

**Use of thermal analysis techniques (TG-DSC) for the characterization of diverse organic
municipal waste streams to predict biological stability**

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calorimetry; Biological Stability; Nuclear Magnetic Resonance; Fourier Transformed Infrared.

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14 **Summary**

15 The use of organic municipal wastes as soil amendments is an increasing practice that can
16 divert significant amounts of waste from landfill, and provides a potential source of nutrients and
17 organic matter to ameliorate degraded soils. Due to the high heterogeneity of organic municipal
18 waste streams, it is difficult to rapidly and cost-effectively establish their suitability as soil
19 amendments using a single method. Thermal analysis has been proposed as an evolving
20 technique to assess the stability and composition of the organic matter present in these wastes. In
21 this study, three different organic municipal waste streams (i.e., a municipal waste compost
22 (MC), a composted sewage sludge (CS) and a thermally dried sewage sludge (TS)) were
23 characterized using conventional and thermal methods. The conventional methods used to test
24 organic matter stability included laboratory incubation with measurement of respired C, and
25 spectroscopic methods to characterize chemical composition. Carbon mineralization was
26 measured during a 90-day incubation, and samples before and after incubation were analyzed by
27 chemical (elemental analysis) and spectroscopic (infrared and nuclear magnetic resonance)
28 methods. Results were compared with those obtained by thermogravimetry (TG) and differential
29 scanning calorimetry (DSC) techniques. Total amounts of CO₂ respired indicated that the organic
30 matter in the TS was the least stable, while that in the CS was the most stable. This was
31 confirmed by changes detected with the spectroscopic methods in the composition of the organic
32 wastes due to C mineralization. Differences were especially pronounced for TS, which showed a
33 remarkable loss of aliphatic and proteinaceous compounds during the incubation process. TG,
34 and especially DSC analysis, clearly reflected these differences between the three organic wastes
35 before and after the incubation. Furthermore, the calculated energy density, which represents the
36 energy available per unit of organic matter, showed a strong correlation with cumulative

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37 respiration. Results obtained support the hypothesis of a potential link between the thermal and
38 biological stability of the studied organic materials, and consequently the ability of thermal
39 analysis to characterize the maturity of municipal organic wastes and composts.

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1. Introduction

The use of organic wastes from diverse origins has become a common practice for increasing soil organic matter and nutrient contents, while simultaneously reducing the biodegradable fraction sent to landfills or incineration (Baffi et al., 2007; Calvo et al., 2004). However, before being applied to soil, organic wastes must be properly treated to avoid possible deleterious effects on soil properties and reduce environmental or health hazards associated with raw wastes. It is therefore important to assess the maturity and stability of their organic matter to ensure its environmental safety, and to provide an efficient agronomic performance in the soil (Baffi et al., 2007; Plaza et al., 2003).

The broad variety of raw materials that make up municipal organic wastes, and the diversity of treatments applied to stabilize them, increase the difficulty of evaluating the quality of these wastes. Different chemical (Senesi, 1989), biological (Adani et al., 2004; ASTM, 1996) and spectroscopic (Chen et al., 1989; Inbar et al., 1989; Smidt et al., 2002) techniques have been used to gain knowledge about the composition of organic matter in wastes, and to assess its degree of stabilization. However, none of these techniques provides sufficient information by itself without being combined with other methods, and many of them cannot be applied to the whole samples without requiring previous extraction or fractionation.

The use of thermal techniques such as thermogravimetry (TG) and differential scanning calorimetry (DSC) has been proposed as a reproducible, informative, rapid, low-cost and small-sample consuming method to characterize the complete quality continuum of organic matter in soils and other materials (Plante et al., 2009). While thermal analysis does require initial investment in analytical instrumentation, this equipment is much less expensive than other analytical instrumentation such as NMR and does not require high labor costs for sample pre-

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4 65 treatment. The rapid and low-cost nature of thermal analyses allows a larger number of aliquots
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6 66 to be tested to help quantify waste stream heterogeneity. Diverse studies have reported the use of
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9 67 thermal techniques to analyze organic wastes (Baffi et al., 2007; Blanco and Almendros, 1994;
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11 68 Provenzano et al., 2000), or to monitor processes of aerobic or anaerobic stabilization such as
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14 69 composting (Dell'Abate et al., 2000; Gómez et al., 2007; Otero et al., 2002; Pietro and Paola,
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16 70 2004). However, these studies are not abundant and most of them are focused on parameters
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19 71 derived from weight loss measurements during the heating process rather than on the data related
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21 72 with the energy released (Otero et al., 2002). The latter measure is expected to provide important
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24 73 information about the biochemical stability of the organic matter (Plante et al., 2011; Rovira et
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26 74 al., 2008). There exists a significant demand to expand the application of thermal analysis
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29 75 techniques to evaluate different organic municipal wastes, and to compare and contrast the
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31 76 information acquired by means of thermal techniques with other, more conventional methods.

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33 77 The objective of this work was to ascertain the potential benefits of adding thermal
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36 78 analysis as an analytical tool to determine the stability and composition of organic matter present
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39 79 in wastes to establish their suitability as organic soil amendments. For this aim, three diverse
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41 80 organic municipal waste streams with different chemical composition and degrees of stability
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43 81 (i.e., municipal waste compost, composted sewage sludge, and thermally-dried sewage sludge)
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46 82 were incubated for 90 days and CO₂ from C mineralization was measured periodically. Samples
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49 83 before and after this process were submitted to thermal analyses and results were compared with
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51 84 other methods that can be used directly on whole waste samples without extraction, including
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53 85 chemical (elemental analysis) and spectroscopic (infrared and nuclear magnetic resonance)
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56 86 techniques. These results together with the C mineralization data obtained during the incubation
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provided useful information about organic matter stability and composition of the samples analyzed that was contrasted with those from thermal analysis.

