- 1 Response to anonymous Referee #1
- 2 3 General Comment
- 4 I found that the authors have improved their manuscript based on my comment and
- 5 suggestion before.
- 6
- 7 Detail Comment
- 8 1. There are several abbreviations in the main text still do not have full name e.g. NF,
- 9 NW, SE, SW (Line 259-260), MILARGO (Line 263).
- 10 Reply: These abbreviations that correspond to northeast, northwest, southeast and southwest,
- 11 respective, have now been included as words.
- 12 The acronym MILAGRO stands for Megacity Initiative: Local And Global Research
- 13 Observations, and has now been included in the revised text.
- 14 15
- 16 2. Figure 1. I suggest the authors include Mexico map in insert and show which part
- 17 of Mexico represent the study location (sampling stations).
- 18 *Reply*: The revised version has a map of Mexico, showing the location of Mexico City.

21 Response to anonymous Referee #222

- 23 Using 1 000 000 hourly ozone measurements this paper makes a convincing case that
- 24 ozone is modulated in Mexico City by the MJO through the modulation of UV light. The
- 25 paper is well written and the analysis is generally sound. I have a few minor comments, but
- after these are addressed the paper should be published.
- 1. Table 1 is a bit mysterious to me. I have some trouble precisely understanding the
- 29 procedure used from the wording "ozone concentrations at average of all 5 stations either 30 greater than the 90% percentile level or less than the 10th percentile level". At any rate the
- numbers in the table are all around 10% which makes sense if one picks the top 10% or
- bottom 10% of ozone. However, I don't understand what the deviations from 10% level
- 33 mean. Is this due to station heterogeneity? The authors should clarify the exact procedure
- 34 used for making this table and discuss how to interpret the findings.
- 35
- 36 *Reply:* We believe the reviewer refers to Table 2 in this comment.
- The actual procedure to calculate extreme low and high ozone was described in the text in
- 39 section 2. Data and Methods (page 8). To define days with extreme high and extreme low
- 40 ozone concentrations, the following procedure as used:
- 41 i) The frequency distributions for the datasets of standard anomalies for the afternoon
- 42 (1200 to 1600 LT) for summer and for winter (using the 1986-2014 period), were
- 43 computed to determine the values that correspond to the 90th and 10th percentiles.
- 44 ii) A day with extreme low ozone concentration is determined when the average standard
- 45 anomaly for the 5 stations for that day is less than the 10^{th} percentile for the season.
- 46 iii) A day with extreme high ozone concentration is determined when the average standard
- 47 anomaly for the 5 stations for that day is greater than the 90th percentile for the season.
- 48 iv) The extreme day identified as above is then related to the phase of the MJO, and then the
- relative frequency is estimated from the number of extreme ozone as a fraction of the totalnumber of days in the particular phase.
- 50 51
- We apologize for the not having a clear enough caption and we have re-written the caption so it now read as follows:
- 54 "Table 2: Relative frequency of extreme ozone days in winter (top two rows) and summer
- 55 (bottom two rows). A high ozone day was defined as one with a mean afternoon (1200 to
- 56 1600 local) ozone anomaly across the 5 observing stations greater than the long-term
- 57 (1986-2014) 90th percentile. Similarly, a low ozone day was defined as one with a mean
- 58 afternoon anomaly across the 5 observing stations less than the long-term 10th percentile.
- Bold values (winter phase 2; summer phase 6) indicate phases with highest mean ozoneconcentrations in those seasons; italics in italics (winter phase 8; summer phase 1) indicate
- 61 phases with lowest mean ozone concentrations in those seasons. Number of days (n) in
- 62 each active phase is given for each season, used to estimate the relative frequency."
- 63
- 64
- 65 2. Line 137. I assume the 30-day basis is a moving window. Please clarify.
- 66

67 68	<i>Reply:</i> Yes, it is a running average or moving window, and we have now added this information in the text in section 2. Data and Methods.
70 71 72	selected to avoid influence from both seasonal variability and also the long-term trend."
73 74	3. Line 159. 'DFJ' should be 'DJF'.
75 76 77	<i>Reply:</i> We thank the reviewer for catching this typographical error, which has now been corrected throughout the manuscript and figure captions.
78	
79 80 81	4. Figure 5 and similar figures. It would be preferable if the projections on all panels are the same.
82	Reply: Figures 5, 6, 8 and 9 have been re-done so that the panels on the first column have
83	the same projection as all other panels. They new figures have been now included in the
84	revised text.
85 86	
80 87	5 Figure 7 How helpful is this as a forecast tool? It might be helpful to put in each figure
88 89	the percentage of days in each category.
90	<i>Reply:</i> We have not attempted to use it as a forecast tool, but it would be simple to do.
91	From the climatological work in this study, a particular phase associated with each day
92 93	would be associated statistically high or low ozone. That would then be compared then with the normalized daily data (averaged over the 5 stations), classified as extreme high or
94	low, to determine the skill of the prediction.
95	We have chosen not to include the percentage of days in Figure 7, since it would be
96 07	confusing but mainly because the corresponding values were already listed in Table 2 and
98	available to readers.
99	
100 101	6. Lines 379-381. It looks to me like days with high ozone feature anomalous westerly winds in DJF.
102	
103	<i>Reply:</i> Yes, you are right, and thank you for pointing this out. As is clearly seen in Fig 10,
104 105 106	surface westerly winds anomalies are observed during winter high O_3 events. We have now corrected the text and it now reads as follows:
100	"In winter, days in phase 8 (lowest ozone concentrations) featured anomalous
108	northeasterly surface winds (blue vectors; Fig. 10), resulting in observed wind speeds up to
109	40% stronger than climatology (red vectors in Fig. 10). Days in phase 2 (highest ozone
110	concentrations) featured anomalous westerly winds, resulting in winds up to 50% weaker
111	in magnitude (Fig. 10) than climatology. In summer, days in phases 8 and 1 (lowest ozone
112	concentrations) featured surface winds very similar to climatology in both magnitude and

