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Emissions of terpenoids, benzenoids, and other biogenic gas-phase organic compounds from agricultural crops and their potential implications for air quality

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Terpenoids, benzenoids, and other biogenic gas-phase OCs

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Abstract

Agriculture comprises a substantial fraction of land cover in many regions of the world, including California's San Joaquin Valley, which is out of compliance with state and federal standards for tropospheric ozone and particulate matter ($PM_{2.5}$). Emissions from vegetation and other biogenic and anthropogenic sources react in the atmosphere to produce ozone and secondary organic aerosol, which comprises a substantial fraction of $PM_{2.5}$. Using data from three measurement campaigns, we examine emissions of reactive gas-phase organic carbon from agricultural crops and their potential to impact regional air quality relative to anthropogenic emissions in California's San Joaquin Valley. Emission rates for a suite of biogenic terpenoid compounds were measured in a greenhouse for 25 representative crops from California in 2008, and ambient measurements of terpenoids and other biogenic compounds in the volatile and intermediate-volatility organic compound range were made over an orange orchard in a rural area of the San Joaquin Valley during two seasons in 2010: summer and spring flowering. When accounting for both emissions of reactive precursors and the deposition of ozone to an orange orchard, the net effect of the orange trees is a net source of ozone in the springtime during flowering, and relatively neutral for most of the summer until the fall when it becomes a sink. Flowering was a major emission event and caused a large increase in emissions including a suite of compounds that had not been measured in the atmosphere before. Such biogenic emission events need to be better parameterized in models as they have significant potential to impact regional air quality since emissions increase by an order of magnitude. In regions like the San Joaquin Valley, the mass of biogenic emissions from agricultural crops during the summer (without flowering) and the potential ozone and secondary organic aerosol formation from these emissions are on the same order as anthropogenic emissions from motor vehicles and must be considered in air quality models and secondary pollution control strategies.

1 Introduction

Biogenic compounds are emitted from vegetation via several mechanisms and pathways. Emissions are typically a function of environmental parameters (e.g. light, temperature) or specialized responses to communicate with, attract, or repel animals, insects, or other plants (Bouvier-Brown et al., 2009; Goldstein and Galbally, 2007). Biogenic emissions from plants are mostly in the gas-phase and span from 1 to over 20 carbon atoms in size (Goldstein and Galbally, 2007). Examples include small compounds such as methanol and acetone, and a broad suite of isomers that are multiples of isoprene (C_5H_8). Prominent examples of these olefinic compound classes include monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$). Their oxygenated counterparts contain 1–2 oxygen atoms and are included in the definition of monoterpenoids and sesquiterpenoids. Plant species can emit a variety of these isomers with one or more double bonds and can include cyclic or bicyclic rings, but a certain suite of compounds has been observed more frequently (Bouvier-Brown et al., 2009; Goldstein and Galbally, 2007). Commonly reported monoterpenes include Δ-limonene, α-pinene, and Δ3-carene, and common sesquiterpenes, which are more difficult to measure, include β-caryophyllene and α-humulene (Bouvier-Brown et al., 2009; Ormeno et al., 2007). Many terpenoids have specific functions and are responsible for the fragrances and flavors associated with various plants (Bouvier-Brown et al., 2009; Lewis et al., 2007; Afsharypuor and Jamali, 2006; Bendimerad et al., 2007; Bernhardt et al., 2003; Azuma et al., 2001; Omura et al., 1999; Kotze et al., 2010). Some studies have also shown plant leaves or flowers to contain other compounds with aromatic rings (i.e. benzenoids) and nitrogen- or sulfur-based functional groups (Lewis et al., 2007; Afsharypuor and Jamali, 2006; Bendimerad et al., 2007; Bernhardt et al., 2003; Azuma et al., 2001; Omura et al., 1999; Kotze et al., 2010; Ormeno et al., 2010).

Much work has been done to understand emissions of biogenic gas-phase organic carbon since most of the compounds are highly reactive and can produce ozone (O_3) and secondary organic aerosol (SOA) as a product of their chemistry with atmospheric

oxidants (Carter, 2007; Ng et al., 2006). Understanding emissions from vegetation is important in California because of the complex interplay of anthropogenic emissions and biogenic emissions from both natural vegetation and agricultural crops (Shilling et al., 2013). Agricultural plantings make up a major fraction of land cover in some re-
5 gions such as California's San Joaquin Valley, which is an extreme non-attainment area for ozone and a non-attainment area for $PM_{2.5}$ (US EPA). A summary of prominent agricultural crops in the San Joaquin Valley is shown in Table 1. Historically, there has been some research on emissions from agricultural crops in California (Arey et al., 1991a–d; Winer et al., 1989, 1992; Karlik et al., 2002). Yet, biogenic emissions from many of
10 these crops and other agricultural plants require further characterization with new advances in instrumentation and contemporary scientific knowledge and concerns. Also, total emissions have previously been thought to be minor relative to natural vegetation (Lamb et al., 1987), and further measurements of terpenoid emissions is necessary to build upon previous work. Models on regional scales and larger need this informa-
15 tion on emission factors from individual plant species to improve parameterizations; these include the MEGAN (Model of Emissions of Gases and Aerosols from Nature) model (Sakulyanontvittaya et al., 2008; Guenther et al., 2012) and the BEIGIS model developed by the California Air Resources Board (2003).

This work includes a survey of volatile organic compound (VOC) and intermediate-
20 volatility organic compound (IVOC) emissions from agricultural crops studied via plant enclosure measurements in a greenhouse to develop emission factors and emission parameters (Table 2), and also an assessment of seasonal emissions from an orange orchard located in a rural area of the San Joaquin Valley. Further objectives of this work include characterizing emissions associated with spring flowering and examining the
25 relative importance of biogenic emissions from agriculture on ozone and SOA formation in the San Joaquin Valley.

2 Materials and methods

This paper uses measurements from three campaigns: a survey using plant and branch enclosures in a greenhouse, a multi-season campaign in an orange orchard, and an urban site in Bakersfield, CA. The principle gas-phase organic carbon measurements in this work were made using a custom gas chromatograph with a mass spectrometer and a flame ionization detector. A broad suite of several hundred compounds was quantified with hourly-time resolution. Extensive detail on the design and operation of the instrument can be found elsewhere (Gentner et al., 2012).

To examine emissions from agricultural vegetation, 25 different crops were studied in the partially controlled environment of the Oxford Tract greenhouse at U.C. Berkeley during the summer of 2008 (all experiment design details available in Fares et al., 2011). The crops included were a mixture of woody trees and shrubs, and herbaceous plants that are prominent in California (Table S1). Plants were all potted, fertilized weekly, and watered daily to provide good growing conditions and avoid water stress. Plants were exposed to natural sunlight and the greenhouse humidity was maintained at 40–60 %. Branches or whole plants were enclosed in Teflon chambers outfitted with temperature and light monitors for several days at a time with several replicates of each species. To avoid any biases caused by plant damage during enclosure, plants were given time to equilibrate before measurements were used to assess emission rates and chemical speciation. In addition to chemically-speciated measurements of VOCs and IVOCs via gas chromatography/mass spectrometry, several other instruments were used to measure ozone, carbon dioxide, and water vapor. Measurements of isoprene and monoterpenes reported from greenhouse enclosure measurements were made in conjunction with a high-time resolution Proton Transfer Reaction Mass Spectrometer (PTR-MS) (Fares et al., 2011).

Based on the results of the greenhouse study, a yearlong measurement site was set-up in a Valencia orange orchard in the San Joaquin Valley (36.3566° N, 119.0923° W), located in Lindcove, which is east of the city of Visalia near the foothills of the Sierra

Nevada mountains. The local area around the site had a large planted area of various citrus trees and some other crops. In addition to biogenic emissions from nearby agriculture, the site was influenced by natural vegetation in the surrounding mountains and anthropogenic sources in the San Joaquin Valley. A detailed description of the site can be found in Fares et al. (2012b). We took two sets of chemically-speciated organic carbon measurements at this site during two different seasons; in April–May 2010 during citrus flowering and summer 2010 (each 10 or more days). Measurements were made at the top of the canopy (4 m), and the site had a similar suite of supporting measurements as the greenhouse study. Year-long measurements of ozone fluxes over the orange orchard were used in this work; these methods have been described elsewhere (Fares et al., 2012b).

Ambient in-situ measurements were made in Bakersfield, CA at the CalNex (California Research at the Nexus of Air Quality and Climate Change) supersite (35.3463° N, 118.9654° W) located in southeast Bakersfield in the southern San Joaquin Valley. Measurement of gas-phase organics took place 18 May–30 June 2010, sampled from the top of an 18 m tower. To reduce losses of highly reactive compounds in the sampling system, ozone was removed at the inlet using sodium thiosulfate treated filters at both ambient measurement sites (discussed in Gentner et al., 2012).

We recently developed a method in Gentner et al. (2013b) that calculates the spatial distribution of emissions in a region based on fixed-location measurements and coincident back-trajectory footprints for each hourly sample determined using the FLEXPART-WRF Lagrangian model for meteorological dispersion (Brioude et al., 2012). Extensive details on the methodology can be found elsewhere (Gentner et al., 2013b). In this work, we use it to examine the transport of biogenic VOCs to the urban site in the southern San Joaquin Valley.

Basal Emission Factors (BEFs) are the standardized emission factors for biogenic compounds from vegetation, and are adjusted based on the environmental parameters considered. BEFs were calculated for each compound class from each plant species studied in the greenhouse by taking the average of the data points with tem-

perature = $30 \pm 2\,°C$, and photosynthetically active radiation (PAR) > $800\,\mu mol\,m^{-2}\,s^{-1}$. These emission rates, or fluxes, are reported in carbon mass per mass dry leaf matter per time (e.g. $ngC\,(gDM)^{-1}\,h^{-1}$). If insufficient data existed at these basal conditions, data were logarithmically extrapolated from lower temperature data to determine BEFs

5 (see Fares et al. (2011) for details).

