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Characterization of Compost-Based Growing Media. A Chemical, Thermal, Spectroscopic and Isotopic Approach

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ABSTRACT

Peat is the best substrate in growing media, but its rapid depletion needs at least a partial substitution. Composting of urban green wastes and agro-industrial by-products can produce good compost (Cm) for this purpose. Cm-based substrates are increasing in the market. However, physical and chemical characterization of Cm-based growing media is the first step for their proper use. This paper reports the results of the fractionation of the bulk organic matter (OM) of four growing media, containing increasing amount (v/v) of Cm [100% Peat; 80% Peat + 20% Cm (CP20); 40% Peat + 60% Cm (CP60); 100% Cm) into well-defined fractions: humic acid-like (HAL), non-humic fraction (NH) and dissolved OM (DOM) and their characterization by a combination of chemical, thermogravimetric (TG), differential thermal analysis (DTA), spectroscopic (Diffuse Reflectance Infrared Fourier Transform-DRIFT) and isotopic (δ ^{15}N) techniques. TG-DTA of bulk growing media, HAL, NH and DOM showed significant differences among increasing Cm in Cm-based growing media. DRIFT spectra confirmed these differences. The N isotope ratio (δ ^{15}N) of all the substrates increased with the amount of Cm in the substrate. The combination of chemical, TG-DTA, DRIFT and δ ^{15}N techniques can be successfully applied for the chemical characterization of Cm-based growing media with a good identification of different matrices.

Keywords: compost, δ ^{15}N, differential thermal analysis, diffuse reflectance infrared Fourier transform, dissolved organic matter, humic substances, non-humic fraction, peat, thermogravimetric analysis

Abbreviations: C, carbon; **Cm**, compost; **DOM**, dissolved organic matter; **FA**, fulvic acid; **FAL**, fulvic acid-like fraction, **HA**, humic acid; **HAL**, humic acid-like fraction; **HS**, humic substances; **HU**, humin; **N**, nitrogen; **NH**, non-humic fraction; **OM**, organic matter; **TOC**, total organic carbon

INTRODUCTION

Peat was considered for many years for its high physical and chemical stability and low degradation rate the best substrate for growing seedlings, plant propagation, vegetable production and ornamental plants growth in pots. Unfortunately, peat is obtained from wetlands, which are being rapidly depleted, causing environmental concerns that have led to many individual countries to limit the extent of peat mining, and prices are increasing as a result. This context stimulated the search for alternative materials (Raviv *et al*. 1986; Abad *et al*. 2001; Garcia-Gómez *et al*. 2002; Guerrero *et al*. 2002; Chong 2005; Pérez-Murcia *et al*. 2006; Grigatti *et al*. 2007a; Herrera *et al*. 2008; Ostos *et al*. 2008).

Developing alternative substrates to peat is necessary for three different reasons: limited peat resources, increased pressure for using wastes/by-products coming from human or agro-industrial activities and the economic necessity to use locally produced waste products. A lot of organic wastes (green wastes), sewage sludge, sawdust, town refuse, etc. have been investigated as peat total or partial substitutes in container media after proper composting (He *et al*. 1995; Burger *et al*. 1997; Raviv 1998; Riberio *et al*. 2000; Benito *et al*. 2005; Hernández-Apaolaza *et al*. 2005). Composting is defined as a biological treatment in which aerobic microorganisms utilize organic matter (OM) as a substrate. The final product (compost) consists of stable OM, water, minerals and ash.

The agronomic value of compost (Cm) and its beneficial or detrimental effects on soil and the environment are closely linked to the nature and dynamics of its constituent OM (He *et al*. 1995). The OM is the most important component of the solid phase directly involved into transformation processes (mineralization/humification). OM improves moisture, nutritional and biological properties of the substrate conditioning plant growth (Chen *et al*. 2002). The soil OM was fractionated into well-defined fractions characterized by different physical and biochemical properties: the humic substances (HS); the non-humic (NH) substances and the dissolved OM (DOM). The HS represent the most stable reservoir of organic C in soils due to their recalcitrancy to microbial degradation and can be divided into three main fractions: humic acids (HA), fulvic acids (FA) and humin (HU) (http://ihss.gatech.edu/ihss2). HS are complex and heterogeneous mixtures of polydispersed materials formed by biochemical and chemical reactions during the decay and transformation of plant and microbial remains: a process called humification (Stevenson 1994; Senesi and Brunetti 1996; Brunetti *et al*. 2007). They have remarkable adsorption and buffer capacity; hence, they can adsorb different nutrients and regulate their uptake, thus contributing to the balanced nutrient supply to the plants and protecting them from the damaging salt-effect. The amount and quality of HS and humic-like substances (HLS) in organic amendments or Cm (HLS are chemically similar to soil native HS but they are formed in an environment different from soil) are, therefore, considered important indicators of the OM maturity and stability for a successful application in agriculture and safe environmental impact of the amendment (Senesi and Brunetti 1996).