- direction. In summer, the wind direction on days in phase 8 was more from the north-
- northwest, while climatology was from the north-northeast, resulting in a very small
- westerly anomaly. Days in phase 6 (highest ozone concentrations) also featured winds with similar direction as the seasonal mean, but with speeds up to 30% faster (Fig. 10). "

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120	Variability of winter and summer surface ozone in Mexico City
121	on the intraseasonal time scale
122	
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126	Bradford S. Barrett ^{1,2} and Graciela B. Raga ¹
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129	

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131 Abstract. Surface ozone concentrations in Mexico City frequently exceed the Mexican standard 132 and have proven difficult to forecast due to changes in meteorological conditions at its tropical 133 location. The Madden-Julian Oscillation (MJO) is largely responsible for intraseasonal 134 variability in the tropics. Circulation patterns in the lower and upper troposphere and 135 precipitation are associated with the oscillation as it progresses eastward around the planet. It is 136 typically described by phases (labeled 1 through 8), which correspond to the broad longitudinal 137 location of the active component of the oscillation with enhanced precipitation. In this study we 138 evaluate the intraseasonal variability of winter and summer surface ozone concentrations in 139 Mexico City was investigated over the period 1986-2014 to determine if there is a modulation by 140 the MJO that would aid in the forecast of high pollution episodes.

141 Over 1 000 000 hourly observations of surface ozone from five stations around the metropolitan 142 area were standardized and then binned by active phase of the MJO, with phase determined using 143 the Real-time Multivariate MJO Index. Highest winter ozone concentrations were found in 144 Mexico City on days when the MJO was active and in phase 2 (over the Indian Ocean), and 145 highest summer ozone concentrations were found on days when the MJO was active and in 146 phase 6 (over the western Pacific Ocean). Lowest winter ozone concentrations were found during 147 active MJO phase 8 (over the eastern Pacific Ocean), and lowest summer ozone concentrations 148 were found during active MJO phase 1 (over the Atlantic Ocean). Anomalies of reanalysis-based 149 cloud cover and UV-B radiation supported the observed variability in surface ozone in both 150 summer and winter: MJO phases with highest ozone concentration had largest positive UV-B 151 radiation anomalies and lowest cloud cover fraction, while phases with lowest ozone 152 concentration had largest negative UV-B radiation anomalies and highest cloud cover fraction. 153 Furthermore, geopotential height anomalies at 250 hPa favoring reduced cloudiness, and thus

154	elevated surface ozone, were found in both seasons during MJO phases with above-normal ozone
155	concentrations. Similar height anomalies at 250 hPa favoring enhanced cloudiness, and thus
156	reduced surface ozone, were found in both seasons during MJO phases with below-normal ozone
157	concentrations. These anomalies confirm a physical pathway for MJO modulation of surface
158	ozone via modulation of the upper-troposphere.

159 1 Introduction

160 Ozone is hazardous to human health (WHO, 2008) and is a ubiquitous problem in many 161 megacities around the world. Tropospheric ozone is a secondary pollutant produced by complex 162 photochemistry from anthropogenic emissions and high ozone events typically affect mid-163 latitude urban areas during summer, while in the tropics, such events can be observed throughout 164 the year. The problem of the incidence of high surface ozone events is exacerbated in Mexico 165 City, a megacity with 21 million inhabitants, because of the intense solar radiation received at its 166 relatively high elevation (more than 2200 m above sea level) and tropical latitude (19.4°N) (Lei 167 et al., 2007). Furthermore, the city is located in a basin, effectively preventing efficient 168 ventilation of the polluted air (Fast and Zhong, 1998; Whiteman et al., 2000; Zhang et al., 2009). 169 Seasonal variability in maximum surface ozone concentrations is not large in Mexico 170 City due to its geographical location (Raga and LeMoyne, 1996). Both in the dry winter (December-February) and wet summer (June-August) months, clear skies and strong insolation 171 172 in the morning hours promote rapid generation of surface ozone via photochemical conversions 173 from anthropogenic precursor emissions near the surface. In both seasons, as the day progresses, 174 the boundary layer becomes unstable from solar radiation and deepens, diluting pollutant 175 concentrations near the surface. The growth of the boundary layer in Mexico City occurs over 176 the course of a few hours, with typical heights reaching at least 1.2 km above the surface 177 (Nickerson et al, 1992; Perez Vidal and Raga, 1998), even during the winter months when 178 insolation is reduced at this latitude. Highest ozone concentrations during the winter months are 179 often seen on days with strong insolation and light or no surface wind (Lei et al., 2007). In 180 summer months, clouds and precipitation generally reduce the number of days with extremely 181 elevated surface ozone concentrations. However, when large-scale atmospheric conditions are

