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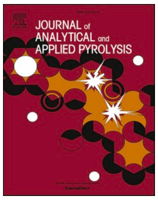

Analytical pyrolysis (Py-GC-MS) for the assessment of olive mill pomace composting efficiency and the effects of compost thermal treatment

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A R T I C L E I N F O

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A B S T R A C T

Composting is an interesting solution for recycling the large amount of residues typically generated in olive oil production areas, particularly olive mill pomace. Bulking agents must be added to wet olive mill pomace for composting. The diversity of the materials used (such as olive tree-pruning residues, animal manure, or straw) and the variable proportion, in which they are mixed, are responsible for the heterogeneity and variability of the quality of the produced compost. For this reason, a comprehensive characterization of compost organic matter is necessary to gain information about its stability and maturity useful as well as to predict its behavior as a soil amendment. In this work, fresh olive mill pomace and four composted olive mill pomace samples were characterized using analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS). Results showed a large variety of pyrolysis products, many of which had a specific biochemical origin. Pyrolysis-GC-MS revealed a decrease in fatty acids and aliphatic compounds content with composting, along with carbohydrates degradation and an increase in phenolic and N-compounds levels. Furthermore, the differences observed in organic matter characteristics had an impact on agronomic aspects (water repellency and phytotoxicity). Thus, the occurrence of fatty acids in incompletely composted materials (mainly palmitic and *cis*-vaccenic acids) was associated with increased phytotoxicity and higher water repellency. The presence of chicken manure in the mixtures was proved to favor the humification process and the production of stabilized compost (characterized by a lower Aliphatic-C/Aromatic-C ratio and higher N-heterocycles content). Furthermore, in this work, the effectiveness of applying thermal treatments to improve compost quality has been evaluated. Analysis of the Py-GC-MS results by means of principal component analysis (PCA) revealed thermal rearrangement, predominantly aromatization, and loss of functional groups of carbohydrates, lignin, and proteins, at temperatures above 225 °C. Interestingly, the results suggest that materials with a non-effective or incomplete composting process can be transformed by thermal treatment into more stable products, exhibiting similar agronomic characteristics as those have that undergone a more efficient biotransformation.

1. Introduction

Recycling agricultural and livestock organic wastes by composting to use them as organic amendments in crop-intensive and organic matter depleted soils is a very attractive and important environmental strategy [1]. Composting promotes the biotransformation of raw organic matter, resulting in a more stable and complex product enriched with humic-like substances. The application of compost contributes to the recovery of poor soils, as it induces an increase in organic matter content and improves its physical-chemical and biological properties [2,3]. In olive oil producing areas, like the Mediterranean countries, olive mil pomace (OMP) is the major by-product generated. Just in Spain, around four million tons are generated per year, many of which are deposited in landfills, leading to severe environmental pollution [4]. Extraction of the residual oil or its use as biomass feedstock for the production of bioenergy and biofuels are suitable valorization strategies [5,6]. However, the high water content (around 60–70 %) of the wet OMP generated by the two-phase decanters employed in modern olive oil production facilities makes the necessary drying step very costly [7]. Several studies have demonstrated that co-composting olive mill

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by-products with complementary residues (i.e. pruning wastes and animal manure) is an interesting option to recycle this material [8,9]. Furthermore, its use can contribute to address the degradation problems related to the decrease of organic matter content of agricultural soils in the south of Spain and other semi-arid regions [10]. OMP compost application improves soil quality and fertility, particularly by increasing the content in organic matter and long-term bioavailable fractions of N, P and K [11].

Properties of compost can vary depending on the composition of initial materials and the progress of the composting process. Compost quality is generally defined on the basis of stability and maturity. Compost stability refers to the resistance of compost organic matter to further rapid degradation [12]. During the composting process, the remaining matter progressively becomes more resistant to biodegradation and will therefore have a higher long-term yield on soil organic matter. Compost maturity is related to humification and to suitability for plant growth. Consequently, many parameters have been considered to assess compost quality degree of evolution, including odor, temperature, color, pH, C/N ratio, metabolic activity, etc. [13]. However, the information obtained can be often incomplete or insufficient [14,15] and further characterization of the structural changes occurring in compost organic matter for in-depth knowledge of its degradation processes and its transformation into humic-like soil substances is required. In this sense, spectroscopic techniques such as UV-Vis, ^{13}C NMR or FTIR have also been employed to evaluate the maturation of compost in terms of humification degree [16-18].

Analytical pyrolysis coupled to gas chromatography and mass spectrometry (Py-GC-MS) is also a very useful analytical method to obtain detailed structural information on organic matter in compost with no need for sample pre-treatment [19,20]. Through this methodology, a sufficient amount of heat reproducibly breaks down the organic bonds of a complex mixture in small and stable molecules called pyrolysates [21]. Thus, the structure and relative intensity of these new products provide insight into the nature of the original material, which can be associated with their biochemical origin; e.g., fatty acids are derived from lipids, substituted phenols from lignin, N-heterocycles from proteins, etc. In general, analytical pyrolysis has been proposed as a reproducible and relatively fast technique for studying qualitative changes in the structure of environmental materials, since it produces a “fingerprint” [22]. Although it shows some limitations, especially related to the occurrence of undesired secondary rearrangements, such as cyclization and aromatization reactions of aliphatic chains in humic acids (HAs) [21, 23], pyrolysis-GC-MS has been demonstrated by several authors as a very useful analytical method for its convenience and ability to yield additional information to wet chemical degradation methods [19–22, 24]. Also, changes in the pyrogram peaks allow the determination of very interesting pyrolytic indices to monitor the degradation and humification of composted organic matter [16,25]. Therefore, an in-depth study of compost organic composition using Py-GC-MS can reveal the chemical changes occurring during composting and can be useful to assess compost quality [26,27].

This study aims to characterize the organic matter in different compost samples prepared with olive mill pomace mixed with other by-products (olive tree pruning residues and animal manure) in variable proportions, using Py-GC-MS. Furthermore, it is interesting to take into account that the use of these organic amendments on agricultural soils still presents some challenges even after composting. Water repellency due to the presence of aliphatic organic compounds with the hydrophobic character in compost, is one of the most critical aspects [11]. The increase in soil water repellency can affect soil infiltration rate [28] and leads to important environmental problems, such as increased erosion [29], loss of soil nutrients and groundwater contamination [30]. In order to reduce this harmful effect, thermal treatment of compost at mild temperatures has been proposed as an effective way to eliminate water repellency [31] by thermal degradation or vaporization of the organic substances responsible for hydrophobicity [32]. In previous studies, we have evaluated the feasibility of using different thermal treatments to increase the quality of several organic amendments based on olive mill pomace [31,33]. It has been proved that thermal treatment reduces water repellency and modifies organic matter characteristics, as revealed by different spectroscopic techniques like ATR-FTIR. However, the changes occurring during the thermal treatment at different temperatures are not fully understood. Therefore, further research is still needed to characterize organic matter composition and the relationship between any induced structural transformations and the reduction of water repellency. Here, we will use Py-GC-MS to provide a deeper knowledge of the structural changes induced by heating at different temperatures. For this purpose, principal component analysis (PCA) is employed as a useful tool to detect trends in samples based on pyrolysates and their relative abundances, to identify marker compounds. Finally, the correlation between the abundance of different organic compounds with agronomic characteristics related to compost stability and maturity will be evaluated.

2. Materials and methods

2.1. Sample collection and description

Four samples of composted olive mill pomace (COMP) and one of raw olive mill pomace (OMP) have been considered in this study, all provided by different producers located in Jaén (Spain). Table 1 shows details of the composition and origin of each one.

Raw OMP sample refers to a non-composted dried olive mill pomace. Sample COMP1 was elaborated using OMP and olive tree pruning (OTP) as raw materials by mobile stacking, turning once a fortnight to avoid any anaerobic processes during the initial four months’ bio-oxidation period, and then allowed to stand without turning for two more months (4 + 2 months). Samples COMP2, 3, and 4 were prepared by mixing OMP, OTP, and chicken manure (CM), and staking in 3 m high and 6 m diameter piles which were turned regularly every 15 days during a seven-month maturation period.

Each sample involved five sub-samples collected in five different pile positions to assure representativeness. They were all desiccated at 65 ºC and then ground and sieved to 200 μm.

OMP: olive mil pomace; COMP: composted olive mill pomace.

Table 1
Samples composition and origin.

