

1 Estimating vehicle carbon dioxide emissions from Boulder, Colorado using horizontal path-integrated
2 column measurements

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9
10 Abstract

11 We performed seven and a half weeks of path-integrated concentration measurements of CO₂, CH₄, H₂O,
12 and HDO over the city of Boulder, Colorado. An open-path dual-comb spectrometer simultaneously
13 measured time-resolved data across a reference path, located near the mountains to the west of the city, and
14 across an over-city path that intersected two-thirds of the city, including two major commuter arteries. By
15 comparing the measured concentrations over the two paths when the wind is primarily out of the west, we
16 observe daytime CO₂ enhancements over the city. Given the warm weather and the measurement footprint,
17 the dominant contribution to the CO₂ enhancement is from city vehicle traffic. We use a Gaussian plume
18 model combined with reported city traffic patterns to estimate city emissions of on-road CO₂ as (6.2 ± 2.2)
19 $\times 10^5$ metric tons (MT) CO₂/year, after correcting for non-traffic sources. Within the uncertainty, this value
20 agrees with the city bottom-up greenhouse gas inventory for the on-road vehicle sector of 4.5×10^5 MT
21 CO₂/year. Finally, we discuss experimental modifications that could lead to improved estimates from our
22 path-integrated measurements.

23 24 1. Introduction

25 Measurements of greenhouse gases, especially CO₂ and CH₄, are critical for monitoring,
26 verification, and reporting as countries and cities work towards decreasing their carbon emissions.
27 Measurements on the city-scale are critical because cities contribute to a large fraction of global
28 emissions (Marcotullio et al., 2013; Seto et al., 2014). However, quantification of city greenhouse gas
29 emissions is challenging, especially for CO₂ since it has a high background and numerous point and
30 diffuse sources including traffic, power plants, and animal and plant respiration. Emissions of pollutants
31 are typically determined using two methods: a top-down approach using atmospheric measurements over
32 a specific site or area to adjust a prior model, and bottom-up inventories that calculate emissions based on
33 sector activity and sector emissions factors. Here we demonstrate a technique for top-down
34 measurements that uses an open-path sensor rather than a point sensor.

35 Quantification of CO₂ fluxes from cities has been determined from eddy covariance flux
36 measurements with a point sensor located on a tower in or near a city (Nemitz et al., 2002; Velasco et al.,
37 2005; Coutts et al., 2007; Bergeron and Strachan, 2011; Velasco et al., 2014). However, for a single
38 sensor, the relatively small footprint of the eddy covariance flux measurements limits the utility of this
39 technique for large cities as do violations of the horizontal homogeneity assumption (Järvi et al., 2018).
40 To overcome this limitation, tower networks of point sensors can measure CO₂ at multiple sites within a
41 city and at background sites outside the city (McKain et al., 2012; Lauvaux et al., 2013; Bréon et al.,
42 2015; Staufer et al., 2016; Lauvaux et al., 2016; Shusterman et al., 2016; Mueller et al., 2017; Verhulst et
43 al., 2017; Sargent et al., 2018; Mitchell et al., 2018). To distinguish the small enhancements compared to
44 the large background, these networks often use expensive, high-precision cavity ringdown (CRDS)
45 instruments resulting in a high cost. The BEACO₂N network (Shusterman et al., 2016), on the other
46 hand, has a much lower cost per sensor. It requires calibration for quantitative results, but the high
47 density of the point sensors can provide lower sensitivity to systematics (Turner et al., 2016). All of these
48 methods use an inversion to determine the total emissions and thus rely on well-known priors and high-
49 resolution mesoscale atmospheric models.

50 More recently, several other approaches have also been applied to city-scale emissions. Aircraft
51 mass balance measurements (White et al., 1976; Ryerson et al., 2001) have been used to determine city

emissions (Mays et al., 2009; Heimbürger et al., 2017). However, the use of an aircraft is costly and labor intensive, and therefore not suited to long-term continuous measurements. Column measurements from the Total Carbon Column Observation Network (TCCON) were used to calculate total South Coast Air Basin (SoCAB) CO and CH₄ emissions, but not CO₂ (Wunch et al., 2009). Data from the Orbiting Carbon Observatory satellite (OCO-2) was recently combined with TCCON data to estimate CO₂ emissions from the LA basin (Hedelius et al., 2018).

As an alternative to these approaches, horizontal, kilometer-scale, open-path instruments could in principle be used to determine CO₂ emissions from cities. Such instruments are capable of continuous measurements over a large area with a single instrument, e.g. (Wong et al., 2016; Dobler et al., 2017; Coburn et al., 2018). These sensors also have the advantage of being insensitive to small changes in local meteorology and are not subject to the same representation errors as point sensors (Ciais et al., 2010). Several such systems have been deployed. A laser absorption spectrometer system (GreenLITE) has mapped CO₂ concentrations over Paris, but not yet quantified emissions (Dobler et al., 2017). The California Laboratory of Atmospheric Remote Sensing Fourier Transform Spectrometer (CLARS-FTS) is a downward-looking slant column Fourier transform spectrometer (FTS) that scans across 28 measurement targets in the Los Angeles Basin to measure CO₂, CH₄, and O₂ (Wong et al., 2015). Based on the measured CH₄:CO₂ ratio and the bottom-up CO₂ inventory from California Air Resources Board, researchers have calculated the LA Basin CH₄ emissions (Wong et al., 2016), but not yet the CO₂ emissions.

Here we present the quantification of city CO₂ emissions using open-path measurements made with a dual frequency comb spectrometer. While dual-comb spectroscopy is a relatively new technique it has a unique set of attributes that make it attractive for open path measurements (Rieker et al., 2014; Coddington et al., 2016; Waxman et al., 2017; Coburn et al., 2018). Dual-comb spectroscopy (DCS) is a high-resolution, broadband technique spanning hundreds of wavenumbers, but with a resolution that exceeds even high-end FTIRs leading to a negligible instrument lineshape (Coddington et al., 2016). This allows for simultaneous measurements of multiple species and path-integrated temperature with low systematic uncertainty and without the need for instrument calibration. Additionally, the eye-safe, high-brightness, single transverse-mode output of a frequency comb allows for beam paths exceeding 10 km while the speed and parallelism of the measurement suppress any spectral distortion from the inevitable turbulence-induced power fluctuations over such a path (Rieker et al., 2014; Waxman et al., 2017).

Figure 1 shows the measurement layout for an initial campaign to quantify CO₂ emissions from Boulder, Colorado. Here we take the light from a dual comb spectrometer near the edge of the city and simultaneously measure two paths: a reference path that points west-southwest towards the mountains and an over-city path that crosses the city to the northeast, covering the main traffic arteries of the city with sensitivity to traffic emissions. We acquire time-resolved data at 5-minute resolution of CO₂, CH₄, H₂O and isotopologues over 7.5 weeks. The dry mole fraction of CO₂ shows a diurnal cycle consistent with a morning build-up from traffic followed by a mid-day decline due to the rising boundary layer. In addition, there is a distinct difference between the weekday and weekend cycles for CO₂, consistent with traffic patterns. In order to demonstrate the utility of this method for emissions quantification, we perform a preliminary estimate of the CO₂ emissions from traffic. To do this, we filter the data for days when the wind is out of the west and not too strong so that there is a measurable daytime enhancement in CO₂ between the reference path and over-city path. Given the weather, beam path location, and observation times, the dominant contribution will be from traffic rather than residential or industrial emissions. We apply a Gaussian plume model to calculate the city emissions based on the expected distributed source (due to traffic) and the path-averaged concentrations. After adjusting for small expected contributions from residential sources and a local utility plant, the measured emission value is scaled to annual city-wide emissions based on city traffic count data. We estimate $(6.2 \pm 2.2) \times 10^5$ metric tons (MT) CO₂/year, compared to the bottom-up City of Boulder inventory estimate of 4.46×10^5 MT CO₂/year. Finally, we discuss improvements to this estimate, which could be realized by more advantageous beam paths that sample a larger spatial and temporal fraction of the full city emissions and by a more detailed inventory model.

103
104 2. Experimental data

105
106 2.1 DCS measurements

107 The dual frequency comb spectroscopy (DCS) system was located on the top floor of the National
108 Institute of Standards and Technology (NIST) building in Boulder, Colorado. This instrument has been
109 described previously (Truong et al., 2016; Waxman et al., 2017). The light from the combs is split to
110 generate two combined dual-comb outputs, one of which is transmitted over the reference path and one of
111 which is transmitted over the city path (see Fig. 1.) Here, we transmit 2-10 mW of light spanning 1.561
112 to 1.656 μm , which includes absorption lines from CO_2 , CH_4 , H_2O and HDO. The returning light from
113 each path is detected and digitized to yield the transmitted optical spectrum at a point spacing of 0.0067
114 cm^{-1} (1.5 picometer) and with effectively perfect (10 ppb) frequency accuracy and narrow instrument
115 lineshape ($\sim 4 \times 10^{-6} \text{ cm}^{-1}$). A typical spectrum from the reference path is shown in Fig. 2. A fit of this
116 transmitted spectrum yields the path-averaged gas concentrations. The absolute frequency accuracy and
117 high frequency resolution of the dual-comb spectrometers translates to a high precision and accuracy in
118 the retrieved concentrations. Further, DCS spectra are undistorted by turbulence due to the simultaneous
119 acquisition of all spectral channels and the fast sample rate of the instrument (1.6 ms/spectrum, averaged
120 up to 5 minutes here) (Rieker et al., 2014).

