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VOLATILE ORGANIC COMPOUNDS FROM GREEN WASTE ANAEROBIC DEGRADATION AT LAB-SCALE: EVOLUTION AND COMPARISON WITH LANDFILL GAS

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ABSTRACT
The chemical composition of volatile organic compounds (VOCs) in landfill gas from municipal waste (MW) landfills primarily depends on the type of degrading waste. To provide first insights into the relationship between VOC chemistry (in landfill gas) and specific waste components, a lab-scale experiment on anaerobic digestion (AD) of green waste (GW) was carried out. The composition of the released C_{4+} VOCs was semi-quantitatively determined and indirectly compared to that generally expected for the overall MW landfill gas. The generated biogas from degrading GW during AD time showed up to 29 different VOCs, mainly including terpenes, followed by alkanes, alkenes, cyclics, aromatics, and halogenated compounds. O- and S-substituted compounds were sporadically detected. Overall, speciation and total concentration of VOCs fluctuated over AD time, likely due to changes in microbial populations and metabolism, as well as substrate depletion, during the AD evolution. As expected, VOC speciation in the GW biogas was lower than that of the typical MW landfill gas, since the latter is generated by a large variety of organic and synthetic waste components following different sequential degradation processes. These results highlighted that, when disposed of at MW landfill sites, the specific GW component may (i) potentially concur to the overall odour charge and toxic effects of MW landfill gas and (ii) detrimentally impact the energy exploitation of MW landfill gas by releasing terpenes, aromatics, and halogenated compounds.

1. INTRODUCTION

Landfilling has long been the prevalent practice for municipal waste (MW) management (treatment and disposal) worldwide (Duan et al., 2021; Kaza et., 2018). Once deposited in landfill, MW generates landfill gas as the result of the direct volatilization of compounds contained in the waste (e.g., plastic foam, air fresheners, detergents, etc.) and the progressive degradation of organic matter mainly based on anaerobic digestion (AD) processes (Chiriac et al., 2011; Christensen et al., 2010; Rasi et al., 2011). MW landfill gas, primarily consisting of CH_4 and CO_2, includes small fractions (normally at concentrations < 1% by vol.) of a wide range of non-methane volatile organic compounds (hereafter, VOCs) (Tassi et al., 2009), having a potential impact on air quality, local population's welfare, and landfill worker health if released to the environment (Nair et al., 2019). VOCs may also damage gas engines, reducing the functional life of equipment and the energy recovery performance (Giraudet et al., 2014; Sevimoĝlu and Tansel, 2013; Shin et al., 2002). Moreover, CH_4 oxidation occurring within landfill cover soils may decrease in presence of significant amounts of VOCs, resulting in a reduced mitigation of CH_4 release to the atmosphere (Alvarez-Cohen and McCarty, 1991; Alvarez-Cohen and Speitel, 2001).

Owing to its biodegradability and relatively high methane yield (Campuzano and González-Martínez, 2016), the organic fraction of municipal waste (OFMW) represents a significant challenge for landfill management. In fact, the OFMW (i) positively contributes to the conversion of landfill gas to energy by increasing its methane content but (ii) negatively contributes to the possible emission of toxic and pollutant organic trace gases into the environment. Nota-

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bly, the OFMW is by far the dominating fraction of MW accounting for almost 50% of the generated waste worldwide (Zamri et al., 2021) and landfilling has remained the main method for its management (Chen et al., 2020). Particularly, the specific component of OFMW represented by the green waste (GW), which includes grass clippings, hedge cuttings, pruning, leaves, and wood from private gardens, public parks, and roadside greenery, has been increasing in recent years with the growth of urbanization and related urban green spaces (Langsdorf et al., 2021; Reyes-Torres et al., 2018). For example, in Beijing (China) the amount of generated GW has increased by about 50,000-100,000 ton year^{-1} (Zhang and Sun, 2016), while an increase of 2 million ton occurred in the USA during the period from 2010 to 2018 (USEPA, 2020). Moreover, a relevant amount of 10.53 million ton of GW was destined for landfilling in the USA in 2018 (USEPA, 2020). Even in territorial areas with a considerable level of separately collected MW destined for recovery, as in the Marche Region (Central Italy), where it was equal to 70.5% in 2019, the GW still represents, with food waste and fines, the largest portion of the residual MW, accounting for 30.8% as overall organic fraction (Boccarossa et al., 2021). In the representative Marche Region, both the mechanically separated outputs from the residual MW are destined for landfilling, either directly in the case of the oversize stream or following only a partial aerobic biostabilization in the case of the undersize stream (Boccarossa et al., 2021).

In the last decades, several studies have been focused on the chemical characterization of VOCs in landfill gas to (i) identify potential odorous or pollutant compounds, (ii) verify the achievement of quality standards required to the optimized energy recovery, and (iii) assess the landfill life-cycle impact perspective (e.g., Allen et al., 1997; Beylot et al., 2013; Nair et al., 2019; Papadias et al., 2012; Parker et al., 2002; Sadowska-Rociek et al., 2009; Saral et al., 2009; Takuwa et al., 2009). On the contrary, to the best of our knowledge, only Staley et al. (2006) have focused on the characterization of VOC compositional features from few, selected waste components (paper, yard waste, and food waste) under anaerobic conditions. However, a deep analysis on the temporal evolution of VOC composition seems to be lacking. The chemical composition of the primary MW landfill gas compounds is known to be the result of the combination of the organic and synthetic waste components disposed of at a given landfill and the extension and evolution of the occurring biodegradation. However, the chemical features of VOCs released from different deposited waste components under anaerobic conditions, over time, have remained poorly known.

