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

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Supplementary Material for:

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

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Summary of Supporting Information: 12 Pages (excluding cover)

Tables

Figures

Emission Algorithms

Temperature and Light (Guenther et al., 1993):

$$E_{L+T} = BEF\left[\frac{\alpha C_L PAR}{\sqrt{1+\alpha^2 PAR^2}}\right] * \left[\frac{\exp\left(\frac{C_{T1}(T-T_S)}{RT_S T}\right)}{0.961+\exp\left(\frac{C_{T2}(T-T_M)}{RT_S T}\right)}\right] \quad \text{(S1)}$$

Empirical coefficients:

$C_L = 1.066$

$C_{T1} = 95000$ J mol^{-1}

$C_{T2} = 230000$ J mol^{-1}

$C_{T3} = 0.961$

$\alpha = 0.0027$

$T_M = 314$ K

R (universal gas constant) = 8.314 J K^{-1} mol^{-1}

Variables:

T: leaf temperature (K)

T_S: leaf temperature at standard conditions (303 K)

Emission rates, also referred to as fluxes, are in terms of compound mass per mass dry leaf matter per time (e.g. ngC gDM^{-1} h^{-1}). Using information on the mass to area of a species' leaves and the leaf density of a canopy, this emission rate can be converted to carbon mass per area ground cover per time (e.g. gC m^{-2} h^{-1}).

Temperature Only (Guenther et al., 1993):

$$E_T = BEF \exp[\beta(T-T_s)] \quad \text{(S2)}$$

β (K^{-1}): a coefficient that scales the exponential dependence on temperature and is calculated by inverting equation S2 using the BEF calculated from samples that meet standard conditions