favorable, such as when a high pressure regime and associated clear skies affect the Mexico City basin, elevated concentrations of surface ozone are also recorded in summer (Raga and Le Moyne, 1996). Hourly surface ozone concentrations routinely exceed the national standard, set at 110 ppb in 1993 (by law NOM-020-SSA1-1993) and modified in 2014 to 95 ppb (by law NOM-020-SSA1-2014). In 2015, hourly maximum O₃ concentrations in every month of the year exceeded the standard set in 2014 at monitoring stations in all five geographic regions: NE, NW, SE, SW and Center (Rodríguez et al., 2016).

189 The problem of air quality in Mexico City has been the subject of numerous field 190 programs over the years, typically limited in time but more comprehensive in terms of the 191 number of parameters measured. One such campaign was MILAGRO: Megacity Initiative: Local 192 and Global Research Observations, a very large international field campaign that took place in 193 March 2006. The results of the large number of publications from that project are summarized 194 by Molina et al (2010). These results provided new insight into several processes related with 195 pollutant transformations and chemical pathways, emerging from the analysis of the data 196 collected with the large suite of sophisticated instrumentation deployed and the modeling 197 performed. However, intensive field campaigns limited to one month, cannot address the 198 seasonal and intraseasonal variability of the high surface ozone within the city. Past studies 199 have examined the variability of surface ozone in Mexico City at different time scales, e.g. 200 hourly (Raga and Le Moyne, 1996; Huerta et al., 2004; Lei et al., 2007), daily (Fast and Zhong, 201 1998), weekly (Stephens et al., 2008), monthly (Rodríguez et al., 2016), and seasonal (Thompson 202 et al., 2008). All of these studies noted a primary relationship between ozone concentration in 203 Mexico City and ultraviolet (UV) radiation, where days with more UV radiation were associated 204 with elevated surface ozone concentrations. Furthermore, UV radiation received at the surface is

205 strongly modulated by cloud cover (El-Nouby Adam and Ahmed, 2016). However, as yet, no 206 study has explored surface ozone variability in Mexico City on the intraseasonal (30-60 day) 207 time scale, despite known relationships between the leading mode of atmospheric intraseasonal 208 variability, the Madden-Julian Oscillation (MJO; Madden and Julian. 1971), and tropical cloud 209 cover (Riley et al., 2011) and circulation (Madden and Julian, 1972; Zhang, 2005). The MJO is 210 largely responsible for intraseasonal variability in the tropics. Circulation patterns in the lower 211 and upper troposphere and precipitation are associated with the oscillation as it progresses 212 eastward around the planet. It is typically described by phases (labeled 1 through 8), which 213 correspond to the broad longitudinal location of the active component of the oscillation with 214 enhanced precipitation.

In this study we evaluate the intraseasonal variability of winter and summer surface ozone concentrations in Mexico City over the period 1986-2014 to determine if there is a modulation by the MJO that would aid in the forecast of high pollution episodes. Based on the relationships between surface ozone and UV radiation, UV radiation and cloud cover, and cloud cover and the MJO, the primary hypothesis tested in this study was the following: *surface ozone varies intraseasonally by phase of the MJO*.

The physical pathway hypothesized to support this intraseasonal variability was as follows: *anomalies in tropical convection associated with the MJO drive variability in upper tropospheric circulation, and that variability can be seen in composite anomalies of height and wind by MJO phase* (e.g., Madden and Julian, 1994; Zhang, 2005). Those circulation anomalies then drive variability in cloud cover and thus variability in UV radiation reaching the boundary layer, which in turn is seen in phase-to-phase variability in surface ozone concentrations in Mexico City. The cloud-UV radiation portion of our hypothesis is supported by Kerr et al.

228 (2008), who found that typical UV transmission ratios range between 0.3 and 0.8 for overcast 229 conditions (Cede et al., 2002) and as little as 0.05 for thick cumulonimbus clouds (McArthur et 230 al., 1999). It is also supported by An et al. (2008), who found a strong relationship between 231 surface ozone concentrations in Beijing and surface UV radiation, particularly in summer, and 232 noted that surface UV was up to 200% more sensitive to total cloud cover than was surface total 233 radiation. The motivation to explore potential relationships between the MJO and surface ozone 234 concentrations came from Barrett et al. (2012), who found differences as large as 25% of the 235 daily mean in afternoon summer ozone concentrations in Santiago, Chile, by phase of the MJO 236 and tied those differences to changes in cloud fraction associated with synoptic-scale circulation 237 variability in different MJO phases.

