

## Volatile organic compound emissions from green waste composting: Characterization and ozone formation

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### ABSTRACT

Composting of green waste separated from the disposed solid waste stream reduces biodegradable inputs into landfills, and contributes valuable soil amendments to agriculture. Agencies in regions with severe air quality challenges, such as California's San Joaquin Valley (SJV), have raised concerns about gases emitted during the composting process, which are suspected to contribute to persistent high levels of ground-level ozone formation. The goal of the current study is to thoroughly characterize volatile organic compound (VOC) emissions from green waste compost piles of different ages (fresh tipped piles, 3–6 day old windrows, and 2–3 week old windrows). Multiple sampling and analytical approaches were applied to ensure the detection of most gaseous organic components emitted. More than 100 VOCs were detected and quantified in this study, including aliphatic alkanes, alkenes, aromatic hydrocarbons, biogenic organics, aldehydes, ketones, alcohols, furans, acids, esters, ether, halogenated hydrocarbons and dimethyl disulfide (DMDS). Alcohols were found to be the dominating VOC in the emissions from a compost pile regardless of age, with fluxes ranging from 2.6 to 13.0 mg m<sup>-2</sup> min<sup>-1</sup> with the highest emissions coming from the younger composting windrows (3–6 days). Average VOC emissions other than alcohols were determined to be 2.3 mg m<sup>-2</sup> min<sup>-1</sup> from younger windrows, which was roughly two times higher than either the fresh tipping pile (1.2 mg m<sup>-2</sup> min<sup>-1</sup>) or the older windrows (1.4 mg m<sup>-2</sup> min<sup>-1</sup>). It was also observed that the older windrows emit a slightly larger proportion of more reactive compounds. Approximately 90% of the total VOCs were found to have maximum incremental reactivity of less than 2. Net ozone formation potential of the emissions was also assessed.

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### 1. Introduction

Disposal of solid organic waste in an environmentally friendly and productive manner is a pressing need in a developing world. Increasing consumption of resources, rapidly filling landfills, and landfill-related global warming concerns (Mor et al., 2006) have challenged the landfill paradigm and are driving communities to reduce, reuse and recycle waste to the maximum extent possible. Compostable materials like yard trimmings and food waste comprise approximately 25% of municipal solid waste by weight in the United States while other organic wastes like paper and wood

make up another 36% (USEPA, 2008). Some two thirds of yard waste generated in the United States is now recycled, much of it by composting and mulching (USEPA, 2008). At least 23 states in the United States have totally or partially banned the disposal of yard waste in landfills (Arsova et al., 2008). The European Union targeted a decrease in the amount of organic waste disposed of in landfills by 20% by 2010 and by 50% by 2050 (Council Directive 1993/31/EC, 1999). In California, nearly 20 million tons, more than 25% of compostable organics, food, lumber, paper and cardboard are still disposed in landfills annually (CalRecycle, 2009a). California's Department of Resources Recycling and Recovery (CalRecycle), formerly known as the Integrated Waste Management Board, adopted a goal in 2007 to reduce the amount of organics being landfilled by 50 percent by 2020 (CalRecycle, 2009b). More than 360 California cities and counties reported collecting source-separated organic wastes in 2008, either at the residential curb or from businesses, or both (CalRecycle, 2008). There are approximately 115

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operating compost facilities in California, and more than 100 other operations that grind green and woody waste into mulch or boiler fuel. The largest of these facilities cover more than 100 acres and are permitted to receive more than 1000 tons per day of organic wastes (CalRecycle, 2010).

Composting is a naturally-occurring biochemical process utilizing controlled aerobic decomposition of organic material. Typical feedstocks include lawn clippings and prunings, tree trimmings, pre- and post-consumer food scraps, farm wastes including manure, food packaging and processing wastes, and sewage treatment plant solids. These materials are ground, blended and arranged in either large static or aerated piles, or elongated piles called windrows which are easily churned with a mechanized turner. The piles are watered and turned over a period of weeks and months. Controlling the levels of oxygen and balancing the carbon:nitrogen ratio through proper mixing of green and brown materials are key drivers for producing high-quality compost. The end product of composting is a moist, crumbly, soil-like product with a not objectionable, earthy odor.

Composting of organic wastes is not only a key strategy in conserving valuable landfill capacity and reducing methane emissions from landfills, but also produces a natural fertilizer and soil conditioner for agricultural land. An average of more than 3600 compost samples analyzed by a California laboratory showed typical compost nutrient values exceeding 1% by weight for nitrogen, phosphorus and potassium, more than 3.5% for calcium, as well as significant amounts of important micro-nutrients and minerals such as iron, manganese and zinc. The addition of compost to agricultural soils reduces soil density and can increase water holding capacity by 1.7–4.4% (UNSW, 2006). This reduces the need for irrigation as well as reducing nutrient-rich runoff into creeks and rivers and percolation of excess fertilizers into groundwater. The world's farmlands have lost between 42 and 78 billion metric tons of carbon since the onset of mechanized agriculture (Lal, 2004). An increase of just one ton of soil carbon in depleted soils can boost production of wheat and corn by 20–40 tons hectare<sup>-1</sup> and 10–20 tons hectare<sup>-1</sup> respectively (Lal, 2004). With an average carbon dry weight of more than 24%, compost should be an effective way to rebuild soil carbon levels, particularly in depleted or intensively farmed soils. Overall, the soil carbon pool is 3.3 times larger than the atmospheric carbon pool, and has the potential to offset 5–15% of global fossil fuel emissions annually (Lal, 2004). When used as a substitute for peat, researchers have estimated that composted organic wastes can produce a greenhouse gas (GHG) benefit of up to 900 kg ton<sup>-1</sup> of wet waste (Boldrin et al., 2009). The ability of compost to produce GHG benefits from avoided fertilizer use and reduction of nitrous oxide emissions from intensively managed crop lands is currently under investigation by CalRecycle and UC Davis.

