RESEARCH ARTICLE



Volatile emissions during storing of green food waste under different aeration conditions

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Abstract Controlled field experiments were carried out for monitoring the emissions of three plastic commercial household waste bins, which were adapted for studying the effect of aeration process in the evolved volatiles, during house storing of green food waste for 2 weeks, prior to collection. Three experimental scenarios were examined based on no aeration ("NA," closed commercial waste bin), diffusion-based aeration ("DA," closed commercial waste bin with tiny holes), and enforced aeration ("EA," closed commercial waste bin with tiny holes and enforced aeration). The monitoring of volatile organic compounds (VOCs) emitted from organic household kitchen waste was performed using solid-phase microextraction-gas chromatography-mass spectrometry (SPME-GC-MS) analysis. Portable sensors were also used for monitoring selected gases and parameters of environmental, bioprocess, and health interest (e.g., CO₂, O₂, H₂S, CH₄, NH₃, % RH, waste temperatures). VOC emissions are strongly dependent on the waste material. The most frequent VOCs identified over the storing waste, showing over 50 % appearance in all examined samples, were terpenes (e.g., di-

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limonene, beta-myrcene, delta-3-carene, alpha-pinene, alphaterpinolene, linalool, etc.), sulfides (dimethyl disulfide), aromatics (benzene, 1-methyl-2-(2-propenyl)), alkanes (e.g., decane, dodecane), ketones (2-propanone), esters (e.g., acetic acid ethyl ester, acetic acid methyl ester), and alcohols (e.g., 3cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)). The prominent role of terpenes in the "pre-compost" odor and especially that of di-limonene was highlighted. In all examined scenarios, the emitted volatiles were increased at raised temperatures and later decreased in time. Aeration of waste bins slightly affected the volatilization process resulting in higher profiles of VOCs; uniformity in the composition of VOCs was also noted. Slight modifications of commercial waste bins may favor the initiation of home composting.

Keywords Household composting · Waste bins · VOC emissions · SPME-GC-MS · Odor nuisance · Organic waste

Introduction

Composting is an aerobic thermophilic process which acquires oxygen, humidity, and moisture and results in the degradation of organic waste. Compost products are carbon dioxide, water, heat, and a stable recovery product which can be used for controlling the soil quality, in restoring land use and in agriculture applications. This biological process includes different phases (e.g., starting, mesophilic, thermophilic, and cooling), depending on the type of microbes involved; each phase differs in time and temperature (e.g., between 20 and 60 °C). A number of parameters can contribute to optimized composting including temperature, humidity, aeration, pH, and the quality of the substrate (e.g., porous, size, structure, C/N ratio) (Li et al. 2013).

Urbanization and rapid economic development strongly impact solid waste management efforts; therefore, economical, social, and environmental optimal solutions are searched out. Composting is suggested as the most relevant method regarding the treatment of organic solid waste and more specific for the treatment of food waste (World Bank 2012). Other waste management methods are recycling, sewage treatment, incineration, and landfill deposition (Domingo and Nadal 2009). However, composting, either industrial or in home, is considered to be the most promising recycling treatment method for household waste and especially for green food waste (Zorpas 2009). This is due to the fact that it can act as a prevention technique minimizing the waste disposed off to landfills (Zorpas et al. 2015). Therefore, the need for collection, transportation, and processing of the food waste is reduced (Anderson et al. 2012). The EU landfill directive sets a decrease of the amount of organic waste disposed in landfills by 50 % by 2050 (Council Directive 1993/31/EC 1999). Towards this effort, according to Eurostat (2012), 42 % of treated municipal waste in the EU in 2012 was recycled or composted. Nevertheless, it is associated to the motivation of people and lack of standardized procedures, as compost process can be carried out using homemade, commercial composting bins or even in an open pile in the backyard. Among the different composting means, commercial home composting bins offering lateral natural ventilation (passive aeration bins) are preferred. The importance of aeration process in compost was early noted by Barrington et al. (2003). Different aeration methods such as pile turning and forced (Arslan et al. 2011), passive (Karnchanawong and Suriyanon 2011), and negative pressure aeration (Lin 2008) were examined in order to succeed ideal aerobic fermentation conditions. However, it was observed that wastes decayed faster in bins with lateral and vertical systems of natural ventilation (Karnchanawong and Suriyanon 2011). Nevertheless, the technical and scientific aspects of bin composting have been scarcely studied; thus, new household composters are still proposed (Papadopoulos et al. 2009).

