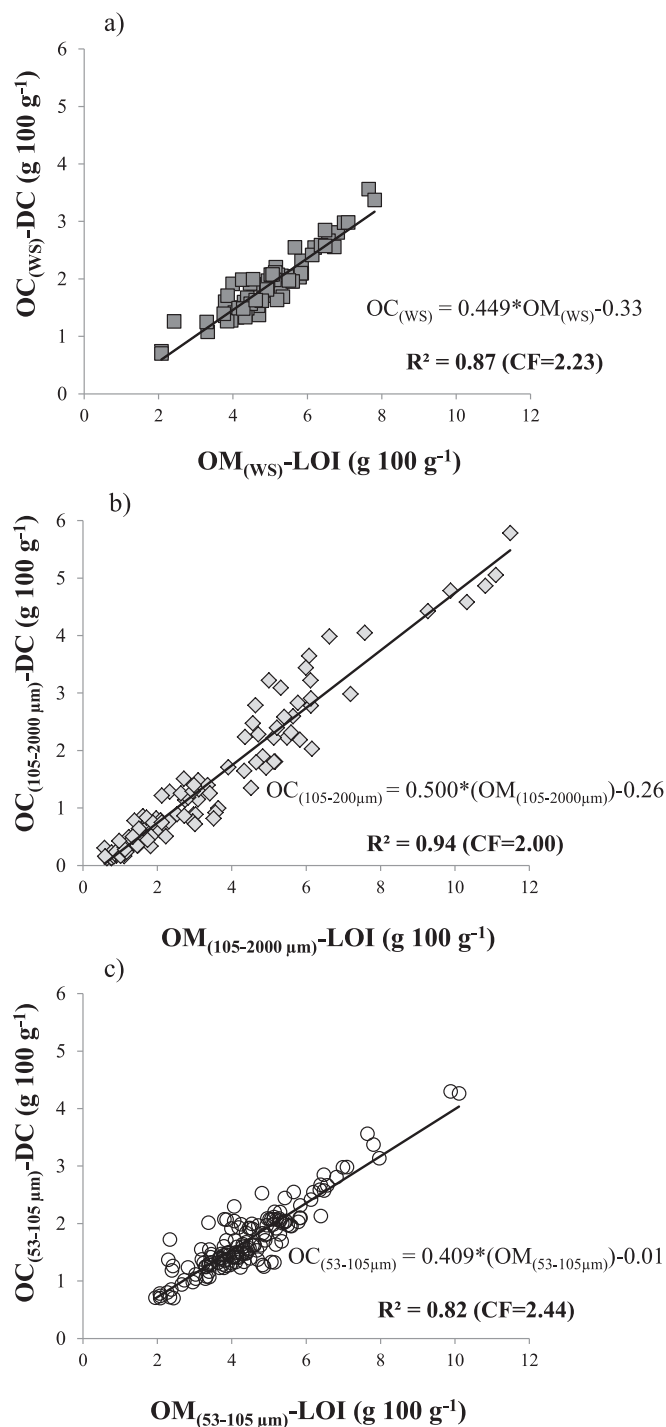


Fig. 2. Linear relationships between a) $OC_{(WS)}$ and $OM_{(WS)}$; b) $OC_{(105-2000 \mu m)}$ and $OM_{(105-2000 \mu m)}$; and c) $OC_{(53-105 \mu m)}$ and $OM_{(53-105 \mu m)}$ determined by dry combustion (DC) and loss-on-ignition (LOI), respectively. CF, conversion factor.

different CF of 2.22 and 2.63 for Cluster A and B, respectively.

4. Discussion

4.1. Soil properties

Soil pH was slightly alkaline to mildly acid, typical of the Pampas area (Berhongeray et al., 2013), with an average of 7.0 and a range between 6.0 and 7.6. Soil organic N showed a mean value of 1.4 g kg^{-1} , ranging from 0.5 g kg^{-1} to 2.8 g kg^{-1} . Considering the soil

Sites

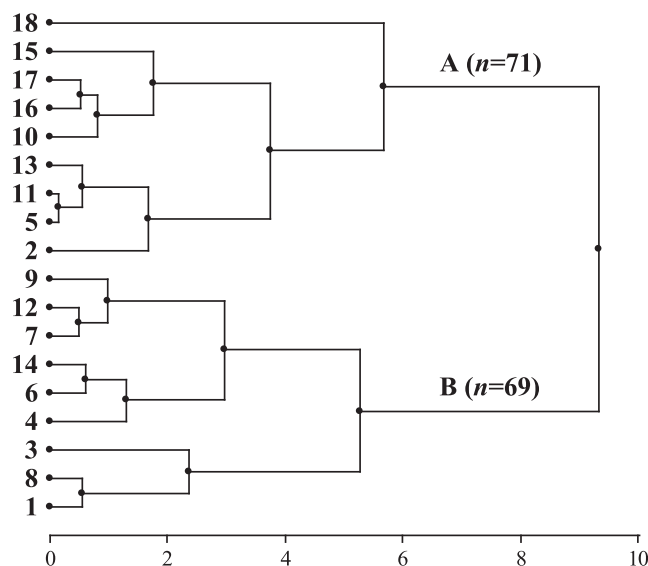


Fig. 3. Cluster analysis with Ward's differences for soil properties by site.

