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Biogenic emissions from *Citrus* species in California

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ABSTRACT

Biogenic Volatile Organic Compounds (BVOC) emitted from plants are the dominant source of reduced carbon chemicals to the atmosphere and are important precursors to the photochemical production of ozone and secondary organic aerosols. Considering the extensive land used for agriculture, cultivated *Citrus* plantations may play an important role in the chemistry of the atmosphere especially in regions such as the Central Valley of California. Moreover, the BVOC emissions from *Citrus* species have not been characterized in detail and more species-specific inputs for regional models of BVOC emissions are needed. In this study, we measured the physiological parameters and emissions of the most relevant BVOC (oxygenated compounds, monoterpenes, and sesquiterpenes) for four predominant *Citrus* species planted in California (*Citrus sinensis* var. 'Parent Navel', *Citrus limon* var. 'Meyer', *Citrus reticulata* var. 'W. Murcott' and 'Clementine'). We used two analytical techniques to measure a full range of BVOC emitted: Proton Transfer Reaction Mass Spectrometry (PTR-MS) and gas chromatography with mass spectrometry. Methanol, followed by acetone and acetaldehyde, were the dominant BVOC emitted from lemon and mandarin trees (basal emission rates up to 300 ng(C) $g(DW)^{-1}$ h^{-1}), while oxygenated monoterpenes, monoterpenes, and sesquiterpenes were the main BVOC emitted from orange trees (basal emission rates up to = 2500 ng(C) $g(DW)^{-1}$ h^{-1}). Light and temperature-dependent algorithms were better predictors of methanol, acetaldehyde, acetone, isoprene and monoterpenes for all the *Citrus* species. Whereas, temperature-dependent algorithms were better predictors of oxygenated monoterpenes, and sesquiterpenes. We observed that flowering increased emissions from orange trees by an order of magnitude with the bulk of BVOC emissions being comprised of monoterpenes, sesquiterpenes, and oxygenated monoterpenes. Chemical speciation of BVOC emissions show that the various classes of terpene emissions among all *Citrus* species are dominated by ocimenes, β-caryophyllene, and linalool, respectively. In addition to utilizing our reported emission factors in BVOC emission models, we recommend that future BVOC emission models consider additional emissions from flowering and harvest, which occur seasonally and may have a significant impact on regional atmospheric chemistry.

1. Introduction

Plants emit biogenic volatile organic compounds (BVOC) to the atmosphere at an estimated global rate of 1–1.5 Pg C yr^{-1} (Guenther et al., 1995). These emissions account for 2–3% of the total carbon exchange between biota and the atmosphere (Crutzen et al., 1999; Kesselmeier and Staudt, 1999). In the presence of sunlight and nitrogen oxides (NO_x), the oxidation of BVOC leads to tropospheric ozone formation (Chameides et al., 1988; Papiez et al., 2009), a greenhouse gas with detrimental effects on plant carbon assimilation and growth (Guderian et al., 1985), as well as human health (for a reference list, see EPA, 2009). BVOC are also precursors to atmospheric aerosol (Kanakidou et al., 2005; Henze and Seinfeld, 2006), accounting for a significant fraction of secondary organic aerosol (SOA) produced in the atmosphere (Goldstein and Galbally, 2007).

Leaves are the main sources of BVOC emission into the atmosphere (Guenther et al., 1995). Because of the role of BVOC emission in ozone and aerosol atmospheric chemistry, modeling efforts have

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been done to characterize BVOC emissions on a regional and global basis (Lamb et al., 1993; Benjamin et al., 1997; Guenther et al., 1995, 2006). These models can predict emissions of a range of BVOC, including those in this study, parameterized by integrating environmental data, plant distribution, biomass density, using emission algorithms which incorporate the basal emission factor (BEF) of the modeled species while accounting for either the light and temperature dependence (Monson et al., 1992; Niinemets et al., 2004), or just the temperature dependence (Tingey et al., 1980; Harley et al., 1996). BEF come from direct emission measurements performed at leaf, branch, or canopy scales using different sampling techniques, and they are defined at standardized conditions of 30 °C and 1000 μmol m^{-2} s^{-1} of photosynthetically active radiation (PAR). Robust compound-specific information on basal emission factors improves the accuracy of emission models since not all BVOC are emitted in the same way.

Isoprene emission, the dominant BVOC emitted to the atmosphere (Guenther et al., 1995) primarily responds to light and temperature because its formation pathway is primarily in the leaf chloroplast, strictly related to photosynthesis, and is released immediately after production (Lichtenthaler et al., 1997).

Monoterpenes are 10-carbon isoprenoids whose emissions are dependent on temperature and, in some cases, on light as well. Monoterpene emissions from many plants have been described as temperature-dependent because their emission is mainly the result of volatilization from storage organs (Kesselmeier and Staudt, 1999; Niinemets et al., 2004).

Sesquiterpenes are another important class of isoprenoids whose emissions depend primarily on temperature, but they are formed by a different biosynthetic pathway than isoprene and monoterpenes (for a review see Duhl et al., 2008). These hydrocarbons, containing 15 carbon atoms, have previously been considered to account for a small percentage of global BVOC emissions (Guenther et al., 1995), but recent results suggest their total emission rates are similar to monoterpenes (Ormeño et al., 2010). Sesquiterpene emissions are of great interest since they contribute to secondary organic aerosol even more than monoterpenes (Lee et al., 2006a,b; Ng et al., 2006).

Unlike emissions of isoprene and monoterpenes, which have been extensively studied, the main knowledge of oxygenated volatile organic compounds (in this paper described with the acronym OVOC) emissions only dates from the last decade (for a review, see Steiner and Goldstein, 2007; Koppmann and Wildt, 2007). Similarly to isoprenoids, OVOC can notably influence the oxidizing capacity and the ozone-forming potential of the atmosphere, while also increasing concentrations of HOx and peroxyacetyl nitrates, and possibly contributing to the formation of organic aerosol (Singh et al., 2001). Methanol is a biogenic volatile emitted by plants to the atmosphere in large quantities from the demethylation of pectins in cell walls (Obendorf, 1990) with global emissions estimated at 100–240 Tg yr^{-1} (Galbally and Kirstine, 2002; Jacob et al., 2005; Millet et al., 2008). Methanol emissions occur under phenological modification of leaf tissues during leaf expansion and senescence (Schade and Goldstein, 2002; Huve et al., 2007; Fall, 2003). Previous studies reported methanol emission in response to oxidative stress following cutting and during drying of grass (Karl et al., 2001) or following leaf wounding (Loreto et al., 2006).

Acetone is the most abundant ketone in the atmosphere (Koppmann and Wildt, 2007); global emissions are estimated at 95 Tg yr^{-1} (Jacob et al., 2002) with considerable sources in rural areas (Goldan et al., 1995; Riemer et al., 1998; Ciccioli et al., 1999).

This compound is emitted primarily from terrestrial ecosystems and oceans, but is also produced in the atmosphere in large amounts from oxidation of hydrocarbons of both anthropogenic and biogenic origin (Goldstein and Schade, 2000). While we know that biogenic acetone is released during senescence (de Gouw et al., 1999) and oxidative stress on plants (e.g. from ozone) (Cojocariu et al., 2005), the biosynthetic pathway of acetone formation in leaves still deserves more investigation.

Acetaldehyde is another OVOC that is directly emitted from oceanic and terrestrial sources, but is also a product of hydrocarbon oxidation in the atmosphere. An estimate of acetaldehyde emission was recently reported by Millet et al. (2009), with values which are similar to acetone. The emission of this OVOC from plants occurs mainly under anoxic conditions in roots (Kreuzwieser et al., 1999) and in leaves (Karl et al., 2002; Graus et al., 2004). It is also emitted by leaves in large quantities during and after abiotic stresses (Fall et al., 1999; Loreto et al., 2006), or after light to dark transitions (Karl et al., 2002).

The objectives of this study were (1) determine the branch-level BEF for each BVOC (including OVOC) emitted from *Citrus* species, and (2) test the performance of current algorithms to predict BVOC emission by comparing modeled vs observed measurements. We focused on four important *Citrus* varieties: orange (*Citrus sinensis* 'Parent Navel'), lemon (*Citrus limon* 'Meyer'), and mandarin (*Citrus reticulata* 'W. Murcott' and 'Clementine'). We chose these species and varieties because citrus cultivation often occurs close to polluted urban areas where urban emissions mix with agricultural emissions. This is the case in the Central Valley of California, a region with extensive agriculture and anthropogenic pollution from large nearby cities (e.g. Fresno, Bakersfield, and Sacramento) and regional agricultural activities, as well as inflow of pollution from populated coastal regions (e.g. the San Francisco Bay area).

2. Material and methods

2.1. Choice of Citrus species and experimental set-up

Experiments were carried out in 2008 from the last week of August to the first week of October in the Oxford Greenhouse at the University of California, Berkeley, USA. For the 4 *Citrus* species, a set of 10 individuals of the same genotype were ordered from a commercial nursery (Willits and Newcomb) and placed in the greenhouse in February to allow for adaptation to the environmental conditions of the greenhouse. Selected species were orange (*C. sinensis* var. 'Parent Navel' grafted on Volk rootstock), lemon (*C. limon* var. 'Meyer' on Volk rootstock), mandarins (*C. reticulata* var. 'W. Murcott' and 'Clementine', both on C-35 rootstock). All trees were 3 years old and potted in 19 L pots; they were irrigated daily and fertilized weekly (Peters Professional, general purpose fertilizer 20-20-20) to promote favorable growing conditions and avoid water stress interference. Temperatures in the greenhouse were controlled with nighttime values around 17 °C and mid-day values up to 31 °C. Plants were exposed to natural sun light which filtered through the glass roof of the greenhouse facility. Photosynthetically active radiation (PAR) ranged from 0 to 1400 μmol m^{-2} s^{-1}. Relative humidity was maintained in the range of 40–60%.