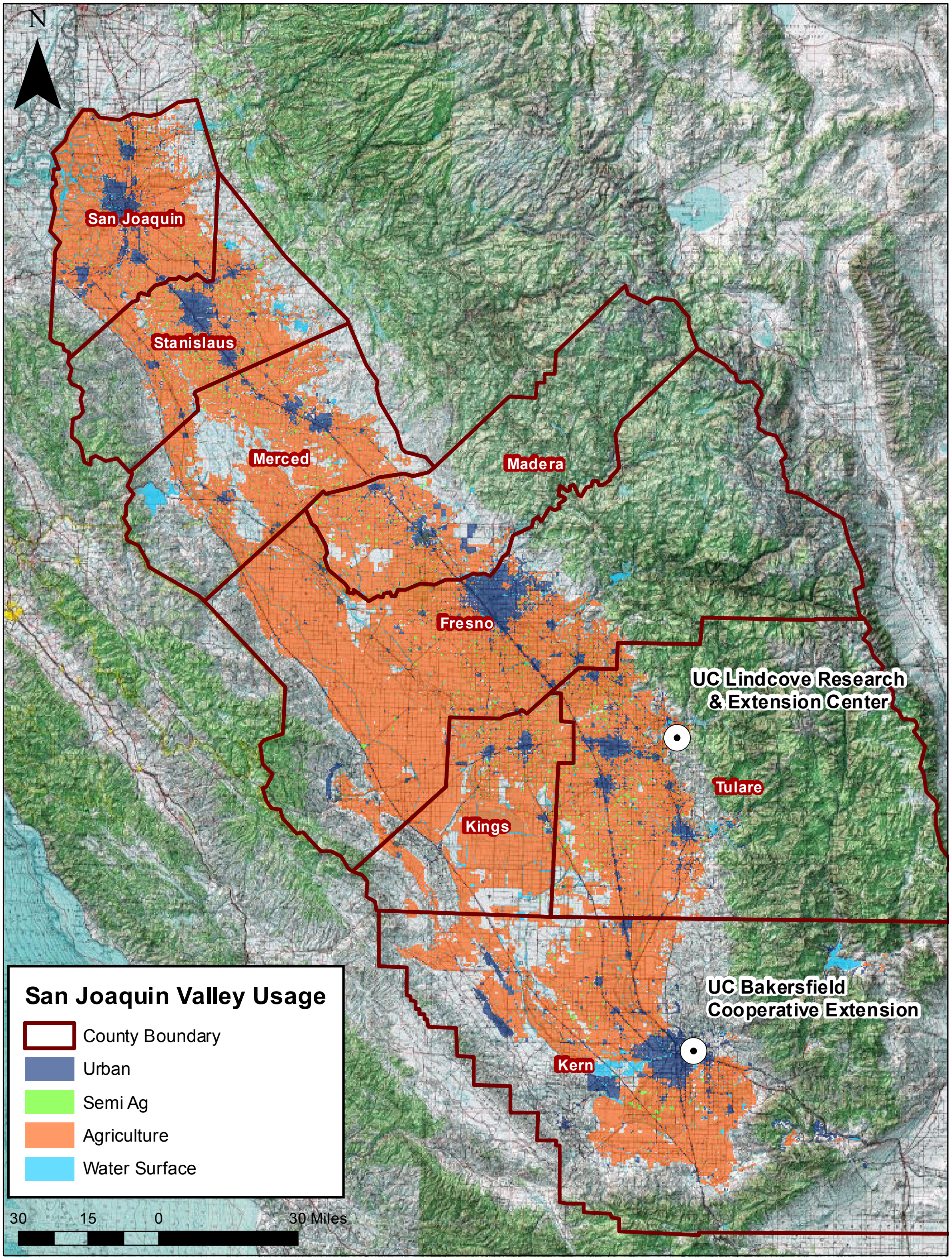

Figure S1: Map of the San Joaquin Valley showing distribution of urban areas and agriculture (note: semi ag represents mainly dairies)

