

# Assessment of compost maturity by using an electronic nose

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## **Abstract**

The composting process produces and emits hundreds of different gases. Volatile organic compounds (VOCs) can provide information about progress of composting process. This paper is focused on the qualitative and quantitative relationships between compost age, as sign of compost maturity, electronic-nose (e-nose) patterns and composition of compost and composting gas at an industrial scale plant,. Gas and compost samples were taken at different depths from composting windrows of different ages. Temperature, classical chemical parameters, O<sub>2</sub>, CO, combustible gases, VOCs and e-nose profiles were determined and related using principal component analysis (PCA). Factor Analysis carried out to a data set including compost physical-chemical properties, pile pore gas composition and composting time led to few factors, each one grouping together standard composting parameters in an easy to understand way. PCA obtained from e-nose profiles allowed the classifying of piles, their aerobic-anaerobic condition, and a rough estimation of the composting time. That would allow for immediate and in-situ assessment of compost quality and maturity by using an on-line e-nose. The e-nose patterns required only 3-4 sensor signals to account for a great percentage (97-98%) of data variance. The achieved patterns both from compost (chemical analysis) and gas (e-nose analysis) samples are robust despite the high variability in feedstock characteristics (3 different materials), composting conditions and long composting time. GC-MS chromatograms supported the patterns.

*Keywords: green wastes, pruning residues, manure, biomass, composting, compost maturity, VOCs.*

## 1. Introduction

In accordance with the waste hierarchy, and for the purpose of reducing greenhouse gas emissions originating from waste disposal on landfills, the European directives about waste (European Union, 2008, 2009) point out the need to facilitate the separate collection and proper treatment of bio-waste in order to produce environmentally safe compost and other bio-waste based materials. Such waste, which includes biodegradable garden and park waste, when decomposing in landfills accounted for some 3% of total greenhouse gas emissions in the EU-15 in 1995. The Landfill Directive (European Union, 2009) obliges European countries to reduce the amount of biodegradable municipal waste that they landfill to 35% by 2016 (of 1995 levels) which will significantly reduce this problem. Composting has proven to be one of the most efficient and effective ways to manage these wastes, from both an economic and an environmental point of view. The composting process reduces toxicity, for example decreasing the concentrations of most pesticides (Büyüksönmez et al., 2000) and other organic pollutants present in feedstocks. Composting also reduces volume and moisture content of residues and transforms them into useful sources of organic matter for agricultural use contributing to enhanced soil quality and resource efficiency (Haug, 1993).

The composting process itself emits some gases into the atmosphere. Compost emissions have been studied in some length with widely varying results. They include non-greenhouse gases such as  $\text{NH}_3$  (Nakasaki et al., 2001) and CO (Hellebrand and Schade, 2008). Though CO is not a direct greenhouse gas, CO emissions have indirect effects on climate through enhanced levels of tropospheric  $\text{O}_3$  and  $\text{CH}_4$  and it might affect local air quality in and near composting facilities (Hellebrand and Schade, 2008).

Greenhouse gases such as nitrous oxide (N<sub>2</sub>O), methane (CH<sub>4</sub>) (Amlinger et al., 2008), and CO<sub>2</sub> and volatile organic compounds (VOCs) (Büyüksönmez, 2012; Büyüksönmez and Evans, 2007; Delgado-Rodríguez et al., 2012a; Komilis et al., 2004; Kumar et al., 2011) were also considered. The amount and type of emissions depends on a number of variables; the type and mix of feedstocks determine the molecules available for biochemical reactions, and their proportions. Feedstocks are considered the most important factor in determining what particular intermediate and potentially compounds develop (Büyüksönmez et al., 2007; Büyüksönmez et al., 2012). Additional managing factors such as temperature, O<sub>2</sub> levels, humidity, pH and duration of composting are also of significance (Akdeniz et al., 2010; Blazy et al., 2014; Büyüksönmez and Evans, 2007; Delgado-Rodríguez et al., 2012b; Romain et al., 2005).

Odours coming from wastes are caused by substances such as some inorganic gases (ammonia and hydrogen sulphide) and VOCs released during the biodegradation of organic residues (Shareefdeen et al., 2005). Electronic noses (e-noses) have proven useful to monitor the odour emissions in composting (Littarru, 2007; Sironi et al., 2007), and the aeration conditions (Rajamäki et al., 2005). A significant relationship between the biological activity (measured by the dynamic respiration index), and the odour molecule production (measured by an e-nose), has been found during high-rate food-waste composting processes (D'Imporzano et al., 2008). Gutiérrez et al. (2014) studied the evolution of total VOC concentration with maturity time, although they concluded the e-nose was unable to accurately predict the odour concentration and maturity time.

The weight of evidence indicates that it could be feasible to determine compost age, as sign of compost maturity, from e-nose patterns, in the same way that an experienced

operator can tell the condition of compost by its odour among other characteristics.

However, to date, few efforts (Romain et al., 2005) have been made to do this.

The objective of this research was to find qualitative and quantitative relationships between compost maturity, expressed as composting time, and e-nose patterns obtained from pore gas of different industrial scale compost piles. A set of compost chemical parameters and composition of pile gases have been also compared.

## **2. Materials and Methods**

### **2.1. Composting facility**

Compost and gas samples were taken from several composting windrows in a commercial composting facility located in Los Palacios, Seville province, SW Spain. Details about the selected composting piles (composting time, number of turnings) are shown in Table 1. Main feedstock at this facility were trimmings and cut branches from garden trees (windrows P4, P5, P14 and finished compost P17), being palm, pine and orange trees particularly abundant in yards and public gardens in the area. The maximum particle size after grinding was 15 cm. Finished compost (P17) was sieved in a 10 mm trommel. Some piles (PF2 and PF4) consisted of fine particles screened out from biomass used for energy in a different location (Huelva, SW Spain). In this case eucalyptus was the most common tree used in the energy plant. A pile composed of mature horse manure (M) was also included. Wheat straw was the main component in the horse bedding. This pile was installed at the facility 500 days ago. Then, after one year of composting compost batches from this pile were used when needed. Compost obtained at the facility was used to make potting soil and growing substrates by mixing

with peat, coconut fibre and pine bark. The composting process was carried out in trapezoidal windrows whose dimensions were 5 m wide in their base, 2.5-3 m high, and 40-50 m long. In the case of piles PF2 and PF4 the pile height was 1 m. The composting process in the facility could be described as: Not intensive, adapted to low water availability, moistening of windrows at start-up only, pile turning every 2 months to avoid excessive drying, residence time greater than 1 year keeping the windrows in the facility during the rainy seasons to take advantage of rain water. Composting under minimal technology level is a usual low-cost approach for green waste composting if a large, well isolated area is available (Haug, 1993).

