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Recent methodologies for studying the soil organic matter

Giacomo Santoiemma¹

Department of Agronomy, Food, Natural Resources, Animals & Environment (DAFNAE), University of Padova, Viale dell'Università 16, 35020 Legnaro PD, Italy

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ABSTRACT

A number of innovative methodologies are currently employed to analyse soil organic matter (SOM). In this review we outline three such methods; (1) Elemental analysis coupled to Isotope ratio mass spectrometry (EA-IRMS), which provides representative data for the elemental composition and isotopic signature of a sample; (2) Pyrolysis – gas chromatography coupled to mass spectrometry (Py-GCMS), a method in which the sample is heated to decomposition to produce smaller molecules which are separated and detected; (3) Nuclear magnetic resonance spectroscopy (NMR), a technique for atomic and molecular level structure elucidation.

We also present some of the most recent works employing these techniques and discuss the suitability of the methods.

1. Introduction

The soil surface comprises the largest carbon stock in terrestrial ecosystems, with a total of 1550 Gt of organic carbon (OC) (Lal, 2004). Of this, soil organic matter (SOM) is the largest source of soil organic carbon (SOC), which plays a fundamental part in restoring and establishing carbon balance, soil elements, environmental sustainability and climatic conditions. SOM affects, directly and indirectly, chemical, biological and physical properties of belowground components (Nadi et al., 2017).

To shed light on these ecosystem services, it is therefore essential to explore the characteristics of this complex ecosystem: during the last decades, the study of SOM through analytical methods has progressed rapidly (Mathers et al., 2000). Here we presented some of the most used and effective analytical techniques to investigate the soil: Elemental analysis coupled with Isotope ratio mass spectrometry (EA-IRMS), Pyrolysis – gas chromatography coupled to mass spectrometry (Py-GCMS), and Nuclear magnetic resonance spectroscopy (NMR).

2. Elemental analysis – isotope ratio mass spectrometry

EA-IRMS is a bulk measurement technique that provides data on the mean elemental composition and isotopic signature of a soil sample (Muccio and Jackson, 2009).

In order to measure the element percentages present in the SOM, the bulk sample must be placed into a tin capsule after weighing. The capsule is then lowered into an elemental analyser combustion oven: the sample is combusted at high temperatures under a stream of O₂ into

NO_x, CO₂ and H₂O residuals. After the combustion process, the sample reaches a reduction chamber through a gas flow; here NO_x are reduced to N₂ while the surplus of O₂ is removed. Then a chemical trap and a moisture trap remove from the sample the water generated during combustion. At last, a separation column (or zeolite molecular sieve) performs the separation of CO₂ and N₂ (Fig. 1).

The remaining material is subsequently passed through to the IRMS, which measures the relative abundance of carbon isotopes (¹²C, ¹³C) present in the SOM. The IRMS can be schematically divided into four parts: ioniser, ion accelerator, magnetic analyser and detectors (Fig. 2).

A hard ionization technique (EI) is used to produce electrons through thermionic emission. This involves heating a wire with consequent generation of an internal electric current, which induce ionization and fragmentation in the neutral molecules of the sample. The ions produced are then accelerated by an electric field and passed to the mass analyser.

The mass analyser is a magnetic sector that employs a magnet to deflect the ion beam along a trajectory of 90°. The trajectory described inside the sector by the ions is given by the balance between the magnetic force $F_n = Bzev$ and the centrifugal force $F_c = mv^2/r$ (Skoog et al., 2017), from which we get the mass/charge ratio:

$$m/z = (B^2 r^2 e) / 2V$$

The final part of the IRMS is the detector, which is essentially a transducer for ions. It converts the ion beam into an electrical signal (measured in nano-Amperes) that can then be processed by the computer. The detection tool, called multicollector, consists of several detectors in series, allowing the identification of ions scattered from the

E-mail address: giacomosanto@gmail.com.

¹ Suggested background music: SHPALMAN by Elio e le Storie Tese: <https://www.youtube.com/watch?v=KbkThh0azrQ>.

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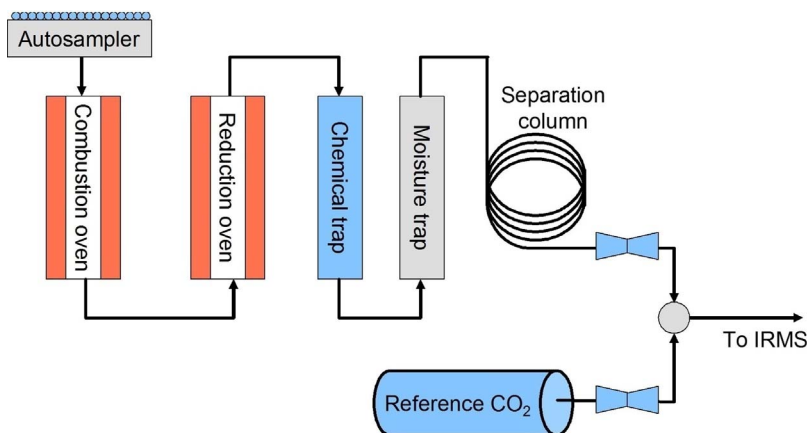


Fig. 1. Elemental analyser. Diagram of instrument operation. Reproduced from Muccio and Jackson (2009) with permission from the Royal Society of Chemistry.

