Volatile organic compound fluxes in the San Joaquin Valley – spatial distribution, source attribution, and inventory comparison

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Abstract. The San Joaquin Valley is an agricultural region in California that suffers from poor air quality. Since traffic emissions are decreasing, other sources of volatile organic compounds (VOCs) are gaining importance in the formation of secondary air pollutants. Using airborne eddy covariance, we conducted direct, spatially resolved flux observations of a wide range of VOCs in the San Joaquin Valley during June 2021 at 23-36°C. Through landcover-informed footprint disaggregation, we were able to attribute emissions to sources and identify tracers for distinct source types. VOC mass fluxes were dominated by alcohols, mainly from dairy farms, while oak isoprene and citrus monoterpenes were important sources of reactivity. Comparisons with two commonly used inventories showed that isoprene emissions in the croplands were overestimated, while dairy and highway VOC emissions were generally underestimated in the inventories, and important citrus and biofuel VOC point sources were missing from the inventories. This study thus presents unprecedented insights into the VOC sources in an intensive agricultural region and provides much needed information for the improvement of inventories, air quality predictions and regulations.

1 Introduction

The San Joaquin Valley in California is one of the regions with the worst air quality in the United States (US EPA and American Lung Association, 2022). Despite decades-long ozone control measures, the National Ambient Air Quality Standard of 70 ppb is frequently exceeded, especially in the summer (Faloona et al., 2020). High ozone contributes to cardiovascular and respiratory health risks, and damages crops and ecosystems. Volatile organic compounds (VOCs), emitted by anthropogenic and biogenic sources, fuel ozone formation when nitrogen oxides (NO_x) are present.

The San Joaquin Valley is an intense agricultural production region, home to millions of cattle and dairy cows, and it is the leading US producer of many types of fruits and nuts (California Department of Food and Agriculture, 2020). It is also an important transportation corridor connecting southern and northern California, and is home to 4.3 million people, the largest urban areas being Fresno and Bakersfield (Public Policy Institute of California, 2018). Moreover, there are ca. 47 000 active oil and gas wells in the San Joaquin Valley (CALGEM, 2022). Agriculture including dairy and cattle farms (Gentner et al.,

2014b; Hu et al., 2012; Gentner et al., 2014a; Marklein et al., 2021; Shaw et al., 2007; Malkina et al., 2011), natural landscapes (Misztal et al., 2014), urban areas, transportation (Hu et al., 2012), oil and gas production (Gentner et al., 2014a) are known VOC sources in the San Joaquin Valley.

35   With reductions in Californian transportation VOC emissions over the last few decades (Warneke et al., 2012), the relative importance of other emission sources contributing to poor air quality is increasing. Based on air quality modelling, Hu et al. (2012) therefore predicted that livestock feed and mobile-source VOC emissions would contribute almost equally to ozone production in the San Joaquin Valley by 2020. However, the VOC sources in the San Joaquin Valley and their emission strengths are not well understood. For example, Pusede et al. (2015) found that unidentified molecules contributed

40   significantly to ozone production in the San Joaquin Valley, especially at high temperatures. A comparison with aircraft observations showed that a regional air quality model underestimated ozone near dairy farms and oil fields (Cai et al., 2016).

        Atmospheric chemistry models used to forecast air quality and guide policy decisions are built on emission inventories. Such inventories are typically based on bottom-up reporting or top-down inference of emissions from concentration measurements using chemical transport models. These strategies all have significant uncertainties since they

45   are indirect. Direct, spatially resolved flux observations enable direct validation of emission inventories. Airborne eddy covariance measurements of VOCs have previously been used to validate inventories in an urban area (Vaughan et al., 2017) and in Californian oak forests (Misztal et al., 2016). A previous airborne VOC flux study covering parts of the San Joaquin Valley region (Misztal et al., 2014; Karl et al., 2013; Misztal et al., 2016) was limited to few VOCs since the available measurement technique (PTR-quadrupole-MS) did not enable the simultaneous observation of many species at the high time

50   resolution necessary for airborne eddy covariance. State of the art instrumentation (PTR-ToF-MS) has dramatically increased the number of compounds observable at the same time (Blake et al., 2004; Krechmer et al., 2018).

In this work, we apply direct observations of spatially resolved emission and deposition fluxes of a wide range of VOCs using airborne eddy covariance. Spatial comparisons help in the identification of inventory biases associated with regionally specific emission sources. We also provide estimates of source emission strengths by footprint disaggregation (Hutjes et al.,

55   2010), a method which has not previously been applied to VOC fluxes. Thus, this work seeks to identify and quantify relevant VOC emission sources in the San Joaquin Valley and their contribution to ozone formation, and validates two commonly used emission inventories with direct observations.

2 Methods

2.1 Flight routes, study region, and meteorological conditions

60   As part of the RECAP-CA (Re-evaluating chemistry of air pollutants in California) campaign, seven flights were conducted over the San Joaquin Valley between June 1 and 22, 2021. Routes were selected to ensure a good coverage of important VOC sources in the southern San Joaquin Valley, including dairy farms, the I-99 highway, oil and gas fields northeast of Bakersfield, urban areas, and oak woodlands in the Sierra Nevada foothills. Each of the seven five-hour long flights was

conducted on a different day and along the same flight tracks (Fig. 1). Every other flight included a 12-15 km long stacked

65 racetrack pattern (Karl et al., 2013) flown at 4-6 different altitudes within the planetary boundary layer (PBL). The flights

containing stacked racetracks were cut short at the northern end, while the others reached up to Fresno. The flight altitude

was kept stable at 300-400 m above ground level (a.g.l.), since low, stable altitude and long legs assure good quality airborne

flux measurements (Karl et al., 2013). The aircraft flew slowly at an airspeed of 50-60 m/s to ensure a high spatial

resolution.

70 Table 1 provides an overview of the meteorological variables for each flight. Average ambient temperatures at 2 m a.g.l.

ranged from 23 to 36°C. There was no precipitation. PBL heights were 800-1000 m a.g.l. Flight days and routes were chosen

so that no cloud cover was encountered. The flights were performed between 11:00 and 17:00 local time to ensure

homogeneous turbulent conditions and a high PBL.

75 **Table 1. Average (± standard deviation) for meteorological variables and modeled OH for each flight. RH: relative humidity, TAS: true air speed. w*: Deardorff velocity (convective velocity scale). "a.g.l.": above ground level. "Fresno flight" indicates whether a flight included Fresno in the north (Y). If it did not (N), stacked racetrack patterns were flown at a suitable location in order to measure vertical flux gradients.**

Flight No	Fresno flight	Date (dd/mm/yyyy)	Flight altitude a.g.l. (m)	TAS (m/s)	PBL height (m a.g.l.)	Wind speed (m/s)	Wind direction (°)	RH (%)	Dewpoint temperature (°C)	Ambient temperature at 2 m (°C)	w* (m/s)	OH (molec/cm³)
SJV1	N	03/06/2021	434 ± 126	57.1 ± 2.5	1303 ± 114	3.2 ± 1.3	335 ± 50	29 ± 4	9.7 ± 2.1	36.2 ± 1.9	1.1 ± 0.4	1.9e+06 ± 6.8e+05
SJV2	N	08/06/2021	430 ± 104	56.4 ± 2.3	1202 ± 52	3.1 ± 0.9	314 ± 45	40 ± 5	2.6 ± 1.2	22.8 ± 1.8	1.6 ± 0.4	2.9e+06 ± 9.7e+05
SJV3	Y	09/06/2021	424 ± 101	56.0 ± 2.7	1266 ± 20	3.5 ± 1.1	304 ± 33	41 ± 5	2.7 ± 0.7	22.6 ± 1.7	1.6 ± 0.4	3.0e+06 ± 8.3e+05
SJV4	Y	13/06/2021	439 ± 111	57.2 ± 2.5	1234 ± 73	2.8 ± 0.9	305 ± 38	48 ± 6	13.3 ± 1.6	31.2 ± 2.0	1.3 ± 0.4	2.6e+06 ± 8.3e+05
SVJ5	Y	15/06/2021	428 ± 114	57.1 ± 2.6	1193 ± 23	3.0 ± 1.2	323 ± 45	42 ± 6	8.3 ± 2.2	28.0 ± 2.0	1.3 ± 0.4	2.9e+06 ± 1.0e+06
SJV6	N	16/06/2021	421 ± 85	57.4 ± 3.2	899 ± 102	2.9 ± 1.1	307 ± 43	33 ± 4	9.4 ± 1.9	32.9 ± 1.3	1.1 ± 0.4	1.9e+06 ± 5.9e+05
SJV7	Y	22/06/2021	415 ± 94	56.9 ± 2.6	826 ± 126	2.6 ± 0.8	284 ± 35	36 ± 7	9.5 ± 2.2	31.6 ± 2.2	1.0 ± 0.3	2.4e+06 ± 9.2e+05

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2.2 Aircraft

A two-engine UV-18A Twin Otter research aircraft was operated by the Naval Postgraduate School out of the Burbank
85 airport, CA. The aircraft is equipped with micrometeorological sensors and is capable of flux measurements (Karl et al.,
2013). The NPS Twin Otter payload during RECAP-CA included total temperature measured by a Rosemount probe, dew
point temperature (chilled mirror, EdgeTech Inc., USA), barometric, dynamic, and radome-angle pressures based on
barometric and differential transducers (Setra Inc., USA), total air speed, mean wind, slip- and attack angles measured by a
radome flow angle probe, GPS pitch, roll and heading (TANS Vector platform attitude, Trimble Inc., USA), GPS latitude,
90 longitude, altitude, ground speed and track (NovAtel, Inc., USA), and latitude, longitude, altitude, ground speed and track,
pitch, roll and heading measured by C-MIGITS-III (GPS/INS, Systron, Inc., Canada).

Air was drawn from a 7.62 cm isokinetic pipe inlet extending above the nose of the plane. Ambient air gets diffused from a
5.2 cm (inner diameter) orifice at the tip (area ratio of about 2) to another diffuser with an area ratio of 5, resulting in a flow
speed inside the tube of about 10 % of the aircraft speed. Vertical wind speed was measured by a five-hole radome probe
95 with 33º half-angles at the nose of the aircraft. Corrections based on "Lenschow maneuvers" (Lenschow, 1986) were applied
to ensure that the vertical wind speed is unaffected by the aircraft movement and flow distortion at the nose. More detailed
descriptions of this particular aircraft can be found in Hegg et al. (2005).

2.3 VOC measurements

100 ### 2.3.1 Sampling and instrument operation

Ambient air was sampled via a 90 cm long heated (40°C) 1/4'' Teflon line through a Teflon filter from the abovementioned
isokinetic inlet (flow speed ca. 6 m/s for 5 m length) with a mass flow controller at 1.5 L/min. The resulting lag time
between the wind sensor and VOC detection was around 3 s.

The Vocus proton transfer reaction time of flight mass spectrometer (Vocus PTR-ToF-MS, Aerodyne Inc., Billerica, MA,
105 USA, (Krechmer et al., 2018)) was operated at 2.0 mbar reactor pressure, 60°C reactor temperature, and an E/N of
ca. 130 Td. The mass resolution was ≈4800 ± 280 (average ± standard deviation). The potential gradient along the focusing
ion-molecule reactor (FIMR) was 590 V. The gradient between skimmer 1 and skimmer 2 was changed once during the
campaign from 6 to 9.1 V, which resulted in an improved sensitivity for some VOCs, but stronger fragmentation for others,
both of which effects were accounted for through calibration. The reagent water flow was 20 sccm, resulting in a high water
110 mixing ratio (10 %v/v–20 %v/v) in the FIMR, so that the instrument showed no humidity dependence in its sensitivity. This
is an advantage in flux measurements because it eliminates the necessity to correct for humidity differences between
different eddies caused by water fluxes. The high water mixing ratio causes a large primary ion (H_3O^+) signal, which is
lowered by a big segmented quadrupole (BSQ) that reduces the transmission of low-mass ions in order not wear down the

115   detector too quickly. However, we kept the voltage of the BSQ relatively low at 200 V so that low-mass VOCs like methanol could be detected with reasonable sensitivity.

Mass spectra were recorded for a mass range of 10-500 Da at 10 Hz time resolution (or 2 Hz time resolution, for one flight out of seven: SJV6). Several times during each flight, zero-air measurements were conducted for 1-5 min, during direction changes of the aircraft, because data acquired during turns cannot be used for flux calculations. Ca. two times during each flight, the zero-air measurement was followed by a pulse of calibration gas of ca. 1-5 min length. These calibration data were

120   used to confirm that the instrument sensitivity after correction for the zero-air background did not change significantly with the lower inlet pressure at our flight altitude and that, consequently, the calibration factors acquired on the ground were applicable to the airborne data.

2.3.2 VOC data treatment and calibration

Raw PTR-ToF-MS data were processed using Tofware 3.2.3. At this stage, no dead time correction was applied. 630 peaks

125   were chosen for peak fitting. Interpolated ion counts from zero air measurements taken in-flight were subtracted from the ambient data. The instrument zero at flight altitude was different from the zero on the ground due to pressure effects that changed the pressure control valve position. According to laboratory testing of pressure effects, the sensitivities at the heights we flew at were the same as on the ground after subtracting the flight zero. Throughout the campaign, one of three distinct gravimetrically manufactured multicomponent VOC standards (Apel-Riemer Environmental Inc., Colorado, USA)

130   was used for ground calibrations every 1-3 days. Gas-standard calibrated compounds are labelled in Table S1. For most VOCs, the sensitivities were stable within 25 % over the campaign. For all m/z without a corresponding gas standard, the sensitivities were derived from a root function (the expected function of a ToF transmission) fitted to reaction rate normalized sensitivities of non-fragmenting and non-clustering gas-standard calibrated VOCs. The estimated uncertainty of the calibration for gas-standard calibrated VOCs was 20 %, while it was 54 % for all other VOCs.

