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Eucalypt smoke and wildfires: Temperature dependent emissions of biogenic volatile organic compounds

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ABSTRACT

Eucalypt contributions to biogenic sources of volatile organic compounds (VOCs) in Australia are estimated at teragram ($Tg = 10^{12}$ g) amounts each year. Biogenic VOCs include plant-specific isoprenoids (isoprene and a range of terpenes) and other reactive organic compounds (i.e., acids, aldehydes and ketones). Atmospheric reactions of VOCs are numerous and many have significant environmental impact. Wildfires increase both the amounts of VOCs released and the complexity of their reactions. Proton-transfer reaction mass spectrometry (PTR-MS), gas chromatography mass spectrometry (GCMS) and direct analysis in real time (DART) mass spectrometry were applied to analyze release of VOCs as a function of temperatures ranging from ambient to combustion. PTR-MS enabled trace level analysis of VOCs from a complex forest atmosphere and revealed the release of terpenes associated with leaf damage during a storm. Temperature profile studies revealed ion abundances (i.e., emissions of VOCs) could be correlated with boiling points and vapor pressures of specific compounds. PTR-MS analysis of VOCs resulting from heating fresh leaf (*E. grandis*) material suggested that emissions of protonated methanol (*m/z* 33) and protonated acetaldehyde (*m/z* 45) were greatest at ~60 °C while *m/z* 137 and 153 (associated with a series of terpenes) showed monotonic increases in ion abundances over a wide temperature range from ambient to 200 °C. GCMS analysis of fresh and senescent leaves of *E. grandis* showed that a series of VOCs (ethylvinylketone, diethylketone, 2-ethylfuran, hexanal and hexenals) are present only in fresh leaves while several terpenes (α and β pinenes, α-phellandrene, eucalyptol, γ-terpinene) were common in both. DART analysis of fresh leaf and stem of *E. sideroxylon* identified tissue-specific VOCs (e.g., methanol and ethanol were more abundant in stems). PTR-MS combustion studies of senescent leaves (*E. grandis*) identified two distinct, temperature-dependent VOC compositions. Before the appearance of smoke, the composition of VOCs remained consistent and correlated well with various naturally occurring isoprenoids, as observed in temperature profile studies. Sampling of eucalypt smoke suggested ions (*m/z* 75, 85, 87, 99, 111 and 125) correlated with protonated mass of oxygenated aldehydes, ketones, furans and substituted benzenes, and were due to pyrolysis of polycarbohydrates (cellulose and lignin) that are common in many types of wood.

1. Introduction

Volatile organic compounds (VOCs) are continually emitted from all types of vegetation and have substantial impact on the global atmosphere. Plants contain a wide range of organic compounds but only a limited set of these compounds are released at rates that could significantly influence the chemical and physical composition of the atmosphere [1–5]. Eucalypts grow widely in Australia and are increasingly grown elsewhere [6]. In Australia, their annual release of VOCs into the environment is estimated at teragram ($Tg = 10^{12}$ g) amounts [7]. Biogenic VOCs of eucalypt include plant-specific isoprenoids (isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$)) and other reactive compounds (organic acids, aldehydes, ketones and alcohols). The type of compounds emitted and their emission rates depend in complex ways upon the type of ecosystem, health of vegetation, time of year, ambient temperature, amount of sunlight, and a range of other environmental factors. Furthermore, atmospheric reactions of VOCs lead to secondary products often containing more functional groups than their parent compounds [8–11].

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Wildfires and prescribed burns could significantly affect the complexity of atmospheric reactions of VOCs and contribute to production of a variety of toxic compounds resulting from pyrolysis of plant oils and fibers [12–15]. Condensable products may be formed from atmospheric reactions of VOCs. These compounds partition between the gas and particle phases appearing in a haze above many forest (such as the Blue Mountains in NSW, Australia) and can influence the flux of solar radiation either by direct absorbance and scattering or indirectly as aerosol and cloud condensation nuclei [16–20].

Considerable recent attention has been directed worldwide toward potential health effects of biogenic VOCs, including those produced during fires (i.e., prescribed burns, wildfires) [15,21–23]. Identification and quantification of biogenic VOCs from various landscapes and during fires are crucial to evaluating their environmental impacts, and are also invaluable for informing and protecting the public and improving protective equipment for firefighters.

Direct analysis and real-time monitoring of VOCs (i.e., without a pre-concentration step) emitted from Australian vegetation, particularly native trees in the genus *Eucalyptus* are a major focus of our research [24]. Measurements of VOCs can be made at a variety of scales, from leaf, branch, canopy, to landscapes. Biogenic VOC species are numerous and their analysis requires the application of several analytical techniques for their accurate identification and sampling. We are utilizing advanced mass spectrometry techniques for real-time monitoring of VOCs from Australian forests at trace concentrations, measuring emissions of VOCs for a variety of plant tissues as a function of temperature, and identifying the composition of smoke from combustion studies under controlled atmospheric conditions.

We applied gas chromatography mass spectrometry (GC-MS), proton-transfer reaction mass spectrometry (PTR-MS) [25,26] and direct analysis in real-time (DART) mass spectrometry [27] to study emissions of VOCs from a series of eucalypts at temperatures ranging from ambient to combustion. Advantages and limitations of each technique for the identification and quantification of plant-derived volatiles are described. This study identified that temperature-dependent emissions of VOCs could be correlated with three major classes of compounds released as a function of increasing temperatures (i.e., from ambient to wildfires). The first class of compounds include acids, aldehydes, ketones, isoprene and low boiling point terpenes that were detected from ambient to ∼100 °C. Terpenes with relatively greater boiling points were the second class and were detected before the onset of pyrolysis. Above 300 °C, pyrolysis of plant fibers (i.e., cellulose and lignin) released the third class of compounds that include a range of substituted furans and benzenes.

