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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, …). 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 characterisation 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 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-labeled 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. Standards are thus required to calculate such factors but not all of them are commercially available. To overcome this difficulty, a selected set of identified pyrolysis products was grouped into given classes reflecting their origin and the relative abundance of the classes was calculated [41]. This approach, coupled with multivariate analysis was then applied in various studies using Py-GC-MS [42-46] or TMAH thermochemolysis [47]. Py-GC with flame ionization detector (FID) is also used for quantitative purposes based on the retention times of previously identified peaks. Ratios of abundances of selected peaks were thus used as soil OM mineralisation (furfural/pyrrole and pyrrole/phenol) and humification (benzene/toluene) indexes. Trends between samples were then deduced thanks to the use of statistical treatments [48-54].

2.4 Selection of analytical pyrolysis method to overcome potential limitations

Due to the natural complexity of natural OM, a large number of pyrolysis products are released and even when coupled to the GC, numerous coelutions may occur, thus making the identifications difficult. It is therefore useful to introduce an additional separation step prior to GC-MS analysis. In this “off-line” or “preparative” pyrolysis, the pyrolysate is collected and further separated by column chromatography into fractions that are further analysed using GC-MS and further quantified [55-58]. However, a loss of the most volatile compounds is associated with this procedure (Table 1).

Most pyrolytic studies are performed at temperatures high enough to provoke a substantial cleavage of organic matter covalent bonds, the released products also including thermally desorbed molecules. Such compounds can be released at sub-pyrolytic temperatures and thus be distinguished from the actual cracking products. A two-step Py-GC-MS including a first heating at T≤300°C was therefore developed to investigate separately the composition of these two organic pools either off-line [35, 56] or on-line, with the so-called "double-shot" pyrolysis [59-61].

When performing pyrolysis, one must be aware of potential artefacts leading to pyrolysis products which are not actual building blocks of the organic matter. Indeed, side reactions such as decarboxylation [12, 62] or dehydration (e.g. diketopiperazine formation from peptide groups; [63]) were reported. It is also well known that upon heating, some aromatization reactions take place [64, 65]. Decarboxylation and aromatization can be limited by using TMAH thermochemolysis but it has been shown that decarboxylation still takes place at high temperature and aromatization is favoured by the presence of clay minerals [12, 66]. Moreover, extensive retention of pyrolysis effluents by the mineral matrix may occur in organic-poor samples [56]. As a result, for organic-poor clayey soils, a demineralization step prior to pyrolysis may be a prerequisite [67]. This step is commonly performed through the use of HF treatment despite potential selective OM losses upon this treatment as also revealed thanks to Py-GC-MS [56, 68]. Another way to isolate the most organic-rich compartment is to perform physical fractionation [69]. However data obtained on that fraction may not be representative of the whole soil.

2.5 Identification of nitrogen compounds through analytical pyrolysis of SOM

When focusing on N-containing products, two major problems have to be faced in SOM pyrolysis. First, it appears that N-containing moieties are poorly detected upon Py-GC-MS [70-72] and second, the identified products are generally limited to aromatic N heterocyclic compounds (pyrroles, indoles) or nitriles. Although the occurrence of some of these chemical functions cannot be excluded in SOM, it is commonly accepted that most of them result from secondary reactions. Moreover, the abundance of N-containing pyrolysis products is not correlated to the N content but is rather related to the speciation of N functions [73]. To overcome this drawback, Py-FIMS was recently suggested to reduce cyclisation of N-containing molecules as soft ionization provides less energy to the sample with respect to Curie point Py-GC-MS [74].

Several attempts to improve our knowledge on soil N were based on the analysis of model compounds (e.g. amino acids) using various types of pyrolysis, such as Py-GC-MS [75], Py-FIMS [18] and TMAH thermochemolysis [76]. These studies confirmed the secondary reactions which occur upon pyrolysis and highlighted the difficulties in detecting non heterocyclic N in soils. Another *a priori* promising approach to detect N-containing pyrolysis products is the use of a specific detector such as atomic emission detection (AED) but only small molecules (ammonia, acetonitrile, hydrogen cyanide, pyridine and pyrrole) could be identified in a forest soil [77].

2.6 Rock-Eval pyrolysis

Although not directly affording molecular information, Rock–Eval pyrolysis is increasingly used in soil science [78-83]. Initially developed for petroleum exploration to rapidly assess the potential quality of a source rock [84], Rock-Eval is now used to assess the thermal stability of soil OM. In this device, a first heating at 200-300 °C under nitrogen is used to release the most volatile compounds (termed S1), followed by a heating at 25-30°C/min up to 650°C which releases products resulting from organic matter cracking (S2 fraction). S1 and S2 are quantified thanks to FID and in parallel, an infrared detector quantifies CO and CO_2 (S3) that are evolved upon pyrolysis of polar moieties [78]. After this pyrolysis step, the residue is submitted to an air oxidation at high temperature (750-850 °C) to convert all remaining organic carbon into CO and CO_2 which are again quantified by infrared spectroscopy. An oxygen index [OI = (100S3/TOC)] and a hydrogen index [HI = (100S2/TOC)], are calculated.

3. Analytical pyrolysis as a soil OM characterization tool

SOM pyrolysis generates a wealth of compounds and most of them can be considered as markers for a given class of biomolecules thus allowing assessment of SOM sources. As shown below, this molecular information is powerful to compare OM molecular composition between different soils, different horizons in a given soil profile, and different fractions resulting from physical or chemical separations.

3.1 Biochemical markers in pyrolysis products

SOM is mainly derived from vegetation biomass which comprises carbohydrates, proteins, lignin (a structural polyphenol occurring in conductive tissues of vascular plants), cutin and suberin (aliphatic biopolyesters occurring in plant cuticle for the former and bark and root for the latter). Pyrolysis products may constitute markers for most of these macromolecules.

