Analytical pyrolysis as a tool to probe soil organic matter

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ABSTRACT

The environmental importance of soil organic matter (SOM) in the ecosystems and in the C biogeochemical cycle is well established. Indeed, it represents the main terrestrial carbon pool and due to its vulnerability, it plays a key role in the global carbon cycle. However, as SOM is mainly composed of products resulting from microbial and physicochemical transformations of vegetal, microbial and animal biomass, it results in a heterogeneous mixture. This complexity, along with organo-mineral interactions, makes challenging the characterization of SOM composition at the molecular scale. Nevertheless, its precise characterization is essential to determine its fate in the environment and eventually to provide recommendations on sustainable practices. Among the available techniques to analyse SOM, thermal degradations appear as especially efficient as they are less selective than some chemical ones, leading to a larger view of the SOM chemical structure. Analytical pyrolysis was thus used in a wide range of soil science fields including studies on pedogenesis and anthropic effects. It allows to characterize SOM at the molecular level, including identification of biomarkers, and to compare different soils and/or different horizons in a given soil profile under various impacts (land use, evolution, etc.). The review of recent developments in data acquisition and/or processing leads us to provide guidelines to select the most appropriate method and to avoid possible pitfalls. Examples will illustrate the wide range of soil science applications and show the potential and limitations of this approach.

1. Introduction

Soil organic matter (SOM) has a crucial effect on many soil properties such as cation exchange capacity, nutrient availability, soil structure stability and water-holding capacity, and its amount is closely associated with soil fertility [1,2]. The maintenance of SOM levels is essential to sustain the productivity of agricultural systems [3,4]. SOM content varies with vegetation and soil microorganism nature, soil mineralogy, geomorphology, environmental parameters and is sensitive to various changes such as land use or climate. SOM also plays a key role upon various amendments [5] and it is involved in xenobiotic transportation [6,7]. When considered at a larger scale, SOM represents the main terrestrial carbon pool and due to its vulnerability, is essential in the global carbon cycle [8,9]. A precise knowledge of the ability of soils to stabilize carbon is especially important to assess the impact of policy changes on CO_2 release.

SOM consists in a complex, heterogeneous mixture mainly composed of products resulting from microbial and physicochemical transformations of organic remains of vegetal, microbial and animal origins. Thus SOM presents a complexity and diversity which makes its characterization challenging. Numerous studies were thus performed to decipher the chemical structure of SOM. However, they only yield a partial picture of SOM composition. Indeed, there are knowledge gaps on molecular identification and quantification of some components (e.g. N-containing moieties, carbohydrates, tannins) and also on spatial organization including organo-mineral interactions. Nevertheless, the precise characterization of SOM is essential to determine the mechanisms involved in its stabilization, to predict its dynamics and eventually to provide recommendations on practices aiming at compensating CO_2 increase or at improving soil fertility management. This is especially true when the soil systems are submitted to anthropogenic changes.

Several analytical approaches have been used to address SOM composition [10]. They include (i) spectroscopy, mainly nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) which give insights into the nature of the chemical functions, (ii) mass spectrometry with Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) which provides molecular identification in complex soluble organic mixtures, (iii) secondary ion

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mass spectrometry (SIMS) potentially used in combination with scanning transmission X-ray microscopy to give spatial elemental and isotopic analysis and (iv) degradations which aim at releasing molecular information through cleavage of the organic network. Among the latter, thermal degradations appeared as promising tools as they are less selective than the most used chemical ones, leading to a larger view of SOM chemical structure. Several types of thermal degradations differing by the design of the pyrolysis units, the temperature ranges, the addition (or not) of a chemical reagent and the nature of the detection unit, were developed during the last 30 years. Analytical pyrolysis thus appears as an efficient tool to characterize SOM and to provide molecular markers, to derive proxies for soil properties and to assess impacts of various changes. In the present review, these different types of pyrolysis are described and examples of their application in soil science are presented, thus illustrating the high potential of these techniques.

2. Different types of analytical pyrolysis

2.1. Advantages and drawbacks of the different analytical pyrolysis devices

Depending on the temperature used, organic matter undergoes either thermodesorption (release of trapped compounds) or pyrolysis (cracking of covalent bonds). Upon pyrolysis, chemical bonds in organic matter are cleaved as soon as the brought energy exceeds that of the given bonds, thus yielding a wealth of molecules. The identification of these molecules and further interpretation of their potential allows the reconstruction of the chemical structure of the starting material.

Several types of pyrolyzer exist, the most common being resistively heated filament, Curie point and microfurnace. Their pros and cons have been recently discussed in terms of heating efficiency, reproducibility and potential secondary reactions [11].

