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Biogenic VOC emissions from fresh leaf mulch and wood chips of *Grevillea robusta* (Australian Silky Oak)

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Abstract

The emissions of VOC from freshly cut and shredded *Grevillea robusta* (Australian Silky Oak) leaves and wood have been measured. The VOC emissions from fresh leaf mulch and wood chips lasted typically for 30 and 20 h respectively, and consisted primarily of ethanol, (*E*)-2-hexenal, (*Z*)-3-hexen-1-ol and acetaldehyde. The integrated emissions of the VOCs were $0.38 \pm 0.04\,g\,kg^{-1}$ from leaf mulch, and $0.022 \pm 0.003\,g\,kg^{-1}$ from wood chips. These emissions represent a source of VOCs in urban and rural air that has previously been unquantified and is currently unaccounted for. These VOCs from leaf mulch and wood chips will contribute to both urban photochemistry and secondary organic aerosol formation. Any CH_4 emissions from leaf mulch and wood chips were $< 1 \times 10^{-11}\,g\,g\,dry\ mass^{-1}\,s^{-1}$.

Keywords: Volatile organic compounds; Emissions; Methane; *Grevillea robusta*; Leaf mulch; Wood chips

1. Introduction

The biogenic volatile organic compounds (BVOCs) emitted from plants are a myriad of hydrocarbons and oxygenated and other organic compounds. These emissions occur during various stages of plant growth, plant injury and plant decay, and they are a significant source of volatile organic compounds (VOCs) in the atmosphere. Globally, emissions from BVOCs account for approximately 86% of the total of VOCs emitted while anthropogenic VOCs make up the rest (Guenther et al., 1995).

BVOC emissions from trees and woody shrubs have been extensively studied (Scholes et al., 2003). The dominant compounds emitted under unperturbed conditions are isoprene, monoterpenes, sesquiterpenes and methanol. There are episodic emissions of C_6 aldehydes, esters and alcohols associated with plant injuries, and episodic emissions of ethanol and acetaldehyde associated with waterlogging (Scholes et al., 2003). Most of these compounds are photochemically reactive in the atmosphere because of their alkenyl bonds and other properties of their structure (Seinfeld and Pandis, 1998). Two key products of the photochemical reactions of these compounds in the atmosphere are gas-phase oxidants (including ozone) and secondary organic aerosols. These gas-phase oxidants and secondary organic aerosol

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can have significant effects on human health when present in high concentrations in near surface air and are climatically active in the global atmosphere.

BVOCs from cut grass emissions have been found to consist of hexenal acetates, hexenals, hexenols, methanol, acetaldehyde, acetone, isoprene and monoterpenes (Kirstine et al., 1998). The emissions released from cut grasses are much larger than the emissions that come from undisturbed pastures. Kirstine and Galbally (2004) calculated that the C_6 compounds produced as a direct product of grass cutting could contribute between 3% and 5% of urban VOC emissions with higher levels occurring in the summer.

Another possible source of BVOC emissions is from garden mulch made by the shredding of wood and leaves. Mulch can be made of many materials including straw, sugar cane, sawdust, pine needles, hay, bark and wood chips.

There have been studies of BVOC emissions both from vegetative litter left after thinning of a forest (Goldstein et al., 2004) and from the kiln drying process during the preparation of sawn timber for commercial use (Englund and Nussbaum, 2000).

The emissions of BVOCs from freshly shredded leaves and wood from the tree species, *Grevillea robusta* (Silky Oak) was the main focus of this study. *G. robusta* was chosen because it is an Australian tree, which can grow in areas with mean annual temperature from 14 to 31 °C and mean annual rainfall from 600 to 1700 mm. It is a relatively fast growing tree and is very commonly found in household gardens in eastern Australia. Because of its abundance and fast growth, it is a tree species that is likely to be frequently pruned and subsequently mulched. Past research on *G. robusta* has included studies of isoprene emissions (Varshney and Singh, 2003) and of its chemical extracts (Kitsuta, 1956; Cannon et al., 1973; Varma et al., 1976; Kleiman and Plattner, 1977).

The term wood chips used in this study represents the chips made from the combination of the wood and bark. This is the common procedure in making wood chips for gardens and mulch. Wood chips made for the paper and particle board industries are generally made from the wood after the bark has been removed. The leaf mulch used in this study is made primarily of leaves that have been stripped from their branches.

2. Materials and methods

The method adopted for this project has been taken from similar experiments involving cut grass using flux measurement chambers developed by CSIRO Atmospheric Research (Kirstine et al., 1998). In this experiment, the chamber was set up indoors in order to minimise the effects of solar radiation and temperature on emission rate. Samples of leaf mulch were taken on 4 July 2003, 26 August 2003 and 4 September 2003. Samples of wood mulch were taken on 11 July, 15 July, 19 August and 28 August of the same year.

2.1. Chipping and mulching

The technique used in this study involved taking branches cut from a mature *G. robusta* tree and shredding either the wood and bark for wood chips or leaves for leaf mulch.