121 In previous work (Waxman et al., 2017), we confirmed the high precision and accuracy possible
122 with open-path DCS. Two DCS instruments, constructed by different teams, measured atmospheric air
123 over adjacent paths over a two-week period. The retrieved path-averaged gas concentrations agreed to
124 better than 0.6 ppm (0.14%) for CO_2 and 7 ppb (0.35%) for CH_4 across the full two week period, where
125 the analysis of the two DCS instruments used a common spectral database (HITRAN 2008, Rothman et
126 al., 2009) to retrieve the concentrations from the absorption spectrum. In the work here, a single DCS
127 instrument probes the concentrations across two different open paths simultaneously, which should
128 further suppress any systematic offsets to below 0.45 ppm (Waxman et al., 2017). In addition, (Waxman
129 et al., 2017) compared the two DCS instruments to a stationary cavity ringdown (CRDS) point sensor
130 whose inlet was approximately at the midpoint of the open path. This comparison actually took place
131 over the reference path during the first two weeks of the present work. During that time, we found a
132 roughly constant difference of 3.4 ppm CO_2 and 17 ppb CH_4 between the DCS and CRDS systems. At
133 present, we attribute this offset to differences in the calibration scheme as the DCS is tied to the HITRAN
134 database while the CRDS is tied to the manometric (or gravimetric depending on the gas) WMO scale.
135 Similar level offsets have been observed in comparison of the TCCON open-path FTS instrument and
136 point sensor-based vertical columns resulting in the TCCON CO_2 scaling factor of 0.9898 (4.08 ppm for a
137 mixing ratio of 400 ppm) (Wunch et al., 2015). This offset does not affect the results here as it is common
138 to both the reference and over-city paths.

139 The reference and over-city paths had different path lengths and therefore used slightly different
140 telescopes and launch powers. For the reference path, 2 mW of dual-comb light is launched from a 2-inch
141 home-built off-axis telescope (Cossel et al., 2017; Waxman et al., 2017). The light travels to a 2.5-inch
142 retroreflector located on a hilltop 1 km to the southwest of NIST and then is reflected back to a detector
143 that is co-located with the launch telescope for a $1950.17 \pm 0.15 \text{ m}$ round-trip path. Return powers vary
144 constantly with air turbulence but we collect about 200 μW for a typical 10 dB link loss. For the city
145 path, 10 mW of dual-comb light is launched from a modified 10-inch diameter astronomical telescope to
146 a 5-inch retroreflector located on a building roof 3.35 km to the northeast for a $6730.66 \pm 0.15 \text{ m}$ round-
147 trip path. We collect about 100 μW for a typical 20 dB link loss. Round-trip path distances were
148 measured with a laser range finder. Telescope tracking of the retroreflector is implemented to
149 compensate for thermal drifts via a co-aligned 850 nm light emitting diode (LED) and Silicon CCD
150 camera (Cossel et al., 2017; Waxman et al., 2017).

151 The measured spectra are analyzed as described in (Rieker et al., 2014; Waxman et al., 2017) at
152 32 second intervals. Briefly, we fit a 7th-order polynomial and HITRAN data to the measured spectrum in
153 100-GHz (0.333 cm^{-1}) sections to remove the underlying structure from the comb themselves (as opposed

154 to the atmospheric absorption). We fit the resulting absorption spectrum twice: once in the region from
155 6171 cm^{-1} to 6271 cm^{-1} (1.595 to $1.620\text{ }\mu\text{m}$) to obtain the path-averaged temperature from the $1.6\text{ }\mu\text{m}$ CO_2
156 band, and once over the entire spectrum to obtain $^{12}\text{CO}_2$, $^{13}\text{CO}_2$, CH_4 , H_2O , and HDO concentrations using
157 the retrieved temperature. We then use the retrieved H_2O concentration to correct the wet CO_2 and CH_4
158 mole fractions to dry mole fractions, hereafter referred to as X_{CO_2} and X_{CH_4} given in units of ppm and ppb
159 (micromole of CO_2 per mole of dry air, and nanomole of CH_4 per mole of dry air). The correction
160 equations are $X_{\text{CO}_2} = \text{CO}_2/(1-\text{H}_2\text{O})$ and $X_{\text{CH}_4} = \text{CH}_4/(1-\text{H}_2\text{O})$.

161 The variations in the retrieved concentrations are due to statistical uncertainty, systematic
162 uncertainty (discussed above), and the true variations in the gas concentrations. Figure 8 of (Waxman et
163 al., 2017) quantified the statistical uncertainty in terms of the Allan deviation over the 2-km reference
164 path for both X_{CH_4} and X_{CO_2} . Figure 3 here provides an Allan deviation for just X_{CO_2} over both the ~ 6.7 -
165 km city and ~ 2 -km reference paths, as calculated from a relatively “flat” 1000-s period of this
166 measurement campaign on the night of 3 to 4 October 2016. As expected, the statistical uncertainty over
167 both paths improves as the square root of integration time until reaching a floor, which we attribute to real
168 variations in the atmospheric gas concentrations. At 30 seconds, the statistical uncertainty of X_{CO_2} is 0.76
169 ppm for the reference path and 0.64 ppm for the over-city path, finally dropping to 0.21 ppm and 0.15
170 ppm, respectively, at about 15 minutes. In most subsequent figures, we show results at a 5-minute
171 averaging time for which the statistical uncertainty is well under 0.3 ppm of X_{CO_2} for both paths and
172 therefore well below the typical atmospheric variations. Note that the uncertainty also improves with path
173 length, as expected due to the stronger absorption. The lower uncertainty over the city path reflects the
174 expected improvement from the $3.4\times$ longer path length lessened by the $2\times$ reduction in return signal
175 power for the longer path length.

176 177 2.2 Meteorological Measurements

178 Meteorological data including pressure, wind direction, and wind speed measurements are
179 obtained from meteorological stations located at NCAR-Mesa and NCAR-Foothills
180 (<ftp://ftp.eol.ucar.edu/pub/archive/weather>), which are approximately the endpoints of our measurement
181 paths (see Fig. 1), as well as a 3-D sonic anemometer located at NIST. The path-averaged air temperature
182 was retrieved from the CO_2 spectra as described above.

183 184 2.3 Traffic data

185 We measure a subset of Boulder traffic, so we use the city traffic data to determine the fraction
186 covered by our footprint (see Fig. 1). Traffic data from the City of Boulder is freely available at:
187 [https://maps.bouldercolorado.gov/traffic-counts/?_ga=2.264109964.1414067815.1500302174-](https://maps.bouldercolorado.gov/traffic-counts/?_ga=2.264109964.1414067815.1500302174-274759643.1492121882)
188 [274759643.1492121882](https://maps.bouldercolorado.gov/traffic-counts/?_ga=2.264109964.1414067815.1500302174-274759643.1492121882). The city provides two types of traffic data that are useful in this work: the
189 Arterial Count Program (ART) and the Turning Movement Count (TMC) data.

190 ART measures traffic at 18 major intersections in Boulder for five days (one work week, Monday
191 through Friday) every year in one-hour bins to create a diurnal cycle. The traffic counts for 2016 are
192 shown in Fig. 4. We use these data to scale our selected measurement time periods to a full day as
193 discussed in section 3.3.4. Note that there is only a 10-20% “peak” in traffic counts at the standard
194 commuter times with generally high traffic levels from 7:00 to $\sim 19:00$, which agrees with the traffic
195 emissions reported by the Hestia inventory model for the similar city of Salt Lake City, UT (Mitchell et
196 al., 2018).

197 TMC measures the number of vehicles at 140 intersections in Boulder for one work day per year
198 during the hours of 7:45-8:45, 12:00-13:00, and 16:45-17:45. One third of each of these sites is measured
199 every year. We have scaled the 2014 and 2015 data to 2016 traffic levels by using total vehicle mile
200 values available from the City of Boulder. We approximate city vehicle emissions by using the TMC
201 locations as our source locations with a source strength scaled based on the location’s fractional traffic
202 count.

203 204 3 Results and Discussion

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3.1 DCS measurements

All 7.5 weeks of DCS measurements of CO₂, CH₄, H₂O, and HDO are shown in Fig. 5. HDO is not used here but is shown for completeness (note that the HDO concentration is scaled by the isotopic abundance in HITRAN). We have insufficient precision to measure time-resolved ¹³CO₂ concentrations over the 2-km path. However, there are very clear enhancements in the over-city path relative to the reference path for the other trace gases, especially for CO₂. These enhancements are observed primarily at night when the boundary layer is lower. For example, on Oct. 13 the CO₂ enhancement reaches 129 ppm and the CH₄ enhancement reaches 265 ppb. Daytime enhancements occur when the wind speed is very low and intermittent (typically below 5 m/s), which allows emitted gases to build up over the city. When the wind increases to steady moderate speeds, the concentrations drop quickly as the emissions are flushed out of the city. The H₂O retrieval is important as accurate knowledge of the time-dependent water concentration is needed to calculate the dry CO₂ and CH₄ mole fractions (see Section 2.1). Also, the correlation of the water concentration between the two paths indicates the two paths sense the same air mass, which is further substantiated in Figure 7a and is central to attributing their different CO₂ concentration to local urban sources.

