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Title: Ambient measurements of monoterpenes near Cannabis cultivation facilities in Denver, Colorado

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Abstract: Colorado was one of the first US states to legalize the industrial-scale cultivation of Cannabis spp. for recreational purposes. In March 2018, there were 609 indoor Cannabis cultivation facilities (CCFs) in operation in Denver County with a recorded 550,000 mature plants (higher than 8 inches) under cultivation at any given time. It is known that cultivation of Cannabis spp. produces emissions of a group of highly reactive hydrocarbons, monoterpenes. There have been limited studies that have quantified concentrations of emitted monoterpenes in air outside CCFs. A field campaign was conducted in August 2016 in Denver County focused on six different CCF clusters near the intersection of interstate highways I-25 and I-70 during which a total of 150 ambient air samples were collected. Monoterpene mixing ratios near CCFs were $\sim 408 \pm 203$ pptv; 4-8 times higher than samples collected from a "background" site located at the Denver City Park (75 ± 25 pptv). The composition of samples taken near CCFs were dominated by d-limonene (30%), β -myrcene (20%), and α -pinene (15%), which is similar to previously reported emission factors for Cannabis spp. Since β -myrcene was only detected in leaf enclosure studies, indoor CCF observations and ambient samples near CCFs and not detected at a background site, this particular compound could be used as a tracer for the Denver Cannabis production industry. The monoterpene speciation in ambient measurements varied across Denver suggesting differences in emissions between different Cannabis spp., or different growth stages. Given the observed variabilities in both composition and emission rates, it is critical for the accuracy of emissions inventories to develop strain specific emission factors. This information, coupled with detailed information on each CCF, would greatly reduce the uncertainties currently present in monoterpene emission estimates for the Cannabis industry and its potential impact on air quality.

Research Data Related to this Submission

Title: Data for: Ambient measurements of monoterpenes near Cannabis cultivation facilities in Denver, Colorado
Repository: Mendeley Data

<https://data.mendeley.com/datasets/z7h7y3m28x/draft?a=5b50fb78-cff7-4ede-bb1d-c648c53fe407>



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Dear Editor-in-Chief:

Please find attached a new manuscript entitled "Ambient measurements of monoterpenes near *Cannabis spp.* cultivation facilities in Denver, Colorado" submitted for publication in *Atmospheric environment*.

The legal commercialization of marijuana for recreational and medical use has effectively created a new and almost unregulated cultivation industry. In the Denver city limits alone there are now more than 600 registered *Cannabis spp.* cultivation facilities (CCFs) with total 550,000 *Cannabis spp.* plants for recreational and medical use, mostly housed in commercial warehouse premises. Measurements inside and outdoor of CCFs have found significant concentrations of highly reactive terpenes that, when released in the atmosphere, could lead to ozone and particulate matter formation. There are limit studies, however, that have completed an ambient measurement of monoterpenes near CCFs and proved that *Cannabis spp.* industry can increase the ambient mixing ratio of biogenic volatile organic compounds (BVOCs).

This work produces ambient measurement data of monoterpenes in Denver County and found that monoterpene mixing ratios near CCFs are 4-8 times higher than were measured at a background site. The BVOC emissions from CCFs has implications on attaining the ozone standard in Denver county. This industry emissions are important not only for Colorado, but also for other states in which the commercial cultivation and sale of *Cannabis spp.* plants has been legalized. Given that the legalization of recreational cannabis in urban areas is a hotly debated topic, our study will be of great interest to a very wide audience. I hope you would consider this manuscript for publication in *Atmospheric Environment*. I have submitted the manuscript via the website.

Suggested reviewers include:

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Please contact me if there are any questions.

Sincerely yours,

A handwritten signature in black ink, appearing to read 'William Vizuite', with a long horizontal flourish extending to the right.

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1 Ambient measurements of monoterpenes near *Cannabis* cultivation 2 facilities in Denver, Colorado.

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14

15 Abstract

16 Colorado was one of the first US states to legalize the industrial-scale cultivation of
17 *Cannabis spp.* for recreational purposes. In March 2018, there were 609 indoor *Cannabis*
18 cultivation facilities (CCFs) in operation in Denver County with a recorded 550,000 mature
19 plants (higher than 8 inches) under cultivation at any given time. It is known that cultivation
20 of *Cannabis spp.* produces emissions of a group of highly reactive hydrocarbons,
21 monoterpenes. There have been limited studies that have quantified mixing ratios of emitted
22 monoterpenes in air outside CCFs. A field campaign was conducted in August 2016 in
23 Denver County focused on six different CCF clusters near the intersection of interstate
24 highways I-25 and I-70 during which a total of 150 ambient air samples were collected.
25 Monoterpene mixing ratios near CCFs were $\sim 408 \pm 203$ pptv; 4-8 times higher than samples
26 collected from a “background” site located at the Denver City Park (75 ± 25 pptv). The
27 composition of samples taken near CCFs were dominated by d-limonene (30%), β -myrcene
28 (20%), and α -pinene (15%), which is similar to previously reported emission factors for
29 *Cannabis spp.* Since β -myrcene was only detected in leaf enclosure studies, indoor CCF
30 observations and ambient samples near CCFs and not detected at a background site, this
31 particular compound could be used as a tracer for the Denver *Cannabis* production industry.
32 The monoterpene speciation in ambient measurements varied across Denver suggesting
33 differences in emissions between different *Cannabis spp.*, or different growth stages. Given
34 the observed variabilities in both composition and emission rates, it is critical for the
35 accuracy of emissions inventories to develop strain specific emission factors. This
36 information, coupled with detailed information on each CCF, would greatly reduce the
37 uncertainties currently present in monoterpene emission estimates for the *Cannabis* industry
38 and its potential impact on air quality.

39

40 **Introduction**

41 On January 1st 2014, the cultivation, processing, and sale of *Cannabis* for recreational
42 use became legal in the state of Colorado. There were 360 facilities growing *Cannabis* for
43 medical purposes in Denver County at the end of 2013. By 2018 the industry expanded to
44 608 medical and recreational *Cannabis* Cultivation Facilities (CCFs) in Denver County
45 (CDOR, 2018). These CCFs are all registered and licensed via the Colorado Department of
46 Revenue (DOR), with a recorded total of >550,000 mature (>8 inches) *Cannabis* plants under
47 cultivation in Denver County at any given time (Hartman et al., 2018). These new CCFs tend
48 to be clustered around major highways, which offer ease of access for incoming raw
49 materials and to the markets for end products. Where CCFs abut residential neighbourhoods,
50 complaints to Colorado Department of Public Health and Environment (CDPHE) regarding
51 odour nuisance have soared (Murray, 2016; Rusch, 2016) as the volatile compounds
52 responsible for the characteristic smell of *Cannabis* are released and dispersed from CCF
53 ventilation systems.

54 There has historically been considerable interest in the volatile organic compounds
55 (VOCs) found in *Cannabis spp.* and its products, and many previous studies have measured
56 these compounds in dried plant material and essential oils (Hood et al., 1973; Turner et al.,
57 1980; Ross and ElSohly, 1996; Rice and Koziel, 2015). Over 100 different compounds have
58 been identified in the headspace above these materials; the most common of which are
59 monoterpenes (C₁₀H₁₆) that include: α -pinene, β -pinene, β -myrcene, d-limonene, and *cis*-
60 ocimene; sesquiterpenes (C₁₅H₂₄) including β -caryophyllene, α -farnesene, and β -humulene;
61 and the terpene alcohols (C₁₀H₁₈O) such as linalool, borneol, and terpineol (Hood et al.,
62 1973; Turner et al., 1980; Ross and ElSohly, 1996; McPartland and Russo, 2001; Rice and
63 Koziel, 2015). It has also been reported that the more odiferous (such as nonanal, decanol,
64 cymene, and benzaldehyde) compounds need only be present in low mixing ratios, but to be
65 discernible to humans and animals (Rice and Koziel, 2015).

66 Only a handful of studies, however, have investigated emissions from growing
67 *Cannabis spp.* plants. Three of these measured mixing ratios of volatiles inside growing and
68 processing rooms in cultivation facilities. The first study took place in small (illicit)
69 operations with ~100 plants per room found mixing ratios of monoterpenes as high as 100
70 ppbv (Martynty et al., 2013), i.e. over an order of magnitude higher than levels observed in
71 high-emitting natural ecosystems such as forests (Ortega et al., 2014; Yanez-Serrano et al.,
72 2015; Acton et al., 2016; Emmerson et al., 2016; Yanez-Serrano et al., 2018). The second

73 study reported average monoterpene levels in CCF budding and flowering rooms to be ~360
74 ppbv (Southwell et al., 2017). Most recently, researchers measured monoterpene mixing
75 ratios between 20 ppbv and 1,000 ppbv inside four CCFs in California and Nevada
76 (Samburova et al., 2019).

77 Wang et al. (2019a) measured emissions of volatiles directly from individual live plants
78 of four different *Cannabis spp.* strains enclosed in chambers. The authors found that although
79 the compounds d-limonene, and β -myrcene were the most commonly emitted compounds
80 from each strain, the relative emission rates varied between strains. Total monoterpene
81 emission rates from plants in the vegetative stage also varied by strain and had a range of 4.9-
82 8.7 $\mu\text{gC dwg}^{-1} \text{h}^{-1}$ (dwg is dry weight in grams). This is actually higher than most pine trees
83 in Colorado (Guenther et al., 1995; Guenther et al., 2006; Ortega and Helmig, 2008; Ortega
84 et al., 2008).

85 In subsequent work, Wang et al. (Wang et al., 2019a) developed a monoterpene
86 emissions inventory of CCFs across Colorado and estimated that total emissions could be as
87 high as 362 tons year⁻¹ for Denver county alone. There is considerable uncertainty in this
88 estimate as assumptions were made in the number of plants per facility (0-50,000), dry
89 weights per plant (1-2500 g) and emission capacity (10-100 $\mu\text{g dwg}^{-1} \text{h}^{-1}$). Prior to the
90 introduction of this industry, it was estimated that Denver County had total emissions of
91 biogenic VOCs (BVOCs) of ~265 tons year⁻¹ (IWDW, 2017). Thus, the addition of the
92 *Cannabis* industry could increase BVOC emissions by up to 362 (+136%) tons year⁻¹ in
93 Denver County (Wang et al., 2019a). Monoterpenes are highly reactive; their atmospheric
94 lifetimes range from seconds to hours and the products of their oxidation reactions include
95 secondary air pollutants such as ground-level ozone and particulate matter (PM) (Seinfeld
96 and Pandis, 2006). When Wang et al. (Wang et al., 2019a) included monoterpene emissions
97 from CCFs in an air quality model in the configuration used by the State of Colorado and
98 EPA, they demonstrated these emissions were sufficient to increase hourly average ozone
99 levels by as much as 1 ppbv per 1000 tons per year of monoterpenes released from CCFs.

100 Given the considerable uncertainties in CCF emissions estimates and the importance of
101 understanding their impacts on local air quality, we carried out a series of ambient sampling
102 studies in the vicinity of CCFs in Denver County, home to 42% of CCFs and 50% of
103 *Cannabis* plants in the state of Colorado (CDOR, 2018). These experiments were designed to
104 determine the composition of monoterpenes released into the atmosphere from active CCFs
105 to constrain model predictions (Wang et al., 2019a) and reduce uncertainties associated with

106 emission factors (Wang et al., 2019b). This study focused on Park Hill, River North Art
107 District, Sunnyside, Lincoln Park and Northeast areas across Denver County each of which
108 contain high numbers of CCFs.

109

110 **Methods**

111 **2.1 Sampling**

112 Ambient air samples were collected onto sorbent cartridges from various locations in
113 the Denver urban area during August 2016 (see Table 1 and Fig. 1). The stainless-steel
114 cartridges (from Markes International, Llantrisant, UK) were loaded with ~400 mg of Tenax
115 TA and Carbograph 5TD in series, to optimise the capture of terpenoids. Air was drawn into
116 the cartridges using small battery-powered pumps, which were placed on a portable platform
117 ~1m above the ground. To reduce the effect of losses due to ozone on the adsorbent surfaces,
118 filters impregnated with potassium iodide were used immediately upstream of the sorbent
119 tubes (Pollmann et al., 2005). Two samples were simultaneously collected at each sampling
120 point at approximately hourly intervals, using one low- and one high-flowrate of ~140 and
121 ~300 cm³ min⁻¹ respectively. Pump flow rates (used to calculate sample volume) were
122 checked periodically during the campaign period and found to remain stable within 1 ml min⁻¹
123 ¹. Before sampling, clean cartridge tubes were kept capped at both ends and stored in sealed
124 containers. Once used, they were re-capped, transferred to a second sealed container, and
125 kept refrigerated until analysis. The total time from collection to analysis was no longer than
126 one week for any sample. This methodology is consistent with the EPA's TO-17 sampling
127 protocol for toxic organic compounds in ambient air by cartridges (USEPA, 1999).