Most compounds without specialized functions can be characterized by two different emission mechanisms, described as dependence on light and temperature or just temperature. Compounds that are emitted immediately after being produced in the leaves are light and temperature dependent, and their emission rates are calculated using the

10 method developed by Guenther et al. (1993). Whereas, emissions based solely on temperature are kept in storage pools inside the leaves and/or stems, and are emitted via volatilization. These emission rates are calculated based on methods in Tingey et al. (1980) and Guenther et al. (1993). Not all compounds are emitted by a single pathway, so we test both methods of emission characterization with the same BEF, determined

15 using the standardized data described in the previous paragraph. Additional information and the equations used (S1 and S2) can be found in the Supplement. For both methods, calculated emission rates from the greenhouse enclosure studies were compared to measured rates via linear correlation. The resulting slopes and coefficients of determination (r^2) are used to determine which method best represents the emissions

20 from each plant for each compound class.

At the Lindcove and Bakersfield sites, comparisons of biogenic to anthropogenic burdens of gas-phase organic carbon were done using chemical mass balance source receptor modeling methods (Gentner et al., 2012) to model anthropogenic emissions from motor vehicles. Total emissions of anthropogenic hydrocarbons in the San Joaquin

25 Valley from motor vehicles are determined using the emission factors derived in Gentner et al. (2012) and fuel use data for the seven counties of the air basin (California Dept. Transportation, 2008). Our estimates of biogenic emissions for the region were compared to the California Air Resources Board emission inventory (2010). The ozone formation potential of these emissions are compared using maximum incremental re-

activity (MIR) determined using the SAPRC VOC reactivity scales (Carter, 2007). Existing information on yields of secondary organic aerosol from atmospheric oxidation are compiled from literature (Gentner et al., 2012; Saathoff et al., 2009; Kim et al., 2012; Ng et al., 2006). Where available, literature values are presented for the reaction constants of newly measured biogenic compounds with atmospheric oxidants (Atkinson and Arey, 2003a, b). Otherwise, theoretical values are estimated using the US EPA's EPI Suite program (2000).

3   Results and discussion

3.1   Greenhouse measurements of individual plant species

There were numerous terpenoid compounds quantified in emissions from crops with considerable diversity of emissions between plant species. Emission parameters and detailed chemical speciation for monoterpenes, oxygenated monoterpenes, and sesquiterpenes measured from the different crops in the greenhouse study are shown in Tables 2 and S2–S5. Monoterpene concentrations were measured as individual species via gas chromatography and as total monoterpenes with the PTR-MS, and agreed to within 20 % (Fares et al., 2011). In addition to the well-known monoterpenes Δ-limonene and α-pinene, there were similar magnitude emission factors for β-myrcene, sabinene, and both isomers of β-ocimene. Oxygenated monoterpene emissions were dominated by linalool and perillene, a little-studied furanoid. We observed only two sesquiterpenes, α-humulene and β-caryophyllene from the crops studied. Consistent with previous work, β-caryophyllene dominated the two, but it is likely that there were other sesquiterpenes outside of the observable range, at concentrations below the limit of detection, or lost in the sampling system prior to detection. A broader suite of sesquiterpenes were measured using a cartridge method and emissions are reported by Ormeno et al. (2010).

Calculated BEFs and beta values for total monoterpenes, oxygenated monoter-penes, and sesquiterpenes are summarized in Table 2 with relevant statistical metrics. Data on the chemical speciation of emissions and the performance of the temperature-only and light + temperature modeling methods are shown in Tables S2–S5. Com-pared to other natural vegetation (e.g. oak trees, Poplar) agricultural crops have low isoprene emission factors. This work focuses on the larger emissions of terpenoids, but a summary of isoprene emission factors can be found in Tables S6 and S7 along with emission factors for methanol, acetaldehyde, and acetone. While it is conven-tionally helpful to group plants together for the purposes of modeling based on either emissions strength or crop type, we have refrained from doing so in this work. There is a considerable amount of uncertainty in the individual emission factors and the relative strength of emissions varies for each plant species depending on chemical class. Such a grouping would be subject to the limitations of this study and in some cases, regional assumptions.

3.1.1 Monoterpenes

Total emissions of monoterpenes were lowest ($< 100\,\mathrm{ng\,C\,(gDM)^{-1}h^{-1}}$) from almond, grape, olive, pistachio, plum and pomegranate (Table 2). For almond and cherry, the monoterpene BEF agreed with previous research (Winer et al., 1992). Emissions from grapes were very low (11 and $91\,\mathrm{ng\,C\,(gDM)^{-1}h^{-1}}$) whereas Winer et al. (1992) did not detect any emissions. The monoterpene BEF for peach, $1211\,\mathrm{ng\,C\,(gDM)^{-1}h^{-1}}$ was significantly higher than other plants in the *Prunus* genus (i.e. almond, plum) measured in this study.

Correlations between measured and modeled monoterpene emissions for both the temperature only and the light + temperature modeling methods were significant for al-mond and olive (Table S2). Some plant species, such as these, are known to have stor-age structures on their leaves where terpenes are typically stored (Vieira et al., 2001). The existence of these "pools" of biogenic compounds is relevant since harvesting or pruning may cause emissions if leaves are damaged during agricultural operations.

Among the herbaceous species, tomato was the highest monoterpene emitter (BEF = 742 ng C (gDM)$^{-1}$h^{-1}). The measured BEF was within the range of previously reported values for Tomato (Winer et al., 1992; Jansen et al., 2008). Tomato is well known to have specialized structures (Freitas et al., 2002; van Schie et al., 2007) filled with terpenes, and the emissions have been shown to dramatically increase after wounding or pathogen infestation (Jansen et al., 2008), suggesting that higher emissions should be expected during harvesting.

Parent Navel Orange (P. N. Orange) had a high monoterpene emission factor with a beta coefficient of 0.14 without flowers (temperature only algorithm), which is consistent with previous published work on oranges (Ciccioli et al., 1999). Emissions of total monoterpenes from other citrus species in this study were very low; 22, 26, and 63 ng C (gDM)$^{-1}$h^{-1} for Eureka lemon, Clementine mandarin, and W. Murcott mandarin, respectively. Monoterpene emissions from P. N. Orange were predominantly β-myrcene and β-trans-ocimene, and mandarins emitted mainly β-cis- and β-trans-ocimene. Previous work has shown much higher emission for Lisbon lemons (Winer et al., 1992), which suggests potential variability in emissions owing to phenological factors.

Our emission measurements of pistachio are considerably lower than previous work classifying Pistachio as a large monoterpene emitter; our BEF is more than two orders of magnitude lower than in Winer et al. (1992). Since pistachio acreage is very large in California, further studies on this crop are warranted as fundamental questions remain about pistachio's BEF. It is possible that although the same variety was used in both studies, specific phenotypic traits of the individuals selected could cause such differences. It is the case here with pistachio as with many other crops surveyed in our study that several replicates of a few individuals for a crop variety were likely inadequate to capture the variability in biogenic emissions within individuals of the same species, between different crops, and during different periods of an individual's life or annual cycle. The results of this portion of the study are also subject to the limitations of the greenhouse environment compared to the field; plants were potted and were exposed

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to lower than typical light and temperature conditions. Thus, it is important to note that the results presented from the greenhouse study comprise a survey of emissions from a broad suite of crops and more extensive measurements are critical to effectively characterize emissions from a particular crop species. Future users of this individual crop data should take caution of the variability between individuals of the same species and their seasonal cycles.

3.1.2 Oxygenated monoterpenes

Oxygenated monoterpene emissions from crops have not been reported extensively in the past. The most prevalent oxygenated monoterpene observed in the greenhouse study was perillene. Emissions of oxygenated monoterpenes were highest from flowering orange (BEF = 4600 ng C $(gDM)^{-1}h^{-1}$), followed by pima cotton and non-flowering orange (2700 and 1300 ng C $(gDM)^{-1}h^{-1}$, respectively). Lower emissions were observed from cherry, peach, almond, and W. Murcott mandarin, with very low emissions from the other crops (Table 2). Modeled and measured emissions of oxygenated monoterpenes from non-flowering orange leaves were not well correlated. The occurrence of perillene may suggest that neither of the modeling methods represent emissions of this furanoid. For flowering oranges, the temperature only method best describes the emission of oxygenated monoterpenes, mainly linalool, confirming the temperature dependency of linalool emissions reported previously (Ciccioli et al., 1999).

3.1.3 Sesquiterpenes

Almond was the highest sesquiterpene emitter of the crops studied according to the calculated BEF (10 000 ng C $(gDM)^{-1}h^{-1}$), while the magnitude of the monoterpene and oxygenated monoterpene emissions were very low. This sesquiterpene BEF was anomalous, so we report it with low confidence. The calculated beta of 0.45 is very high, and all the measurements for almond were below 25 °C. Using a beta of 0.1, the BEF would be 1200 (a factor of 10 lower, but still a significant emission). Sesquiterpene

emissions were very low or not detected for other non-citrus woody crops. Sesquiterpene emissions from tomato were $59\,\mathrm{ng\,C\,(gDM)^{-1}h^{-1}}$, slightly lower than the range reported in previous work for different varietals (Winer et al., 1992). After almond trees, P.N. Orange trees had the highest sesquiterpene emission rates, with the flowering specimen being twice that of the non-flowering trees.

3.2 Emissions from flowering citrus trees

Many trees and herbaceous plants produce flowers once or more every year. In the greenhouse enclosure studies, flowering increased monoterpene emissions from orange trees by a factor of three. The presence of flowers has been shown previously to dramatically influence the magnitude and composition of emissions from orange trees (Ciccioli et al., 1999; Hansen et al., 2003; Arey et al., 1991a). In the greenhouse study β-myrcene and β-trans-ocimene were the dominant monoterpenes emitted from orange trees and were three times greater from the flowering specimen (Table S3). β-cis-ocimene was also observed from the flowering plants. Emissions of the oxygenated monoterpene linalool increased by a factor of ~3.5 from the flowering plant. β-caryophyllene emissions also increased by a factor of two for the flowering orange tree. Increased emissions from the flowering orange tree were observed for all compounds measured (Fares et al., 2011), but there were no flowering individuals from the other *Citrus* species for comparison.