DOM is considered the active and more mobile OM fraction that plays a key role in a wide variety of chemical physical and biological processes. It is related to organic C and N availability, metal complexation and enhanced plant growth. The DOM composition is a mixture of low mole-

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cular weight compounds (free amino acids and sugars) and chemically heterogeneous macromolecules like enzymes, amino-sugar complexes, polyphenols and HS (Chefetz *et al.* 1998; Chen *et al.* 1998; Zhou *et al.* 2000; Peuravuori *et al.* 2005; McDowell *et al.* 2006). The non-humic (NH) fractions are characterized by low molecular weight molecules such as carbohydrates, proteins, amino acids and uronic acids (Chen *et al.* 2002).

The investigation of all these organic fractions could give additional value to the conventional parameters (pH, electrical conductivity, bulk density, water holding capacity, organic C and total N) normally used to define the quality (stability and maturity) of the growing media (Inbar *et al.* 1993).

Thermal analysis and Fourier Transform Infrared (FT-IR) spectroscopy are two widely-applied analytical techniques to study the molecular structure of the OM and its different fractions. Thermal degradation techniques, such as thermogravimetric analysis (TG) and differential thermal analysis (DTA), have been used for many years to elucidate structural features of OM in whole soils, HS and Cm, providing important information on the chemical characteristics of the samples (Provenzano *et al.* 1998; Francioso *et al.* 2003, 2005; Smidt and Lechner 2005; Francioso and Montecchio 2007; Carballo *et al.* 2008). Thermal analysis has the advantage that it is simple, fast, reproducible and can be performed on the whole sample without requiring any pretreatment. TG has also been used to assess Cm stability and maturity (Dell'Abate *et al.* 2000; Mondini *et al.* 2003; Baffi *et al.* 2007; Smidt and Tinter 2007).

FT-IR spectroscopy being a modern non destructive analytical method more and more often is used for the structure elucidation and quantification of a large variety of organic, inorganic and biological samples. Today FT-IR spectroscopy is more frequently applied in environmental analyses including soil OM, HA and FA (Francioso *et al.* 1998; Filip and Bielek 2002; Francioso *et al.* 2003), organic wastes (Grube *et al.* 2006; Smidt *et al.* 2008) and Cm (Chefetz *et al.* 1996; Provenzano *et al.* 2001; Smidt *et al.* 2008). The isotope signature of N in organic materials has often been evaluated since this parameter can give information on their provenance and their undergone transformations (Choi *et al.* 2002, 2003; Lynch *et al.* 2006). Isotope fractionation during composting is actually the result of N losses and/or N microbial transformation that lead to an enriched, homogeneous and relatively stable $\delta\ ^{15}N$ signature of the organic N in stabilized Cm (Lynch *et al.* 2004, 2006). Therefore the technique could be useful to distinguish among organic matrices of different origin present in a mixture (traceability), and/or to follow N transformations during the composting process.

This study aimed i) to fractionate the bulk OM of peat, Cm and Cm-based growing media prepared using an increasing amount of Cm into well-defined fractions (HAL, NH and DOM) and ii) to characterize their molecular structure by a combination of chemical, thermal (TG-DTA), spectroscopic (DRIFT) and isotopic ($\delta\ ^{15}N$) techniques.

MATERIALS AND METHODS

Growing media

The studied growing media were: Peat, Cm and two mixtures (v/v) 80% Peat and 20% Cm (CP20), 40% Peat and 60% Cm (CP60). A homogeneous mixture of each sample was obtained. The growing media were dried in an air-forced oven at 60°C to constant weight and milled to below 0.25 mm by a Tecator Cyclotec, 1093 PBI.

The Cm utilized was 80-days old, obtained by mixing (v/v) 60% plant trimming and 40% urban and agro-industrial sewage sludge and it was supplied by *Nuova Geovis* (Bologna, Italy). The peat used was a German white *Sphagnum* peat (Floratorf) distributed by Floragard (Italy) (**Table 1**).

Table 1 Main chemical properties of the peat, Cm and Cm-based growing media (CP20, CP60). All data are expressed on a dry-matter basis.