The composting process also emits some gases into the atmosphere. The amount and type of emissions depends on a number of variables, including the feedstock, age of the pile, temperature, O<sub>2</sub> levels, humidity and pH (Romain et al., 2005). Compost emissions include volatile organic compounds (VOCs) and greenhouse gases such as nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>) (Hellebrand, 1998). For nitrogen-rich feedstocks such as animal manures or sewage sludge, ammonia (NH<sub>3</sub>) is another emission of concern. When compost facilities contain such feedstocks or when compost piles are not well maintained, they may also emit substantial odors. (CalRecycle, 2007; Tsai et al., 2008). California has one of the largest commercial compost sectors in the nation, partially due to a 20-year focus on reducing the amount of waste sent to landfills, and partially due to a demand for the product from the state's sizeable agriculture sector. The California Air Resources Board's 2008 emissions inventory estimates indicated that ROG (Reactive

Organic Gases, or non-exempt VOC) emissions from composting were approximately 38.02 tons day<sup>-1</sup>. These emissions accounted for less than 1% of the total ROG emissions in California. (CARB, 2008). Even small amounts of ROG are a major concern in places like California's San Joaquin Valley (SJV), which has "extreme" non-attainment status with the federal Clean Air Act for its persistent high ozone concentrations during the warm, sunny and cloudless summer and autumn months.

Air quality officials in the SJV have drafted first-in-the nation rules to limit emissions from greenwaste compost piles. Both the San Joaquin Valley Unified Air Pollution Control District's Rule 4565 and the South Coast Air Quality Management District's Rule 1133.2 already regulate emissions from compost piles comprised of animal manure or sewage sludge (SJVUAPCD, 2007; SCAQMD, 2003). Prohibitory rules such as the ones under consideration might impede the composting infrastructure and pre-empt future benefits in soil carbon sequestration and agricultural-related GHG emissions reductions before basic information about actual contributions of these emissions in ozone formation are known.

There have been numerous efforts to measure the flux rates of total VOCs from compost piles, with widely varying results. But we know of no study attempting to characterize the entire range of VOC emissions from a green waste compost operation. The purpose of the present study is to address the composition of green waste compost emissions and to estimate the ozone formation potential of those emissions. Emission estimation with a detailed speciation profile was carried out for more accurate input on the contribution of compost operations to tropospheric ozone production in the Valley.

## 2. Material and methods

### 2.1. Field experiments

Two compost facilities, each located within California's San Joaquin Valley, were chosen for sampling. The first facility (Site 1) is permitted to receive up to 2000 tons day<sup>-1</sup> of urban green waste as well as farm waste. Most of the feedstocks come from the San Francisco Bay Area, about 40 miles to the northwest, where several cities encourage residents to dispose of lawn clippings and yard prunings, as well as food waste, in a green waste can. This facility is characterized by small, intensively managed windrows. The second facility (Site 2) is about 1/10th as large and receives its feedstock exclusively from within the San Joaquin Valley. This site only handles green and woody wastes, but no food waste. Windrows at Site 2 are larger in terms of height and width. Experiments in duplicate were carried out on fresh tipping piles, newly formed compost windrows (3–6 days old), and 2–3 week old windrows at each facility in September and October of 2009, respectively. VOC samples in each experiment were collected in duplicate to enhance the sample representativeness. Strongly emitting or 'hot' locations in the sources were not sought.

Environmental flux chambers similar to the USEPA surface emission isolation flux chambers were used at the first compost facility for the collection of emissions from the tipping pile or compost windrows. A flux chamber (Odotech, Inc., Montreal, Quebec, Canada) is a dome shaped enclosure used to sample gaseous emissions from a defined surface area (0.13 m<sup>2</sup>) as shown in Fig. 1 (Sun et al., 2008). Four flux chambers were used in the study to cover a larger surface area and were placed on the top of the windrow. Zero air, generated from zero air generators (Perma Pure, Toms River, NJ), was swept at the rate of 5 L min<sup>-1</sup> through each of the flux chambers. These generators have an ultra violet lamp for the removal of bacteria and oxidizes NO to NO<sub>2</sub> which is readily removed by system adsorbent, an activated carbon/alumina