Storage and compost of food waste emits a complicated mixture of volatile organic compounds (VOCs) and inorganic gases (Drew et al. 2007). The latter are of great concern in compost emissions, accounting 5 % of the global greenhouse budget (Lou and Nair 2009); therefore, greenhouse gases (GHGs) are widely studied as high global warming potentials contributing to climate change (Anderson et al. 2010; Lou and Nair 2009). In the same context, VOCs contribute to the formation of ground-level ozone by reacting with NOx; more than 100 VOCs were found to be emitted from compost facilities including aliphatic alkanes, alkenes, aromatic hydrocarbons, biogenic organics, aldehydes, ketones, alcohols, furans, acids, esters, ethers, halogenated hydrocarbons, and reduced

sulfides (Kumar et al. 2011; Muller et al. 2004). Therefore, biofilters are examined for eliminating odors in waste treatment plants (Gutiérrez et al. 2015).

A big number of analytical instruments have been employed for monitoring the gaseous waste emissions. Among them, gas chromatography combined with mass spectrometry (GC-MS) is considered to be the gold standard allowing for qualitative and quantitative results. Adsorbentbased materials such as thermal desorption tubes (TD-GC-MS) (Romain et al. 2005) and solid-phase microextraction (SPME-GC-MS) (Fiedler et al. 2001) fibers are mainly used, offering sample pre-concentration, thus better sensitivity. SPME is a low-cost, simple, solvent-free method widely applied to numerous environmental applications. Other applicable analytical methods for measuring odor nuisance include the utilization of diffusive samplers (Bruno et al. 2007), enoses (Romain et al. 2005), olfactometers (Fischer et al. 2008), and combination of them (e.g., olfactometry, GC-MS, gas detector tubes) (Mao et al. 2006). Moreover, real-time monitoring of organic fraction of municipal solid waste is enabled using proton transfer reaction time-of-flight mass spectrometry (PTR-TOF MS) (Papurello et al. 2012).

Composting process is a function of various parameters, some of which are difficult to control; e.g., pH, C/N ratio, phytotoxicity, and presence of toxic metals. Nevertheless, it is known that aeration affects the overall emissions, improving the quality of the compost (Romain et al. 2005). According to our knowledge, few studies investigated volatile emissions, except GHGs, during storage of organic waste and even less of storing conditions at home composting, parameters that are of the close interest of waste management operators (Quirós et al. 2014). The aim of the present study was to analyze the household waste emissions of green food waste, when stored in modified waste bins for 15 days, under different aeration conditions. This is especially important for countries with limited composting facilities, where separation at source and collection of different waste fractions are promoted.

Materials and methods

Substrate

Field experiments were conducted using plastic household commercial waste bins modified to examine the aeration effect. The modified bins were filled with a total waste mass of 50 kg. The selected food substrate (freshly, uncooked, mostly green kitchen waste without meat, fish and dairy products) was placed in different layers after being cut into small pieces: bread (10 kg), green vegetables such as lettuces and cucumbers (15 kg), kitchen paper (2 kg), rice and potatoes (5 kg), tomatoes (3 kg), and fruits such as oranges, apples, and lemons (15 kg). The waste bins were placed in the open space and left for 15 days under environmental conditions (early June, Athens, Greece).

Experimental setup and sampling

Four household commercial plastic waste bins (140 L, height $106 \times$ width 55 cm) were employed serving three different aeration scenarios: no aeration ("NA"), aeration through diffusion ("DA"), and enforced aeration ("EA"; two waste bins were used for reproducibility reasons, EA1 and EA2). DA was achieved through the opening of 36 ventilation holes (2.5 mm diameter) at the bottom and on top of the left and right side walls of the waste bin and a 10-cm-diameter hole on the lid, which was enclosed with a metal net for protection from various insects. EA was enabled through the further adaptation of a commercial plastic electric fan installed on the cover lid of the DA; it was set in use for approximately 8 h/day (i.e., 2 h off-1 h on). The specifications of the fan were the following: power 220/50 V, consumption 20 W, speed 2300 r.p.m., and airflow 50 m³/h. Finally, a small hole (1 cm diameter) was opened on the cover of each waste bin for facilitation of the sampling procedure. Headspace samples were taken in selected days; 2 h after placing of wastes on the 1st, 4th, 5th, 10th, 11th, and 15th day. The samples were taken between 13:00 and 15:00 hours for a time period of 15 days. No further addition of waste was performed.

A series of three preliminary experimental cycles were previously performed aiming at setting various experimental details: examining different waste bin scenarios and aeration profiles, identifying VOC retention times and revealing marker compounds, selecting fiber conditions, and optimizing the chromatographic conditions (data not presented). Since waste bins are gradually filled by consumers, storage time and local food habits were also taken into consideration.