128

129 **2.2 Sampling locations**

130 Sampling points were selected based on locations of registered CCFs (CDOR, 2019),
131 with latitudes and longitudes confirmed in the field using handheld GPS. Figure 1 shows the
132 clusters of CCFs targeted in this study, the 6 sampling locations and the background (BG)
133 site. Details pertaining to sampling dates, times, and locations can be found in Table 1 and
134 S1.

135 All experiments were conducted in Denver County near the I-70 highway and to the
136 northwest, west, and northeast of central Denver as shown in Fig. 1. Selection of the CCF
137 sampling sites were determined by ease of access to sufficient radial locations at which to
138 collect samples. In experiments 1-3, paired samples were collected radiating in upwind and
139 downwind directions from a central CCF. Depending on the street layout, sampling points

140 were either aligned in a north-south or southwest-northeast direction to align as closely as
141 possible with the prevailing wind. Sampling points were spaced ~150-200 m apart, and each
142 was visited only once. Experiments 4, 5, and BG (background) consisted of the collection of
143 paired samples at a single point, at hourly intervals over an 8-hour period (roughly 08:00-
144 16:00 Local Time, LT). Experiment BG was conducted at Denver City Park (104.943°W,
145 39.751°N) where the nearest CCF was 2 km away.

146 Experiment 6 focused on the Park Hill area of Denver County. In this experiment
147 samples were taken at two points near CCFs (19 m and 103 m) just to the north of the Park
148 Hill residential area, and at two further points within it (433 m and 655 m). Sampling
149 alternated between these sites resulting in 2-hourly, rather than hourly, samples at each.
150 Experiment 6 was motivated by the high number of odour complaints from local Park Hill
151 residents (Murray, 2016; Rusch, 2016).

152

153 **2.3 Analysis method and instrument**

154 Cartridges containing the ambient air samples were thermally desorbed and analyzed
155 by a Gas Chromatograph (GC) (Agilent Technologies, model 7890A) coupled to both a Mass
156 Spectrometer (MS) (model 5975C) and Flame Ionization Detector (FID), following published
157 protocols (Harley et al., 2014). Thermal desorption (TD) was achieved by heating the tubes to
158 275°C in a UNITY TD (model UNITY, Markes International, Llantrisant, UK). The analytes
159 were then focused onto a small cryotrap, which was then rapidly heated to 300 °C and
160 injected on to the GC. Helium was used as the carrier gas in the capillary column (RESTEK
161 Rtx-5 model 10224, 30 m, 0.32 mm, ID, 0.25 µm film thickness). The GC oven temperature
162 cycle started at 35 °C and was held at that temperature for 1 minute, subsequently increasing
163 at 10 °C per minute to 260 °C for each cartridge. Ion fragments and retention time on the
164 column were detected and recorded by MS and FID to optimize capability to distinguish
165 different species present in the sample. To account for changes in MS sensitivity and
166 potential losses during the adsorption and desorption processes, 2 ml of an internal standard
167 (decahydronaphthalene (DHN)), was added to each GC sample. Additional cartridges
168 containing 100 scc (130 ml at local atmospheric pressure) of a camphene (214.6 ppbv) and
169 isoprene (335 ppbv) gas standard were processed with each experiment for calibration
170 purposes. VOC mixing ratios in the sample were deduced by analyzing peak areas and
171 comparing them against those recorded for either camphene ($m/z = 93$) or isoprene ($m/z = 67$)
172 depending on m/z of the detected VOC and correcting for sample volume for each sample.

173 The analysis method and calculations followed the protocol developed by Harley et al.
174 (2014) for separation and quantification of low-mixing ratio VOCs that elute at similar times.
175 The retention time and major ion fragments for specific VOCs taken from the National
176 Institute of Standards and Technology (NIST) database and a previous study (Harley et al.,
177 2014) were used to distinguish the individual monoterpenes (Table S2). The lower detection
178 limits (LDL) of GC-MS samples are taken to be three standard deviations of blank values.
179 The LDL of terpenes is 4 pptv for a 7 liters samples size. Below these limits, a non-detected
180 (ND) symbol is reported in the results.

181 Particular attention was given to distinguishing between d-limonene and β -
182 phellandrene, which co-elute. Following the procedure of Harley et al. (2014), a second
183 major d-limonene peak at $m/z=68$ was used to calculate the mixing ratio of d-limonene and
184 thus accurately determine the mixing ratios of each compound. Fragment ion signals of
185 isoprene ($m/z = 67$) and sesquiterpenes ($m/z = 93$ and 133) were also detected in samples by
186 GC-MS, but are not reported here. The isoprene signal at $m/z = 67$ has a strong co-elution
187 with other (anthropogenic) VOCs at almost identical retention times, and the sesquiterpene
188 fragment signals were not of sufficient magnitude to identify individual sesquiterpenes from
189 the NIST database. Thus, this study only reports specific monoterpene mixing ratios and
190 composition in the samples.

191 The results show no apparent breakthrough effect in the high-flowrate samples with a
192 difference in total monoterpene mixing ratios $< \pm 10\%$ between the two pump flowrates. All
193 results presented here use only the low-flowrate pump data (N=74) to avoid system error. In
194 one single case, the low-flowrate cartridge failed to capture the BVOCs, so the high flowrate
195 data was used.

196

197 **2.4 Meteorological Data and back-trajectory estimate**

198 Meteorological data for each sampling period were obtained from the National
199 Weather Service (NWS) and Road/Runway Weather Information System (RWIS) networks
200 (Utah, 2019). Wind speed, wind direction, and temperature data from the nearest
201 meteorological station were used to identify the up-wind and down-wind directions and the
202 source locations for the samples, and to estimate back-trajectories. A full list of available
203 weather stations in the vicinity is given in Table S3.

204 Due to the short life time of monoterpenes in the urban area, back-trajectories are only
205 calculated for 3 hours duration using the approximation given in Eq. 1 (Stohl, 1998;

206 Walmsley and Mailhot, 2010). At each time step, the current air mass location x and y and the
207 u and v downwind and crosswind windspeed vectors from the nearest meteorological site at
208 time t_0 are used to calculate the previous location x' and y' at time $t_0 - \Delta t$. Here, the timestep Δt
209 is 5 minutes. The u and v vectors are calculated from Eq. 2 using the wind direction (wwd)
210 and wind speed (ws) data from the closest weather station in time to the sampling location.

$$211 \begin{cases} x' = x - u(x, y, t_0) \times \Delta t \\ y' = y - v(x, y, t_0) \times \Delta t \end{cases} \quad \text{Eq.1}$$

$$212 \begin{cases} u = ws(x, y, t_0) \times \cos(270^\circ - wwd(x, y, t_0)) \\ v = ws(x, y, t_0) \times \sin(270^\circ - wwd(x, y, t_0)) \end{cases} \quad \text{Eq.2}$$

213

214 **3 Results**

215 **3.1 The ambient monoterpenes mixing ratios and CCFs**

216 Table S1 shows the location, sample duration and mixing ratios (pptv) for all
217 individual monoterpenes detected and the total amount of monoterpenes identified for each
218 sample. Total monoterpene mixing ratios ranged from 44-926 pptv, with the lowest levels
219 found at the BG site (average of 75 ± 25 pptv from 8 samples). Excluding this site, the average
220 monoterpene mixing ratios were 408 ± 203 pptv (from 67 samples). Figure 2 shows that
221 morning (6:00-11:00 LT) monoterpene mixing ratios are strongly correlated with the distance
222 to the closest upwind CCF ($R^2 = 0.78$, p -value $\ll 0.001$, where the p -value is derived from
223 the null hypothesis in F-test the probability of no relationship between the two variables that
224 we observed). As expected from Gaussian plume dispersion models, mixing ratios decrease
225 as the square of the distance from the source increases. As shown in Fig 2, mixing ratios at
226 the BG site (2,260 m from the nearest CCF) varied between 66-116 pptv. By contrast, mixing
227 ratios >500 pptv, i.e. approximately 5 times that of BG mixing ratios, were found at distances
228 of 5-100 m downwind of the closest CCF. At a distance of 5 m, the average and standard
229 deviation of mixing ratio were 632 ± 163 pptv (N=5); at 12 m, these were 626 ± 215 pptv (N=8),
230 and at 100-200 m, these were 392 ± 104 pptv (N=10). The relatively high standard deviations
231 are reflections of different emission rates from the different CCFs and the number of
232 additional CCFs that lie on the back-trajectory and thus contribute to the monoterpenes
233 sampled at a particular location.

234 Experiment 2, located at the River North Art District, was conducted near an isolated
235 CCF with no other CCFs within 1.5 km. Two samples were taken together simultaneously
236 every 30 minutes from 6:15 to 9:00 LT at 8 different locations resulting in a total of 16
237 samples. 6 of these locations were either directly upwind or downwind of the CCF. Figure 3A

238 shows the sampling time, distance from the CCF (marked by a green diamond) and total
239 monoterpene mixing ratios for each of these 6 sample locations. During this experiment, the
240 windspeed ranged from 0.9-2.6 m s⁻¹ (average of 1.5 m s⁻¹) and the average wind direction
241 (211°±37°) is indicated by the blue arrow. As expected, total monoterpene mixing ratios were
242 highest at 5 m downwind of the CCF peaking at 823 ppt and decreased with downwind
243 distance (682 ppt at 107 m; 534 ppt at 239 m). These levels are ~4-7.5 times higher than the
244 maximum recorded at the BG site (116 pptv). The mixing ratios gradient upwind of the CCF
245 was 410-550 ppt over a similar distance. During the sampling period, the wind direction is
246 consistent and wind speed is slow. Thus, it is likely that emissions from this CCF also
247 diffused upwind of the CCF.

248 Figure 3B shows the monoterpene composition at the closest (5 m and -31 m) and
249 farthest (239 m and -282 m) distances of upwind and downwind sampling locations shown in
250 Fig. 3A. If the sample taken at 5 m distance from the CCF is representative of the emission
251 flux, it is evident that the fraction of β-myrcene decreases rapidly with distance. At the same
252 time, α- and β-pinene, and to a lesser extent camphene and p-cymene comprise more of the
253 total fraction of monoterpenes. This is consistent with the relative reactivities of the
254 monoterpenes with the highly reactive β-myrcene oxidizing far more rapidly than the more
255 stable compounds such as α- and β-pinene. The atmospheric lifetime of α-pinene is ~5× that
256 of β-myrcene against both the OH radical and ozone (Hites and Turner, 2009; Hens et al.,
257 2014; Yanez-Serrano et al., 2018).

258 The experiment times in this study varied from 6:00-9:00 LT or 8:00-15:00 LT, but
259 measurements collected between 8:00-9:00 LT are available for all experiments. At this hour,
260 the samples are least impacted by photochemistry losses that occur later in the day and by
261 dilution with the mid-day development of the planetary boundary layer (PBL). The PBL
262 heights for all experiments were estimated by the HYSPLIT model with High-Resolution
263 Rapid Refresh (HRRR) meteorological data (NOAA, 2019) and showed in Fig. S1. Although
264 the modeled PBL in the BG experiment is higher than others at 8:00-9:00 LT, the lower PBL
265 from 10:00-15:00 LT cannot explain the lowest monoterpene mixing ratios detected in BG
266 experiment. Therefore, the PBL in different experiments is a weaker force than other factors.
267 The distance to emission source, wind directions, and photochemistry dominate the ambient
268 monoterpene mixing ratios in our samples and provided an opportunity to investigate the
269 emission source strengths of CCFs upwind of all experimental locations. Figure 4 shows the
270 average mixing ratios for all experimental sites using only data from these times. Taking

271 wind speed and direction data from the closest meteorological site, we estimated 3-hour back
272 trajectories at 8:00, 8:30 and 9:00 LT for each of these sites. These are shown in Fig. S2. The
273 back-trajectory paths were analyzed to identify known CCFs located along the pathway that
274 therefore contributed to the air samples taken. The average number of CCFs along each back-
275 trajectory are indicated by grey bars shown in Fig. 4. The 3-hour back-trajectories from the
276 BG site (Fig. S2) do not pass over any CCFs, providing confidence that this measurement is
277 not influenced by CCF emissions. The wind direction data from the Denver International
278 Airport (DIA) were consistent with the results of the back-trajectories. In table S4, the
279 meteorological data from DIA also showed that the wind direction in experiments 1-6 were
280 mainly from the southwest and during the BG experiment it was mainly from the east.