It has been known for long that lignin markers include 4-vinylphenol, 2-methoxyphenol (guaiacol) and 2,6-dimethoxyphenol (syringol) [85] although syringic acid (dimethoxy-4-hydroxybenzoic acid) may, at least partly, be of tannin origin [26]. More direct evidence is provided by Py-FIMS with the detection of lignin dimers [20]. Carbohydrates are known to produce furan derivatives and levoglucosan [86] whereas cutin and suberin can be recognized through their monomers (mainly aliphatic hydroxyacids and diacids; [25]). Black carbon (BC) is the product of incomplete combustion of biomass and fossil fuels and pyrolysis may *a priori* seem to be unsuitable for its characterization. Indeed, (i) heating itself causes molecular rearrangements as aforementioned and (ii) a significant fraction of BC comprises thermally stable polycondensed aromatics usually considered as not pyrolysable. However, using high temperature (750 °C) Py-GC-MS, benzene, toluene, naphthalene, biphenyl, dibenzofuran and benzonitrile can be released and considered as BC markers [87].

Aboveground and belowground inputs can be distinguished thanks to pyrolysis especially when performed in the presence of TMAH [25]. TMAH thermochemolysis indeed revealed the preservation of suberin biopolyester in soils. Recently, the roots and aerial parts of more than 30 plants potentially living during Holocene were separately analysed by Py-GC-MS and the derived vegetation markers could then be used to investigate the molecular composition of archeological records [88].

Thanks to these markers, SOM can be traced in the environment and more especially in their transfer towards the hydrosystems. Py–GC-MS and thermochemolysis thus yielded complementary information about the sources of dissolved OM in Australian catchments in relation to vegetation changes [89]. The simultaneous use of several pyrolytic techniques (Py–MS and Py–GC-MS, with and without TMAH) was also recommended to follow the evolution of the OM chemical structure from a grass upland soil towards the soil leachates [38]. TMAH thermochemolysis of water-extracted OM from several soil horizons along a podzolization sequence evidenced exportation of OM from deep horizons of well-developed podzols to the rivers of the Rio Negro Basin [90].

3.2 Examples of characterization of bulk soils through analytical pyrolysis

The aforementioned markers have been extensively used to determine the sources and evolution of SOM. They revealed variations in SOM composition with degradation, differences in vegetation cover and /or along soil profiles.

107 lipid-free soil samples from 27 sites across a semi-arid/arid environment in South Africa were analysed using Py-GC-MS [91]. This study revealed a higher abundance of poorly altered plant-derived lignin and cellulose in pyrolysates from the semi-arid area than in the arid one where low molecular weight aromatic products were more abundant. This was interpreted as differences in the extent of degradation of plant OM. Another example of the efficiency of pyrolysis in revealing differences related to vegetation cover is the Py-GC-MS

of 7 soils collected along a glacier-retreat chronosequence [44]. Some compound classes, such as pyridines, furfurals, phenols, aromatic hydrocarbon precursors or cyclopentanones, were distinguished among the pyrolysis products. Thanks to statistical analysis, they indicated the appearance of lignin-containing vegetation 60-100 years after glacier-retreat. Moreover, ^{13}C-labelled TMAH thermochemolysis revealed that whereas the lipid-free topsoil reflected differences in vegetation (grasses, heather and spruce) between three adjacent sites in a peaty gley soil profile, these characteristics were lost in the deeper horizons [29].

Although most studies deal with surface samples, pyrolysis can also be used to investigate SOM composition along a given soil profile. Py-MBMS thus showed an increase in pyrolysis products of more highly decomposed plant materials as a function of increasing sample depth. Samples from different forest sites could also be distinguished monitoring the effect of forest management practices [16]. Rock-Eval pyrolysis provided information about the heterogeneity of the OM in two horizons of adjacent forest and cropped soils, although without any estimation of the individual components composing the SOM [79]. However, it revealed trends with depth which pointed to the importance of the first stage of oxidation in these samples.

Py-FIMS was also shown to provide a valuable help in soil classification. Indeed, it supported the classification of Black Soils from the Baltic region of Germany as Chernozems [92]. In the same way, multivariate analysis performed on intensity ratio of selected Py-GC peaks, such as furfural/pyrrole and pyrrole/phenol considered as SOM mineralisation indices and benzene/toluene used to reflect SOM humification, revealed that this technique is appropriate to distinguish humus forms in Mediterranean forest soils [54].

3.3 Examples of characterization of soil chemical fractions through analytical pyrolysis

SOM is commonly separated into chemical fractions which are either supposed to contain OM with different stability and/or to concentrate OM. These fractions are obtained following base or acid treatment as well as oxidation. The analysed fraction can be the released OM as well as the residue. In the latter case, analytical pyrolysis provides molecular insight into OM source and degradation extent.

3.3.1 Humic substances

In addition to the bulk soil, the so-called humic substances are commonly studied through pyrolysis. They are isolated from soils following a classical procedure involving base and acid extractions [93]. Fulvic acids, humic acids and humin were considered for long as representing SOM pools of increasing stability. However, caution should be exercised about the representativity of such fractions as it is now more and more accepted that molecular structures can be altered by the isolation treatment [94]. Moreover, comparison between the lipid-free peat and the sum of its humic fractions clearly demonstrated loss of some soil constituents upon fractionation in a two-step off-line thermochemolysis study with a first heating at 300 °C with HMDS and a second one at 400 °C with TMAH [35]. While the first step was especially efficient in the release of carbohydrate-derived products, phenolic compounds, fatty acids and cutin/suberin monomers dominated the trace obtained at 400 °C. Nevertheless, the humic fractions are studied to investigate the effects of humification, changes in vegetation and land use on SOM as illustrated below.

An index for the degree of decomposition of the NaOH non-extractable OM from different horizons of Arctic tundra soils was proposed using Py-GC-MS [95]. It is based on the lipid to polysaccharide ratio determined from relative abundances of previously selected compound classes. In a TMAH thermochemolysis study of a wide set of humic acids, aliphatic and aromatic compounds were separately quantified and their total abundances were correlated with humification degree and NMR-derived carbon distribution [42].