Parameters	Growing media			
	Peat	CP 20	CP 60	Cm
pH (H_2O)	5.92 ± 0.31	7.46 ± 0.29	7.87 ± 0.22	8.27 ± 0.23
Ash (%)	6.9 ± 0.21	30.1 ± 0.50	46.7± 0.32	59.1 ± 0.37
TOC (%)	52.1 ± 0.02	41.0 ± 1.21	28.9 ± 0.74	22.6 ± 0.72
HL^a-C (%)	26 ± 0.05	22.4 ± 0.05	12.8 ± 0.18	10.4 ± 0.12
NH-C (%)	2.1 ± 0.07	2.3 ± 0.06	2.2± 0.07	2.2 ± 0.08
DOM-C (%)	0.21 ± 0.003	0.55 ± 0.005	0.55 ± 0.001	0.54 ± 0.006
Total N (%)	1.32 ± 0.02	1.60 ± 0.01	1.80 ± 0.01	2.12 ± 0.01
C/N ratio	43.4	25.6	16.0	10.7

HL ^{a}: humic-like fraction = HAL+FAL - ± standard deviation

Quantitative analysis

The four substrates were analyzed for total organic C (TOC) and total N using an elemental analyser (EA-1110 - Thermo Fisher). The humic-like C was measured by dichromate oxidation after extraction and fractionation, according to Ciavatta *et al.* (1991). Two g of substrate were extracted under N_2 with 100 ml of 0.1 M NaOH and stirred at 65°C for 48 h. The suspension was centrifuged at 6000 × *g* for 20 min and then filtered at 0.8 µm. An aliquot was used to determine the total extracted C by dichromate oxidation. Twenty-five ml of the extract were then acidified with 5 M HCl to pH < 2 to precipitate the HAL. The supernatant, containing the fulvic-like acids (FLA) and the NH compounds was separated from the precipitated HAL by centrifugation at 5000 × *g* for 20 min. The FLA were separated from the NH by passing the supernatant through a polyvinylpyrrolidone column in order to separate coloured polyphenol compounds (Ciavatta and Govi 1993). The recovered FLA were then added to the HAL, redissolved in 0.5 M NaOH before C determination by dichromate oxidation (Ciavatta *et al.* 1991). The NH was indirectly determined as a difference between the total extracted C and the humic-like C.

The DOM was extracted by using deionised water according to Chen *et al.* (1998) with an extraction ratio 1:10. Samples were shaken for 2 h, afterwards the suspension was centrifuged at 10,000 × *g* for 30 min and filtered through a 0.45 µm filter membrane. An aliquot of the extract was used to determine the C content by dichromate oxidation (Ciavatta *et al.* 1991).

Preparation of HAL, NH and DOM fraction for qualitative analysis

In order to carry out the qualitative analysis on the HAL, NH and DOM fractions, the same procedures of extraction and fractionation previously described were used. Then the obtained fractions were dialyzed at different cut off, 8000 Da for HAL fraction, 1000 Da for both NH and DOM before being freeze-dried.

Thermal analysis

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out simultaneously using a TG-DTA92 instrument (SETARAM, France). About 10 mg of sample was weighed on an alumina crucible and isothermally heated to 30°C for 10 min under air flow ($8\ l\ h^{-1}$) and then heated from 30 to 800°C. The heating rate was $10°C\ min^{-1}$. Indium and calcinated caolinite were used as the reference materials. Each sample was analyzed and mean values of the three replicates were estimated for each mixture and lyophilized sample.

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy

DRIFT spectra were recorded with a Bruker TENSOR series FT-IR Spectrophotometer (Ettlingen, Germany) equipped with an apparatus for diffuse reflectance (Spectra-Tech. Inc., Stamford, CT). Spectrum was collected as Kubelka-Munk units using KBr (Aldrich Chemical Co. Milwaukee, WI) as background reference. Each spectrum was recorded from 4000 to 400 cm^{-1} and averaged over 100 scans (resolution 4 cm^{-1}). Analyses of spectral data were performed with Grams/386 spectral software (Galactic Industries, Salem, NH).

Spectral sections from 1850 to 600 cm^{-1} were baseline-corrected to an absorbance value of 0.00 at 1850 cm^{-1}. We decided to study this region because it is sensitive to the structural changes. Area integration of the region from 3020 to 2750 cm^{-1} was used to compare the aliphatic component between samples. Data were expressed as average of three replicates ± standard deviation.

δ^{15}N measurements

Nitrogen isotopic ratio was determined using an elemental analyser (CHNS-O mod. EA 1110) coupled with an isotope ratio mass spectrometer (IRMS, FINNIGAN-MAT mod. Delta Plus). The isotopic composition of the samples was expressed as δ units according to the following formula:

$$\delta\,^{15}N = [(R_{sample} - R_{standard})/R_{standard}] \times 1000$$

where R = $^{15}N/^{14}N$ and the standard is atmospheric N_2.