The sample of wood chips or leaf mulch was then delivered to the laboratory where it was placed into a flux measurement chamber to determine emission rates. Two types of samples were studied: (i) chips made from wood with the bark intact and (ii) mulch made from leaves. When mulch made from leaves was required, branches with high amounts of foliage were chosen. The leaves were then stripped from the branches and put through a wood chipper or a rotary lawnmower to produce the leaf mulch, typically pieces with approximately 1 cm^2 surface area. If chips were required, woody branches that were <2.5 cm in diameter were chosen. Leaves were stripped off the branches before the branches were put through the wood chipper so that only wood and bark were present in the wood chips. Immediately after chipping or mulching, the prepared samples were placed into glass jars, which were sealed with a Tedlar® sheet to minimise the loss of emissions, for transport to the laboratory.

Once in the laboratory, a sub-sample of the wood chips or leaf mulch was weighed and placed in a 1 cm deep layer in the base of the flux measurement chamber. This amount was typically between 0.5 and 1.0 kg of fresh chip/mulch material.

Another sub-sample of wood chips or leaf mulch was taken, weighed and then dried in an oven at ~70 °C overnight. After drying, the sub-sample was weighed again and the dry mass-to-fresh mass ratio of the chip/mulch material was determined. This ratio was used to determine the dry mass of wood chips or leaf mulch placed in the chamber.

2.2. Chamber system and emission measurement

The chamber used is a variation of that described in Meyer et al. (2001). The system consists of two parts: (i) the flux measurement chamber and (ii) its controller/logger. The flux measurement chamber used for this study consists of two sections, the top, commonly regarded as the chamber, and the base which has a solid bottom and is used to contain the chips or mulch. The base is made from a flat rectangle of anodised aluminium with a 20 cm lip around the edge that seals with the chamber top. The top is essentially an open bottomed mainly transparent box, 490 mm wide by 690 mm long by 400 mm tall. The chamber is made of an anodised aluminium frame and perspex windows lined with Tedlar® sheets on the inside. The chamber top has two pneumatically operated lids. When the lids were up, two fans, one in each opening, were activated (one fan drives air into the chamber, the other fan extracts air from the chamber) to flush the chamber and return the air in the chamber to as near to ambient conditions as possible. When the chamber lids were open, the concentrations of VOCs and CO_2 in the chamber air were virtually indistinguishable from ambient air. When the lids were closed, the chamber has a closed constant volume of air. The chamber is not completely sealed since it has a small leak tube to prevent the build up of pressure differences between inside and outside the chamber.

Air was drawn from the flux chamber at approximately $1\,l\,min^{-1}$ and was continuously monitored for the concentrations of carbon dioxide (CO_2), methane (CH_4) and VOCs. The chambers were operated in an automatic static mode, closing once per hour for 20 min, followed by 40 min open. The chamber air concentration data for the periods following chamber closure were used to determine emission rates each hour and these emission rates were subsequently combined to give the total integrated emissions for the duration of the experiment. The emission measurement procedure is based on previous studies (Galbally et al., 1985; Kirstine et al., 1998) and is designed to ensure that during the period of closure, the rate of emission that causes the build up of the emitted species in the chamber is comparable to the undisturbed emission in the open atmosphere. Each mulch chip experiment continued until the mulch/chips ceased to emit detectable VOCs. Emissions were detectable for 1–2 days after the tree material was cut and shredded.

Emission rates were calculated from the increase in the concentration inside the chamber during the 20 min intervals following the closure of the chamber lids. The flux of VOCs from the material in the chamber (F) is calculated as:

$$F = \left(\frac{\Delta C}{\Delta t'}\right) V_1 \tag{1}$$

where V_1 is the internal volume of the chamber plus base ($0.1478\,m^3$) and ΔC is the change in concentration in density units ($g\,m^{-3}$) of the gas being analysed. The gas in the chamber is normally measured in volumetric or molar mixing ratio units by the continuous analysers and the conversion of mixing ratio to density units at atmospheric pressure is made using the ideal gas equation. $\Delta t'$ is the time interval corresponding to ΔC, corrected for leakage as described by Eq. (2).

Chamber leakage is defined as the gross rate of air lost from the chamber (v_g) which is the sum of the rate of natural air leakage of the chamber and the rate at which air is purposely withdrawn from the chamber as a result of sampling (Meyer et al., 2001). When there is chamber leakage, the concentrations measured by the continuous analysers are lower than the concentrations that would occur in a fully sealed chamber. In the emission estimate allowance is made for this chamber leakage via a corrected time interval $\Delta t'$ calculated using Eq. (2) developed by Marynick and Marynick (1975):

$$\Delta t' = \frac{1 - e^{-v_g V^{-1} \Delta t}}{v_g V_1^{-1}} \tag{2}$$

where Δt is the difference in time between the initial and final concentration (s); $\Delta t'$ the time difference corrected for chamber leakage (s); v_g the gross rate of air lost from the chamber ($m^3\,s^{-1}$) and V_1 the internal volume of the chamber plus base (m^3).