3.2 Diurnal Cycles

The diurnal cycle of X_{CO₂} and X_{CH₄} for both the reference path and the over city path are shown in Fig. 6 for weekdays (midnight to midnight Monday through Friday) and weekends (midnight to midnight Saturday and Sunday). We choose to include Monday as a weekday and Saturday as a weekend because the influence of emissions from the previous day is expected to be low. The diurnal cycle of the wind direction and the wind speed measured at NCAR Foothills are also shown in the top panel of Fig. 6. All diurnal cycles are the median values over the full 7.5 weeks of measurements and the bars reflect the 25%/75% quartile values.

The diurnal cycle of the reference path CO₂ is nearly flat and nearly identical for both weekends and weekdays. It has a slight maximum between 9 and 10 am, with average values of 410 to 420 ppm. The diurnal cycle of the city path CO₂ shows a different trend with a stronger diurnal variation. Overnight from about 6 pm (18:00) to 9 am, there is an enhancement in the CO₂ relative to the reference path as the CO₂ from the city sources builds up due to the low winds out of the west and a presumed collapsing nighttime boundary layer. During the weekdays, this enhancement increases in the morning consistent with the rise in traffic. After the morning, the combination of the presumed rising boundary layer, increased wind speed, and shift in average wind direction out of the west (270°) to the southeast (135 °) result in a drop in the city path CO₂. Moreover, this shift in wind direction means that the reference path no longer samples the clean air from the direction of the mountains but rather sees a very similar CO₂ enhancement as the city path. (Fortunately, as discussed below, there are days when the wind does not shift direction so that there is a measured enhancement of the city path compared to the reference path.) In the early evening, as the wind speed drops and the wind direction shifts back to out of the west, the enhancement of the city path over the reference path reappears and continues overnight as the boundary layer presumably drops. In general, the CO₂ mixing ratios tend to be higher on the weekdays, sometimes exceeding 500 ppm, while weekend mixing ratios are entirely below 490 ppm. This difference is reflected in the median values as well, which reach about 440 ppm during the weekdays but only 430 ppm during the weekend.

The diurnal cycle of the reference path CH₄ is relatively flat for both weekends and weekdays at just over 1.9 ppm, with a slight peak between 9 and 10 am. The diurnal cycle of the city path CH₄ shows an enhancement, relative to the reference path, between midnight and about 9 am. We attribute this enhancement to sources of CH₄ within the city combined again with low nighttime winds and collapsing boundary layer. These sources may be leaking natural gas infrastructure such as observed in Boston (Phillips et al., 2013; McKain et al., 2015; Hendrick et al., 2016), Washington, D.C. (Jackson et al., 2014), and Indianapolis (Lamb et al., 2016). Unlike for CO₂, the CH₄ diurnal cycle appears unrelated to

255 traffic (nor would we expect it to be for clean-burning vehicles) as it does not increase during high traffic
256 times.

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258 3.3 Estimate for CO₂ emissions due to traffic

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260 3.3.1 Measurement day selections

261 To select test case days to estimate the city emissions, we filter the X_{CO₂} time series for time
262 periods with daytime enhancement and a moderate wind strength predominantly out of the west (270 °).
263 Given that the prevailing daytime winds are from the southeast (135°) and often strong, this limits the test
264 case days significantly. However, as is clear from Fig. 1, for these wind conditions, the city path samples
265 a significant fraction of the traffic emissions and the reference path samples no traffic emissions. We
266 consider only daytime enhancements because the nighttime boundary layer behavior is significantly more
267 complicated than a well-mixed daytime stable boundary layer. We find two days that meet these criteria:
268 Saturday 22 October 2016 from 11:00 to 16:00. and Tuesday 25 October 2016 from 7:00 to 16:00. Both
269 days have moderate wind speeds (on average, 5 m/s) as measured at both meteorological sites. There are
270 additional days with daytime enhancement in X_{CO₂}, but the wind direction is variable. Additionally, there
271 are many days with no daytime enhancement in X_{CO₂} because the high wind speeds (6 m/s or higher)
272 prevented buildup of CO₂. We use Oct. 22 as a proxy for all weekend days and Oct. 25 as a proxy for all
273 weekdays. The X_{CO₂} and X_{CH₄} mixing ratios as well as wind speed and wind direction for these two case
274 study days are shown in Fig. 7.

275 In order to confirm that the reference path measured clean background air and the over-city path
276 measured city emissions, we calculated footprints for the two test case time periods using the Stochastic
277 Time-Inverted Lagrangian Transport (STILT-R) model (Fasoli et al., 2018). The input meteorology file
278 consisted of a uniform wind field with wind data from the NCAR Foothills lab, boundary layer height
279 from the North American Regional Reanalysis (NARR), uniform turbulent velocity variance calculated
280 from the Pasquill stability class (determined from wind speed and solar insolation) from the ground up to
281 the boundary layer, and the hyper near-field scaling described in Fasoli et al., (2018). Average footprints
282 for the two time periods are shown in Fig 7. The footprint for the reference path covers undeveloped areas
283 extending from the near foothills into the mountains. The footprint for the over-city path also has
284 contributions from the same general mountain region. In addition, this path has sensitivity to an extended
285 area within the city and therefore to a large fraction of the traffic emissions. Note the open-path geometry
286 leads to a much larger extended footprint for this path than would be the case for a single point sensor
287 located at the same height within the city.

288 The variability in the reference CO₂ on both days is a real atmospheric effect. (In processing, any
289 data is removed if the signal power is low, which is indicative of poor telescope alignment or strong
290 weather-related attenuation over the beam path, so the variability is not due to variable signal strength.)
291 We attribute this variability to the smaller footprint of the reference path relative to the over-city path, as
292 seen in Fig. 7. If the CO₂ in the air is not fully mixed, then the temporal and spatial variability will be
293 more evident in the path with the smaller footprint.

294 To convert from the measured enhancement to an emissions rate, we require a model that
295 connects the source strength to the plume concentration. Since we do not have a high-resolution, spatially
296 resolved inventory for Boulder similar to the Hestia model for Salt Lake City (Mitchell et al., 2018), we
297 use the existing Boulder traffic inventory (see Section 2.3) in conjunction with a Gaussian plume model.
298

299 3.3.2 Gaussian plume calculations

300 The standard Gaussian plume model that includes total reflection at the Earth's surface is
301 (Seinfeld and Pandis, 2006):

$$302 \quad c(x, y, z, t) = \frac{q}{2\pi\sigma_y\sigma_z u} \exp\left(\frac{-(y-y_0)^2}{2\sigma_y^2}\right) \left[\exp\left(\frac{-(z-H)^2}{2\sigma_z^2}\right) + \exp\left(\frac{-(z+H)^2}{2\sigma_z^2}\right) \right] \quad (1)$$

303 where (x,y,z) is the location in space for which the plume concentration is being calculated, (x_0,y_0,H) is the
 304 emissions location, $c(x,y,z)$ is the concentration at location (x,y,z) and time t , q is the emissions strength
 305 (usually in kg/s), σ_y and σ_z are the plume variances in the y and z direction as a function of travel distance
 306 and Pasquill stability class (Seinfeld and Pandis, 2006), and u is the wind speed in m/s. The wind is
 307 assumed to be in the x-direction. The plume variances are calculated as:

$$308 \quad \sigma_y = \exp\left[I_y + J_y (\ln \Delta x) + K_y (\ln \Delta x)^2\right] \quad (2)$$

309 and

$$310 \quad \sigma_z = \exp\left[I_z + J_z (\ln \Delta x) + K_z (\ln \Delta x)^2\right] \quad (3)$$

311 where $I_y, J_y, K_y, I_z, J_z,$ and K_z are from a look-up table based on the Pasquill stability class, which depends
 312 on the wind speed and solar insolation (Seinfeld and Pandis, 2006) and Δx is the x-distance relative to the
 313 plume origin. This plume model does not include any reflection at the boundary layer height; however,
 314 due to the small spatial scales, this effect is negligible here.