OC content, this study showed a range of SOC (0.7 g kg^{-1} – 3.6 g kg^{-1}) in coincidence with other LOI method studies (Cambardella et al., 2001; Abella and Zimmer, 2007). This soil OC range of values is important, because Donkin (1991) found that LOI-DC relationships were strongest in soils with soil OC concentrations lower than $5 \text{ g } 100 \text{ g}^{-1}$. Regarding soil texture, the amount of fine fractions (silt-plus-clay), whose mean values were 466 g kg^{-1} , showed high and positive significant relationships for all soil fractions with a silt-plus-clay content (data not shown). The highest relationships were found between $OC_{(WS)}$ and $OM_{(WS)}$ with a R^2 of 0.66, whereas the lowest relationship was found for CPF. In the case of MPF, relationships were similar to WS.

4.2. Relationships between determinations by DC and LOI and conversion factor

The OC and OM values showed a wide edaphic variability for all fractions evaluated ($CV = 28$ – 102%). As expected, the greatest variability was obtained for CPF because this fraction is highly influenced by crop residue input, which is strongly affected by the climatic conditions in this region over the years (Galantini et al., 2004; Martínez et al., 2016; Martínez et al., 2017a). In addition, Galantini and Suñer (2008) stated that the C content in the constituents of the labile fraction is variable and the quantity of each of them will be a determinant of the characteristics of the isolated material.

Relationships between DC and LOI for each soil fraction were high and significant ($P < 0.001$), but the highest relationship was found for CPF ($R^2 = 0.94$), as was partially hypothesized. Conversely, relationships between DC and LOI in MPF were lower than in WS. These results demonstrate that under these conditions LOI can accurately estimate C in all soil fractions, although the prediction was more accurate in CPF. In addition, these results verified different C contents for each fraction, with similar values to those reported in the literature, mainly for WS (Galantini et al., 1994; Pribyl, 2010; Martínez et al., 2017b). These results partially confirm the hypothesis, because a different C content was found in CPF in comparison to WS and to MPF. Given that no studies have been reported in the literature that estimate OC from OM in POM fractions (Cambardella et al., 2001), and considering the 1.724 factor determined by Van Bemmelen (1890) for soil, the CF obtained in this study was higher, although within the range (1.4–2.4) proposed by Pribyl (2010). This indicates that using the 1.724 factor instead of the value obtained in the study would result in an overestimation of

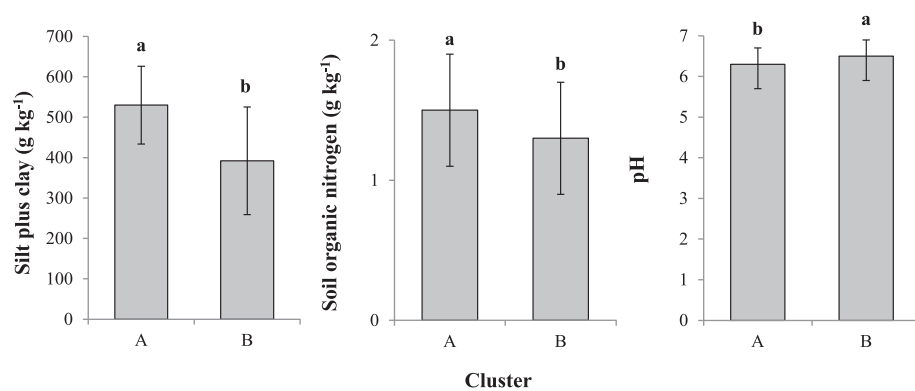


Fig. 4. Mean values of soil properties included in cluster analysis. Vertical bars indicate the standard deviation. Different letters indicate significant differences in soil properties by soil group ($P < 0.05$).

approximately 40% of the C content in WS, thus showing that using the universal CF for estimating the C content could be erroneous. The accuracy with which CF is estimated depends on the methods used for measuring OC and OM (Pribyl, 2010). In this case, the CF for CPF was calculated from an OC-OM relationship with a high R^2 , which is a measure that could be used for comparing relative reproducibility (Pribyl, 2010). Several authors (David, 1988; Konen et al., 2002; Martínez et al., 2017b) stated that DC-LOI relationships are only valid for specific soil data sets. For this reason, LOI estimates should be calibrated against the most reliable determination of C by DC for each soil type and region (Pribyl, 2010). In this case, using LOI helped to understand the relationship between the two methods for determining OC and OM in soil and different particle-size fractions for a large number of Mollisols with contrasting edaphic properties over a large area of the Argentinean Pampas. In addition, the present study made it possible to assess the C content of each particle-size fraction evaluated with great accuracy, and it established a suitable CF for estimating the C content of these fractions. In particular, the close relationship between $OC_{(105-2000 \mu m)}:OM_{(105-2000 \mu m)}$ in CPF and the convenience of using the LOI method would make POM easier to determine. However, more research is needed for finding out which factors may improve the estimation of OC in WS and in MPF using the LOI method.