Methods

Headspace SPME-GC-MS was used for VOC analysis. The SPME fiber (85 µm carboxen/polydimethylsiloxane on a Stableflex fiber, Supelco) was stabilized on a ring stand and through a utility clamp was placed in the hole of the waste bin cover and exposed over the headspace of the wastes for 30 min. Subsequently, it was thermally desorbed to an HP 5890/5972 GC/MS system. A 60-m SPB-624 capillary column with 1.4-mm stationary phase and an internal diameter of 0.25 mm (Supelco) was utilized for high-resolution chromatographic separation. Column head pressure of helium purge gas was set to 25 psi. GC program was selected as follows: 35 °C initially for 5 min, ramp of 4 °C/min up to 180 °C, and hold for 20 min. The mass range of mass selective detector was set from 35 to 350 amu with 1.8 scans per second. Chromatographic peaks were identified with the help of Wiley 138 library.

Portable sensors were further used for monitoring daily the evolved inorganic gases. Carbon dioxide was monitored through the use of Anagas CD 98 plus (Environmental Instruments, UK) and oxygen, hydrogen sulfide, methane, and ammonia by Oldham MX 2100 (UK) multi-gas detector. The detector of portable CO_2 sensor was infrared, whereas that of the all other gases were electrochemical, enabling for possible cross sensitivities. The ambient temperature and relative humidity during sampling were measured by a portable thermometer-hygrometer (model H 270, Dostmann Electronics, Germany). Finally, a K-type thermocouple was used for daily measuring the biomass temperature inside and above the mass waste (headspace air temperature).

Results and discussion

A variety of VOCs were emitted from the modified household waste bins including almost all chemical classes: terpenes, reduced sulfides, aromatics, alkanes, ketones, esters, and alcohols. Table 1 presents the qualitative results of the SPME-GC-MS analyses of VOCs appeared in more than half of the samples (in all three scenarios). The most prominent VOCs that were identified despite the aeration scenarios were dilimonene, beta-myrcene, delta-3-carene, alpha-pinene, alphaterpinolene, and linalool, showing over 90 % appearance in all samples examined. Terpenes were considered the most prominent chemical category; they originated from evaporation and decomposition, as they are present in peels, fleshes, oils, and juices of citrus fruits (vegetable matter biodegradation product). On the other hand, the only sulfur compound detected was disulfide dimethyl, which is attributed to microbial activity. In general, volatile sulfur compounds such as hydrogen sulfide (H₂S), methyl mercaptan, dimethyl sulfide, carbon sulfide, and dimethyl disulfide are responsible for the malodor in composting plants (Zhang et al. 2013).

Although di-limonene is not considered a bad odorant, however, it is usually detected in waste management operations and associated with odor nuisance in high concentrations. It may play an important role in the perception of waste odor in combination with certain microbial volatiles. Nevertheless, the perception of malodorous substances on the human nose should not be seen as a result of a single component but as a synergy or antagonism between compounds. The odor threshold values for limonene is 38 ppb, whereas for disulfide dimethyl 2.2 ppb (Nagata 2003). The latter known offensive odorant sulfide is usually detected as a food waste aerobic decomposition product, due to the microbial decay of organic matter and moisture, resulting from the presence of sulfur contents in food waste (Komilis et al. 2004; Wu et al. 2010).

In Fig. 1, a representative chromatogram of VOCs of a modified household waste bin is presented. The dominant

Table 1 VOCs with high frequency of appearance in all samples	VOCs category	Compound	Percentage of appearance (%)	
	Terpenes	Di-limonene	100	
		Beta-myrcene	100	
		Delta.3-carene	100	
		Alpha-pinene	95	
		Alpha-terpinolene	90	
		Linalool	90	
		Alpha-terpinene	85	
		Beta-phellandrene	80	
	Sulfides	Disulfide dimethyl	75	
	Aromatics	Benzene, 1-methyl-2-(2-propenyl)	75	
	Terpenes	Alpha-terpineol	75	
	Alkanes	Decane	70	
	Terpenes	Gamma-terpinene	70	
		Isoterpinolene	70	
	Ketones	2-Propanone	65	
	Esters	Acetic acid, ethyl ester	60	
	Terpenes	Alpha-cubebene	55	
	Esters	Acetic acid, methyl ester	50	
	Alkanes	Dodecane	50	
	Alcohols	3-Cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)	50	

peak of limonene is highlighted; some other peaks are also shown. In the same context, the most prominent VOCs, showing over 67 % appearance per aeration process, are presented in Table 2. According to Table 2, the most prominent chemical classes identified were again terpenes (e.g., di-limonene, betamyrcene, D-3-carene, alpha-pinene, alpha-terpinolene, etc.). Esters (e.g., acetic acid ethyl ester), ketones (e.g., 2propanone), and alkanes (e.g., decane) were also present. The only sulfide compound detected was dimethyl disulfide.

