1 Potential Regional Air Quality Impacts of Cannabis Cultivation Facilities in

2 Denver, Colorado

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13 Abstract

14 The legal commercialization of cannabis for recreational and medical use has effectively created a new and almost unregulated cultivation industry. In 2018, within the 15 16 Denver County limits, there were more than 600 registered cannabis cultivation facilities 17 (CCFs) for recreational and medical use, mostly housed in commercial warehouses. 18 Measurements have found concentrations of highly reactive terpenes from the headspace above 19 cannabis plants that, when released in the atmosphere, could impact air quality. Here we 20 developed the first emission inventory for cannabis emissions of terpenes. The range of 21 possible emissions from these facilities was 66-657 metric tons/year of terpenes across the state 22 of Colorado; half of the emissions are from Denver County. Our estimates are based on the 23 best available information and highlight the critical data gaps needed to reduce uncertainties. 24 These realizations of inventories were then used with a regulatory air quality model, developed 25 by the State of Colorado to predict regional ozone impacts. It was found that most of the 26 predicted changes occur in the vicinity of CCFs concentrated in Denver. An increase of 362 27 metric tons/year of terpene emissions in Denver County resulted in increases of up to 0.34 ppb 28 in hourly ozone concentrations during the morning and 0.67 ppb at night. Model predictions 29 indicate that in Denver County every 1,000 metric tons/year increase of terpenes results in 1 30 ppb increase in daytime hourly ozone concentrations and a maximum daily 8-hour average 31 (MDA8) increase of 0.3 ppb. The emission inventories developed here are highly uncertain, 32 but highlight the need for more detailed cannabis and CCFs data to fully understand the 33 possible impacts of this new industry on regional air quality.

Keywords: *Cannabis spp.*; emission inventory; biogenic volatile organic compound; terpene;
 particulate matter; ozone; air quality

36 1. Introduction

37 The rapid expansion of one of the United States' newest industries, the commercial 38 production and sale of recreational cannabis, was recently likened to the millennial "dot com" 39 boom (Borchardt, 2017). With an increasing number of states passing bills to legalize 40 recreational cannabis, the enterprise is set to rival all but the largest of current businesses. The 41 cultivation, sale, and consumption of recreational cannabis annual sales revenues had reached 42 \$1.5 billion in the US state of Colorado by 2017 (CDOR, 2018b), exceeding revenues 43 generated by grain farming in the state. The commercial cultivation and sale of cannabis is not 44 subject to the same strict environmental monitoring and reporting procedures as other 45 industries of similar size. While the relaxation of laws has provided certain medicinal and 46 economic opportunities for the states involved, the potentially significant environmental 47 impact on air quality due to the production of cannabis has largely been ignored.

48 Previous research on the wider impacts of cannabis production has been limited due to 49 its federal status as an illegal or controlled substance (Crick et al., 2013; Eisenstein, 2015; 50 Andreae et al., 2016; Stith and Vigil, 2016). As a result of this status, most studies have focused 51 on the pharmacological and health effects of the psychoactive constituents of Cannabis spp. 52 (Ashton, 2001; Borgelt et al., 2013; WHO, 2016), or the societal impacts associated with the 53 illicit nature of the industry (IDCP, 1995; Sznitman and Zolotov, 2015; WHO, 2016). The few 54 assessments to date on the environmental impacts of the production of Cannabis spp. have 55 centered on the detrimental effects of outdoor cultivation on ecosystems and watersheds due 56 to land clearance and high water demand (Bauer et al., 2015; Carah et al., 2015; Butsic and 57 Brenner, 2016). Studies have also quantified the energy consumption of the industry and the 58 resulting greenhouse gas emissions associated with indoor cultivation (Mills, 2012). Little 59 attention has been paid to the possible biogenic volatile organic compounds (BVOCs) emitted 60 from the growing of cannabis and its impact on indoor and outdoor air quality.

61 The only studies that have measured the composition of gaseous emissions from 62 cannabis have been limited to headspace samples above the plants (Hood et al., 1973; Turner 63 et al., 1980; Martyny et al., 2013). These studies have shown high concentrations of VOCs 64 such as monoterpenes ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$), and cannabinoids. These studies also 65 measured thiols, a sulfur-containing compound responsible for the characteristic odor of 66 Cannabis spp. (Rice and Koziel, 2015b, a). The principle (trace) components are reported to 67 be: α - and β -pinene, β -myrcene, d-limonene, cis-ocimene, β -caryophyllene, β -farnesene and α -68 humulene (Hood et al., 1973; Turner et al., 1980; Hillig, 2004; Fischedick et al., 2010; Martyny 69 et al., 2013; Marchini et al., 2014; Rice and Koziel, 2015b). The precise mix of chemical 70 species, however, was strongly dependent on strain and the growing conditions (Fischedick et 71 al., 2010). It should be noted that the pharmacologically active ingredients, e.g., 72 Tetrahydrocannabinol (Δ^9 -THC), generally have low volatility and therefore are rarely 73 detected in the gas-phase (Martyny et al., 2013). Measurements in (illicit) CCFs in conjunction 74 with law enforcement raids in Colorado in 2012 found VOC concentrations of terpenes to be 75 50-100 ppb within growing rooms (Martyny et al., 2013). In these cases, the CCF operation 76 contained fewer than 100 plants, compared with the thousands of plants found in currently 77 licensed premises (CDOR, 2018a). Further, the Spokane Regional Clean Air Agency (SRCAA) 78 study in Washington state measured indoor VOCs in seven flowering rooms and two dry bud 79 rooms across four different CCFs. The average terpene concentration was 361 ppb (27-1,676 80 ppb) in those facilities (Southwellb et al., 2017). These indoor measurements indicate the 81 presence of BVOCs, but only limited studies have actually determined the chemical profile of 82 gases actually emitted by the growing plants. For comparison, summertime outdoor 83 monoterpene concentrations in forested regions of Colorado are typically less than 4 ppb 84 (Ortega et al., 2014).

85 Terpenoids, such as monoterpenes $(C_{10}H_{16})$ and sesquiterpenes $(C_{15}H_{24})$, are highly 86 reactive compounds with atmospheric lifetimes ranging from seconds to hours (Fuentes et al., 87 2000; Seinfeld and Pandis, 2006). They are primarily biogenic in origin (Fuentes et al., 2000; 88 Guenther et al., 2012) and their reactions alter the atmospheric oxidizing capacity, resulting in 89 a range of low volatility products that can partition into the aerosol phase and, depending on 90 the concentration of nitrogen oxides (NO_x), lead to the formation of ozone (Laothawornkitkul 91 et al., 2009; Guenther et al., 2012). Both ozone and aerosols are climate-relevant components 92 of the atmosphere as well as criteria air pollutants (USEPA, 2016).