In this study, an AD experiment was conducted at lab-scale using GW, a key organic component of MW, as substrate to simulate the anaerobic degradation that typically occurs in landfills with the aim of investigating the VOC release in the time evolution and in the relation with potential sources. Semi-quantitative analyses of a wide range of VOCs (C_{4+}) in the biogas generated during the AD of GW were repeatedly carried out. The specific objectives of this study were to (i) compare indirectly the VOCs released at lab-scale from GW AD with those generally expected from a MW landfill and (ii) explore the potential contribution of deposited GW on MW landfill gas composition in terms of VOCs.

2. MATERIALS AND METHODS

2.1 AD experiment

2.1.1 Substrate and inoculum

The considered GW used as substrate was obtained from the collection center of the Fano town district in the Marche Region that is located at the pertaining landfill operated by the "ASET" public multi-utility group. At this facility, first the GW was visually separated from impurities (such as plastic, paper/cardboard, glass, and metal). Then, the GW was shredded by a mobile grinder and further reduced by an electric blender at the laboratory to favor the substrate uniformity in size to a few millimeters (Raposo et al., 2011).

To the purpose of the experiment, an inoculum consisting of anaerobic sludge (hereafter, INO), obtained from the anaerobic digestion treatment stage at a municipal wastewater treatment plant, was added to provide initial microbial community and improve the stability of the experimental system (Carchesio et al., 2014, 2020).

Both the substrate and inoculum were characterized in terms of moisture, total solids (TS), and volatile solids (VS), the latter being an indirect measure of the organic matter content (Tatàno et al., 2015). Moisture and TS contents were determined by loss-on-drying at 105°C, while VS content was measured by loss-on-ignition at 550°C (IRSA, 1984). The considered properties are shown in Table 1. GW moisture and VS contents fell within the ranges reported in the literature as representative for the physico-chemical quality of green waste (i.e., 21.1-67.9% FM - fresh matter - and 30.0-98.9% TS, respectively: Reyes-Torres et al., 2018). As far as INO is concerned, the resulting moisture content was at the lower limit of the range of 96.5-98% FM derivable in Londong (2006) as indicative for a well anaerobically digested sludge, while VS content remained at the upper limit of the range of 30-60% TS reported for digested sludge (Acaia and Ragazzi, 1991).

2.1.2 Experimental setup

Two parallel AD reaction lines were implemented using a mixture of GW with INO (hereafter, just GW line) and only INO as blank control, respectively. The substrate to inoculum ratio in the mixture was fixed at 2:1 on a VS basis (Carchesio et al., 2020). The AD experiment, which lasted 49 days, was performed in batch mode with two lab-scale digesters consisting of a dark glass bottle (inner volume: 1 L) equipped with a pierceable rubber cap and filled up

TABLE 1: Properties of the substrate and inoculum.

	Green Waste (GW)	Inoculum (INO)
Moisture (% FM)	49.9	96.5
Total Solids, TS (% FM)	50.1	3.5
Volatile Solids, VS (% TS)	67.1	60.2

FM = fresh matter

to approximately 0.5 L (Figure 1a). The operating temperature was set to mesophilic conditions (38°C) (Carchesio et al., 2020) and the digester contents were homogeneously mixed using heating magnetic stirrers at speed of roughly 300 rpm (Figure 1a). Small amounts of Na_2CO_3 powder (around 1 g) were initially added to both digesters to raise the pH up to approximately 8 and prevent the inhibition of AD process in the early phase of the experiment (Carchesio et al., 2020). The pH values in the GW digester evolved in time respecting the range of 6.0–8.3, where the anaerobic digestion is expected to occur (Angelidaki and Sanders, 2004). To avoid high overpressure in the digester headspaces, biogas was periodically evacuated in both GW and INO digesters, particularly after each dedicated biogas sampling.

From each digester, eight biogas samples were periodically collected (precisely, at 2, 7, 12, 16, 21, 33, 40, and 49 days after AD started). The biogas samples were collected inserting a needle, connected to a syringe through a three-way-valve, in the digester headspace from the pierceable rubber cap (Figure 1a). Thus, the biogas samples were transferred and stored into glass vials (Labco Exetainer®, 12 cm^3), equipped with a pierceable rubber cup, using an inlet and outlet needle to insert the samples and rinse deionized water filled vials, respectively (Figure 1b).

2.2 Chemical analysis

Semi-qualitative analysis of VOCs (C_{4+}) was performed using solid phase microextraction method (SPME) to pre-concentrate VOCs (Arthur and Pawliszyn, 1990) and a Thermo Trace Ultra gas-chromatograph (GC) equipped with a Thermo DSQ quadrupole mass spectrometer (MS) as analytical instrument. The SPME fibre, constituted of divinylbenzene (DVB)-carboxen-polydimethylsiloxane (PDMS), was inserted into the vials through the pierceable rubber and exposed to the gas for 30 min at 20°C. Thus, adsorbed VOCs were released, exposing the SPME fibre for 2 min at 230°C in the injection port of the Thermo Trace Ultra GC. Analytes were separated by employing a film thickness TR-V1 fused silica capillary column (30 m x 0.25 mm, inner diameter = 0.25 μm) and He as carrier gas (1.3 mL min^{-1}). The column operated at three temperature ramps: 35°C (held 10 min) to 180°C (held 3 min) at rate of 5.5°C min^{-1} and then to 230°C (held 6 min) at rate of 20°C min^{-1}. Finally, analytes were detected by the quadrupole mass spectrometer that operated in electron ionization mode (EI), with ionization energy of 70 eV and source temperature set at 250°C, and in full scan mode (35 to 400 m/z). VOC species were identified by the retention time of chromatographic peak and comparing the mass spectra with those reported in the NIST05 library (NIST, 2005). A relative quantitative analysis of VOC compounds was carried out as follows: the areas of the peaks measured in each sample were normalized to the lowest peak area (represented by the symbol "+"), determining five classes with increasing area ranges, each one represented by an increasing number of "+" symbol. For example, a VOC compound labelled with three "+" symbols showed a peak area approximately three times higher than the lowest peak area range. The relative quantities of VOCs pertaining to the same functional group were summed and the resulting percentage of each functional group was computed according to the sum of "+" symbols of the VOCs in each sample (hereafter, % ΣVOCs).