281 As the number of *Cannabis spp.* plants under cultivation in individual CCFs is not
282 publicly available, the relative source strength of each CCF could not be determined.
283 Nevertheless, there was a strong correlation between the maximum measured mixing ratios
284 (of 403-864 pptv) with the number of contributing CCFs in the northern region of Fig. 4.
285 These mixing ratios are ~3-8 times higher than those at the BG site. Interestingly, experiment
286 5 had similar total monoterpene mixing ratios as the other experiments, but appeared to be
287 influenced by about 30 CCFs. This could be the result of the number, strain, or growth stage
288 of the plants in those CCFs, or the activities or venting practices at the time of the
289 measurement.

290

291 **3.2 Monoterpene composition**

292 Figure 4 shows the composition of monoterpenes based on the average of
293 measurements taken from 8:00-9:00 LT at each experimental site within 200 m of the CCF.
294 Compared to the BG site, the samples taken near CCF clusters had higher proportions of d-
295 limonene (18-35%), α -pinene (16-32%), p-cymene (6-16%) and 3-carene (4-12%), but
296 fractions of β -pinene and eucalyptol were lower. The dominant monoterpene, however,
297 differed between the CCF sites with α - and β -pinene (up to 27% and 17%) dominating in the
298 western and north-western part of the Denver County (experiments 1 and 5), and β -myrcene
299 and d-limonene (up to 20% and 33%) in northern of the Denver County (experiments 2 and
300 4). Experiment 6 at north-eastern part of the city also showed a relatively large proportion of
301 sabinene (12%), a minor contribution elsewhere. The differences in terpene compositions
302 associated with the different CCF cluster locations suggest a mixture of *Cannabis spp.* strains
303 under cultivation across Denver. Thujene, camphene, β -myrcene, and 3-carene were

304 observed in the vicinity of CCFs, but were below detection limits at the BG site, suggesting
305 that the monoterpene composition from the *Cannabis* industry in Denver differs from the
306 other local vegetation, such as landscaping, lawns, trees and gardens.

307 Figure 5(A) shows the composition of monoterpene and terpenoids emissions
308 measured by (Wang et al., 2019b) from four *Cannabis spp.* strains: Critical Mass (CM),
309 Lemon Wheel (LW), Elephant Purple (EP), and Rockstar Kush (RK). The dominant
310 compounds among these strains were β -myrcene (20-60%), eucalyptol (18-40%) and d-
311 limonene (3%-10%). Figure 5(B) shows the same data as Fig 4, but normalized to percentage
312 (%) for comparison. Comparing the compositions of ambient air and enclosure samples, it
313 appears that β -myrcene is ubiquitous between strains but absent from background air in
314 Denver (BG site on Fig. 5(B)) and may therefore be exclusive to *Cannabis* in an urban
315 context. Interestingly, the proportion of sabinene measured at experiment 6 was similar to
316 that from the Critical Mass strain (Wang et al. 2019b).

317 Figure 5 (C) presents monoterpene compositions measured in indoor grow rooms of
318 four different CCFs in the US states of California and Nevada (Samburova et al., 2019).
319 Their results indicate that different monoterpene compounds dominate in each of the CCFs:
320 β -myrcene (CCF 1: 55% and 3: 42%), β -pinene (CCF 2: 68%), and d-limonene (CCF 4: 58%)
321 as the composition of BVOCs emitted from *Cannabis spp.* varies by strain, growth stage,
322 growth environment and agronomic practice. This result may explain the reason for the lack
323 of eucalyptol found in the ambient environment despite being seen in direct emissions from
324 all four strains tested by Wang et al. (2019b). β -myrcene was detected in all samples from
325 *Cannabis spp.* Fig. 5(A)-(C) show that γ -terpinene and terpinolene were present in the direct
326 emissions sampled from *Cannabis spp.* plants and from grow rooms, but were not detected in
327 the ambient measurements.

328 Figure 6 show the hourly fractional monoterpene composition for experiments 4-6,
329 and at the BG site from 08:00-15:00 LT. Total mixing ratios are reported at the top of each
330 bar. Peak mixing ratios were recorded at 09:00 LT at all experiments (10:00 LT at
331 experiment 6 which was only sampled 2-hourly). Mixing ratios generally fall in the afternoon
332 across the experiments due to increasing PBL height and photochemical loss. There is an
333 anomaly to this pattern as seen in experiment 5 where secondary peaks occur at 12:00 and
334 14:00 LT. It may be that the relatively constant mixing ratios seen at experiment 5 were due
335 to the close proximity of the sampling to the ventilation outlet of the CCF (~5 m) Inside
336 CCFs, the environment is typically maintained at constant conditions of light, temperature

337 and CO₂ concentrations, but other activities such as plant movement, harvesting, trimming
338 and air handling can contribute to how emissions are vented into the ambient atmosphere.

339 The monoterpene fractional compositions of experiments 4 and 5 also changed with
340 time. In experiment 5, the fraction of β -myrcene was 10% at 8:00 LT, increased to 62% at
341 noon, and then decreased to 45% by 15:00 LT. Experiment 4 showed a similar pattern in that
342 d-limonene and β -myrcene were low in the morning, but increased to their peak mixing ratios
343 at noon. This mid-day increase at noon cannot be explained by photochemistry, as β -myrcene
344 and d-limonene have higher rate constants (shorter lifetimes) than α -pinene and β -pinene at
345 ambient conditions. Thus, this could be the result of compositional changes at the emission
346 source. Some previous laboratory and field studies have shown that the monoterpene
347 emission fraction from a plant are known to be environmental condition dependent, such as
348 light, temperature and insect (Sharkey et al., 1991; Staudt et al., 1997; Jones et al., 2011;
349 Yanez-Serrano et al., 2018), but the *Cannabis* plants in this study is unknown.

350

351 **3.3 Comparison with air quality model predictions**

352 Figure 7A shows the measured hourly monoterpene mixing ratios for experiments 1-6
353 between 06:00-15:00 LT with the BG samples (taken between 08:00-15:00 LT) shown as
354 black dots. In the early morning hours, from 6:00-9:00 LT, the median mixing ratios of total
355 monoterpenes were 444 to 505 pptv, with an inter quartile range (IQR; Q3-Q1) of 135 to 282
356 pptv (6:00-9:00 LT). From 10:00 LT, monoterpene mixing ratios decreased initially due to
357 the dilution effect of the evolution of the PBL and then from the increase in photochemical
358 loss rates. By contrast, experiment 5 exhibited two peaks (668 and 680 pptv at 12:00-13:00
359 LT and 14:00-15:00 LT respectively), most likely due to the close proximity of the sampling
360 point to the CCF ventilation outlet preventing chemical loss or dilution prior to sampling.

361 We previously reported monoterpene mixing ratios across Denver County simulated
362 by the Western Air Quality Study model (ENVIRON and AlpineGeophysics, 2017) when
363 estimated CCF emissions were included (Wang et al., 2019a). Although the modeling episode
364 is in 2011 that covers a different period than this study in 2016, it still provides a qualitative
365 comparison between predictions from an estimated inventory and real-world measurements
366 providing context for that inventory. Figure 7B and 7C compare modeled hourly mixing
367 ratios in August (with and without CCF emissions) with those measured here. As shown in
368 Fig. 7B, the median mixing ratio without CCF emissions was 88 pptv at 06:00 LT and 12
369 pptv at 12:00 LT across all relevant grid cells, which is similar to the data from the BG site

370 (median = 67.5 and IQR = 34.5). When Denver CCF emissions of 362 tons year⁻¹ were
371 included in the model (Fig. 7C), the median rose to 511 pptv at 06:00 LT and 40 pptv at
372 12:00 LT, very close to the average of the samples collected at CCF sites at 06:00 LT (505
373 pptv) although somewhat lower than observations at 12:00 LT (165 pptv).

374

375 **4 Conclusion**

376 This is the first study to provide evidence of elevated outdoor mixing ratios of
377 monoterpenes in the vicinity of CCFs in Denver where the *Cannabis* industry is legalized.
378 The results recorded total monoterpene mixing ratios are ~4-8 times higher around CCFs than
379 observed at a background location. Monoterpene mixing ratios decreased ~1.5 pptv per meter
380 distance away from each individual CCF. While the total number of CCFs within 500 m
381 strongly correlated with measured mixing ratios, some clusters of CCFs had higher than
382 expected mixing ratios in the vicinity. This is likely due to differences in emission source
383 strengths due to differences in the number, strain and growth stage of plants, and crop
384 management activities taking place in each CCF. This information is currently unavailable to
385 the research community and could not be used in this study. Analysis of monoterpene
386 composition showed geographic variability suggesting that different clusters of CCFs may
387 have different monoterpene emission profiles due to variability in strains or life cycle. One
388 monoterpene, β -myrcene, was identified in samples taken downwind of CCFs. But this
389 compound was not detected in background measurements at a site remote from CCFs. Since
390 β -myrcene and its oxidized products have been measured in leaf enclosure studies and inside
391 CCFs, it could be a potential tracer for CCF emissions in the ambient environment (Boge et
392 al., 2013).

393 The sampling studies reported here were limited in both time and space. Future
394 campaigns across more sample locations and during different seasons would be beneficial to
395 better understanding the impact CCF emissions have on terpene mixing ratios in Denver. Our
396 study, however, clearly demonstrates that emissions from growing *Cannabis spp.* are
397 detectable at measurable mixing ratios at distances from CCFs, suggesting this single
398 industry strongly influences the composition of the urban atmosphere in Denver. Given the
399 fairly unique “signature” of compounds from *Cannabis spp.* and the proximity to clusters of
400 CCFs we are confident that the VOCs we sampled did indeed originate from CCFs.

401 Our findings suggest that the introduction and rapid growth of previously niche
402 industries (e.g. artisan coffee roasters, craft breweries, etc that are highly odiferous) can also

403 be expected to have similar impacts. Previous studies have also shown the usage of volatile
404 chemical products (VCPs), such as acetone, chlorinated hydrocarbons, monoterpene and
405 aldehydes, in household cleaning and personal care products affect VOC mixing ratios in
406 urban areas (McDonald et al., 2018). McDonald et.al showed that monoterpenes mixing ratio
407 in indoors measurement in Los Angeles was ~7-9 ppb, which is higher than in forest in
408 Colorado (Ortega et al., 2014) but lower than indoor CCF (20-1,000 ppb) (Samburova et al.,
409 2019). Another urban ambient measurement study in New York City indicated that a spike
410 signals of monoterpene and other VCPs in excess of 3.5 ppb (Shah et al., 2019). Therefore,
411 we suggest an urgent need for more studies and better understanding, already in place for
412 existing traditional industries and products, to protect urban populations from increasing
413 exposure to these chemicals and their secondary air pollutants.

414

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427

Table 1. The summary of sampling dates, duration, number of sampling points and distance to the closest meteorological site.