In Colorado, the commercial growing of *Cannabis spp.* is restricted to secure and locked premises, resulting in indoor operations in most counties (CDOR, 2018a). Since legalization, the number of cannabis cultivation facilities (CCFs) has risen to 1,400 across the state of Colorado in 2018, including more than 233 registered recreational and 375 medical

97 CCFs within the Denver city limits alone. In Denver, the CCFs are commonly housed in 98 commercial warehouses and the majority of these are located near transport links such as train 99 hubs and major interstate highways (CDOR, 2019; Mills, 2012). Denver and the Front Range area are currently classified as "moderate" nonattainment of the ozone standard (USEPA, 100 101 2017). Due to that status, a federally mandated State Implementation Plan (SIP) was developed 102 and mutually agreed upon between the state of Colorado and the United States Environmental 103 Protection Agency (EPA) (CDPHE, 2009). Under the terms of the SIP, Colorado Air Quality 104 Control Commission (AQCC) developed regulatory models to predict reductions in ozone 105 precursors (CDPHE, 2009). These studies have found that ozone concentrations in Denver are 106 VOC-sensitive, meaning that an increase in VOC concentrations will increase ozone 107 production (UNC-IE and ENVIRON, 2013). The location of CCFs in a VOC sensitive region 108 in Denver suggests a potential emission source that may impact regional air quality (UNC-IE 109 and ENVIRON, 2014). This work used the best available information to produce the first 110 emission inventory of VOCs from CCFs in Colorado. Colorado's regulatory model was then 111 used to determine the extent that these emissions could impact regional air quality.

112 **2.** Materials and Methods

113

2.1 Emission Rate calculation

Figure 1a shows the locations of the licensed 739 recreational and 733 medical CCFs in Colorado as of March 2018 (CDOR, 2018a). Eq. (1) was first used to estimate an emission rate for each CCF, and then all CCFs were used to build a bottom-up BVOC emission inventory.

117

$$ER_i = \sum_j EC_{ij} \times DPW_{ij} \times PC_{ij} \tag{1}$$

118 Where, ER_i (µg h⁻¹) is the total emissions rate for CCF *i* based on the sum of emission 119 rates for all j cannabis strains; EC_{ij} is the emission capacity (µg dwg⁻¹ h⁻¹) for cannabis strain *j* 120 in facility *i*, DPW_{ij} is the dry plant weight per plant (g) for cannabis strain *j*, and *PC* is the plant 121 count number for strain *j* in facility *i*.

Since state legalization only occurred in 2014, and given the current federal illicit status of *Cannabis spp.*, there is a lack of available data for the three parameters used in Eq. (1). The following describes the assumptions made for a range of potential values of *EC*, *DPW*, and *PC* given the best information available.

126 **2.1.1 Emission Capacity (EC)**

127 The only data of *EC* from a leaf enclosure measurement are of three strains namely: 128 Critical Mass, Lemon Wheel and Rockstar Kush, that were 45 days old (Wang et al., 2018). 129 This study found that at this growth stage the *EC* for total monoterpenes varied among strains: 10 µg gdw⁻¹ h⁻¹ for Critical Mass, 7 µg gdw⁻¹ h⁻¹ for Lemon Wheel, and 6 µg gdw⁻¹ h⁻¹ for 130 Rockstar Kush. The Department of Revenue (DOR) in Colorado has classified Cannabis spp. 131 in a CCF into four different growth stages: immature (0-24 days old), vegetative (25-79 days 132 133 old), flowering (80-132 days old), and at harvest (132-140 days old) (Hartman et al., 2018b). Wang et al. (2018) only sampled during the vegetative stage, and to our knowledge emission 134 135 rates of monoterpenes from buds or flowers do not exist. It is not known how much EC will 136 change during these different growth stages, but the grey literature does report that CCFs 137 actively select cultivars to maximise the amount of monoterpenes found in the bud tissues.

The Spokane Regional Clean Air Agency (SRCAA), in collaboration with Washington State University (Southwellb et al., 2017; Wen et al., 2017), measured monoterpenes in flowering rooms of CCFs in Washington state. They found concentrations of monoterpenes in grow room with 80 days old plants (1,660 ppb) to be >10 times higher than the 48 days old plants (150 ppb). CCFs in Colorado house a wide variety of strains at both vegetative and 143 flowering stages of growth suggesting that the emission rate of monoterpenes from CCFs is higher than that measured from foliage by Wang et al. (2019). Currently, no database exists 144 145 that can provide the number of plants by strain and growth stage. For the base case, it was assumed that each CCF grew only one strain and that all plants were at the vegetative growth 146 stage resulting in a single and constant EC for each CCF; taken to be 10 µg gdw⁻¹ h⁻¹ of total 147 monoterpenes based on the reported EC from the Critical Mass cultivar (Wang et al., 2019). 148 149 Given the uncertainty in EC, the variety of possible plant stages and cultivars, the EC used in 150 simulation 1 EC was multiplied by a factor of 5 and 10 in simulations 2 EC and 3 EC as a 151 sensitivity analysis.

152 2.1.2 Dry Plant Weight (DPW)

No published studies report the DPW of a Cannabis spp. plant. Both the states of 153 154 Colorado (METRC, 2018) and Washington (LCB, 2017; Topshelfdata, 2017) track the mass 155 of the commercially sold portion of the plant, the "dry bud." The Colorado database, however, 156 is not publicly accessible and was not available for this study. In Washington, using data from 157 all type of facilities (outdoor and indoor) from August-October 2017, it was found that the 158 average dry bud mass per plant was 210 g (0-586 g) shown in Fig. S1a. The Washington 159 database also includes the "wet bud" weight defined as the mass of the bud after it was just 160 harvested (Fig. S1b), but prior to the 7-10 day drying process. The total waste weight, or the 161 remaining mass of the plant after the buds have been harvested, is also recorded. As shown in 162 Eq. (2), the sum of these two masses should equal the total mass of the wet plant.

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171

$$M_{wet \, plant} = M_{wet \, buds} + M_{waste} \tag{2}$$

164 Where, $M_{wet plant}$ is the mass of the entire wet plant (g), and $M_{wet bud}$ is the mass of the 165 wet bud (g), and $M_{wet waste}$ is the mass of the waste (g).

Data from August-October of 2017 were used with Eq. (2), to estimate the wet plant weight resulting in an average of 3,770 g (6-13,405 g) shown in Fig. S1c. The large range in mass is due to the different growing conditions found in CCFs, and the type of strain being grown. The ratio of the wet and dry bud mass data from Washington was used as a surrogate to determine the percentage of water found in the total plant material as shown in Eq. (3).

 $R_{D/W} = M_{dry\ bud} / M_{wet\ bud} \tag{3}$

172 Where, $R_{D/W}$ is the ratio of the masses of the dry to wet bud, and $M_{dry \ bud}$ (g) is the 173 mass of the harvested buds after 7-10 days of drying (Fig. S1d). 174 It was assumed that the same factor could be applied to the total wet plant weight to 175 estimate the *DPW* as shown in Eq. (4).

