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Emission of oxygenated volatile organic compounds (OVOCs) during the aerobic decomposition of orange wastes

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ARTICLE INFO

Article history:
Received 9 October 2014
Revised 26 January 2015
Accepted 27 January 2015
Available online 11 April 2015

Keywords:
Oxygenated volatile organic compounds (OVOCs)
Emission fluxes
Orange wastes
Aerobic decomposition

ABSTRACT

Oxygenated volatile organic compounds (OVOCs) emitted from orange wastes during aerobic decomposition were investigated in a laboratory-controlled incubator for a period of two months. Emission of total OVOCs (TOVOCs) from orange wastes reached 1714 mg/dry kg (330 mg/wet kg). Ethanol, methanol, ethyl acetate, methyl acetate, 2-butanone and acetaldehyde were the most abundant OVOC species with shares of 26.9%, 24.8%, 20.3%, 13.9%, 2.8% and 2.5%, respectively, in the TOVOCs released. The emission fluxes of the above top five OVOCs were quite trivial in the beginning but increased sharply to form one "peak emission window" with maximums at days 1–8 until leveling off after 10 days. This type of "peak emission window" was synchronized with the CO_2 fluxes and incubation temperature of the orange wastes, indicating that released OVOCs were mainly derived from secondary metabolites of orange substrates through biotic processes rather than abiotic processes or primary volatilization of the inherent pool in oranges. Acetaldehyde instead had emission fluxes decreasing sharply from its initial maximum to nearly zero in about four days, suggesting that it was inherent rather than secondarily formed. For TOVOCs or all OVOC species except 2-butanone and acetone, over 80% of their emissions occurred during the first week, implying that organic wastes might give off a considerable amount of OVOCs during the early disposal period under aerobic conditions.

Introduction

Oxygenated volatile organic compounds (OVOCs), as ubiquitous and abundant components in the global troposphere (Singh et al., 2001), have received special attention because of their important roles in tropospheric chemistry. Consequently their mixing ratios and fluxes, as well as their global budgets, have been widely investigated (Jacob et al., 2002; Seco et al., 2007; Kumar et al., 2011; Laffineur et al., 2012). The short-chain OVOCs with high activity, such as methanol, ethanol, formaldehyde, acetaldehyde, acetone and 2-methyl-3-buten-2-ol, can sequester reactive nitrogen to form peroxyacetyl nitrate and are easily photolyzed to produce free radicals such as HOx (Arnold et al., 1986; Singh et al., 1995; Atkinson, 2000), and thus influence the oxidizing capacity and ozone-forming potential of the atmosphere and contribute significantly to the formation of secondary organic aerosols (Singh et al., 1995; Seco et al., 2007; Kumar et al., 2011). On the local scale, some OVOCs are primary irritants and offensive odor pollutants with very low sensory thresholds (Devos et al., 1990; Table 1), and

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http://dx.doi.org/10.1016/j.jes.2015.01.006

Table 1 – The odor threshold and production of detected oxygenated volatile organic compounds (OVOCs) during the two-month incubation of orange wastes in the present study.

Compounds	Production (mg/dry kg)	Threshold [a] (mg/m^3)	Compounds	Production (mg/dry kg)	Threshold [a] (mg/m^3)
Alcohols			*Ketones*		
Methanol	425	186	2-Propanone	12.1	34.7
Ethanol	462	55.0	2-Butanone	48.5	23.4
1-Propanol	0.47	6.03	2-Pentanone	19.9	5.50
2-Methyl-1-propanol	2.94	2.57	3-Pentanone	1.56	1.15
1-Butanol	0.72	1.51	2-Heptanone	1.70	0.68
2-Methyl-2- butanol	0.33	7.08	2,3-Butanedione	27.4	0.02
3-Methyl-1-butanol	0.49	0.16	3-Hydroxy-2-butanone	18.5	
2-Pentanol	8.56		Sum	130	
1-Hexanol	0.97	0.19	*Esters*		
2-Methyl-3-buten-2-ol	15.0		Methyl formate	1.94	234
1-Penten-3-ol	0.32	1.48	Ethyl formate	0.33	57.5
3-Hexen-1-ol	0.33		Methyl acetate	238	19.1
Sum	917		Ethyl acetate	348	9.77
Aldehydes			Propyl acetate	0.62	2.45
Acetaldehyde	43.4	0.34	Butyl acetate	0.71	0.93
2-Methyl-propanal	0.35	0.12	2-Methylpropyl acetate	2.14	2.34
2-Methyl-butanal	0.04		3-Methylbutyl acetate	15.0	0.12
Pentanal	0.10	0.02	2-Methylbutyl acetate	1.91	
Hexanal	0.10	0.06	Methyl propionate	0.28	11.2
Sum	44.0		Ethyl propionate	0.50	0.39
Acetals			Methyl butyrate	0.59	0.02
1,1-Diethoxy-ethane	0.01		Ethyl butyrate	10.2	0.11
2,4,6-Trimethyl-1,3,5-trioxane	2.01		Methyl hexanoate	0.41	0.01
Sum	2.03		Sum	621	
			Total OVOCs	1714	

[a] Devos et al. (1990).

their emission and presence in ambient air are widely regulated. For example, acetaldehyde, propionaldehyde, butyraldehyde, isobutyaldehyde, valericaldehyde, isovaleraldehyde, isobutyl alcohol ethyl acetate, methyl isobutyl ketone, propionic acid, butyric acid, valeric acid and isovaleric acid have long been regulated for odor control by the Ministry of the Environment of Japan (1971).

