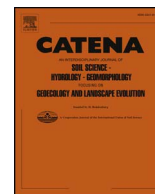




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Thermal separation coupled with elemental and isotopic analysis: A method for soil carbon characterisation

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ABSTRACT

A new analytical approach (Thermally Based Separation, TBS) for the characterisation of inorganic (IC) and organic (OC) carbon pools in alluvial soils has been tested. The method does not involve any chemical pre-treatment of samples and relies on different thermal stabilities of IC and OC pools, which can be accurately determined with an EA-IRMS analytical system. Elemental (C, g/kg) and isotopic ($\delta^{13}\text{C}$, ‰) carbon data were used to check the reliability of the TBS method by calculating the mass balances using the measured IC and OC fractions and total carbon (TC). TBS was applied to 7 soil samples from the Padanian alluvial plain (NE Italy) that were collected from different depths and characterised by textural/geochemical heterogeneity. The method allowed for a mean carbon elemental recovery of 99% (SD = 2%), and mean isotopic deviation ($\Delta^{13}\text{C}$) between theoretical ($\delta^{13}\text{C}_{\text{OC}} X_{\text{OC}} + \delta^{13}\text{C}_{\text{IC}} X_{\text{IC}} / (X_{\text{OC}} + X_{\text{IC}})$) and measured $\delta^{13}\text{C}_{\text{TC}}$ of 0.2‰ (SD = 0.3‰). A comparison of TBS with other conventional methods for carbon separation provided insights into the possible effects of sample acidification on the soil organic pools. The results suggest a higher robustness of TBS compared to conventional methods in the determination of organic and inorganic carbon pools in soils. This is because TBS bypasses any possible fractionation derived from the hydrolysis of soil organic matter and therefore accurately determines the carbon isotopic composition of the OC and IC fractions. TBS appears to be more robust than conventional methods and is independent from the IC/OC ratio of the samples, from the unpredictable complexity of soil organic matter and from the arbitrary application of the acidification routine. On this basis, TBS represents a very promising approach for a correct and complete characterisation of soil carbon pools.

1. Introduction

Soils are vital for agriculture and the functioning of the terrestrial ecosystems. They represent an essential planetary resource both in terms of food security and as a carbon stock (Sanderman et al., 2017). Unfortunately, conventional agriculture and ongoing climatic changes are threatening this important resource, and their negative effects on soil properties deserve detailed investigation. In fact, conventional agricultural management strongly contributes to greenhouse gas (GHG) emissions in the atmosphere (Lal, 2004; Johnson et al., 2007). Soil ecosystems partly offset GHG emissions by sequestering C in both organic and inorganic pools (Egan et al., 2018), some of which could keep C 'locked' for decades or even centuries (Sollins et al., 2009). Moreover, the characterisation of carbon pools (organic and inorganic) is of fundamental importance in the study of soil fertility, organic matter turnover and ecological functionality. Therefore, determination of the total C (TC) and both organic and inorganic fractions is a very important task that requires rapid and precise analytical protocols for

thorough soil analysis.

TC determination by dry combustion is straightforward, whereas separation and analysis of inorganic and organic carbon (IC and OC) fractions is more complex, time-consuming, costly, and usually requires the use of dangerous chemicals. Various physico-chemical pre-treatments of the sample have been proposed for the analysis of distinct carbon fractions in different environmental matrices (Walkley and Black, 1934; Froelich, 1980; Cachiers et al., 1989; Caughey and Barcelona, 1994; Serrano et al., 2008; Meyer et al., 2013). Unfortunately, all of these analytical protocols invariably require acidification of the sample to remove IC prior to the determination of the OC fraction, either when measured directly by dry combustion (Verardo et al., 1990; Bisutti et al., 2004; Phillips et al., 2011) or when using colorimetric techniques (Soon and Abboud, 1991) after wet chemical oxidation (e.g., Walkley and Black, 1934). The use of acidification pre-treatment, although very popular, and included in methodological standards (e.g., EN13137, 2001), is highly contentious. Several studies have investigated the effects of acidification methods and acid types on

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different environmental matrices and found that the procedures can lead to C losses, in turn resulting in nonlinear, sometimes significant, deviations in elemental and isotopic values (e.g., Serrano et al., 2008; Brodie et al., 2011 and the references therein; Schlacher and Connolly, 2014 and the references therein).

Alternatively, OC fraction measurement can be based on thermal methods (thermogravimetry – TG; Differential Scanning Calorimetry – DSC; Infrared Gas Analysis - IRGA) that exploit distinctive oxidation temperatures (e.g. Boyle, 2004; Lopez-Capel et al., 2005a; Leifeld, 2007; Hsieh and Bugna, 2008; Fernández et al., 2012; Pallasser et al., 2013; Emdondson et al., 2015). Accordingly, the OC fraction is measured within a temperature interval between 200 and 500 °C, whereas calcite, dolomite and other common soil carbonate minerals breakdown at higher temperatures, above 650 °C (Cuthbert and Rowland, 1947; Manning et al., 2005; Pallasser et al., 2013). The IC fraction of soil samples can also be determined using dry combustion, following the preliminary thermal oxidation of OM (Rabenhorst, 1988; Dorodnikov et al., 2007). To satisfy the pressing demand for an analytical protocol that is precise, fast and cost effective, thermal separation prior to elemental and isotope determination has been investigated to quantify and characterise distinct soil carbon pools. Thermal separation and isotopic analysis have been coupled, providing a powerful tool for the discrimination of the distinct carbon pools in heterogeneous environmental materials, such as soils (Lopez-Capel et al., 2005b, 2006; Bisutti et al., 2007; Manning et al., 2005, 2008; Natali and Bianchini, 2015). In fact, the carbon isotopic composition ($^{13}\text{C}/^{12}\text{C}$) represents a very useful tracer for the discrimination of organic and inorganic soil compounds, since the former are distinctly ^{13}C -depleted with respect to the latter (Cerling, 1984; Bird and Pousai, 1997).