2. Materials and methods

2.1. Organic wastes

The municipal waste compost (MC) sample used in the study was collected from a waste treatment facility located in Toledo, Spain. The MC consisted of the organic fraction of municipal wastes (e.g., cardboard, paper, food and yard wastes, and other organic solids) subjected to a conventional windrow composting process for two months. The composted sewage sludge (CS) sample was collected from a three-month windrow composted mixture of three sludges from three municipal wastewater treatment plants in Madrid, Spain. The thermally dried sewage sludge (TS) sample was taken from a wastewater treatment plant also located in Madrid. The TS was produced by heating sewage sludge at 70-80 °C with a stream of hot air in trommel for 20 minutes, resulting in a pasteurized 2-4 mm homogeneous granular product. The sludges from which both CS and TS were derived consisted of a blend of primary and biological sludges which were subjected to aerobic digestion followed by mechanical dewatering with centrifuge for pre-treatment.

2.2. Incubation experiment

Three replicate aliquots (2 g, air dry-equivalent) of MC, CS, and TS were adjusted to 55 % of water-holding capacity, and placed in 50 mL glass tubes. Samples were pre-incubated for three days at 25 °C, and then for 90 days at 28 °C. This near-ambient incubation temperature was selected to simulate temperature conditions expected to be experienced after agronomic land

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4 109 application rather than a conventional heat stability test. Mineralization rates were measured
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6 110 periodically by sealing the tubes with a rubber septum cap for 20 to 40 min to allow CO₂ to
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9 111 accumulate in the headspace. The headspace was then mixed by drawing air from the headspace
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11 112 into a gas-tight syringe and plunging the air back into the tube. After mixing, a 2-mL sample was
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13 113 drawn and immediately injected into a LiCOR-7000 CO₂/H₂O infrared gas analyzer (LICOR
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15 Biosciences, Lincoln, NE). Using a set of calibrations, measures were converted to CO₂
16 114 concentrations in the tubes and then to respiration rates that were normalized to the initial C
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18 115 concentration of each waste.
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25 117 2.3. Analytical methods

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27 118 The pH and electrical conductivity of the organic wastes were measured on mixtures of
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29 119 1:5 sample:water. Total C (TC) and N contents of the samples before and after incubation were
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31 120 determined using an Elementar Analysensysteme (Hanau, Germany) Vario MACRO CHNS
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33 121 elemental analyzer. Inorganic C (IC) content was determined with a Shimadzu (Duisburg,
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35 122 Germany) TOC-5000A analyzer equipped with a SSM-5000 solid sample module, and total
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37 123 organic C (TOC) content was computed as the difference between TC and IC.
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42 124 *Fourier transform infrared spectroscopy*

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45 125 Aliquots of the three replicates of each waste (i.e., MC, CS, and TS), before and after
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47 126 incubation, were combined into composite samples for analysis with Fourier transform infrared
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49 127 (FTIR) spectroscopy. The FTIR spectra of each resultant composite were recorded over the range
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51 128 from 4000 to 400 cm⁻¹ on pellets obtained by pressing a mixture of 1 mg of sample and 400 mg
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53 129 of dried KBr under reduced pressure. A Nicolet 5PC FTIR spectrophotometer (Madison, WI)
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55 130 operating with a peak resolution of 2 cm⁻¹ and Omnic 6.0 were used to obtain spectra.
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CPMAS ^{13}C -nuclear magnetic resonance Spectroscopy

Solid-state cross-polarization magic-angle spinning ^{13}C nuclear magnetic resonance (CPMAS ^{13}C -NMR) spectra were also obtained from composite samples on a Bruker (Billerica, MA) Avance 400 MHz NMR spectrometer, operating at a frequency of 100.62 MHz. Approximately 200 mg of sample was packed into a zirconium rotor of 4-mm outer diameter with a Kel-F cap. The rotor spin rate was set at 5 kHz. Forty thousand scans were accumulated for each sample with a pulse delay of 0.5 s and a contact time of 3 ms. The NMR-free induction decay signals were digitized and Fourier transformed after application of a line broadening of 80 Hz. The CPMAS ^{13}C -NMR spectra were then baseline corrected and integrated into the following chemical shift regions: 0-45 ppm for aliphatic C; 45-110 ppm for substituted-aliphatic C, including alcohols, amines, carbohydrates, ethers, methoxyl, and acetyl C; 110-160 ppm for aromatic C; and 160-240 ppm for carboxyl and carbonyl C in carboxylic acids, ketones, esters and amides. The ^{13}C chemical shifts are reported relative to adamantane.

Thermal analyses

Thermal analyses were performed using a Netzsch STA 409PC Luxx simultaneous thermal analyzer equipped with a type-S (Pt/PtRh) TG-DSC sample carrier (Netzsch-Gerätebau GmbH, Selb, Germany). Prior to analysis, waste samples before and after incubation were air-dried and lightly ground in a mortar. Samples (5 mg) were placed in a Pt/Rh crucible with an identical and empty crucible used as the reference, and heated from ambient to 725 °C at 5 °C min⁻¹ under an oxidizing atmosphere of 30 mL min⁻¹ of synthetic air (20% O₂ and N₂ balance) and 10 mL min⁻¹ of N₂ as a protective gas. A 15-minute isothermal stop at 105 °C was used to drive off moisture present in the samples before proceeding to the exothermic region.

Differential scanning calorimetry (DSC) data were corrected for baseline drift using instrumental correction runs and the non-parametric baseline fitting function of Peakfit software (Systat Software Inc., Chicago IL).