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2.3.3 VOC identification from mass spectra

The PTR-ToF-MS method provides exact masses that can be linked to chemical formulas, but often not with certainty to molecular structures. Depending on the predominant source type, detected ions may be mixes of different isomers. Moreover, some VOCs fragment strongly, ending up being detected at masses other than their parent mass.

140   The monoterpenes measured at $C_{10}H_{16}H^+$ (m/z 137.13) may include fragments of $C_{10}H_{18}O$ (m/z 155.14) monoterpenoids and monoterpene alcohols (e.g. eucalyptol (Kari et al., 2018), linalool, cineole, terpineol (Tani, 2013)).

Gasoline vapor as well as oil and gas emissions include cycloalkanes that fragment on $C_5H_8H^+$ (m/z 69.07), the ion that is typically attributed to isoprene in PTR-MS. Gueneron et al. (2015) showed that several cyclohexanes fragment on $C_5H_8H^+$, especially at higher E/N, similar to the instrument conditions in our study. Pfannerstill et al. (2019) reported in

145   measurements of oil and gas emission-dominated air over the Persian Gulf that isoprene measured by GC-FID was

significantly lower than the $C_5H_8H^+$ signal in PTR-ToF-MS, and attributed the remaining $C_5H_8H^+$ after isoprene subtraction to emissions from oil and gas extraction. Furthermore, longer-chain aldehydes, such as nonanal, also fragment onto $C_5H_8H^+$ (Buhr et al., 2002). Such aldehydes may be relevant in dairy emissions (Rabaud et al., 2003). Fragments of both the long-chain aldehydes and the cycloalkanes also appear on $C_8H_{15}^+$ (m/z 111.12) and/or $C_9H_{17}^+$ (m/z 125.13). To distinguish

150   isoprene from interfering fragments of aldehydes and cycloalkanes, we used the following approach: We derived the ratio of m/z 69.07 vs (m/z 111.12 + m/z 125.13) from the isoprene-free nonanal calibration gas standard. This ratio was compared to that seen over oil and gas fields northeast of Bakersfield, were the m/z 69.07 signal is most likely dominated by cycloalkane fragments. Both ratios were the same at ~ 17 (at a gradient between skimmer 1 and skimmer 2 of 6 V) or ~ 45 (at a skimmer gradient of 9.1 V). This isoprene-free ratio of m/z 69.07/(m/z 111.12 + m/z 125.13) was used to correct the isoprene signal:

155

$$Isoprene_{corr} = m69.07 - [(m111.12 + m125.13) \cdot slope_{nonanal}] \qquad (1)$$

For an accurate isoprene flux correction, this equation was applied to the fluxes of m/z 69.07 and (m/z 111.12 + m/z 125.13) directly, not to the mixing ratios first. Similarly, acetaldehyde was corrected for ethanol fragments (Buhr et al., 2002).

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2.4 WRF-Chem model simulation

We conducted model simulations over the study period using the Weather Research and Forecasting-Chemistry model (WRF-Chem v. 4.2.2) configured as described in Li et al. (2021). Following a WRF-Chem simulation at 12 km horizontal resolution

165   over the Continental US to provide the initial and boundary condition, we performed a 4 km horizontal resolution nest run over California. We utilized the RACM2_Berkeley2.0 chemical mechanism (Goliff et al., 2013; Browne et al., 2014; Zare et al., 2018) with the following updates: We included the new TUV scheme for the calculation of photolysis and a newer SOA VBS scheme (Ahmadov et al., 2012) for better representation of SOA formation. Isopropanol, propylene glycol, and glycerol were added as new species to represent the VOC chemistry from VCP emissions (Coggon et al., 2021).

170   Anthropogenic emissions were provided by the fuel-based inventory for vehicle emissions (FIVE-VCP), developed by McDonald et al. (2012) and updated by Harkins et al. (2021). The FIVE-VCP inventory was further updated to include emissions from volatile chemical products (Coggon et al., 2021). We also re-speciated the FIVE-VCP inventory to the updated RACM2_Berkeley2.0 mechanism. The biogenic emissions are provided by the Biogenic Emission Inventory System (BEIS) v3.14. It is the default scheme to estimate volatile organic compounds from vegetation and NO from soil developed

175   by the United States Environmental Protection Agency (EPA). We updated the BEIS emissions for isoprene and monoterpenes from the urban land cover type based on Scott and Benjamin (Scott and Benjamin, 2003)

The only WRF-Chem outputs used in this study were $J(O^1D)$, H_2O, and O_3 for the chemical vertical divergence correction (Sect. 2.5.3).

2.5 Airborne Eddy Covariance fluxes

2.5.1 Flight segment selection

In order to minimize uncertainties (Lenschow et al., 1994; Karl et al., 2013), flight segments were chosen for flux calculation along the following criteria: length of at least 10 km, stable aircraft roll and pitch (within 8°), stable altitude (within ±50 m). PBL heights were estimated from aircraft soundings by stark drops in dew point, water concentration, toluene concentration and temperature. Soundings were conducted at least at the beginning and end of each flight and before each stacked racetrack. The PBL heights such derived agreed well with PBL heights from the High-Resolution Rapid Refresh (HRRR) model, except for the flight leg in the Sierra Nevada foothills where the PBL height was often substantially over- or underestimated. Datapoints outside the PBL were disregarded for flux calculation.

2.5.2 Continuous wavelet transformation

Lag times were derived for each VOC in each segment by calculating the covariance and searching for the covariance peak in a window of 4 s around 0 (Fig. S1). Different VOCs have different levels of stickiness, causing lag times to differ between compounds (Taipale et al., 2010). Since we used a mass flow controller in front of the inlet pump, pressure changes additionally affected the lag time. Furthermore, as reported by Taipale et al. (2010), lag times may vary because pumping speed changes over time. Thus, a variable lag time ensures that the flux is not underestimated. When there was no covariance peak above the noise, a constant lag time (the lag time of isoprene) was applied for the respective VOC and segment, since it is possible that positive fluxes occurred during half of the segment and negative fluxes during the other half of the segment. Airborne fluxes were calculated using continuous wavelet transformation (Torrence and Compo, 1998), which de-convolutes the variance within a timeseries along both the frequency and the time (here equalling distance) domains. Using the lag times, 10 Hz wind and VOC time series were aligned. Wavelet transformation of the data generated the local wavelet co-spectra for each data point along the flight track. Integration over all frequencies yielded the flux timeseries. Points containing > 80 % spectral power within the cone of influence, the region in which edge-effects can lead to spectral artifacts, were removed. A running mean of 2 km was applied to the 10-Hz fluxes to eliminate turbulence effects causing artificial emission and deposition, and sub-sampled to 200 m. For the flight where data was recorded only in 2 Hz resolution, disjunct Airborne Eddy Covariance (Karl et al., 2009) was applied. Otherwise, these data were treated the same as the 10 Hz data. A comparison between results of 10 Hz fluxes from one flight and the same data averaged to 2 Hz before doing the wavelet transformation confirmed a very minor high frequency loss, with an overall reduced average flux of e.g. 0.5 % for isoprene and 0.4 % for benzaldehyde. As the cospectra (Fig. S1) illustrate, almost 100 % of the flux was at frequencies below 1 Hz (the Nyquist frequency which can be resolved by 2 Hz sampling, Fig. S1). This implies that the eddies were sufficiently large at our flight altitude that no significant information was lost by 2 Hz sampling. Previous aircraft campaigns operated at

210 an even lower 0.7 s time resolution (Misztal et al., 2014; Karl et al., 2013) without a need for correction for high-frequency losses. The Nyquist frequency for 10 Hz measurements is 5 Hz (Fig. S1).

We note that particularly polar VOCs such as long-chain oxygenated VOCs (OVOCs) can be retained in the inlet system, leading to a dampened covariance peak and therewith a possible underestimation of their flux. However, the cospectra for most OVOCs, including sticky ones like cresol, ethanol or methanol, compared well with the complete cospectra. The

215 stickiest among the gas-standard-calibrated VOCs was nonanal, for which the cospectrum suggests around 50 % spectral loss. Thus, the fluxes reported for long-chain OVOCs reported here may represent a lower limit.

2.5.3 Chemical vertical flux divergence correction

Due to oxidative loss following the reaction with hydroxyl radicals (OH) and ozone, the flux of reactive VOCs measured at

220 flight altitude is smaller than at the surface. In order to correct for this chemical loss, gradients of fluxes of isoprene, trimethylbenzene, and dimethylfurane from stacked racetrack flights were used to derive approximate OH concentrations. The resulting OH for each of these three VOCs and their isomers covers a certain range. In order to derive OH concentrations for the whole flight track, not just the racetrack locations, we used the steady state box model described in Laughner and Cohen (2019). Input parameters are measured NO_x concentrations, VOC reactivity (calculated from all

225 measured VOCs, CO, and methane, multiplied by 1.3 to account for unmeasured species), an organic nitrate branching yield of 0.052 based on the measured VOC composition, and OH production rates calculated using simulated $J(O^1D)$, H_2O and O_3 from WRF-Chem. Model performance was verified with data from the CalNex campaign, for which direct OH and total OH reactivity measurements are available (Griffith et al., 2016).

The VOC fluxes were then corrected according to:

230
$$\frac{dF}{dz} = k_{OH+VOC} * [OH][VOC] \qquad (2)$$

$$F_s = z * \frac{dF}{dz} + F_z \qquad (3),$$

where F_s is the flux at the surface and F_z the flux at flight altitude, z is the flight altitude, k_{OH+VOC} is the OH reaction rate of the respective VOC, and [OH] and [VOC] are the concentrations of hydroxyl radicals and VOC, respectively. The ozone

235 correction was done the same way using ozone concentrations from WRF-Chem. OH and ozone reaction rates and references are listed in Table S1.

The speciation of monoterpenes measured as $C_{10}H_{16}H^+$ was assumed to be the same as the monoterpene composition in Pusede et al. (2014). The resulting reaction rate was verified to represent (i) the ratios of inferred surface flux (after O_3 and OH correction) to measured aircraft flux at altitude, with the gradient observed in stacked racetracks, and (ii) the

240 monoterpene oxidation product/monoterpene ratio with expected yields according to the reaction rate used. Both methods

confirmed that the assumed average OH reaction rate coefficient of 5.91e-11 cm^3 $molec^{-1}$ s^{-1} and an ozone reaction rate coefficient of 9.59e-17 cm^3 $molec^{-1}$ s^{-1} are reasonable. Since the citrus emissions may include more reactive monoterpene species (e.g., with a weighted average monoterpene OH reaction coefficient of 1.56e-10 cm^3 $molec^{-1}$ s^{-1} following the composition in Lu et al. (2019)), which would require a larger correction, the citrus monoterpene emissions reported here are

245 a lower limit.

2.5.4 Physical vertical flux divergence correction

After the correction for oxidative loss (Sect. 2.5.3), remaining vertical gradients in the VOC fluxes were due to physical vertical flux divergence. Physical vertical flux divergence is caused by horizontal advection and entrainment into the free

250 troposphere. Entrainment causes the flux divergence to differ between chemical species. The vertical racetrack data did not show conclusive vertical gradients in non-reactive VOCs. We attribute this to impacts of inhomogeneous local emissions and the larger uncertainty of the fluxes on the short (~10 km) racetrack legs. Therefore, we used data from complete flights to determine the vertical flux divergence over areas that were covered at several relative flight altitudes (z/z_i, i.e., flight altitude normalized by PBL height). Vertical divergence was calculated separately for each VOC.

255 Fluxes of each VOC were binned into ten different z/z_i bins, removing any bins containing less than 3 % of the data and any data points that did not have a counterpart in the other bins within 6 km distance (~ footprint size). The vertical divergence slope was then derived from a linear regression of the median flux of each altitude bin vs. z/z_i (Fig. S2). For VOCs whose fluxes in the remaining data were below the detection limit, the vertical divergence correction equation of NO_x fluxes from the same campaign (Zhu et al., 2023) was applied.

260 The relative slope was derived by normalizing it by the intercept, i.e., C= slope/intercept. Then, the final surface fluxes F_0 were calculated from the fluxes at altitude z (F_z) following:

$$F_0 = \frac{F_z}{1 + C \cdot \frac{z}{z_i}} \qquad (4)$$

C is negative for VOCs that are emitted at the surface. However, C can be positive for VOCs that are deposited at the surface, or for OVOCs that are being formed while the air moves from the surface to the point of observation.

265 Data points where the vertical divergence correction was larger than 3 times the median correction factor of the respective VOC were substituted with "nan" in order to not introduce extremely high uncertainties. 95 % of the measurements were conducted between $z/z_i = 0.2$ and $z/z_i = 0.66$, causing a relatively small physical vertical divergence and small uncertainties thereof. The most substantial divergence correction had to be applied in the Sierra Nevada foothills, where the aircraft was sometimes close to the top of the PBL (Fig. S3). The vertical divergence correction amounted to a factor of 1.0 ± 1.3

270 (average ± standard deviation). Average correction factors for each VOC are listed in Table S1.

2.5.6 VOC flux uncertainties

The flux detection limit was calculated following Langford et al. (2015). For each VOC and for each flight segment, a VOC white noise time series was created, and wavelet fluxes using this white noise time series and the measured wind were

275 calculated. If the resulting random flux was smaller than the random covariance (i.e., covariance at ±220-240 s lag time), the random covariance of the respective segment was used instead of the white noise-derived flux. The overall precision was propagated from the 2σ detection limit and the random uncertainty of the flux calculation which was calculated following Lenschow et al. (Lenschow et al., 1994; Karl et al., 2013). The accuracy was propagated from the uncertainty of the calibration, the systematic uncertainty of the flux calculation (Lenschow et al., 1994), and the uncertainties of the divergence

280 corrections. The uncertainty of the chemical vertical divergence correction was estimated to be 20 % of the correction applied. The uncertainty of the physical vertical divergence correction was estimated using a Monte Carlo uncertainty propagation, assuming a 17 % uncertainty each for the slopes and boundary layer heights, since 17 % was the average day-by-day variability in the vertical divergence slopes of benzene. The resulting median uncertainty of the vertical divergence correction was 17 % (average: 51 %). The final uncertainties were unique to each VOC. Precision ranged from 4 %-220 %

285 (for gas standard calibrated VOCs 4-150 %), accuracy from 7-400 % (for gas standard calibrated VOCs 7-120 %), and the total uncertainty from 33 % to 136 % (for gas standard calibrated VOCs 33-87 %).