During the spring field measurement campaign at the orange orchard, a broad array of biogenic gas-phase organic compounds was measured in ambient air (Table 3). Flowering occurring at the field site and in the region had a major impact on the distribution of biogenic compounds in ambient air. There was a dramatic increase in both the magnitude and diversity of chemical species emitted during the flowering process. Due to strong nocturnal inversions, many were measured at ppb-level concentrations at night owing to their build-up in the shallow boundary layer where ozone had been scavenged to concentrations below 10 ppb. Perhaps of more interest is that daytime concentrations averaged above 10 ppt for most compounds, when their emissions are most

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relevant to photochemistry. Additionally, several of the most prominent compounds had daytime concentrations that regularly exceeded 1 ppb (Table 3).

β-myrcene was the principal monoterpene observed during flowering, while linalool was overall the most abundant terpenoid compound observed. Yet, there were high concentrations of a wide variety of compounds during the flowering period that had strong diurnal patterns (Fig. 1). While many of the biogenic compounds observed at the site were terpenoids, there was a diverse array of functionalized aromatic compounds (i.e. benzenoids) that were clearly biogenic and associated with flowering (Tables 3–5). This was evidenced by their strong correlations to β-myrcene and linalool (Tables 5 and 6), which are known from the greenhouse and field site measurements to be associated with flowering. To our knowledge, several of the compounds observed and measured have not been previously reported in other studies of ambient air. These compounds were initially identified through high quality matches to mass spectra libraries and Kovat's indices for appropriate retention times, and then later confirmed with authentic standards after the campaign. Table 4 summarizes their chemical structures and reactivity. Many of the compounds we observed during flowering have been attributed to floral scents or essential oils from flowers in various botany and ecology studies, which include a variety of compounds with aromatic rings, as well as nitrogen, sulfur, and/or oxygen-containing functional groups (Lewis et al., 2007; Afsharypuor and Jamali, 2006; Bendimerad et al., 2007; Bernhardt et al., 2003; Azuma et al., 2001; Omura et al., 1999; Kotze et al., 2010).

There were several previously unidentified peaks observed during measurements of the flowering Parent Navel orange in the greenhouse studies that have very good retention time matches to these flowering compounds measured at this site; including indole, methyl anthranilate, benzeneethanol, benzyl nitrile, 2-aminobenzaldehyde, and possibly sabina ketone. In the greenhouse measurements, these compounds were observed only from the flowering specimen, supporting the conclusion that flowering is the source. At the field site, daytime concentrations of methyl anthranilate, indole, and benzyl nitrile were over 1 ppb, similar or greater than the dominant monoterpene β-

myrcene. Lavender lactone, benzeneethanol, 2-amino-benzaldehyde, and benzeneac-etaldehyde had significant median daytime concentrations at, or above, 100 ppt. Sabina ketone and methyl benzoate had lower concentrations similar to the linalool oxide iso-mers, but still appeared to be emitted in significant amounts. Cis-3-hexenyl acetate, a well-known plant-wounding compound, had considerable nighttime concentrations around 1 ppb despite no harvest or pruning activity, and correlated well with other flow-ering compounds suggesting that is also released as part of the flowering process. In addition to these compounds, we also observed several high molecular weight straight alkanes and alkenes associated with flowering (e.g. *n*-heptadecane, 1-heptadecene), which have been reported in other floral and essential oil analyses (Lewis et al., 2007; Afsharypuor and Jamali, 2006; Bendimerad et al., 2007; Bernhardt et al., 2003; Kotze et al., 2010; Winer et al., 1992). Emissions of benzyl alcohol and benzaldehyde were recently observed in a flowering tree enclosure study (Baghi et al., 2012). The diurnal patterns of the flowering-related compounds were similar to that of monoterpenes, but were more prevalent (Figs. 1 and 2). A regression of the flowering related compounds to the sum of monoterpenes yielded a ratio of 4.0 (on a mass basis), but the sum of monoterpenes included compounds that were related to flowering (i.e. β-myrcene, sabinene, and both β-ocimenes).

There were several sesquiterpenes observed at the site during flowering, several of which we were not able to identify, but the concentrations measured were considerably lower than many of the other terpenoids. The dominant observed sesquiterpenes were β-caryophyllene, aromadendrene, trans-β-farnesene, valencene and trans-nerolidol (all confirmed with standards). Given the high reactivity of sesquiterpenes, the lower magnitude of concentrations does not necessarily imply lower emissions, but could also be a result of sesquiterpene compounds reacting at more rapid rates in the atmo-sphere than other terpenoid compounds. Sampling methodology can sometimes be responsible for underestimates of ambient concentrations, but the sampling and mea-surement techniques used in this study are suitable for sesquiterpene measurements.

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It is very likely that only a fraction of the emitted sesquiterpenes were measured due to their short atmospheric lifetimes, reacting with both OH and ozone.

We were only able to detect and identify a few sesquiterpenes. Yet, previous work (Ormeno et al., 2010) has shown that a wide array of sesquiterpenes are emitted from agricultural crops (flowering and non-flowering) and that emissions of sesquiterpenes should be roughly equivalent to those of monoterpenes. In the spring, measured sesquiterpenes were 5 % of monoterpenes, on average by carbon mass, but flowering is an episodic event and is not representative of an annual average. Previous work with the MEGAN model estimates sesquiterpene emission to be 9–16 % of monoterpenes, but sesquiterpene data for input into the MEGAN model is limited (Sakulyanontvittaya et al., 2008). Figure 3 shows the relative amounts of sesquiterpenes to monoterpenes and it is evident that there is a dynamic range of observed ratios that varies over the course of the day and it is quite possible that additional, unaccounted sesquiterpenes will increase the ratio.

The concentrations of sesquiterpenes during flowering were higher than previous work done in a ponderosa pine forest, where concentrations of individual sesquiterpenes were on the order of 10 ppt (Bouvier-Brown et al., 2009), but there are extremely few published ambient air measurements of sesquiterpenes with which to compare our observations. Our summertime measurements did not have the capacity to measure sesquiterpenes due to chromatographic and detector difficulties.

3.3 Seasonal differences in biogenic emissions

While there were considerable year-round concentrations of monoterpenes at the site, there was a strong increase in biogenic emissions during the flowering period. A comparison indicates the daytime concentration of monoterpenes was approximately three times greater during spring flowering compared to summer non-flowering conditions (Figs. 4 and 5). The diurnal pattern of monoterpenes between the two seasons was similar, despite higher concentrations in the spring during flowering (Fig. 4). Given the similarities between Δ-limonene during the two seasons, the difference can

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be attributed to the other monoterpenes associated with flowering. Over the summer, Δ-limonene was the predominant monoterpene, but during flowering β-myrcene, sabinene, and trans-β-ocimene were equally prevalent (Fig. 4, Table 7). A variety of other monoterpenes were present during both seasons, but made up relatively minor fractions.

While we measured fewer biogenic compounds during the summer campaign relative to the spring, we still observed a variety of monoterpenes in ambient air. We did not observe many of the compounds that were associated with flowering, including many of the oxygenated monoterpenes and benzenoids. There were similar diurnal patterns in the summer as in the spring due to boundary layer effects, with ambient ozone still getting below 10 ppb at night due to stomatal deposition, and reaction with biogenic VOCs and NO (Fares et al., 2012b).

The chemical speciation of monoterpenes is summarized in Table 7. There is a similar distribution and diversity of monoterpenes between the two seasons, with the exception of β-myrcene, sabinene and trans-β-ocimene, which increased significantly with flowering. Concentrations of total monoterpenes during the summer were similar to those observed at a California ponderosa pine forest in warm temperatures (26°C daytime mean), but the distribution of monoterpenes was significantly different; there was much more Δ-limonene and less α- and β-pinene compared to the pine forest (Bouvier-Brown et al., 2009). Δ-limonene was the most prevalent monoterpene observed in the summer and its diurnal patterns and interquartile concentrations were similar but slightly higher in the spring (Fig. 5b, Table 3). Para-cymene is a known non-flowering aromatic emitted from plants with a wide variety of sources and a few minor anthropogenic sources (e.g. gasoline). Similar to Δ-limonene, Fig. 5c shows that it was similar between the two seasons in both prevalence and diurnal pattern. The potential anthropogenic contribution to para-cymene is negligible given the relatively low concentrations of dominant gasoline tracers. The relatively comparable concentrations of several monoterpenes during the two measurement periods in the orange orchard imply similar emission rates during those two periods.

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3.4 Transport of biogenic emissions in the San Joaquin Valley

The relative magnitude of biogenic vs. anthropogenic emissions varied depending on location in the San Joaquin Valley as shown by the comparison of the Bakersfield and Lindcove sites (Fig. 6). Given the geographic distribution of agriculture and urban areas in the San Joaquin Valley, the transport of biogenic emissions from more vegetated areas is important, and can affect atmospheric reactivity and secondary pollutant formation throughout the valley. By comparing various pairs of monoterpenes, we assessed the timescales for transport of biogenic emissions through their aging by the three primary atmospheric oxidants (OH, O_3, NO_3). Each monoterpene measured at Bakersfield reacts at different rates with each oxidant, so by picking monoterpene pairs appropriately, we determined the most important oxidants for aging and their timescales. A comparison of Δ-limonene to $α$-pinene shows a distribution of ratios (Fig. 7). While some of this variability is possibly due to differences in emissions, it is evident that aging is playing an important role in the variability of observed ratios. Δ-limonene reacts faster than $α$-pinene with all three atmospheric oxidants, but given the average concentrations of the oxidants, oxidation by OH is the fastest and will have the strongest influence on the observed ratios. We used 24 h oxidant average concentrations of 0.25 pptv, 41 ppbv, and 0.29 pptv for OH, O_3, and NO_3, respectively, at the Bakersfield site based on observations (with steady state calculations for NO_3) and literature values (Bouvier-Brown et al., 2009; Brown et al., 2009; Rollins et al., 2012;). A comparison of Δ-limonene to para-cymene (not shown) similarly demonstrates the importance of aging by OH as the differences in reaction rates are more pronounced than between Δ-limonene and $α$-pinene. A similar comparison of camphene to $α$-pinene, demonstrates the constant initial emission ratio for the sources in the region and the effects of aging by ozone and nitrate radicals since there is less variability in the observations given that their OH reaction rates are identical (Fig. 7b). These monoterpene ratios clearly indicate the presence of these oxidation mechanisms and show the predominance of oxidation by OH, but are dependent on the timescales and diurnal patterns

of biogenic compounds arriving to Bakersfield. Overall, our findings are consistent with recent work reporting the presence of nitrate chemistry and also a study showing the dominance of OH oxidation of biogenic emissions (Rollins et al., 2012; Donahue et al., 2012).