Experiment	Date	Sample duration (minutes)	Sample count	Numbers of sampling locations (sites)	Distance to Meteorological site	Meteorological Site Identification
1	Aug 2, 2016 6:10-12:10 LT	55	20	10	1.7 km	CO144
2	Aug 11, 2016 6:15-9:00 LT	30	16	8	2.8 km	CO144
3	Aug 15, 2016 6:10-9:00 LT	30	16	8	4 km	AENC2, CO011
4	Aug 10, 2016 7:35-16:10 LT	50	32	2	1.7 km	CO003
5	Aug 17, 2016 7:45-15:35 LT	50	16	1	1.5 km	CO006
6	Aug 3, 2016 7:54-16:13 LT	50	34	4	1.7 km	CO003
BG	Aug 19, 2016 7:45-15:20 LT	50	16	1	2.6 km	CO003

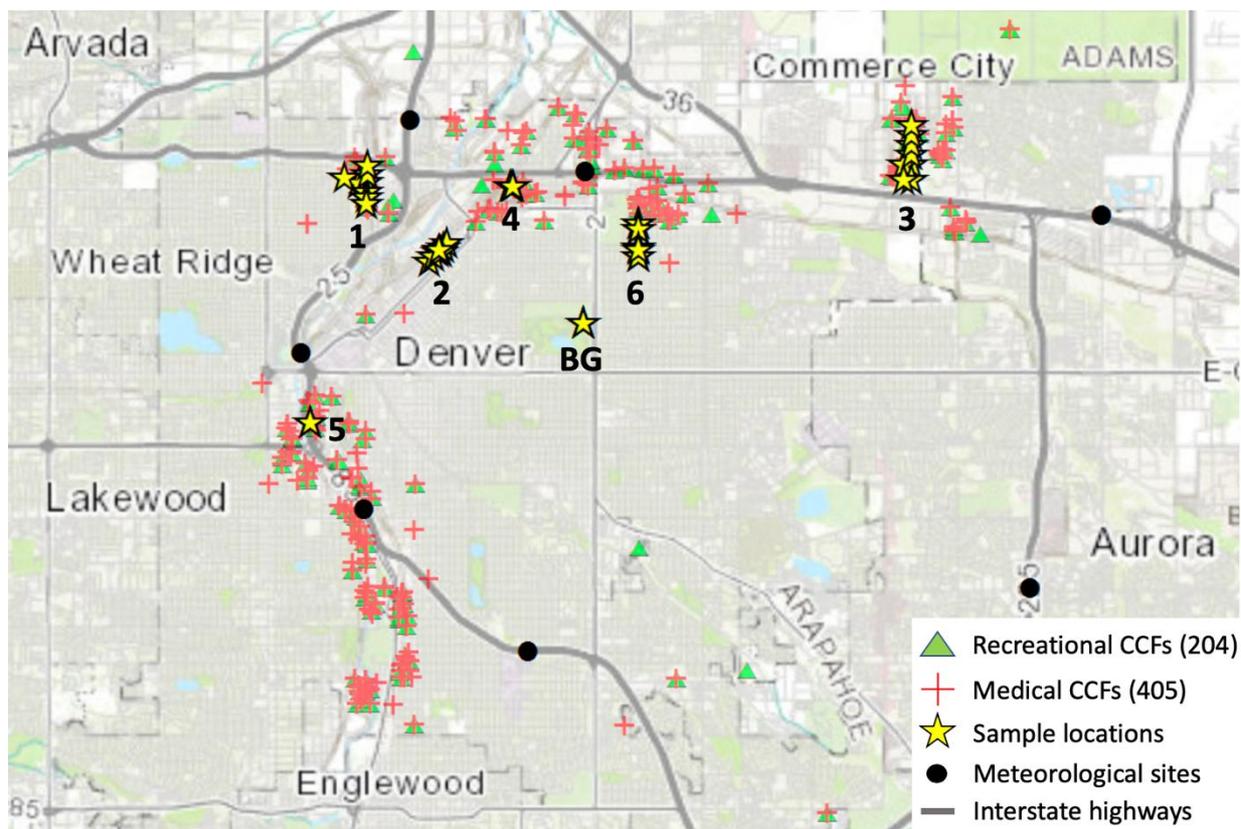


Fig. 1 Map of Denver, CO showing sampling locations listed in Table 1 (yellow stars), medical *cannabis* cultivational facilities (CCFs, red crosses), recreational CCFs (green triangles), and meteorological sites (black dots). The total number of CCFs in Denver County are given in parentheses. The base map was supplied by Esri (Esri, 2013).

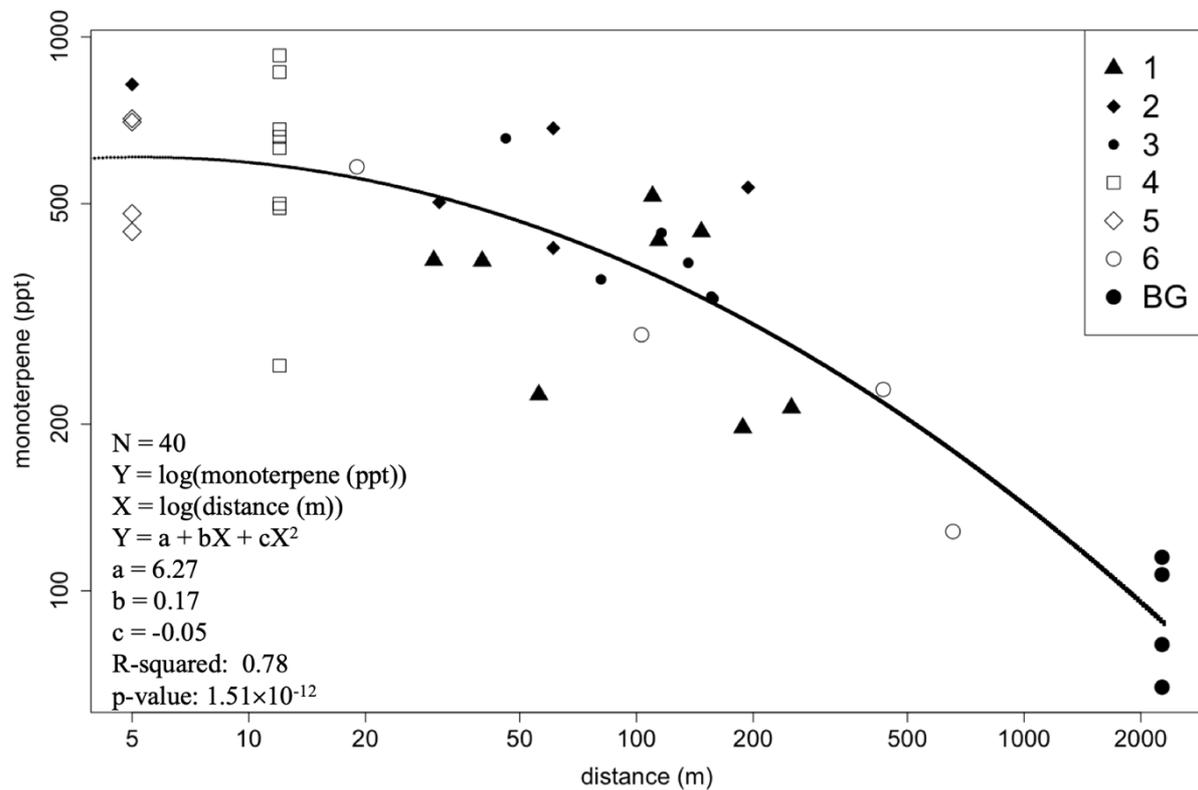


Fig. 2 Monoterpene mixing ratios in samples taken between 06:00-11:00 LT for all experimental sites versus distance to the closest upwind CCF. Note that both axes are log scale. The curved line is the predicted regression model whose equation is shown in the left of the plot area. The null hypothesis (p-value) is the probability of there being no relationship between the two observed variables.

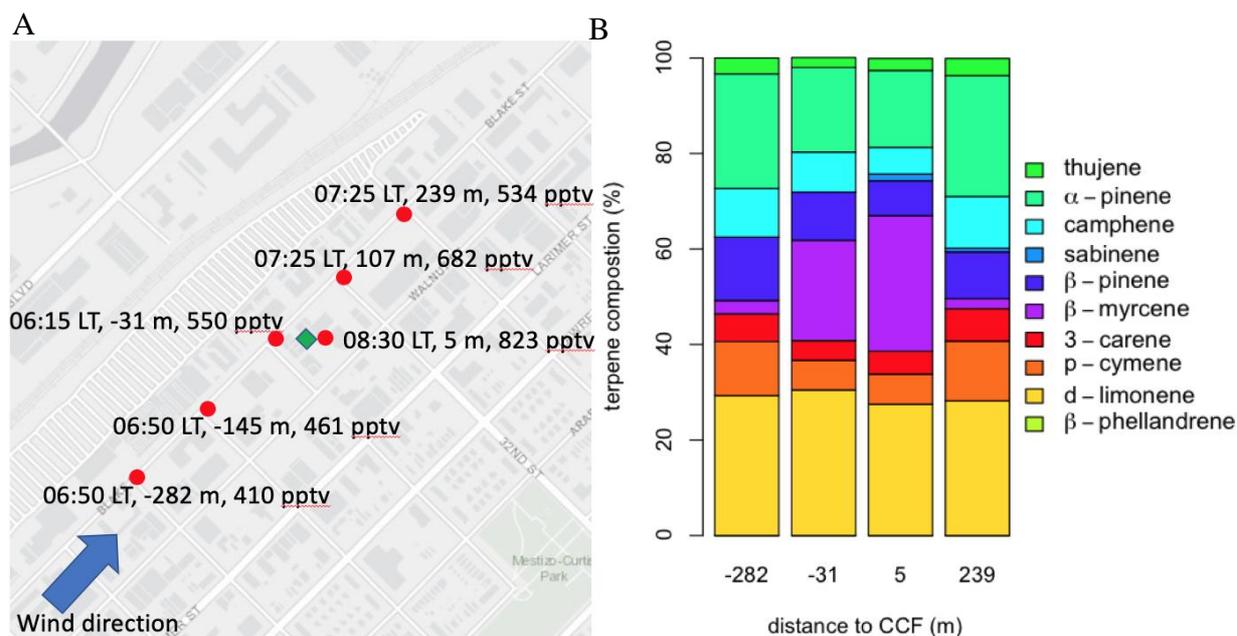


Fig. 3 Experiment 2: Panel (A) shows the sampling locations (red dots), corresponding mixing ratios and sampling times. Also shown are the upwind (-) and downwind (+) distances (meters) from the CCF (green diamond). The blue arrow indicates the average wind direction during the sampling period. Panel (B) shows fractional monoterpene composition at the two closest and two farthest sampling distances. The base map was supplied by Esri (Esri, 2013)

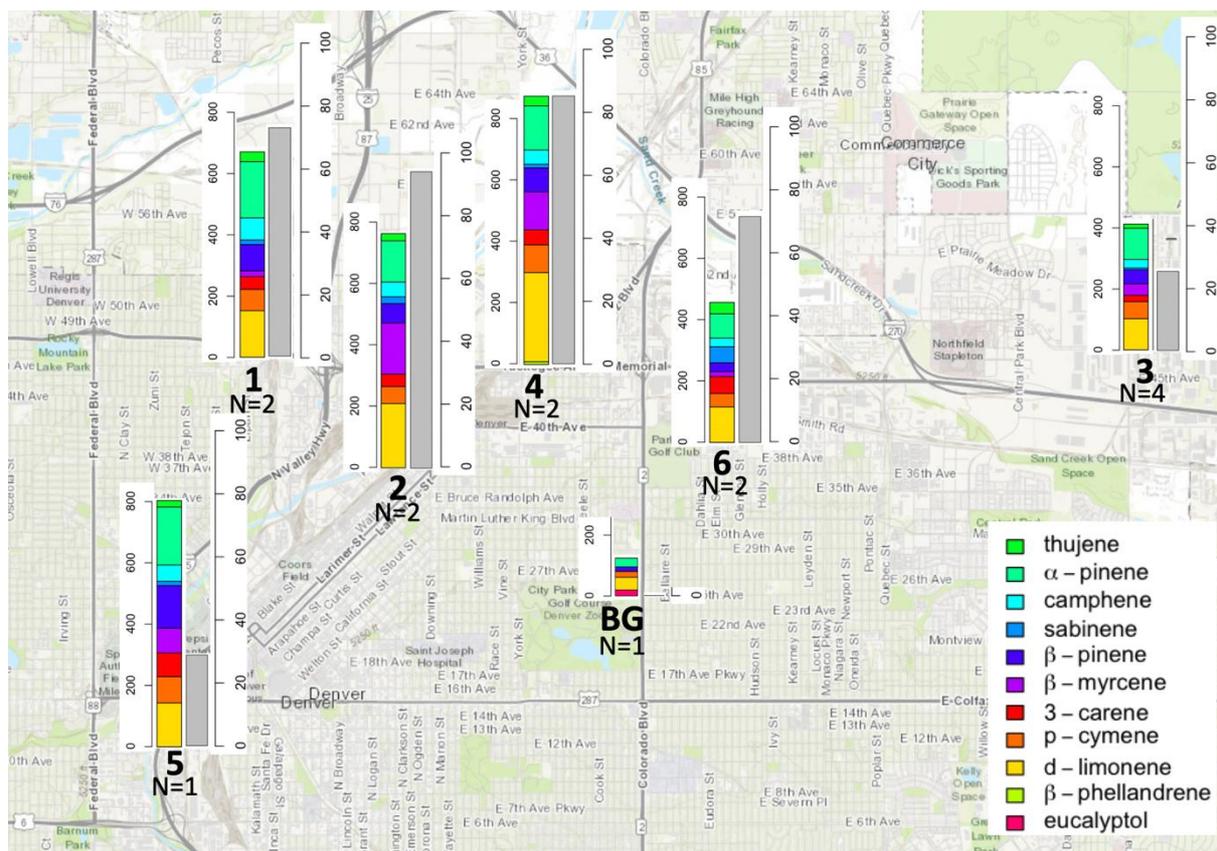


Fig. 4 The average total mixing ratios (pptv) of individual monoterpene and terpenoid, and the number of samples at each experiment between 8:00-9:00 LT. The estimated number of CCFs along the estimated back-trajectories (Fig. S2) are shown by the grey bars. The base map was supplied by Esri (Esri, 2013)