Ref. code	Composition (% w/w)	Maturation time (months)	Origin
OMP	Raw OMP		Hermejor de la Reina organic oil factory (Villanueva de la Reina, Jaén)
COMP1	30 % OMP 70 % Olive tree pruning	4 + 2	Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA) (Mengíbar, Jaén)
COMP2	80 % OMP 10 % Olive tree pruning 10 % Chicken manure	7	Alcanova S.L, oil factory (Alcaudete, Jaén)
COMP3	80 % OMP 10 % Olive tree pruning 10 % Chicken manure	7	Olive-growing cooperative N. S. Remedios (Noguerones, Jaén)
COMP4	50 % OMP 25 % Olive tree pruning 25 % Chicken manure	7	Hermejor de la Reina organic oil factory (Villanueva de la Reina)

2.2. *Chemical and agronomic characterization*

For preliminary characterization of samples, pH was measured in 1:10 (w/v) water-soluble extract with a CRISON pH-meter. Total carbon and total nitrogen were determined with a LECO TruSpec CHN 620–100–400 analyzer. A more detailed characterization including micronutrients and other specific parameters for the analysis of organic amendments can be found in [31]. In addition, basic agronomic testing was also carried out.

Water repellency (W*R*) was examined according to the water drop penetration time test (WDPT) [34]. This test consists in determining the time it takes for a drop of distilled water, placed on the organic amendment surface, to fully penetrate the material [35]. The WDPT value was calculated as the average of the time taken for 5 distilled water drops to be absorbed, thrown from 5 mm high to avoid kinetic energy excess. Thus, samples can be classified into five categories according to Bisdom et al. [36]: wettable (≤ 5 s); slightly water repellent (6–60 s); strongly water repellent (61–600 s); severely water repellent (601–3600 s) and extremely water repellent (> 3600 s).

The germination index (GI) was determined using the Zucconi test [37]. Briefly, 4 g of dry samples were moistened with deionized water to 60 % field capacity and let stand for 30 min. Then, deionized water was added to a 1:10 w/v concentration and stirred mechanically for 30 min, centrifuged at 3000 rpm for 15 min and filtered (0.45 mm). 1 mL of the so-obtained extract was added to a Petri dish with filter paper and 10 *Raphanus sativus* L. seeds were incubated at 28 °C for 72 h in the dark. Then the number of seeds germinated was counted and the root length of those germinated was measured. Results were expressed as the GI resulting from the percentage of germination and root elongation over the control sample (incubated with deionized water).

2.3. *Thermal treatment*

In order to study the changes induced by heating in the samples of compost, the four composted mixtures were subjected to different thermal treatments. About 60 g of each were placed in porcelain containers and brought up to temperatures of 175, 225 and 275 °C in a pre-heated oven (Binder FED GmbH) at 5 °C/min ramp rate. Final temperature was maintained for 5 h [32]. A total of 12 thermally treated samples were obtained in this way, which were also characterized in terms of variables of agronomic interest (water repellency and germination index).

2.4. *Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS)*

Pyrolysis-Gas Chromatography/Mass Spectrometry analyses (Py-GC-MS) were carried out using a SCION GC-MS System (Bruker Daltonics, Germany) coupled to a Multi-Shot Pyrolyzer® EGA/Py-3030D (Frontier Lab, Fukushima). The samples (< 1 mg) were placed in the sample cup and introduced into the pre-heated pyrolyzer micro-furnace for single-shot pyrolysis at 600 °C for 10 s. Pyrolysis products were purged into the SCION 436-GC. The temperature of the transfer line to the chromatograph was set to 300 °C to prevent the condensation of the products. The GC injection was operated at 300 °C in split mode with split ratios of 1:10 for 0.01 s, 1:50 for 5 min and 1:10 until the end. Chromatographic separation was performed on a fused silica BR-5MS capillary column (5 % diphenyl-95 % dimethyl polysiloxane, 30 m × 0.25 mm I.D., 0.25 µm film thickness, Bruker). Helium (purity 99.99 %) was used as carrier gas at a constant flow speed of 1.0 mL/min. The temperature of the chromatographic column was progressively increased as follows: (i) 60 °C for 5 min; (ii) from 60 to 300 °C at a rate of 5 °C/min; (iii) the capillary column was maintained at 300 °C for 30 min. The mass spectrometer parameters were: electron impact ionization (EI full scan, 70 eV); scan range from *m/z* 50–700; GC-MS interface capillary temperature 300 °C. The MS transfer line was 278 °C and the ion source temperature was kept at 280 °C. Octafluoronaphtalene (OFN) was used for mass spectrometer tuning.

Identification of pyrolysis products was undertaken using MS Data Review software (version 8.0), based on their *m/z* value and fragmentation pattern when compared with the National Institute of Standards Library database (NIST, version 17). The relative retention times and spectra reported in the literature were also considered. The relative abundance of each peak was calculated as a percentage of the total chromatographic area for comparison among Py-GC-MS data. Compounds retained from 1.9 to 50 min and with an abundance above 0.10 % were considered for identification. Reproducibility ($n = 3$) was checked for both retention times and relative abundances showing mean RSD values of 1.7 % and 18 %, respectively for untreated samples, and 1.4 % and 7.4 % for thermally treated samples, respectively.

The similarity between the relative abundances (I) of homologous peaks (k) in two pyrograms (i and j), was also determined by a numeric index of similarity S_{ij} using the (1).

$$S_{ij} = \left[\sum\nolimits_{k=1}^{n}\left(I_i^k \middle/ I_j^k\right)\right] \Big/ n \tag{1}$$

with $I_i^k < I_j^k$, and n as the number of total peaks considered [25].

S_{ij} compares a pair of pyrograms without discriminating peaks and it ranges from 0 to 1: the closer the values are to unity, the greater the similarity. Five conventional levels have been suggested [25]: very high (> 0.85), high (0.85–0.75), medium (0.75–0.70), low (0.70–0.60) and very low (< 0.60).

The Shannon-Weaver diversity index (H) was calculated according to the eq. (2).

$$H = -\sum\nolimits_{i=1}^{S} P_i \ln P_i \tag{2}$$

where S is the number of pyrogram peaks with normalized area and P_i is the area of peaks i with respect to the total area of identified pyrolysis products [38].

2.5. *Principal component analysis*

Solo+MIA software (Eigenvector Research, Inc.) version 8.9.1, was used for principal component analysis (PCA), in order to investigate tendencies among samples and their correlation with the identified pyrolysis products according to loadings plots. In this study, the relative abundances (calculated as peak area divided by total chromatogram area in percentage) of compounds detected in Py-GC-MS chromatograms were established as variables. Data were mean-centered prior to PCA model development.

3. Results and discussion

3.1. *Preliminary characterization of compost samples*

An initial assessment of samples quality and maturity is shown in

Table 2
Characterization of samples. Mean ± Standard Deviation (n = 3).

Sample	pH	C (%)	N (%)	C/N	GI (%)	WDPT (s)
OMP	5.8 ± 0.3	54.6 ± 0.8	1.5 ± 0.1	36.4 ± 1.8	43.7 ± 2.2	2580 ± 52
COMP1	6.1 ± 0.4	51.9 ± 0.5	1.5 ± 0.1	34.6 ± 1.3	93 ± 5	930 ± 29
COMP2	8.9 ± 0.2	28.8 ± 0.9	1.7 ± 0.1	16.9 ± 1.3	110.4 ± 3.3	150 ± 16
COMP3	9.0 ± 0.2	22.6 ± 0.5	1.8 ± 0.1	12.9 ± 0.9	168.9 ± 4.4	65 ± 6
COMP4	8.8 ± 0.2	27.9 ± 0.3	1.7 ± 0.1	16.5 ± 0.9	165.6 ± 6.3	345 ± 14

Table 2 including an approach for both the chemical parameters and the assays of agronomic interest. Composted mixtures showed higher pH values and a decrease in C/N in comparison with raw OMP, as reported in other studies [39]. Nevertheless, COMP1 showed levels of pH, total organic carbon and C/N ratio very similar to raw OMP. This may be due to the high olive tree pruning percentage used during its elaboration (70 %), together with the absence of chicken manure, when compared to the rest of the composted materials. It should be noted that this sample is highly different from the rest, not only in terms of composition but also regarding how and for how long it was composted.