It is evident from this analysis that the observed biogenic compounds are emitted within several hours of transport to the site, which can inform our exploration of the spatial distribution of emissions. Using the FLEXPART footprint modeling method (Gentner et al., 2013b), we determined the spatial distribution of biogenic sources that emit monoterpenes, which advect to the Bakersfield ground site. Figure 8 shows the distribution for the sum of monoterpenes over the 6 h of transport and Fig. S1 shows the distribution of individual chemical species. While many of the compounds appear to have similar sources in the San Joaquin Valley, some areas are stronger than others as emitters of different monoterpenes. Overall, there are three areas that emit monoterpenes that impact Bakersfield: cropland to the east/southeast of the site, cropland to northwest, and a relatively small patch of cropland in the mountains to the southwest. The spatial distribution of these emissions appear to be consistent with the location of croplands, but influence from natural vegetation is expected especially in the case of areas near or in the mountains with pine trees and other significant natural emitters of monoterpenes.

3.5 Impacts on air quality

The principal motivation for studying biogenic emissions from agriculture was to improve our understanding of the impact of biogenic emissions on air quality in the San Joaquin Valley. Terpenoid compounds are known to be very reactive and have the potential to form both tropospheric ozone and SOA. Our work has highlighted orange trees as large emitters, but many other crops have been shown in this and other studies to have non-negligible emissions (Winer et al., 1992). Previous work has concluded that emissions from agricultural croplands are minor (Lamb et al., 1987). While, this may be true for some crop types, particularly with respect the isoprene emissions. Over-

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all, the extent of land coverage and leaf mass, together with the range of observed emission factors for all compound classes, is likely to result in croplands representing a significant fraction of biogenic emissions in agricultural regions.

3.5.1 Relative magnitude of biogenic vs. anthropogenic emissions

To provide a relative comparison for biogenic emissions in context of the region, we estimated the ambient concentration of anthropogenic emissions due to motor vehicles during the spring campaign at the rural Lindcove site using the source receptor modeling methods described in Gentner et al. (2012). Figure 6 shows the diurnal pattern and relative prevalence of anthropogenic and biogenic source contributions for both Lindcove and Bakersfield. Biogenic sources do not contribute many primary emissions in Bakersfield, but are very important at the Lindcove site, especially in the spring. This effect is due to the differences in the biogenic factor as the anthropogenic contribution is similar between the two sites except for major spikes due to commuting periods in Bakersfield (Fig. 6b). While a similar chemical mass balance analysis is not possible for the summer, a comparison of anthropogenic compounds (e.g. m/p-xylene, isooctane) between the two seasons shows that nighttime concentrations are similar, but daytime concentrations of motor vehicle emissions are ∼30 % lower. This is likely due to a combination enhanced photochemical processing and increased dilution during the summer months when the top of the mixed boundary layer is generally higher. Nevertheless, it appears that during the summer in rural parts of the San Joaquin Valley anthropogenic emissions from motor vehicles will be slightly higher or the same order as biogenic emissions of terpenoids based on the sum of monoterpenes presented in Fig. 5a and a similar abundance as the springtime anthropogenic vehicular contribution (Fig. 6b).

During flowering of citrus trees the mass of observed biogenic compounds was on average 14 times that of inferred anthropogenic compounds from vehicular emissions at the Lindcove site. In contrast, the mass of anthropogenic contributions from motor vehicles was 48 times the observed monoterpenoids from biogenic sources in Bak-

ersfield. Contributions from isoprene or oxygenated VOCs from biogenic sources will slightly reduce this difference at Bakersfield, but are not included as these emissions cannot be attributed to agriculture. Daytime monoterpene concentrations measured with GC/MS at Lindcove were on average 6 ± 2 times greater during flowering than in the summer. This is largely consistent with observations from year-long PTR-MS measurements at the Lindcove site that reported a 10× increase in the monoterpene BEF between the flowering and non-flowering periods (Fares et al., 2012a). Given that the concentration of quantified flowering compounds was 4 times greater than the sum of monoterpenes, in total we found that flowering increases carbon emissions by $\sim 25\times$ in total, with the source profile for flowering shown in Table 6. This difference in emissions between flowering and non-flowering plants needs to be considered in emissions and air quality modeling, since during flowering periods the chemistry of the atmosphere may be significantly different. These seasonal events need to be taken into account to accurately model the large changes in biogenic emissions from agriculture and air quality in the San Joaquin Valley. Important emission events were spring flowering, pruning, harvesting, and fertilizer application (Fares et al., 2012a). During these events large increases in emissions of terpenoids were measured (monoterpenes, sesquiterpenes, and oxygenated terpenes). It is important to note that many agricultural regions, like the San Joaquin Valley, are comprised of a diverse mixture of crop types. These plants have different phonological and management cycles, meaning that emission events, such as flowering, will occur at different times and there is less likely to be a singular burst in emissions. The timing and intensity of these events will have to be determined for each major crop type in a region of interest.

3.5.2   Ozone formation potential

To assess the ability of agricultural terpenoid emissions and flowering events to impact air quality via the contributions of reactive precursors to ozone and SOA, we developed metrics to compare them to motor vehicle emissions. The ability of a compound to produce ozone is quantified through the use of literature MIR values [$gO_3 g^{-1}$ com-

pound]. We use MIR to compare sources on a similar basis despite differences in NO_x availability as the San Joaquin Valley has a complex spatial distribution of emissions and meteorology. Gasoline exhaust, diesel exhaust, and non-tailpipe emissions have MIR ozone formation potentials (OFPs) of 4.5, 2.5, and 2.0 $gO_3\,g^{-1}$, respectively (Gentner et al., 2013a). For the monoterpene profile observed during the spring (including para-cymene, but excluding β-myrcene which is grouped with the flowering profile), the OFP was calculated to be 4.1 $gO_3\,g^{-1}$. The flowering source profile in Table 6 has an OFP of 3.6–5.4 $gO_3\,g^{-1}$ with the range of potential values for unknown values determined from compounds with similar structures and general values provided with the framework. Linalool, which comprises 44 % of the flowering profile, has a known OFP of 5.4 $gO_3\,g^{-1}$. These calculated values infer that per mass of emissions, the biogenic emissions have a greater ability to produce ozone than gasoline emissions. This effect may be slightly reduced as terpenoids are generally more reactive with ozone, and will also act as a loss mechanism for tropospheric ozone. Overall, we observed that crops are relatively minor emitters of isoprene, a highly effective ozone precursor. Emissions of isoprene from natural vegetation, such as the oak trees in the foothills surrounding the San Joaquin Valley, play an important role in ozone formation and must also be considered in modeling efforts.

3.5.3 Secondary organic aerosol formation potential

Predicting the exact SOA yields and formation from flowering-related compounds is not feasible given the high level of uncertainty associated with predicting SOA yields for these compounds as many of them have barely been studied. However their potential to form SOA can be estimated using literature on well-characterized Δ-limonene and α-pinene yields from OH oxidation and ozonolysis experiments (Saathoff et al., 2009; Kim et al., 2012), and work by Ng et al. (2006) that compares a suite of terpenoid compounds including Δ-limonene and α-pinene. SOA yields from Δ-limonene and α-pinene range from 0.25–0.35 and 0.1–0.2 $gOA\,g^{-1}$, respectively, for ozonolysis at an organic particle loading of 10 $\mu g\,m^{-3}$ (Saathoff et al., 2009). SOA yields from OH

oxidation at similar particle loadings are significantly lower at approximately 0.05 and 0.04 gOA g^{-1} for Δ-limonene and α-pinene, respectively (Kim et al., 2012). Given the lifetimes to OH and O$_3$ presented in this work, that implies average SOA yields of 0.1 and 0.07 gOA g^{-1} at OA = 10 µg m^{-3}. Assessing the behavior of other monoterpenoids associated with flowering and their reaction rates with OH and O$_3$ suggests a slightly lower SOA yield for β-myrcene than α-pinene and an SOA yield for linalool around 0.004. So overall this infers that under similar loadings, the monotepenoid emissions have a greater SOA yield than the gasoline exhaust (0.023 ± 0.007 gOA g^{-1}), but not quite that of diesel exhaust (0.15 ± 0.07 gOA g^{-1}) based on the yields for gasoline and diesel derived in Gentner et al. (2012). Estimating SOA yields for the benzenoids associated with flowering is much more difficult given the uncertainties, but SOA yields for C$_{7-8}$ aromatics in Gentner et al. (2012) were approximately 0.05 gOA g^{-1} compound for OH oxidation at an organic particle loading of 10 µg m^{-3}. So benzenoid compounds can be assumed to be 0.05 gOA g^{-1} or greater given their decreased initial volatility due to initially present functional groups. In general, this work identifies the critical research need to improve estimates of SOA yields from the biogenic compounds discussed in this study through theoretical or experimental studies.

3.5.4 Overall comparison in the San Joaquin Valley

Detailed modeling using spatially resolved chemical models coupled with emissions will be necessary to fully understand the relative impact of biogenic emissions on air quality using the new information derived in this study. Here we use this information and the case study of the San Joaquin Valley in a back-of-the-envelope calculation to demonstrate the need for further modeling based on the magnitude of emissions from agricultural crops and their potential ozone and SOA. Considering the spatial distribution of emissions and chemistry are essential to account for transport and NO$_X$ emissions/chemistry, but the objective here is to inform the necessity of that future research. The work presented here addresses emissions of monoterpenoids and larger

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compounds, and does not include isoprene or small oxygenated VOCs and alcohols that are also emitted from vegetation. As the focus is on the relative impacts of agriculture, we do not consider the potential transport of emissions from natural vegetation (e.g. pine trees, oak trees) in the foothills or mountains. We use available metrics from literature to assess potential ozone and SOA formation with the caveat that they may not fully capture the differences in NO_x availability and thus the chemical regimes between urban and rural areas in the valley. It is with these caveats that we estimate the magnitude of emissions from agricultural vegetation relative to motor vehicles and their potential to impact air quality.