Although OVOCs are major biogenic volatile organic compounds from living plant leaves (Seco et al., 2007; Laffineur et al., 2012) or fruit (Buettner and Schieberle, 2001; Umano et al., 2002; Brat et al., 2003), as metabolites formed largely from pectin (Laffineur et al., 2012), fatty or amino acid precursors (Peterson and Reineccius, 2002), they can be formed during the decomposition or decay of organic matters such as plant litters (Isidorov and Jdanova, 2002; Gray et al., 2010), green wastes (Kumar et al., 2011) and vegetable, fruit and garden wastes (Defoer et al., 2002). Thus, OVOCs are also major non-methane organic compounds in waste gases from various waste treatment processes including transferring (Dorado et al., 2014), landfilling (Davoli et al., 2003; Dincer et al., 2006; Tassi et al., 2009) and composting (Eitzer, 1995; Smet et al., 1999; Pierucci et al., 2005; Romain et al., 2005; Staley et al., 2006; He et al., 2010; Kumar et al., 2011; Lehtinen et al., 2013). Emission of OVOCs from these treatment facilities may not only burst into their airborne ambient levels in the neighborhood (Davoli et al., 2003; Dincer et al., 2006) and contribute to ground-level ozone formation (Kumar et al., 2011), but also trigger complaints of sensory irritation by local residents.

Organic wastes share a comparatively larger portion of municipal solid wastes (MSWs) in the developing world, such as in China (Tian et al., 2007). They are easily decomposed by microbes, and give off various OVOCs. For example, Gray et al. (2010) found OVOCs contributed over 84% and 98% to total VOCs emitted from plant litter during abiotic and biotic decomposition, respectively. Kumar et al. (2011) reported that OVOCs accounted for 83.8%–98.7% of the total VOCs emitted from green waste composting. Defoer et al. (2002) also found OVOCs shared over 23% of total VOCs released during the aerobic composting process of vegetable, fruit and garden wastes. Therefore, the study of OVOC emission in the degradation of organic waste helps to understand their fate during the processing of MSW as well as to improve MSW operation design.

Many previous studies have measured the composition and production of OVOCs from laboratory-controlled composting or pilot-scale landfill using different combinations of organic wastes (Smet et al., 1999; Staley et al., 2006; Kumar et al., 2011). OVOCs are present in fleshes and juices of fruits, particularly citrus (Umano et al., 2002; Brat et al., 2003). For example, OVOCs accounted for over 98% of volatile compounds extracted from flesh of citrus fruit (Umano et al., 2002). Fruit and vegetable wastes, such as biodegradable wastes, are decomposed initially by an aerobic process in the early stage of disposal (in dustbins and transfer stations, and early in landfills) by consuming oxygen from the air or remaining in the wastes (Statheropoulos et al., 2005; Zhang et al., 2012). Rather than studying OVOC

production during decomposition of composite organic wastes, the present study instead specifically tested orange wastes and measured emission rates of OVOCs during a 2-month laboratory incubation under aerobic conditions. The origin of OVOCs was also discussed along with the investigation of relationships between the emission fluxes and internal respiration rates (CO_2 emission fluxes) or incubation temperature.

1. Materials and methods

1.1. Experimental design

Newhall navel oranges (*Citrus sinensis* (L.) Osbeck, *Rutaceae*) used in the present study were purchased from a local market. Since oranges not suitable for sale are disposed whole as wastes and OVOCs are mainly present in the flesh of oranges (Umano et al., 2002; Brat et al., 2003), we did not isolate peels from flesh for our simulation. To accelerate the degradation, oranges were shredded with a slow speed, high torque shredder into pieces of about 0.5 cm × 1 cm in size (Sponza and Ağdağ, 2005). To obtain dry weights, part of the fresh shredded oranges was weighed before and after drying in an oven at 60°C for 24 hr. The water content of Newhall navel oranges averaged 80.8%.

For laboratory simulation, self-made glass reactors, each with a capacity of 11 L, were employed. The design and operation of the reactors have been described by Wang and Wu (2008). Briefly, the reactors were modified glass cylinders, each containing an air inlet, an air outlet and a leachate recirculation system. Two small fans were installed inside the chamber to ensure that the headspace air was well mixed. A thermocouple probe was inserted at half-depth of the waste to monitor its internal temperature. 5 cm washed gravel and a thin layer of glass fiber were placed at the bottom of each reactor to form an effective drainage layer. Aluminum foil was used to wrap the outer surface of the reactor to avoid light during the whole incubation. All the connecting tubes were made of Teflon.

The simulation was carried out in triplicate. At the start of the experiment, each reactor was loaded with about 2 kg shredded oranges along with 50 mL leachate from aerobic decay of residential municipal solid waste to initiate the decomposition. The incubation was carried out at room temperature (25 ± 0.5°C). During incubation, deionized water was occasionally added to maintain enough leachate, which was recirculated by a peristaltic pump (Wang and Wu, 2008). Except during sampling, ambient air was continuously introduced into the reactor at a rate of 0.5 L/min and effused from the oranges. According to Binner et al. (2003), an aeration rate of about 0.25 L/(min·kg^{-1}) food wastes as used in the present study is enough to ensure aerobic conditions. The orange wastes were monitored at regular intervals until there was less than a 0.2% daily increase in cumulative CO_2 yield, as described by Staley et al. (2006).