Ventilation allows high oxygen supply to the wastes by enhancing the activity of microorganisms and leading to aerobic conditions. Thorough aeration prevents anaerobic



Fig. 1 A representative chromatogram of VOCs evolved from a modified household waste bin after 5 days of storing. The numbered peaks indicate the following VOCs: (1) 2-propanone, (2) acetic acid

methyl ester, (3) furan, 2-methyl, (4) acetic acid ethyl ester, (5) disulfide dimethyl, (6) 2-butanone-3-hydroxy, (7) alpha-pinene, (8) sabinene, (9) beta-myrcene, (10) di-limonene, (11) beta-phellandrene, (12) linalool

No aeration (NA)	%	Aeration through diffusion (DA)	%	Enforced aeration (EA)	%
Alpha-pinene	100	Decane	100	Alpha-terpineol	100
Beta-myrcene	100	Beta-myrcene	100	Alpha-terpinolene	100
Delta.3-carene	100	Delta.3-carene	100	Gamma-terpinene	100
Di-limonene	100	Alpha-terpinene	100	Beta-phellandrene	100
Alpha-terpinolene	100	Di-limonene	100	Di-limonene	100
Gamma-terpinene	86	Linalool	100	Delta.3-carene	100
Benzene, 1-methyl-2-(2-propenyl)	86	Disulfide dimethyl	83	Beta-myrcene	100
Linalool	86	Alpha-pinene	83	Alpha-pinene	86
Acetic acid, ethyl ester	71	Benzene, 1-methyl-2-(2-propenyl)	83	Linalool	86
Disulfide dimethyl	71	Alpha-terpineol	83	Isoterpinolene	86
Decane	71	Beta-phellandrene	67	Alpha-terpinene	86
Alpha-terpinene	71	Alpha-terpinolene	67	2-Propanone	86
Beta-phellandrene	71	Isoterpinolene	67	Alpha-cubebene	71
Alpha-cubebene	71			Dihydrocarvone	71
Beta-elemene	71			3-Cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)	71
				Disulfide dimethyl	71
				Acetic acid, ethyl ester	71

 Table 2
 VOCs with high frequency of appearance in the three scenarios

conditions in the organic waste that could promote the formation of malodorous sulfur compounds by Gram-negative bacteria and increases the emission rate of microbial VOCs (Muller et al. 2004). According to Li et al. (2013), in composting processes, the aeration rate affects microbial activity, substrate degradation rate, and temperature variation. In pararell, Domingo and Nadal (2009) mentioned that incomplete processes of aerobic degradation results in alcohol, ketones, esters, and acids. Furthermore, Wang and Wu (2008) detected many terpenes (i.e., limonene, beta-myrcene, sabinene, alpha-pinene) under controlled aerobic conditions in laboratory incubation experiments, as a result of orange wastes decomposition. Finally, the combined effect of aeration and moisture to selected odorous compounds of solid waste composting (limonene, beta-pinene, 2-butanone, undecane, phenol, toluene, dimethyl sulfide, and dimethyl disulfide) was examined through modeling; aeration rate strongly affected the emissions, whereas moisture effect varied based on the compound (Delgado-Rodriguez et al. 2012).

In Table 3, a comparison of VOCs identified in both the literature and in the present study is shown. Nevertheless, this comparison is only indicative since waste emissions found in the literature originate mostly from composting facilities and may have both different substrate components and treatment history that may significantly change VOC profiles and categories. Key articles on the field of gaseous emissions and especially on the influence of aeration rate during early storage/composting are missing from the literature.

Monitoring composting emissions is quite important for a number of environmental, health, and waste management reasons (Pagans et al. 2006a; Maulini-Duran et al. 2014). It allows for detection of toxic compounds in the emissions, dispersion, and control of odor, as well as for monitoring the composting process. Volatile emissions, especially in densely populated cities, are related to a wide range of environmental, health, safety, and social impacts (Statheropoulos et al. 2005): odor nuisance (Mayrhofer et al. 2006), occupational exposure of collectors (Anderson et al. 2012), airborne dust and aerosols production (Fischer et al. 2008), frequency of collection and types of waste bins (Drew et al. 2007), costs for collection and transportation, storage time, and relevant place inside or outside the house. Nevertheless, the main risks associated with domestic waste composting facilities are chemical and environmental and risks on the surrounding environments (Domingo and Nadal 2009). It was reported that a mixture of terpenes, i.e., (+)-3-carene, (-)-limonene, alpha-pinene, and alpha-terpineol in high concentration, can cause eye irritations, whereas compounds such as limonene and alphapinene can result in sensitization of the skin and allergy (Muller et al. 2004).