Total exothermic energy content (in J) was determined by integrating the DSC heat flux (in mW) over the exothermic region 150–725 °C. Thermogravimetric mass loss (in mg) was determined for the same range. Data recorded at < 150 °C were discarded, thus obviating weigh losses and energy changes associated to moisture loss during the isothermal stop at 105 °C, which could mask data in the temperature range under study. Energy density (J mg⁻¹ OM) was also determined over the exothermic region (150–725 °C) by dividing energy content by thermogravimetric mass loss (Rovira et al., 2008). The temperature at which half of the exothermic mass loss has occurred (TG-T₅₀), and the temperature at which half of the exothermic energy has been released (DSC-T₅₀) were also calculated for samples before and after incubation. The thermostability index (R₁), which was proposed to evaluate the level of maturation of organic matter in composts (Dell'Abate et al., 1998), was also calculated using the modified temperature ranges proposed by Baffi et al. (2007). This index is expressed as the ratio between the weight loss associated with the exotherm in the higher temperature range (410-725 °C, Exo₂) and the weight loss occurring in the lower temperature range associated with the first exothermic reactions (150-410 °C, Exo₁).

2.4. Data analysis

Results of analyses performed on samples before laboratory incubation are reported as means with measures of variability. However, the three aliquot samples on which analyses were performed were pulled from the same original sample, representing pseudo-replication, so the

variability calculated is only analytical. Conversely, respiration results from the incubation and thermal analyses performed on samples after incubation are reported with standard errors of the mean because the aliquot samples underwent the incubation separately, and thus represent independent replicates. Pearson Product Moment Correlation Coefficients (r-value) were calculated to determine the strength of association between soil cumulative respiration and TOC and several thermal parameters obtained for all the samples before the incubation.

3. Results and discussion

The chemical properties (Table 1) of the organic wastes (MC, CS, and TS) generally fell within the ranges previously reported for these kinds of materials (Fernández et al., 2007; García-Gil et al., 2004). Total organic C concentrations for TS were almost twice that found for CS and MC, while N contents were particularly high in TS and CS, something characteristic of sewage sludges (Warman and Termeer, 2005).

Mineralization of organic C during the 90-day incubation was significantly greater from TS samples compared to MC samples, and particularly compared to CS samples (Fig.1). At the end of the incubation, 19.8% of the original organic C present in the TS samples was mineralized, compared to 4.5% in the CS samples, and 11.7 % in the MC samples (Table 1). While the incubation technique used perhaps represents only potential reactivity at relatively low temperatures, these results indicate that organic matter from CS was more stable than that from the MC, and both more stable than TS. This can be explained by how these wastes were pre-treated and it is consistent with results observed in previous experiments where soils amended with TS or CS were incubated to study C mineralization kinetics (Fernández et al., 2007). The TS was submitted to a drying process that minimized microbial activity, reducing the presence of

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4 198 pathogens and preserving labile organic matter from decomposition. The outcomes of thermal
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6 199 drying is the preservation of large amount of labile C, high C concentrations typical of raw
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9 200 organic wastes, and the subsequent large quantity of C lost as CO₂ during incubation. Under the
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11 201 optimal conditions of temperature and moisture in the incubation, microorganisms continue the
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13 202 mineralization process interrupted by the thermal-drying process. In contrast, the other two
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15 203 wastes have been submitted to composting processes, one of the most common treatments for
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17 204 stabilizing organic wastes. Composting leads, if properly completed, to a stabilized, biologically
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19 205 mature and sanitized final product, free of pathogens and rich in humic-like substance (Ahmad et
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21 206 al., 2007; Hargreaves et al., 2008; Plaza et al., 2005). These differences in the treatments explain
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23 207 the larger C mineralization from TS after 90 days of incubation and suggest that, in this case, the
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25 208 composting process was probably more efficient for CS than for MC. The final characteristics
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27 209 and quality of any waste compost can widely vary and depends on many different factors
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29 210 including the composting facility design, initial materials, the composition of the raw materials,
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31 211 the composting procedure and conditions, the time of maturation, etc.
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39 212 *FTIR spectra*

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42 213 The FTIR spectra (Fig. 2) of the three wastes showed a common broad band around
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44 214 3405-3418 cm⁻¹ (especially sharp and intense for CS), usually attributed to vibrations of O-H
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46 215 stretch from bonded and non-bonded hydroxyl groups and water, and two distinct peaks in the
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48 216 range of 2925-2850 cm⁻¹ due to aliphatic C-H stretching of methylene groups. The spectra also
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50 217 featured a common band around 1640 cm⁻¹, generally attributed to absorptions of several groups
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52 218 including aromatic C=C and C=O stretching of carboxylates and amide groups and OH bending
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54 219 vibrations for water, though the relative contribution of each component to this band cannot be
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ascertained. Unlike the others, the TS spectra showed a small band around 1540 cm^{-1} that can be associated with amide II vibrations. Smidt et al. (2002) found this band in fresh sewage sludge but not in composted sludge, and it was also observed in some nitrogen-rich composts of different origins (Inbar et al., 1989). In contrast, the band located around 1420 cm^{-1} , often associated with the presence of carbonates that also absorb at 875 cm^{-1} , was more intense in the CS and MC spectra, while the nitrate band at 1384 cm^{-1} , highly reproducible and characteristic of well composted materials (Smidt et al., 2002), appeared perfectly distinguishable as a sharp and intense peak only in the CS. Finally, the asymmetric and sharp form of the band detected around 1034 cm^{-1} in the original CS samples and its growing intensity in the TS spectrum after incubation (TS90), could indicate a relative increase of inorganic compounds due to the mineralization process associated with an efficient composting in the case of CS or with the incubation in the case of TS. This band is generally attributed to C-O stretching of polysaccharide-like substances but it is also specifically associated with Si-O asymmetric stretch of silicate impurities (Smidt and Meissl, 2007). Grube et al (2006) and Provenzano et al (2001) previously concluded that the FTIR spectra of samples before and after composting are qualitatively similar in terms of the presence or absence of peaks, and that differences are essentially in relative intensity of peaks, which our data confirm.