176

 $DPW = M_{wet \, plant} \times R_{D/W} \tag{4}$

The average of DPW was 754 g (1-2,260 g). For the development of these emission 177 inventories, a base value of 750 g was assumed for DPW based on the average calculated from 178 179 the Washington database. As a sensitivity test, a DPW of 1,500 g representing the mean plus one standard deviation range was chosen. Finally, a DPW of 2,500 g, the maximum yield 180 181 recorded by Washington State Liquor and Cannabis Board, was taken as the upper statistical 182 boundary as shown in Fig. S1e. As the total plant count and reported yields are 3 and 4 factor 183 higher respectively in Colorado than Washington state (LCB, 2017; Topshelfdata, 2017; 184 Hartman et al., 2018b), we took this maximum on the assumption that Cannabis spp. cultivated 185 in CCFs in Colorado in summer season is grown under more optimal conditions than those 186 grown in Washington State resulting in considerably higher yields.

187 **2.1.3 Plant Count (PC)**

Counts of all plants larger than 8 inches have been recorded by the Colorado DOR on a monthly basis since 2014. As of June 2018, there are a total of 1.06 million plants (Hartman et al., 2018a, b). We therefore used 1 million as the base number for the emission inventory. The DOR data only provides county-level information rather than actual number of plants per CCF. The plants were then distributed equally among the CCFs to calculate an average of 905 plants per facility in Denver County and 521 outside of the county.

194 Two sensitivity simulations were conducted based on the assumption that the cannabis 195 industry in Colorado will continue to expand at similar rates in the future. From June 2016 to 196 June 2018 the total number of plants recorded by DOR grew from 826,963 to 1,062,765, an 197 annual average increase of 118,000. Assuming this rate of expansion remains constant, there 198 would be 2 million plants in the state of Colorado by 2025 and this value was used in simulation 6 PC. It was assumed in simulation 7 PC that growth would accelerate in the future to the 199 200 point at which each recreational and medical CCF would contain the maximum number of 201 plants permitted under a Tier 1 license leading to a state-wide total of nearly 4 million plants. 202 The maximum number of plants that can be grown under each licensing tier is shown in 203 supplemental Table S2 (CDOR, 2019). The average plant count per CCF for each PC 204 sensitivity simulation are shown in Table S1.

205 2.2 Emission Inventories for Cannabis Cultivation Facilities (CCF)

Given the large gaps in knowledge, this study will focus only on variabilities in EC, DPW, and PC and will hold other parameters constant. For example, to maximize growing conditions relative humidity, temperatures, CO_2 concentrations, and fertilizer usage are all optimized and vary widely by CCF. Further, this study did not consider other processes such as trimming, harvesting and drying buds which may also release BVOCs.

For this study, it was assumed that all CCFs operated in the same way at a temperature of 30°C and 1000 μ mol m⁻² s⁻¹ of photosynthetically active radiation (PAR). In addition, it was assumed that all emissions from the plants inside a CCF enter the atmosphere. Ventilation to the atmosphere varies widely by the operation, and there are no current regulations or industrywide practices that are being used to mitigate emissions.

In total, seven scenarios of emission inventories were created to explore sensitivities in EC, DPW, and PC as shown in Table 1. In scenarios 1-3, the PC was held to a total of 1 million and a 750 g DPW was assumed. The EC of 10 µg gdw⁻¹ h⁻¹ as reported by Wang et al. (2018) was used in 1_EC, with a sensitivity that multiplied that rate by a factor of 5 (scenario 2_EC), and 10 (scenario 3_EC). The remaining scenarios in Table 1 kept the EC constant at 10 µg gdw⁻¹ h⁻¹. Scenarios 4_DPW and 5_DPW explored the sensitivity of increasing DPW, and scenarios 6_PC and 7_PC increased the total plant count.

223 2.3 Model description and analysis tools

224 2.3.1 Model protocols and evaluation

225 The Comprehensive Air Quality Model with Extensions, CAMx6.10 (ENVIRON, 2013; ENVIRON and Alpine., 2017b), was used to predict ground-level ozone concentrations. 226 227 The model and protocols used in this study are based on the Western Air Quality Modeling 228 Study (WAQS) for 2011 (ENVIRON and Alpine., 2017b; Adelman et al., 2016). The WAQS 2011b baseline model simulation period runs from June 15th to September 15th, 2011, and is 229 230 driven with meteorological data from WRF version 3.3 for the same time period and domain. 231 The model was initialized using Three-State Air Quality Modeling Study standard boundary 232 and initial conditions (ENVIRON and Alpine., 2017b). The model domain is a 2-way nested 233 grid at 12 and 4 km grid cell resolutions (Fig. 1b). Anthropogenic emissions were derived from 234 EPA National Emission Inventory (NEI) version 2011 NEIv2 with updates for point and area 235 sources of oil and gas emissions in the western US. The biogenic emissions inventory was 236 based on the Model of Emissions of Gases and Aerosols from Nature version 2.1 237 (MEGANv2.1) (Guenther et al., 2012). All data and supporting documentation are publicly available via the Intermountain West Data Warehouse (IWDW) website (WAQS, 2017).

239 The revision 2 of Carbon Bond 6 (CB6r2) (Ruiz and Yarwood, 2013) chemistry 240 mechanism was used in all model runs. This groups all monoterpenes as a single compound 241 species, TERP. Thus, the total monoterpenes EC reported in Wang et al. (2018) was converted 242 into the TERP species. TERP undergoes oxidation reactions with the nitrate radical (NO₃), the 243 hydroxyl radical (OH), ozone (O₃), and singlet oxygen. It should be noted that the TERP 244 category includes a wide variety of monoterpenes whose reaction rate constants may differ from TERP ($k_{298} = 6.77 \times 10^{-11}$ molecules cm⁻³ s⁻¹). For example, the rate constant of β -myrcene 245 with OH radical (Hites and Turner, 2009) is 3.35×10^{-10} molecules cm⁻³ s⁻¹ (k₂₉₈), which is 4 246 time higher than TERP and 5.6 times faster than α -pinene (Carter, 2010). 247

248 The details of the WAQS model setup protocol (ENVIRON and Alpine., 2017b) and 249 model performance (Adelman et al., 2016) can be found in IWDW website. In summary, the 250 model performance evaluation concluded that this simulation had met all performance goals 251 for both maximum daily 1-hour (MDA1) and maximum daily 8-hour average (MDA8) ozone. 252 In the performance review report, it was found that the WAQS model had a positive bias for 253 ozone simulated in a 4 km \times 4 km resolution domain, when compared with EPA Air Quality System (AQS) surface monitors (MDA1: 0.8%, MDA8: 0.9%). On days when ozone 254 255 concentrations higher than 60 ppb were measured, the model had a negative bias of -6.2% for 256 MDA1 and -6.3% for MDA8. The model evaluation result also noted that the model 257 performance was best during the spring and summer months.