2.5.7 Flux footprints and land cover

We used the KL04+2D model to derive a spatially resolved flux footprint for each flux data point along the flight track (Kljun et al., 2015; Metzger et al., 2012). A detailed description of the footprint calculation can be found in Zhu et al. (2023).

290 The resulting footprints are shown in Fig. 1.

Land cover data were obtained from CropScape 2018 (National Agricultural Statistics Service, 2018). Additional emission sources were taken from the Vista-CA methane inventory (Hopkins et al., 2019). Since we found high monoterpene emissions over citrus processing facilities (such as juice factories and citrus packing warehouses) and large ethanol emissions from an ethanol biofuel plant, we derived our own inventory of citrus processing and packing facilities for the

295 study area using Google Maps (Pfannerstill, 2022b) and the ethanol biofuel production plant location from a business inventory (SafeGraph, 2022).

The KL04+2D footprint algorithm was compared with the half-dome footprints (Weil and Horst, 1992) applied for airborne VOC fluxes by Misztal et al. (2014) (Fig. S4), and with the Kljun et al. (2015) algorithm applied for airborne fluxes by Hannun et al. (2020) (Fig. S5). Matches with known point sources and VOC flux increases observed (dairy farms, methanol)

300 were used to check whether an algorithm's result explained the observed VOCs. From this comparison, the KL04+2D algorithm showed the best match (Figs. S4, S5).
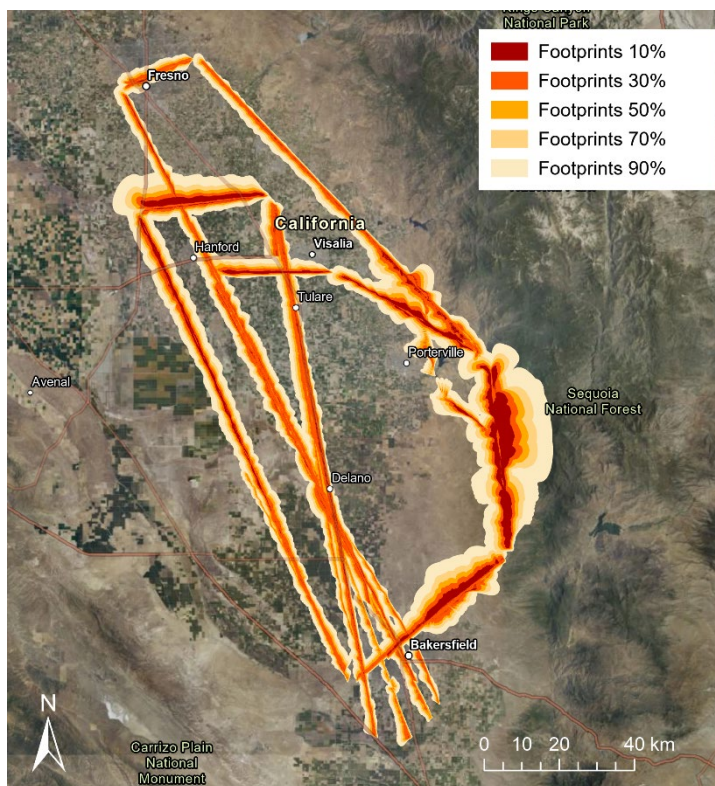
Figure 1: Footprints along the flight tracks. The different colors show the areas where the 10th, 30th, 50th, 70th, and 90th percentiles of the measured fluxes originated. Footprints were derived from the KL04+ model. Map: NAIP imagery via ESRI ArcGIS Pro.

2.6 Inventory comparison

Two commonly used inventories were compared with our observations. The inventory developed by the California Air Resources Board (CARB) includes anthropogenic emissions of VOCs from mobile sources, stationary sources and other emissions from miscellaneous processes such as residential fuel combustion and managed disposal. The mobile emissions are estimated from EMission FACtor (EMFAC) v1.0.2 and OFFROAD emission models. The stationary emissions are estimated from a survey of facilities within local jurisdiction and the emission factors from the California Air Toxics Emission Factor (CATEF) database. The biogenic emissions included in the CARB inventory are obtained from the Model of Emissions of Gases and Aerosols from Nature v3 (MEGAN) (Guenther et al., 2012). It is gridded at 4 km spatial scale and has hourly time resolution.

The second combined inventory consists of anthropogenic emissions from FIVE-VCP (described in Sect. 2.4) and biogenic emissions from the Biogenic Emission Inventory System (BEIS). We obtained the hourly BEIS v3.14 biogenic VOC

emissions at 4 km spatial resolution during the study period from WRF-Chem (described in Sect. 2.4). The sum of BEIS and

320   FIVE-VCP is hereafter called "BEIS+FIVE-VCP". Toluene and xylene are usually lumped with other aromatic VOCs in

FIVE-VCP and were separated out from the lump for comparison with the observations.

For VOC flux comparison with the inventory, each footprint (corresponding to a measured flux) was matched to the inventory grid cells that it overlapped with, weighted by the percentage of the overlap, if the overlap was > 10 % of the area of the grid cell and the sum of all overlaps amounted to at least 100 %. The measured and inventory data for each grid cell

325   were matched in time. Only for the purpose of plotting maps, an average of all flyovers was calculated for each grid cell.

330

3 Results and discussion
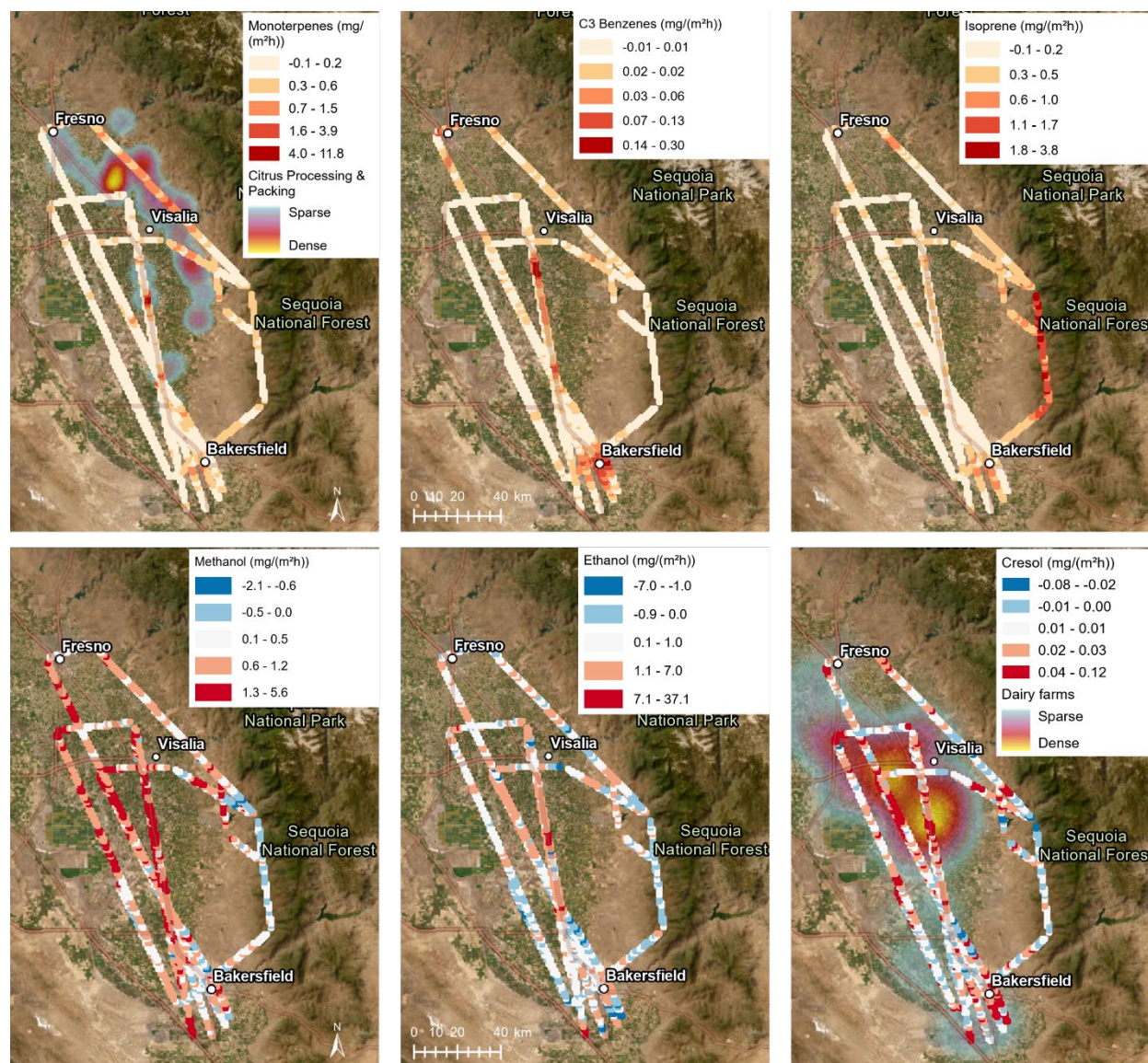
Figure 2: Fluxes in the San Joaquin Valley shown for 6 example VOCs. Values result from all flights, averaged to a 1 km grid (points enlarged for better visibility). Blue colors indicate deposition fluxes. The monoterpene emission distribution is shown together with a heat map of citrus packing and processing facilities. Methanol, ethanol and cresol emissions distributions are comparable to the distribution of dairy and cattle farms (shown as heat map in last panel). Satellite imagery map from ESRI ArcGIS Pro.

335

3.1 Overview of the VOC flux observations

340   VOC flux observations from seven flights on different days were spatially averaged to 1 km with the result shown in Fig. 1.
As described by Zhu et al. (2023) and shown in Fig. 1, the footprints were mostly close to the flight track and had an average
extent of 2.6 km. The spatial distributions of the fluxes were clearly source-dependent (Fig. 2). Monoterpene emissions were
highest (> 0.6 mg m^{-2} h^{-1}) in the areas where citrus orchards, citrus packaging and processing facilities are located, and
moderate in the urban areas (mostly in the range of 0.3-0.6 mg m^{-2} h^{-1}), where both trees and anthropogenic sources like

345   fragrance use may contribute to the monoterpene emissions (Peng et al., 2022). Aromatic emissions (example in Fig. 2: C3
benzenes, likely mainly trimethylbenzene) were highest (> 0.03 mg m^{-2} h^{-1} and up to 0.3 mg m^{-2} h^{-1} for C3 benzenes) in the
urban areas and along the highway I-99. Isoprene emissions were negligible in the croplands, and high (0.6-3.8 mg m^{-2} h^{-1})
in the oak woodlands of the Sierra Nevada foothills (Sequoia National Forest), as previous airborne flux observations in the
region have also shown (Misztal et al., 2014; Misztal et al., 2016). The isoprene emissions in the oak woodlands were in the

350   same range as reported by Misztal et al., although visually up to 1/3 of the oaks appeared to be dead (Fig. S6), potentially
from climate stress (Wang et al., 2022) and/or Sudden Oak Death (Frankel, 2019). Enhanced isoprene emissions in
Bakersfield (up to ~1 mg m^{-2} h^{-1}) may indicate isoprene-emitting urban trees. The negligible isoprene fluxes observed in the
croplands confirm that crops are negligible isoprene emitters (Gentner et al., 2014b). The spatial distributions of methanol,
ethanol, and cresol emissions were similar to each other (Fig. 2). They all resembled the distribution of dairy and cattle

355   farms, which likely are their main sources. Like other oxygenated VOCs (OVOCs), methanol and ethanol were deposited in
some parts of the study area, especially in the oak woodlands of the Sequoia National Forest. Maximum deposition fluxes
reached -2.1, -7.0, and -0.08 mg m^{-2} h^{-1} for methanol, ethanol, and cresol, respectively.
The mass flux measured in the San Joaquin Valley was overwhelmingly dominated by OVOCs (including alcohols, acids,
carbonyls, and other OVOCs) with 81 % of the total (Fig. 3). Alcohol emissions alone contributed almost half, mostly due to

360   methanol (21 %) and ethanol (18 %). Acids (18 %) and carbonyls (9 %) also were relevant OVOC emissions. We attribute
the dominance of OVOC emissions mainly to the abundance of dairy farms in the study area (see Fig. 1 and below), with
200 farms in the flux footprints and ca. 1400 in the whole San Joaquin Valley (Hopkins et al., 2019). In an airborne study of
VOC mixing ratios in the San Joaquin Valley, OVOCs even accounted for 91 % of the total (Liu et al., 2022). This reflects
that a relevant fraction of the reactive VOCs is lost before it reaches the point of observation, which makes it difficult to

365   determine primary emission contributions from concentration-based studies and underscores the value of direct flux
measurements.
When the fluxes are scaled by OH reactivity (Fig. 3), which is an indicator for the VOCs' relevance for ozone formation, the
OVOCs contribute 42 %, but now the terpenoids (isoprene, mono- and sesquiterpenes) contribute equally 42 % of the total,
mainly because of isoprene (32 %) followed by monoterpenes (10 %). This fraction is much higher than the concentration-

370   based BVOC contribution to OH reactivity of 6 % found in the SJV by Liu et al. (2022), since such observations are skewed
towards long-lived species and do not reflect the primary emission contributions (see above).