2. Materials and methods

2.1. Proton transfer reaction mass spectrometry (PTR-MS)

A high sensitivity PTR-MS (Ionicon Analytik, Innsbruck, Austria) with an upper mass range of 512 u [25,26] was operated in standard mode with inlet tubing and chamber temperatures ranging from 30 to 60 °C. PTR-MS comprises of a hollow cathode discharge ion source producing the reactant/reagent ions (H_3O^+ and $(H_2O)_nH^+$), a drift tube reactor where VOCs are introduced for proton-transfer reactions and a quadrupole mass analyzer. A mass flow controller supplies a flow of water vapor (8–10 ml/min) from the headspace of a water reservoir to supply a constant flow of reagent ions. A voltage (∼600 V) applied to a drift tube (∼9.2 cm) consisting of a series of stainless steel rings provides a homogenous electric field for transporting ions out to the analyzer. A reduced drift tube voltage of 500 V was used in some experiments to limit fragmentation [24]. The standard operating mode refers to conditions that satisfy $E/N \sim 120$ Td (Townsend) where E is the electric field and N is the number density of the drift tube buffer gas molecules [25,26]. Mass spectra were collected via PTR-MS control software and were processed utilizing Microsoft Excel (Microsoft Inc.) and Origin (Microcal Software, Inc.). A standard mixture of VOCs (Apel-Riemer Environmental, Inc. Denver, CO, USA) was used for calibrating and converting mass spectral data (ion counts per second (c/s) to concentrations. Conversion of PTR-MS mass spectral data to concentrations has been well documented since 1995 [25,26] including methodologies and calibration procedures for measurements of biogenic VOC in forests [28]. The calibration gas mixture included methanol, acetone, acetonitrile, acetaldehyde, isoprene, benzene, toluene and camphene. PTR-MS was calibrated by serial dilution of the calibration gas. Background signal (VOC free) was determined with a supply of ultrapure nitrogen (Linde Gas). Data were recorded in scanning or multiple ion detection (MID) modes with dwell times of 5 ms to 1 s resulting in acquisition times of several seconds (MID) to ∼200 s (scan mode).

Proton-transfer reactions of H_3O^+ (typical count rates of 10^6 counts/s) enable ionization of trace levels of VOCs in air. VOCs with a higher proton affinity than water (166.5 kcal/mol) are detected in trace levels (parts per billion by volume (ppbv: 10^{-9}) according to Equation (1):

$$H_3O^+ + \text{VOC} \rightarrow [(\text{VOC}) + \text{H}]^+ + H_2O \tag{1}$$

Concentrations of VOCs are calculated by applying pseudo first-order kinetics (i.e., high ratio of $[H_3O^+]$ to trace levels of $[(\text{VOC})+\text{H}]^+$) according to Equation (2):

$$\begin{aligned}[(\text{VOC}) + \text{H}]^+)] &= [H_3O^+]_0\{1-\exp(-k[\text{VOC}]\text{Dt})\} \\ &\cong [H_3O^+]_0 k[\text{VOC}]\text{Dt}\end{aligned} \tag{2}$$

where $[H_3O^+]_0$ represents the concentration of primary reagent ions in the absence of VOCs, k corresponds to rate constants for proton transfer reactions and Dt is the time H_3O^+ ions require to traverse the drift tube (∼0.1 ms with standard instrumental parameters and determined by the length of the drift tube and the drift tube voltage). Trace level concentrations of VOCs justify the approximation in Equation (2). Reaction rate constants (k) are reported for many proton transfer processes [25,26] and a value of 2×10^{-9} cm^3/s was applied for all masses. Measured rate constants for monoterpenes were detected using PTR-MS range from 2.2 to 2.5×10^{-9} cm^3/s [29]. Uncertainties in measured concentrations of VOCs are estimated to be ±20% based on differences in theoretical versus measured k values or errors associated with calibration curves.

2.2. Gas chromatography mass spectrometry (GCMS)

GCMS was performed on a TRACE GC Ultra^{TM} (Thermo Scientific, Inc. San Jose, CA, USA) gas chromatograph equipped with an autosampler and a headspace gas-tight syringe. A 15 m × 0.25 mm i.d. capillary column (factorFour^{TM} VF-1 ms (1 μm film thickness); Varian Inc. Palo Alto, CA, USA) was used. Mass spectra were collected on a single quadrupole mass spectrometer (TRACE DSQ^{TM}) operated in electron ionization (EI) mode. GCMS library (NIST 2.0) search was utlilized for the identification of compounds.

2.3. Direct analysis in real time (DART) time-of-flight mass spectrometry (TOF-MS)

DART experiments were performed at the University of Pacifica (Stockton, CA, USA) on an AccuTOF-DART^{TM} (JEOL, Peabody, MA, USA) time-of-flight mass spectrometer providing highly accurate mass measurements and isotope abundance measurements with a resolving power of ~7 k.

DART ionization [27] is facilitated by a flow of gas (typically helium) through an electrode with a high potential that generates high-energy species (metastable gaseous atoms or molecules). These react with atmospheric water and produce H_3O^+ and water cluster according to Equations (3) to (5).

$$He(2^3S) + H_2O \rightarrow H_2O^{+\bullet} + He(1^1S) + e^- \quad (3)$$

$$H_2O^{+\bullet} + H_2O \rightarrow H_3O^+ + {}^\bullet OH \quad (4)$$

$$H_3O^+ + nH_2O \rightarrow [(H_2O)nH]^+ \quad (5)$$

A gap (a few centimeters) is used for placing samples between the DART ionization source and the capillary inlet of the mass spectrometer. Plant tissues were held via tweezers in DART ionization path and VOCs emitted from plant tissues were ionized through proton transfer reactions similar to those described earlier for PTR-MS. Gas heaters were used for adjusting the temperature of the helium gas, which in turn enabled the heating of the plant material.

2.4. Mass loss calorimeter

Combustion studies were performed utilizing a mass loss calorimeter (Fire Testing Technology, West Sussex, UK) consisting of a cone heater mounted in a sealed chamber. Cone heaters (comprised of a set of coiled copper tubing 6.5 cm in height) provide uniform heating up to 1000 °C. Use of a sealed chamber enables combustion under controlled conditions. An integrated balance is used for recording mass loss as materials burn. VOCs and smoke were carried via a heated transfer line to PTR-MS for analysis.

2.5. Materials source & sample preparation

The focus of this study was to identify the utility of different analytical techniques for characterizing the temperature dependence (up to combustion temperatures) of emissions of VOC from eucalypts, rather than a species by species comparison. We thus selected eucalypts for study based on availability in New South Wales and California. Eucalypt leaves were collected from living trees growing on campus at the University of New South Wales or from Mount Annan Botanic Gardens, NSW, with senescent leaves collected from fallen branches. For DART experiments, small branches were provided as a gift from a local nursery (Green Tumb, Ventura, CA, USA). For temperature-profile experiments, leaves were excised (2–5 mm pieces) and placed in sealed vials. For PTR-MS analysis, vials were heated in a beaker containing sand and VOCs were extracted via PEEK^{TM} tubing (Upchurch Scientific, Oak Harbor, WA, USA) connecting the vials to the heated transfer line of PTR-MS. For GCMS analysis, vials were incubated in a temperature-controlled sample block and VOCs were drawn via a heated gas-tight syringe. Measurements of VOCs at Bago State Forest (NSW) were achieved by pumping forest air from a canopy height of 45 m through sampling lines (Teflon thin-walled 1/4 inch OD) at approximately 10–15 l/min. The flow rate of forest air into the PTR-MS was between 50 and 250 ml/min. The overall delay time through the sampling line was about 11 s and was measured by spiking VOCs into the sampling inlet. Temperature, wind speed, and rainfall were continuously recorded.