Table 1 Composting piles

Pile Name	Feedstocks	Composting time (day)	Pile turnings	Sampling date
P4	Garden pruning	106	1	06/11/2013
P5	Garden pruning, fines from biomas, 2:1	145	2	06/11/2013
P14	Garden pruning, rice husk, 2:1	423	5	18/11/2013
P17	Garden pruning	510	8	18/11/2013
PF2	Fine particulate material from biomass	58	1	29/09/2014
PF4	Fine particulate material from biomass	111	2	29/09/2014
M	Horse manure	500	7	6/10/2014

## 2.2. Gas sampling and analysis

Pore gas samples were taken by drilling a gas probe (Compost Probe SON2IN, RAE Systems Inc., San José, CA, USA) into the windrow and pumping gas samples to a

multi-gas analyser, to e-nose and to sampling bags for GC-MS determinations. Compost temperature was measured simultaneously by inserting a probe at the same depths. Determinations with multi-gas analyser and e-nose were done in triplicate and single samples were used for GC-MS. The probe was inserted to a depth of 0.2, 0.4, 0.6, 0.8 and 1 m for analyses with the multi-gas monitor (MultiRAE IR PGM-54, RAE Systems, San José, CA, USA) by using its integrated sampling pump with a flow rate of 0.2 L min<sup>-1</sup>. This instrument incorporated sensors to determine the concentrations of O<sub>2</sub>, CO<sub>2</sub>, CO, total-VOCs and combustible (LEL sensor) gas. The VOCs sensor incorporated a 10.6 eV lamp for photoionization. Enough time (approximately 120 s) was left to purge the probe and sampling line and to obtain stabilized readings. The instrument does not detect water but its condensation on UV lamp could cause a loss of VOCs signal (Ojala et al., 2006). To avoid this effect, sampling lines were kept to a minimum and a Teflon filter (0.45 µm pore size) (RAE Systems, San José, CA, USA) was used as aerosol and particulate material trap. The instrument was calibrated by user by using standard gases contained in gas cylinders: 100 ppb<sub>v</sub> isobutene for VOCs, 0.88% CH<sub>4</sub> for the combustible gases (LEL) sensor and 50 ppm<sub>v</sub> CO. Although CO<sub>2</sub> measurements were registered, these data were not used because CO<sub>2</sub> sensor was calibrated to 5,000 ppm<sub>v</sub> and most of the readings overranged.

After using the gas monitor, e-nose measurements were performed at two depths in which aerobic (20 or 40 cm) or anaerobic (usually 40-60 cm) conditions were prevailing. In this work, PEN3 e-nose (Portable Electronic Nose, Airsense Analytics GmbH, Hagenover, Schwerin, Germany) was used. This e-nose has an array of 10 different metal oxide sensors (MOS) positioned inside a small chamber (1.8 mL). Orzi et al. (2010) described a similar e-nose with the same sensor configuration and a more general description on the basis and use of e-nose can be found in Romain et al.

(2005). The analytical system has a special integrated sampling system, which by an automatic control (auto-ranging) prevents overloading of the sensors and also leads to better and faster qualitative and quantitative analysis. A time of 50 s was selected as stabilization time, after which sensor readings were taken during 10 s.

Gas samples were collected in 2 L Tedlar bags (Supelco, Bellefonte, PA, USA) with a vacuum pump from the aerobic and anaerobic sampling point at each pile. As Tedlar bags can produce background signals for some VOCs such as N-dimethyl acetamide, acetic acid and phenol (Koziel et al. 2005; Trabue et al. 2006), the bags were previously pre-conditioned by cleaning them three times with N<sub>2</sub>. Following this procedure the background signal detected in synthetic air samples used as control was negligible. VOCs were analysed by means of GC-MS. The samples were protected from light exposure and analysed within 24 h. VOCs were pre-concentrated using solid phase microextraction (SPME) method. An SPME fibre coated with Carboxen/polydimethylsiloxane (Supelco, Bellefonte, PA, USA), was employed to capture VOCs in Tedlar bags. The SPME fibre was manually inserted into the bag for 30 min. The SPME fibre coating containing volatile compounds was inserted into the GC injection port at 230 °C and remained for 3 min for desorption. After each sample injection, fibres were kept inside the SPME needle to prevent possible contamination and were conditioned with helium at 250 °C for 10 min before reuse. The GC-MS system (GCMS-QP2010SE, Shimadzu Corporation, Tokio, Japan) was equipped with an Agilent HP-5MS fused silica capillary column (30 m long, 0.25 mm internal diameter, 0.25 µm film thickness). The GC was equipped with a split/splitless injection port operating in splitless mode. The oven temperature was programmed from 35 °C (5 min) to 270 °C (20 min) by increasing the temperature at 5 °C min<sup>-1</sup>. The transfer line was heated at 280 °C. The carrier gas was helium with a constant flow of 1 mL min<sup>-1</sup>



(mean velocity  $36 \text{ cm s}^{-1}$ ). The mass spectrometer was operated in scan mode (33–350  $m/z$ ). Identification of volatile compounds was achieved comparing the GC retention times and mass spectra with those, when available, of the pure standard compounds. All mass spectra were also compared with the data system library (NIST 08).

### 2.3. Compost sampling and analysis

Compost samples were taken from each pile at the same positions in which e-nose readings were carried out, that is, in triplicate for aerobic and anaerobic sampling points. On each pile, sampling sites were distributed as evenly as possible along it, halfway the top of the heap. Each sample was about 5 L.

Compost samples were analysed following standard procedures for soil improvers and growing media of the European Committee for Standardization (CEN). Moisture and laboratory compacted bulk density were determined following EN 13040 (CEN, 1999d). The results were expressed on a dry matter basis. Particle size distribution was determined by a sieve shaker (CISA MODRP.09 Sieve Shaker).