Overall, TS featured an FTIR spectrum more characteristic of fresh sewage sludge, while the CS spectrum was typical of stabilized sewage sludge (Smidt et al., 2002). The FTIR spectrum of MC can be considered more similar to CS, but its characteristics pointed to a less advanced state of stabilization.

CPMAS ^{13}C NMR spectra

The organic matter present in soils is typically composed of plant residues inputs with high contents of cellulose and lignin and their decomposition products, but in the case of organic municipal wastes, the composition is usually more heterogeneous with an origin sometimes difficult to determine. The limits of the CPMAS ^{13}C NMR technique must be also taken into account when applied to sewage sludges because NMR can significantly underestimate the proportion of alkyl C (Smernik et al., 2003).

For all samples, the most intense peaks in the solid-state CPMAS ^{13}C NMR spectra and corresponding estimates of C distribution derived from the NMR integration were in the chemical shift regions between 0-45 ppm and between 45-110 ppm (Figure 3, Table 2). The signals in the first region (0-45 ppm) are generally assigned to aliphatic-C, and are commonly prominent in spectra of sewage sludges and other organic wastes (Castaldi et al., 2005; Smernik et al., 2003). In this case, all the wastes analyzed featured two peaks at 22 and 29 ppm (especially well defined in TS samples), which can be assigned to terminal methyl groups and methylene groups in long chain aliphatic compounds of varying origin, such as fatty acids, lipids, cutin acids and other biopolymers (Kögel-Knabner, 1997). The substituted-aliphatic C region (45-110 ppm) contained the largest proportion of signal for all of the samples analyzed (43.0–56.0 %). One of the most prominent peaks in the spectra (especially in MC and TS), was at around 70 ppm, usually attributed to the singly oxygen-substituted C_2 through C_6 carbons of sugars residues in carbohydrates. Peaks around 103 ppm are normally assigned to the doubly oxygen-substituted anomeric (C_1) carbons in carbohydrates. (Smernik et al., 2003) while the secondary peaks found at around 55 ppm are associated with methoxyl in lignin and in

hemicellulose, and peaks around 64 ppm to crystalline components of hexoses and pentoses (Gómez et al., 2007).

The aromatic region (160-110 ppm) represented the lowest proportion of C for the TS and MC samples. This region can be divided in two sub-regions: 160-140 ppm for aromatic carbons linked to O or N, and 140-110 ppm usually associated with non-substituted and C-substituted aromatic carbons (Almendros et al., 2000). While the first sub-region is poorly represented in the spectra of all the samples analyzed, the second presented a peak at 121 ppm that was well defined in the TS spectrum only.

The region between 160-240 ppm showed signals (especially intense for TS) around 171 ppm and 221 ppm. Resonances in this area are generally assigned to carboxylic acid and carbonyl C but also the amide C in proteins and esters. The most intense peak, around 171 ppm, is traditionally attributed to carboxyl group, but aliphatic esters and amides may also contribute to this signal intensity (Almendros et al., 2000). It has been suggested (Vane et al., 2003) that the signal near 30 ppm would indicate that the amide C are also contributing to the signal at 171 ppm, which could indicate the presence of non-digested proteinaceous material in this waste apart from other compounds.

Changes in NMR spectra before versus after incubation were consistent with the relative amounts of CO₂ respired during incubation. CS samples had the lowest amounts of CO₂ respired, and featured few remarkable changes in NMR spectra. On the other hand MC and TS samples were more intensely mineralized during the incubation, and showed more distinct changes in the NMR spectra. For the MC, the most significant decrease was in the substituted-aliphatic region (45-110 ppm), most probably due to the mineralization of hemicellulose and other carbohydrates. For the TS, the most significant decrease was in the aliphatic region (0-45 ppm), probably

resulting from the mineralization of easily degradable compounds. TS also featured a significant decrease in the intensity of the peak at 171 ppm that could be related, at least in part, to the breakdown of amides, from which some products could have been transformed into simpler aliphatic-N groups, subsequently contributing to the relative increase in the 45-110 ppm region.

Thermal analysis

The TG curves (Fig. 4) of TS samples featured the largest weight loss (50.2 %), a value close to that found for untreated sewage sludges (Jindarom et al., 2007). In contrast, the other two wastes, MC and CS, featured weight losses around 25 %. When TS samples were analyzed after incubation, the weight loss associated with the TG decreased to 39 %, a sign of the intense mineralization of this waste and the relative increase of the inorganic fraction. Increases in the ash contents (i.e., less weight loss) of organic wastes are commonly observed as a consequence of biological stabilization processes (Gómez et al., 2007). Meanwhile, only small TG changes were detected for the incubated CS and MC samples with respect to initial samples, which would point to the higher stability of these composted materials in comparison with the TS.