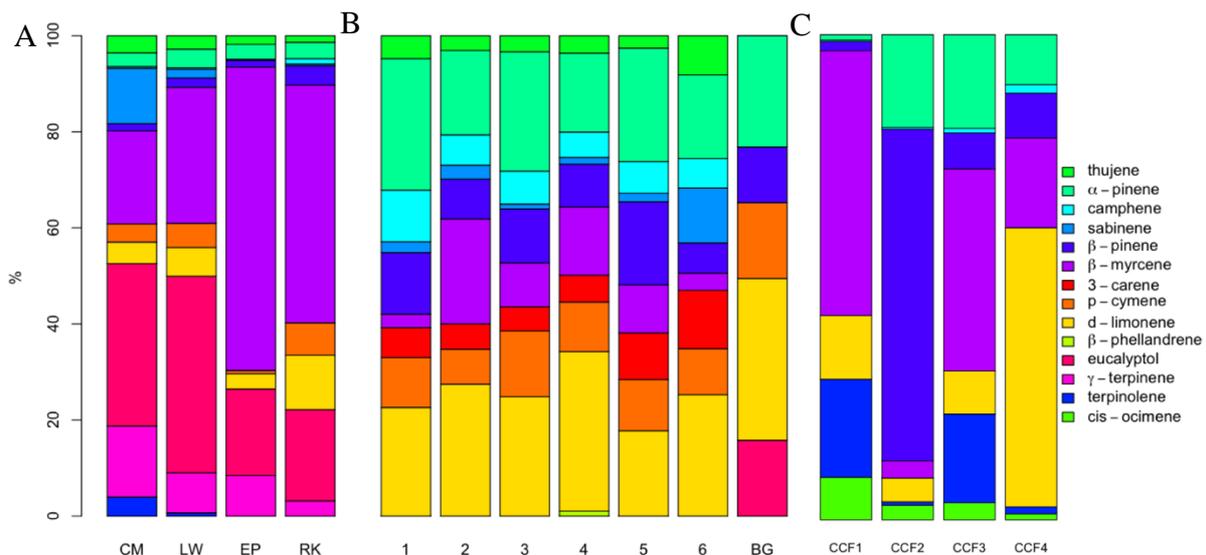


Fig. 5 (A) The monoterpene and terpenoid composition (%) of emissions from Critical Mass (CM), Lemon Wheel (LW), Elephant Purple (EP), and Rockstar Kush (RK; Wang et al., 2019b). and (B) in ambient air samples taken at experiments 1–6 and BG. (C) The monoterpene composition (%) in the grow room of four different indoor facilities measured by Samburova et al. (Samburova et al., 2019).

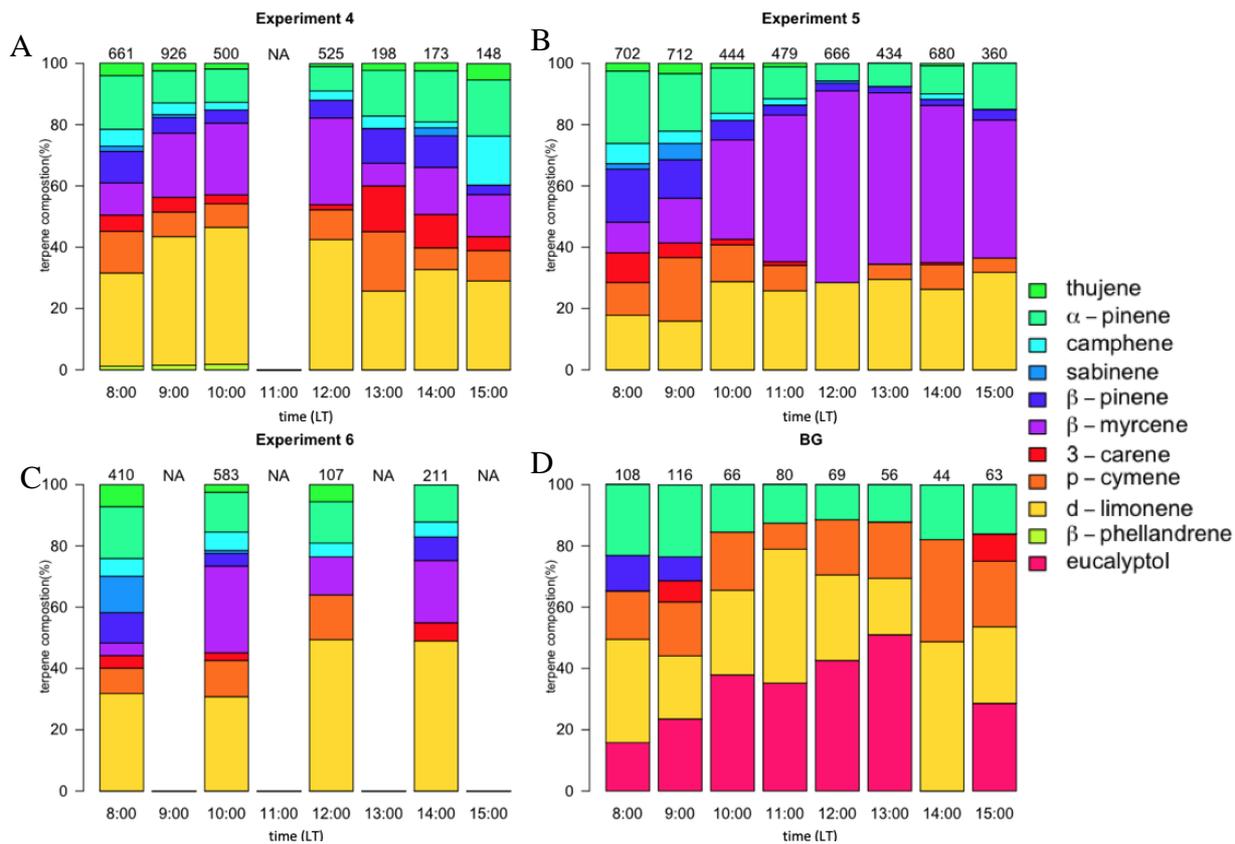


Fig. 6 Monoterpene composition from experiments (A) 4, (B) 5, (C) 6, and (D) background (BG) between 08:00 and 15:00 LT. The numbers on the top of each bar are the total monoterpene mixing ratios (pptv).

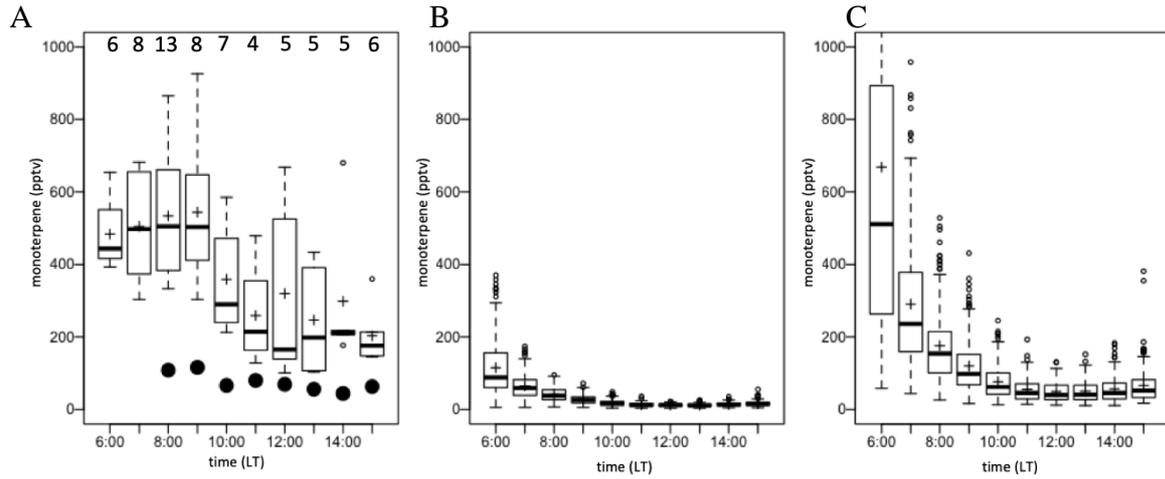


Fig. 7 (A) Measured hourly timeseries of monoterpane mixing ratios (pptv) at 6 experiments (box plot) and from the background (BG) site (black circles). The number on the top of each box is samples number. Predicted monoterpane mixing ratios (pptv) at the sampling sites simulated by the western air quality study model (WAQS 2011b) (ENVIRON and AlpineGeophysics, 2017) (B) in the absence of CCF emissions, and (C) with predicted monoterpane emissions of $362 \text{ ton year}^{-1}$ (Wang et al., 2019a). The black cross in each boxplot is the mean of each box, and open circles denote outliers ($>Q3 + 1.5 \times \text{inter quartile range (IQR)}$).

Table S1. The details of measurement date, time, locations, and the total and explicit monoterpene mixing ratio (pptv)