Emission rates E were obtained by dividing the flux F by the dry mass of the mulch or chips in the chamber:

$$E = \frac{F}{\text{dry mass of sample}} \tag{3}$$

The experiments were conducted indoors in an air-conditioned laboratory. Consequently, the air drawn into the chamber would have a very low concentration of ozone in it, and negligible hydroxyl concentration. It is assumed that no gas-phase chemical reactions occur in the chamber under these conditions. The VOCs were measured both

when the chamber is open and closed, and the measurements when the chamber was open indicated that the background VOC concentrations in the laboratory were low.

2.3. Canister and adsorbent tube sampling

Air samples were also withdrawn from the chamber and drawn through either mixed bed adsorbent tubes or into canisters, for subsequent analysis to determine the chemical speciation of *G. robusta* BVOC emissions.

The canisters used for sample collection were 3 l stainless-steel canisters passivated by the Summa process and fitted with two 1/4 in Swagelok stainless-steel bellow valves and a dip tube (Scientific Instrumentation Specialists of Moscow Idaho, USA). The canister samples were taken at ambient air pressure and each canister was flushed with approximately 15 l of sample air. The thermal desorption tubes contained Tenax/CarbosieveSIII (Markes International, 2006; UK) and the sampling rate was 76 ml min^{-1} for 5 min. Canisters and thermal desorption tubes were kept sealed until analysed, typically 3 (0–13) days after collection. The two different sampling systems were used because of the known limitations with canister and tube sampling of oxygenated VOCs and the unknown composition of the emissions.

For each experiment, air samples using a 3 l canister and two mixed bed adsorbent tubes in series were taken from the chamber while the chamber lids were open. This was labelled the *initial concentration* air sample. The chamber lids were then closed manually and the mulch left for 15 min inside the sealed chamber to allow the emissions to accumulate, after which a second batch of air samples were taken. This was labelled the *final concentration* air sample. The composition of the emitted gases was determined by subtracting the initial from the final composition. This procedure was done in the first hour of the experiment and repeated after 24 h of sampling. The blank canister and blank tube samples were taken in the same way as described above, except that there was no mulch or wood chips in the chamber at the time of taking the air samples. One thermal desorption tube and two canister samplings were conducted for the leaf emissions, and two thermal desorption tube and four canister samplings were conducted for the wood emissions.

2.4. Chemical analysis

The absorbent tube and canister samples taken from the chamber were analysed by a Hewlett-Packard HP6890 gas chromatograph system coupled with an Agilent 5973 mass selective detector and a canister auto-sampler (Entech Instruments Inc. Model 7016BCA). Up to eight pressurised canisters can be connected to the auto-sampler at any one time. As the canister air samples were collected at atmospheric pressure, the canisters were pressurised with ultra-high-purity nitrogen gas (to ~200 kPa) in preparation for analysis. A measured volume of air, up to 1 l, was taken from the canister by the auto-sampler and the VOCs within this sample were collected in a pre-concentrator (Entech Instruments Inc. Model 71000), passed through a series of three cold traps and injected onto the GC column for analysis. The column was either an AT1 or a BP1 of dimensions 60 m length by 250 μm i.d. with a 1 μm internal film thickness. The initial column temperature was −50 °C and the final was 240 °C. The temperature was kept at −50 °C for 4.5 min, increased at 15 °C min^{-1} to −10 °C, 5 °C min^{-1} to 150 °C and then 25 °C min^{-1} to 240 °C where it stayed for ~4.2 min. The carrier gas used was ultra-high-purity helium. This was set to 4 ml min^{-1} for 0.5 min and at 0.75–1 ml min^{-1} for the rest of the run.

The thermal desorption tubes were placed manually into the pre-concentrator sampling port on the Entech auto-sampler where they were desorbed at 240 °C, concentrated in the series of cold traps, and then run through the GC–MS under the same flow rate and temperature program as the canister samples.

Compounds were identified using the MS library NBS75K.L (G1033a Rev C.00.00 NIST/EPA/NIH Mass Spectral Database). A compound was considered for acceptance if the match was above 85%. Those compounds with a match below 85% were only considered for acceptance if on manual inspection their spectra matched. A comparison of the boiling points of the compounds versus gas chromatograph retention times was used to provide further evidence of the compound's identity. These are shown in Table 2.

Gas standards were not available for all the gases being considered, so a qualitative analysis of the speciation of VOC emissions was conducted using the mass spectral total ion count (TIC). The areas of the chromatographic peaks were divided by the

volume of air utilised in the VOC pre-concentration step to give the peaks in "concentration" units of area l^{-1}. This allowed a comparison of canister and tube data. Also the peak "concentrations" were summed and then each peak concentration was normalised by dividing its "concentration" by the sum of the observed "concentrations" to give the percentage contribution of the peak to the whole of the VOC emissions detected for that sample. Direct comparison between the different sets of data was possible because the internal standards showed a consistent peak area over time.

Significant contamination was observed in the blank adsorption tubes for the aldehyde series heptanal to decanal. These compounds were not observed in the canisters. These compounds were removed from subsequent data analyses and interpretation.