2.2. Enclosure systems to measure BVOC and photosynthetic parameters

Two identical dynamic branch enclosures were built to enable sampling BVOC emissions from two plants at a time (for a detailed experimental design see Fares et al., 2010). For each measurement we enclosed a single branch which contained 10–500 g of leaf fresh biomass, an amount large enough to ensure that BVOC concentration inside the system was sufficient to achieve an adequate signal/noise ratio during BVOC emission monitoring (Tholl et al., 2006; Ortega and Helmig, 2008). The cylindrical enclosure (volume 84 L) was made of a rigid Teflon frame and coated with transparent Teflon FEP film (0.025 mm thick, Richmond Air Craft products, Inc.)

allowing good illumination to leaves. This structure was made completely of Teflon to minimize reactions of BVOC on the chamber walls. The air flushed through the inlet of the enclosure was first purified using a zero air generator (Aadco mod. 737) to remove CO_2, hydrocarbons, and ozone. After purification, it was enriched with CO_2 from a pure cylinder connected to a mass-flow controller (MKS Instruments, Inc.) to simulate ambient CO_2 concentration of 380 ppm. The air flow at the enclosure inlet was maintained at 8.5 L min^{-1} using a mass-flow controller (MKS Instruments, Inc.). A short section of ¼ inch Teflon tubing leading to a shower-based Teflon ring with multiple holes allowed for a uniform distribution of the air flow inside the enclosure and facilitated air mixing. Under these conditions, we calculated an air retention time in the enclosure of ~10 min.

During plant enclosure, the stems were gently wrapped with the Teflon film to avoid mechanical damage as much as possible. In all cases, measurements started 24 h after plant enclosure to compensate for potential enclosure effects. The pure air flowed in continuously during the 2–3 days of measurements. Each enclosure was equipped with a radiation sensor (LICOR quantum sensor mod. Li-190), a relative humidity and temperature sensor (Omega engineering mod. HX93AV-RP1), and with a system of fine wire thermocouples touching the abaxial side of the leaves to measure their temperature (Omega Engineering, Precision Fine Wire thermocouples).

Measurements of photosynthetic parameters and BVOC were carried out by switching between the plant enclosure outflows every 15 min with a system of 2- and 3-way solenoid valves (TEQCOM Industries) controlled by a datalogger (Campbell Scientific, mod. CR10) that recorded data every minute. The first 3 min of each cycle were dedicated to the measurement of the zero air entering the enclosures. Fluxes were calculated using the differential approach described by Fares et al. (2008). CO_2 and water exchanges were measured with a closed-path infrared gas analyzer (IRGA, LICOR mod. 6262) and enclosed leaf area was measured with a leaf area meter (LICOR mod. 3100C). The nocturnal CO_2 exchange was used to determine respiration rates. After BVOC sampling, enclosed leaves were dried by lyophilization and weighed in order to express BVOC emission rates on a dry mass basis.

2.3. PTR-MS system

A PTR-MS was used for on-line measurements of BVOC. For a detailed description of the instrument see Lindinger et al. (1998) or de Gouw and Warneke (2007). The instrument sampled from the main sampling line at 0.4 L min^{-1} and was optimized to an E/N ratio of 128 Td using a drift tube pressure, temperature, and voltage of 2.02 hPa, 45 °C, and 600 V, respectively. The reaction time was 100 μs and the count rate of $H_3O^+H_2O$ ions was less than 3% of the count rate of H_3O^+ ions, which was $\sim 5 \times 10^6$ counts s^{-1}. BVOC fluxes were calculated with a differential approach from fast concentration measurements in multiple ion detection mode, including the following compounds with a dwell time of 1 s each: methanol (mass to charge ratio (m/z) 33), acetaldehyde (m/z 45), acetone (m/z 59), isoprene (m/z 69), monoterpenes (m/z 81 and 137), and products of lipoxygenation (3-Z-hexenol, 2-E-hexenal, 3-Z-hexenal, 2-E-hexenol at m/z 93, 97, 99, 101, respectively). Each measurement cycle was repeated for an 11 min measuring time. The instrumental background was measured by directing the sample flow through a catalyst-based purifier for the first 3 min before starting the measurement of the sample air. The purifier consisted of a stainless steel tube filled with platinum-coated quartz wool (Shimadzu) heated to 350 °C, which efficiently removed the VOC but not the water vapor from the sample. This is important because the background compounds may depend on the humidity of the sampled air.

Gravimetrically-prepared gas standard cylinders (Apel & Riemer) of pure nitrogen with small mixing ratios (4–5 ppm) of methanol, acetaldehyde, acetone, and a mixture of monoterpenes (α-pinene, D-limonene, Δ-3-carene) were automatically measured twice a day by diluting with purified air to obtain concentrations in the range of 10–50 ppb, which are similar to those expected in the plant enclosures. The count signal was then transformed to ppb after subtracting the averaged background levels and taking into account the measured sensitivities for each calibrated compound (i.e. counts ppb^{-1}, Davison et al., 2009). For oxygenated compound concentrations, we calculated normalized sensitivities (counts/concentration) based on calculated proton transfer reaction rate coefficients and the instrument specific transmission coefficient calculated from a transmission curve. This curve was determined at an array of masses from 33 to 219 m/z using our gas standards at concentrations of 50 ppb. Due to poor transmission coefficients of masses above m/z 150, we discarded measurements of masses above that molecular weight (e.g. oxygenated monoterpenes (m/z 155) and sesquiterpenes (m/z 205)). During measurements, markers of cell wall degeneration resulting from wounding effects (3-Z-hexenol, 2-E-hexenal, 3-Z-hexenal, 2-E-hexenol, m/z 93, 97, 99, 101) were detected in trace concentrations after inserting the branch in the enclosure. Therefore emission rates were only considered reliable after observing negligible emission of these markers (enclosure concentrations < 50 ppt, which is close to the instrumental detection limit); in most cases this was one day after the enclosure of the leaf material (data not shown).

2.4. GC/MS-FID system

In parallel with PTR-MS, hourly-resolved VOC concentrations and emissions were measured using an automated in-situ gas chromatograph (Agilent mod. 5890) equipped with both a mass-selective detector (Agilent mod. 5971) and a flame ionization detector (GC/MS-FID) (further details on this instrument can be found in Millet et al., 2005). The instrument pre-concentrated ~600 mL of the enclosure effluent onto two separate adsorbent traps over a 30 min period and thermally-desorbed them onto capillary columns; the FID-analyzed sample was collected on a glass bead/Carbopak B/Carboxen 1000 adsorbent mix and injected onto a DB-624 column, while the MSD-analyzed sample was collected on Tenax-TA, then injected onto a Rtx-5 column. Calibrations were performed using gas-phase monoterpene standards and liquid standards for more reactive compounds (e.g. sesquiterpenes and unstable monoterpenes).

We report emissions of monoterpenes, sesquiterpenes, and oxygenated monoterpenes using this instrumentation. A comparison of isoprene and monoterpenes measured using both the GC/MS-FID and the PTR-MS systems shows agreement within 20% ($r = 0.97$, PTR-MS Flux = 0.81 × GC/MS-FID Flux) calculated using a trust-region Levenberg–Marquardt least orthogonal distance regression method to account for uncertainties in both the measurements. Due to the poor transmission to the PTR-MS quadrupole, sesquiterpenes and oxygenated monoterpenes were consistently underestimated with PTR-MS (PTR-MS Flux = 0.20 × GC/MS-FID Flux). Thus, for these two classes of compounds, we solely considered emission values from GC/MS-FID.

2.5. Emission algorithms

Emissions of some BVOC species respond strongly to both light and temperature, while emission of other BVOC species are almost completely dependent on temperature only, therefore two different algorithms are typically applied to model emissions (Niinemets et al., 2004). In the first case, BVOC can be emitted after being synthesized in the leaves through an enzymatic control, which is dependent on

light and temperature. To test for dependencies on light and temperature, we modeled fluxes (E_{L+T}) using the algorithm proposed by Guenther et al. (1993) (hereafter called L + T algorithm):

$$E_{L+T} = \mathrm{BEF}\left[\frac{\alpha C_L \mathrm{PAR}}{\sqrt{1+\alpha^2 \mathrm{PAR}^2}}\right] \times \left[\frac{\exp\left(\frac{C_{T1}(T-T_S)}{RT_S T}\right)}{0.961+\exp\left(\frac{C_{T2}(T-T_M)}{RT_S T}\right)}\right] \quad (1)$$

where the empirical coefficients are α (0.0027), C_L (1.066), C_{T1} (95,000 J mol^{-1}), C_{T2} (230,000 J mol^{-1}) and T_M (314 K); R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the leaf temperature (K) and T_S is the leaf temperature at standard conditions (303 K) (Guenther et al., 1993; Guenther, 1997). Basal emission factors (BEF) were calculated for each species as an average of the data that met the following conditions: 1. Temperature = 30 ± 2 °C, 2. PAR > 800 μmol m^{-2} s^{-1}, negligible concentrations of lipoxygenation markers, and photosynthetic rates comparable to literature and never below 2 μmol m^{-2} s^{-1}.

A second emission mechanism assumes BVOC are synthesized and stored in specific pools inside the leaves and emitted to the atmosphere by volatilization. These diffusive processes are modeled assuming they depend only on temperature. Emissions of BVOC were modeled with the algorithm (E_T) proposed by Tingey et al. (1980) (hereafter called T algorithm):

$$E_T = \mathrm{BEF}\exp[\beta(T-T_s)] \quad (2)$$

Where β (K^{-1}) is a coefficient that represents the exponential dependence on temperature and was calculated inverting Eq. (2) and applying the measured BEF during the day.

