Odours and volatile organic compounds emitted from municipal solid waste at different stage of decomposition and relationship with biological stability

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Pre-print of: Scaglia, Barbara, et al. "Odours and volatile organic compounds emitted from municipal solid waste at different stage of decomposition and relationship with biological stability" in Bioresource technology (Ed. Elsevier), vol. 102, issue 7 (April 2011), p. 4638-4645.
The final version is available at DOI 10.1016/j.biortech.2011.01.016

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ABSTRACT

Odours and volatile organic compounds (VOC) emission during biological process used to treat MSW were studied under standardized conditions in order to detect potential risk for workers and population. Results obtained indicated that odours and VOCs emitted depends on the biological stability of waste measured by the Dynamic Respiration Index (DRI) and a very good correlation were found between these parameters (OU_E vs. DRI, $r = 0.957$, $p < 0.001$, $n = 6$; VOC vs. DRI $r = 0.969$, $p < 0.001$, $n = 6$).

GC-MS study of the VOCs was able to investigate on the nature of the molecule emitted. Two groups of molecules could be detected. The first group of molecules were degraded during the process and so their presence depended on the DRI, such as correlation found confirmed, i.e. alcohols vs. DRI, $r = 0.84$, $p < 0.05$, $n = 6$; aliphatic hydrocarbon vs. DRI, $r = 0.87$, $p < 0.05$, $n = 6$; ketones vs. DRI, $r = 0.84$ $p < 0.05$, $n = 6$; nitrogen compounds vs. DRI, $r = 0.87$ $p < 0.05$, $n = 6$; < 0.05; terpenes vs. DRI, $r = 0.95$ $p < 0.01$, $n = 6$). The second group, i.e. aromatic and halogenated compounds and furan persisted in the waste sample, becoming the more representative compound of the treated final waste. Nevertheless, molecules concentration was always lower than TLV-TWA. Odours perceived was due, above all, to N compounds produced during the biological process. However, it was not possible to indicate for the treated waste the specific molecules responsible for the odours detected.

Keywords: Dynamic Respiration Index; GC-MS; Mechanical Biological Treatment; Odours; VOC.

1. Introduction

The landfill represents the most common way of municipal solid waste (MSW) disposal. On the other hand, the anaerobic degradation of the biodegradable fraction of the landfilled MSW causes several environmental problems such as the production of methane, VOC odors and leachate, the presence of vectors – insects, rodents, and birds – public health hazard, explosions and plants toxicity. All these negative impacts and the long time required to stabilize the materials are the major issues that make landfills unsustainable. On the contrary, a landfill is defined sustainable if there is a safe disposal of waste, and its subsequent degradation to the inert state in the shortest possible time-span.

The strength of environmental impacts of MSW depends fundamentally on both the quantity and the characteristics of the organic fraction of MSW (OFMSW). The reduction of OFMSW in landfills can be obtained by three different approaches: i) separated collection of OFMSW to produce compost; ii) waste burning to produce energy and iii) mechanical-biological treatment (composting-like process) to produce a stabilized material.

The Mechanical Biological Treatment (MBT) refers to a series of mechanical and biological management of MSW performed with the purpose to reduce its the impact when being landfilled. MBT is extensively used in Europe, mainly in Italy, Germany and Austria, although many other countries, such as England and Spain and East Europe, have now started adopting MBT as their main strategy to reduce the organic fraction of MSW before landfilling.

From a processing point of view, MBT consists on the mechanical screening of MSW in order to separate the fraction characterized by low water content (generally lower than 250-300 g kg^{-1} wet weight – w.w.) and a high energetic content (EC) (EC generally > 12000 kJ kg^{-1} w.w.) (e.g. plastic and paper), from the fraction characterized by a high water content because of the high organic fraction (OF) contained (generally > 500 g kg^{-1} w.w.) and low

energetic value (EC generally < 9.000 kJ kg^{-1} w.w.) (e.g. kitchen and garden refuse waste). The fraction with high EC is then used to produce solid recovered fuel (SRF) and burned to produce electricity. On the other hand, the fraction rich in the organic matter is biologically treated in order to reduce the OF contained before being disposed in a landfill. Biological process represents the core of the MBT treatment.

Biological process consist in an solid-state aerobic process (composting-like process) during which forced aeration in the biomass allows the microbial oxidation of the OF contained in the MSW reducing its potential impact (waste reactivity) when MSW is landfilled (Scaglia et al., 2008; Scaglia et al., 2010). Biological processes, since uses forced aeration, are sources of gas emissions because of the presence in the exhaust air of inorganic and organic molecules coming from the microbial metabolism or due to the presence of volatile molecules present in the MSW (Pagans et al., 2006). From a chemical point of view, gas emissions are represented by CO_2 and methane, but, also, by nitrogen, sulphur, hydrocarbons, alcohols, ketones, esters and aromatic compounds (Homas and Fischer, 1992). Some of these compounds represent odours causing annoyance for the population (Pagans et al., 2006), whereas other compounds can be toxic for humans (Jung and Park, 2005).

Because of the rapid increase of the number of operative MBT plants in Europe, the quali-quantitative characterization of emission from MBT plants becames necessary to correctly plan new MBT plants and to preserve the health of the plant workers and of the inhabitant close to the plant (Biasioli et al., 2004).