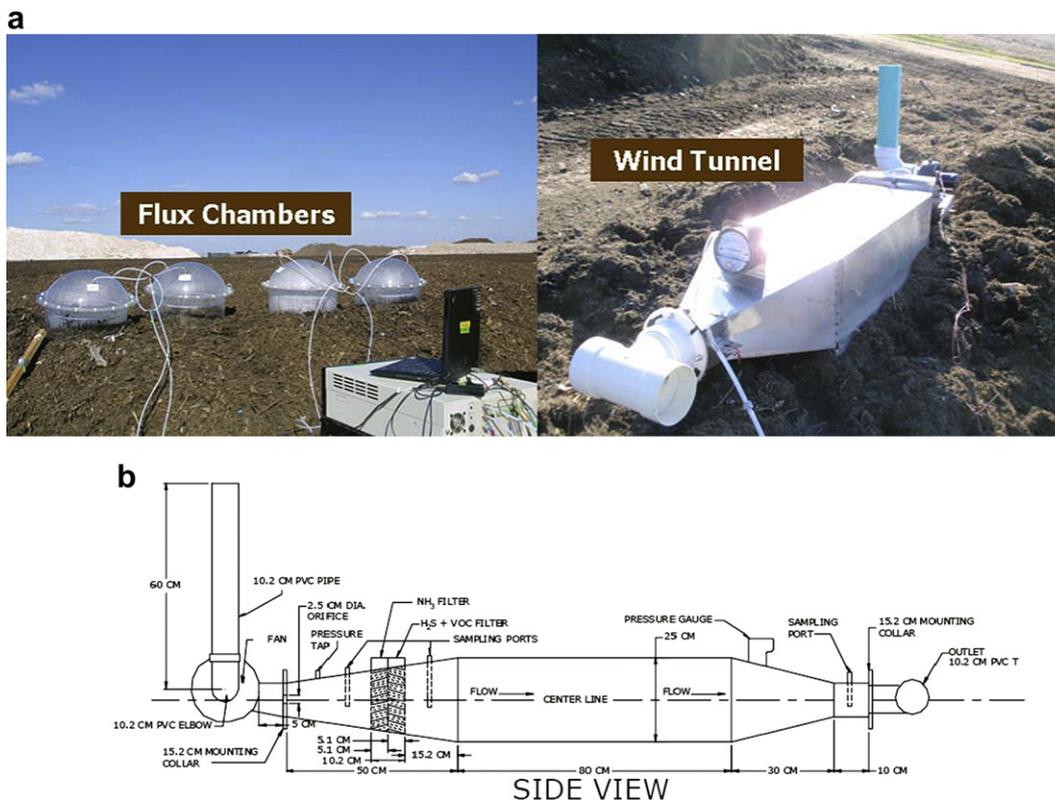


Fig. 1. Flux chambers and the dilution tunnel with the schematic of the dilution tunnel.

mixture for the removal of trace quantities of hydrocarbons, sulfur di- and trioxide, NO<sub>x</sub> and O<sub>3</sub>, a carbon monoxide catalyst to convert CO to CO<sub>2</sub>, and a 1.0 μm particulate filter with a 93 percent rating down to 0.1 μm to ensure that any airborne particles that may have been in the background air are removed. The zero air generated was found to be quite clean. Moreover, an inlet air sample was also collected and analyzed to ensure its quality. Returned air from each of the chambers was set to flow at 5 L min<sup>-1</sup> so that the net pressure drop between the atmosphere and the chamber was zero. Return flow from all four chambers were combined and passed through a cold trap (0 °C, for reduction of water vapor) before collection by the sampling media. The contents of the cold traps were analyzed in the laboratory for VOC composition.

After experiencing high water content in the flux chamber samples, a dilution tunnel was used to provide dilution of emissions at Site 2. As a result, no cold trap was needed. The dilution tunnel is a rectangular stainless steel enclosure with an open bottom portion that covers 0.32 m<sup>2</sup> of emitting surface area and which has a volume of 0.08 m<sup>3</sup>, shown in Fig. 1 with its schematic. The dilution tunnel is placed 1 cm into the top of the selected windrow to fix the tunnel surface into the compost. Details of the dilution tunnel are provided elsewhere (Schmidt and Bicudo, 2002). The first sampling port in the tunnel allows the sampling of inlet air, the second port allows for the sampling of post filter air and the third port is used for sampling at the tunnel outlet. A 12 cm long perforated stainless steel tube in the tunnel was connected to each sampling port. The perforated tube ensures that samples representative of the full flow are collected. The outlet baffle of the tunnel helps avoid back pressure caused by ambient wind during sampling. Air is blown through the tunnel to mix with and transport the surface emissions towards the outlet. The dilution tunnel is equipped with chemisorbant and activated carbon filled chambers at the intake to clean the air being pulled into the chamber. The

bulk speed in the dilution tunnel, which is measured using a pressure gauge installed on the tunnel, can be adjusted to between 0.13 and 0.47 m s<sup>-1</sup> (roughly 0.5 to 1.5 km h<sup>-1</sup>) with resulting air exchanges of 10 to 35 per minute. The velocity profile in the tunnel is fairly uniform and consistent. (Schmidt and Bicudo, 2002)

The use of the dilution tunnel in lieu of the flux chambers provides a larger covered surface area and a defined, controlled air exchange rate. Air flow through the dilution tunnel also provides dilution of emissions, which helps to reduce the high humidity from compost emissions. After each experiment, the tunnel/chamber is wiped clean with dry paper towels and flushed on a clean surface with zero air. All Teflon tubing is also purged with zero air after every experiment.

## 2.2. VOC sampling and analyses

Multiple sampling techniques were applied to collect a wide range of VOCs in order to characterize the complex mixture of compost emissions. Evacuated 6 L passivated stainless steel SUMMA polished canisters were used to collect VOC samples using USEPA method TO-15 (USEPA, 1999a). Charcoal tubes (Orbo 32, Sigma-Aldrich, St. Louis, MO) containing 400 mg and 200 mg of activated carbon in two successive sections were used for sample collection and breakthrough determination, respectively, for less volatile/semi volatile organic compounds at a sampling rate of 1.5 L min<sup>-1</sup> for 2 to 3 h (NIOSH, 2003). Charcoal tubes supplemented canister samples to ensure that a full range of hydrocarbons were measured. USEPA TO 11 was applied for the measurement of carbonyl compounds (aldehydes and acetone) with sorbent tubes containing 300 and 150 mg of silica gel impregnated with 2,4-dinitrophenylhydrazine (DNPH) in the front (main sample) and backup (to assess breakthrough) sections of the tube, respectively (SKC West Inc. Fullerton, CA) (USEPA, 1999b).

Samples were collected at a flow rate of 200–500 mL min<sup>-1</sup> for 2–3 h. Backup sorbent sections of charcoal and DNPH tubes were analyzed to demonstrate lack of breakthrough during sample collection. Neither charcoal nor DNPH tube type showed sample breakthrough at any time. Sampled tubes and field blanks were capped and placed in polypropylene bags immediately after collection and stored under refrigeration at 4 °C prior to analysis.

Alcohols, which constitute a major fraction of compost VOC emissions, were measured using an INNOVA photo-acoustic multigas monitor (Model-1412, INNOVA AirTech Instrument, Ballerup, Denmark). The INNOVA was configured for methanol, ethanol, 2-propanol, ammonia, trimethylamine and water vapor through the use of respective optical filters and was calibrated by the instrument manufacturer. The method quantification limit of the INNOVA for alcohols was less than 1 ppm. The INNOVA is an approved method for alcohol measurements by the California Air Resource Board (CARB, MSO 2000-08). The analyzer monitored all the compounds at one minute intervals, and the average values over 2–3 h, in parallel with other sampling techniques, were used in data calculation.