1.2. OVOCs analysis

The analytical method used for the identification and quantification of the OVOCs was similar to that employed by Blunden et al. (2005). OVOC species were analyzed by a gas chromatography–mass spectrometry detector (GC–MSD) system (6890/5973N, Agilent Technologies, Santa Clara, CA, USA) coupled with an Entech Preconcentrator (Entech Instruments Inc., Simi Vally, CA, USA). Details about sample analysis, standard preparation and calibration were similar to those presented previously (Yi et al., 2007; Wang and Wu, 2008). Briefly, an Entech Preconcentrator with three stages of cryo-trapping was applied to concentrate OVOCs before GC–MS analysis. A HP-1 capillary column (60 m × 0.32 μm × 1.0 μm, Agilent Technologies, Santa Clara, CA, USA) was used with helium as carrier gas. The GC oven temperature was programmed initially at −50°C, holding for 3 min, increasing to 10°C at 15°C/min, then increasing again to 120°C at 5°C/min, and finally to 250°C at 10°C/min and holding for 10 min. The MSD was run in scan mode with the mass range of 35–250 amu. The ionization method was electron impacting.

The identification of each compound was based on its retention time and mass spectrum. Target compounds were quantified by using a multi-point external calibration method. To prepare calibration curves, all OVOCs were first diluted with pure nitrogen to around 1000 mg m^{-3} as a primary standard mixture. The standard mixture was further dynamically diluted with pure nitrogen to 0 (pure nitrogen), 10, 100, 500 and 1000 μg/m^3 using mass flow controllers and a mixing chamber. The diluted gas standards were analyzed in the same way as the incubation samples. Except for methanol and ethanol, all OVOCs had good dose–response correlation ($R > 0.99$) in the range 0–1000 μg/m^3. Each day before sample analysis the system was calibrated with a 10 μg/m^3 standard mixture. If the responses were more than 20% different from the initial calibration curves, recalibration was conducted. After that the analytical system was challenged first with a humidified zero air sample to ensure that the analytical system was clean. The method detection limits of VOCs ranged from 0.05 to 0.63 μg/m^3 with a sample volume of 250 mL. The relative standard deviations were less than 7% after 10 replicate analyses of a standard mixture (10 μg/m^3) in 10 consecutive days. The recoveries of spiked samples (10 μg/m^3) were 88%–110%. Methanol and ethanol, due to their high solubility in the water phase, were easily removed with water during the preconcentration process, and their recoveries were therefore below 50%, and their dose–response correlation coefficients (R) were below 0.95 in the range 0–1000 μg/m^3. Thus, their quantitative results might be underestimated. Nevertheless, the relative standard deviations of methanol and ethanol were 7% and 4%, respectively, after 10 replicate analyses of a standard mixture (10 μg/m^3), which was humidified similarly to the incubation samples. The present method is sensitive and accurate for the measurement of trace OVOCs with weak polarity, but not as good for measuring OVOCs with strong polarity such as volatile fatty acids (VFAs) because they can be removed along with water in the Entech Preconcentrator, thermally decomposed in the hot inlet and/or poorly separated by the HP-1 capillary column. So we did not include VFAs in this study. Considering that VFAs were important components of OVOCs detected in the juice and flesh of citrus fruit (*e.g.*, Umano et al., 2002; Brat et al., 2003) as well as during the decay of organic wastes (*e.g.*, Romain et al., 2005), they should be taken into consideration in future studies on OVOC emissions from orange wastes.

1.3. Flux measurement

Fluxes of OVOCs were measured by a dynamic flow-through chamber technique. Briefly, dry clean air (with CO_2 level comparable to that in ambient air) from a gas cylinder instead of ambient air was passed through the chamber after being humidified by deionized water. After 60 min (over 5 cycles of residence time), when a steady state was reached, air samples were collected from the outlet with 1 L Teflon sampling bags (SKC Inc., Eighty Four, PA, USA). After sampling, again ambient air was passed through the chamber to maintain the aerobic condition. The emission fluxes (F, μg/(kg·hr)) were calculated as below:

$$F = Q \times [C_o(t) - C_i(t)]/M_w \quad (1)$$

where, Q (L/hr) is the airflow rate of compressed air through the chamber, $C_o(t)$ (μg/L) is the concentration in the outgoing air, and $C_i(t)$ (μg/L) is the concentration in the incoming air. For OVOCs $C_i(t)$ is zero and for CO_2 it is the level in the gas cylinder. M_w (kg) is the mass of orange wastes used for the simulation study. CO_2 concentrations were measured by a HP 4890D gas chromatograph coupled with a methanizer and a flame ionization detector.