Anaerobic processes for composting food waste are most undesirable, since they are responsible for the production of CH₄, CO₂, N₂O, H₂S, and NH₃, as well as the production of a variety of VOCs (Pavlostathis and Giraldo-Gomez 1991; McKinley and Williams 2007). These types of emissions are malodorous and may impact health. Examples of other undesirable conditions include temperatures over 70 °C, moisture content less than 30 %, and pH level less than 4.5 (Li et al. 2013). Moreover, increased NH₃ (Li et al. 2013; Pagans et al. 2006b) can be correlated with high pH in combination with high temperature and low C/N ratio. Furthermore, high peaks of CO₂ and NH₃ are correlated with high substrate

Table 3 Categories of compounds identified in this study and in literature

	VOCs identified (in the present study)	Experimental details (Literature)	Literature
Alkanes		In paper and yard wastes, food waste composting plants	(Komilis et al. 2004), (Mao et al. 2006)
	Pentane-2 methyl	r or	
	Pentane-3 methyl		
	Hexane		(Mao et al. 2006)
	Heptane		
	Decane		Komilis et al., (2004)
	Undecane		(Delgado-Rodriguez et al. 2012), (Komilis et al. 2004)
	Dodecane		(Komilis et al. 2004), (Maulini-Duran et al. 2014)
	Tridecane		(Komilis et al. 2004)
	Tetradecane		(Maulini-Duran et al. 2014)
Esters		In food wastes (1-week sample), laboratory composter, food waste	(Komilis et al. 2004), (Krzymien et al. 1999), (Mao et al. 2006)
	Acetic acid, ethyl ester	composing plants	(Imppola et al. 2003)
	Acetic acid, methyl ester		(Wang and Wu 2008), (Mao et al. 2006), (Imppola et al. 2003)
	Acetic acid, butyl ester		(Imppola et al. 2003)
	Propanoic acid, ethyl ester		(Krzymien et al. 1999)
	Butanoic acid, ethyl ester		
	1-Butanol, 3-methyl acetate		
	Hexanoic acid, methyl ester		(Krzymien et al. 1999), (Imppola et al. 2003)
	Hexanoic acid, ethyl ester		(Krzymien et al. 1999), (Imppola et al. 2003)
	Octanoic acid, ethyl ester		
	Octanoic acid, methyl ester		(Maulini-Duran et al. 2014)
Acids		In food wastes (1-week sample), laboratory composter, food waste composting plants	(Komilis et al. 2004), (Krzymien et al. 1999), (Mao et al. 2006)
	Acetic acid	I GI GI	(Mao et al. 2006), (Imppola et al. 2003)
Alcohols		In paper and food waste, composting facilities, food waste composting plants	(Komilis at al. 2004), (Muller et al. 2004), (Fischer et al. 2008), (Mao et al. 2006)
	Ethanol	Punto	(Krzymien et al. 1999), (Wang and Wu 2008), (Mao et al. 2006), (Imppola et al. 2003)
	Ethanol, 2-butoxy		
	1-Octanol		
	3-Cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)		
Ketones	2-Propanone	In yard wastes, food waste composting plants	(Komilis et al. 2004), (Mao et al. 2006) (Krzymien et al. 1999) (Wang and Wu 2008)
	2-1 ториноне		(Mao et al. 2006)
	2-Pentanone		
	2-Butanone		(Krzymien et al. 1999), (Maulini-Duran et al. 2014), (Bruno et al. 2007), (Wang and Wu 2008), (Mao et al. 2006), (Imppola et al. 2003) (Delgado-Rodriguez et al. 2012)
	2-Butanone, 3-hydroxy		(Imppola et al. 2003)
Terpenes		Orange wastes, yard wastes, composting facilities, food wastes, food waste composting plants, laboratory composter	(Wang and Wu 2008), (Komilis et al. 2004), (Muller at al. 2004), (Mao et al. 2006) (Krzymien et al. 1999)
	Alpha-pinene		(Krzymien et al. 1999), (McKinley and Williams 2007), (Muller et al. 2004), (Bruno et al. 2007), (Wang and Wu 2008), (Mao et al. 2006), (Imppola et al. 2003)
	Di-limonene		 (McKinley and Williams 2007), (Muller et al. 2004), (Maulini-Duran et al. 2014), (Bruno et al. 2007), (Wang and Wu 2008), (Mao et al. 2006), (Imppola et al. 2003), (Delgado-Rodriguez et al. 2012)
	Alpha-terpinene		(Wang and Wu 2008)