3. Results and discussion

3.1. Real-time monitoring of VOCs from Australian forest

We measured changes in concentration of differing VOCs as a function of time as part of a study to investigate the impact of VOCs on ecosystems and climates. Emissions of VOCs from plants are highly affected by diurnal and seasonal temperature variations [2,3,6,30–34]. While a range of reactive hydrocarbons are released by plants into the atmosphere, isoprene and monoterpenes are amongst the most characterized compounds due to their important reactions leading to atmospheric pollutants.

Isoprene and monoterpenes are commonly emitted from a variety of eucalypts and their emission rates are highly dependent on temperature, light intensity as well as the age of trees. Biological precursors of isoprene and monoterpenes are isopentenyl pyrophosphate (IPP) and its isomer dimethylallyl diphosphate (DMAPP). Isoprene, a five carbon hydrocarbon (2-methyl-1,3-butadiene) is produced in plants by enzymatic (catalyzed by isoprene synthase) conversion of dimethylallyl diphosphate (DMAPP). Monoterpenes (10 carbons) are synthesized by the addition of IPP and DMAPP [1,35]. Isoprene and monoterpenes are actively involved in the chemistry of the lower atmosphere and both react with ozone and hydroxyl radicals generating highly reactive oxygen species (ROS). In other reaction pathways, atmospheric reactions of NO (from natural and anthropogenic sources) with ozone lead to the formation of NO_3 radicals. Concentrations of nitrate radicals remain low during daylight due to photolysis and increase at night. Isoprene reacts with NO_3 radicals generating C_5-hydroxynitrates, methylvinylketone and methacrolein. Monoterpene reactions with NO_3 radicals generate hydroxynitrates and di-hydroxycarbonyls as well as acetone [8,9].

Mass spectrometric analyses are ideal for studies of the complex atmospheric chemistry described above. In recent years, proton transfer reaction mass spectrometry (PTR-MS) has enabled the analysis of VOCs in real-time [25,26]. Trace level detection of atmospheric VOCs by PTR-MS is facilitated by selective proton transfer reactions with H_3O^+ (proton affinity of 166.5 kcal/mol) since proton affinities of major components of air (N_2 and O_2) are less than those of water. This unique process enables direct sampling of forest air from various elevations without pre-concentration steps that could bias specific compounds. PTR-MS is ideal for real-time monitoring of VOCs at low concentrations (ppbv to pptv). While the unit mass resolving power of quadrupole mass analyzers can sometimes result in ambiguous identification of some compounds, recent incorporation of time-of-flight analyzers (PTR-TOFMS) has substantially improved capabilities of PTR mass spectrometers and their applications in environmental sciences [36]. Even so, some isobaric compound cannot be distinguished by PTR-TOFMS analysis.

Fig. 1 shows PTR-MS analysis of VOCs performed in Bago State Forest, NSW during November (late spring season in southern hemisphere). Dominant species of this tall open eucalypt forest with average tree height of 40 m are *E. delagatensis* (Alpine Ash) and *E. dalympleana* (Mountain Gum). Concentrations of isoprene (*m/z* 69) and total terpenes (*m/z* 137) were monitored with respect to temperature changes. It should be noted that while major sources of these ions (i.e., *m/z* 69 and 137) are considered to be isoprene and terpenes, other isobaric compounds and their fragments could also contribute to these ions. For example sesquiterpenes share a common fragment ion at *m/z* 137 with monoterpenes. During the first 36 h of this study, isoprene concentrations varied in accordance with daily temperatures with a maximum range of 1 ppbv (at ~18 °C), while concentrations of monoterpenes was steady at

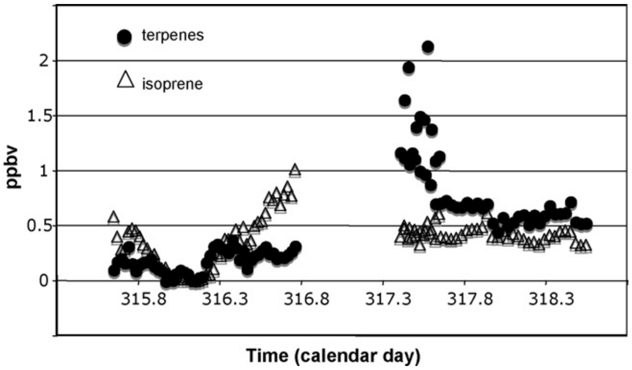

Fig. 1. Concentrations of isoprene (*m/z* 69) and total terpenes (*m/z* 137) measured by PTR-MS analysis of forest air at Bago State Forest in November 2006.

<0.5 ppbv levels. A storm during the latter part of this study resulted in a substantial damage to trees. During this storm, concentrations of monoterpenes increased by four-fold (up to 2 ppbv) due to leaf damage that resulted in the release of VOCs into the atmosphere. In contrast, isoprene levels remained at low (at 0.5 ppbv) concentrations in response to cold temperatures (~8 °C). It is important to note that baseline concentrations of VOCs were calculated based on PTR-MS background measurements when ultrapure nitrogen was analyzed. These results highlight the power of PTR-MS for monitoring low levels of VOCs within complex forest atmospheres and reveal that forest storms [37] could increase the concentration of VOCs even during cold seasons when it is presumed that emissions of VOCs remain low.

3.2. Temperature dependent emissions of VOCs

Emissions of VOCs from plants are highly dependent on diurnal temperature variations, and concentrations of VOCs in the atmosphere increase directly in response to increasing temperatures. We are applying several methods to identify the range of compounds that could be emitted from various species as a function of temperature (from ambient to combustion temperatures).