238

239 2 Data and methods

The government monitoring network, Red Automática de Monitoreo Atmosférico (Automated Atmospheric Monitoring Network, RAMA) has been operational since January 1986 measuring all criteria pollutants, with instrumentation certified by the US Environmental Protection Agency (EPA). In particular, the instrument to measure ozone is produced by Thermo Environmental Instrument Model 49, by UV absorbance. The RAMA currently has 33 stations within the Mexico City basin, but only a few have records dating back to 1986.

We selected five stations with the longest periods of record (Table 1), one station from each of the five geographic regions in the metropolitan area identified by several previous studies and summarized by Raga et al. (2001). Hourly observations from Tlalnepantla (TLA, in the <u>northwest sector of the city, NW</u>), Xalostoc (XAL, in the <u>northeast sector, NE</u>), Merced (MER, in the Center), Pedregal (PED, in the <u>southwest sector, SW</u>), and Universidad Autónoma

251 Metropolitana-Iztapalapa (UIZ, in the southeast sector, SE) were available beginning in January 252 1986 and up to December 2014. See Figure 1 for station locations and Table 1 for numbers of 253 observations and elevations of each station. Since the ozone time series were non-stationary, 254 standard anomalies (also called normalized anomalies) were calculated by subtracting a mean 255 value from each observation and then dividing that result by a standard deviation (Wilks, 2011). 256 Those mean values and standard deviations for each hour were estimated applying a 30-day 257 (approximately monthly) running window, and the 30-day period was selected to avoid influence 258 from both seasonal variability and also the long-term trend. We did not stratify by day of the 259 week based on Stephens et al. (2008), who found that ozone in Mexico City exhibited relatively 260 little variability by day of the week. Furthermore, we defined a "low" ozone concentration day 261 as one with mean afternoon (1200 to 1600 local time) ozone standard anomalies (averaged across the five observing stations) below the 10th percentile. Percentiles were determined separately for 262 263 each season using standard anomalies on all days in that season from 1986 to 2014. Similarly, we 264 defined a "high" ozone concentration day as one where mean afternoon ozone standard anomalies exceeded the 90th percentile, again calculating winter and summer percentiles 265 266 separately.

The MJO phase was determined using the Real-time Multivariate MJO (RMM) index (Wheeler and Hendon, 2004). The daily RMM is based on time series of two principal components derived from empirical orthogonal functions of equatorially (5°S to 5°N) averaged 200-hPa zonal wind, 850-hPa zonal wind, and outgoing longwave radiation. The projection of daily data onto the empirical orthogonal functions serves as a time filter and makes the RMM useful in a real-time setting (Wheeler and Hendon, 2004). The RMM is divided into eight phases, and each phase corresponds to the broad geographic location of the MJO tropical convective

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graciela binimelis d..., 14/10/16 8:41 A.M. Eliminado: calculated on graciela binimelis d..., 14/10/16 8:41 A.M. Eliminado: basis signal on that day. An active MJO was defined in this study as one with RMM amplitude, which
is the square root of the sum of the squares of the two principal components RMM1 and RMM2
(Wheeler and Hendon, 2004), greater than 1.0 (LaFleur et al., 2015). Each day's hourly standard
ozone anomalies were binned using the phase of active MJO of that day. Mean values for each
MJO phase were then calculated, first annually and then for each season (DJF, and JJA).

281 Values of geopotential height (in m) and u- and v vector wind components at 250 hPa (in 282 m s⁻¹), along with total cloud cover, high cloud cover, and low cloud cover (expressed as fractions from 0 to 1) and downward UV radiation received at the surface (UV-B, in W m⁻²) at 283 284 1800 UTC (1200 local time) were derived from the ERA-Interim reanalysis (Dee et al., 2011). 285 We chose to examine 250 hPa in part based on the results of Li et al. (2012), who connected 286 intraseasonal ozone variability across east Asia with variability in upper-troposphere 287 geopotential heights by MJO phase. Additionally, we are aware that cloud cover in reanalysis has 288 biases, and we selected the ERA-Interim product because it specifically includes an improved 289 deep convective cloud triggering mechanism over tropical land masses (Bechtold et al., 2004) 290 and thus shows skill over other products (Dee et al., 2011).

We selected the winter (Dec-Feb; DJF) and summer (June-August; JJA) seasons for this study because of the homogeneity in synoptic-scale weather patterns in those seasons. More details on the climatological variability of ozone in Mexico City can be found in Klaus et al. (2001).

Finally, daily values of surface wind at the Tacubaya station (TCBY in Fig. 1) were taken from the NOAA National Centers for Environmental Information (NCEI) Integrated Surface Database (ISD; Smith et al., 2011). Anomalies of those values, calculated with respect to seasonal means, were binned by MJO phase to give composite anomalies for each season. For

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graciela binimelis d..., 12/10/16 2:01 P.M. Eliminado: J 300 UV and total cloud cover in Mexico City itself, the gridded ERA-Interim value at the point

301 closest to the mean latitude and longitude of the five RAMA stations was selected.