4.3. Grouping soils by properties

Grouping soils by soil properties resulted in two groups of soils with a high proximity between them. When analyzing the linear regressions between OC and OM in different particle-size fractions, significant differences in slopes were only found in WS, obtaining a different CF, and therefore showing different C contents in both groups (Fig. 5).

Cluster A soils (higher content of silt-plus-clay and SON, and lower pH) showed a higher C content than Cluster B soils, with a lower CF. Considering the positive influence of the silt-plus-clay content in SOM fractions (Galantini et al., 2004) and the negative correlation between soil OC and pH, i.e. a higher soil OC content with a lower pH (Schmidt and Amiotti, 2017), it could be inferred that soils with a higher fertility have a lower CF than soils of poor fertility in these Mollisols. This result was in agreement with Eyherabide et al. (2014), who reported that the CF is likely to be higher in coarse-textured soils due to the greater percentage of particulate organic fractions with a lower C content. Other authors (Buschiazzo et al., 1991; Quiroga et al., 2006) reported the influence of silt-plus-clay content on soil C turnover in several Mollisols. Also, the silt-plus-clay content becomes relevant because it can affect LOI conditions, thus affecting the intercept of regression. Grewal et al. (1991) referred to this effect as the intercept effect and suggested that it increases in soils with a higher clay content. When this value is negative with a high temperature, it suggests dehydroxylation, dehydration or carbonate removal (Pribyl, 2010), resulting in a high CF. It is important to note that this effect would only be detected when WS was considered; these causes, however, might be neglected when LOI measurements were made on particle-size fractions, due to their composition of sand and organic materials. Also, in the present study the relationships between OC and OM in particulate organic fractions were not adjusted to the fraction percentage of each one with respect to the total soil. Conversely, a positive intercept value shows that SOM removal has not been complete (Pribyl, 2010); therefore, the intercept values found in this study for all soil fractions demonstrate that LOI conditions have been adequate. Under these conditions, grouping soils together by their soil properties, i.e. SON, silt-plus-clay and pH, allowed us to obtain a different CF for converting OM to estimates of OC.

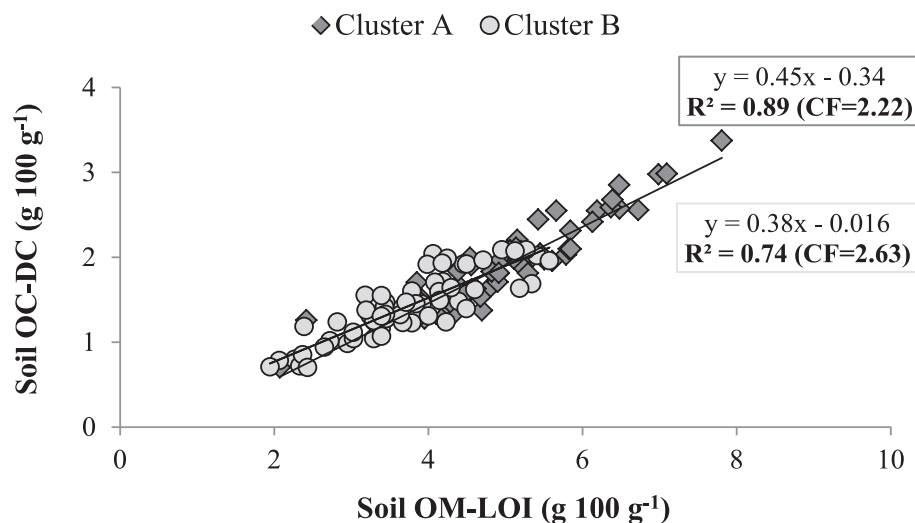


Fig. 5. Linear relationships between OC and OM in whole soil grouped by cluster analysis.

5. Conclusions

Under the particular conditions of these Mollisols with a wide range of edaphic properties, the LOI method can predict OC in the 105–2000 µm particle-size fraction with reliable accuracy. LOI would be a precise, inexpensive and simple method that can quickly estimate C in coarse POM. Results from this study also suggest that in order to determine C in WS and in MPF, the method should be modified for improving the accuracy of the estimation. Nevertheless, LOI may be useful for estimating soil OC in these soils when only rough estimates are required.

The CF varied according to the fraction considered, with values of 2.23, 2.00 and 2.44 for WS, CPF and MPF, respectively. These results demonstrate that C data for soils under these conditions could be overestimated when using the widespread CF. By grouping soils together by soil properties –i.e. silt-plus-clay, SON and pH– different CF were obtained in WS according to the soil fertility, with a lower value in high fertility Mollisols.

This study is of great relevance when SQ is assessed through the analysis of different soil organic C fractions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geodrs.2017.12.004>.

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