According to the results of the water-drop penetration time test, OMP showed the highest water repellency (2580 ± 52 s). Although composting reduced this parameter, COMP1 sample was still classified as severely water repellent according to the Bisdom et al. classification [36], whereas COMP2 to COMP4 were strongly water repellent. COMP3 presented the lowest hydrophobicity (65 ± 6 s). The seed germination test is a powerful tool to examine the potential phytotoxicity of organic amendments, one of the most relevant aspects to be considered. Only raw OMP with a seed germination index (GI) below 50% can be regarded as highly phytotoxic [40]. Concerning the composted materials, they all show GI values above 80%, which indicates their non-phytotoxic character. In particular, GI > 100 % was reported for COMP2, 3 and 4, meaning that they are phytonutrient or phytostimulant amendments.

C: total organic carbon; N: total nitrogen; GI: germination index; WDPT: water drop penetration time test. (Detailed characterization is found in [31]).

3.2. Identified pyrolysis products in OMP and COMP samples

A total of 108 different compounds were identified by analytical pyrolysis of OMP and compost samples. Pyrograms of raw olive mill pomace and a compost sample from the same producer (i.e., COMP4) are depicted in Fig. 1.

Identified chemical compounds that represent at least 0.5 % of the total peak area in any of the studied materials are listed in Table 3, totaling 50 major pyrolysis products. To facilitate comparison between individual samples, the identified products have been grouped into several classes, regarding their chemical structure and possible origin [20,26,41–43]: (a) benzene and substituted benzenes; (b) N-heterocycles; (c) phenol and substituted phenols; (d) substituted furans; (e) carbocyclic and aliphatic compounds and (f) fatty acids. Note that the overall percentage of total peak area for each chemical group in all analyzed samples is marked in bold in Table 3.

Overall percentages of the total peak area for each chemical group are included and marked in bold (which includes minor compounds not reported in the table).

RT: Retention Time.

Raw OMP stands out mainly for its very high fatty acids content, which constitutes 22.84% of total peak area. Among them, it can be noted the presence of two intense peaks at 29.4 and 33.1 min, corresponding to palmitic (C16:0) and oleic (C18:1 ω-9) acids respectively. This is not surprising since OMP still contains lipids remaining after the olive oil extraction from the olive fruit [44]. Aliphatic compounds, mainly high molecular weight n-alkanes and n-alkenes (MW > 112) and aliphatic alcohols, such as 1-decene and tridecan-1-ol, were also abundant in OMP pyrolysate, accounting for 7.03 % of total peak area.

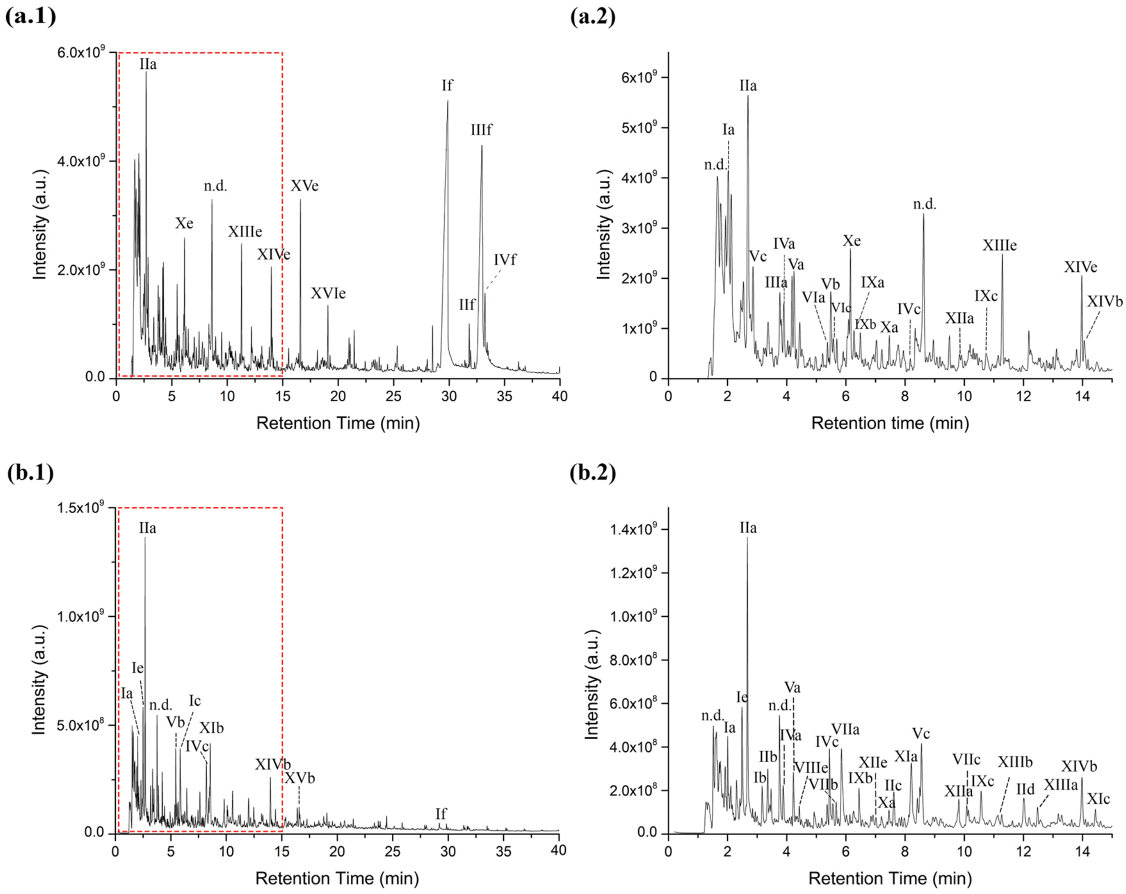
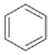
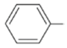
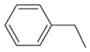
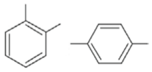
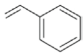
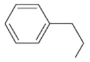
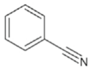
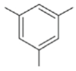
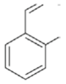
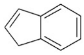
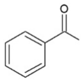
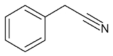
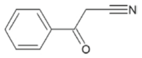
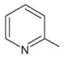
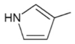
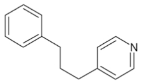
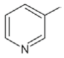
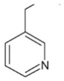
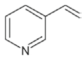
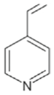
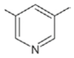
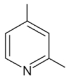
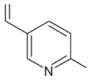


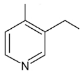
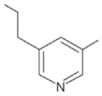
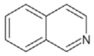
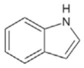
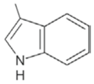
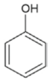
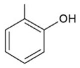
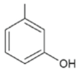
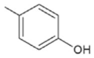
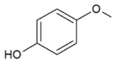
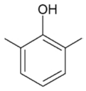
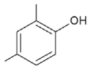
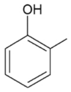
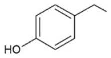
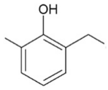
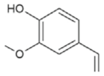
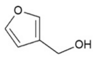
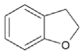
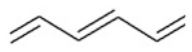
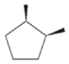
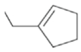
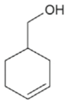
Fig. 1. Py-GC-MS chromatograms obtained for raw OMP (a.1) and COMP4 (b.1), both respectively collected and elaborated by Hermejor de la Reina organic oil factory (Villanueva de la Reina, Jaén). Zoomed-in views of each pyrogram are represented in (a.2) and (b.2). Compounds corresponding to each label are listed in Table 3.

Table 3
Major identified pyrolysis products (> 0.5% of total peak area in any of the samples) from OMP and COMP samples.