Although TG thermograms showed some differences, DSC curves (Fig. 4) more clearly reflected the differences between the three organic wastes analyzed. The TS yielded the most intense DSC signal, mainly due to its higher C content (Table 1). DSC curves of both TS and MC had a typical bimodal peak distribution previously observed in fresh and composted wastes (Baffi et al., 2007; Pietro and Paola, 2004), with the first maximum at 320 °C (MC) and 350 °C (TS) and the second maximum at 494 °C. Conversely, DSC curves for CS (Fig. 4) did not feature a clear bimodal pattern. Instead, its curve more closely resembled those found for organic matter analyzed in bulk soils with an intense peak around 330 °C followed by a shoulder at 445 °C and

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4 308 a secondary peak near 540 °C. Although the presence or absence of a bimodal pattern has been
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6 309 suggested to be caused by organo-mineral interactions in soils (Duguy and Rovira, 2010; Plante
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9 310 et al., 2011), this explanation is unlikely in the case of organic wastes with low mineral content.
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12 311 Commonly, the low-temperature part of the exothermic region has been linked to the
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14 312 burning of carbohydrates and other aliphatic compounds as simple lipids and amino acids, and
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16 313 consequently associated with the most easily-degradable fraction of the organic matter.
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18 314 Meanwhile, the high-temperature part has been generally attributed to reaction of aromatic
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21 315 compounds or other polyphenols, distinctive of a more humified and stable fraction of the
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23 316 organic matter (Dell'Abate et al., 2000; Plante et al., 2009). However, this generalization does
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26 317 not completely agree with some of the results observed for these organic wastes, particularly for
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31 319 The DSC curves of CS and MC slightly differed before and after incubation. Specifically,
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33 320 CS showed an increase of the DSC intensity in the range near 450 °C. This variation could be
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38 322 observed during advanced states of composting and associated with the humification process.
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41 323 More interestingly, the DSC curve of the TS, which presented a particularly well-defined and
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43 324 intense peak near 500 °C (Fig. 4), showed a significant reduction of the intensity of this peak
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48 326 maximum displaced to a lower temperature. This suggests that at least part of the components
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51 327 that contributed to this secondary peak in the TS curve were easily altered or mineralized during
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53 328 the incubation. According to the FTIR and CPMAS ¹³C NMR results described above, it could
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56 329 be possible that the presence of proteinaceous material in the TS were partly responsible for this
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DSC peak. Some pyrolysis studies have shown the contribution of long chained hydrocarbons and nitrogen compounds to the reactions above 400 °C (Leinweber et al., 1992).

Among the different parameters calculated from the DSC and TG results (Table 3), those indexes calculated exclusively with thermogravimetric data (i.e., R_1 and $TG-T_{50}$), featured weak correlations with cumulative respiration expressed as % of initial C ($r = 0.460$ and 0.320 , respectively; Table 4). Both, the R_1 index, which was intended to express the relative amount in weight (TG) of the more thermally stable fraction of organic matter with respect to the less stable one (Dell'Abate et al., 2000) or the $TG-T_{50}$, proposed to establish a balance of energy input necessary to loss half of the weight (Rovira et al., 2008) did not show a clear trend that explains the different stability of the organic matter present in the wastes analyzed. This could be due to different factors such as the presence of easily degradable compounds that contributed to significant weight losses at high temperatures or the absence of clear bimodal patterns in some the wastes analyzed (Rovira et al., 2008). Of the parameters that included energy data, the balance of energy input necessary to released half of the energy ($DSC-T_{50}$) did not show a clear trend for samples before and after incubation despite the good correlation found with the biological stability of the samples. However, energy density, which combines both, TG and DSC, information, exhibited a clear trend and its values for all the samples before incubation were significantly correlated with cumulative respiration expressed as % of initial C ($r = 0.988$, Table 4). The results obtained indicated that the waste that yields the greatest energy per unit of organic matter was the TS, followed by MC and CS. A similar trend was found for samples after incubation. Intense C mineralization also represented an important decrease in the energy stored in the organic matter. These results match with those from the respirometric study and suggest

that with the same input of energy, microorganisms would obtain a higher energy benefit from degrading TS than MC or CS.

4. Conclusions

Given the complexity of the composition of organic municipal waste streams, their different origins and the diverse treatments that they can be submitted to, the use of thermal analysis as a complimentary method provides useful and valuable information about the nature and composition of the organic wastes. Advanced analytical techniques such as ^{13}C -NMR can provide detailed chemical characterization of organic wastes, while thermal analysis techniques can provide more rapid and cost-effective assessments of stability that are indirectly related to chemical composition. Results obtained in the current study showed the potential of using thermal energy-related parameters, such as energy density, to establish a relation between the energy available per unit of organic matter for microbial activity and the biological stability of the wastes. However, it is still necessary to test the observed trend with other organic wastes to fully understand the relationship between thermal and biological stability before establishing DSC-TG thermal analysis as regular method to characterize organic wastes.