By now, no regulation is imposed by the European Union with respect to the presence of odours in air coming from MBT plants (Drew et al., 2007). Nevertheless, national or local rules are present (e.g. Italian regional rules and German rules) (Adani et al., 2001; German Federal Minister for Environment, Nature Conservation and Nuclear Safety; 2001). These rules, generally, focuse the attention on the measurement and regulation of the odours emitted

by a composting or MBT plant by measuring the odour perceived by a human panel (i.e., dynamic olfactometry) (CEN, 2003). Nevertheless this approach only allows to measure the degree of annoyance of the plant for population close to the plant but says nothing about the hazardous of the organic molecules emitted. Thus, the impact of a MBT plant concerning air quality needs to be completed by detecting not only odour impact but also the kind of molecules emitted (Sironi el at., 2007).

The measurement of both odours and volatile organic compounds is usually carried out in the full-scale plants in order to detect the exposure of workers and the diffusion of gaseous emissions around the plant (Sánchez-Monedero et al., 2003). These measurements are very useful to measure and describe the impacts that occur for a particular existing plant. Nevertheless these measurements and relative results and cannot be applied to other MBT plants as, in situ data, are influenced by process parameters, atmospheric conditions and waste characteristics (Sánchez-Monedero et al., 2003). In addition, the management of the solid-state aerobic process may be not optimal, increasing the volatile emissions. In particular, the maintenance of optimal aeration conditions (optimal O_2 concentration in the biomass) of the biomass (D'Imporzano et al., 2008; Suler and Finstein, 1977; Hamelers, 2004) limits the formation of the anaerobic conditions in the biomass avoiding the production of intermediates of the anaerobic metabolism (e.g. sulphur and nitrogen compounds). Odour impact is most evident during the first phase of aerobic process when oxygen limitation for the aerobic biological process becames more evident. Oxygen limitation could be due to both the high rate of O_2 consumption because of the large amount of degradable organic matter present in the biomass and to insufficient air diffusion.

Differently of the molecules that have a microbial origin, hazardous compounds emitted during the process do not relate directly to the microbial activity, but depend, firstly, by both their presence and concentration in the MSW (Staley et al., 2006). On the other hand, biomass

120 temperature could play an important role in the volatilization of these compounds that
121 depends on their vapour pressure (Pierucci et al., 2005). Thus, both biological process and
122 waste characteristics play an important role in the VOC emission during the MBT process.
123 Recently D'Imporzano et al. (2008) correlated VOC emission during composting
124 process with the biological process by using the biological stability, i.e. dynamic respiration
125 index (DRI), as a descriptor of the stage of the biological process. DRI has been used
126 extensively to provide a complete picture of the potential waste impact due to biological
127 waste reactivity (Scaglia et al., 2008; Scaglia et al., 2010) including odors impact
128 (D'Imporzano et al., 2008).
129 In this way DRI, because of the particular conditions adopted for its measurement, i.e.
130 large amount of sample tested by simulating full scale aerobic treatment, could be a good
131 candidate to became an index to measure the potentiality of the impact of the waste in terms
132 of odors and, in general, of volatile organic compounds. The study of the odors emission
133 under controlled condition is not new (Staley et al., 2006).

134 The aim of this work is to correlate the degradation degree, i.e. biological stability, of
135 waste collected directly form a full scale MBT plant at different stages of biological process,
136 with the odours and VOC emitted from waste at different stage of biological treatment,
137 studied under standardized and controlled conditions. Obviously, these conditions do not
138 reflect necessarily what effectively full-scale plant emitted. Nevertheless, we think that this
139 study can suggest the use of DRI as an indicator of the potentiality of odour and/or hazardous
140 organic molecules production of waste during a biological process.
141
142 **2. Materials and Methods**
143 *2.1 Sample collection*

144 Waste samples were directly collected from the full-scale plants located in the North
145 Italy. MBT consisted in the MSW screening (hole diameter of 60 mm). Oversized fraction
146 was used to produce SRF burned in an incinerator. On the other hand, the undersized fraction
147 was successively treated by a composting-like process consisting in an high rate phase of 28
148 d, followed by a successive curing phase, for a total of 90 days of treatment.
149 Waste, during biological process was sampled at the start of the process (t = 0 d) (Sa
150 and Sb), at the end of the active phase (t = 28 d) (Ia and Ib) and at the end of the curing phase
151 (90 d) (Ea and Eb). Sampling was performed by using standard procedures (CEN, 2006).
152 Each sample, of about 40–50 kg of wet weight (w.w.), was then brought to the laboratory and
153 stored at 4°C and processed within 3–5 days from the date of its reception. A homogeneous
154 sub-sample of 1–3 kg (depending on the particle size) was taken from each biomass for the
155 successive chemical characterizations, previously to sample preparation.
156
157 *2.2. Experimental laboratory apparatus adopted*
158 Trials of biological treatment were performed by using a 30-L adiabatic reactor
159 (Costech International, Cernusco S.N., Italy; DiProVe, Milan, Italy) (Adani et al., 2001).
160
161 *2.3. MSW characterization*
162 *2.3.1. Chemical properties*
163 Dry matter (DM), volatile solids (VS) and total organic carbon (TOC) were
164 determined according to standard procedures (APHA, 1998). Total N-Kjeldahl (TKN) was
165 analysed on fresh samples according to the analytical method established for wastewater
166 sludge (IRSA CNR, 1994). pH was determined according to standard procedures (The US
167 Department of Agriculture & The US Composting Council, 2001). Dissolved organic matter
168 (DOM) was determined as reported previously in D'Imporzano et al. (2008). In particular 50