315 We modify this equation in several ways: 1) Since we measure the column-integrated
 316 concentration over a finite beam path at an angle to the wind direction, we integrate the plume
 317 concentration along this beam path and then normalize to the length of the beam path. 2) We sum over
 318 the emissions locations in the city that contribute emissions to our measurements. Thus our overall
 319 measurement equation is:

$$320 \quad (c - c_0) = \frac{Q}{L} \sum_{(x_j, y_j)} \int_0^L \frac{f_j}{2\pi\sigma_y\sigma_z u} \exp\left(\frac{-(s \sin \theta - y_j)^2}{2\sigma_y^2}\right) \left[\exp\left(\frac{-(15-1)^2}{2\sigma_z^2}\right) + \exp\left(\frac{-(15+1)^2}{2\sigma_z^2}\right) \right] ds \quad (4)$$

321 where $(c - c_0)$ is our path-integrated concentration enhancement measurement (in MT/m³ and MT
 322 metric tons; 1 MT = 1000 kg) along our path s which goes from 0 to L , Q is the total city emissions in
 323 MT/hour, L is our path length in m, (x_j, y_j) are the source emissions locations, f_j is the fraction of traffic at
 324 source location (x_j, y_j) relative to traffic over all locations in the city from the TMC database, u is the wind
 325 speed in m/s, θ is the angle of the beam path with respect to the wind direction, and σ_y and σ_z are the
 326 plume dispersions in m in the y and z directions, which depend on the sources distance from the beam
 327 path. In writing (4), we assume the wind is in the $+\hat{x}$ direction (which assumption is relaxed below). We
 328 assume that all plume emission locations are vehicle tailpipes at 1 m above the ground, and the beam path
 329 runs 15 m above ground so all measurement heights are at 15 m above ground.

330

331 *Grid rotation for variable wind directions*

332 To calculate (4), we grid the emissions locations using UTM (Universal Transverse Mercator)
 333 coordinates obtained from Google Earth, where we then define north as $+\hat{y}$ and east as $+\hat{x}$. We translate
 334 the coordinate system such that the DCS path begins at the origin (0,0) and travels a distance L at angle
 335 θ with respect to the x-axis. Eq. (4) is then valid provided the wind is directly in the $+\hat{x}$ direction. More
 336 generally, the wind is at a time varying small angle $\phi(t)$ with respect to $+\hat{x}$. Therefore, we apply a
 337 rotation about the origin (Prussin et al., 2015):

$$338 \quad \begin{bmatrix} \cos \phi & \sin \phi \\ -\sin \phi & \cos \phi \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} x' \\ y' \end{bmatrix}$$

339 to generate new traffic coordinates (x'_j, y'_j) and a new parameterized DCS beam path of $(s \cos(\theta'), s$
 340 $\sin(\theta'))$ where $\theta' = \theta - \phi(t)$. In this new coordinate system, the wind is along the $+\hat{x}$ direction and Eq. (4)
 341 holds with the substitutions $\theta \rightarrow \theta'$ and $y_j \rightarrow y'_j$, and where the σ_y and σ_z are calculated based on the
 342 distance $\Delta x = |x'_j - (y'_j / \tan \theta')|$.

343

344 *Time dependent estimate of $Q(t)$*

345 The rotated Eq. (4) can be solved for Q in terms of the measured or estimated values of $c(t) - c_0(t)$, $u(t)$,
 346 $\Delta\phi(t)$, $\sigma_y(t)$, $\sigma_z(t)$, θ , L , and f_i , where the first five quantities are time dependent. The resulting, time-

347 dependent $Q(t)$ for each test case day is shown in the bottom panels of Fig. 7 and has a mean value and
348 standard deviation of $Q_{\text{Oct22}} = 31 \pm 17$ MT CO₂/hour for October 22 and $Q_{\text{Oct25}} = 165 \pm 45$ MT CO₂/hour
349 for October 25 for the 5-minute averaged data as shown.

350

351 *Uncertainty in $Q(t)$*

352 Seven measured parameters factor in to the emissions calculation of $Q(t)$ for the two days. These
353 are given in Table I along with the instrumental measurement precision and the observed variability. Note
354 that solar insolation is used solely in the determination of the Pasquill stability class (Seinfeld and
355 Pandis, 2006). The stability class is relatively insensitive to the variations in solar insolation observed on
356 the two test case days. As can be seen in the table, the uncertainty is dominated by the natural variability
357 in parameters like wind speed, wind direction, and CO₂ concentration rather than the DCS spectrometer
358 precision. The observed variability over the 5-9 hour period is typically at least a factor of 2 larger than
359 the instrument precision. The variability in these parameters leads to the observed variability in $Q(t)$. We
360 use the mean of $Q(t)$ as our emissions value and the standard deviation (at 5-minute time-averaging) as its
361 uncertainty. In using this standard deviation as a measure of the uncertainty, we attempt to capture the
362 uncertainty associated with the discrepancies between, for example, the weather-station measurements of
363 wind direction and speed relative to the true wind direction (which results in greater or fewer number of
364 plumes from the given traffic locations intercepting the measurement path). This variability appears in
365 $Q(t)$ as the nominal measured wind direction varies. Future systems with redundant, distributed DCS
366 beam paths would provide a superior estimate of all these uncertainties.

367 In addition, there are assumptions, and possible uncertainties, inherent to the Gaussian plume
368 model. First, the model does not include the effects of buildings, trees, or other objects that could break
369 up the plume between the emissions location and the beam path. Second, we assume that all CO₂
370 emissions come from the discrete locations shown in Fig. 1, while in reality the emissions are likely
371 substantially more diffuse. The assumption of discrete emissions simplifies modeling and is feasible due
372 to the city traffic data but may result in a bias due to the coarse distribution of traffic measurements.
373 Third, we approximate the measurement height at 15 m above ground although the beam height differs
374 over the path since Boulder is not perfectly flat. Finally, we use standard $I_y, J_y, K_y, I_z, J_z,$ and K_z values
375 which were derived for rural areas (Turner, 1970) which may be different than urban or suburban areas.
376 However, the greatest differences between rural and urban conditions are expected to be at night (Turner,
377 1970).

378 We further ran plume calculations in STILT-R using both wind fields derived from the local
379 meteorological stations shown in Figure 1 and using the North American Mesoscale Forecast System
380 (NAM, <https://www.ncdc.noaa.gov/data-access/model-data/model-datasets/north-american-mesoscale-forecast-system-nam>).
381 The High Resolution Rapid Refresh (HRRR, <https://rapidrefresh.noaa.gov/hrrr/>)
382 and North American Regional Reanalysis (NARR, [https://www.ncdc.noaa.gov/data-access/model-
383 data/model-datasets/north-american-regional-reanalysis-narr](https://www.ncdc.noaa.gov/data-access/model-data/model-datasets/north-american-regional-reanalysis-narr)) wind projections did not match the
384 measured winds at the meteorological stations. These calculations produced emissions values ranging
385 between 55 MT/hour and 770 MT/hour, depending on the wind fields and vertical dispersion
386 parameterization used. This brackets our emissions calculations by approximately a factor of three in
387 each direction and shows how sensitive these kilometer-scale measurements are to vertical dispersion.

388

389 3.3.3 Corrections for non-traffic sources of CO₂

390 There are a number of non-traffic sources of CO₂ that could contribute to our measured X_{CO_2}
391 enhancement including local power plants, residential emission, and biological activity. These non-traffic
392 sources should have relatively minor contribution for several reasons. First, the footprint of the over-city
393 path does not overlap the large power plant to the east of the Boulder city limits. Second, the temperature
394 during the two test case days was 24 °C and 20 °C (68 °F and 75 °F) on October 22 and 25th leading to
395 minimal residential and commercial heating. Third, the measurements occurred in October after leaf
396 senescence so there should be negligible biological activity. Nevertheless, as discussed below, we do

397 adjust our measurements to account for the relatively minor contribution from non-traffic sources before
398 scaling up to an estimate of the annual traffic emissions.

399 We first consider power plants. There are two power generation facilities on the Department of
400 Commerce (DOC) campus located near the NIST building that houses the dual-comb spectrometer: the
401 site's Central Utilities Plant (CUP), and the National Oceanic and Atmospheric Administration (NOAA)
402 building's boilers. To calculate their average CO₂ emissions, we used available fuel consumption data
403 (October 2016 monthly average for the CUP and mid-November to mid-December 2016 average for the
404 NOAA boilers; October data was unavailable) and the EPA emissions factor (EPA, 1995). We then
405 modeled the CUP and boiler plume emissions using WindTrax (Flesch et al., 1995, 2004) with wind
406 speed and direction data from the NCAR-Mesa site. We find that due to the moderate wind speeds (~5
407 m/s) during our case study days and the height mismatch between the emission stacks and our
408 measurement path over the DOC campus, there is negligible enhancement over the reference path. Given
409 the location of the emission sources and the wind direction during our measurement periods, the
410 emissions also do not cross the over-city beam path. Therefore, we apply no correction for these two
411 power plant emissions.

412 The University of Colorado also has a power plant that falls within the main footprint associated
413 with the over-city beam path, shown in Fig. 7a, and whose emissions are expected to intersect our over-
414 city beam path. The EPA Greenhouse Gas Reporting Program (GHGRP,
415 <https://www.epa.gov/ghgreporting>) lists the 2017 emission from the power plant as 2.7×10^4 MT CO₂ or
416 an average of 3.1 MT/hour. (No breakdown by season or hour is provided.) We apply this correction to
417 our previous daily values and add a conservative uncertainty equal to this correction in quadrature with
418 the previous uncertainty. The new adjusted values are then 28 ± 17 MT CO₂/hour for October 22 and 162
419 ± 45 MT CO₂/hour for October 25.

420 The large Valmont power station lies just outside the city limits to the east of Boulder; however,
421 given its location and the dominant westerly wind, emissions from this source does not reach our beam
422 paths. There are no other power generation facilities within the city that report to the GHGRP, so we
423 make no further corrections based on power plants.