3.2.1. Proton transfer reaction mass spectrometry (PTR-MS)

Our initial studies identified that a range of VOCs are emitted from eucalypt leaf tissue at ambient to elevated temperatures [24]. These compounds included acetaldehyde (MH^+ 45), acetone (MH^+ 59), acetic acid (MH^+ 61), isoprene (MH^+ 69) and terpenes (MH^+ 135 and 137), oxygen-containing terpenes (MH^+ 153 and 155) and sesquiterpenes (MH^+ 205). Fragment ions at *m/z* 81, 93, 95, 137, 149 are common to many monoterpenes and sesquiterpenes. Fig. 2A shows PTR-MS of VOCs emitted from heating *E. grandis* leaf at 160 °C. Relative abundances for several compounds identified from a temperature profile study are presented in Fig. 2B. These results show emissions of VOCs are least at ambient temperatures and increase with heating. As temperature rises, rates of emission of each compound reach a maximum at temperature close to their boiling points and vapor pressures. As heating continues, a different class of compounds is emitted from leaves, via a process similar to distillation. For example, ion abundances (Fig. 2B) corresponding to protonated mass of methanol (*m/z* 33) and acetaldehyde (*m/z* 45) showed maximums at 60 °C. In comparison, *m/z* 137 showed monotonic ion abundance increases over a wide temperature range. This pattern is expected since several monoterpenes $C_{10}H_{16}$ (such as pinene, limonene, myrcene, terpinene, etc) and oxygen-containing terpenes $C_{10}H_{18}O$ produce *m/z* 137 and have similar boiling points. Fragment ions from oxygen-containing terpenes ($C_{10}H_{16}O$ and $C_{10}H_{18}O$) and sequiterpenes ($C_{15}H_{24}$) contribute to *m/z* 137 [24,29].

3.2.2. Gas chromatography mass spectrometry (GCMS)

Chemical compositions of a variety of eucalypts have been well studied by GCMS mainly due to their potential value in perfumes and medicines [38–42]. These studies provide a basis for suggestion as to the types of compounds present in various eucalypts. Our studies are focused on the effects of temperature on the

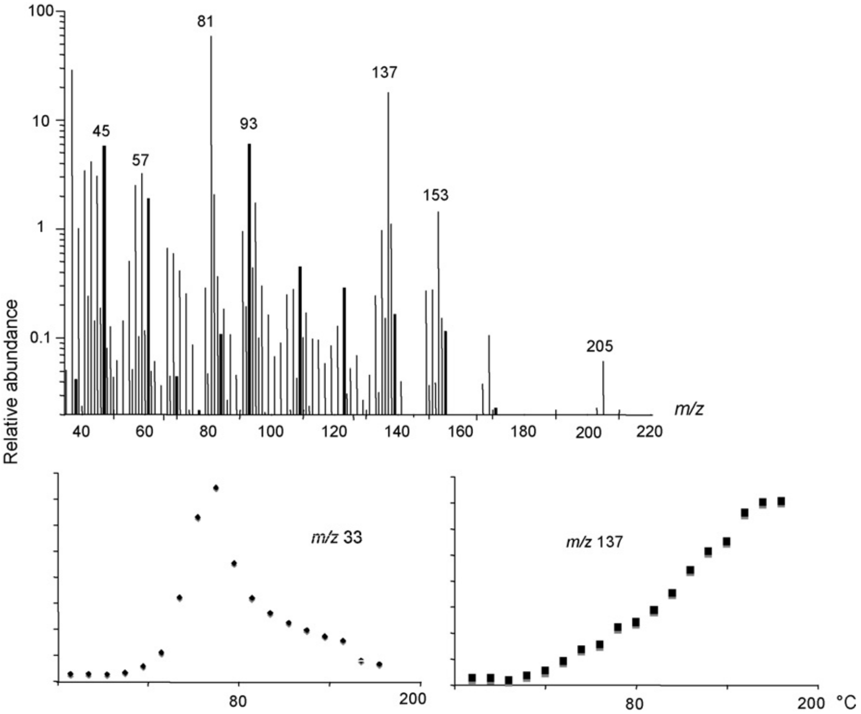

Fig. 2. PTR-MS of VOCs emitted from heating *E. grandis* leaf (A) at 160 °C and (B) temperature profiles of *m/z* 33 (methanol) and *m/z* 137 (monoterpenes and sesquiterpenes).

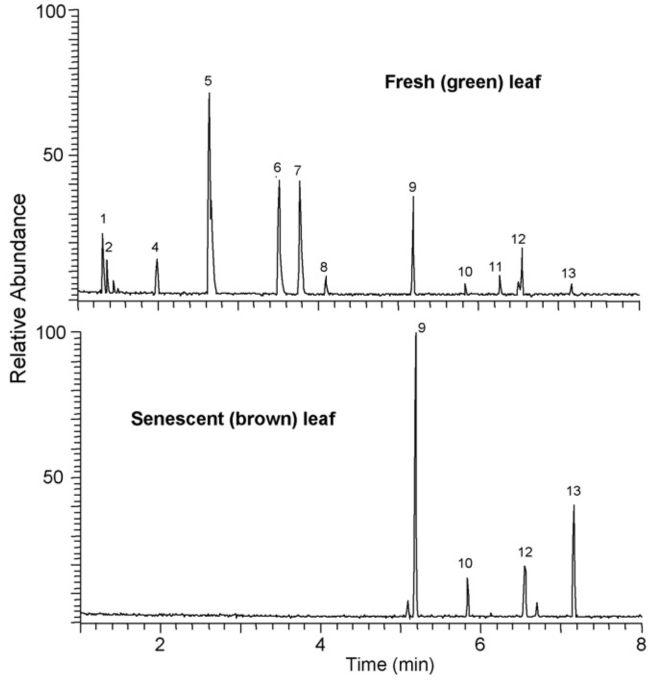

Fig. 3. GCMS chromatograms of VOCs after 5 min incubation of leaves of *E. grandis* in sealed headspace vials at 40 °C (A) fresh (green) leaf and (B) senescent (brown) leaf. (1) ethylvinylketone, (2) diethylketone, (3) 2-ethylfuran, (4) 1,1-diethylcyclopropane, (5) hexanal, (6) 2-hexenal, (7) 3-hexene-1-ol, (8) 1-hexenol, (9) α-pinene, (10) β-pinene, (11) α-phellandrene, (12) eucalyptol, (13) γ-terpinene.

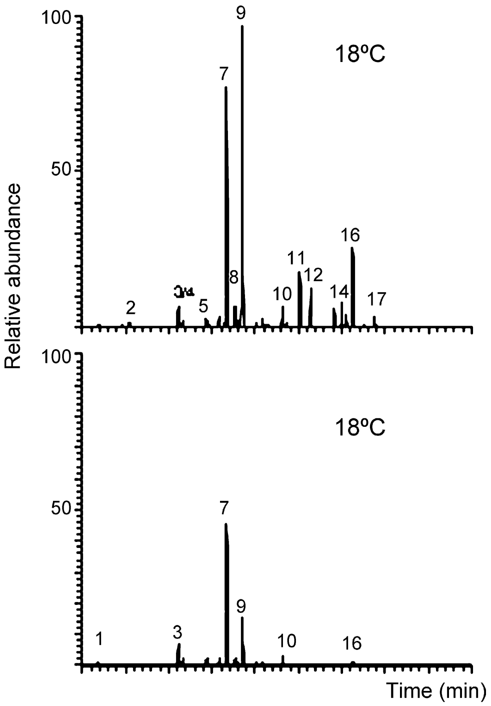

Fig. 4. GCMS chromatograms of VOCs after 5 min incubation of fresh leaves of *E. Corymbia Ficifolia* in sealed headspace vials at (A) 80 °C and (B) 18 °C. (1) $C_6H_{10}O$, (2) $C_6H_{12}O$, (3–8, 10) C_6H_{10}, $C_{10}H_{18}O$ (9, 11–16) and $C_{10}H_{16}O$ (17).

release of various VOCs from eucalypts rather than analyzing specific terpenes for each species. Since the types of terpenes and their concentrations vary in response to seasonal changes and environmental factors, cross comparisons of VOCs emitted from different eucalypts from different sites tend to be confounded.