Modeled fluxes were analyzed for linear correlation with measured observations, and the slope coefficient and R-square values (R^2) were calculated with a statistical program (Matlab v. R2010a) in

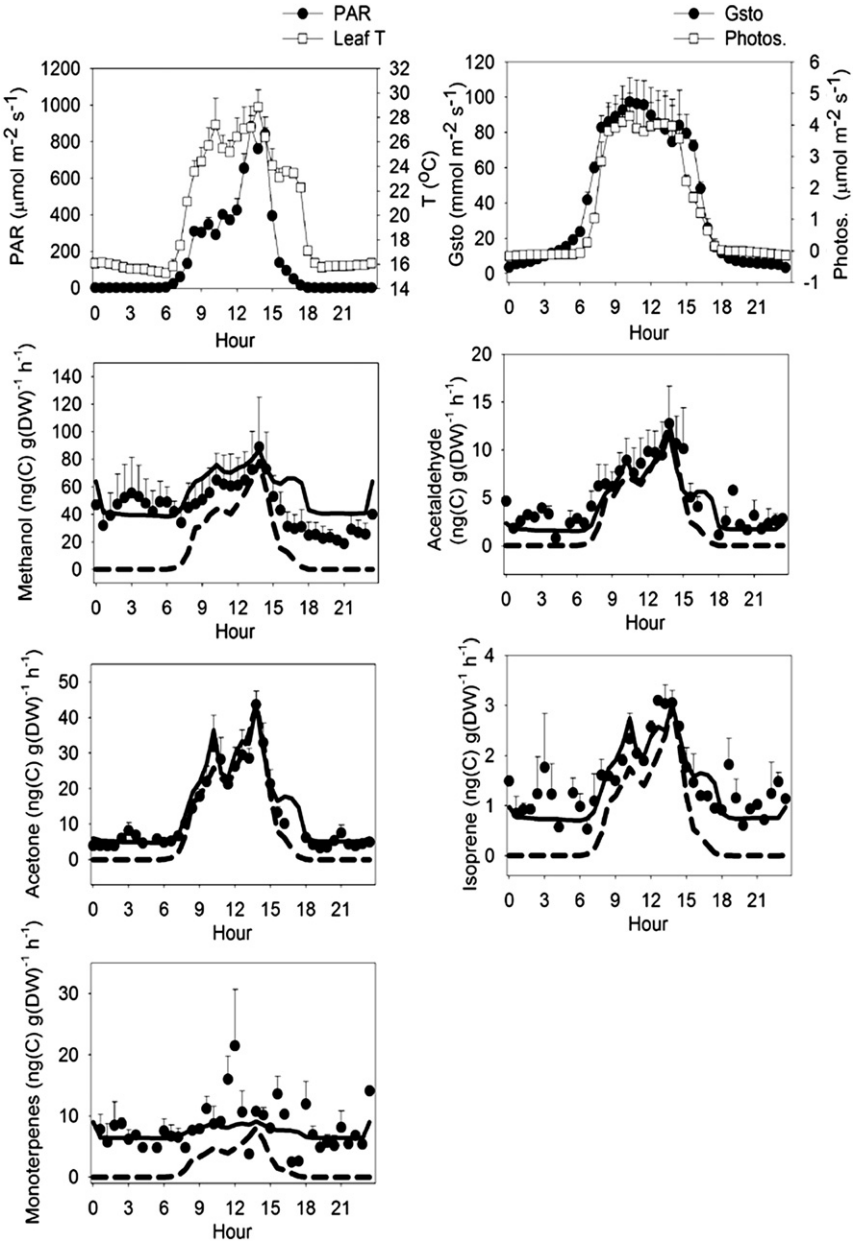

Fig. 1. Diurnal pattern of photosynthesis and stomatal conductance, and BVOC emission from Meyer lemon. Points (±std. error, $n = 4$) refer to measured emissions. Continuous lines refer to BVOC emission modeled with the T algorithm. Broken lines show BVOC modeled emission with the L + T algorithm.

order to estimate which modeled emissions better represent the actual BVOC emission from leaves.

3. Results and discussion

Our study is the first using PTR-MS to detect BVOC emission and BEF for *Citrus* species in California. We show the diurnal emission dynamics for all BVOC and physiological parameters, including photosynthesis and stomatal conductance (Figs. 1–4). Photosynthesis was only weakly correlation with all the BVOC groups we studied (data not shown), in particular during flowering, suggesting that photosynthesis cannot be considered a valid proxy for BVOC emission from citrus trees. Stomatal conductance was also not significantly correlated with BVOC emissions (data not shown). This result is in agreement with published observations that stomatal closure does not impede monoterpene emissions (Brilli et al., 2007). The lack of stomatal control over BVOC emission has been previously described by Niinemets et al. (2004), who showed that emission of some compounds like isoprenoids are less sensitive than other compounds (e.g. organic acids) to stomatal opening due to their partitioning to the gaseous phase and fast release into the atmosphere.

3.1. OVOC emissions: methanol

In lemon and mandarins, methanol was the oxygenated compound with the highest emissions (Fig. 1) and a BEF ranging from 140 to 300 ng(C) g(DW)$^{-1}$ h^{-1} for 'Meyer' lemon and 'Clementine'

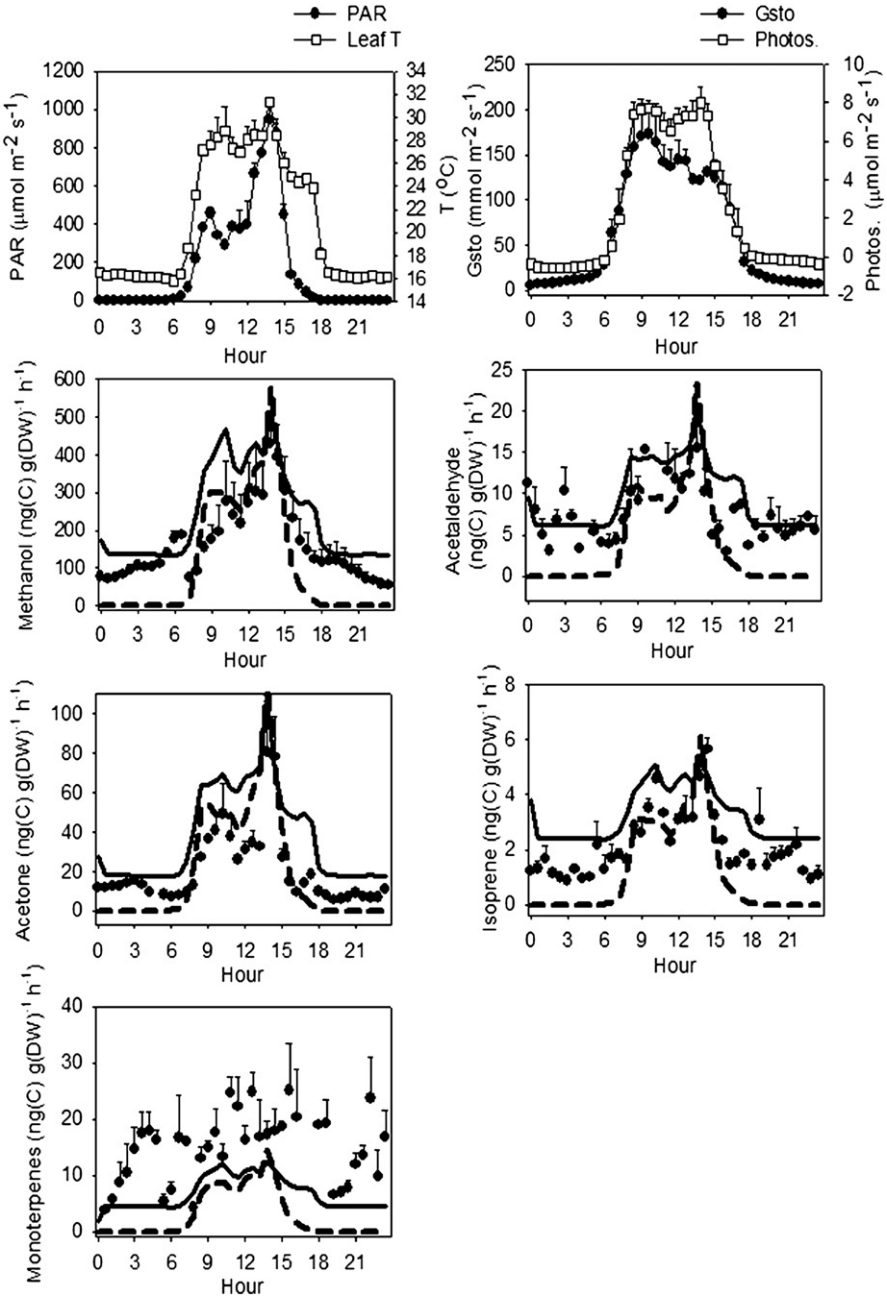

Fig. 2. Diurnal pattern of photosynthesis and stomatal conductance, and BVOC emission from Clementine mandarin. Points (±std. error, $n = 4$) refer to measured emissions. Continuous lines refer to BVOC emission modeled with the T algorithm. Broken lines show BVOC modeled emission with the L + T algorithm.