When considering the relative contributions shown in Fig. 3, it is important to note that the contribution of isoprene is almost entirely due to the flight leg performed in the Sierra Nevada foothills. Depending on the wind direction, it is possible that these emissions contribute less to air quality in the center of the San Joaquin Valley than Fig. 3 suggests.

375
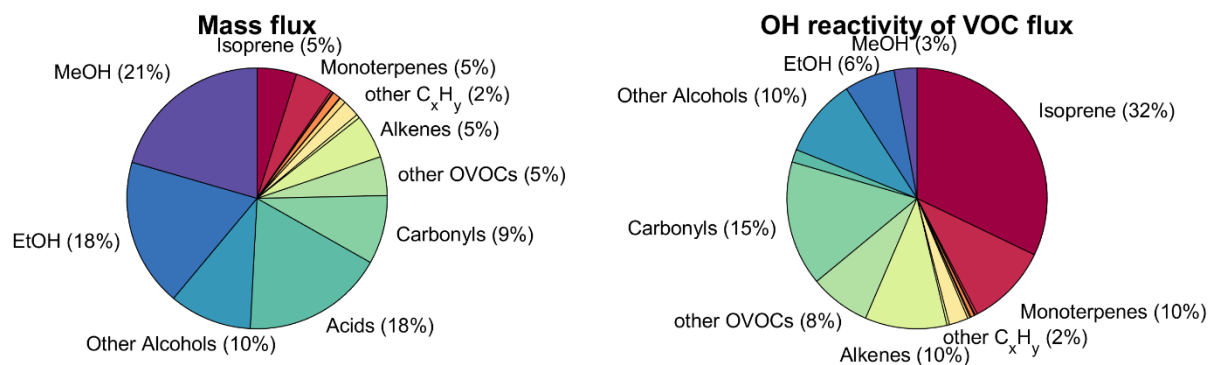
Figure 3: Pie charts showing the median composition of the measured net VOC flux mixture, with VOC group contribution to measured mass flux, and OH reactivity flux. The VOCs included in each group are listed in Table S1. VOC classes contributing less than 2 % of the total were not labeled. SQT: Sesquiterpenes.

380

3.2 Source attribution

The San Joaquin Valley contains a multitude of potential VOC sources, with crop agriculture, dairy and cattle farms, major highways, oil and gas production, urban areas, and natural sources. In order to attribute VOC emissions to their sources, we

385 used a footprint disaggregation method that applies multivariate linear regression of the measured fluxes using land cover information weighted by footprint density as predictors (Hutjes et al., 2010; Hannun et al., 2020). We compiled the spatial distribution of landcover types and point sources using CropScape for land cover (National Agricultural Statistics Service, 2018), Vista-CA for the locations of dairy and cattle farms, composting sites, digesters, landfills, and wastewater treatment plants (Hopkins et al., 2019), a business registry for ethanol biofuel manufacturing locations (SafeGraph, 2022), a registry of

390 active oil and gas wells (CALGEM, 2022), and locations of citrus processing and packaging facilities collected from Google Maps which we uploaded to ArcGIS online (Pfannerstill, 2022b). Using these sources as input, we first identified the crop types and Vista-CA sources that were present in at least 10 % of the footprints or covered at least 10 % of a footprint. The remaining source types were used as input for a multivariate linear regression for footprint disaggregation. The number of crop types was reduced further by performing a test with adding crop types in each regression loop. Only citrus crops

395 (combining oranges and other citrus) and other tree fruit crops (combining cherries, nectarines, peaches, pomegranates, apples, pears) significantly improved the regression. All remaining crop types were summed up under a "cropland" category. The grasslands in the slopes of the Sierra Nevada were removed from the results since they are strongly impacted by the

hillslope effect, which causes pollution from the valley to be transported up along the slopes and makes it appear as positive emission fluxes in the measurements, although it is not emitted by the grass itself. Grasslands are expected to be negligible
400   VOC sources (Bamberger et al., 2010; Brunner et al., 2007) except immediately after cutting (Brilli et al., 2012; Davison et al., 2008). Figure 4 shows the relative composition of emissions attributed to eight relevant source types found in the San Joaquin Valley.

The footprint disaggregation results (Fig. 4) show reasonable emission compositions for the sources presented, although the separation of sources is not always complete. For example, the oil and gas category includes isoprene, since most of the oil
405   and gas wells overflown were located in the Sierra Nevada foothills northeast of Bakersfield, close to the oak woodlands. Vice versa, the oak shrubland category includes hydrocarbons that may be stemming from the oil and gas production (but partly may be PTR-MS fragment ions from terpenoids emitted in the oak region (Kari et al., 2018; Tani, 2013)).

Apart from the overall composition of each source's emissions, we also identified tracer m/z for the sources (Table 2). These were m/z whose emissions in the disaggregation result were above 3x the overall median emission of that m/z, above 2x the
410   standard deviation of emissions between the sources, and higher than in the disaggregation result of at least six other source categories.

The composition of the dairy/CAFO (concentrated animal feeding operation) category was dominated by fermentation-related VOCs, with a mass fraction of 12 % methanol (1.1 kg facility^{-1} h^{-1}), 34 % ethanol (3.0 kg facility^{-1} h^{-1}), 12 % other alcohols, and 21 % acids dominated by acetic acid (1.8 kg facility^{-1} h^{-1}) (Fig. 4, Table 2). This composition is in agreement
415   with direct measurements of dairy cattle VOC emissions (Gierschner et al., 2019; Oertel et al., 2018; Shaw et al., 2007; Stackhouse et al., 2011; Sun et al., 2008; Yuan et al., 2017), of silage, the fodder used for cows in industrial agriculture (Hafner et al., 2013; Malkina et al., 2011), and of manure (Hales et al., 2015; Sun et al., 2008), which all are rich in alcohols and acids. For example, Yuan et al. (2017) reported a mole fraction of 55-87 % alcohols and 4-32 % carboxylic acids from CAFO emissions. Less important in amount, but relevant "tracers" for dairy and cattle emissions (Table 2) in agreement with
420   previous studies (Yuan et al., 2017; Borhan et al., 2012; Gierschner et al., 2019) also included strongly odor-active sulfur-containing VOCs (hydrogen sulfide, methane thiol, dimethyl sulfide or ethane thiol, benzothiazole), and phenolic species (phenol, cresols). The emission strengths can vary strongly between individual dairy farms (Gentner et al., 2014a; Yuan et al., 2017) based on feed composition (Hafner et al., 2013; Hales et al., 2015; Malkina et al., 2011), management practices, or animal age and state (Shaw et al., 2007; Gierschner et al., 2019; Stackhouse et al., 2011). This is confirmed by our
425   observations, where e.g. methanol fluxes from dairy-dominated footprints had a variance of 2.2 mg m^{-2} h^{-1} associated with a median of 1.0 mg m^{-2} h^{-1}.
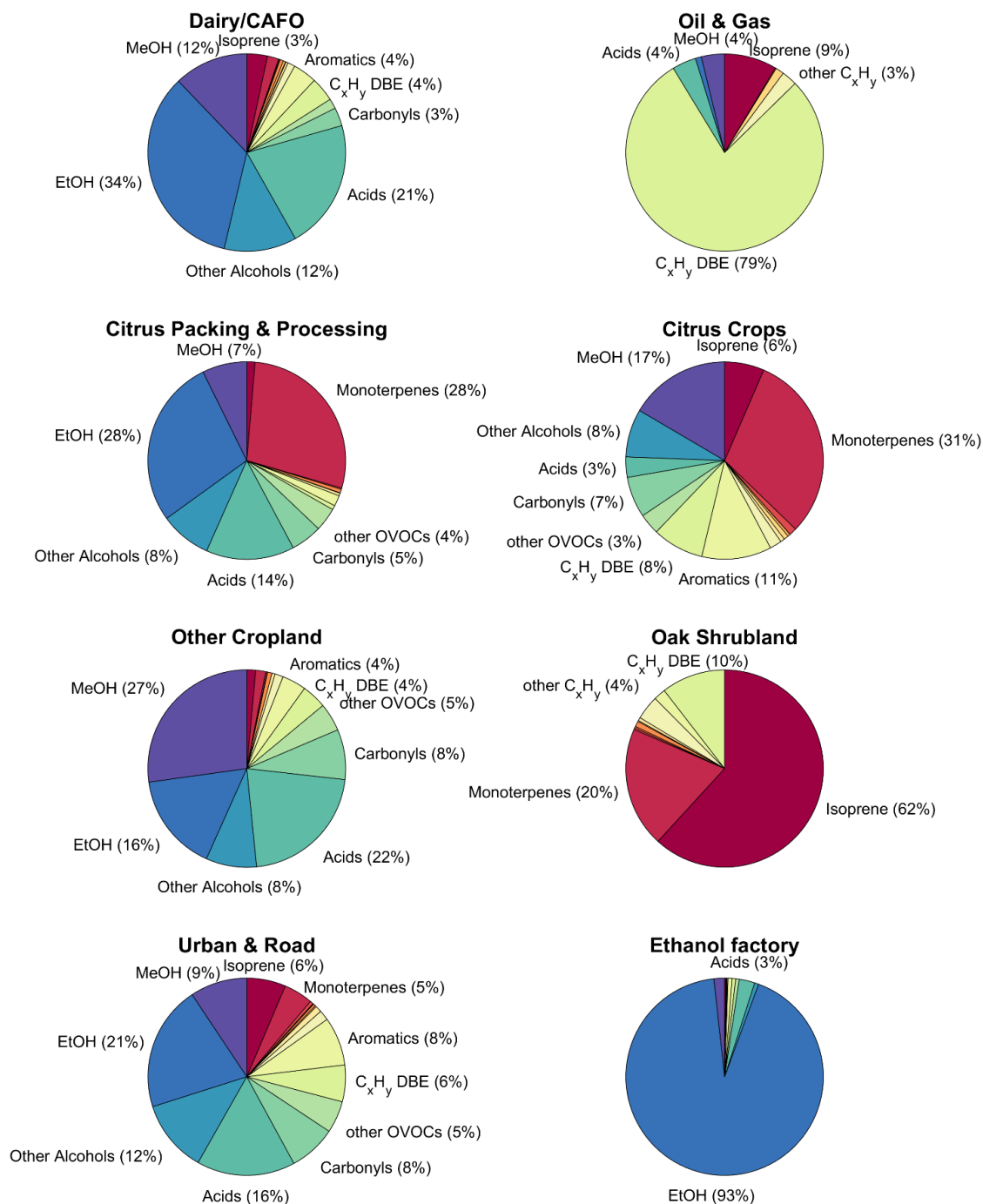
Figure 4: Pie charts showing the composition of the measured VOC emissions by mass from the footprint disaggregation result.
430   **CxHy DBE: Hydrocarbons with double bond equivalents (i.e., alkenes, cycloalkanes, and potentially unknown aromatics). For oil and gas sources, this category includes $C_{15}H_{24}$ (European Chemical Agency, 2006) and $C_{10}H_{16}$ (Gueneron et al., 2015) isomers that are sorted into the sesquiterpene and monoterpene categories, respectively, for other sources. Since the PTR-MS is blind to most alkanes, the VOC composition, especially of the oil & gas category, can be expected to be incomplete.**

435 The oil and gas category mainly consisted of hydrocarbons (82 %, Fig. 4). Since the PTR-MS method is blind to most alkanes, we can only report hydrocarbons with double bonds or longer-chain (cyclo)alkanes, and aromatics. Interestingly, two m/z that are usually attributed to biogenic emissions were significantly enhanced in the oil and gas emissions: $C_{15}H_{24}H^+$ (m/z 205.19) and $C_{10}H_{16}H^+$ (m/z 137.13; Table 2). In the oil and gas category, we attributed them to petroleum emissions and included them into the hydrocarbons with double bond equivalents category, since $C_{15}H_{24}$ can be a component of petroleum

440 kerosene (European Chemical Agency, 2006) and $C_{10}H_{16}H^+$ here is likely a PTR-MS product of decahydronaphthalene (Gueneron et al., 2015). Tracers for this source category included C4-C17 hydrocarbons, covering almost the entire mass and volatility range that can be measured with the method used. Example m/z are $C_{14}H_{24}H^+$ (anthracene or phenantrene), and $C_8H_{15}^+$ and $C_9H_{17}^+$, which both are fragments of substituted cyclohexanes (Gueneron et al., 2015).

The citrus packing and processing category includes juice factories, fragrance extraction, and citrus packaging facilities.

445 Emissions from these consist of 28 % (8.75 kg facility^{-1} h^{-1}) monoterpene and 28 % ethanol emissions as the largest contributors by mass (Fig. 4). While there were 45 citrus processing and packaging facilities identified in the study area, one of them stood out with extremely large emissions: A facility in Tipton, CA. In Fig. 2, this is shows up as the largest monoterpene source location, with 11.8 mg m^{-2} h^{-1} emitted on average in Tipton over all flights, while only a small fraction of the measurement footprint is covered by the facility. This facility does not only produce juices, but also extracts

450 monoterpenes for the fragrance industry (Ventura Coastal, 2023). It is possible that ethanol is used as a solvent in the extraction process. Also, fruit juices contain significant amounts of ethanol (Gorgus et al., 2016). Since citrus fruits emit monoterpenes especially when they are being handled, and monoterpene emissions were enhanced around citrus packaging facilities, we conclude that citrus packing also contributes to the agroindustrial source of monoterpenes summed up in this category. Tracers observed in the citrus processing and packing emissions (Table 2) were rich in $C_{10}H_{16}$ monoterpenes, but

455 also included aromatic monoterpenes ($C_{10}H_{15}$), monoterpenoids (e.g. $C_{10}H_{18}O$, $C_9H_{14}O$, $C_9H_{14}O_2$, $C_{10}H_{18}O_2$), sesquiterpenes ($C_{15}H_{24}$), sesquiterpenoids ($C_{15}H_{22}$), diterpenes ($C_{20}H_{32}$), and the plant metabolite dodecane ($C_{12}H_{26}$).