Peak No.	Pyrolysis product	*m/z*	RT (min)	% Of total peak area					Origin	Chemical structure
				OMP	COMP					
					1	2	3	4		
(a) Benzene and substituted benzenes				11.4	9.8	11.1	13.2	12.6		
Ia	benzene	78	2.01	3.4	1.6	1.7	1.9	1.2	Unspecific	
IIa	toluene	92	2.68	3.5	3.1	4.1	5.5	5.9	Unspecific	
IIIa	ethylbenzene	106	3.76	0.9	1.3	1.9	0.0	0.0	Unspecific	
IVa	(o-, p-) xylene	106	3.89	0.9	1.0	0.3	1.6	1.1	Unspecific	
Va	styrene	104	4.23	1.1	1.3	1.3	1.6	1.1	Unspecific	
VIa	propyl benzene	120	5.37	0.3	0.4	0.0	0.6	0.0	Unspecific	
VIIa	benzonitrile	103	6.02	0.0	0.0	0.0	0.0	0.5	Proteins	
VIIIa	mesitylene	120	6.26	0.0	0.0	0.0	0.0	0.7	Unspecific	
IXa	1-ethenyl-2-methyl benzene	118	6.27	0.6	0.0	0.0	0.0	0.0	Unspecific	
Xa	indene	116	7.46	0.4	0.0	0.0	0.0	0.5	Unspecific	
XIa	acetophenone	120	7.97	0.0	0.0	0.5	0.5	0.5	Lignin	
XIIa	benzyl nitrile	117	9.82	0.3	0.1	0.6	1.0	1.3	Proteins	
XIIIa	benzene propane nitrile	131	12.5	0.0	0.0	0.0	0.0	0.6	Proteins	
(b) N-Heterocycles				**2.3**	**1.9**	**12.7**	**18.5**	**15.1**		
Ib	2-methyl pyridine	93	3.17	0.0	0.0	0.5	0.7	1.0	Proteins	
IIb	3-methyl-1 H- pyrrole	81	3.40	0.0	0.0	0.6	0.7	1.2	Proteins	
IIIb	4-(3-phenylpropyl) pyridine	197	3.76	0.0	0.0	0.0	0.0	2.1	Proteins	
IVb	3-methyl pyridine	93	3.77	0.0	0.0	0.0	2.3	0.0	Proteins	
Vb	3-ethyl pyridine	107	5.45	0.9	0.6	1.9	2.6	1.3	Proteins	
VIb	3-ethenyl pyridine	105	5.67	0.4	0.4	0.7	0.9	0.6	Proteins	
VIIb	4-ethenyl pyridine	105	5.67	0.0	0.0	0.0	0.0	0.6	Proteins	
VIIIb	3,5-dimethyl pyridine	107	6.45	0.0	0.3	0.9	1.3	0.0	Proteins	
IXb	2,4-dimethyl pyridine	107	6.46	0.6	0.0	0.0	0.0	0.8	Proteins	
Xb	5-ethenyl-2-methyl pyridine	119	8.08	0.0	0.0	1.2	0.3	0.3	Proteins	
XIb	3-ethyl-4-methyl pyridine	121	8.56	0.0	0.0	2.9	4.3	2.3	Proteins	

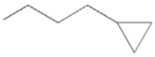
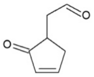
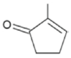
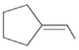
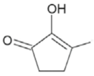
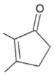
(*continued on next page*)

Table 3 (*continued*)

Peak No.	Pyrolysis product	*m/z*	RT (min)	% Of total peak area					Origin	Chemical structure
				OMP	COMP					
					1	2	3	4		
										
XIIb	3-methyl-5-propyl pyridine	135	10.9	0.0	0.0	0.0	0.6	0.0	Proteins	
XIIIb	isoquinoline	129	13.2	0.0	0.0	0.0	0.5	0.5	Proteins	
XIVb	indole	117	14.1	0.4	0.0	1.8	1.6	1.5	Proteins	
XVb	3-methyl indole	131	16.4	0.0	0.3	0.5	0.3	0.5	Proteins	
(c) Phenol and substituted phenols				**1.5**	**4.9**	**13.1**	**8.3**	**10.3**		
Ic	phenol	94	5.88	0.0	1.5	2.5	2.3	2.6	Lignin	
IIc	2-methyl phenol	108	7.65	0.0	0.7	1.8	1.3	1.0	Lignin	
IIIc	3-methyl phenol	108	8.24	0.0	1.0	2.8	0.0	0.0	Lignin	
IVc	p-cresol	108	8.27	0.4	0.0	0.0	2.1	2.5	Lignin	
Vc	mequinol	124	8.42	0.0	0.0	0.0	0.0	0.8	G-lignin	
VIc	2,6-dimethyl phenol	122	9.04	0.0	0.3	0.4	0.5	0.0	Lignin	
VIIc	2,4-dimethyl phenol	122	10.1	0.0	0.0	0.6	0.5	0.5	Lignin	
VIIIc	2-ethyl phenol	122	10.3	0.0	1.0	0.5	1.0	0.0	Lignin	
IXc	4-ethyl phenol	122	10.6	0.5	0.0	1.3	0.0	1.2	Lignin	
Xc	2-ethyl-6-methyl phenol	136	12.5	0.0	0.4	0.5	0.5	0.0	Lignin	
XIc	4-vinyl guaiacol	150	14.4	0.0	0.0	0.5	0.0	0.5	G-lignin	
(d) Substituted furans				**0.0**	**1.0**	**1.5**	**1.4**	**1.2**		
Id	3-furyl alcohol	98	3.59	0.0	0.0	0.4	0.5	0.0	Holocellulose	
IId	2,3-dihydrobenzo furan	123	12.1	0.0	1.0	1.1	0.9	1.2	Holocellulose	
(e) Carbocyclic and aliphatic compounds				**7.0**	**9.5**	**8.4**	**7.1**	**3.8**		
Ie	1,3,5-hexatriene	80	1.92	0.0	1.6	1.7	2.2	1.2	Unspecific	
IIe	*cis*-1,2-dimethyl cyclopentane	98	2.11	0.0	2.2	0.0	0.0	0.0	Unspecific	
IIIe	1-ethyl-1-cyclopentene	96	2.35	0.0	0.5	0.0	0.0	0.0	Unspecific	
IVe	3-cyclohexene-1-methanol	112	2.46	0.0	0.6	0.0	0.0	0.0	Lignin	

(*continued on next page*)

Table 3 (*continued*)

Peak No.	Pyrolysis product	*m/z*	RT (min)	% Of total peak area					Origin	Chemical structure
				OMP	COMP					
					1	2	3	4		
Ve	pentyl cyclopropane	112	2.86	1.4	0.0	0.0	0.0	0.0	Unspecific	
VIe	2-oxo-3-cyclopentene-1-acetaldehyde	124	3.39	0.0	0.9	0.0	1.1	0.6	S-lignin	
VIIe	1-nonanol	144	4.03	0.0	0.0	1.3	0.6	0.0	Lipids	$C_9H_{20}O$
VIIIe	2-methyl-2-cyclopenten-1-one	96	4.42	0.0	0.0	0.7	0.7	0.5	Holocellulose	
IXe	ethylidene cyclopentane	96	4.43	0.0	0.7	0.0	0.0	0.0	Unspecific	
Xe	1-decene	140	6.15	1.1	1.2	0.0	0.0	0.0	Lipids	$C_{10}H_{20}$
XIe	2-hydroxy-3-methyl-2- cyclopenten-1-one	112	6.94	0.0	0.0	1.2	0.5	0.0	Holocellulose	
XIIe	2,3-dimethyl-2-cyclopenten-1-one	110	7.19	0.0	0.0	0.6	0.7	0.5	Holocellulose	
XIIIe	1-dodecanol	186	11.3	1.2	0.0	0.0	0.0	0.0	Lipids	$C_{12}H_{26}O$
XIVe	1-tridecene	182	13.9	0.9	0.0	0.0	0.0	0.0	Lipids	$C_{13}H_{26}$
XVe	(*E*)-5-octadecene	252	16.6	1.4	0.6	0.0	0.0	0.0	Lipids	$C_{18}H_{36}$
XVIe	tridecan-1-ol	200	19.1	0.5	0.0	0.0	0.0	0.0	Lipids	$C_{13}H_{28}O$
(f) Fatty Acids and Fatty Acids derivatives				**22.8**	**15.7**	**0.2**	**0.1**	**0.15**		
If	palmitic acid	256	29.4	9.6	1.9	0.2	0.1	0.1	Lipids	$C_{16}H_{32}O_2$
IIf	*cis*-vaccenic acid (*ω*-7)	282	32.9	2.6	11.9	0.0	0.0	0.0	Lipids	$C_{18}H_{34}O_2$
IIIf	oleic acid (*ω*-9)	282	33.1	8.7	1.2	0.0	0.0	0.0	Lipids	$C_{18}H_{34}O_2$
IVf	arachidic acid	312	33.2	1.1	0.0	0.0	0.0	0.0	Lipids	$C_{20}H_{40}O_2$

Benzene and substituted benzene compounds constituted 11.4 % of the total area, being benzene (3.4 %) and toluene (3.5 %), the most abundant compounds detected.