Canisters were connected directly to the GC-MS through two stage (carbo trap and cryogenic trap) automatic high performance cryofocusing units (Lotus Consulting, Long Beach, CA) for analysis by a Varian CP-3800 gas chromatograph coupled to a Varian Saturn 2200 ion trap mass spectrometer (Varian Inc., Palo Alto, CA). A DB-624 fused silica capillary column (Agilent, Santa Clara, CA) with dimensions 60 m × 0.32 mm × 1.8 μm was used for the separation of analytes. Detailed analytical conditions were described previously in Kumar et al. (2010). A gaseous standard calibration gas mixture of over 60 compounds including alkanes, alkenes, aromatics, alcohols, ketones, acetates etc. at 100 ppb was purchased from Scott Specialty Gases (Plumsteadville, PA), and was diluted by a factor of 10 in a clean canister with ultra pure nitrogen and used for GC-MS calibration. The absolute accuracy of the concentration measurement for most of compounds was estimated to be ±10%.

Individual sections of each charcoal tube and DNPH silica cartridge were extracted in separate vials using 1.5 mL of CS<sub>2</sub> and 5 mL of acetonitrile solvent, respectively, followed by 15 min of sonication. The supernatant phase of the charcoal extracted solvent was transferred into an autosampler vial and analyzed by an Agilent 6890A gas chromatograph coupled with an Agilent 5973N mass spectrometer with a ZB-624 capillary column (Phenomenex, Torrance, CA) with dimensions 30 m × 0.25 mm × 1.4 μm. The instrument was calibrated with a mixture of known concentration of several groups of compounds to verify the linearity of the measurements. Samples extracted from DNPH cartridges were transferred into an autosampler vial and analyzed by isocratic reverse phase high performance liquid chromatography (HPLC) on an Agilent 1100 equipped with an ultraviolet absorption detector operated at 360 nm following USEPA TO-11 (USEPA, 1999b). A 250 mm × 4.6 mm Ultra C18 column (Restek, Bellefonte, PA) was used for carbonyls separation. The mobile phase consisted of acetonitrile and water in the ratio of 70:30 at a flow rate of 1 mL min<sup>-1</sup>. Three point calibration curves (0.015 μg mL<sup>-1</sup>, 0.15 μg mL<sup>-1</sup>, and 1.5 μg mL<sup>-1</sup>) were obtained using a standard solution containing 15 carbonyl compounds in acetonitrile obtained from Supelco (Bellefonte, PA). Further analytical details were provided in our previous paper (Kumar et al., 2010). Sorbent tubes used for the inlet air sampling and field blanks were also extracted and analyzed. A solvent blank was analyzed prior to each batch of analyses to ensure that the instrument and solvent were both contamination-free.

Liquid condensate samples collected in the cold trap during flux chamber experiments were also analyzed on the Agilent GC-MS

with a polar DB-WAXetr column (Agilent) to more fully characterize the gas emissions. Aqueous samples were directly injected into the GC-MS. During each 2–3 h experiment, up to 150 mL of condensate was collected. More than 30 compounds, predominantly polar compounds such as alcohols, acids and ketones were measured in these samples.

All volatile organic compounds were identified primarily by their mass spectrum using a National Institute of Standards and Technology (NIST) library match, by retention time, and by literature values of retention index (Harangi, 2003; Ettre, 2003). Additional tests with individual compounds were also performed to ensure compound identification. The majority of the peaks were identified in the sample chromatogram. Compounds classified in the same chemical class were calibrated using known standards of similar molecules (Beck et al., 2007; Molhave et al., 1997; Filipy et al., 2006). Unknown compound peaks were less than 5% of total signal area and were not used in our emission calculations. A blank run was performed before each batch of compost samples to ensure the sampling system was clean and to prevent any possibility of sample carryover. Inlet field blanks were also analyzed and subtracted from the compost samples. VOCs quantified by the various techniques were summed up to calculate total VOC (TVOC).

As with our previous projects (Howard et al., 2008, 2010a,b; Kumar et al., 2008, 2010) we conducted a Mobile Ozone Chamber Assay (MOChA) on 1000L of source sample supplemented with mini-surrogate VOC and NO<sub>x</sub> as background to assess ozone formation potential of the VOC mixtures. By matching observed net incremental ozone with model calculations (Howard et al., 2008) one can assert that the VOCs measured adequately characterize the source.

The MOChA chamber is a rectangular wood box approximately 4' by 8' in dimensions which is mounted on a 12' metal trailer and is pulled behind a pickup truck to research sites. The box is equipped on the inside with 26, 4-foot long UV lights installed on one inner side of the chamber, capable of generating 50 W m<sup>-2</sup> of UV radiation, and two 12' fans to prevent heating of the box above normal summer (ozone season) temperatures.

A 1,000-liter Teflon bag inside the MOChA chamber is filled with the air sample drawn from the sampling port of the wind tunnel using Teflon-coated diaphragm pumps at a flow rate of approximately 50 L min<sup>-1</sup> until the bag is full, which takes approximately 20 min. A Teflon membrane filter is used at the sampling inlet point of bag to remove particulate matter from the sample. Nitrogen oxide (NO<sub>x</sub>) in the concentration range of 45–55 ppb is introduced into the bag using a gas cylinder (10.1 ± 0.5 ppm as NO<sub>2</sub> in air) to simulate the typical NO<sub>x</sub> level of rural/agricultural areas of SJV during summer ozone episodes. The background reactive organic gases (or minisurrogate) consists of a 55 ± 1% ethylene, 33 ± 1% hexane, and 12 ± 1% xylene mixture by volume, and are also introduced in the bag. The purpose of the minisurrogate is to take the source emissions and mix them with a representative, well-defined atmosphere acting as the receiving air with which emissions from any source will mix. Then we assess how much more ozone is formed than would be formed by the receiving air itself. Once the Teflon bag is full with the combined sample and the introduced gas mixtures, the lights are turned on, exposing the bag within the MOChA chamber for 180 min. Probes measure temperature and relative humidity, while dedicated instruments measure concentrations of oxides of nitrogen (as NO, NO<sub>2</sub> and NO<sub>x</sub>) and ozone from sample removed from the Teflon bag at 0–5, 20–30, 55–65, 85–90, 115–120, 145–150, and 175–180 min. After each experiment the Teflon bag is emptied and flushed (re-filled and emptied again) with clean air produced by a Zero-Air generator. A new Teflon bag was used for each week in the field. Moreover, each

bag is checked for contamination at regular intervals and is replaced with the spare bag whenever required.

