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## Chemical sensing of plant stress at the ecosystem scale

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## Abstract

Significant ecosystem-scale emissions of methylsalicylate (MeSA), a semivolatile plant hormone thought to act as the mobile signal for systemic acquired resistance (SAR) (Park et al., 2006), were observed in an agroforest. Our measurements show that plant internal defence mechanisms can be activated in response to temperature stress and are modulated by water availability on large scales. Highest MeSA fluxes (up to 0.25 mg/m<sup>2</sup>/h) were observed after plants experienced ambient night-time temperatures of ~7.5°C followed by a large daytime temperature increase (e.g. up to 22°C). Under these conditions estimated night-time leaf temperatures were as low as ~4.6°C, likely inducing a response to prevent chilling injury (Ding et al., 2002). Our observations imply that plant hormones can be a significant component of ecosystem scale volatile organic compound (VOC) fluxes (e.g. as high as the total monoterpene (MT) flux) and therefore contribute to the missing VOC budget (de Carlo et al., 2004; Goldstein and Galbally, 2007). If generalized to other ecosystems and different types of stresses these findings suggest that semivolatile plant hormones have been overlooked by investigations of the impact of biogenic VOCs on aerosol formation events in forested regions (Kulmala et al., 2001; Boy et al., 2000). Our observations show that the presence of MeSA in canopy air serves as an early chemical warning signal indicating ecosystem-scale stresses before visible damage becomes apparent. As a chemical metric, ecosystem emission measurements of MeSA in ambient air could therefore support field studies investigating factors that adversely affect plant growth.

## 1 Introduction

Volatile organic compounds (VOCs) critically influence the composition of the Earth's atmosphere by fueling tropospheric chemistry (Atkinson, 2000), thereby modulating its oxidation capacity and providing condensable material for organic aerosol formation (Kanakidou et al., 2005). On a global scale the emission strength of biogenic

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VOCs ( $\sim 1000 \pm 600$  Tg/y) dominates the annual VOC budget, accounting for up to 90% of the reduced carbon flux entering the atmosphere (Guenther et al., 1995). In recent years indirect evidence was presented suggesting that substantial amounts of unknown VOCs are emitted from terrestrial plants (Carlo et al., 2004; Goldstein and Galbally, 2007), which are currently not included in comprehensive biogenic emission inventories (Kesselmeier and Staudt, 1999). Whether these biogenic VOC emissions are large enough to influence atmospheric chemistry in profound ways depends on the magnitude of their ecosystem scale fluxes as well as their physiochemical properties.

Here we report significant ecosystem-scale fluxes of the plant hormone MeSA above a walnut (*Paradox Hybrid*; *Juglans californica*  $\times$  *Juglans regia*) agroforest. MeSA is a biologically active compound thought to be one of the key airborne messenger molecules synthesized by plants in response to stress (e.g. Shulaev et al., 1997; Baldwin et al., 2006). MeSA has been shown to act as a mobile signal for systemic acquired resistance (SAR) by being converted to salicylic acid (SA) in plants (Park et al., 2006). SA is known to promote the expression of defence related genes in response to herbivores and pathogens (Li et al., 2002). While two major biochemical routes for immune responses (jasmonic acid and salicylic acid pathway) exist (e.g. Beckers and Speol, 2006), the methyl ester of SA (MeSA) presents the less soluble and more volatile form making it a suitable candidate for plant to plant communication through the air (rather than the phloem alone). In the past, laboratory experiments exposing plants to mixing ratios exceeding 60 ppbv (and ranging up to 40 ppmv) were used to study the ecological role of MeSA (Shulaev et al., 1999; Peñuelas et al., 2006). Because real ecosystems are challenged by a number of stresses that cannot realistically be reproduced in the laboratory, it is currently only assumed that the biochemical machinery that produces biologically active volatiles in laboratory experiments operates in similar ways in the real world. One of the big uncertainties to date in understanding the ecological importance of MeSA is the fact that typical emission rates and concentrations in the real canopy atmosphere in response to naturally occurring stresses are not known (Baldwin et al., 2006; Peñuelas et al., 2006). Here we report – to our knowledge – the first

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measurements of MeSA in ambient air and quantify ecosystem scale emissions in an agroforest.