The citrus crop emissions composition with mass fractions of 31 % monoterpenes and 17 % methanol agrees with a study performed on Californian citrus plants and in a San Joaquin Valley citrus plantation, where methanol and monoterpenes were the largest emissions, approximately equal in molar contributions (Fares et al., 2012; Fares et al., 2011). The aromatic

460 fraction of the citrus crop emissions (11 %) included aromatic monoterpenes ($C_{10}H_{15}$) and their fragments. Other aromatic emissions from citrus observed here (toluene, Table 2) have previously been reported as well (Misztal et al., 2015).

Emissions of the "other tree fruits" category (not shown in Fig. 4 for space reasons, see Fig. 5 and Table 2) were enhanced in monoterpene emissions compared to the other cropland, and exhibited a plant metabolite as a tracer: methyl salicylate, a methyl ester of a plant hormone that is considered to be a stress indicator (Niinemets and Monson, 2013). The monoterpene

465 enhancement is in accordance with the literature, where fruit trees such as cherry and peach have been shown to be monoterpene emitters (e.g. Gentner et al., 2014b; Rapparini et al., 2001).

The emission mass fractions in the "other cropland" category look similar to the dairy emissions, which is likely because the dairy farms are usually located in the middle of cropland and cannot completely be separated out. However, in the cropland category, the methanol emission fraction is, at 27 % of the total, much higher than in the dairy category (Fig. 4), which
470 indicates that some actual crop emissions were captured by the disaggregation. Methanol has been reported to be emitted by many crops (König et al., 1995; Das et al., 2003; Gonzaga Gomez et al., 2019; Karl et al., 2001; Warneke, 2002; Gentner et al., 2014b; Loubet et al., 2022), including almonds (Gentner et al., 2014b), one of the major crops in the San Joaquin Valley. There were no specific tracer VOCs identified for the "other cropland" category.

The oak shrublands emissions were dominated by isoprene (62 %, 0.73 mg m^{-2} h^{-1}) and monoterpenes (20 %, Fig. 4). The
475 oaks of the Sierra Nevada foothills are known isoprene emitters (Misztal et al., 2014). Tracer m/z identified for the oak shrubland emissions also included monoterpene alcohols ($C_{10}H_{18}O$) and sesquiterpene alcohols ($C_{15}H_{26}O$).

The emission composition of the urban & road category was similar to the composition of VOC emissions in Los Angeles (Pfannerstill et al., submitted), with a large ethanol contribution (21 %, Fig. 4 and significant aromatics emissions (8 %). Tracer species identified for this source category included chloramine (potentially from cleaning (Mattila et al., 2020)),
480 several aromatics (styrene, C2 benzenes [e.g. xylene], C3 benzenes [e.g. trimethylbenzene]) indicative of traffic emissions, and para-chlorobenzotrifluoride, a coating solvent (Stockwell et al., 2020).

In Pixley, CA, the largest single ethanol source of the study area was observed: An ethanol biofuel factory, which according to the disaggregation emits 106 kg of ethanol per hour. The footprint disaggregation result of almost exclusively ethanol emissions (93 %, Fig. 4) for this facility is reasonable.

485 Figure 5 shows quantitative results of the footprint disaggregation. Area fluxes per mass (Fig. 5a) were highest in the "developed" category (total of ~4.2 mg m^{-2} h^{-1}) which includes roads and urban areas, followed by cropland and citrus crop emissions of each ~3 mg m^{-2} h^{-1}. A notable result was the deposition of OVOCs (alcohols, acids, carbonyls) of in total -0.9 mg m^{-2} h^{-1} in the oak shrublands. With an emission flux of 1.1 mg m^{-2} h^{-1}, the resulting net mass flux of the oak shrublands was close to zero. Deposition of oxygenated VOCs on leaf surfaces and even uptake into leaves (Seco et al., 2007; Canaval
490 et al., 2020) and soils (Rinnan and Albers, 2020) are known phenomena. Point source emissions (Fig. 5b) were highest from ethanol biofuel manufacturing (~115 kg h^{-1} facility^{-1}), followed by citrus processing/packing (~31 kg h^{-1} facility^{-1}), and dairy farms (~9 kg h^{-1} facility^{-1}).

Considering the OH reactivity instead of the mass of emissions by area (Fig. 5c) changes the order of source importance: The oaks were the largest source of OH reactivity per area (0.21 m s^{-2}) followed by citrus crops (0.17 m s^{-2}) and developed
495 areas (0.16 m s^{-2}). Among the point sources, scaled by OH reactivity, the ethanol manufacturing factory (Fig. 5d) was still largest (0.59 m^3 s^{-2} facility^{-1}), and was closely followed by citrus processing (0.43 m^3 s^{-2} facility^{-1}). Dairy farms emitted an OH reactivity of 0.22 m^3 s^{-2} facility^{-1}.

The relevance of each of these sources for air quality in the San Joaquin Valley depends on their abundance in the region. It should be noted that there is only one ethanol biofuel factory in the valley, but ca. 1400 dairy farms, 47 000 active oil or gas
500 wells, and 45 citrus processing facilities. The areas of citrus crops, other tree fruits, other cropland, oak shrublands, and

developed areas in the whole San Joaquin Valley are approximately 970, 1140, 17540, 3880, and 3960 km², respectively. (The oak area depends strongly on where the border of the valley is drawn.) Previous studies have reported that dairy farms are a major contributor to ozone formation in the San Joaquin Valley, only second to road transport (Howard et al., 2008) and predicted that traffic and dairies would contribute equally by 2020 (2012). We refrain from upscaling our results to the
505   whole San Joaquin Valley for two reasons: The source separation resulting from the disaggregation is not perfect, and the contribution of the oak woodlands depends strongly on where along the slope of the Sierra Nevada the border of the valley is drawn. However, it becomes clear from our observations that citrus-related emissions – including crops and citrus processing or packing – are a previously disregarded source of highly reactive VOCs in the San Joaquin Valley with important ozone formation capabilities. Locally, in Pixley, ethanol biofuel manufacturing is a substantial VOC source with potential for
510   secondary air pollution contribution.
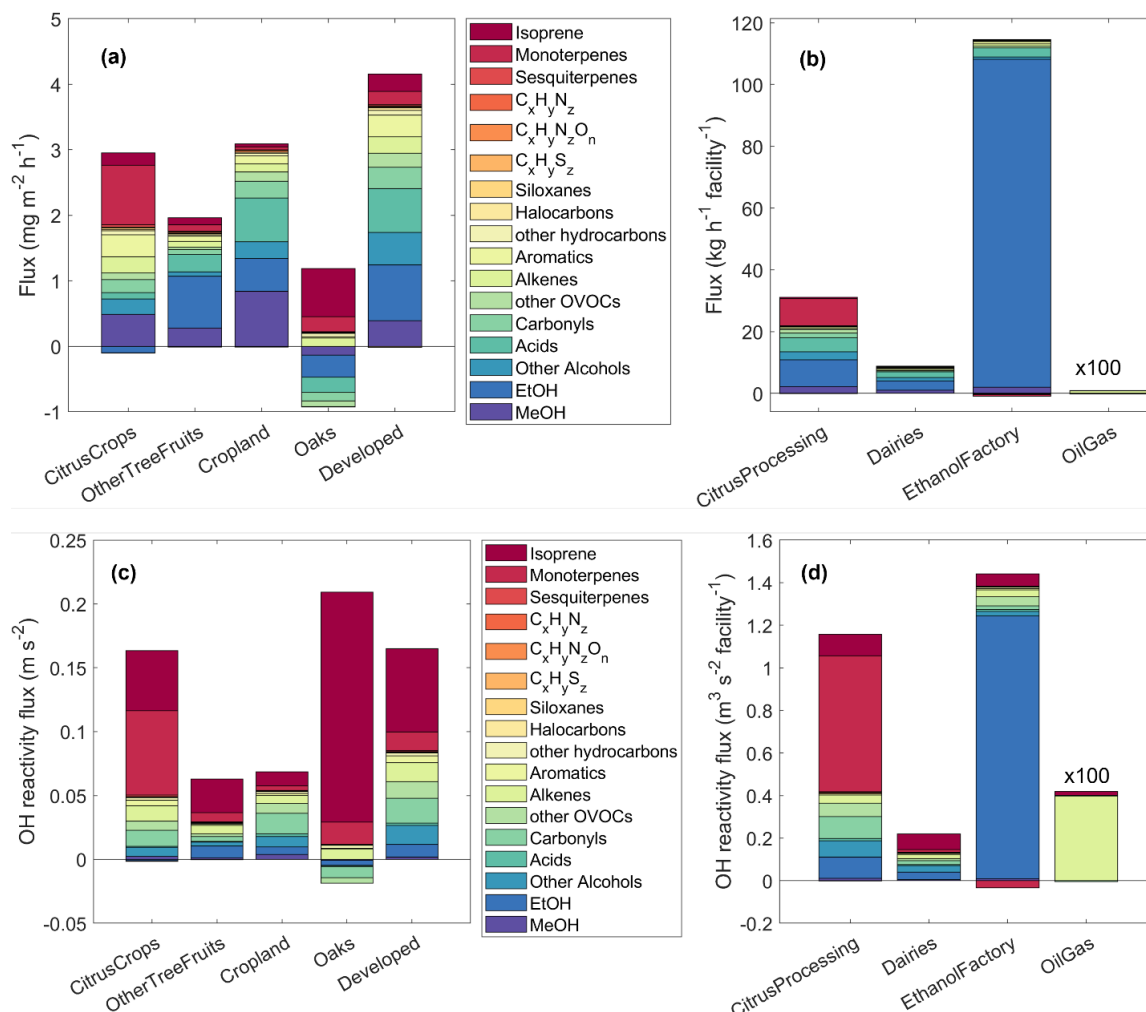
Figure 5: Quantitative footprint disaggregation results shown as mass fluxes (a, b) and OH reactivity fluxes (c, d). The fluxes for area sources were given per area (a, c), while point sources (b, d) are reported as fluxes per facility. Negative fluxes signify

515

deposition. Note that the oil and gas well emissions were multiplied by 100 to become visible, and that their expectedly significant alkane emissions were not captured by the measurements. "Developed" includes urban areas and roads.

Table 2: List of tracer m/z specific to the different sources, resulting from the footprint disaggregation. Point source emissions are given in kg facility^{-1} h^{-1}, and area source emissions in mg m^{-2} h^{-1}. The complete disaggregation results with emissions of each VOC attributed to each source are given in Table S2. No specific tracers were found for the general cropland emissions.

Source	Mass (amu, protonated)	Chemical Formula (protonated)	Potential ID	Source emission (kg facility^{-1} h^{-1})
Citrus Processing	93.055	$C_3H_9O_3+$	Glycerol, C_3 acid/ester water cluster	1.29E-01
	103.039	$C_4H_7O_3+$	Isoprene ox	5.81E-02
	103.075	$C_5H_{11}O_2+$	Ethyl propionate, etc.	4.54E-02
	105.091	$C_5H_{13}O_2+$	Pentanediol	3.67E-02
	109.101	$C_8H_{13}+$	Sesquiterpene fragment	1.07E-01
	133.050	$C_5H_9O_4+$	$C_5H_8O_4$	1.12E-01
	135.117	$C_{10}H_{15}+$	Aromatic monoterpenes	5.04E-02
	137.132	$C_{10}H_{17}+$	Monoterpenes	8.75E+00
	139.112	$C_9H_{15}O+$	Nopinone etc	1.19E-02
	155.107	$C_9H_{15}O_2+$	Norpinonaldehyde etc	1.21E-02
	155.143	$C_{10}H_{19}O+$	Citronellal, monoterpene alcohols	1.01E-02
	159.138	$C_9H_{19}O_2+$	C_9 acid/ester	2.22E-02
	163.075	$C_{10}H_{11}O_2+$	Safrole, carbofuran	1.67E-02
	167.034	$C_8H_7O_4+$	Phthalic acid	2.66E-02
	171.065	$C_8H_{11}O_4+$	$C_8H_{10}O_4$	6.53E-03
	171.138	$C_{10}H_{19}O_2+$	Linalool oxide	4.72E-03
	171.211	$C_{12}H_{27}+$	Dodecane (plant metabolite)	4.90E-04
	175.060	$C_7H_{10}O_5H+$	Shikimic acid	6.28E-04
	203.179	$C_{15}H_{23}+$	Aromatic sesquiterpene, sesquiterpenoid	2.52E-03
	205.195	$C_{15}H_{25}+$	Sesquiterpenes	6.40E-02
	273.258	$C_{20}H_{32}H+$	Diterpenes	5.56E-04
Ethanol Biofuel Factory	47.049	C_2H_7O+	Ethanol	106.14
Oil & Gas production	57.070	C_4H_9+	Butene	9.79E-04
	71.086	$C_5H_{11}+$	Pentene	4.45E-05
	83.086	$C_6H_{11}+$	Cyclohexene, hexadiene	8.72E-04
	85.101	$C_6H_{13}+$	Hexene, hexanol fragm	4.64E-05
	97.101	$C_7H_{13}+$	Heptadiene, heptanal fragm	1.72E-04
	111.117	$C_8H_{15}+$	Dimethylcyclohexane fragment	1.19E-04
	119.086	$C_9H_{11}+$	Propenyl benzene, methyl styrene, indane	4.84E-05
	125.132	$C_9H_{17}+$	Trimethylcyclohexane fragment	3.81E-05
	129.164	$C_9H_{21}+$	C_9H_{20} hydrocarbons	1.85E-06
	133.101	$C_{10}H_{13}+$	Phenylbutene and isomers	4.68E-05
	135.117	$C_{10}H_{15}+$	Tetramethyl benzene	1.64E-04