In addition to be efficient in following up humification, pyrolytic studies of humic substances can also provide information on the origin of the OM. A comparison between humic acids from five reference European soils was performed [96]. While Py-GC-MS showed differences in the chemical structures of these humic acids, TMAH thermochemolysis allowed distinction between different vegetation covers and land uses through differences in cutin and lignin composition. Similarly, Py-GC-MS and further statistical analysis highlighted variation in humic acid quality in five cover vegetation types and also over the course of the season [43].

Differences in vegetation under various climatic regions were revealed through factor analysis performed on a large number of pyrolysis products which showed large variations between the humic acids of eighteen topsoil samples [97]. It therefore appears that vegetation is a major factor determining the humic acid composition in A-horizons as further confirmed in a study of a large set of soils in maritime temperate forests [98] and of soils under different types of cultivation [46].

3.3.2 Other chemical fractions

Chemical treatments were applied to isolate SOM compartments in an attempt to better understand SOM dynamics and/or composition. The remaining organic residue after hydrolysis or oxidation was assumed to represent the most stable fraction and analytical pyrolysis was used to investigate its molecular composition.

The acid insoluble SOM has been analysed using Py-GC-MS in litter samples and organic soil horizons. Although this fraction is also termed “Klason lignin”, it was shown that lignin was only accounting for 34 to 68 % of its pyrolysis products [99]. The Curie point pyrolysate of a forest soil refractory material, *i. e.* the non-hydrolysable residue remaining after successive base and acid hydrolyses as well as HF/HCl demineralisation, was shown to be dominated by alkane/alkene doublets pointing to a strong aliphatic character [100] but further study using off-line pyrolysis showed that the aliphatic chains only account for a small part of the refractory OM and that the latter is mostly composed of melanoidins (condensation products from proteins and carbohydrates) and of black carbon [101]. The Py-GC-MS of the refractory OM isolated from a tropical soil with a ^{14}C age of ca. 8300 years showed a lack of aliphatic chains and the presence of more condensed melanoidins with respect to the above study [102]. A similar refractory OM from another forest soil was shown to comprise a complex mixture of lignin, condensed tannins, higher plant waxes, suberin and polysaccharides attributed to cellulose by Py-GC-MS and TMAH thermochemolysis [103]. Using only HCl hydrolysis, a so-called non-acid hydrolysable fraction was isolated from two soils [104]. Py-MBMS analysis revealed the incomplete hydrolysis of carbohydrates and peptides suggesting a mineral protection.

Py-GC-MS was also used to follow modifications undergone by soil OM upon oxidation using various reagents. Persulfate oxidation is used to isolate condensed SOM thanks to the removal of most of the amorphous SOM and is thus considered to mimic humification. Py-GC-MS of a soil before and after persulfate oxidation showed that this treatment mainly affected lignin and short chain aliphatics but not long chain aliphatics [105]. The same selectivity on the aliphatics was reported upon H_2O_2 oxidation through off-line TMAH thermochemolysis [57]. H_2O_2 oxidation is supposed to remove OM sorbed onto clay particles and thus to leave SOM located within clay interlayers. In contrast, long chain aliphatics and more generally high molecular weight products are selectively lost upon sodium hypochlorite oxidation whereas alkylaromatics, carbohydrate and protein markers are selectively retained as observed using Py-FIMS [39]. This clearly demonstrates that this treatment is unable to isolate the refractory SOM due to limitation in reagent access and suggests some protection within the mineral matrix. This was confirmed by 10% HF treatment which was able to remove these labile constituents. Chemical oxidation with acidified potassium dichromate is a commonly used method to assess the amount of BC in soils. BC quantification in soils remains an analytical challenge due to its refractory character [106]. However, pyrolysis under high hydrogen pressure was recently proposed as a quantification method [107-109] and it revealed that BC isolated by such an oxidation may contain a significant contribution of long chain aliphatics, hence an overestimation of BC [110].

The aforementioned chemical treatments (hydrolysis and oxidation) were also performed to isolate and characterize SOM linked through specific bonds. TMAH thermochemolysis of mineral soils showed that saponification is efficient in releasing ester-bound suberin markers [111]. The same conclusion was reached for microwave-assisted TMAH hydrolysis of a forest soil using Py-GC-MS and TMAH thermochemolysis [112]. Moreover, they showed that microwave-assisted acid hydrolysis would only affect the unprotected or unaltered lignin moieties in SOM.

Whereas in most studies analytical pyrolysis was used to characterize the insoluble residue, it has also been applied to soluble fractions released upon chemical treatment. A sequential NaOH – $Na_2P_2O_7$ treatment was applied to separate free OM from that bound in metal-organic complexes in two soil profiles [113]. Whereas all pyrolysates were dominated by polysaccharide-derived products, the $Na_2P_2O_7$ extracts contained slightly more lignin, proteins, and lipids. When applied to both NaOH extractable and non-extractable fractions, Py-GC-MS showed conspicuous differences, with a relative enrichment in aliphatic units in the non-extractable SOM [46].

Lipids are isolated from SOM through solvent extraction and are classically analyzed by GC-MS. The potential of Py-MAB-TOF-MS for soil lipid analysis was tested. When compared with GC-FID, a broader group of compounds could be detected but additional work is required for their complete identification [21].

3.4 Characterization of soil physical fractions through analytical pyrolysis

Another way to identify compartments with different stability is to perform physical separation into density or particle-size fractions. Differences in molecular composition between physically separated SOM fractions are also revealed through analytical pyrolysis.

3.4.1 Density fractionation

Density fractionation, commonly performed with sodium polytungstate solutions allows separation between the uncomplexed fraction or light fraction (LF), which mainly consists of poorly decomposed OM, and the heavy fraction, considered as mineral-associated.

Py-GC-MS of these fractions from soils in the San Juan Mountains, Colorado, showed that the light fraction mainly comprised plant lignin while the heavy one had very little unaltered lignin but an abundance of polysaccharides and proteins [71]. In another study, the free and intra-aggregate light fractions (obtained by density separation without and after disruption of aggregates, respectively) were shown to be similar but they strongly differ from the organomineral fraction corresponding to the residual dense material [114]. Off-line TMAH thermochemolysis also allowed comparison between the free and dense (after sonication) fractions in 4 horizons of a soil profile, leading to the conclusion that the dense fractions of the deepest horizons were more influenced by a microbial reworking than those from the upper horizons [58].