In comparison with OMP, composted materials show hardly any lipid remains in their composition (only 0.1–0.2 % of palmitic acid) with the exception of COMP1, which still contains a significant quantity of fatty acids and their derivatives (15.72 %). It is clear that lipid biodegradation in this sample has not been as complete as for the rest of composted materials under study. Furthermore, *cis*-vaccenic acid (C18:1 ω-7) has been detected in much higher abundance when compared to OMP (11.9 vs. 2.6 % of total peak area). *Cis*-vaccenic acid is commonly used as a bacterial biomarker since it is produced by many species of heterotrophic bacteria. Thus, the presence of this monounsaturated fatty acid points to the activity of strictly anaerobic bacteria but also Gram-negative communities (e.g., *Pseudomonas*, *Paracoccus*, *Salmonella* and *E. coli* among others) [45,46]. During composting, microorganisms are involved in aerobic matter degradation and stabilization. Microbial activity, composition and abundance change considerably during the transition between thermophilic, mesophilic and maturation composting phases [47]. Previous studies reveal a decrease in bacterial community during the thermophilic and maturation phases, but a very marked increase during mesophilic conditions, together with fungi predominance [48,49]. Consequently, the high content of *cis*-vaccenic acid detected in COMP1 also indicates the presence of a significant quantity of Gram-negative bacteria [50], most likely due to the anaerobic processes taking place during the last two months of maturation without turning the pile, meaning it is not a fully composted material.

Regarding the rest of COMP samples, they are characterized by similar concentrations of aromatic compounds, including benzene and substituted benzenes (11.1–13.2 %), and phenolic compounds (8.26–13.1 %). This is in agreement with Plaza et al. [51] who reported that condensed aromatic compounds, COOH, phenolic-OH content and aromaticity increased in the final steps of olive-mill pomace composting. The higher content in nitrogen-containing compounds, mainly N-heterocycles (12.7–18.5 %), in the pyrolysates of these samples must be due to the presence of chicken manure (10–25 %) in the initial mixture of organic materials. The inclusion of this livestock waste shows a very positive effect on the composting process if compared to the use of only olive tree pruning as bulking agent, also in terms of fatty acids content as already pointed out. However, some compositional differences can also be found among COMP2, 3, and 4 through a more in-depth evaluation.

Both COMP2 and COMP3 contain 10 % of olive tree pruning and chicken manure. Sample COMP3 is notable for its more complex substituted benzenes (13.2 % of total peak area) and its lack of any G-lignin and S-lignin units. In COMP2, aliphatic compounds are more abundant, notably: 1-nonanol (1.3 %); cyclopentenone derivatives (1.2 %); 1-hexadecanol (0.2 %) and 1-hexacosene (0.1 %). Furthermore, nitrogen-containing compounds' content is about 6 % less than in COMP3 and COMP4. This result suggests that protein decomposition has not been completed yet in this material, which implies a lower level of humification and a higher C/N ratio [52]. Despite this, the formation of low molecular weight phenolic compounds associated with lignin decomposition [53], as well as methoxyphenols such as 4-vinyl guaiacol (0.5 %) and syringol (0.2%), shows little variation when compared to the other two samples.

On the other hand, COMP4 was prepared using a higher proportion of these raw materials (25 % each). As a result, the pyrolysis products mainly identified were N-heterocycles (15.1 %), mostly more evolved pyridine and pyrrole derivatives, primarily derived from chicken manure pyrolysis [41,54]. This sample is particularly characterized by a much greater variety (meaning not more quantity) of other N-compounds, the vast majority of which have not been detected in any of the other composted materials (note that many of the identified products are not listed in Table 3). In particular, several benzene derivatives had been identified: benzyl nitrile (1.3%), benzene propane nitrile (0.6 %) and benzonitrile (0.4 %). Moreover, this material has a slightly higher content of pyrrole derivatives (2.1 %), finding here five pyrrole rings: 3-methyl-1 H-pyrrole (1.2 %); 2,5-dimethyl-1 H-pyrrole (0.2 %); 3-ethyl-1 H-pyrrole (0.2%); 2-ethyl-1 H-pyrrole (0.2 %) and 2,3,5-trimethyl-1 H-pyrrole (0.2 %). The higher content of olive tree pruning can be responsible for this finding, due to the largest amount of chlorophyll pigments, primary precursors of such compounds [55]. As regards lignin-derived phenolic compounds (10.0%), the most relevant are syringol and guaiacol units (0.7% and 0.5%, respectively), and other interesting molecules such as mequinol (0.8 %), apocynin (0.4 %, vanillin-related compound) and eugenol (0.2%).

It is apparent from our results that, as composting of olive mill pomace progresses, the abundance of fatty acids and aliphatic compounds follows the order: raw OMP > low-evolved COMP ≫ evolved COMP. The opposite happens for phenolic compounds and nitrogen heterocycles. Py-GC-MS analysis has also allowed the identification of some furan derivatives products in COMP samples: 3-furyl alcohol and 2,3-dihydrobenzofuran. Furans are derived from polysaccharide fraction of microorganisms. However, these molecules were poorly represented in the pyrograms (0.4–1.2% of total peak area), as also reported in some previous studies [26,56]. Such low content of furan derivatives in samples, suggests the degradation of carbohydrates like holocellulose as composting advances [26]. Despite this, one of the main routes of cellulose degradation is depolymerisation to anhydrosugars and furans, so it might be expected that, during OMP and COMP pyrolysis, a higher proportion of furans would have been identified. Therefore, pyrolysis at high temperatures (600 °C) leads to an increase in protein decomposition (cracking reactions) and Maillard reaction between amino acids and sugars, responsible for the scarce furan production [57,58].

The index of similarity, S_{ij}, is useful to quantify differences between raw OMP and the four compost samples of different origins and characteristics (see Table 4).

Values in parentheses are the number of common peaks between two pyrolysates out of the 108 main peaks of each pyrogram.

The results reveal very low similarity between OMP and compost samples, ranging from 0.380 to 0.477. The highest index of similarity corresponds to the pair OMP and COMP1, which once again confirms that this sample is more similar to a raw material than to a mature compost. Differences between COMP1 and the remaining compost samples are still high (values around 0.6), which also indicates differences in maturation. The highest similarity index is found for COMP3 and COMP4 (0.761), both considered more mature according to the above-discussed results, despite the differences in the starting materials.

Table 4
Pyrolytic index of similarity (S_{ij}) of analysed samples.

Samples	COMP1	COMP2	COMP3	COMP4
OMP	0.477 (19)	0.389 (10)	0.380 (12)	0.429 (15)
COMP1		0.658 (21)	0.571 (21)	0.603 (13)
COMP2			0.760 (33)	0.711 (25)
COMP3				0.761 (30)

3.3. *Py-GC-MS characterization of changes with thermal treatment*

The transformations that happen when composted OMP is subjected to mild thermal treatments (175, 225 and 275 °C) were studied by Py-GC-MS. A total of 181 pyrolysis products were tentatively identified in the thermally treated samples. Fig. 2 shows the pyrograms collected for COMP1 and COMP3 samples as an example.

The exam of the global pyrolysis profiles revealed differences, especially between COMP1 and the rest of the materials. Compared to the pyrogram of the non-thermally treated sample, it can be observed how the abundance of n-alkanes and n-alkenes, as well as fatty acids such as palmitic and *cis*-vaccenic acids, clearly decreases with heating from 225 °C onwards. Interestingly, with treatments at 275 °C, N-containing derivatives of palmitic acid are formed, namely palmitoleamide and palmitoleonitrile. Amides can be formed by the thermal treatment of carboxylic acid and an amine without any catalyst present, generally at reaction temperatures above 140 °C [59]. For COMP2 to COMP4, an increase in benzene-derived compounds and N-heterocycles is particularly noticeable along with temperature rise. Considering the composition of these samples, it is worth emphasizing the occurrence of nitrogen-containing benzene derivatives such as benzonitrile (6.0 min) and benzyl nitrile (9.8 min). An interesting feature is observed at 175 °C for all samples to a greater or lesser extent: the increase in abundance of peaks due to high molecular weight carbocycles (MW > 390), long-chain alkanes (hentriacontane) and phytosterols like β-sitosterol and uvaol. Stigmasta-3,5-diene, which is typically formed by dehydration of β-sitosterol, was also detected. These compounds originate largely from epidermal plant cuticles and their increase with heating at 175 °C can be explained by preferential thermal degradation of other biocomponents, especially carbohydrates at this temperature [42].