Source	Mass (amu, protonated)	Chemical Formula (protonated)	Potential ID	Source emission (mg m⁻² h⁻¹)
	137.132	$C_{10}H_{17}+$	Decahydronaphthalene	2.19E-03
	139.148	$C_{10}H_{19}+$	$C_{10}H_{18}$ hydrocarbons	2.14E-05
	146.976	$C_6Cl_2H_5+$	Dichlorobenzene	4.41E-05
	151.148	$C_{11}H_{19}+$	Methyl-caren	6.57E-05
	179.179	$C_{13}H_{23}+$	Heptylbenzene and isomers	6.91E-05
	193.195	$C_{14}H_{25}+$	Anthracene, phenantrene	2.51E-05
	203.179	$C_{15}H_{23}+$	$C_{15}H_{22}$ petroleum hydrocarbons	7.83E-06
	205.195	$C_{15}H_{25}+$	$C_{15}H_{24}$ petroleum hydrocarbons	1.71E-04
	207.211	$C_{15}H_{27}+$	$C_{15}H_{26}$ petroleum hydrocarbons	5.75E-06
	221.226	$C_{16}H_{29}+$	C_{16} hydrocarbon, 3DBE	3.61E-06
	231.211	$C_{17}H_{27}+$	C_{17} hydrocarbon, 5 DBE	4.34E-06
	235.242	$C_{17}H_{31}+$	C_{17} hydrocarbon, 3 DBE	2.98E-06
Dairy & cattle farms	33.033	CH_5O+	Methanol	1.08E+00
	34.995	H_3S+	Hydrogen sulfide	1.58E-03
	43.054	C_3H_7+	Propanol fragment	7.06E-01
	44.049	C_2H_6N+	Vinylamine, acetaldimine	3.34E-03
	45.033	C_2H_5O+	Acetaldehyde	2.06E-01
	47.049	C_2H_7O+	Ethanol	3.03E+00
	49.011	CH_5S+	Methane thiol	5.47E-03
	61.028	$C_2H_5O_2+$	Acetic acid	1.78E+00
	63.026	C_2H_7S+	Ethane thiol, dimethyl sulfide	2.30E-02
	63.944	S_2+	Sulfur	2.66E-03
	73.065	C_4H_9O+	Methyl ethyl ketone	4.53E-02
	74.060	C_3H_7NOH+	Dimethylformamide	6.67E-03
	83.013	$C_4H_3O_2+$	Fragment	5.68E-03
	87.080	$C_5H_{11}O+$	C_5 carbonyls	5.60E-03
	95.049	C_6H_7O+	Phenol	2.83E-02
	103.075	$C_5H_{11}O_2+$	Ethyl propionate, etc.	9.36E-03
	107.070	$C_4H_{11}O_3+$	C4-acid water cluster	2.56E-02
	109.065	C_7H_9O+	Cresols, anisole	3.93E-02
	121.086	$C_5H_{10}O_2H_2OH+$	Valeric acid watercluster	9.85E-03
	129.127	$C_8H_{17}O+$	C_8 carbonyls	2.51E-03
	136.022	C_7H_6NS+	Benzothiazole	6.03E-03
	141.055	$C_7H_9O_3+$	$C_7H_8O_3$	1.19E-02
	145.122	$C_8H_{17}O_2+$	C_8 acid	4.80E-03
	155.107	$C_9H_{15}O_2+$	C_9 acid/ester	3.07E-03
	173.044	$C_7H_9O_5+$	$C_7H_8O_4$	5.56E-03
	223.169	$C_{14}H_{23}O_2+$	$C_{14}H_{22}O_2$	7.25E-04
Source	**Mass (amu, protonated)**	**Chemical Formula (protonated)**	**Potential ID**	**Source emission (mg m⁻² h⁻¹)**
Citrus Crops	93.070	C_7H_9+	Fragment of aromatic monoterpenes, toluene	0.076
	137.132	$C_{10}H_{17}+$	Monoterpenes	0.906
	151.112	$C_{10}H_{15}O+$	Monoterpenoids - e.g. carvone, thymol	0.005
	205.195	$C_{15}H_{25}+$	Sesquiterpenes	0.036

Other Tree Fruits	137.132	$C_{10}H_{17}+$	Monoterpenes	0.095
	153.055	$C_8H_9O_3+$	Methyl salicylate (plant metabolite)	0.014
Developed (urban & road)	51.995	ClH_3N+	Chloramine	0.005
	82.945	$CHCl_2+$	Chlorinated fragment	0.007
	97.101	$C_7H_{13}+$	Heptadiene, heptanal fragm	0.006
	105.070	C_8H_9+	Styrene, cyclooctatetraene	0.028
	107.086	$C_8H_{11}+$	Xylene, C_2 benzenes	0.045
	121.101	$C_9H_{13}+$	Trimethyl benzene, C_3 benzenes	0.022
	136.022	C_7H_6NS+	Benzothiazole	0.007
	156.951	C_2H_6I+	Iodoethane	0.002
	181.003	$C_7H_4ClF_3H+$	Para-chlorobenzotrifluoride	0.006
Oak shrubland	38.015	C_3H_2+	Alkyl fragment	0.010
	69.070	C_5H_9+	Isoprene	0.733
	155.143	$C_{10}H_{19}O+$	Citronellal, monoterpene alcohols	0.003
	223.206	$C_{15}H_{27}O+$	Cadinol, farnesol, sesquiterpenoids	0.002

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3.3 Inventory comparison

A comparison of observed median fluxes with the California Air Resources Board (CARB) Inventory and the combination of the BEIS (biogenic) and FIVE-VCP (anthropogenic) Inventory, hereafter "BEIS + FIVE-VCP", is given in Fig. 6. In both inventories, median isoprene emissions were strongly overestimated. In the CARB inventory (Fig. 6a), methanol,
525 acetaldehyde and acetone emissions were relatively close to the observations (within a factor of 2). All other CARB VOCs included were underestimated in the medians, notably the aromatics and typical dairy emissions such as ethanol, acids, cresol and phenol.

While most CARB inventory VOC emissions were lower than observations, the BEIS + FIVE-VCP inventory emissions (Fig. 6b) scatter more around the 1:1 line with observations. Within a factor of 2 were methanol, ethanol, monoterpenes,
530 long-chain acids, and acetaldehyde; within a factor of 3 toluene and xylene. The inventory underestimated the median emissions of cresol, phenol, benzaldehyde, benzene, and acetic acid, and overestimated acetone and potentially sesquiterpene emissions. The sesquiterpene emissions observations are a lower limit because their speciation is unknown, and conservative reaction rates were assumed for the correction of ozone and OH loss between surface and flight altitude.
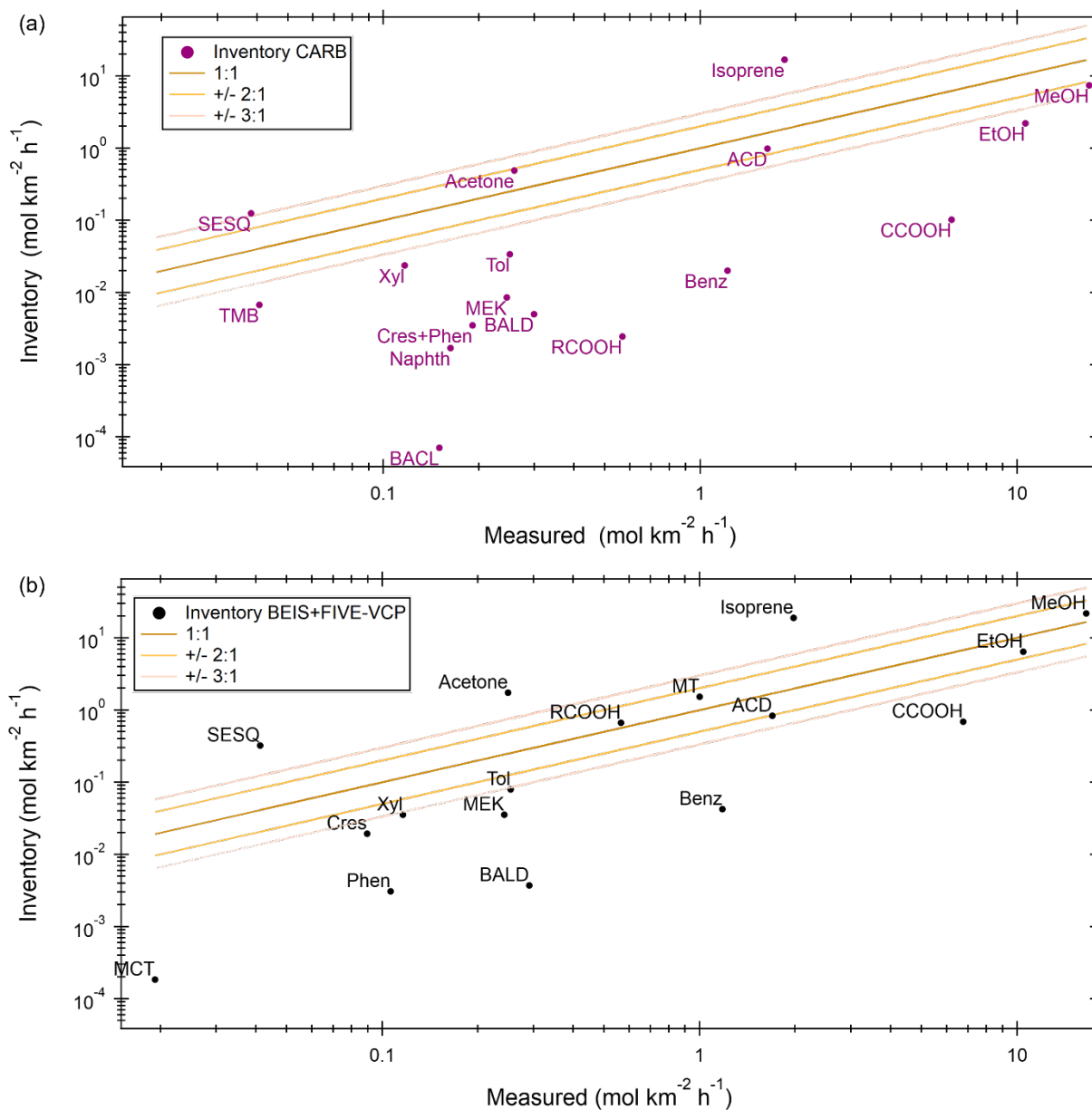
Figure 6: Comparison of median values between measured and inventory emissions of individual VOCs for (a) CARB and (b) BEIS+FIVE-VCP. Cres: Cresol, Phen: Phenol, MCT: Methanethiol, SESQ: sesquiterpenes, TMB: trimethylbenzene, BALD: benzaldehyde, BACL: Biacetyl, Naphth: naphathalene, MEK: methyl ethyl ketone, Benz: benzene, Xyl: Xylene, Tol: Toluene, TMB: Trimethylbenzene, MT: monoterpenes, MeOH: methanol, EtOH: ethanol, CCOOH: acetic acid, ACD: acetaldehyde, RCOOH: Higher organic acids, "Measured" values can slightly differ in comparison to each inventory because of a different distribution and coverage of inventory grid cells.
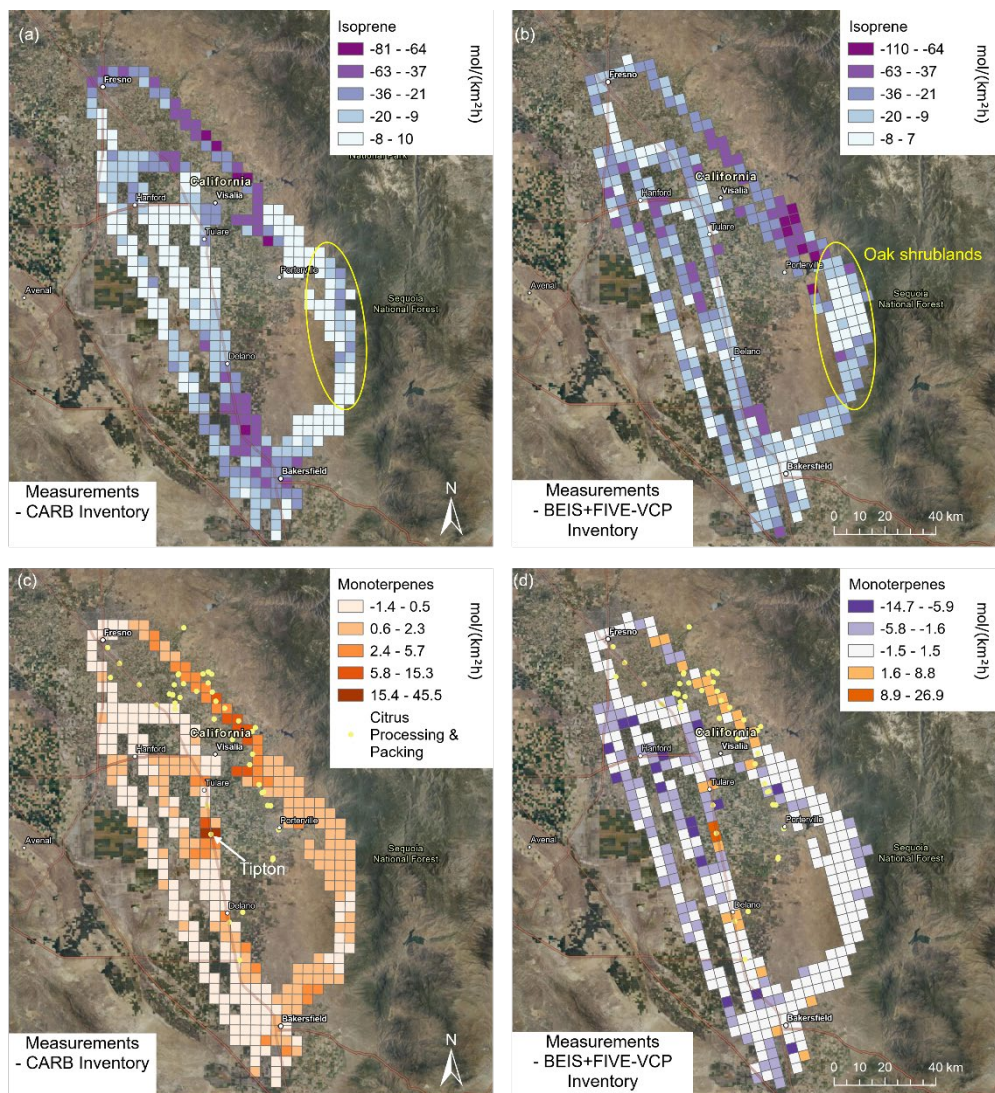
Figure 7: Differences between measurement and inventory emissions for terpenoids observed in the San Joaquin Valley. (a), (c):
CARB Inventory, (b, d) BEIS+FIVE-VCP inventory. Orange colors designate observations > inventory emissions, purple colors
the opposite. Color scales were chosen accordingly (diverging where there are both over- and underestimations in the inventory,
orange where there are mainly underestimations, purple where there are mainly overestimations). Important sources are indicated
in the maps (oak shrublands for isoprene, citrus processing and packing for monoterpenes, with Tipton highlighted as the place
with a juice and fragrance extraction factory). Satellite maps from NAIP Imagery via ESRI ArcGIS Pro.