3.4.2 Particle-size fractionation

Particle-size fractionation is commonly performed on SOM as the clay fractions are known to be the most organic-rich due to clay-OM interactions.

Py-FIMS revealed that fine clay fractions were enriched in carbohydrates and peptides and depleted in lignin dimers and lipids when compared to coarse clay fractions [115]. Using the same technique, the SOM in nano-size structures of a Canadian black Chernozem was shown to accumulate carbohydrates, N-heterocyclics, peptides and alkylaromatics whereas that of the bulk clay fraction was enriched in phenols, lignin monomers, lipids and fatty acids [116]. In a study dedicated to organic nitrogen, five particle-size fractions were separated from soil samples collected at 3 different depths. Py-GC-AED performed at 3 temperatures (300, 400 and 500 °C) revealed trends with particle-size and depth for ammonia, acetonitrile, hydrogen cyanide, pyridine and pyrrole [77]. Particle-size fractions were also separated from tropical earthworm casts and surrounding soil [117]. Py-GC-MS analysis performed with a polar column could not differentiate SOM between the size fractions but higher lignin content was observed in the casts when compared to the surrounding soil aggregates.

4. Examples of applications of analytical pyrolysis in soil studies

Analytical pyrolysis was applied on SOM to address the various aspects of its fate under natural and/or anthropic impacts, including SOM evolution as well as management or fire effect.

4.1 Analytical pyrolysis as a tool to derive proxies for soil biological features.

In combination with measurements indicative of biological activity, pyrolysis techniques have enabled to reveal differences in biodegradability depending on SOM composition or accessibility to microorganisms. They were also used to investigate the relationship between SOM composition and the activity of enzymes involved in SOM degradation.

Bioavailability of SOM was studied on 5 Arctic soils through laboratory incubation [118]. Some Py-GC-MS compounds were selected as representative of the main biochemical classes and changes in their relative proportion before and after incubation were correlated with CO_2 emission, *i.e.* soil degradation. A similar approach was developed to predict the relative respiration for soils based on the Py-GC-MS fingerprint [41]. As expected, in these studies, the cumulative respiration was well represented by the initial abundance of polysaccharides.

Physical and chemical characteristics responsible for OM degradation were determined from the pyrolysis of humic acids after incubation and multivariate analysis [45]. The lack of correlation of aromatics with mineralization highlighted the dual origin of the latter, lignin and black carbon. A recent study using Rock-Eval pyrolysis to determine the thermal stability of a subarctic forest soil organic carbon showed that the thermolabile fraction was related to carbon susceptibility to decomposition assessed through laboratory incubation [83].

In a study which aimed at testing whether variation in the activity of enzymes that mediate SOM turnover and nutrient cycling could explain differences in SOM chemical structure, β-1,4-N-acetyl-glucosaminidase was negatively correlated with polysaccharides and positively correlated with lignin but there were not always significant correlations between enzymes and substrates. This may reflect differences in time scale for SOM chemistry evolution and enzyme dynamics [71]. However, β-glucosidase was strongly correlated with N-containing pyrolysis products. Fungal to bacterial ratios were also determined from quantitative polymerase chain reaction and were positively correlated with lignin derivatives and negatively with the N-bearing products [119]. Similarly, xylanase activity was positively correlated to the xylan/xylose ratio derived from Py-FIMS [120].

4.2 Analytical pyrolysis as a tool to investigate SOM formation and evolution

Pyrolysis is an efficient tool to reveal molecular transformations in OM. It was therefore successfully applied to investigate the chemical transformation of litter, including the relative biodegradability of its constituents, during its degradation leading to soil formation as well as the evolution of SOM. Isotope labelling and long-term experiments are especially suitable for this purpose.

Py-GC-MS of NaOH-extractable OM fraction from litter and underlying soil horizons showed that decomposition of lignin is fast, even more than cellulose [121]. This extensive degradation of lignin was confirmed by comparing the pyrochromatograms of maize leaves and soil cultivated with maize [122]. A common decomposition sequence with lignin degradation and polysaccharide accumulation was observed in a Py-GC-MS study of light and heavy fractions of soils from various geochemical environments [71]. The formation of microbial by-products and their stabilization on mineral surfaces was put forward as the primary mechanism for long-term carbon stabilization. However, a higher degradation of polysaccharides with respect to lignin was reported upon 80 day-incubation of crop residues and Py-GC-MS comparison of original and incubated samples [123]. In podzols where the local removal of SOM can be considered as mimicking SOM degradation, adjacent depleted mottles and surrounding NaOH-extractable SOM samples were compared using Py-GC-MS [124]. A strong depletion in lignin along with a selective preservation of more resistant aliphatic units associated with an increase in microbial activity was observed in the mottles. A similar role of microorganisms can be put forward in the formation of the diagnostic E horizons of podzols although an additional involvement of aluminium and iron is known.

Isotope labelling is a powerful tool to investigate the dynamics of SOM. When combined with molecular analysis such as pyrolysis, it may provide additional insight into the source of SOM. Natural labelling is possible in a chronosequence when the change in vegetation involves plants with different photosynthetic pathways, such as C3 and C4. In a 23 year-old vegetation change from the C3 plant wheat to the C4 plant maize, naturally ^{13}C-enriched material was thus added to the soil, and residence times could be assessed from pyrolysis coupled to GC and isotope ratio mass spectrometry (Py-GC-irMS). N-containing moieties and polysaccharides, with long residence times (ca. 50 yrs) were shown to be preserved during soil decomposition and humification processes [122].

Labelled material input in *in situ* experiments allows specific following up of degradation of this material. A 2 yr degradation experiment was thus set up with dual labelled ^{13}C and ^{15}N pine fine roots and needles in a temperate conifer forest soil [125]. Needles were shown to degrade faster and to contribute more to the humic substances and the dense fraction than roots. Moreover, the physical breakdown of roots appeared as a limitation step in their decomposition. Incubation of ^{13}C and ^{15}N labelled ponderosa pine litter of either needles or fine roots in mesocosms was also used to elucidate processes involved in OM degradation in soil. Most of the compounds revealed by Curie point Py-GC-irMS were identical in litter and in soil. However the assignation of the compounds to different classes of precursors allows distinguishing litter, soil and humin composition [126].