## 2 Methods

### 2.1 Identification of MeSA using GC-MS

5 A field deployed Gas Chromatograph with Mass Spectrometer (GC-MS; HAPSITE Smart, INFICON, East Syracuse, NY) was used for in-situ identification of MeSA in ambient air within and above the walnut agroforest and in emission samples from walnut leaves. The GC-MS used a 30 m×0.32 mm ID, 1 μm SPB-1 column, temperature programmed with an initial hold of 2 min at 50°C followed by an increase to 80°C at 15 C min<sup>-1</sup> followed by an increase to 110°C at 3 C min<sup>-1</sup> and then to 200°C at 9 C min<sup>-1</sup>. Identification was confirmed by comparison of mass spectra in the NIST database and an authentic standard (SigmaUltra, Sigma Aldrich, CAS 119-36-8, Milwaukee, WI), shown in Fig. 1a, and by comparison of retention index with the authentic standard. Samples (~2 L) were pre-concentrated on an internal Tenax adsorbent concentrator (INFICON, East Syracuse, NY). An assessment of artifacts demonstrated that MeSA blank levels were negligible. No other compounds exhibiting a nominal molecular weight of MeSA (152 amu) were detected on GC-MS mass scans.

### 2.2 Proton-Transfer-Reaction Mass Spectrometer (PTR-MS)

20 A high sensitivity Proton-Transfer-Reaction Mass Spectrometer was used for gradient measurements of selected VOCs. The instrument is based on soft chemical ionization using protonated water ions (H<sub>3</sub>O<sup>+</sup>). It combines the advantage of online analysis while maintaining linearity and low detection limits (Ionicon, Austria) (Hansel et al., 1999). The detection limit for methyl salicylate and total monoterpenes for a 5 s integration time was 2 and 5 pptv respectively. The instrument was operated at 2.3 mbar drift pres-

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sure and 540 V drift voltage and calibrated using two multicomponent ppmv VOC standards: VOC standard 1 contained a mixture of methanol, acetonitrile, acetaldehyde, acetone, isoprene, methyl vinyl ketone, methyl ethyl ketone, benzene, toluene, m,o,p xylenes and camphene; VOC standard 2 contained a mixture of benzene, toluene, m,o,p xylenes + ethylbenzene, chlorobenzene, trimethylbenzenes, dichlorobenzenes and trichlorobenzenes. Ultrapure methyl salicylate (SigmaUltra, Sigma Aldrich, CAS 119-36-8, Milwaukee, WI) was injected into the instrument to determine the instrument specific response for this compound (Fig. 1b). The instrument sequentially sampled of six independent  $\frac{1}{4}$  inch Teflon (PFA) sampling lines mounted at 1.5, 4.5, 9, 11, 14 and 23 m on a 30 m tall Rohn Tower. A valve switching system changed sampling lines every 5 min. Gradients were calculated from the 5 min averages. High flow rates through the sampling lines resulted in delay times of less than 8–12 s, measured by spiking a VOC pulse at each sampling inlet.

### 2.3 Ozone measurements

Ozone concentrations were also measured via the 6-level sampling manifold by UV absorbance (2B Technologies, Model 205). Ozone concentrations were measured every 10 s and then averaged over the entire 5 min sampling time on each level, excluding only the first 15 s to insure adequate flushing of the connecting gas lines. The ozone analyzer was compared with laboratory instruments both prior to and following the experiment and found to agree with  $\pm 5\%$  with a detection limit of 2 ppbv. It was zeroed periodically by placing an ozone scrubber on the 1.5 m inlet and laboratory tests indicated no measurable loss of ozone within any of the PFA inlet lines.