424 In addition, there are also likely diffuse emissions from residential and commercial furnaces and
425 water heaters that use natural gas. The City of Boulder Community Greenhouse Gas Emissions Inventory
426 reports twenty percent of the city emissions, or 3.18×10^5 MT CO₂e, were from natural gas in 2016
427 ([https://www-
428 static.bouldercolorado.gov/docs/2016_Greenhouse_Gas_Emissions_Inventory_Report_FINAL-1-
429 201803121328.pdf?_ga=2.130927943.970967930.1525795820-107394975](https://www-static.bouldercolorado.gov/docs/2016_Greenhouse_Gas_Emissions_Inventory_Report_FINAL-1-201803121328.pdf?_ga=2.130927943.970967930.1525795820-107394975)). The natural gas usage varies
430 strongly by month with building heating requirements. Although our measurements occurred in October,
431 the measurement days were quite warm (20-24 C) so that residential and commercial building heating
432 was unlikely and the use of an annual average would overestimate any contribution. Instead, we scale the
433 natural gas usage according to the monthly breakdown provided by the United States Energy Information
434 Administration database for Colorado (<https://www.eia.gov/dnav/ng/hist/n3010co2m.htm>). The mean
435 daytime (approximately sunrise to sunset, 7 am to 6 pm) temperature in October was 18.2 C while the
436 mean temperature (including day and night) for October was 15.7 C. Our daytime-only measurements
437 therefore had a mean temperature that was much closer to the mean temperature (day and night) of
438 September, which was 19.2 C. Therefore, we scale the Boulder annual natural gas consumption by the
439 September 2016 nature gas usage, which was 2.4% of the Colorado annual total according
440 (<https://www.eia.gov/dnav/ng/hist/n3010co2m.htm>). The estimated total emissions from residential and
441 commercial natural gas usage in Boulder over our measurement days is then 10.2 MT CO₂/hour. We
442 apply this correction to our measured values and include a (conservative) uncertainty equal to this
443 correction. The new adjusted values are then $Q_{\text{Oct22,adj}} = 18 \pm 20$ MT CO₂/hour for October 22 and $Q_{\text{Oct25,adj}}$
444 $= 152 \pm 46$ MT CO₂/hour for October 25.

445 Once leaf senescence has completed, neither plants nor soil respiration contribute to CO₂ signal
446 (Matyssek et al., 2013). The National Phenology Network (USA National Phenology Network, 2018)
447 data shows that for the site nearest to Boulder (64 km north of Boulder), the leaf fall dates were

448 September 15, 2016 for box elder trees October 6, 2016 for Eastern cottonwoods. Thus by our
449 measurement dates leaf senescence should be fully complete and plants will not contribute to the city CO₂
450 enhancement. We note that a wide range of biogenic contributions to CO₂ have been noted in the
451 literature (Gurney et al., 2017; Mitchell et al., 2018; Sargent et al., 2018).

452

453 3.3.4 Scaling to annual emissions

454 In order to compare with the city inventory, we scale our results to an annual total. To do this, we
455 use the hourly traffic data of Fig. 4 to scale $Q_{\text{Oct}22,\text{adj}}$ and $Q_{\text{Oct}25,\text{adj}}$ to a daily emission. Based on Figure 4,
456 34% of the total traffic counts occur during the 5-hour measurement period on Oct. 22 and 52% of the
457 total traffic counts occur during the 8-hour measurement period on Oct. 25 (excluding the 13:00 to 14:00
458 period). The daily emissions are then $Q_{\text{Oct}22,\text{day}} = Q_{\text{Oct}22,\text{adj}} \times (5 \text{ hours}) \div (0.34)$ and $Q_{\text{Oct}25,\text{day}} = Q_{\text{Oct}25,\text{adj}} \times (8$
459 $\text{hours}) \div (0.52)$ (The traffic data in Fig. 4 is based on weekday measurement and we assume that the
460 hourly distribution is the same for weekends; this may lead to a slight overestimate in the weekend data
461 where a larger fraction of emissions occurs between 11 am and 4 pm than on weekdays.) We then scale to
462 annual emissions by assuming that the emissions on Oct. 22 are representative of all 112 weekend/holiday
463 days and the emissions on Oct. 25 are representative of all 253 workdays. Including their uncertainty, this
464 calculation yields $(6.2 \pm 1.8) \times 10^5$ MT CO₂/year.

465 The scaling relies heavily on the traffic count data supplied by the city of Boulder, which does not
466 have an associated uncertainty value. A comparison of these data over several years shows a typical 7%
467 statistical variation at a given TMC location, after removing a linear trend. We assume this reflects day-
468 to-day fluctuations in traffic. In addition, there will be seasonal variations, which is not captured in the
469 extrapolation from our two test case days to the annual emissions. Due to the lack of seasonal data for
470 Boulder traffic, we use the detailed Hestia traffic inventory for Salt Lake City, UT given in Figure 2 of
471 (Mitchell et al., 2018). These data show a variation of $\pm 18\%$ in traffic emissions between “summer” and
472 “winter” months. Combined in quadrature with the 7% statistical uncertainty in the TMC traffic count
473 data, this leads to an additional $\sim 20\%$ uncertainty to the scaled annual estimate. As noted earlier, we have
474 not applied any additional uncertainty on the reliance on the TMC data as a proxy for emissions locations.

475 Including the additional uncertainty on the scaling to annual emissions, we estimate an annual
476 emission rate of $(6.2 \pm 2.2) \times 10^5$ MT CO₂/year for traffic carbon emissions for Boulder CO.

477

478 4 Comparison with city estimates

479 The city vehicle emissions estimate comes from total vehicle miles traveled based on data from
480 the transportation department, miles per gallon inputs from the EPA state inventory tool, and vehicle type
481 distribution from the Colorado Department of Public Health and the Environment (Kimberlee Rankin,
482 City of Boulder, personal communication). The City of Boulder estimates total vehicle emissions of
483 4.50×10^5 metric tons (MT) of CO₂ in 2016 ([https://www-
484 static.bouldercolorado.gov/docs/2016_Greenhouse_Gas_Emissions_Inventory_Report_FINAL-1-
485 201803121328.pdf?_ga=2.130927943.970967930.1525795820-107394975](https://www-static.bouldercolorado.gov/docs/2016_Greenhouse_Gas_Emissions_Inventory_Report_FINAL-1-201803121328.pdf?_ga=2.130927943.970967930.1525795820-107394975)). On-road emissions account
486 for greater than 99% of the transportation emissions, so we have scaled this value down by one percent
487 for an on-road emissions value of 4.46×10^5 MT CO₂. We assume that all traffic emissions are CO₂ rather
488 than a mix of CO₂ and CH₄. There is no uncertainty provided by the city on this value.

489 In comparison, we estimate $(6.2 \pm 2.2) \times 10^5$ MT CO₂/year MT CO₂/year, which is 139% of the
490 city estimate but agrees within the given uncertainty. Interestingly, other studies have also found that
491 emissions measurements were higher than the reported inventory values. Brioude et al., (2013) found
492 top-down aircraft estimates of Los Angeles county and the South Coast Air Basin (SoCAB) CO₂ were
493 1.45 times larger than the Vulcan 2005 inventory (Gurney et al., 2009). An earlier aircraft campaign over
494 Sacramento, CA found an average CO₂ emission, with 100% uncertainty, that was 15-20% higher than
495 the Vulcan estimate (Turnbull et al., 2011). Lauvaux et al. (2016) compared Indianapolis city CO₂
496 emissions measured by a network of CRDS instruments to the HESTIA inventory (Gurney et al., 2012)
497 during INFLUX (Davis et al., 2017). They found that despite the building-scale resolution in the
498 HESTIA inventory, it still under-estimated the annual CO₂ flux by 20%. An updated version of HESTIA

499 predicted very similar emissions estimates for on-road, residential, and commercial sectors, so the
500 discrepancy was attributed to missing sources of CO₂, including animal (primarily human and companion
501 animal) respiration, biofuel combustion, and biosphere respiration (Gurney et al., 2017).

502

503 4.1 Improvements in future measurements

504 Future improvements should include additional and different beam paths, selected based on
505 prevailing wind directions. (Our initial assumption that the mountain path would generally act as a
506 reference path was incorrect since the prevailing daytime winds are not out of the west but rather the
507 southeast.) An east-west running beam north of the city and one south of the city would allow us to utilize
508 a larger fraction of the data as the predominant midday wind direction during the fall is out of the north to
509 north-east (see Fig. 1). Even longer beam paths would also interrogate a larger fraction of the city and
510 measure a correspondingly larger fraction of the vehicle emissions. Vertically-resolved data from e.g. a
511 series of stacked retroreflectors would better test the assumption of vertically-dispersing Gaussian
512 plumes.

513 Additionally, more extensive modeling to cover variable wind directions and speeds would allow
514 the incorporation of a much larger fraction of the data than the two days selected here. An inversion-
515 based model similar to (Lauvaux et al., 2013) could potentially be applied to a small city like Boulder;
516 however this would depend heavily on the quality of the bottom-up emissions inventory used to generate
517 the priors. Indeed, one of the major future improvements would be to generate a detailed Hestia inventory
518 of Boulder, CO similar to that generated for Salt Lake City, UT (Mitchell et al., 2018).