In this paper, we further explored the potential of a thermal separation method to selectively extract the different soil organic and inorganic fractions on the basis of their distinctive thermal stability. This thermally-based separation (TBS) is very efficient, especially if an automated elemental analyser (EA) is coupled with an IRMS device; in this case, the quantitative estimate of the various carbon pools can be cross-checked and validated with a C (g/kg)- $\delta^{13}\text{C}$ (‰) mass-balance calculation between the TC values and those of the OC and IC fractions. In particular, the thermal separation of carbon pools has been tested on alluvial soils from the Padanian plain, which are characterised by large elemental (TC) and isotopic ($\delta^{13}\text{C}_{\text{TC}}$) variability; the results, compared with those obtained with conventional sample acidification pre-treatment, have been critically discussed.

The purpose is twofold, firstly to define an approach for routine determination of soil OC and IC contents for laboratories simply equipped by EA, and secondly to provide a tool for thorough characterisation of C pools in soil and the related physico-chemical and biological processes, in laboratories where EA is coupled with an IRMS device.

2. Materials and methods

2.1. Overview of TBS methodology

TBS is an analytical approach that involves the use of EA-IRMS and a muffle furnace in the thermal separation and analysis (elemental and isotopic) of the OC and IC fractions (Fig. 1). The method exploits the separation of different carbon fractions on the basis of their different temperature stabilities, which are compound specific. The OC fraction has a lower destabilisation temperature compared to IC and can be separated, and analysed with EA-IRMS, setting the combustion module (EA) at a temperature between 450 and 550 °C. On the other hand, pre-heating the samples with a muffle furnace in the same temperature interval induces complete oxidation of the OC, leaving only the IC fraction, which can be subsequently analysed by EA-IRMS setting the combustion module at 950 °C. The choice of separation temperature depends on the nature of the OC and IC fractions and can be critical in

case of overlap of the respective thermal stability fields. Therefore, the method must be calibrated, for any type of matrix, investigating the 450–550 °C interval to define the most appropriate temperatures that allow correct separation and analysis of the OC and IC fractions. This methodology has been successfully applied to a set of complex environmental matrices (see Natali and Bianchini, 2015), and the specific application to soil samples has been tested in this work.

Elemental and isotopic carbon composition of the different carbon pools were implemented at the Department of Physics and Earth Sciences of the University of Ferrara, using an Elementar Vario Micro Cube EA in line with an ISOPRIME 100 IRMS operating in continuous-flow mode. The system allows variation of the combustion module temperature of up to 1050 °C; this, theoretically, permits extraction of different components with distinctive destabilisation temperatures and to analyse the respective elemental and isotopic composition. Powdered samples are introduced in tin capsules that are wrapped and weighed; these capsules, which allow loading of up to 40 mg of sample, are subsequently introduced into the Vario Micro Cube autosampler to be analysed. Flash combustion takes place in a sealed quartz tube filled with copper oxide grains (padded with corundum balls and quartz wool) that acts as catalyst, in excess of high purity (6 grade purity) O_2 gas. The formed CO_2 gas, carried by dry He (5 grade purity), passes through a water-trap filled with Sicapent®, ensuring the complete removal of moisture; then, it is quantitatively determined on a thermoconductivity detector (TCD) and finally reaches the IRMS compartment for the determination of carbon isotopic ratios. The detection of the distinct isotopic masses of the sample are compared to those of reference CO_2 (5 grade purity) gas, which has been calibrated using a series of reference materials, in turn calibrated against IAEA international standards, such as the limestone JLS-1 (Kusaka and Nakano, 2014), the peach leaves NIST SRM1547 (Dutta et al., 2006), the Carrara Marble (calibrated at the Institute of Geoscience and Georesources of the National Council of Researches of Pisa), and the synthetic sulfanilamide provided by Isoprime Ltd. Mass peaks were recalculated as isotopic ratios by the Ion Vantage software package. The elemental precision, estimated by repeated standard analyses, and accuracy, estimated by the comparison between reference and measured values, were on the order of 5% of the absolute measured value. The uncertainty, increased for contents approaching the detection limit (0.01 g/kg). The carbon isotope ratios were expressed in the standard (δ) notation in per mil (‰), relative to the international Vienna Pee Dee Belemnite (V-PDB) isotope standard (Gonfiantini et al., 1995). The $\delta^{13}\text{C}$ values were characterised by an average standard deviation of $\pm 0.1\%$ defined by repeated analyses of the above-mentioned standards.

2.2. Investigated samples

The soils of the easternmost Padanian Plain (N Italy) developed from alluvial (and deltaic) deposits (Bianchini et al., 2012, 2013; Natali and Bianchini, 2017). They are characterised by limited profile development, in which the lack of soil maturity is related to young depositional age (Holocene), fluvial reworking and extensive agricultural activities (ploughing). The samples considered in this study were selected from a sample set previously studied by Di Giuseppe et al. (2014) that provided a complete geochemical characterisation. They include 4 samples (AR6A, AR16A, AR19A, AR34A) collected at a depth of 20–30 cm, corresponding to the plough horizon and 3 samples (AR32B, AR34B, AR41B) collected at a depth of 90–110 cm, corresponding to layers unaffected by agricultural activities. On the basis of the available data, the selected samples are representative of the whole population and show wide textural (sand 5–32, silt 18–52, clay 25–76%) and geochemical (SiO_2 46.9–52.5, Al_2O_3 12.9–21.1, CaO 1.0–11.7 wt%) variability (Table 1).

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