### 2.4 The Canopy Horizontal Array Turbulence Study (CHATS) field site

The Canopy Horizontal Array Turbulence Study (CHATS) took place from March through June 2007, and is the third in the series of Horizontal Array Turbulence Study (HATS) experiments. The HATS experiments have been instrumental in testing and

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developing sub-filter-scale models for large-eddy simulations of planetary boundary layer turbulence. The CHATS campaign took place in a deciduous walnut orchard near Dixon, California (N 38° 29' 15", W 121° 50' 45"). CHATS included a thirty-meter tower instrumented with assorted turbulence instrumentation, fast and slow chemistry measurements, aerosol samplers, and radiation instrumentation. A high-resolution scanning backscatter LIDAR characterized the turbulence structure above and within the canopy; a scanning Doppler LIDAR, mini SODAR/RASS system, and a helicopter-observing platform provided details of the large-scale flow. Ultimately, the CHATS data set aims to improve parameterizations responsible for transporting energy and chemicals to and from vegetation which is a critical component of global and regional land, atmosphere, and chemical models. Complete details for CHATS are summarized by Patton (2008)<sup>1</sup> and can be found at <http://www.eol.ucar.edu/rtf/projects/CHATS/isff/>.

### 2.5 Flux calculation using an Inverse Lagrangian Transport Scheme

Ecosystemscale fluxes of VOCs were calculated based on concentration gradients throughout the canopy and applying an Inverse Lagrangian Transport Model (Raupach, 1986; Nemitz et al., 2000; Karl et al., 2004).

The VOC fluxes were computed according to,

$$\mathbf{C} - C_{\text{ref}} = \mathbf{D} \cdot \mathbf{S} \quad (1)$$

where  $\mathbf{C}$  is the VOC concentration ( $\mu\text{g}/\text{m}^3$ ) vector for each level,  $C_{\text{ref}}$  is the VOC concentration ( $\mu\text{g}/\text{m}^3$ ) at reference height (e.g. 14 m),  $\mathbf{D}$  (m) represents a dispersion matrix and  $\mathbf{S}$  ( $\text{mg}/\text{m}^2/\text{h}/\text{m}$ ) the resulting VOC source/sink vector.  $\mathbf{D}$  can be expressed as a function of Lagrangian timescale (TI) and profiles of the standard deviation of the vertical wind speed ( $\sigma_w$ ) divided by the friction velocity ( $u^*$ ). The calculation was performed using a  $10 \times 4$  dispersion matrix. Integration over all source and sink terms ( $S$ ) yields

<sup>1</sup>Patton, E. G.: The Canopy Horizontal Array Turbulence Study, B. Am. Meteorol. Soc., submitted, 2008.

the canopy scale VOC flux ( $\text{mg}/\text{m}^2/\text{h}$ ). Fluxes were calculated for 30 min intervals. The parameterization of **D** was based on turbulence measurements inside and above the canopy and calculated using the far- and near-field approach described by Raupach (1986). The Lagrangian timescale was parameterized according to Raupach (1986).

## 5 2.6 Canopy environment model estimates of leaf temperatures

Leaf temperatures of sun and shade leaves at each canopy depth were estimated using a canopy environment model (Guenther et al., 1995). This model calculates direct and diffuse, visible and near infrared solar radiation incident on sun and shade leaves at each canopy depth based on solar angle, above canopy solar radiation, canopy structure, and leaf characteristics. Wind speed, humidity and ambient temperature at each canopy depth are estimated using empirical functions. Leaf temperature is calculated using an energy balance approach that includes solar radiation, infrared radiation, convective heat flux, and latent heat flux terms. Daytime sun leaf temperature estimates can be several degrees warmer than ambient temperature due to increased solar radiation absorption, especially if water stress limits the ability of a leaf to cool by transpiration, while nighttime temperatures are several degrees cooler than ambient temperatures due to radiative losses of infrared energy.

## 2.7 Measurement of Henry's Law Constants (HLC)

HLC for Methylsalicylate (MeSA) and Methyljasmonate (MeJA) were measured using the single (Mackey et al., 1979) and double stripping cell configuration using PTRMS (Karl et al., 2003), where clean air (zero air) is introduced through a sintered glass disk into a stripping vessel, which contains distilled water and traces of MeSA and MeJA. On the way through the vessel the VOC reaches an equilibrium concentration in the air bubbles according to Henry's Law. Using a PTR-MS it can be shown that the HLC can be obtained from the declining countrate over time ( $cps(t)$ ) plotted as a ratio to the initial countrate ( $cps_0$ ) according to:  $\ln \frac{cps(t)}{cps_0} = -\frac{F}{HVRT}t$ , (Eq. 2) where  $F$  is the flowrate,

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$V$  is the water volume,  $R$  is the ideal gas law constant,  $T$  is the temperature and  $t$  is the time since start of the stripping experiment.