2. Results and discussion

2.1. Compositions of the released OVOCs

Fig. 1 presents an example of chromatograms of OVOCs released from orange waste. Forty OVOCs were identified and quantified, including 12 alcohols, 5 aldehydes, 7 ketones, 14 esters and 2 acetals. Alcohols dominated in released OVOCs and were followed by esters, ketones and aldehydes (Table 1, Fig. 2), just as those detected in citrus fruit flesh (Umano et al., 2002) and juice (Buettner and Schieberle, 2001; Brat et al., 2003) and in intermediates of aerobic metabolism of organic materials (Eitzer, 1995; Staley et al., 2006). Alcohols were also observed as major VOCs emitted from green wastes (lawn clippings, yard prunings, and food wastes, as well as green and woody wastes) (Kumar et al., 2011) and biowastes (70% garden waste, 20% kitchen waste and 10% nonrecyclable paper) (Smet et al., 1999) during the aerobic composting process. Ethanol was found to be the most abundant species among the OVOCs released, followed by methanol, ethyl acetate, methyl acetate, 2-butanone and acetaldehyde. Other OVOCs were minor and altogether accounted for less than 10% in TOVOCs. Although 2,4,6-trimethyl-1,3,5-trioxane and 1,1,-diethoxy-ethane, as products from the condensation of acetaldehyde, were previously observed in fruit such as capers (Ozcan and Chalchat, 2007) and fermentative food such as grape wine (Lee and Noble, 2003) and pomaces (Ruberto et al., 2008), they have never been reported in citrus fruits, and in our study they were merely trivial constituents detected in emitted OVOCs. This profile of emitted OVOCs was consistent with that of OVOCs in citrus fruit flesh (Umano et al., 2002) or juice (Buettner and Schieberle, 2001; Brat et al., 2003), with ethanol, acetaldehyde, and ethyl acetate being the predominant compounds extracted. Also, the results in the study were quite similar to previous studies, which revealed that ethanol, ethyl acetate, 2-butanone and acetaldehyde typically showed high levels in odor sources such as municipal solid wastes (Staley et al., 2006) and waste treatment facilities (Eitzer, 1995; Smet et al., 1999; Dorado et al., 2014; Lehtinen et al., 2013).

As shown by Fig. 2, during the whole incubation the ratio of aldehydes to TOVOCs drastically decreased due to large loss of inherent acetaldehyde, while the percentage of ketones gradually increased with enhancement of acetone and 2-butanone. The share of alcohols decreased during the early

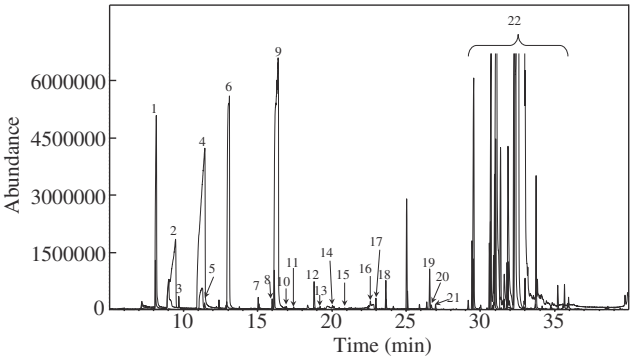

Fig. 1 – Typical chromatogram showing selected oxygenated volatile organic compounds (with production of more than 1 mg/dry kg) and some terpenoids from oranges at day 0 (solid line), day 2 (dotted line), and day 22 (dash line) of aerobic incubation. The numbered peaks indicate compounds: 1 acetaldehyde; 2 methanol; 3 methyl formate; 4 ethanol; 5 acetone; 6 methyl acetate; 7 2,3-butanedione; 8 2-butanone; 9 ethyl acetate; 10 2-methyl-1-propanol; 11 2-methyl-3-buten-2-ol; 12 2-pentanone; 13 3-pentanone; 14 2-pentanol; 15 3-hydroxy-2-butanone; 16 2-methylpropyl acetate; 17 2,4,6-trimethyl-1,3,5-trioxane; 18 ethyl butyrate; 19 3-methylbutyl acetate; 20 2-methylbutyl acetate; 21 2-heptanone; 22 monoterpenes.

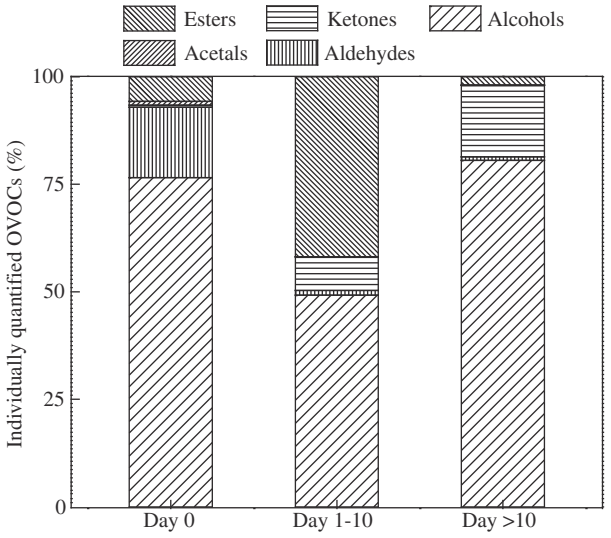

Fig. 2 – Percent contribution of five classes of oxygenated volatile organic compounds (OVOCs) to total oxygenated volatile organic compounds (TOVOCs) released at different stages of incubation.

