# Flux Measurements of Biogenic Precursors to Ozone and Particulate Matter in the Central Valley

**DRAFT FINAL REPORT**

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**Principal Investigator**

Professor Allen H. Goldstein

Department of Environmental Science, Policy and Management
University of California at Berkeley

**Co-Principal Investigator**

Dr. John F. Karlik
University of California Cooperative Extension
Bakersfield

**Contributing Researchers**

Dr. Silvano Fares, Post-Doctoral Researcher, UC Berkeley
Dr. Elena Ormeno Lafuente, Post-Doctoral Researcher, UC Berkeley
Drew Gentner, PhD Candidate, UC Berkeley
Jeong-Hoo Park, PhD Candidate, UC Berkeley
Robin Weber, Staff Research Associate, UC Berkeley
Megan McKay, Staff Research Associate, UC Berkeley


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## GLOSSARY of SYMBOLS and ACRONYMS

| | |
|---|---|
| ARB | California Air Resources Board |
| BEIGIS | Biogenic Emission Inventory Geographical Information System |
| BEIS | Biogenic Emission Inventory System (U.S. EPA) |
| BVOC | biogenic volatile organic compounds |
| BEF | Basal Emission Factor |
| $CO_2$ | carbon dioxide |
| EPA | Environmental Protection Agency |
| GAP | Gap Analysis Project |
| GC-FID | gas chromatography-flame ionization detection |
| GC-MS | gas chromatography-mass spectroscopy |
| GIS | geographical information system |
| LAI | leaf area index |
| LMD | leaf mass density |
| LDL | lower detection limit |
| LOD | limit of detection |
| NCAR | National Center for Atmospheric Research |
| NMOC | non-methane organic compound |
| $NO_x$ | oxides of nitrogen ($NO + NO_2$) |
| NO | nitric oxide |
| $NO_2$ | nitrogen dioxide |
| $N_2O$ | nitrous oxide |
| $O_3$ | ozone |
| OVOC | oxygenated volatile organic compounds |
| PAR | photosynthetically active radiation |
| ppbC | parts per billion carbon |
| ppb | parts per billion |
| ppmC | parts per million carbon |
| ppm | parts per million |

## GLOSSARY of SYMBOLS and ACRONYMS (continued)

| | |
|---|---|
| pptC | parts per trillion carbon |
| ppt | parts per trillion |
| PVC | polyvinyl chloride |
| PTRMS | proton transfer reaction mass spectrometer |
| RH | relative humidity |
| ROG | reactive organic gases |
| ROM | Regional Oxidant Model |
| RSI | relative sensitivity index |
| SCAQMD | South Coast Air Quality Management District |
| SCAQMP | South Coast Air Quality Management Plan |
| SJV | San Joaquin Valley |
| SJVAB | San Joaquin Valley Air Basin |
| SJVAQS | San Joaquin Valley Air Quality Study |
| SLA | specific leaf area |
| SoCAB | South Coast Air Basin |
| TPD | metric tons per day |
| UAM | Urban Airshed Model |
| UCB | University of California at Berkeley |
| UCCE | University of California Cooperative Extension |
| VOC | volatile organic compounds |

PROPOSED TASKS AND WORK DESCRIBED IN THIS REPORT

The tasks identified in the original proposal are outlined below. Sections within this report containing results from each task are also identified. This project was divided into a first phase of plant enclosure measurements made in a greenhouse, and a second phase of flux and concentration measurements made at the canopy scale in a field setting.

**Task 1. Choose crops for plant level emission measurements.**

Plant selection was informed by known emission behavior as reported in the literature and the dominant crop types grown in California.

**Task 2. Measurements of BVOC emission using an enclosure**

Plant enclosures at a UCB greenhouse were used to study emissions of crop plants. Crop selection for field flux measurements was informed by the enclosure results.

**Task 3. Canopy Scale Flux Measurements.**

A tower was set up in a citrus orchard with a temperature controlled instrument structure to house analytical instrumentation. BVOC flux and concentration measurements were made above the crop canopy. $CO_2$, $H_2O$, temperature, wind speed, and relative humidity were also measured.

**Task 4. Progress Reports.**

We have delivered via email quarterly progress reports to fit the needs of the ARB project manager.

**Task 5. Draft and Final Reports.**

This report is submitted in fulfillment of Task 5.

**Task 6. Presentation of research results at ARB.**

This presentation remains to be scheduled.

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# ABSTRACT


## Abstract

The Central Valley of California is out of compliance with current air quality standards for ozone and particulate matter (PM). Ozone and PM air quality model simulations focused on the Central Valley are critical for State Implementation Plan development for ozone and particulate matter (PM). Model simulations are sensitive to emission sources, deposition/sinks, chemical reactions, and meteorology. Biogenic volatile organic compounds (BVOCs) participate in ozone and PM formation, and comprise a substantial fraction of ARB VOC emission inventories. Also, as regulatory controls are extended to agriculture, there is a renewed focus on crop biogenic emissions as well as ozone deposition to crops. While inputs to the ARB's BVOC emission inventory model have been evaluated using field measurements, modeled emissions have not been evaluated using in-situ micrometeorological flux measurements for important valley floor crop environments, nor have emissions from native and naturalized plants frequently found in the Central Valley been characterized with recent measurement methods. Enclosure and landscape-scale BVOC flux measurements are both critical for emission model performance evaluation, and for reducing uncertainties in emission inventories. In addition, recent field measurements suggest that emissions of fast reacting terpene species may be significantly underestimated (Kurpius and Goldstein, 2003), and no measurements of emissions from crops are available to evaluate this potential emission for modeling purposes.

Crops cultivated on the valley floor may comprise a large source of monoterpenes, sesquiterpenes, and other compounds, but their emission potentials have not been measured extensively nor with recent measurement techniques.

A two phase study has been conducted. In phase I, BVOC emissions at the branch or whole plant scale were characterized for more than 20 key crop species in a greenhouse. All crops studied had very low emission rates of isoprene. These results are consistent with previous studies in California for several of the same crop species. Emissions of terpenes and oxygenated hydrocarbons (particularly methanol, but also acetaldehyde, and acetone) represented the dominant fraction of the total BVOC emission for the crops studied. Oxygenated VOC dominated emissions for some crops such as tomato, grape, potato, miscanthus, mandarins, and lemon. All crops studied, with the exception of orange, fall in the category of low monoterpene emitters. The 'Parent Navel' orange tree emitted more terpenes than the other crop plants studied, and emissions of terpenoids and many other BVOC increased dramatically during the flowering event. However, emissions from orange per g dry leaf are still far less than emissions from the major BVOC emitting California plant species occurring in the natural environment.

Based on the species we measured, we conclude that the agricultural crops studied generally have low emission rates of isoprene and other terpenoid compounds compared to many plants found in natural or urban landscapes. Based on these phase I data and crop coverage data, a citrus orchard was selected to conduct landscape-scale, micrometeorological BVOC flux measurements.

In phase II, canopy scale flux measurements were performed at the selected citrus orchard site. In-situ measurements were made continuously over a full year of BVOC emissions and micrometeorology to evaluate BVOC emission model performance and improve the representation of emissions and atmospheric processes. Chemical species and micrometeorological variables were measured continuously at high temporal resolution (tens of minutes, hourly) over the course of one year. Vegetation metrics utilized in BVOC emission models were collected simultaneously with the measurements. Measured canopy scale BVOC emission rates of methanol, acetone, isoprene, and monoterpenes are reported. Emissions were generally low, with highest emissions for methanol, then monoterpenes, then acetone, and isoprene emissions were essentially zero. During flowering, harvesting, and pruing, emissions increased substantially for short periods. Continuous ambient speciated VOC measurements were made during two specific study periods including a summer period and a flowering period to assess the biogenic contribution to observed VOCs at different times of the day. A wide array of specific BVOCs were measured with many novel compounds identified that go beyond the traditional terpenoid compounds expected.

Data reported here include emissions of methanol, acetaldehyde, acetone, isoprene, monoterpenes, sesquiterpenes, oxygenated sesquiterpenes, and a variety of other chemicals for the major crop species grown in California. We report basal emission factors and make recommendations for their use in BVOC emission model evaluation and development. This data will be used by ARB staff to reduce uncertainty in BVOC emission inventories for the agricultural regions of California. This project also provides a one year long observational database of BVOC fluxes in a California orange grove demonstrating the diurnal and seasonal cycles of emissions and atmospheric concentrations that can be used to compare with BVOC emission and air quality models.

Even though emissions were generally low, BVOC emitted from crop species may still play a significant role in the chemistry of the atmosphere in areas like in the San Joaquin Valley of California, where there are large areas planted with agricultural crops. Also, events such as flowering, pruning or harvesting when leaves are present may result in pulses of emissions. Therefore, it is important to model emissions for the agricultural landscape as non-zero, and to evaluate the importance of crop BVOC emissions in regional air quality models.

## 1.0 EXECUTIVE SUMMARY

It is now well known that volatile organic compounds (VOC) are emitted from vegetation, including urban landscapes, agricultural crops, and natural plant communities in unirrigated areas. The overall magnitudes of biogenic volatile organic compound (BVOC) emissions of an individual plant are affected by its leafmass and by its intrinsic BVOC emission rates, as well as by environmental factors such as temperature and light intensity. An accurate estimate of the magnitude of BVOC emissions relative to anthropogenic VOC emissions in California's airsheds is critical for formulating effective strategies to reduce concentrations of fine particles, ozone, and other secondary air pollutants which affect human health and reduce yields of agricultural crops.

The contribution of crops cultivated on the Central Valley floor to emissions of monoterpenes, sesquiterpenes, and other compounds could be important for regional air quality, but their emission potentials had not previously been measured extensively. Enclosure measurements from a range of plant species prominent in the Valley, followed by a one year campaign of canopy scale measurements at a specific site was conducted to evaluate biogenic VOC emission potential from crops suitable for advancing emission inventory models.

In Phase 1 (2008-2009), measurements of highly reactive and oxygenated BVOC for major crop types were made via a dynamic enclosure apparatus at UC Berkeley. Highly reactive and oxygenated BVOC emissions of key California crop species were measured with in-situ GC-MS/FID and PTR-MS instruments. Crops were measured under ambient conditions of light and temperature in a greenhouse. Measurements for plant species showed distinct diurnal profiles of

emissions. Light intensity and temperature, which have been shown to be the key variables in BVOC emission, were recorded. The emission measurements were used to develop basal emission factors (BEF) for use by ARB staff in improving the California Biogenic Emission Inventory (BEIGIS) model. The emission behavior of crop plants measured during the first year of the study informed crop selection for the second phase of the study.

In Phase 2, a field site was developed in a citrus orchard near Visalia California for measuring canopy scale BVOC fluxes. The site included a telescoping tower to hold inlet lines and sensors, and a temperature controlled container to house analytical instrumentation. For one full year, canopy level flux measurements were made in-situ above the crop canopy via PTR-MS with eddy covariance, with concurrent eddy covariance flux measurements of BVOC, $CO_2$, $H_2O$, and $O_3$. Concentration measurements of speciated VOC and meteorological data were collected simultaneously during a spring flowering period and a summer period.

Previous modeling of crop emissions at regional and global scales has been poorly constrained due to lack of information about the species-specific BEF and temperature and light dependence. The results reported here can now be used as input parameters for new modeling efforts. Specifically, our results are intended for use in the California ARB's BEIGIS Model and the MEGAN (Model of Emissions of Gases and Aerosols from Nature) model developed by Guenther et al. (2006) to provide more detailed estimates on the regional and global BVOC emissions from crops, thus decreasing the error in model emission estimates, and providing more accurate inputs for regional air quality models.

All crops studied had very low emission rates of isoprene. These results are consistent with previous studies in California for several of the same crop species Therefore, the BEF reported in Guenther et al. of 16000 ng(C) g(DW)$^{-1}$ h$^{-1}$ could be lowered for the crops studied, particularly since this value seems to be based on agronomic crops rather than those more typical in California.

Measured emission of monoterpenes was more comparable with the value reported by Guenther et al. (400 ng(C) g(DW)$^{-1}$ h$^{-1}$). All crops studied, with the exception of orange, fall in the category of low monoterpene emitters. Emissions from some of these species are in the same order of magnitude of data observed in past research and now used as BEF for regional/global models BEIGIS (Scott and Benjamin, 1997) and MEGAN (Guenther et al. 2006).

We observed in our study a low (<1000 ngC gDM$^{-1}$ h$^{-1}$) amount of OVOC emitted by crops, with methanol often representing the major compound emitted. Current parameterization for regional/global model is still poor for this class of compounds. In MEGAN, a BEF of 800 μg m$^{-2}$ h$^{-1}$ is generally associated with croplands based on few previous studies on alfalfa and ryegrass (Warneke et al. 2002, Schade and Custer 2004). We note that California's croplands are dominated by permanent crops (orchards, vineyards), rather than agronomic crops like alfalfa, maize, or soybeans. The MEGAN model BEF, which we approximately convert to ng(C) g(DW)$^{-1}$ h$^{-1}$ using a leaf area index of 2 and a specific leaf mass of 100 g m$^{-2}$, equals 6000 ng(C) g(DW)$^{-1}$ h$^{-1}$ and is a higher value than most of our measured crops with the exception of tomato.

We conclude that the agricultural crops studied generally have low emission rates of isoprene and other terpenoid compounds compared to many plants found in natural or urban landscapes. Isoprene is generally considered the most important single BVOC in terms of impact on atmospheric chemistry, but our results show that emissions of isoprene from these crops were uniformly extremely low. Emissions of terpenes and oxygenated hydrocarbons (particularly methanol, but also acetaldehyde, and acetone) represented the dominant fraction of the total BVOC emission for the crops studied. Oxygenated VOC dominated emissions for some crops such as tomato, grape, potato, miscanthus, mandarins, and lemon. Terpene emissions dominated for other crops such as orange. However, these statements are based on limitations of sample size, experimental design, and low emission rates measured, so we offer these generalizations with caution.

The 'Parent Navel' orange tree emitted more terpenes than the other crop plants studied, and emissions of terpenoids and many other BVOC increased dramatically during the flowering event. However, emissions from orange per g dry leaf are still far less than emissions from the major BVOC emitting California plant species occurring in the natural environment. BVOC may increase during other events during the crop cycle, including harvesting and management practices such as pruning, potentially accounting for a significant fraction of the annual budget of emissions from orange orchards. We expect increases in emissions to occur for other crops during flowering (insect-pollinated flowers probably moreso than for wind-pollinated flowers) and certain management practices, but these effects were not the focus of this study.

Even though emissions were generally low, BVOC emitted from crop species may still play a significant role in the chemistry of the atmosphere in areas like in the San Joaquin Valley of California, where there are large areas planted with agricultural crops. Therefore, it is important to model emissions for the agricultural landscape as non-zero, and to evaluate the importance of these emissions in regional air quality models.

## 2.0 INTRODUCTION AND BACKGROUND

### 2.1 General Introduction

As the result of several decades of cost-effective air pollution control programs by the California Air Resources Board (ARB), and a succession of regional air quality agencies, air pollution in the California South Coast Air Basin (SoCAB) reached a fifty year low in 2000. The reduction in ozone first stage alerts in the SoCAB, for example, from a high of 121 in 1978 to none in 1999 and 2000 (SCAQMD 2000). This was a profound achievement given the enormous growth in population and emission sources in the SoCAB over the period of these control programs. A new eight-hour ozone standard of 0.070 ppm was approved by the ARB effective May 2006, which proved to be much more difficult to meet. Figure 1 shows the number of days per year exceeding this eight-hour standard from 1980 to 2009, making clear that while improvements have occurred in SoCAB and the San Francisco Bay Area, the San Joaquin Valley still experiences a similar number of exceedance days as occurred 30 years ago.

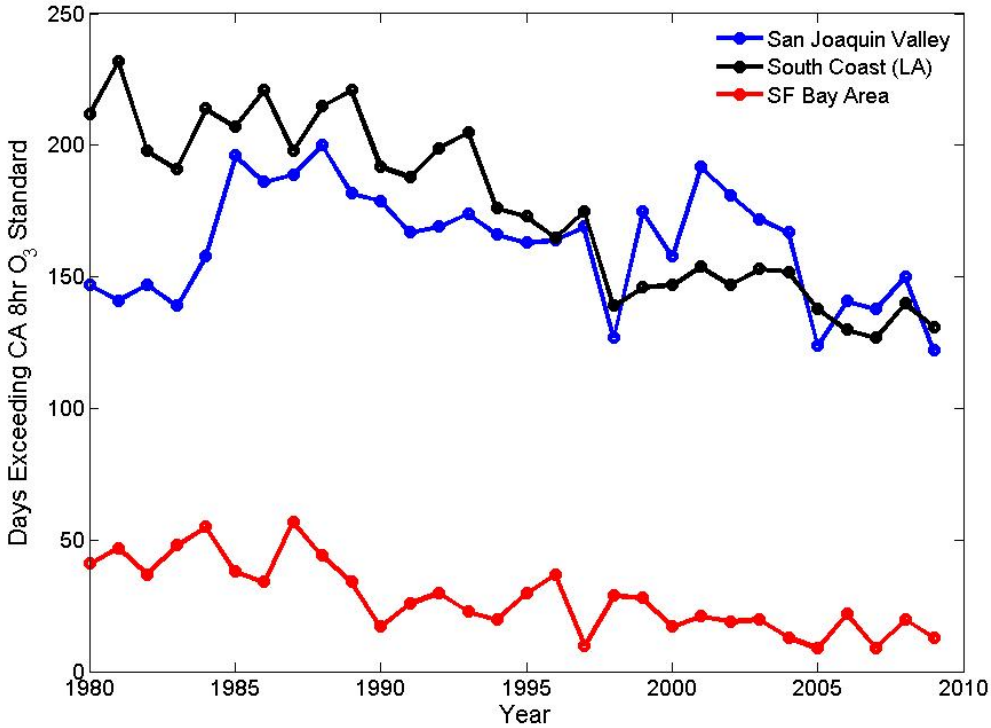



Figure 2-1. Days exceeding the current California 8 hour ozone standard from 1980 through 2009 in the San Joaquin Valley, South Coast, and San Francisco Bay Area air sheds (data from ARB).

For particulate matter the situation is similar, and the San Joaquin Valley is designated a nonattainment area for both PM2.5 and PM10 with regard to both the US Federal and California State standards.

One possible contributing factor to the disparity in progress in various California airsheds is the role of volatile organic compounds (VOC) from vegetation, or biogenic VOC (BVOC). VOC react in the presence of $NO_x$ and sunlight to form ozone, and oxidized VOC can partition from gas to particle phase forming secondary organic aerosols that dominate the organic aerosol source in at least some California airsheds (Williams et al. 2010).

Modeling studies by the ARB suggest that development of specific emission control strategies for reducing ambient ozone in certain areas of California is dependent upon estimated emissions of BVOC. These studies, for example using the Urban Airshed Model (UAM), showed that emissions of hydrocarbons from vegetation can make the difference between $NO_x$ vs. VOC emission controls being the most effective in reducing ozone concentrations (Jackson 1996). Concern about the possible critical role of BVOC emissions is reinforced by (a) the fact that on average many BVOC are as reactive, or more reactive, in the atmosphere than emissions from mobile or stationary anthropogenic sources (Carter 1994, Benjamin et al. 1998); and (b) a growing body of research from studies throughout the world indicates that BVOC can constitute a significant and even dominant contribution to the overall VOC inventory in both regional California airsheds (Lamanna and Goldstein 1999, Steiner et al. 2008) and the global atmosphere (Guenther et al. 1995). It is becoming increasingly clear that on a global level BVOC oxidation is the major source of SOA (Goldstein and Galbally 2007), but it is not yet understood how important the contribution of BVOC is to SOA in California airsheds.

Given the key role played by BVOC in the atmosphere, and the enormous costs associated with further reducing VOC and $NO_x$ in California to meet state and federal air quality standards (AQS), it is critical to quantify the essential databases needed to assemble reliable BVOC emission inventories; to expand and refine predictive methods for emission rates and leaf mass; and to further develop and validate key components of ARB BVOC models such as BEIGIS. Indeed, placing the air quality role of BVOC on a more quantitative basis must be ranked as a high priority of state and federal air quality regulators.

The interactions between meteorology, geography, extensive and intensive agriculture, and air pollution problems in California are a subject of increasing concern for the California Air Resources Board and California's regional Air Pollution Control Districts. The Central Valley of California represents this state's major agricultural region, with 6,396,000 acres harvested in 1997. Both urban and agricultural sectors are expanding within the Central Valley, leading to increasing interfacial conflict and questions about the role of agriculture in the environment, particularly in terms of continuing air quality problems in the region. The high ambient ozone and PM levels in this region affect human health, and the ozone levels also cause yield reductions up to 30% for some crops (Winer et al. 1990). The conjunction of extensive and intensive agriculture, confinement of polluted air by surrounding mountains, and high summer levels of solar radiation, make this area an ideal outdoor laboratory for investigating plant-atmosphere interactions, and their impact on air quality.

The California Air Resources Board is under increasing pressure to promulgate regulations for agricultural practices, yet effective policy for air quality attainment is contingent upon a thorough understanding of emissions of VOC, $NO_x$, and other pollutant precursors, as well as their fate and transport in the atmosphere. At present, policy development is constrained by lack of data for specific agricultural enterprises, including the emission of BVOC compounds from crop plants.

Although great strides have been made in understanding of BVOC emissions, there remains a paucity of data needed to properly assess the spectrum of chemicals which comprise the

emissions of green plants, including major crop types. Such data are needed to address many of the most important air pollution-related problems, including effects on human health and crop development.

## 2.2 Background

It is now well known that reactive BVOC are emitted from vegetation, including urban landscapes, agricultural crops, and natural plant communities in unirrigated areas. The global budget of VOC is dominated by biogenic emissions (Guenther et al. 1995) and green plants are contributors to VOC emissions in all California airsheds (Arey et al. 1991; 1995; Benjamin et al. 1997, Goldstein et al. 2001). The magnitudes of BVOC emissions of an individual plant are affected by its leaf mass and by its rates of emission of isoprene, terpenes and other VOC, as well as by environmental factors such as temperature and light intensity. Vegetative emissions are typically more reactive than the VOC emissions from automobiles, and can have higher ozone-forming potential (Carter 1994). The emission rates of isoprene, the VOC emitted by plants in greatest quantity, have been found to generally follow plant phylogenetic relationships (Benjamin et al. 1996, Csiky and Seufert 1999, Karlik and Winer 2001, Karlik et al. 2002). An accurate estimate of the magnitude of biogenic contributions is important in formulating air quality attainment strategies to reduce peak ozone concentrations, because an effective strategy will take into account the relative strength of NOx and VOC emissions.

For air quality attainment, it is also critical to understand rates of ozone formation and ozone deposition. Recent research suggests the role of biogenic emissions may be even greater than previously thought, because certain emissions may also play a role in ozone deposition. Ozone deposition and resulting plant injury occurs through stomatal uptake (Agrios 1997). Fowler et al.

(2001) argued that non-stomatal deposition in a forest environment was due to temperature dependent thermal decomposition on surfaces. However, Kurpius and Goldstein (2003) found that over a pine forest $O_3$ flux due to chemical loss by reaction with BVOC was even larger than the stomatal uptake, and scaled with temperature just like monoterpene emissions. Furthermore, the lifetimes of principal monoterpenes such as α-pinene, β-pinene, Δ-3-carene, and d-limonene are sufficiently long (11 to 190 min) to make these compounds unlikely candidates for reacting with substantial amounts of $O_3$ within the canopy (Valentini et al. 1997). Kurpius and Goldstein (2003) proposed, rather, that a wider suite of hydrocarbons, including monoterpenes, sesquiterpenes, and related compounds with lifetimes with respect to reaction with $O_3$ less than 10 min, could contribute significantly to gas-phase within-canopy $O_3$ loss. Holzinger et al. (2005) observed the oxidation products of at least some of these reactions above the same forest canopy, and Goldstein et al. (2004) confirmed that when terpene emissions increased due to mechanical disturbance $O_3$ gas-phase within canopy losses increased. Measurements above the ponderosa pine forest found sesquiterpenes α-bergamotene, longifolene, α-farnesene, and β-farnesene, and although the amount of sesquiterpene mass quantified above the canopy was small (averaging a total of 3.3 ppt during the day), these compounds contributed 8.5% to the overall ozone reactivity above the canopy (Bouvier-Brown et al. 2009a). In branch enclosures at the same site, the monoterpene-to-sesquiterpene emission rate was shown to be similar (Bouvier-Brown et al. 2009b).

In an orange orchard in Spain, Ciccioli et al. (1999b) found substantial within-canopy removal of the sesquiterpene β-caryophyllene, likely through reaction with $O_3$. Sesquiterpenes react with $O_3$ much faster than the monoterpenes (Arey et al. 1991), and the temperature dependence of their emissions is similar (Ciccioli et al. 1999b, Winer et al. 1992, Bouvier-Brown et al. 2009b).

Sesquiterpenes have been observed in a variety of plant species (Arey et al. 1991, Winer et al. 1992, Hakola et al. 2006, Helmig et al. 2006) and for many plants sesquiterpene emission rates can equal or exceed monoterpene emission rates (Winer et al. 1992, Helmig et al. 2006, Ormeño Lafuente et al. 2010). However, due to measurement limitations there has historically been a high degree of uncertainty regarding the specific sesquiterpenes emitted from plants and the magnitude of the emissions (Ciccioli et al. 1999a). Depending on the magnitude of the within-canopy $O_3$-hydrocarbon chemistry, fluxes of hydrocarbons that react rapidly with $O_3$ could be significantly underestimated (Makar et al. 1999) or not observed at all by above-canopy flux measurement techniques (Ciccioli et al. 1999b).

In the Central Valley as well as other regions, air quality degradation is manifested in visibility reduction. Atmospheric aerosols contribute to the radiative forcing of climate, contribute to haze and visibility reduction (Fehsenfield et al. 1992), and provide cloud condensation nuclei (Andreae and Crutzen 1997, Novakov and Penner 1993). The aerosol-forming potential of terpenes was recognized as early as 1960 (Went 1960), and these compounds are now believed to contribute significantly to secondary organic aerosol growth (Zhang et al. 1992). It has recently been reported (O'Dowd et al. 2002) that aerosol particles produced over forests are composed primarily of organic species derived from oxidation of biogenically emitted terpenes. Bonn and Moortgat (2003) suggest that new particle formation in rural areas is most likely initiated by reactions of sesquiterpenes and ozone. Yields of organic aerosols from photooxidation of terpenes range from 5 to 100% with the highest values observed for sesquiterpenes (Andreae and Crutzen 1997, Lee et al. 2006a and b). Thus, the inferred magnitude of $O_3$-hydrocarbon reactions in plant canopies has important implications for secondary organic aerosol growth

(Kurpius and Goldstein 2003, Andreae and Crutzen 1997, Zhang et al. 1992), and is globally important as a source of SOA (Goldstein and Galbally 2007, Hallquist et al. 2009).

Certain BVOC compounds important in atmospheric chemistry also play key roles in plant-insect relationships, and may affect pest management strategies. Compounds involved include terpenes, sesquiterpenes, salicylic acid, jasmonic acid, and indole (Paré and Tumlinson 1999, Turlings et al. 2000, Alborn et al., 2000, Schmelz, et al., 2001, 2003, Engleberth et al., 2003, Aldrich et al., 2003, Röse and Tumlinson, 2004). A very important type of plant defense against insect herbivores is the release of volatile compounds that attract natural enemies of the herbivores (Tumlinson et al., 1993, Stowe et al., 1995, Turlings et al., 1995, Seybold et al., 2006). Blends of volatile terpenes, sesquiterpenes, and other compounds (Figure 2), released in response to insect feeding and not to mechanical damage alone (Turlings et al., 1990, Korth et al. 1995), allow insect parasitoids (Turlings et al., 1995) and predators (Dicke et al., 1993) to distinguish between infested and non-infested plants and thus aid in location of hosts or prey. These phytodistress signals, which result in an active interaction between herbivore-damaged plants and a third trophic level, have been described for several plant species (Dicke et al., 1993, Turlings et al., 1991, Turlings and Tumlinson, 1991). This group of BVOC that have been studied regarding their role in plant-insect interactions are highly reactive with OH and $O_3$ and their oxidation should lead to secondary organic aerosol formation and growth, but these compounds have generally not yet been included in BVOC models such as BEIGIS that are used as inputs to models assessing regional air quality.

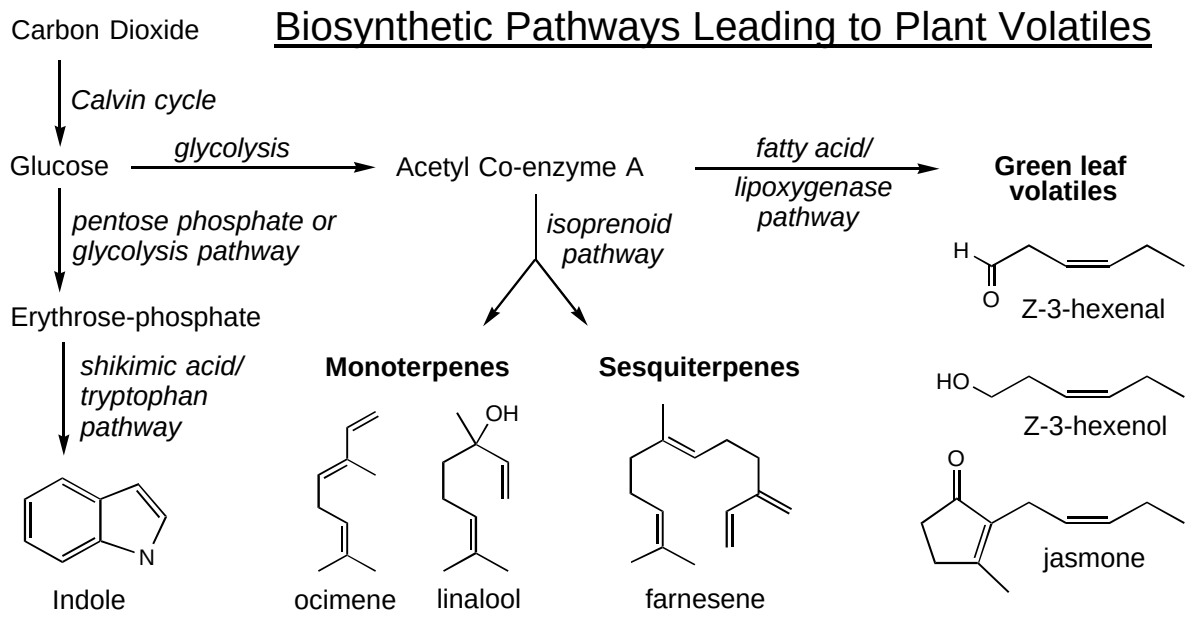



Figure 2-2**.** Biosynthetic pathyways leading to plant volatiles. From Paré and Tumlinson, 1999.

To answer questions about plant emissions, requisite analytical techniques are required. While gas chromatography coupled with a flame ionization detector and mass spectroscopy provides excellent analytical methods for quantifying concentrations of VOC in the atmosphere or air samples, study of many compounds less amenable to cartridge sampling, including certain oxygenated and short-lived BVOC, is now possible through the use of proton-transfer mass spectroscopy (PTR-MS). In this instrument, a stream of ambient air (or standard mixture) is passed through a chamber in which $H_3O^+$ is present in the vapor phase. Gases with proton affinity higher than water become protonated, and are measured with a quadrupole mass spectrometer as the parent mass plus one proton. This analytical method is particularly useful for quantifying oxygenated compounds and the total sum of terpenes (which have the same molecular weight but varying chemical structures), and allows real-time detection for many compounds in the low parts-per-trillion range.

In support of an ARB Program to develop a biogenics emission inventory for California's Central Valley, including the Sacramento and San Joaquin Valley Air Basins, Winer and co-workers (Winer et al. 1989, 1992, Arey et al. 1991a,b) measured the rates of emission of speciated hydrocarbons from more than thirty of the most important (based on acreage) agricultural and natural plant types relevant to California's Central Valley. Four dozen individual compounds were identified as emissions from agricultural and natural plant species studied. Data obtained in that study demonstrated again there can be large variations in emission rates from a single specimen of a given plant species, as well as from multiple specimens of a cultivar. Mean emission rates for total monoterpenes ranged from none detected in the case of beans, grapes, rice and wheat to as high as 12-30 µg per hour for pistachio and tomato (normalized to dry leaf and total biomass, respectively). Agricultural species were found to be overwhelmingly monoterpene emitters and not isoprene emitters (Winer et al. 1992), and the low or negligible isoprene emission from crops was observed in a subsequent ARB-funded project (Karlik and Winer, 2001, Karlik et al. 2002)

However, studies related to emission of short-lived compounds from crop plants in California have not been published in recent years, despite the extensive acreages of these plants, although crop plants compose the dominant landscape type in the Central Valley, by far. The present study has provided opportunity to enhance understanding of the emission of highly reactive BVOC from crop plants with regard to air quality, including the identities and rates of emission for use in emission model development and testing.

## 2.3 Rationale and Significance for the Present Study

The Central Valley is home to about 60% of California's $30 billion of agricultural production. More than 500,000 acres of cotton and corn were grown in 2002 in just the southern half of the Central Valley, in addition to fruit and nut crops (Table 1). At the same time, air quality in the Central Valley is among the worst in the nation, both in terms of ozone levels and particulate matter. Measurements of highly reactive mono- and sesquiterpene emissions and related compounds are needed to quantify the importance of their oxidation products to ozone formation and deposition, secondary aerosol loading in the atmosphere, and other potential impacts on atmospheric chemistry and regional air quality. The paucity of data regarding these compounds is a result of past emphases, and because the requisite analytical techniques were not available until now. This integrated study has investigated the emission of these highly reactive compounds from selected crop species, and their concentrations and fluxes above the canopy of a selected crop found in the San Joaquin Valley. This work expands our understanding of the role major crop species may play in ozone formation and deposition and formation of secondary aerosols.

Table 2-1. Planted areas for several of the agronomic and permanent crops with largest areas of land cover in the eight counties of the San Joaquin Valley, the southern half of California's Central Valley.

| Crop | Botanical Name | Acreage[1] |
|---|---|---|
| Cotton | Gossypium spp. | 653,000 |
| Maize | Zea mays | 501,000 |
| Tomatoes | Lycopersicon esculentum | 222,000 |
| Grapes, Table Varieties | Vitis vinifera cv. | 84,900 |
| Grapes, Raisin Varieties | Vitis vinifera cv. | 241,000 |
| Almonds | Prunus dulcis | 453,000 |
| Apples | Malus domestica | 15,800 |
| Peaches | Prunus persica | 51,300 |
| Pistachios | Pistacia vera | 97,024 |
| Walnuts | Juglans regia | 124,000 |
| Navel Oranges | Citrus sinensis | 124,000 |

[1] Data from 2002 crop reports, respective county Agriculture Commissioner's offices.