Here we obtain a HLC of  $33.5 \pm 4.0$  M/atm for MeSA and  $5018 \pm 1003$  M/atm for MeJA.

### 3 Results

5 We identified MeSA as a dominant reactive VOC constituent in ambient air based on mass spectral analysis using gas-chromatographic pre-separation (GC-MS). Canopy air concentrations were also measured using an online Proton-Transfer-Reaction Mass Spectrometer (PTR-MS) (Lindinger et al., 1998). Figure 2a, b depict the vertical mixing ratio gradients of MeSA throughout the canopy observed in a walnut orchard during the  
10 Canopy Horizontal Array Turbulence Study (CHATS) obtained by PTR-MS. We calculated the average daytime emission profile throughout the canopy for the period shown in Fig. 2a using an Inverse Lagrangian Transport (ILT) model (Fig. 2c). Peak emission rates occurred at the upper part of the canopy and coincided with the height at which night-time leaf temperatures reached a minimum (Fig. 2d). Figure 3 plots ambient  
15 air temperature, soil moisture and vapor pressure deficits (VPD) (Fig. 3a) along with MeSA and monoterpene (MT) mixing ratios (Fig. 3b), MT fluxes (Fig. 3c) and MeSA fluxes (Fig. 3d) observed during the study. Soil moisture was declining until JD146, when irrigation of the section of the plantation that was within the footprint of our measurements was started. It is noted that no rain events were recorded during the part  
20 of the study shown in Fig. 3. The highest emissions of MeSa were observed on Julian day (JD) 133 ( $0.25 \text{ mg/m}^2/\text{h}$ ) and declined thereafter. Corresponding average canopy mixing ratios were 250 pptv on this day. The average MeSA flux over the entire study was comparable to the total MT flux (Fig. 4a) and therefore represented a major component of reactive biogenic VOC emissions in this agroforest. Daytime canopy-scale  
25 stomatal resistances ( $R_s$ ) before irrigation calculated based on the Penman-Monteith equation exhibited average values of 214 s/m with a median of 197 s/m. After the irrigation cycle was initiated (JD146)  $R_s$  decreased to a mean of 177 s/m and a median

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of 162 s/m. The ~20% lower Rs after irrigation was found to be statistically significant based on the Wilcoxon rank sum test (WRST) ( $P=0.0017$ ,  $n=911$ ). Similarly VPD was found to be 10% higher before irrigation (WRST:  $P=6\times 10^{-7}$ ,  $n=911$ ) and was as high as 3.4 kPa on JD133 (Fig. 3a). Systematically higher Rs and VPD before irrigation indicate that trees experienced the onset of drought stress to a point where they were forced to reduce water loss.

Based on canopy scale MeSA concentrations, fluxes, Rs and measured HLC we can calculate internal MeSA mixing ratios in leaves (e.g.  $C_i=7.8$  ppbv on JD 133) and, assuming most of it is dissolved in leaf water, estimate a range of liquid concentrations (e.g. ~40  $\mu\text{g/l}$  on JD133 and 21  $\mu\text{g/l}$  on JD148). For comparison a concentration range of ~100–250 ng/gFW was reported by Park et al. (2006) in primary inoculated and uninoculated systemic mosaic tobacco leaves; their observations would correspond to a liquid concentration of ~125–310  $\mu\text{g/l}$  assuming that 80% of leaf fresh weight (FW) consisted of water. On JD143 and JD144 the leaves in the orchard were sprayed with an insecticide (DuPont, ASANA XL) for the only time during the experiment. In order to avoid contamination all chemical instrumentation had to be shut down. MeSA fluxes and mixing ratios were measured approximately 24 h (JD145) after the application of the insecticide. MeSA emissions after spraying were not statistically different at the 5% significance level compared to days before the application of the insecticide (Two Sample T-Test:  $P(\text{before}=\text{after})=0.1495$ ;  $P(\text{before}>\text{after})=0.0748$ ,  $n=32$ ). A number of biotic and abiotic stresses (e.g. herbivores/pathogens, ozone, temperature, drought) can induce the production of MeSA; during CHATS we can rule out the presence of a significant herbivore infestation due to a highly managed agroforest showing no sign of apparent physical leaf damage. With peak daytime ozone mixing ratios ranging between 39 and 70 ppbv during the study, plants did not experience acute exposure to ozone (e.g. study maximum (average) daily AOT40 <130 (60) ppbv h at  $\text{VPD}>1.5$  kPa (Karlsson et al., 1998) and total study AOT40=1.2 ppm h (Fuhrer et al., 1997)). Consequently ozone mixing ratios did not exhibit a statistically significant correlation with MeSA emission rates ( $R^2=0.24$ ). Similarly no significant correlation ( $R^2=0.02$ ) be-