Date	latitude	longitude	Start Time	Sample Time	Experiment	Flow rate (ccm)	T (degC)	Total monoterpene	thujene	alpha-pinene	camphene	sabinene	beta-pinene	beta-myrcene	d 3-carene	p-cymene	d-limonene	beta-phellandrene	eucalyptol
8/2/16	39.778525	-104.99948	6:10	0:55	1	140	18	393	19	107	43	5	53	16	18	45	87	ND	ND
8/2/16	39.778397	-105.00159	6:10	0:55	1	140	18	445	23	119	44	10	52	14	25	60	99	ND	ND
8/2/16	39.778525	-104.99948	7:45	0:55	1	140	22	624	26	201	63	11	78	16	40	61	128	ND	ND
8/2/16	39.778397	-105.00159	7:45	0:55	1	140	22	543	29	119	62	15	71	17	33	60	136	ND	ND
8/2/16	39.776583	-104.99944	8:50	0:55	1	140	25	392	22	74	44	11	56	10	25	54	96	ND	ND
8/2/16	39.775576	-104.99934	8:50	0:55	1	140	25	430	23	79	40	9	51	11	23	53	141	ND	ND
8/2/16	39.774296	-104.99949	8:50	0:55	1	140	25	515	12	46	22	20	49	7	12	22	324	ND	ND
8/2/16	39.780115	-104.99927	10:05	0:55	1	140	28	226	11	36	18	6	22	11	9	31	82	ND	ND
8/2/16	39.781952	-104.99933	10:05	0:55	1	140	28	213	11	26	15	7	19	7	8	28	92	ND	ND
8/2/16	39.779458	-105.00506	11:15	0:55	1	140	31	198	17	24	6	20	15	14	7	31	66	ND	ND
8/11/16	39.764605	-104.98091	6:15	0:30	2	140	17	550	11	97	46	ND	56	116	23	34	167	ND	ND
8/11/16	39.764942	-104.98046	6:15	0:30	2	140	17	416	11	117	45	ND	48	37	23	57	65	14	ND
8/11/16	39.762729	-104.98332	6:50	0:30	2	140	18	410	14	99	42	ND	54	11	24	46	120	ND	ND
8/11/16	39.763659	-104.98213	6:50	0:30	2	140	18	461	15	99	52	ND	37	67	24	50	118	ND	ND
8/11/16	39.76545	-104.97973	7:25	0:30	2	140	20	682	18	227	63	5	52	19	45	66	187	ND	ND
8/11/16	39.766338	-104.97866	7:25	0:30	2	140	20	534	19	135	58	5	52	11	36	67	151	ND	ND
8/11/16	39.76462	-104.98009	8:30	0:30	2	140	22	823	20	133	46	11	60	233	40	52	227	ND	ND
8/11/16	39.764981	-104.98069	8:30	0:30	2	140	22	505	20	101	37	27	50	57	31	44	138	ND	ND
8/15/16	39.782	-104.859	6:10	0:30	3	140	16	654	9	114	29	ND	51	207	20	42	180	ND	ND
8/15/16	39.782	-104.861	6:10	0:30	3	140	16	442	8	93	20	ND	44	91	27	31	128	ND	ND
8/15/16	39.779	-104.859	7:00	0:30	3	140	16	303	8	101	19	ND	40	6	11	36	82	ND	ND
8/15/16	39.779	-104.861	7:00	0:30	3	140	16	337	8	94	24	ND	41	22	23	31	105	ND	ND
8/15/16	39.784	-104.859	7:50	0:30	3	270	18	333	10	96	27	ND	40	26	15	43	76	ND	ND
8/15/16	39.786	-104.859	7:50	0:30	3	140	18	391	14	103	28	8	45	24	26	52	91	ND	ND
8/15/16	39.788	-104.859	8:30	0:30	3	140	22	339	14	68	19	7	35	52	16	43	85	ND	ND
8/15/16	39.79	-104.859	8:30	0:30	3	140	22	360	10	86	23	ND	40	28	15	57	102	ND	ND
8/10/16	39.777721	-104.96233	7:35	0:50	4	140	22	681	29	144	71	12	93	46	49	67	155	14	ND
8/10/16	39.777721	-104.96179	7:35	0:50	4	140	22	630	31	126	37	33	103	37	59	35	169	ND	ND
8/10/16	39.777721	-104.96233	8:35	0:50	4	140	26	865	28	135	44	10	68	147	50	68	306	8	ND
8/10/16	39.777721	-104.96179	8:35	0:50	4	140	26	661	27	116	36	11	68	69	35	90	201	8	ND
8/10/16	39.777721	-104.96233	9:30	0:50	4	140	29	492	24	82	27	10	32	49	40	74	137	18	ND
8/10/16	39.777721	-104.96179	9:30	0:50	4	140	29	926	23	97	35	9	48	194	44	74	389	14	ND
8/10/16	39.777721	-104.96233	10:25	0:50	4	140	30	253	7	35	14	ND	8	46	9	39	95	ND	ND
8/10/16	39.777721	-104.96179	10:25	0:50	4	140	30	500	9	54	12	ND	22	117	15	39	223	9	ND
8/10/16	39.777721	-104.96233	12:30	0:50	4	140	34	144	3	19	8	ND	5	33	ND	22	54	ND	ND
8/10/16	39.777721	-104.96179	12:30	0:50	4	140	34	525	5	42	16	ND	31	148	9	51	223	ND	ND
8/10/16	39.777721	-104.96233	13:20	0:50	4	140	34	391	8	57	22	ND	23	93	24	32	134	ND	ND
8/10/16	39.777721	-104.96179	13:20	0:50	4	140	34	198	5	29	8	ND	19	15	29	31	51	ND	ND
8/10/16	39.777721	-104.96233	14:20	0:50	4	140	32	218	5	42	15	ND	12	34	17	35	58	ND	ND
8/10/16	39.777721	-104.96179	14:20	0:50	4	140	32	173	5	29	ND	5	18	27	19	12	58	ND	ND
8/10/16	39.777721	-104.96233	15:20	0:50	4	140	33	214	ND	41	9	ND	11	37	9	34	73	ND	ND
8/10/16	39.777721	-104.96179	15:20	0:50	4	140	33	148	8	27	24	ND	5	20	7	15	43	ND	ND
8/17/16	39.730705	-105.01388	7:45	0:50	5	140	21	702	18	165	46	12	121	70	68	75	125	ND	ND
8/17/16	39.730705	-105.01388	8:45	0:50	5	140	24	712	24	134	28	37	90	104	34	147	113	ND	ND
8/17/16	39.730705	-105.01388	9:45	0:50	5	140	27	444	7	66	10	ND	28	144	8	53	128	ND	ND
8/17/16	39.730705	-105.01388	10:45	0:50	5	140	28	479	6	50	10	ND	16	229	6	40	124	ND	ND
8/17/16	39.730705	-105.01388	11:45	0:50	5	140	30	666	ND	37	ND	5	17	417	ND	ND	190	ND	ND
8/17/16	39.730705	-105.01388	12:45	0:50	5	140	31	434	ND	33	ND	ND	9	243	ND	22	128	ND	ND
8/17/16	39.730705	-105.01388	13:45	0:50	5	140	32	680	5	62	12	ND	14	349	5	54	179	ND	ND
8/17/16	39.730705	-105.01388	14:45	0:50	5	140	32	360	ND	54	ND	ND	12	162	ND	17	114	ND	ND
8/3/16	39.770228	-104.92952	7:54	0:50	6	140	21	410	29	69	24	49	41	17	17	34	130	ND	ND
8/3/16	39.769301	-104.92952	7:54	0:50	6	140	21	383	35	69	25	42	9	11	79	42	70	ND	ND
8/3/16	39.76553	-104.92952	8:54	0:50	6	140	24	303	24	54	24	17	24	8	12	50	90	ND	ND
8/3/16	39.763845	-104.92952	8:54	0:50	6	140	24	583	44	75	33	63	77	14	26	86	164	ND	ND
8/3/16	39.770228	-104.92952	9:54	0:50	6	140	27	585	15	76	35	6	24	165	15	69	180	ND	ND
8/3/16	39.769301	-104.92952	9:54	0:50	6	140	27	290	19	60	18	6	20	11	12	43	100	ND	ND
8/3/16	39.76553	-104.92952	10:55	0:50	6	140	29	231	12	32	17	6	14	27	16	34	74	ND	ND
8/3/16	39.763845	-104.92952	10:55	0:50	6	140	29	128	11	26	9	ND	6	11	6	23	36	ND	ND
8/3/16	39.770228	-104.92952	12:18	0:50	6	140	31	101	6	14	5	ND	ND	12	ND	15	50	ND	ND
8/3/16	39.769301	-104.92952	12:18	0:50	6	140	31	165	7	19	ND	ND	5	19	7	25	84	ND	ND
8/3/16	39.76553	-104.92952	13:20	0:50	6	140	33	107	6	11	5	ND	ND	27	7	16	35	ND	ND
8/3/16	39.763845	-104.92952	13:20	0:50	6	140	33	103	ND	12	5	ND	ND	17	5	20	44	ND	ND
8/3/16	39.770228	-104.92952	14:20	0:50	6	140	34	206	ND	25	10	ND	16	42	12	ND	101	ND	ND
8/3/16	39.769301	-104.92952	14:20	0:50	6	140	34	211	ND	20	12	ND	ND	32	10	36	100	ND	ND
8/3/16	39.76553	-104.92952	15:23	0:50	6	140	34	164	6	22	6	ND	ND	17	12	33	69	ND	ND
8/3/16	39.763845	-104.92952	15:23	0:50	6	140	34	145	8	19	8	ND	ND	14	9	33	54	ND	ND
8/3/16	39.765	-104.92952	15:27	0:45	6	140	34	188	11	27	9	ND	14	9	12	28	77	ND	ND
8/19/16	39.7505	-104.9435	7:45	0:50	BG	140	15	108	ND	25	ND	ND	12	ND	ND	17	36	ND	17
8/19/16	39.7505	-104.9435	8:35	0:50	BG	140	16	116	ND	27	ND	ND	9	ND	8	20	24	ND	27
8/19/16	39.7505	-104.9435	9:30	0:50	BG	140	17	66	ND	10	ND	ND	ND	ND	ND	12	18	ND	25
8/19/16	39.7505	-104.9435	10:25	0:50	BG	140	19	80	ND	10	ND	ND	7	ND	7	35	ND	28	7
8/19/16	39.7505	-104.9435	11:55	0:50	BG	140	21	69	ND	8	ND	ND	ND	ND	12	19	ND	29	19
8/19/16	39.7505	-104.9435	12:50	0:50	BG	140	22	56	ND	7	ND	ND	ND	ND	10	10	ND	29	10
8/19/16	39.7505	-104.9435	13:40	0:															

1 Table S2 The GC-MS retention time and fragment of explicit monoterpenes

Terpene	Retention time (min)	fragment ion used for quantitation	fragment(%)
thujene	8.4	93	28.6
alpha-pinene	8.56	93	26.3
camphene	8.89	93	18.8
sabinene	9.3	93	26.6
beta-pinene	9.43	93	25.5
beta-myrcene	9.54	93	23.7
alpha-phellandrene	9.93	93	32.1
alpha-terpinene	10.13	93	15.4
p-cymene	10.28	119	38.8
d-limonene	10.32	68, 93	12
beta-phellandrene	10.36	93	34
eucalyptol	10.43	93	6
cis-beta-ocimene	10.56	93	22.4
gamma-terpinene	10.87	93	20
terpinolene	11.38	121	14.5
caryophyllene	16.9	93	-

2

3 Table S3 Colorado meteorological stations

Site	Longitude	Latitude	Altitude (m)	Time period (min)
KBJC	-105.10417	39.90085	1692	20
KAPA	-104.84841	39.55991	1789	5
KDEN	-104.65622	39.84658	1647	5
KEIK	-105.05033	40.01169	1550	20
KBDU	-105.22582	40.03943	1612	20
KFTG	-104.55000	39.78333	1709	60
KMNH	-104.63389	39.21667	2152	20
KBKF	-104.75806	39.71331	1700	60
AENC2	-104.85572	39.82425	1608	60
LOOC2	-105.25028	39.72417	2287	60
CTPC2	-105.08406	39.41908	2154	60
BTAC2	-105.36139	40.01806	2052	60
CO006	-105.01654	39.74421	1583	10
CO003	-104.94333	39.78024	1597	10
CO148	-105.00041	39.71298	1594	10
CO144	-104.98839	39.79054	1584	10
CO146	-105.09575	39.78393	1627	10
CO011	-104.81014	39.77152	1643	10
CO024	-104.82871	39.69712	1702	10
CO145	-104.95799	39.68458	1632	10
CO161	-104.91108	39.64095	1706	10

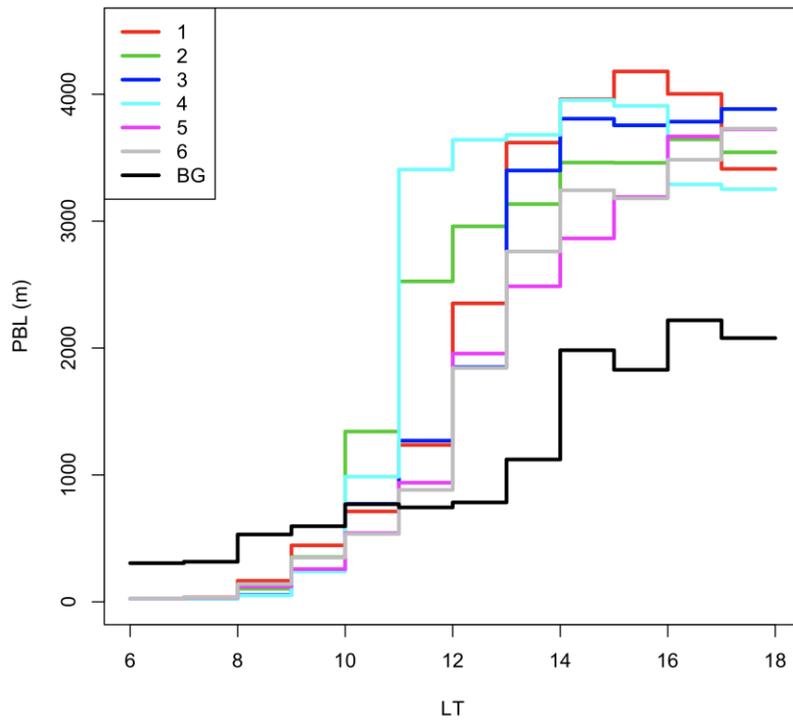
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5

6 Table S4 Denver airport meteorological information at 8:00-9:00 LT and PBL in Denver
7 County estimated by HISPLIT model.
8

Experiment	8:00-9:00 LT		
	Wind Direction	Wind Speed (m/s)	PBL (m)
1	W	3.5	177
2	WSW	3.5	103
3	WSW	2.2	50
4	SW	6.2	77
5	WSW	3.1	101
6	S	2.7	123
BG	ESE	1.3	528