Fresh compost samples were used for the determination of electrical conductivity and pH in a 1:5 (v:v) aqueous extract (CEN, 1999a, b). Only sample fractions with a particle size below 5 mm were used, after grinding, for organic matter content (OM), chemical oxygen demand (COD) and nitrogen determinations. It was assumed that the transformation (degradation during composting) would be slower and less intense in the coarser ( $>5 \text{ mm}$ ) fractions. To include these coarser fractions in the sample intended for OM-related parameters could difficult the observation of the more intense changes which have taken place in the smaller fractions ( $<5 \text{ mm}$ ). OM was determined by dry combustion at  $450^\circ\text{C}$  (CEN, 1999c) and total N content was determined by distillation

after Kjeldahl digestion. Organic carbon content (OC) was calculated from OM by multiplying by the factor 0.58. COD and absorbance at 465 nm (A465) were determined after water extraction following the procedure indicated by Zmora-Nahum et al. (2005).

Compost samples from the WEPAL programs (Houba et al., 1996) were also analysed for quality control of analytical procedures. The results obtained for these samples agreed  $\pm 5\%$  with the certified results.

#### 2.4. Statistical analysis

The data sets from compost chemical analyses and e-nose were elaborated through statistical methods such as principal component analysis (PCA) for data reduction. In the case of compost chemical data the statistical analysis was carried out with the program SPSS 19 for Windows (SPSS, 2010). For e-nose results, the data reduction is displayed in a two dimensional figure, in which the axes correspond to the first two principal components and samples are distributed in this two dimensional space. The legends for the x- and y-axes contain the value of the variance achieved by the PCA component. Partial least squares regression (PLS) has been used for prediction of composting time, using the actual values as input results for the e-nose template. Each composting time was assigned to its corresponding e-nose measurements, and the descriptor was recalculated from PLS regression. These statistical analyses were done by the e-nose built-in software (WinMuster, 2010).

### 3. Results and Discussion

### 3.1. Temperature and gases profile in composting windrows

Pore gases and temperature changes with depth averaged for all piles are shown in Fig. 1. Compost temperature increased gradually with depth to reach 60 °C at 60 cm depth. Maximum temperature values were recorded at 80 cm in piles P4 (68 °C, Fig. 1), P5 (68 °C), and PF4 (69 °C) indicating the high microbial activity and degradability of that fresh material. Moisture content in the piles (Table 2) was low in view of the recommended requirements (minimum of 40% (Diaz and Savage, 2007)). Reached temperature values were surprisingly high despite the low moisture content in the piles (Table 2), although the pile size would contribute to maintain the generated heat. Matured composts (P17, M) exhibited temperatures in the range 50-60 °C in deeper (60-80 cm) layers, due also to the larger size of piles or the aeration during the screening process.

VOCs, CO and combustible gases increased with depth, and conversely, O<sub>2</sub> content decreased gradually to values lower than 2% at 60 cm. The increase with depth of gas content (All, Fig. 1) could be considered as normal in composting (Bueno Márquez et al., 2008) because sometimes anaerobic conditions appeared in the core part of the pile (Kumar et al., 2011). Even so, there appeared clear differences between the various composting piles. Surface (20 cm) total-VOCs contents were negligible in green waste (P4, Fig. 1) but significant in fine biomass and manure piles (15.5, 31.5 ppm<sub>v</sub> respectively, data not shown). He et al. (2012) found a maximum VOCs concentration of 85 ppm<sub>v</sub> during storage of forest residues. O<sub>2</sub> diffusion to internal layers (40 and 60 cm) was greater in coarse texture material, such as P4 (Fig. 1). The depletion in O<sub>2</sub> with depth was indicative of anaerobic conditions inside the composting pile and favoured the presence of VOCs, combustible gases and CO. The maximum CO concentration

was 787 ppm<sub>v</sub> at 80 cm in pile PF4, a value lower than those found during storage of forest residues (0.16 -1.52 % CO) (He et al., 2012; Kuang et al., 2009).

Table 2. Characteristics of the composted materials

	Unit	PF2 <sup>a</sup>	P4	P17	M
Moisture	g kg <sup>-1</sup>	113 (67) <sup>b</sup>	156 (37)	270 (33)	327 (31)
BD <sup>b</sup>	g L <sup>-1</sup>	424 (54)	nd	394 (25)	nd
pH 1:5 vol		6.15 (0.60)	8.17 (0.17)	8.11 (0.06)	8.98 (0.14)
EC <sup>c</sup> 1:5 vol	mS m <sup>-1</sup>	34.2 (7.5)	83.7 (14.4)	108 (8.4)	250 (27)
OM <sup>d</sup>	g kg <sup>-1</sup>	366 (51)	340 (21)	290 (24)	373 (27)
OC <sup>e</sup>	g kg <sup>-1</sup>	212	197	168	216
Kjeldahl-N	g kg <sup>-1</sup>	3.2 (0.7)	10.4 (0.6)	6.80 (0.6)	11.3 (0.5)
C/N		68.1 (11.9)	19.1 (1.3)	25.0 (3.7)	19.2 (1.0)
PARTICLE SIZE DISTRIBUTION					
>25 mm	%	0.5 (0.8)	3.0 (1.9)	0.0 (0.0)	0.0 (0.0)
10-25 mm	%	0.9 (1.7)	4.9 (1.9)	0.0 (0.0)	3.3 (1.0)
5-10 mm	%	2.9 (3.3)	8.5 (1.7)	2.4 (1.1)	8.8 (1.8)
2-5 mm	%	17.1 (4.8)	21.2 (10.8)	16.2 (2.6)	23.7 (1.6)
1-2 mm	%	15.8 (0.7)	48.6 (6.6)	40.2 (19.1)	17.4 (1.6)
<1 mm	%	62.8 (9.0)	13.8 (2.0)	41.2 (18.3)	46.8 (1.4)

<sup>a</sup> Pile PF2: Fine particulate material from biomass, Pile P4: Garden pruning, Pile P17 final compost from garden prunings, Pile M: Mature manure.

<sup>a</sup> Values in brackets are standard deviation, n=6; <sup>b</sup>BD: Compacted bulk density on a dry matter basis; <sup>c</sup>EC: Electrical conductivity; <sup>d</sup>OM: Organic Matter; <sup>e</sup>OC: Total Organic Carbon; nd not analysed.

Nitrogen gases were not measured during the composting process. The low N content (<10 g kg<sup>-1</sup>, Table 2) in the composting substrates makes high nitrogenous (NH<sub>3</sub>, N<sub>2</sub>O) emissions unlikely (Chou and Büyüksönmez, 2006), apart from M compost. It is worth noting that no noticeable odour was detected except near M pile.