Data analysis

The difference between means was estimated using Tukey's test with a significant level of $P<0.05$.

RESULTS AND DISCUSSION

Chemical characteristics

The chemical characteristics of the substrates are shown in **Table 1**. The pH values increased as the Cm content increased in the medium. The pH in CP20, CP60 and in Cm was higher than an ideal substrate according to Abad *et al.* (2001), while pH of peat was clearly in the optimal range. Also the ash content increased as the Cm level increased in the medium, since the Cm used contained the 60% of ashes.

The TOC and HAL-C content decreased as the % of Cm increased in the mixtures. The TOC and HAL-C content of Cm was less than a half with respect to peat's one and this influenced the organic and HAL-C of the two mixtures. The NH-C was at the same concentration in all the growing media while the DOM-C content in the two mixtures seemed to depend on the presence of Cm. In fact the DOM-C content was not statistically different in Cm, CP60 and CP20 while it was significantly lower in peat sample ($P < 0.05$). Quantitatively the DOM-C extracted from peat represented the 0.4% of the TOC while in Cm it increased up to 2.4% (6 times higher than in peat). These findings are important because the DOM fraction of a substrate represents the biologically and chemically active and mobile organic fraction involved in nutrients availability, metal complexation and microbial activity (Chefetz *et al.* 1998; McDowell *et al.* 2006).

The N content increased as the Cm increased in the growing media, being Cm characterized by a higher N content than peat. Increasing amount of not stabilized N might cause N immobilization processes in growing media thus negatively affecting plant growth, with concerns for users (Griffin and Hutchinson 2007; Grigatti *et al.* 2007b) The different composition of the media clearly influenced also their C/N ratio: it rapidly decreased as the Cm content increased in the medium.

TG-DTA analysis

The TG-DTA data of the studied growing media (Peat, CP20, CP60, Cm) and their relative organic fractions (HAL, NH and DOM) are shown in **Figs 1, 2**.

The DTA profiles were mainly characterized by the presence of two exothermic reactions. The first peak (250-350°C-Exo1) is considered to be the result of the thermal degradation of polysaccharides, pectin, hemicellulose, cellulose and microbial cell walls, decarboxylation of acidic groups and dehydration of hydroxylate in aliphatic structures; the second peak (350-500°C-Exo2) is related to the breakdown of aromatic structures and cleavage of the C-C although it could also be attributed to aliphatic macromolecules in the form of long chain hydrocarbons and N compounds (Dell'Abate *et al.* 2000; Provenzano *et al.* 2001; Francioso *et al.* 2003; Peuravuori *et al.* 2005; Francioso and Montecchio 2007; Lyons *et al.* 2008).

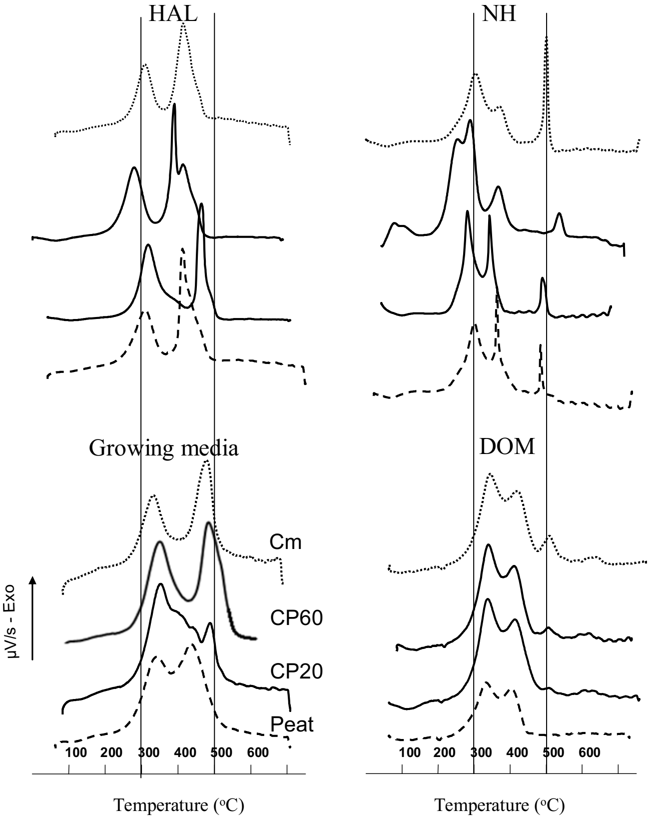

Fig. 1 DTA curves of increasing compost-based growing media (Peat, CP20, CP60 and Cm) and their organic fractions (HA, DOM and NH).