3. RESULTS

The VOC compounds identified during AD time of GW and INO digesters, respectively, are listed in Table 2. Up to 29 different VOCs were detected in the GW biogas samples, including: alkanes (5), alkenes (5), aromatics (4), cyclics (2), terpenes (5), halogenated (3), S-substituted compounds (1), as well as compounds pertaining to four different O-substituted classes (i.e., ketone, alcohol, ether, and aldehyde) (Table 2). Differently, gas samples from the INO AD at every sampling time showed only five VOCs (i.e., methylpentane, hexane, trimethylpentene, methylcyclopentane, and cyclohexane) pertaining to alkanes, alkenes, and cyclic groups (Table 2).

In the individual GW biogas samples, the number of measured VOC species ranged from 12 to 25 (Figure 2). In particular, the number of different VOC species showed a peak in the initial stage of AD (25), decreased during the next two weeks (18), then increased again up to 25 at day 21 and, subsequently, decreased to 12 (Figure 2). In gener-

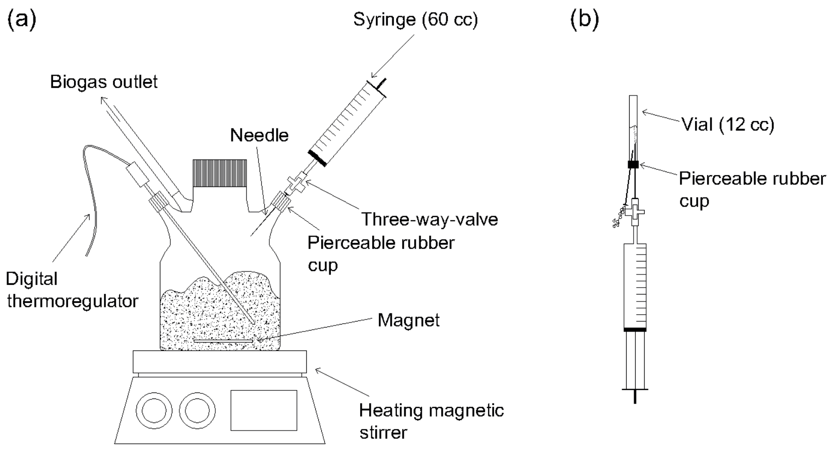

FIGURE 1: Experimental equipment used for the AD of GW and INO (a) and biogas sampling scheme (b).

TABLE 2: Summary of semi-qualitative analysis of VOC (C_{4+}) composition in GW and INO biogas samples during AD time.

	Day 2		Day 7		Day 12		Day 16		Day 21		Day 33		Day 40		Day 49	
	GW	INO	GW	INO	GW	INO	GW	INO	GW	INO	GW	INO	GW	INO	GW	INO
Alkanes																
Methylpentane	++	+	++	+	++	+	++	+	++	+	++	+	++	+	++	+
Hexane	+++	+	+++	+	+++	+	+++	+	+++	+	+++	+	+++	+	+++	+
Dimethylhexane	+															
Methyloctane	+		+		+		+		+		+		+		+	
Nonane	+		+		+		+		+		+		+		+	
Alkenes																
Methylbutene	++		++		++		++		++		++		++		++	
Hexene	+		+		+		+		+							
Methylpentene	+		+		+		+		+							
Trimethylpentene	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Dimethylhexene	+		+													
Aromatics																
Toluene	+		+		+		++		+++		+		+		+	
Ethylbenzene									+							
Xylene									+							
Styrene	+								+							
Halogenated																
Trichloroethylene	+								+							
Chlorohexane	+		+		++		+		++		+		+		+	
Trichloromethylpropane	+				+		+		+							
S-Substituted																
Dimethylsulfide	+															
Cyclics																
Methylcyclopentane	++	+	++	+	++	+	++	+	++	+	++	+	++	+	++	+
Cyclohexane	++	+	++	+	++	+	++	+	++	+	++	+	++	+	++	+
Terpenes																
α-Pinene	+++++		+++++		+++++		+++++		+++++		+++++		+++++		+++++	
Camphene	+++		+++		+++		+++		+++		++					
β-Pinene	+		+		++		++		++		+					
Carene	+		+		+		+		++		+					
Limonene	++		++		++		+++		+++		++		++		+	
O-substituted																
Ethylhexanol									+							
Butoxyethanol									+							
Dimethylcyclohexanone	+															
Benzaldehyde	+								++							

"+" = detected; empty space = not detected.
The number of symbols "+" indicates the magnitude of selected peak area ranges (i.e., greater number of "+" means larger peak area).