g of material was extracted in water (1:20 solid:liquid ratio, w:w) using a Dubnoff bath (60 rpm for 30 min at 40°C). The suspension obtained was filtered firstly using fast cellulose filter (Whatman paper filter N.4) and then on 0.45 µm Millipore membrane (Advantec MFS, Pleasanton, CA). For each DOM, organic carbon (DOC) was determined (ISO, 2002). All the analyses were performed in triplicate.

2.4. Biological reactivity parameters

2.4.1. Dynamic respiration index (DRI)

The samples were optimized for the moisture content (750 g kg^{-1} w.w. of the water-holding capacity) (Adani et al., 2001), and tests were performed by setting O_2 concentration at 140 ml L^{-1} in the outlet airflow (Adani et al., 2001). This value was maintained by a feedback control that automatically adapted airflow rate as a function of the O_2 concentration in the outlet airflow.

The hourly *DRI* (DRI_h) was determined by measuring the difference in the O_2 concentration (ml L^{-1}) between the respirometer inlet and outlet airflow, and was calculated as reported by Adani et al. (2006) (Eq. 1):

$$DRI_h\ (mg\ O_2\ kg\ DM^{-1}\ h^{-1}) = Q \cdot \Delta O_2 \cdot Vg^{-1} \cdot 31.98 \cdot DM^{-1} \quad (1)$$

where DRI_h is the hourly *DRI*, Q (l h^{-1}) is the airflow rate, ΔO_2 (ml L^{-1}) is the difference in the O_2 concentration in the inlet and outlet air flow of the reactor, Vg (L mol^{-1}) is the volume of 1 mole of gas at the inlet air temperature, 31.98 (g mol^{-1}) is the molecular weight of O_2 and DM (kg) is the initial total dry-matter content.

The *DRI* was calculated as the average of the 24 DRI_h values taken over the 24-hour period, characterized by the most intense biological activity (mobile mean), avoiding lag

phase (Adani et al., 2004) (Eq. 2). Each sample was tested twice. On average, about 58 h was required to determine the final *DRI* (Adani et al., 2004).

$$\text{DRI}\ (mg\ O_2\ kg\ DM^{-1}\ h^{-1}) = \sum_{\theta=0}^{24}(DRI_h)/24 \qquad (2)$$

DRI test were performed in duplicate, for a total of 6 trials.

2.5. Gaseous emission from MSW

2.5.1. Procedure for gas emission sampling

Emission sampling was performed during respirometric test. In particular, sampling occurred during maximum microbial activity, identified by the maximum DRI measured during the test, i.e. DRI_{MAX}. Gaseous emission produced from biomasses were caught up into a Nalophan™ bags connected adopting the following flows: 18 l kg DM^{-1} h^{-1}, 11 l kg DM^{-1} h^{-1} and 3 kg DM^{-1} h^{-1} for samples at t = 0, t = 28 days and t = 90 days, respectively. Different bag volumes for each sample (3 l and 20 l, respectively for GC-MS and olfactometric analyses) were filled for the successive analyses.

2.5.2. Gaseous emission and CG-MAS detection

Volatile organic compounds (VOC) from air samples were analyzed by SPME/GC-MS (Davoli et al., 2003). A manual SPME device and divinylbenzene (DVB)/ Carboxen/polydimethylsiloxane (PDMS) 50-30 µm fiber - Supelco, Bellefonte, PA, USA) was used. The compounds were adsorbed from the air samples by exposing the fiber, preconditioned for 3 h at 250°C , as suggested by the supplier, in Nalophan bags for 30 min at room temperature. A solution of deuterated p-xylene in methanol was used as internal standard (IS) for quantitative analysis. VOC analysis was performed using an Agilent 5975C

Series GC/MSD. Volatiles were separated using a capillary column for VOC (Meta.VOC, Teknokroma, Sant Cugat del Vallès (Barcelona, Spain) of 30 m x 0.32 mm and a film thickness of 3.0 µm. Carrier gas was helium at a flow-rate of 1 ml min^{-1}. VOC were desorbed exposing the fiber in the GC injection port for 3 min at 250 °C. A 0.75 mm i.d. glass liner was used and the injection port was in splitless mode. The temperature program was isothermal for 3 min at 35 °C, raised to 200°C at a rate of 8 °C/ min. The transfer line to the mass spectrometer was maintained at 250 °C. The mass spectra were obtained by electronic impact at 70 eV, a multiplier voltage of 1294 V and collecting data at a m/z range of 33–300. Compounds were tentatively identified by comparing their mass spectra with those contained in the NIST (USA) 98 library. A semi-quantitative analysis, for all the identified compounds, was performed by direct comparison with the internal standard. Results were expressed as µg m^{-3}.

2.6. Odour detection

2.6.1. Dynamic olfactometry

Olfactometric analyses were carried out in conformity with the standardized EN method n. 13725 (CEN, 2003). An Olfaktomat-n 6 olfactometer (PRA-Odournet B.V., Amsterdam, NL), based on the forced choice method, was used as a dilution device.