10
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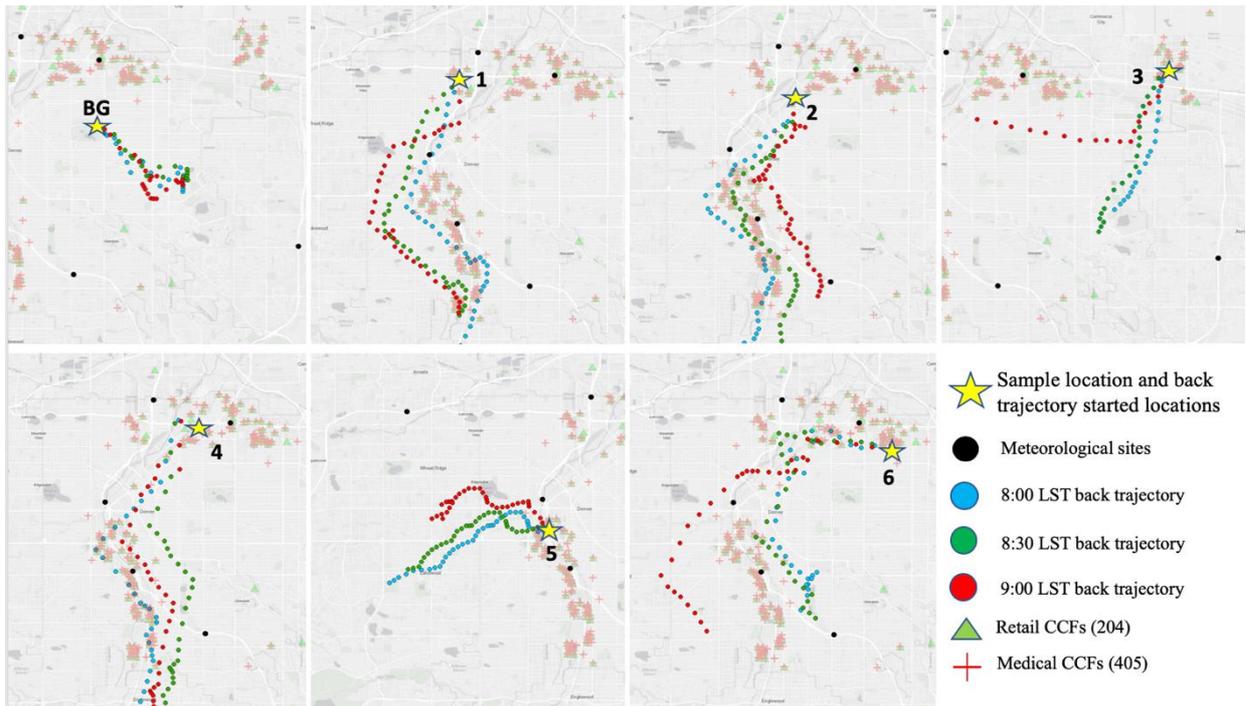
13 Fig. S1. The hourly PBL height (m) in Denver for all experiments. The data is from

14 HYSPLIT model (NOAA, 2019) for all experiments.

15

16

17



19

20 Fig. S2. The 3 hours back-trajectory pathways for all experiments (Table 1) ending at 8:00
 21 LT (blue circle), 8:30 LT (green circle) and 9:00 LT (red circle) for all experiments. The
 22 back-trajectories are calculated using local weather station data. The yellow stars are the
 23 sampling location, the black dots are the meteorological sites the green triangles are the
 24 recreational CCFs, and the red crosses are the medical CCFs. The base map was supplied by
 25 Esri (Esri, 2013)

26

27

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Table[Click here to download Table: Table 1_submit.docx](#)

Table 1. The summary of sampling dates, duration, number of sampling points and distance to the closest meteorological site.

Experiment	Date	Sample duration (minutes)	Sample count	Numbers of sampling locations (sites)	Distance to Meteorological site	Meteorological Site Identification
1	Aug 2, 2016 6:10-12:10 LT	55	20	10	1.7 km	CO144
2	Aug 11, 2016 6:15-9:00 LT	30	16	8	2.8 km	CO144
3	Aug 15, 2016 6:10-9:00 LT	30	16	8	4 km	AENC2, CO011
4	Aug 10, 2016 7:35-16:10 LT	50	32	2	1.7 km	CO003
5	Aug 17, 2016 7:45-15:35 LT	50	16	1	1.5 km	CO006
6	Aug 3, 2016 7:54-16:13 LT	50	34	4	1.7 km	CO003
BG	Aug 19, 2016 7:45-15:20 LT	50	16	1	2.6 km	CO003

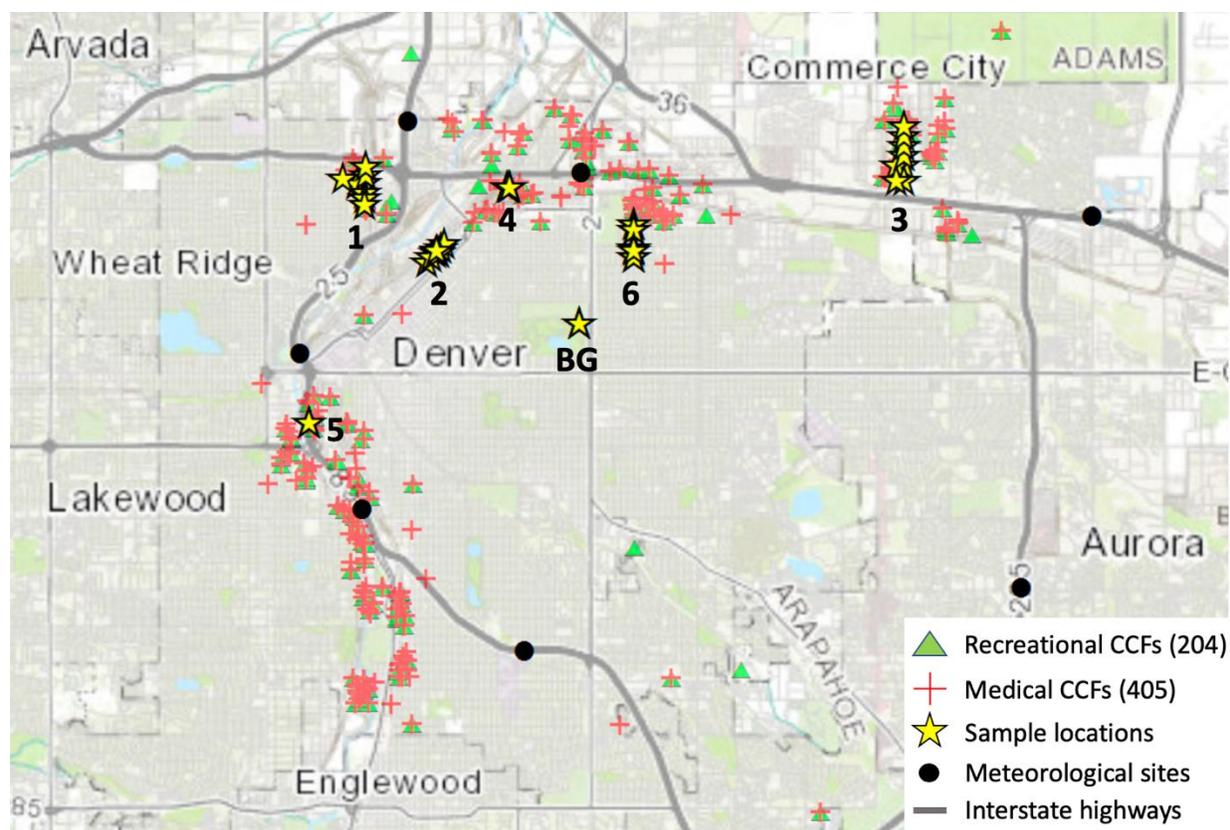


Fig. 1 Map of Denver, CO showing sampling locations listed in Table 1 (yellow stars), medical *cannabis* cultivational facilities (CCFs, red crosses), recreational CCFs (green triangles), and meteorological sites (black dots). The total number of CCFs in Denver County are given in parentheses. The base map was supplied by Esri (Esri, 2013).

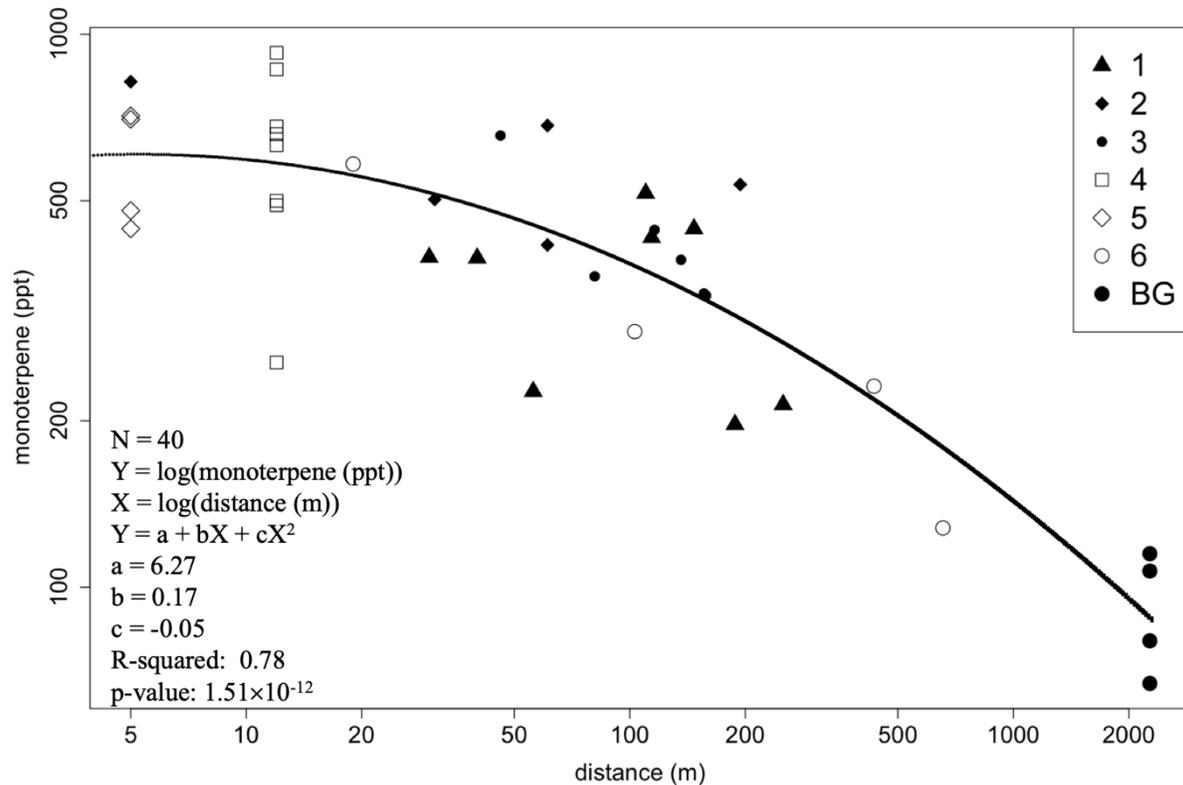


Fig. 2 Monoterpene mixing ratios in samples taken between 06:00-11:00 LT for all experimental sites versus distance to the closest upwind CCF. Note that both axes are log scale. The curved line is the predicted regression model whose equation is shown in the left of the plot area. The null hypothesis (p-value) is the probability of there being no relationship between the two observed variables.

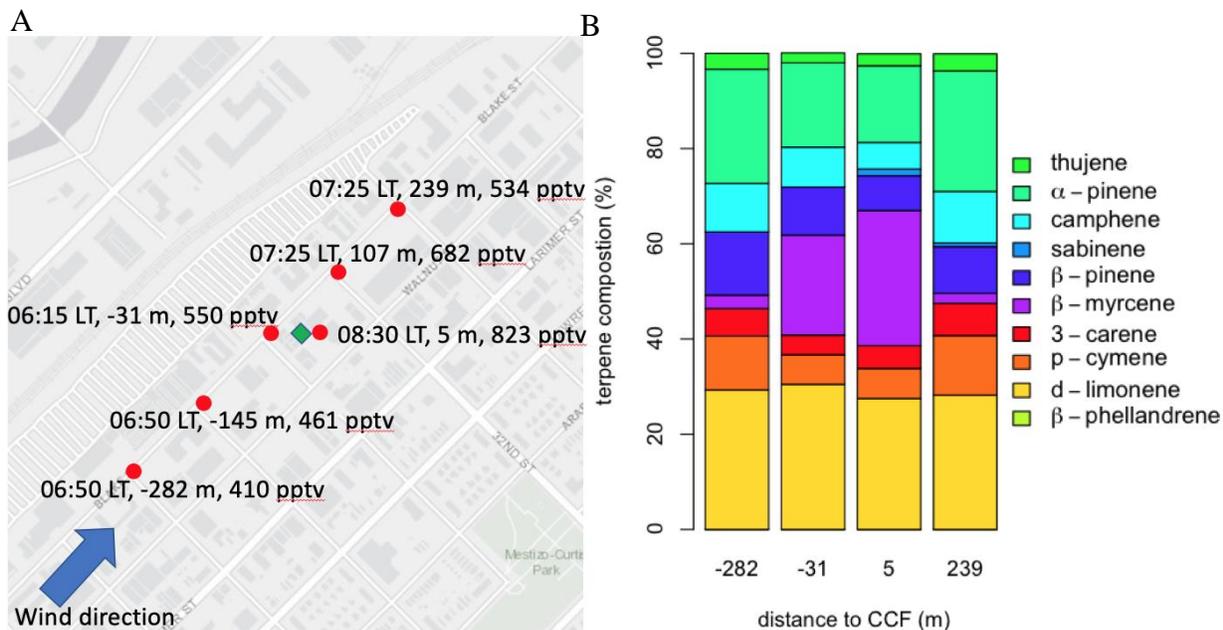


Fig. 3 Experiment 2: Panel (A) shows the sampling locations (red dots), corresponding mixing ratios and sampling times. Also shown are the upwind (-) and downwind (+) distances (meters) from the CCF (green diamond). The blue arrow indicates the average wind direction during the sampling period. Panel (B) shows fractional monoterpene composition at the two closest and two farthest sampling distances. The base map was supplied by Esri (Esri, 2013)