Since numerous isobaric compounds (such as various $C_{10}H_{16}$) are emitted from eucalypts, it becomes essential to incorporate a chromatography step when seeking to accurately quantify many VOCs. Gas chromatography has been successfully interfaced with PTR-MS [43]. Databases of electron ionization mass spectral facilitate compound identification with the availability of well-established libraries.

We applied GCMS for analysis of VOCs of a variety of plant tissues. GCMS analyses of VOCs emitted from fresh and senescent leaves of *E. grandis* when heated at 40 °C for 5 min are compared in Fig. 3. A series of compounds with lower retention times (i.e., lower boiling points and/or weaker binding to GC column) were only present in fresh leaves. These compounds were identified through library searches and in order of increasing retention times (from 1.3 to 4.1 min) are ethylvinylketone, diethylketone, 2-ethylfuran, 1,1-diethylcyclopropane, hexanal, 2-hexenal, 3-hexene-1-ol, and 1-hexenol. Several isoprenoids with retention times of 5.2–7.2 min (i.e., α-pinene, β-pinene, α-phellandrene, eucalyptol (cineole) and γ-terpinene) were found common in both types of leaves (i.e., fresh and senescent). These results suggest that variation in fuel sources is a significant influence on the composition of smoke from forest fires. These results also show that even senescent leaves contain high concentrations of terpenes, and that these can be released into the environment during the normal process of decomposition and consumption by soil organisms.

In another experiment, we studied the effects of heating on release of VOCs from fresh leaves of *Eucalyptus Ficifolia*. GCMS analyses of fresh leaves incubated for 5 min in sealed headspace vials at 18 and 80 °C are compared in Fig. 4. VOCs identified by library searches are reported with their retention times and molecular formulas (i.e., $C_6H_{10}O$ at 1.4 min; $C_6H_{12}O$ at 2.1 min; C_6H_{10} at 3.2, 3.9, 4.3, 4.5, 5.0, 5.2 and 5.6 min; $C_{10}H_{18}O$ at 4.7, 5.7 6.0, 6.8, 7.0, 7.1, 7.3 min; and $C_{10}H_{16}O$ at 7.7 min). Concentrations of most VOCs increased dramatically in response to increasing temperatures from 18 to 80 °C. The intensity for the peak with a retention time of 4.7 (identified as eucalyptol) increased five-fold while compounds with greater boiling points (i.e., peak with retention time of 7.3 min) showed a more dramatic increase of peak intensity (about 20-fold). These results suggest that compounds with high boiling points can easily be released into the atmosphere during even relatively 'cool' fires and these VOCs could serve as new sources of fuels in fires and contribute to air pollution.

3.2.3. *Direct analysis in real time (DART) time-of-flight mass spectrometry (TOF-MS)*

Analysis of VOCs from eucalypt tissues in open air can be facilitated by DART technology [27]. DART mass spectra obtained from plant tissues (an intact leaf and a stem cut in the middle) of *E. sideroxylon* are shown in Fig. 5. These spectra were collected with a helium temperature of 100 °C. DART mass spectra identify several VOCs (i.e., methanol, ethanol, acetone, terpenes, and sesquiterpenes), however, structurally informative fragments are not available to fully distinguish each terpene. For example, *m/z* 137, 155 and 205 are associated with protonated $C_{10}H_{16}$, $C_{10}H_{18}O$ and $C_{15}H_{24}$. DART mass spectrum of the cut stem (Fig. 5A) shows abundant ions at *m/z* 47.04, 65.05 and 93.08 that are absent in the DART mass spectrum of the leaf (Fig. 5B). These ions could be related to alcohols (ethanol and methanol) and suggest stem tissues contain higher concentrations of these alcohols. Protonated ethanol is assigned to *m/z* 47.04 and proton-bound dimer of ethanol could be associated with *m/z* 93.08. Additionally, *m/z* 65.05 is associated with proton-bound dimers of methanol. Mass spectra for these experiments were recorded above *m/z* 40 to eliminate abundant background ions (i.e., water clusters, etc.) and methanol is iden-

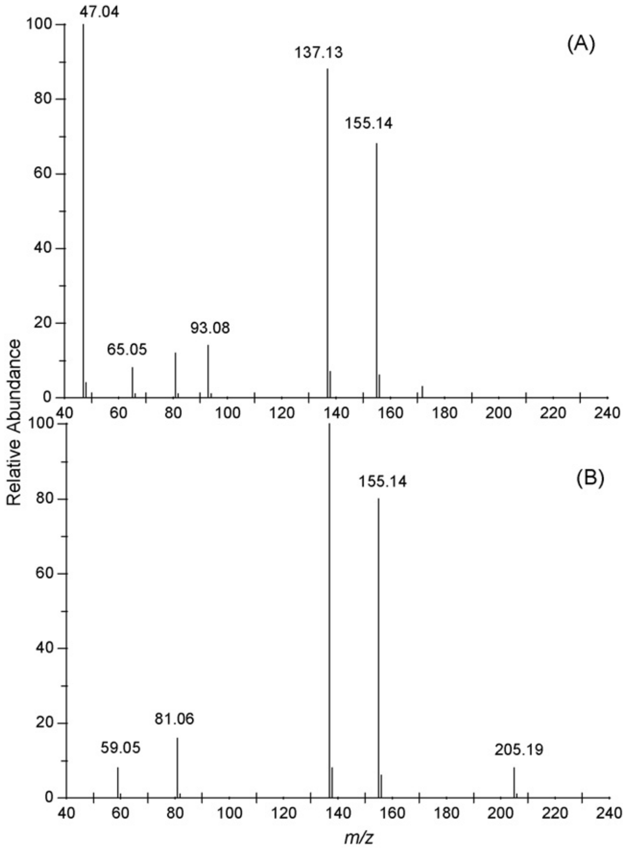

Fig. 5. DART TOF-MS of VOCs emitted at 100 °C from *E. sideroxylon* (A) stem cut in the middle and (B) intact leaf.

tified through its proton-bound dimer at *m/z* 65. Proton-bound dimers could be generated in the small sample gap of the DART ionization source. Proton-bound dimers of alcohols and their fragments corresponding to the loss of water have been reported in PTR-MS analysis of alcohols [24]. With increasing temperatures >100 °C (i.e., raising the temperature of the helium gas), concentrations of terpenes increased dramatically leading to the formation of proton-bound terpene dimers. These studies suggest that DART mass spectrometry would be ideal for monitoring emissions of VOCs from various tissues (i.e., root, leaf, stem and flower) of living plants, although high concentrations of VOCs could contribute to artifact ions (i.e., proton-bound dimers).