519

520 5 Conclusions

521 We demonstrate the use of an open-path dual frequency comb spectroscopy system for
522 quantifying city emissions of carbon dioxide. We send light over two paths: a reference path that
523 samples the concentration of gases entering the city from the west, and an over-city path that measures the
524 concentrations of gases after the air mass has crossed approximately two-thirds of the city including two
525 major commuter arteries. The measured diurnal cycle shows a significant traffic-related enhancement in
526 the carbon dioxide signal during weekdays in the over-city path compared to the reference path. We
527 select two case study days with appropriate wind conditions and apply Gaussian plume modeling to
528 estimate the total vehicular carbon emission. We then scale these results up to annual city-wide emissions
529 using traffic data from the City of Boulder. We find overall traffic related carbon emissions that are
530 approximately 1.4 times greater than the city's bottom-up traffic emissions inventory but with an
531 uncertainty that encompasses the city inventory estimate. Further improvements to this method should
532 include improved design of reference and over-city paths and a more detailed inventory model for
533 Boulder CO, which together should further reduce the overall uncertainty in the estimate.

534

535 Author contributions: EMW, KCC, IC, and NRN designed the experiment. WCS helped build the
536 hardware for the open-path measurements. EMW, KCC, and GWT ran the experiment. FG wrote the
537 processing code for the data analysis. EMW processed the data and did the Gaussian plume modeling.
538 KCC did the STILT-R modeling. EMW, KCC, IC, and NRN cowrote the manuscript.

539

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546

547 5. References

548

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753 Appendix A: Modification of the Gaussian plume equation

754

755 Equation 1 is the standard Gaussian plume equation as discussed in Section 3.3.2 (Seinfeld and
756 Pandis, 2006). It is reproduced here,

$$757 \quad c(x, y, z, t) = \frac{q}{2\pi\sigma_y\sigma_z u} \exp\left(\frac{-(y - y_0)^2}{2\sigma_y^2}\right) \left[\exp\left(\frac{-(z - H)^2}{2\sigma_z^2}\right) + \exp\left(\frac{-(z + H)^2}{2\sigma_z^2}\right) \right]$$

758

759 where the standard variables are as defined in Section 3.3.2.

760

761 *Path-integrated substitutions*

762 The DCS returns the average concentration along a line path. We denote distance along this path
763 by the variable s , where s runs from 0 to L . This path is assumed to lie in the x-y plane at an
764 angle θ with respect to the x-axis (which is assumed to be the wind direction in the standard
765 Gaussian plume equation). With these definitions, the contribution to the DCS signal from the
766 plume is,

$$767 \quad (c - c_0) = \frac{1}{L} \int_0^L c(s \cos \theta, s \sin \theta, z, t) ds$$

768 or:

769

$$770 \quad (c - c_0) = \frac{1}{L} \frac{q}{2\pi\sigma_y\sigma_z u} \int_0^L \exp\left(\frac{-(s \sin \theta - y_0)^2}{2\sigma_y^2}\right) \left[\exp\left(\frac{-(z - H)^2}{2\sigma_z^2}\right) + \exp\left(\frac{-(z + H)^2}{2\sigma_z^2}\right) \right] ds$$

771

772 *Accounting for multiple point sources*

773 Rather than a single source at (x_0, y_0) , we have multiple sources at locations (x_j, y_j) , each with a
774 source strength $f_j q$, where f_j is the fractional source strength out of the total value q . We now sum
775 over all sources to find the total enhancement. We also change the units of q from kg/s to
776 MT/year and thus change the emissions variable to Q to indicate the unit change. This gives,

$$777 \quad (c - c_0) = \frac{Q}{L} \sum_{(x_j, y_j)} \int_0^L \frac{f_j}{2\pi\sigma_y\sigma_z u} \exp\left(\frac{-(s \sin \theta - y_j)^2}{2\sigma_y^2}\right) \left[\exp\left(\frac{-(z - H)^2}{2\sigma_z^2}\right) + \exp\left(\frac{-(z + H)^2}{2\sigma_z^2}\right) \right] ds$$

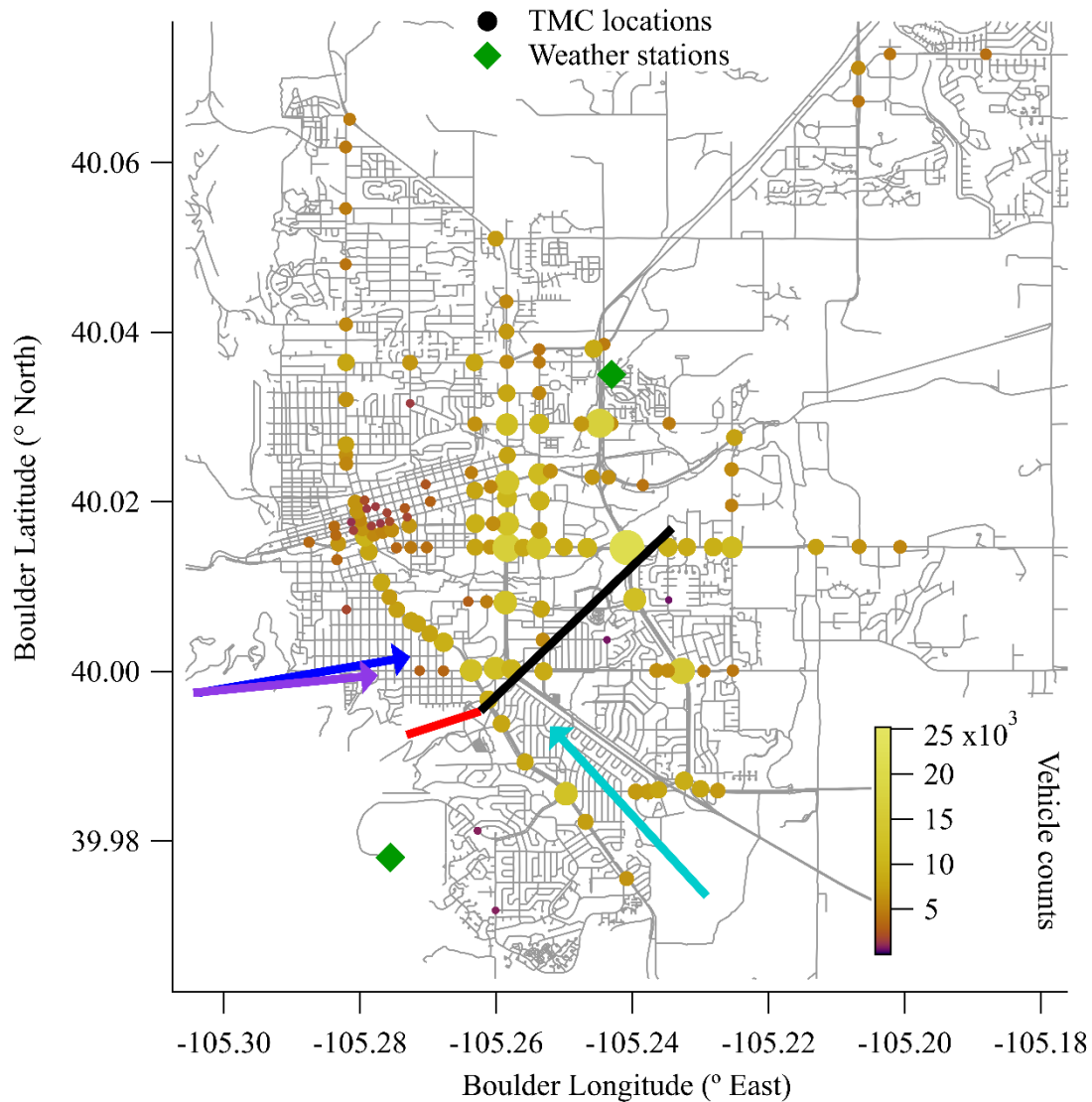
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779 *Height substitutions*

780 We assume that the point source emissions locations are 1 meter above ground ($z = 1$) and city
781 topographic data indicates that our beam path is approximately 15 meters above ground ($H = 15$).
782 These substitutions finally lead to Eq. (4) in the main text.