10 days of the incubation, and then increased after 10 days, whereas the contribution of esters to TOVOCs increased in the initial 10 days and then decreased after 10 days. The ratio of acetals was very low during the whole decomposition. The change of ketone ratio in the present study was consistent with that in a previous study, which revealed that the relative proportion of ketones increased with compost age (Romain et al., 2005). This result can be explained by the fact that ketones are produced as concomitants of possible microbial metabolites when the large bio-organic compounds such as lignins and proteins are being turned into humus as the compost ages (Eitzer, 1995). However, the changes of alcohol, aldehyde, and ester percentages were not in line with those in a previous study, which revealed that the relative proportions of alcohols and aldehydes peaked in the middle of the composting process, while the ratio of ester to total VOCs fluctuated during the composting process (Romain et al., 2005).

2.2. Emission profiles

As demonstrated in Figs. 1 and 3, the emission profiles of the released OVOCs from orange wastes varied with incubation time. For a few OVOCs including acetaldehyde, hexanal, 1-hexanol, 1-penten-3-ol, 3-hexen-1-ol and 2,4,6-trimethyl-1,3,5-trioxane, their emission fluxes were very high at day 0, decreased sharply and then leveled off after 10 days, and they did not reveal a correlation with internal respiration rate (CO_2 emission fluxes) and biomass temperature (Fig. 4), both of which could indicate biological activity (Haug, 1993). The results suggested that evaporation of inherent OVOCs in navel oranges was the major mechanism for their emission. Oranges as a pool of OVOCs were shredded before incubation, meaning that these compounds were not locked in clumps, but rather volatilized rapidly due to the increase of surface area (Eitzer, 1995). As revealed by previous studies, OVOCs are metabolites formed largely from fatty or amino acid precursors during normal ripening and maturation and can be

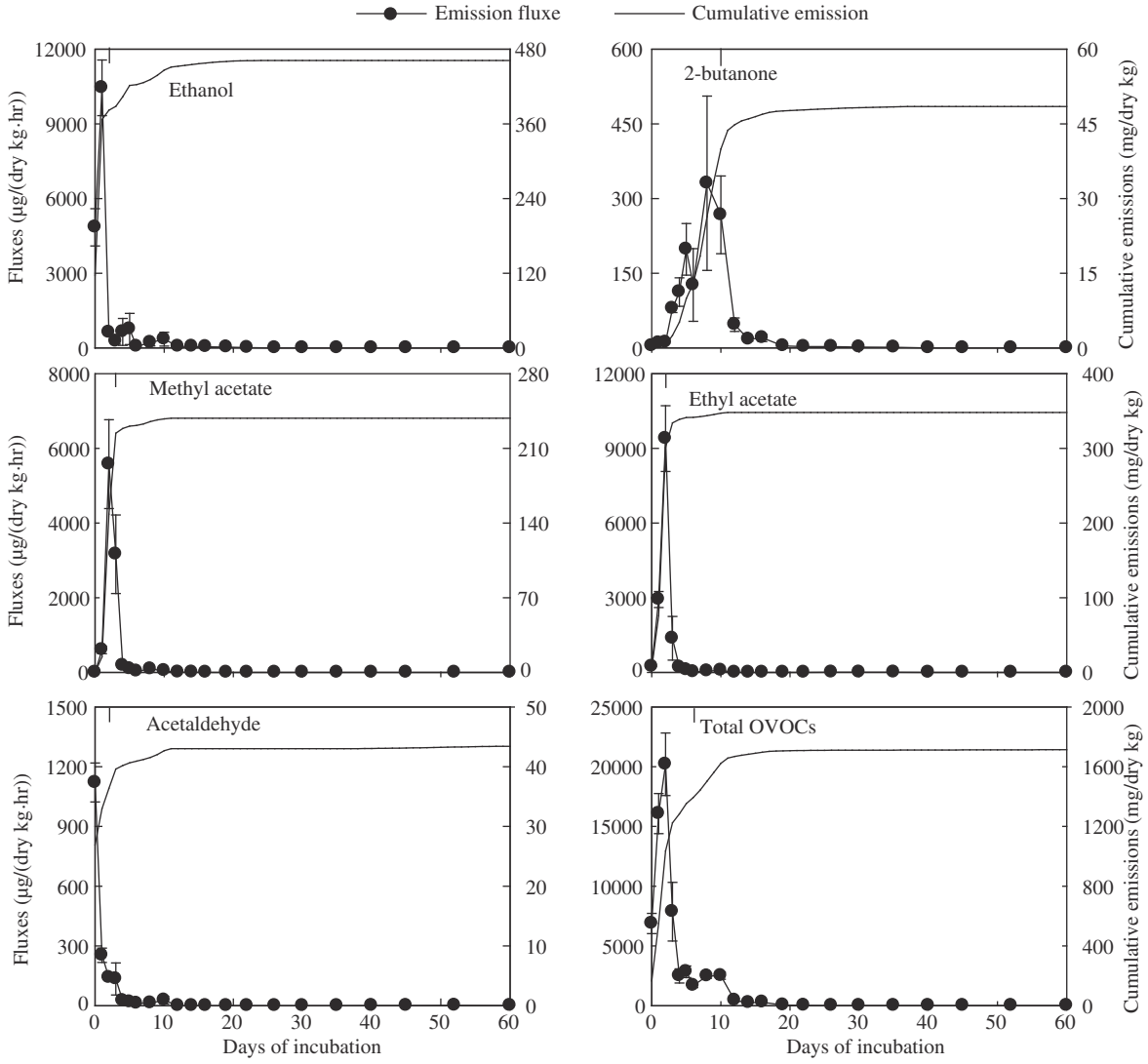

Fig. 3 – Emission fluxes and cumulative emissions of some major oxygenated volatile organic compounds (OVOCs) and total oxygenated volatile organic compounds (TOVOCs) from orange wastes. Error bars represent the standard deviation and dashed lines denote cumulative emission over 80%.