258 2.3.2 Process Analysis

259 CAMx runs used in this analysis had the process analysis (PA) option enabled 260 (ENVIRON, 2013). The CAMx configuration used here produces two additional files needed 261 for PA: the integrated reaction rate (IRR) and integrated process rate (IPR). These files include 262 the rates of change in concentration of every species due to chemistry and transport for every grid cell and timestep. Python-based Process Analysis (pyPA) and the Python Environment for 263 264 Reaction Mechanisms/Mathematics (PERMM) (Henderson et al., 2010; Henderson et al., 265 2011) were then applied to post-processing the CAMx PA output. PERMM was used to 266 aggregate the chemical and physical process rates for selected model grid cells and layers 267 allowing for tracking of plumes within the planetary boundary layer (PBL).

268 **3. Results**

269 **3.1** Emissions Inventory

270 The seven scenarios were used to estimate a range of emissions of BVOCs from CCFs 271 for the entire state of Colorado. As shown in Table 2, the base case (BC) scenario estimates 272 731,442 ton/year of all VOCs being emitted in Colorado, of which 47% are BVOCs. The BC 273 scenario does not include any emissions from the cannabis industry. Table 2 also shows the 274 seven scenarios that did include CCF emissions ranked in order of their increases in state-wide 275 BVOC emissions. As expected the CCF BVOC emissions scaled linearly with each factor that was changed in Eq. (1). In scenario 3_EC, a 10-fold increase in the emission rate (100 µg gdw-276 277 ¹ h⁻¹) resulted in a 657 metric tons/year increase. Similarly, scenario 2 EC assumes 50 µg gdw⁻ 278 ¹ h⁻¹ and produces 329 metric tons/year. Scenarios 4 and 5 showed the sensitivity of terpene 279 emissions from CCFs to variation in DPW while holding PC constant and an EC of 10 µg gdw⁻ ¹ h⁻¹. It was estimated that an additional 66 ton/year of emissions were produced when a 750 g 280 281 DPW is assumed. This doubles to 131 metric tons/year with a DPW of 1500 g and reaches 219 282 metric tons/year with a DPW of 2500 g. Comparing scenario 1 EC with scenario 6 and 7 shows 283 how the growth in PC will impact emissions of BVOCs. In Colorado, a doubling of the PC 284 increases BVOC emissions by 131 metric tons/year in scenario 6 PC and 261 metric tons/year 285 for the 4 million plants in scenario 7 PC. The largest increases in BVOC emissions were 286 predicted in scenarios 3 EC and 2 EC showing that the total emission rate of BVOCs from 287 CCFs were most sensitive to EC.

288 In March 2018, Denver County housed 41% of CCFs and 55% of all cannabis plants in 289 Colorado (Hartman et al., 2018a). As a result, about 43% of state-wide CCF BVOC emissions 290 occur there (Table 2). Current emission inventories of Denver County show negligible amounts 291 of biogenic emissions accounting for only 0.1% of the total state-wide BVOC emissions. CCF 292 emissions increased BVOC emission rates in Denver Country up to 136% in scenario 3 EC. 293 This changes the total VOC emission rate in Denver County by up to 3.5%. Other cities in 294 Colorado do not have as high a concentration of CCFs, and thus the relative increases were 295 smaller as shown in Table 2.

The introduction of additional cannabis BVOC emissions into model simulations increased the predicted TERP concentrations. Figure 2 shows the maximum increase in TERP concentrations for three scenarios for Denver County over the entire 90-day simulation period. Regardless of the scenario, the largest increases in TERP occurred near the largest 300 concentrations of CCFs. The absolute maximum changes ranged from 0.5-5.0 ppb located at 301 the Elyria Swansea and Globeville neighborhoods in north-central Denver. Increases in TERP 302 were also predicted to the north due to the dominant wind flows in that direction throughout 303 the simulation period. Figure S2 shows the maximum increase in TERP concentrations for the 304 1 EC, 5 DPW, and 3 EC scenarios in the $4 \text{ km} \times 4 \text{ km}$ domain for the entire 90-day simulation 305 period. As expected substantially lower increases in TERP concentrations were predicted for 306 other cities in Colorado: 0.26 ppb in Colorado Springs and 0.24 ppb in Pueblo. Figure 3 shows 307 the hourly changes in TERP concentrations across the entire $4 \text{ km} \times 4 \text{ km}$ domain. The largest 308 increases for all scenarios occurred at night with a peak of 5 ppb at 4:00 AM local standard 309 time (LST). Given that the hourly emissions of terpenes from CCFs were assumed constant for 310 24 hours, these larger nighttime changes can be primarily ascribed to the lack of 311 photochemistry and a shallow nocturnal PBL. These results suggest that the increases of TERP 312 are highly correlated with locations of CCFs, accumulate at night, and have significant losses during the day. 313

314 **3.2 Regional Ozone impacts**

Predicted increases in hourly ozone concentrations in excess of 0.1 ppb only occurred 315 316 when terpene emissions were in excess of 219 metric tons per year, with scenarios 4 DPW, 317 6 PC, and 1 EC having little impact on predicted ozone. Thus, this analysis will focus on two 318 scenarios, 5 DPW, and 3 EC to explore potential regional ozone impacts in the present and 319 future. Figure 4 shows the hourly changes in ozone concentrations across the entire $4 \text{ km} \times 4$ 320 km domain for these two scenarios. During the daytime, the increase in TERP emissions results 321 in a peak ozone increase of 0.34 ppb at 9:00 AM LST for 3 EC with only minimal changes in 322 5 DPW. Figure 5 shows, for Denver County and the Front Range Metropolitan Area, the 323 locations of the daytime (6:00 AM - 6:00 PM LST) maximum increases in hourly ozone 324 concentrations for all 90 days when emissions were added for scenarios 5 DPW and 3 EC. 325 Ozone increases for the entire 4 km \times 4 km domain can be found in Fig. S3. The largest 326 predicted ozone concentrations occurred in Denver County with impacts of 0.11 ppb in 327 5 DPW, and 0.34 ppb in 3 EC as shown in Fig. 5. Both scenarios show that daytime increases 328 in ozone were limited to Denver County and just to the northwest, west, and southwest of 329 Denver County.