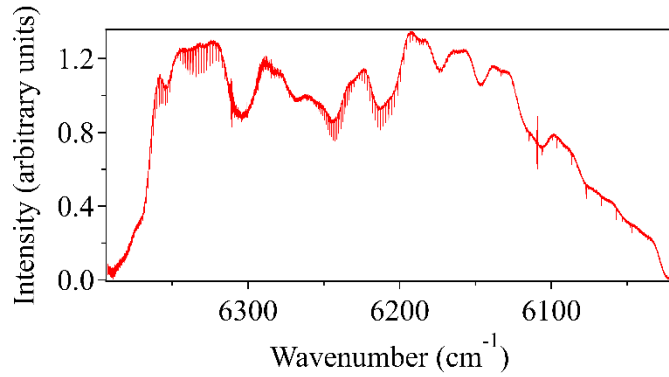
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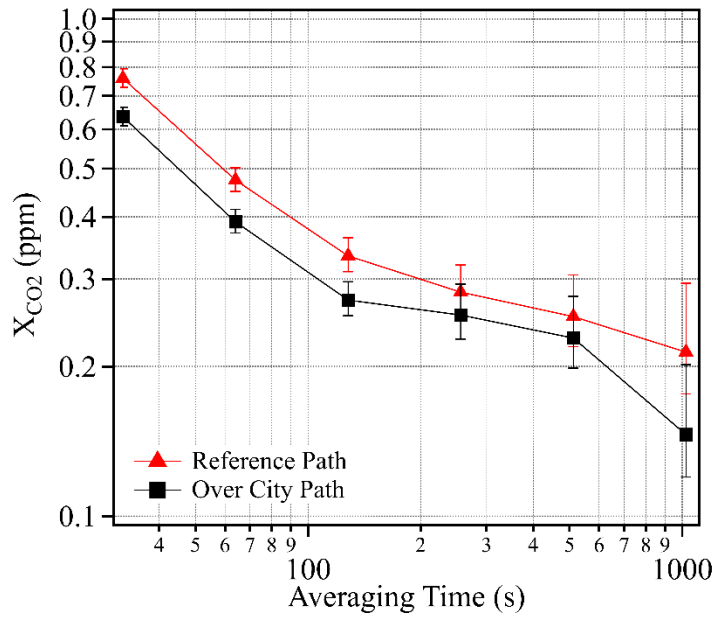
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Figure 1: Measurement layout. The two measurement paths are shown by red (reference) and black (over-city) lines. The two weather stations that provided wind speed and direction data are given by the green diamonds. The colored circles are Turning Movement Count (TMC) locations, which are used as a proxy for the traffic source locations. Both color and size represent the number of traffic counts at each location. Dominant wind directions for the campaign overall (aqua) and the test case days (purple for 10/22 and blue for 10/25) are given by colored arrows.



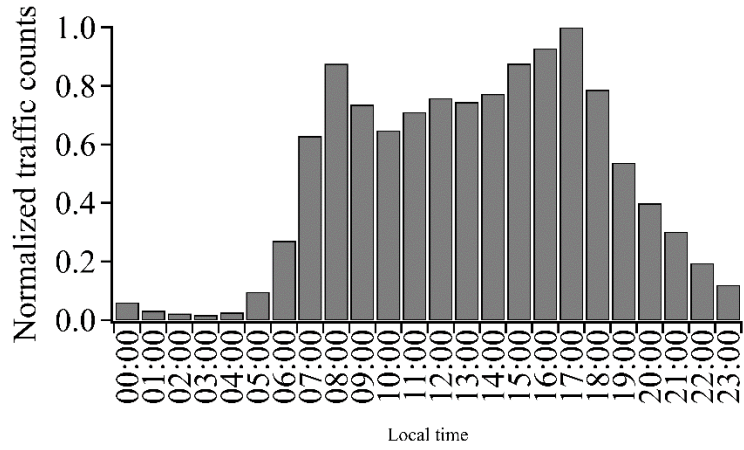
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Figure 2: Typical 32-second spectrum measured over the 2-km reference path. CO₂ bands are observed in the 6350 cm⁻¹ and 6225 cm⁻¹ regions, while CH₄ and H₂O are measured between 6150 and 6050 cm⁻¹. The larger, slowly varying structure is from the comb intensity profile. The atmospheric absorption appears as the small and narrow dips.

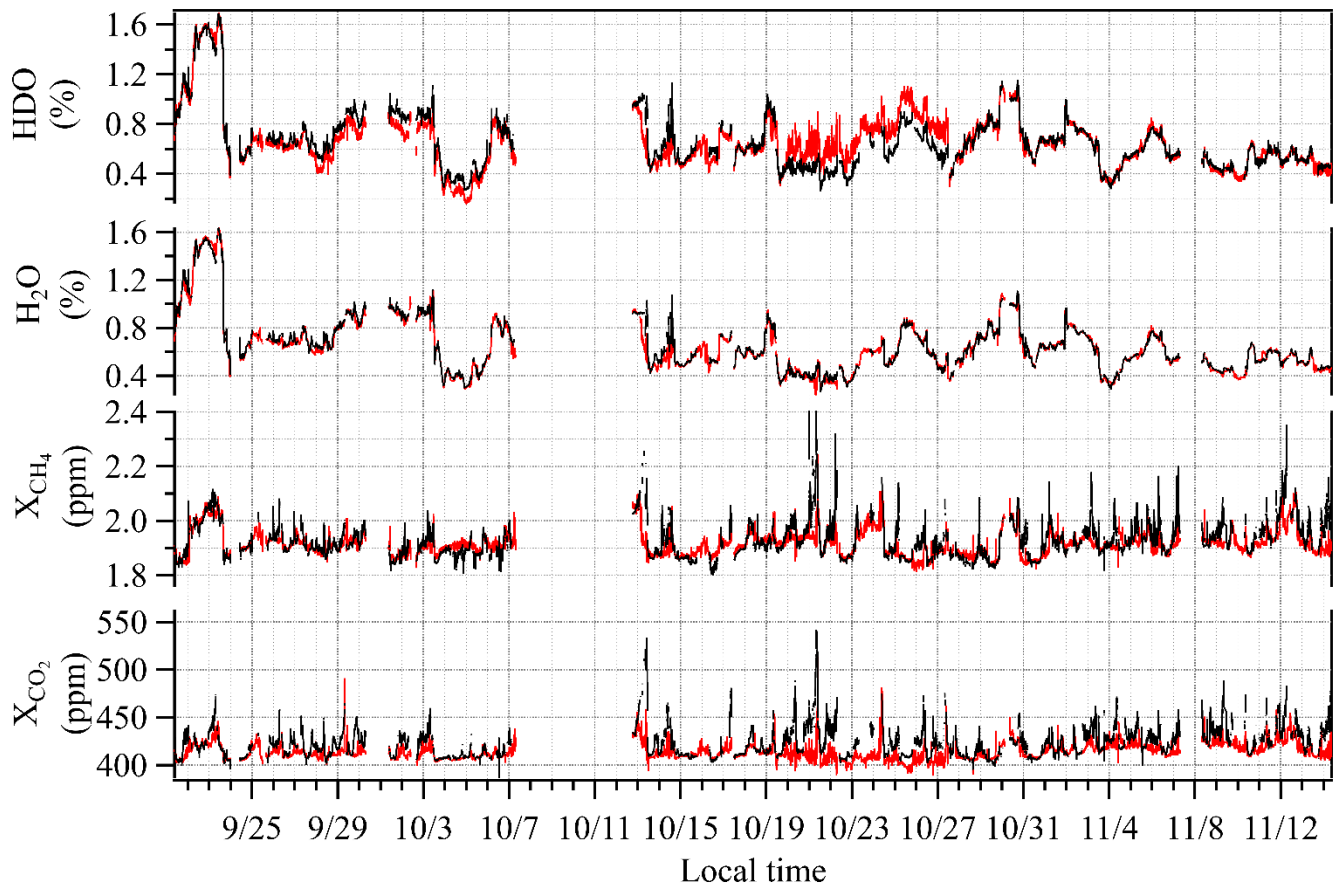


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Figure 3: Statistical uncertainty as quantified by the Allan deviations for X_{CO_2} over both the reference path (red triangles) and city path (black squares) from a well-mixed, three-hour time period on the night of October 3, 2016.