The gas chromatography working standard was an accurate pressure diluted version (5 ppb level) of Scott Specialty Gases standard of 100 ppb of each of 42 C_1–C_{10} hydrocarbons (accurate to $\pm 10\%$) including alkanes, alkenes, arenes and isoprene. This was used to calibrate the total VOCs measurements from the canisters and tubes.

CO_2 concentrations were measured using a GasHound Model LI-800 (LI-COR, Inc., Lincoln, NE, USA) CO_2 non-dispersive infrared (NDIR) gas analyser. According to the manufacturer, its accuracy was 2% of the reading for CO_2 concentrations >350 ppmv. The standard used for calibrating the GasHound was a high-pressure cylinder of clean baseline air. The concentration of CO_2 in this air standard was determined by GASLAB at CSIRO Aspendale by calibration to a precision of ± 0.04 ppm against a suite of other CO_2 in air standards held by them and whose concentrations were based on the internationally accepted World Meteorological Organisation X93 CO_2 mole fraction calibration scale. The zero air used for setting the GasHound zero was a cylinder of high-purity zero air (BOC Australia).

CH_4 and VOC concentrations were measured using a total hydrocarbon analyser (TEI Model 55C, Thermo Environmental Instruments, TEI, Franklin MA, USA). This instrument is a gas chromatograph with flame ionisation detection, a GC–FID, system. The instrument is normally considered a non-methane hydrocarbon (NMHC) analyser. We ascertained from previous studies that the analyser also responds to oxygenated VOCs and that the analyser needs to be calibrated according to the mixture of VOCs that it is measuring. The TEI 55C analyser measures NMHC and VOC concentrations in parts per million CH_4 equivalents, ppmC, which is a non-SI unit. This unit is the molar (or volumetric) mixing ratio in parts per million multiplied by the number of carbon atoms in the NMHC or VOC molecule. This quantity, ppmC, is additive across different species of hydrocarbons of different carbon numbers. The unit was developed as a method of combining the concentrations of a suite of different hydrocarbons together. This unit is applicable to FID-based detection as the FID responds quantitatively to total carbon number for NMHCs. When calculating VOC fluxes from the continuous analyser, the MW of CH_4 was used to provide a CH_4 equivalent concentration.

One calibration gas used for the TEI 55C analyser was a National Institute of Standards and Technology Standards Reference Material 1660a nominal 4 ppm CH_4 and 1 ppm propane in air certified to 0.02 and 0.005, respectively. This calibration was used for CH_4.

The TEI 55C analyser was also calibrated by comparison of its readings with the results of VOC concentrations from canister samples taken simultaneously and then analysed by the Entech/Agilent system. It was determined that the nominal VOC concentrations obtained by the TEI 55C continuous analyser should be multiplied by a factor of 2.8 to bring them into equivalence with the full VOC speciation analysis. This was further investigated, and was found to arise because of a decreasing response of the TEI 55C analyser (a) to higher molecular mass VOCs including both alkanes and aromatic compounds and (b) to oxygenated VOCs. The emission estimates presented subsequently include this calibration.

These instruments were connected to the sampling chamber. The CO_2 analyser extracted air at $0.4\,l\,min^{-1}$ and the CH_4/VOC analyser extracted air at $0.6\,l\,min^{-1}$.

3. Results

3.1. Leaf mulch emissions

An example typical of the VOC concentration data obtained during the period when wood chips or leaf mulch were in the chamber is presented in Fig. 1. The recurrent peaks in VOC concentration that are seen, represent the BVOC concentration

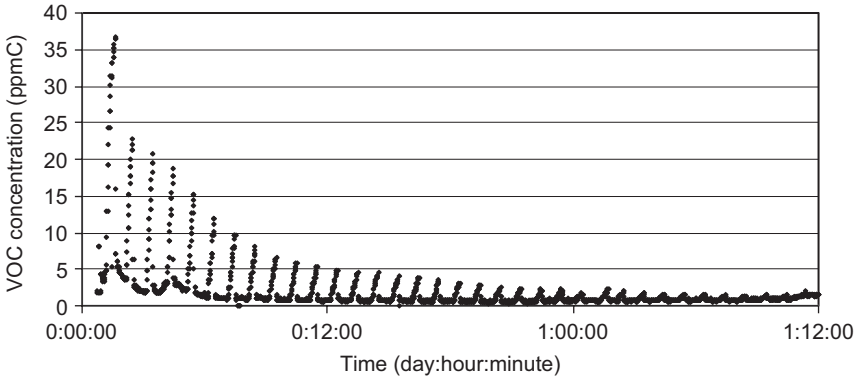

Fig. 1. VOC concentrations in the chamber from *G. robusta* leaf mulch versus time since mulching (4–7 September 2003).