Chemical transformation in litter during its decomposition was also investigated using Py-MBMS. A higher decomposition rate was observed when the litter is placed in its native environment than under other vegetation, due to higher specialization of the decomposer community [17]. The preservation of root constituents in soils, especially in acidic ones, was also revealed by the survival of its suberin marker, despite the chemical lability of the ester-bound functions, in a study involving saponification and TMAH thermochemolysis [111].

SOM evolution can be traced using in situ long term experimental sites, including chronosequences or within specific environments. OM evolution upon long term (85 years) cultivation was investigated through Py-FIMS and Py-GC-MS [20]. Whereas the virgin soil contained relatively more lignin dimers, lipids, sterols, and long chain fatty acids than the cultivated soil, the latter was richer in carbohydrates, phenols and lignin monomers, alkyl aromatics and N-containing compounds. Py-FIMS was also used to study fine and coarse clay fractions from a long term series (up to 98 years) which underwent continuous fertilizer deprivation [115]. While the chemical composition of the fine fraction remained stable along the series, that of the coarse one was degraded and finally approached that of the fine fraction.

SOM also evolves under the impact of anthropic or natural changes in environmental conditions. Py-GC-MS was used to describe the chemical composition of NaOH-extractable SOM following secondary succession in *Imperata* grasslands [121]. Samples from different stages of secondary succession, primary forest, and 9 years of *Acacia mangium* plantation were collected and analyzed. Degradation of NaOH-extractable SOM was more efficient under forest than under grassland despite a larger contribution of carbohydrates in the latter. Decomposition seemed to be mostly related to the abundance of N-compounds.

Newly vegetated areas after mining activities are appropriate to study the very early stage of SOM development thanks to differentiation between old lignite or new plant derived carbon sources [127]. Markers for the lignite contribution could be identified from the pyrolysis products present in the lignite substrate but absent from the vegetation. Differences in the extent of degradation and in vegetation inputs were noted according to the environment.

Climatic and environmental conditions are the main drivers of soil type differentiation. Andosols are formed on volcanic substrate and are characterized by thick OM-rich surface horizons contrary to Cambisol, in which horizons are poorly differentiated. Fulvic and humic acids along with bulk soil of diagnostic horizons from three Andosols were compared with a

Cambisol using double shot Py-GC-MS [60]. In agreement with their higher OM content, the andic horizons yielded richer pyrograms although more products were thermodesorbed from the Cambisol.

4.3 Pyrolysis as a tool to evaluate soil management impact

Agricultural soil management is of prime interest to optimize productivity of culture and particularly to preserve or improve soil quality. As SOM is a key parameter of soil quality, numerous studies focus on SOM abundance. Pyrolysis was used to investigate potential modifications in the chemical composition of OM (bulk SOM or chemical fractions such as NaOH extract) upon changes in soil management. The latter include tillage vs no tillage, organic or mineral amendments, liming, cropping and reforestation. However in many cases, several types of managements are combined, such as different amendments and/or no tillage making conclusion on the effect of a single parameter difficult to evaluate.

The impact of tillage on SOM composition was often evaluated through the comparison of OM from whole soil or/and soil fractions arising from no-tilled and tilled sites. As tillage could influence SOM distribution, and consequently OM incorporation in soil structures, the chemical composition of SOM from such experimental fields provides insight into OM fate [48, 128, 129]. The inclusion of OM in aggregates seems to play a major role on the composition of OM extracted from different soil fractions. Indeed, in a soil from Belgium, a higher contribution of less-decomposed plant-derived SOM in silt- and clay-size separates is observed upon Py-FIMS when reduced tillage is compared to conventional tillage, but only when microaggregates are considered [129]. Similarly, thermochemolysis after HF treatment revealed that soils under reduced tillage underwent either a preferential incorporation or selective preservation of rather fresh lignin when compared with a soil under conventional practice [67]. Buurman et al. [128] have investigated by Py-GC-MS the composition of NaOH-extractable SOM from soils under Brazilian savanna, no-tillage and conventional tillage, along with the corresponding free and occluded light fractions isolated by density fractionation and sonication. The comparison of the native soil with tilled or non-tilled experimental soil revealed significant differences between the samples, reflecting different origin of OM as well as different degradation rates and pathways in free and occluded fractions.

Differences between organic or inorganic amendments on soil were addressed to evaluate their influence on the evolution of SOM. When whole soil or soil fractions are characterized, differences in SOM composition are observed with manure enrichment when compared to conventional practices such as mineral fertilising [49-51, 130-132]. TMAH thermochemolysis was used to assess the effect of intensive cattle husbandry outdoor during winter when pasture plants are not growing [47]. Using multivariate analysis, the OM profile of the most impacted soil could not be discriminated from the profile of the cattle excrements. Composition changes after manure input have also been evaluated by using humification and mineralization indices derived from pyrolysis products; they evidence the stimulation of microbial biomass due to available OM provided by compost or manure input [49-51]. Through double shot pyrolysis, humic acids extracted from soil under conventional management appeared more aromatic than those from organic management but undisturbed soil exhibited an intermediate stage of decomposition [130].

Different mulching practices were also used to indirectly address the effect of tillage. Plant residue mulching was thus considered to represent no till treatment. After statistical analyses on relative abundances of pyrolysis products, this practice was shown to result in a more stable SOM as well as straw mulching, whereas compost mulched soils appear more degradable [49]. Differences between organic amendments can also be revealed both in whole soil and in pyrophosphate extracts thanks to statistical analysis of pyrolytic indices as shown in a comparison between composted and non-composted amendments derived from vine pruning waste and sewage sludge [53]. Indeed, soils amended with non-composted waste could be distinguished from those with composted waste and the nature of the amendment also has an effect on the chemical composition of the SOM. The effects of periodic inputs of farmyard manure or crop wastes, in the presence or not of N fertiliser, on soil humic acids were investigated by Curie point Py-GC-MS [132]. An increase in lignin-derived products was observed in plots receiving organic inputs when compared to untreated plots and further increase in aliphatic products is noted with manure amendment. An additional N fertilization seemed to favour degradation of aliphatic chains.