TG-DTA of substrates

Peat and Cm showed a different thermal behaviour. Peat was characterized by a high content of OM (about 93%) with a mass loss related to Exo1 (336°C) of 48% and to Exo2 (446°C) of 44.6% (**Fig. 2**) suggesting an equilibrium between the presence of polysaccharides, aliphatic compounds, carboxylic groups and aromatic compounds. Cm presented the lowest content of OM (35%) and the highest ash content among the substrates (**Table 1**). In spite of the quantitative differences, the ratio between the two exothermic peaks Exo2/Exo1 (0.93) was similar to that of peat (0.80), but DTA of Cm showed a shift of Exo2 towards higher temperature (495°C) compared to peat suggesting a higher content of aromatic polycyclic structures in Cm.

The thermal behaviour of CP20 and CP60 was clearly influenced by the two sources (Peat and Cm). The OM content decreased with the increase in the amount of Cm in the mixture with values of 68 and 46% in CP20 and CP60, respectively. In CP20 88% of the total OM was lost with the first exothermic reaction (**Fig. 2**). As showed by DTA this mass loss is basically related to the overlapping of two exothermic reactions at 330°C (corresponding to Exo1 of Peat and Cm) and a not well resolved peak at 446°C (corresponding to Exo2 of Peat). The remaining OM (12% of the total) was lost with the second exothermic reaction at 495°C and was due to the presence of Cm in the mixture, and in particular to its aromatic component (**Fig. 1**).

The CP60 DTA curve was characterized by two well separated exothermic reactions at 332 and at 496 °C. This thermal behaviour was very similar to that of Cm (**Fig. 1**), but the lower Exo2/Exo1 ratio of CP60 (0.58) compared to

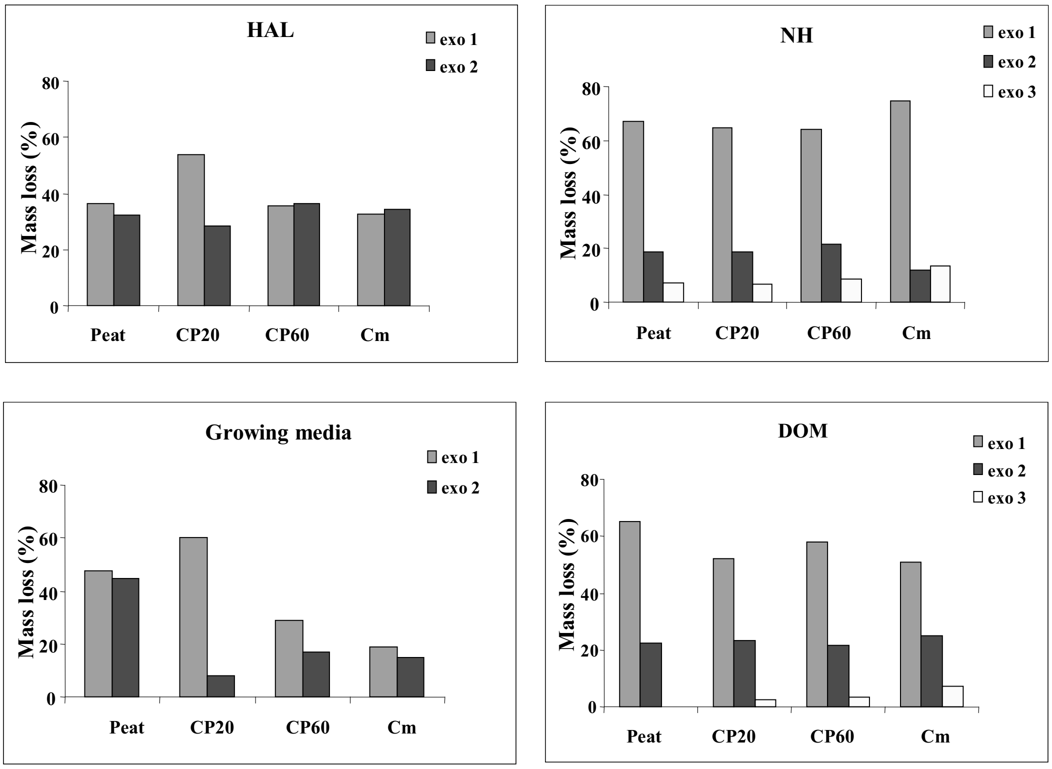

Fig. 2 Thermogravimetry data of increasing compost-based growing media (Peat, CP20, CP60 and Cm) and their organic fractions (HA, DOM and NH).

that of Cm (0.80) suggesting the presence of a greater amount of polysaccharides, pectin, hemicellulose and aliphatic compounds due to the presence of peat.