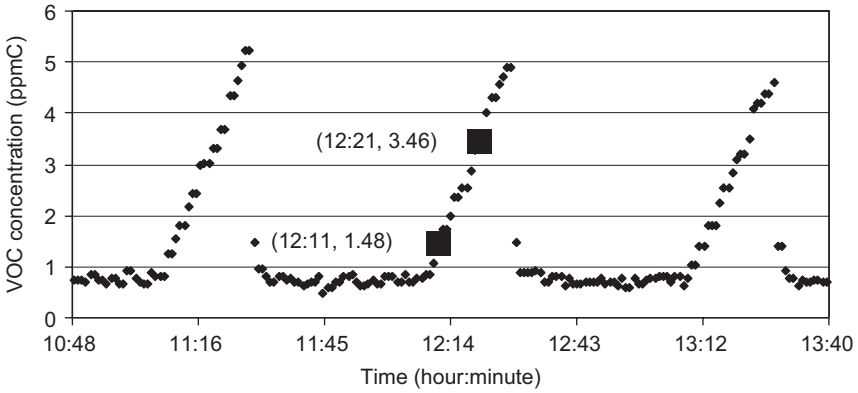

Fig. 2. Close up of VOC concentrations from Fig. 1, over a 3-h time frame, at approximately 12 h after the *G. robusta* leaves had been mulched.

build up that occurs during the 20 min in every hour that the chamber is sealed (i.e., when the lids were closed).

Fig. 2 zooms in on three of the peaks in Fig. 1 obtained approximately 12 h after the leaves were mulched. In Fig. 2, it is easy to see the increase in concentration that occurs after the lids are closed, and the rapid return to ambient concentrations that occurs as soon as the lids are opened. The gradient of the increase in concentration following the closure of the lids is used to calculate the emission rate. An emission rate was calculated for every hour that the mulch or chips were in the chamber during the experiment. For illustration, two data points 10 min apart are highlighted in Fig. 2 and were used to determine the rate of emission during this lid closure using Eqs. (1) and (2). The emission rate calculated from these two points, corresponds to a data point in Fig. 3 at 12:00 h on 4–7 September 2003 of VOC emission rate of 2.2×10^{-9} g g dry mass^{-1} s^{-1}. Fig. 3 shows a comparison of VOC emissions obtained from the three experiments on *G. robusta* leaf mulch. There is remarkable agreement of the time-course and magnitude of emissions from these three samples of leaf mulch, which suggests some constancy of the underlying processes that produce the VOC emissions within the leaf mulch. The emissions appear to cease at some time around 30 h.

The time scale has been adjusted for the leaf mulch sample dated 4–7 July, which was placed in the chamber 7 h after it had been mulched, but has been plotted here as though it was freshly cut when it was placed in the chamber. This is because the sample was stored in a sealed glass jar during the 7 h and presumably the bulk of the volatiles were prevented from escaping from the biomass due to their equilibration with the gas phase in the small volume remaining above the mulch in the jar.

Fig. 4 presents the equivalent emissions of CO_2 from the *G. robusta* leaf mulch, and demonstrates that CO_2 behaves in a similar manner to VOC,

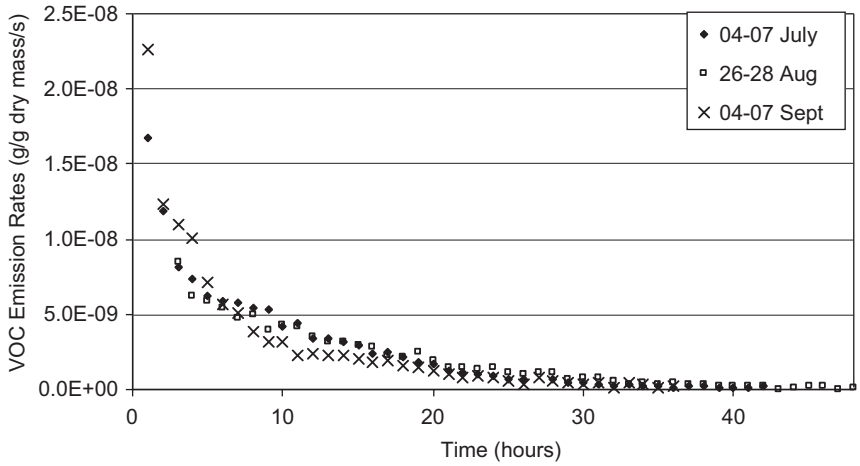

Fig. 3. VOC emission rates from *G. robusta* leaf mulch versus time since mulching.

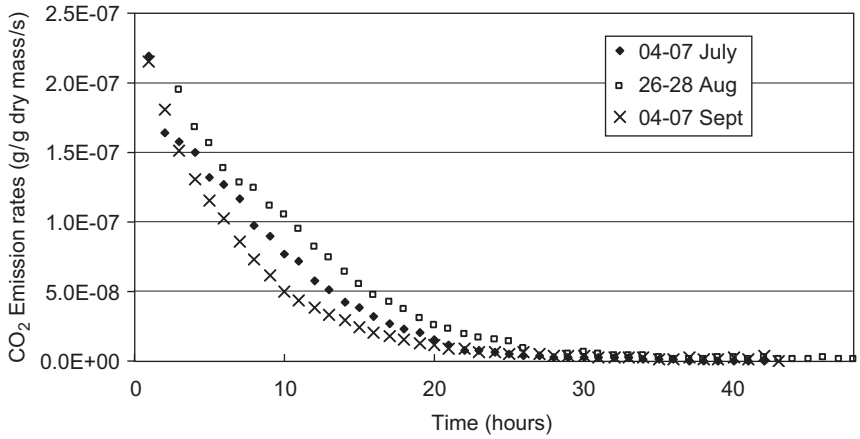

Fig. 4. CO_2 emission rates from *G. robusta* leaves versus time since mulching.