### 2.3.1 Statement of the Problem

As discussed above, quantifying BVOC emissions and understanding the atmospheric reactivity of isoprene, monoterpenes and other BVOC are critical elements in the development of effective ozone attainment strategies. ARB-funded research has produced a wealth of data related to biogenic hydrocarbon emissions in California and substantial progress has been made in characterizing the atmospheric chemistry of BVOC. Agricultural crops are the predominant

landcover in the Central Valley, yet their emissions had not been characterized by advanced analytical techniques.

### 2.3.2 Objectives

The overall objective of this project was to provide critical information to resolve key questions related to the magnitude of certain BVOC compounds emitted by crops. Because BVOC emission inventories depend upon scaling up of leaf-level or branch-level emission factors via species-specific leaf mass estimates within a geographic region, the proposed research addressed components within two levels of inventory development. These included quantitative measurements of emission of BVOC for a carefully chosen list of crop species. These results provide critical data for the contribution of crop plants to VOC in the lower atmosphere, and hence ozone formation, formation of secondary organic aerosols, and the relative role of chemical vs surface reaction for rates of ozone deposition. Although agricultural crops, in general, have low to moderate emission rates for the BVOC compound isoprene (Winer et al., 1992, Karlik and Winer, 2001, Karlik et al., 2002), their production of shorter-lived reactive compounds, e.g. monoterpenes and sesquiterpenes, and their production of oxygenated VOCs, is not well known. The extensive plantings of various crop types and corresponding high values for leaf mass may result in significant emissions of reactive BVOC if even moderate rates of emission are found.

To address the deficiency of data for principal crop types, a two-phased study was conducted. The objectives and tasks were as follow:

Objective 1 (Phase 1): Measurement of BVOC emissions for major crop types

Task 1. Choose crops for plant level emission measurements.

Plant selection was informed by any known emission behavior of monoterpenes and other reactive VOC, and by analyzing the extent of planting of the crop type in the San Joaquin Valley. For example, pistachios and tomatoes were found to be emitters of monoterpenes (Benjamin et al. 1996) and cotton and maize occupy large acreages and have been shown to release volatile compounds upon herbivory in laboratory studies (Röse et al. 1996, Schnee et al. 2002). Table 1 shows crop plants with large landcover extent and also key genera and families. Selection of plants to be measured was further informed by a literature search that preceded the measurements made in Phase I. This search considered recent studies and also phylogenetic relationships of plants found in agricultural landscapes, both in terms of opportunities to generalize emission behavior at the genus and family levels, and also to be sure key genera and species were not omitted from consideration. Details of crop selection are in chapter 3.

Task 2. Measurements of BVOC emission using plant or branch enclosures

We purchased multiple representatives of each crop type defined in Task 1 and grew them in the Oxford greenhouse at UC Berkeley. To measure emissions, we developed dynamic branch enclosures that could be easily placed around the individual plant or branch of interest. Measurements of BVOC emissions were made by both PTRMS and GC-MS/FID as described in detail below in chapter 3. Simultaneously, temperature, photosynthetically active radiation, carbon dioxide and water were measured to document the environment and the physiological status of the plant. Enclosure methods have been used in California studies (Winer et al. 1983,

1992, Arey et al. 1995, Karlik and Winer, 2001, Bouvier-Brown et al., 2009), in other regions of the United States (Kempf et al. 1996, Helmig et al. 2003, 2006), in other parts of the world (Street et al. 1996, Hakola et al. 2006, Holzke et al. 2006), and the BEMA project (Seufert et al. 1997, Owen et al. 1997), among others. Enclosure measurements are the best suited method for measuring emissions of highly reactive compounds (Helmig et al. 2003) because no atmospheric oxidants are present while the branch remains under relatively natural conditions.

Objective 2 (Phase 2): Flux measurements of BVOC from selected crop canopy.

Task 3: Canopy Scale Flux Measurements. A crop type and site was selected based on the results of chamber BVOC emission measurements from Task 2, the area of the crop in the San Joaquin Valley, and the ability to find a site with suitable characteristics. Initially two intensive measurement campaigns of at least three-weeks were proposed to be conducted in the field. We changed that original plan to one full year of measurements in one location in order to define the full seasonal cycle of BVOC emissions. We ultimately selected an orange grove, in which a tower was set up as a platform for sensors and inlet lines, coupled to an array of analytical instruments. Flux and concentration measurements were made in and above the crop canopy along with a suite of meteorological, ecophysiological, and environmental variables, as described in chapter 4.

In the following report we describe in detail how each of these objectives were met, the results obtained, and their implications and significance.

# 3.0 BVOC MEASUREMENTS OF SELECTED CROP SPECIES VIA AN ENCLOSURE APPARATUS

## 3.1 Introduction

Seminal studies of BVOC emissions in California were carried out in the South Coast Air Basin (SoCAB) (Winer et al. 1983, 1989) and green plants are expected to be contributors to VOC emissions in all California airsheds (Arey et al. 1995, Winer et al. 1995, Chinkin et al. 1996, Benjamin et al. 1997). Modeling studies by the California Air Resources Board (ARB) indicated that development of specific emission control strategies for reducing ambient ozone concentrations in some areas of California is dependent upon estimated fluxes of biogenic hydrocarbons (Jackson 1996). These studies, using the Urban Airshed Model with Carbon Bond IV chemistry, showed that emissions of hydrocarbons from vegetation can determine whether NOx emission controls or VOC emission controls are most effective in reducing ozone concentrations. Similar conclusions concerning the potential importance of biogenic hydrocarbon emissions in determining the efficacy of control programs for anthropogenic emissions have been reached for other airsheds and regions (Chameides et al. 1988); specifically, an accurate estimate of the magnitude of biogenic contributions is important in formulating strategies to reduce peak ozone concentrations, because an effective strategy will take into account the relative strength of NOx and VOC emissions.

Agricultural cultivation often occurs close to polluted urban areas where urban emissions mix with agricultural emissions. This is the case of the Central Valley of California, a region with extensive agriculture and anthropogenic pollution from large nearby cities (e.g. Fresno,

Bakersfield, and Sacramento), as well as inflow of pollution from populated coastal regions (e.g. the San Francisco Bay area).

Plants emit biogenic volatile organic compounds (BVOC) to the atmosphere at an estimated global rate of 1-1.5 Pg C $y^{-1}$ (Guenther et al. 1995). These emissions account for 2-3 % of the total carbon exchange between biota and the atmosphere (Crutzen et al. 1999, Kesselmeier and Staudt 1999, Monson and Fall 1989, Loreto and Sharkey 1990). In the presence of sunlight and nitrogen oxides ($NO_x$), the oxidation of BVOC leads to tropospheric ozone formation (Chameides et al. 1988, Papiez et al. 2009), a greenhouse gas with detrimental effects on plant carbon assimilation and growth (Guderian et al. 1985), as well as human health (for a reference list, see EPA 2009). BVOC are also precursors to atmospheric aerosol (Kanakidou et al. 2005, Henze and Seinfeld 2006), accounting for a significant fraction of secondary organic aerosol (SOA) produced in the atmosphere (Goldstein and Galbally 2007).

Isoprene is the BVOC emitted in greatest quantity by the plant kingdom worldwide (Guenther et al. 1995) and is the dominant BVOC emitted by deciduous forests (Geron et al. 1995). Among the plant species that have been measured, emission rates of isoprene differ by more than three orders of magnitude (Benjamin et al. 1996) and the resulting ozone-forming potential (OFP) of individual trees and shrubs ranges over nearly four orders of magnitude (Benjamin et al. 1998). Monoterpenes are 10-carbon isoprenoids whose emissions are dependent on temperature and, in some cases, on light as well. Many monoterpenes have been described as temperature-dependent because their emission is mainly the result of volatilization from storage organs (Kesselmeier and Staudt, 1999).

Sesquiterpenes are another important class of isoprenoids whose emissions depend primarily on temperature, but they are formed by a different biosynthetic pathway than isoprene and monoterpenes (for a review see Duhl et al. 2008). These hydrocarbons, containing 15 carbon atoms, have previously been considered to account for a small percentage of global BVOC emissions (Guenther et al. 1995), but recent results suggest their total emissions are similar to monoterpenes (Ormeño et al., 2010). Sesquiterpene emissions are of great interest since they generally have higher secondary organic aerosol yields than monoterpenes (Lee et al. 2006a, 2006b; Ng et al. 2006). Current empirical BVOC emission models for regional and global scales use emission algorithms which incorporate the basal emission factor (BEF) of the modeled species while accounting for either the light and temperature dependence (Monson et al. 1992, Niinements et al. 2004), or just the temperature dependence (Tingey et al. 1980, Harley et al. 1996).

Unlike emissions of isoprene and monoterpenes, which have been extensively studied, the main knowledge of oxygenated volatile organic compounds (OVOC) emissions only dates from the last decade (for a review, see Steiner and Goldstein 2007). Similarly to isoprenoids, OVOC can notably influence the oxidizing capacity and the ozone-forming potential of the atmosphere, while also increasing concentrations of HOx and peroxyacetyl nitrates, and possibly contributing to the formation of organic aerosol (Singh et al. 2001).

Methanol is a plant volatile emitted to the atmosphere in large quantities from the demethylation of pectins in cell walls (Obendorf 1990) with global emissions estimated at 100-240 Tg $y^{-1}$

(Galbally and Kirstine 2002, Jacob et al. 2005, Millet et al. 2008). Its emission occurs under phenological modification of leaf tissues during leaf expansion, senescence (Schade et al. 2002, Huve et al. 2007, Fall 2003), and oxidative stress (Karl et al. 2001, Loreto et al. 2006).

Acetone is another important OVOC emitted primarily from terrestrial ecosystems and oceans, but is also produced in the atmosphere in large amounts from oxidation of hydrocarbons of both anthropogenic and biogenic origin (Goldstein and Schade, 2000). Acetone is the most abundant ketone in the atmosphere (Koppmann and Wildt 2007); global emissions are estimated at 95 Tg $y^{-1}$ (Jacob et al. 2002) with considerable sources in rural areas (Goldan et al. 1995, Riemer et al. 1998, Ciccioli et al. 1999). While we know that acetone is released during senescence (de Gouw et al. 1999) and oxidative stress on plants (e.g. from ozone) (Cojocariu et al. 2005), the biogenic sources of acetone are not fully explained.

Acetaldehyde is another OVOC that is directly emitted from oceanic and terrestrial sources, but is also an oxidation product of hydrocarbon oxidation in the atmosphere. Acetaldehyde emissions from plants occur mainly under anoxic conditions in roots (Kreuzwieser et al. 1999) and possibly also in leaves (Karl et al. 2002, Graus et al. 2004). It is also emitted by leaves in large quantities during and after abiotic stresses (Fall et al. 1999, Loreto et al. 2006), or after light to dark transitions (Karl et al. 2002). In general, OVOC emission from biogenic sources are products of catabolism and depend mostly on temperature, but also to some degree on light conditions.

Modeling efforts have been done to characterize BVOC emissions on a regional and global basis (Lamb et al. 1993, Benjamin et al. 1997, Guenther et al. 1995, 2006). These models can predict emissions of a range of BVOC, including those in this study, under varying environmental conditions. Emissions are typically parameterized by integrating environmental data, plant distribution, biomass density, and basal emission factors for each type of vegetation (standardized to conditions of 30 $^{o}$C and 1000 μmol $m^{-2}$ $s^{-1}$ of photosynthetically active radiation (PAR)). Basal emission factors come from direct emission measurements performed at leaf, branch, or canopy scales using different sampling techniques. Robust compound-specific information on basal emission factors improves the accuracy of the emissions model since not all BVOC are emitted in the same manner. Emission rates respond primarily to light and temperature because their formation pathway is primarily in the leaf chloroplast, strictly related to photosynthesis, and they are released immediately after production (Lichtenthaler et al. 1997).

## 3.2 Enclosure Study Objectives

The objectives of the enclosure study were (1) identify and quantify BVOC emissions from various crop species, (2) determine the basal emission factors (BEF) for each BVOC emitted, and (3) test the performance of current algorithms to predict BVOC emission by comparing modeled versus observed measurements. These objectives were fulfilled using a fast BVOC sensor, the proton transfer reaction mass spectrometer (PTR-MS) (Lindinger et al. 1998), which allowed on-line measurements of BVOC in parallel with measurement of physiological parameters and environmental conditions, and a gas chromatograph with a mass selective detector and flame ionization detector (GC/MS-FID) to identify emissions of chemically-speciated monoterpenes and sesquiterpenes. We measured emissions using a dynamic plant

enclosure (Winer et al. 1983, 1989, 1992; Karlik and Winer 2001,Tholl et al. 2006, Ortega and Helmig 2008; Bouvier-Brown et al., 2009), which we specifically designed for this experiment.

## 3.3 Experimental Methods for the Enclosure Studies

### 3.3.1 Choice of Crops for the Present Investigation

Crops comprise the most important landcover classification for the Central Valley. We focused our attention on the most important crop species cultivated in California, with common varieties: orange (*Citrus sinensis* 'Washington Navel'), lemon (*Citrus limon* 'Meyer'), mandarin (*Citrus reticulata* 'W. Murcott' and 'Clementine'), almond (*Prunus dulcis* 'Nonpareil'), grape (*Vitis vinifera* 'Crimson Seedless' and 'Pinot Noir'), pistachio (*Pistacia vera* 'Kerman'), tomato (*Lycopersicon esculentum* 'Mortage Lifter'), carrot (*Daucus carota* 'Bolero Nantes' and 'Red Label'), cherry (*Prunus avium* 'Bing'), Japanese plum (*Prunus salicina* 'Satsuma'), olive (*Olea europea* 'Manzanillo'), pomegranate (*Punica granatum* 'Wonderful').

We used a greenhouse facility in Berkeley, California, to house 5-10 plants for each of the 22 potted species and varieties studied. For citrus, 10 individuals of each of five genotypes were ordered from a commercial nursery (Willits and Newcomb). Other plants came from Fowler Nurseries and East Bay Nursery. Detailed information about the species, their cultivar, and the number of plants actually sampled is shown in Table 3-1.

Plants were placed in the greenhouse in February to allow adaptation to the greenhouse conditions. For each crop species, three to six plants were randomly sampled from July 25 to October 22, 2008, after they had adapted to greenhouse conditions for at least five months. Plants

were watered daily and fertilized weekly to ensure favorable growing conditions. Temperature in the greenhouse was controlled to have night values around 17 $^{o}$C and mid-day values up to 31 $^{o}$C; daytime temperatures in the greenhouse typically ranged between 25-30 $^{o}$C. A glass roof on the greenhouse allowed sunlight, including photosynthetically active radiation (PAR), to reach the plants. Light conditions changed with the ambient environment outside the greenhouse (0 to 1500 µmol $m^{-2}$ $s^{-1}$). Relative humidity was maintained in the range of 40-60 %.

Table 3-1. Plants selected for enclosure measurements.

| Common Name | Scientific Name | Variety and Type |
|---|---|---|
| *Herbaceous plants* | | |
| Alfalfa | Medicago sativa L. | Lucerne |
| Carrot 1 | Daucus carota L. | Bolero Nantes |
| Carrot 2 | Daucus carota L. | Red Label |
| Corn (Maize) | Zea mays L. | Eureka |
| Cotton 1 | Gossypium barbadense L. | Pima |
| Cotton 2 | Gossypium hirsutum L. | Upland |
| Onion | Allium cepa L. | Walla Walla |
| Potato | Solanum tuberosum L. | Red La Soda |
| Tomato | Lycopersicon esculentum L. | Mortgage Lifter |
| *Woody plants* | | |
| Almond | Prunus dulcis Mill. D.Webb | Nonpareil |
| Apricot | Prunus armeniaca L. | Blenheim |
| Cherry | Prunus avium L. | Bing |
| Grape 1 | Vitis vinifera L. | Crimson Seedless (Table Variety) |
| Grape 2 | Vitis vinifera L. | Pinot Noir (Wine Variety) |
| Lemon | Citrus limon L. | Allen Eureka (on Cuban Shaddock rootstock) |
| Mandarin | Citrus reticulata Blanco | W. Murcott (on C-35 rootstock) |
| Mandarin | Citrus reticulata Blanco | Clementine (on C-35 rootstock) |
| Olive | Olea europaea L. | Manzanillo |
| Orange | Citrus sinensis L. Osbeck | Parent Navel (on Volk rootstock) |
| Peach | Prunus persica L. Batsch. | Carson |
| Pistachio | Pistacia vera L. | Kerman |
| Plum | Prunus salicina Lindley | Satsuma |
| Pomegranate | Punica granatum L. | Wonderful |

### 3.3.2 Enclosure Apparatus

Two identical dynamic branch enclosures were designed to sample BVOC emissions from two plants at a time. Either a branch (woody species) or the entire plant (herbaceous species) was enclosed in an 84 L cylindrical enclosure constructed out of Teflon. The enclosure was made of a rigid Teflon frame and coated with transparent Teflon FEP film (0.025 mm thick, Richmond Air Craft products, Inc.) to allow penetration of PAR to the leaves. This structure was made completely of Teflon to minimize reactions of BVOC on the chamber walls. For each sample a 10 to 500 g branch of leaf fresh biomass was enclosed to ensure that the analyte concentration inside the system was sufficient to achieve an adequate signal/noise ratio during BVOC emission monitoring (Tholl et al. 2006, Ortega and Helmig 2008). The air flushed through the inlet of the enclosure was first purified using a zero air generator (Aadco mod.737) to remove $CO_2$, hydrocarbons, and ozone. After purification, it was enriched with $CO_2$ from a pure cylinder connected to a mass-flow controller (MKS Instruments, Inc.) at a constant concentration of 380 ppm to simulate ambient $CO_2$. The air flow at the enclosure inlet was maintained between 8.5 and 10 L $min^{-1}$ using a mass-flow controller (MKS Instruments, Inc.). A short section of ¼ inch Teflon tubing leading to a shower-based Teflon ring with multiple holes allowed for a uniform distribution of the air flow inside the enclosure and facilitated air mixing. Under these conditions, we calculated an air residence time in the enclosure of ~10 minutes.

Each enclosure was equipped with a radiation sensor (LICOR quantum sensor model Li-190), a relative humidity and temperature sensor (Omega Engineering model HX93AV-RP1), and a system of fine wire thermocouples touching the leaves to measure their temperature (Omega

Engineering, precision fine wire thermocouples). $CO_2$ and $H_2O$ were measured by an infrared gas analyzer (Li-Cor 6262).

### 3.3.3 Temperature and Light Measurement

Measurements of photosynthetic parameters ($CO_2$, $H_2O$) and BVOC were carried out by switching between the two enclosure outflows every 15 min with a system of two- and three-way solenoid valves (TEQCOM Industries), controlled by a datalogger (Campbell Scientifics, model CR10). The first three min per cycle were dedicated to the measurement of the zero air entering the enclosures.

### 3.3.4 Analytical Instrumentation: PTR-MS

A PTR-MS was used for on-line measurements of BVOC. For a detailed description of the instrument see Lindinger et al. (1998) or de Gouw and Warneke (2007). The instrument sampled from the main sampling line at 0.4 L $min^{-1}$ and was optimised to an E/N ratio of 128 Td using a drift tube pressure, temperature, and voltage of 2.02 hPa, 45 $^{o}$C, and 600 V, respectively. The reaction time was 100 μs and the count rate of $H_3O^+H_2O$ ions was less than 3% of the count rate of $H_3O^+$ ions, which was ~5x$10^6$ counts $s^{-1}$. BVOC fluxes were calculated with a differential approach from fast concentration measurements in multiple ion detection mode, including the following compounds with a dwell time of 1 second each: methanol (mass to charge ratio (m/z) 33), acetaldehyde (m/z 45), acetone (m/z 59), isoprene (m/z 69), monoterpenes (m/z 81 and 137), and products of lipoxygenation (3-Z-hexenol, 2-E-hexenal, 3-Z-hexenal, 2-E-hexenol at m/z 93, 97, 99, 101, respectively). Each measurement cycle was repeated for an 11 min measuring time. The instrumental background was measured by directing the sample flow through a catalyst-based purifier for the first 3 minutes before starting the measurement of the sample air. The

purifier consisted of a stainless steel tube filled with platinum-coated quartz wool (Shimadzu) heated to 350 $^{o}$C, which efficiently removed the VOC but not the water vapor from the sample. This is important because the instrument response may depend on the humidity of the air.

### 3.3.5 Analytical Instrumentation: GC/MS-FID

Hourly-resolved VOC concentrations were measured using an automated in-situ gas chromatograph (Agilent mod. 5890) equipped with both a mass-selective detector (Agilent mod. 5971) and a flame ionization detector (GC/MS-FID) (further details on this instrument can be found in Millet et al. 2005). The instrument sampled from the plant enclosures through an insulated ¼" Silcosteel line that was heated to maintain a temperature above 50°C, pre-concentrated ~600 mL of the enclosure effluent onto two separate adsorbent traps over a 30 minute period, and thermally-desorbed them onto capillary columns; the FID-analyzed sample was collected on a glass bead/Carbopak B/Carboxen 1000 adsorbent mix and injected onto a DB-624 column, while the MSD-analyzed sample was collected on Tenax-TA, then injected onto a Rtx-5 column.

### 3.3.6 Calibration

The PTRMS was calibrated using gravimetrically-prepared gas standard cylinders (Apel and Riemer) of pure nitrogen with low ppm mixing ratios of methanol, acetaldehyde, acetone, and a mixture of monoterpenes (α-pinene, d-limonene, Δ-3-carene) which were automatically measured twice a day by diluting with purified air to obtain concentrations in the range of 10-50 ppb. The instrument was calibrated at mixing ratios similar to those expected in the plant enclosures. The count signal was then transformed to ppb after subtracting the averaged background levels and taking into account the measured sensitivities for each calibrated

compound (i.e. counts/ppb, Davison et al. 2009). For oxygenated compound concentrations, we calculated normalized sensitivities (counts/concentration) based on calculated proton transfer reaction rate coefficients and the instrument-specific transmission coefficient calculated from a transmission curve. This curve was determined at an array of masses from 33 to 219 m/z using our gas standards at concentrations of 50 ppb. Due to poor transmission coefficients of masses above m/z 150, we discarded measurements of masses above that molecular weight (e.g. oxygenated monoterpenes (m/z 155) and sesquiterpenes (m/z 205)). During measurements, markers of cell wall degeneration resulting from wounding effects (3-Z-hexenol, 2-E-hexenal, 3-Z-hexenal, 2-E-hexenol, m/z 93, 97, 99, 101) were detected in trace concentrations after inserting the branch in the enclosure. Therefore emission rates were only considered reliable after observing negligible emission of these markers (enclosure concentrations < 50 ppt, which is close to the instrument detection limit); in most cases this was one day after the enclosure of the leaf material (data not shown).

For the GC/MS-FID, calibrations were performed using gravimetrically-prepared gas standard cylinders (Apel and Riemer) of pure nitrogen containing low ppm mixing ratios of isoprene and a variety of monoterpenes (limonene, α-pinene, Δ3-carene, nopinone, & α-terpinene) by diluting with purified air to obtain concentrations in the range of 10-50 ppb, similar to those expected in the plant enclosures. Liquid standards were used for more reactive compounds (e.g. sesquiterpenes and unstable monoterpenes) and they were volatilized through a heated injection port into the heated sampling line.

### 3.3.7 Plant Measurement Procedures

Several environmental factors influence emissions of BVOC from vegetation, and among them light and temperature are most important (Guenther et al. 1993). For this reason ambient air temperature and photosynthetically active radiation (PAR) were recorded while sampling each plant. Due to the light dependency of the isoprene metabolic pathway, sampling was ideally carried out at a light intensity greater than 1000 μmol $m^{-2}$ $s^{-1}$.

When placing plants into the enclosure, the stems were gently wrapped with Teflon film to avoid mechanical damage as much as possible. In all cases, the measurements started 24 hours after plant enclosure to compensate for potential enclosure effects. The pure air flowed in continuously during the 2-3 days of measurements. Measurements of photosynthetic parameters and BVOC were carried out by switching between the plant enclosure outflows every 15 minutes with a system of 2- and 3-way solenoid valves (TEQCOM Industries) controlled by a datalogger (Campbell Scientific, mod. CR10). The first three minutes of each cycle were dedicated to the measurement of the zero air entering the enclosures. Fluxes were calculated using the differential approach described by Fares et al. (2008). $CO_2$ and water exchanges were measured with a closed-path infrared gas analyzer (IRGA, LICOR mod. 6262). After BVOC sampling, leaf area was measured with a leaf area meter (LICOR mod. 3100C), enclosed leaves were dried and weighed in order to express BVOC emission rates on a dry mass basis.

## 3.4 Results and Discussion for Greenhouse Enclosure Studies

We report speciated emissions of methanol, acetaldehyde, acetone, isoprene, monoterpenes, oxygenated monoterpenes, and sesquiterpenes. A comparison of monoterpenes measured in the plant enclosure experiments using both the GC/MS-FID and the PTR-MS systems shows agreement within 20% (r = 0.97, PTR-MS Flux = 0.81 * GC/MS-FID Flux) calculated using a trust-region Levenberg-Marquardt least orthogonal distance regression method to account for uncertainties in both the measurements. Due to their poor transmission to the PTR-MS quadrupole, sesquiterpenes and oxygenated monoterpenes were consistently underestimated with PTR-MS (PTR-MS Flux = 0.20 * GC/MS-FID Flux). Thus, for these two classes of compounds, we only considered emission values from GC/MS-FID. To minimize possible bias from emissions due to mechanical damage, we did not report initial emissions following plant enclosure but only emissions once branches were acclimated.

BEF were calculated for each species as an average of the data that encountered the following conditions: 1) temperature = 30 ± 2 $^{o}$C, and 2) PAR > 800 μmol $m^{-2}$ $s^{-1}$.

As generally considered, we assumed that BVOC can be emitted to the atmosphere through two different mechanisms. First, BVOC are emitted after being synthesized in the leaves through an enzymatic control which depends on light and temperature. To show these dependencies from light and temperature, we modelled fluxes ($E_{L+T}$) using the algorithm proposed by Guenther et al. 1993, hereon called L+T algorithm:

$$E_{L+T} = BEF\left[\frac{\alpha C_L PAR}{\sqrt{1+\alpha^2 PAr^2}}\right] * \left[\frac{\exp\left(\frac{C_{T1}(T-T_S)}{RT_S T}\right)}{C_{T3} + \exp\left(\frac{C_{T2}(T-T_M)}{RT_S T}\right)}\right] \quad \text{(Equation 3-1)}$$

where the empirical coefficients are α (= 0.0027), $C_L$ (= 1.066) ,$C_{T1}$ ( = 95000 J $mol^{-1}$), $C_{T2}$ ( = 230000 J $mol^{-1}$), $C_{T3}$ ( = 0.961) and $T_M$ ( = 314 K); R is the universal gas constant (= 8.314 J $K^{-1}$ $mol^{-1}$), T is the leaf temperature ($^oK$) and $T_S$ in the leaf temperature at standard conditions (= 303 °K).

The second emission mechanism assumes that BVOC are synthesized and stored in specific pools inside the leaves and emitted in the atmosphere by volatilization. This volatilization process depends mainly on temperature. Emissions of BVOC were modelled with the algorithm ($E_T$) proposed by Tingey et al., (1980) hereon reported as T algorithm:

$$E_T = BEF \exp[\beta(T - T_s)] \quad \text{(Equation 3-2)}$$

$\beta$ ($K^{-1}$) (beta) is a coefficient that represents an exponential dependence on temperature. We calculated $\beta$ by inverting Equation 2 and applying the measured BEF during the day. Modelled fluxes were correlated linearly with measured observations and the slope coefficient and r-squared were calculated in order to estimate which modelled emissions better represented the actual BVOC emission from leaves.

### 3.4.1 Data Summaries

In the following tables we present data for the crops measurements made via the enclosure system including BEF and $\beta$ determined for major species and classes of compounds (Tables 3-2 and 3-3), measured isoprene emissions (Table 3-4), comparison between model and measured emissions (Tables 3-5 and 3-6), and speciated monoterpene (Table 3-7, Figure 3-1), oxygenated terpene (Table 3-8, Figure 3-2), and sesquiterpene (Table 3-9, Figure 3-3) composition.

Table 3-2. Basal emission factors (ngC $gDM^{-1}$ $h^{-1}$) and beta values for methanol, acetaldehyde, acetone and isoprene for crop plants investigated.

| | Methanol | | Acetone | | Acetaldehyde | | Isoprene | |
|---|---|---|---|---|---|---|---|---|
| *Species* | *BEF±StDev(N)* | *Beta (r)(N)* | *BEF±StDev(N)* | *Beta (r)(N)* | *BEF±StDev(N)* | *Beta (r)(N)* | *BEF±StDev(N)* | *Beta (r)(N)* |
| Alfalfa | N.M. | | N.M. | | N.M. | | N.M. | |
| Almond | 620±300 (29)[24] | 0.032 (0.30)(233)* | 84±110 (6)[24] | 0.11 (0.17)(107)* | 89±60 (27)[24] | 0.12 (0.42)(192)* | | |
| Carrot (RL) | 610±230 (19)[26] | 0.050 (0.53)(87) | 5600±6400 (19)[26] | 0.19 (0.68)(86) | 540±360 (19)[26] | 0.22 (0.88)(76) | 77±62 (4) | 0.13 (0.66)(73) |
| Carrot (BN) | 510±190 (51)[27] | 0.098 (0.58)(242) | 35±9 (51)[27] | 0.068 (0.69)(233) | 41±11 (51)[27] | 0.15 (0.65)(180) | 5.4±1.7 (5) | 0.071 (0.33)(188) |
| Cherry | 590±310 (46)[26] | 0.043 (0.33)(251)* | 91±21 (38)[26] | 0.12 (0.74)(185) | 150±67 (38)[26] | 0.19 (0.65)(166) | 9.8±1.9 (3) | 0.078 (0.37)(165) |
| Corn | N.M. | | N.M. | | N.M. | | N.M. | |
| Cotton (Pima) | N.M. | | N.M. | | N.M. | | N.M. | |
| Cotton (Upland) | N.M. | | N.M. | | N.M. | | N.M. | |
| Table Grape | 3600±950 (17)[24] | 0.064 (0.39)(113)* | 140±52 (17)[24] | 0.12 (0.70)(108) | 360±100 (17)[24] | 0.19 (0.53)(102) | N.A. | |
| Wine Grape | N.M. | | N.M. | | N.M. | | N.M. | |
| Liquidambar | 350±140 (31)[26] | 0.12 (0.59)(182) | 53±19 (31)[26] | 0.11 (0.67)(174) | 70±39 (31)[26] | 0.13 (0.34)(150)* | N.A. | |
| Miscanthus | 870±350 (21)[27] | 0.084 (0.67)(87) | 170±32 (21)[27] | 0.077 (0.72)(83) | 340±100 (21)[27] | 0.15 (0.71)(78) | N.A. | |
| Olive | 150±15 (8)[26] | 0.073 (0.83)(40) | 16±2 (8)[26] | 0.098 (0.83)(38) | 36±5 (8)[26] | 0.15 (0.73)(29) | N.A. | |
| Onion | N.M. | | N.M. | | N.M. | | N.M. | |
| Peach | N.M. | | N.M. | | N.M. | | N.M. | |
| Pistachio | 48±57 (15) | 0.092 (0.43)(246) | 24±4 (15) | 0.054 (0.39)(311) | 23±13 (15) | 0.20 (0.62)(238) | 7.3±4.5 (15) | 0.052 (0.19)(266) |
| Plum | 210±50 (7)[26] | 0.11 (0.79)(38) | 89±16 (7)[26] | 0.11 (0.91)(36) | 84±26 (7)[26] | 0.18 (0.91)(23) | N.A. | |
| Pomegranate | 240±29 (4)[24] | 0.038 (0.65)(28) | 52±8 (4)[24] | 0.092 (0.73)(27) | 190±35 (4)[24] | 0.24 (0.71)(17) | N.A. | |
| Potato | 550±91 (5)[24] | 0.11 (0.54)(27) | 550±60 (5)[24] | 0.17 (0.95)(25) | 640±90 (5)[24] | 0.26 (0.91)(20) | N.A. | |
| Tomato | 9800±5700 (8)[27] | 0.16 (0.57)(86) | 410±170 (8)[27] | 0.082 (0.46)(82)* | 570±190 (8)[27] | 0.13 (0.72)(81) | 43±32 (2) | 0.017 (0.07)(74) |
| Orange Parent Navel (No Flw) | 480±400 (15) | 0.059 (0.28)(535) | 240±200 (15) | 0.097 (0.49)(528) | 650±830 (15) | 0.13 (0.38)(530) | 35±38 (15) | 0.15 (0.53)(469) |
| Orange Parent Navel (Flowers) | 880±280 (36)[26] | 0.029 (0.33)(151)* | 500±130 (36)[26] | 0.12 (0.77)(151) | 1700±1100 (36)[26] | 0.15 (0.66)(151) | 92±29 (4) | 0.18 (0.73)(145) |
| Mandarin W. Murcott | 190±130 (21)[28] | 0.064 (0.49)(111)* | 69±41 (21)[28] | 0.12 (0.84)(107) | 16±7 (21)[28] | 0.11 (0.67)(87) | 7.9±3.0 (6) | 0.11 (0.64)(89) |
| Mandarin Clementine | 300±160 (36)[27] | 0.10 (0.64)(204) | 54±36 (36)[27] | 0.12 (0.82)(197) | 23±28 (36)[27] | 0.068 (0.37)(175)* | 5.1±1.5 (8) | 0.089 (0.51)(169) |
| Lemon Eureka | 140±60 (39)[25] | 0.046 (0.29)(240)* | 50±15 (39)[25] | 0.16 (0.91)(232) | 18±9 (39)[25] | 0.13 (0.47)(190)* | 3.5±0.35 (5) | 0.11 (0.48)(205) |

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 *

Table 3-3. Basal emission factors (ngC $gDM^{-1}$ $h^{-1}$) and beta values for monoterpenes, oxygenated monoterpenes and sesquiterpenes for crop plants investigated.