al, VOC variety in GW biogas samples was mainly provided by terpenes, alkenes, and alkanes (up to 5 different compounds for each group) (Figure 2). In the last period of GW AD, the number of VOC species of the former two groups dropped to 2 (Figure 2). These pair of compounds were detected at all GW AD sampling times among terpenes and alkenes (α-pinene and limonene, and trimethylpentene and methylbutene, respectively) (Table 2). Differently, at least four alkanes were detected during the GW AD time (i.e., methylpentane, hexane, methyloctane, and nonane) (Table 2). The prevalent speciation of aromatics (4 and 2) and halogenated (3) was observed in combination with the overall peaks in the number of species (Figure 2), whereas among these VOCs only toluene and chlorohexane were detected during the whole GW AD time (Table 2). Similarly, two cyclic VOCs (i.e., methylcyclopentane and cyclohexane) were constantly detected during the whole GW AD time (Table 2). Instead, two and three oxygenated compounds occurred at days 2 and 21 of GW AD, respectively (Figure 2). Finally, dimethylsulfide (DMS) was detected only at day 2 of GW AD (Table 2).

Concerning the relative quantities of VOC functional groups, substantial variations were observed during the GW AD (Figure 3). In particular, terpene group dominated up to day 40 (ranging from 30 to 41% ΣVOCs) and then decreased approaching the GW AD end (27% ΣVOCs) when on the contrary alkanes became dominant (Figure 3). However, α-pinene was by far the most abundant VOC detected during the whole GW AD (Table 2). Alkanes and alkenes (dominated by hexane and methylbutene, respectively: Table 2), representing large relative fractions of VOCs (overall ranging from 16 to 32% and from 11 to 19% ΣVOCs, respectively), showed the lowest relative abundance at day 21 of GW AD when on the contrary the highest relative abundance of aromatics (overall ranging from 3 to 13% ΣVOCs) and oxygenated compounds (5 and 9% ΣVOCs at day 2 and 21, respectively) occurred (Figure 3). Cycling compounds, consisting of comparable fractions of methylcyclopentane and cyclohexane (Table 2), globally ranged from 9 to 18% ΣVOCs and showed particularly an increasing trend approaching the GW AD end after day 21 (Figure 3). Some variations of relative abundances of halogenated group (overall ranging from 3 to 9% ΣVOCs) were observed during GW AD time (Figure 3). DMS found at day 2 of GW AD accounted for 3% ΣVOCs (Figure 3).

With final regard to the INO AD, the related biogas samples regularly consisted of 40% ΣVOCs each of alkanes and cyclic compounds and 20% ΣVOCs of alkenes.

4. DISCUSSION

Lab-scale AD tests are known to be a reliable tool to assess the anaerobic biodegradability and the biochemical methane potential of selected organic substrates (Carchesio et al., 2020; Raposo et al., 2011). In this study, the AD experiment was conducted to simulate, under an-

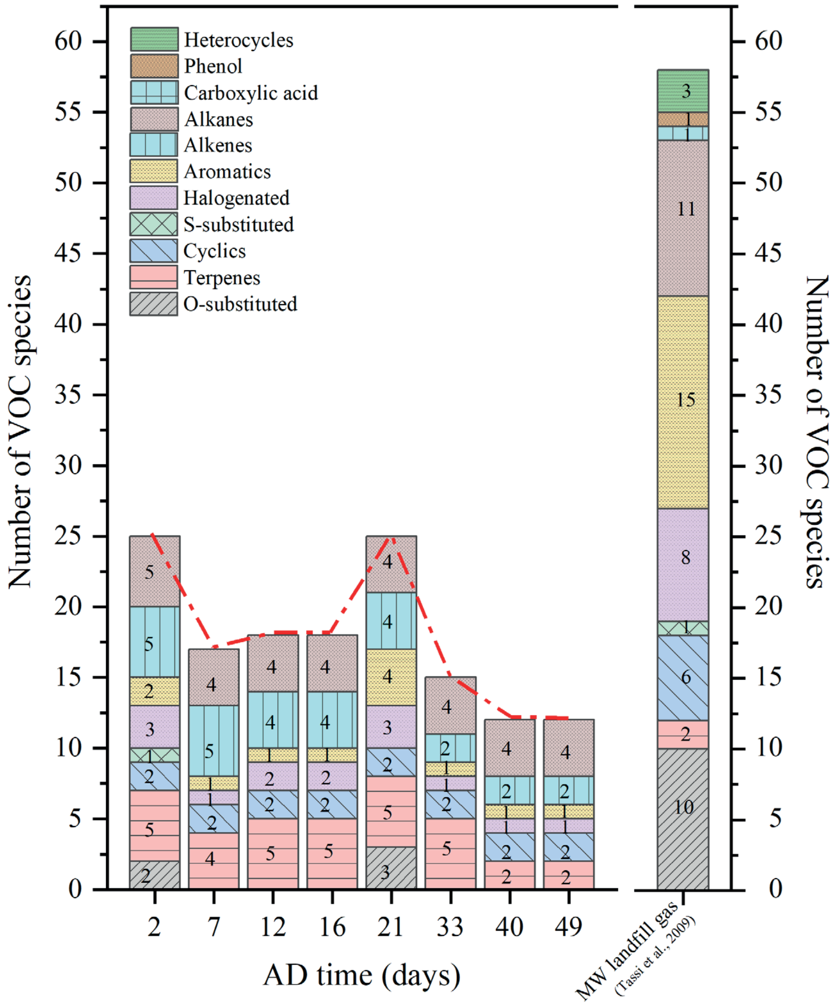

FIGURE 2: Stacked column diagram showing the evolution of the number of species in the VOC functional groups detected in GW biogas during AD time and the number of species in the VOC functional groups in a typical MW landfill gas (Tassi et al., 2009). MW landfill gas column includes both the pertaining recovery wells 1 and 2 because they correspond. Dashed red line shows the total VOC species number.