The measuring range of the olfactometer starts from a maximum dilution factor of 33,000 with a dilution step factor of 2. Results of olfactometry were expressed as odour concentration value (OU_E Nm^{-3}). On the other hand, the odour emission rate (OE) was calculated by using the following equation:

$$OE = CQ/S$$

in which OE is the odour emission rate (OU_E m^{-2} h^{-1}), C is the odour concentration (OU_E Nm^{-3}), Q is the incoming air rate to the flux chamber (0.35 m^3 h^{-1}) and S the surface covered by the chamber (0.196 m^2).

2.7. Statistical analyses

All statistical analyses, otherwise reported in the specific point, were performed using the SPSS statistical software (version 17) (SPSS, Chigaco, IL).

3. Results and Discussion

3.1. Chemical characterization and biological reactivity of the samples

Organic matter degradation during the biostabilization process leaded to a significant reduction of the content of VS and TOC measured in sample taken at different processing time (Table 1) and to an increase of the biological stability (Table 2) of the mass as also indicated by the DRI trends. The DRI measured for starting (t=0 days) and final samples (t = 90 days) were of 1,635± 53 and 147± 59 mg O_2 kg $DM^{-1}h^{-1}$ (Table 2), respectively, in agreement with the literature data obtained for similar waste and process (Scaglia et al., 2010). These data suggested that process studied represented well the typical waste and MBT performances.

3.2. Volatile emission characterizations

Results of dynamic olfactometric analyses (Table 2) showed a high level of odour perceived by the panellist used to perform the test when no-treated wastes were analysed. The OU_E became small after biological treatment (t = 28 and t = 90 days) (Table 2). Therefore, to low DRI values corresponded low OU_E values and vice versa, and a very good correlation was found between these two parameters: OU_E vs. DRI, $r = 0.88$; $p < 0.01$; $n = 6$.

Odours produced depend on the presence in the exhaust air of organic volatile compounds (Smet et al., 1999). GC-MS analysis allowed detecting the highest concentration (as $\mu g\ m^{-3}$) of volatile organic compound at the start of the process (Sample Sa and Sb) (VOC = 14,431 ± 306 $\mu g\ m^{-3}$) (Table 2). Then, a progressive reduction of the VOCs concentration occurred for the intermediated samples (after 28 days of process) (Sample I_a and I_b) (OU_E = 4,539 ± 573 $\mu g\ m^{-3}$) and for the final samples (after 90 days of process) (Sample E_a and E_b) (OU_E = 205± 30 $\mu g\ m^{-3}$) (Table 2). A total reduction of 98.6% of the VOC concentration was calculated from the start to the end of the process. VOCs concentration also correlated well with both OU_E and DRI (VOC vs. OU_E, $r = 0.957$; $p < 0.001$; $n = 6$; VOC vs. DRI $r = 0.969$; $p < 0.001$; $n = 6$; respectively) confirming that VOCs were responsible of the odours perceived by panellist and that their presence was related to the biological reactivity of the waste, i.e. their biological stability.

VOCs are the products of the anaerobic respiration or fermentation processes that occur in the biofilm-particle, when oxygen became a limiting factor of the aerobic oxidation of the microbial-available substrate, i.e. the dissolved organic matter (DOM) (Hamelers, 2004; D'Imporzano et al., 2008). Oxygen concentration in the particle-biofilm depends on the oxygen concentration in the air, the oxygen uptake rate to degrade substrate and temperature. Even if a correct airflow rate is maintained during the biological process, such as in this case, O_2 in the particle-biofilm can became the limiting factor the oxidation of DOM (D'Imporzano et al., 2008). This could occur when there is a high DOM concentration that determines a very high OUR that limits the presence of oxygen in the particle-biofilm because of O_2 fast depletion (Hamelers, 2004). High biomass temperature could contribute, also, in the O_2 depletion in the particle-biofilm, because it reduces the oxygen solubility in water (D'Imporzano et al., 2008). These conditions occur, typically, during the first stages of the

biological process when no degraded substrate (untreated MSW) is present and a high temperature characterizes the biological process.

A high DOM content was detected for the starting sample analysed (Table 1). In addition, high temperature was registered during DRI test performed on these samples (Table 2). Both these conditions suggested low O_2 presence in the biofilm-particle and so, the preferential presence of anaerobic/semi-anaerobic conditions that were responsible for the high VOCs production. On the contrast, DOM concentration considerably decreased for samples taken after 28 d and 90 d of the biological process (Table 1), in a same way that biomass temperature registered during DRI test (Table 2). These conditions lead to a strong reduction of VOCs produced because of both less available substrate, and to the higher O_2 concentration in the biofilm-particle with respect to the starting conditions. The strong negative correlations found for VOCs and OU_E, vs. DOC content (VOCs vs. DOM: $r = 0.988$, $p < 0.0001$, $n = 6$ and, OU_E vs. DOM: $r = 0.926$, $p < 0.008$, $n = 6$) seems to confirm this hypothesis.