| | Monoterpenes | | Oxygenated Monoterpenes | | Sesquiterpenes | |
|---|---|---|---|---|---|---|
| Crop | 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)* | 150±28 (6)[24] | 0.16 (0.90)(32) | 10000±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)* | | | 56±36 (3)[27] | N.B. |
| Cherry | 84±59 (26)[26] | 0.067 (0.34)(121)* | 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)* | 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)* | 47±4.8 (2)[26] | 0.19 (0.94)(4) | N.D. | |
| Miscanthus | 140±89 (17)[27] | 0.044 (0.20)(63)* | 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)* | 39±55 (15)[26] | 0.15 (0.36)(22)* | N.D. | |
| Plum | 37±20 (5)[26] | 0.010 (0.04)(26)* | 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)* |
| Potato | 150±9.8 (3)[24] | 0.064 (0.47)(16)* | 22±9.3 (3)[27] | N.B. | 40±13 (3) | N.B. |
| Tomato | 740±260 (7)[27] | 0.11 (0.31)(68)* | N.D. | | 59±15 (3)[27] | N.B. |
| Orange P.N. (No Flower) | 2500±3400 (116)[26] | 0.14 (0.35)(522)* | 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)* | 3200±780 (11)[24] | 0.28 (0.92)(36) |
| Mandarin W. Murcott | 63±25 (20)[28] | 0.080 (0.47)(99)* | 150±190 (8)[29] | 0.23 (0.79)(20) | N.D. | |
| Mandarin Clementine | 26±18 (22)[26] | 0.064 (0.27)(141)* | N.D. | | N.D. | |
| Lemon Eureka | 22±22 (24)[25] | 0.036 (0.15)(166)* | 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 *

Table 3-4. Isoprene flux and environmental parameters for crop plants studied.

| | Isoprene Flux (ngC $gDM^{-1}$ $h^{-1}$) | | Leaf Temperature ($^oC$) | | PAR (µmol $m^{-2}$ $s^{-1}$) | | Sample Size (N) |
|---|---|---|---|---|---|---|---|
| Crop | *Min* | *Max* | *Min* | *Max* | *Min* | *Max* | |
| Alfalfa | | | | | | | 0 |
| Almond | 0.014 | 16 | 16.4 | 27.6 | 259 | 1040 | 53 |
| Carrot (RL) | 5.1 | 137 | 19.6 | 30.6 | 268 | 1020 | 29 |
| Carrot (BN) | 0.20 | 12 | 22.7 | 30.2 | 201 | 1020 | 58 |
| Cherry | 1.0 | 20 | 23.7 | 29.2 | 201 | 1150 | 39 |
| Corn | | | | | | | 0 |
| Cotton Pima | | | | | | | 0 |
| Cotton Upland | | | | | | | 0 |
| Table Grape | 4.8 | 29 | 20.0 | 27.8 | 220 | 977 | 24 |
| Wine Grape | | | | | | | 0 |
| Liquidambar | 1250 | 5600 | 24.9 | 27.1 | 202 | 863 | 31 |
| Miscanthus | 2.5 | 55 | 25.6 | 30.6 | 215 | 634 | 21 |
| Olive | 9.0 | 14 | 26.1 | 28.0 | 205 | 936 | 8 |
| Onion | | | | | | | 0 |
| Peach | | | | | | | 0 |
| Pistachio | 0.43 | 23 | 18.6 | 30.8 | 203 | 1040 | 86 |
| Plum | 3.1 | 12 | 25.6 | 27.7 | 257 | 904 | 7 |
| Pomegranate | 2.2 | 9.5 | 20.4 | 26.2 | 201 | 972 | 6 |
| Potato | 0.25 | 21 | 23.2 | 25.6 | 612 | 959 | 5 |
| Tomato | 16 | 73 | 23.0 | 28.6 | 263 | 1060 | 11 |
| Orange P.N. (No Flower) | 1.1 | 3100 | 21.0 | 31.6 | 205 | 1140 | 158 |
| Orange P.N. (Flowers) | 3.5 | 130 | 21.0 | 28.9 | 210 | 1100 | 51 |
| Mandarin W. Murcott | 0.22 | 12 | 22.2 | 32.0 | 234 | 1100 | 34 |
| Mandarin Clementine | 0.33 | 8.6 | 21.6 | 32.6 | 210 | 1110 | 62 |
| Lemon Eureka | 0.25 | 5.9 | 21.9 | 32.8 | 201 | 1070 | 64 |

Table 3-5. Statistics for algorithms for light and temperature (L&T) and temperature (T) for methanol, acetaldehyde, acetone, and isoprene for crop plants studied.

| | Methanol | | | | Acetone | | | | Acetaldehyde | | | | Isoprene | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *L&T* | | *T* | | *L&T* | | *T* | | *L&T* | | *T* | | *L&T* | | *T* | |
| Crop | $r^2$ | *Slope* | $r^2$ | *Slope* | $r^2$ | *Slope* | $r^2$ | *Slope* | $r^2$ | *Slope* | $r^2$ | *Slope* | $r^2$ | *Slope* | $r^2$ | *Slope* |
| Alfalfa | | | | | | | | | | | | | | | | |
| Almond N.S. | N.S. | N.S. | N.S. | N.S. | N.S. | N.S. | N.S. | 0.23 | 0.41 | 0.31 | 0.35 | | | | | |
| Carrot (RL) | 0.34 | 1.08 | 0.35 | 0.44 | 0.35 | 0.48 | 0.30 | 0.39 | 0.64 | 0.92 | 0.59 | 0.80 | 0.38 | 0.80 | 0.35 | 0.61 |
| Carrot (BN) | 0.31 | 0.83 | 0.33 | 0.61 | 0.49 | 1.06 | 0.56 | 0.68 | 0.58 | 1.13 | 0.55 | 0.93 | 0.17 | 0.38 | 0.15 | 0.27 |
| Cherry | 0.13 | 0.88 | 0.11 | 0.61 | 0.66 | 1.02 | 0.68 | 0.87 | 0.48 | 1.03 | 0.46 | 0.79 | 0.10 | 0.16 | 0.12 | 0.14 |
| Corn | | | | | | | | | | | | | | | | |
| Cotton Pima | | | | | | | | | | | | | | | | |
| Cotton Upland | | | | | | | | | | | | | | | | |
| Table Grape | 0.10 | 0.53 | 0.13 | 0.32 | 0.46 | 0.94 | 0.52 | 0.66 | 0.66 | 1.69 | 0.62 | 1.13 | | | | |
| Wine Grape | | | | | | | | | | | | | | | | |
| Liquidambar | 0.47 | 0.59 | 0.47 | 0.68 | 0.46 | 0.58 | 0.47 | 0.67 | 0.01 | 0.03 | 0.01 | 0.03 | | | | |
| Miscanthus | 0.40 | 0.77 | 0.40 | 0.65 | 0.34 | 0.60 | 0.49 | 0.53 | 0.70 | 0.98 | 0.66 | 0.97 | | | | |
| Olive | 0.62 | 1.13 | 0.74 | 0.90 | 0.42 | 0.81 | 0.62 | 0.75 | 0.76 | 1.16 | 0.77 | 1.05 | | | | |
| Onion | | | | | | | | | | | | | | | | |
| Peach | | | | | | | | | | | | | | | | |
| Pistachio | N.S. | N.S. | 0.12 | 0.13 | N.S. | N.S. | N.S. | N.S. | 0.44 | 0.52 | 0.44 | 0.41 | N.S. | N.S. | N.S. | N.S. |
| Plum | 0.67 | 1.11 | 0.81 | 0.94 | 0.80 | 1.19 | 0.89 | 1.02 | 0.74 | 1.27 | 0.87 | 0.99 | | | | |
| Pomegranate | 0.64 | 1.60 | 0.52 | 0.57 | 0.49 | 1.11 | 0.49 | 0.63 | 0.71 | 2.39 | 0.65 | 1.16 | | | | |
| Potato | N.S. | N.S. | 0.15 | 0.19 | 0.90 | 1.61 | 0.93 | 0.97 | 0.94 | 2.26 | 0.89 | 1.00 | | | | |
| Tomato | 0.16 | 0.35 | 0.17 | 0.28 | 0.12 | 0.49 | 0.33 | 0.43 | 0.67 | 1.12 | 0.64 | 0.91 | N.S. | N.S. | N.S. | N.S. |
| P.N. (No Flw) | 0.19 | 0.50 | 0.40 | 0.51 | 0.62 | 0.97 | 0.73 | 0.81 | 0.50 | 0.79 | 0.53 | 0.61 | N.S. | N.S. | N.S. | N.S. |
| P.N. (Flowers) | 0.19 | 1.21 | 0.16 | 0.60 | 0.74 | 1.04 | 0.74 | 0.77 | 0.54 | 0.81 | 0.53 | 0.58 | 0.58 | 1.28 | 0.62 | 0.91 |
| W. Murcott | 0.31 | 0.33 | 0.32 | 0.30 | 0.59 | 0.61 | 0.67 | 0.63 | 0.42 | 0.65 | 0.54 | 0.65 | 0.53 | 0.84 | 0.61 | 0.80 |
| Clementine | 0.50 | 0.59 | 0.53 | 0.51 | 0.63 | 0.66 | 0.60 | 0.60 | N.S. | N.S. | 0.11 | 0.17 | 0.44 | 0.98 | 0.45 | 0.73 |
| Eureka Lemon | 0.11 | 1.41 | N.S. | N.S. | 0.87 | 0.99 | 0.90 | 1.03 | 0.24 | 0.86 | 0.18 | 0.65 | 0.35 | 0.53 | 0.34 | 0.45 |

N.S. = Results not significant (e.g. $r^2 < 0.10$ or negative slope)
Note: Table 3-5 gives information on sample size (N)

Table 3-6. Statistics for algorithms for light and temperature (L&T) and temperature (T) for monoterpenes, oxygenated monoterpenes and sesquiterpenes for crop plants studied.

| | Monoterpenes | | | | Oxygenated Monoterpenes | | | | Sesquiterpenes | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | L&T | | T | | L&T | | T | | L&T | | T | |
| Crop | $r^2$ | *Slope* | $r^2$ | *Slope* | $r^2$ | *Slope* | $r^2$ | *Slope* | $r^2$ | *Slope* | $r^2$ | *Slope* |
| Alfalfa | 0.72 | 1.36 | 0.7 | 0.92 | | | | | | | | |
| Almond | 0.6 | 0.36 | 0.61 | 0.27 | 0.72 | 1.41 | 0.84 | 0.89 | 0.62 | 3.26 | 0.94 | 0.81 |
| Carrot (RL) | N.S. | N.S. | N.S. | N.S. | N.S. | N.S. | N.S. | N.S. | | | | |
| Carrot (BN) | 0.14 | 0.4 | 0.11 | 0.24 | | | | | N.S. | N.S. | N.S. | N.S. |
| Cherry | 0.64 | 2.52 | 0.6 | 1.37 | 0.69 | 1.57 | 0.78 | 0.87 | | | | |
| Corn | | | | | | | | | | | | |
| Cotton Pima | N.S. | N.S. | N.S. | N.S. | 0.32 | 0.4 | 0.34 | 0.27 | | | | |
| Cotton Upland | 0.51 | 1.02 | 0.43 | 0.66 | N.S. | N.S. | N.S. | N.S. | | | | |
| Table Grape | N.S. | N.S. | N.S. | N.S. | 0.11 | 0.68 | 0.11 | 0.28 | 0.25 | 0.56 | 0.28 | 0.32 |
| Wine Grape | 0.11 | 0.43 | N.S. | N.S. | N.S. | N.S. | N.S. | N.S. | 0.14 | 0.35 | N.S. | N.S. |
| Liquidambar | 0.5 | 0.16 | 0.63 | 0.17 | 0.64 | 1.65 | 0.81 | 1.07 | | | | |
| Miscanthus | 0.7 | 1.23 | 0.73 | 0.97 | 0.25 | 0.94 | 0.5 | 0.7 | 0.35 | 1.18 | 0.47 | 0.7 |
| Olive | 0.98 | 0.26 | 0.84 | 0.16 | 0.47 | 1.4 | 0.28 | 0.42 | | | | |
| Onion | N.S. | N.S. | N.S. | N.S. | | | | | | | | |
| Peach | 0.96 | 1.78 | 0.97 | 1.17 | 0.93 | 1.84 | 0.95 | 1.21 | | | | |
| Pistachio | 0.15 | 0.18 | 0.17 | 0.16 | N.S. | N.S. | N.S. | N.S. | | | | |
| Plum | 0.13 | 0.21 | N.S. | N.S. | 0.4 | 1.08 | 0.25 | 0.69 | | | | |
| Pomegranate | N.S. | N.S. | N.S. | N.S. | 0.63 | 1.01 | 0.69 | 0.68 | 0.29 | 1.87 | N.S. | N.S. |
| Potato | 0.12 | 1.31 | 0.2 | 0.53 | 0.12 | 0.13 | N.S. | N.S. | N.S. | N.S. | N.S. | N.S. |
| Tomato | 0.33 | 0.18 | 0.27 | 0.11 | | | | | N.S. | N.S. | N.S. | N.S. |
| Orange nflw) | 0.57 | 0.74 | 0.63 | 0.61 | 0.44 | 0.84 | 0.68 | 0.87 | 0.88 | 2.14 | 0.8 | 1.17 |
| Orange flw) | 0.6 | 0.78 | 0.61 | 0.58 | 0.43 | 1.37 | 0.37 | 0.74 | 0.92 | 2.13 | 0.89 | 1.11 |
| Mand W. Mur | 0.32 | 0.08 | 0.41 | 0.08 | 0.18 | 0.26 | 0.34 | 0.4 | | | | |
| Mand Clem | N.S. | N.S. | N.S. | N.S. | | | | | | | | |
| Lemon Eureka | N.S. | N.S. | N.S. | N.S. | | | | | | | | |

N.S.: Results not significant ( $r^2 < 0.10$ or negative slope)
Note: Table 3-5 gives information on sample size (N)

Table 3-7. Composition of monoterpene emissions expressed as fraction of one for crop plants studied via enclosures.

| Crop | limonene | β-cis-ocimene | β-trans-ocimene | β-myrcene | a-phellandrene | β-phellandrene | Δ3-carene | Δ2-carene | α-terpinene | γ-terpinene | α-thujene | sabinene | α-pinene | β-pinene |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alfalfa | 0.00 | 0.00 | 0.58 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.42 | 0.00 |
| Almond | 0.09 | 0.00 | 0.23 | 0.36 | 0.02 | 0.00 | 0.26 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 |
| Carrot (RL) | 0.28 | 0.03 | 0.03 | 0.37 | 0.00 | 0.01 | 0.03 | 0.00 | 0.11 | 0.06 | 0.00 | 0.00 | 0.06 | 0.03 |
| Carrot (BN) | 0.02 | 0.19 | 0.01 | 0.23 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.15 | 0.34 | 0.01 |
| Cherry | 0.00 | 0.94 | 0.06 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Corn | | | | | | | | | | | | | | |
| Cotton Pima | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.34 | 0.64 | 0.00 |
| Cotton Upland | 0.00 | 0.01 | 0.19 | 0.00 | 0.00 | 0.39 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.41 | 0.00 |
| Table Grape | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.98 | 0.00 |
| Wine Grape | 0.00 | 0.00 | 0.23 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 | 0.00 | 0.64 | 0.03 | 0.04 |
| Liquidambar | 0.55 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.17 | 0.27 | 0.00 |
| Miscanthus | 0.48 | 0.04 | 0.23 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.21 | 0.00 | 0.02 | 0.02 | 0.00 |
| Olive | 0.00 | 0.05 | 0.93 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 |
| Onion | 0.85 | 0.00 | 0.15 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Peach | 0.00 | 0.00 | 1.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Pistachio | 0.87 | 0.05 | 0.01 | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 | 0.01 | 0.01 |
| Plum | 0.00 | 0.00 | 1.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Pomegranate | | | | | | | | | | | | | | |
| Potato | 0.61 | 0.22 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.17 | 0.00 |
| Tomato | 0.00 | 0.00 | 0.00 | 0.00 | 0.07 | 0.75 | 0.01 | 0.14 | 0.02 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 |
| Orange (no flw) | 0.07 | 0.04 | 0.27 | 0.56 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 0.01 | 0.00 |
| Orange (flw) | 0.02 | 0.00 | 0.30 | 0.67 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 |
| Mand. W. Murcott | 0.13 | 0.33 | 0.32 | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.04 | 0.00 | 0.09 | 0.02 | 0.04 |
| Mand. Clementine | 0.17 | 0.06 | 0.14 | 0.01 | 0.01 | 0.00 | 0.14 | 0.00 | 0.00 | 0.00 | 0.00 | 0.40 | 0.05 | 0.03 |
| Lemon Eureka | | | | | | | | | | | | | | |

Table 3-8. Composition of oxygentated monoterpene emissions expressed as fraction of the total for crop plants studied via enclosures.

| Plant | Linalool | Perillene | Eucalyptol |
|---|---|---|---|
| Alfalfa | | | |
| Almond | 0.10 | 0.90 | 0.00 |
| Carrot (RL) | 0.94 | 0.06 | 0.00 |
| Carrot (BN) | | | |
| Cherry | 0.00 | 1.00 | 0.00 |
| Corn | | | |
| Cotton Pima | 0.00 | 1.00 | 0.00 |
| Cotton Upland | 0.04 | 0.96 | 0.00 |
| Table Grape | 0.00 | 1.00 | 0.00 |
| Wine Grape | 0.00 | 1.00 | 0.00 |
| Liquidambar | 0.00 | 1.00 | 0.00 |
| Miscanthus | 0.26 | 0.00 | 0.74 |
| Olive | 0.00 | 1.00 | 0.00 |
| Onion | | | |
| Peach | 0.00 | 1.00 | 0.00 |
| Pistachio | 0.16 | 0.84 | 0.00 |
| Plum | 0.03 | 0.97 | 0.00 |
| Pomegranate | 0.00 | 1.00 | 0.00 |
| Potato | 0.00 | 1.00 | 0.00 |
| Tomato | 1.00 | 0.00 | 0.00 |
| Orange P.N. (No Flower) | 0.93 | 0.06 | 0.01 |
| Orange P.N. (Flowers) | 0.97 | 0.02 | 0.01 |
| Mandarin W. Murcott | 0.06 | 0.94 | 0.00 |
| Mandarin Clementine | 0.46 | 0.54 | 0.00 |
| Lemon Eureka | | | |

Table 3-9. Composition of sesquiterpene emissions expressed as fraction of the total for crop plants studied via enclosures

| Plant | β-caryophyllene | α-humulene |
|---|---|---|
| Alfalfa | | |
| Almond | 0.77 | 0.23 |
| Carrot (RL) | 1.00 | 0.00 |
| Carrot (BN) | 1.00 | 0.00 |
| Cherry | | |
| Corn | | |
| Cotton Pima | 0.54 | 0.46 |
| Cotton Upland | | |
| Table Grape | 0.69 | 0.31 |
| Wine Grape | 1.00 | 0.00 |
| Liquidambar | 1.00 | 0.00 |
| Miscanthus | 0.07 | 0.93 |
| Olive | 1.00 | 0.00 |
| Onion | | |
| Peach | | |
| Pistachio | 0.00 | 1.00 |
| Plum | | |
| Pomegranate | 0.90 | 0.10 |
| Potato | 0.98 | 0.02 |
| Tomato | 1.00 | 0.00 |
| Orange P.N. (No Flower) | 1.00 | 0.00 |
| Orange P.N. (Flowers) | 1.00 | 0.00 |
| Mandarin W. Murcott | 0.33 | 0.67 |
| Mandarin Clementine | 0.17 | 0.83 |
| Lemon Eureka | | |

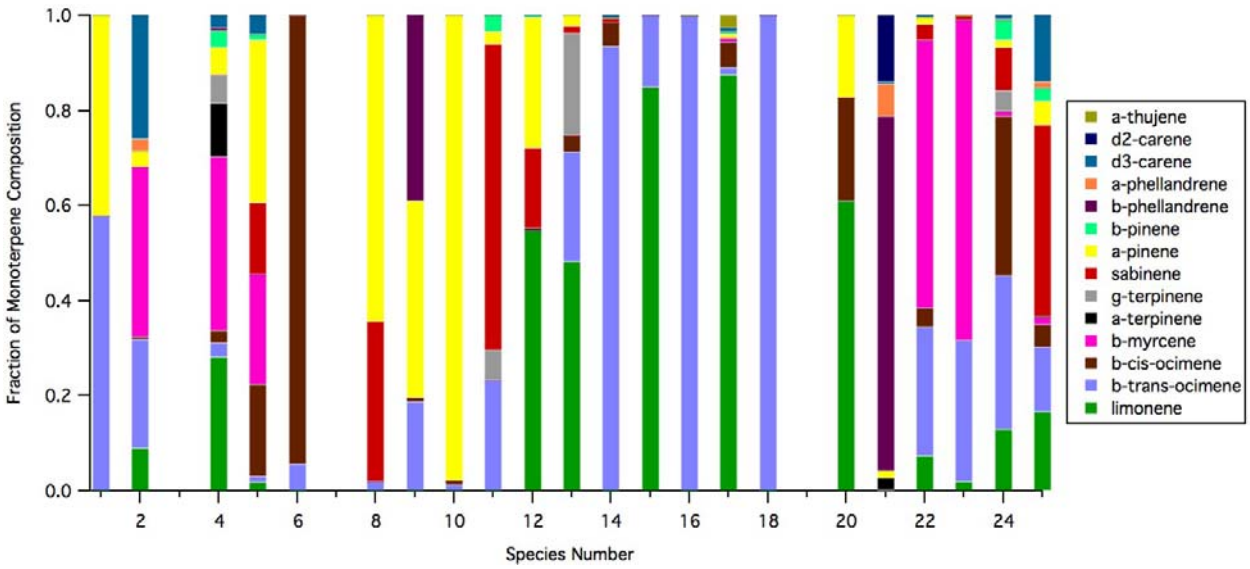



Figure 3-1. Monoterpene composition from enclosure measurements for crops studied.

Species Codes: 1-Alfalfa, 2-Almond, 3-Apricot 4-Carrot (RL), 5-Carrot (BN), 6-Cherry, 7-Corn, 8-Cotton Pima, 9-Cotton Upland, 10-Table Grape, 11-Wine Grape, 12-Liquidambar, 13-Miscanthus, 14-Olive, 15-Onion, 16-Peach, 17-Pistachio, 18-Plum, 19-Pomegranate, 20-Potato, 21-Tomato, 22-P.N. Orange (No Flw), 23-P.N. Orange (With Flw), 24-W. Murcott Mandarin, 25-Clementine Mandarin, 26-Eureka Lemon

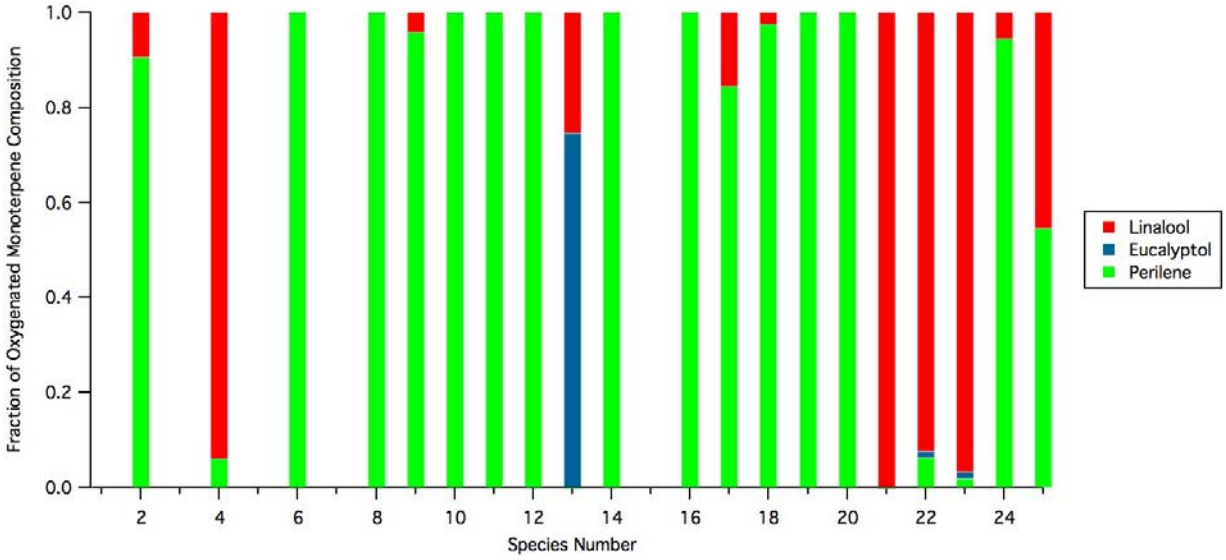



Figure 3.2. Oxygenated monoterpene composition from enclosure measurements for crops studied.

Species Codes: 1-Alfalfa, 2-Almond, 3-Apricot 4-Carrot (RL), 5-Carrot (BN), 6-Cherry, 7-Corn, 8-Cotton Pima, 9-Cotton Upland, 10-Table Grape, 11-Wine Grape, 12-Liquidambar, 13-Miscanthus, 14-Olive, 15-Onion, 16-Peach, 17-Pistachio, 18-Plum, 19-Pomegranate, 20-Potato, 21-Tomato, 22-P.N. Orange (No Flw), 23-P.N. Orange (With Flw), 24-W. Murcott Mandarin, 25-Clementine Mandarin, 26-Eureka Lemon

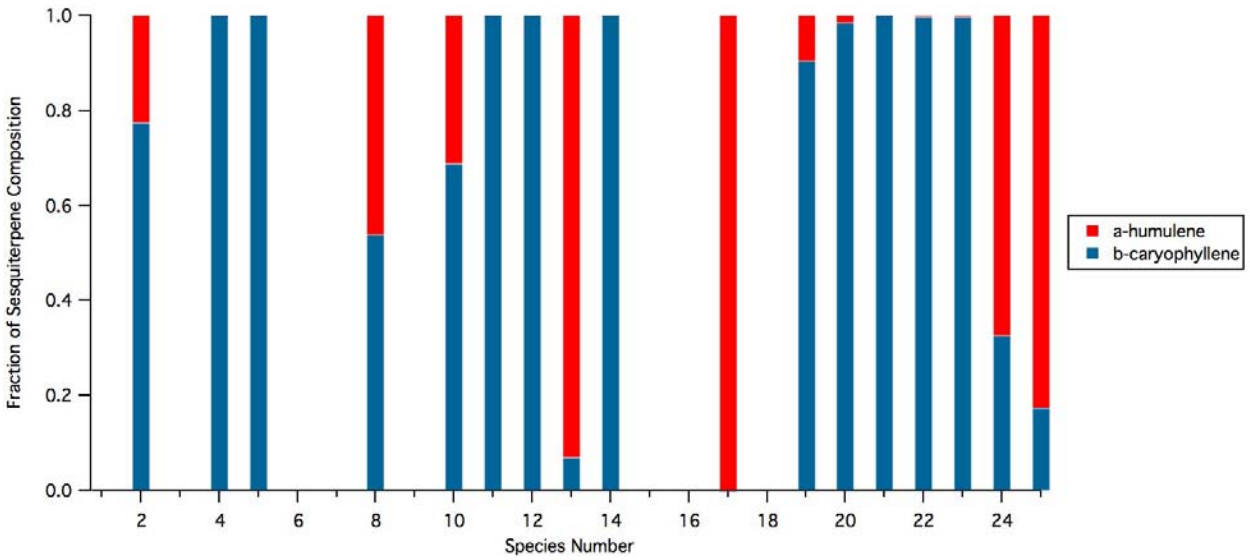



Figure 3-3. Sesquiterpene composition from enclosure measurements for species and varieties studied.

Species Codes: 1-Alfalfa, 2-Almond, 3-Apricot 4-Carrot (RL), 5-Carrot (BN), 6-Cherry, 7-Corn, 8-Cotton Pima, 9-Cotton Upland, 10-Table Grape, 11-Wine Grape, 12-Liquidambar, 13-Miscanthus, 14-Olive, 15-Onion, 16-Peach, 17-Pistachio, 18-Plum, 19-Pomegranate, 20-Potato, 21-Tomato, 22-P.N. Orange (No Flw), 23-P.N. Orange (With Flw), 24-W. Murcott Mandarin, 25-Clementine Mandarin, 26-Eureka Lemon

### 3.4.2 Discussion of Crop Emissions

For each plant species examined there were two to eight individuals measured for several days at a time in the individual plant enclosures. The BEF and photosynthetic uptake values were determined at basal conditions of 30 ± 2.0°C leaf temperature and PAR > 800 when possible. Calculated BEF and $\beta$ values (temperature dependence of emissions) are summarized in Table 3-2 and 3-3 for the important classes of BVOC based on our enclosure measurements, which also include information on the number of individual measurements for each species where sample size (N) is given for the number of 15-minute averages that met the measurement conditions. Values were determined using both the GC/MS and PTR-MS data, with calculations done using IGOR Pro and MATLAB. Values for methanol, acetaldehyde, acetone, isoprene, and were determined using PTR-MS measurements, and values for sesquiterpenes and oxygenated

monoterpenes were determined using GC/MS measurements. Values for monoterpenes were determined using PTR-MS data unless they were not available or inadequate, in which case GC/MS data were used. Due to occasional instrument malfunctions, there are a few species that had insufficient or no measurements to report for either the GC/MS or the PTR-MS measured species. Because of the relatively low temperature and light conditions in the greenhouse environment, typical basal conditions were frequently not met during plant enclosure periods. Although we offer data for BEF when PAR was below 800, we present these data with caution since we have found in past experimental work that low PAR levels cause emissions to drop sharply, and we are not convinced plants give representative emissions at low PAR. We also note that conditions in the Central Valley during the smog season often have PAR above 1200 and temperature above 35 $^{o}$C. Thus, our enclosure temperatures and PAR and corresponding emission results do not fully represent the conditions in which crop plants are often found.

For BVOC with clear temperature dependencies (with the exception of isoprene discussed further below), we accommodated the sub-basal conditions by calculating BEFs at several standard temperatures below 30°C (i.e. 24-29°C ± 2°C) using only data points that had above 200 PAR to ensure daytime conditions. These BEFs and their standard deviations were then adjusted from the average temperature of the measurements (noted in Tables 3-2 and 3-3) used to 30°C values using the beta calculated for that species and compound. $\beta$ values were calculated using the temperature dependent algorithm developed by Tingey et al. The slope and correlation coefficients (r) were determined using a trust-region Levenberg-Marquardt least orthogonal distance method to account for uncertainties in both measurements. In cases where our calculation of $\beta$ had low confidence (noted in Tables 3-2 and 3-3), we used a default beta of 0.10,

which was chosen as an intermediate value for a wide variety of species and compounds. The sample size (N) given with the BEF or $\beta$ indicates the number of data points used to establish the value.

We assessed the performance of both temperature and light + temperature algorithms using our BEF and beta values. Emissions were calculated using the leaf temperature and PAR data measured on the 15-minute intervals in the greenhouse using formulas from Tingey et al. (temperature) and Guenther et al. (light + temperature). We performed regressions of calculated to observed values using a trust-region Levenberg-Marquardt least orthogonal distance method, and report the slope, coefficient of determination ($r^2$), and sample size for these analyses. The results of our model assessment are shown in Tables 3-5 and 3-6. While there are cases in which the models and results agreed well with the measurements, in many cases neither the temperature nor the light + temperature algorithm described the system well. Most of the poor correlations between model and measurements likely occurred because the fluxes were near the detection limit, but may also be due to the limited data for each plant species.

### 3.4.3 Isoprene Emissions

Isoprene is the dominantBVOC emitted on a global scale, accounting for approximately 1/3 of all known BVOC emissions (Guenther et al. 2006). Its production and emission depends directly on the photosynthetic metabolism since specific leaf reservoirs (as opposed to temporary pools in the intercellular-spaces) are never filled up with this compound.

For isoprene, which is known to have strong light dependencies, we only calculated BEFs at strict basal conditions of 30 ± 2°C, PAR > 800, which limited our results to less than half of our test species. To assess the isoprene emissions from the other species, we report the range of isoprene emissions observed and the associated leaf temperature and PAR range (Table 3-4).

All crops measured in this study can be classified as low isoprene emitters, with most emission values not exceeding 10 ngC $gDM^{-1}$ $h^{-1}$ and none exceeding 100 ngC $gDM^{-1}$ $h^{-1}$ (Table 3-4). *Liquidambar styraciflua*, which we measured for comparison, is considered a high isoprene emitter, with previous research showing BEF up to 75000 ngC $gDM^{-1}$ $h^{-1}$ based on leaf cuvette measurements (Circh et al. 1992, Harley et al. 1996). We recorded lower emission values for this species, ranging up to 5600 ngC $gDM^{-1}$ $h^{-1}$. These lower values occurred at least in part because the light and temperature conditions when our measurements occurred (25-27°C, 0-860 PAR) were below the basal conditions for both light and temperature (30°C, 1000 PAR), and in part because we used branch enclosures which typically show emissions 60% as high as measured by leaf cuvettes due to self-shading (Guenther et al. 1994, Harley et al. 1997). The main point of reporting the measurements for liquidambar here is to demonstrate that the emissions from all crops studied were always less than 2%, and generally less than 0.2%, of what we observed for this major isoprene emitting species.

The few crop species that did emit isoprene at rates between 10-100 ngC $gDM^{-1}$ $h^{-1}$ were tomatoes, carrots, and 'Parent Navel' orange. For example, isoprene emission from tomato was very low in comparison with mono-and sesquiterpenes, 43 ng(C) $g(DW)^{-1}h^{-1}$) (Table 3-2, 3-3), but still one of the highest emission rates among the crop species under investigation. The high

photosynthetic rate for tomato (up to 15 umol $m^{-2}$ $s^{-1}$, (data not shown) suggests that this species (and all the other crops studied here) allocates a minimal fraction of the assimilated carbon for isoprene production. Carrots also showed a low isoprene emission rate up to 77 ng(C) $g(DW)^{-1}$ $h^{-1}$) (Table 3-2), but only one of the carrot varieties had this rate, so we present this value with caution. 'Parent Navel' orange isoprene emissions were 35 and 92 ng(C) $g(DW)^{-1}h^{-1}$), two orders of magnitude lower than monoterpenes, andwhile for other citrus species such as mandarins and lemon isoprene emissions were tiny, between 3 and 7 ng(C) $g(DW)^{-1}h^{-1}$), (Table 3-2, 3-3), suggesting that *Citrus* species are not significant isoprene emitters and that the methyl-erythritol-phosphate biosynthetic pathway in the leaves (Hampel et al. 2005) produces mainly monoterpenes rather than isoprene in *Citrus* sp., especially in navel orange. Isoprene emissions had about the same correlation with the T algorithm as with the L+T algorithm for the mandarins and lemon (Table 3-5). This was especially the case at low emission rates occurring in the dark or under low light conditions in which the L+T algorithm systematically underestimates BVOC emission rates for all species. In general for this study, the small rate of isoprene emissions makes it difficult to determine which algorithm better predicts isoprene emission.