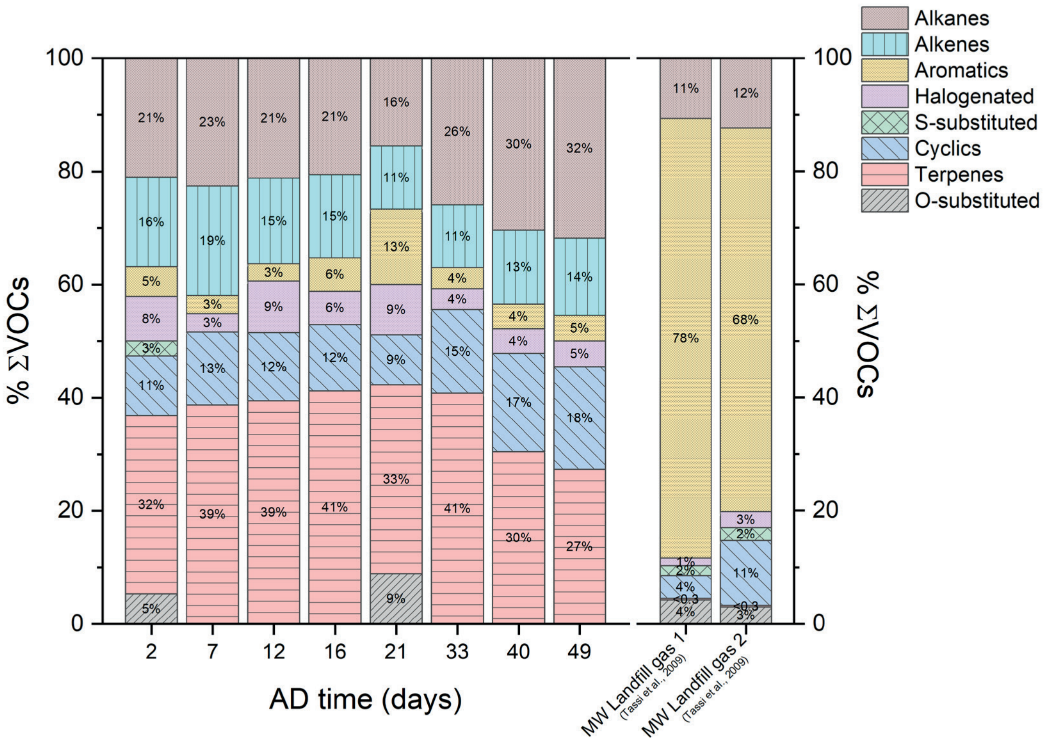

FIGURE 3: Stacked column (100%) diagram illustrating the amount of each VOC functional group in GW biogas during AD time expressed as % ΣVOCs (as indicated in Section 2.2). The relative amounts of VOC functional groups in MW landfill gas from pertaining recovery wells 1 (MW landfill gas 1) and 2 (MW landfill gas 2) (Tassi et al., 2009) were also reported and expressed as % ΣVOCs. In both MW landfill gases, terpenes, heterocycles, phenol, and carboxylic acid accounted for < 0.3% ΣVOCs.

aerobic condition and in a limited temporal scale, the digestion of a key component of MW as the short-term analogue of its landfilling (Bogner and Lagerkvist, 1997), with the aim of investigating the consequential release of VOCs. Effectively, the AD represents the predominant and long temporal phase of MW degradation expected within the landfill body and promoted by the development of anaerobic bacteria consortia (Christensen et al., 2010). Basically, the AD converts the organic matter into small molecules and finally into the main gaseous components of CO_2 and CH_4 through four sequential stages: (i) hydrolysis, (ii) acidogenesis, (iii) acetogenesis, and (iv) methanogenesis (Li et al., 2014, 2019).

4.1 VOC composition and sources in GW biogas

GW biogas samples were characterized by large relative abundance of terpenes (Figure 3), particularly dominated by α-pinene (Table 2). On the other hand, terpenes are strictly related to degradation of yard trimmings, vegetable food, and fruits (Komilis et al., 2004; Maulini-Duran et al., 2014; Wang and Ting, 2008). Generally, compounds pertaining to this functional group, including monoterpenes and sesquiterpenes, are synthesized by plants (as defence against biotic and abiotic stressors and attractor for pollinators) and stored in tissues, leaves, needles, and resins (Gershenzon and Dudareva, 2007; Mewalal et al., 2017; Ormeño et al., 2008). Terpenes are also identified in some fruits and vegetables (Aharoni et al., 2004; Muchlinski et al., 2020). The production of terpenes depends on plant species, and it changes in function of diverse vegetative components such as roots, leaves, and barks (Courtois et al., 2012, 2009). For example, conifer trees such as Pinus, Picea, and Abies predominantly emit α-pinene, β-pinene, camphene, and limonene (Bowman et al., 1997; Kopaczyk et al., 2020). Accordingly, high contents and variety of terpene species released from the experimental GW AD were likely dictated by the expected mixture of the investigated GW and the related decaying rates of the diversified matrices. It is worth noting that terpenes are known to be highly odorous compounds (Wenjing et al., 2015) as they have low odor thresholds (Gallego et al., 2012). The odor threshold identifies the charge of selected gaseous compounds or mixtures as the lowest concentration which generally produce a sensorial response to the human sense of smell (Gallego et al., 2012). In particular, the concentration of α-pinene detected by olfactometry is about two and one order of magnitude (in terms of $\mu g\ m^{-3}$) lower than camphene and limonene, respectively (Gallego et al., 2012). Moreover, α-pinene threshold is about three times lower than hexane (Gallego et al., 2012). Considering the relatively high abundance of α-pinene detected in the GW biogas samples (Table 2), this compound may play a fundamental role on the odorous charge of GW biogas. Moreover, high amounts of terpenes are known to be detrimental for materials normally employed in biogas collection and exploitation systems (such as pipelines, valves, and pumps) and to affect the removal efficiency of impurities (Arrhenius and Engelbrektsson, 2016; Bragança et al., 2020).