The nature of plant residues cultivated on experimental fields in Germany and in Brazil has significantly modified SOM. However neither the addition of N fertilizer in a Brazilian soil nor the different rates of N fertilization applied on four sites in Germany have induced any effect on the SOM composition assessed by Py-GC-MS [133, 134]. Despite the aforementioned differences, the relative effects of agricultural management and land use varied depending on the experiments. Indeed, the contrast between arable and permanent pasture was higher than between organic and conventional management [131].

Liming, an agricultural practice used to reduce soil acidity, is also supposed to affect soil fauna and microbial activity. Its effect on SOM was considered by Rosenberg et al. [135]

using TMAH thermochemolysis. Acid/aldehyde ratio of lignin monomers indicated a lower oxidation of lignin after liming along with an increase in suberin monomers. Thus, in addition to other analyses, liming has been evidenced to be responsible for an increasing root input in soil.

Pyrolysis GC-MS is a useful tool to evaluate changes at the molecular scale in SOM following conversion of grassland to cultivated land or reforestation of a site. The conversion of grassland to cultivated land led to a significant decrease in lignin compounds after only 3 months and principal component analysis based on pyrolysis product classes allowed distinction between the different sites. However, after one year of cultivation, the arable soil signature was no longer discriminated from grassland [136]. The same observation was reported in a chronosequence of short coppice rotation conversion with poplar (7 and 14 years) of previous alfalfa site and an adjacent forest site which were investigated by Py-FIMS. Despite rapid changes in microbial community, the SOM trace remained highly similar to the alfalfa one after 7 years whereas, after 14 years, SOM appeared more similar to the forest SOM [137].

Land use conversion could be revealed even after NaOH extraction. Double shot pyrolysis of humic and fulvic acids isolated from a native forest soil, a soil under coffee culture and a pasture has evidenced the influence of land use on the molecular composition of the extracts in both thermal desorption and pyrolysis chromatograms [61]. The different compounds from desorption chromatograms were dominated by carbohydrate- and lignin-derived moieties, and their higher abundance in samples from soil under coffee and pasture was interpreted as recent lignocellulose input to the soil. A Shannon diversity index calculated on desorption and pyrolysis products revealed a lower diversity under coffee as a result of simplification in the structure of the trophic system under monoculture. The effect of cropping was also evidenced by Py-FIMS, 4-9 years of *Miscanthus* cropping leading to a significant alteration of SOM quality [134].

Fulvic and humic acids, humin and a soil fraction refractory to acid hydrolysis were separated from native and long-term (*ca*. 100 years) cultivated samples from Colorado in order to isolate fractions with different stability, further analyzed by Py-MBMS [104]. The compounds were gathered in different classes and the obtained results were subjected to PCA. Statistical analysis revealed variations in chemical composition of the different extracts and the whole soil. A relative enrichment in the higher molecular weight compounds in the whole soils along with a higher heterogeneity was observed after long-term cultivation in agreement with a previous study using Py-GC-MS and Py-FIMS [20]. However, the non-acid hydrolysable fraction, considered as being more resistant, did not reflect any change upon land use.

The NaOH-extractable and non-extractable fractions isolated from the fine fraction (<50µm) from soil under native vegetation were compared with those of reforested agricultural sites years in order to distinguish vegetation and land use characteristics through Py-GC-MS analysis [46]. The molecular composition of SOM was still bearing the fingerprint of the native vegetation after 35 years of reforestation especially when the non-extractable fraction is considered. A similar conclusion was reached by Vancampenhout et al. [98] after 60 yr of reforestation with pine. When the NaOH–$Na_4P_2O_7$ extracts of soil profiles sampled in a native grassy cerrado and after 8 years of riparian forestation are examined through Py-GC-MS, strong differences are observed between the topsoils with a significant increase in lignin [138]. However, the persistent influence of the native vegetation is observed in the subsoil.

The effects of reclamation and regeneration processes on estuarine SOM were investigated by comparing the Py-GC-MS traces of profiles from a reclaimed salt marsh, a natural one and a regenerated one [139]. The reclaimed site appeared strongly different through the whole profile when compared with the other two sites. Although the regeneration started more than 40 years, the regenerated salt marsh has not yet fully recovered natural characteristics.

4.4 Analytical pyrolysis as a tool to evaluate fire impact

Due to the apparent persistence of pyrogenic OM in soil, interest in this SOM fraction is increasing. As previously mentioned, analytical pyrolysis of residues resulting from fire event such as BC appears inappropriate *a priori* (see section 3.1) and NMR analysis is often favoured. However, analytical pyrolysis, sometimes coupled with other analytical techniques (XANES, NMR), has provided elements on molecular alteration of OM with temperature and evidence of past fire events as illustrated below.

Analytical pyrolysis of soil affected by fire was used to evaluate the effect of temperature on SOM. Knicker et al. [140] evidenced modification of the molecular composition of SOM samples (bulk and humic fractions) induced by fire through comparison with unaffected samples. Py-GC-MS revealed a contribution of uncharred lignin within the input of charred biomass. Chemical differences between burnt and unburnt SOM were more precisely investigated by de la Rosa et al. [141] through a triple shot pyrolysis-GC-MS (340, 520 and 600°C). The 320°C pyrolysis evidenced the loss of labile OM from the burnt sample and the second pyrolysis showed enrichment in heterocyclic nitrogen compounds and aliphatic nitriles, related to a pyrogenic origin. The comparison of pyrolysis traces (obtained from double shot pyrolysis) of soil submitted to wildfire under two types of vegetation (Eucalypt and *Pinus pinaster*) revealed a similar pattern of OM modification with fire [142]. Wildfire induced loss of thermolabile compounds and thermal cracking of long-chain SOM components. The combination of XANES and Py-FIMS to investigate changes in OM structure with increasing heating temperature (from 100°C to 700°C) confirmed the distinction of alteration occurring at temperatures lower and higher than 400°C [143]. A similar pattern of degradation was reported upon pyrolysis of pine forest soils which underwent fire of different intensity [144]. Some authors have looked for fire history traces [46, 145, 146]. Distinction between samples from sites either burnt or unburnt was made possible by statistical analysis performed on Py-GC-MS product classes especially in the NaOH extracts analysis [46]. The high abundance of some molecules (benzene, toluene, benzonitrile, PAHs) produced by pyrolysis of NaOH-extractable SOM or pyrolysis of BC with coil probe pyrolysis system has been described as indicative of the occurrence BC [87, 147, 148].