Net ozone formation from MOChA is calculated using the following equation (Carter et al., 1995) because an increase in NO represents a net production of ozone from NO<sub>2</sub> photolysis – independent of VOC reaction:

$$\text{Net O}_3 \text{ formation } (\Delta\text{O}_3) = \left( \text{O}_3^{\text{final}} - \text{O}_3^{\text{initial}} \right) - \left( \text{NO}^{\text{final}} - \text{NO}^{\text{initial}} \right) \quad (1)$$

Flux rates (mass time<sup>-1</sup> area<sup>-1</sup>) of a compound are calculated using the air flow rate in the dilution tunnel/flux chamber, the concentration of the compound in the outlet sample, and the surface area covered by the tunnel/chamber.

$$\text{Flux Rate } \left( \text{mg m}^{-2} \text{min}^{-1} \right) = \left[ \text{Sample concentration } \left( \text{mg m}^{-3} \right) \times \text{Sweep flow rate } \left( \text{m}^3 \text{min}^{-1} \right) \right] / \text{Exposed surface area } \left( \text{m}^2 \right)$$

### 3. Results

Detailed physico-chemical properties of the green waste compost materials along with their variability are given in Table 1. The fresh tipping pile was measured for fewer parameters due to its less homogeneous nature. The water content of younger compost material (3–6 days) was found to be in the range of 50% by mass and decreases by 20% in older compost material (2–3 weeks). 100% Moisture saturation in the composting material was almost always present. The average temperature at approximately 30 cm and 1 m deep inside of the compost windrow was slightly higher in older windrows. Another important parameter was C:N ratio, which decreased from 28 to 18 from younger to older material. This decrease in C:N ratio was more prominent at Site 2. The rest of the parameters were in the same range in both types of compost material.

Most of the previous studies on compost emissions were attempts to estimate the total emissions of non-methane non-ethane organic carbon (NMNEOC) for either a typical compost windrow or an entire facility. This is the first study intending to fully speciate green waste compost VOC emissions. In recent decades, an understanding has been developed that different volatile organic compounds contribute differently to ozone production (Carter, 2010). Some of the compounds (e.g. acetone) are exempted in the federal ROG list. Therefore, it would be unfair to use TVOC as equivalent to gaseous carbon in an ozone precursor inventory. Table 2 depicts the compounds identified in the emission samples as a result of all techniques applied. Data are averaged for the two compost facilities in order to develop a representative gas

**Table 1**  
Physico-chemical characteristics of the green waste compost materials.

Parameters, unit	Fresh tip <sup>a</sup>	3–6 Days	2–3 Weeks
C/N Ratio by mass	–	28 ± 8	18 ± 5
Density, g mL <sup>-1</sup>	–	0.25 ± 0.05	0.26 ± 0.08
Porosity, % by volume	–	64 ± 6	61 ± 4
Moisture saturation, %	61 ± 18	100 ± 0	100 ± 0
pH, in Water	–	7.1 ± 1.4	8.0 ± 0.1
T at ~30 cm depth, °C	56 ± 23	60 ± 12	73 ± 9
T at ~1 m depth, °C	44 ± 7.9	64 ± 8	65 ± 2
Water content, % by wet mass	–	50 ± 9	39 ± 12
Organic content, % by dry mass	–	63 ± 9	52 ± 8
TOC, % by dry mass	–	37 ± 5	30 ± 5

<sup>a</sup> Fewer parameters were studied for the fresh tipping pile since its composition was less homogeneous than the windrows.

composition. Over 100 VOCs were detected and quantified in an effort to characterize the complete compost gas emission. These compounds included aliphatic alkanes, alkenes, aromatic hydrocarbons, biogenic organics, aldehydes, ketones, alcohols, furans, acids, esters, ethers, halogenated hydrocarbons and dimethyl disulfide (DMDS). Lighter alcohols dominated the emission profile comprising 66–85% of the total emissions. Flux rates for total VOCs, alcohols and methane are reported in Table 3. The remaining 15–34% of (1.2 to 2.3 mg m<sup>-2</sup>min<sup>-1</sup>) average VOC flux included all other compounds. Methane and ammonia (also shown in Table 3) were measured for only 1 or 2 samples of each type of compost pile to provide additional information. Methane emissions increased

**Table 2**

List of compounds found in the air emissions from green waste compost operations.