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tween MeSA and ozone fluxes (Fig. 4b) was observed, suggesting that MeSA production was not primarily induced due to oxidative stress. The correlation between MeSA fluxes and VPD for the whole study exhibited an  $R^2$  of 0.58 (Fig. 4c). Among all environmental and chemical data available during CHATS we found that the best predictor of MeSA fluxes was the difference between the minimum nighttime temperature of the previous night and the following maximum daytime temperature ( $\Delta T$ ). Figure 4d shows a plot of mean daytime MeSA fluxes versus  $\Delta T$ . The correlation between these quantities was statistically significant exhibiting an  $R^2$  of 0.95 before irrigation and an  $R^2$  of 0.65 after irrigation. For comparison correlations with maximum daytime temperatures (e.g.  $R^2$ : 0.43) or minimum temperatures of the previous night (e.g.  $R^2$ : 0.21) alone were rather poor. MeSA emissions were therefore likely a result of temperature stress possibly enhanced due to the onset of drought stress, which increases daytime leaf temperatures. Initial emission bursts typically followed a night with low temperatures that could induce chilling injury (e.g. ambient temperature,  $T_{\text{ambient}}=7.5^\circ\text{C}$ , calculated minimum leaf-temperature,  $T_{\text{leaf,min}}=4.6^\circ\text{C}$  on JD133) and a subsequent temperature change of  $\sim 20^\circ\text{C}$  over the following day (e.g.  $\Delta T=21.3^\circ\text{C}$  on JD133). A similar temperature change ( $T=19^\circ\text{C}$ ) occurred on JD148 after the irrigation schedule was started. The corresponding MeSA emission was clearly enhanced, but the average daytime canopy-scale flux was lower on JD148 than on JD133. These observations suggest that large temperature changes can trigger an ecosystem wide immune response; this is supported by the occurrence of lipid derived wound VOCs observed in PTR-MS mass scans on JD133 and confirmed by GC-MS analyses indicating that 3-Z-hexenal was a dominant component. For example noontime mixing ratios (fluxes) of the sum of hexenal isomers were on the order of 1.5 ppbv ( $0.8\text{ mg/m}^2/\text{h}$ ) on this day, declining to 0.3 ppbv ( $0.1\text{ mg/m}^2/\text{h}$ ) over the following week.  $C_6$  wound VOCs such as 3-Z-hexenal are commonly observed when lipids are damaged and have been detected during mechanical wounding (Fall et al., 1999), herbivore infestations (Arimura et al., 2005), freezing (Fall et al., 2001) and drying (Karl et al., 2001) events, acute ozone exposure (Heiden et al., 1999) and after drastic changes of a plant's light environment (Graus

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et al., 2004). From Figure 4d MeSA fluxes can be obtained as a function of  $\Delta T$ . The pre-irrigation (JD133) and post-irrigation (JD148) emission events exhibited slopes of  $0.032 \pm 0.004 \text{ mg/m}^2/\text{h}/^\circ\text{C}$  and  $0.015 \pm 0.009 \text{ mg/m}^2/\text{h}/^\circ\text{C}$  respectively. MeSA emission pulses were thus a factor of  $\sim 2$  lower after irrigation of the plantation started. Systematically higher daytime Rs and VPD before JD148 indicate that these differences could have been caused by a drought stressed ecosystem. Observations in this agroforest therefore support the idea that chilling injury at temperatures below  $10\text{--}15^\circ\text{C}$  can result in greater membrane damage at times when plants experience water deficit (Wright, 1974).