BC is often considered to be more resistant to biodegradation than bulk SOM. However the SOM chemical composition from sites which have experienced a fire event 1, 4 and 10 years ago revealed a decrease in charcoal contribution to SOM and thus a degradation of pyrogenic carbon [149]. In addition, in soils from Spain, despite typical pyrogenic features were identified in fire affected SOM, they were overprinted by uncharred OM signal after five years [140]. The use of Py-GC-MS contributed to evidence biodegradation of charred material. Nocentini et al. [150] have analyzed particle-size fractions of charcoal separated from soil samples. They concluded that the fractions were produced by different plants under different fire conditions, hence different turnover rates depending on the considered fractions [150]. Py-GC-MS of the NaOH-extractable OM from a colluvial soil profile that covers more than 8500 yr showed episodes of burning and revealed that BC may become NaOH-extractable after long periods of degradation [147].

4.5 Palaeoenvironmental implications of analytical pyrolysis studies

Palaeosols are important archives for past climate and vegetation. Chemical characterization of SOM through pyrolysis in such environments may therefore be a powerful tool for palaeoreconstruction purposes.

To this end, the NaOH-extractable SOM from two soil profiles was investigated through Py-GC-MS followed by principal component analysis on the whole set of identified pyrolysis products [151]. The results support a climatic evolution towards colder and drier conditions, less suitable for microbial activity and provide information on the vegetation during the studied period.

The Rock-Eval pyrolysis indices OI and HI are often considered as proportional to the elemental O/C and H/C ratios and are therefore used as indirect measurement of O and H content. Zaccone et al. [80] thus followed peat humification along a Holocene permafrost bog profile and distinguished three periods corresponding to different stages of permafrost likely related to climatic variations. However, in a study using pure biochemicals, it was shown that some oxygen-devoid molecules may lead to a S3 signal, hence a significant OI value [81] and the analysis of peat samples also led to contradictory results [82]. However, S1 peak was shown to mainly correspond to low molecular weight molecules and S2 to lipids and biological standards (biomass) whereas carbohydrates, lignins and terrigenous plant standards are most responsible for the S3 signal [81].

7. Conclusion

Analytical pyrolysis has been used for more than 30 years in soil science and has been shown to be a powerful tool in SOM characterization. The present review illustrates the use of various types of analytical pyrolysis in soil science.

Initially focused on humic substances, analytical pyrolysis is now also applied to bulk soil and physical SOM fractions. It provides information at the molecular level on most of the SOM thanks to the lack of selectivity in the nature of the cleaved bonds. It allowed the identification of biochemical markers among pyrolysis products, which can then be used to compare different soil horizons or soils belonging to various ecosystems. These comparative studies are mainly focused on the investigation of SOM evolution under different types of impacts, such as environmental changes or anthropic pressure.

To better address the relevance of the observed differences, statistics are increasingly used. They represent a powerful improvement as long as they are not performed at the expense of a careful characterization of SOM composition. In addition, when SOM studies are performed on soil fractions, one must be aware that they may not be representative of the bulk soil. Analytical pyrolysis data may also gain at being constrained using additional analytical approaches such as spectroscopic methods (*e. g.* XANES or NMR) or mass spectrometry (*e. g.* FT-ICR MS or SIMS).

Pyrolysis is therefore already used for a large array of applications in soil science, ranging from laboratory incubations, with the aim to derive proxies of soil biological features, to larger scales with field experimentations. Although it remains difficult to derive quantitative data from pyrolysis studies, semi-quantitative analyses can be obtained through the comparison of abundance ratios of selected pyrolysis products. However, new developments must be pursued. Different types of pyrolysis devices have been set up depending on the purposes of the carried out studies. They include GC separation step or *in situ* derivatisation of the pyrolysis products to overcome the limitations that may be encountered in pyrolysis studies especially in the detection of high molecular weight or polar pyrolysis products. These new developments would especially aim at characterizing soil organic nitrogen which remains challenging, potentially through the use of new derivatisation reagents. This characterization is still a gap to fill to improve our ability to couple C and N biogeochemical cycles.