302

303 **3 Results**

304 **3.1 Variability of the ozone time series**

305 The diurnal cycle of ozone concentrations at each of the stations exhibited a daily 306 minimum around 0700 local time just prior to sunrise and a peak between 1200 and 1500 local 307 time, with highest concentrations at the southern-most stations (PED and UIZ) and lowest in the 308 northern-most station (XAL) (Fig. 2a). Additionally, highest ozone concentrations occurred one 309 to two hours earlier in spring (March-May; MAM) than in winter (December-February; DJF) at 310 both PED and XAL (Fig. 2b), and peak ozone at PED in the south occurred one to two hours 311 after peak ozone in XAL in the north, as a result of weak northeasterly surface winds 312 transporting ozone and photochemical precursors southward during the day (Bossert 1997).

Mean ozone concentrations in spring were nearly 30% higher at all stations than the rest of the year (Fig. 3, with observations smoothed by a 30-day running mean), and the effects of increased UV radiation during the "mid-summer drought" (*canícula*) (Magaña et al. 1999) were reflected as a secondary peak in ozone concentrations in August. Minimum O₃ concentrations were observed in all five stations during September, when daily maximum precipitation was observed in Mexico City.

One of the challenges in examining intraseasonal variability of ozone is the need for a stationary record over a long period. In Mexico City, ozone concentrations have steadily decreased from the early 1990s to the 2010s (Fig. 4a; also Rodríguez et al., 2016) as a result of pollution control measures (Molina and Molina, 2004). In order to remove the long-term trend, while keeping the intraseasonal variability at hourly resolution, hourly observations were converted to standard anomalies as described in Section 2. Results of this transformation of hourly observations to standard anomalies for station PED are shown in Figures 4a (original hourly observations) and 4c (hourly standard anomalies). Standard anomalies for the other four stations show very similar results.

We note that overnight minimum observations from 1991 to 1993 were probably overestimated in the observational record (Fig. 4a), an artifact also seen in the other four stations (not shown). However, because in this study we focused on afternoon values (from 1200 to 1600 local time), that potential overestimation did not materially impact our results.

By transforming each hourly observation into a standard anomaly, the distribution of relative frequencies shifted from highly non-Gaussian, with peaks near zero and very long right tails (Fig. 4b), to more Gaussian, with peaks near -0.5 and reduced skewness (Fig. 4d). Although the peaks in these transformed distributions were less than zero, and the right tails were longer than the left tails, the means of each of the distributions of standard anomalies in Figure 4d were very near zero, falling between -0.03 and 0.

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339 **3.2** Synoptic patterns associated with low and high ozone

340 Before examining ozone variability by MJO phase, it was important to first establish the 341 synoptic-scale patterns associated with days of low and high ozone concentrations (defined in 342 Section 2) in each season.

In winter (DJF), the synoptic pattern on days with low afternoon surface ozone concentration featured a 250-hPa ridge over northwest Mexico and the southwest U.S. (height anomalies up to +50 m) and a 250-hPa trough over central, eastern, and southern Mexico and the

346 southern and eastern U.S. (height anomalies -10 to -40 m) (Fig. 5a). Mean circulation at 250-hPa 347 on low DJF ozone days was nearly westerly off the central Mexican west coast turning to 348 southwesterly over central Mexico (Fig. 5a). This synoptic pattern would favor enhanced 349 cloudiness over Mexico City (and thus reduced UV radiation and lower ozone concentrations) 350 via two mechanisms: first, through quasi-geostrophic ascent associated with the 250-hPa trough, 351 and second, through advection of moisture and high-level clouds from the subtropical Pacific 352 (around 20°N) associated with westerly and west-northwesterly winds (Fig. 5a). Indeed, positive 353 total cloud fraction anomalies were seen with this height and circulation pattern, and those cloud 354 fraction anomalies (+0.05 to +0.10) extended over central and southern Mexico and 355 northeastward into the Gulf of Mexico (Fig. 5b). Those anomalies were likely comprised 356 primarily of high cloud (+0.05 to +0.15; Fig. 5c), given the resemblance between the pattern of 357 total cloud cover (Fig. 5b) and high cloud cover (Fig. 5c). A region of positive low cloud cover 358 anomalies (up to +0.15; Fig. 5d) was also seen in central Mexico on winter days with lowest O_3 359 concentrations, likely associated with surface wind convergence over the Sierra Madre Oriental 360 Mountains, although low cloud fraction anomalies over Mexico City itself were less than +0.05. 361 The synoptic pattern for winter days with high surface ozone concentration was opposite 362 that for the low ozone days. Over northwest Mexico and the southwest U.S., a trough was seen at 363 250-hPa (anomalies -10 to -70 m), while a ridge was seen over central, southern, and eastern

Mexico and the southern and eastern U.S. (anomalies to +50 m; Fig. 5e). Circulation at 250 hPa over central Mexico was southwesterly (compared to westerly for low ozone days). Negative total cloud fraction anomalies (-0.05 to -0.15) over central and southern Mexico were associated with this circulation pattern (Fig. 5f). This pattern would promote clearer than normal skies (and thus enhanced UV radiation and surface ozone production) by both favoring quasi-geostrophic

369 subsidence over central Mexico (associated with the above-normal heights and ridging at 250 370 hPa) and by advecting dry, cloud-free air toward central Mexico from the tropical East Pacific 371 Ocean originating near 10°N (Fig. 5g). Similar to low ozone days, most of the negative total 372 cloud fraction anomalies were likely result of the reduction in the presence of high cloud (Fig. 373 5g), given similarity of the anomaly patterns between total (Fig. 5f) and high (Fig. 5g) cloud 374 fraction. The low cloud fraction anomaly over Mexico City itself (Fig. 5h) was close to zero, 375 although negative low cloud fraction anomalies (-0.05 to -0.15) were seen over the low-land 376 states bordering the Gulf of Mexico (Fig. 5h).