The structural changes occurring in the molecular composition of compost samples with temperature are reflected in the evolution of the abundance of the main established chemical groups in the pyrograms. Roughly, the results showed an increase in the relative abundance of benzene derivatives and N-heterocycles, along with a decrease in the levels of phenolic compounds, aliphatic hydrocarbons, fatty acids and furan derivatives with the thermal treatments (see Figure S1 in the Supplementary Material). Additionally, the Shannon-Weaver index can be used as a representation of the diversity of the chemical compounds found. The untreated mature compost show higher complexity in organic matter in comparison with the immature COMP1, which has a lower value for this diversity index. As can be seen in Figure S2 (Supplementary material), the thermal treatment induces different changes depending on the starting material and the temperature. The most significant finding is that the treatment at 275 °C leads to similar values of the Shannon-Weaver index for all the samples. This is also observed in the high pyrolytic index of similarity (S_{ij}) observed for the samples treated at 275 °C (Supplementary Material, Table S1).

For a more in-depth study of the effects of the thermal treatments, Principal Component Analysis (PCA) was performed. The relative abundances of all the identified pyrolysis products were considered as variables. The first two PCs captured 72.2% of the total variance. The inspection of scores plotted in the space defined by PC1 and PC2 (Fig. 3a), revealed interesting clustering and tendencies in the analyzed samples. PC1 establishes a clear distinction between two samples of COMP1 (those at 65 °C, without thermal treatment, and heated at 175 °C) with positive score values and the rest of the samples. Looking at the loading plots (Fig. 3b-f), this difference is mainly due to the higher content of *cis*-vaccenic, oleic and palmitic acids in both samples (Fig. 3f), as well as other aliphatic compounds, being particularly relevant 1-decene, (*E*)− 5-octadecene and *trans*-1,2-dimethylcyclopentane (Fig. 3e). Furthermore, a clear effect of the thermal treatment is observed along the axis defined by PC2 with scores values increasing with the temperature of the treatment. The samples of mature compost (COMP2, 3 and 4) heated to 175 °C, group together with the untreated mixtures. This indicates that this temperature does not induce important

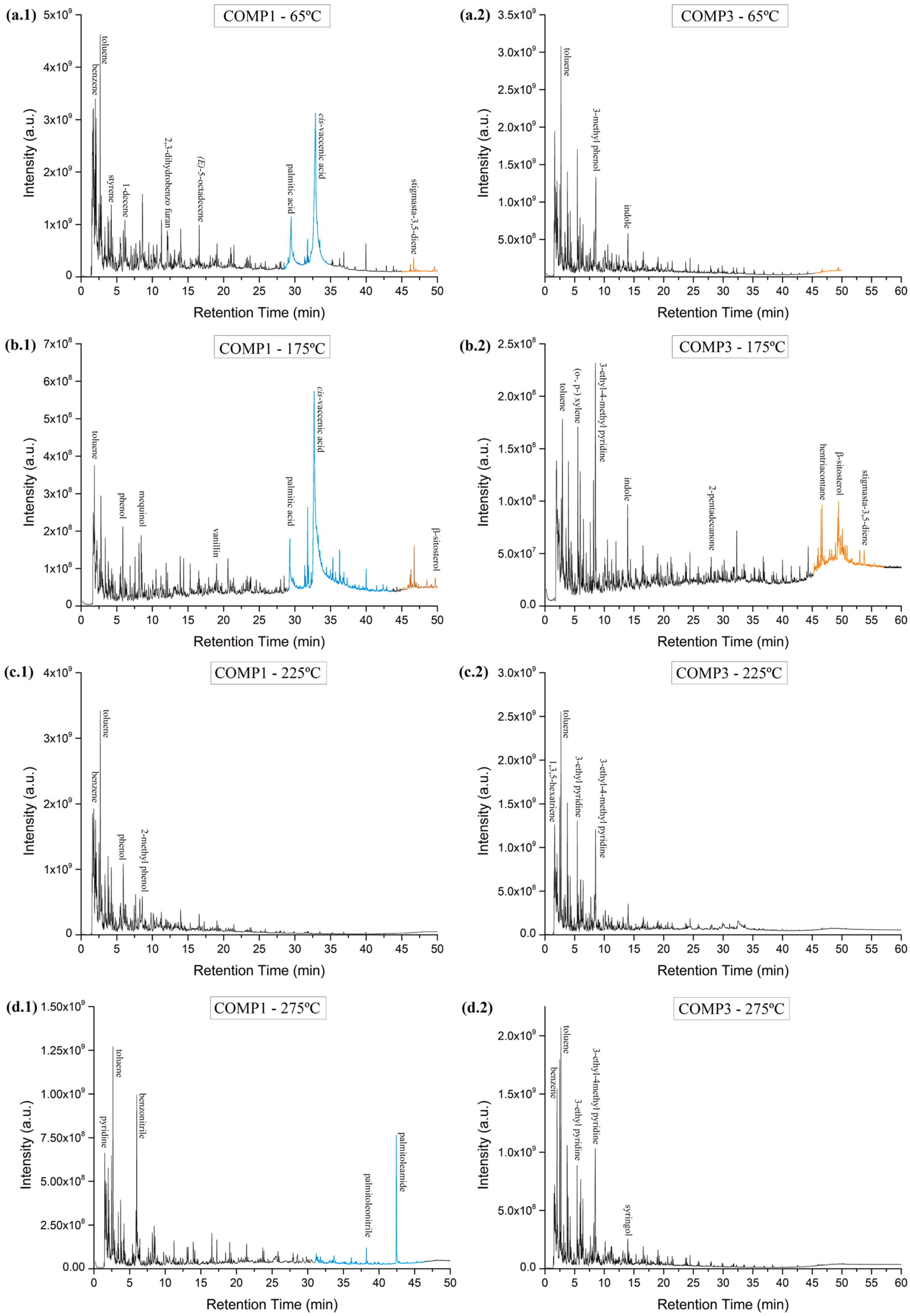


Fig. 2. Pyrograms of the composted materials (1) COMP1 and (2) COMP3 with thermal treatments at different temperatures: non-treated-65 ºC (a); 175 ºC (b); 225 ºC (c) and 275 ºC (d). Fatty acids and their derivatives are marked in blue, and high molecular weight carbocycles (MW > 390) in orange.