TG-DTA of HAL

The DTA curves of HAL were similar for all the substrates and characterized by the presence of two exothermic reactions at about 300°C (Exo1) and about 420°C (Exo2) (**Figs. 1, 2**). In HAL of peat sample and even more in CP20 HAL the mass loss related to Exo1 was higher than that related to Exo2, so that the Exo2/Exo1 ratio was always below 1. Increasing amount of Cm in the mixtures caused an increase in the Exo2/Exo1 ratio with values ranging from 1.03 (CP60) to 1.05 (Cm) that indicates a higher content in aromatic compounds deriving from Cm.

TG-DTA of DOM

Thermal behaviour of DOM was similar for all the substrates. The greatest amount of total OM is lost in two exothermic reactions (Exo1, Exo2) and it is generally characterized by a high content of carbohydrates, aliphatic compounds and carboxylic groups as suggested by the high mass losses related to Exo1. This was particularly evident for Peat-DOM which Exo2/Exo1 ratio was 0.35, whereas Cm-DOM showed a higher content of aromatic compounds as highlighted by the higher Exo2/Exo1 ratio (0.49). Moreover, a third exothermic peak (Exo3 at about 500°C) was present in Cm-DOM, and in the two mixtures (CP20 and CP60). This peak seems to be characteristic of Cm since it is lacking in a peat DTA curve (**Fig. 1**) and it increases with the amount of Cm in the mixtures (**Fig. 2**). We suggest this peak to be related to the presence of amidic groups, as confirmed by DRIFT data (**Fig. 3**) that during heating of the sample form N-heterocyclic aromatic compounds due to the Maillard reaction (Knicker 2007). On the basis of these results we suggest that bioavailable organic N that could be easily immobilized in the presence of Cm.

TG-DTA of NH

The NH fraction is obtained at the end of the fractionation procedure of the HS and is constituted by the remaining organic components that are soluble in acidic conditions and are not adsorbed on a cross-linked polyvinylpyrrolidone polymer (Ciavatta and Govi 1993). This organic fraction is characterized by the presence of simple and cyclic carbohydrates, amino-sugars, fatty acids and uronic acids (Chen *et al.* 2002). The DTA curves of Peat and CP20 NH were similar to thermal profile of cellulose (DTA curve not reported) (**Fig. 1**), while the CP60 and Cm differed from this pattern. The mass losses were similar, except for Peat-NH and Cm-NH Exo3 where the last one was double respect to the former (13.2 and 7%, respectively).

DRIFT analysis

The spectra of peat, Cm, CP20, CP60 and their organic fractions (DOM, HAL and NH) were shown in **Fig. 3**. The main attributions were assigned according to the literature (Chefetz *et al.* 1996, 1998; Ouatmane *et al.* 2000; Xiao *et al.* 2001; Chen *et al.* 2002; Ouatmane *et al.* 2002; Jouraiphy *et al.* 2005; Grube *et al.* 2006; Francioso and Montecchio 2007; Carballo *et al.* 2008; Smidt *et al.* 2008). In general the spectra of the substrates showed a similar profile. The broad band at around 3300 cm^{-1} is due to vibrations of OH groups; the peaks between 2930 and 2860 cm^{-1} are due to C–H stretch in aliphatic substances; the peaks between 1700 and 1600 cm^{-1} are assigned to C=O vibration of carboxylic acids, amides, ketones and/or quinones and the C=C vibration of aromatic components. A weak peak at 1511 cm^{-1} was attributed to aromatic skeletal of lignin. Another broad band at around 1440 cm^{-1} arose from the bending motion of CH_2 group and also the C–O stretch vibration of carbonates. The intense peak between 1150 and 1000 cm^{-1} is usually attributed to polysaccharides and to mineral compounds. Finally, the band at 874 cm^{-1} may be assigned to the C–O out-of-plane bend of carbonates.

Peat and Cm spectra were different. The spectra of the mixtures were affected by the different amount of Cm and