### 3.4.4 Monoterpenes, Oxygenated Monoterpenes, and Sesquiterpenes

There was a wide array of oxygenated VOC and terpenoid compounds that were quantified in the crops emissions with considerable diversity between the species. Detailed chemical speciation for monoterepenes, oxygenated monoterpenes, and sesquiterpenes as measured by our in-situ GC/MS system are shown in Figures 3-1, 3-2, and 3-3, and given numerically in Tables 3-7, 3-8, and 3-9. Monoterpene concentrations were measured as individual species with the GC/MS and as total monoterpenes with the PTR-MS, and agreed to within 20%. In addition to several well-

studied monoterpenes, there was a considerable amount of β-myrcene, sabinene, and both isomers of β-ocimene. Oxygenated monoterpene emissions were dominated by linalool and perillene, a little-studied furanoid. Using the GC/MS system we only observed two sesquiterpenes, α-humulene and β-caryophyllene. Consistent with previous work, β-caryophyllene dominated the two, but it is likely that there were other sesquiterpenes that were outside of the GC/MS observable range or at concentrations below the limit of detection.

3.4.4.1 *Monoterpenes*

Emissions of monoterpenes were lowest (< 100 ngC $gDM^{-1}$ $h^{-1}$) from almond, grape, olive, pistachio, plum and pomegranate (Table 3-3). For almond and cherry, the BEF for monoterpenes agreed with previous research (Winer et al. 1992). We detected very low emission from grape (11 and 91 ng(C) $g(DW)^{-1}$ $h^{-1}$) whereas Winer et al. (1992) did not detect any emission. The monoterpene BEF for peach, 1211 ngC $gDM^{-1}$ $h^{-1}$ was anomalous compared to other plants in the *Prunus* genus (almond, plum) measured in this study which all had BEFs more than one order of magnitude below that of peach.

Pistachio var. Kerman was characterized by Winer et al. (1992) as a strong monoterpene emitter (12 μg $g(DW)^{-1}h^{-1}$), whereas we recorded an emission more than two orders of magnitude lower. We measured pistachio emissions under basal conditions (30 $^{o}$C) and the data were collected at an average temperature of 34 $^{o}$C in the cited study, so the difference of temperature cannot explain this discrepancy. Since pistachio acreage is now large and increasing in the Central Valley, revisiting this crop for additional measurement would be appropriate. We speculate that although the same variety was used in both studies, specific phenotypic traits of the individuals

selected could cause such differences. Pistachio plants are dioecious, with male and female flowers on separate trees. Female plants were measured in this study, since they are the principal gender found in pistachio orchards, but unfortunately no information about this feature is available in Winer et al. (1992). Further research comparing BVOC emission differences in male and female trees could reveal interesting results about the effect of genetically-determined features on plant emissions. However, there remain fundamental questions about possible compounds and emission strength from pistachio.

The correlation between measured and modeled monoterpene emissions (whether the T or L+T algorithm) was significant ($P > 0.05$) for almond (Table 3-6), which is known to have extrafloral nectary glands on the petiole (Kerner, 2008), a potential source of monoterpenes obeying the T algorithm. In olive, monoterpene emissions correlated about the same with either algorithm. Olive posseses glandular trichomes on leaves (Vieira et al. 2001). Since both olive and almond feature specific storage structures where terpenes are typically stored in high amounts, it is likely that high BVOC amounts can be released to the atmosphere if leaves are wounded during agricultural operations. However, unlike harvesting processes in some parts of the world, in the Central Valley trees are typically shaken to remove fruit, so leaf wounding attributable to harvest should be minimal.

Among the herbaceous species, tomato was the highest monoterpene emitter BEF = 742 ng(C) $g(DW)^{-1}$ $h^{-1}$, (Figure 3-1, Table 3-3). The BEF we measured was one order of magnitude lower than that recorded by Winer et al. (1992) but consistent with results from 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 beenshown to dramatically increase after wounding or pathogen infestation (Jansen et al. 2008), thus suggesting that during harvesting procedures higher emissions should be expected. Potato showed a low emission of monoterpenes (basal factor = 154 ng(C) g(DW)$^{-1}$h$^{-1}$) (Table 3-3), and this emission was poorly correlated with the modeled emissions for both algorithms ($r^2$=0.12 and 0.2 respectively) (Table 3-6), although slightly better for the temperature algorithm, and this species is known to have glandular trichomes (Lyshede 1980).

Orange had the highest levels of monoterpene emissions, BEF = 2520 ng(C) g(DW)$^{-1}$ h$^{-1}$, Table 3-3. The β coefficient of the T algorithm for total monoterpenes from oranges without flowers was on average 0.14, similar to that reported by Ciccioli et al. (1999). In a study performed with GC/MS, Winer et al. (1992) reported a leaf emission rate for navel orange of 800 ng(C) g(DW)$^{-1}$ h$^{-1}$) at 21 $^{o}$C, similar to what we observed in our study. Ciccioli et al. (1999) performed field measurements using a branch enclosure and GC/MS measurement techniques; they recorded emission rates from a 'Valencia' orange of the same order of magnitude as values presented in this study.

Lemon and mandarins emitted total monoterpenes at a very low rate (22, 26, and 63 ng(C) g(DW)$^{-1}$ h$^{-1}$ for 'Eureka' lemon, 'Clementine' mandarin, and 'W. Murcott' mandarin, respectively (Table 3-3). For mandarins, the most abundant monoterpenes species were β-cis and β-trans isomers of ocimene with minor amounts of limonene, sabinene, and pinene. Clementine mandarin had twice the rate of photosynthesis of navel orange, but lower emission of BVOC. Lemon and mandarins, which had negligible monoterpene emissions, featured lower β

coefficients than orangeIn study of Winer et al. (1992) the emissions for lemon var. 'Lisbon' at 31 $^{o}$C appeared to be 3600 ng g(DW)$^{-1}$ h$^{-1}$, which is much higher than ours, but the difference may be attributed to the conditions of light and temperature in the Winer et al. study as well as genotypic and phenotypic dissimilarities.

The correlation between measured and modeled BVOC emissions was significant for 'Parent Navel' orange, both when emissions were modeled using the L+T algorithm and the T algorithm (Tables 3-5, 3-6). The possibility that some of the BVOC species (e.g. those stored in secretory structures) are more temperature dependent, and other are more light dependent (e.g. those originated from *de novo* synthesis) seems the most likely explanation, as already noted in Simon et al. (2005).

3.4.4.2 <u>*Oxygenated monoterpenes*</u>

Oxygenated monoterpene emissions have not been reported extensively in the past. The dominant oxygenated sesquiterpene emission observed in this study was perilene. Emmissions of oxygenated monotperenes were highest from flowering orange (BEF = 4600 ngC g(DW)$^{-1}$h$^{-1}$), with high emissions also by pima cotton and non-flowering orange (BEF 2700 and 1300 ngC g(DW)$^{-1}$h$^{-1}$, respectively) followed by lower emissions form cherry, peach, almond, and murcott mandarin, with very low emission from the other crops (Table 3-3). Modeled and measured emissions of oxygenated monoterpenes from non-flowering orange leaves were not significantly correlated, probably because the emissions were very low. The occurrence of perillene may suggest that the T and L+T algorithms do not represent the emission of this furanoid. For flowering oranges, the T algorithm best describes the emission of oxygenated monoterpenes,

mainly linalool (slope = 0.74), confirming the high temperature dependency of emissions for this compound.

3.4.4.3 *Sesquiterpenes*

Almond was the highest sesquiterpene emitter of the crops we studied according to the calculated BEF (10000 ng(C) $g(DW)^{-1}$ $h^{-1}$), while the magnitude of the monoterpene and oxygenated monoterpene emissions was very low for this species. 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. If we apply 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. For example, sesquiterpene emissions of tomato were 59 ng(C) $g(DW)^{-1}$ $h^{-1}$ with sesquiterpenes emitted consistent with Winer et al. (1992).

The sesquiterpene emission rates for orange trees found in this study are consistent with Hansen and Seufert (2003), who measured BVOC emissions with a branch enclosure and agree with our finding that β-caryophyllene is the main sesquiterpene emitted by navel orange (Table 3-9). Hansen and Seufert (2003) demonstrated that the L+T algorithm better represented the actual β-caryophyllene emissions than the T algorithm, while our results reveal that slopes are closer to one with the T algorithm than with L+T algorithm. This suggests that temperature is a more important environmental parameter controlling the emission of sesquiterpenes in orange plants without flowers as traditionally stated for this type of species (Tingey et al., 1991). The β coefficient for sesquiterpenes in oranges was on an average 0.28, although recent literature suggests a β coefficient used for modeling purposes to be about half of that calculated in this

study (Sakulyanontvittaya et al. 2008). Our value is however in agreement with previous estimates (Ciccioli et al. 1999) and justified by the higher vaporization energy required to transfer β-caryophyllene from the liquid to the gas phase, owing to their lower vapor pressure in comparison with monoterpenes.

### 3.4.5 Small Oxygenated VOC: Methanol, Acetone, and Acetaldehyde

#### 3.4.5.1 *Methanol*

Methanol was emitted at rates comparable to monoterpenes for the non-citrus woody species (Table 3-2, 3-3), with values ranging from 48 (pistachio) to 3600 ngC $g(DW)^{-1}h^{-1}$ for table grape, the highest. Interestingly, for almond and grape we observed spikes in emissions coincident with the stomatal aperture in the morning, between 06:00 and 07:00. This agrees with the hypothesis that methanol is produced in high amounts during tissue elongation during the night, it accumulates in the intercellular spaces and is then released in the early morning as soon as stomata open in response to light (Huve et al. 2007).

Among herbaceous species, tomato showed the highest methanol emission of the all crop species studied (BEF = 9800 ng(C) $g(DW)^{-1}h^{-1}$) (Table 3-2). This is partly explained by the high photosynthetic rates (up to 14.7 μmol $m^{-2}s^{-1}$) suggesting the plant is growing and expanding very rapidly. Carrots also showed reasonably high methanol emissions of 608 and 507 ng(C) $g(DW)^{-1}h^{-1}$ for 'Bolero Nantes' and 'Red Label' varieties, respectively. For all the herbaceous species, methanol emission is better represented by the T algorithm. This is in agreement with previous findings related to isoprenoids, although methanol is unlikely accumulated in storing organs as terpenes.

In lemon and mandarins, methanol was the oxygenated compound with the highest emissions as compared to acetone or acetaldehyde (Table 3-2) and a BEF ranging from 140 to 300 ng(C) g(DW) $^{-1}$h$^{-1}$ for 'Eureka' lemon and 'Clementine' mandarin, respectively (Table 3-2). For oranges, the emission of methanol was of the same order of magnitude compared to that of the other *Citrus* species. However, the carbon invested in methanol emission was still a very minor percentage of the carbon assimilated through photosynthesis (~ 0.032 % averaged for all species during the central hours of the day in which measurements were carried out). It is important to note that for compounds not directly linked to photosynthetic metabolism, there could be a delay in the re-emission of photosynthetically-fixed carbon in the atmosphere; such is the case for OVOC, which depends on the duration of the catabolic processes that release such compounds. In our experiments however, the long acclimation phase in the enclosures and the observation of a stable photosynthetic signal before starting BVOC measurements supports the hypothesis that a mismatch between carbon photosynthetic uptake and carbon released via OVOC emission did not occur.

Methanol is emitted as a result of pectin demethylation during cell wall elongation during leaf expansion (Fall and Benson, 1996; Galbally and Kirstine, 2002), with plant growth globally recognized as the primary source of methanol in the atmosphere (Galbally and Kirstine, 2002). Leaf expansion is particularly enhanced during the night, but methanol emission seems to be regulated by the stomata (Huve et al. 2007). For this reason we observed the highest levels of methanol emission during the central hours of the day when stomatal conductance was at the highest levels (ranging 100 mmol m$^{-2}$ s$^{-1}$, data not shown). Since stomata never completely closed at night (assessed to levels around 5 mmol m$^{-2}$ s$^{-1}$, data not shown), emissions at night,

recorded at temperatures ~ 17-19 $^{o}$C, were up to half of the maximum daily emissions measured. The modeled emissions according to the T and L+T algorithm correlated similarly with the measured emission, while the slope of the linear regression was closer to 1.0 for the T algorithm, except for Eureka lemon, in which both the $r^2$ and the slope were more favorable to the L+T algorithm. We want to highlight that the light-dependency of methanol emissions is purely dependent on the diffusive resistance of stomata, and not to the activation of a biosynthetic pathway as for isoprene and some monoterpenes (Lichtenthaler et al. 1997). This has been confirmed by Folkers et al. (2008), who demonstrated that a limited fraction of newly assimilated carbon is reemitted as methanol. This implies that other factors influencing stomatal aperture (exposure to pollutants, increase of atmospheric $CO_2$) may affect methanol emission, and the T or L+T algorithm should be used depending on the prevailing environmental driving factor. High temperatures indeed may suggest the use of a T algorithm, considering the temperature dependency of methanol emission reported by Folkers et al. (2008).

3.4.5.2 *Acetone*

The highest acetone emission was from 'Red Label' carrot, 5600 ng(C) g(DW)$^{-1}$h$^{-1}$) (Table 3-2), but this value is two orders of magnitude greater than the 'Bolero Nantes' variety, so we offer this value with caution. The next highest value was 550 ng(C) g(DW)$^{-1}$ h$^{-1}$) for potato. Emissions of acetone were lower for lemons and mandarins than for orange, and for citrus seemed to be represented about equally by the T or L+T algorithm. We tend to exclude that plant tissues were wounded during enclosure, given the absence of C-6 compounds that are typical indications of wounding (data not shown) and the relatively low amount of methanol emitted. Spikes in acetone emission from 'Bolero Nantes' carrot and tomato during the night

culminated right before 05:00, and in these cases emissions seemed not to be under stomatal control, since stomatal conductance was at its minimal value (10 mmol $m^{-2}$ $s^{-1}$). This dynamic also complicates the interpretation of the correlation and slope of the modeled emission according the T and L+T algorithm, although the T algorithm seems to explain better the acetone emission in all species. These results suggest that acetone emission mechanisms are still unexplained and further research should be addressed at investigating the causes of its release in the atmosphere as it is the most abundant ketone in the atmosphere (Koppmann and Wildt 2007).

3.4.5.3 *Acetaldehyde*

Of all the crops except oranges, acetaldehyde was emitted in highest amount from potato (BEF = 640 ng(C) g(DW)$^{-1}$ h$^{-1}$) (Table 3-2). This compound has been shown to be synthesized in the roots under anoxic conditions (Kreuzwieser et al. 1999). The large tuber belowground may therefore be a source of acetaldeyde. Grape was the non-orange woody species which emitted the highest amount (360 ng(C) g(DW)$^{-1}$h$^{-1}$). Mandarins and lemon emitted acetaldehyde at rates below 100 ng(C) g(DW)$^{-1}$ h$^{-1}$) and emission was slightly better represented by the L+T algorithm.

Past field studies (Ciccioli et al. 1999; Smith et al. 1996) attributed acetone and acetaldehyde compounds to atmospheric oxidation processes (e.g. photooxidation of linalool) because no detectable emission was observed from branch enclosures. Given the low retention time in our enclosures (~10 minutes) and the limited presence of reactive oxidants (OH, ozone), we exclude gas-phase reaction as the production source in the enclosure, and thus associate fluxes of acetone and acetaldehyde with direct plant emission. We do recognize that additional gas-phase

chemistry in the ambient atmosphere may enhance the apparent emission of these two compounds during field studies. Although no proxies of membrane lipoxygenation (C-6 compounds) were detected during OVOC measurement after one day of enclosure, we cannot exclude a minimal wounding disturbance to navel orange that may have lead to acetaldehyde emissions (previously reported by Fall et al. (1999) and Loreto et al. (2006)).

### 3.4.6 Emissions from Flowering and Non-Flowering Oranges

Flowering is an important phenomenon that occurs twice annually in most of the *Citrus* plantations in California's Central Valley. We found that flowering dramatically increases emissions of monoterpenes from navel orange, approximately tripling the rate to 7800 ng(C) $g(DW)^{-1}$ $h^{-1}$ (Table 3-3) while the net photosynthesis rates decreased more than 50%. A sharp increase in emissions during flowering was also noted for oxygenated monoterpenes, the sesquiterpenes, and for the small oxygenated VOC (Table 3-2). Isoprene increase was also noted but even with the increase isoprene emission is so small as to be insignificant. Figure 3-4 shows the emission dynamics over three days for two orange trees measured at the same time, one flowering and one without flowers. These observations are in agreement with previous results showing the presence of flowers dramatically influences the magnitude and composition of BVOC emitted from oranges (Ciccioli et al. 1999; Hansen and Seufert 1999; Arey et al. 1991).

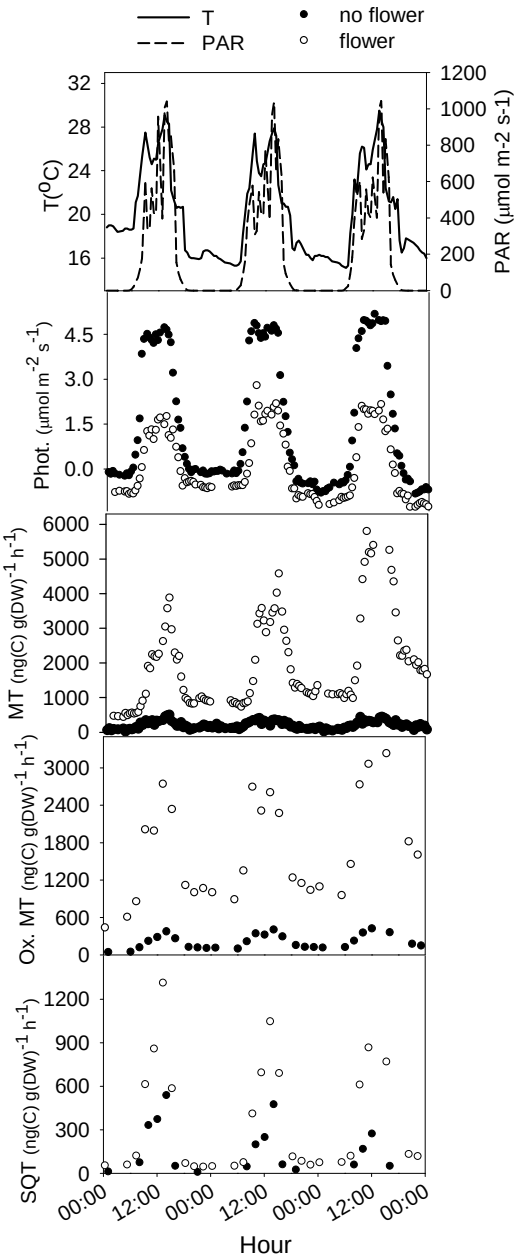



Figure 3-4. For three days of continuous measurements on 'Parent Navel' orange plants in June we report (from the top): environmental parameters (temperature and PAR), photosynthesis, and emissions of monoterpenes (MT), oxygenated monoterpenes (Ox. MT) and sesquiterpenes (SQT) of a flowering (open circles) and a non-flowering (closed circles) individual.

Monoterpene species emitted from flowering and non-flowering branches were substantially different. For non-flowering plants, β-myrcene was the main monoterpene emitted (56%), followed by β-trans-ocimene (27%) (Table 3-7). For flowering plants, 67% of the total monoterpene emission was β-myrcene followed by β-trans-ocimene (30%). β-trans-ocimene is a compound already reported in emissions from flowering *Citrus* trees and known to attract pollinators (Dudareva and Pickersky 2000). Linalool was the dominant oxygenated monoterpene observed from flowering 'Navel Orange' plants (97%) (Table 3-8), which agrees with findings of Ciccioli et al. (1999) and Arey et al. (1991) and is also consistent with the reported presence of linalool synthase in flowers (Pickersky et al. 1994). We identified perillene, representing 6% of the oxygenated monoterpene emissions from non-flowering citrus, but 94% of oxygenated monoterpenes from W. Murcott mandarin. This is the first time this furanoid has been identified as an emission from *Citrus*. Volatile furanoids are very rarely found in plants. To our knowledge, cis- and trans-linalool oxide and now perillene are the only furanoids found in plant BVOC emissions (Noe et al 2006). β-Caryophyllene was the main sesquiterpene emitted from both flowering and non-flowering oranges (Table 3-9). For the flowering plants, the T algorithm rather than the L+T algorithm better predicted emissions of β-caryophyllene (slope of 1.11 vs 2.13); this is contrary to the findings from Hansen and Seufert (2003) who hypothesized the role of light in enhancing volatilization of β-caryophyllene from storage pools by triggering oxidative process which lead to membrane degradation and release of β-caryophyllene.

During daytime hours, monoterpenes represented, on average, 0.02 % and up to 0.9 % of photosynthesized carbon in non-flowering and flowering plants, respectively.

Emissions from plant species that have the ability to store BVOC, such as *Citrus*, mainly originate from the volatilization of BVOC accumulated within specific leaf reservoirs. Thus emissions depend more on temperature than on plant physiology, and this is generally the case we observed for *Citrus*. A clear decoupling between photosynthesis and BVOC emissions in flowering oranges was observed, mainly due to the role of flowers as strong BVOC emitter in the atmosphere. We also recorded a higher mitochondrial respiration activity in the flowering plants averaging 0.93±0.04 μmol $m^{-2}$ $s^{-1}$ at night versus 0.3±0.05 μmol $m^{-2}$ $s^{-1}$ in non-flowering plants, which suggests that during the flowering processes *Citrus* sp. decreases its net carbon uptake. Consistently, a previous study in grapefruit showed that net carbon uptake was decreased because flowering respiration was enhanced rather than photosynthesis being decreased (Bustan and Goldschmidt 1998). In addition, the increased carbon lost as terpenes during flowering also minimally contributes to a decrease of net carbon uptake, although our enclosure system did not allow an exact partition between BVOC emitted by flowers and leaves since the were both enclosed at the same time.

Although we did not sample BVOC from flowering individuals for the other *Citrus* species, we expect a similar change in emission intensity and composition. This difference in emission between flowering and non-flowering plants should be taken into account in emissions and air pollution modeling, since during flowering periods the chemistry of the atmosphere may be significantly different. In the Central Valley of California a massive flowering event takes place in early spring, with flowers growing faster but persisting longer on the trees.

### 3.4.7 Comparison of Results of The Current Study to Previously Reported Values

All crops studied had very low emission rates of isoprene (Table 3-4). These results are consistent with previous studies in California for several of the same crop species (Winer et al. 1992, Karlik and Winer 2001). Furthermore, these results are consistent for plants within plant phylogeny, and specifically for the rose family and more specifically the *Prunus* genus (almond, peach, plum) (Benjamin et al. 1996, Karlik et al. 2002). Therefore, the BEF reported in Guenther et al. of 16000 ng(C) $g(DW)^{-1}$ $h^{-1}$ could be lowered for the crops studied, particularly since this value seems to be based on agronomic crops rather than those more typical in California. Emission of monoterpenes is more comparable with the value reported by Guenther et al. (400 ng(C) $g(DW)^{-1}$ $h^{-1}$). All crops studied, with the exception of orange, fall in the category of low monoterpene emitters. Emissions from some of these species are in the same order of magnitude of data observed in past research and now used as BEF for regional/global models BEIGIS (Scott and Benjamin, 1997) and MEGAN (Guenther et al. 2006). We observed in our study a low (<1000 ngC $gDM^{-1}$ $h^{-1}$) amount of OVOC emitted by crops, with methanol often representing the major compound emitted. Current parameterization for regional/global model is still poor for these classes of compounds. In MEGAN, a BEF of 800 μg $m^{-2}$ $h^{-1}$ is generally associated with croplands based on few previous studies on alfalfa and ryegrass (Warneke et al. 2002, Schade and Custer 2004). We note that California's croplands are dominated by permanent crops (orchards, vineyards), rather than agronomic crops like alfalfa, maize, or soybeans. These values, which we approximately convert to ng(C) $g(DW)^{-1}$ $h^{-1}$ using a leaf area index of 2 and a specific leaf mass of 100 g $m^{-2}$, equals to 6000 ng(C) $g(DW)^{-1}$ $h^{-1}$, is a higher value than most of our measured crops with exception of tomato.

### 3.5 Implications for California's Agricultural Landscape

The aim of this study was to provide information on BVOC emissions through determination of the basal emission factors and light and temperature dependence for crop species cultivated in large areas in California.

Based on the species we measured, we conclude that the agricultural crops studied generally have low emission rates of isoprene and other terpenoid compounds compared to many plants found in natural or urban landscapes. Isoprene is generally considered the most important single BVOC in terms of impact on atmospheric chemistry, but our results show that emissions of isoprene from these crops were uniformly low. Emissions of terpenes and oxygenated hydrocarbons (particularly methanol, but also acetaldehyde, and acetone) represented the dominant fraction of the total BVOC emission for the crops studied. Oxygenated VOC dominated emissions for some crops such as tomato, grape, potato, miscanthus, mandarins, and lemon. Terpene emissions dominated for other crops such as orange. However, these statements are based on limitations of sample size, experimental design, and low emission rates measured, so we offer these generalizations with caution.

The 'Parent Navel' orange tree emitted more terpenes than the other crop plants studied, and emissions of terpenoids and many other BVOC increased dramatically during the flowering event. However, emissions from orange per g dry leaf are still far less than emissions from the major BVOC emitting California plant species occurring in the natural environment. BVOC may increase during other events during the crop cycle, including harvesting and management practices such as pruning, potentially accounting for a significant fraction of the annual budget of

emissions from orange orchards. We expect increases in emissions to occur for other crops during flowering (insect-pollinated flowers probably moreso than for wind-pollinated flowers) and certain management practices, but these effects were not the focus of this study.

It is useful to put the measured emissions in perspective from the plant carbon budget point of view. Our results show that overall an almost negligible amount of photosynthesized carbon is re-emitted into the atmosphere and lost as BVOC (< 0.1 %) from most of the crop species studies. This is in stark contrast to the dominant isoprene, methylbutenol, and terpene emitting species so far identified in California's natural landscape such as oaks and pines which emit on the order of 2-3% of their photosynthesized carbon as BVOC (Bouvier-Brown et al., in review; Kesselmeier et al. 2002), and the flowering orange whose total BVOC emissions to the atmosphere accounted for 2.8 % of carbon fixed during photosynthesis.

Even though emissions were generally low, BVOC emitted from crop species may still play a significant role in the chemistry of the atmosphere in areas like in the San Joaquin Valley of California, where there are large areas planted with agricultural crops. Therefore, it is important to model emissions for the agricultural landscape as non-zero, and to evaluate the importance of these emissions in regional air quality models.

Previous modeling of crop emissions at regional and global scales has been poorly constrained due to lack of information about the species-specific BEF and temperature and light dependence. The results reported here can now be used as input parameters for new modeling efforts. Specifically, our results are intended for use in the California ARB's BEIGIS Model and the

MEGAN (Model of Emissions of Gases and Aerosols from Nature) model developed by Guenther et al. (2006) to provide more detailed estimates on the regional and global BVOC emissions from crops, thus decreasing the error in model emission estimates, and providing more accurate inputs for regional air quality models.

Based on the emissions measured from the crops species studied in the greenhouse during phase I of this project, we chose orange as the crop to study in detail with flux measurements at the orchard scale for phase II. In addition, the large difference in emissions between the flowering and non-flowering orange trees led us to change our strategy for phase II. In the original proposal we had planned to measure fluxes at the whole canopy scale for two different crops over short periods. Based on the results in phase I we decided to measure fluxes over an orange orchard over a full year in order to characterize fluxes under a variety of conditions including flowering and non-flowering periods.

# 4.0 FLUX MEASUREMENTS OF BVOC FROM CITRUS

## 4.1 Introduction and Site Description

The overall biogenic VOC emissions of an individual plant are affected by its green-leaf biomass and by its intrinsic rates of emission of isoprene, monoterpenes and other BVOC, as well as by environmental factors such as temperature, light intensity, and phenology. Emission rates, expressed as μg BVOC per gram dry leaf mass per hour, vary by more than three orders of magnitude among plant species (Benjamin et al. 1996, Benjamin et al. 1998), and trees with both high biomass and high emissions rates may be dominant BVOC emitters in urban or rural settings. In this section, we describe the year-long observations of fluxes and vertical concentration gradients of BVOC measured in a commercial orange orchard.

### 4.1.1 Site Selection and Infrastructure

The experimental site was a citrus orchard owned by Jim and Milo Gorden (Figure 4-1), about three km (two miles) west of the UC Lindcove Research and Experiment Station (36°21'23.68"N and 119°5'32.14"W, 131 m above sea level). Power for measurements was arranged through Southern California Edison, and three overhead poles were installed to bring 120/240 V single-phase power 300 feet from the Edison line to an insulated seatainer equipped with a temperature control system which was used to house analytical instrumentation. The seatainer was brought to the site Aug 12, 2009. A tower (Floatograph FM50 telescoping mast) was erected on a concrete base between the next two citrus trees west of the seatainer (Figure 4-2). Instruments and sampling lines were installed on the tower (Figure 4-3) and connected to the seatainer. A security fence was installed after the tower had been outfitted. A schematic diagram of instruments and inlet line heights is shown in Figure 4-4.

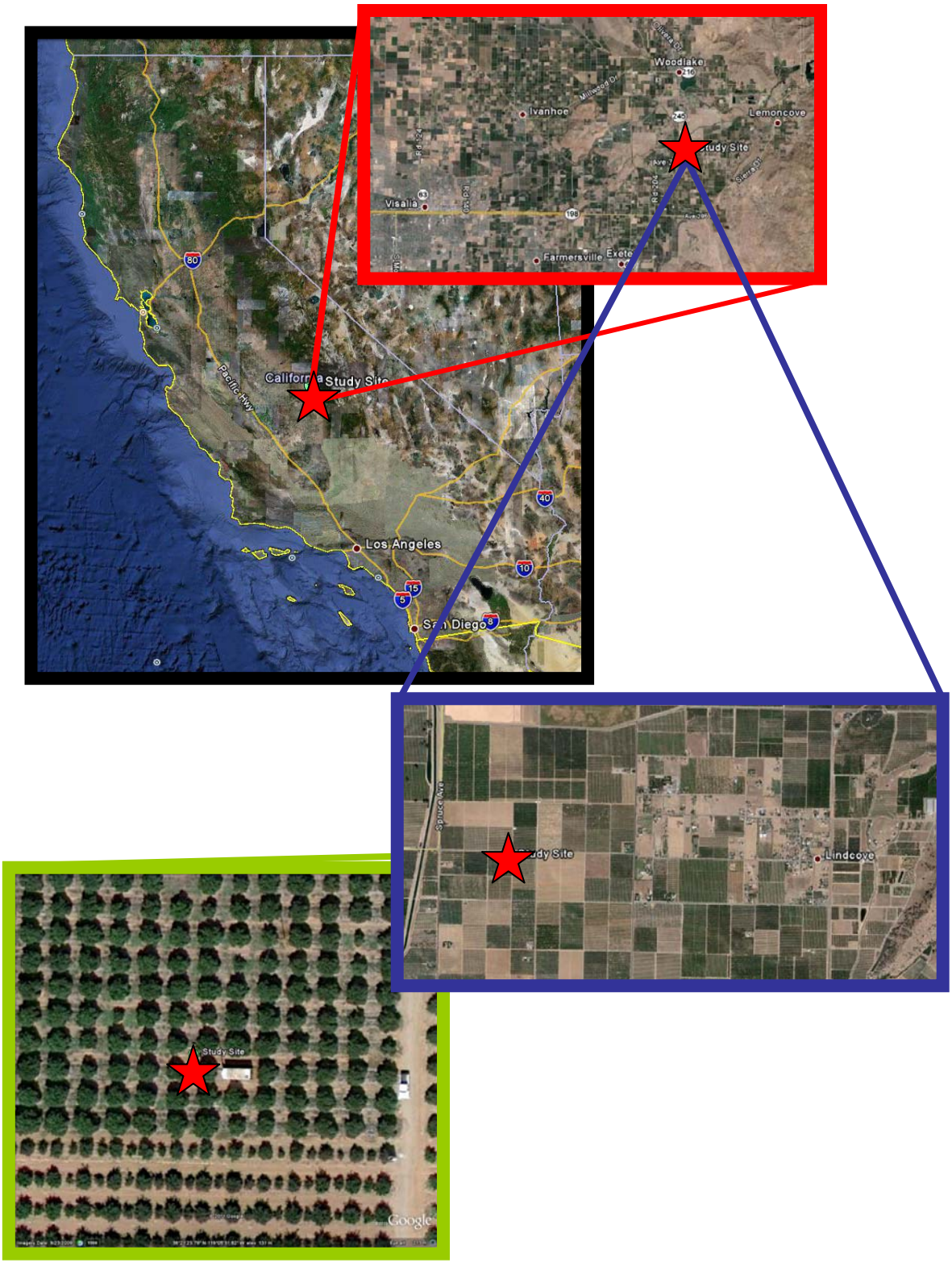



Figure 4-1. Site location for flux measurements, San Joaquin Valley, Tulare County, east of Visalia, about 3 km west of the UC Research and Extension station at Lindcove.

Figure 4-2. Image showing seatainer and concrete pad with tower for flux measurements. Citrus variety is 'Valencia' orange. To the south (lower) is 'W. Murcott' mandarin.