Based on fuel sales for the valley and the results of Gentner et al. (2012, 2013a), gas-phase gasoline exhaust emissions are 1.8×10^8 g day^{-1}, non-tailpipe gasoline emissions are 4.6×10^7 g day^{-1}, and diesel emissions are 4.6×10^7 g day^{-1}. Together this combines to 2.7×10^8 g day^{-1} and an ozone formation potential of 1.0×10^9 g O_3 day^{-1}, with the reactivity dominated by gasoline sources. Using the SOA yields from Gentner et al. (2012), potential SOA from motor vehicles is 8.0×10^6 g OA day^{-1} (Table 8).

Biogenic emissions from agriculture are estimated using a range of emission factors from agriculture measured in the greenhouse study that is consistent with the range of input BEFs into the BEIGIS model; leaf scale BEFs of 80–3000 ng C (gDM)$^{-1}$ h^{-1} correspond to field-level emission factors of 0.1–2 nmol m^{-2} s^{-1}, given a mean specific leaf area of 85 cm^2 g^{-1} and a canopy leaf area index of 3.0 m^2 leaf area m^{-2} land area (Fares et al., 2012b). These leaf mass density and leaf area factors are derived from the orange orchard, and are applied here with caution to the diversity of crops found in the Valley. This range of estimates includes the summertime BEF measured in the orange orchard (0.13 nmol m^{-2} s^{-1}) (Fares et al., 2012a). We assume a total land cover by agriculture of 3 million acres in the San Joaquin Valley (Table 1).

In terms of total mass from agricultural sources, baseline monoterpene emissions are estimated to be on the same order as anthropogenic sources with a range of 0.1–3×10^8 g day^{-1}. The CARB emission inventory of 1.8×10^7 g monoterpenes day^{-1} from agriculture in the San Joaquin Valley is at the low end of our estimated range. Our

estimated emission factor does not include sesquiterpenes and emissions during flow-ering or other emission events, which will increase emissions by 24× and at least 2×, respectively, with the timing depending on the diversity of crop types and management practices.

With regard to the production of ozone from organic precursors, monoterpene emissions from agriculture have the ability to produce $0.6–12 \times 10^8 \, g \, O_3 \, day^{-1}$, making them equally important as organic emissions from motor vehicles, but further analysis with NO_X sensitivity is essential to elucidate the relative importance for the region. As this is a baseline value, it is evident that emissions occurring during flowering will have a major impact on ozone production given the substantial increase in emissions, and additional considerations for sesquiterpene emissions will increase ozone production as well.

Estimating SOA has a significant amount of uncertainty associated with it, but for comparison with motor vehicles we estimate that monoterpene emissions from agriculture can contribute $1–30 \times 10^6 \, g \, OA \, day^{-1}$, across the range of emissions and SOA yields (at $10 \, \mu g \, m^{-3}$). This means that baseline monoterpene emissions have a similar ability as motor vehicles ($8.0 \times 10^6 \, g \, OA \, day^{-1}$) to produce SOA and does not include sesquiterpene emissions or other emission events such as flowering. The valley-wide magnitude of flowering emissions is highly uncertain and warrants further work. Rough estimates with a range of flowering emissions are given with potential ozone and SOA formation in Table 8.

3.5.5 Citrus: a case study on the net effect of agricultural crops on ozone uptake and formation

Many woody-plants, including orange trees, remove some ozone from the ambient atmosphere via uptake through their stomata. This process, stomatal deposition, along with soil/plant surface deposition and the reaction of ozone with reactive biogenic compounds in the air produces a flux of ozone into the plant canopy, which was measured for a full year at the Lindcove field site. Chemical deposition via reaction with BVOCs

was estimated to be 10–26 %, while stomatal deposition and soil deposition were each responsible for approximately ∼ 30 % of ozone losses (Fares et al., 2012b). A full discussion of these fluxes and their partitioning into different mechanisms has been published elsewhere (Fares et al., 2012b).

To determine the net effect of the orange orchard on regional ozone, we compared the measured ozone flux into the canopy with the amount of ozone likely to be produced downwind based on emissions and OFP values. Monoterpene BEFs from the field site for spring and summer were used from Fares et al. (2012a), with the summer flux multiplied by 2 during non-flowering emission events (harvest, pruning, fertilizer application) when emissions measured by PTR-MS exceeded modeled emissions. Based on the work of Ormeno et al. (2010) sesquiterpene emissions were assumed to be equivalent to monoterpene emissions and were assumed to have an OFP of 4 $gO_3 g^{-1}$ based on the range of potential OFPs. Emissions of floral compounds during the spring flowering period were estimated by multiplying monoterpene emissions by 4.0 per the results of Fig. 2. Additionally, downwind chemical removal of ozone beyond the measured flux reported previously (Fares et al., 2012b), was accounted for using the monoterpene emissions and the probability of reaction with ozone. Figure 9 summarizes the results of this analysis with total emissions, ozone fluxes into the canopy, ozone production, and the net effect. The net effect on a weekly timescale of these processes is shown in Fig. 10 over the period of ozone exceedances in the region. The orchard is a net source of ozone in the springtime during flowering, and is neither a major source nor sink for most of the summer. The orchard is a sink in the fall and in the early spring before flowering begins. Given that flowering occurs at different times for different crops throughout the valley, that time period's net ozone production may not translate to a valley-wide effect. The net effect of ozone deposition was not included in the previous basin-wide comparison of agriculture to motor vehicles as exhaust emissions contain significant amounts of alkenes that can also remove ozone initially.

3.5.6 Implications

This work has demonstrated the importance of biogenic organic carbon emissions from agricultural crops relative to vehicular emissions in terms of total emissions and the formation of ozone and SOA in the San Joaquin Valley. Further highly resolved modeling of emissions and chemistry is warranted based on this new information. Recent work examined flowering emissions in the urban area of Boulder, CO and temporarily incorporated flowering into the MEGAN model (Baghi et al., 2012). The study concluded the impacts of flowering in Boulder, CO were minor (equivalent to 11 % of the monoterpene flux). Our results suggest a larger temporary annual impact of flowering in agricultural regions with high densities of flowering foliage, but is dependent on the composition of crops and flowering timing. When the magnitude of the flowering event is considered across a region, it may have a substantial effect on the biogenic emission inventory and likely on atmospheric composition and air quality, especially in regions prone to air quality problems. It is important to note that the majority of flowering occurs in the spring, conveniently before the primary periods of ozone exceedances in the San Joaquin Valley when contributions to ozone precursors would be particularly important.

The newly characterized compounds in this study should be included in the MEGAN and BEIGIS models since their emissions during flowering were on the same order as or greater than all the terpenoids observed. Further work is necessary to better characterize the basal emission factors, dependent parameters, and, in the case of the novel compounds, their ozone and SOA formation potential. Emissions due to flowering and other seasonal events need to be assessed for other major crops, and possibly natural vegetation. The modeling of biogenic emissions from agriculture has a major advantage over natural vegetation: the ability to gain more detailed information on the composition of vegetation species. This data, along with emission factors provides the necessary components to more regional emissions and potentially identify potential regional changes in emissions with shifts or rotations in crop plantings.

Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/13/28343/2013/ acpd-13-28343-2013-supplement.pdf.

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Table 1. Planted areas for permanent crops with largest land cover in the San Joaquin Valley.

Crop	Acreage
Cotton	653 000
Maize	501 000
Almonds	453 000
Grapes (Raisin Varieties)	241 000
Tomatoes	222 000
Walnuts	124 000
Navel Oranges	124 000
Pistachios	97 024
Grapes (Table Varieties)	84 900
Peaches	51 300
Apples	15 800

Data from 2002 crop reports, respective county
Agriculture Commissioners' offices.

Table 2. Basal emission factors ($ng\,C\,(gDM)^{-1}\,h^{-1}$) and beta values for monoterpenes, oxygenated monoterpenes and sesquiterpenes from enclosure studies (N = sample size, r = correlation coefficient).

Crop	Monoterpenes		Oxygenated Monoterpenes		Sesquiterpenes	
	BEF±StDev (N)	Beta (r)(N)	BEF ± StDev (N)	Beta (r)(N)	BEF ± StDev (N)	Beta (r)(N)
Alfalfa	270 ± 160 (2)	0.10 (0.84)(11)	N.D.		N.D.	
Almond	68 ± 51 (23)[24]	0.065 (0.23)(157)a	150 ± 28 (6)[24]	0.16 (0.90)(32)	10 000 ± 3300 (6)[24]	0.45 (0.92)(31)
Carrot (RL)	78 ± 45 (15)[25]	N.B.	22 ± 12 (3)[25]	0.099 (0.51)(11)	N.D.	
Carrot (BN)	48 ± 36 (43)[27]	0.063 (0.29)(166)a			56 ± 36 (3)[27]	N.B.
Cherry	84 ± 59 (26)[26]	0.067 (0.34)(121)a	670 ± 250 (16)[26]	0.30 (0.94)(40)	N.D.	
Corn	N.D.		N.D.		N.D.	
Cotton Pima	47 ± 21 (10)[27]	0.027 (0.25)(31)a	2700 ± 3100 (5)	0.13 (0.35)(26)	N.D.	
Cotton Upland	41 ± 16 (4)	0.12 (0.74)(16)	81 ± 83 (4)	0.18 (0.26)(7)	N.D.	
Table Grape	11 ± 4.9 (2)[28]	N.B.	26 ± 13 (5)	0.029 (0.27)(23)	45 ± 15 (5)	0.095 (0.69)(13)
Wine Grape	91 ± 50 (13)[27]	0.17 (0.67)(20)	44 ± 10 (3)[25]	N.B.	52 ± 22 (8)[27]	N.B.
Liquidambar	350 ± 260 (31)[26]	0.098 (0.35)(174)a	47 ± 4.8 (2)[26]	0.19 (0.94)(4)	N.D.	
Miscanthus	140 ± 89 (17)[27]	0.044 (0.20)(63)a	48 ± 19 (6)[28]	0.16 (0.80)(11)	180 ± 31 (6)[28]	0.076 (0.76)(11)
Olive	60 ± 32 (8)[26]	0.15 (0.68)(28)	7.5 ± 0.91 (2)[26]	0.066 (0.51)(4)	N.D.	
Onion	350 ± 110 (3)[28]	N.B.	N.D.		N.D.	
Peach	1200 ± 270 (2)[24]	0.23 (0.97)(10)	240 ± 55 (2)[24]	0.23 (0.97)(10)	N.D.	
Pistachio	40 ± 22 (47)[28]	0.098 (0.47)(207)a	39 ± 55 (15)[26]	0.15 (0.36)(22)a	N.D.	
Plum	37 ± 20 (5)[26]	0.010 (0.04)(26)a	30 ± 11 (4)[28]	0.14 (0.68)(6)	N.D.	
Pomegranate	32 ± 26 (4)[25]	N.B.	26 ± 9.8 (4)[27]	0.14 (0.78)(5)	61 ± 8.6 (5)[27]	0.024 (0.23)(9)a
Potato	150 ± 9.8 (3)[24]	0.064 (0.47)(16)a	22 ± 9.3 (3)[27]	N.B.	40 ± 13 (3)	N.B.
Tomato	740 ± 260 (7)[27]	0.11 (0.31)(68)a	N.D.		59 ± 15 (3)[27]	N.B.
Orange P.N. (No Flowers)	2500 ± 3400 (116)[26]	0.14 (0.35)(522)a	1300 ± 1900 (33)[26]	N.B.	1500 ± 970 (20)[25]	0.25 (0.74)(58)
Orange P.N. (Flowers)	7800 ± 4300 (36)[26]	0.15 (0.71)(151)	4600 ± 1300 (11)[24]	0.072 (0.38)(36)a	3200 ± 780 (11)[24]	0.28 (0.92)(36)
Mandarin W. Murcott	63 ± 25 (20)[28]	0.080 (0.47)(99)a	150 ± 190 (8)[29]	0.23 (0.79)(20)	N.D.	
Mandarin Clementine	26 ± 18 (22)[26]	0.064 (0.27)(141)a	N.D.		N.D.	
Lemon Eureka	22 ± 22 (24)[25]	0.036 (0.15)(166)a	N.M.		N.M.	