Both OU_E and VOC are quantitative data and say nothing about the quality, i.e. the origin and the nature of the organic or inorganic molecules emitted during the biological processes. This fact appears more important for the MSW that is characterized, also, by the production during the storing or during the biological transformation, of hazardous molecules of non-biogenic origin that could be of high risk for health of workers in MBT plant (Elliott et al., 1996). In consequence, air samples were analysed by GC-MS and data obtained referenced. In total 147 VOCs were detected in the air emitted during the test performed on MSW sampled at different MBT process stage (Table 3). The number of molecules was larger for the starting samples than for the others, and a progressive reduction of the VOC complexity (molecule number) occurred within the biological process (Table 3). Because of this complexity, in this study, only the principal organic compounds that represented at the least the 10% of the class in which organic compounds are comprised, were considered

315 (Staley et al., 2006) (Table 3). The organic compounds detected agree with those reported in
316 literature as typical of MSW emission under aerobic conditions (Pierucci et al., 2005; Staley
317 et al., 2006), and they accounted for 69 ± 0 % (sample S), 90 ± 13 % (Samples I) and 77±11
318 % (Samples E) of all molecules detected in this study, (Pierucci et al., 2005; Staley et al.,
319 2006). VOC detected were resumed in ten different chemical class of compounds: aliphatic
320 hydrocarbon, alcohols, esters, ketones, terpenes, furans, nitrogen, sulphur, aromatic
321 hydrocarbon and halogenated organic compounds (Figure 1). This classification allowed a
322 first description of the VOCs emitted by samples taken at different degradability stages.
323 VOCs presented in the air of the starting samples (Sa and Sb samples) consisted (on a
324 relative basis, i.e. %) above all (average of 2 measures) of aliphatic hydrocarbons (41±12%),
325 terpenes (31±7%), ketones (11±4%) and aromatic hydrocarbons (8±6%) compounds (Figure
326 1). Changes in VOC pattern occurred, specifically, during the active phase of the
327 biostabilization process. Samples after 28 d of biological process (Ia and Ib samples) were
328 characterized by the high presence of terpens (67±7%) and less of aromatic compounds
329 (9±4%). The samples taken at the end of the biological process (Samples Ea and Eb), i.e. after
330 90 days of process, were constituted, mainly, of aromatics compounds (68±24%), while the
331 other compounds constituted a marginal fractions of the VOCs. Obviously these patterns
332 represent the relative abundance of VOCs in the sample studied and must be related to the
333 absolute VOC concentration values (Table 3). From the Table 3, two different trends
334 concerning VOC production during the biological process can be observed. In particular, a
335 first group of organic compounds reduced their concentration during the biological process.
336 They were representative of compounds that were extensively degraded during the biological
337 process: i.e. alcohols, aliphatic hydrocarbon, ketones, nitrogen and sulphur compounds.
338 Biological degradation was confirmed, indirectly, by the high correlations found between the
339 biological stability index (DRI) and the classes of compounds above cited (alcohols vs. DRI, r

340 = 0.84, p <0.05, *n* = 6; aliphatic hydrocarbon vs. DRI, r = 0.87, p <0.05, *n* = 6; ketones vs.
341 DRI, r = 0.84 p <0.05, *n* = 6; nitrogen compounds vs. DRI, r = 0.87 p <0.05, *n* = 6; <0.05;
342 although no correlation was found for sulphur compounds). Terpenes also correlated well
343 with DRI (DRI, r = 0.95 p <0.01, *n* = 6), but probably in this case both biological degradation
344 and stripping phenomena occurred (Pierucci et al., 2005).
345 A second group of compounds did not show strong reduction of their concentration
346 with the biological process, i.e. aromatic hydrocarbons, furans, and halogenated organic
347 compounds. These molecules represent xenobiotic compounds (aromatic and halogenated
348 compounds) or products (e.g. furans) of the thermal decomposition of other molecules.
349 Nevertheless, the no-degradation was apparent; in fact, taking into consideration that
350 concentration depends on the airflow rate used during DRI detection, it can be deduced that
351 degradation/stripping of these molecules occurred, at least, at a rate similar to that of airflow
352 rate of sample taken at different biological stage.
353 More representative organic compounds for each class were reported in Table 3.
354 Limonene was the most representative terpen in the starting samples, i.e. it represented the
355 68% ± 14 of the total terpens emitted. Limonene composes typically vegetable materials (food
356 fractions of the MSW, Pierucci et al., 2005), but it could also represents an intermediate of the
357 aerobic metabolism of microorganisms (Eitzer, 1995). At the end of the aerobic process, the
358 concentration of the limonene was very low because of its biodegradation. Stripping
359 phenomena, enhanced during the first stage of biological process by the high biomass
360 temperature could also contributed to the limonene reduction in the air (Pierucci et al., 2005).
361 The presence of alcohols (Table 3) especially in the fresh material was, probably, the
362 consequence of microbial alcohol formation from waste substrate during the period of storage
363 under nearly anaerobic conditions at low pH (Staley et. al., 2006), and during first
364 biostabilization stage in which O_2 could be a limiting factor for the aerobic degradation.

Thus, successive more oxidizing conditions during biological process leaded to the complete degradation of alcohols and so to the absence of these compounds in the air. Ketones were represented especially by butanone and acetone that were present during first stage of the process (Table 3). It has been reported that bacteria are able to oxidize alcohols to ketone (Widdel, 1986) probably during storing or under O_2 limitation; on the other hand these compounds can be also released from plastic packaging (Staley et. al., 2006). Again, subsequent oxidizing conditions determined the degradation of these compounds that practically disappeared in the GC-MS spectra of air sampled after biological treatment (Table 3).