	VOCs identified (in the present study)	Experimental details (Literature)	Literature
	Isolimonene		
	Alpha-terpineol		(Muller et al. 2004)
	Beta-myrcene		(Krzymien et al. 1999), (Muller et al. 2004), (Wang and Wu 2008)
	Gamma-terpinene		(Muller et al. 2004), (Wang and Wu 2008)
	Delta.3-carene		(McKinley and Williams 2007), (Muller et al. 2004), (Wang and Wu 2008)
	Sabinene		(Wang and Wu 2008)
	Beta-phellandrene		(McKinley and Williams 2007), (Wang and Wu 2008)
	Alpha-terpinolene		(Muller et al. 2004), (Wang and Wu 2008)
	Isoterpinolene		
	Alpha-cubebene		
	Alpha-selinene		
	Valencene		
	Beta-elemene		
Aromatics		Paper and yard wastes, food waste, usually xenobiotic	(Komilis et al. 2004)
	Toluene		(Komilis et al. 2004), (Mao et al. 2006), (Imppola et al. 2003), (Delgado-Rodriguez et al. 2012)
	p-Xylene		(Komilis et al. 2004), (Maulini-Duran et al. 2014), (Mao et al. 2006), (Imppola et al. 2003)
	Benzene-1-methyl-4-(1 methyl ethyl)		
Chlorinated compounds		Non-carboy samples and in ambient air of municipal solid waste composting facilities	(Komilis et al. 2004)
	Benzene, chloro		
Sulfides		Mostly in food wastes but also in yard wastes (one week sample), laboratory composter, composting facilities, food waste composting plants	(Komilis et al. 2004), (Krzymien et al. 1999) (Fischer et al. 2008), (Muller et al. 2004), (Mao et al. 2006)
	Disulfide dimethyl		 (Krzymien et al. 1999), (McKinley and Williams 2007), (Zhang et al. 2013), (Fischer et al. 2008), (Muller et al. 2004), (Maulini-Duran et al. 2014), (Mao et al. 2006), (Imppola et al. 2003), (Delgado-Rodriguez et al. 2012)
Furans		Composting facilities	(Muller et al. 2004), (Fischer et al. 2008)
	Furan, 2-methyl		(Fischer et al. 2008), (Muller et al. 2004)
	2-Furan carboxaldehyde		
	2-Furan methanol		
	Furan, 2-pentyl		(Muller et al. 2004), (Maulini-Duran et al. 2014)

 Table 3 (continued)

temperature. On the other side, reduction of NH_3 emission may be associated with high moisture content.

In Fig. 2, a more close view of the processes carried out in the different modified waste bins is presented. CO_2 evolution versus time (Fig. 2a) increases very rapidly, takes a maximum, and then decreases (day 4). The same pattern is repeated for all adapted waste bins for day 5 to day 10. Then, for day 12, there is an increase that stops on day 14. There is a clear difference between EA waste bins and the other two scenarios. This profile is further confirmed by monitoring O_2 in all waste bins (Fig. 2b). Temperature profiles show the same profiles as CO_2 and O_2 with distinct increases that may be related to microbial activity. These profiles might be closely related to composting processes and might be used as indicators for assessing the performance of the adapted waste bins. In Fig. 2c, the production of H_2S is shown. Its measurement is considered quite important for odor emissions. As is shown, H_2S production during the early composting process was not constant presenting fluctuations. The evolved gas increased at raised temperatures and then its production rate decreased in time. The patterns of relative humidity are presented in Fig. 2d, whereas Fig. 2e, f presents the temperature inside and above the waste. The breakdown of organic matter bonds results in release of thermal energy during the composting process. The relative humidity and temperature within the waste bins were raised in all cases due to the presence of organic waste fraction and the

0

0 2



10 12 14

Fig. 2 Parameters relating to the processes occurring in the modified waste bins

10 12 14

6 8

Time (days)

20

0 2

4

6 8 Time (days)

active action by microorganisms. The humidity and temperatures achieved were bigger than the environmental values showing the potentiality of the decay process. Although NH₃ and CH₄ concentration values are not presented, however, these gases were also measured. Ammonia is considered an environmental indicator of compounds acidification, eutrophication, and photochemical oxidation, whereas methane is directly related to anaerobic conditions. Methane values were not detected, although these may be produced below sensor's limit of detection (>1 ppm_v). On the other hand, small concentration values of ammonia were measured only on the 10th–12th date $(1-2 \text{ ppm}_v)$ in DA waste bin; this is attributed probably to the combination of the high relative humidity and high temperatures observed at these dates. Another interesting observation is that CO₂ concentrations in EA1 and EA2 bins, when measured just after enhanced aeration, presented an increased trend.