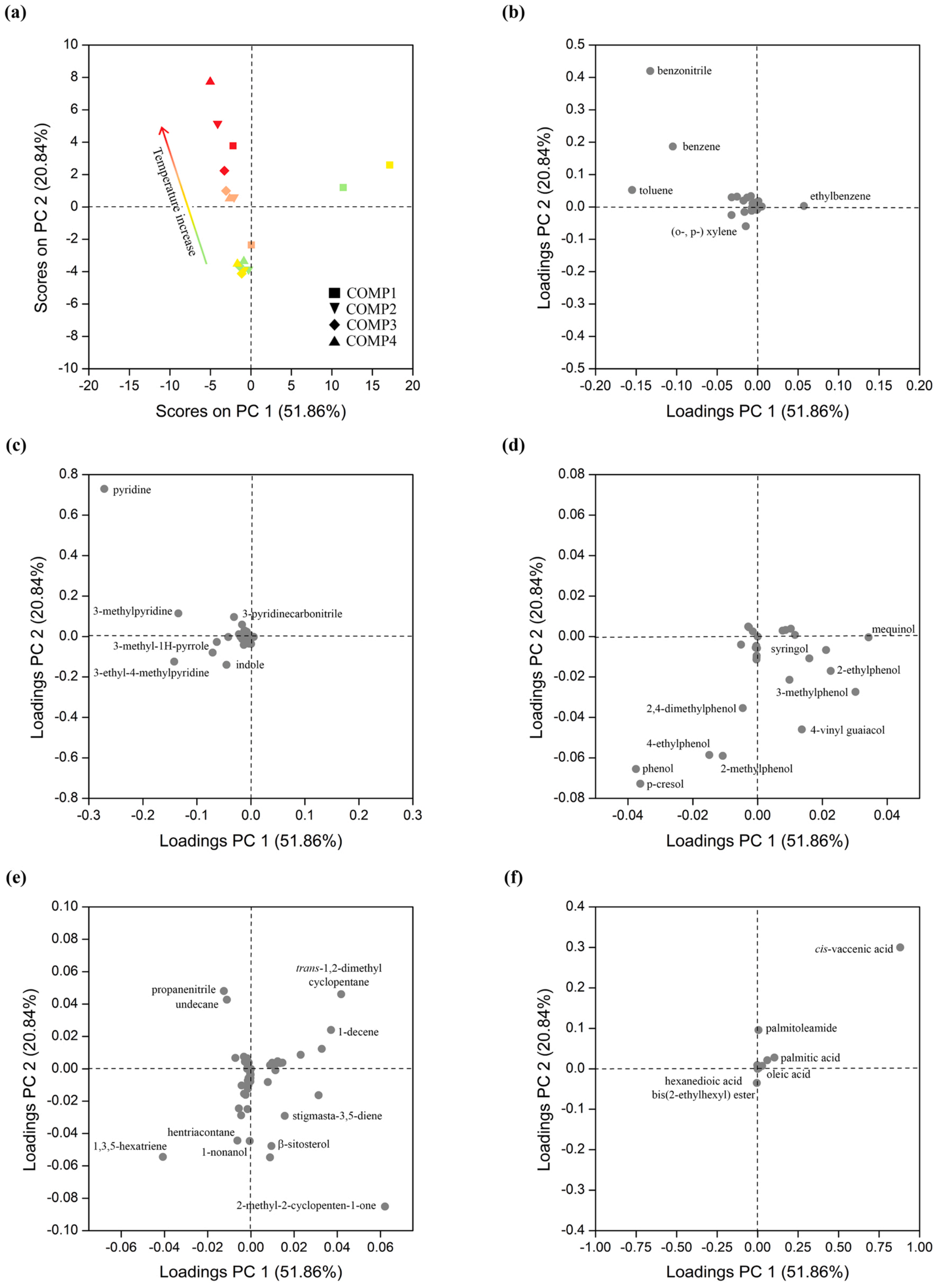


Fig. 3. (a) PCA score plot of the identified pyrolysis products. Color code is from green to red as temperature increases. PCA loadings graphs have been separated according to chemical groups as follows: (b) benzene and substituted benzenes; (c) N-heterocycles; (d) phenol and substituted phenols; (e) carbocyclic and aliphatic compounds and (f) fatty acids and fatty acids derivatives.

changes in the characteristics of the organic matter present in mature compost. This can be explained because, at 175 °C, probably only labile compounds are degraded and their amount was already low in mature compost since these materials were mainly biodegraded during the composting process. Interestingly, COMP1 sample heated at 225 °C is also very close to this cluster. This finding suggests that materials with an incomplete composting process can be transformed by thermal treatment into a more stable compost, exhibiting similar characteristics to mixtures that have undergone a more efficient composting process. Furthermore, when the compost were heated at higher temperatures

(225 and 275 °C), their molecular composition clearly changes and samples spread over PC2 axis (with increasing positive scores as temperature raises).

The combined analysis of the scores (Fig. 3a) and loadings plots (Fig. 3b-f) allowed us to better understand the molecular structural changes that occurred in compost organic matter due to these thermal treatments. Benzene derivatives were detected in the untreated samples with relative abundances between 9.8 % and 13.2 %. Among them, the major compounds were toluene (3.1–5.9 %), benzene (1.2–1.9 %), styrene (1.1–1.6 %) and xylene (0.9–1.6 %). There is an increase in benzene derivatives with heating, reaching relative abundances between 18.1 % and 23.1 % (see Figure S1). Looking at PCA results, we can attribute this rise at higher temperatures mainly to benzene and toluene with positive values in scores and loadings for PC2 in Fig. 3a and b. This behavior reflects the aromatization and loss of aliphatic functional groups mainly from lignin and carbohydrates. The increase in benzene derivatives is accompanied by a concomitant decrease in phenols (Fig. 3d) revealing a loss of hydroxyl groups from 175 °C to 225 °C and 275 °C, which represents lignin dehydroxylation, possibly in combination with carbohydrate aromatization. A similar effect has been described during biochar production, although in that case temperatures above 300 °C were employed [42]. Furthermore, samples heated at 275 °C are characterized by a higher abundance of benzonitrile (Fig. 3b), a product formed upon pyrolysis of phenylalanine-containing peptides [60].

The total content of identified N-heterocycles also rises with temperature, showing an increasing rate of about 7 % in COMP1, and reaching relative abundances around 25 % in the rest of materials, in which these pyrolysis products predominate at 275 °C. Looking at the loading and score plots (Fig. 3c and a), pyridine is the most abundant nitrogen-containing compound in samples under 275 °C, ranging in relative abundances from 4.2 % to 9.7 %. On the contrary, methyl pyridine derivatives and pyrroles are more abundant in the samples treated at lower temperatures. Dealkylation of the pyrolysis products has been reported to occur with artificial charring of biomass together with an increase in abundance from pyrroles to pyridines [42,43]. Our results show a similar trend, even when dealing with milder temperatures.

Furthermore, a decrease in carbocyclic and aliphatic compounds was observed with heating as can be deduced from the positive scores values of PC2 at higher temperatures (Fig. 3a) and the negative loading values for these compounds (Fig. 3e). This is particularly interesting since the presence of long hydrophobic chains in compost can have an impact on soil water repellency. As already mentioned, high molecular weight compounds (MW > 390), like different phytosterols and hentriacontane (a long-chain n-alkane (C_{31}) derived from leaf waxes), were detected in samples thermally treated up to 175 °C. The content in other aliphatic compounds (n-alkanes, n-alkenes and n-alcohols) also decreased with treatments above 175 °C. A similar trend of decrease with temperature was observed for furans derivatives, which represented a minor fraction in the pyrograms.

Fatty acids and fatty acids derivatives were identified mainly in COMP1 without thermal treatment and heated at 175 °C. In fact, at 175 °C, an increase in fatty acids total peak area was observed. As can be seen in the loading plot (Fig. 3f), this rise was mainly due to a higher relative contribution of *cis*-vaccenic acid. This could be explained by the thermal degradation of more labile polysaccharide fractions at such temperature in poorly composted materials (COMP1), leading to an enrichment of the compost in lipidic compounds. In the rest of composted materials, fatty acids and derivatives were not detected or in proportions lower than 0.2 % of total peak area. In COMP2, 3 and 4 treated at 175 °C, hexanedioic acid, bis(2-ethylhexyl) ester in relative percentages ranging from 0.4 % to 0.9 % was identified. This compound has been isolated from *Streptomyces* sp. [61,62], which plays a key role in lignin decomposition during the thermophilic phase of composting, as shown by Lu et al. [63]. These results suggest that at this temperature, lipidic compounds contained in compost are preserved. However, at 225 and 275 °C, fatty acids were totally eliminated in COMP2, 3 and 4. In the case of the less evolved sample (COMP1), only small quantities of palmitoleamide and palmitoleonitrile were detected, while the rest lipid-derived products were not, which indicates the potential of these thermal treatments to improve its quality.

The relationship between the molecular composition of non- and thermally treated compost samples and variables of agronomic interest (water repellency and germination index) is shown by the Pearson's coefficient matrix (Table 5).

WDPT: water drop penetration time test; GI: germination Index; B: benzene and substituted benzenes; N-het: N-heterocycles; P: phenol and substituted phenols; AL: carbocyclic and aliphatic compounds; FA: fatty acids and fatty acids derivatives; F: substituted furans. Statistical significance: * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$.

As seen in Table 5, water repellency (expressed as log (WDPT+1)) is directly correlated with the content of aliphatic compounds (0.5920) and furans (0.7235) and inversely correlated with the content of benzene derivatives (−0.7563). Thus, the treatments at 275 °C clearly decrease water repellency by increasing the relative content of aromatic moieties in compost. This is in agreement with the results shown in our previous work where a hydrophobicity index defined from the FTIR spectra of compost was also shown to correlate with water repellency, decreasing with thermal treatment at 275 °C [31].

Furthermore, the use of analytical pyrolysis has allowed the understanding of the increase in water repellency observed with heating at 175 °C (and 225 °C in the case of less mature compost) [31]. At this temperature, all the pyrolysates showed an enrichment in aliphatic substances, particularly high molecular weight carbocycles, long-chain alkanes and phytosterols. Probably, the thermal degradation of the more labile polysaccharide materials increased the relative amount of more resistant structures, like plant cuticles responsible for the formation of these compounds in the pyrolysates and the increase in water repellency. Regarding phytotoxicity, according to our results, it can be mainly attributed to the presence of fatty acids and other aliphatic compounds, showing inverse correlations of − 0.6982 and − 0.5061, respectively, with the germination index. Thermal treatment reduced toxicity by decreasing the amount of these substances and promoting the enrichment of compost in N-heterocycles, which showed a certain positive correlation with the GI (0.5571).