377 Summer days with low surface ozone concentration featured a slight anomalous ridge 378 (height anomalies of +5 to +15 m) over northern Mexico and much of the U.S. (Fig. 6a). This 379 synoptic-scale pattern would favor cloudiness because positive geopotential height anomalies at 380 250 hPa over northern Mexico and the southwest U.S. would be associated with a stronger 381 summer anticyclone, signifying a more intense monsoon circulation, easterly winds at 250 hPa in 382 central and southern Mexico (Fig. 6a), and precipitation in central and southern Mexico. Indeed, 383 low ozone days featured positive anomalies in total cloud fraction (Fig. 6b), high cloud fraction 384 (Fig. 6c), and low cloud fraction (Fig. 6d), with anomalies of each fractional cloud cover variable 385 ranging from +0.05 to +0.15. The regions of positive total and high cloud cover anomalies 386 extended over much of central Mexico, but anomalies in low cloud fraction were confined to 387 Mexico City and the states bordering it (Fig. 6d). Summer days with high ozone concentration 388 featured less ridging over northwestern Mexico and the southwest U.S., with 250-hPa height 389 anomalies of -10 to -20 m (Fig. 6e). This synoptic-scale pattern with weaker ridging over 390 northwest Mexico and the southwest U.S., and stronger ridging over Central America, is 391 opposite of the climatological monsoon circulation and would favor less precipitation in central

Mexico. Indeed, negative anomalies in fraction of total cloud cover (Fig. 6f), high cloud cover (Fig. 6g), and low cloud cover (Fig. 6h) were seen on days with high ozone concentrations, with anomaly magnitudes of -0.05 to -0.15 over much of central and southern Mexico (total and high cloud cover) and the states bordering Mexico City and along the Sierra Madre Occidental mountains (Fig. 6h). In the next section, these seasonal ozone pattern composites are compared to pattern composites for MJO phases with greatest ozone anomalies.

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399 3.3 Intraseasonal ozone variability

400 On an annual basis, afternoon (1200 to 1600 local time) surface ozone concentrations in 401 Mexico City were found to vary by MJO phase. Highest ozone concentrations were noted on 402 days when MJO was active and in phases 3, 4, and 5, while lowest ozone concentrations were 403 noted on days when the MJO was active and in phases 1 and 2 (Fig. 7a). This variability was 404 seen at all five stations, regardless of geographic position within the basin. Normalized 405 anomalies of surface UV radiation and total cloud fraction from ERA-Interim reanalysis strongly 406 supported the observed surface ozone variability: MJO phases with highest ozone concentrations 407 also had highest UV anomalies and lowest total cloud fraction anomalies, while MJO phases 408 with lowest ozone concentrations had the most negative UV and the most positive cloud fraction 409 anomalies (Fig. 7d). We found this agreement remarkable, particularly so because the two data 410 sets independently presented the same intraseasonal pattern.

411 On a seasonal basis, surface ozone concentrations in Mexico City were also found to vary 412 by MJO phase. However, the dependence on phase was found to change between winter and 413 summer, meaning a phase associated with higher ozone concentrations in winter would not 414 necessarily be associated with higher ozone concentrations in summer. We attribute these

differences to seasonality in both the convective properties of the MJO itself (e.g., Zhang and Dong, 2004; Wu et al., 2006) and in the extratropical atmosphere, whose circulation the MJO modulates (Gloeckler and Roundy, 2013). Despite the phase-to-phase variability in maximum and minimum ozone concentrations throughout the year, in all seasons, there remained good agreement between phases with highest (lowest) ozone concentrations and phases with highest (lowest) UV and lowest (highest) total cloud fraction. That is, the sunnier phases were consistently associated with the highest ozone concentrations.

422 In winter months (DJF), highest ozone concentrations were found on days when the MJO 423 was in phase 2, and lowest ozone concentrations were found on days when the MJO was in phase 424 8 (Fig. 7b). Highest UV radiation, and lowest total cloud fraction, were seen on days when the 425 MJO was in phase 2, and lowest UV radiation and second-highest cloud fraction were seen on 426 days when the MJO was in phase 8 (Fig. 7e). In summer months (JJA), highest ozone 427 concentrations were found on days when the MJO was in phases 5, 6, and 7, and lowest ozone 428 concentrations were found on days when the MJO was in phases 1 and 8 (Fig. 7c). Highest UV radiation, and lowest total cloud fraction, was seen on days when the MJO was in phase 6, and 429 430 lowest UV radiation and highest total cloud fraction were seen on days when the MJO was in 431 phase 1. In both winter and summer, UV radiation and cloud cover anomalies strongly supported 432 observed surface ozone anomalies, whereby the cloudiest MJO phases featured lowest ozone and 433 the sunniest phases featured highest ozone. We again consider this agreement remarkable, given 434 the independence of the ozone and reanalysis data sets. Summer months (JJA) featured the greatest range in mean ozone concentrations by MJO phase: a difference in 0.25 standard 435 436 anomaly units between the phases with the highest ozone concentrations (phases 5 and 6) and the

phases with the lowest ozone concentrations (phases 1 and 8) (Fig. 7c). Summer months alsofeatured the largest spread in both UV and total cloud fraction standard anomalies (Fig. 7f).