Notes: N.M. = No Measurements, N.D. = Below Detection Limit, N.A. = No Basal Condition Met, N.B. = Beta Value Analysis Inaccurate.
When the BEF was determined at a lower temperature and adjusted, the temperature it was determined at is indicated after the BEF as [°C], the value was adjusted using the calculated beta unless the correlation coefficient for beta was below 0.5, then a default beta of 0.1 was used and the beta column is marked with a. Data on citrus species measured in the same greenhouse campaign are reproduced from Fares et al. (2011) for comparison to the other crops and assessment of implications on air quality. Chemical speciation of emissions can be found in Tables S2–S5.

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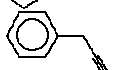Conclusions | References

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Table 3. Interquartile ranges [pptv] for measured biogenic compounds in spring and summer.

| | Spring (Flowering) | | Summer | |
Compound	Day (10:00–17:00)	Night (20:00–6:00)	Day (10:00–17:00)	Night (20:00–6:00)
isoprene	24.8–67.4	55.5–375.8	61.3–197.8	107.4–852.8
α-thujene	3.8–13.7	16.4–122.0	2.5–3.7	4.6–19.1
α-pinene	6.9–13.0	12.6–90.8	3.2–6.8	5.4–20.7
camphene	4.4–6.8	6.2–40.2	3.7–7.7	7.0–26.5
sabinene	23.6–67.6	62.7–977.5	11.5–23.2	15.7–33.7
β-myrcene	324.1–1143.2	407.9–2285.4	4.4–9.3	8.4–49.8
β-pinene	BDL-17.7	12.8–52.3		
α-phellandrene	1.3–3.1	2.1–5.1	2.3–6.7	7.0–35.1
cis-3-hexenyl acetate	165.3–353.7	213.3–790.2		
Δ3-carene	23.0–51.1	37.0–162.0	3.2–5.2	5.2–38.5
Benzaldehyde	69.5–276.0	78.6–434.3		
α-terpinene	5.3–12.0	12.0–102.1		
cis-β-ocimene	23.9–65.9	39.5–162.5		
trans-β-ocimene	134.8–380.3	197.6–1267.1		
Δ-limonene	183.6–365.0	275.2–2250.5	158.9–271.9	204.1–1606.0
p-cymene	17.8–41.1	26.0–238.6	7.8–16.6	16.4–176.5
γ-valeroactone	6.2–11.3	11.2–103.3		
γ-terpinene	16.4–32.4	30.6–247.6	1.6–7.5	4.1–15.5
terpinolene	6.7–15.6	14.2–85.8	1.7–2.7	6.8–22.2
trans-linalool oxide	1.7–5.1	3.3–18.0		
cis-linalool oxide	9.2–14.9	11.6–50.6		
benzeneacetaldehyde	57.1–242.4	86.8–455.7		
linalool	1657.3–6037.5	2436.4–18 342.1		
lavender lactone	122.5–278.6	216.3–1033.1		
sabina ketone	16.8–111.9	58.8–255.1		
2-amino-benzaldehyde	174.0–443.1	189.2–806.2		
indole	984.6–2707.4	1408.4–3696.6		
methyl anthranilate	906.6–2742.4	1151.8–6856.5		
benzeneethanol	188.2–420.4	215.8–966.7		
benzyl nitrile	836.6–1780.8	971.7–3212.2		
methyl benzoate	14.9–32.8	19.8–57.6		
β-caryophyllene	9.7–19.6	7.0–18.4		
aromadendrene	7.2–25.0	10.2–31.9		
trans-β-farnesene	3.1–21.5	6.9–41.7		
valencene	BDL-17.1	13.3–59.2		
trans-Nerolidol	22.7–150.9	64.0–301.1		
n-pentadecane	12.6–29.5	14.6–35.8		
n-hexadecane	8.1–37.3	5.4–34.9		
n-heptadecane	36.6–83.7	38.7–101.4		
8-heptadecene	1.2–7.1	2.0–52.0		
1-heptadecene	79.0–204.3	105.5–285.5		
hexanal	35.8–162.7	81.0–337.8		
octanal	11.6–25.3	17.3–73.9		
nonanal	55.0–120.4	68.6–184.2		
decanal	6.9–21.1	11.3–40.1		

Notes: Entries left blank indicate that compound was not observed during the summer campaign.
BDL: Below Detection Limit.

Table 4. Novel compounds from measurements of ambient air during flowering.

Name(s)	Structure	k_{OH} [cm^3 s^{-1} molecules^{-1} × 10^{11}]	Lifetime to OH oxidation [min]
Indole		15.4	20
Methyl Anthranilate (benzoic acid, 2-amino-, methyl ester)		3.48	89
Benzeneacetaldehyde (phenyl acetaldehyde)		2.63	117
Benzeneethanol (phenylethyl alcohol)		0.957	323
Benzyl Nitrile (benzneacetonitrile)		0.962	321
Lavender Lactone (γ-lactone, dihydro-5-methyl-5-vinyl-2(3H)-furanone)		2.76	112
Methyl Benzoate (Methyl Benzenecarboxylate, Niobe Oil)		0.0844	3660
Sabina Ketone (5-isopropylbicyclo[3.1.0]hexan-2-one)		0.626	493
2-amino-benzaldehyde		5.23	59

Notes: Chemical Structures from NIST Chemistry WebBook http://webbook.nist.gov/chemistry/
[OH] = 0.25 pptv.

Table 5. Compounds highly correlated with flowering emissions (represented by β-myrcene).

Compound	mol mol^{-1} β-myrcene	±Std. Dev.	Correlation Coeff. (r)
linalool	7.1	0.2	0.92
methyl anthranilate	1.2	0.04	0.95
indole	0.62	0.02	0.93
benzyl nitrile	0.38	0.03	0.78
Δ-limonene	0.35	0.03	0.73
trans-β-ocimene	0.31	0.01	0.93
benzeneacetaldehyde	0.26	0.02	0.76
2-amino-benzaldehyde	0.23	0.007	0.95
benzeneethanol	0.22	0.007	0.94
lavender lactone	0.18	0.01	0.78
cis-3-hexenyl acetate	0.15	0.006	0.93
benzaldehyde	0.081	0.006	0.78
1-heptadecene	0.040	0.002	0.91
cis-β-ocimene	0.025	0.002	0.79
Δ3-carene	0.023	0.002	0.79
cis-linalool-oxide	0.015	0.0005	0.93
octanal	0.014	0.0009	0.82
n-heptadecane	0.011	0.0006	0.85
terpinolene	0.0096	0.0009	0.70
methyl benzoate	0.0071	0.0006	0.75
valencene	0.0067	0.0005	0.83
decanal	0.0060	0.0006	0.71
aromadendrene	0.0048	0.0002	0.88
n-pentadecane	0.0041	0.0002	0.91
trans-linalool oxide	0.0032	0.0003	0.76
β-caryophyllene	0.0030	0.0002	0.83

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Table 6. Source profile for flowering emissions from citrus trees.

Compound	
linalool	44.3 %
methyl anthranilate	17.0 %
indole	10.1 %
benzyl nitrile	8.0 %
β-myrcene	7.9 %
cis-3-hexenyl acetate	2.3 %
benzeneethanol	2.2 %
lavender lactone	1.9 %
2-amino-benzaldehyde	1.9 %
1-heptadecene	1.2 %
benzaldehyde	1.0 %
benzeneacetaldehyde	0.92 %
sabina ketone	0.61 %
n-heptadecane	0.44 %
methyl benzoate	0.17 %
cis-linalool oxide	0.12 %
trans-linalool oxide	0.04 %
8-heptadecene	0.04 %

Table 7. Summary of monoterpene composition for both seasonal campaigns at Lindcove.

Compound	Spring (Flowering)	Summer
β-myrcene	34.2 %	2.4 %
sabinene	12.8 %	2.2 %
Δ-limonene	24.2 %	87.6 %
γ-terpinene	2.0 %	1.0 %
cis-β-ocimene	2.9 %	–
trans-β-ocimene	13.6 %	–
α-thujene	1.7 %	1.1 %
Δ3-carene	3.7 %	1.3 %
α-pinene	0.7 %	0.80 %
α–terpinene	0.77 %	–
α–phellandrene	0.93 %	1.3 %
terpinolene	0.84 %	0.7 %
β–pinene	0.91 %	2.60 %
camphene	0.70 %	1.6 %

Table 8. Metrics of secondary pollutant formation, emissions, and potential impacts of biogenic emissions from agricultural crops compared to motor vehicles in California's San Joaquin Valley.