The correlation between emitted VOCs and the aeration was examined by studying the relative response factors of VOCs, as presented in Table 4. The trends of selected VOCs were estimated per waste bin, in an attempt to highlight their time evolution behavior; increased, decreased, or mixed trends were observed. Some volatiles showed a clear decreased behavior such as 2-propanone, whereas the rest a more mixed behavior. This is mainly attributed to the fact that compost emissions are affected by a number of parameters next to aeration: waste quality and composition, mixing, humidity, temperature, weather conditions, etc. (Quirós et al. 2014). Since there was not observed a clear correlation between aeration conditions and emitted VOCs, GC peaks were further normalized and seen through their average response

factors $A_i/A_{limonene}$ (integrated area under curve in arbitrary units), as shown in Fig. 3. The most prominent VOCs in NA waste bin appeared to be di-limonene, followed by acetic ethyl ester, hexane, beta-myrcene, and ethanol. In DA waste bin, dilimonene remains the most prominent volatile, although a slight decrease is observed in its evolution profile; acetic acid ethyl ester peak follows, along with hexane and beta-myrcene. Finally, in EA waste bins, a richer VOC profile is observed, especially in low and high molecular weight volatiles. Dilimonene remains the most abundant volatile, followed by acetic acid, acetic ethyl ester, hexane, beta-myrcene, acetic ethyl methyl ester, and 2-butanone. The abundant presence of terpenes in all cases can be attributed to the waste material (mainly seasonal citrus), constituting about 30 % of the waste. As noted by Pierucci et al. (2005), it is of interest the uniformity of results, despite the aeration scenarios, and especially the prominent role of terpenes. In all three scenarios, the high concentration profile of di-limonene observed on the 1st days is gradually decreased until the 4th day, whereas a second steep increase is followed until the 15th day. This observation is in agreement with similar aerobic degradation waste studies and is associated with the volatilization of terpenes originated from biomass, whereas the secondary peak is related to the microbial decomposition activity (Papurello et al. 2012). Overall, aeration of waste bins seems to enhance the degradation (volatilization) process resulting in higher abundant profiles of VOCs. This is in agreement with Komilis et al. (2004), which stated that an important effect of the enforced aeration consisted in releasing compounds embedded in the organic material mixture. Moreover, Wang and Wu (2008) reported that fruit wastes degrade faster under aerobic conditions and

20

0

2

4 6 8 10 12 14

Time (days)

No	Day	Volatile organic compounds (VOCs)	RR ^a NA ^b	Trend ^c	RR ^a DA ^b	Trend ^c	RR ^a EA ^b	Trend ^c
1	5	Disulfide dimethyl	0.0052		0.0013		0.0055	
	10		0.0045	D	0.0005	М	0.0076	Ι
	15		0.0014		0.0037		0.0652	
2 5 10	5	Alpha-pinene	0.0016		0.0014		0.0033	
	10		0.0029	М	0.0016	М	0.0018	М
	15		0.002		0.0012		0.0022	
3 5	5	2-Propanone	0.1274		0.0421		0.0556	
	10		0.0101	D	0.0163	D	0.0254	D
	15		0.0079		0.0092		0.0183	
4	5	Beta-myrcene	0.0444		0.1229		0.0887	
	10		0.1197	М	0.1549	Ι	0.1002	Ι
	15		0.1157		0.2428		0.1908	
5	5	Delta.3-carene	0.005		0.0034		0.0057	
	10		0.0011	М	0.0207	М	0.0056	D
	15		0.0047		0.0031		0.0051	
6	5	Alpha-terpinene	0.0023		0.0019		0.0049	
	10		0.0029	Ι	0.0037	М	0.0029	М
	15		0.0044		0.0016		0.0041	
7	5	Benzene, 1-methyl-2-(2-propenyl)	0.0099		0.0307		0.0119	
	10		0.0144	Ι	0.0129	D	0.0111	D
	15		0.0165		0.0017		0.0109	
8	5	Decane	0.0032		0.0022		0.0054	
	10		0.0012	М	0.0015	М	0.0045	D
	15		0.0018		0.0027		0.0035	
9	5	Alpha-terpinolene	0.0037		0.0023		0.003	
	10		0.0035	D	0.002	М	0.0043	М
	15		0.0029		0.0022		0.0031	
10	5	Linalool	0.0009		0.0048		0.0121	
	10		0.0063	М	0.0024	D	0.0038	D
	15		0.0014		0.0007		0.0021	