3.3. Combustion studies and composition of smoke

Earlier studies in smoke analysis were often the part of efforts to optimize combustion of wood, biomass and wastes into fuels, or were conducted to identify toxic chemicals in relation to public health [21–23]. Smoke is a complex mixture of numerous chemicals including carbon monoxide, carbon dioxide, nitrogen oxides, hydrocarbons, water vapor and particles. Smoke composition varies depending on the types of wood or other vegetative material, the temperature of fire, and the wind conditions as they affect the oxygen available for combustion.

Australian studies of wildfires report flame tip temperatures could range widely from 300 to over 900 °C depending on three major variables of wind speed, fuel type and topography of a region. At any point in time, flames contain unburnt fuel, air and combustion products [44]. Wildfires generate high levels of smoke containing various VOCs and particulates with potential health hazards [45–48]. Our studies are aimed at identifying the range of compounds that could be emitted from eucalypts at elevated temperatures including combustion studies to mimic the effects of bushfires. This information is important when evaluating the environmental impacts of smoke-related compounds. Additionally, this data would be valuable in informing and protecting the public and in improving protective equipment for firefighters.

Eucalypt emits a wide range of VOCs at ambient temperature and our studies (described above) have shown that the range of compounds and their concentrations could change dramatically with increasing temperatures. Aside from the volatile compounds, eucalypts contain a range of biopolymers such as cellulose and lignin that are common to many types of wood. Pyrolysis studies of wood have shown that initially water and low molecular weight volatile compounds are released and then, with increasing temperature, compounds arising from pyrolysis of biopolymers are formed. The predominant components of celluloses in softwood and hard wood are galactoglucomannan and glucuronxylan. Pyrolysis of these polycarbohydrates in the initial stages involves dehydration, decarboxylation and decarbonylation reactions leading to the release of water, CO and CO_2. At temperatures above 300 °C, depolymerization reactions involving glycosidic linkages generate the monosaccharide levoglucosan, which decomposes further to low molecular weight VOC's (i.e., furfurals and 2,3-butanedione). In addition, oxygen-containing furan structures (i.e., dibenzofuranols, benzonaphthofuran) can be formed. In comparison, lignin is pyrolyzed over a wide temperature range. Below 300 °C, formaldehyde is produced and with increasing temperatures, substituted phenols (i.e., guaiacols) are generated [49–55].

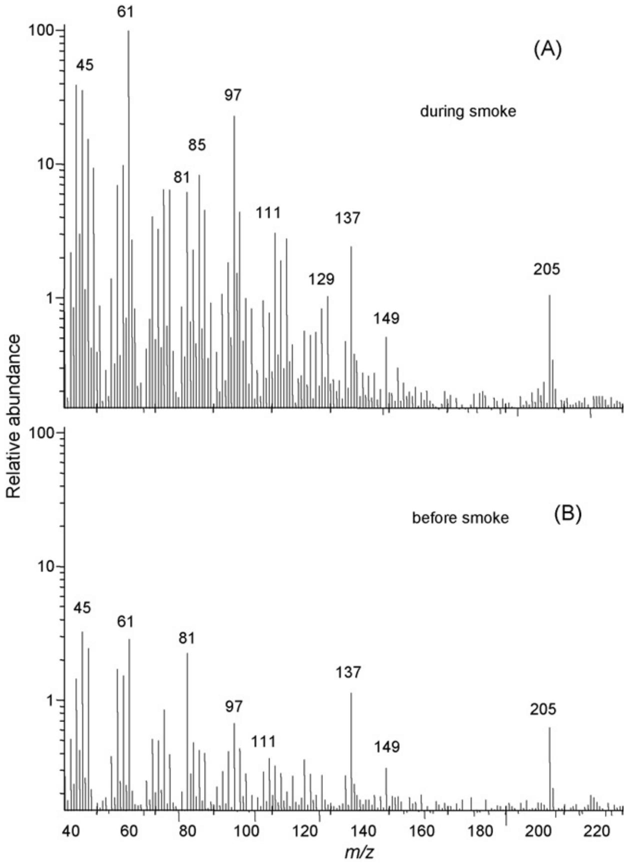

Fig. 6. PTR-MS of VOCs emitted from heating senescent leaves of *Eucalyptus grandis* (A) during smoke ($T_{\text{cone heater}}$ 600 °C) and (B) before smoke ($T_{\text{cone heater}}$ 450 °C).

PTR-MS analyses of VOCs emitted from senescent leaves of eucalypts at cone heater temperatures of 450 and 600 °C are shown in Fig. 6. In this experiment, samples were placed 10 cm away from the bottom coil of the cone heater (i.e., the temperature of the cone heater does not reflect the temperature of the sample). VOCs and smoke were sampled at a height of 2 cm from the top of the cone heater (i.e., 12 cm from the leaves). Appearance of smoke was observed with increasing temperatures (cone heater >530 °C). Ions at *m/z* 137 and 205 correspond to $(M+H)^+$ of monoterpenes and sesquiterpenes. Oxygen-containing monoterpenes could also contribute to *m/z* 137 through loss of water. Another fragment ion that is common to sesquiterpenes and monoterpenes is observed at *m/z* 81, and similarly *m/z* 137 and 149 could be assigned to fragment ions of sesquiterpenes. These spectra were recorded at a reduced drift voltage (500 v) to minimize fragmentation as previously reported [24]. Note the intensity of terpene-related fragment ions at *m/z* 93, 95, 107 and 121 remains relatively low in Fig. 6B (before the appearance of smoke).