There were also night time variations in ozone observed for the modeling domain. In scenario 5_DPW and 3_EC, nighttime increases were more than double the increases predicted

332 during the day. The largest changes in hourly ozone concentrations of 0.67 ppb occurred at 333 0:00 AM LST (i.e. midnight) for 3 EC. Figure 6 shows the location and magnitude of the 334 maximum changes in hourly ozone concentrations during the night (6:00 PM - 6:00 AM LST) 335 in 5 DPW and 3 EC. The extent of ozone increases at night are primarily to the north of 336 Denver indicating a northern outflow. The maximum increase in hourly ozone for the whole of 337 Colorado is shown in Fig. S3, with visibly little changes at night in other cities. These model 338 results suggest that the additional emissions of TERP have immediate impacts on local ozone 339 production chemistry during both the day and night, but little wider impact.

A critical metric for the attainment of the NAAQS ozone standard in Denver County is the maximum daily average 8-hour ozone concentration (MDA8). Figure 7 shows the maximum difference in MDA8 for each grid cell centered on Denver County, across the entire 90-day simulation period for the 5_DPW, and 3_EC scenarios. Maximum increases in MDA8 are 0.14 ppb for 3_EC (Fig. 7b) co-located with the maximum increases in TERP concentrations.

346 **3.2.1 Ozone impact at night**

The maximum hourly ozone increase of 0.67 ppb for the 3_EC scenario occurred on Thursday, July 28th, 2011, at 0:00 AM LST (i.e. midnight) near the largest concentration of CCFs (see Fig. 8). In subsequent hours the plume of ozone moved slowly to the east before being dispersed by the rise of the morning PBL at 6:00 AM LST.

351 To better understand why ozone increased at night, the PA model output was analyzed 352 to quantify the chemical and physical processes producing ozone. Plume tracking was used so 353 that only grid cells where the increase in ozone (i.e. the plume) occurred were included in our 354 analysis, which ran from July 27th, 9:00 PM to July 28th, 6:00 AM LST. The number of vertical 355 model layers included in the analysis also varied to incorporate the hourly evolution of the PBL. 356 Figure S4 provides snapshots of the horizontal grid cells used and the vertical layers that were 357 aggregated throughout the simulation time period. Fig. S5 shows the changes in final ozone 358 concentrations (compared to the base case) for the grid cells and vertical layers included in the 359 analysis, as well as the physical and chemical process rates that account for these changes. 360 Figure S5 shows that the process most responsible for increases in ozone concentrations was 361 chemical production.

For the chosen vertical layers and grid cells Table 3a shows the total rate of the oxidation reactions with TERP across the entire period. Throughout this time, the additional

364 TERP emissions lead to an increase in the number of oxidation reactions thereby generating more secondary VOC products and radical species. The chemical losses of TERP increased 365 366 due to reactions with: OH (from 0.01 ppb to 0.1 ppb; +900%), nitrate radical (NO₃) (from 0.39 ppb to 1.58 ppb; +305%), and O₃ (from 0.04 ppb to 0.2 ppb; +400%). Further analysis confirms 367 368 that night-time oxidation chemistry leading to changes in ozone concentration are driven by 369 NO₃. In the 3 EC scenario, TERP emissions only increased the annual VOC emission in 370 Denver County by 3.5%, but this is sufficient to increase the VOC + NO₃ reaction rates by 371 125%. These increases produce more peroxyl radicals $(TRO_2=HO_2 + RO_2)$ driving further 372 oxidation and further radical production. Table 3b also shows that the generation of OH 373 radicals from reactions of TERP with O₃ increased by 267%. Ultimately, these increases in 374 initial TERP reactions with NO₃ and O₃ increase the NO to NO₂ conversions via the TRO₂ 375 pathway by 44%, reducing the availability of NO to react with O₃. Thus, the increased ozone 376 concentration predicted at night is actually due to the 1 ppb (0.8%) reduction in the loss of 377 ozone to reactions with NO rather than an increase in actual production of ozone (Table 3c). 378 The increased TERP emissions also increase production of NO_x termination products (NO_z) by 379 27% with organic nitrate (NTR; representing \sim 71% of this NO_z product) increasing from 0.66 380 ppb to 1.6 ppb (+142%). This increase in NO_z production at night also results in lower NO 381 concentrations and thus lower ozone titration.

382

3.2.2 Ozone impact during the day

383 The maximum daytime hourly ozone increase of 0.34 ppb occurred at 9:00 AM on Monday, July 18th, 2011, as shown in Fig. 9. On this day, the meteorological conditions 384 385 favoured the maximum possible production of ozone. This day featured "upslope flows" that 386 are a common meteorological condition linked to ozone exceedances periods (Pfister et al., 387 2017). We thus chose to focus on July 18th to understand the daytime changes in chemistry that occur from increased BVOC emissions. As expected, the location of predicted ozone increases 388 389 coincides with the location of the strongest terpene emissions in the domain as shown in Fig. 390 9a. For the daytime hours of 6:00 AM - 2:00 PM LST, the PA option was used to quantify 391 changes in chemical processes for the grid cells and model layers shown in Fig. S6. For these 392 grid cells and layers, Fig. S7 shows the changes in final ozone concentrations compared to the 393 base case and the physical and chemical process rates that impact those concentrations. Table 394 S3 sums the key chemical processes for these hours. The increases in CCF emissions resulted 395 in a 100% increase in OH reactions with TERP producing intermediate oxidation products and 396 ultimately increasing OH production by 0.6%. As a result of this oxidation chemistry, there 397 was an increase of 0.9% in NO to NO₂ conversion by TRO₂ pathway, ultimately leading to a

398 0.1% increase in ozone production.

399 3.2.3 Ozon

.3 Ozone impact sensitivity

400 The maximum modelled daytime hourly ozone increase due to additional CCF 401 emissions occurred on July 18th. Using this day multiple sensitivity simulations were 402 performed, where CCF emissions from Denver County were incrementally increased up to 403 3,800 ton/year. Figure 10 shows the increase in terpene emissions from Denver County versus 404 the largest daily increase in hourly ozone concentrations. Figure 10a shows a linear relationship, 405 indicative of a VOC limited environment, where hourly ozone concentrations are predicted to 406 increase by 1 ppb for every 1,000 ton/year increase in TERP emissions during the day, and 407 0.85 ppb at night. Also shown is the sensitivity to the MDA8 ozone where there is a 0.30 ppb 408 increase for every 1,000 ton/year of TERP emissions. According to projected emission 409 inventories provided by the state of Colorado, the ozone non-attainment area was expected to 410 see reductions of 26.4% of NO_x and 24.6% of VOC emissions by the year 2017 (ENVIRON 411 and Alpine., 2017a). Under these reduced anthropogenic emission scenarios, Fig. 10b shows 412 how ozone would then respond to additional CCF TERP emissions. Figure 10b continues to 413 show a linear relationship, where hourly ozone concentrations are predicted to increase by 1.5 414 ppb for every 1,000 ton/year increase in TERP emissions during the day, and 1.8 ppb at night. 415 In the future case, the MDA8 ozone increases by 0.38 ppb increase for every 1,000 ton/year of 416 TERP emissions. Therefore, Denver will still be VOC-limited and ozone is predicted to more 417 sensitive to CCF emissions of terpenes.