Propane	2 Pinen-3-one	Acetone <sup>a</sup>
Pentane isomers	Thujen-2-one	2 Butanone
3 Methyl hexane	(Umbellulone)	2 Pentanone
Dimethyl hexane isomers	Verbenone	3 Pentanone
Trimethyl hexane isomers	trans-Verbenol	3,3 Dimethyl 2-butanone
Epoxy cyclooctane	Linalool	Methyl isobutyl ketone
Others ≥ C7 straight and cyclic Hydrocarbons	Eucalyptol	(MIBK)
	Terpineol	3 Pentene 2-one
	Borneol	3 Methyl 2-pentanone
Propene	Allylanisole	2 Hexanone
2 Methyl 1-propene	Saftrol	Methyl hexanone isomers
n-Butene & isomers	(1,3-Benzodioxole,	Octanone
2 Methyl 1,3-butadiene	5-(2-propenyl))	Nonanone
(Isoprene)		2 Butanedione (Diacytol)
2 Methyl 3-butene 2-ol	Formaldehyde	1 Hydroxy 2-propanone
2 Methyl 1,3 pentadiene	Acetaldehyde	3 Hydroxy 2-butanone
2,4-Heptadienal	Propionaldehyde	Methyl phenylethanone
Acetyl cyclomethylpentene	Crotonaldehyde	
2 Ethyl 3-hexen 1-ol	(2-Butenal)	<sup>a</sup> Methyl acetate
Methyl hexyne	Butyraldehyde	Ethyl acetate
Methyl cycloheptene	Isovaleraldehyde	Propyl acetate
Acetyl methylcyclohexene	Valeraldehyde	Isoamyl acetate
Other alkenes	2 Methyl pentenal	Methyl butylacetate
	Hexanal	Bornyl acetate
	Hexenal	Methyl isobutanoate
Benzene	Heptanal	Methyl butanoate
Toluene	Heptenal	Methyl isopentanoate
Xylene isomers	Octanal	Ethyl butanoate
Styrene	Nonanal	Methyl pentanoate
C-3 Benzene isomers	Decanal	Propyl butanoate
C-4 Benzene isomers	Dimethyl octenal	Methyl hexanoate
Isopropenyl toluene	Benzaldehyde	Butyl butanoate
4 Methyl benzenemethanol		Isomer of butylbutanoate
Naphthalene	Furan	Heptyl hexanoate
Dichlorobenzene isomers	3 Methyl furan	Other esters
Trichlorobenzene isomers	2 Methyl furan	
	2,5 Dimethyl furan	Acetic acid
α-Pinene	2 Ethyl 5-methyl furan	Propionic acid
β-Pinene		Methyl propionic acid
4 Carene	2 Butyl furan	Butanoic acid
3 Carene	2 Pentyl furan	Methyl butanoic acid
Camphene		Pentanoic acid
Terpinene	Methyl hexanone isomers	Hexanoic acid
Terpinolene	Methanol	Acetyl benzoic acid
Limonene	Ethanol	Dimethyl disulfide
Adamantane	2 Propanol	
α-Phellandrene	1 Propanol	Methylthymyl ether
β-Phellandrene	2 Butanol	Dichlorodifluoro methane <sup>b</sup>
l-Fenchone	1 Butanol	Chloro difluoro methane <sup>b</sup>
Copaene	2 Methyl 1-butanol	Trichloromonofluoromethane <sup>b</sup>
Camphor	& isomer	
cis-Linalool oxide	Pentanol	
trans-Linalool oxide	Hexanol	
	2,3 Butanediol	
	Pentanol	
	Hexanol	
	2,3 Butanediol	

<sup>a</sup> Exempted from federal ROG list.

<sup>b</sup> Exempted from federal and California ROG list.

**Table 3**  
Average flux emissions ( $\text{mg m}^{-2} \text{min}^{-1}$ ) from green waste compost operation.

Flux emission	Fresh tip	3–6 Days	2–3 Weeks
Total VOC except alcohols	$1.20 \pm 0.51$	$2.28 \pm 0.87$	$1.37 \pm 0.10$
Alcohols	$2.81 \pm 0.11$	$12.95 \pm 0.62$	$2.62 \pm 0.05$
Methane <sup>a</sup>	0.04	0.36	1.98
Ammonia <sup>a,b</sup>	$0.06 \pm 0.02$	$0.27 \pm 0.04$	$0.11 \pm 0.01$

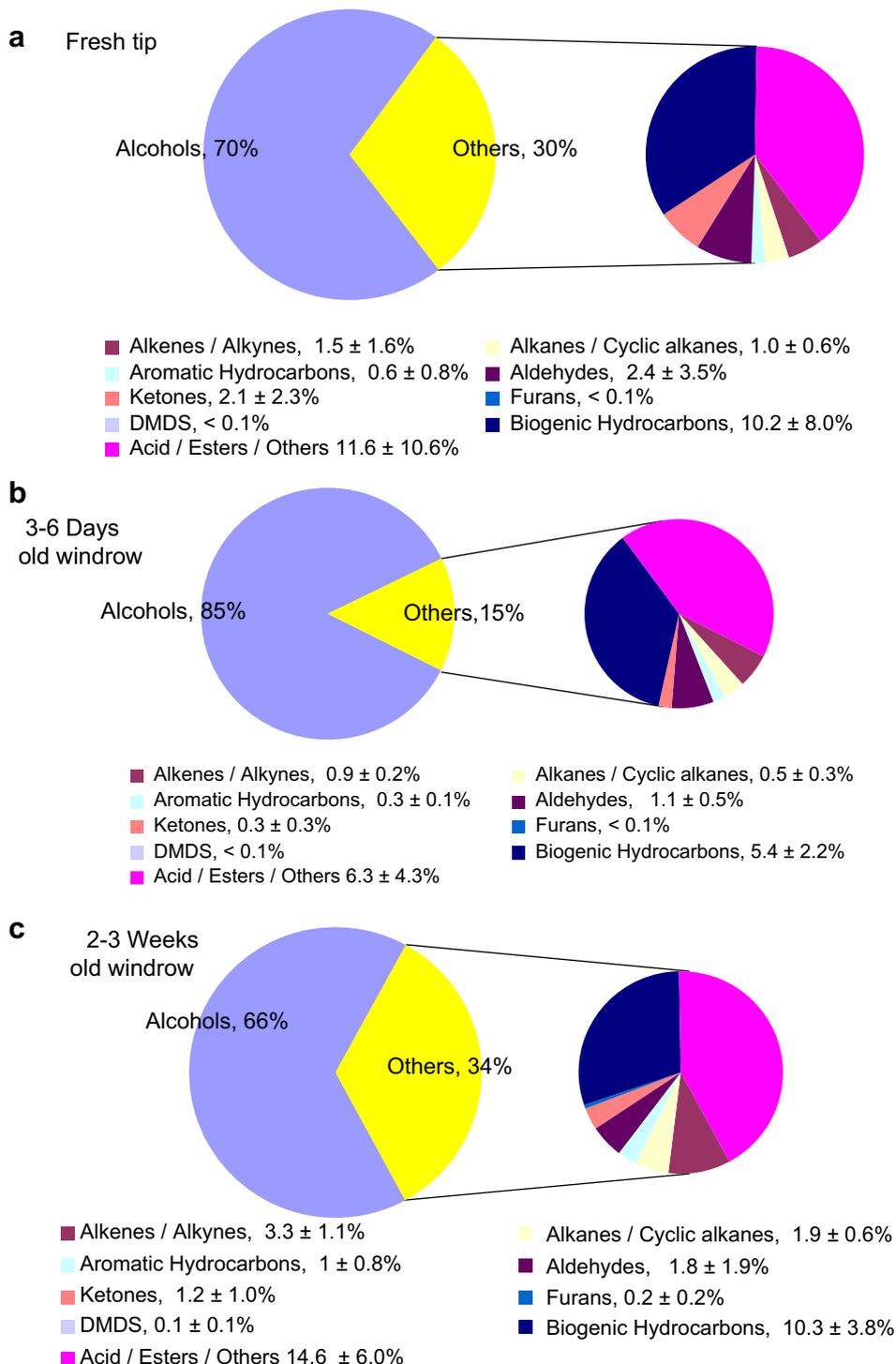
Note: Uncertainty is the standard deviation (SD) of TVOC of individual samples except noted while SD may vary for individual compound or group of compounds.