Aliphatic compounds were mainly represented in the waste samples by decane, 2,6 di-methyl decane, undecane and dodecane compounds. These alkenes have been reported to come from cooked and heated oil, but also from food packaging (Risch and Hotchkiss, 1991, Reineccius, 1991; Appendini and Hotchkiss, 2002). These molecules were readily degraded and stripped (otherwise they cannot be detected as VOC in the air stream) during biological process and disappear completely in the exhaust air. The nitrogen and sulphur compounds were mainly present at the start of the process. Trimethylamine, which is a product of the decomposition of plants and animals, was representative of N-compounds. Sulfur compounds were represented mainly by allyl mercaptant, a typical product of the organic matter degradation. The presence of these molecules was indicative of anaerobic/microearophilic metabolism. Furans, which have been reported to be toxic and maybe carcinogenic, were represented by the furan 2-penthyl, a natural based compound typically found in fruit and other food (Rogers and Williams, 1938) but also coming from thermal degradation of other molecules (e.g. pentose) (Ruther and Baltes, 1994).

Aromatic hydrocarbons were represented by xylenes, styrene and benzenes. Their presences are generally related to the initial presence in the MSW of synthetic materials (i.e.

plastic polymers) and household hazardous MSW (i.e. some plastics, solventa, etc.) (Pierucci et al., 2005; Staley et al., 2006).

Tetrachloroethylene (PCE) and 2-propanol, 1-chloro, were representative of halogenated organic compounds. PCE is a solvent used for dry cleaning and it represents one of the most widely contaminants of ground water (Vieria et al., 2005) and it has been classified as toxic chemical. 2-propanol, 1-chloro is used to manufacture propylene oxide and propylene glycol and then used to produce plastic polymer (e.g. polyurethane). 2-propanol, 1-chloro was reported to be a probable human carcinogen (Ashby, 1996). These compounds were more observed in the final sample, probably because of relative concentration due to airflow reduction and their recalcitrance.

The molecules above discussed were also investigated as responsible for human annoyance (odours) and worker harmful (molecules toxicity). In Table 3, for each molecule the odours threshold, i.e. the minimal concentration of molecules that cause the perception of the odours (OTV), is reported. Comparing these values with molecules concentration it can be seen that only terpens, sulphur and nitrogen compounds showed concentration above OTV. Therefore, it could be supposed that, effectively, these molecules contributed to the odour perceived by the panellists during olfactometric tests. This fact was supported by the very good correlations found for these compounds and the OU_E (nitrogen compounds vs. OU_E, $r = 0.97$, $p < 0.01$, sulphur compounds vs. OU_E $r = 0.85$, $n = 6$; <0.05). Terpens, also, correlated with OU, but it was not statistically significant ($r = 0.71$, $p < 0.10$, $n = 6$). Probably both absolute concentration and OTV should be considered to understand what molecules contribute to OU_E. From data reported in Table 3 we calculated, for the samples studied, the ratio: class compound concentration / average OTV. This ratio represents the contribution of molecules to the odours considering both quantitative aspects (concentration) and qualitative

(OTV) aspects. Results (not showed) indicated that N compounds contributed to the odours of factor of magnitude 150 with respect to both terpens and S compounds.

This appears true for starting and intermediate samples, as in the final ones it was not possible to find appreciable concentration of N and S compounds and terpens above OTV, although OU_E were high (2,569 ± 709 OU). However, the presence of many other molecules may enhance (synergistic effect) or suppress (antagonist effect) the odour (Ruth, 1986). In addition, Gralapp et. al. (2001) and Bruno et. al. (2007) suggested that human odorous response (OU measurement) may be based, also, on compounds that are not detected by GC-MS analysis.

Xenobiotic compounds such as aromatic hydrocarbons and halogenated organic compounds showed very low concentration with respect OTV, i.e. no odour was perceived. Nevertheless, these molecules could represent a risk for worker and population, as they are toxic and maybe carcinogenic. In Table 3 we reported the Threshold Limit Value – Time Weighted Average (TLV-TWA), i.e. the level to which it is believed a worker can be exposed day after day for a working lifetime without adverse health effects (average exposure on the basis of a 8h/day, 40h/week work schedule). From the results obtained, it could be seen that hazardous molecules concentrations were very low with respect to the TLV-TWA.

4. Conclusion

Potential odours and VOCs emission during biological process used to treat MSW can be studied under standardized conditions in order to detect potential risk for worker and population.

Odours and VOCs emitted depend on the decomposition degree of the waste, i.e. biological stability.

GC-MS study of the VOCs was able to investigate about the nature of the molecule emitted. Two groups of molecules could be detected. The first group of molecules was degraded and they were not representative of air emitted from biologically treated samples. On the other hand, xenobiotic molecules and furans (second group of molecules) persisted in the waste sample becoming the more representative of treated waste. Nevertheless, xenobiotic molecules were in a concentration much lower than TLV-TWA.

Odours perceived were mainly due to N compounds produced during the biological process. However, it was not possible to indicate for the treated waste, specific molecules responsible for the odours.