418 **4.** Conclusion

419 This study provides the first VOC emission inventory to be compiled for the cannabis 420 industry in Colorado, the first time such analysis has been conducted anywhere in the USA. 421 Given the current state of knowledge of emission rates and growing practices, there are 422 considerable uncertainties in the basic parameters required to build such an inventory. Using 423 realistic bounds on each parameter, we developed seven scenarios, which resulted in estimated 424 emission rates that ranged over an order of magnitude. The highest emissions occur in Denver 425 County, with rates ranging between 36-362 metric tons/year for the different scenarios, from a 426 total of 66-652 metric tons/year across Colorado as a whole.

427 We included these additional terpene emissions in the Comprehensive Air Quality 428 Model with Extensions (CAMx), the model used by the state of Colorado for regulatory 429 monitoring and projections. Taking the worst case (3 EC) and median scenario (5 DPW) we 430 consider representative of current uncertainty upper boundary and future industry expansion; 431 we find that these projected increases in emissions lead to maximum increases in terpene 432 concentrations of up to 5.0 ppb. The largest impacts were seen in locations with the highest 433 terpene emissions coming from CCFs, i.e. in Denver County. We further found that these 434 increases in terpene concentrations affected the local atmospheric chemistry and air quality 435 with ground-level ozone concentrations increasing by as much as 0.34 ppb during the day and 436 0.67 ppb at night. In general, simulated nighttime increases were higher than those during the davtime were, and we take the nighttime of July $27^{\text{th}} - 28^{\text{th}}$ as a case study to further investigate. 437 By applying process analysis (PA), following the evolving plume of VOCs and ozone, we find 438 439 that the initial reactions of the additional terpenes with OH, NO₃ and ozone result in increased 440 formation of peroxyl radicals which increases the NO to NO₂ conversion rate; also removes 441 the NO_x to generate more NO_z product. This effectively reduces the loss of ozone by reaction 442 with NO, increasing the total ozone concentration.

We acknowledge, however, the considerable uncertainties that surround our projections and call for the need for continued efforts to reduce these such that a more accurate assessment of the regional air quality implications of this industry can be made. Future studies that include ambient BVOC measurements are critical for comparisons with model predictions. Additionally, in the model chemical mechanism more accurate and mechanistic representation of terpene species is needed that can reflect the current cannabis emission composition. Currently, the model surrogate "TERP", which represents all monoterpene species in the 450 mechanisms, may not represent the precise rate constant for BVOC emissions from cannabis. 451 Further data are needed to reduce uncertainties in emission inventory estimates specifically 452 those regarding CCF-specific information on plant counts, and weight by cultivar and growth 453 stage, coupled with information about the agronomical practices of Cannabis cultivation in 454 CCFs. Additional measurements of emission capacities of different cannabis strains at different 455 growth stages are also needed. Further, the emission inventory version is for the year 2011; it 456 may not be suitable to estimate the ozone impacts by the CCF industry.

457 We chose to focus on ozone, since Denver is a moderate non-attainment area with an 458 ozone State Implementation Plan (SIP) (ENVIRON and Alpine., 2017b, a; Colorado, 2018) in 459 accordance with the EPA regulations. But assessments of the impact of these additional terpene 460 emissions on particulate matter (PM_{2.5}) is warranted given the high secondary organic aerosol (SOA) yields of terpenes from 0.3 to 0.8 (Iinuma et al., 2009; Lee et al., 2006; Fry et al., 2014; 461 462 Slade et al., 2017). It should also be borne in mind that investigations of indoor air quality are 463 needed given the findings of Martyny et al. (2013) and Southwellb et al. (2017) that indoor 464 terpene concentrations reached 50-100 ppb in growth rooms and 30-1,600 ppb in flowering 465 room, likely initiating intense photochemistry under the powerful grow lamps in use in CCFs.

466 **Code availability:**

- 467 1. The source code of the CAMx6.10 model can be downloaded on the Environ website:
 468 <u>http://www.camx.com</u>
- 469 2. The process analysis tools and source codes including PseudoNetCDF, pyPA, and
- 470 PERMM, can be downloaded on GitHub: <u>https://github.com/barronh/pseudonetcdf</u>,
 471 https://github.com/barronh/pypa, and https://github.com/barronh/permm
- 472 3. Python 2.7 is used to treat the model output and can be downloaded on anaconda
 473 python website: <u>https://www.anaconda.com/distribution/</u>

474 **Data availability:**

- 475 The air quality model input data and output data (~2.3TB) of WAQS2011b episode
- 476 for Colorado can be downloaded on IWDW website:
- 477 <u>https://views.cira.colostate.edu/iwdw/</u>

478 Author contribution

Chi-Tsan Wang and Dr. William Vizuete are lead researchers in this study responsible for research design, experiments, analyzing results and writing the manuscript. Dr. Christine Wiedinmyer and Dr. Kirsti Ashworth are also co-head researchers, and guided the research design, assessed model results, and contributed to writing the manuscript. Dr. John Ortega, and Dr. Peter Harley helped in collecting data and writing the manuscript. Dr. Quazi Z. Rasool helped to analyze model results and contributed in writing the manuscript.

485 **Competing interests**

486 The Authors declare that they have no conflict of interest.

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- 694

695 Tables

- 696 **Table 1.** Simulation scenarios and assumed values for emission capacity (*EC*) rate, dry plant
- 697 weight (*DPW*), and the plant count (*PC*) for Colorado and Denver County. The base case (BC)
- 698 scenario has no cannabis emissions.

	EC	DPW	Р	С
Name	(ug gdw ⁻¹ hr ⁻¹)	(gdw plant ⁻¹)	Colorado	Denver County
BC	0	0	0	0
1_EC	10	750	$1.0 imes 10^6$	5.5×10 ⁵
2_EC	50	750	1.0×10^{6}	5.5×10 ⁵
3_EC	100	750	$1.0 imes 10^6$	5.5×10 ⁵
4_DPW	10	1,500	1.0×10^{6}	5.5×10 ⁵
5_DPW	10	2,500	$1.0 imes 10^6$	5.5×10 ⁵
6_PC	10	750	$2.0 imes 10^6$	1.1×10 ⁶
7_PC	10	750	$4.0 imes 10^6$	2.2×10 ⁶

- 700 **Table 2.** The estimated BVOC and total VOC emission rates (metric tons/year) for the base
- 701 case (BC) scenario. Also shown are the increases in VOC emissions for all scenarios shown in
- 702 Table 1 for Colorado, Denver County, Colorado Springs, Pueblo, and Boulder. The numbers
- in parenthesis are the percentage increases compared with the BC scenario.