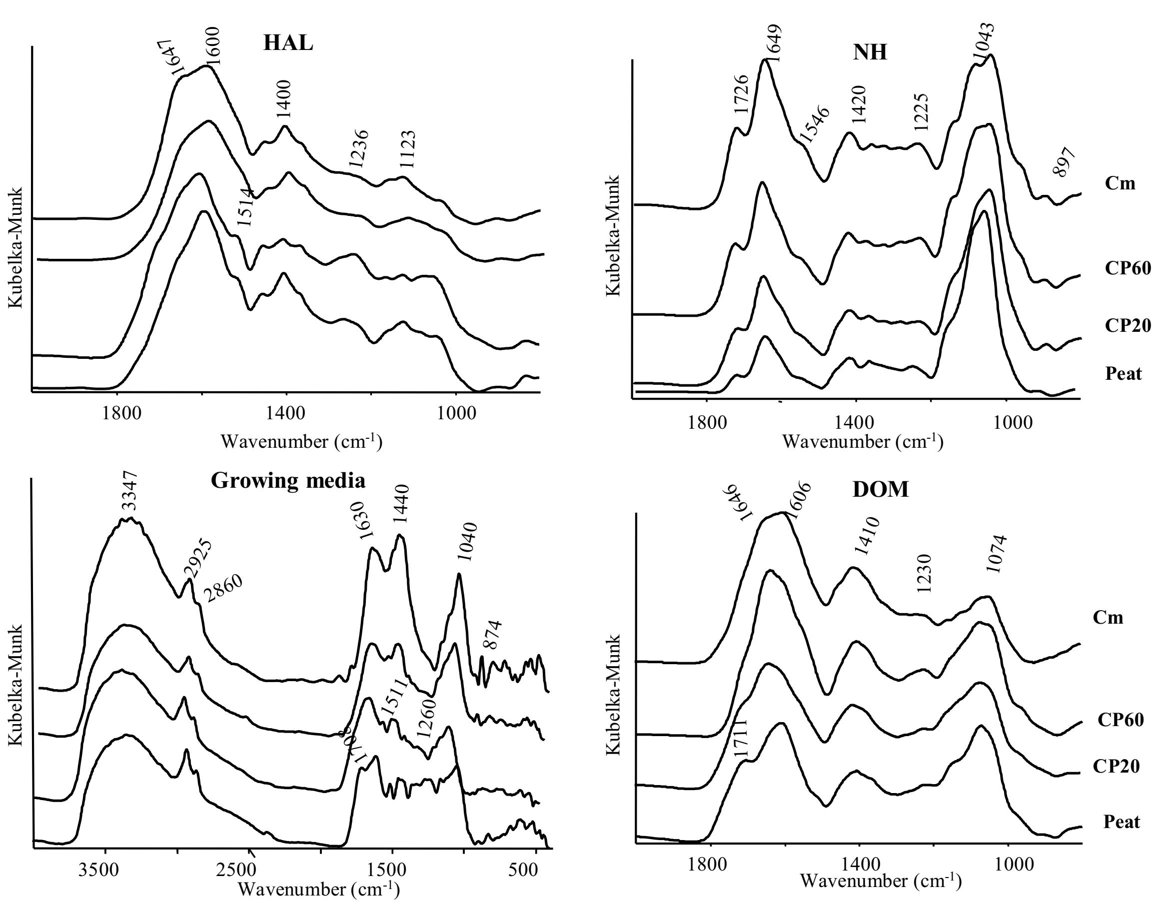

Fig. 3 DRIFT spectra of increasing compost-based growing media (Peat, CP20, CP60 and Cm) and their organic fractions (HA, DOM and NH).

peat, confirming the findings of the thermal analysis. Peat spectrum was characterized principally by lignin (1510 cm^{-1}) while in Cm spectrum was prevalent the calcium carbonate (1440, 874 cm^{-1}). Infact, in Cm spectrum, bands due to its mineral component are prevalent because it contained the 60% of ash (**Table 1**). Further, the content in CH groups of peat and Cm significantly ($P < 0.05$) differed as determined by the integration area values (22.1 ± 0.3 for peat and 16.3 ± 0.6 for Cm). CP20 spectrum was dominated by the signals of peat while, on the contrary, the spectral profile of CP60 is, very similar to that of Cm for the presence of the carbonates, and the broad band at 1040 cm^{-1}, that, considered the high amount of Cm, should be attributed to mineral compounds.

The spectra of the HAL were characterized by a shoulder at around 1650 cm^{-1} attributed to aromatic vibration bands, carboxylate bands (1593, 1403 cm^{-1}), and carbohydrates (1230-1100 cm^{-1}) (**Fig. 3**). In peat and CP20 spectra the lignin band (1514 cm^{-1}) was also evident. The main structural change between Peat-DOM and Cm-DOM concerns the different protonation state of carboxylic groups (1711 cm^{-1}). In the mixtures, the intensity of the band due mainly to the stretching of C-N of secondary amides (1230 cm^{-1}) increased with the amount of Cm. This behaviour is consistent with the thermal analysis showing an increased mass loss of Exo3 with the increase of Cm in the substrates (**Fig. 2**).

The NH spectra (**Fig. 3**) were similar and mainly characterized by the bands of carbohydrates (1043 and 897 cm^{-1}), carboxylic acids (1726 and 1225 cm^{-1}) and amide I (1649 cm^{-1}) and amide II (1546 cm^{-1}). As expected, Peat-NH showed a prominent broad band at 1048 cm^{-1} principally due to the stretching of carbohydrates in hemicellulose and cellulose residues as also confirmed by DTA analysis (**Fig. 2**).