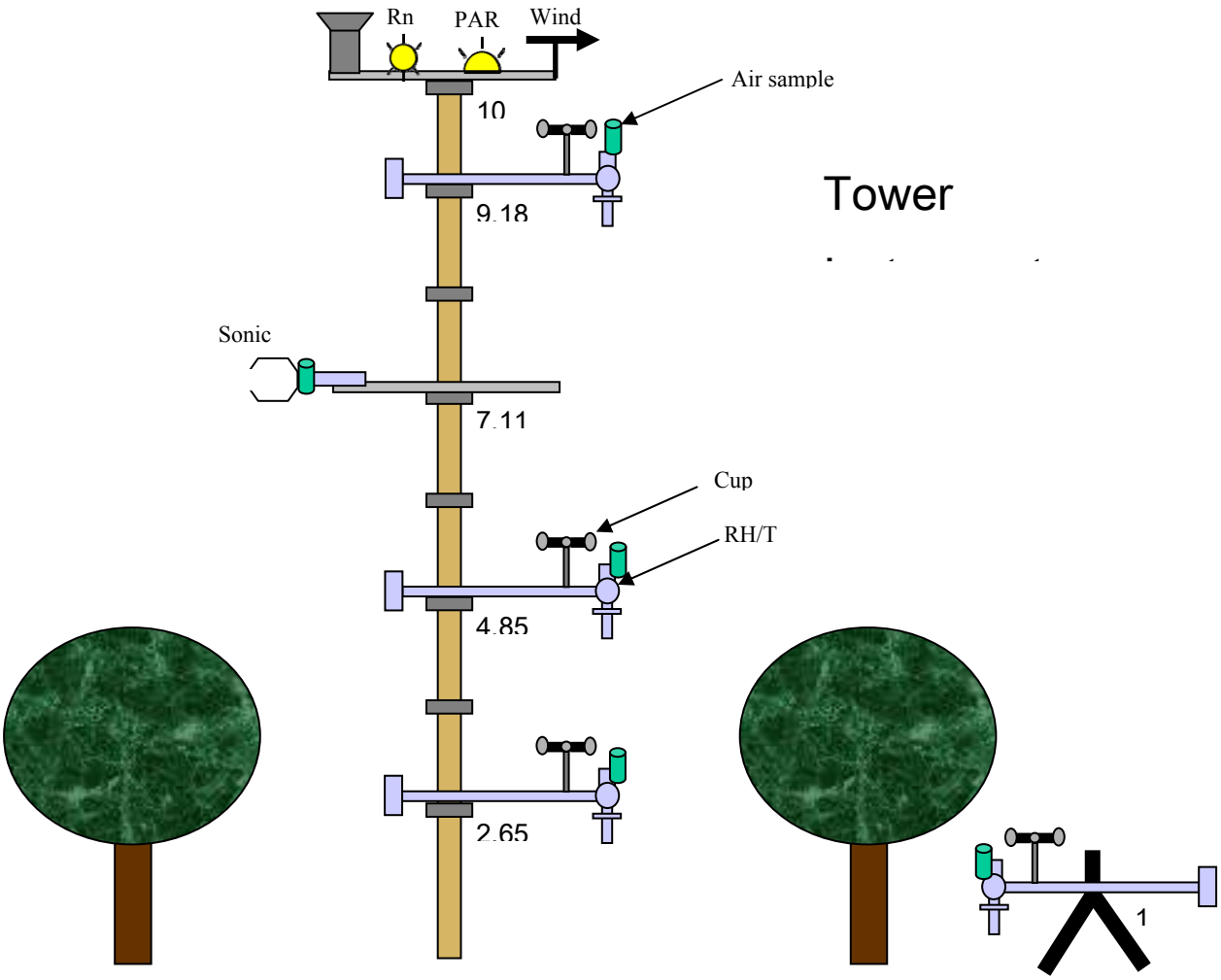



Figure 4-3. Tower with sensor arrangement and inlet heights.

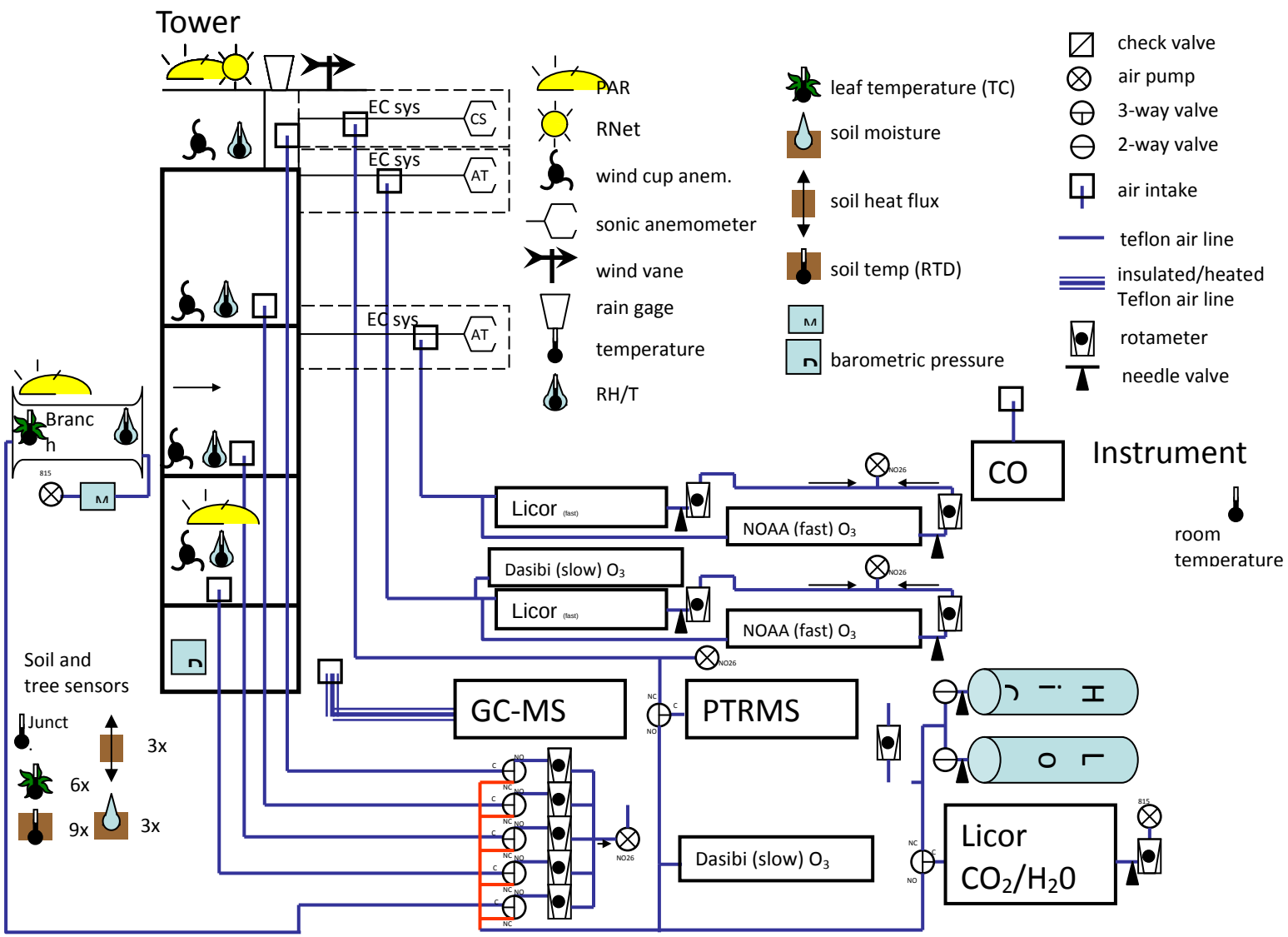



Figure 4-4. Schematic of sensors and analytical instruments.

### 4.1.2 Climate and Meteorology

The site is characterized by a Mediterranean climate typical of Central California, with warm dry summers and cold wet winters. Our daily-averaged annual air temperature data (Figure 4-5) was similar to the annual air temperature averaged over a period of 12 years as recorded at the CIMIS station (California Irrigation Management Information System) located at the UC Lindcove research station.

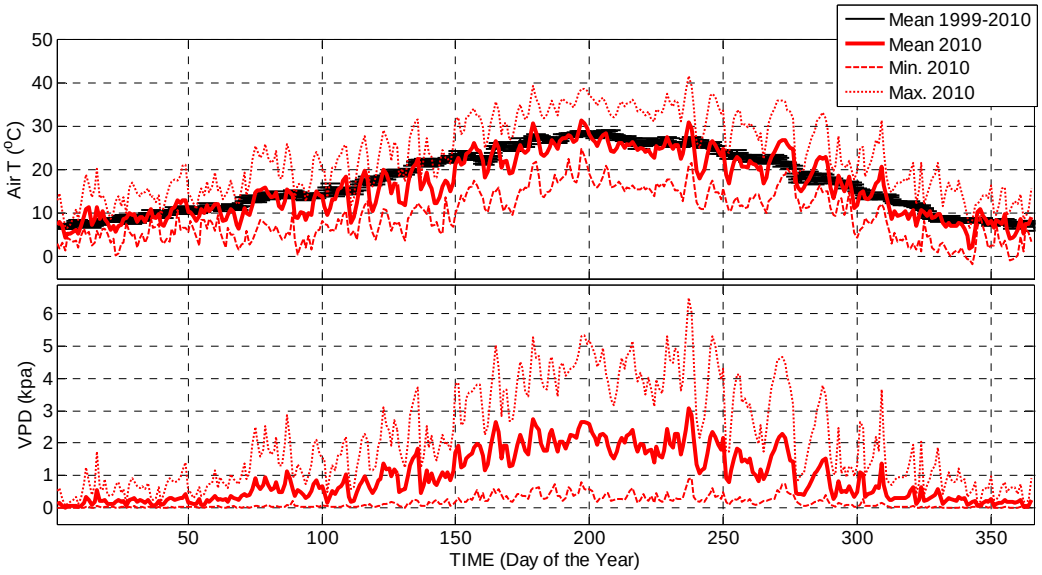



Figure 4.5 In red bold, daily averages of air temperature and vapor pressure deficit (VPD) at the citrus research site. The continuous lines show daily minima, the broken lines show daily maxima. The black line shows the average daily temperature (± sd from year 1999 to year 2010) from the CIMIS research station, located at the UC Lindcove citrus research station three km east of our measurement site.

Hourly mean values of temperature, vapor pressure deficit, photosynthetic active radiation (PAR) and turbulence (u*) are shown in Figure 4-6, separating three well defined periods: summer, flowering (day-of-year 116 to 145) and fall-winter.

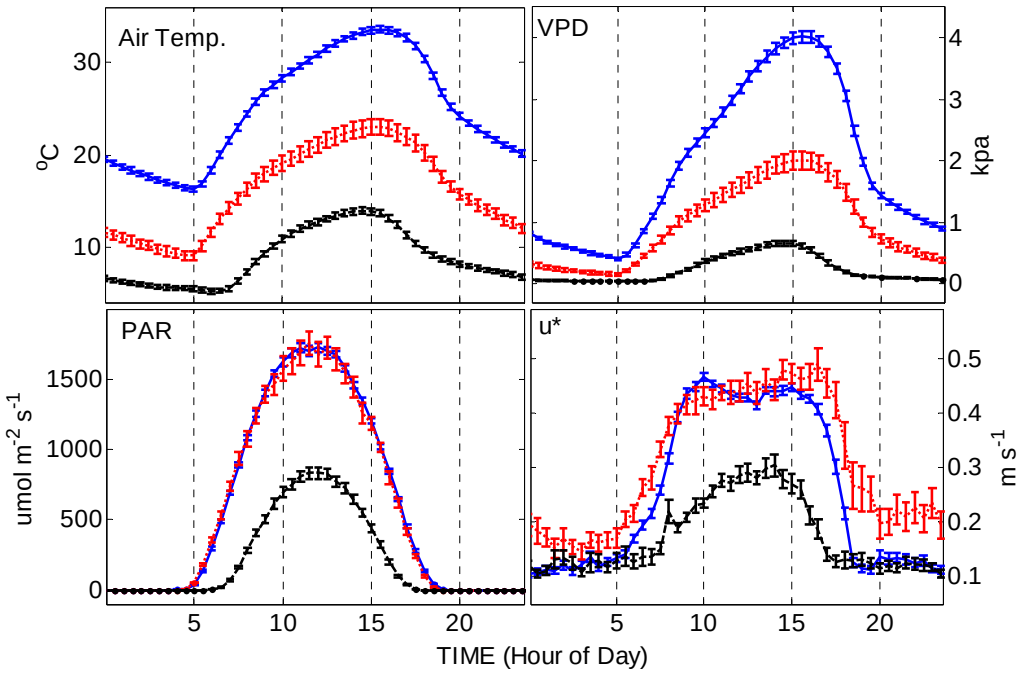



Figure 4-6 Hourly mean values (± sd) of air temperature, vapor pressure deficit (VPD), photosynthetically active radiation (PAR) and u*. In black, data averaged for the winter period (day of the year 1 to 80 and 325 to 365); in red, data averaged for the flowering period (day of the year 116 to 145); in blue, data averaged for the summer period (day of the year 116 to 145).

The typical wind pattern in this area brings daytime air across the valley from the west and then up the mountain slopes of the Sierra Nevada Mountains from the nearby urban area of Visalia, while at night a gentle downslope wind reverses the direction (Figure 4-7). The total precipitation over the one year measurement period was 979 mm, much higher than the annual precipitation averaged for the previous 12 years measured at the CIMIS station (245 ± 132 mm).

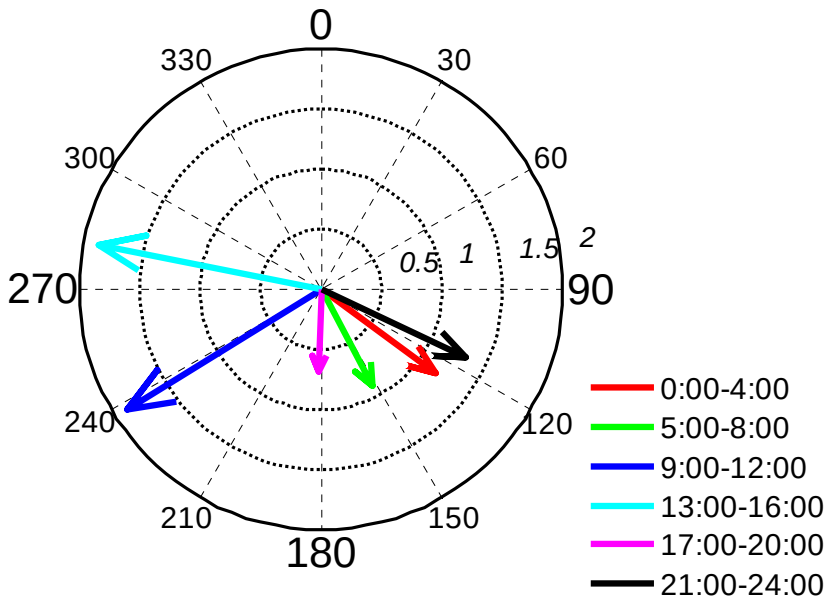



Figure 4-7. Wind rose plot with arrows indicating the wind direction (in degrees, 0 = N) for different hours of the day, and x axis showing the wind speed. Data are averaged for the full measurement period.

### 4.1.3 Soil

Soil data for the block where orange trees were located were taken from the peer-reviewed soils-to-go website housed at the UC Kearney Ag Center, http://soilstogo.uckac.edu. These data indicate an agricultural soil well suited for citrus (Table 4-1). The soil taxonomic name was a fine, mixed, thermic abruptic durixeralf.

Table 4-1. Soil properties according to location in the soil profile.

| | |
|---|---|
| Soil Name: | San Joaquin Loam; 0 To 2 Percent Slopes |
| Soil Symbol: | 154 |
| Acres within the Map Unit: | 3120.87 |
| Farmland Class: | Farmland of statewide importance |
| Slope Gradient: | 1 |
| Flood Frequency: | None |
| Drainage Class: | Moderately well drained |
| Available Water (inches) 0 to 10 Inches: | 1.46 |
| Available Water (inches) 0 to 20 Inches: | 3.06 |
| Available Water (inches) 0 to 40 Inches: | 3.38 |
| Available Water (inches) 0 to 60 Inches: | 3.38 |
| Nonirrigated Capability Class: | 4 |
| Irrigated Capability Class: | 3 |
| First Horizon: 0 cm-33 cm | |
| Horizon Name: | H1 |
| Layer: | H |
| Top Depth: | 0 cm |
| Bottom Depth: | 33 cm |
| Sand: | 42.1% |
| Silt: | 37.9% |
| Clay: | 20.0% |
| Organic Matter: | 1.5% |
| Saturated Hydraulic Conductivity (ksat): | 9.00 cm/sec |
| Available Water Capacity (awc): | 0.15 cc |
| Calcium Carbonate (CaCO3): | 0% |
| Calcium Sulfate (CaSO4): | 0% |
| Sodium Absorption Ratio (SAR): | 0.00 |
| Electrical Conductivity (ECe): | 0.00 dS/m |
| pH: | |

Second Horizon: 33 cm-51 cm

| | |
|---|---|
| Horizon Name: | H2 |
| Layer: | H |
| Top Depth: | 33 cm |
| Bottom Depth: | 51 cm |
| Sand: | 59.6% |
| Silt: | 17.9% |
| Clay: | 22.5% |
| Organic Matter (om): | 1.5% |
| Saturated Hydraulic Conductivity (ksat): | 2.70 cm/sec |
| Available Water Capacity (awc): | 0.17 cc |
| Calcium Carbonate (CaCO3): | 0% |
| Calcium Sulfate (CaSO4): | 0% |
| Sodium Absorption Ratio (SAR): | 0.00 |
| Electrical Conductivity (ECe): | 0.00 dS/m |

---

Third Horizon: 51 cm-64 cm

| | |
|---|---|
| Horizon Name: | H3 |
| Layer: | H |
| Top Depth: | 51 cm |
| Bottom Depth: | 64 cm |
| Sand: | 27.6% |
| Silt: | 29.9% |
| Clay: | 42.5% |
| Organic Matter (om): | 1.5% |
| Saturated Hydraulic Conductivity (ksat): | 0.22 cm/sec |
| Available Water Capacity (awc): | 0.05 cc |
| Calcium Carbonate (CaCO3): | 0% |
| Calcium Sulfate (CaSO4): | 0% |
| Sodium Absorption Ratio (SAR): | 0.00 |
| Electrical Conductivity (ECe): | 0.00 dS/m |

---

Fourth Horizon: 64 cm-142 cm

| | |
|---|---|
| Horizon Name: | H4 |
| Layer: | H |
| Top Depth: | 64 cm |
| Bottom Depth: | 142 cm |
| Sand: | |
| Silt: | |
| Clay: | |
| Organic Matter (om): | |
| Saturated Hydraulic Conductivity (ksat): | |
| Available Water Capacity (awc): | 0.00 cc |
| Calcium Carbonate (CaCO3): | |
| Calcium Sulfate (CaSO4): | |
| Sodium Absorption Ratio (SAR): | |
| Electrical Conductivity (ECe): | |

---

Fifth Horizon: 142 cm-198 cm

| | |
|---|---|
| Horizon Name: | H5 |
| Layer: | H |
| Top Depth: | 142 cm |
| Bottom Depth: | 198 cm |
| Sand: | |
| Silt: | |
| Clay: | 17.5% |
| Organic Matter (om): | 0.3% |
| Saturated Hydraulic Conductivity (ksat): | 0.91 cm/sec |
| Available Water Capacity (awc): | 0.11 cc |
| Calcium Carbonate (CaCO3): | 0% |
| Calcium Sulfate (CaSO4): | 0% |
| Sodium Absorption Ratio (SAR): | 0.00 |
| Electrical Conductivity (ECe): | 0.00 dS/m |

### 4.1.4 Trees

The block of trees in which the tower and instruments were located was 'Valencia' orange on trifoliate rootstock, with a planting date in the 1960's. The square block had dimensions of 650 ft N-S and E-W, so the area was about 420,000 sq ft or about 10 acres. The block immediately south was 'W. Murcott' mandarin on trifoliate interstock. To the east was 'Lane Late' orange on trifoliate rootstock, and to the west 'Valencia' on either Carizzo or trifoliate rootstock. The seatainer and tower were in the SE corner of the block, in the third row north counting from the south end of the block, and tower was between the 7$^{th}$ and 8$^{th}$ trees counting from the east edge of the block. Tree no. 6 was removed to make a space for the seatainer. Avenue 314, a rural two-lane road with asphalt cover, was the closest road, and located 600 ft north of the tower.

### 4.1.5 Leaf Mass and Leaf Area Determinations from Whole-Tree Harvest

We harvested a 'Valencia' citrus tree from within the study block to measure citrus leaf mass and leaf area. These data are critical for relating flux measurements at the canopy versus the leaf or branch scale, and for scaling emissions in biogenic emission models. The tree harvested for measurement was surrounded by other citrus trees on all sides so there was no edge effect of proximity to a road. The tree height was 3.7 m as measured with a telescoping pole. The radius in each of the cardinal directions was measured with a tape; the radii varied from 1.6 to 2.5 m with a mean of 1.97 m. Approximating the tree crown as a circle, the planar area as seen from above was 12.2 m$^2$.

The tree was harvested over a three-day period in August, 2010, taking care to keep leaves from drying prematurely. Leaves were removed from stems and placed in paper bags for drying.

Initially, thirteen samples of leaves of about 1 kg each fresh mass were measured for leaf area with a LiCor 3100C leaf area meter, but to do so was too time consuming and leaves began to wilt, interfering with area measurements. Therefore, five fresh subsamples of leaves were measured for leaf area and then oven-dried to obtain leaf mass, so the ratio of leaf mass to leaf area could be calculated. The mean specific leaf area (SLA) of citrus leaves was 85.4 $cm^2$ $g^{-1}$ with a standard deviation of 6.00, and a coefficient of variation of 7.02%. The reciprocal, leaf mass density (LMD), was 0.0118 g $m^{-2}$. All leaves from the citrus tree were placed in paper bags and placed into a vacant greenhouse, where day temperatures reached 50 $^{o}$C. After 12 days all bags were weighed, and six bags were oven-dried for two days to check for complete drying. Mass difference between those oven-dried and the values from greenhouse weighing ranged from 0 to 0.68%, so less than 1% for all. We therefore concluded that the greenhouse arrangement provided dry mass. The sum of dry mass values for all leaves from the citrus tree was 14,830 g.

Calculation of leaf area using the SLA value above gave a total of 126.7 $m^2$ for the tree. Dividing by tree planar area gave a value of 10.3 for tree LAI. Using an exact 20 ft x 24 ft (6.10 m x 7.32 m) spacing for trees, each tree would occupy 44.6 $m^2$ and the plant population would be 90.7 plants per acre (224 plants per ha). With this spacing the orchard LAI would be 2.84. However, the spacing of trees in the orchard was not exact. Counting trees using GoogleEarth gave 96 trees per acre (237 plants per ha), and the corresponding planar area per tree was therefore 42.2 $m^2$, with corresponding LAI of 3.00. The grower concurs with an in-row spacing slightly less than 24 ft, so the LAI value of 3.00 is preferred.

### 4.1.6 Wood Mass and Total Mass

After leaves were removed, we gathered branches and weighed them. The larger section of the trunk was also weighed, but we did not assign diameters to trunk vs branches so in effect we have totals for above-ground wood. The central root system was removed with a backhoe, but we did not attempt to gather fine roots, e.g. with a pneumatic spade. Therefore, the roots collected represent less than 100% of the root mass. Wood samples from roots, trunk, and branches were oven dried to give a conversion factor for fresh weight to dry weight. The root dry mass was 49.6 kg, the trunk was 48.8 kg, and branches 39.2 kg. We also collected the immature oranges on the tree and dried a sample for a fresh-to-dry conversion. There were 7.84 kg of immature oranges present on a dry-mass basis. Therefore, the total above-ground wood mass was 88.0 kg, Total dry mass for the tree harvested, including leaves and immature fruit, was 160 kg.

### 4.1.7 Carbon and Nitrogen Determinations

After drying, three leaf samples and three samples of wood, one each of roots, trunk, and branches, were sent to the ANR Analytical Lab at UC Davis. The mean value for N in leaves was 2.13%, and for C 40.7%. For the tree harvested, the N total for leaves was 316 g and C was 6.04 kg.

For wood samples, the N value for root, trunk, and branches was 0.67%, 0.81% and 0.48%, respectively, and for C 46.2%, 46.9% and 45.8%, respectively. We did not replicate samples of roots, trunk or branches; in calculations for N and C from these plant parts we used their respective lab values.

Table 4-2. Nitrogen and carbon content of a citrus tree harvested August, 2010.

| Plant Part | Nitrogen (g) | Carbon (kg) |
|---|---|---|
| Leaves | 316 | 6.04 |
| Branches | 318 | 18.4 |
| Trunk | 233 | 22.4 |
| Total Above-Ground | 866 | 46.8 |
| Roots | 331 | 22.9 |
| Total for Tree | 1198 | 69.7 |

It is possible to estimate the N and C content for one acre of one hectare of citrus trees by multiplying the above values by the respective plant populations.

## 4.2 Experimental Methods

### 4.2.1 PTRMS System for Flux and Gradient Measurements

From January 2010 to October 2010, VOC mixing ratios were measured in situ with a proton-transfer-reaction mass spectrometer (PTR-MS), which has been described elsewhere in detail (Lindinger et al. 1998). During each hour, air was sampled through five individual gas inlets made of Teflon with 4 mm internal diameter each of which was protected by a Teflon filter (PFA holder, PTFE membrane, pore size 2μm) 30 cm from the inlet. The filters were replaced every two weeks, a time interval considered adequate to avoid contamination or flow problems based on past research (Holzinger et al. 2005). One inlet was used to sample air at 4.85 m from 0 to 30

min for eddy-covariance flux measurements of methanol, acetone, isoprene, monoterpenes and an oxidation product, with m/z of 33, 59, 69, 81, and 113, respectively. The measurement cycle duration for these five masses, including water, was 1.5 s. The sampling tube was 15 m long and heated at a constant temperature of 40 $^{o}$C to avoid condensation inside the tubing. A sample flow of 10 L min$^{-1}$ was generated with a diaphragm pump maintained by a mass flow controller (MKS Instruments). Four additional inlets were used to sample vertical gradients at height-levels within (1.0 m, 3.76 m) and above (4.85 m and 9.18 m) the canopy sequentially for 6 min each during the second 30 min of each hour. In order to avoid different retention times of the air in the inlet lines, we used tubing with the same length for each inlet line (20 m). Table 1 lists the m/z monitored, the corresponding compounds, and the dwell time for each mass.

| m/z | Compound | Formula | Dwell time (s) | Norm. sensitivity (ncps $ppbv^{-1}$) | Detection limit (ppbv)*[3] | Mid-day mixing ratio*[4] (ppbv) | Mid-day flux *[5] (nmol $m^{-2}$ $s^{-1}$) | mean 95% CI*[6] | N (tot 30-min files) | N (after filtering) | Quality test (1, 2, 3)*[7] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ***33*** | ***methanol*** | CH3OHH+ | 0.2, 0.5 | 5.9 ± 0.02 | 1.15 ± 0.24 | 6.1 , 15.06, 13.07 | 1.4, 8.9, 5.2 | 0.15, 0.48, 0.16 | 5013, 5149 | 3001, 5141 | 1444, 454,3115 |
| *45* | *acetaldehyde* | C2H4OH+ | 0.5 | 10.6 ± 0.04 | 0.36 ± 0.09 | 1.07, 1.4, 2.6 | n.a. | n.a. | 5149 | 5114 | n.a. |
| ***59*** | ***acetone*** | C3H6OH+ | 0.2, 1 | 13.8 ± 0.04 | 0.14 ± 0.04 | 1.16, 2.1 , 3.6 | 0.07, 1.05, 0.64 | 0.07, 0.12, 0.05 | 5013, 5149 | 3012, 5116 | 1444, 454,3115 |
| ***69*** | ***isoprene**** [1] | C5H8H+ | 0.2, 1 | 8.7 ± 0.03 | 0.03 ± 0.02 | 0.22, 0.19, 0.3 | 0.06, 0.06, 0.08 | 0.006, 0.00, 0.01 | 5013, 5149 | 3015, 4993 | 1444, 454,3115 |
| *71* | *MVK+MCR** [2] | C4H6OH+ | 1 | 10.07 ± 0.03 | 0.04 ± 0.02 | 0.06, 0.17, 0.27 | n.a. | n.a. | 5149 | 4898 | n.a. |
| ***81, 137*** | ***monoterpenes*** | C6H9+ | 0.2, 1 | 10.5 ± 0.03 | 0.03 ± 0.02 | 0.08, 0.21, 0.08 | 0.21, 0.77, 0.34 | 0.01, 0.04, 0.01 | 5013, 5149 | 3014, 5111 | 1444, 454,3115 |

Table 4-3. BVOC species measured during the field campaign in 2010. Bold indicates compounds (m/z) for which fluxes were measured.

[1] Furans and methylbutenol fragment were also a minor contributor to m/z 69 from intercomparison with GC-MS.

[2] Sum of methylvinylketone and methacrolein

[3] The limit of detection (LOD) is calculated setting a minimum acceptable signal to noise ratio equal to 2

[4] Median concentration values at 4.85 m above ground in winter, flowering, summer periods, respectively, in the central hours of the day: 12:00 to 14:00

[5] Median values in winter, flowering, summer periods, respectively in the central hours of the day: 12:00 to 14:00 for the 30-min periods which were assigned to quality categories 1 and 2

[6] Measure of the Confidence Interval as the mean noise for the 30-min fluxes which were assigned to quality categories 1 and 2

[7] Number of flux observations with 1= good quality (distinct maximum in the covariance, $r^2$ >0.2), 2=low quality (slightly visible maximum in the covariance), 3=poor quality (or no visible maxima)

Each sampling line was connected to a 3-way solenoid valve (TEQCOM Industries) controlled by a datalogger (mod. CR10x, Campbell Sci.). Air was continuously pulled from each sampling line to avoid memory effects of the air retained in the lines.

The instrument sampled from the main sampling line at 0.4 L $min^{-1}$ and was optimised to an E/N ratio of 128 Td using a drift tube pressure, temperature, and voltage of 2.02 hPa, 45 $^{o}$C, and 600 V, respectively. The reaction time was 100 μs and the count rate of $H_3O^+ H_2O$ ions was less than 3% of the count rate of $H_3O^+$ ions, which was typically ~$5x10^6$ counts $s^{-1}$. Each measurement cycle lasted ~2 minutes, totalling 13 measured cycles per level for each hour. The first two cycles were discarded to prevent potential errors due to missed synchronization between the PTRMS and the datalogger clocks. The instrumental background signal was measured by directing the sample flow through a catalyst-based purifier for the first 3 minutes before starting the measurements in the second half of each hour, similar to Holzinger et al. (2005). The purifier consisted of a stainless steel tube filled with platinum-coated quartz wool (Shimadzu) heated to 350$^{o}$C, which efficiently removed the VOC but not the water vapor from the sample. This is important because the instrument background signals may depend on the humidity of the sampled air.

A gravimetrically-prepared gas standard cylinder (Apel & Riemer) of pure nitrogen with known mixing ratios (4-5 ppm) of methanol, acetaldehyde, acetone, isoprene, methylvinylketone, benzene, hexenal, and d-limonene was automatically measured twice a day (at hours 02:00 and

16:00) by dynamically diluting with purified air to obtain concentrations in the range of 10-50 ppb, which are similar to those expected in the ambient atmosphere. The count signal was then transformed to ppb after subtracting the averaged background levels and taking into account the measured sensitivities for each calibrated compound (i.e. counts/ppb, Davison et al. 2009). For concentrations of the other masses for which authentic standards were not available, we calculated normalized sensitivities (counts/concentration) based on theoretical proton transfer reaction rate coefficients and the instrument specific transmission coefficient calculated from a transmission curve. This curve was determined at an array of masses from 33 to 219 m/z using gas standards at concentrations of 50 ppb (Apel & Riemer). We observed changes in the relative abundance of the main monoterpene fragment (m/z 81) versus the unfragmented monoterpene mass (m/z 137), suggesting themixture of monoterpenes present changed over both diurnal and seasonal timescales. Due to this behaviour, and because our primary standard only contained 1 monoterpene (limonene) that preferentially was observed at m/z 81, we quantified the total monoterpene concentrations as the theoretical concentration of monotepenes summed over m/z 81 and m/z 137. The theoretical based determination of concentration for total monoterpenes was 20% higher than total monoterpenes calibrated twice a day using the sum of m/z 81 and m/z 137 solely based on limonene standard.

### 4.2.2 BVOC Flux Calculation

Wind velocity and sonic virtual temperature fluctuations were measured at 10 Hz with a three-dimensional sonic anemometer (Applied Technologies, Inc., Boulder, CO) mounted on a horizontal beam where the air inlet was attached. The wind data were rotated according to the planar fit method (Wilczack et al. 2001). The time lag interval between the instantaneous vertical

wind velocity and the BVOC concentration measurement varied due to changes in clock synchronization between the PTRMS clock and the datalogger where sonic data were stored. To calculate and then correct for this lag time, for each specific 30-min measurement period vertical wind velocity and concentration were correlated in a ± 10s time window following the principle of the maximum covariance. In cases in which a clear covariance peak was not observed, we used the lag time measured closest in absolute temporal scale.

Fluxes of BVOC ($F_c$, nmol $m^{-2}$ $s^{-1}$, Equation 4-1) were calculated using the continuous flow disjunct eddy covariance method (Davison et al. 2009) in which fluxes are calculated from a subsample of the horizontal wind data corresponding to data collected with the PTRMS after subtracting the lag time (Δt):

$$F_c = \frac{\sigma}{N}\sum_{i=1}^{N} w'(i - \Delta t / \Delta t_w)c'(i) \qquad \text{(Equation 4-1)}$$

where σ is the air density (mol $m^{-3}$), $w' = w - \overline{w}$ is the instantaneous deviation of the vertical wind speed (w) from its average, $c' = c - \overline{c}$ is that of the BVOC concentration (nmol $mol^{-1}$), $\Delta t_w$ is the sampling interval in the wind measurements (0.1 s), and N is the number of PTR-MS measurement cycles (1680) during the flux averaging time (29.5 min).

A de-spiking routine was applied to exclude points clearly resulting from interferences. Fluxes were multiplied by a frequency response correction factor compensating for high frequency data losses, calculated by comparing normalized cospectra of each mass with sensible heat (Wolf and Laca 2007). Flux values were discarded if at least one of the following conditions were met: 1. measured ambient concentration close to the detection limit of the specific VOC. 2. Results

from the stationary test for the various BVOC were above 60 % (Foken and Wichura, 1966). 3. the footprint area was outside the boundaries of the orchard (Hsieh et al. 2000). 4. turbulence was low ($u^* < 0.15$), which occured very frequently at night (Fig. 4-6).

The uncertainty was measured according to the method proposed by Wienhold et al. (1994) determining the signal noise of the covariance by calculating the time shifts between vertical wind velocity and BVOC concentration far beyond the true lag-time. We used the same procedure recently adopted by Ruuskanen et al. (2011) using a lag window of 40 s and rated the 30-min flux data in three classes: 1 (good quality), 2 (low quality), 3 (poor quality), as reported in Table 4-3. All data processing was computed using a Matlab routine.

## 4.3 Results and Discussion

### 4.3.1 Results from PTR-MS measurements

This project offered the opportunity to perform the most extensive in-situ measurements of a suite of BVOC concentration and fluxes observed to-date in a citrus orchard. In Fig. 4-8, for each measured compound reported in Table 4-3 we show the concentration at 4.85 m averaged every 30-min for the full measurement year. We also show vertical gradients averaged over the diurnal cycle by interpolation of mean mixing rations at the measurement heights of 1 m, 3.76 m, 4.85 m and 9.18 m (Figs. 4-9, 4-10).