Due to the high complexity of SOM pyrolysate, pyrolysis is often followed by a gas chromatographic (GC) separation step prior to identification by mass spectrometry (MS). However, several drawbacks are associated with Py-GC–MS [12] among which the fact that only pyrolysis products that are GC-amenable are detected. Consequently, the most polar products or the heaviest ones potentially escape the detection. There are several ways to circumvent this limitation. To overcome the polarity problem, a polar column may be used instead of the classical apolar one [13] or derivatization into less polar products can be performed as detailed below (Section 2.2). Condensation of the heaviest compounds may occur before analysis. Optimization of the device into a so-called non-discriminating pyrolysis system by minimizing transfer losses at the pyrolyzer-analytical system (GC–MS) interface [14] or pyrolysis-molecular beam mass spectrometry (Py-MBMS), in which pyrolysis products are swept into the mass spectrometer by supersonic jet expansion [15–17] were developed to minimize such condensation. Direct coupling of the pyrolysis unit to the mass spectrometer (Py-MS) including pyrolysis field ionization mass spectrometry (Py-FIMS) in which the heating unit is inside the mass spectrometer source [18] can also be used. Py-GC–MS and Py-FIMS led to consistent and complementary results as assessed from a study where both methods are used on the same samples [19,20]. Comparison between the data obtained from the two techniques shows that Py-FIMS allowed detection of lignin dimers and quantification of the pyrolysis products. However, Py-FIMS spectrum is much more difficult to interpret as it results from the superimposition of the mass spectra of all the released products and multivariate analysis (principal component analysis) has often to be used for pattern recognition [16]. It thus cannot yield information at the same precision level as Py-GC–MS (isomer distinction for

example). As a result, Py-MS is especially powerful to provide sample fingerprinting as recently shown for soil fatty acids using a modified system involving metastable atom bombardment (MAB) to reduce chemical fragmentation during ionization, compared to electron impact ionization [21]. However, as discussed below, Py-GC–MS remains the most commonly used pyrolysis device for analytical purposes. The advantages and drawbacks of the different pyrolysis devices are gathered in Table 1.

2.2. Derivatization

As aforementioned, derivatization allows overcoming polarity problems in GC identification (Table 1). The most common derivatization reaction is methylation, mainly performed with tetramethylammonium hydroxide (TMAH) which combines the properties of a base and of a methylation reagent [22,23]. Pyrolysis in the presence of TMAH is also termed thermochemolysis or thermally assisted hydrolysis and methylation. Py(TMAH)-GC–MS has been extensively used for 20 years, especially for assessing the degradation extent of lignin moieties in soil (e.g. [24]) but it also revealed cutin/suberin markers [25] as well as tannin [26] and carbohydrate [27] ones (Fig. 1). However, this technique does not allow for distinguishing free hydroxyl groups from preexisting methoxyl groups due to complete methylation with TMAH. Consequently, some tannins or demethylated compounds may be falsely considered as lignin products. To this end, thermochemolysis using ^{13}C-labelled TMAH was developed, the labelled methoxyl groups corresponding to initially free hydroxyl groups [26,28,29]. Moreover, as transesterification takes place in addition to methylation of free OH groups, it is difficult to differentiate free and bound acid/alcohol fractions. This can be partly achieved through the use of tetraethylammonium acetate instead of TMAH as tetraalkylammonium acetates are less basic than hydroxides and they only alkylate free acids [30,31]. Silylation is a commonly used derivatization reaction in lipid analysis. It takes place in situ upon pyrolysis when the latter is performed in the presence of hexamethyldisilazane (HMDS) as initially developed on pure amino acids and carbohydrates [32,33]. Since these pioneer papers, it has been shown that the silylation efficiency was improved thanks to the use of trimethylchlorosilane as a catalyst [34] and recently, HMDS was proven to be efficient also at low temperature (300 °C) to silylate carbohydrates from a peat sample [35]. Other reagents that have not yet been used in soil science, such as trimethylsulfonium hydroxide which can operate at lower temperature than TMAH, may also be of interest. Such alternative reagents have been recently reviewed in Shadkami and Helleur [36]. Among these reagents, the use of TMSH in thermochemolysis coupled with individual compound isotopic measurement to determine the carbon isotope composition of soil mesofauna fatty acids must be noted [37].

2.3. Quantitative issues

A major drawback with pyrolysis is the difficulty in deriving quantitative data (Table 1). This is due either to mineral matrix effect which may prevent pyrolysis products to be released (as discussed in Section 2.4) or to direct measurement of pyrolysis product abundances. Ion intensities in in-source Py-MS should a priori give access to absolute yields but large variations were noted depending on the pyrolysis conditions [38]. However, this method was further developed to derive relative abundances of various pyrolysis product classes [39]. In Py-GC–MS, relative abundances can also be calculated from the intensity of two characteristic mass spectrometry fragments [40] or from the ratios of the areas of the corresponding GC peaks but the response factors have to be taken into account for comparison between compound classes.