## 4 Conclusions

Our observations suggest that environmental factors can induce an ecosystem-wide immune response resulting in significant emissions of semivolatile plant hormones adding to the biogenic contribution of SOA. The atmospheric significance of plant hormones stems from their physiochemical properties. The vapor pressure of MeSA for example ( $4.5 \times 10^{-5} \text{ atm}$ ) is two orders of magnitudes lower than that of commonly observed monoterpenes (e.g. alpha-pinene); the resulting saturation vapor pressure ( $C^* = 270 \mu\text{g/m}^3$ ;  $T = 25^\circ\text{C}$ ) is in the range of carboxylic acids. For comparison  $C^*$  for Methyl jasmonate (MeJA) is  $2.6 \mu\text{g/m}^3$  ( $T = 25^\circ\text{C}$ ), close to values obtained for dicarboxylic acids. For typical ambient aerosol mass concentrations between  $1\text{--}50 \mu\text{g/m}^3$  (17), 0.4–18% of MeSA could partition into the particle phase directly without prior oxidation in the atmosphere (Pankow, 1994). This fraction is likely a lower limit due to the neglect of gas-phase oxidation, which is expected to be fast with respect to reaction with the OH radical (e.g.  $k_{\text{OH}} = 1.1 \text{ e}^{-11} \text{ cm}^3/\text{s}$ ). Plant hormones could therefore make an important contribution to biogenic secondary organic aerosol formation (Kanakidou et al., 2005) if concentrations and emission rates observed during this study are generalized to other ecosystems.

While a large body of literature on the defensive function of herbivore-induced VOCs

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inferred from laboratory experiments exists (Baldwin et al., 2006; Farmer, 2001), effects of environmental parameters on plant-specific constitutive responses, in particular, the relationship between abiotic and biological stresses have not been studied systematically in the field. Whether higher production rates of MeSA (and SA) during periods of moderate water limitation could help stressed plants to deal with imminent pathogen or herbivore infestations more successfully under field conditions merits further investigation in the future. Ecosystem-scale measurements of MeSA within emerging ecological networks (e.g. the National Ecological Observatory Network – NEON (<http://www.neoninc.org/>)) could potentially play an important role in improving our understanding of plant health under naturally occurring conditions.