	Colorado		Denver County		Colorado Springs		Pueblo		Boulder	
Name	BVOC	Total VOC	BVOC	Total VOC	BVOC	Total VOC	BVOC	Total VOC	BVOC	Total VOC
BC	340,268	731,442	265	10,465	5,184	15,143	5,870	9,184	3,677	9,820
3_EC	657 (+0.19%)	+0.09%	362 (+136%)	+3.5%	60 (+1.20%)	+0.40%	53 (+0.90%)	+0.58%	26 (+0.70%)	+0.26%
2_EC	329 (+0.10%)	+0.04%	181 (+68%)	+1.7%	30 (+0.58%)	+0.20%	27 (+0.45%)	+0.29%	13 (+0.35%)	+0.13%
7_PC	261 (+0.08%)	+0.04%	116 (+44%)	+1.1%	42 (+0.80%)	+0.27%	22 (+0.38%)	+0.24%	12 (+0.33%)	+0.12%
5_DPW	219 (+0.06%)	+0.03%	121 (+45%)	+1.2%	20 (+0.39%)	+0.13%	18 (+0.30%)	+0.19%	9 (+0.23%)	+0.09%
4_DPW	131 (+0.04%)	+0.02%	72 (+27%)	+0.69%	12 (+0.23%)	+0.08%	11 (+0.18%)	+0.12%	5 (+0.14%)	+0.05%
6_PC	131 (+0.04%)	+0.02%	72 (+27%)	+0.69%	12 (+0.23%)	+0.08%	11 (+0.18%)	+0.12%	5 (+0.14%)	+0.05%
1_EC	66 (+0.02%)	+0.01%	36 (+14%)	+0.35%	6 (+0.12%)	+0.04%	5 (+0.09%)	+0.06%	3 (+0.07%)	+0.03%

705 Table 3. All data summed from July 27th, 9:00 PM LST to July 28th, 5:00 AM LST for grid 706 cells and layers shown in Fig. S4. The base case (BC) scenario column shows the absolute 707 predicted values and, the subsequent columns show the predicted changes due to emissions 708 from the 3 EC scenario. Percentages in parenthesis are the changes in 3 EC relative to BC. 709 Shown are the (a) total amount of VOC and TERP consumed due to oxidation (ppb), the (b) 710 total amount of hydroxyl radical (OH) and total peroxyl radicals (TRO₂) that were generated 711 and their sources (ppb), and the (c) total amount of Nitrogen Dioxide (NO₂) and NOx 712 termination products (NO_z) produced and their sources (ppb).

713 (a)

	BC	3_EC
VOC + OH	1.36	1.68 (+23.5%)
TERP + OH	0.01	0.10 (+900%)
$VOC + NO_3$	0.91	2.05 (+125%)
$TERP + NO_3$	0.39	1.58 (+305%)
$VOC + O_3$	1.80	1.97 (+9.40%)
$TERP + O_3$	0.04	0.20 (+400%)

714

715 (b)

	BC	3_EC
OH generation (from VOC + O ₃)	1.00	1.10 (+10.0%)
from TERP + O ₃	0.03	0.11 (+267%)
TRO ₂ generation	34.2	42.8 (+25.1%)
from VOC initial reactions	3.25	5.03 (+54.8%)
from TERP initial reactions	0.47	1.98 (+321%)

716

717

(c)

	BC	3_EC
NO to NO ₂	198	197 (-0.70%)
$NO + O_3$	158	157 (-0.80%)
$NO + TRO_2$	3.50	5.04 (+44.0%)
NO _z generation	4.91	6.24 (+27.1%)
NTR generation	0.66	1.60 (+142%)
PAN generation	1.54	1.56 (+1.30%)
PANX generation	0.54	0.66 (+22.2%)
HNO ₃ generation	2.17	2.42 (+11.5%)

719 Figures

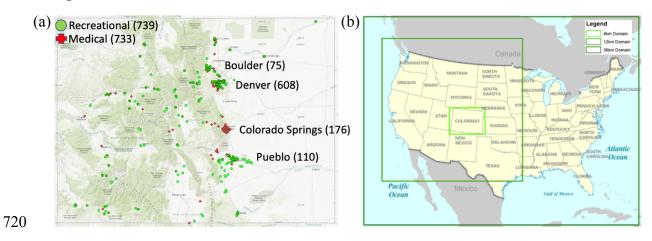
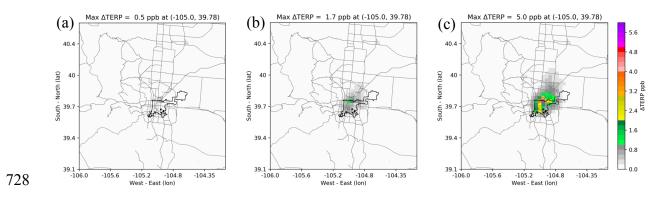


Figure 1. (a) The locations of medical (red) and retail (green) Cannabis cultivation facilities
(CCFs) in Colorado as of March 1, 2018. The corresponding values are the number of CCFs
found within each city. (b) The 36km × 36km resolution of Western Air Quality Model Study
(WAQS) and nested inner 12km × 12km resolution domains and 4km × 4km resolution domain
used by the Comprehensive Air Quality Model with Extensions (CAMx) (ENVIRON and
Alpine., 2017b).



729 Figure 2. The maximum increase in TERP concentrations (ppb) for Denver County and Front

Range over the entire 90-day simulation for the (a) 1_EC, (b) 5_DPW, and (c) 3_EC scenarios.

The black outlines Denver County and the grey lines are state and interstate highways.

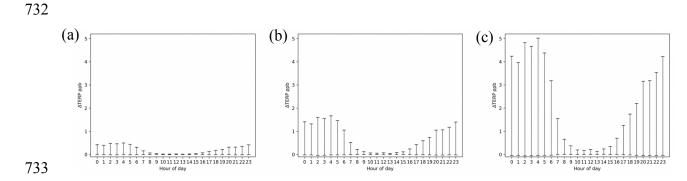


Figure 3. The hourly changes in TERP concentrations across the entire 4 km × 4 km domain,
over the 90 days simulation for the (a) 1_EC, (b) 5_DPW and (c) 3_EC scenarios.

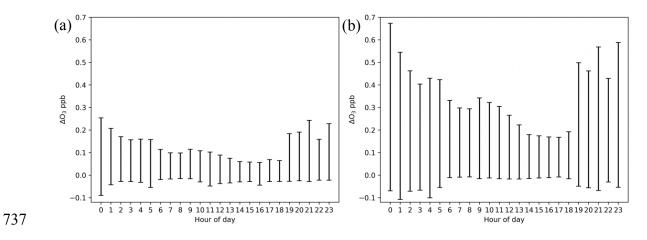


Figure 4. The predicted differences in hourly ozone concentrations (ppb) across the entire
Colorado domain, over the 90 days simulation for the (a) 5_DPW and (b) 3_EC scenarios.