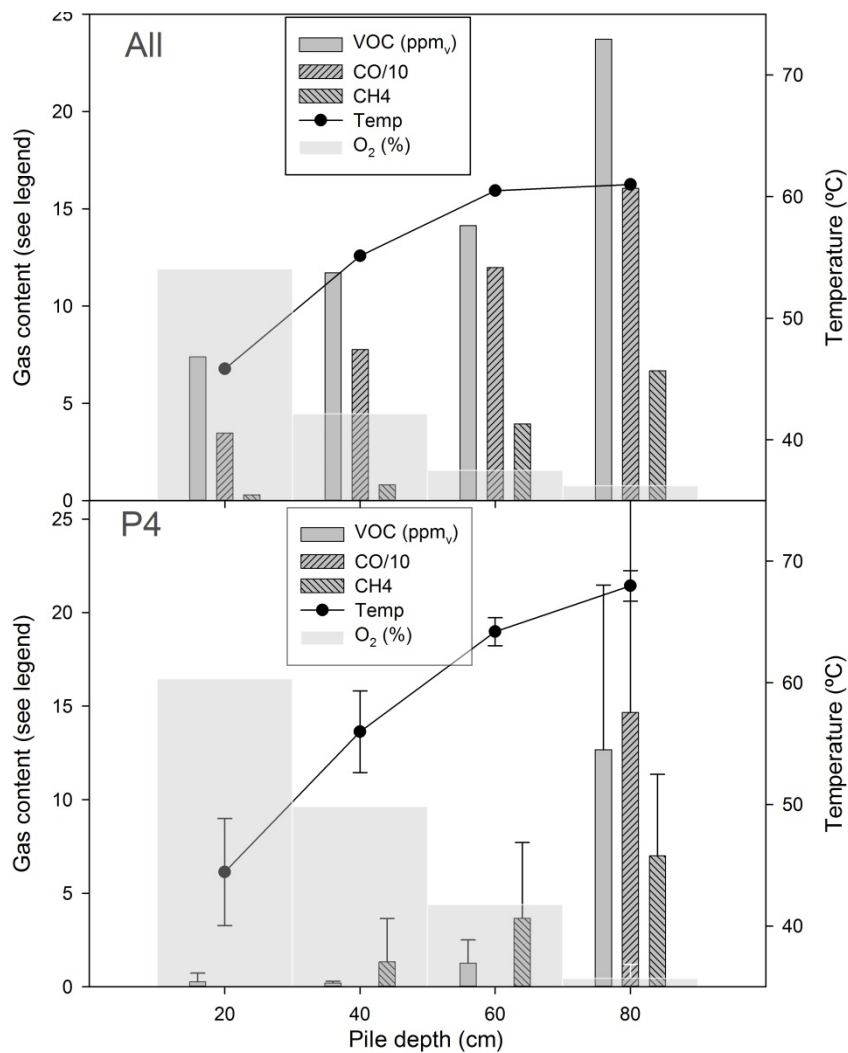


Fig. 1: Temperature and interstitial gas composition at different depths: O<sub>2</sub> (%), VOCs (ppm<sub>v</sub>), CO (ppm<sub>v</sub>) and combustible gases (% CH<sub>4</sub>): average for all piles (upper) and for pile P4.

### 3.2. Compost characteristics

Composting piles differed in their physical-chemical properties (Table 2). Fine biomass (PF2) contained a high percentage (78.6%) of fine particles (<2 mm), and exhibited slightly acidic pH, moderate OC content, low N content and high C/N ratio. Green waste (P4) had the greater percentage (16.4%) of coarser particles (>5 mm), and

moderate OC and N contents. Its C/N ratio (19.2) likely indicated that the particles smaller than 5 mm were at least partially degraded, in spite of the short time (106 days) from the process start. Finished compost (P17), which was already screened, did not contain coarse particles (97.6 % particles <5 mm) and its C/N ratio (25) was greater than that of P4. Its N content was lower than that of P4 although it could be considered in the usual range for green wastes. Green waste heterogeneity or breaking of coarser particles during the screening process could explain the apparent C/N increase and N decrease. Mature horse manure (M) had the highest basic pH and N contents, an adequate C/N ratio and a moderate percentage of coarse particles (12.1% particles >5 mm).

Factor analysis concerning the compost physical-chemical characteristics and the corresponding pore gas contents is shown in Table 3. The Kaiser-Meyer-Olkin Measure of Sampling Adequacy and the Bartlett's test of sphericity indicated the suitability of the used data for structure detection using Factor Analysis. Factor analysis found 5 factors which account for much variation (83.8 % of variance) in the original data. The obtained factors can be regarded as logical ones from the knowledge of the composting process evolution. Factor 1 was the most important one (42.9 % of variance) and it included (Table 3) composting time, OM content, electrical conductivity, moisture content, the extract absorbance at 465nm and C/N ratio. These parameters are usual process variables related to OM degradation during composting: the more composting time has passed the more mineralized and moist (likely due to rain) the material. The negative sign for OM content and C/N ratio agreed with the usual OM degradation and C/N decreasing trends during composting. Factor 2 (15.4 % of variance) connected VOC and CO contents in the interstitial pile gas to COD (chemical oxygen demand of water extract) in the compost samples. This relationship among these parameters could

have two non-selective implications: degradation of the compost organic matter increased water soluble organic species as a previous step to volatilization, or some of the VOCs generated were partially soluble in the water layer surrounding the compost particles, increasing COD. Factor 3 included coarser fractions (particles greater than 5 mm). Factor 4 grouped the N content of compost in direct relationship with the intermediate particle sizes (Fraction 1-2 and Fraction 1-5 mm) and in opposite relationship with the finest particles percentage (Fraction <1mm) likely due to the finest particles containing dust and soil with a lower N content. Finally, the factor 5 (11.4 % of variance) related combustible gas (CH<sub>4</sub>) content and temperature with O<sub>2</sub> content in opposite direction (lack of oxygen favoured anoxic conditions and an increase of temperature with depth). It is noteworthy that factor 5, which includes usual indicators of the biodegradation process during composting (temperature and O<sub>2</sub> content) accounted for such a poor part of the variation of the results. Presumably, temperature and O<sub>2</sub> content should have related to other gases contents (VOCs, CO) in greater magnitude. VOCs generation could have been controlled by the own nature of the green waste rather than by the likely low aeration of piles. These results agree with those of Büyüksönmez and Evans, (2007) who found for pruning that the composition of VOCs showed a large variation while the emission levels did not vary to the same extent of VOCs from woodchips.

