



Methods assessment for organic and inorganic carbon quantification in calcareous soils of the Mediterranean region

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ABSTRACT

In calcareous soils, two methods for measuring soil organic carbon (SOC) have been traditionally used: 1) wet oxidation, and 2) dry combustion in which SOC is measured either directly by removing soil inorganic carbon (SIC) from samples through an acid pretreatment, or indirectly by subtracting SIC measured by a calciometer from total soil C. These methods have well documented experimental limitations that may result in erroneous quantification of C stocks and cycling in calcareous Mediterranean soils. An alternative approach is ramped combustion, which takes advantage of the large difference in the temperatures at which SOC and SIC combust or decompose. Our aim in this study was to test the capability of a continuous, ramped combustion technique combining differential scanning calorimetry and evolved gas analysis to quantify SIC and SOC in calcareous soil samples, and compare this technique with conventional techniques. We also sought to use thermal analysis to test the efficacy of acid fumigation for carbonate removal, and to evaluate the effects of acid fumigation on SOC quality. SIC and SOC concentrations from a set of 23 soil samples differing in carbonate concentrations were well correlated among conventional and ramped combustion methods, indicating that ramped combustion is an effective method to simultaneously quantify SIC and SOC in calcareous soil samples. Ramped combustion was also effective in demonstrating incomplete carbonate removal in several samples, though quantification was made difficult by sample mass issues due to hydrophilicity after fumigation. Ramped combustion also revealed substantial qualitative changes in the thermal lability of residual organic matter, as evidenced by changes in CO₂-EGA thermogram shape and peak temperatures. As a result, ramped combustion appears to be a preferable single-sample method for the simultaneous quantification of SOC and SIC in calcareous soil, providing a relatively rapid, cost- and labor-effective method that precludes the use of hazardous reactants such as those used in wet oxidation and acid fumigation.

1. Introduction

In recent decades, interest in the global C cycle has intensified research related to the terrestrial part of this cycle, and in particular, on C storage and cycling in soils. In the Mediterranean region, this study is especially relevant, as substantial amounts of agricultural land are set on organic C-depleted soils with varying proportions of inorganic C (SIC) in the form of primary (inherited from parent materials) and secondary (pedogenic) carbonates. In addition to Calcisols, Leptosols, Cambisols and Luvisols are the dominant soil orders in the Mediterranean Basin (Soil Atlas of Europe, 2005). Many of these soils contain different types and concentrations of carbonates because limestone and other calcareous rocks are the parent materials of a large proportion of them (Lewin and Woodward, 2009; Verhey and de la

Rosa, 2005). This, added to the xeric moisture regime present in most of the region (Aguilera et al., 2013; Wainwright, 2009), generates optimal conditions for dissolution, leaching and re-precipitation of carbonates (Yaalon, 1997). These climatic conditions, together with the fact that this region has been densely populated and intensively exploited for long periods in history, also result in soil organic carbon (SOC) contents that are typically lower than in temperate areas (Jones et al., 2005; Verhey and de la Rosa, 2005), especially in cultivated soils where net primary production in these dryland agrosystems is relatively low (Aguilera et al., 2013). Irrigation is often adopted, and known to alter soil C dynamics, by changing SOC accumulation and turnover rates (Apesteguía et al., 2015; Zamanian et al., 2016), and SIC processes by favoring dissolution, leaching and precipitation (Bughio et al., 2016; de Soto et al., 2017).

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The study of SOC and SIC contents and dynamics is therefore especially challenging in these soils for agricultural and environmental research, particularly in relation to measurements of CO₂ emissions from calcareous soils (Chevallier et al., 2016). Because of the ubiquity of organic and inorganic C, there is substantial demand for high-throughput analytical methods able to generate accurate and inexpensive measurements (Chatterjee et al., 2009). In the absence of SIC, total soil carbon can be equated to SOC, and dry combustion is considered the most accurate method (Bisutti et al., 2004) and can be used as a reference to calibrate other methods (Bisutti et al., 2004). Moreover, dry combustion is also the most common method used for measurements of $\delta^{13}\text{C}$ in organic carbon turnover studies (e.g., Balesdent and Mariotti, 1996; Deneff et al., 2001; Derrien and Amelung, 2011) due to the fact that the coupling of elemental analyzers with isotope ratio mass spectrometry (IRMS) is relatively simple and common. In calcareous soils (in which SIC accounts for a part of total soil C), however, the measurement of SOC by dry combustion cannot be direct due to the presence of SIC. In these soils, the measurement of SOC remains challenging and straightforward methods are not yet available (Schmidt et al., 2012). Two different approaches for measuring SOC have been traditionally used in calcareous soils: 1) wet oxidation, which can be considered a “direct” method of measurement in which the oxidizable fraction (assumed to equal SOC) is measured, leaving intact the SIC fraction; and 2) dry combustion, in which SOC is measured either directly by removing SIC from samples through an acid pretreatment, or indirectly by subtracting SIC measured by a calcimeter or other method of analysis from total soil C (Rodríguez et al., 2016). Debate over the advantages and disadvantages of different methods has been ongoing for decades (e.g., Tabatabai, 1996). Both approaches have demonstrated experimental limitations related to incomplete quantification of SOC or SIC removal, which may lead to under or overestimations of SOC.