Short-chain alkanes and alkenes constituted a relevant fraction of the overall GW biogas composition (Figure 3).

Particularly, they may be related to the degradation of long-chain aliphatic compounds that constitute cuticular wax coating the surface of plant leaves, stems, and flowers (Eglinton and Hamilton, 1967; Mitra et al., 2020; Sharma et al., 2018). The relatively high contents of methylbutene revealed in the alkene group (Table 2) may be attributed to the reactivity and degradability of longer-chain alkenes. Differently, the resulting dominance of hexane, known to be potentially toxic, among alkanes (Table 2) may be ascribed to the relatively high stability of C_6 structure (Capaccioni et al., 1995; Randazzo et al., 2020).

Aromatics and halogenated compounds, which may pose potential concerns to the environment and human health (Dincer et al., 2006) as well as to the biogas exploitation having detrimental effects on engine systems (de Arespacochaga et al., 2014; Piechota, 2021), were detected in the GW biogas (Figure 3). Firstly, aromatic compounds were likely produced by the biodegradation of lignin, a natural polymer enveloped inside the lignocellulosic biomass that consists of hemicellulose and cellulose (Liew et al., 2012; Lubbers et al., 2019; Zimmermann, 1990). For example, it is known that styrene may be produced by decarboxylation of cinnamic acid, a precursor organic acid for lignin and flavonoid biosynthesis (Mooney et al., 2006; Salvador et al., 2013). On the contrary, no evidence was found for halogenated compounds as constituent of plant and vegetal tissues. However, it is worthy mentioning that both aromatic and halogenated compounds may be assimilated by plants from contaminated air (Cape, 2003; Keymeulen et al., 1995; Mosaddegh et al., 2014) and then released after death. Consequently, the detected presence of halogenated compounds and partly of aromatics in the GW biogas may be considered of xenobiotic origin.

Cyclic compounds were detected in all biogas samples from GW AD (Figure 2). On the other hand, leaf waxes are covered by a barrier formed by different alicyclic compounds (Andrae et al., 2019; Chen et al., 2020; Staiger et al., 2019) which may be consequently released during degradation processes.

As expected, limited variety and relative amount in oxygenated compounds were found in only two GW biogas samples (Figures 2 and 3). Typically, these compounds are intermediates or by-products of aerobic decomposition processes (Li et al., 2021; Mustafa et al., 2017; Wu and Wang, 2015). Consequently, they are efficiently produced only at oxidizing conditions, e.g., during the alternative composting process. Nevertheless, some O-substituted compound species have been recognized to occur also at anaerobic conditions, deriving from both degradation of fresh waste and direct volatilization of compounds contained in waste (Duan et al., 2021; Staley et al., 2006; Zheng et al., 2020). Particularly, benzaldehyde (Table 2), a highly odorous compound (Gallego et al., 2012), can be produced by enzymatic hydrolysis of some fruit kernels (Verma et al., 2017).

As far as finally DMS is concerned, its initial detection in GW AD (Table 2) may derive from decomposition of organic waste containing sulfur (Wu et al., 2020; Zheng et al., 2020).

4.2 Temporal evolution of VOC composition in GW biogas

Significant variations in VOC composition and relative abundance of functional groups were revealed during GW AD (Figures 2 and 3).

Initially, a first peak in VOC species (25) was observed in the GW biogas at day 2 of AD, including different compounds of aromatics, DMS, halogenated and O-substituted compounds (Figure 2). Effectively, DMS, aromatics, O-substituted and halogenated compounds are normally emitted and volatilized during fresh waste degradation (Duan et al., 2014; Zhao et al., 2015). Moreover, high amounts of oxygenated compounds were detected during the acidogenesis (Chiriac et al., 2011), suggesting that this AD stage was dominant at day 2. From day 7 to day 16, no significant changes in VOC features were observed (i.e., terpenes, alkanes, and alkenes remained the dominant groups) (Figure 2), implying a certain stability of the AD process. The second peak in number of VOC species (25), observed at day 21 (Figure 2), possibly derived from changes in microbial metabolism. It is known that microbial diversity and activity are sensitive to variations in physico-chemical conditions during AD time (e.g., variations in nutrients, particularly ammonia content) and shifts among different AD stages (Fitamo et al., 2017; Mao et al., 2019; Pan et al., 2021), metabolizing and releasing different VOC species (Zhang et al., 2020). However, the release of gas pockets trapped within the GW substrate cannot be excluded as suggested by the occurrence of xenobiotic compounds pertaining to aromatic and halogenated compounds (see Section 4.1). The decrease in variety of VOC species observed during the last temporal stage of the GW AD may be ascribed to the gradual GW substrate depletion as highlighted by the drastic reduction of terpene species (from 5 at day 33 to 2 at conclusive day 49) (Figure 2).