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Table 3 Factor Analysis is primarily used for data reduction using principal components method

of extraction and Varimax rotation

Kaiser-Meyer-Olkin measure of sampling adequacy		0.583
Bartlett's test of Sphericity	Aprox. Chi-square	1208.05
	df	190
	Sig.	0.000

Component	Initial Eigenvalues			Rotation Sums of Squared Loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	8.573	42.86	42.86	4.268	21.34	21.34
2	3.088	15.44	58.31	3.441	17.20	38.54
3	2.493	12.47	70.77	3.424	17.12	55.66
4	1.477	7.39	78.16	3.340	16.70	72.36
5	1.120	5.60	83.76	2.279	11.39	83.75

	Rotated component matrix				
	Component				
	1	2	3	4	5
Composting time	<b>.886</b>	-.193	-.233	-.183	.152
Organic mater	<b>-.803</b>	.139	-.393	.083	.180
E.C.	<b>.762</b>	-.089	.041	.453	.380
Moisture content	<b>.744</b>	-.123	.037	.304	.058
Absorbance 465 nm	<b>.700</b>	-.058	.352	.332	.206
C/N	<b>-.690</b>	.235	-.422	-.463	-.164
pH	<b>.614</b>	-.520	.383	.415	.101
CO	-.138	<b>.922</b>	-.171	-.131	.006
COD	-.159	<b>.921</b>	-.107	-.136	.063
Total-VOCs	-.190	<b>.919</b>	-.150	-.077	.092
Fraction 10-25 mm	.097	-.102	<b>.891</b>	.232	.022
Fraction >25 mm	.192	-.120	<b>.842</b>	.123	.071
Fraction 5-10 mm	.033	-.202	<b>.790</b>	.363	.011
Fraction <1 mm	-.192	.182	-.450	<b>-.811</b>	-.145
Fraction 1-2 mm	.215	-.183	.095	<b>.773</b>	.260
Fraction 2-5 mm	.029	.014	.181	<b>.678</b>	-.182
N	.320	-.205	.407	<b>.669</b>	.352
O <sub>2</sub>	-.151	-.267	-.116	.098	<b>-.833</b>
CH <sub>4</sub>	.151	-.208	-.135	.161	<b>.764</b>
Temperature	-.033	.447	.360	.253	<b>.674</b>

E.C.: electrical conductivity; COD: Chemical oxigen demand;

### 3.3. Sample classification using e-nose



PCA analysis carried out by the e-nose using surface (aerobic) – deep (anaerobic) as starting groups misclassified some samples which were initially classed as "aerobic" but appearing in the "anaerobic" one. These misclassified samples were assigned to a new 'misassigned' class, and then, the result of the PCA is shown in Fig. 2. Two components were enough to explain 98.3 % of the variance using the readings corresponding only to three e-nose sensors: one for aromatic compounds, one for methane-aliphatic compounds and the third sensor covering a broad range of chemical compound types. Fig. 3 showed the chromatograms of surface and deep gas samples taken from the pile P17. Many alkanes, terpenes, cycloalkanes, aldehydes and aromatic compounds were the main VOCs appearing in these chromatograms. These compounds, primarily terpenes (natural compounds released from the feedstock) and to a lesser extent alcohols, ketones and benzenes, are usual VOCs detected in green waste composting as a result of biological breakdown. (Büyüksönmez and Evans, 2007). During the storage of forest residues the identified VOCs also included alcohols, terpenes, aldehydes, acids, acetone, benzene, ethers, esters, sulfur and nitrogen compounds (He et al., 2012; Svedberg et al., 2004). Chromatograms in Fig. 3 showed some of these VOCs, mainly alkanes (peaks 2: Isooctane; 3: Hexane, 2,4-dimethyl-; 4: Pentane, 2,3,4-trimethyl-; 7: Cycloheptane) and aldehydes (6: Hexanal; 9: Heptanal; 17: Nonanal) in lower or null concentrations in deep samples. Peaks of aromatic compounds (5: Toluene; 8: Xylene; 12: Phenol) and some terpenes (15: *p*-Cymene; 16: Eucalyptol) were similar in surface and deep samples likely due to a greater resistance to degradation of these compounds. Pinene and camphene were detected in greater concentration in the deep sample. These results were in correspondence with the higher loadings of methane-aliphatic, aromatic, and broadrange sensors in the PCA.

Thus, results of GC-MS analysis confirmed the sample classification between aerobic-anaerobic samples carried out by e-nose.