which is, that the leaf mulch emits CO_2 after mulching and emission rates decline with time after mulching, ceasing some time around 30 h later. Fig. 4 shows that the CO_2 emissions from these three chamber leaf experiments are in good agreement with respect to the time-course and magnitude of emissions. (Note that the data collected on 4–7 July has been brought forward 7 h as discussed above.)

The total emissions of VOCs and CO_2 from the leaf mulch following mulching, calculated as the integrals underneath the emission rate curves in Figs. 3 and 4, are presented in Table 1. As would be expected from the figures, the total emissions from the three experiments are in good agreement with standard deviations of 12% and 10% for VOCs and CO_2, respectively. The ratio of VOC to CO_2 emissions are around 1:16 on a mass basis. There was no significant perturbation of the CH_4 concentration when the chamber was closed compared

Table 1
Comparison of average total VOC, CO_2 and CH_4 emissions (10^{-3} g g dry mass^{-1}) from *G. robusta* leaf mulch and *G. robusta* wood chips

	Leaf mulch			Wood chip		
	Mean	SD (%)	Min–max	Mean	SD (%)	Min–max
VOC	0.38	12	0.32–0.41	0.022	14	0.019–0.025
CO_2	6.26	10	5.34–6.59	2.54	17	2.11–2.98
CH_4	<0.001	–	<0.001	<0.001	–	<0.001

with the concentration when the chamber was open. Any CH_4 emissions coming off the leaf mulch were below the measurement detection limit of 1×10^{-11} g g dry mass^{-1} s^{-1}.

3.2. Wood chip emissions

The experiments to measure the BVOC emissions from wood chips showed similar results to leaf mulch experiments. Emissions were determined using the same procedures as for the leaf mulch. The wood chip emission rates for VOC and CO_2 are given in Figs. 5 and 6, respectively. The sample taken during 28–30 August is considered the best representation of the emissions because it was placed into the chamber within an hour of being chipped. The BVOC emissions per unit mass of wood chips are much smaller than the equivalent emission per unit of leaf mulch. The emission rates decline with time after chipping, ceasing some time around 20 h later, slightly earlier than the emissions from leaf mulch.

The integrals of the emission rates shown in Figs. 5 and 6 give the integrated masses emitted by the wood chips, and these emissions are presented in Table 1. The ratio of VOC to CO_2 emissions for wood chips is around 1:116 which is quite different from the equivalent ratio of 1:16 for leaf mulch. Wood chips emitted far fewer VOCs per unit of CO_2 emitted than leaf mulch.

CH_4 emissions from wood chips, as in the case of leaf mulch, were below the detection limit of 1×10^{-11} g g dry mass^{-1} s^{-1}.

3.3. Chemical composition of the mulch and chip emissions

The composition of the emissions from leaf mulching and wood chipping have been examined through the tube and canister sampling. Table 2 lists the compounds that were positively identified and showed an increase in concentration over the time the chamber was closed. The compounds listed were consistently present in the replicate sampling and constituted >0.1% of the total VOC "concentration". Many other compounds were identified in trace amounts.

There are a number of substantial differences between the composition detected by the adsorption tubes and the canisters. As mentioned earlier, there are known deficiencies in both sampling techniques for tube and canister sampling of atmospheric oxygenates. The known deficiencies for adsorption tubes are that more volatile compounds can pass right through the adsorbent beds leading to only fractional retention, and less volatile compounds can be irreversibly adsorbed onto the tubes leading to reduced recovery. The tubes that were used, and the volumes sampled should have given quantitative recovery for compounds in Table 2, since Tenax is recommended by Markes International for trapping n-C_7–n-C_{30} and Carbosieve is recommended for ethane to n-C_5 compounds. Canisters are appropriate for sampling more volatile compounds, but more polar compounds may condense onto the canister walls as also may higher molecular mass polar compounds. Quantitative recovery is expected for acetone and toluene. The recovery of other compounds is not well known.