Methyloctane, nonane, methylbutene, toluene, chlorohexane, α-pinene, and limonene were steadily detected in all GW biogas samples and not appeared in the INO gas samples (Table 2). Consequently, they could be considered as markers of the GW AD. On the contrary, methylpentane, hexane, trimethylpentene, and each cyclic compound were also found in the INO gas samples (Table 2). However, in GW biogas the relative abundance of hexane was steadily higher than methylpentane, trimethylpentene, methylcyclopentane and cyclohexane, while their relative abundances were comparable in INO gas (Table 2). This suggests that a significant portion of hexane was direct released from the GW anaerobic degradation.

α-pinene and hexane were the most abundant species in each GW biogas sample and showed an overall relative enrichment in the AD time (Table 2) implying a relatively high release rate of these compounds from the investigated GW regardless of the evolution of AD stages. Instead, the other terpene compounds revealed in GW biogas were dependent on the proceeding of the AD experiment: in particular, the terpenes/alkanes ratios were 1.5 at the beginning of GW AD (day 2), then increased to > 1.5 from day 7 to day 33, when methanogenesis was expected (Brown et al., 2012; Liew et al., 2012), and finally dropped to ≤ 1 at the conclusive stages of AD when only α-pinene and limonene were found. The previous conditions suggest that the release of terpene species from GW AD was more affected by type and rate of biochemical process and substrate depletion than alkanes. Finally, the tendency of increasing alkanes/alkenes ratios over AD time was also observed, indicating a relative depletion of alkenes likely due to the progressive exhaustion of the GW substrate.

4.3 Comparison of GW biogas and MW landfill gas

In order to perform indirectly a coherent comparison between GW biogas and MW landfill gas, the chemical composition of MW landfill gas determined by Tassi et al. (2009) was specifically considered, according to: (i) analogous geographic, climatic, and socio-economic context (i.e., both the considered MW landfill and GW collection center are located in Central Italy); and (ii) common analytical method. Particularly, Tassi et al. (2009) reported compositional data of MW landfill gas from two recovery wells including a wide variety of 58 VOCs (C_{4+}) (Figure 2). In the considered MW landfill gas, aromatics showed the highest VOC speciation (15), followed by alkane (11), O-substituted (10, including 2 aldehydes, 3 esters, and 5 ketones), halogenated (8), and cyclic (6) compounds (Figure 2). Finally, heterocycles (3), terpenes (2), S-substituted compound (1), phenol (1), and carboxylic acid (1) were also revealed, whereas no alkenes (C_{4+}) were detected (Figure 2). In the considered MW landfill gas, aromatics constituted relatively the most abundant VOC group, followed by alkanes, cyclics, and O-substituted compounds (Figure 3). Significant contents of halogenated and S-substituted compounds (i.e., dimethylsulfoxide) were relatively observed in the considered MW landfill gas, while terpenes, heterocycles, phenol, and carboxylic acid occurred up to 0.3% ΣVOCs (Figure 3).

The lower speciation and relative abundance of terpenes in MW landfill gas characterized by Tassi et al. (2009) (i.e., only α-pinene and eucalyptol were identified with resulting incidence < 0.3% ΣVOCs), as compared with the GW biogas generated and characterized in the present experimental study, may likely be dictated by (i) large terpenes loss by volatilization in the early phases of degradation of deposited waste or (ii) relatively low presence of deposited waste containing terpenes. On the other hand, the AD experiment in the present study was conducted in a confined and controlled volume, avoiding biogas losses and using a terpenes-rich substrate (see Sections 2.1.2 and 4.1). Generally, terpenes in MW landfills may derive from both biodegradation of green and food wastes, and direct volatilization of industrial substances contained in household detergents and air fresheners (Duan et al., 2021; Allen et al., 1997). In particular, α-pinene and limonene are generally the dominant terpene species in MW landfill gas (Duan et al., 2021), indicating that they are easily released during degradation processes of organic and synthetic waste.

The relatively high speciation of alkanes recognized in MW landfill gas (Figure 2) was caused by the enrichment of long-chain alkanes (C_{7+}). Presumably, the large variety of long-chain alkanes (C_{7+}) detected in MW landfill gas (Tassi et al., 2009) was ascribed to the degradation of plastics, frequently disposed of at landfills, releasing a large variety of high molecular weight alkanes (Meunmee et al., 2016). Similarly, the higher variety of aromatic compounds in MW landfill gas than GW biogas (Figure 2) may be caused by the direct release of these compounds from anthropogenic waste commonly disposed of at landfills such as solvents, petroleum-derived products, and plastics (Duan et al., 2021). Indeed, toluene was a dominant aromatic in both MW landfill gas (Tassi et al., 2009) and GW biogas (Table 2), suggesting that this compound can be easily released by degradation processes regardless waste composition. However, MW landfill gas showed alkanes/aromatics ratio significatively lower (about 0.16) than those revealed in GW biogases (ranging from 1 to 8). On the other hand, aromatics in GW biogas are related to the decomposition of the recalcitrant lignin and the possible release as xenobiotic compounds (see Section 4.1). Differently, in MW landfill they are also produced by the direct volatilization of compounds contained in deposited synthetic waste.

Similar to alkanes and aromatics, the relatively high speciation of cyclic compounds in MW landfill gas (Figure 2) was ascribed to the wide range of waste typologies deposited in MW landfill (Tassi et al., 2009).