Isotopic analysis

The N isotope ratio of the whole substrates increases with the amount of Cm in the substrate (**Fig. 4**). Mature Cm is generally characterized by high δ ^{15}N values as a result of N fractionation during composting process (Lynch *et al.* 2006). On the contrary Peat has a characteristic δ ^{15}N value always close to zero ‰ since in peat-forming ecosystems, the N source is only due to atmospheric deposition (Schmidt *et al.* 1992).

The HAL fraction showed the same trend of the unfractionated substrate with δ ^{15}N values increasing with the increase in the amount of Cm, although the values were generally lower compared to the unfractionated substrate. Data on N isotope fractionation in humic and HL fractions of different origin are not available in literature. However, the trend we found turns out to follow the same trend observed for C for which a great amount of data indicate that the humic or HL fractions are depleted in ^{13}C compared to

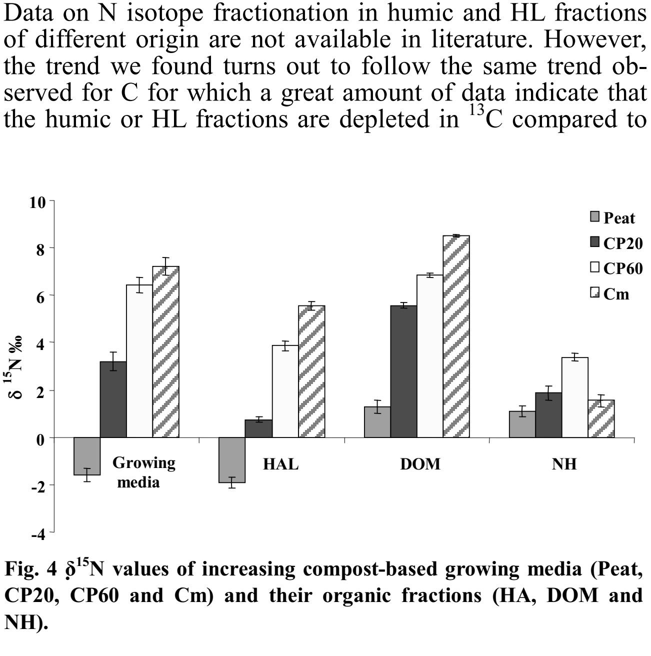

Fig. 4 δ^{15}N values of increasing compost-based growing media (Peat, CP20, CP60 and Cm) and their organic fractions (HA, DOM and NH).

the unfractionated material (Lichtfouse *et al.* 1995; Hiradate *et al.* 2004). The DOM shows once more the increase in δ ^{15}N values already observed with the increase in the amount of Cm, but, unlike the humic fraction, the DOM was characterized by values higher than the unfractionated substrates. This enrichment could be possibly due to the prevalent presence in this fraction of microbial-derived or microbial-transformed N which are normally enriched in the heavier isotope (Blair *et al.* 1985; Nadelhoffer and Fry 1988). Unlike the two previous fractions and the unfractionated substrates, unexpected values were found in the NH fraction, and in particular in that from Cm that was characterized by very low δ ^{15}N values. Both peat and the mixture containing 80% of peat (CP20) had δ ^{15}N values higher than the humic fraction and this is consistent with fractionation mechanisms observed by Esteves *et al.* (2007) in the NH fraction extracted from soils. However, a further increase in Cm in CP60 did not cause the expected increase in δ ^{15}N that was on the contrary lower than the value measured for the humic fraction. This tendency was even more pronounced in the NH from Cm that was characterized by a great fractionation leading to very low ^{15}N values.

CONCLUSIONS

Although peat is the best substrate in growing media its rapid depletion needs to force towards at least its partial substitution. Among the potential substitutes, Cm represents a real source and Cm-based substrates are a good chance to decrease the peat use. In this way we can save peat and we can transform urban green wastes and agro-industrial by-products into excellent products after a proper composting process. Nevertheless, in order to obtain the best results it is absolutely necessary the chemical characterization of Cm-based substrates.

The combination of TG-DTA, DRIFT and δ ^{15}N techniques on the whole substrate seemed to be worthwhile to recognize the different matrices of the mixture. Among the fractions, the DOM seemed to be characteristic for the different growing media because the presence of Cm was well recognized in this fraction. The specific exothermic peak at high temperature, and the specific DRIFT band related to N compounds in Cm-based growing media, might be promising to evaluate the bioavailable N in DOM.

However further investigations on different kinds of Cm-based growing media are needed.

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