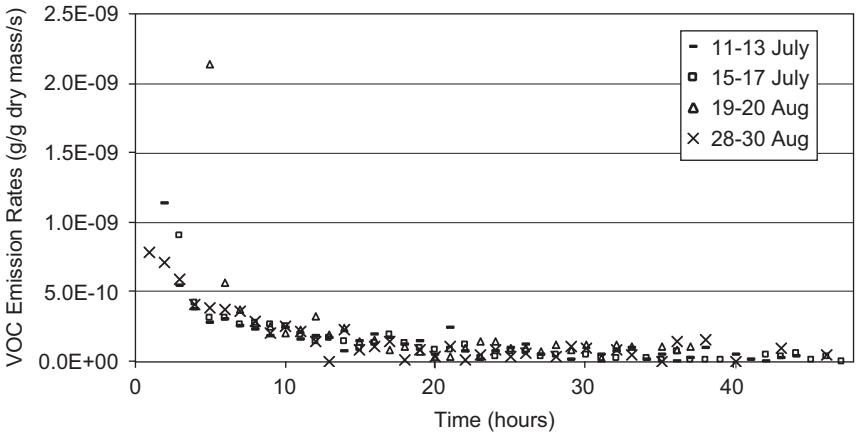

Fig. 5. VOC emission rates from *G. robusta* wood chips versus time since chipping.

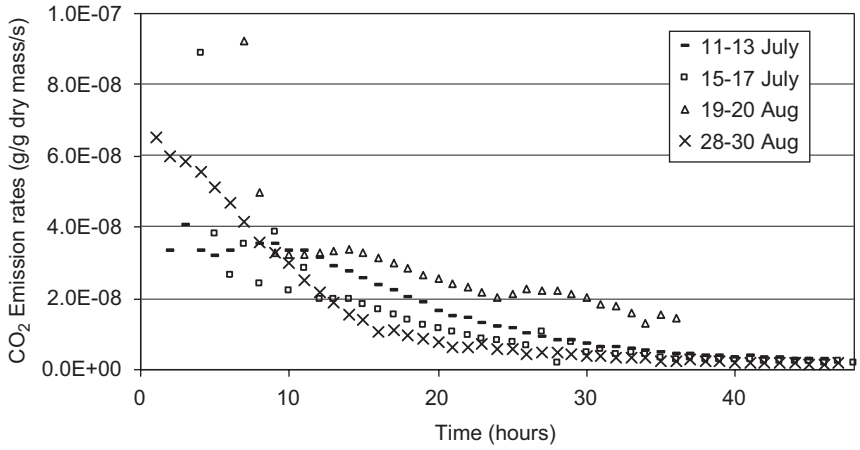

Fig. 6. CO_2 emission rates from *G. robusta* wood chips versus time since chipping.

Table 2
Comparison of the major compounds emitted by *G. robusta* leaf mulch and wood chips as percent of total emitted VOCs for the two sampling techniques used, during the first hour and in the 24 h following cutting

Compound	Retention time (min)	BP (at 760 mmHg)	Leaves (% of total)				Wood (% of total)			
			Tubes		Canisters		Tubes		Canisters	
			1 h ($n=1$)	24 h ($n=1$)	1 h ($n=2$)[a]	24 h ($n=1$)	1 h ($n=2$)	24 h ($n=1$)	1 h ($n=4$)[a]	24 h ($n=1$)
Acetaldehyde	9.9	20.1	[b]	69	14	n.d.	5	23	14	1
Ethanol	14.5	78.2	10	11	38	13	46	n.d.	58	3
Acetone	15.98	56	<1	n.d.	1	3	3	6	4	n.d.
1-Penten-3-ol or 2-pentanone	24.44	114.5/105	3	n.d.	2	n.d.	n.d.	n.d.	n.d.	n.d.
3-Pentanone	24.74	101.9	1	n.d.	<1	n.d.	n.d.	n.d.	n.d.	n.d.
3-Pentanol	25.19	116.2	1	n.d.	<1	n.d.	n.d.	n.d.	n.d.	n.d.
(*E*)-2-Pentenal	27.05	120	<1	n.d.	<1	n.d.	n.d.	n.d.	n.d.	n.d.
Toluene	28.31	110.6	<1	n.d.	<1	n.d.	<1	n.d.	0.5	n.d.
2-Methyl-4-pentenal	29.1	115	6	n.d.	1	n.d.	n.d.	n.d.	n.d.	<1
Hexanal	29.22	131	6	n.d.	4	4	10	1	3.0	n.d.
(*E*)-2-Hexenal	31.41	146.5	27	26	15	23	10	2	<1	n.d.
(*Z*)-3-Hexen-1-ol	31.79	156	30	4	11	39	7	n.d.	7	n.d.
(*Z*)-3-Hexen-1-ol acetate	37.6	169	3	n.d.	2	n.d.	n.d.	n.d.	n.d.	n.d.

[a]Values presented are average values. The variation from highest to lowest values observed ranged from 50% to 200%.
[b]Acetaldehyde was not quantified in these tubes due to high blank values.

The major contributors to these emissions (>10%) from leaf mulch and woodchips (indicated by LM and WC, respectively) are ethanol (LM and WC), (*E*)-2-hexenal (LM and WC), (*Z*)-3-hexen-1-ol (LM and WC) and acetaldehyde (LM and WC). The moderate contributors are hexanal (LM and WC), acetone (LM and WC), a compound not adequately identified perhaps 1-penten-3-ol or 2-pentanone (LM only), 2-methyl-4-pentenal (LM only) and (*Z*)-3-hexenal-1-acetate (LM only). The minor contributors $<\sim$1% are 3-pentanone (LM only), 3-pentanol (LM only), (*E*)-2-pentenal (LM only) and toluene (LM and WC).