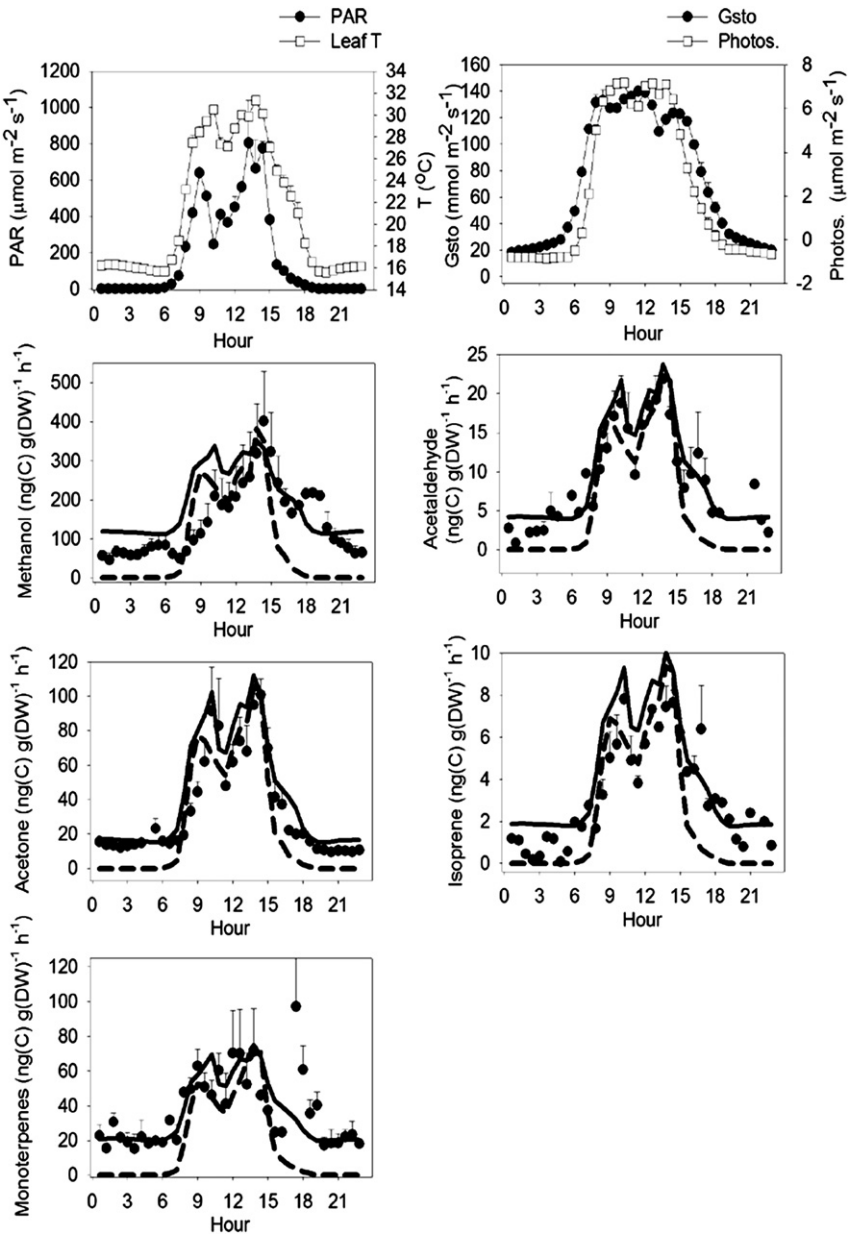

Fig. 3. Diurnal pattern of photosynthesis and stomatal conductance, and BVOC emission from A. Murcott mandarin. Points (±std. error, $n = 4$) refer to measured emissions. Continuous lines refer to BVOC emission modeled with the T algorithm. Broken lines show BVOC modeled emission with the L + T algorithm.

mandarin, respectively (Table 1). For oranges, the emission of methanol was even higher than the other *Citrus* species, but lower than isoprenoid emissions. Methanol is emitted as a result of pectin demethylation when cell walls elongate during leaf expansion (Fall and Benson, 1996; Galbally and Kirstine, 2002) and plant growth is recognized as the primary global source of methanol to the atmosphere (Galbally and Kirstine, 2002). We observed nocturnal methanol fluxes from many plants that were up to half of the daytime maximum observed values even though nighttime temperatures were only ~17–19 °C, consistent with emission during leaf expansion at night. In Table 2 we show how measured fluxes correlate with modeled fluxes using the T, and L + T algorithm. The drivers of methanol emission do not strictly depend on light, so we did not expect good correlation of measured fluxes of methanol with modeled fluxes using the L + T algorithm. Indeed, the low R^2 and slope values in our study suggest that the L + T algorithm is not a good predictor for methanol emissions from *Citrus* species (Table 2). This result is consistent with evidence that light-dependency of methanol emissions is purely dependent on the diffusive resistance of stomata (Huve et al., 2007), and not on the activation of a biosynthetic pathway as for isoprene and some monoterpenes (Lichtenthaler et al., 1997). This has been confirmed by Folkers et al. (2008), who demonstrated that only a limited fraction of methanol emissions is from re-emission of newly assimilated carbon, and recommended modeling of methanol emissions as a temperature-dependent process. However, temperature also was not well correlated with methanol emission in our study. We conclude that, in our study, neither of the proposed algorithms was a good predictor for methanol emissions. We suggest that to accurately model methanol emissions it is necessary to combine the current algorithms with more information on the phenological status of the plant, which affects tissue expansion, the primary source of methanol emission. Moreover, an

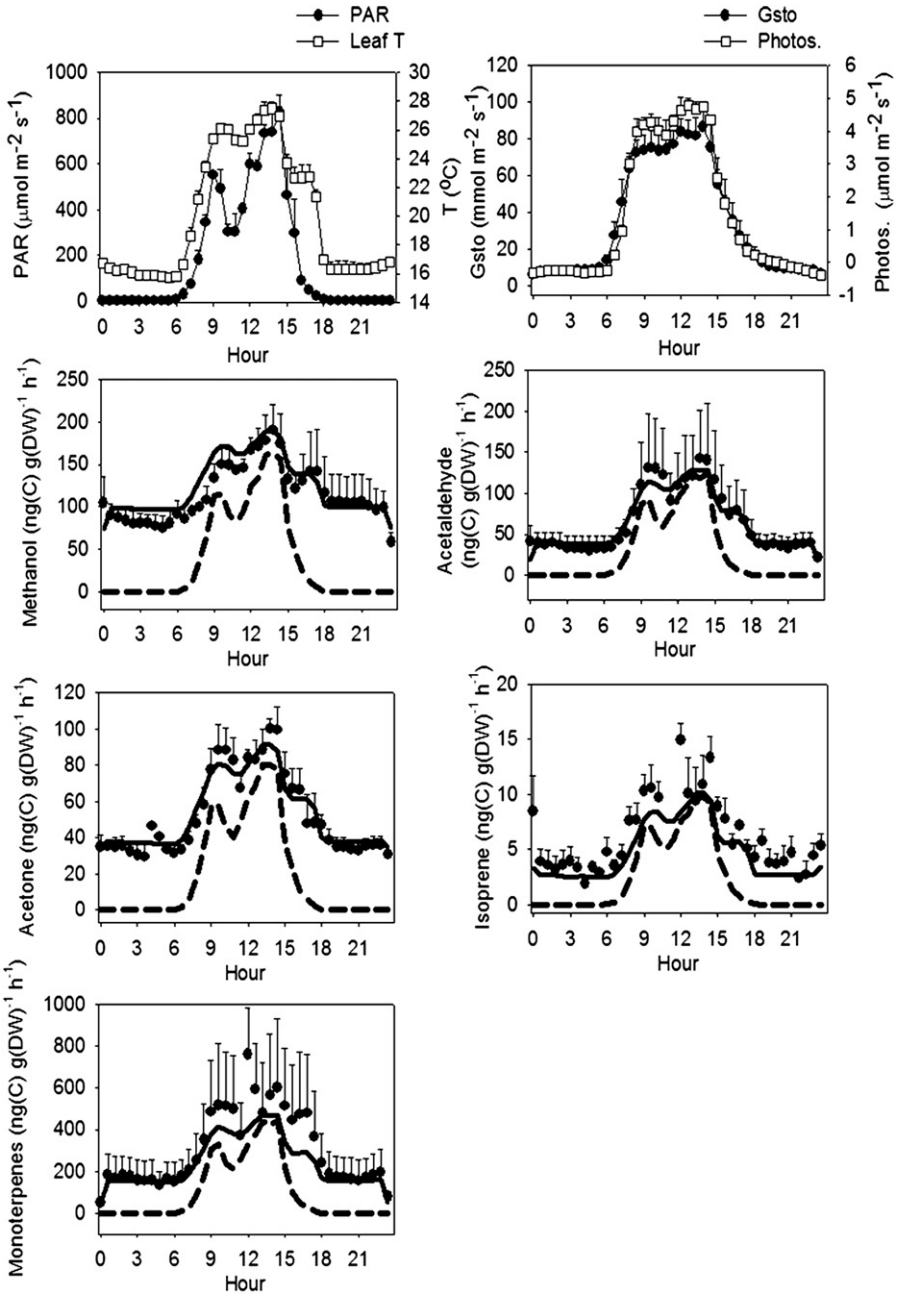

Fig. 4. Diurnal pattern of photosynthesis and stomatal conductance, and BVOC emission from Parent Navel orange. Points (±std. error, $n = 4$) refer to measured emissions. Continuous lines refer to BVOC emission modeled with the T algorithm. Broken lines show BVOC modeled emission with the L + T algorithm.

improved modeling approach should consider increases of methanol emission in response to oxidative stress imposed by cutting (Karl et al., 2001) or leaf wounding (Loreto et al., 2006).

3.2. OVOC emissions: acetaldehyde and acetone

Our study demonstrates direct biogenic emission of acetaldehyde and acetone from *Citrus*. Interestingly, past field studies of citrus (Ciccioli et al., 1999; Smith et al., 1996) attributed emissions of acetaldehyde and acetone to atmospheric oxidation processes (e.g. photooxidation of linalool) because no detectable emission was observed from branch enclosures. Given the low retention time in our enclosures (~10 min) and the limited presence of reactive oxidants (OH, ozone), we exclude gas-phase reaction as the production source in the enclosure, and thus associate fluxes of acetone and acetaldehyde with direct plant emissions. We recognize that additional gas-phase chemistry in the ambient atmosphere may enhance the apparent emission of both compounds during field studies.