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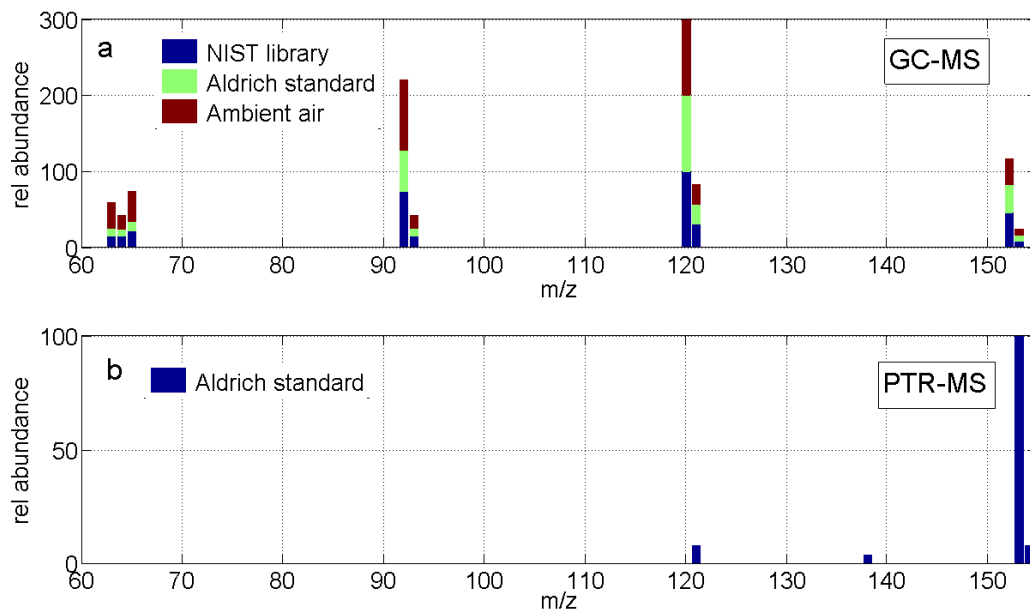
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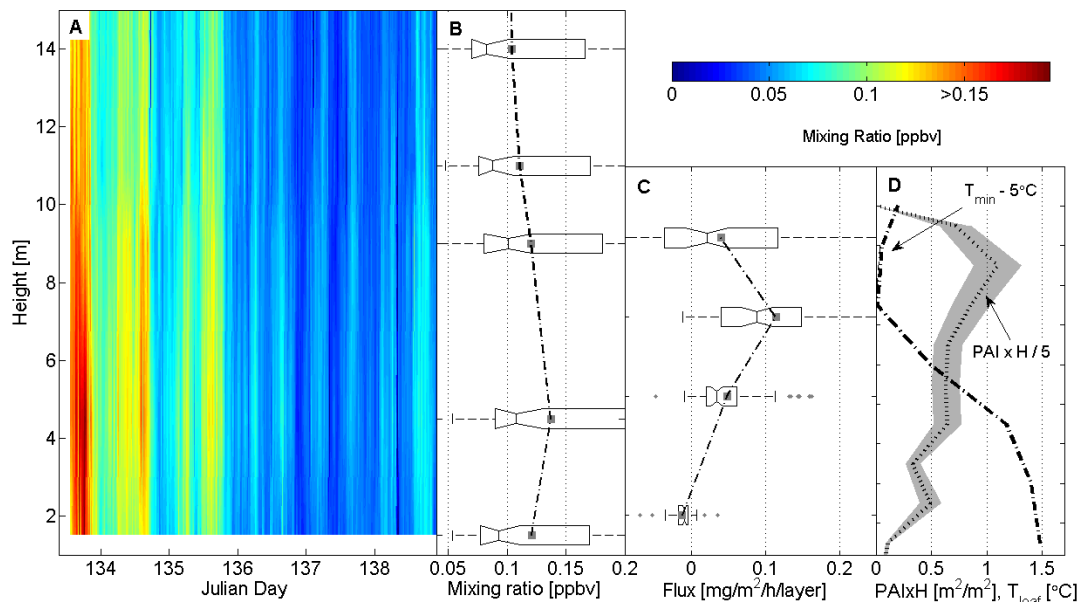
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**Fig. 1.** (a). Stacked bar plot of electron-impact ionization mass spectra of methyl salicylate (NIST library, an authentic standard (SigmaUltra, Sigma Aldrich, CAS 119-36-8, Milwaukee, WI) and ambient air measurements). (b). Proton-transfer-reaction mass spectra of methyl salicylate using an authentic standard (SigmaUltra, Sigma Aldrich, CAS 119-36-8, Milwaukee, WI).

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**Fig. 2.** (a) Vertical gradient of mixing ratios (colour coded). (b) Vertical gradient of daytime (10–18 local time) mixing ratios. Statistical box plot shows lower quartile, median and upper quartile (vertical lines of notched box), mean (gray squares connected with dashed line), whiskers (include 95% of data) and extreme values (gray dots). (c) Vertical flux gradient integrated over each flux layer and calculated for mixing ratio profiles shown in (a). (d) Vertical distribution of normalized plant area index ( $\text{PAI} \times \text{H}$ ) and minimum night-time leaf temperatures ( $T_{\text{leaf}}$ ) (an offset of 5°C was subtracted from  $T_{\text{leaf}}$  in order to plot both quantities on the same axis).