Since emissions are spatially highly variable within the San Joaquin Valley according to source distribution, spatial comparisons of observed emissions with the inventories provide additional information and can regionally differ from the median comparison shown in Fig. 6. Figure 7 shows the difference between measurements and inventory for isoprene and monoterpene emissions. Both inventories display similar patterns for isoprene (Fig. 7 a, b). Observations and inventories matched well in the oak shrublands, with only a slight tendency to overestimation especially in the BEIS inventory, potentially because of the reduced fraction of live oak trees (see Fig. S6 and Sect. 3.1). Isoprene emissions were strongly

overestimated by both inventories northeast of Visalia, in the region with intense citrus production (see Fig. 7d). The CARB inventory overestimated isoprene emissions in Bakersfield, while the BEIS + FIVE-VCP inventory matched relatively well there and instead showed a stronger overestimation in the dairy region around Hanford. For monoterpene emissions (Fig. 7c, d), the two inventories were distinctly different. The CARB inventory underestimated monoterpene emissions almost

560   throughout the study region, with especially strong underestimations in the regions with intense citrus processing. The monoterpene emission hotspots of the juice and fragrance factory in Tipton (and to a lesser extent of a juice factory in Delano) have clearly not been included in either of the two inventories. Contrary to the CARB inventory, the BEIS+FIVE-VCP inventory overestimated monoterpene emissions from large swaths of the croplands. However, it underestimated monoterpene emissions in the citrus regions similarly to the CARB inventory. An unrealistic land cover underlying the

565   inventory is likely the reason for mismatches between observed and predicted isoprene and monoterpene emissions (Misztal et al., 2016).
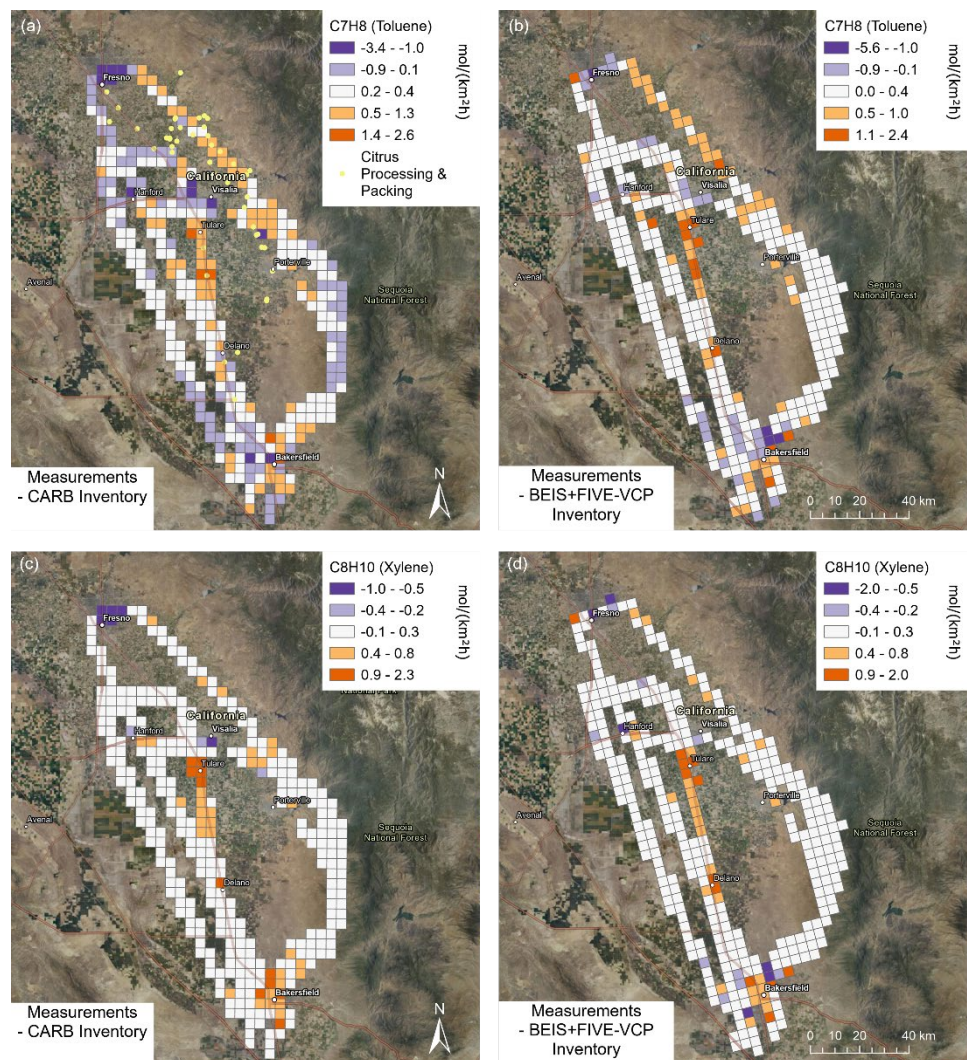
Figure 8: Differences between measurement and inventory emissions for two aromatic VOCs observed in the San Joaquin Valley. (a), (c): CARB Inventory, (b), (d) BEIS+FIVE-VCP inventory. Satellite maps from NAIP Imagery via ESRI ArcGIS Pro. Orange colors indicate where the inventory is underestimating emissions, purple colors where it is overestimating. The C$_7$H$_8$ signal potentially includes fragments of aromatic monoterpenes besides toluene.

The benzenoid emissions comparison (Fig. 8) showed distinct patterns where toluene and xylene were both underestimated by the inventories along the highway and in Bakersfield but overestimated in Fresno and Visalia. Toluene emissions were also underestimated in the citrus production regions northeast of Visalia, potentially because of citrus toluene emissions (Misztal et al., 2015), but this signal may be influenced by fragments of aromatic monoterpenes (Kari et al., 2018).
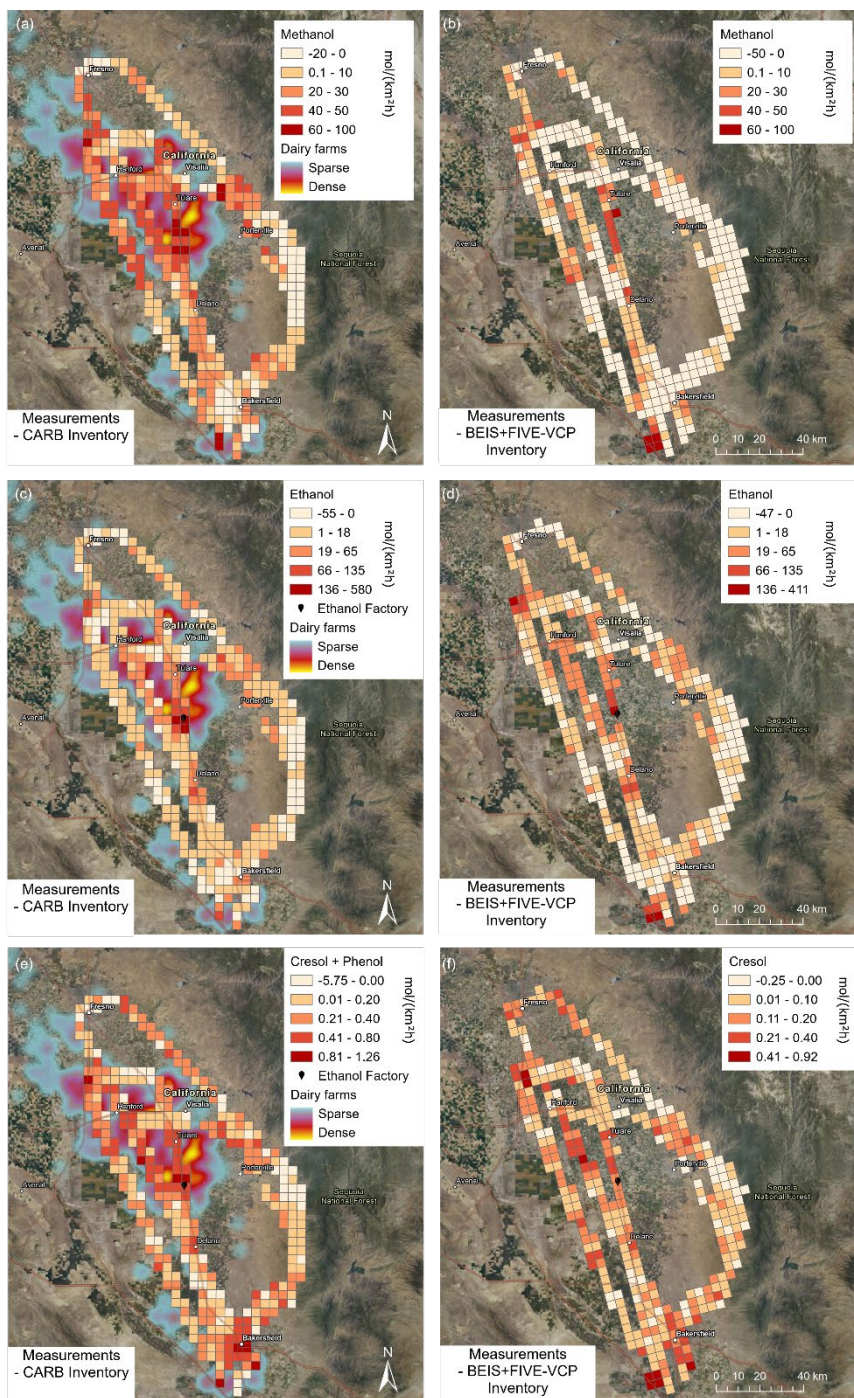
Figure 9: Differences between measurement and inventory emissions for some dairy and cattle farm VOC emissions observed in the San Joaquin Valley. (a), (c), (e): CARB Inventory, (b), (d), (f) BEIS+FIVE-VCP inventory. Important sources are indicated by the density of dairy farms and, for ethanol (c, d), by the ethanol biofuel factory location. The CARB inventory includes the sum of cresol and phenol (e), while cresol is shown separately for BEIS+FIVE-VCP. Satellite maps from NAIP Imagery via ESRI ArcGIS Pro.

Typical dairy VOC emissions are shown in comparison with the inventories in Fig. 9, and they all tend to be underestimated.

585 Both inventories predicted lower than observed methanol emissions with especially strong differences in the dairy-intense regions (Fig. 9 a, b), while matching reasonably well in the urban areas of Bakersfield and Fresno. However, the differences were generally larger in the CARB inventory than in the BEIS+FIVE-VCP inventory. For ethanol emissions (Fig. 9 c, d), the ethanol biofuel factory was the location of the largest underestimation in both inventories. Both inventories also clearly underestimated ethanol emissions in the dairy-intense regions and matched better in the urban areas. Cresol and Phenol were

590 underestimated by both inventories in the dairy regions, but also in the urban areas. For other dairy-relevant emissions not shown here (e.g. methanethiol and acetic acid), we find a similar result where the inventories underestimate these emissions. This may explain why a model based on the CARB inventory underestimates observed enhanced ozone near dairy farms (Cai et al., 2016).