Acetaldehyde was emitted in considerable amounts, especially from navel orange when flowering (BEF = 1700 ng(C) g(DW) $^{-1}$ h^{-1}), while lemon and mandarins emitted at minimal rates (BEF ~ 20 ng(C) g(DW) $^{-1}$ h^{-1}) (Table 1). Acetaldehyde emission from leaves has been described as a product of catabolism and observed in large quantities during and after abiotic stresses (Fall et al., 1999; Loreto et al., 2006), or after light to dark transitions (Karl et al., 2002; Graus et al., 2004). In general, emissions are better represented by the L + T algorithm, with slopes closer to 1 in all *Citrus* species, with the exception of 'Clementine' mandarin, where no significant correlation was found (Table 2). This suggests that light is

Table 1
Photosynthesis (mg(C) g(DW)$^{-1}$ h^{-1}) and BVOC basal emission factors (ng(C) g(DW)$^{-1}$ h^{-1}) of *Citrus* species. The β value calculated from the Tingey (T) algorithm is reported below each BVOC species. Data ± standard errors refer to basal conditions of Temperature = 30 ± 2 °C and Photosynthetically Active Radiation (PAR) > 800 μmol m^{-2} s^{-1} extrapolated from the observations (note that temperatures rarely reached 30 °C in the greenhouse). PTR-MS was used to measure fluxes of methanol, acetaldehyde, acetone, isoprene, monoterpenes. GC/MS-FID was used to measure fluxes of sesquiterpenes and oxygenated monoterpenes. $N = 4$ for all tree species for PTR-MS measurement except flowering Navel orange and mandarins ($N = 2$). $N = 4$ for Navel orange measured with GC/MS-FID. n.d. = not detected; n.a. = GC/MS-FID measurements not available.

Species	'Meyer' lemon	'Clementine' mandarin	'W. Murcott' mandarin	'Parent Navel' orange (no flowers)	'Parent Navel' orange (with flowers)
Photosynthesis	1.65 ± 0.50	3.93 ± 0.63	2.42 ± 0.01	2.04 ± 0.11	0.61 ± 0.02
Methanol	140 ± 30	300 ± 80	190 ± 65	480 ± 200	880 ± 140
β	0.046 ± 0.006	0.087 ± 0.030	0.064 ± 0.018	0.059 ± 0.011	0.059 ± 0.004
Acetaldehyde	18 ± 4.5	23.3 ± 10.8	16 ± 3.5	650 ± 415	1700 ± 550
β	0.13 ± 0.013	0.068 ± 0.008	0.11 ± 0.015	0.13 ± 0.007	0.15 ± 0.007
Acetone	50 ± 7.15	54 ± 18	69.4 ± 20.5	240 ± 90	500 ± 65
β	0.159 ± 0.004	0.116 ± 0.001	0.127 ± 0.004	0.078 ± 0.009	0.12 ± 0.001
Isoprene	3.16 ± 0.05	4.72 ± 0.05	8.4 ± 0.84	13.22 ± 1.90	45.32 ± 23.62
β	0.106 ± 0.002	0.062 ± 0.046	0.113 ± 0.016	0.123 ± 0.007	0.173 ± 0.002
Monoterpenes	22 ± 9	26 ± 7.4	63 ± 12.5	2500 ± 1700	7800 ± 2150
β	0.03 ± 0.020	0.064 ± 0.009	0.084 ± 0.015	0.14 ± 0.016	0.15 ± 0.014
Oxy. MT	n.a.	n.d.	150 ± 95	1300 ± 950	4600 ± 650
β	n.a.	n.d.	0.23 ± 0.040	0.18 ± 0.070	0.072 ± 0.040
Sesquiterpenes	n.a.	n.d.	n.d.	1500 ± 485	3200 ± 274
β	n.a.	n.d.	n.d.	0.40 ± 0.070	0.28 ± 0.030

related to those catabolic processes responsible for acetaldehyde release, although we cannot provide a detailed explanation for the specific pathway which is triggered by light and leads to acetaldehyde emission.

Acetone was also emitted from leaves, with the highest emission observed from oranges, with BEF > 200 ng(C) g(DW)$^{-1}$ h^{-1}. There is still a lot of uncertainty about the biogenic sources of acetone, but a previous study showed that that acetone is released from leaves during senescence (de Gouw et al., 1999). Another study showed an increase in acetone release after and oxidative stress generated by ozone exposure (Cojocariu et al., 2005), thus suggesting that emission of acetone is not only correlated with temperature and light, when these environmental factors are present that can trigger oxidative stress (e.g. heat stress, photooxidation). In our study, acetone emissions seemed to be better represented by the T algorithm for lemon and mandarins (i.e. slopes closer to 1 or better R^2), while for oranges, acetone emissions correlated similarly with both algorithms; thus, such correlations do not allow us to make a strong recommendation regarding which algorithm better represents acetone emissions to the atmosphere for all species studied.

3.3. Isoprenoid emission: monoterpenes

Orange had the highest levels of monoterpene emissions (BEF = 2500 ng(C) g(DW)$^{-1}$ h^{-1}, Table 1, Fig. 6). Clementine mandarin had twice the rate of photosynthesis of navel orange, but lower emission of BVOC. Lemon and mandarins emitted a low, if not negligible, amount of total monoterpenes (22, 26, and 63 ng(C) g(DW)$^{-1}$ h^{-1} for lemon, 'Clementine' mandarin, and 'W. Murcott' mandarin, respectively) (Table 1). For mandarins, the most abundant monoterpene species were β-cis and β-trans isomers of ocimene with minor amounts of limonene, sabinene, and pinene. For all species, the diurnal pattern of monoterpene emission (Figs. 1–4) was similar to that found by Ciccioli et al. (1999) for *Citrus* species, with peaks during the central hours of the day under the highest levels of light and temperature, and photosynthetic values for mid-day peaks between 4 and 7 μmol m^{-2} s^{-1}.

BEF values reported in this study are mostly within the same order of magnitude as those found in previous research. In a study performed with GC/MS, Winer et al. (1992) reported a leaf emission rate for navel orange of 900 ng(C) g(DW)$^{-1}$ h^{-1} at 21 °C, similar to what we observed in our study if we normalize this value for basal conditions. Winer et al. also reported emissions for lemon var. 'Lisbon' at 31 °C of 3600 ng g(DW)$^{-1}$ h^{-1}, which is much higher than our observations, but the difference may be attributed to genotypic and phenotypic dissimilarities. Ciccioli et al. (1999) performed field measurements using a branch enclosure and GC/MS measurement techniques; they recorded emission rates from a Valencia orange on the same order of magnitude as values presented in this study.

The correlations between measured and modeled BVOC emissions were highly significant for 'Parent Navel' orange ($p < 0.001$), both when emissions were modeled using the L + T algorithm ($R^2 = 0.57$) and the T algorithm ($R^2 = 0.63$, Table 2); correlation slopes were also similar (0.64 vs 0.61). The possibility that some of the BVOC compounds (e.g. those stored in secretory structures) are more temperature-dependent, and other are more light dependent (e.g. those originated from *de novo* synthesis) seems the most likely explanation, as previously reported in Simon et al. (2005). This different sensitivity to light and temperature can be explained by

Table 2
R-square (R^2) coefficients of the linear correlation between measured and modeled fluxes of *Citrus* species cultivated in California. The left member shows correlation with L + T modeled fluxes, while the right member shows correlation with fluxes according to the T algorithm. In parenthesis is the slope of each of the linear correlation between modeled and measured values. n.s. = non significant values ($p > 0.05$).

Species	'Meyer' lemon	'Clementine' mandarin	'W. Murcott' mandarin	'Parent Navel' orange (no flowers)	'Parent Navel' orange (with flowers)
Methanol	0.11 (1.41)–n.s.	0.50 (0.59)–0.53 (0.51)	0.31 (0.33)–0.32 (0.30)	0.19 (0.50)–0.40 (0.51)	0.19 (1.21)–0.16 (0.60)
Acetaldehyde	0.24 (0.86)–0.18 (0.65)	n.s.–0.11 (0.17)	0.42 (0.65)–0.54 (0.65)	0.50 (0.79)–0.53 (0.61)	0.54 (0.81)–0.53 (0.58)
Acetone	0.87 (0.99)–0.90 (1.03)	0.63 (0.66)–0.60 (0.60)	0.59 (0.61)–0.67 (0.63)	0.62 (0.97)–0.73 (0.81)	0.74 (1.04)–0.74 (0.77)
Isoprene	0.35 (0.53)–0.34 (0.45)	0.44 (0.98)–0.45 (0.73)	0.53 (0.85)–0.61 (0.80)	n.s.–n.s.	0.58 (1.28)–0.62 (0.91)
Σ Monoterpenes	n.s.–n.s.	n.s.–n.s.	n.s.–n.s.	0.57 (0.64)–0.63 (0.61)	0.60 (0.78)–0.61 (0.58)
Σ Oxy. Monot.	n.s.–n.s.	n.s.–n.s.	n.s.–n.s.	0.44 (0.84)–0.68 (0.87)	0.43 (1.37)–0.37 (0.74)
Σ Sesquiterpenes	n.s.–n.s.	n.s.–n.s.	n.s.–n.s.	0.88 (2.14)–0.80 (1.17)	0.92 (2.13)–0.89 (1.11)