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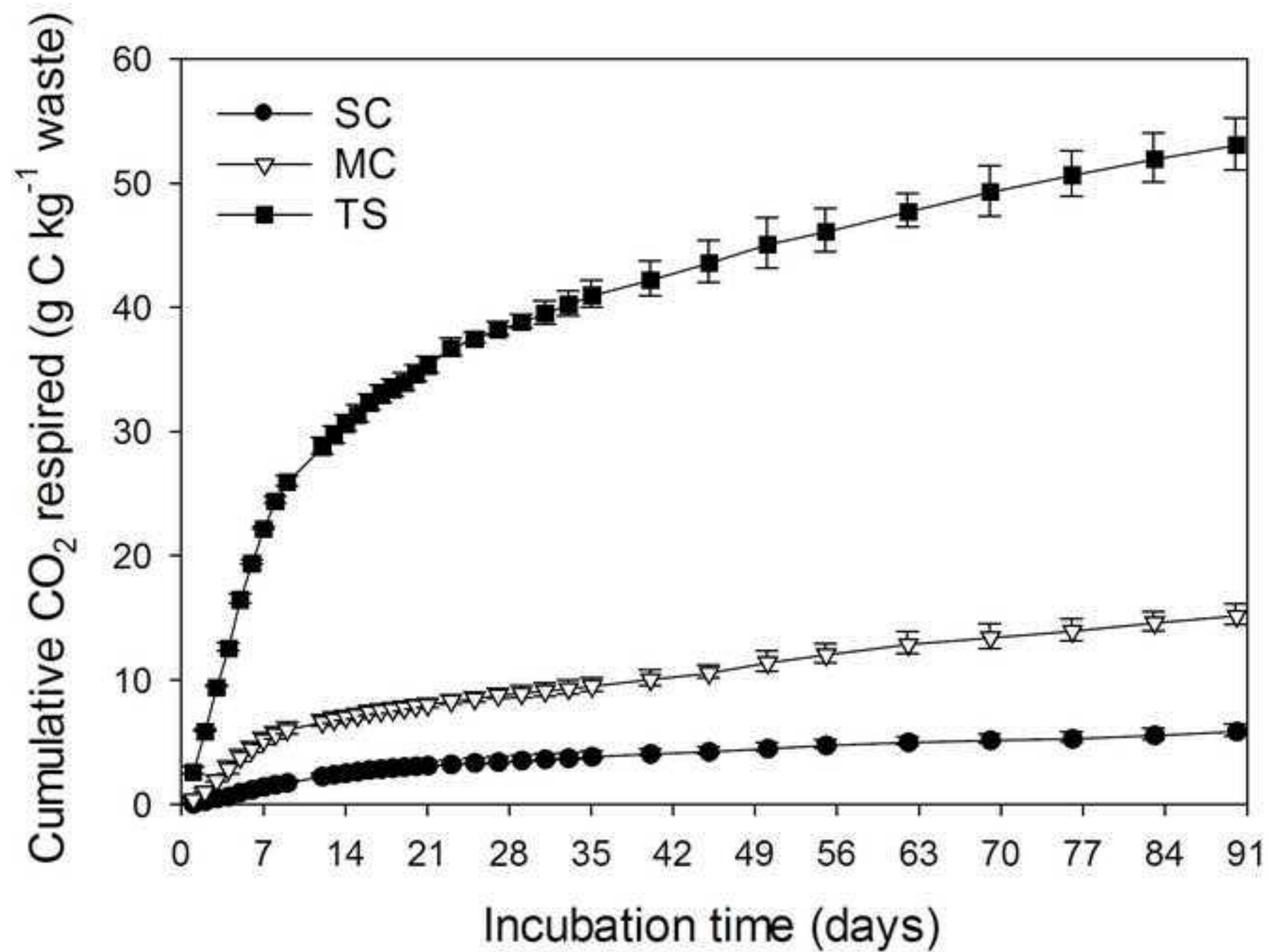
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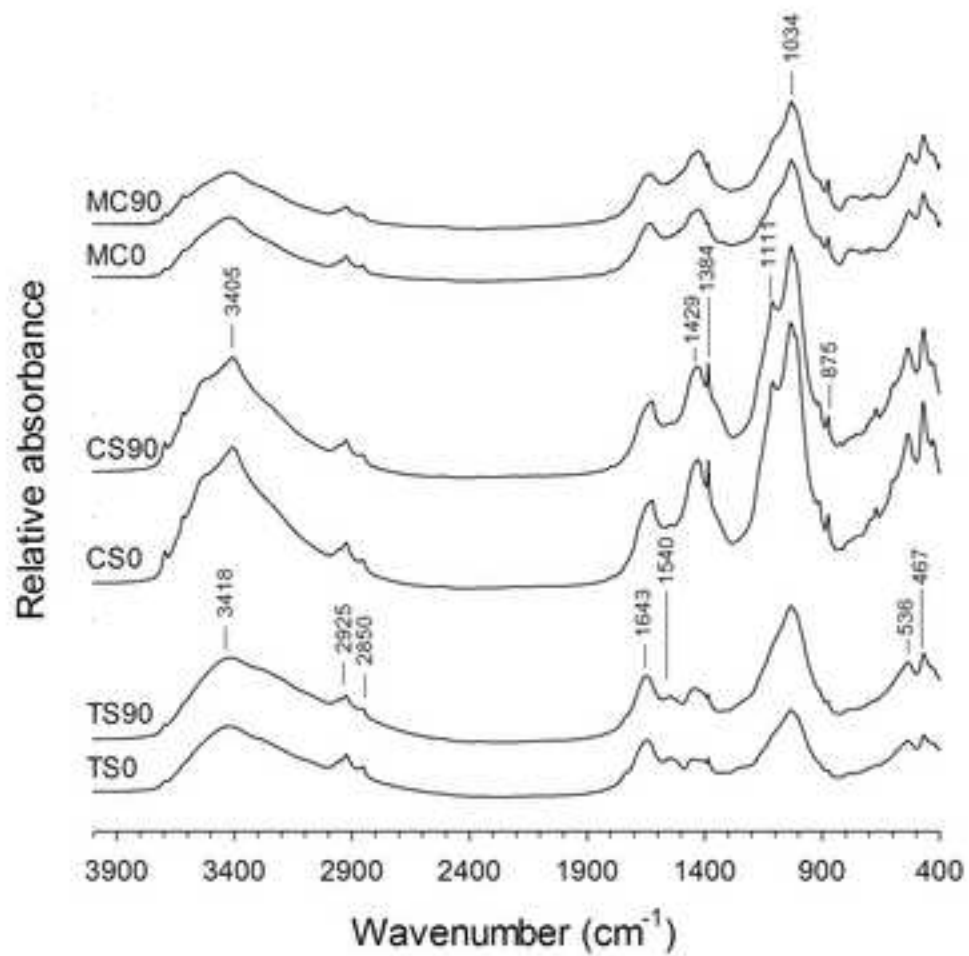