Although alkenes (C_{4+}) may be released during degradation of plastics such as packaging and films (Muenmee et al., 2016) commonly disposed of at MW landfills, they are not or scarcely found in MW landfill gas (Allen et al., 1997; Tassi et al., 2009). Presumably, the expected overall landfill conditions disadvantage the presence of alkenes, since these compounds are extremely reactive in an aerobic environment (Li et al., 2021). Differently, the anaerobic conditions imposed in the adopted lab-scale system (see Section 2.1.2) permitted the accumulation of alkenes in the GW biogas (Figure 2).

Halogenated compounds in MW landfill gas (Tassi et al., 2009) markedly differed from those identified in GW biogas (Figure 2). These VOCs are recalcitrant and normally considered anthropogenic contaminants contained in synthetic substances used in textile, chemical, pharmaceutical, and dry-cleaning industries (Randazzo et al., 2020). As a wide range of industrial products, such as solvents, paints, adhesives, and pesticides, are generally deposited with unsorted waste (Allen et al., 1997), relatively higher content and variety of halogenated compounds were expected in MW landfill gas than GW biogas. However, the presence of chlorohexane was revealed in all GW biogas samples (Table 2) while it was absent in typical MW landfill gas (Tassi et al., 2009). Presumably, the occurrence of chlorohexane during GW AD was related to the possible use of specific organochlorine pesticides eventually adsorbed, accumulated, and metabolized by the vegetal tissues (Gonzalez et al., 2003; Strandberg and Hites, 2001; Waliszewski et al., 2004)

The relatively low abundance and speciation of O-substituted compounds in GW biogas were likely dictated by the anaerobic conditions controlling the biogas production (Figures 2 and 3). In fact, oxygenated compounds are typically related to aerobic degradation processes occurring at the beginning of MW degradation in landfills (Liu et al., 2015; Nie et al., 2018), particularly in sites characterized by air permeation since biodegradation of alkanes to O-substituted compounds is more efficient (Randazzo et al., 2020).

S-substituted group in MW landfill gas consisted only in dimethylsulfoxide (DMSO: Tassi et al., 2009). Considering that DMS, found instead in GW biogas (Table 2), is unstable at oxidizing conditions (Taylor and Kiene, 1989), its absence in MW landfill gas may be caused by the possible occurrence of oxidation processes at aerobic conditions (Long et al., 2017; Wu et al., 2010) in the landfill body, particularly favoured by the permeation of meteoric water or atmospheric air.

Finally (Figure 2), the lack of phenols and heterocycles in the GW biogas agreed with the origin of these functional groups, being generally released from chemical products and intensely cooked foods such as meat and coffee, respectively (Randazzo et al., 2020), whereas carboxylic acids (i.e., intermediate hydrophilic products of anaerobic processes: Cao et al., 2021), were not detected likely because they were dissolved in fermentation broth (Duan et al., 2021).

5. CONCLUSIONS

The results of this study showed that terpenes dominated in both relative abundance (i.e., ranging from 27 to 41% ΣVOCs) and number of species (up to 5 compounds) the GW biogas and were strictly related to the specific waste component used as substrate for the AD experiment. Significant amounts and high speciation (up to 5 compounds) were exhibited by alkanes and alkenes accounting from 27 to 46% ΣVOCs as sum. The previous VOC groups were followed in the order by aromatics (up to 4 compounds), halogenated and O-substituted compounds (up to 3 each), cyclics (2 compounds), and S-substituted compound (1) that relatively represented, as sum, from 19 to 40% ΣVOCs. Alkanes, alkenes, cyclics, aromatics, DMS, and O-substituted compounds were to be ascribed to the degradation of plant tissues and other general vegetal organic components (e.g., fruits and flowers). Differently, a fraction of aromatics and halogenated compounds could be considered xenobiotic.

Overall, the temporal changes in number and amount of VOC species during GW AD may be caused by (i) subsequent AD stages induced by the progressive establishment of different microbial consortia, and (ii) degree of substrate conversion. Indeed, a comprehensive assessment of biodegradation processes occurring during GW AD requires complementary analyses such as main gas composition, isotopic composition of C-CO_2 and C-CH_4, and microbiological characterization.

Significative differences in VOC composition were indirectly observed between GW biogas and MW landfill gas, since MW landfill gas is expected to derive from a large variety of deposited waste components including a wide range of synthetic materials (such as solvents, plastics, paints, and dry-cleaning products). Moreover, MW landfill gas in the landfill body may be often (or at least initially) affected by oxidation processes related to air circulation possibly driven by permeating meteoric water. Differently, at the experimental lab-scale implemented in this study, whereas environmental and process conditions were fixed and steady and the investigated substrate was isolated in a closed digester, biogas oxidation was avoided or at least minimized.

The results of this study showed that the disposal of GW in MW landfills may concur to the odorous charge and potential toxic effects of the globally generated MW landfill gas, since it provides to landfill gas the content of terpenes and xenobiotic compounds pertaining to aromatic and halogenated groups. Moreover, significative charges of terpenes, aromatics, and halogenated compounds generable by the anaerobic degradation of GW may concur to negatively affect the energy exploitation of the landfill gas by potentially damaging gas collection, conveying, and engine systems. Indeed, these potential detrimental effects may be also expected in the alternative waste management option based on the possible bioenergy recovery through AD from the separately collected GW streams in biogas plants.

Future lab-scale experiments to be carried out using different waste components than GW, may be useful to predict the expected contributions (particularly in terms of VOCs) to the composition of landfill gas generated (and eventually released to the atmosphere) at MW landfill environments.

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