Fig 2

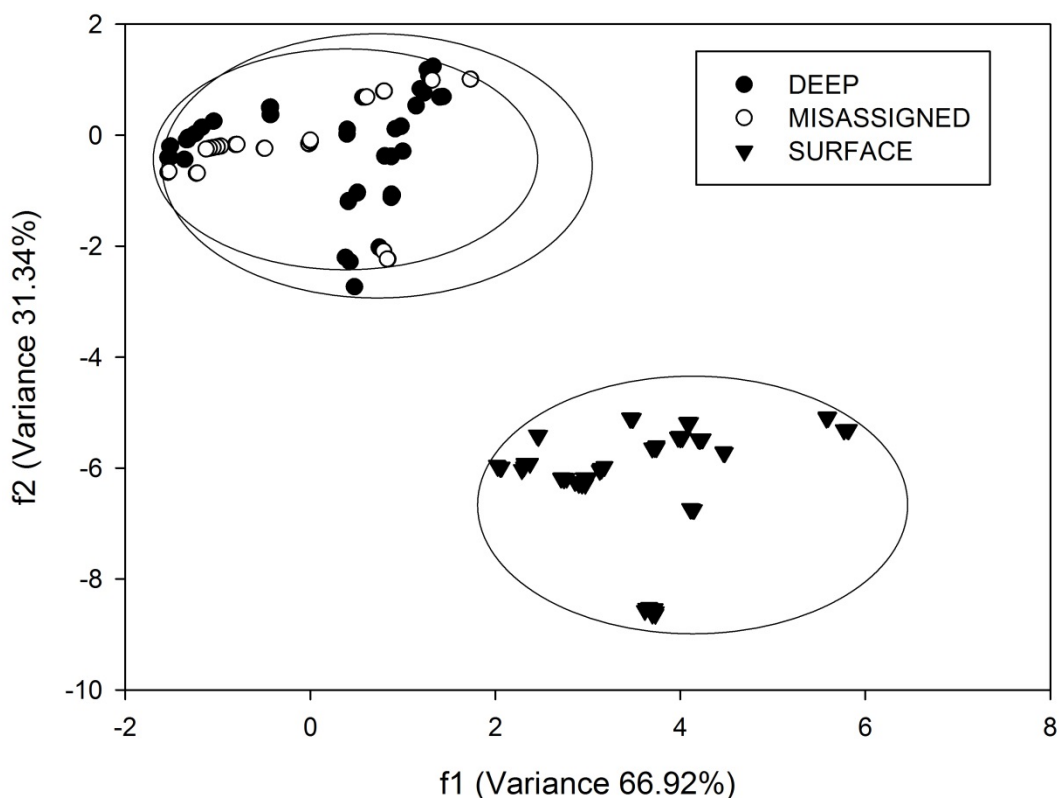


Fig. 2: PCA for e-nose results of pile gas samples. Contour lines show classes for superficial and deep gas samples. Three sensor readings (aromatic, broadrange, and methane-aliphatic) were used.

The misassigned gas samples corresponded to M, P4 and P5 surface samples, and their composition are shown in Table 4. These samples were taken at 20, 40 and 40 cm depth respectively and their average O<sub>2</sub> content was 10.8, 9.7 and 10.7% respectively although the variability among replicates was high (Table 4). Reported minimum level of oxygen to keep aerobic condition could vary from 12% (Chica Pérez and García Morales, 2008) to 15% (Diaz and Savage, 2007). Consequently, anaerobic conditions

could have evolved in the misassigned samples, at least in some microsites, changing their VOCs profile. In support of this argument detectable levels of VOCs were measured in all these samples and combustible gases (LEL) were also detected in some of M and P4 samples.

PCA analysis has also been carried out by using each pile class as starting groups, including both surface and deep samples in each group (Fig. 4). In this case, the two first components were enough to explain 96.7 % of the variance (most of the variance corresponding to the x axis function) using the readings corresponding to dilution factor (loading on y-axis) and 3 e-nose sensors, detecting sulphur-organic compounds (loading on y-axis), broad-alcohols and aromatic compounds (loading on x-axis). These results agree with those obtained by Gutiérrez et al. (2014) who found that the concentration of alcohols decreased with time of maturity.

Table 4. Gas composition of samples incorrectly classified from e-nose pattern (3 replications per depth).

Pile	Depth (cm)	O <sub>2</sub> (%)	VOCs (ppm <sub>v</sub> )	LEL (% CH <sub>4</sub> )
M	20	19.3	2.6	0.0
		4.2	34.4	3.0
		9.0	34.1	2.0
P4	40	9.0	0.2	0.0
		10.4	0.3	4.0
		9.6	0.1	0.0
P5	40	0.0	7.4	0.0
		5.8	0.1	0.0
		20.0	0.6	0.0

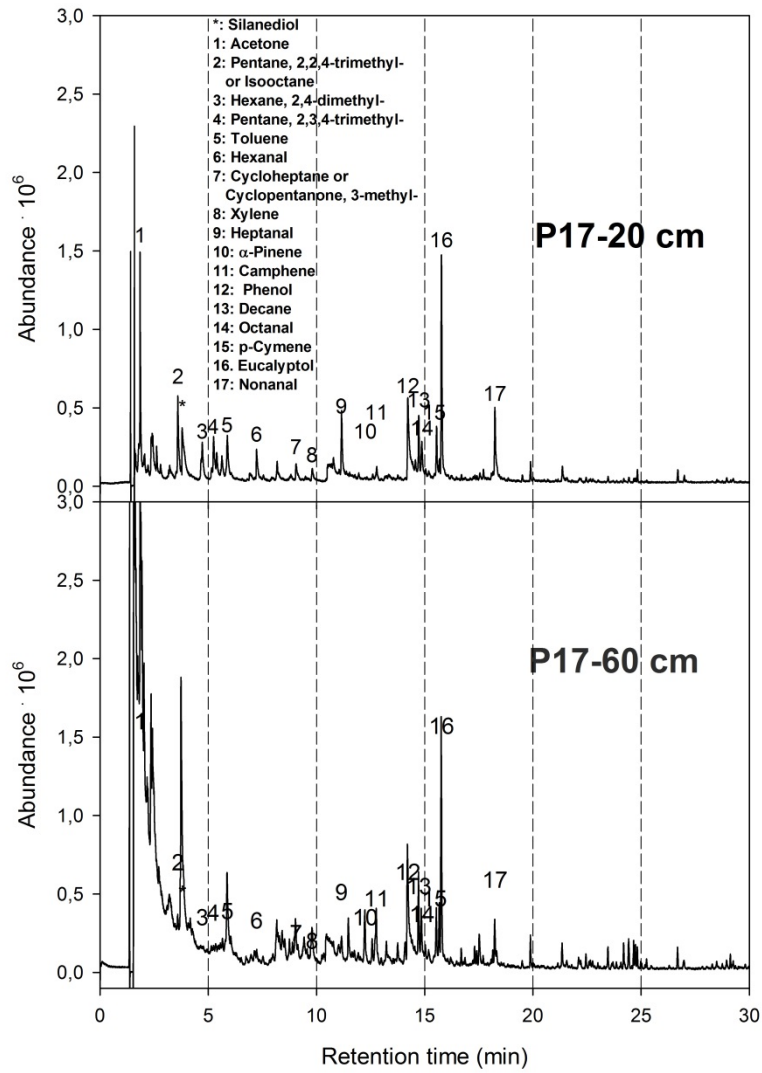


Fig. 3: Total ion chromatogram (TIC) using SPME-GC-MS of volatile organic compounds (VOCs) of surface and deep gas samples of pile P17. (a) P17-20 cm, b) P17-60 cm..