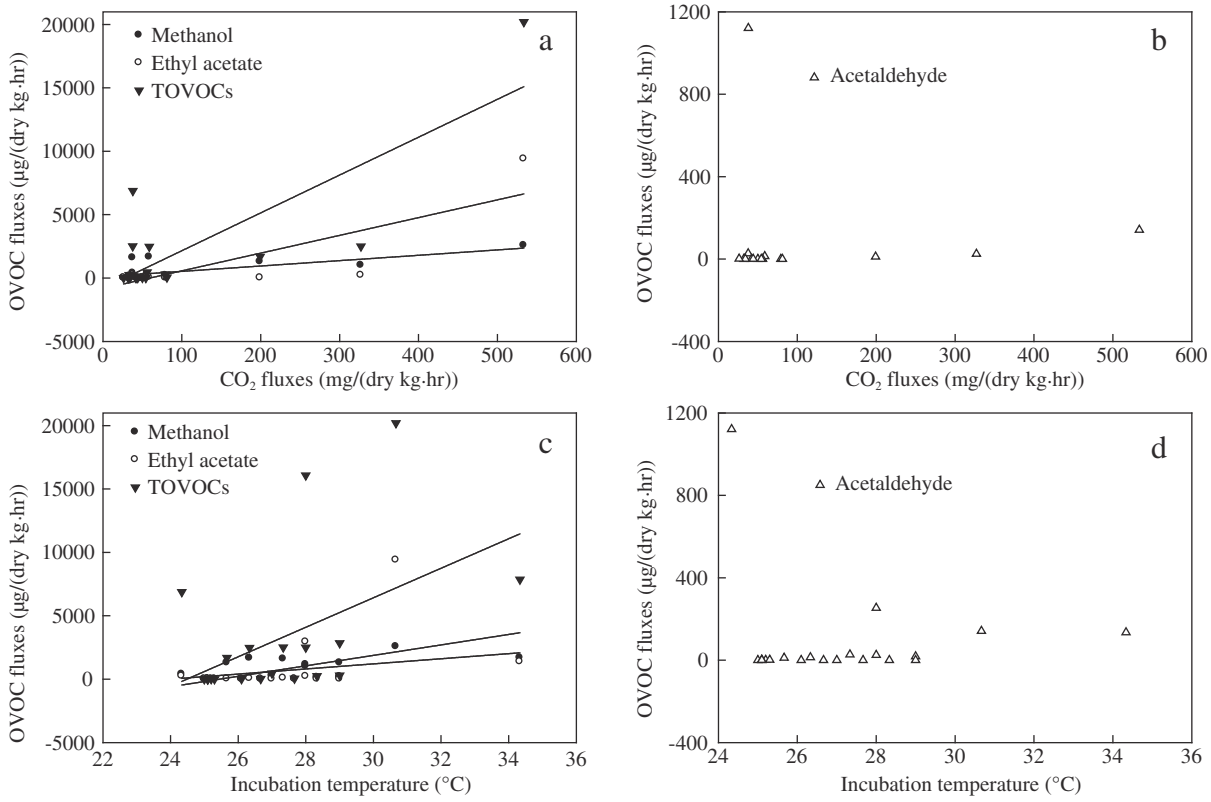

Fig. 4 – Fluxes of some major oxygenated volatile organic compounds (OVOCs) and total oxygenated volatile organic compounds (TOVOCs) from orange wastes in relationship to waste respiration rate (a, b) and incubation temperature (c, d). The regression equations for methanol are $y = 4.23x + 102.04$ ($n = 17$, $r = 0.7282$, $p = 0.0009$) and $y = 201.37x - 4833.15$ ($n = 21$, $r = 0.6070$, $p = 0.0035$), those for ethyl acetate are $y = 14.01x - 835.95$ ($n = 17$, $r = 0.8329$, $p < 0.0001$) and $y = 412.49x - 10{,}497.20$ ($n = 21$, $r = 0.4600$, $p = 0.0359$), and those for TOVOCs are $y = 29.86x - 835.71$ ($n = 17$, $r = 0.8329$, $p < 0.0001$) and $y = 1163.72x - 28{,}490.22$ ($n = 21$, $r = 0.4954$, $p = 0.0224$).

emitted transiently upon cell wounding (Peterson and Reineccius, 2002; Koppmann and Wildt, 2007).