<sup>a</sup> Average of 1–2 samples only.

<sup>b</sup> Uncertainty of each sample.

from  $0.04 \text{ mg m}^{-2} \text{min}^{-1}$  from the fresh tipping pile to  $0.36 \text{ mg m}^{-2} \text{min}^{-1}$  in the younger windrow to  $1.98 \text{ mg m}^{-2} \text{min}^{-1}$  in the older windrow. Ammonia was found to be at the highest level in the younger windrow and lowest in the fresh tipping pile.

Further details on the emissions flux of each group of VOCs measured across all three ages of compost material are displayed in Fig. 2a–c. The younger stage compost windrow (3–6 days) had the highest alcohols emission ( $12.95 \text{ mg m}^{-2} \text{min}^{-1}$ ) constituting 85% of total flux, followed by acids/esters, biogenic emissions, and aldehydes. Dimethyl disulfide (DMDS) and a few furans were also



**Fig. 2.** Contribution of VOC groups in the emission profile of different aging compost windrows (values in  $\pm$  represent standard deviation).

detected in small amounts with other VOC groups. In the older compost windrow (2–3 weeks), non-alcoholic VOC emissions ( $1.37 \pm 0.10 \text{ mg m}^{-2} \text{ min}^{-1}$ ) decreased to almost half of the younger windrow ( $2.28 \pm 0.87 \text{ mg m}^{-2} \text{ min}^{-1}$ ). Alcohols emissions also decreased and represented 66% ( $2.62 \pm 0.05 \text{ mg m}^{-2} \text{ min}^{-1}$ ) of total older windrow emissions while saturated and unsaturated hydrocarbons increased as a relative proportion. Total emissions from the fresh tipping pile were similar to those from the older windrow, with 70% ( $2.81 \pm 0.11 \text{ mg m}^{-2} \text{ min}^{-1}$ ) alcohols plus other relatively low reactivity compounds.

Table 4 shows the most abundant individual VOCs comprising approximately 95% of total emissions and their weighted average contribution in the emissions profile during the composting process studied. A weighted average provides an estimate of the approximate relative duration of each type of emission profile: 1 week as a fresh tipping windrow, 1 week as a young windrow and 4 weeks as an older windrow. Table 4 also lists each compound's maximum incremental reactivity (MIR) and equal benefit incremental reactivity (EBIR) referenced from Carter (2010). Maximum incremental reactivity (MIR) is an ozone yield scale derived by adjusting the  $\text{NO}_x$  emissions in a base case to yield the highest incremental reactivity of the base reactive organic gas mixture, while equal benefit incremental reactivity (EBIR) is an ozone yield

**Table 4**

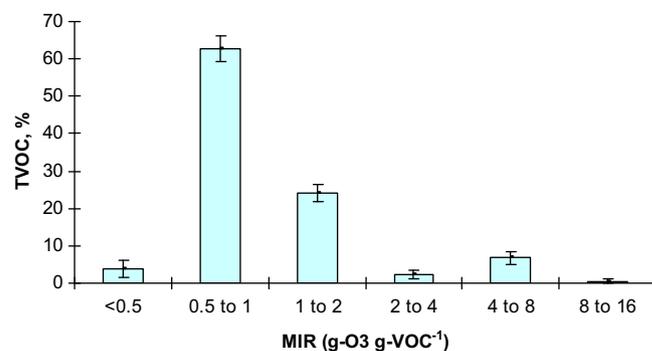
Relative reactivity ( $\text{g-O}_3\text{g-VOC}^{-1}$ ) and percent of weighted average compost pile emissions. [% VOC units are  $(\text{mg m}^{-2} \text{ min}^{-1} \text{ compound})/(\text{mg m}^{-2} \text{ min}^{-1} \text{ TVOC}) * 100$ ].