The composition of VOCs up to the point before the appearance of smoke (cone heater <530 °C) remained consistent and correlated well with various compounds identified in temperature profile studies (i.e., heating eucalypt leaf to 200 °C). Correlating PTR-MS data (Fig. 2A) with compounds previously identified from pyrolysis studies of wood [49] provided the list (Table 1) of possible compounds related to eucalypt smoke. Relative abundances of smoke related ions (Fig. 6) increased dramatically in comparison to compounds associated with terpenes (i.e., *m/z* 137, 149, 205). For example, abundances of ions *m/z* 61, 97 and 111 increased 10-fold.

Table 1
Smoke related VOCs [50] correlated with their protonated mass from PTR-MS*.

$(M+H)^+$	Possible compounds
42	acetonitrile
43	propene
45	ethanol, acetaldehyde, dimethylamine
47	formic acid
57	acrolein
59	acetone, glyoxal
61	acetic acid, hydroxyacetaldehyde, methyl formate
69	furan
75	propionic acid, 1-hydroxy-2-propanone (acetol), 2-hydroxypropanal
79	benzene
81	pyrazine
83	methylfuran, hexanal
85	cyclopentanone, 2-methyl-2butenal, 2(5H)-furanone
87	2,3-butanedione, 2-butenoic acid (crotonic acid), 1,4-butyrolactone
93	toluene
95	phenol
97	furfural, 2-methyl-2-cyclopentene-1-one, dimethylcyclopentene
99	furfuryl alcohol, 3-methyl-2(5H)-furanone
107	benzaldehyde
111	5-methylfurfural, dihydroxybenzenes (catechol, hydroquinone, resorcinol)
113	dimethylcyclopentanone, 2-hydroxy-3-methyl-2-cyclopentene-1 -one
115	3-hydroxy-2-penten-1,5-lactone
117	hexanoic acid, 1-acetyloxy-2-propanone, indene
121	vinylphenol
123	dimethylphenols, ethyl phenol, benzoic acid
125	2-methoxyphenol (guaiacol), dihydroxytoluene, trimethylcyclopentenone
127	levoglucosenone, 5-hydroxymethyl-2-furaldehyde, 2-methyl-3-hydroxy-2-pyrone
129	naphthalene

* Some ions (eg. *m/z* 81, 93, 95, 107, 121) could be fragment ions associated with terpenes [24].

While these results identify several key and smoke-related compounds, the identity of these compounds needs to be further verified by incorporating gas chromatography and high-resolution mass spectrometry. For example, *m/z* 59 could be attributed to protonated acetone ($C_3H_7O^+$ 59.05 u) or glyoxal (1,2-ethanedione, $C_2H_3O_2^+$ 59.01 u). Acetone is well classified within the list of biogenic VOCs while glyoxal is a smoke-related compound and has also been identified in cigarette smoke [56,57], and a mass spectrometer with a resolving power of 1500 (i.e., PTR-TOFMS) would be required to differentiate these compounds.

These combustion studies are being expanded to distinguish smoke-related compounds for a variety of eucalypts with different contents of cellulose and lignin (i.e., hardwood versus softwood). A combustion chamber is ideal for generating smoke in a range of atmospheric conditions (i.e., air with 21% oxygen versus lower oxygen content), and will enable elucidation of conditions that could promote specific reaction pathways and products. For example, combustion studies have reported that while oxygen was required for the production of dioxins from carbon from fly ash, reduced oxygen concentration (between 5 and 10%) maximized their rates of formation [58].

4. Conclusions

Mass spectrometry and chromatography enabled identification of VOCs emitted from Australian eucalypts. Emissions of VOCs were classified in three major classes. The first class of compounds (acids, aldehydes, ketones, isoprene and low boiling point terpenes) were detected from ambient to ∼100 °C, followed by the second class containing plant-specific terpenes. The third major class of VOCs was released at high temperatures (>300 °C) upon pyrolysis of plant fibers (i.e., cellulose and lignin). GCMS was a reliable approach for the identification of VOCs by providing retention times that could be matched with reference compounds and structurally informative fragmentation patterns that uniquely identify the majority of compounds. Some terpenes have indistinguishable mass spectra and require additional information (i.e., GC retention times) for further identification. PTR-MS enabled trace level detection of VOCs from a complex forest atmosphere, and DART TOF-MS provided high mass accuracy and was unique in analyzing plant tissues in open air. Identification of smoke-related compounds will require further analysis incorporating gas chromatography and high-resolution mass spectrometry. Combining these techniques may well be required in many studies where the aims is to quantify VOCs at ambient to high temperatures across diverse plant materials.

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References

[1] R. Fall, in: C.N. Hewitt (Ed.), Reactive Hydrocarbons in the Atmosphere, Academic Press, San Diego, USA, 1999, p. 41.
[2] J. Kesselmeier, M. Staudt, J. Atmos. Chem. 33 (1999) 23.
[3] A. Guenther, C. Greon, T. Pierce, B. Lamb, P. Harley, R. Fall, Atmos. Environ. 34 (12–14) (2000) 2205.

[4] C. Geron, S. Owen, A. Guenther, J. Greenberg, R. Rasmussen, J.H. Baie, Q.-J. Li, B. Baker, Atmos. Environ. 40 (2006) 1759.

[5] S. Moukhtar, C. Couret, L. Rouil, V. Simon, Sci. Total Environ. 354 (2006) 232.

[6] K.M. Cooke, S. Hassoun, S.M. Saunders, M.J. Pilling, Chemosphere 3 (2001) 249.

[7] C. He, F. Murray, T. Lyons, Atmos. Environ. 34 (4) (2000) 645.

[8] R. Atkinson, Atmos. Environ. 34 (12) (2000) 2063.

[9] R. Atkinson, J. Arey, Chem. Rev. 103 (12) (2003) 4605.

[10] R. Holzinger, D.B. Millet, B. Williams, A. Lee, N. Kreisberg, S.V. Hering, J. Jimenez, J.D. Allan, D.R. Worsnop, A.H. Goldstein, J. Geophys. Res. 112 (2007) D10s24, doi:10.1029/2006JD007599.

[11] S.M. Saunders, S. Pascoe, A.P. Johnson, M.J. Pilling, M.E. Jenkin, Atmos. Enviorn. 37 (2003) 1723.

[12] P.J. Crutzen, M.O. Andreae, Science 250 (4988) (1990) 1669.

[13] K.C. Ryan, Environ. Int. 17 (1991) 169.

[14] G. Helas, Phil. Trans. R. Soc. Lond. A 351 (1995) 297.

[15] R. Holzinger, C. Warneke, A. Hansel, A. Jordan, W. Lindinger, D.H. Scharffe, G. Schade, P.J. Crutzen, Geophys. Res. Lett. 26 (8) (1999) 1161.