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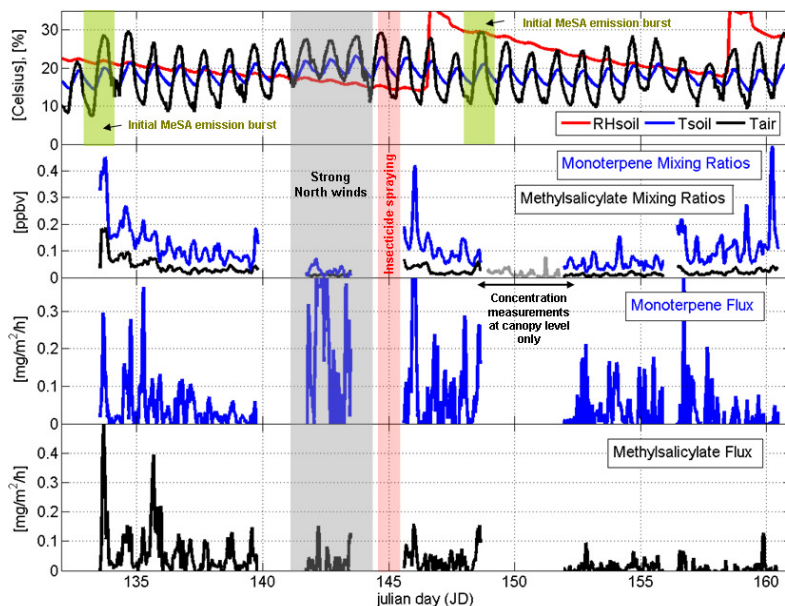
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**Fig. 3.** (a) Air temperature (black), Vapor Pressure Deficit (VPD) (blue) and soil moisture (red). (b) Mixing ratios of MT (blue) and MeSA (black). Days when measurements of MeSA were performed at only one level are coloured gray. (c) Canopy scale integrated total MT flux. (d) Canopy scale integrated MeSA flux. Data collected between JD140 and JD144 were omitted from any analysis due to strong north winds resulting in a biased flux and concentration footprint.

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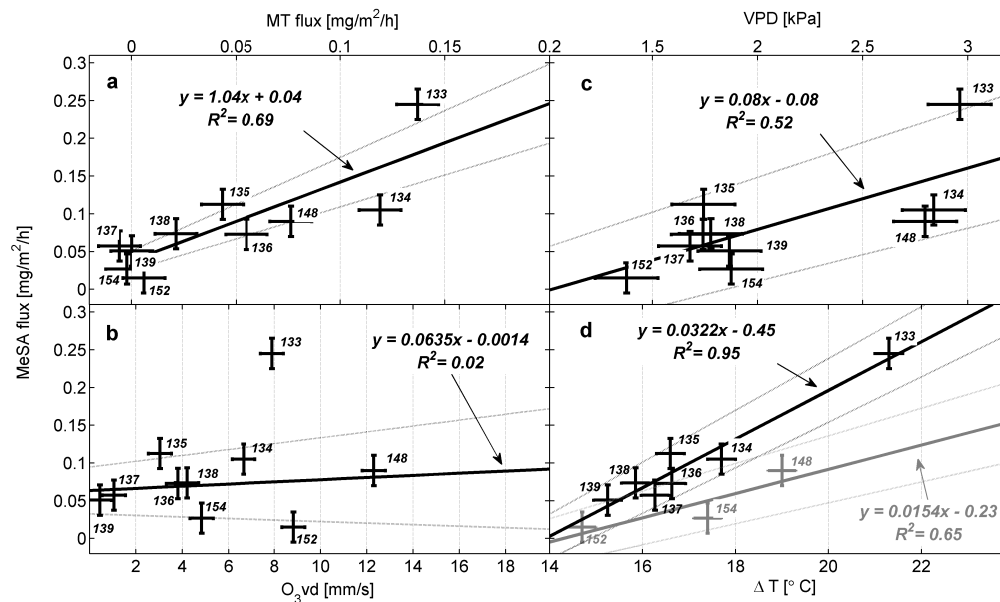
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**Fig. 4.** (a), MeSA flux plotted vs MT flux. (b) MeSA flux plotted vs O<sub>3</sub> deposition velocity (vd). (c) MeSA flux plotted vs VPD. (d) MeSA flux plotted versus ΔT before irrigation (black) and after irrigation (gray). Data point labels indicate Julian Day. Fitting equation and R<sup>2</sup> shown for each x/y weighted fit. Dotted lines represent prediction bounds based on the standard deviation of the fitting parameters.

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