Acknowledgements

Financial support was provided by the Spanish Ministerio de Educación y Ciencia (Project CTM2009-14073-C02-01).

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Tables

Table 1 - Chemical characterization of the analyzed samples

Sample	pH	DM ($g\ kg^{-1}$w.w.)	VS ($g\ kg^{-1}$DM)	TKN ($g\ kg^{-1}$DM)	TOC ($g\ kg^{-1}$DM)	DOM ($g\ C\ kg^{-1}$DM)
Start a	5.71	637 ± 37	490.6 ± 91	7.7 ± 0.2	274.7 ± 9.3	282.8 ± 1.8
Start b	5.42	634.2 ± 10.7	442.5 ± 16.4	7.5 ± 0.1	266.9 ± 4.9	264.8 ± 2.6
Grand Mean	5.57±0.21a	635.6±2a*	466.6±34b	7.6±0.1a	270.8±5.5b	273.8±12.7c
28 d a	7.63	828 ± 12.7	439.5 ± 28.9	9.7 ± 0.9	237.7 ± 14.4	144.9 ± 13.1
28 d b	7.42	827.1 ± 9.1	379.5 ± 22.4	7.8 ± 0.1	202.3 ± 0.8	133.5 ± 10.1
Grand Mean	7.53±0.15b	827.6±1b	409.5±42.4b	8.8±1.3a	220±25	139.2±8.1b
90 d a	7.65	805.3 ± 19.7	333.2 ± 32.5	7.8 ± 0.5	154.7 ± 17.8	32.8 ± 4
90 d b	7.77	794.7 ± 5.6	347.7 ± 4.5	8.3 ± 0.1	181.9 ± 1.2	42.0 ± 8.9
Grand Mean	7.71±0.08b	800 ± 7.5c	340.5±10.3a	8.1±0.4a	168.3±19.2a	37.4±6.5a

* number followed by the same letter in the same column are not statistically different (Test Tukey, $p<0.05$)

563 **Table 2** – Biological stability characterization and volatile emission values of the analyzed samples

564

Sample	RT* (Days)	DRI_{DM} (mgO_2 kg DM^{-1} h^{-1})	DRI_{DM} MAX (mgO_2 kg DM^{-1} h^{-1})	Temp. (°C)	VOC ($\mu g\ m^{-3}$)	Odour ($OU_E\ Nm^{-3}$)
Sa	0	1,672	1,863	41	14,215	32,944
Sb	0	1,597	1,814	46	14,648	24,147
Grand Mean		1,635±53 c*	1,675±267 c	43. 5±3.5b	14,431±306c	28,546±6,220b
Ia	28	954	990	43.5	4,944	5,838
Ib	28	865	881	50	4,133	3,966
Grand Mean		910±63 b	936±77 b	47.6±3.3b	4,539±573b	4,902±1,324a
Ea	90	188	203	24.5	184	3,070
Eb	90 2C	105	108	25.5	226	2,067
Grand Mean		147±59 a	156±67 a	25±0.7a	205± 30a	2,569±709 a

565 * number followed by the same letter in the same column are not statistically different (Test Tukey, $p<0.05$)

566 **Table 3-.** Dominant molecules for each air emission sample accounting for at least the 10% of each class of compounds.

Molecule class		MSW Sa	Sb	Ia	Ib	Ea	Eb	OTV[a] ($\mu g\ m^{3-1}$)	TLV-TWA[b] ($\mu g\ m^{3-1}$)
	p-xylene	58	64	0	67	19	46	4,767[1c]	433,361[1c]
	o-xylene	0	0	51	0	30	61	4,767[1c]	433,361[1c]
	styrene	132	150	48	5	0	0	1,361[c]	212,592[c]
	benzene	0	0	57	0	0	0	38,267[c]	31,889[c]
	1 ethyl 4 methyl benzene	0	0	0	79	0	0	432[2c]	245,298[2c]
	1 methyl 2 (1 methylethyl) benzene	0	112	35	0	0	0	30,253[3c]	60,507[3c]
	1 ethyl 4(1 methylethyl) benzene	0	0	0	95	0	69	432[2c]	245,298[2c]
	1 methyl 3(1 methylethyl) benzene	0	189	0	0	3	0	30,253[3c]	60,507[3c]
	2 ethyl 1,3 dimethyl benzene	0	174	18	26	0	0	432[2c]	245,298[2c]
	1,2,3 trimethyl benzene	103	399	0	0	0	0	2,703[4c]	122,843[4c]
	1 methoxy 4 methyl 2(1methylethyl) benzene	0	0	8	16	15	0	NA	NA
total		**293**	**1088**	**217**	**288**	**67**	**176**		

furans	2,4 dimethyl furan	0	0	0	0	0	1	90,450[5d]	NA
	2 pentyl furan	140	83	163	234	0	1	90,450[5d]	NA
total		**140**	**83**	**163**	**234**	**0**	**2**		
ketones	acetone	70	88	11	2	4	4	30,826[c]	1,778,414[c]
	2 butanone	656	1192	5	9	0	0	15,895[c]	588,716[c]
	4,4 dimethyl 2 pentanone	0	0	0	0	12	0	1,634	233,422
	2,4 dimethyl 3 pentanone	19	0	0	29	0	0	1,634[6c]	233,422[6c]
	3ethylcyclopentanone	0	0	20	31	0	0	NA	NA
	3 methyl, 2hexanone	0	0	0	0	1	1	56[7c]	233,034[7c]
	5 methyl, 2 hexanone	7	4	0	0	0	5	56 [c]	233,034 [c]
	2 methyl, 3hexanone	0	0	31	0	0	0	56[8c]	233,034[8c]
	3,3,5 trimethyl, cyclohexanone	0	0	0	28	0	0	1,128 [c]	28,209 [c]
	5 vmethyl 2 (1 methylethyl), trans cyclohexanone	258	243	12	31	0	0	NA	NA