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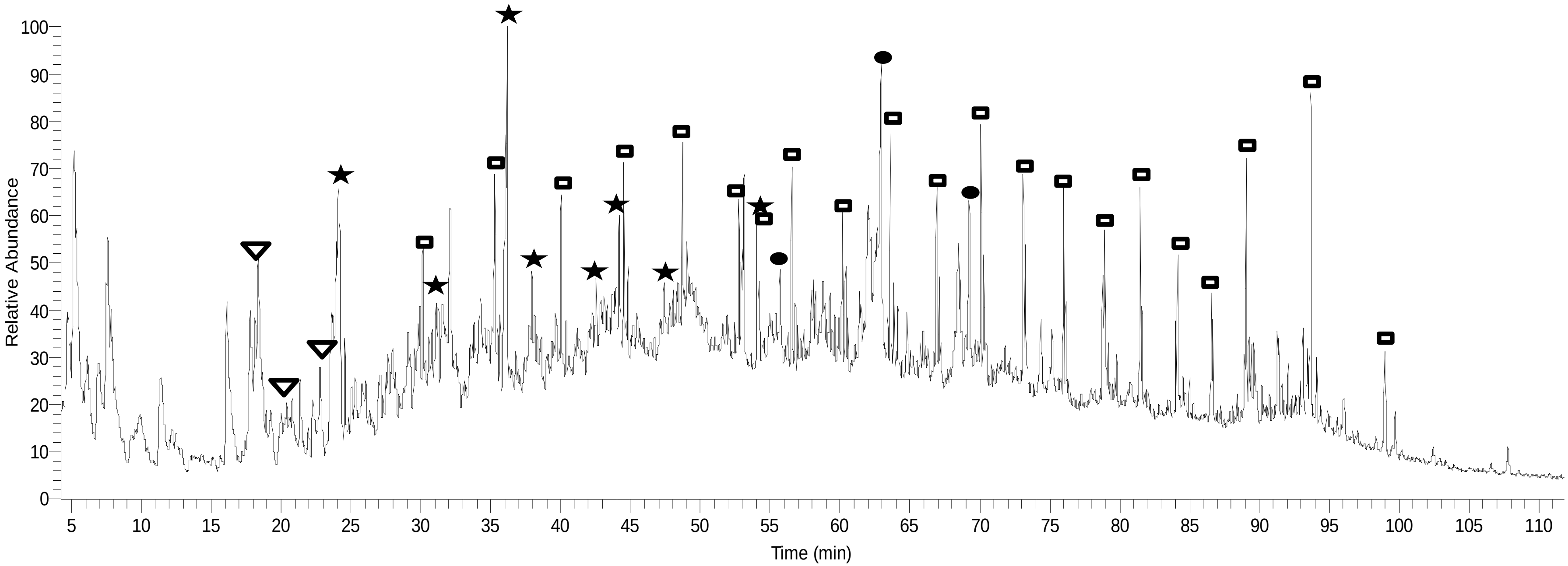
Figure caption

Figure 1 : Pyrochromatogram of a grassland soil (Brittany, West France) without (top) and in the presence of TMAH (bottom).
▼ Cutin/suberin-derived compounds, ● Carboxylic acids, ✱ Lignin-derived compounds, ▣ Alkane/alkene, ▽ Carbohydrate-derived compounds

Table 1: Summary of main advantages and drawbacks of analytical pyrolysis devices for SOM analysis. Note that a comparison between the different pyrolyzers was already published [11].

	Advantages	Drawbacks
Pyrolysis coupled with flame ionization detection (Py-FID)	Semi-quantitative analysis	No identification of the compounds
Pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS)	Individual identification of the compounds	No quantitative analysis, lack of detection of non GC-amenable compounds
Py-GC-MS with a derivatization reagent (e.g. TMAH, HMDS)	Individual identification of the compounds, detection of polar compounds	No quantitative analysis
Pyrolysis coupled with mass spectrometry (Py-MS) (Py-Field Ionization MS or Py Molecular Beam MS)	Quantitative analysis, detection of additional compounds (such as lignin dimers)	Complexity of the mass spectrum
Double or triple shot Py-GC-MS	Individual identification of the compounds, discrimination according to thermal stability	Long analysis time
Pyrolysis coupled with atomic emission detection (Py-AED	Detection of nitrogen compounds	Selective detection, lack of overview
Off line-GC-MS	Separation of compound classes making the identification easier	Larger amount of sample needed, loss of the most volatile compounds
Rock Eval (FID/Infrared)	Information on thermal stability	No information at the molecular level

Figure(s)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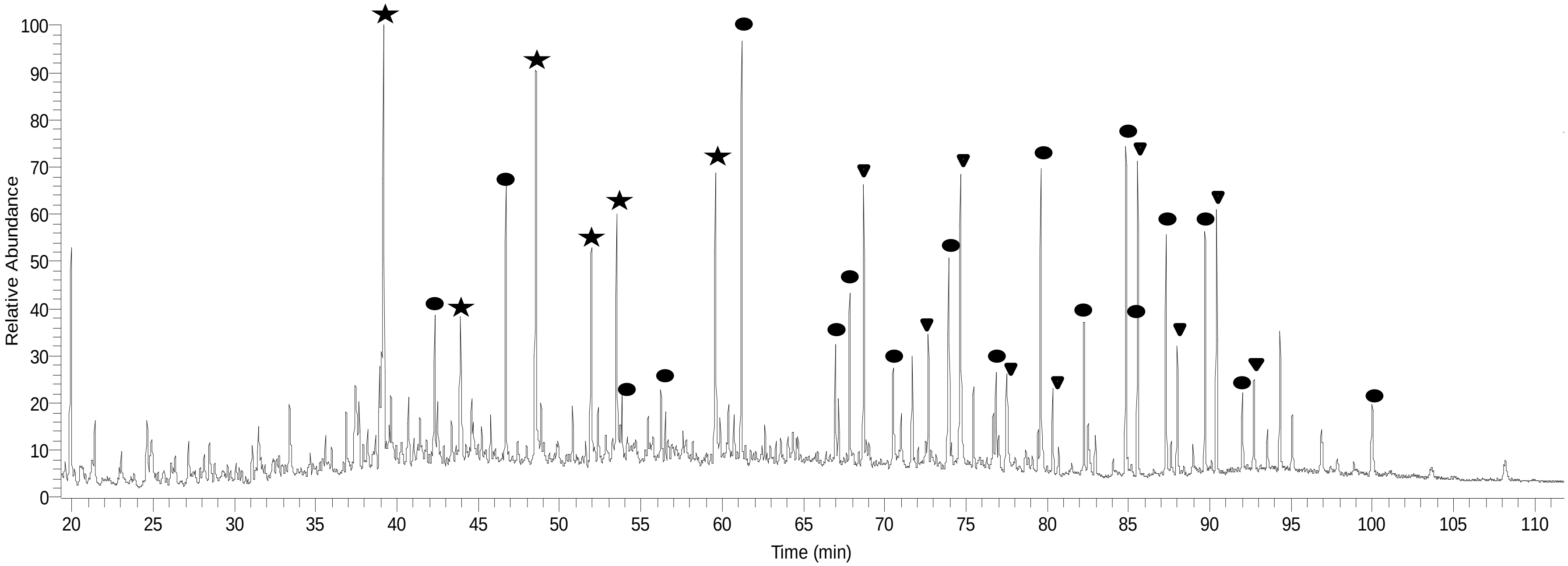
Time (min)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