### 3.4. Predicting maturity from e-nose data

Partial least squares regression (PLS) has been applied from the PCA pattern classifying piles (Fig. 4) using the known composting time values (Table 1) as training values. The PLS predicted the composting time values shown in Fig. 5. In general terms, the predicted time corresponded with the actual time for P4 and P5 deep samples, M deep samples, P14 and P17 (surface and deep samples). The PLS overestimated the composting time in the case of PF2 and PF4 pile. The input composting time assigned to these piles corresponded to the known time period in the composting facility but it did not include the unknown time period that this material was left for (before and after biomass screening) in the energy plant before the material was moved to the composting plant. Presumably the actual degradation time would be greater and additionally the small particle size of this material would have favoured a quicker transformation before the composting (He et al., 2012; Jirjis, 1995). The PLS also overestimated the predicted composting time for P4, P5 and M surface samples (the misassigned samples in pattern of Fig.2). Air diffusion from the atmosphere around the piles into the more external pile layers, primarily in coarser P4 and P5 composts, could have favoured sample gas dilution altering the model prediction. This explanation seems reasonable considering that the VOCs production rates usually decreased with composting time (Gutiérrez et al. 2014; Komilis et al., 2004). Additionally the oxygen influx could have provoked the oxidation of some VOCs releasing new VOCs and altering their composition and consequently their classification and PLS value.

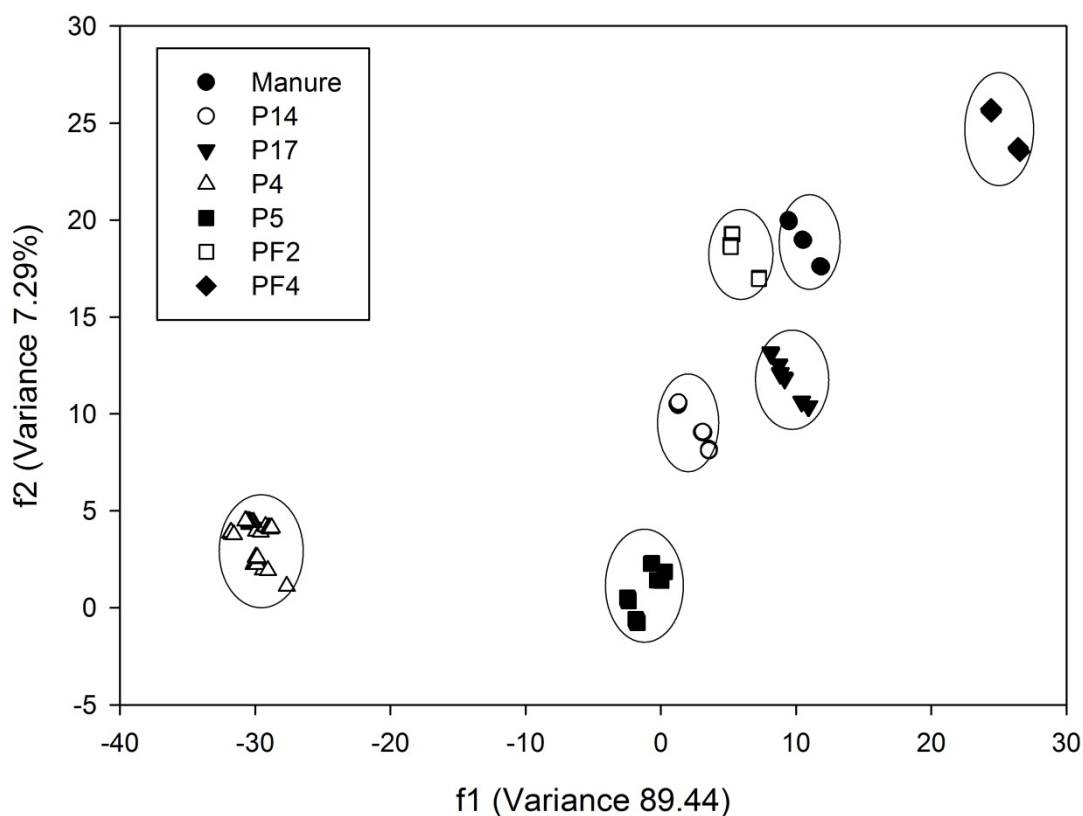


Fig. 4: PCA for e-nose results of pile gas samples. Contour lines show classes for deep gas samples of the different aged piles. Four sensor readings (aromatic, aromatic-aliphatic, broad-alcohol, and dilution factor) were used.

#### 4. Conclusions

Factor Analysis carried out to a data set including compost physical-chemical properties, pile pore gas composition and composting time led to few factors, each one grouping together standard composting parameters (process variables related to OM degradation during composting; pile gas composition and soluble organic matter; particle size and N content; temperature and aerobic-anoxic conditions) in a logical and easy to understand way. PCA obtained from e-nose profiles allowed the pile classification among aerobic and anaerobic ones and a rough estimation of the composting time. The e-nose patterns required only 3-4 sensor signals to account for a

great percentage (97-98%) of data variance. The achieved patterns from compost (chemical analysis) and gas (e-nose analysis) samples are robust despite the high variability in feedstock characteristics, composting conditions and long composting time. GC-MS chromatograms supported the patterns.

These are promising results in order to tune e-nose systems for in-situ assessment of compost quality and maturity.