	2 nonanone	0	182	14	0	0	0	11,531[d]	NA
total		**1010**	**1709**	**93**	**130**	**17**	**10**		
alogenated compound	1 chloro, 2 propanol	0	0	9	13	13	0	NA	NA
	tetrachloroethylene	0	0	13	0	14	4	183,238[c]	339,330[c]
total		**0**	**0**	**22**	**13**	**27**	**4**		
esters	acetic acid methyl ester	37	4	0	0	0	0	13,917[c]	605,070[c]
	methyl propionate	258	0	0	0	0	0	NA	NA
total		**295**	**4**	**0**	**0**	**0**	**0**		
	2.,2 dimethyl hexane	0	23	33	18	0	0	457,073[9c]	175,7979[c]
	butyl cyclohexane	0	0	36	13	0	0	85,854[10 c]	1,030,253[10 c]
	pentyl cyclohexane	62	0	22	60	0	0	85,854[10 c]	1,030,253[10 c]
	Heptane	3	0	30	0	0	0	613,246[c]	1,635,323[c]
	2,2,4,4,6,8,8 heptamethyl nonane	0	0	39	53	3	0	245,953[11c]	1,046,607[11c]
	decane	720	958	0	50	0	0	4,400[e]	NA
	2,6 dimethyldecane	48	1220	0	0	0	0	NA	NA
	undecane	1,262	0	0	0	0	0	7,800[e]	NA

	dodecane	1,733	773	0	0	0	0	14,550[e]	NA
	tetradecane	0	28	34	0	0	0	NA	NA
total		**3828**	**3002**	**194**	**194**	**3**	**0**		
N compounds	trimethylamine	269	24	269	0	0	0	1[a]	24,121[a]
	2 methyl pyridine	0	7	0	0	0	0	NA	NA
total		**269**	**31**	**269**	**0**	**0**	**0**		
alcohols	2 butoxy ethanol	30	0	0	0	0	0	NA	NA
	2 butanol	6	66	65	0	0	0	7,866[a]	302,535[a]
	1-methoxy 2 propanol	53	16	0	0	0	0	75,000-500,000[12d]	NA
	1 butoxy 2 propanol	25	110	38	54	0	0	NA	NA
	2 ethyl 1 hexanol	84	412	14	37	0	0	41.7[13d]	NA
	3 7 dimethyl 3 octanol	106	0	0	0	0	0	691.6[14d]	NA
total		**304**	**604**	**117**	**91**	**0**	**0**		
sulphur compounds	dimethyl disulfide	0	68	9	8	0	0	1-346.5[d] 48.3[c]	NA
	disulfide carbon	0	0	14	0	4	0	342[c]	31,071 [c]

	disulfide methyl propyl	6	20	0	20	1	0	49[15d]	NA
	allyl mercaptan	428	0	0	0	0	0	0.2[d]	NA
	dimethyl trisulfide	3	0	0	0	0	0	NA	NA
	sulfide allyl methyl	59	0	0	0	0	0	0.7[16d]	NA
	1(methylthio) 1propene	123	0	0	0	0	0	4	1,840
totañ		**619**	**88**	**23**	**28**	**5**	**0**		
terpenes	limonene	2993	3042	2233	3135	5	0	200[e]	NA
	camphor[a]	127	529	14	20	3	0	1,678[c]	12,428[c]
total		**3,120**	**3,571**	**2,247**	**3,155**	**8**	**0**		

[a] OTV: odour threshold value

[b] TLV-TWA: Threshold Limit Value – Time Weighted Average

[c] data from: Amore and Hautala, 1983.

[d] data from: Ruth, 1986

[e] data from: Lornage et al., 2005

[1] surrogate m-xylene

575 [2] surrogate cumene (1 methylethyl benzene)

576 [3] surrogate 1 methyl 4 methylethyl benzene

577 [4] surrogate 1,3,5 trimethylbenzene

578 [5] surrogate 2 methyl furan

579 [6] surrogate 4,4 dimethyl 2 pentanone

580 [7] surrogate 5 methyl 2 hexanone

581 [8] surrogate 5 methyl 3 hexanone

582 [9] surrogate hexane

583 [10] surrogate cyclohexane

584 [11] surrogate nonane

585 [12] surrogate propyl alchol

586 [13] surrogate hexane

587 [14] surrogate octanol

588 [15] surrogate ethyl methyl sulfide

589 [16] surrogate allyl sulfide

590 **Legends to Figures**

591

592 **Fig. 1**- Composition on classes of MSW volatile emissions (SPME CG-MS data).

593

Fig. 1