439 An examination of the frequency of "extreme" ozone days in each MJO phase (here a day 440 with an "extreme" ozone value was defined for each season as an afternoon standard anomaly either above the 90th percentile value or below the 10th percentile value) provides additional 441 442 insight into the character of the MJO modulation of ozone. In both winter and summer, the 443 phases associated with highest ozone concentrations (phase 2 in winter and phase 6 in summer) 444 featured the fewest occurrences of days with extremely low ozone (days with concentrations below the 10th percentile; Table 2). Those phases also featured either the highest (in summer) or 445 near-highest (in winter) occurrences of days with concentrations above the 90th percentile (Table 446 447 2). Furthermore, the phases associated with lowest ozone concentration (phase 8 in winter and 448 phase 1 in summer) featured the highest occurrences of days with low ozone (Table 2) and 449 below-normal occurrence of days with high ozone. These results confirm that one manner in 450 which the MJO modulates ozone concentration in Mexico City is to reduce (or augment) the frequency of days with afternoon ozone concentrations either below the 10th or above the 90th 451 452 percentiles.

To examine physical mechanisms for the observed variability in ozone concentration and cloud cover by MJO phase, composite anomalies of 250-hPa height and *u*- and *v*- wind components were created for each active MJO phase for each season. Seasonal anomalies of total cloud fraction, high cloud fraction, and low cloud fraction were also composited for each active MJO phase. In both seasons, anomalies of each variable were found for all eight MJO phases. However, for the remainder of this paper, we focus only on the synoptic-scale conditions in phases with maximum and minimum surface ozone. In DJF, minimum ozone concentrations

460 occurred on days when the MJO was active and in phase 8. In that phase, anomalous 250-hPa 461 ridging was seen over northwest Mexico and the southwest U.S. (anomalies up to +50 m) and 462 anomalous 250-hPa troughing over northeast Mexico and the southeastern U.S. (anomalies to -60 463 m) (Fig. 8a). This height pattern resembled the seasonal pattern for winter days with above-464 normal cloudiness and low ozone (Figs. 5a), with troughing over central Mexico favoring both cloud formation via ascent and cloud advection from the subtropical East Pacific Ocean. Indeed, 465 466 on days in MJO phase 8, total cloud cover anomalies were positive over nearly all of Mexico, 467 ranging from +0.05 to +0.15 (Fig. 8b). Anomalies in high cloud cover were smaller in magnitude 468 (up to +0.05), and over Mexico City, high cloud cover anomalies were zero (Fig. 8c). Positive 469 low cloud anomalies were confined to the states to the east of Mexico City (Fig. 8d), which when 470 combined with high cloud cover anomalies, suggest that the anomalies in total cloud cover (Fig. 471 8b) were composed of anomalies at multiple levels.

472 Maximum winter ozone concentrations occurred on days when the MJO was active and 473 in phase 2, and on those days, a synoptic-scale pattern opposite to that of phase 8 was seen: 474 anomalous 250-hPa troughing was seen over northern Mexico and the south-central U.S. (height 475 anomalies of -10 to -30 m) and anomalous 250-hPa ridging was seen over central and southern 476 Mexico and Central America (height anomalies +5 to +20 m) (Fig. 8e). This height pattern 477 resembled the seasonal pattern for high ozone and low cloud fraction (Fig. 5e), with anomalous 478 ridging favoring clearer than normal skies via subsidence and advection of dry air from the 479 tropical East Pacific. Indeed, below-normal total cloud fraction (anomalies -0.05 to -0.15; Fig. 8f), high cloud fraction (anomalies -0.05 to -0.15; Fig. 8g), and low cloud fraction (anomalies -480 481 0.05 to -0.10; Fig. 8h) were seen on days when the MJO was in phase 2 over much of central and 482 southern Mexico.