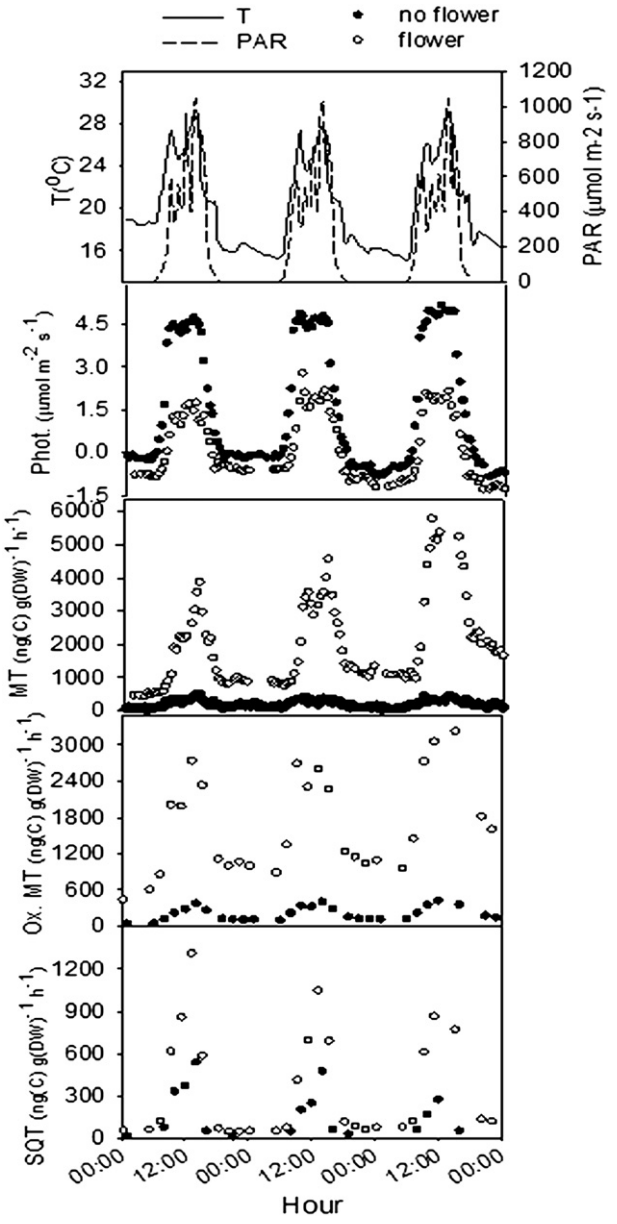

Fig. 5. For three days of continuous measurements on Parent Navel orange plants in June we report (from the top): environmental parameters (Temperature and PAR), photosynthesis, and emissions of monoterpenes (MT), oxygenated monoterpenes (Ox. MT) and sesquiterpenes (SQT) of a flowering (open circles) and a non-flowering (closed circles) individual.

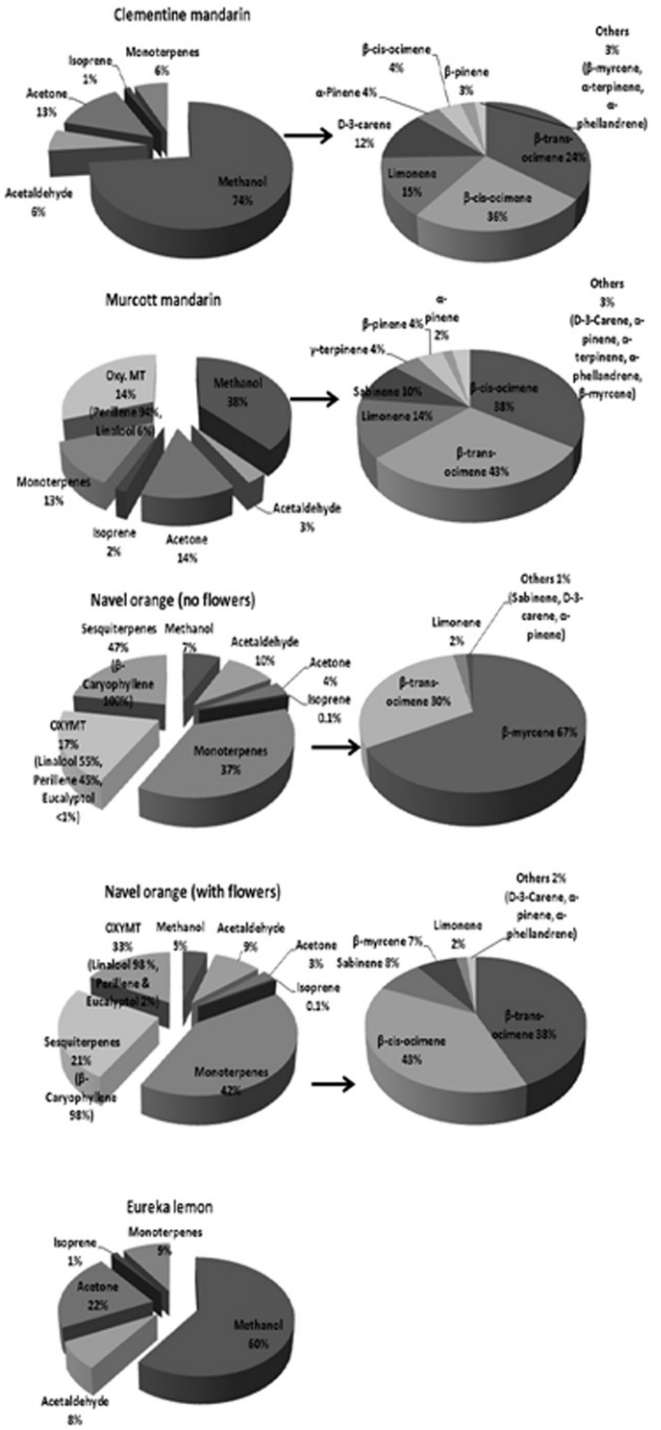

Fig. 6. Pie chart showing the percentage of each BVOC species emitted from the 4 *Citrus* species investigated. The arrow indicates the percentage of each monoterpene species. Data are calculated from the basal emission factor, emission values are reported in Table 1.

different degrees of stomatal control over different classes of monoterpenes based on their different partitioning in the liquid and gas phase inside the leaves (Niinemets et al., 2004).

For modeling purposes, we also provide the β coefficient of the T algorithm for total monoterpenes from oranges. This value of 0.14 is similar to that reported by Ciccioli et al. (1999). Lemon and mandarins, which had negligible monoterpene emissions, had lower β coefficients than orange. Modeled and measured emissions of oxygenated monoterpenes from non-flowering orange leaves were not significantly correlated, probably because the emissions were very low. We observed emissions of perillene, a chemical in the furanoid class which has been previously observed in plant essential oils. The poor fit between measured and modeled emissions suggests that the T and L + T algorithms do not adequately represent the emission of these compounds.

3.4. Isoprenoid emission: sesquiterpenes

The sesquiterpene emission rates for orange trees found in this study are consistent with Hansen and Seufert (1999), who measured BVOC emissions with a branch enclosure and agree with our finding that β-caryophyllene is the main sesquiterpene emitted by navel orange. Nevertheless, Hansen and Seufert (2003) demonstrated that the L + T algorithm better represented the actual β-caryophyllene

emissions than the T algorithm, and suggested that light enhances volatilization of β-caryophyllene from storage pools by triggering oxidative process which lead to membrane degradation. Our results instead reveal that slopes are closer to 1 with the T algorithm than with L + T algorithm. This suggests that temperature is a more important environmental parameter controlling the emission of sesquiterpenes in orange plants as traditionally stated for an isoprenoid- storing species (Tingey et al., 1991).

The β coefficient for sesquiterpenes in oranges was 0.34 on average, twice the value adopted in recent literature calculated by combining all the recent information on existing plant functional types in which a temperature dependency has been described (Sakulyanontvittaya et al., 2008). Our value is however in agreement with previous estimates (Ciccioli et al., 1999) and justified by the higher vaporization energy required to transfer sesquiterpenes from the liquid to the gas phase, owing to their lower vapor pressure in comparison with monoterpenes.

3.5. Isoprenoid emission: isoprene

Isoprene is the most abundant non-oxygenated BVOC emitted on a global scale (Guenther et al., 2006). Its production and emission depend directly on photosynthetic metabolism since specific leaf reservoirs (as opposed to temporary pools in the intercellular-spaces) are never filled up with this compound. In our study, isoprene emissions were negligible in comparison with monoterpenes (Table 1), suggesting that *Citrus* species are not significant isoprene emitters and that the methyl-erythritol-phosphate biosynthetic pathway in the leaves (Hampel et al., 2005) produces mainly monoterpenes rather than isoprene in *Citrus* sp., especially in navel orange. Isoprene emissions correlated better with the L + T algorithm as would be expected based on its known production and emission mechanisms (Table 2, Fig. 4).

3.6. Emissions during flowering events

Flowering is an important phenomenon that occurs once per year in most of the *Citrus* plantations in California's Central Valley, with the largest production of flowers occurring during a 2-week event between late March and April. In Fig. 5 we show photosynthesis and emission dynamics over 3 days for 2 orange trees measured at the same time, one flowering and one without flowers. During flowering, net photosynthesis rates decreased more than 50%, Based on the analysis of gas exchange at night, we observed higher mitochondrial respiration activity in the flowering plants averaging 0.93 ± 0.04 μmol m^{-2} s^{-1} vs 0.3 ± 0.05 μmol m^{-2} s^{-1} in non-flowering plants, demonstrating that during the flowering processes *Citrus* spp. decreases its net carbon uptake. Flowers may represent a respiratory surface not included in the total leaf area, but the contribution of flowers to the total area was ~5%, therefore we considered the flower area negligible. Our results are consistent with a previous study in grapefruit which showed that net carbon uptake was decreased because flowering respiration was enhanced rather than photosynthesis being decreased (Bustan and Goldschmidt, 1998).

A decoupling between photosynthesis and BVOC emissions in flowering oranges was observed, mainly due to the role of flowers as strong BVOC emitters to the atmosphere. Emissions from plant species that have the ability to store BVOC, such as *Citrus*, mainly originate from the volatilization of BVOC accumulated within specific leaf reservoirs. Thus emissions should depend more on temperature than on plant physiology, but OVOC emission from flowering oranges was better predicted by the L + T algorithm, thus suggesting that light stimulates OVOC emissions by promoting a biosynthetic pathway unrelated to photosynthesis. We found that flowering dramatically increased emissions of monoterpenes from navel orange to 7800 ng(C) $g(DW)^{-1}$ h^{-1}, in agreement with previous studies (Ciccioli et al., 1999; Hansen and Seufert, 1999; Arey et al., 1991). Monoterpene species emitted from flowering and non-flowering branches were substantially different. For non-flowering plants, β-myrcene was the main monoterpene emitted (67%), followed by β-E-ocimene (Fig. 6). For flowering plants, 81% of the total monoterpene emissions were β-Z- and β-E-ocimene, a compound previously reported in emissions from flowering *Citrus* trees and known to attract pollinators (Dudareva and Pichersky, 2000). Linalool was the dominant oxygenated monoterpene observed from flowering plants (98%), in agreement with findings from Ciccioli et al. (1999) and Arey et al. (1991), and also consistent with the reported presence of linalool synthase in flowers (Pichersky et al., 1994). Interestingly, we identified perillene, representing 45% of the oxygenated monoterpene emissions from non-flowering plants. This is the first time this furanoid has been identified as an emission from *Citrus*. Volatile furanoids are very rarely found in plants. To our knowledge, Z- and E-linalool oxide and now perillene are the only furanoids found in plant BVOC emissions (Noe et al., 2006).