Table 4 Relative response factors of selected volatile organic compounds and their trends in time

^a RR: relative response = $A_i/A_{limonene}$

^b Waste bin type: NA no aeration, DA diffusion based aeration, EA enforced aeration

^c Trend: D decrease trend, I increase trend, M mixed trend

Chanakya et al. (2007) noticed that fruit waste decay results in organic acids and a large leachate fraction.

Comparing the released volatiles with urban waste disposal bin emissions (Statheropoulos et al. 2005), it is of interest to notice the absence of many xenobiotic VOCs such as aromatic and halogenated compounds usually detected in landfills (Scaglia et al. 2011), thus highlighting the "green origin" of compost wastes. Last but not least, it is related to the representative waste synthesis protocol that was followed. The results of the current study are in agreement with the emissions of composting plants in Greece and Finland (Imppola et al. 2003), where alcohols (ethanol), ketones (2-butanone, 3-hydroxy-2-butanone), acids (acetic acid), esters (methyl acetate, ethyl acetate, ethyl butanate, butyl acetate, methyl hexanoate, ethyl hexanoate), aromatic hydrocarbons (toluene, xylenes), terpenes (limonene, alpha-pinene, beta-pinene), and sulfur compounds (dimethyl disulfide) were detected.

Consequently, monitoring emissions of storing household waste is important for better understanding, as well as for controlling the compost process. Therefore, it is quite fundamental to develop indexes, markers, and profiles of VOCs and gases related to the type of waste material, as well as to correlate with undesired processes and conditions (e.g., odor nuisance, anaerobic conditions). Especially in urban cities, waste bin type (closed, open, enforced or passive aeration) and environmental conditions (e.g., season, environmental conditions) are of significant importance. Another important factor is the type of food waste (substrate dependant): cooked or



Fig. 3 The effect of aeration process in the production of VOCs per waste bin (*NA*, no aeration waste bin, *DA*, diffusion based aeration waste bin, *EA*, enhanced aeration waste bin). The VOCs are placed by their retention time

uncooked, with/without animal protein (i.e., meat, fish, dairy products), amount of organic fraction, etc. Undoubtedly, an optimum amount of oxygen is necessary in composting for achieving aerobic activity; low concentration will lead to anaerobic conditions, whereas the opposite to excessive cooling.

The identification of gaseous emissions from household food waste during storing in modified bins and the possibility of composting were examined. Within the limits of this experimental setup, volatile emissions during waste storing in the bins were reported. The limitations of the study include, among others, the variety of real-life waste bins; storing freshly uncooked and green kitchen waste does not completely represent all different waste bin scenarios. Secondly, the selected food substrates were placed in layers, instead of being mixed and trashed in the bins; top layer of oranges, apples, and lemons further impacts the emission profile. Thirdly, the waste was stored in the bins with and without aeration (no turning or mixing). Although multivariate data analysis techniques were not applied to the data, they could contribute in highlighting hidden correlations between identified VOCs and the examined aeration scenarios. Finally, further measurements on key composting quality factors such as C/N ratio along with longer time period could better highlight home composting cycle.

Conclusions

The effect of composting aeration on biological decomposition, during the storage of green food waste, was characterized by the emitted VOCs. Three different aeration conditions were tested: without aeration, with aeration (diffusion), and intermittently enforced aeration. Important parameters of short storing and composting bioprocess were additionally monitored for 15 days. The emitted VOCs highly depend on the type of waste in the bin; other factors that affect the process are ambient conditions and decomposition time of fresh food. The release of gaseous emissions from the very early stages was notable. Despite the uniformity of results, the important role of terpenes and, more specifically, that of di-limonene in the released odor was noticed. There are indications that slight modifications of commercial waste bins may assist composting of green food waste, allowing possibly for different house storing and collecting schemes; however, further examination of compost quality during the full composting cycle is needed. Aeration process assists the degradation of organic waste fraction. These emissions may be used as indicators of performance in the modified commercial waste bins. Nevertheless, further studies are needed for optimizing this approach (i.e., pile turning, daily batch-feeling, waste variety, longer period of time, optimum aeration) and for studying potential social, economic, nutritional, and environmental impacts of green food waste.

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