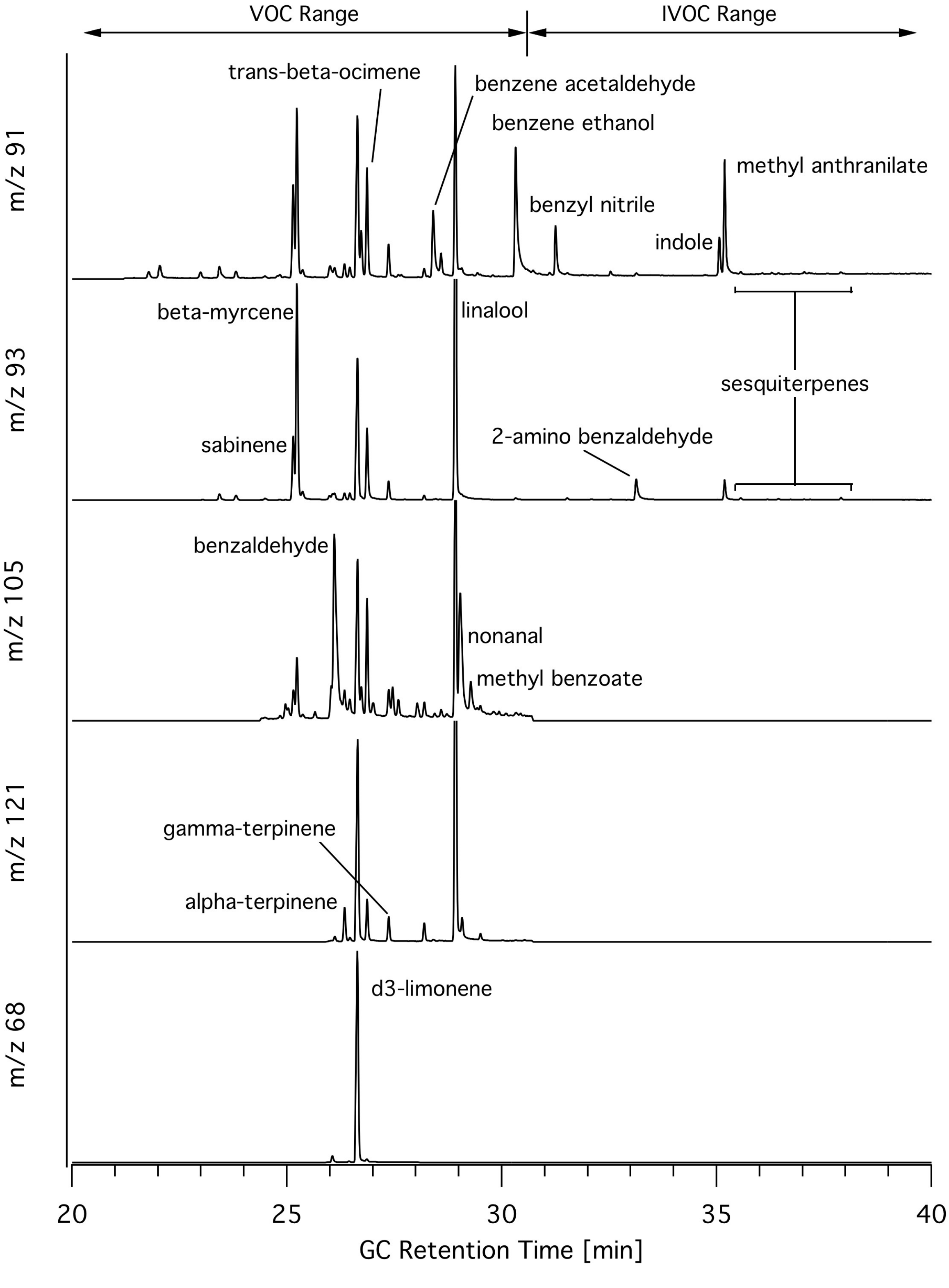

Figure S2: Example chromatogram from the Lindcove orange orchard in spring 2010 during flowering. A selection of the most prominent biogenic compounds are shown on representative mass to charge (m/z) ratios.