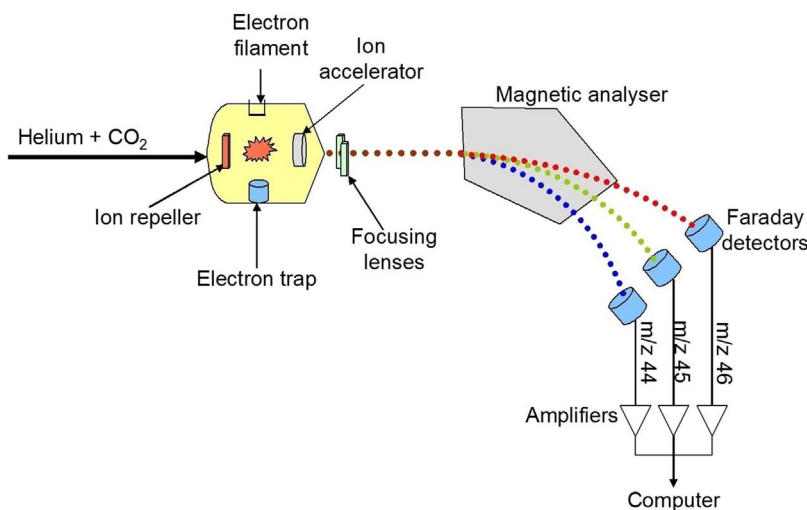


Fig. 2. Isotope ratio mass spectrometer. Diagram of instrument operation. Reproduced from Muccio and Jackson (2009) with permission from the Royal Society of Chemistry.

analyser simultaneously. The final results are typically expressed as $\delta^{13}\text{C}$, which is a relative value of deviation from an international standard, expressed as a permille (‰). The δ value of C is calculated as:

$$\delta^{13}\text{C} = \left(\frac{[^{13}\text{C}/^{12}\text{C}]_{\text{sample}} - [^{13}\text{C}/^{12}\text{C}]_{\text{standard}}}{[^{13}\text{C}/^{12}\text{C}]_{\text{standard}}} \right) \cdot 1000(\text{‰})$$

The standard reference established for ^{13}C is the Pee Dee Belemnite carbonate.

Both the presence of C3 or C4 plants (which have a different photosynthetic pathway) and carbonates affect soil $\delta^{13}\text{C}$ values.

For example, the $\delta^{13}\text{C}$ mean values of air, C3 and C4 plants (Ghashghaie et al., 2001) are as follows:

$$\delta^{13}\text{C}_{\text{CO}_2\text{air}} = -8\text{‰}$$

$$\delta^{13}\text{C}_{\text{C}_3\text{plant}} = -27\text{‰}$$

$$\delta^{13}\text{C}_{\text{C}_4\text{plant}} = -11\text{‰}$$

$\delta^{13}\text{C}$ is also correlated with the age of the SOM (Balesdent et al., 1990) for a number of reasons: (i) association between isotopic fractionation and microbial respiration (Accoe et al., 2002), (ii) quicker mineralisation of ^{13}C -poored components (Billings and Richter, 2006) and (iii) decrease in $\delta^{13}\text{C}$ of CO_2 in the past, as result of fossil combustion (Suess effect) over the last 150 years (Swart et al., 2010).

3. Pyrolysis – gas chromatography – mass spectrometry

Py-GCMS is a method that leads to sample decomposition through

heating in order to produce smaller compounds separable by gas chromatography and detectable by mass spectrometry (Yang et al., 2011).

After weighing, each SOM sample is introduced to a Fe-Ni capsule. Tetramethylammonium hydroxide is then added allowing the detection of phenolic hydroxyl and carboxylic groups as methyl derivatives (these are more volatile) (Templier et al., 2005). The sample is pyrolysed and the products are injected and separated into the gas chromatograph (GC). The GC is coupled to a quadrupole mass spectrometer (Fig. 3).

Ions produced by EI are filtered in the quadrupole depending on their trajectories in the electric fields applied to the rods, which alternate positive and negative charges. Results appear as a spectrum of the relative abundance of detected ions, which is the total ion current chromatogram. This represents the cumulative intensity across the total mass range (detected at each point) as a function of the mass/charge (m/z) ratio for all the detected ions. The compounds in the sample (which can be molecules or single atoms) are recognised through a typical fragmentation pattern, relying on the large databases available for identification and structure elucidation of chemical compounds.

4. Nuclear magnetic resonance spectroscopy

NMR spectroscopy is a technique for determining the atomic and molecular structure of materials. During NMR, the soil sample, properly demineralized to avoid damage to the instrument (Alexis et al., 2012), is situated into an external static magnetic field, which causes a distribution of the nuclei spins among distinct energy levels. This energy difference (ΔE) depends on both the external magnetic and the surrounding magnetic field of the nuclei. Therefore, depending on the

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