For the remaining OVOCs listed in Table 1 such as the four major OVOCs (ethanol, 2-butanone, methyl acetate and ethyl acetate), their emissions were quite trivial or below detection limits in the beginning and increased immediately to form one "peak emission window" with a maximum at days 1–8, and then decreased sharply until leveling off after 10 days (Fig. 3). If they were just inherent, their emission rates would substantially decrease with incubation time. The results indicated that these OVOCs would be secondarily formed during the incubation rather than being inherent. In fact, 13 OVOCs including 2-pentanol, 2-methyl-3-buten-2-ol, 2-methylpropanal, 2-methylbutanal, pentanal, 3-hydroxy-2-butanone, methyl formate, 2-methylpropyl acetate, 2-methylbutyl acetate, 3-methylbutyl acetate, methyl propionate, ethyl propionate and 1,1-diethoxy-ethane (Table 1) were absent in released OVOCs at day 0 when oranges were fresh and occurred only in the subsequent decomposition process. It is worth noting that emission fluxes of TOVOCs peaked at day 2 and were about three times those at day 0 (Fig. 3), implying that OVOCs emitted from aerobic decaying orange wastes were mainly derived from secondary products of orange substrates rather than primary volatilization of the inherent pool in oranges. Quite similarly, Kumar et al. (2011) found that the flux rates of alcohols were low from the fresh tipping pile, peaked in the younger windrow (3–6 days old), and then decreased in the older windrow (2–3 weeks) during the composting of green organic wastes, and that emission fluxes of total alcohols that peaked in the younger windrow were about five times of those in the fresh tipping pile.

As reported by previous studies (Warneke et al., 1999; Rappert and Müller, 2005; Gray et al., 2010), OVOCs in organic materials such as food and plant litter can be formed through abiotic or biotic degradation of substrates. It is well known that non-enzymatic thermo-chemical reactions such as auto-oxidation and Maillard reactions can lead to the formation of OVOCs in the gases emitted from plant litters (Warneke et al., 1999; Rappert and Müller, 2005). Orange wastes used in this study were exposed to air, which could cause the production of OVOCs from substrates by auto-oxidation. Warneke et al. (1999) reported that even at room temperature, considerable amounts of OVOCs could be produced during the decay of plant litter. The incubation temperature in this study was 24.3°C at the beginning and increased with time to a peak at 34.3°C during the aerobic decomposition of orange wastes, which could lead to the production of OVOCs from orange wastes by Maillard reactions. Warneke et al. (1999) found Maillard reactions were responsible for the emissions of acetone during the initial 4 hr of heating of plant materials. Schade and Custer (2004) also reported that methanol emission from an agricultural field plot was attributed to Maillard reactions of soil organic matter

during one of the hottest weeks of the heat wave during the summer of 2003 in Europe. OVOCs from biomaterials such as fruit, vegetable and leaf litter could also be formed through the biological conversion of tissue cells by enzymes (Peterson and Reineccius, 2002; Rappert and Müller, 2005) or microorganisms (Isidorov et al., 2003; Rappert and Müller, 2005; Ramirez et al., 2010). Oranges used in this study were shredded into small pieces with ruptured plant membranes, and thus might be rapidly degraded *via* enzyme activity with available substrates (Fall et al., 1999). OVOCs could also be produced from the microbial metabolisms of primary composition (pectin, protein, cellulose, sugar) (Galbally and Kirstine, 2002), which have high contents in oranges (Brat et al., 2003). Many species of microorganisms (fungi, yeasts and bacteria) are reported to produce OVOCs such as methanol, 2, 3-butanedione, 3-hydroxy-2-butanone and so on (Galbally and Kirstine, 2002; Rappert and Müller, 2005; Mayrhofer et al., 2006; Bäck et al., 2010). Although OVOCs may be secondarily formed from orange wastes by abiotic processes and this study was not designed to distinguish between biotic and abiotic sources of OVOCs, our observation of a strong synchronization of OVOC emission fluxes with CO_2 fluxes and temperature (Fig. 4) suggested that OVOCs as secondary products might be mainly attributed to biotic processes rather than abiotic processes. While abiotic VOC productions might be concurrent, their rates were likely to be far lower than the rates of biotic OVOC production. Gray et al. (2010) reported that the emissions of VOCs including OVOCs from litter by biotic degradation (non-sterile control) were between 0 and 11 times those by abiotic degradation (sterile controls) over a 20-day incubation period, and that abiotic sources of OVOCs were generally less important than biotic sources.

2.3. *Production*

Cumulative production of five major OVOCs and TOVOCs during the incubation period is presented in Fig. 3. For all OVOC species except 2-butanone and acetone, over 80% of their emissions occurred during the first week. In particular, over 90% of the four major OVOC (ethanol, methyl acetate, ethyl acetate and acetaldehyde) emissions and about 85% of TOVOC emission occurred during the first week. Also as shown in Fig. 5, TOVOCs, alcohols, ketones and esters had maximal production at days 1–10 of the incubation, while total aldehydes and acetals attained maximal production at day 0, and after 10 days their production all became minor and accounted for less than 10% in the total production. These results indicated that OVOCs were mainly released at the early stage of orange waste decomposition, which was consistent with previous studies. Knox (1990) observed that the levels of alcohols were greatest in fresh refuse, and other studies also found that OVOCs (alcohols, carbonyl compounds, esters and ethers) were principally emitted at the early stage of waste decomposition (Smet et al., 1999; Muezzinoglu, 2003; Chiriac et al., 2011; Kumar et al., 2011; Delgado-Rodríguez et al., 2012) and bio-drying (He et al., 2010). Considering that organic waste is an important component of MSWs, and that municipal wastes may stay in dustbins or transfer into stations up to a week before reaching landfills or incinerators, and their decomposition largely takes place