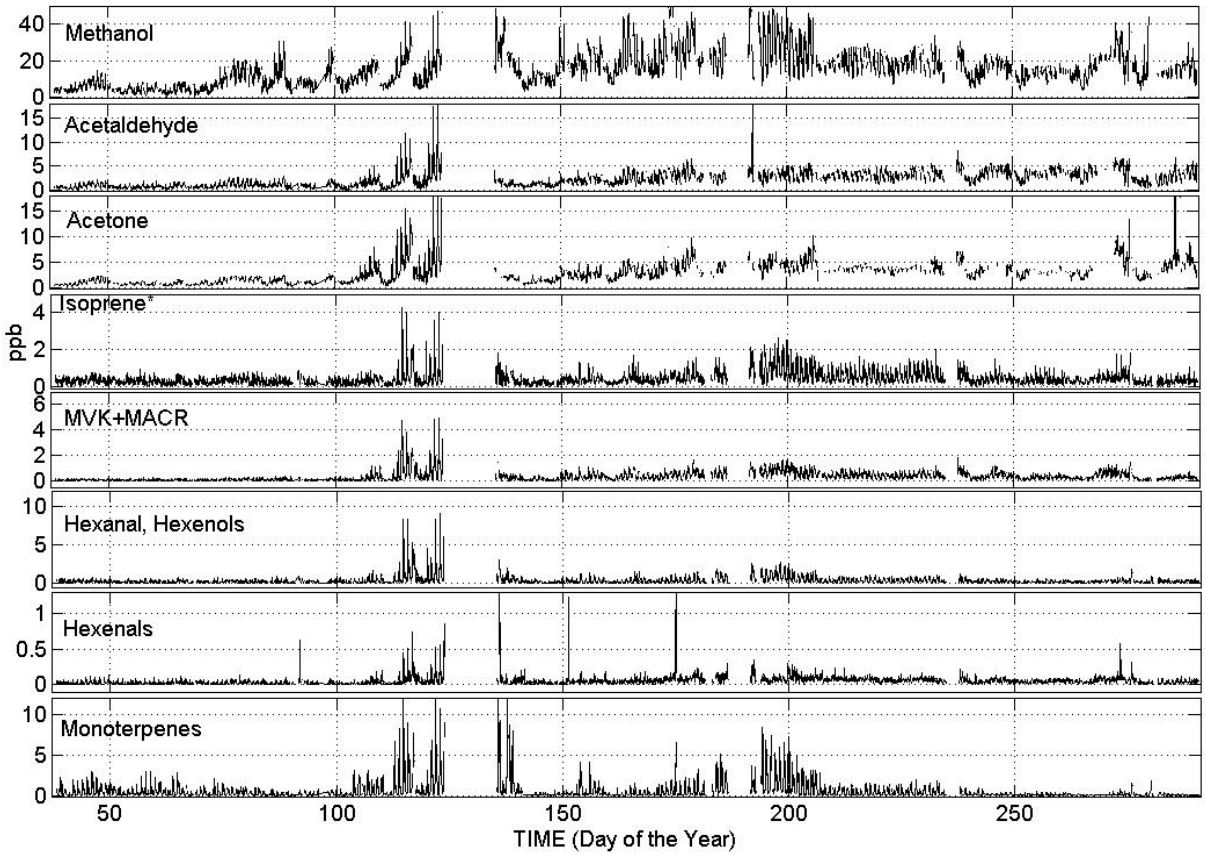



Figure 4-8. Concentration of the major BVOC species measured hourly by PTRMS at 4.85 m above ground at the citrus site between February and November, 2010. The asterisk on isoprene is to note that a minor contribution of furans and methyl-butenol occurred at the m/z 69.

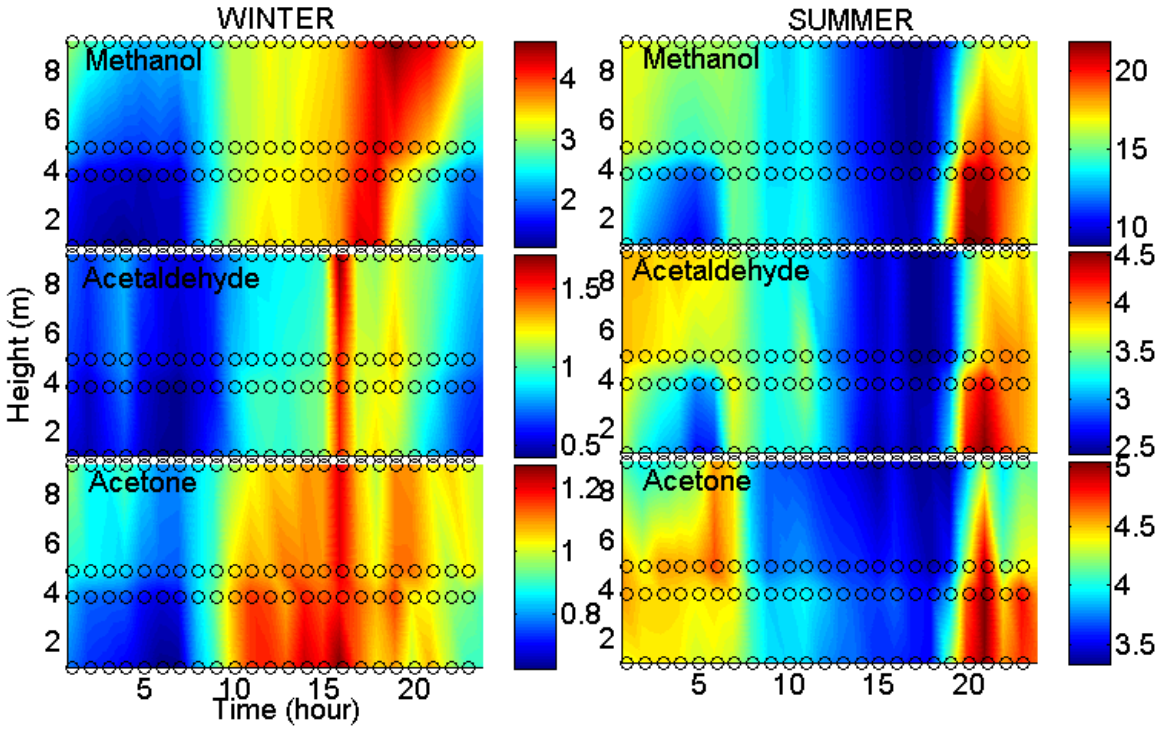



Figure 4-9. Hourly average concentration (ppbv) for winter and summer seasons as a function of height for the major OVOC of this study: methanol, acetaldehyde and acetone. OVOC species measured (measuring heights shown with circles) by PTRMS within (1.0 m, 3.76 m) and above (4.85 m and 9.18 m) the canopy of an orange orchard.

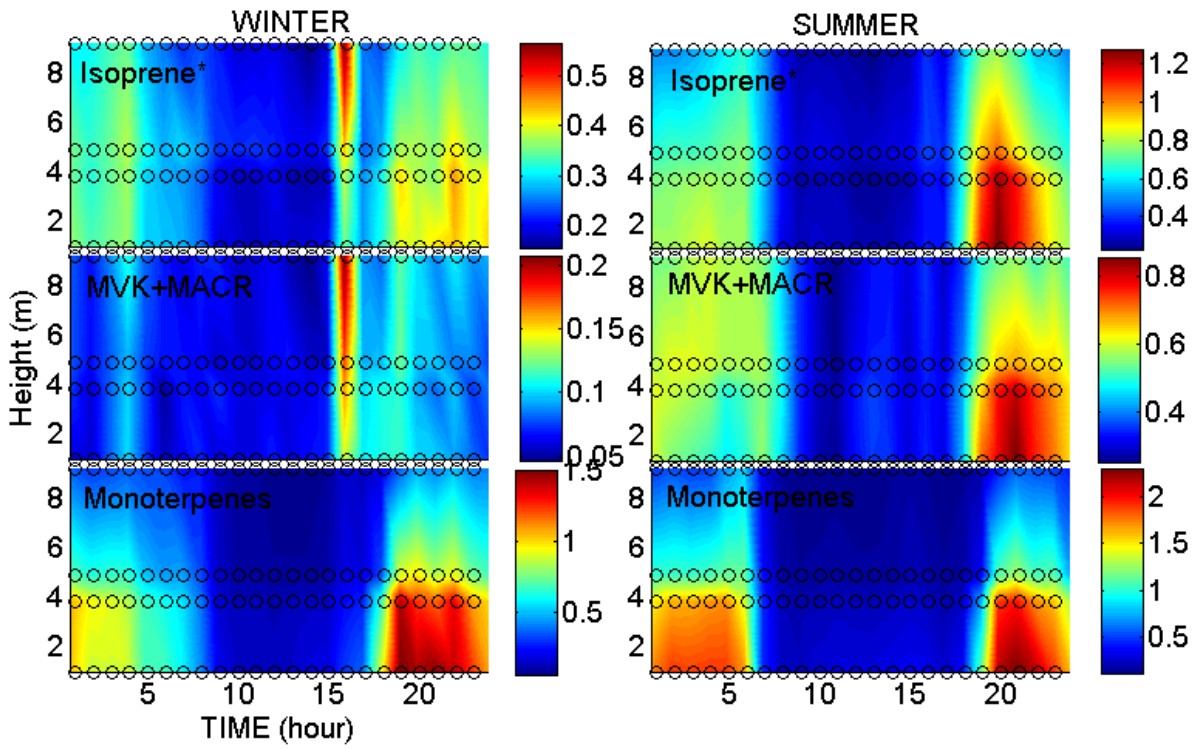



Figure 4-10. Hourly average concentration (ppbv) for winter and summer seasons as a function of height for the major isoprenoids of this study: isoprene, its oxidation products (sum of methylvinylketone and methacrolein), and sum of monoterpenes. BVOC species measured (measuring heights shown with circles) by PTRMS within (1.0 m, 3.76 m) and above (4.85 m and 9.18 m) the canopy of an orange orchard. The asterisk on isoprene is to note that a minor contribution of furans and methylbutenol occurred at the m/z 69.

For all compounds, it was evident that the ambient concentration follows a diurnal cycle that is highly dependent on the depth of the boundary layer. During the day, when convective heat movement expanded the boundary layer thus increasing the mixing layer volume, ambient concentrations were lower. At the end of the day, when the boundary layer was shallower, the concentration of BVOC increased. The boundary layer dynamic also influences fluxes. When we recorded large gradients during the night hours, the vertical mixing was so low that fluxes were almost negligible, helping to explain the daily dynamic of measured fluxes (Fig. 4-11) with maximum peaks in the central hours of the day (Fig. 4-12).

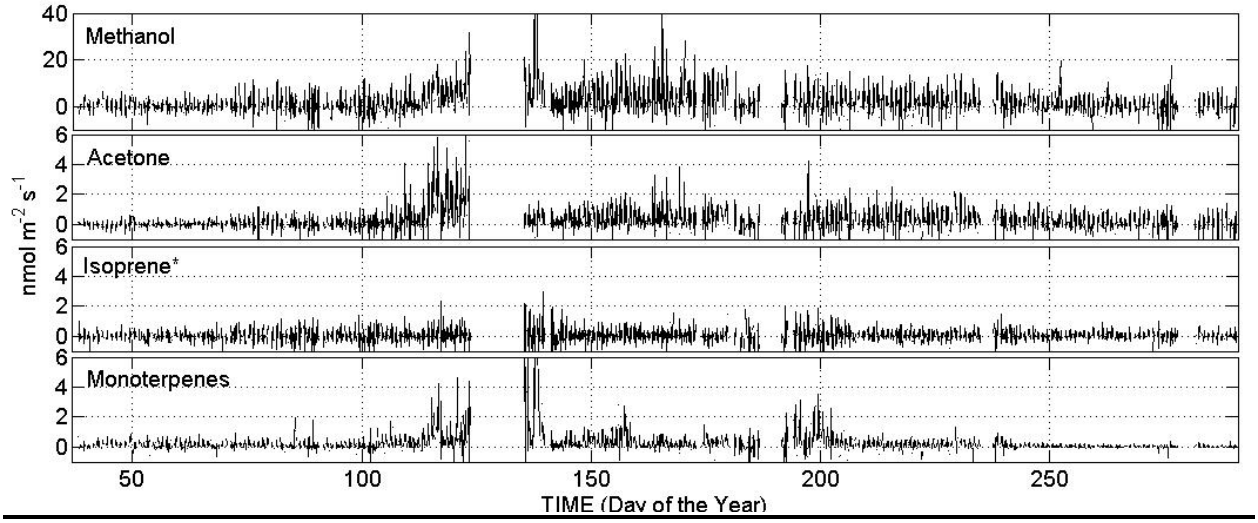



Figure 4-11. Fluxes of the major BVOC species measured hourly by PTRMS eddy covariance at the citrus site between February and November, 2010. The asterisk on isoprene is to note that a minor contribution of furans and methylbutenol occurred at the m/z 69.

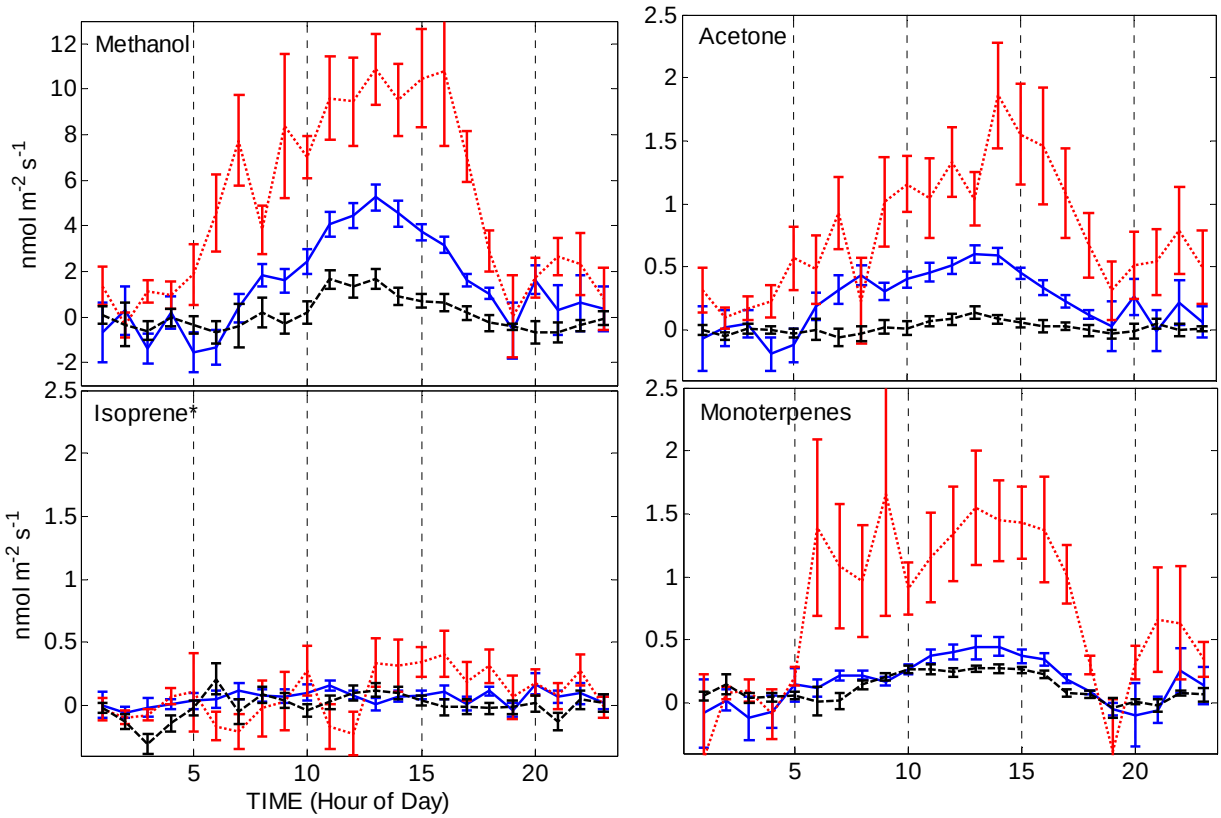



Figure 4-12. Hourly average fluxes of BVOC species measured by PTRMS at the citrus site during the winter (black line), flowering (red line) and summer (blue line) periods.

4.3.1.1 *OVOC concentrations and fluxes*

Methanol was the compound measured in highest amount, with peak values up to 50 ppbv, in agreement with our measurements of high methanol emissions using branch enclosures in the greenhouse facility. The diurnal emission of methanol is clearly visible in Fig. 4-12, with higher values in the spring-summer seasons. This higher methanol emission during this period is consistent with previous results showing that increased emission occurs due to phenological modification of leaf tissues during leaf expansion, (Schade and Goldstein 2002, Huve et al. 2007, Fall 2003) and oxidative stress (Karl et al. 2001, Loreto et al. 2006), as a result of pectin

demethylation when cell walls elongate during leaf expansion (Fall and Benson 1996, Galbally and Kirstine 2002), with plant growth recognized as the primary global source of methanol to the atmosphere (Galbally and Kirstine 2002). In the diurnal cycle of gradient concentration shown in Figure 4-12 for the winter and summer period, a slight gradient is visible in the morning between 09:00 and 11:00 during summer. The gradient is less visible during the central hours of the day, although these are the hours when maximum fluxes were recorded, rising up to a summer time average of 6 nmol $m^{-2}$ $s^{-1}$, and reaching peaks above 10 nmol $m^{-2}$ $s^{-1}$ during the flowering period in the day of the year 116 to 145. Higher fluxes during mid-day hours of methanol has been previously described, with light-dependent emissions (Huve et al. 2007), and evidence of newly assimilated carbon re-emitted as methanol following a temperature dependence (Folkers et al. 2008). Strong nocturnal gradients decreasing from the atmosphere to the canopy suggest that some deposition occurs at night. This may be explained by the presence of dew on leaves, which we measured using sensors for leaf humidity (data not shown). Previous research (Karl et al. 2004) showed that deposition on wet leaves can be responsible for a large percentage of total deposition, the latter enhanced by hydrolysis reactions (Jayne et al. 1992). Despite this evident deposition process at night, a negative flux would have been hard to detect with the eddy covariance method because of the low turbulence which causes systematic underestimation of nighttime fluxes. Most of the night time flux measurements have been discarded due to low atmospheric turbulence ($u^* < 0.15$). Some positive gradients, however, are evident in the early evening hours (19:00 – 23:00), in particular in the summer period. At these hours leaves are not wet and a foliar emission may be generated as methanol is produced during tissue expansion. This positive gradient from the canopy to the atmosphere in the early evening is less visible for the winter period, when the higher water condensation on leaf surfaces

especially during the night hours and the limitations to the biosynthetic pathways of methanol formation during the winter (e.g. decrease in plant growth and photosynthesis) occur. Flowering has been described to produce a burst of terpenoid and non-terpenoid compounds (Arey et al. 1991, Ciccioli et al. 1999; Fares et al. 2011), and we observed an increase of ambient concentrations up to 50 ppb and fluxes above 10 nmol $m^{-2}$ $s^{-1}$, in agreement with the branch enclosure studies (Chapter 3), where in the latter case the basal emission factor (BER) was about three times higher, and there was a decoupling of emissions from photosynthesis.

Acetaldehyde and acetone were also measured in concentrations up to 15 ppb during the flowering period (Fig. 4-9), with ambient concentrations of each of these compounds equal to about one third of methanol. Acetone is the most abundant ketone in the atmosphere (Koppman and Wildt 2007), released during senescence (de Gouw et al. 1999) and oxidative stress on plants (e.g. from ozone) (Cojocariu et al. 2005), with global emissions estimated at 95 Tg $y^{-1}$ (Jacob et al. 2002). Our results agree with previous research which found that rural areas can have significant sources of acetone (Goldan et al. 1995, Riemer et al. 1998, Ciccioli et al. 1999; Schade and Goldstein 2001). Acetaldehyde is emitted by leaves in large quantities during and after abiotic stresses (Fall et al. 1999, Loreto et al. 2006). An estimate of global emission similar to acetone was recently reported by Millet et al. (2009) for acetaldehyde. The good correlation of acetaldehyde vs acetone (slope = 1.1, $r^2$=0.8, data not shown) confirms a similar origin of these compounds, as previously observed (Karl et al. 2003, Schade and Goldstein 2001). The orchard behaved as a source of acetone and acetaldehyde during summer, with a visible positive gradient in the early evening, and became predominantly a sink during winter (Fig. 4-11). Nocturnal deposition due to dew could have played a significant role in the wintertime deposition of these

two compounds, similar to methanol. The physicochemical properties of these three organic compounds differ in terms of the reactivity in the liquid phase thus affecting their solubilities and Henry`s law constants (Noziere and Riemer 2003), with acetone being less reactive than acetaledyde (Duncan et al. 1999). A minor deposition of acetone is evident as a small gradient in Figure 4-12. Acetaldehyde in particular has been shown to be emitted by citrus plants especially during flowering (section 3), although this compound is also produced by atmospheric oxidation processes (e.g. photooxidation of linalool), as described by Ciccioli et al. (1999), and Smith et al. (1996). Acetone is another OVOC emitted by citrus leaves that also forms in atmosphere through oxidation processes. We directly measured acetone fluxes with eddy covariance (Table 4-3, Fig. 4-11). Flowering significantly increased acetone emission, as shown from the enhanced atmospheric concentrations and the hourly fluxes (Fig. 4-12), reaching levels up to 2 nmol $m^{-2}$ $s^{-1}$, a value almost three times higher than the typical summer emissions. This OVOC burst during flowering events indicates that this phenological stage of plants could be important for the chemistry of the atmosphere, since these compounds can be involved in regional photochemistry.

4.3.1.2 *Concentrations and fluxes of isoprenoids*

Isoprene was measured in relatively low concentrations, rarely above 2 ppbv, except during the flowering season, when nocturnal peak concentrations increased to 5 ppbv (Fig. 4-8). Isoprene fluxes were negligible in all seasons (Fig. 4-11, 4-12), in agreement with previous findings showing that orange is not a significant isoprene emitter (Winer et al. 1992, Ciccioli et al. 1999; section 3). During the winter period, the orchard was acting more as an isoprene sink based on our observations of the concentration gradients (Fig. 4-11). An evident deposition phenomenon is occurring at ~16:00. We hypothesize that isoprene is transported to the orchard through

advection plumes from a source far away from our measuring footprint; however, the most common oak species in proximity is deciduous, and in winter the rate of isoprene production is low for oaks that retain leaves. Similar to isoprene, its primary oxidation products methylvinylketone and metacrolein (MVK+MACR) follow the same pattern during the winter and in summer. Deposition of MVK+MACR has been recently observed by Karl et al. (2010) in a tropical forest, as a result of uptake and degradation inside leaves by enzyme activity. During summer, both isoprene and MVK+MACR follow the same dynamic patterns, with a notable positive gradient suggesting emission from the soil to above the canopy in the early evening hours. Despite this positive gradient, the low turbulence did not allow measurement of a significant flux during those hours, but this phenomenon suggests that a minimal production of isoprene can exist in the early night hours. This may be explained by the post-illumination consumption of residual substrate pools (e.g. dimethylallyldiphosphate) produced during photosynthesis in the light hours, although a strong post-illumination decay in isoprene emission has been described to happen in a few minutes (Rasulov et al. 2009) which does not correspond to the time delay observed in our study (2-3 h). The positive fluxes of MVK+MACR during the same hours are consistent with recent findings (Jardine et al. in prep.) that isoprene oxidation products can be emitted directed from leaves as result of intercellular oxidation of isoprene with ROS (Reactive Oxygen Species). ROS production in the orchard site should be enhanced by high levels of tropospheric ozone, for which we measured levels exceeding 100 ppb in the summer afternoon hours.

Monoterpenes were the isoprenoids emitted in largest amount. Even in winter a positive gradient from the ground to above the canopy was detected (Fig. 4-10), although fluxes were quite small

(<0.3 nmol $m^{-2}$ $s^{-1}$). Fluxes of limonene, the most abundant monoterpene species, have been described being emitted in a high percentage from soils using soil enclosure in a navel orange orchard (Ciccioli et al. 1999). During flowering, fluxes increased above 1.5 nmol $m^{-2}$ $s^{-1}$, in agreement with our branch-level experiments in the greenhouse and previous research (Arey et al. 1991, Ciccioli et al. 1999, Hansen and Seufert 2003). Concentration and fluxes of monoterpenes reached their maximum during the flowering period (Fig. 4-8).

Sesquiterpenes are a very important class of isoprenoids which have been identified as the more abundant isoprenoids emitted from oranges when emissions have been tested with branch enclosures (Ciccioli et al. 1999). These compounds are very reactive with tropospheric ozone (Atkinson and Arey, 2003) and therefore have very short atmospheric lifetimes. β-caryophyllene is the main sesquiterpene emitted from citrus based on our greenhouse measurements and according to Ciccioli et al. 1999. We estimated an atmospheric lifetime of ~ 30-80 s for this compound when ozone concentrations are between 40 and 100 ppb, typical of hot days in the Central Valley. We tried to minimize the residence time of the air in the sampling line (~ 2.2 s), but the high reactivity with ozone, the poor transmission efficiency of β-caryophyllene in the PTRMS, and likely losses in our sampling lines resulted in very low concentration measurements of these compounds, for which we cannot provide a quantitative analysis based on our field measurements. A discrepancy in magnitude between β-caryophyllene measured in branch enclosure and ambient atmosphere above a citrus orchard was also noted by Ciccioli et al. (1999), with enclosure fluxes being very high, even higher than monoterpenes, similar to what we found in our greenhouse enclosure experiments. In the field, Ciccioli et al. observed low fluxes of β-caryophyllene using REA technique in comparison with enclosure measurement, and

justified this by the high estimated resident time (360-480 s) of the molecule in the air space between the soil and the sensor above the canopy. Turbulence at our site was low similar to that observed by Ciccioli et al. therefore, it is reasonable to hypothesize a similarly long residence time for β-caryophyllene relative to its atmospheric lifetime. Our results therefore suggest that using our sesquiterpene BEF estimates from the controlled greenhouse experiements in models is more appropriate than relying on the field based measurements because they are more quantitative than what we could achieve in the field where oxidant (ozone) levels were high and sesquiterpene lifetimes were very short.

#### 4.3.1.3 *Seasonality in emission factors*

The year-long data set allowed us to calculate the basal emission factors of the temperature-dependent BVOC (BEF, Guenther et al. 1995, Tingey et al. 1991) for the most important seasons (Table 4-4) using a logarithmic temperature dependence. It is important to note that in the greenhouse we measured emissions from Parent Navel orange while in the field we measured emissions from Valencia orange, so the absolute values of BEFs are not expected to agree. In agreement with the greenhouse enclosure experiments in 2008 (section 3 of this report), BEF for monoterpenes were much higher during the flowering period than in summer. In the 2008 greenhouse experiments, BEF during flowering was about three times higher than in summer. In the field, the leaf-scaled flowering BEF was 10 times higher than the summer BEF, and the winter BEF was 6 times higher than summer BEF. The larger flowering versus summer difference in the field likely results from a much larger density of flowers on the orange plants in the field. These differences demonstrate that flowering is a very important phenological stage when the emission of monoterpenes and other BVOC is enhanced, as shown in the next section,

where speciated isoprenoids during flowering season and summer season have been characterized with a GC-MS.

| | 2008 Cuvette | 2010 Field (using beta from 2008) |
|---|---|---|
| ***Monoterpenes*** | n.a., 7796±4315, 2520±3410 | 1994 ± 1119, 3258 ± 3693, 319.4 ± 293 |
| *β* | n.a., 0.15, 0.14 | |
| ***Methanol*** | n.a., 882±277, 483±401 | 346 ± 595, 1222 ± 522, 349 ± 458 |
| *β* | n.a., 0.03, 0.06 | |
| ***Acetone*** | n.a., 503±134, 240±204 | 84 ± 317, 806 ± 481, 123 ± 155 |
| *β* | n.a., 0.12, 0.1 | |

Table 4-4. BVOC basal emission factors (BEF, ng(C) $gDW^{-1}$ $h^{-1}$) of 'Valencia' orange for winter, flowering, and summer periods, respectively. The β value calculated from the Tingey (T) algorithm is reported below for each BVOC species. Data ± standard deviations refer to basal conditions of temperature = 30 ± 2 $^{o}$C and PAR = 1000 ± 100 umol $m^{-2}$ $s^{-1}$ extrapolated from the observations. BEF for the 2010 field experiment were calculated using β values from the greenhouse experiment using plant cuvettes because in the greenhouses the environmental conditions were close to basal condition thus providing a more robust dataset for β calculation. β from summer 2008 was used to calculate BEF for winter period.

Our results confirm that many BVOC species (e.g. terpenes such as ocimene) are emitted in large amounts during flowering to attract pollinators (Dudareva and Pickersky 2000). BEF variations between winter, flowering and summer seasons were also observed for methanol and acetone, with higher values during flowering, probably due to enhanced pectin demethylation during the flowering time (Galbally and Kirstine 2002) which correspond to the spring period, when vegetative growth activity of plants is enhanced. Seasonal variation of emission factors has also been observed for an oak forest (Geron et al. 2000), a hardwood forest (Karl et al. 2003) and a pine forest (Schade and Goldstein 2006, Holzinger et al. 2006). In particular, Karl et al. (2003) observed a BEF for acetone higher in fall, ascribing this major emission to decaying plant material, and Schade and Goldstein (2006) saw enhanced emissions of acetone and methanol in the spring during budbreak and elongation of pine needles. Our results highlight the importance

of calculating BEF for different seasons for a proper parameterization of emission models, as also suggested through measurements by Goldstein et al. (1998), Keenan et al (2009) and Niinemets et al. (2010).

### 4.3.2 Overview of GC/MS-FID instrument

Chemical speciation of VOC was achieved using the same gas chromatograph as in the greenhouse experiments (Hewlett Packard 5890 Series II) that was equipped with a quadrapole mass selective detector (Hewlett Packard 5971) and a flame ionization detector. The instrument was operated *in situ* with a custom system that automated sample collection and analysis. Ambient samples were collected for the first 30 minutes of every hour via an inlet located at a height of 4 m, mounted on a pole attached to the seatainer. The inlet was not co-located with the tower inlets due to the need for a short sampling line to minimize line losses of VOCs. To accurately preserve gas-phase VOCs in the ambient sample, ozone and particulate matter was removed at the inlet using 47 mm glass fiber filters (Pall, type A/E) that were coated in sodium thiosulfate according to the method vetted by Pollmann et al. (2005). After ozone and particulate removal, the sample traveled down a ¼" heated Silcosteel line at ~1 L $min^{-1}$ to a preconcentration system, where two separate channels sub-sampled off the main flow each at ~20 mL $min^{-1}$. Ozone removal was confirmed by measuring the remainder of the main flow with a spectroscopic ozone analyzer (Dasibi model 1008-AH).

### 4.3.3 Calibration Procedures

The instrument was calibrated for more than 100 individual VOC using a mix of gas and liquid standards. Three gas standard tanks with ppm concentrations (Apel-Riemer, Scott Gas) were

dynamically diluted into a ~1 L $min^{-1}$ flow of pure air supplied from a zero air generator (Aadco Inc.) to get ppt- to ppb-level concentrations. Multi-point calibrations were run at the beginning and end of each 3-4 week measurement campaign, and daily single point standards were run to verify the calibrations. Pure air from the zero air generator was also used to run daily blank runs to account for any artifacts or biases in the system. For identified compounds without standards, their response factors on the MSD were determined by multiplying the fraction of the quantifying ion in a representative mass spectrum by the total ion response factor calculated from known compounds of similar chemical class. This method, while approximate, provides concentration data with a reasonable amount of uncertainty when standards are not available for relatively stable hydrocarbons.

#### 4.3.4 Measurement Protocols

The instrument was equipped with two independent measurement channels sampling from the same inlet line. Channel 1 was focused on measuring a broad range of VOC including those with lower volatilities (ranging from isopentane to heptadecane). Channel 2 measured low-molecular weight compounds that are more volatile (e.g. propene – isopentane). Prior to subsampling from the inlet line for the two channels, an internal standard (n-octane, 5.0 ppm) was constantly added to the sample flow at 2 mL/min, such that after the dynamic dilution its concentration was ~2 ppb. The internal standard was used to correct for any drift in the sensitivity of the mass selective detector and to confirm overall instrument analytical stability. The entire sampling line and all other elements of the sampling/preconcentration system that pertain to channel 1 were constructed with passivated steel or other highly inert materials that were heated to constant temperatures at or above 90°C using resistive heaters. This was done to minimize losses of any

VOC due to adsorption, absorption, or condensation, especially for compounds with lower volatility.

The channel 2 sub-sample was run through a custom-made water trap to remove water that would have otherwise adsorbed onto the channel 2 adsorbent trap. This was accomplished by passing the channel 2 Teflon sample line through an aluminum block that was cooled to 0°C and routinely purged when sample was not being collected.

The samples in both channels were concentrated on custom-made multilayer adsorbent traps via a system of three 12-port rotary valves (Valco, Valcon E) to facilitate the automation of sampling and injection. The adsorbent traps were constructed out of 1/8" Sulfinert steel tubing and contained the following sequence of adsorbents held in place by glass wool on each end. Channel 1: 60 mg glass beads (Alltech, 60/80 mesh, DCMS-treated), 20 mg Tenax TA (Supelco, 60/80 mesh), 30 mg Carbopak B (Supelco, 60/80 mesh), and 40 mg Carbopak X (Supelco, 60/80 mesh). Channel 2: 60 mg glass beads, 30 mg Carbopak B, 40 mg Carbopak X, and 40 mg Carboxen 1000 (Supelco, 60/80 mesh). During sample collection the adsorbent traps were thermoelectrically cooled to a constant 15°C and 5°C for channel 1 and 2, respectively. Following the preconcentration of ~1 L samples on each adsorbent trap, the analytes were thermally desorbed at 320°C with a reverse flow of helium and injected directly onto their respective capillary columns where chromatographic separation was assisted by a ramped temperature program in the GC oven. The effluent from the traps was injected onto a DB-624 (60 m × 0.32 mm × 1.8 μm) and a HP-Plot-Q (30 m × 0.32 mm × 20.0 μm) for channel 1 and 2, respectively.

All flows were measured and controlled using mass-flow controllers (MKS Instruments), and system temperatures were monitored using T-type thermocouples (Thermo Scientific). All system data were recorded on a data- logging system (Campbell-Scientific, model SDM-CD16AC).

### 4.3.5 GC/MS-FID Measurements Made During Intensive Study Periods

The GC-MS was deployed for two periods, once in spring during flowering and once in summer to correspond to warmer temperatures and higher levels of ambient ozone.

#### 4.3.5.1 *Spring flowering measurements*

During the spring measurement campaign, which spanned from April 15 to May 6, a broad array of VOC were measured in ambient air, including over 40 identified BVOC – most of which had authentic standards to confirm their identification. Table 4-5 summarizes the relevant VOCs measured during the spring flowering period.