[16] T. Novakov, M.O. Andreae, E. Gabriel, T.W. Kirchstetter, O.L. Mayol-Bracero, V. Ramanthan, Geophys. Res. Lett. 27 (24) (2000) 4061.

[17] V. Ramanathan, P.J. Crutzen, J.T. Kiehl, D. Rosenfeld, Science 294 (5549) (2001) 2119.

[18] M.L. Roderick, G.D. Farquhar, Science 298 (5597) (2002) 1410.

[19] I.A. Podgorny, F. Li, V. Ramanathan, Geophys. Res. Lett. 30 (1) (2003) 1028, doi:10.1029/2002GL015979.

[20] A.H. Goldstein, I.E. Galbally, Environ. Sci. Technol. 41 (5) (2007) 1514.

[21] D.J. Freeman, F.C.R. Cattell, Environ. Sci. Technol. 24 (1990) 1581.

[22] N.E. Clinton, P. Gong, K. Scott, Atmos. Environ. 40 (2006) 3686.

[23] P.M. Lemieux, C.C. Lutes, D.A. Santoianni, Energy Combust. Sci. 30 (2004) 1.

[24] S.D. Maleknia, T.L. Bell, M.A. Adams, Int. J. Mass Spectrom. 262 (2007) 203.

[25] A. Hansel, A. Jordan, R. Holzinger, P. Prazeller, P.W. Vogel, W. Lindinger, Int. J. Mass Spectrom. Ion Proc. 149–150 (1995) 609.

[26] W. Lindinger, A. Hansel, A. Jordan, Int. J. Mass Spectrom. Ion Proc. 173 (1998) 191.

[27] R.B. Cody, J.A. Laramee, H.D. Durst, Anal. Chem. 77 (8) (2005) 2297.

[28] C. Ammann, C. Spirig, A. Neftel, M. Steinbacher, M. Komenda, A. Schaub, Int. J. Mass Spectrom. 239 (2004) 87.

[29] A. Tani, S. Hayward, C.N. Hewitt, Int. J. Mass Spectrom. 223–224 (2003) 561.

[30] S. Hayward, A. Tani, S.M. Owen, C.N. Hewitt, Tree Phys. 24 (7) (2004) 721.

[31] C.N. Hewitt, S. Hayward, A. Tani, J. Environ. Monitor. 5 (1) (2003) 1.

[32] T.M. Ruuskanen, P. Kolari, J. Back, M. Kulmala, J. Rinne, H. Hakola, R. Taipale, M. Raivonen, N. Altimir, P. Hari, Boreal Environ. Res. 10 (6) (2005) 553.

[33] A. Lee, G.W. Schade, R. Holzinger, A.H. Goldstein, Atmos. Chem. Phys. 5 (2) (2005) 505.

[34] J. De Gouw, C. Warneke, Mass Spectrom. Rev. 26 (2007) 223.

[35] T.D. Sharkey, A.E. Wimberley, A.R. Donohue, Ann. Bot. (2007) 1.

[36] H. Tanimoto, N. Aoki, S. Inomata, J. Hirokawa, Y. Sadanaga, Int. J. Mass Spectrom. 263 (2007) 1.

[37] R. Fall, T. Karl, A. Jordan, W. Lindinger, Atmos. Environ. 35 (22) (2001) 3905.

[38] P.J. Dunlop, C.M. Bignell, B. Hibbert, M.I.H. Brooker, Aust. J. Bot. 46 (6) (1988) 683.

[39] C.M. Bignell, P.J. Dunlop, J.J. Brophy, C.J.R. Fookes, Flav. Frag. J. 12 (3) (1997) 177.

[40] C.M. Bignell, P.J. Dunlop, J.J. Brophy, Flav. Frag. J. 12 (3) (1997) 185.

[41] D.R. Batish, H.R. Singh, N. Setia, S. Kaur, R.K. Kohli, Z. Naturforsch. 61c (2006) 465.

[42] D.J. Boland, J.J. Brophy, A.P.N. House (Eds.), Eucalyptus oils: Use, Chemistry, Distillation and Marketing, Inkata Press, Melbourne, 1991.

[43] C. Lindinger, P. Pollien, S. Ali, C. Yeretzian, I. Blank, T. Mark, Anal. Chem. 77 (2005) 4117.

[44] A.L. Sullivan, P.E. Ellis, I.K. Knight, Int. J. Wildland Fire 12 (2003) 101.

[45] J.P. Greenberg, H. Friedli, A.B. Guenther, D. Hanson, P. Harley, T. Karl, Atmos. Chem. Phys. 6 (1) (2006) 81.

[46] T.J. Christian, B. Kliess, R.J. Yokelson, R. Holzinger, P.J. Crutzen, W.M. Hao, B.H. Saharjo, D.E. Ward, J. Geophys. Res. 108 (D23) (2003) 4719.

[47] T.J. Christian, B. Kleiss, R.J. Yokelson, R. Holzinger, P.J. Crutzen, W.M. Hao, T. Shirai, D.R. Blake, J. Geophys. Res. 109 (D02311) (2004) 1.

[48] T.G. Karl, T.J. Christian, R.J. Yokelson, P. Artaxo, W.M. Hao, A. Guenther, Atmos. Chem. Phys. 7 (22) (2007) 5883.

[49] R.J. Evans, T.A. Milne, Energy Fuels 1 (1987) 123.

[50] A. Bhargava, B.Z. Dulgogorski, E.M. Kennedy, Fire Safety J. 37 (2002) 659.

[51] S. Saka, in: D.N.-S. Hon, N. Shiraishi (Eds.), Wood and Cellulose Chemistry, Marcel Dekker AG, Basal, Switzerland, 2001, p. 51.

[52] F. Font, M. Esperanza, A.N. Garcia, Chemosphere 52 (6) (2003) 1047.

[53] Z. Jin, T. Akiyama, B.Y. Chung, Y. Matsumoto, K. Liyama, S. Watanabe, Phytochemistry 64 (5) (2003) 1023.

[54] N.W. Tame, B.Z. Dulgogorski, E.M. Kennedy, Prog. Energy Combust. Sci. 33 (2007) 384.

[55] D.E.A. Butt, J. Anal. Appl. Pyrol. 76 (2006) 38.

[56] A.E. Mullick, J.M. McDonald, G. Melkonian, P. Talbot, K.E. Pinkerton, J.C. Rutledge, Am. J. Physiol. Heart Circ. Physiol. 283 (2002) H591.

[57] P. Prazeller, T. Karl, A. Jordan, R. Holzinger, A. Hansel, W. Lindinger, Int. J. Mass Spectrom. 178 (1998) L1.

[58] R. Addink, K. Olie, Environ. Sci. Technol. 29 (6) (1995) 1583.