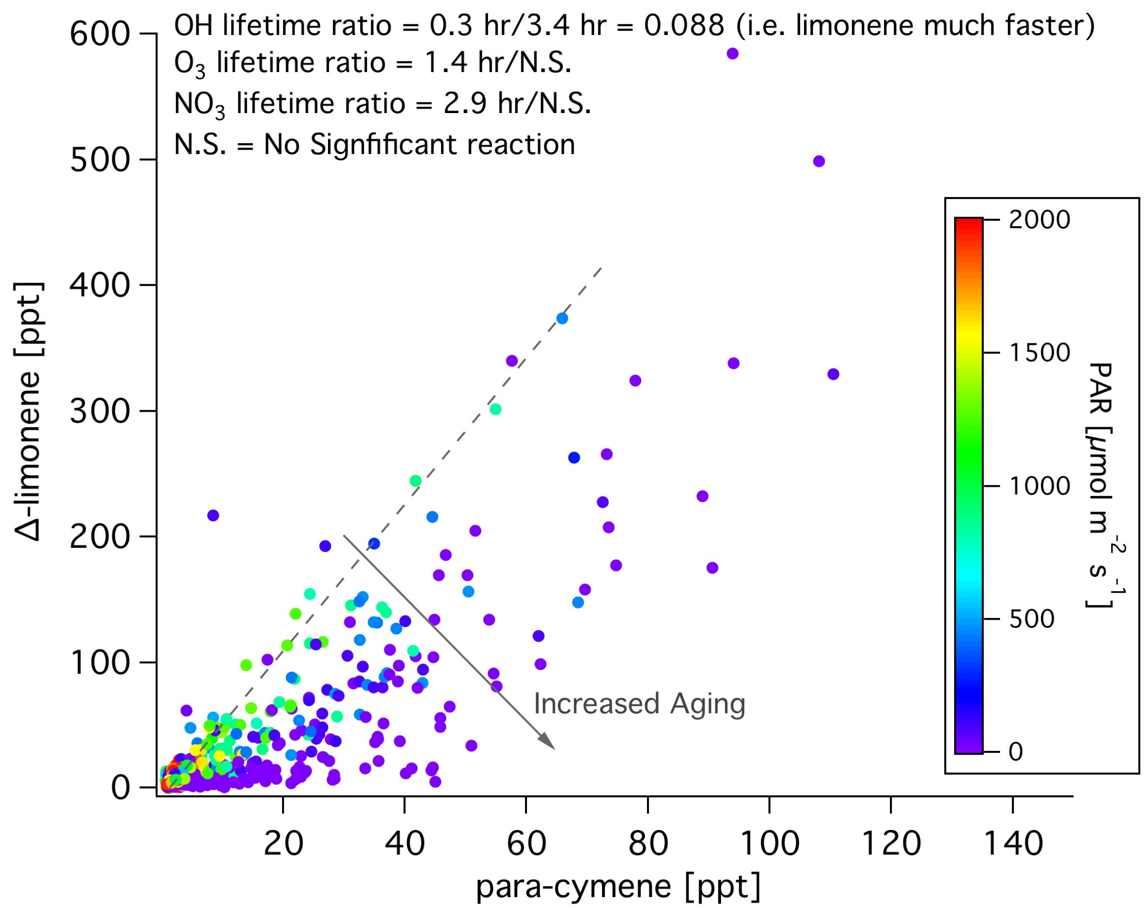

Figure S3: BVOC transport in the San Joaquin Valley: Observations of monoterpene pair Δ-limonene and p-cymene at Bakersfield site. Ratios of lifetimes to all three atmospheric oxidants show faster processing of Δ-limonene. Given the concentrations of radicals, OH oxidation has the fastest timescales and the importance of OH oxidation is also indicated by the most aged parcels coinciding with PAR (representative of OH production). Reaction with ozone is likely to also play a role. See Figure 7 for other comparisons.