This hypothesis is further explored in Fig. 10, which shows ratios of OH reactivity emissions (summed from all available

595 VOC emissions, not including deposition fluxes) between inventories and observations. Because of the strong overestimation of highly reactive isoprene emissions almost throughout the study region (see Fig. 7), the emission of OH reactive species was overestimated by a factor of at least 2 by the two inventories almost everywhere (Fig. 10 a, b). However, the CARB inventory clearly shows some underestimation of OH reactive emissions (by a factor of 2-5) in the dairy-intense region, which also includes the two largest single sources of OH reactivity observed: the ethanol biofuel factory in Pixley and the

600 citrus processing facility in Tipton, closely north of Pixley (see Fig. 7). These also were the locations where the BEIS+FIVE-VCP inventory underestimated the flux of OH reactive emissions. Since overestimated isoprene in the inventories was clearly dominant in causing the OH reactivity flux mismatch, we removed it from the sums in Fig. 10 c and d. Now it becomes apparent that the CARB inventory underestimated the remaining OH reactive emissions throughout the study region, usually by a factor of 3 and more. For BEIS+FIVE-VCP, the picture is different with underestimated OH reactive

605 emissions of a factor of 3 and more in the oak shrublands (pointing at missing biogenic VOCs), underestimation at dairy farms at the south and northwest ends of the flight tracks and the abovementioned citrus and ethanol processing. In the urban areas, the BEIS+FIVE-VCP inventory had a tendency towards overestimating the OH reactivity source. In conclusion, our observations support the finding by Cai et al. (2016) that the dairy farm regions emit more ozone-relevant VOCs than predicted by the CARB inventory. However, some of this is not solely caused by dairy farms, because intense point sources

610 of monoterpenes and ethanol contribute to the mismatch.
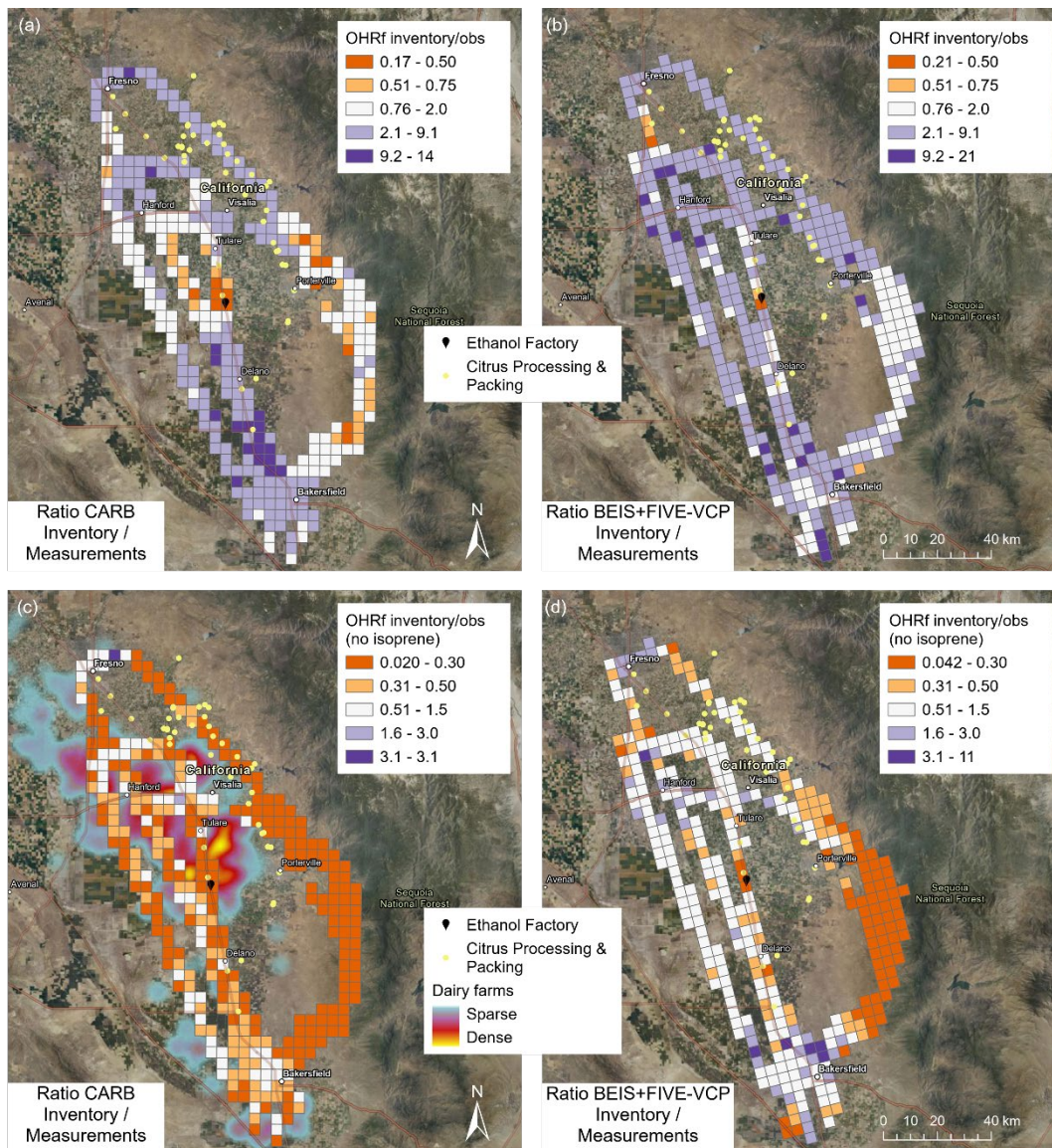
Figure 10: Inventory/observations ratio of OH reactivity emissions (OHRf) summed from all VOCs for a) CARB, b) BEIS + FIVE-VCP; and inventory/observations ratio of summed OH reactivity emissions _without_ isoprene for c) CARB and D) BEIS+FIVE-VCP. Satellite maps from NAIP Imagery via ESRI ArcGIS Pro. Orange colors indicate where the inventory is underestimating emissions, purple colors where it is overestimating.

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3.4 Temperature relationship of VOC emissions

620 The flight days were chosen so that measurements were conducted under a wide range of summer temperatures. Average flight temperatures ranged from 23 to 36°C (Table 1). In order to investigate measured and inventory fluxes dependence on temperature, the data were sorted into three different temperature bins. All data points in grid cells that were not covered in at least 6 out of 7 flights and in each temperature bin were removed. The non-temperature related point sources of the ethanol production and citrus extraction facilities were also removed from the temperature dependence analysis. Figure 11

625 shows a comparison of the observed fluxes with the two inventories grouped by those temperature bins.
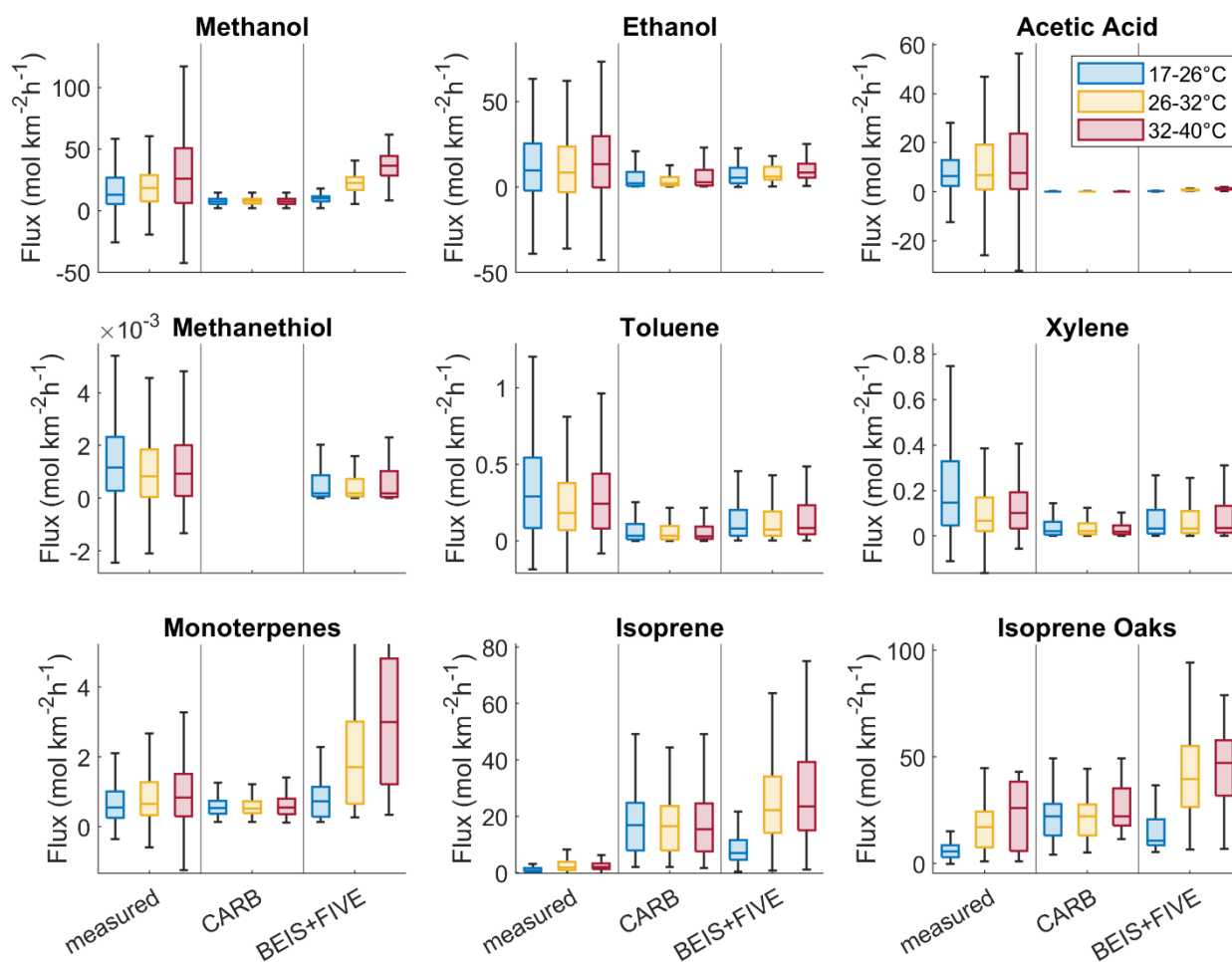
Figure 11: Fluxes of example VOCs grouped into three temperature bins, in comparison between measurements, CARB, and BEIS+FIVE-VCP inventories. All data points in grid cells that were not covered in at least 6 out of 7 flights and in each temperature bin were removed. Each of the temperature bins includes 310-366 data points (except the subset of oak shrubland
630 **data with 20-60 data points)**

Some of the VOC emissions increased with temperature, while others did not appear to have temperature relationships (Fig. 11). Methanol, ethanol, and acetic acid showed overall increased emissions with temperature in agreement with a study that reported increasing contributions of small oxygenated VOCs to OH reactivity in the San Joaquin Valley with increasing temperature (Pusede et al., 2015). This may be related to the main source of alcohols and acids here, dairy farms (Table 2), and specifically silage (Hafner et al., 2013), whose VOC emissions can volatilize more at higher temperatures as has been shown in experiments (Hafner et al., 2012). However, wind speed (Hafner et al., 2012) and management practices such as opening silage plastic covers (Heguy et al., 2016) play a role in this volatilization, which may explain why the temperature dependence is not more prominent in our observations. For methanol, the temperature dependence of agricultural crop emissions is a contributing factor, too (Gonzaga Gomez et al., 2019; Loubet et al., 2022). The CARB inventory did not reflect the observed emission increases of these OVOCs with temperature, while the BEIS+FIVE-VCP did better (although underestimating acetic acid emissions significantly).

Methanethiol also is a dairy farm emission, but it does not come from silage (Hafner et al., 2013). Its main source is expected to be the cows themselves (Shaw et al., 2007; Gierschner et al., 2019), and it was not temperature dependent (Fig. 11). Toluene and xylene did not display temperature-related patterns, potentially because their main source in the study region was traffic. When toluene emissions are mostly solvent-related, they do increase with temperature (Pfannerstill et al., submitted).

The biogenic VOC emissions – monoterpenes and isoprene – were clearly temperature related, as is known (Guenther et al., 2012). The observed monoterpene emission increase with temperature was not as strong as predicted by the BEIS + FIVE-VCP inventory, but stronger than in the CARB inventory. The isoprene emissions were clearly temperature related in the oak woodlands, where the observed flux range was in between the CARB and BEIS+FIVE-VCP predictions. There were no significant isoprene emissions observed in the rest of the study region, especially not in the croplands (Fig. 2). Therefore, the overall isoprene emission medians were low. The overall isoprene emissions predicted by the inventories, with a clear temperature increase in BEIS+FIVE-VCP, suggest an unrealistic biogenic emission source assumed as a basis of both the inventories.

4. Conclusions

This study provides unprecedented insight into the sources and sinks of volatile organic compounds in the San Joaquin Valley, including their spatial distribution and their contribution to OH reactivity. Using a landcover-informed footprint disaggregation method, we were able to attribute and quantify emissions of various sources, and to identify tracer compounds for distinct source types.

We found that developed areas, dairies, and citrus (including citrus crops and packing or processing) are important sources of anthropogenic VOCs and reactivity in the San Joaquin Valley. Citrus processing and biofuel manufacturing sources were apparently not included in the two commonly used inventories that we compared with, CARB and BEIS+FIVE-VCP.

665 Spatially resolved differences in inventory mismatches showed that the inventories generally underestimated dairy, citrus, and highway traffic emissions, but strongly overestimated isoprene emissions in the croplands. The oak woodlands in the Sierra Nevada foothills were a significant sink for oxygenated VOCs. Apart from the expected temperature dependence of biogenic VOC emissions, we also observed evidence for temperature-dependent dairy silage VOC emissions.

The results of this study provide the opportunity to improve emission inventories and have impacts for air quality modelling and policy in the San Joaquin Valley.

670

Code availability. The VOC airborne eddy covariance code and the footprint code are available online (Pfannerstill, 2022a; Zhu and Pfannerstill, 2022).

Data availability. The meteorological and VOC (flux) data used for this manuscript can be found at
675 https://csl.noaa.gov/projects/sunvex/ .

Author contribution. EP, CA, BS, RW and AB performed the field investigation, QZ, RS and CH the modeling, EP conducted the formal analysis with help from QZ and CA; AG, RC and JS conceptualized and supervised the study. AG and RC acquired funding. EP wrote the original draft of the manuscript and all authors reviewed and edited the final version.

680

Competing interests. At least one of the co-authors is a member of the editorial board of Atmospheric Chemistry and Physics. The peer-review process was guided by an independent editor, and the authors also have no other competing interests to declare.

685 **Disclaimer.** The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency. EPA does not endorse any products or commercial services mentioned in this publication.

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