4. Discussion

This study has shown that both VOCs and CO_2 are emitted from fresh leaf mulch and fresh wood chips from *G. robusta*. The integrated mass emissions from the freshly mulched leaf samples were $6.3 \pm 0.6\,mg\,CO_2\,g^{-1}$ dry mass of leaf mulch, and $0.38 \pm 0.04\,mg\,VOCs\,g^{-1}$ dry mass of leaf mulch. Emission rates were at their greatest immediately after mulching and decreased exponentially with time, until emissions ceased between 28 and 30 h after mulching; by this time the leaves had visibly dried out. The integrated mass emissions from freshly chipped wood were $2.6 \pm 0.8\,mg\,CO_2\,g^{-1}$ dry mass of wood chips, and 0.022 ± 0.003 $mg\,VOCs\,g^{-1}$ dry mass of wood chips. Emission rates were highest immediately after wood chipping and decreased exponentially, with VOC emissions falling below detection limits around 20 h after chipping and CO_2 emissions detectable for 30 h.

There are three biological processes that should be considered in relation to these VOC and CO_2 emissions. These are the (a) ongoing living processes of the plant material, (b) the plant response to the mechanical trauma and (c) the dying of the plant material. Each of these processes will probably be occurring in different parts of the plant material throughout these measurements.

Because the chamber is located inside a building, it is assumed that plant photosynthesis is not occurring, and this is reflected in the absence of isoprene and monoterpenes in the VOC emissions. The CO_2 emissions are taken to be indicative of ongoing cell metabolism through plant respiration. Currently, it is not known if there are any VOCs produced in plants associated with aerobic respiration.

Ethanol and acetaldehyde were amongst the major compounds found in the leaf mulch and wood chip emissions. These compounds are normally associated with anaerobic glycolysis in plants (Lehninger et al., 1993). Perhaps mechanical trauma can stimulate this situation in some of the cells in plant material particularly if the plant interior contains active microbes. We note CO_2 emissions continue during this period when ethanol and acetaldehyde are detected, indicating that aerobic glycolysis is continuing in at least part of the plant material, even if not in all of it. The ethanol emissions are a larger fraction of total emissions from wood chips than from leaf mulch.

Other major compounds that were emitted from leaf mulch and wood chips include (*Z*)-3-hexen-1-ol, (*E*)-2-hexenal, hexanal and 2-methyl-4-pentenal (Table 2). The first three of these compounds are also emitted by cut grass (Kirstine et al., 1998; Kirstine and Galbally, 2004). This is to be expected since the biochemical processes occurring in the leaves as a result of being mulched, are the same as those in the grasses when they are cut and are identified as a widespread wound defence mechanism (Heldt, 1997; Matsui, 2006).

The integrated emissions from leaf mulch per unit mass are 10–20-fold higher that the equivalent emissions from wood chips. This presumably relates to the more biochemically active role of leaf cells which have the components and mechanisms for photosynthesis as well as respiration and active wound defence mechanisms compared with the stem which is made up of a small fraction of living bark cells along with dead xylem and dead pith cells.

The lifetime of the vegetative material that makes up this leaf mulch and wood chips can most probably be defined by the presence of positive CO_2 emissions. As the leaves die, the emissions of VOCs and CO_2 drop off, as is shown in continuous sampling. Broadly, the disappearance of VOC emissions along with the cessation of CO_2 emissions is indicative that the VOC emissions are associated with at least one of the three processes indicated above.

There has recently been an indication of CH_4 emissions from plants (Keppler et al., 2006). In the case of leaf mulch and wood chips examined here, any CH_4 emissions were below the measurement detection limit of $1 \times 10^{-11}\,g\,g\,dry\,mass^{-1}\,s^{-1}$.

5. Conclusion

The usage of wood chips and leaf mulch for ground and garden cover has increased recently in urban Australia, but to our knowledge no information has previously been published on the VOC emissions from freshly chipped wood used as ground cover in urban areas. This study provides information on mulch emissions from freshly cut and shredded leaves and wood for one commonly occurring urban tree, *G. robusta* (Australian Silky Oak). From this investigation, it was observed that the VOC emissions from fresh leaf mulch and wood chips lasted typically for 30 and 20 h, respectively, and consisted primarily of ethanol, (*E*)-2-hexenal, (*Z*)-3-hexen-1-ol, and acetaldehyde. The integrated emissions of the VOCs were $0.38 \pm 0.04\,g\,kg^{-1}$ from

leaf mulch, and $0.022 \pm 0.003\,g\,kg^{-1}$ from wood chips. These emissions represent a new currently unaccounted for source of VOCs in urban air that will contribute to both urban photochemistry and secondary organic aerosol formation. Any CH_4 emissions from leaf mulch and wood chips were below the measurement detection limit of $1 \times 10^{-11}\,g\,g\,dry\ mass^{-1}\,s^{-1}$.

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