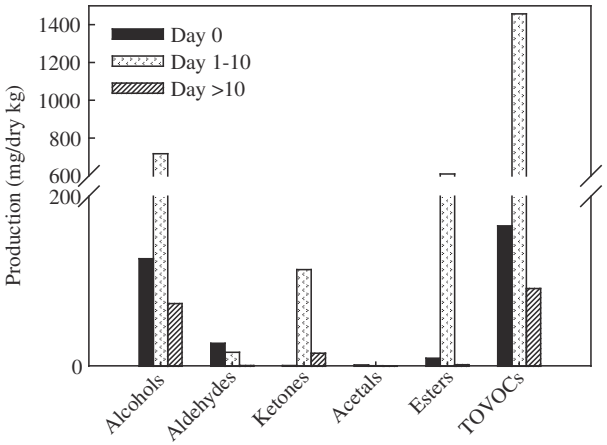

Fig. 5 – Comparison of production of the five classes of oxygenated volatile organic compounds (OVOCs) and total oxygenated volatile organic compounds (TOVOCs) at day 0, days 1–10 and day >10.

under aerobic conditions during the collection and distribution processes and the early times in landfills (Statheropoulos et al., 2005; Zhang et al., 2012), the results in the present study suggested that considerable amounts of OVOCs are emitted during early disposal of organic wastes and thus contribute to malodor from these waste treatment facilities.

Table 1 presents the production of detected OVOCs during the two-month incubation of orange wastes. Total yields of OVOCs reached 1714 mg/dry kg (330 mg/wet kg). Alcohols as the most dominant OVOC group in total had emission of 917 mg/dry kg (176 mg/wet kg), accounting for 53.5% of the TOVOCs released. Total ester emission was 621 mg/dry kg (119 mg/wet kg) and contributed 36.2% of the TOVOC emission. Total ketones, aldehydes and acetals accounted for 7.6%, 2.6% and 0.1% in OVOCs emitted, respectively. Ethanol, methanol, ethyl acetate, methyl acetate, 2-butanone and acetaldehyde, as the six most abundant OVOC species, had an emission of 462, 425, 348, 238, 48.5 and 43.4 mg/dry kg, accounting for about 26.9%, 24.8%, 20.3%, 13.9%, 2.8% and 2.5% of the TOVOCs released, respectively. The above six major species altogether contributed 91.3% of the TOVOC emission.

In comparison, the production of the two major OVOC groups (alcohols and esters) from orange wastes during the aerobic decomposition in the present study was 0–1 order higher, with TOVOCs 2–3 orders higher, than that reported previously by Smet et al. (1999) for biowastes (70% garden waste, 20% kitchen waste and 10% nonrecyclable paper) during aerobic decomposition, or by Staley et al. (2006) for residential MSWs (municipal solid wastes) and yard waste during aerobic and anaerobic degradation, although the TOVOC production from orange wastes was much lower than that (2031–108,580 mg/dry kg) from litter of 12 plant species during aerobic biotic decomposition mg/dry kg (Gray et al., 2010). This indicated that citrus fruit waste, even when making up a small part in biowastes, would contribute a large portion to OVOC emission. Allen et al. (1997) found that the alcohols, ketones and esters were 2–3 orders of magnitude higher at sites for the disposal of fruit wastes than other sites in a landfill.

3. Conclusions

In the present study we measured 40 OVOCs emitted from orange wastes during laboratory-controlled aerobic decomposition for a period of 2 months. Emission of OVOCs from orange wastes totaled 1714 mg/dry kg (330 mg/wet kg). Ethanol, methanol, ethyl acetate, methyl acetate, 2-butanone and acetaldehyde were the six most abundant OVOC species, contributing 26.9%, 24.8%, 20.3%, 13.9%, 2.8% and 2.5% to the TOVOCs released, respectively. The emission fluxes of the above top five OVOCs were very low at day 0 and peaked at days 1–8, and then decreased sharply until leveling off after 10 days of incubation. This time series was correlated significantly with CO_2 fluxes and incubation temperature, indicating that these OVOC species were mainly derived from secondary metabolites of orange substrates from biotic processes. For acetaldehyde, its emission flux was maximized at day 0 and then decreased sharply to nearly zero in about 4 days, implying it was primarily from evaporation of the inherent pool. For all OVOCs except 2-butanone and acetone, over 80% of their emissions occurred during the first week. In particular, over 90% of the four major OVOC (ethanol, methyl acetate, ethyl acetate and acetaldehyde) emissions and about 85% of TOVOC emissions occurred during the first week. These results suggest that OVOCs were mainly released from orange waste at the early stage of aerobic decomposition. For organic wastes or plant leaves littered on soil surfaces, their degradation all takes place initially under aerobic conditions, and they would also give off OVOCs since they have compositions quite similar to orange wastes. So this study will help to understand their aerobic degradation processes in relation to the emission of OVOCs and will also provide information useful for waste management and odor control.

Acknowledgments

This work was supported by the Ministry of Science and Technology of China (No. 2012IM030700), and the National Natural Science Foundation of China (Nos. 41025012, U0833003, 41273095 and 41103067). Thanks are given to Zhengyue Li, Dejun Li, Xiang Ding, Zhigang Yi, and Longfeng Li for their help in this research.

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