3.4. *Pyrolytic indices for the estimation of the degree of maturation and humification of OMP compost*

Variations in the relative abundance of the distinct chemical structures can be summarized in the form of pyrolytic indices based on ratios of specific peak areas of the pyrograms. Taking into account the results of the PCA analysis, some pyrolytic indices are proposed to consider the effect of the thermal treatment (see Table S1 in the Supplementary Material).

The index AL/AR, corresponding to the ratio of aliphatic to aromatic compounds, was calculated considering all the identified pyrolysis products. This is a very interesting parameter since it reflects clearly the different degrees of evolution of the original compost samples and the effect of temperature (see Fig. 4a). As can be seen, COMP1, an incompletely composted material, had a much higher value of AL/AR than the other samples. Thermal treatment at 175 °C increased slightly the value of this index for all the samples, while heating at higher temperatures produced a decrease, which was particularly intense in the case of the COMP1. The latter behavior reflects the increase in aromaticity in compost and the thermal degradation of aliphatic compounds (mainly lipids) present in this material at temperatures higher than 225 °C. These results are in agreement with those of our previous study from ATR-FTIR spectra of these samples, showing a decrease of the bands at 2920 and 2850 cm^{-1} (characteristic of aliphatic -CH_2- chains) at these temperatures [31]. According to García-Ruiz et al. [64] and Aranda et al. [65], these recalcitrant aromatic compounds might contribute to the low rate

Table 5
Pearson's correlation coefficients for composted olive mill pomace samples (n = 16).

	log (WDPT+1)	GI (%)	Σ B	Σ N-het	Σ P	Σ AL	Σ FA	Σ F
log (WDPT+1)								
GI (%)	-0.0321							
Σ B	-0.7563 ***	0.3086						
Σ N-het	-0.4118	0.5571 *	0.3676					
Σ P	0.4581	-0.0084	-0.6325 **	-0.1135				
Σ AL	0.5920 *	-0.5061 *	-0.6758 **	-0.5495 *	0.3114			
Σ FA	0.1554	-0.6982 **	-0.4478	-0.6945 **	-0.0201	0.3823		
Σ F	0.7235 **	-0.1761	-0.7814 ***	-0.3008	0.7415 ***	0.6428 **	0.1696	

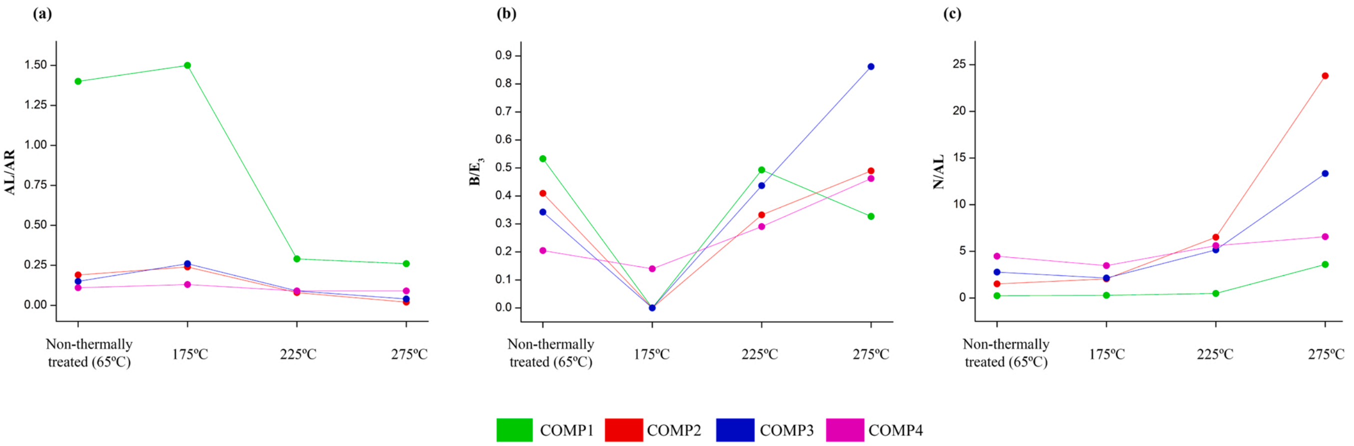


Fig. 4. Pyrolytic indices varying with temperature: (a) AL/AR: Aliphatic-C/Aromatic-C (b) B/E_3: Benzene/Toluene, and (c) N/AL: N-compounds/Aliphatic-C. Compost samples are marked in green for COMP1; red for COMP2; blue for COMP3 and purple for COMP4.

of carbon decomposition of this compost when applied to soils under field conditions, improving the physical and chemical fertility.

The ratio benzene to toluene (B/E_3) is commonly employed as a measurement of the extent of humification in soils [66]. Benzene and substituted benzenes are derived especially from pyrolytic degradation of condensed aromatic structures, while toluene comes from non-condensed ones with aliphatic chains. However, considering our results this humification index, originally defined for soil organic matter (SOM), seems not to be appropriate for the estimation of the degree of humification in compost. COMP1 showed the highest B/E_3 index (0.52) and the value was even higher for raw OMP (0.98, data shown in Table S1), whereas more evolved materials had lower values. Hernández et al. [67] reported similar findings with decreasing levels of benzene during composting of sewage sludge with sawdust. The formation of benzene by pyrolytic cyclization reactions from aliphatic substances (more abundant at the beginning of the composting process) has been suggested as a plausible explanation [67,68]. Furthermore, both OMP and olive leaves are rich in complex polyphenols that could also be responsible for benzene formation during pyrolysis [69]. The behavior of this index with the thermal treatments corroborates these findings. At 175 ºC there was a decrease in B/E_3 for all the compost samples (more pronounced for those with higher initial values). It is clear that labile compounds thermally degraded at this temperature (like polyphenols, organic acids or carbohydrates) were precursors of pyrolytic benzene in non-thermally treated samples and therefore responsible for the higher values of this index in immature compost. Then B/E_3 increased due to the condensation of aromatic structures, more stable at higher temperatures. The same trend can be observed for the ratio between N-containing aromatic compounds (sum of N-heterocycles, benzonitrile and benzyl nitrile) and aliphatic compounds (N/AL), which clearly rose with temperatures from 225 ºC. These recalcitrant aromatic compounds behave more similarly to soil humic substances [23].

Other useful indices are the ratio between non-alkylated and alkylated N-containing aromatic compounds, (BN+BzN+Py)/N-alk, and the ratio between benzene and phenol derivatives (Bs/Ps) (see Table S2, Supplementary Material). They reflect the dealkylation and dehydroxylation of the pyrolysis products with increasing temperatures, respectively.

4. Conclusions

Analytical pyrolysis (Py-GC-MS) has allowed the characterization of organic matter in composted olive mill pomace, showing a highly heterogeneous chemical composition depending on the mixture of original organic wastes and the composting process. Thus, composting involved a decrease in the content of fatty acids and aliphatic compounds of lipidic origin along with carbohydrate degradation and a progressive increase in phenolic and N-containing compounds in the pyrolysates. The use of chicken manure in the mixtures seemed to favor the composting process leading to materials with improved agronomic properties. PCA analysis was very useful to interpret the changes occurring in the molecular composition of compost organic matter with temperature. Furthermore, several useful pyrolytic indices are proposed to monitor the molecular changes induced by thermal treatment. An increase in benzene derivatives and N-heterocycles accompanied by a concomitant decrease in phenols revealed lignin dehydroxylation and demethoxylation when heating up to 275 ºC. In general, dealkylation of the pyrolysis products took place together with the increase of nitrobenzene and pyridine. Thus, the so-obtained materials may have intermediate properties between compost and biochar, since similar molecular changes have been reported to occur with artificial charring of biomass at higher temperatures. The effect of the treatment was particularly noticeable for the lowest quality material, although temperatures of 275 ºC were necessary to obtain a good-quality organic amendment similar to those obtained from more evolved compost samples heated at 225 ºC. The correlation of relevant agronomic characteristics (like water repellency and phytotoxicity) with the relative amount of certain groups of substances (identified by Py-GC-MS) demonstrates the usefulness of determining the molecular structures present in OMP compost as a first step towards predicting its behavior in soil.

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CRediT authorship contribution statement

M.P. Rueda and F. Comino: Data curation, Formal analysis, Writing – original draft. **V. Aranda**: Conceptualization, Writing – review & editing, Project administration, Funding acquisition. **A. Domínguez-Vidal**: Conceptualization, Investigation, Writing – review & editing, Supervision. **M.J. Ayora-Cañada:** Conceptualization, Investigation, Writing – review & editing, Project administration, Funding acquisition, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jaap.2022.105711.

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