Soil organic C determination by wet oxidation is applied worldwide in many laboratories, particularly those lacking expensive analytical instruments. It has been the standard method since the early twentieth century, following the protocol described by Walkley and Black (1934). The interest in using wet oxidation in calcareous soils is the possibility of obtaining a direct measurement of SOC unaffected by the presence of carbonates. In this method, SOC is oxidized by addition of excess oxidant to air-dried, ground soil samples, while leaving inorganic carbon undecomposed. Oxidizable carbon is determined indirectly by titration of the remaining oxidant. The main problem of the method is that oxidation of SOC may be incomplete (Chatterjee et al., 2009; Nelson and Sommers, 1996; Skjemstad et al., 1998), particularly as heat is added only through the exothermic reaction of combining the acid and oxidant. Generally, the oxidized organic carbon represents 75–85% of the total organic carbon as measured by dry combustion, which makes the use of a correction factor necessary (Grewal et al., 1991). Heating samples during the reaction generally improves SOC recovery (Tiessen and Moir, 1993), though the duration and temperature of heating need to be adjusted appropriately, and the acid dichromate oxidizing solutions decompose at 150 °C, which can lead to overestimation (Pansu and Gautheyrou, 2006). Soil type and the nature of the organic material have been reported as factors influencing the proportion of oxidized carbon (Neal and Younglove, 1993). The correction factor must therefore be determined experimentally for different soil types. Moreover, several additional factors affecting the accuracy of the method, depending on the characteristics or composition of the soil sample, were summarized by Bisutti et al. (2004). Among others, interferences caused by the presence of Cl⁻, Fe²⁺, MnO₂, presence of refractory compounds that may resist oxidation such as pyrogenic C, and uncertainties concerning the redox state of the organic matter, which is assumed to be zero. Another important limitation is that the wet oxidation method cannot be coupled with subsequent isotopic studies of SOC.

Soil organic C determination by dry combustion is very commonly

used because of the accuracy of the method and the possibility for its use for measurements of $\delta^{13}\text{C}$. Its use in calcareous soils is, however, problematic because of the need to differentiate organic versus inorganic carbon. The removal of carbonates by acid pretreatment coupled with analysis by dry combustion of samples with and without pretreatment has been reported as the only method applicable for isotopic analysis of organic carbon in soils with carbonates (Midwood and Boutton, 1998). Most commonly used acids are HCl, H₃PO₄, and H₂SO₃ due to their capability to react with carbonates (Bisutti et al., 2004). Although $\delta^{13}\text{C}$ of organic carbon has been reported to remain unaffected after HCl treatment (Midwood and Boutton, 1998), this method faces the problem that dissolution in liquid acid and washing may produce organic carbon dissolution and removal during the pretreatment (Bisutti et al., 2004; Chatterjee et al., 2009; Midwood and Boutton, 1998). Also, incomplete carbonate removal would result in overestimations of SOC and erroneous $\delta^{13}\text{C}$ values. Acid fumigation with high concentration HCl (Harris et al., 2001; Ramnarine et al., 2011) has partially solved the problem, reducing or eliminating C losses by dissolution during the liquid treatment. Nevertheless, a correct handling of the method is required during acid pretreatments, and its effects on the organic fraction of soils are still not well studied. The other possible approach for SOC analysis with dry combustion, when isotopic analyses are not considered, consists of the subtraction of SIC obtained separately from the total soil C obtained by dry combustion. In soils with high SIC contents, this approach faces the unavoidable problem of “catastrophic cancellation”, which occurs when a relatively small value (SOC) is calculated as the difference between two, much larger, measured values (total carbon and SIC; Bisutti et al., 2004). This is especially true when the error around each term is greater than the calculated difference. In addition, inaccuracies in the determination of SIC need to be added to the determination of SOC.

As noted above, the most frequent methods used for SIC determinations are based in the reaction of carbonate-containing samples with concentrated solutions of strong acids, HCl in most cases. The most common method is the quantification of the volume of CO₂ released in the reaction, using volumetric (Allison and Moodie, 1965) or pressure calcimeters (Fonnesbeck et al., 2013; Sherrod et al., 2002). By comparing with calibrated standards, this volume can be used to determine the carbonate content in samples. Acidimetry based in back-titration of the remaining acid after reaction with the sample is another possible approach (Pansu and Gautheyrou, 2006), and gravimetric measurement of the mass lost as CO₂ is released has also been proposed as more rapid, inexpensive and accurate (Goh et al., 2013; Rodríguez et al., 2016). As all these approaches are dependent on the reaction of soil carbonates with acid, the limitations of this reaction include different reaction times for different types of carbonates, the size-dependent reactivity of carbonates, and the interference caused by H₂O formation during the reaction. Also, these methods are often insufficiently precise in the cases of low carbonates contents (Pansu and Gautheyrou, 2006).

An alternative approach for SOC analysis in calcareous soils takes advantage of the large differential in the temperatures at which SOC and SIC combust or decompose. The loss on ignition (LOI) method for SOC determination consists of heating dried soil samples up to 550 °C, until mass constancy is achieved. Soil organic matter is assumed to correspond to the mass difference before and after heating, and the difficulty relies on estimating SOC from organic matter because the usual factor of 1.72 has been found to vary substantially depending on soil type (Pribyl, 2010). In general, a mass-based (i.e., thermogravimetric) approach can be problematic because some mass loss is not attributable to organic matter combustion but may be due to dehydroxylation of clays. Also, the threshold temperature of 550 °C may be too high in some soils to correspond solely to SOC, and different thresholds have been proposed for simultaneous determination of SOC (375 °C) and SIC (800 °C) in calcareous soils using LOI (Wang et al., 2012). The different thermal behavior of SOC and SIC was also used by Bisutti et al. (2007) to test the validity of a method to determine organic

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