	Ozone Formation Potential [$g\,O_3\,g^{-1}$]	SOA Yield [$g\,OA\,g^{-1}$]	Emission Estimates for SJV [$10^{-7} \times g\,d^{-1}$]	Potential Production	
				Ozone [$10^{-8} \times g\,O_3\,d^{-1}$]	SOA [$10^{-6} \times g\,OA\,d^{-1}$]
Agriculture: Monoterpenes	4.1	~ 0.1	1–30[a]	0.6–12	1–30
Agriculture: Flowering Compounds	3.6–5.4	~ 0.03[b]	24–720[c]	8.6–390	7.2–220
Gasoline Exhaust[d]	4.5	0.023 ± 0.007	18	8.0	2.7
Non-tailpipe Gasoline Emissions	2.0	0.0024 ± 0.0001	4.6	0.93	0.1
Diesel Exhaust[d]	2.5	0.15 ± 0.07	4.6	1.2	5.1

References: Vehicular ozone formation potential values are MIR values from Gentner et al. (2013a).

[a] Range is set as BEF $= 80$–$3000\,ng\,C\,(gDM)^{-1}h^{-1}$.

[b] SOA yield for flowering is lower estimate assuming a conservative yield of 0.05 for unstudied aromatics. Linalool (44 % of flowering source profile) has a very low SOA yield as well (0.004).

[c] Estimated as 24× baseline monoterpene emissions.

[d] Both gasoline and diesel exhaust include products of incomplete combustion (excluded in SOA calculations per Gentner et al., 2012) and gasoline exhaust also includes cold start emissions (estimated as equivalent to 60 % of gasoline running exhaust (Gentner et al., 2013a).
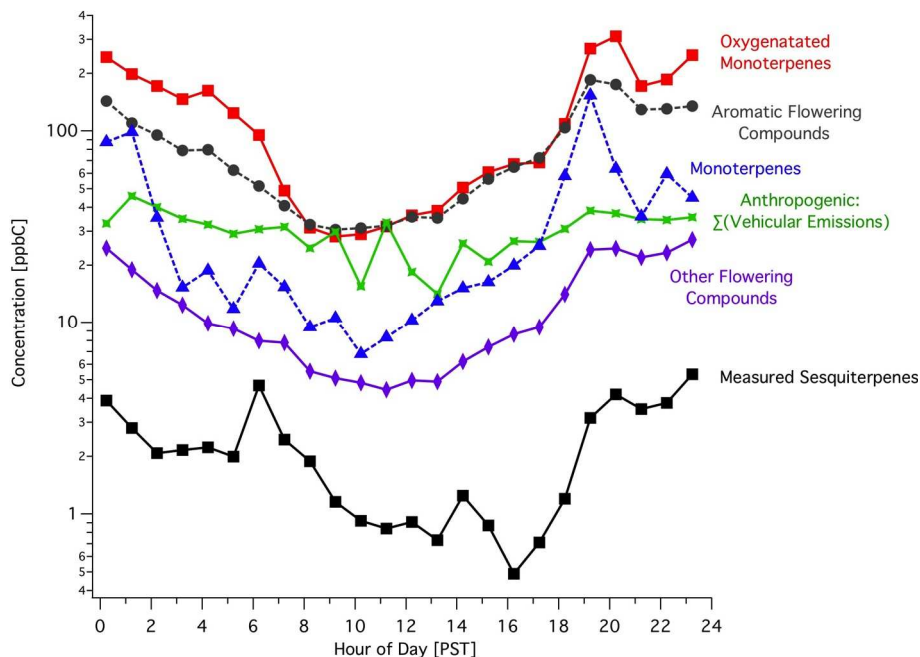
Fig. 1. Average diurnal patterns of different compound classes shown on a logarithmic scale during flowering at the Lindcove site. Anthropogenic emissions from motor vehicles are shown for comparison. Floral emissions of oxygenated monoterpenes and aromatics dominate total biogenic emissions. Observed sesquiterpenes are lower than total sesquiterpenes as not all sesquiterpenes could be quantified.

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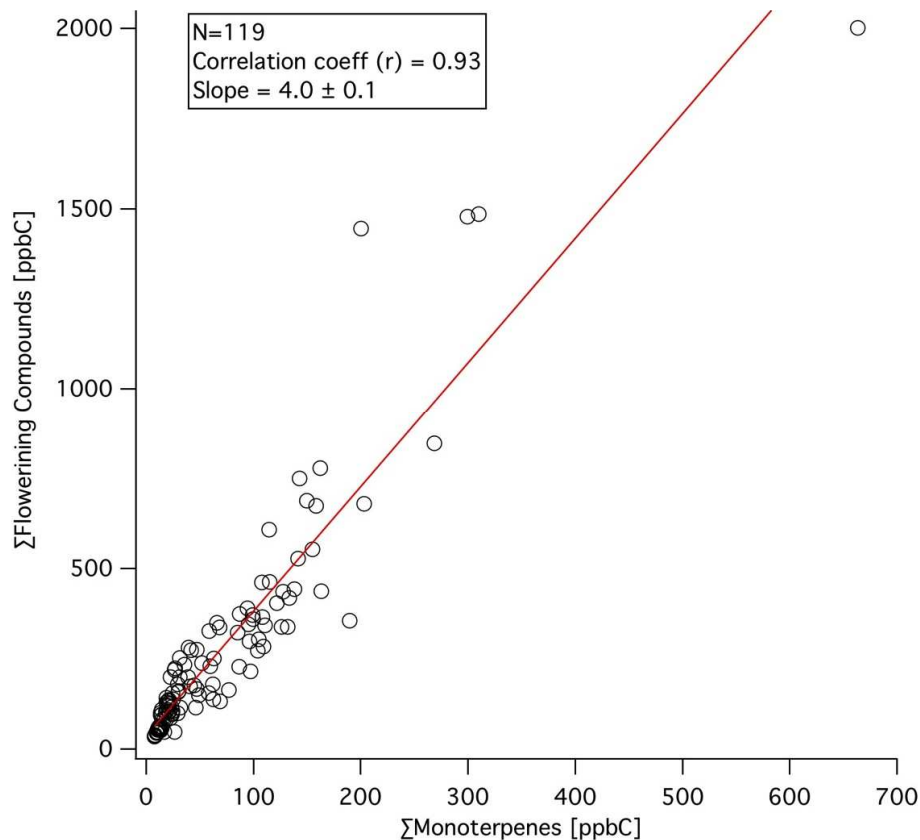
Fig. 2. Comparison of total observed flowering compounds to the sum of monoterpenes during the spring at the Lindcove site. Concentrations were well correlated with a slope of 4.0, but can be expected to vary somewhat with the density of blossoms over the whole period of flowering.

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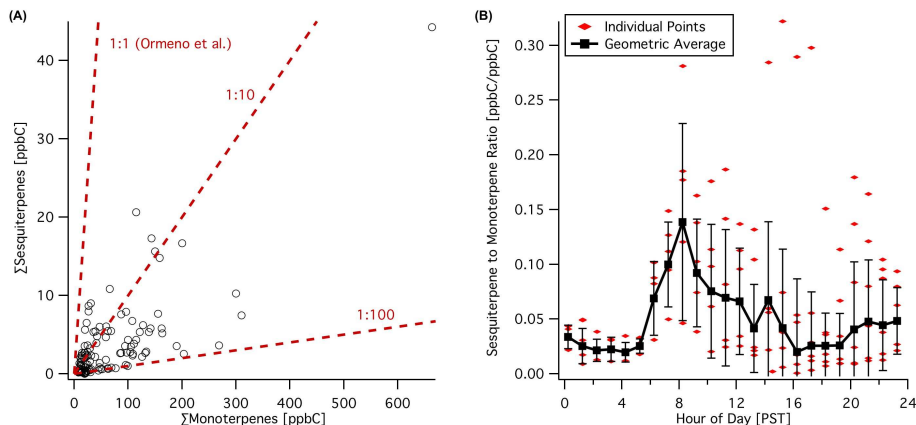
Fig. 3. (A) The comparison of quantified sesquiterpenes to monoterpenes during the spring at Lindcove show considerable variance in their ratio to each other. The 1 : 1 ratio expected by Ormeno et al. (2010) is shown, but is not reached due to measurements of a partial suite of sesquiterpenes and their greater atmospheric reactivity. **(B)** The diurnal pattern of sesquiter-penes to monoterpenes shows a higher ratio during the day than at night. Ratios are the highest early in the morning possibly due to lower levels of atmospheric oxidants (OH and O_3) in the morning and the presence of fresh presence of fresh emissions accumulating after sunrise in a shallow boundary layer.

Fig. 4. Diurnal pattern and composition of monoterpenes in **(A)** spring during flowering and in **(B)** summer.

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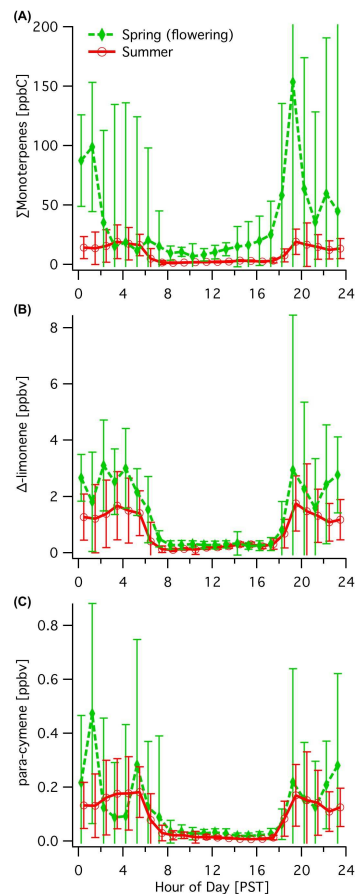
Fig. 5. Seasonal comparison of diurnal concentration patterns for **(A)** total monoterpenes, **(B)** Δ-limonene, and **(C)** para-cymene shown with standard deviations. The seasonal comparison of Δ-limonene and para-cymene concentrations demonstrates similar seasonal abundances that are slightly higher during flowering.