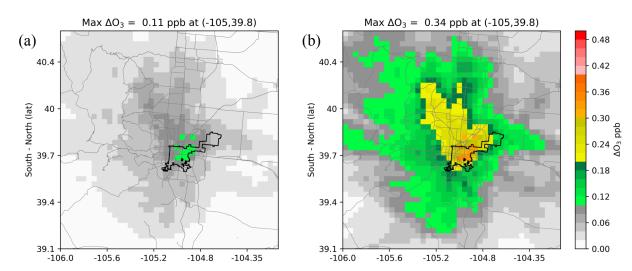


Figure 5. The predicted changes in hourly ozone concentrations for the Denver region from 6
 AM – 6 PM LST for all 90 days of the simulation for the (a) 5 DPW and (b) 3 EC scenarios.

The grey lines indicate major highways and the black line outlines Denver County.

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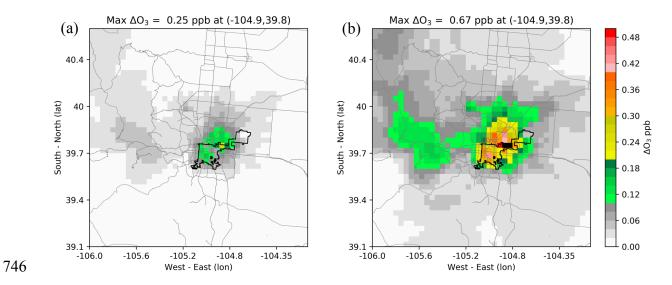


Figure 6. The predicted changes in hourly ozone concentrations for the Denver region from 6
PM – 6 AM LST for all 90 days of the simulation for the (a) 5 DPW and (b) 3 EC scenarios.

749 Black regions within the map indicate ozone increase values greater than 0.5 ppb. The grey

750 lines indicate major highways and the black line outlines Denver County.

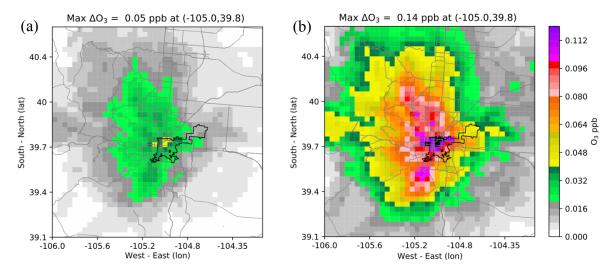


Figure 7. The predicted maximum increases in the maximum daily average 8-hour (MDA8)
ozone concentration (ppb) for the (a) 5_DPW and (b) 3_EC scenarios for the Denver region
over the 90-day simulation period. The black indicates ozone increase values greater than
0.12 ppb.

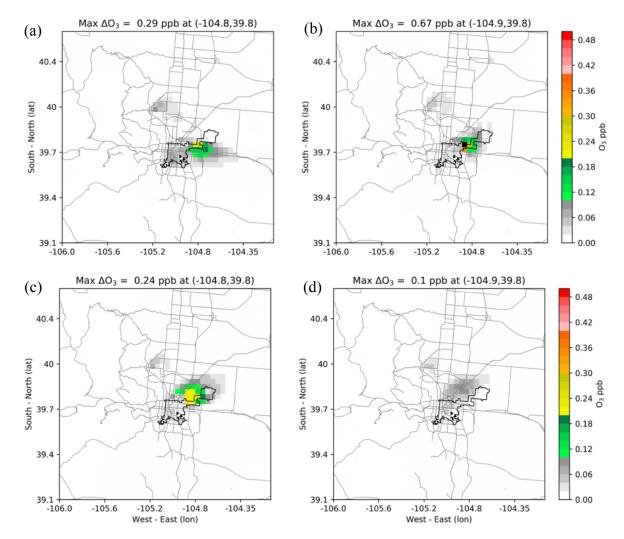


Figure 8. For the 3_EC scenario on July 28th, 2011, the largest hourly predicted ground level
ozone increases at (a) July 27th, 9 PM LST, and for July 28th, at (b) 0 AM LST (i.e. midnight),
(c) 3 AM LST and (d) 6 AM LST.

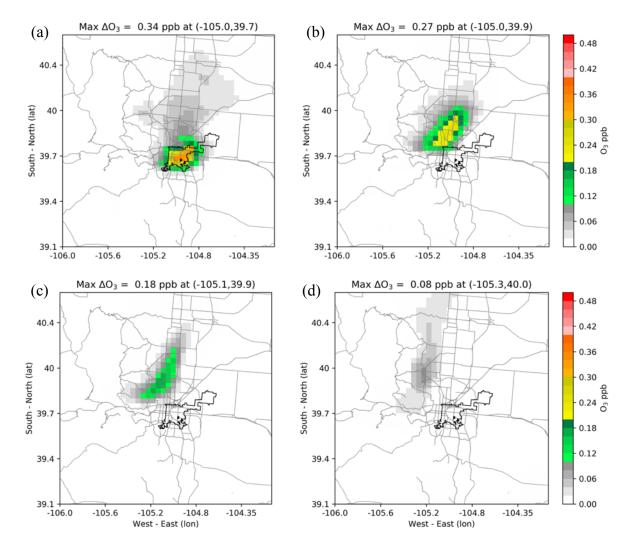


Figure 9. For the 3_EC scenario on July 18th, 2011 the largest hourly predicted ground level
ozone increases at (a) 9 AM LST, (b) 12 PM LST (i.e. noon), (c) 2 PM LST, and (d) 5 PM
LST. The maximum of 0.34 ppb occurred at 9 AM LST.

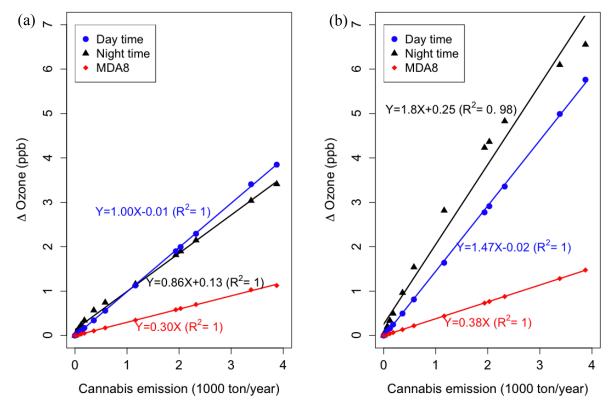


Figure 10. For July 18th during (a) 2011 and (b) 2017 the predicted maximum increase in
hourly ozone concentrations during daytime hours (6 AM – 6 PM LST) in blue, and nighttime
hours (6 PM– 6 AM LST) in black versus additional terpene emissions in Denver County. Also
shown is the response in maximum daily average 8-hour ozone concentration (MDA8) in red.