Table 4-5. VOC measured at the site by GC/MS-FID, including all identified BVOC and relevant anthropogenic VOC for the spring flowering period (April 15-May 6).

| **Monoterpenes ($C_{10}H_{16}$)** | **Aromatics** | **Miscellaneous** |
|---|---|---|
| α-phellandrene | Toluene | Ethanol |
| α-pinene | Ethylbenzene | Isoprene |
| α-terpinene | p-xylene | Acetone |
| α-thujene | m-xylene | Methacrolein |
| β-myrcene | o-xylene | *Diacetyl* |
| β-pinene | 1-ethyl-2-methylbenzene | Methyl Ethyl Ketone |
| *Camphene* | 1-ethyl-3-methylbenzene | Ethyl Acetate |
| Cis-ocimene | 1-ethyl-4-methylbenzene | Tetrahydrofuran |
| 3-carene (Δ) | n-propyl_benzene | Methyl n-butyl Ketone |
| Limonene (Δ) | Biphenyl | *4-Methylene-5-Hexenal* |
| γ-terpinene | Cumene | Cis-3-hexenyl acetate |
| *γ-valeroactone* | Benzaldehyde | α-methyl-γ-butyrolactone |
| Linalool | *Benzeneacetaldehyde* | Nonanal |
| Linalool oxide (cis) | *Benzene Ethanol* | *Lavender Lactone* |
| Linalool oxide (trans) | *Benzyl Nitrile* | *Methyl Benzoate* |
| Nopinone | | *Sabina Ketone* |
| Para-cymene | **Chlorinated Compounds** | *Methyl Pyridine* |
| *Sabinene* | Chloroform | *Indole* |
| Terpinolene | Chlorobenzene | *Methyl Anthranilate* |
| | 1-2-dichlorobenzene | *Neryl Acetone* |
| **Sesquiterpenes ($C_{15}H_{24}$)** | 1-3-dichlorobenzene | *E-Nerolidol* |
| Trans-β-farnesene | 1-4-dichlorobenzene | 1-heptadecene |
| α-humulene | | Heptadecane |
| *Valencene* | | |

Note: Compounds without authentic standards are shown in *italics*

The effect of flowering at the field site and in the region had a major impact on the distribution of BVOC in the ambient air. There was a dramatic increase in both the magnitude and diversity of BVOC emitted during the flowering process. Due to strong nocturnal inversions, many of the BVOC 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 BVOC, when their

emissions are most relavent to photochemistry. Additionally, several of the most prominent BVOC had daytime concentrations that regularly exceeded 1 ppb, as summarized in Table 4-6.

Table 4-6. Innerquartile ranges for measured BVOC in spring and summer (in pptv).

| | **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 | 21.8-42.3 | 30.2-239 | 62.2-118 | 253 -683 |
| α-thujene | 6.22-21.7 | 14.2-221 | 9.61-12.3 | 52.3-128 |
| α-pinene | 9.75-17.5 | 14.2-123 | 7.06-17.8 | 36.0-58.5 |
| Camphene | 6.85-12.8 | 10.5-54.2 | 12.3-27.5 | 47.3-98.4 |
| Sabinene | 24.2-151 | 84.0-2240 | 16.4-34.5 | 23.4-46.1 |
| β-myrcene | 532-1340 | 555-3340 | 8.17-16.3 | 53.2-116 |
| β-pinene | BDL-13.3 | 3.77-50.3 | | |
| α-phellandrene | 0.875-2.06 | 1.40-4.35 | 5.95-17.7 | 14.6-67.0 |
| cis-3-hexenyl Acetate | 180-359 | 212-685 | | |
| Δ3-carene | 22.8-45.5 | 27.5-126 | 2.46-6.2 | 28.2-52.2 |
| Benzaldehyde | 130-251 | 153-462 | | |
| α-terpinene | 5.60-13.0 | 9.9-104 | | |
| cis-ocimene | 27.7-66.7 | 46.7-176 | | |
| Δ-limonene | 127-247 | 167-1280 | 108-273 | 737-1340 |
| Para-cymene | 23.4-46.7 | 38.0-306 | 35.8-111 | 390-839 |
| γ-valeroactone | 14.3-208 | 30.2-167 | | |
| γ-terpinene | 42.5-83.3 | 64.9-578 | 26.1-52.1 | 108-495 |
| Terpinolene | 7.61-14.5 | 12.0-77.2 | 2.63-5.86 | 17.2-41.9 |
| trans-linalool Oxide | 5.82-16.3 | 8.84-47.9 | | |
| cis-linalool Oxide | 25.8-35.2 | 30.8-119 | | |
| Benzeneacetaldehyde | 64.6-156 | 73.9-313 | | |
| Benzeneethanol | 343-619 | 416-1380 | | |
| Methyl Benzoate | 21.1-36.4 | 25.8-77.1 | | |
| Benzyl Nitrile | 1680-3180 | 1840-5470 | | |
| Linalool | 1270-2960 | 1400-7490 | | |
| Lavender Lactone | 190-489 | 290-1360 | | |
| Sabina Ketone | 0.536-73.4 | 24.5-267 | | |
| 2-aminobenzaldehyde | 276-601 | 289-1050 | | |
| Indole | 1720-3930 | 2160-6930 | | |
| Methyl Anthranilate | 1840-4550 | 2230-10700 | | |
| trans-β-farnesene | 0.778-11.9 | 3.04-28.5 | | |
| Valencene | BDL-36.0 | 22.3-122 | | |
| E-Nerolidol | 12.0-90.2 | 29.8-274 | | |

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

β-myrcene was the principal monoterpene observed during flowering, while linalool was overall the most dominate terpenoid compounds observed. Yet, there were high concentrations of a wide variety of BVOC during the flowering period that had strong diurnal patterns, as shown in Figures 4-13, 4-14, and 4-15.

While many of the BVOC observed at the site were terpenoids, there was a diverse array of functionalized aromatic compounds that were clearly biogenic and associated with flowering. This is evidenced by their strong correlations to β-myrcene and linalool (Table 4-7), which are known to be associated with flowering from the 2008 greenhouse studies. Of the compounds observed and measured, several have not been previously reported, to our knowledge, in other studies of ambient air. Tentative identifications were made for these compounds through high quality matches to mass spectra libraries and checking their Kovat's indices for an appropriate retention time. In Table 4-8 we summarize their chemical structures and previous records of the compounds. Since many of these novel compounds are associated with flowering, we report the results of statistical regressions to the more well-known β-myrcene and report the results in Table 4-7 with a few other compounds that have good correlations. There were several previously unidentified peaks observed during measurements of the flowering 'Parent Navel' orange in the 2008 greenhouse studies that have very good retention time matches to these flowering compounds measured at this site: indole, methyl anthranilate, benzeneethanol, benzyl nitrile, 2-aminobenzaldehyde, and possibly sabina ketone. In the greenhouse measurements, these compounds were obsevered only from the flowering specimen, supporting the conclusion that flowering is the source. 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 benzeneacetaldehyde had significant median daytime concentrations at, or above, 100 ppt. Sabina ketone and methyl benzoate had lower concentrations similar to the linalool oxide isomers, 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 flowering compounds suggesting that it might be released as part of the flowering process.

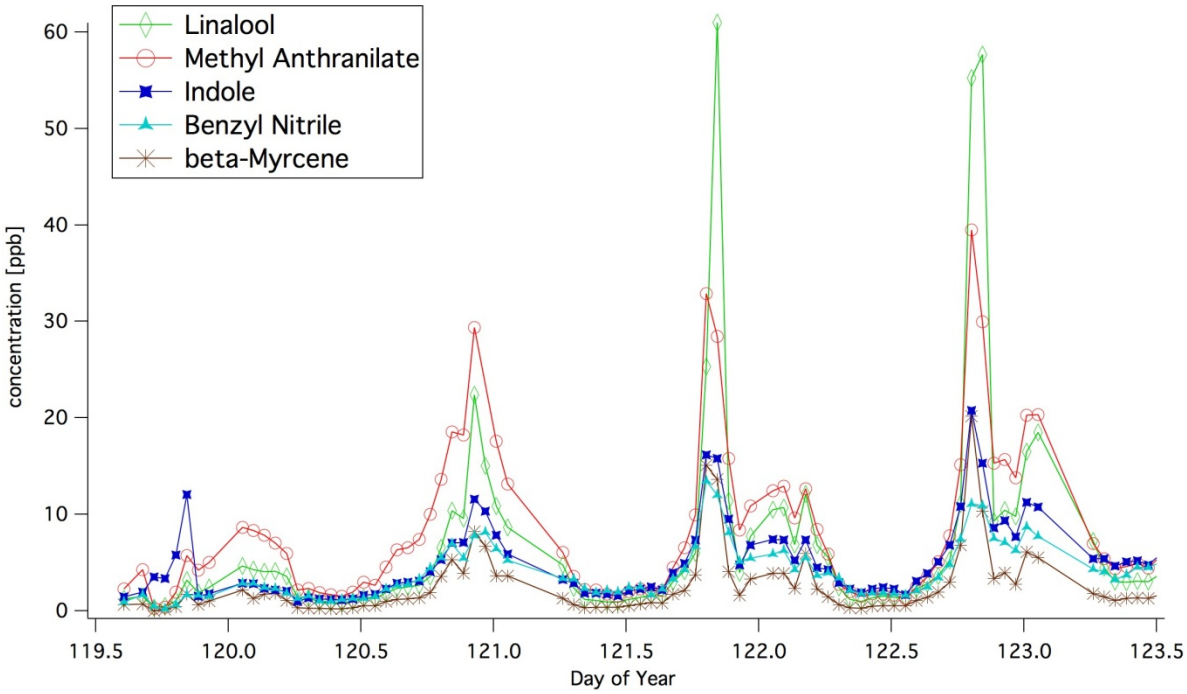



Figure 4-13. Ambient concentrations of linalool and other BVOC during the flowering period.

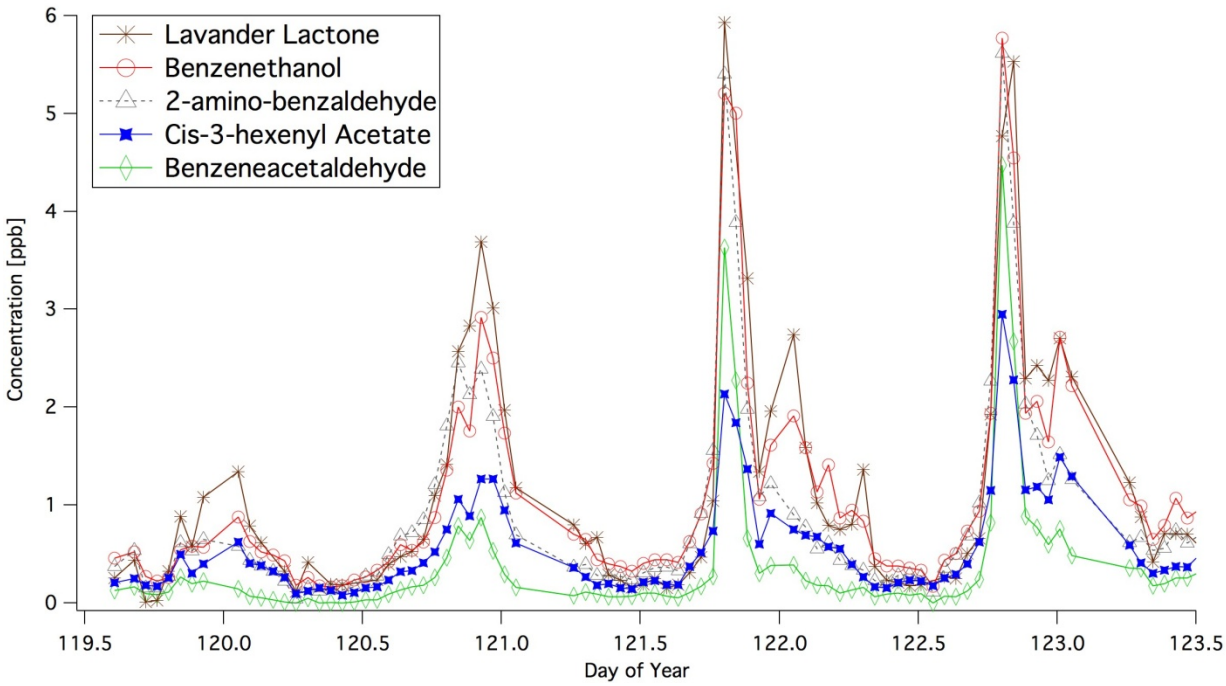



Figure 4-14. Ambient concentrations of lavender lactone and other BVOC during the flowering period.

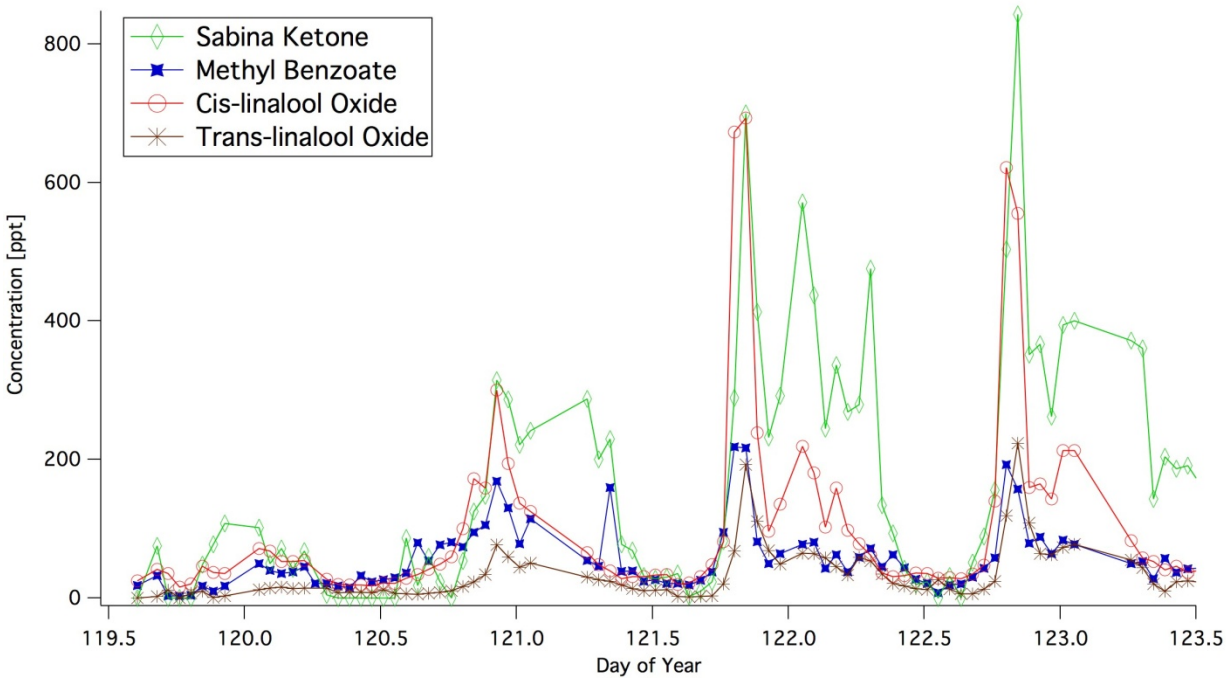



Figure 4-15. Ambient concentrations of sabina ketone and other BVOC during the flowering period.

Table 4-7. Relative prevalence of flowering-related BVOC to β-myrcene.

| Compound | mol/mol β-myrcene | ±95% CI | Correlation Coeff. (r) |
|---|---|---|---|
| Cis-3-hexenyl acetate | 0.148 | 0.0029 | 0.85 |
| Δ3-carene | 0.0198 | 0.0007 | 0.85 |
| Benzaldehyde | 0.123 | 0.0032 | 0.85 |
| α-terpinene | 0.0121 | 0.0008 | 0.84 |
| Cis-β-ocimene | 0.0241 | 0.0012 | 0.85 |
| Limonene | 0.294 | 0.015 | 0.85 |
| γ-terpinene | 0.0638 | 0.0047 | 0.85 |
| Terpinolene | 0.0098 | 0.0005 | 0.85 |
| Trans-linalool oxide | 0.0083 | 0.0004 | 0.84 |
| Cis-linalool oxide | 0.0383 | 0.0007 | 0.84 |
| Benzeneacetaldehyde | 0.198 | 0.0042 | 0.85 |
| Linalool | 3.57 | 0.076 | 0.85 |
| Lavender Lactone | 0.345 | 0.010 | 0.79 |
| Methyl Benzoate | 0.0113 | 0.0004 | 0.85 |
| Benzeneethanol | 0.324 | 0.0046 | 0.85 |
| Benzyl Nitrile | 0.799 | 0.021 | 0.85 |
| Sabina Ketone | 0.0337 | 0.0022 | 0.84 |
| 2-amino-benzaldehyde | 0.298 | 0.0054 | 0.85 |
| Indole | 1.18 | 0.026 | 0.85 |
| Methyl anthranilate | 2.49 | 0.045 | 0.84 |

Table 4-8. Novel compounds from measurements of ambient air.

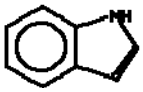
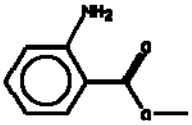
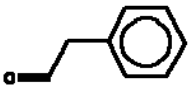
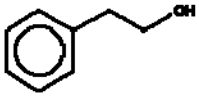
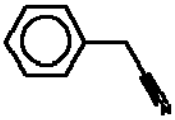
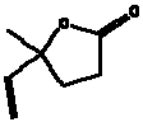
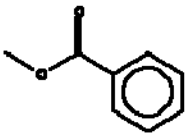
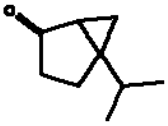
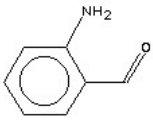
| Name(s) | Structure | Previous Records |
|---|---|---|
| Indole |  | Essential oils (orange and jasmine blossom)<br>Animal waste<br>Key structure in plant chemistry<br>Used as fly attractant[1] |
| Methyl Anthranilate (benzoic acid, 2-amino-, methyl ester) |  | Natural in several grape varieties<br>Widely used as bird/animal repellant[1] |
| Benzeneacetaldehyde (phenyl acetaldehyde) |  | Green Tea[2], Honey[3]<br>Perfume and Flavor Industries[4]<br>Measured during MINOS campaign[4] |
| Benzeneethanol (phenylethyl alcohol) |  | Soil Bacteria[5]<br>Potato Plants[6] |
| Benzyl Nitrile (benzneacetonitrile) |  | No previous record aside from pharmacological studies |
| Lavender Lactone (γ-lactone, dihydro-5-methyl-5-vinyl-2(3H)-furanone) |  | Honey[7] |
| Methyl Benzoate (Methyl Benzenecarboxylate, Niobe Oil) |  | Insect Attractant[8] |
| Sabina Ketone (5-isopropylbicyclo [3.1.0]hexan-2-one) |  | Essential Oil in Sweet Kenyan Oranges[9] |
| 2-amino-benzaldehyde |  | *Magnolia kobus* Flowers[10] |

Table References:
(Chemical Structures from NIST Chemistry WebBook http://webbook.nist.gov/chemistry/; [1] U.S. EPA Pesticide Biopesticide Active Ingredient Fact Sheets http://www.epa.gov/opp00001/biopesticides/ingredients/index.htm#1A; [2] Shimoda et al., 1995; [3] Shimoda et al., 1996; [4] Xu et al., 2003; [5] Gu et al., 2007; [6] Weissbecker et al., 1997; Alissandrakis et al., 2007; [8] Schiestl and Roubik, 2003; [9] Njoroge, et al., 2005; [10] H. Azuma et al., 2001)

There were several sesquiterpenes observed at the site during flowering, but the concentrations measured were considerably lower than many of the other terpenoids measured. 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 than other terpenoid compounds. Sampling methodology can sometimes be responsible for the attenuation of ambient concentrations, but given that the sampling and measurement techniques used in this study are suitable for sesquiterpene measurements, it suggests that reported concentrations are likely close to ambient levels. We observed a number of sesquiterpenes, many of which we were not able to identify. We measured a considerable amount of trans-beta-farnesene (confirmed with standard) and we were able to tentatively identify valencene and nerolidol (isomer unknown). Their diurnal patterns are shown in Figure 4-16.

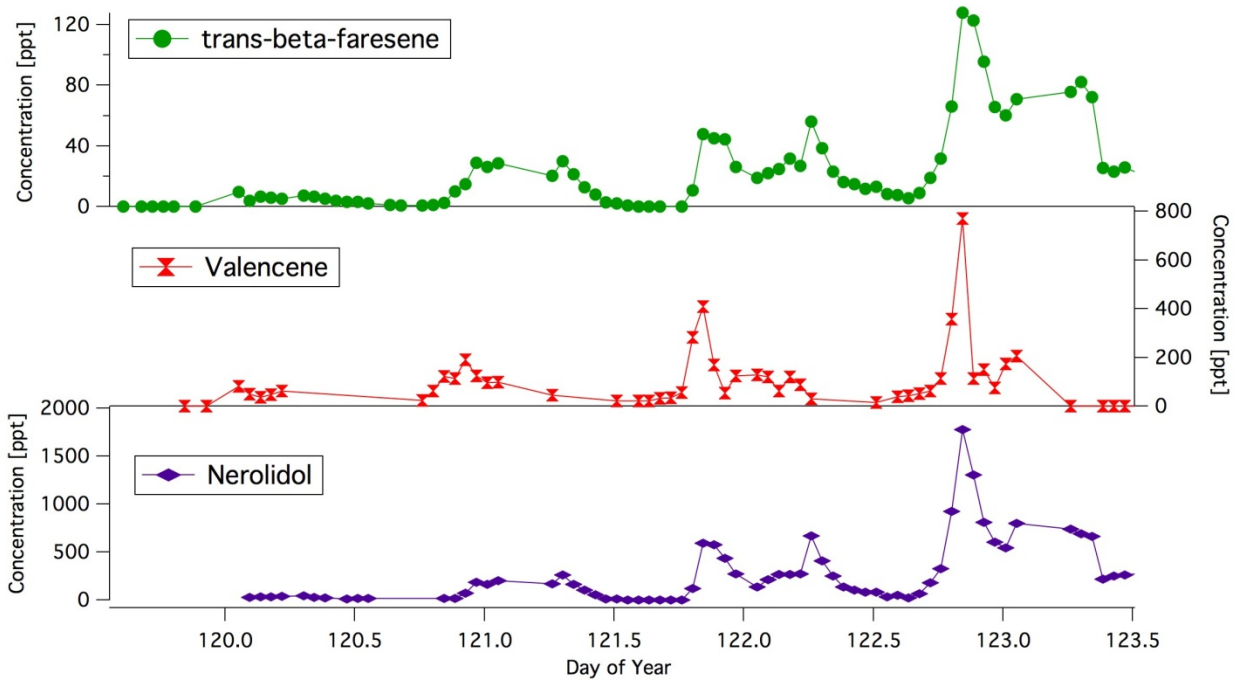



Figure 4-16. Sesquiterpenes observed during the flowering period.

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 ambient air measurements of sesquiterpenes published with which to compare our observations. It should be noted that our summertime measurements did not have the capacity to measure sesquiterpenes due to chromatographic and detector difficulties.

#### 4.3.5.2 *Summer measurements*

While we measured many fewer BVOC during the summer campaign, we still observe a variety of monoterpenes in ambient air – summarized in Table 4-9. We did not observe many of the compounds that appear to be associated with flowering. We observed similar diurnal patterns in the summer as in the winter due to boundary layer effects, with ambient ozone still getting below 10 ppb.

Table 4-9. VOC measured at the site by GC/MS-FID, including all identified BVOCs and relevant anthropogenic VOCs for the summer measurement period (Aug. 12-Sep. 2).

| **Monoterpenes ($C_{10}H_{16}$)** | **Aromatics** | **Chlorinated Compounds** |
|---|---|---|
| α-phellandrene | Toluene | Chloroform |
| α-pinene | Ethylbenzene | Chlorobenzene |
| α-thujene | p-xylene | 1,2-dichlorobenzene |
| β-myrcene | m-xylene | 1,3-dichlorobenzene |
| *Camphene* | o-xylene | 1,4-dichlorobenzene |
| 3-carene (Δ) | 1-ethyl-2-methylbenzene | |
| Limonene (Δ) | 1-ethyl-3-methylbenzene | **Miscellaneous** |
| γ-terpinene | 1-ethyl-4-methylbenzene | Ethanol |
| Nopinone | n-propyl benzene | Isoprene |
| Para-cymene | *Biphenyl* | Acetone |
| Terpinolene | | *Diacetyl* |
| | | Ethyl Acetate |

Note: Compounds without authentic standards are shown in *italics*

4.3.5.3 *Comparison and Seasonality in Terpenoid Concentrations*

The chemical speciation of monoterpenes is shown in Figures 4-17 and 4-18, and summarized in Table 4-10. There is a similar distribution and diversity of monoterpenes between the two seasons, with the exception of β-myrcene and sabinene, 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 limonene and less α- and β-pinene compared to the pine forest (Bouvier-Brown et al. 2009). Limonene was the most prevalent monoterpene observed in the summer and its innerquartile concentrations were very similar between the two seasons; 127-147 ppt vs. 108-273 ppt for daytime summer and winter concentrations, repectively, and 167-1280 ppt vs. 737-1340 ppt at night (Table 4-6). The relatively comparable concentrations of several monoterpenes during the two measurement periods in the orange orchard imply similar emission rates during those two periods.

Table 4-10. Summary of chemical speciation of monoterpenes.

| | *Spring (Flowering)* | *Summer* |
|---|---|---|
| β-myrcene | 43.8% | 4.2% |
| Sabinene | 22.5% | 11.8% |
| Δ-limonene | 16.9% | 50.1% |
| γ-terpinene | 5.6% | 17.1% |
| Cis-β-ocimene | 2.2% | - |
| α-thujene | 2.1% | 5.1% |
| Δ3-carene | 1.5% | 2.1% |
| α-pinene | 1.2% | 2.6% |
| α-terpinene | 1.0% | - |
| α-phellandrene | 1.0% | 1.7% |
| Terpinolene | 0.8% | 1.5% |
| β-pinene | 0.7% | 2.6% |
| Camphene | 0.7% | 3.9% |

While there were considerable year-round concentrations of monoterpenes at the site, there was a strong increase in biogenic emissions during the flowering period. The stacked timeseries (Figures 4-17 and 4-18) show that total concentrations of monoterpenes was approximately three times greater in spring flowering compared to summer non-flowering conditions. This increase was largely due to the emissions of β-myrcene and sabinene attributed to flowering. This result is consistent with our flowering studies in the greenhouse experiments, which saw large amounts of β-myrcene associated with the flowering citrus plants.

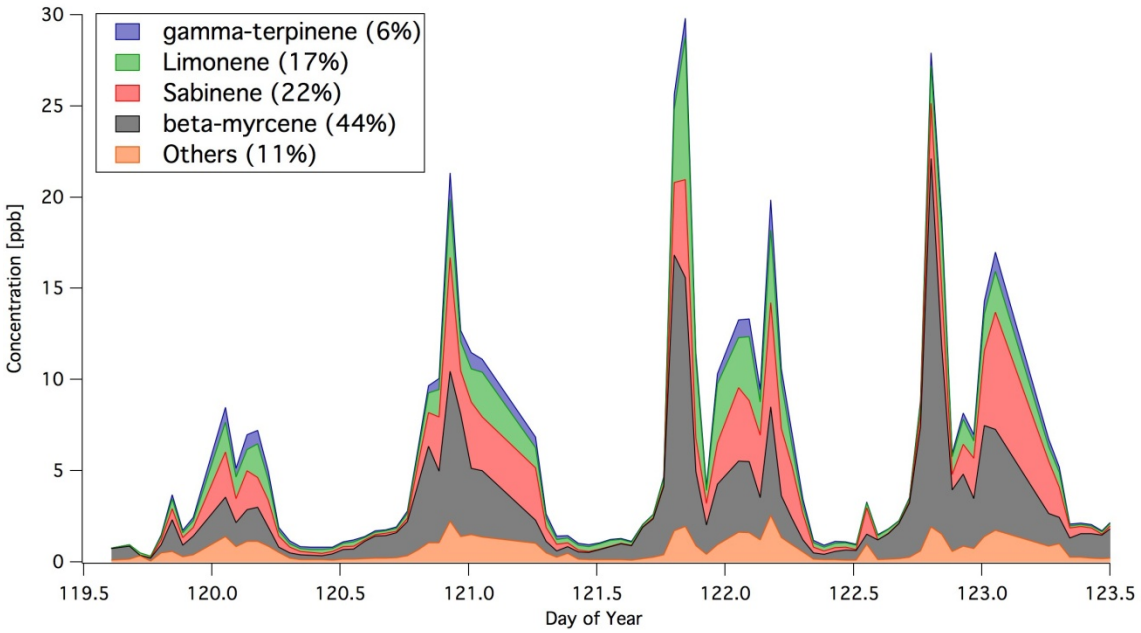



Figure 4-17. Monoterpene composition in spring during flowering.

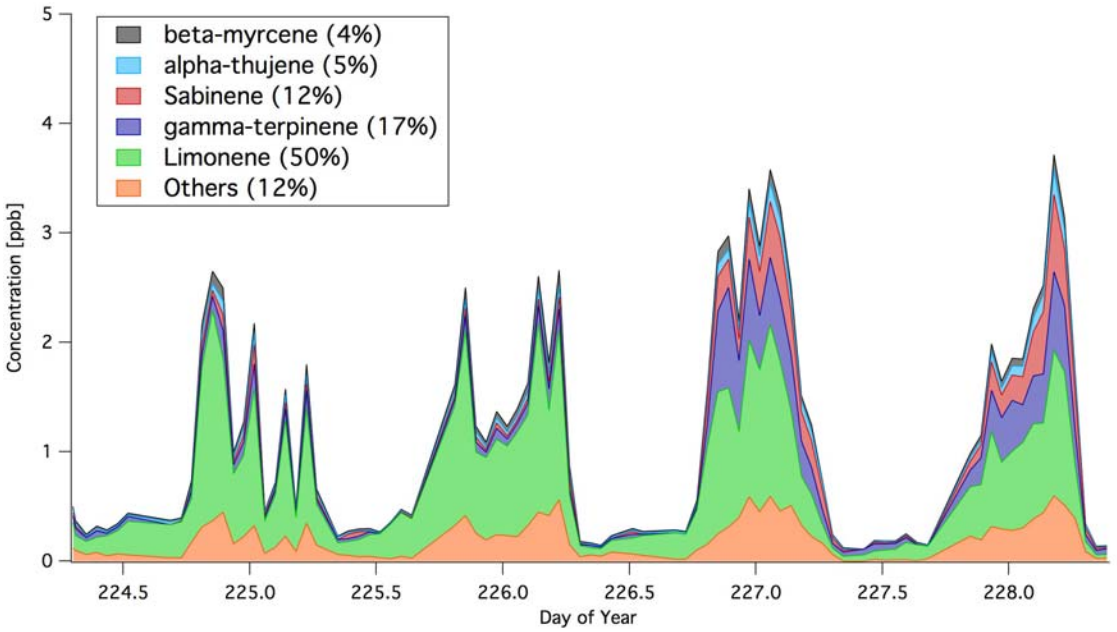



Figure 4-18. Monoterpene composition in summer.

Limonene concentrations were very similar between spring flowering and summer non-flowering periods, as shown in Figure 4-19. Para-cymene is a well-known BVOC with a wide variety of sources and a few minor anthropogenic sources (e.g. gasoline). Similar to limonene, Figure 4-20 shows that its prevalence at the field site was similar, if not slightly greater, in the summer than the spring flowering period. The potential anthropogenic contribution to para-cymene is negligible given the relatively lower concentrations of dominant gasoline components.

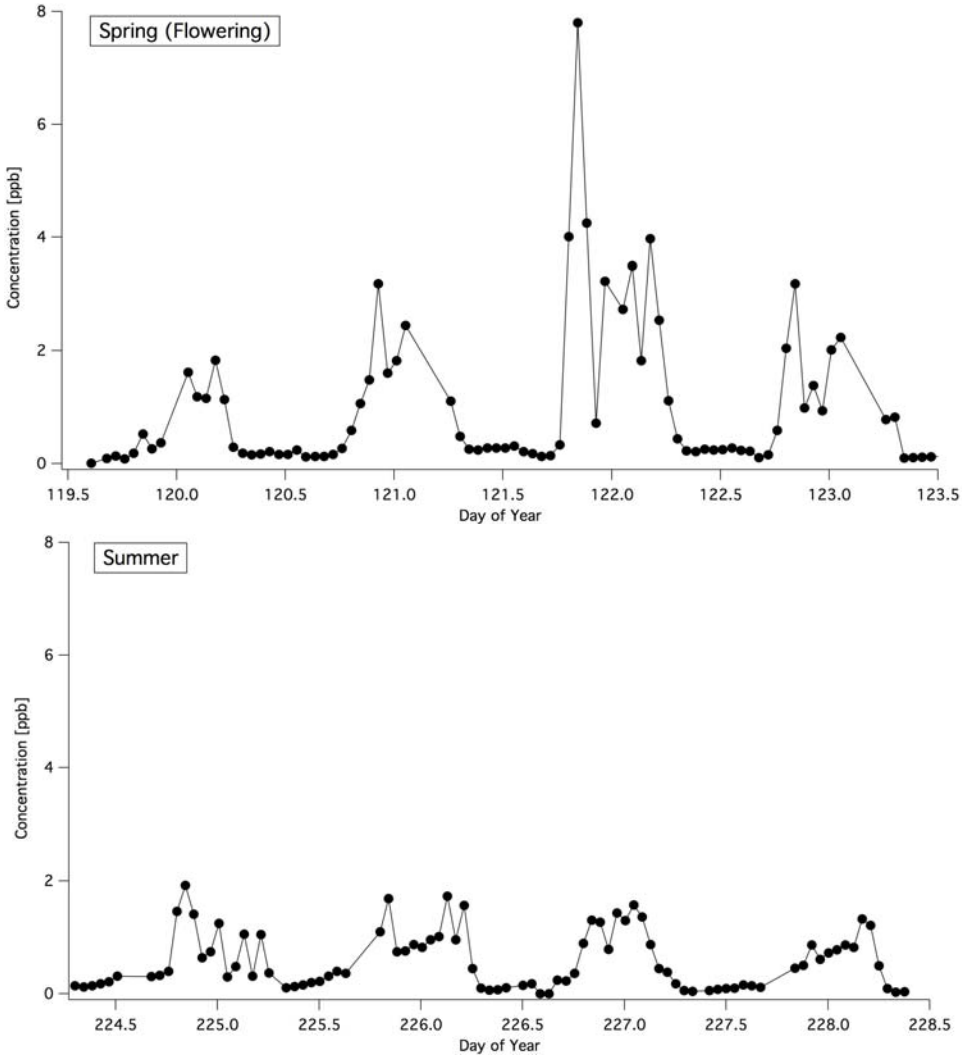



Figure 4-19. Seasonal comparison of ambient limonene concentrations.