For flowering oranges, it is unclear whether the T or L + T algorithm best describes the emission of monoterpenes, a similar situation to that for non-flowering oranges. With regard to sesquiterpenes, β-caryophyllene was the main sesquiterpene emitted from flowering oranges and the T algorithm better predicted emissions of this compound rather than the L + T algorithm (slope of 1.11 vs 2.13). The T algorithm was also preferred for non-flowering oranges. This result is in agreement with current opinion that sesquiterpene emissions respond primarily to temperature rather than to light (Sakulyanontvittaya et al., 2008).

4. Conclusions

The aim of this study was to provide new data on the basal emission factors and the daily emission dynamic of dominant *Citrus* species cultivated in California which may also be applicable to citrus in other regions, especially those with Mediterranean climate.

We found that oxygenated VOC (methanol, acetaldehyde, and acetone) represented the dominant fraction of the total BVOC emission for mandarin and lemon. For orange, monoterpenes were the major BVOC emitted. Emissions of all compounds including OVOC, monoterpenes, sesquiterpenes and oxygenated monoterpenes were up to one order of magnitude higher during flowering.

It is important to include crop emissions in models of BVOC emissions at regional and global scales, and the predictive capabilities of the model depend on the correct parameterization of the species-specific emission potential. In this study, we provide BEFs for principal *Citrus* species and varieties, and report the observed temperature and light dependencies of emissions for each BVOC. Light and temperature-dependent algorithms were better predictors of methanol, acetaldehyde, acetone, isoprene and monoterpene emissions for all the *Citrus* species, while only temperature-dependent algorithms were better predictors for oxygenated monoterpene and sesquiterpene emissions. Our results will be useful in atmospheric chemistry models to estimate whether BVOC emitted from these crop species play a significant role in regional air quality, especially when *Citrus* plantations are close to urban and polluted areas as found in the Central Valley of California, where BVOC can combine with anthropogenic emissions to contribute to ozone and secondary aerosol production.

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References

Arey, J., Corchnoy, S.B., Atkinson, R., 1991. Emission of linalool from Valencia orange blossoms and its observation in ambient air. Atmos. Environ. 25, 1377–1381.

Benjamin, M.T., Sudol, M., Vorsatz, D., Winer, A.M., 1997. A spatially and temporally resolved biogenic hydrocarbon emissions inventory for the California South Coast Air Basin. Atmos. Environ. 31, 3087–3100.

Brilli, F., Barta, C., Fortunati, A., Lerdau, M., Loreto, F., Centritto, M., 2007. Response of isoprene emission and carbon metabolism to drought in white poplar saplings. New. Phytol. 175, 244–254.

Bustan, A., Goldschmidt, E.E., 1998. Estimating the cost of flowering in a grapefruit tree. Plant Cell Environ. 21, 217–224.

Chameides, W.L., Lindsay, R.W., Richardson, J., Kiang, C.S., 1988. The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. Science 241, 1473–1475.

Ciccioli, P., Brancaleoni, E., Frattoni, M., Di Palo, V., Valentini, R., Tirone, G., Seufert, G., Bertin, N., Hansen, U., Csik, O., Lenz, R., Sharma, M., 1999. Emission of reactive terpene compounds from orange orchards and their removal by within-canopy processes. J. Geophys. Res. 104, 8077–8094.

Cojocariu, C., Esher, P., Heinz-Haberle, K., Matyssek, R., Rennemberg, H., Kreuzwieser, J., 2005. The effect of ozone on the emission of carbonyls from leaves of adult *Fagus sylvatica*. Plant Cell Environ. 28, 603–611.

Crutzen, P.J., Fall, R., Galbally, I., Lindinger, W., 1999. Parameters for global ecosystems model. Nature 399, 535.

Davison, B., Taipale, R., Langford, B., Misztal, P., Fares, S., Matteucci, G., Loreto, F., Cape, J.N., Rinne, J., Hewitt, C.N., 2009. Concentrations and fluxes of volatile organic compounds above a Mediterranean macchia ecosystem in western Italy. Biogeosciences 6, 1655–1670.

De Gouw, J.A., Howard, C.J., Custer, T.J., Fall, R., 1999. Emissions of volatile organic compounds from cut grass and clover are enhanced during the drying process. Geophy. Res. Lett. 26 (7), 811–814.

de Gouw, J., Warneke, C., 2007. Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer reaction mass spectrometry. Mass Spectrom. Rev. 26, 223–257.

Dudareva, N., Pichersky, E., 2000. Biochemical and molecular aspects of floral scents. Plant Physiol. 122, 627–634.

Duhl, T.R., Helmig, D., Guenther, A., 2008. Sesquiterpene emissions from vegetation: a review. Biogeosciences 5, 761–777.

EPA, 2009. Reference List of Deleterious Effect of Ozone on Human Health. http://www.epa.gov/o3healthtraining/refsfigs.html#refs Last access on November 10, 2010.

Fall, R., Benson, A.A., 1996. Leaf methanol – the simplest natural product from plants. Trends Plant Sci. 1, 296–301.

Fall, R., Karl, T., Hansel, A., Jordan, A., Lindinger, W., 1999. Volatile organic compounds emitted after leaf wounding: on-line analysis by proton-transfer-reaction mass spectrometry. J. Geophys. Res. – Atmos. 104, 15963–15974.

Fall, R., 2003. Abundant oxygenates in the atmosphere: a biochemical perspective. Chem. Rev. 103, 4941–4951.

Fares, S., Loreto, F., Kleist, E., Wildt, J., 2008. Stomatal uptake and stomatal deposition of ozone in isoprene and monoterpene emitting plants. Plant Biol. 10, 44–54.

Fares, S., Park, J.H., Ormeno, E., Gentner, D.R., McKay, M., Loreto, F., Karlik, J., Goldstein, A.H., 2010. Ozone uptake by citrus trees exposed to a range of ozone concentrations. Atmos. Environ. 44, 3404–3412.

Folkers, A., Huve, K., Ammann, C., Dindorf, T., Kesselmeier, J., Kleist, E., Kuhn, U., Uerlings, R., Wildt, J., 2008. Methanol emissions from deciduous tree species: dependence on temperature and light intensity. Plant Biol. 10, 65–75.

Galbally, I.E., Kirstine, W., 2002. The production of methanol by flowering plants and the global cycle of methanol. J. Atmos. Chem. 43, 195–229.

Goldan, P.D., Kuster, W.C., Fehsenfeld, F.C., Montzka, S.A., 1995. Hydrocarbon measurements in the southeastern United States – the rural oxidants in the southern environment (ROSE) program 1990. J. Geophys. Res. 100, 25945–25963.

Goldstein, A.H., Schade, G.W., 2000. Quantifying biogenic and anthropogenic contributions to acetone mixing ratios in a rural environment. Atmos. Environ. 34, 4997–5006.

Goldstein, A.H., Galbally, I.E., 2007. Known and unexplored organic constituents in the earth's atmosphere. Environ. Sci. Technol. 41 (5), 1514–1521.

Graus, M., Schnitzler, J.P., Hansel, A., Cojocariu, C., Rennenberg, H., Wisthaler, A., Kreuzwieser, J., 2004. Transient release of oxygenated volatile organic compounds during light-dark transitions in Grey poplar leaves. Plant Physiol. 135 (4), 1967–1975.

Guenther, A., Zimmerman, P.R., Harley, P.C., Monson, R.K., Fall, R., 1993. Isoprene and monoterpene emission rate variability – model evaluations and sensitivity analyses. J. Geophys. Res. – Atmos. 98 (D7), 12609–12617.

Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P., 1995. A global model of natural volatile organic compounds emissions. J. Geophys. Res. 100, 8873–8892.

Guenther, A., 1997. Seasonal and spatial variations in natural volatile organic compound emissions. Ecol. Appl. 7, 34–45.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P.I., Geron, C., 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). Atmos. Chem. Phys. 6, 3181–3210.

Guderian, R., Tingey, D.T., Rabe, R., 1985. Effects of photochemical oxidants on plants. In: Guderian, R. (Ed.), Air Pollution by Photochemical Oxidants. Ecological Studies, vol. 52. Springer, Berlin-Heidelberg-New York, pp. 129–333.

Hansen, U., Seufert, G., 2003. Temperature and light dependence of β-caryophyllene emission rates. J. Geophys. Res. 108. doi:10.1029/2003JD003853 Art. No. 4801.

Hansen, U., Seufert, G., 1999. Terpenoid emission from *Citrus sinensis* (L.) OSBECK under drought stress. Phys. Chem. Earth B – Hydrol. Oceans Atmos. 24 (6), 681–687.

Hampel, D., Mosandl, A., Wust, M., 2005. Biosynthesis of mono- and sesquiterpenes in carrot roots and leaves (*Daucus carota* L.): metabolic cross talk of cytosolic mevalonate and plastidial methylerythritol phosphate pathways. Phytochemistry 66, 305–311.

Harley, P., Guenther, A., Zimmerman, P., 1996. Effects of light, temperature and canopy position on net photosynthesis and isoprene emission from sweetgum (*Liquidambar styraciflua*) leaves. Tree Physiol. 16 (1–2), 25–32.