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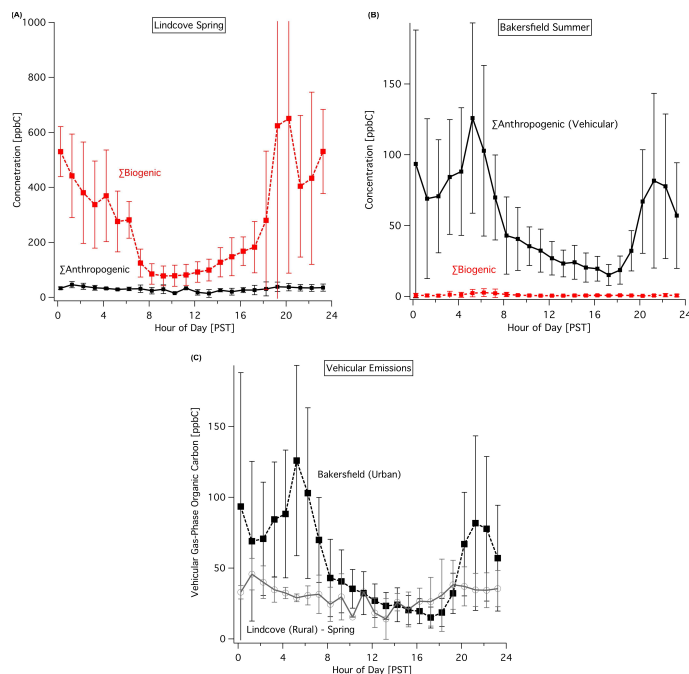
Fig. 6. Diurnal patterns of the sum of biogenic compounds vs. anthropogenic compounds from motor vehicles at the **(A)** Lindcove orange orchard site in the spring and **(B)** the urban Bakersfield site (biogenic compounds are largely monoterpenes). **(C)** A comparison of motor vehicle compound concentrations between the Bakersfield and Lindcove site shows similar daytime levels, but nighttime and morning values vary due to the build-up of local emissions in the nocturnal boundary layer.

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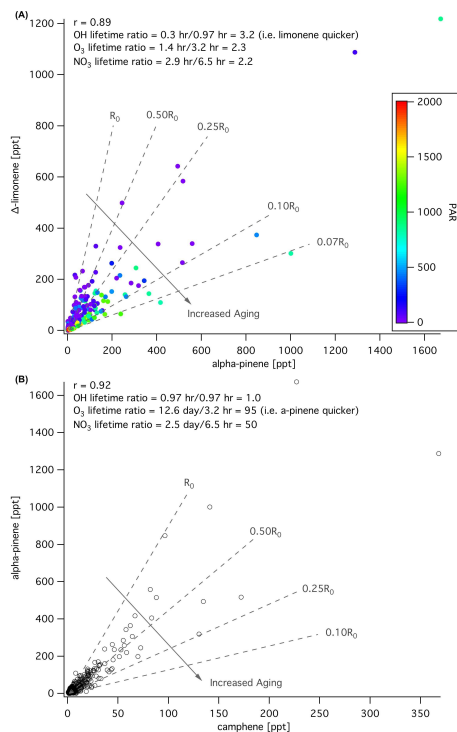
Fig. 7. Observations of monoterpene pairs at the Bakersfield site. **(A)** Δ-limonene vs. α-pinene. Ratios of lifetimes to all three atmospheric oxidants show faster processing of Δ-limonene. Given the concentrations of radicals, OH oxidation has the fastest timescales and the importance of OH oxidation is also indicated by the most aged parcels coinciding with PAR (representative of OH production). **(B)** A comparison of α-pinene vs. camphene at Bakersfield shows evidence of aging by O_3 and NO_3 as α-pinene and camphene's lifetimes to OH are identical.
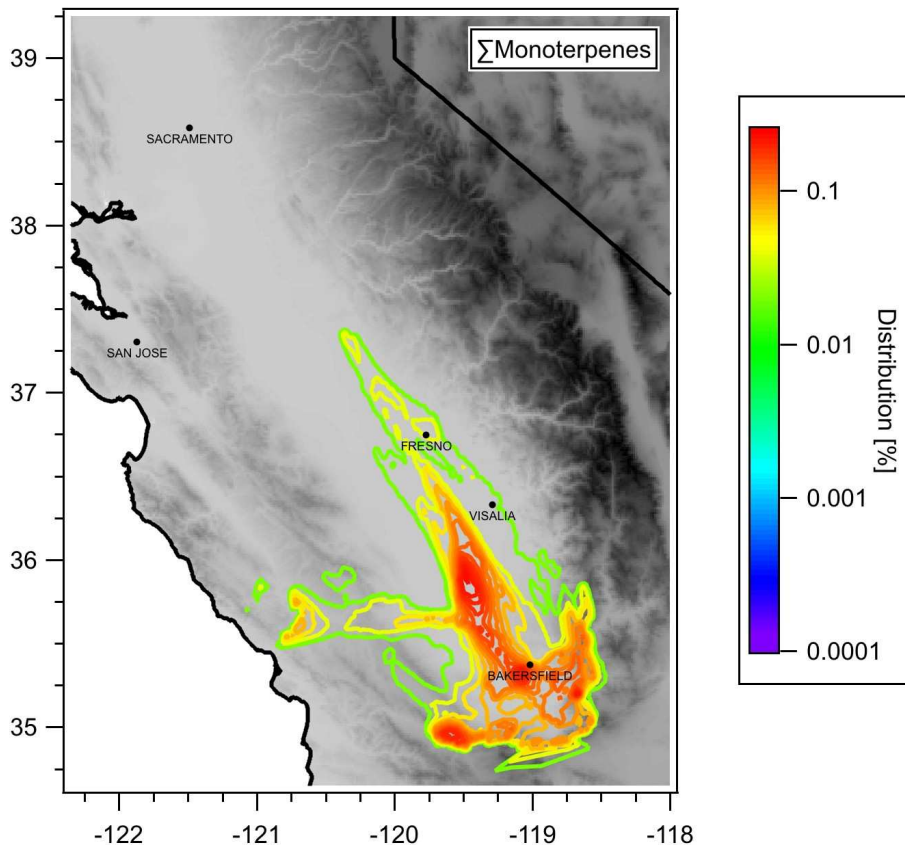
Fig. 8. Spatial distribution of monoterpene sources in the southern San Joaquin Valley shown using the statistical source footprint of the sum of monoterpenes over 6 h of transport prior to arrival at the CalNex ground site in Bakersfield, CA.
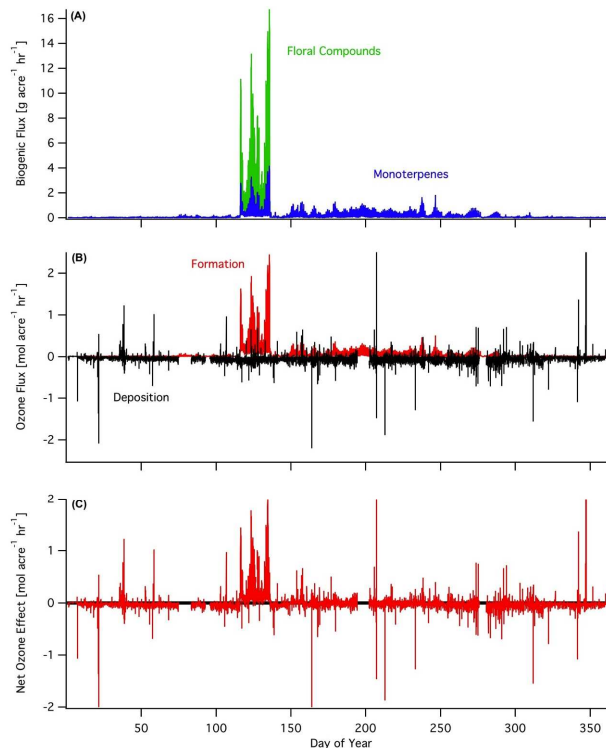
Fig. 9. The components of the net ozone flux for the Lindcove orange orchard. **(A)** Modeled fluxes of monoterpenes and floral compounds are greatest in the spring during flowering, but are significant throughout the summer. Sesquiterpene emissions are assumed to be equivalent to monoterpene emissions. **(B)** Ozone formation and deposition fluxes per acre throughout the year show variable ozone formation with more constant deposition (stomatal and chemical). Formation is calculated as potential O_3 (i.e. assuming a VOC-limited regime). **(C)** The combined effect of these fluxes produces a net flux into the canopy except when biogenic emissions are high.

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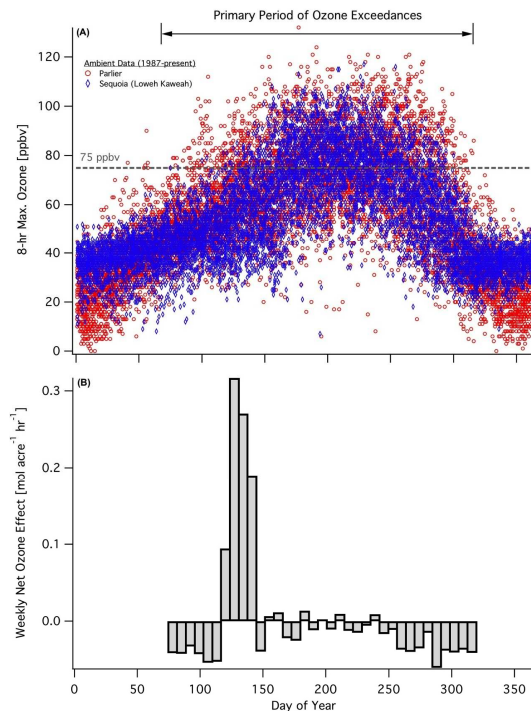Back | Close

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Fig. 10. (A) Ambient ozone data since 1987 (CARB) show exceedances above 75 ppbv at both the center of the valley and downwind in the Sierra Nevada mountains with the primary period of concern from day 70 to 320. No trends were apparent in the data from 1987 till present. **(B)** The weekly net effect of the orange orchard on ozone over this period is shown to be net source of ozone in the springtime during flowering, and relatively neutral for most of the summer until the fall when it becomes a sink.