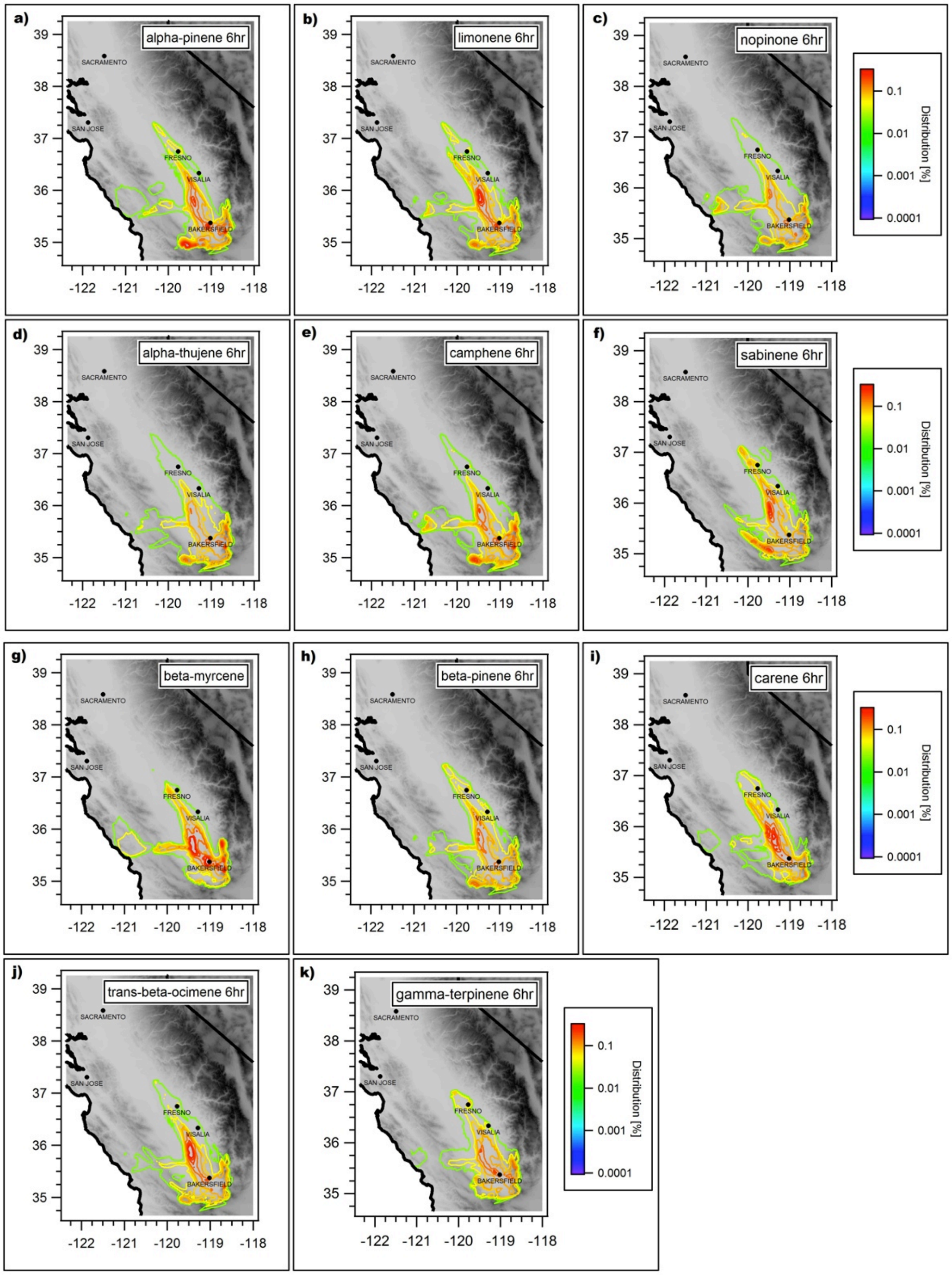

Figure S4: Spatial distribution of individual monoterpene emissions transported to Bakersfield. Together they comprise the map shown in figure 8.

Table S1: Plants studied during greenhouse enclosure campaign

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	W. Murcott (on C-35 rootstock)
Mandarin	Citrus reticulate	Clementine (Clemenules)(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

Table S2: Statistics for modeling methods using light and temperature (L&T) and temperature only (T) from greenhouse enclosures

	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 (no flowers)	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 (flowers)	0.6	0.78	0.61	0.58	0.43	1.37	0.37	0.74	0.92	2.13	0.89	1.11
Mandarin W. Murcott	0.32	0.08	0.41	0.08	0.18	0.26	0.34	0.4				
Mandarin Clementine	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)

Slopes are calculated as predicted emission rates (using calculated BEFs) vs. observed emission rates at measured light and temperature conditions.

Data on citrus species measured in the same greenhouse campaign are reproduced from Fares et al. (2011) for comparison to the other crops and assessment of implications on air quality. Table 2 gives information on sample size (N)

Note: A better reported coefficient of determination or slope does not imply our endorsement of a particular modeling method. When testing and using the crop survey data in this paper, users of this data should consult literature on the temperature or temperature & light dependence of a species and consider the relevant uncertainties in this study (discussed in Sections 3.1 and 3.1.1).

Table S3: Composition of monoterpene emissions measured in enclosure studies

Crop	Δ-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%	0%	58%	0%	0%	0%	0%	0%	0%	0%	0%	0%	42%	0%
Almond	9%	0%	23%	36%	2%	0%	26%	0%	0%	0%	0%	0%	3%	0%
Carrot (RL)	28%	3%	3%	37%	0%	1%	3%	0%	11%	6%	0%	0%	6%	3%
Carrot (BN)	2%	19%	1%	23%	0%	0%	4%	0%	0%	0%	0%	15%	34%	1%
Cherry	0%	94%	6%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Corn														
Cotton Pima	0%	0%	2%	0%	0%	0%	0%	0%	0%	0%	0%	34%	64%	0%
Cotton Upland	0%	1%	19%	0%	0%	39%	0%	0%	0%	0%	0%	0%	41%	0%
Table Grape	0%	1%	1%	0%	0%	0%	0%	0%	0%	0%	0%	0%	98%	0%
Wine Grape	0%	0%	23%	0%	0%	0%	0%	0%	0%	6%	0%	64%	3%	4%
Liquidambar	55%	0%	0%	0%	0%	0%	0%	0%	1%	0%	0%	17%	27%	0%
Miscanthus	48%	4%	23%	0%	0%	0%	0%	0%	0%	21%	0%	2%	2%	0%
Olive	0%	5%	93%	0%	0%	0%	1%	0%	0%	0%	0%	1%	0%	0%
Onion	85%	0%	15%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Peach	0%	0%	100%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Pistachio	87%	5%	1%	1%	0%	0%	1%	0%	0%	0%	3%	0%	1%	1%
Plum	0%	0%	100%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Pomegranate														
Potato	61%	22%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	17%	0%
Tomato	0%	0%	0%	0%	7%	75%	1%	14%	2%	0%	0%	0%	2%	0%
Orange P.N. (no flowers)	7%	4%	27%	56%	0%	0%	0%	0%	0%	0%	0%	3%	1%	0%
Orange P.N. (flowers)	2%	0%	30%	67%	0%	0%	0%	0%	0%	0%	0%	1%	0%	0%
Mand. W. Murcott	13%	33%	32%	1%	0%	0%	1%	0%	0%	4%	0%	9%	2%	4%
Mand. Clementine	17%	6%	14%	1%	1%	0%	14%	0%	0%	0%	0%	40%	5%	3%
Lemon Eureka														