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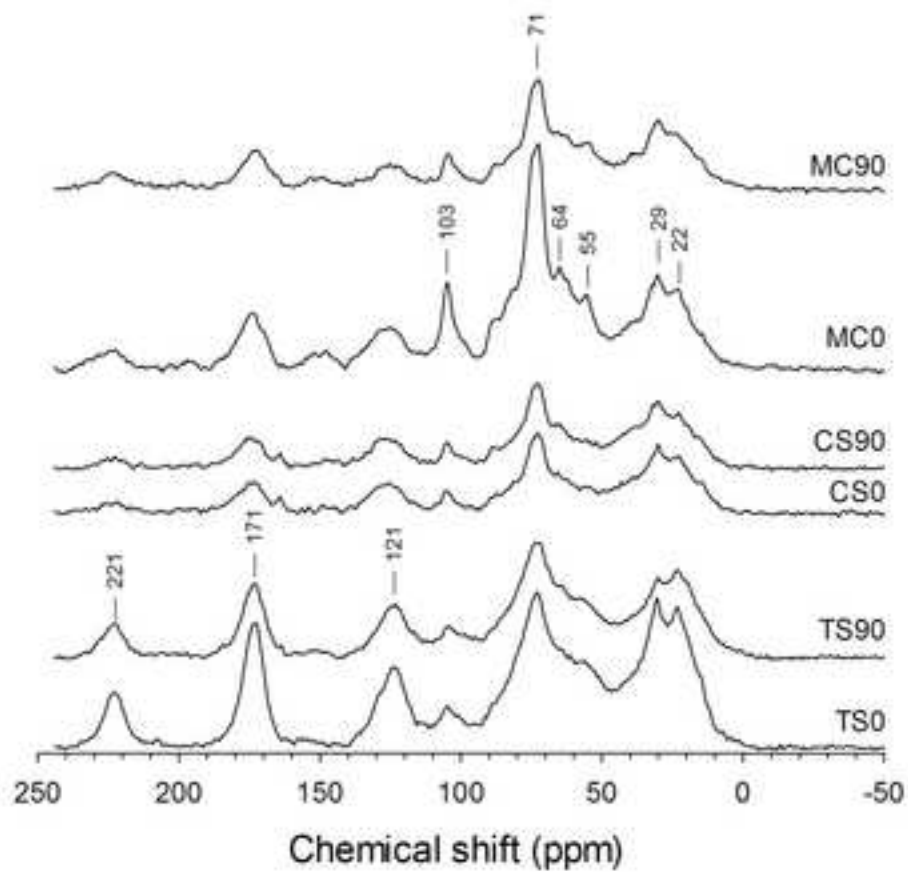
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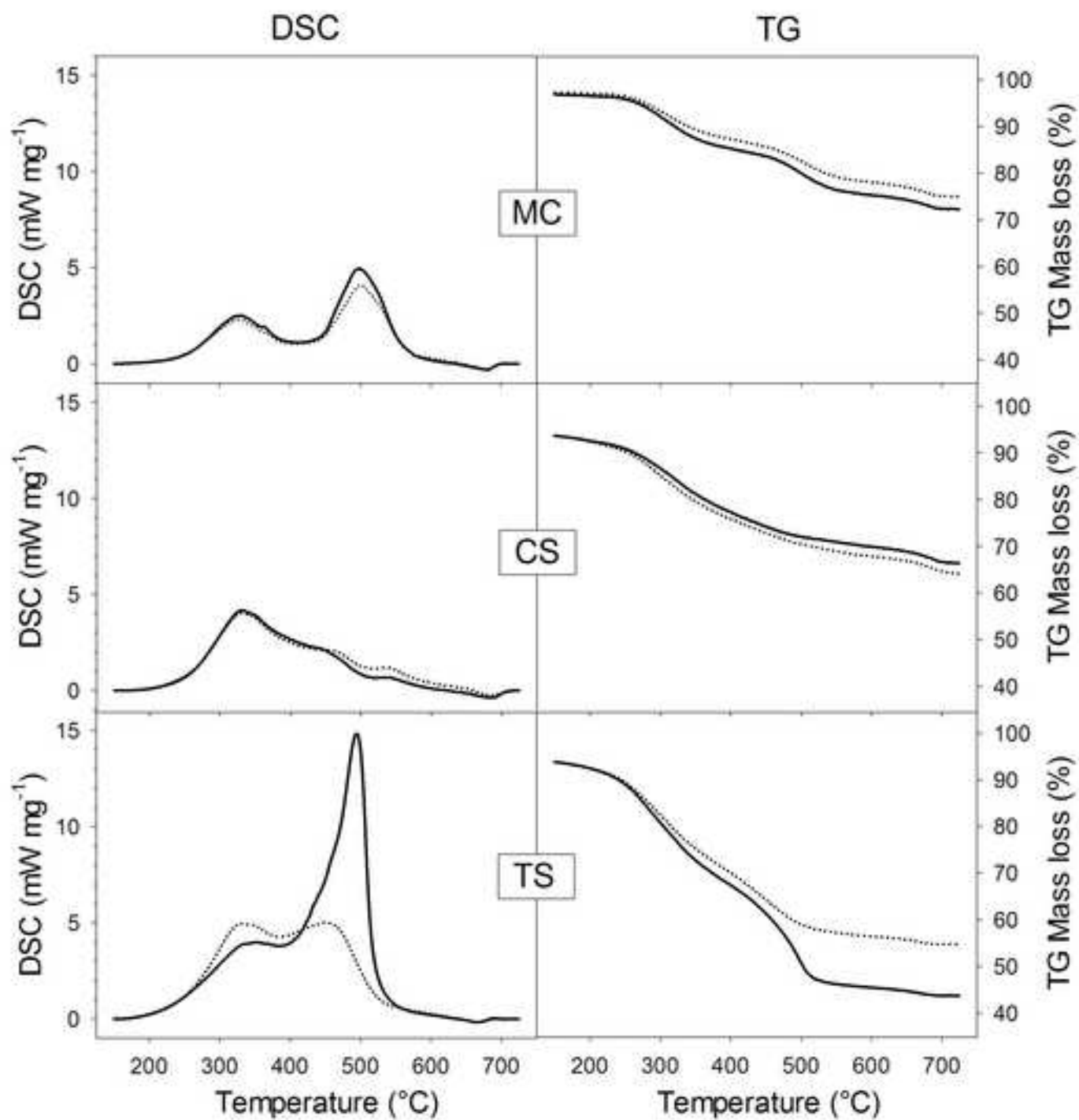
Highlights