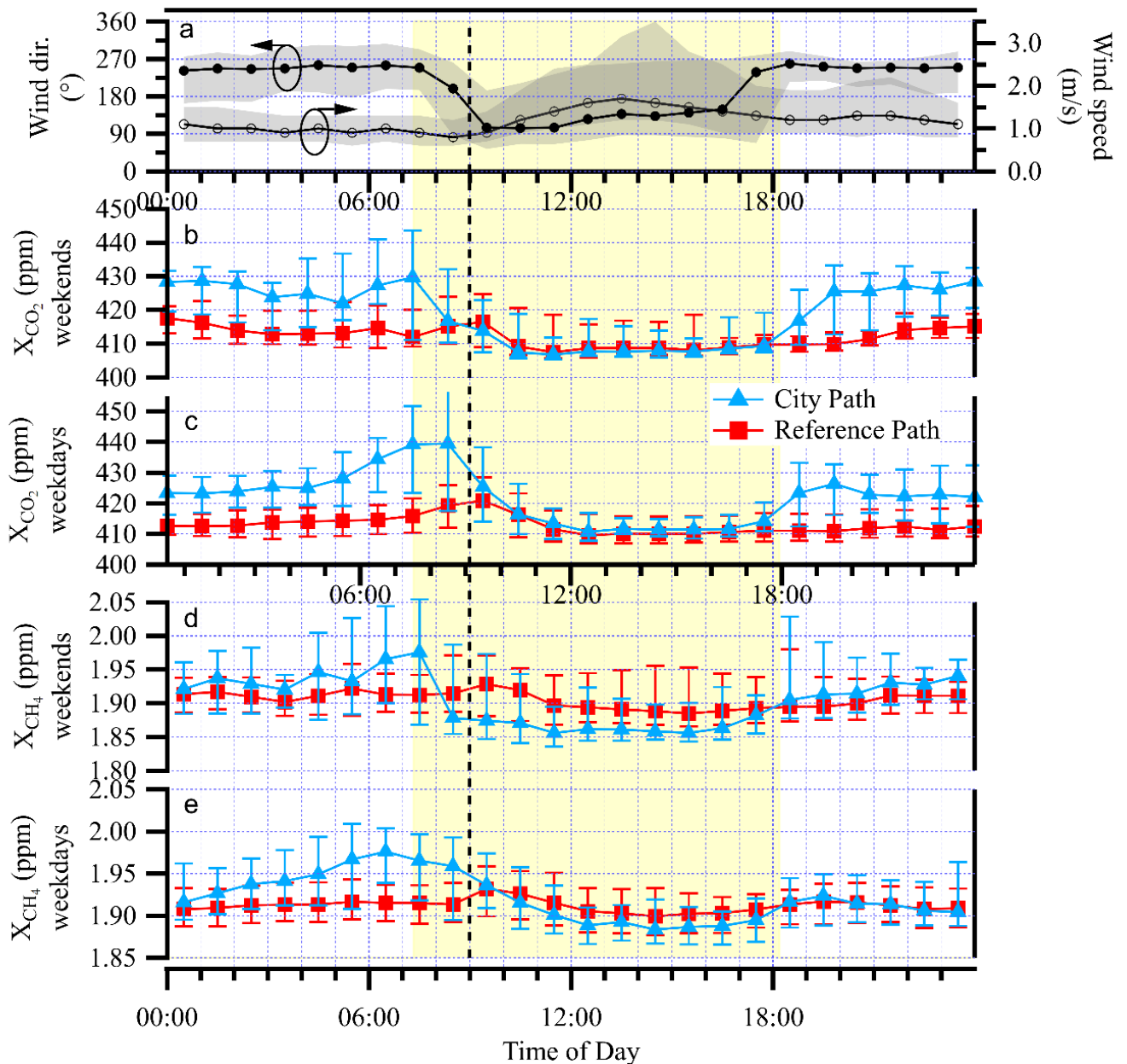


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 804 Figure 4: City-wide traffic counts from the Boulder Arterial Count Program (ART), normalized to a peak
 805 of unity.



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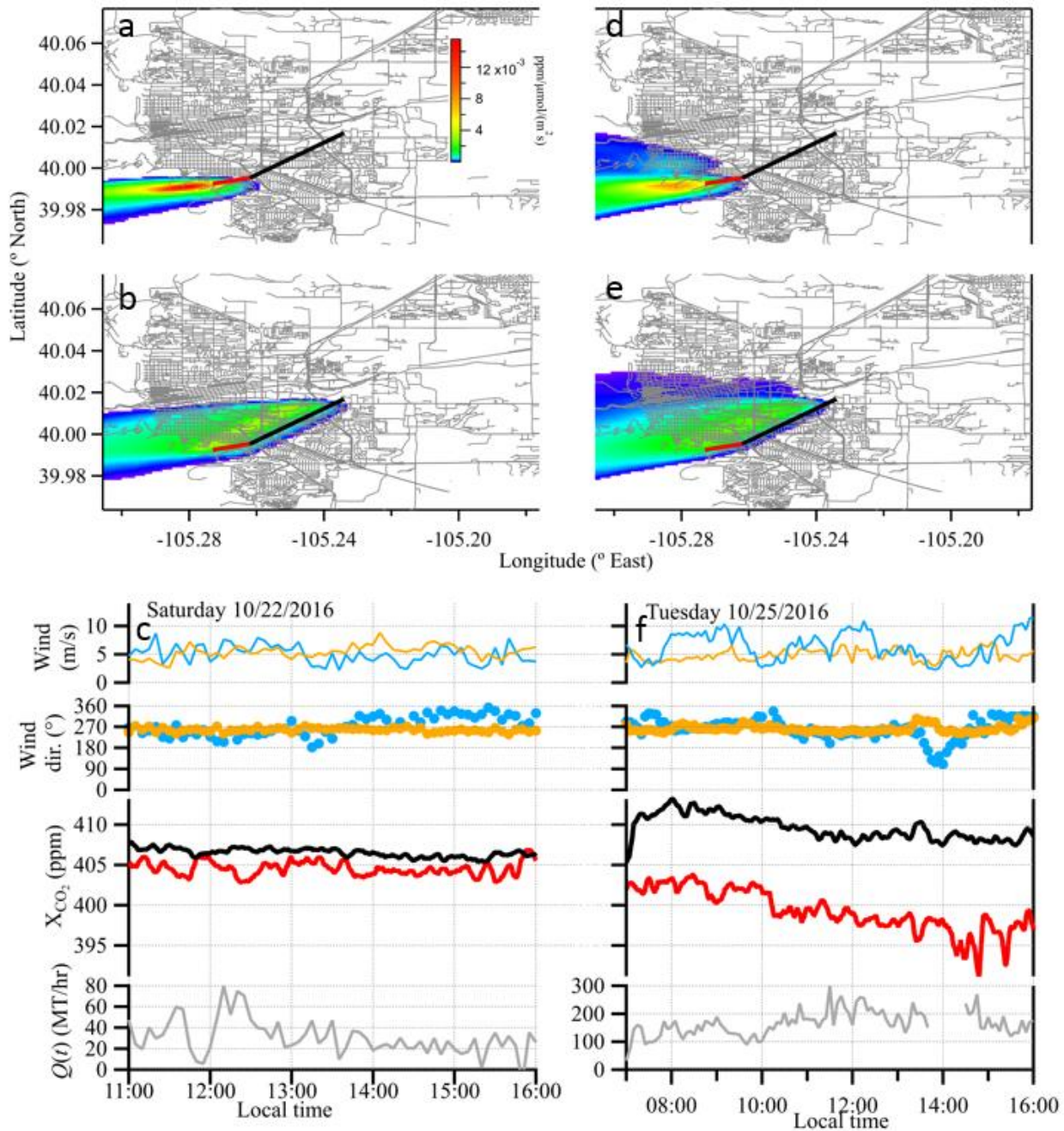
Figure 5: 7.5 weeks of dual-comb spectroscopy data for the reference path (red) and the over-city path (black) smoothed to 5-minute time intervals. Enhancements in the over-city path relative to the reference path are observed in CO_2 and CH_4 but not in H_2O or HDO . (Note: the HDO concentration includes the HITRAN isotopic scaling.)



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815 Figure 6: Diurnal cycle analysis. Data is the median of the full 7.5 weeks. (a) The mean direction in
 816 which the wind is blowing (black trace, left axis) and wind speed (gray trace, right axis) both from the
 817 NCAR Foothills measurement station, shaded regions reflect the 25th to 75th quartiles; (b) the weekend
 818 and (c) weekday median X_{CO_2} values for the over-city path (blue triangles) and reference path (red
 819 squares). Uncertainty bars represent the 25%-75% range of values encountered. (d) and (e) Same data for
 820 X_{CH_4} . The vertical dashed black line marks 9:00 local time and the yellow shaded region highlights the
 821 region from sunrise to sunset on Oct. 22, 2016.



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 823 Figure 7: Footprint calculations and time series data for the two case study days. Left column: Saturday,
 824 October 22, 2016; right column: Tuesday, October 25, 2016 data. Upper panels (a, d): Footprints for the
 825 reference path. Middle panels (b, e): Footprints for the over-city path. The footprints are averaged over
 826 over the respective time windows and open paths. Lower panels (c,f): Wind and CO₂ data at 5-minute time
 827 intervals. Reference and over-city measurement paths are shown in red and black, respectively. Data plots
 828 show X_{CO₂} over the reference path (red) and city path (black), wind speed and wind direction
 829 measurements taken at NCAR Mesa (blue) and NCAR Foothills (orange), and the calculated $Q(t)$. On Oct. 25,
 830 $Q(t)$ data near 14:00 has been removed since the reference path wind direction is out of the southeast to east,
 831 resulting in city contamination along the reference path. All data is smoothed to 5-minute time intervals.

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Table I: Parameters used to calculate the emission rate from Eq. (4). The measurement precision refers to the instrument uncertainty in the measurement quantity. The variability refers to the observed environmental variability over the measurement period. The variability from the enhancement, the wind direction, and the wind speed drive the observed variability in the estimated $Q(t)$. (The distance from a given source location to the DCS measurement path, Δx_j , varies with location and has a 5-m uncertainty.)

Quantity	Measurement precision	10/22 11:00-16:00		10/25 7:00-16:00	
		Mean	Variability	Mean	Variability
Pathlength L	0.15 m	6730.66 m	0	6730.66 m	0
Enhancement ($c-c_0$)	0.28 ppm (ref.) 0.25 ppm (city)	1.99 ppm	0.97 ppm (49%)	10.3 ppm	1.9 ppm (19%)
Wind speed u	0.3 m/s	5.2 m/s	1.0 m/s (19%)	5.6 m/s	1.3 m/s (23%)
Solar insolation	5%	570 W/m ²	76 W/m ² (13%)	275 W/m ²	185 W/m ² (67%)
Wind direction ϕ	2°	265°	21°	264°	15°

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