Data on citrus species measured in the same greenhouse campaign are reproduced from Fares et al. (2011) for comparison to the other crops and assessment of implications on air quality

Table S4: Composition of oxygenated monoterpene emissions measured in enclosure studies

Plant	**Linalool**	**Perillene**	**Eucalyptol**
Alfalfa			
Almond	10%	90%	0%
Carrot (RL)	94%	6%	0%
Carrot (BN)			
Cherry	0%	100%	0%
Corn			
Cotton Pima	0%	100%	0%
Cotton Upland	4%	96%	0%
Table Grape	0%	100%	0%
Wine Grape	0%	100%	0%
Liquidambar	0%	100%	0%
Miscanthus	26%	0%	74%
Olive	0%	100%	0%
Onion			
Peach	0%	100%	0%
Pistachio	16%	84%	0%
Plum	3%	97%	0%
Pomegranate	0%	100%	0%
Potato	0%	100%	0%
Tomato	100%	0%	0%
Orange P.N. (No Flowers)	93%	6%	1%
Orange P.N. (Flowers)	97%	2%	1%
Mandarin W. Murcott	6%	94%	0%
Mandarin Clementine	46%	54%	0%
Lemon Eureka			

Data on citrus species measured in the same greenhouse campaign are reproduced from Fares et al. (2011) for comparison to the other crops and assessment of implications on air quality

Table S5: Composition of sesquiterpene emissions measured in enclosure studies

Plant	β-caryophyllene	α-humulene
Alfalfa		
Almond	77%	23%
Carrot (RL)	100%	0%
Carrot (BN)	100%	0%
Cherry		
Corn		
Cotton Pima	54%	46%
Cotton Upland		
Table Grape	69%	31%
Wine Grape	100%	0%
Liquidambar	100%	0%
Miscanthus	7%	93%
Olive	100%	0%
Onion		
Peach		
Pistachio	0%	100%
Plum		
Pomegranate	90%	10%
Potato	98%	2%
Tomato	100%	0%
Orange P.N. (No Flowers)	100%	0%
Orange P.N. (Flowers)	100%	0%
Mandarin W. Murcott	33%	67%
Mandarin Clementine	17%	83%
Lemon Eureka		

Data on citrus species measured in the same greenhouse campaign are reproduced from Fares et al. (2011) for comparison to the other crops and assessment of implications on air quality

Table S6: Basal emission factors (ngC gDM^{-1} h^{-1}) and beta values for methanol, acetaldehyde, acetone and isoprene for non-citrus crop plants investigated (N = sample size, r = correlation coefficient)

	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)*	N.A.	
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)

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 S7: Observed isoprene fluxes (with environmental parameters) for plant species studied during greenhouse enclosure campaign

	Isoprene Flux (ngC gDM^{-1} h^{-1})		Leaf Temperature (^{o}C)		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

Note: The values in this table are provided to show minimal isoprene emissions for most crops since BEFs could not be calculated for many of the compounds