- Thermal analysis was used to assess stability and composition of organic matter in three diverse municipal waste streams.
- Results were compared with C mineralization during 90-day incubation, FTIR and ^{13}C -NMR.
- Thermal analysis reflected the differences between the organic wastes before and after the incubation.
- The calculated energy density showed a strong correlation with cumulative respiration.
- Conventional and thermal methods provide complimentary means of characterizing organic wastes.









bars indicated standard errors.

Figure 2: Fourier transform infrared (FTIR) spectra of municipal waste compost (MC), composted sewage sludge (CS) and thermally dried sewage sludge (TS) before (0) and after (90) 90 days of incubation.

Figure 3 CPMAS ^{13}C NMR spectra of municipal waste compost (MC), composted sewage sludge (CS) and thermally dried sewage sludge (TS) before (0) and after (90) 90 days of incubation.

Figure 4: Differential scanning calorimetry (DSC) and thermogravimetry (TG) curves of municipal waste compost (MC), composted sewage sludge (CS) and thermally dried sewage sludge (TS) before (solid line) and after (dotted line) 90 days of incubation.

Table 1: Main chemical properties of air-dried samples, and amount of CO₂ respired during 90 days of laboratory incubation of municipal waste compost (MC), composted sewage sludge (CS) and thermally dried sewage sludge (TS).

	pH	EC (dS m ⁻¹)	Total C (%)	Organic C (%)	Total N (%)	Total CO ₂ respired	
						(mg C g ⁻¹ waste)	(% initial OC)
MC	6.34 ± 0.01	10.82 ± 0.32	15.6 ± 0.48	13.1 ± 1.04	1.4 ± 0.06	15.30 ± 0.84	11.7 ± 1.3
CS	7.15 ± 0.01	7.76 ± 0.07	13.8 ± 0.06	13.2 ± 0.02	2.1 ± 0.02	5.99 ± 0.50	4.5 ± 0.4
TS	7.00 ± 0.01	2.35 ± 0.06	28.1 ± 0.54	26.8 ± 0.86	4.2 ± 0.06	53.17 ± 2.08	19.8 ± 0.9

Table 2: CPMAS Decay ^{13}C NMR relative peak area (%) for municipal waste compost (MC), composted sewage sludge (CS) and thermally dried sewage sludge (TS) before (0) and after (90) 90 days of incubation.

	Aliphatic C (0-45 ppm)	Substituted-aliphatic C (45-110 ppm)	Aromatic C (110-160 ppm)	Carboxyl and carbonyl C (160-240 ppm)
	(%)			
MC	28.6	56.0	6.7	8.7
MC90	32.1	53.9	5.6	8.3
CS0	37.7	43.0	9.7	9.6
CS90	37.7	44.9	9.6	7.8
TS	32.2	43.3	9.9	14.6
TS90	30.3	47.5	8.9	13.3

Table 3: Energy, mass loss, energy density, DSC₅₀, TG₅₀, Exo₁, Exo₂ and R₁ (Exo₂/Exo₁) values calculated for the range of temperatures between 150 °C and 725 °C, of municipal waste compost (MC), composted sewage sludge (CS) and thermally dried sewage sludge (TS) before (0) and after (90) 90 days of incubation.

	Energy	Mass loss	Energy density	DSC ₅₀	TG ₅₀	Exo ₁	Exo ₂	R ₁
	(J)	(mg)	(J mg ⁻¹ OM)	(°C)	(°C)	(%)	(%)	(Exo ₂ /Exo ₁)
MC	21.10 ± 1.34	1.23 ± 0.04	17.15 ± 0.70	465 ± 2.1	427 ± 5.5	11.91±0.45	12.64±0.39	1.06±0.02
MC90	18.74 ± 2.53	1.11 ± 0.07	16.83 ± 1.27	460 ± 4.0	435 ± 7.2	10.28±0.83	11.99±0.49	1.17±0.05
CS0	20.67 ± 0.95	1.37 ± 0.06	15.13 ± 0.13	365 ± 0.6	363 ± 1.0	17.08±0.90	10.26±0.35	0.60±0.02
CS90	22.20 ± 0.56	1.48 ± 0.08	15.07 ± 1.14	375 ± 2.5	357 ± 10.5	18.47±1.80	11.09±0.78	0.61±0.09
TS	46.57 ± 1.61	2.51 ± 0.06	18.55 ± 0.22	450 ± 3.5	386 ± 3.1	27.43±0.80	22.73±0.57	0.83±0.03
TS90	34.11 ± 1.15	1.95 ± 0.05	17.49 ± 0.40	392 ± 7.0	359 ± 3.1	24.82±0.52	14.24±0.66	0.57±0.03

Table 4: Pearson correlation coefficients (R-value) for the cumulative respiration (% initial OC) and the initial total organic carbon (TOC) content and thermal parameters calculated for all the samples before incubation.

	TOC %	TG - OM loss (mg)	DSC - Energy (mJ)	Energy density (mJ mg OM ⁻¹)	DSC-T ₅₀ (°C)	TG-T ₅₀ (°C)	R ₁ (Exo ₁ /Exo ₂)
Cum resp. (% initial OC)	0.857 ^{**}	0.826 ^{**}	0.885 ^{**}	0.980 ^{***}	0.768 [*]	0.320	0.460

^{*}, ^{**} and ^{***} represents P< 0.05, 0.01 and 0.001 respectively.