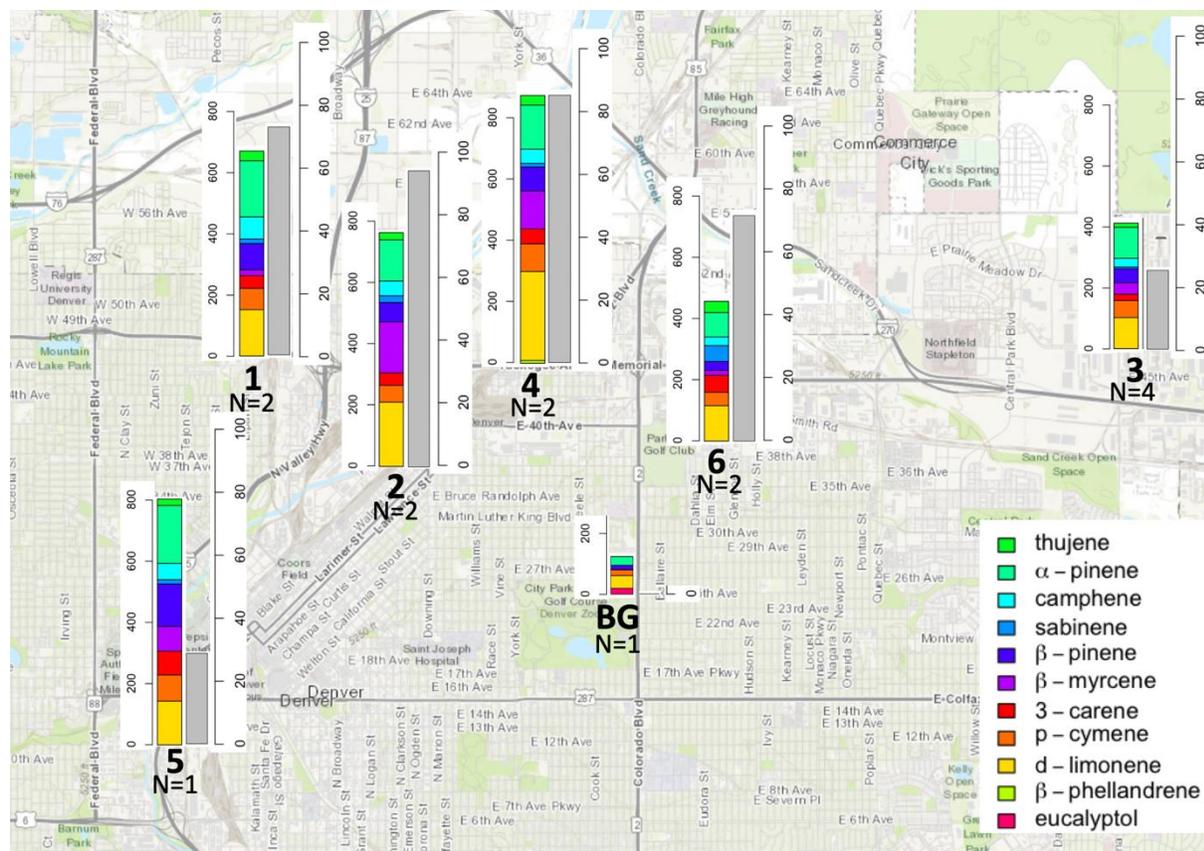


Fig. 4 The average total mixing ratios (pptv) of individual monoterpene and terpenoid, and the number of samples at each experiment between 8:00-9:00 LT. The estimated number of CCFs along the estimated back-trajectories (Fig. S2) are shown by the grey bars. The base map was supplied by Esri (Esri, 2013)

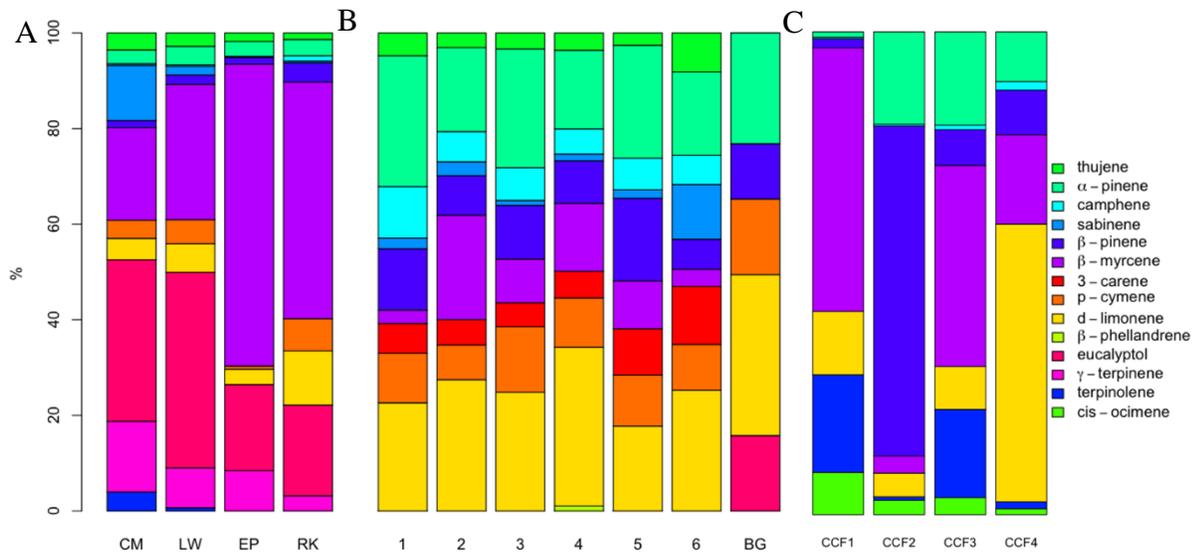


Fig. 5 (A) The monoterpene and terpenoid composition (%) of emissions from Critical Mass (CM), Lemon Wheel (LW), Elephant Purple (EP), and Rockstar Kush (RK; Wang et al., 2019b). and (B) in ambient air samples taken at experiments 1–6 and BG. (C) The monoterpene composition (%) in the grow room of four different indoor facilities measured by Samburova et al. (Samburova et al., 2019).

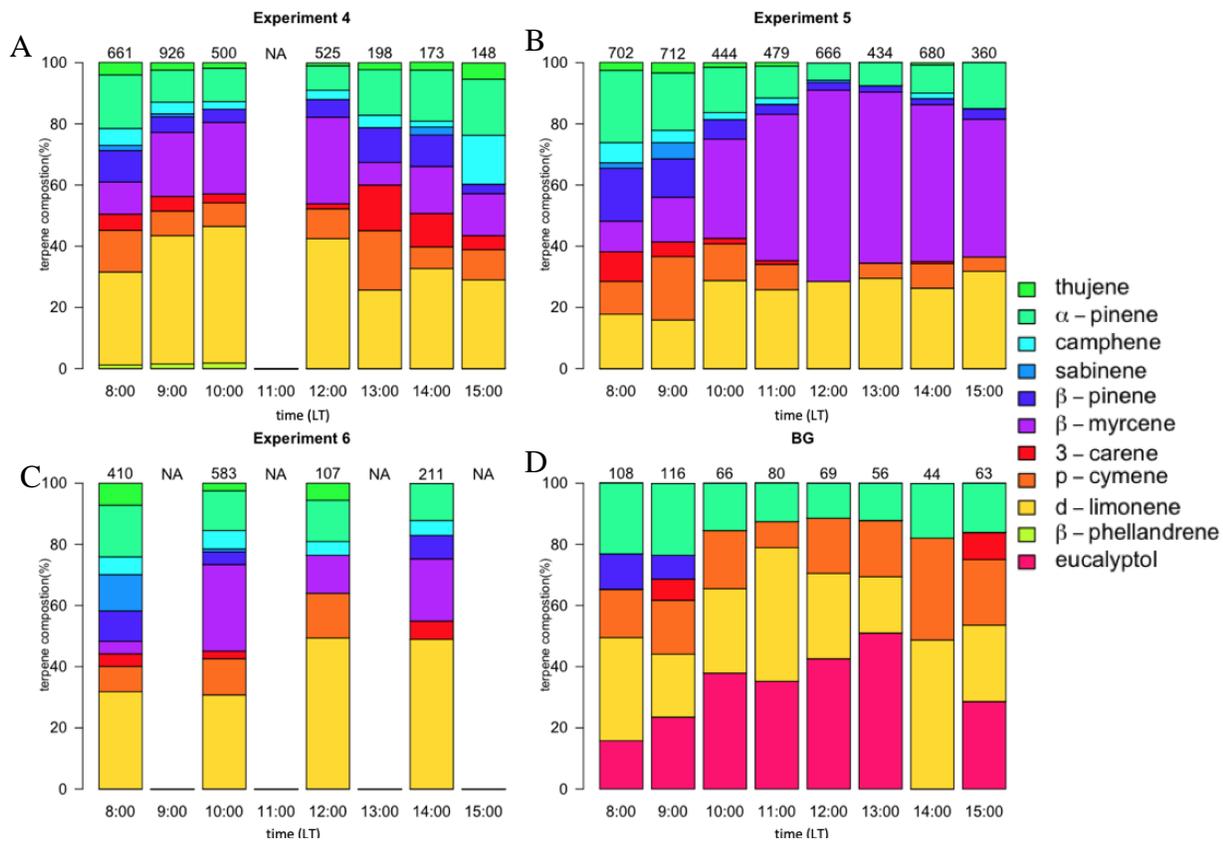


Fig. 6 Monoterpene composition from experiments (A) 4, (B) 5, (C) 6, and (D) background (BG) between 08:00 and 15:00 LT. The numbers on the top of each bar are the total monoterpene mixing ratios (pptv).

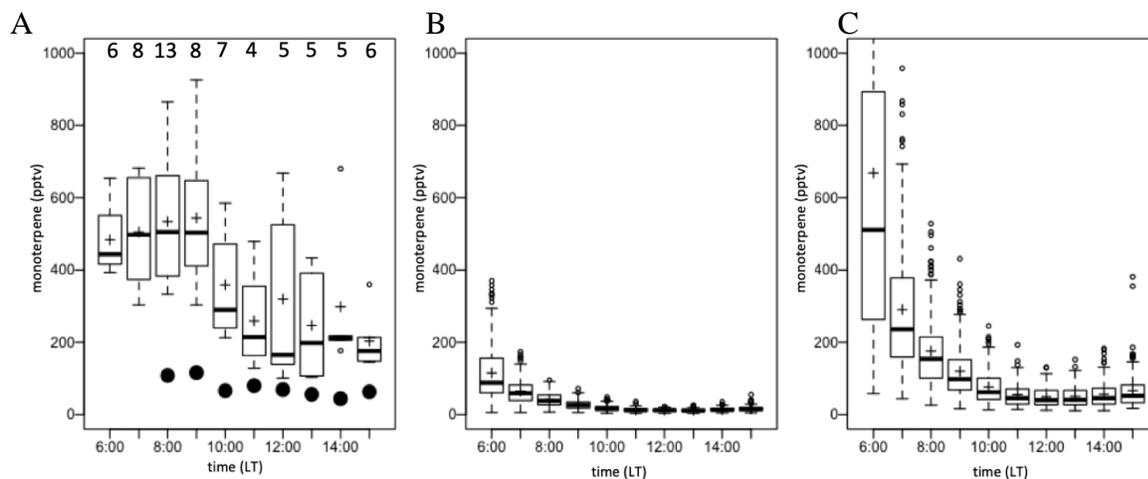


Fig. 7 (A) Measured hourly timeseries of monoterpene mixing ratios (pptv) at 6 experiments (box plot) and from the background (BG) site (black circles). The number on the top of each box is samples number. Predicted monoterpene mixing ratios (pptv) at the sampling sites simulated by the western air quality study model (WAQS 2011b) (ENVIRON & Alpine., 2017) (B) in the absence of CCF emissions, and (C) with predicted monoterpene emissions of 362 ton year⁻¹ (Wang, Wiedinmyer, Ashworth, Harley, Ortega, Rasool, et al., 2019). The black cross in each boxplot is the mean of each box, and open circles denote outliers ($>Q3 + 1.5 \times$ inter quartile range (IQR)).

Supplementary Material

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