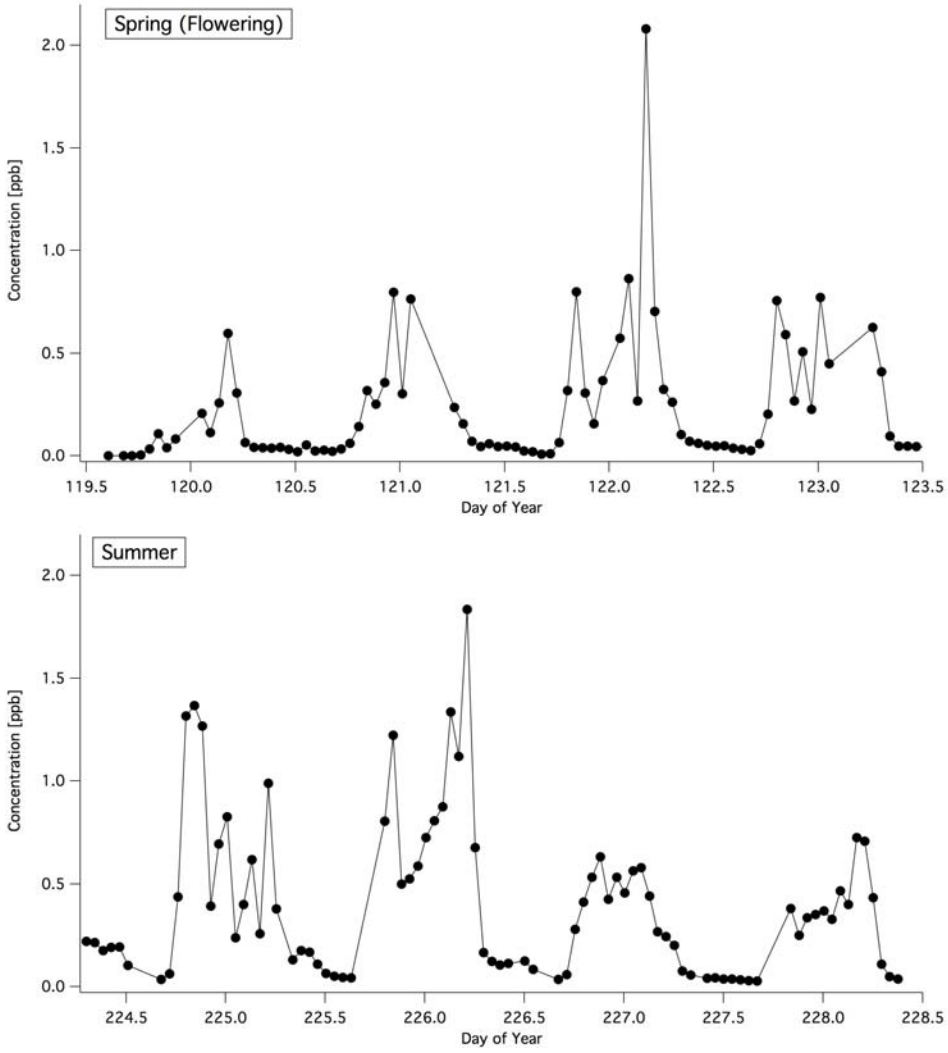



Figure 4-20. Seasonal comparison of ambient para-cymene concentrations.

## 4.4 Intercomparison of BVOC Instrumentation

The PTR-MS and GC/MS were run simultaneously twice during the yearlong measurements at the Lindcove site, and overlapped in their measurements of several compounds. We do not expect perfect agreement since their inlets were not co-located and they operated at different measurement frequencies. The instruments agreed well for measurements of acetone and for the sum of xylene isomers, ethylbenzene, and benzaldehyde, which is represented by mass 107 on

the PTR-MS. There is a slight discrepancy in the summer when GC measurements of benzaldehyde were not available to be included. Measurements of isoprene were in good agreement during the summer, but the PTR-MS infers more isoprene during the spring, and this could be due to additional signal from furan or methyl butenol on m/z 69 where isoprene is measured. Agreement for measurements of toluene was varied with PTR-MS sometimes measuring twice as much toluene as the GC/MS; this suggests one or more additional compounds must have contributed to m/z 93 on the PTR-MS. During the summer measurement period, the PTR-MS observed 1/3 less total monoterpenes than the GC/MS instrument. This discrepancy was larger during the Spring. We continue to investigate the differences between these observations, and have not yet finalized the GC/MS data. Submission of the final GC/MS data set is still pending further data processing.

### 4.5 Implications for California's Biogenic Emission Modeling

In comparison to our 2008 greenhouse study where we surveyed 25 agricultural crops, each for a short period of time, our field measurements focused on the emissions from one cultivar of orange over the course of a year. The reason for choosing this species was that *Citrus* are among the most widely cultivated crops in California, and our greenhouse enclosure meausrements highlighted oranges as one of the highest BVOC emitter among crop species, particularly during flowering. *Citrus sinensis* 'Navel' and 'Valencia' are principal orange cultivars grown in California's Central Valley. As shown by the results of the greenhouse studies there is significant variance in basal emission factor between different citrus species. From comparison between the greenhouse study and the field study, differences in BEF are also evident between the two orange

cultivars. The differences among *Citrus* species should be taken into account when attempting to model the BVOC emissions.

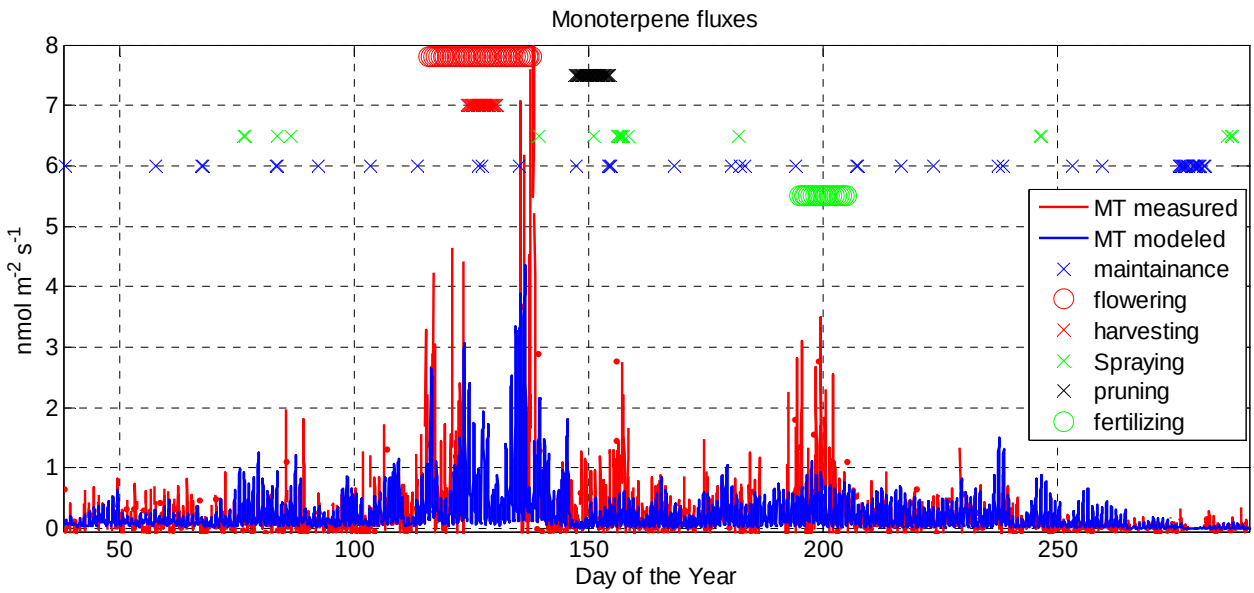



Figure 4-21. Monoterpene emissions (fluxes) measured with PTRMS in the citrus orchard. Modeled fluxes are calculated using a temperature algorithm, using β (0.14 for winter, fall, and summer, 0.15 for flowering period) based on the greenhouse experiments.

Figure 4-21 shows monoterpene emissions measured during the year with PTR-MS, and modeled using an algorithm based on temperature dependencies previously described in this report, with β values coming from the greenhouse experiment for Valencia orange. Of major importance were the large increases we observed in emissions from the orange grove and regional concentrations of BVOC that occurred during seasonal events. Our measurements of both BVOC fluxes and regional concentrations show that these specific events contribute a significant amount of the total annual emissions. At our site these events were spring flowering, pruning, harvesting, and fertilizer application. During these times we measured large increases

in emissions of terpenoids (monoterpenes, sesquiterpenes, and oxygenated terpenes) and also the lower-molecular weight OVOCs measured. Figure 4-21 clearly shows the measured emissions are higher than modeled emissions in certain periods of the year. In other words, the model is not able to represent fluxes during certain periods which correspond to flowering (DOY 116-136), harvesting (DOY 140-145), pruning (DOY 150-160), and fertilizer applications (DOY 195-205).

To accurately model biogenic emissions from agriculture and air quality in the San Joaquin Valley, the seasonal events need to be taken into account since we measured significant changes in both basal emission factors and beta factors for most compounds – a result that is supported by our observations of flowering in the greenhouse study. Some crops such as *Citrus* are pruned during the summer when the effect of emissions is going to have a much larger effect on secondary air pollution formation, whereas for example almonds and pistachios are pruned in the winter when there is no foliage so emissions and their effects are minimized.

The chemically-speciated measurements at the site using the GC/MS-FID yielded information on large emissions of previously-unobserved aromatic BVOC associated with flowering in the region. This burst of emissions could have an effect on the biogenic emission inventory for the region if the emissions are extrapolated across all the *Citrus* of the valley during the periods of flowering. These compounds should be included in the MEGAN and BEIGIS models since their emissions during flowering were on the same order as all the terpenoids observed. Further study will likely be necessary to determine their basal emission factors, beta values, and potential contributions to ozone and SOA formation, and to assess flowering emissions from other major

crops grown in California. The information in this report may be used to revise basal emission factors and beta values, with a strong emphasis on seasonality and emission events.

## 5.0 SUMMARY AND CONCLUSIONS

It is now well known that reactive organic gases are emitted from vegetation, including urban landscapes, agricultural crops, and natural plant communities in unirrigated areas. The global budget of volatile organic compounds is dominated by biogenic emissions (Guenther et al. 1995) and BVOC emissions play important roles in tropospheric ozone formation, production of organic acids important in acidic deposition in rural areas, global tropospheric chemistry, and production of secondary organic aerosols that are important contributors to fine particulate matter (Fesenfeld et al. 1992, Goldstein and Galbally, 2007). Vegetative emissions are as reactive as or more reactive than the VOC emissions from automobiles, and can have higher ozone-forming potential (Carter 1994, Benjamin et al. 1998).

In general, broadleaved plants, such as oaks and eucalyptus, have as their largest BVOC emission the five-carbon compound isoprene, whereas pines and other conifers have as their largest BVOC emission the family of ten-carbon compounds, the monoterpenes, and methanol emissions can be high from a wide variety of plants. The magnitudes of BVOC emissions of an individual plant are affected by its leafmass and by its rates of emission of isoprene, monoterpenes and other VOC, as well as by environmental factors such as temperature and light intensity.

Accurate estimates of the magnitude of BVOC emissions relative to anthropogenic VOC emissions in California's airsheds are critical for formulating effective strategies to reduce concentrations of fine particles, ozone, and other secondary air pollutants which affect human health and reduce yields of agricultural crops. To obtain such estimates requires several distinct databases. The present study focused on emission measurements for principal agricultural crops.

### 5.1 BVOC Emission Measurements from Crop Species

All crop species measured in this study have low isoprene emission rates, less than 1 μg per g dry leaf mass. These low values are one to three orders of magnitude below those of the important BVOC emitting plants found in urban and natural landscapes. Emissions of monoterpenes were low, but not insignificant, with tomato and orange the two plants with

highest monoterpene emissions. Our results for monoterpenes differ from those of Winer et al., 1992. Since pistachio is now a large-area crop (49,600 acres in Kern Co., in 2009, the leading pistachio-producing county) and is still expanding, we recommend additional emission rate measurements for this crop.

Methanol emissions may be important from some crops, but the reactivity of methanol in the atmosphere is far lower than isoprene or monoterpenes, so methanol emissions are not as important in terms of impact on regional air quality.

Flowering events in citrus were found to lead to a large increase of emissions, in agreement with previous work. The flowering event is of short duration but may result in a significant fraction of emission for that crop type for the year. Flowering events may be important for other crops as well, especially for insect-pollinated crops having larger flowers with nectaries.

## 5.2 Canopy-Scale Measurements of BVOC from Citrus

To accurately model biogenic emissions from agricultural crops and their impact on air quality in the San Joaquin Valley, seasonal events causing increases in emission need to be taken into account. We measured significant changes in both basal emission factors and beta factors for most compounds – a result that is supported by our observations of flowering in the greenhouse study. This burst of emissions during flowering could have a significant effect on the biogenic emission inventory for the region if the emissions are extrapolated across all the *Citrus* of the Valley.

Harvensting events may also contribute to the overall emission profile for a crop, particularly if leaves are disturbed. However, harvest practices vary considerably among crops, from cutting/drying for alfalfa to hand-collection of fruit which will result in disturbance of leaves, to shaking of trees to drop fruit to the ground.

Pruning practices may also affect emissions, particularly if plants are pruned mechanically when foliage is present. Citrus represents a crop where pruning occurs during the warmer part of the

year, done mechanically, and with leaves cut. Other deciduous crops, like almonds or pistachios, are pruned during or near winter when leaves are absent and outside of the smog season.

## 5.3 Using the Information from This Study

For a biogenic emission inventory, the total emissions are a product of the emission rate and leaf mass, so for crops where planted area is enormous, emissions even with low rates may be important. In air quality models, these emissions should be represented by a number other than zero. Values for the oxygenated VOC, although small, can be inserted into BEGEIS.

Since crop emissions per g dry leaf mass as measured are, in general, small or very small, it may be that the contribution of natural vegetation surrounding the Central Valley provides the dominant portion of BVOC in California, yet the concentration of many BVOC in agricultural areas of the Central Valley will be dominated by the local crops due to their short atmospheric lifetimes.

## 6.0 RECOMMENDATIONS FOR FUTURE RESEARCH

Further research should be undertaken to provide data vital for spatial allocation and quantification of BVOC emissions, in support of ARB's statewide modeling mission to determine the relative importance of VOC vs. $NO_x$ emission controls in various airsheds. Biogenic emission inventories contain four terms that estimate emissions of each compound: species-specific emission rate, amount of leaf mass, allocation of leaf mass in the landscape, and adjustment of light and temperature so as to model emission rate. Research may be needed to address any or all of these terms to bring the relative precision and accuracy of each into similarity with the others.

### 6.1 Potential Future Research

#### 6.1.1 Overall Objectives

The overall objectives of the proposed research are to provide information critical to resolve key contemporary questions related to BVOC emission inventories. Because these inventories depend upon scaling up of leaf-level or branch-level emission factors, the proposed research addresses components within several levels of inventory development.

#### 6.1.2 Specific Research Needs

(1) Despite rapid population growth, the San Joaquin Valley remains largely rural and extensive natural plant communities, including large expanses of oak woodlands, exist below the atmospheric boundary layer on the south and east sides of the Valley. Although agricultural crops, in general, have low to moderate rates of BVOC emissions, certain tree and shrub species found in urban landscapes and in natural plant communities of California have medium to high BVOC emissions rates and ozone-forming potential (OFP). Plants with both high emissions rates and high leafmass per plant, including several of the oak species, may contribute substantial BVOC emissions to the SJVAB and other airsheds. To date, there have been no canopy scale emission measurements of isoprene from oaks in California which is the major emitting species. Additional measurements of oaks to validate scaling, determine seasonality of emissions, and to investigate the emission of compounds in addition to isoprene are warranted.

(2) Refinement of methods for measuring and validating LAI and its corollary, leaf mass density, is needed. Data from satellite instruments which measure LAI indirectly should be validated with ground-based measurements, especially for plant species of most interest in emission inventories. Further research is required to understand the utility and uncertainty of the GAP or other GIS databases in the natural plant communities adjacent to the San Joaquin Valley through quantification and validation. Further assessment of GAP in key airsheds would give both a qualitative description and quantitative measure of accuracy. Additionally, field data may provide an indication of the degree of change in California's natural plant communities, and hence the reliability of other plant maps and databases derived from earlier surveys. Quantification of GAP through measurement of leafmass per volume ratios and leafmass per unit of areal coverage of selected species should provide data vital to translation of landcover information into quantity of foliage per species.

(3) There remains a need to quantify and understand, through parallel measurements of the same plant specimens, the relationship between BVOC emissions values obtained through leaf-level, branch-level, and whole plant sampling. One approach would be a large-enclosure study, modeled after the whole-tree enclosure work of Pier and McDuffie (1997) for oaks, but with sampling at the various scales added. Ideally the location for this research would be chosen to allow flux measurements at a landscape scale, and could also be used to evaluate canopy models for shading. This work would be in cooperation with NCAR researchers, and intercomparison of data would allow understanding of BVOC emission scaling issues which to date have been never been directly addressed.

(4) Emission inventories to date have focused upon isoprene and monoterpenes, but compounds such as methyl butenol, sesquiterpenes, and other oxygenated hydrocarbons may represent significant or even dominant emissions by some plants. Research is needed to determine whether significant fractions of BVOC emissions by key California species have gone unmeasured.

(5) Both emission and deposition of aerosols and deposition of their oxidized organic precursors in California airsheds should be measured. This is an enormous task, and little to no data is currently available. For example, do plant species vary in their ability to "capture" aerosols and oxidized organics? In addition to gaseous emissions, what fraction of $PM_{10}$ or $PM_{2.5}$ is attributable to physical processes and removal of plant tissue such as cuticular wax or cortex. Although pollen grains and plant spores are larger than $PM_{10}$, their presence may be a factor in air quality in California.

(6) The net air quality effects of California's flora should be examined through compilation of data pertaining to both emission of BVOC and deposition of pollutant compounds, including ozone and aerosols.

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# 8.0 APPENDICES

## APPENDIX A.

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

## Appendix B: Data sets description

I. Data set **CITRUS_MET_VOC_FLUX_V3**

General:

This data set contains ambient VOC mixing ratios and fluxes as measured by PTRMS, coordinated with meteorological and micro-meteorological measurements, H2O, CO2, and ozone ambient mixing ratios and fluxes, and various other measurements useful to interpret the VOC data. Measurements are half-hour averages (or totals, in the case of precipitation) with the time stamp representing the beginning of the half-hour. Rows of data are presented in order of a full year of measurements from January 1 to December 31, the time-stamp for this presentation order to be found in the first "DOY" (day of year) column. Actually, the measurements were taken from November 15, 2009 to November 14, 2010, and the 2009 data are to be found at the end of the data table. Analysts interested in the actual date of measurements should attend to columns 1, 2, and 3, listing the year, month, and day-of-month, respectively.

Data items filled with the value -99999 denote "no measurement".

Column descriptions (numbering refers to column number):

0. "doy": Day of year. Day of year + decimal day fraction. Note that daylight savings time (PDT) is not is not used here, and all times are local standard time (Pacific Standard Time = PST). Time is the beginning of the half-hour averaged measurement.
1. "year": Year of measurement.
2. "month": Month of measurement.
3. "dom": Day of month.
4. "hour": Hour of day.
5. "minute": Minute within hour.
6. "rnet": Net radiation in W $m^{-2}$, measured at approximately 10 m above the ground.
7. "par_1": Photosynthetically active radiation in μmol $m^{-2}$ $s^{-1}$, measured at approximately 10 m above the ground.
8. "wspeed_1": Wind speed in m $s^{-1}$, measured at 9.18 m above the ground.
9. "wspeed_2": Wind speed in m $s^{-1}$, measured at 4.85 m above the ground.
10. "wspeed_3": Wind speed in m $s^{-1}$, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.
11. "wspeed_4": Wind speed in m $s^{-1}$, measured at 1 m above the ground.
12. "wdir": Wind direction in degrees from true north, measured at approximately 10 m off the ground.
13. "airtemp_1": Air temperature in degrees Celsius, measured at 9.18 m above the ground.

14. “airtemp_2”: Air temperature in degrees Celsius, measured at 4.85 m above the ground.
15. “airtemp_3”: Air temperature in degrees Celsius, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.
16. “airtemp_4”: Air temperature in degrees Celsius, measured at 1 m above the ground.
17. “rh_1”: Relative humidity in percent, measured at 9.18 m above the ground.
18. “rh_2”: Relative humidity in percent, measured at 4.85 above the ground.
19. “rh_3”: Relative humidity in percent, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.
20. “rh_4”: Relative humidity in percent, measured at 1 m above the ground.
21. “leaftemp”: Citrus tree leaf temperature in degrees Celsius.
22. “leafwet”: Citrus tree leaf dew condition as wet/dry (1 = wet, 0 = dry).
23. “soiltemp_5cm”: Soil temperature in degrees Celsius, measured at 5 cm depth.
24. “soiltemp_10cm”: Soil temperature in degrees Celsius, measured at 10 cm depth.
25. “soiltemp_15cm”: Soil temperature in degrees Celsius, measured at 15 cm depth.
26. “soilmoist_5cm”: Soil water content as volumetric fraction of water, measured at 5 cm depth.
27. "soilmoist_20cm": Soil water content as volumetric fraction of water, measured at 20 cm depth.
28. "soilmoist_50cm": Soil water content as volumetric fraction of water, measured at 50 cm depth.
29. "shf": Soil heat flux in W $m^{-2}$, measured at 10 cm depth.
30. "co2_1": Ambient mixing ratio of $CO_2$ in ppm, measured at 9.18 m above the ground.
31. "co2_2": Ambient mixing ratio of $CO_2$ in ppm, measured at 4.85 above the ground.
32. "co2_3": Ambient mixing ratio of $CO_2$ in ppm, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.
33. "co2_4": Ambient mixing ratio of $CO_2$ in ppm, measured at 1 m above the ground.
34. "h2o_1": Ambient mixing ratio of $H_2O$ in parts per thousand, measured at 9.18 m above the ground.
35. "h2o_2": Ambient mixing ratio of $H_2O$ in parts per thousand, measured at 4.85 above the ground.
36. "h2o_3": Ambient mixing ratio of $H_2O$ in parts per thousand, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.
37. "h2o_4": Ambient mixing ratio of $H_2O$ in parts per thousand, measured at 1 m above the ground.
38. "o3_1": ": Ambient mixing ratio of $O_3$ in ppb, measured at 9.18 m above the ground.
39. "o3_2": Ambient mixing ratio of $O_3$ in ppb, measured at 4.85 above the ground.

40. "o3_3": Ambient mixing ratio of $O_3$ in ppb, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.
41. "o3_4": Ambient mixing ratio of $O_3$ in ppb, measured at 1 m above the ground.
42. "precip": Total rainfall in the half hour in cm, measured at approximately 10 m above the ground.
43. "Pa": Ambient atmospheric pressure in millibars, measured at approximately 1.5 meters above the ground.
44. "co": Ambient mixing ratio of CO in ppb, measured at approximately 4 meters above the ground.
45. "flux_co2": Vertical flux of $CO_2$ in μmol $m^{-2}$ $s^{-1}$, measured at 7.11 meters above the ground.
46. "flux_h2o": Vertical flux of $H_2O$ in μmol $m^{-2}$ $s^{-1}$, measured at 7.11 meters above the ground.
47. "flux_o3": Vertical flux of $O_3$ in μmol $m^{-2}$ $s^{-1}$, measured at 7.11 meters above the ground.
48. "flux_ustar": Friction velocity in m $s^{-1}$, measured at 7.11 meters above the ground.
49. "flux_sheat": ": Sensible heat in W $m^{-2}$, measured at 7.11 meters above the ground.
50. "flux_lheat": Latent heat in W $m^{-2}$, measured at 7.11 meters above the ground.
51. "flux_molength": Monin-Obukov length in meters, measured at 7.11 meters above the ground.
52. "flux_tmean": Mean air temperature from sonic anemometer in degrees Celsius, measured at 7.11 meters above the ground.
53. "flux_stationary": Flag denoting passed stationary test for flux measurements. (Fluxes for each five minute period within the half hour are within 60% for the half-hour value.) 1 = stationary test passed, 0 = failed.
54. "flux_ubar": Horizontal with speed from sonic anemometer in m $s^{-1}$, measured at 7.11 meters above the ground.
55. "Ra": Aerodynamic resistance in s $m^{-1}$, for canopy height of 3.7 meters above the ground.
56. "Rb": Boudary layer resistance to ozone in s $m^{-1}$, for canopy height of 3.7 meters above the ground.
57. "Rbw": Boudary layer resistance to water in s $m^{-1}$, for canopy height of 3.7 meters above the ground.
58. "Rc": Canopy conductance to ozone in s $m^{-1}$, for canopy height of 3.7 meters above the ground.
59. "Vdo": Ozone deposition velocity in m $s^{-1}$, for canopy height of 3.7 meters above the ground.
60. "Gcanopy": Canopy conductance to ozone in m $s^{-1}$, for canopy height of 3.7 meters above the ground.
61. "O3c": Ozone concentration at leaf level in ppb, for canopy height of 3.7 meters above the ground.
62. "transpir": Transpiration in mmol $m^{-2}$ $s^{-1}$.

63. "maintenance": Flag field denoting times when field instrument maintenance operations are in progress. (1 = maintenance occurring, 0 = no maintenance)
64. "treetrimming": Flag field denoting times when tree trimming operations may be in progress. Information provided by the farmer. (1 = tree trimming possibly occurring, 0 = no trimming)
65. "spraying": Flag field denoting times when pesticide/fungicide/chemical application operations may be in progress. Information provided by the farmer. (1 = pesticide spraying possibly occurring, 0 = no spraying)
66. "harvesting": Flag field denoting times when fruit harvesting operations may be in progress. Information provided by the farmer. (1 = harvesting spraying possibly occurring, 0 = no spraying)
67. "methanolL1": Ambient mixing ratio of methanol in ppb, measured at 9.18 m above the ground.
68. "acetaldehydeL1": Ambient mixing ratio of acetaldehyde in ppb, measured at 9.18 m above the ground.
69. "acetoneL1": Ambient mixing ratio of acetone in ppb, measured at 9.18 m above the ground.
70. "isopreneL1": Ambient mixing ratio of isoprene in ppb, measured at 9.18 m above the ground.
71. "MVK_MACRL1": Ambient mixing ratio of methyl vinyl ketone and/or methacrolein in ppb, measured at 9.18 m above the ground.
72. "monoterpenesL1": Ambient mixing ratio of monoterpines in ppb, measured at 9.18 m above the ground.
73. "methanolL2": Ambient mixing ratio of methanol in ppb, measured at 4.85 m above the ground.
74. "acetaldehydeL2": Ambient mixing ratio of acetaldehyde in ppb, measured at 4.85 m above the ground.
75. "acetoneL2": Ambient mixing ratio of acetone in ppb, measured at 4.85 m above the ground.
76. "isopreneL2": Ambient mixing ratio of isoprene in ppb, measured at 4.85 m above the ground.
77. "MVK_MACRL2": Ambient mixing ratio of methyl vinyl ketone and/or methacrolein in ppb, measured at 4.85 m above the ground.
78. "monoterpenesL2": Ambient mixing ratio of monoterpines in ppb, measured at 4.85 m above the ground.
79. "methanolL3": Ambient mixing ratio of methanol in ppb, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.
80. "acetaldehydeL3": Ambient mixing ratio of acetaldehyde in ppb, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.

81. "acetoneL3": Ambient mixing ratio of acetone in ppb, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.
82. "isopreneL3": Ambient mixing ratio of isoprene in ppb, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.
83. "MVK_MACRL3": Ambient mixing ratio of methyl vinyl ketone and/or methacrolein in ppb, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.
84. "monoterpenesL3": Ambient mixing ratio of monoterpines in ppb, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.
85. "methanolL4": Ambient mixing ratio of methanol in ppb, measured at 1 m above the ground.
86. "acetaldehydeL4": Ambient mixing ratio of acetaldehyde in ppb, measured at 1 m above the ground.
87. "acetoneL4": Ambient mixing ratio of acetone in ppb, measured at 1 m above the ground.
88. "isopreneL4": Ambient mixing ratio of isoprene in ppb, measured at 1 m above the ground.
89. "MVK_MACRL4": Ambient mixing ratio of methyl vinyl ketone and/or methacrolein in ppb, measured at 1 m above the ground.
90. "monoterpenesL4": Ambient mixing ratio of monoterpines in ppb, measured at 1 m above the ground.

91. "benzeneL1": Ambient mixing ratio of benzene in ppb, measured at 9.18 m above the ground.
92. "tolueneL1": Ambient mixing ratio of toluene in ppb, measured at 9.18 m above the ground.
93. "xyleneL1": Ambient mixing ratio of xylene in ppb, measured at 9.18 m above the ground.
94. "benzeneL2": Ambient mixing ratio of benzene in ppb, measured at 4.85 m above the ground.
95. "tolueneL2": Ambient mixing ratio of toluene in ppb, measured at 4.85 m above the ground.
96. "xyleneL2": Ambient mixing ratio of xylene in ppb, measured at 4.85 m above the ground.=
97. "benzeneL3": Ambient mixing ratio of benzene in ppb, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.
98. "tolueneL3": Ambient mixing ratio of toluene in ppb, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.
99. "xyleneL3": Ambient mixing ratio of xylene in ppb, measured at 3.76 m above the ground between 11/15/2009 and 12/16/2009, and at 2.65 m above the ground after 12/16/2009.
100. "benzeneL4": ": Ambient mixing ratio of benzine in ppb, measured at 1 m above the ground.

101. "tolueneL4": ": Ambient mixing ratio of toluene in ppb, measured at 1 m above the ground.

102. "xyleneL4": ": Ambient mixing ratio of xylene in ppb, measured at 1 m above the ground.

103. "methanol_flux": Vertical flux of methanol in nmol $m^{-2}$ $s^{-1}$, measured at 7.11 meters above the ground.

104. "acetone_flux": Vertical flux of acetone in nmol $m^{-2}$ $s^{-1}$, measured at 7.11 meters above the ground.

105. "isoprene_flux": Vertical flux of isoprene in nmol $m^{-2}$ $s^{-1}$, measured at 7.11 meters above the ground.

106. "monoterpenes_flux": Vertical flux of monoterpenes in nmol $m^{-2}$ $s^{-1}$, measured at 7.11 meters above the ground.

II. Data Set: **GC/MS VOC Measurements at Lindcove Field Site in Spring and Summer**

Please see the comma separated values file for VOC data using the GC/MS-FID instrument during 2 measurement periods: spring-flowering (April 15$^{th}$-May 6$^{th}$) and summer (Aug. 12$^{th}$-Sept. 2$^{nd}$).

**THIS DATA IS CURRENTLY PRELIMINARY; A FINAL VERSION OF THE DATA WILL BE DELIVERED SUMMER 2011.**

III. Data Set: **Data from 2008 Greenhouse Measurements**

See file: 2008_Greenhouse_Data.csv

**Summary of Information in File**

| Data Column | Description | Units |
|---|---|---|
| Species_Num | Catalog number for species | |
| Plant_Num | Plant sample number | |
| DOY | Start time of 15 minute measurement period | Fractional Day of Year |
| checkPTRtime | | |
| checkFIDtime | | |
| PAR | Photosynthetically Active Radiation | |
| RH | Relative humidity | % |
| Greenhouse_Temp | Temperature in greenhouse | °C |
| Leaf_Temp | Temperature of leaves in plant enclosure | °C |
| P_mbar | Pressure | mbar |
| Transpiration | | $mol \bullet m^{-2} \bullet s^{-1}$ |
| VPD | Vapor Pressure Deficit | kPa |
| Sto_Conductance | Stomatal conductance | $mol \bullet m^{-2} \bullet s^{-1}$ |
| CO2Flux_umol | | $\mu mol \bullet m^{-2} \bullet s^{-1}$ |
| CO2Flux_ugC | | $\mu gC \bullet gDM^{-1} \bullet s^{-1}$ |
| Dry_Mass | Mass of leaves in enclosure | g |
| m[###]Conc | Concentration in enclosure of given mass measured using PTR-MS | ppb |
| m[###]Flux | Flux of given mass measured using PTR-MS | $ng \bullet gDM^{-1} \bullet hr^{-1}$ |
| m[###]FluxC | Carbon flux of given mass measured using PTR-MS | $ngC \bullet gDM^{-1} \bullet hr^{-1}$ |
| GC_MNT_Flux | Flux of monoterpenes measured using GC/MS | $ng \bullet gDM^{-1} \bullet hr^{-1}$ |
| GC_SQT_Flux | Flux of sesquiterpenes measured using GC/MS | $ng \bullet gDM^{-1} \bullet hr^{-1}$ |
| GC_OXY_Flux | Flux of oxygenated monoterpenes measured using GC/MS | $ng \bullet gDM^{-1} \bullet hr^{-1}$ |
| GC_MNT_FluxC | Carbon flux of monoterpenes measured using GC/MS | $ngC \bullet gDM^{-1} \bullet hr^{-1}$ |
| GC_SQT_FluxC | Carbon flux of sesquiterpenes measured using GC/MS | $ngC \bullet gDM^{-1} \bullet hr^{-1}$ |
| GC_OXY_FluxC | Carbon flux of oxygenated monoterpenes measured using GC/MS | $ngC \bullet gDM^{-1} \bullet hr^{-1}$ |
| GC_Flux_[Compound Name] | Carbon flux of given compound measured using GC/MS | $ngC \bullet gDM^{-1} \bullet hr^{-1}$ |

| | | |
|---|---|---|
| GC_Conc_[Compound_Name] | Concentration of given compound measured using GC/MS | ppb |
| GC_Conc_sumMNT | Concentration of monoterpenes measured using GC/MS | ppb |
| GC_Conc_sumSQT | Concentration of sesquiterpenes measured using GC/MS | ppb |
| GC_Conc_sumOXY | Concentration of oxygenated monoterpenes measured using GC/MS | ppb |

Note: GC/MS measurements appear as two identical points in sequence because the measurement period was 1 continuous 30 minute sample. GC/MS measurements were taken on a separate inlet from the PTR-MS, $CO_2$, and water measurements and switched plant enclosures on a different schedule. In order to include all the measurements in this database and organized by each plant measured, we have left the data in this expanded form.

**Plant Species Catalog Numbers**

1 Alfalfa
2 Almond
3 Apricot
4 Carrot (Red)
5 Carrot (BN)
6 Cherry
7 Corn
8 Cotton (Pima)
9 Cotton (Upland)
10 Table Grape
11 Wine Grape
12 Liquidambar
13 Miscanthus
14 Olive
15 Onion
16 Peach
17 Pistachio
18 Plum
19 Pomegranate
20 Potato
21 Tomato
22 Parent Navel Orange
23 Murcott Mandarin
24 Clementine Mandarin
25 Eureka Lemon
26 Meyer Lemon