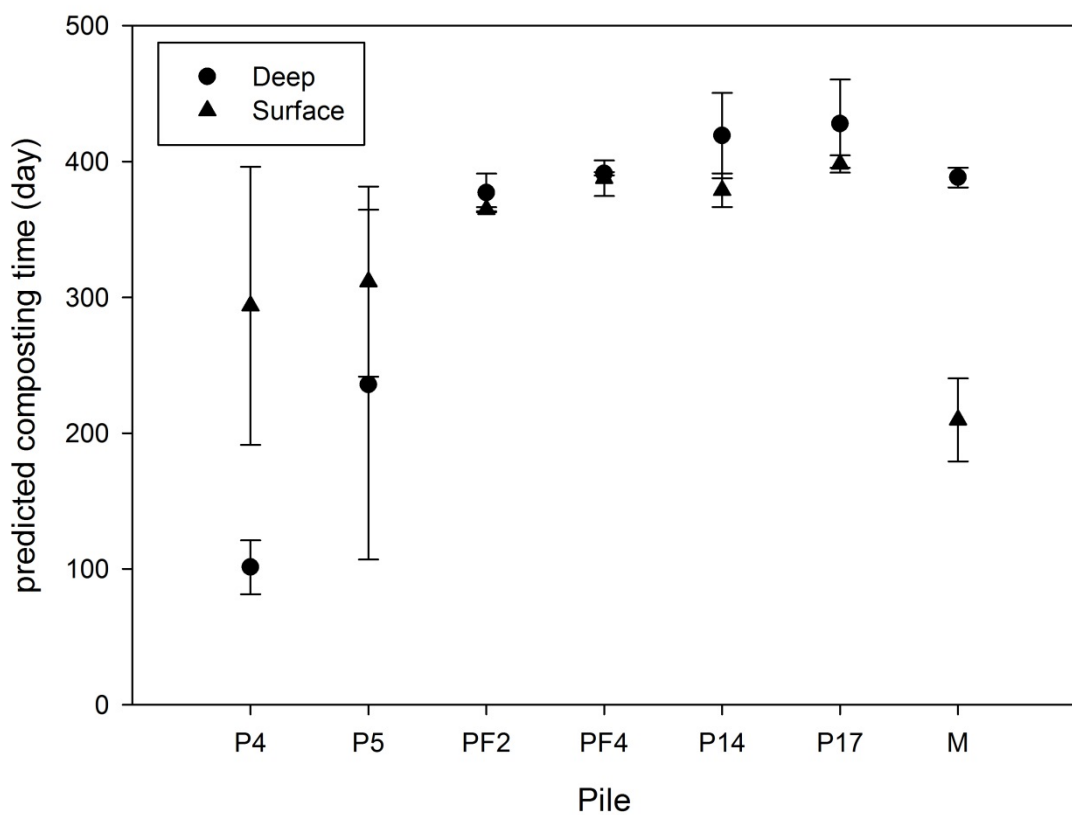


Fig. 5: PLS prediction of composting time from e-nose data of deep and surface gas samples.

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Appendix A. Supplementary material

ANNEX. Volatile organic compounds identified in all the piles by SPME-GC-MS.

Compound Name	Text no	CAS number	Formula	Molecular Weight	Ret. Time (min)	Identification ion m/z	Similarity
Acetone	1	67 - 64 - 1	C <sub>3</sub> H <sub>6</sub> O	58	1.85	58, 43	95
2-Butanone		78 - 93 - 3	C <sub>4</sub> H <sub>8</sub> O	72	2.43	43, 72	89
Pentane, 2,2,4-trimethyl- or Isooctane	2	540 - 84 - 1	C <sub>8</sub> H <sub>18</sub>	114	3.59	57, 56	98
Cyclopentanol		96 - 41 - 3	C <sub>5</sub> H <sub>10</sub> O	86	3.88	57, 86	87
Silanediol, dimethyl-		1066 - 42 - 8	C <sub>2</sub> H <sub>8</sub> O <sub>2</sub> Si	92	3.37	77, 45	92
2,4-Dimethylhexane	3	589 - 43 - 5	C <sub>8</sub> H <sub>18</sub>	114	4.72	43, 57, 85	93
4-Carene		29050 - 33 - 7	C <sub>10</sub> H <sub>16</sub>	136	5.17	93, 79, 136	90
2,3,4-Trimethylpentane	4	565 - 75 - 3	C <sub>8</sub> H <sub>18</sub>	114	5.27	43, 70, 71	96
Toluene	5	108 - 88 - 3	C <sub>7</sub> H <sub>8</sub>	92	5.87	91, 92	84
2,5-Dimethylcyclopentanone		4041 - 09 - 2	C <sub>7</sub> H <sub>12</sub> O	112	6.52	112, 69, 42	85
Hexanal	6	66 - 25 - 1	C <sub>6</sub> H <sub>12</sub> O	100	7.24	56, 44, 41	93
Diethylacetaldehyde		97 - 96 - 1	C <sub>6</sub> H <sub>12</sub> O	100	8.18	43, 72	88
Ethyl isobutyl ketone		623 - 56 - 3	C <sub>7</sub> H <sub>14</sub> O	114	8.57	57, 87, 114	95
4-Isopropylheptane		52896 - 87 - 4	C <sub>10</sub> H <sub>22</sub>	142	8.75	57, 98	88
Cyclopentanone, 3-methyl-	7	6672 - 30 - 6	C <sub>6</sub> H <sub>10</sub> O	98	9.04	98, 69, 55	89
Xylene	8	106 - 42 - 3	C <sub>8</sub> H <sub>10</sub>	106	9.79	106, 91	88
Heptanal	9	111 - 71 - 7	C <sub>7</sub> H <sub>14</sub> O	114	11.15	70, 55, 44	96
3,4-Dimethylcyclopentanone		58372 - 16 - 0	C <sub>7</sub> H <sub>12</sub> O	112	11.23	42, 69, 112	90
3,7,7-Trimethylbicyclo[4.1.0]heptane		6069 - 97 - 2	C <sub>10</sub> H <sub>18</sub>	138	11.96	67, 81, 95, 138	91
α-Pinene	10	80 - 56 - 8	C <sub>10</sub> H <sub>16</sub>	136	12.23	93, 92, 91, 136	96
Camphene	11	79 - 92 - 5	C <sub>10</sub> H <sub>16</sub>	136	12.76	93, 107, 121	93
tert-Butylbenzene		98 - 06 - 6	C <sub>10</sub> H <sub>14</sub>	134	13.41	91, 119, 134	89
trans-Carane		18968 - 23 - 5	C <sub>10</sub> H <sub>18</sub>	138	14.08	95, 123, 138	92
Phenol	12	108 - 95 - 2	C <sub>6</sub> H <sub>6</sub> O	94	14.21	94, 66	95
Decane	13	124 - 18 - 5	C <sub>10</sub> H <sub>22</sub>	142	14.73	43, 57, 71, 142	92
Octanal	14	124 - 13 - 0	C <sub>8</sub> H <sub>16</sub> O	128	14.89	43, 57, 69	86
p-Cymene	15	99 - 87 - 6	C <sub>10</sub> H <sub>14</sub>	134	15.54	134, 119	91
Eucalyptol	16	470 - 82 - 6	C <sub>10</sub> H <sub>18</sub> O	154	15.77	154, 139, 108	94
L-Fenchone		7787 - 20 - 4	C <sub>10</sub> H <sub>16</sub> O	152	17.69	69, 81, 152	90
Nonanal	17	124 - 19 - 6	C <sub>9</sub> H <sub>18</sub> O	142	18.25	41, 57	96
2,6,6-Trimethylbicyclo[3.1.1]heptan-3-one		18358 - 53 - 7	C <sub>10</sub> H <sub>16</sub> O	152	19.36	55, 69, 83, 152	94
Camphor		76 - 22 - 2	C <sub>10</sub> H <sub>16</sub> O	152	19.50	95, 108, 152	95