Henze, D.K., Seinfeld, J.H., 2006. Global secondary organic aerosol from isoprene oxidation. Geophys. Res. Lett. 33, L09812. doi:10.1029/2006GL025976.

Huve, K., Christ, M., Kleist, E., Niinemets, U., Uerlings, R., Walter, A., Wildt, J., 2007. Simultaneous growth and emission measurements demonstrate an interactive control of methanol release by leaf expansion and stomata. J. Exp. Bot. 58 (7), 1783–1793.

Jacob, D.J., Field, B.D., Jin, E.M., Bey, I., Li, Q., Logan, J.A., Yantosca, R.M., Singh, H.B., 2002. Atmospheric budget of acetone. J. Geophys. Res. 107 (D10), 4100.

Jacob, D.J., Field, B.D., Li, Q., Blake, D.R., de Gouw, J., Warneke, C., Hansel, A., Wisthaler, A., Singh, H.B., Guenther, A., 2005. Global budget of methanol: constraints from atmospheric observations. J. Geophys. Res. 110 (D8), D08303.

Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G., Wilson, J., 2005. Organic aerosol and global climate modelling: a review. Atmos. Chem. Phys. 5, 1053–1123.

Karl, T., Guenther, A., Lindinger, C., Jordan, A., Fall, R., Lindinger, W., 2001. Eddy covariance measurements of oxygenated volatile organic compound fluxes from crop harvesting using a redesigned proton-transfer-reaction mass spectrometer. J. Geophys. Res. – Atmos. 106 (D20), 24157–24167.

Karl, T., Curtis, A.J., Rosenstiel, T.N., Monson, R.K., Fall, R., 2002. Transient releases of acetaldehyde from tree leaves-products of a pyruvate overflow mechanism? Plant Cell Environ 25, 1121–1131.

Kesselmeier, J., Staudt, M., 1999. Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology. J. Atmos. Chem. 33, 23–88.

Koppmann, R., Wildt, J., 2007. Oxygenated volatile organic compounds. Chapter 4. In: Koppmann, R. (Ed.), Volatile Organic Compounds in the Atmosphere. Blackwell Publishing Ltd, pp. 129–172.

Kreuzwieser, J., Scheerer, U., Rennenberg, H., 1999. Metabolic origin of acetaldehyde emitted by poplar (*Populus tremula* × *P. alba*) trees. J. Exp. Bot. 50, 757–765.

Lamb, B., Gay, D., Westberg, H., 1993. A biogenic hydrocarbon emission inventory for the USA using a simple forest canopy model. Atmos. Environ. 27 (11), 1673–1690.

Lee, A., Goldstein, A.H., Keywood, M.D., Gao, S., Varutbangkul, V., Bahreini, R., Ng, N.L., Flagan, R.C., Seinfeld, J.H., 2006a. Gas-phase products and secondary aerosol yields from the ozonolysis of ten different terpenes. J. Geophys. Res. 111, D07302. doi:10.1029/2005JD006437.

Lee, A., Goldstein, A.H., Kroll, J.H., Ng, N.L., Varutbangkul, V., Flagan, R., Seinfeld, J.H., 2006b. Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes. J. Geophys. Res. 111, D17305. doi:10.1029/2006JD007050.

Lichtenthaler, H.K., Schwendler, J., Disch, A., Rohmer, M., 1997. Biosynthesis of isoprenoids in higher plant chloroplasts proceeds via a mevalonate-independent pathway. FEBS Lett. 400, 271–274.

Lindinger, W., Hansel, A., Jordan, A., 1998. On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS). Medical applications, food control and environmental research. Int. J. Mass. Spectrom. Ion. Process. 173, 191–241.

Loreto, F., Barta, C., Brilli, F., Nogues, I., 2006. On the induction of volatile organic compound emissions by plants as consequence of wounding or fluctuations of light and temperature. Plant Cell Environ. 29, 1820–1828.

Millet, D.B., Donahue, N.M., Pandis, S.N., Polidori, A., Stanier, C.O., Turpin, B.J., Goldstein, A.H., 2005. Atmospheric volatile organic compound measurements during the Pittsburgh Air Quality Study: results, interpretation, and quantification of primary and secondary contributions. J. Geophys. Res. 110 (D7), D07S07.

Millet, D.B., Jacob, D.J., Custer, T.G., de Gouw, J.A., Goldstein, A.H., Karl, T., Singh, H.B., Sive, B.C., Talbott, R.W., Warneke, C., Williams, J., 2008. New constraints on terrestrial and oceanic sources of atmospheric methanol. Atmos. Chem. Phys. 8, 6887–6905.

Millet, D.B., Atlas, E.L., Blake, D.R., Blake, N.J., Diskin, G.S., Holloway, J.S., Hudman, R.C., Meinardi, S., Ryerson, T.B., Sachse, G.W., 2009. Halocarbon emissions from the United States and Mexico and their global warming potential. Environ. Sci. Technol. 43 (4), 1055–1060.

Monson, R.K., Jaeger, C., Adams, W., Driggers, E., Silver, G., Fall, R., 1992. Relationship among isoprene emission rate, photosynthesis and isoprene synthase activity as influenced by temperature. Plant Physiol. 92, 1175–1180.

Ng, N.L., Kroll, J.H., Keywood, M.D., Bahreini, R., Varutbangkul, V., Flagan, R.C., Seinfeld, J.H., Lee, A., Goldstein, A.H., 2006. Contribution of first- versus second-generation products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons. Environ. Sci. Technol. 40 (7), 2283–2297.

Niinemets, U., Loreto, F., Reichstein, M., 2004. Physiological and physico-chemical controls on foliar volatile organic compound emissions. Trends Plant Sci. 9, 180–186.

Noe, S.M., Ciccioli, P., Brancaleoni, E., Loreto, F., Niinemets, U., 2006. Emissions of monoterpenes linalool and ocimene respond differently to environmental changes due to differences in physico-chemical characteristics. Atmos. Environ. 40, 4649–4662.

Obendorf, R.L., 1990. Methanol accumulation in maturing seeds. J. Exp. Bot. 41, 489–495.

Ormeño, E., Gentner, D.R., Fares, S., Karlik, J., Park, J.H., Goldstein, A.H., 2010. Sesquiterpenoid emissions from agricultural crops: correlations to monoterpenoid emissions and leaf terpene content. Environ. Sci. Technol. 44, 3758–3764.

Ortega, J., Helmig, D., 2008. Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques – part A. Chemosphere 72, 343–364.

Papiez, M.R., Potosnak, M.J., Guenther, A.B., Matsunaga, S.N., Stockwell, W.R., 2009. The impacts of reactive terpene emissions from plants on air quality in Las Vegas, Nevada. Atmos. Environ. 43 (27), 4109–4123.

Pichersky, E., Raguso, R.A., Lewinsohn, E., Croteau, R., 1994. Floral scent production in Clarkia (Onagraceae), localization and developmental modulation of monoterpene emission and linalool synthase activity. Plant Physiol. 106, 1533–1540.

Riemer, D., Pos, W., Milne, P., Farmer, C., Zika, R., Apel, E., Olszyna, K., Kliendienst, T., Lonneman, W., Bertman, S., Shepson, P., Starn, T., 1998. Observations of non-methane hydrocarbons and oxygenated volatile organic compounds at a rural site in the southeastern United States. J. Geophys. Res. 103 (D12), 28111–28128.

Sakulyanontvittaya, T., Duhl, T., Wiedinmyer, C., Helmig, D., Matsunaga, S., Potosnak, M., Milford, J., Guenther, A., 2008. Monoterpene and sesquiterpene emission estimates for the United States. Environ. Sci. Technol. 42 (5), 1623–1629.

Schade, G.W., Goldstein, A.H., 2002. Plant physiological influences on the fluxes of oxygenated volatile organic compounds from ponderosa pine trees. J. Geophys. Res. 107 (D10), 4082.

Simon, V., Dumergues, L., Solignac, G., Torres, L., 2005. Biogenic emissions from *Pinus halepensis*: a typical species of the Mediterranean area. Atmos. Environ. 74, 37–48.

Singh, H., Chen, Y., Staudt, A., Jacob, D., Blake, D., Heikes, B., Snow, J., 2001. Evidence from the Pacific troposphere for large global sources of oxygenated organic compounds. Nature 410 (6832), 1078–1081.

Smith, A.M., Rigler, E., Kwok, E.S.C., Atkinson, R., 1996. Kinetics and products of the gas-phase reactions of 6-methyl-5-hepten-2-one and trans-cinnamaldehyde with OH and NO_3 radicals and O_3 at 296 $\pm$ 2 K. Environ. Sci. Technol. 30, 1781–1785.

Steiner, A., Goldstein, A.H., 2007. Biogenic volatile organic compounds. In: Koppmann, R. (Ed.), Volatile Organic Compounds in the Atmosphere. Blackwell Publishing Ltd.

Tingey, D., Manning, M., Grothaus, L., Burns, W., 1980. Influence of light and temperature on monoterpene emission rates from slash pine. Plant Physiol. 65, 797–801.

Tingey, D.T., Turner, D.P., Weber, L.C., 1991. Factors controlling the emission of monoterpenes and other volatile organic compounds. In: Sharkey, T.D., Holland, E.A., Mooney, H.A. (Eds.), Trace Gas Emissions by Plants, vol. 65. Academic, San Diego, California, pp. 797–801.

Tholl, D., Boland, W., Hansel, A., Loreto, F., Rose, U.S.R., Schnitzler, J.P., 2006. Practical approaches to plant volatile analysis. Plant J. 45, 540–560.

Winer, A., Arey, J., Atkinsons, R., Aschmann, S.M., Lomg, W.D., Morrison, L., Olszyk, D.M., 1992. Emission rates of organics from vegetation in California's Central Valley. Atmos. Environ. 26, 2647–2659.