VOCs	MIR <sup>a</sup>	EBIR <sup>b</sup>	% VOC	SD <sup>c</sup>	Cumulative %
Isopropyl alcohol	0.61	0.25	42.31	2.74	42.31
Ethyl alcohol	1.53	0.59	18.16	3.49	60.47
Methyl alcohol	0.67	0.19	12.79	1.36	73.26
Acetic acid	0.68	0.21	5.94	0.39	79.20
Limonene	4.55	0.96	2.27	1.01	81.47
$\alpha$ -Pinene	4.51	0.89	1.36	0.4	82.83
Butanoic acid	1.82	0.56	1.35	0.8	84.18
Camphor	0.49	0.13	1.18	0.81	85.36
Methylthymyl ether	N.A.	N.A.	0.73	0.63	86.09
Bornyl acetate	N.A.	N.A.	0.63	0.11	86.72
Pinene Isomers	3.52	0.79	0.60	0.18	87.32
Eucalyptol	N.A.	N.A.	0.58	0.24	87.90
Propionic acid	1.22	0.35	0.53	0.14	88.43
Naphthalene	3.34	0.49	0.50	0.51	88.93
Acetone	0.36	0.09	0.47	0.51	89.40
3 Hydroxy 2-butanone (Acetoin)	N.A.	N.A.	0.43	1.71	89.83
2 Methyl 1-Propene	6.29	1.18	0.41	0.44	90.24
2 Butanol	2.4	0.75	0.39	0.37	90.63
Hexanoic acid	N.A.	N.A.	0.39	0.25	91.02
Terpineol	4.63	0.89	0.35	0.26	91.37
Heptyl hexanoate	N.A.	N.A.	0.31	0.49	91.68
3 Methyl butanoic acid	4.23	0.96	0.28	0.13	91.96
Methyl propionic acid	1.2	0.39	0.26	0.13	92.22
Methyl cycloheptene	N.A.	N.A.	0.24	0.15	92.46
Camphene	4.51	0.89	0.24	0.07	92.70
1 Methyl, 3-1-methyl ethyl benzene	5.49	0.89	0.23	0.23	92.93
Pentanoic acid	N.A.	N.A.	0.23	0.18	93.16
Propene	11.66	2.73	0.22	0.22	93.38
Thujen-2one (Umbellulone)	N.A.	N.A.	0.22	0.17	93.60
Undecane	0.61	0.16	0.20	0.17	93.80
2 Butene	14.24	3.08	0.17	0.15	93.97
Isovaleraldehyde	4.97	1.23	0.15	0.13	94.12
Acetaldehyde	6.54	1.61	0.14	0.08	94.26
Methyl butylacetate	1.09	0.40	0.14	0.74	94.40
Others >80			5.60		100.00

<sup>a</sup> MIR, Maximum Incremental Reactivity.

<sup>b</sup> EBIR, Equal Benefit Incremental Reactivity (Carter, 2010), N.A.: not available.

<sup>c</sup> Standard deviation (%) represents the variability between the 3 sample types' mean.



**Fig. 3.** Average contribution of VOC into the ozone formation according to the reactivity.

scale derived by adjusting the  $\text{NO}_x$  emissions in a base case scenario so VOC and  $\text{NO}_x$  reductions are equally effective in reducing ozone. The standard deviation of each compound represents the variability between the means of the 3 different types of sources. Iso-propanol, ethanol and methanol comprise more than 73% of the total emissions. Acetic acid and limonene/pinene isomers are the top contributors after alcohols. These three alcohols and acetic acid have relatively low reactivity and may not contribute significantly to ozone production unless they are in very high concentration. A few compounds with very high reactivity (up to  $14 \text{ g-O}_3 \text{ g-VOC}^{-1}$ ) such as C3–C4 alkenes were also observed. A number of biogenic organic compounds that are also regarded to be highly reactive were also observed in the top non-alcoholic contributions. Several acids from low to medium reactivity are also found in the list. Among aldehydes, reactive acetaldehyde and isovaleraldehyde are the most abundant.

The overall compost emissions, divided into 6 MIR categories, are depicted in Fig. 3. Variability shown in the bar graphs indicates the deviation among different sources. More than 60% of the TVOC emissions fall in the reactivity range of 0.5–1  $\text{g-O}_3 \text{ g-VOC}^{-1}$ . Around 25% of the TVOC emissions were found in the 1–2  $\text{g-O}_3 \text{ g-VOC}^{-1}$  category, with smaller amounts in the other categories. Reactivity of above 8  $\text{g-O}_3 \text{ g-VOC}^{-1}$  was observed for less than 1% of emissions. Overall only about 10% of VOCs had reactivity above 2  $\text{g-O}_3 \text{ g-VOC}^{-1}$ .

Excessive water vapor precluded MOChA operation at Site 1 because of fog formation in the chamber. The MOChA results from site 2 showed net incremental ozone formation of 20 to 30 ppb for the 4 successful experiments on the various sources. These represented fairly small concentrations above the background (mini-surrogate VOCs plus  $\text{NO}_x$ ) formation of 60 ppb net ozone. Model calculations agreed fairly well within an average of  $\pm 10$  ppb, which was comparable to our previous projects for low ozone-forming sources (Howard et al., 2010b).

#### 4. Conclusion

Characterization of VOC emissions from green waste during different stages of composting was conducted to investigate their contributions to potential ozone formation based on VOC reactivity. For a complex source such as composting, an approach using multiple sampling techniques was developed to measure the widest potential range of VOCs. Results indicate that compost piles emit more than 100 VOCs, but that these emissions are dominated by alcohols ranging from 66–85% of the total VOC emissions. Other compounds including the majority of acids, biogenic hydrocarbons, alkenes and carbonyl compounds constitute 15–34% of total VOC emissions ( $1.2\text{--}2.8 \text{ mg m}^{-2} \text{ min}^{-1}$ ), depending on the age of the compost pile. The young compost windrow (3–6 days), had the

highest emission flux, but also exhibited the highest percentage of less-reactive alcohols in the emissions profile. Older compost windrows exhibited lower emission fluxes, but also a higher proportion of alkenes and more reactive compounds. Overall, only around 10 % of the average VOC emissions were found to have medium to high potential for ozone formation. Ozone closure experiments conducted using a Mobile Ozone Chamber Assay confirms that the measured VOC speciation accounts for the observed incremental ozone formation.

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