483 In JJA, minimum ozone concentrations occurred on days when the MJO was in phase 1. 484 In that phase, anomalous 250-hPa ridging was seen over northwest Mexico and the southwest 485 U.S. (anomalies up to +20 m) and anomalous 250-hPa troughing in the tropical East Pacific 486 Ocean (anomalies to -20 m) (Fig. 9a). This height pattern resembled the seasonal pattern for 487 summer days associated with below-normal cloudiness and high ozone (Figs. 6a), with ridging to 488 the north characteristic of the summer monsoon in central Mexico. Indeed, above-normal total 489 cloud fraction (+0.05 to +0.15; Fig. 9b), above-normal high cloud fraction (+0.05 to +0.15; Fig. 490 9c), and above-normal low cloud fraction (+0.05 to +0.10; Fig. 9d) were seen over central and 491 southern Mexico for days in MJO phase 1. Summer maximum ozone concentrations were seen 492 on days when the MJO was in phase 6. In that phase, a weaker-than-normal ridge at 250 hPa was 493 seen as anomalous heights of -10 to -20 m over much of central Mexico (Fig. 9e). This height 494 pattern resembled the seasonal pattern for summer days associated with above-normal cloudiness 495 and high ozone (Figs. 6e), as it is largely opposite of that which characterizes the central Mexico 496 summer monsoon. Indeed, below-normal total cloud fraction (-0.05 to -0.15; Fig. 9f), high cloud 497 fraction (-0.05 to -0.15; Fig. 9g), and low cloud fraction (-0.05; Fig. 9h) were all seen on days 498 when the MJO was in phase 6.

The final physical variable examined for intraseasonal variability by MJO phase was the surface wind vector at 1800 UTC (1200 local time) at Tacubaya (TCBY in Fig. 1) in the centerwest portion of the metropolitan area (Fig. 1). <u>In winter, days in phase 8 (lowest ozone</u> concentrations) featured anomalous northeasterly surface winds (blue vectors; Fig. 10), resulting in observed wind speeds up to 40% stronger than climatology (red vectors in Fig. 10). Days in phase 2 (highest ozone concentrations) featured anomalous westerly winds, resulting in winds up to 50% weaker in magnitude (Fig. 10) than climatology. In summer, days in phases 8 and 1

506 (lowest ozone concentrations) featured surface winds very similar to climatology in both 507 magnitude and direction. In summer, the wind direction on days in phase 8 was more from the 508 north-northwest, while climatology was from the north-northeast, resulting in a very small 509 westerly anomaly. Days in phase 6 (highest ozone concentrations) also featured winds with 510 similar direction as the seasonal mean, but with speeds up to 30% faster (Fig. 10). Despite these 511 variations by MJO phase across all seasons, we do not consider the surface wind anomalies to be 512 physically consistent or representative of a large-scale pattern, for two reasons. First, because 513 Mexico City is located in a basin, surface flow fields do not normally respond to synoptic-scale 514 pattern variability (Stephens et al., 2008). Indeed, the majority of the day-to-day variability in 515 surface wind speed and direction is controlled by mesoscale, thermally-driven mountain-valley circulations (Doran et al., 1998). With the exception of "cold surge" events in winter that have 516 517 been associated with cloudy days, the two dominant ozone patterns identified by De Foy et al. 518 (2005) only served to identify whether the ozone maximum would be in the southern or northern 519 parts of the metropolitan area. Second, the wind anomalies by MJO phase resulted in only subtle 520 changes in either direction, or speed, or both (Fig. 10). Moreover, none of the wind anomalies 521 identified in DJF would meet the northerly "cold surge" of De Foy et al. (2005), suggesting that 522 the "cold surge" events can occur during different MJO phases unrelated to modulation from the 523 MJO. Finally, the smallness of the surface wind variability by MJO phase supports our argument that variability in surface ozone concentrations by MJO phase are primarily driven by variability 524 in total cloud cover and surface UV radiation, which in turn are related to anomalies in upper-525 tropospheric circulation. 526

Eliminado: In winter, days in phase 8 (lowest ozone concentrations) featured anomalous westerly surface winds (blue vectors; Fig. 10), resulting in observed wind speeds up to 50% weaker than climatology (red vectors in Fig. 10). Days in phase 2 (highest ozone concentrations) featured small or weakly anomalous easterly winds, resulting in winds similar to climatology but up to 40% stronger in magnitude (Fig. 10). In summer, days in phases 8 and 1 (lowest ozone concentrations) featured surface winds very similar to climatology in both magnitude and direction. In summer, the wind direction on days in phase 8 was more from the north-northwest while climatology was from the north-northeast. Days in phase 6 (highest ozone concentrations) also featured winds with similar direction as the seasonal mean but with speeds up to 30% faster (Fig. 10). graciela binimelis d..., 14/10/16 8:51 A.M

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528 4 Conclusions

547 In this study, we investigated the intraseasonal variability of winter (DJF) and summer 548 (JJA) surface ozone concentrations in Mexico City. After standardizing over 1 000 000 hourly 549 observations of surface ozone from five stations around the metropolitan area, we binned them 550 by phase of the active MJO. We found that highest winter ozone concentrations occurred on days 551 when the MJO was active and in phase 2 (in the Indian Ocean), and highest summer ozone 552 concentrations occurred on days when the MJO was active and in phase 6 (in the western Pacific 553 Ocean) in summer. Lowest ozone concentrations were found on winter days in MJO phase 8 (in 554 the eastern Pacific Ocean) and summer phase 1 (in the Atlantic Ocean). This intraseasonal 555 variability in surface ozone concentrations agreed well with anomalies in cloud cover and UV-B 556 radiation: phases with highest ozone concentration had highest UV-B radiation and lowest cloud 557 cover, while phases with lowest ozone concentration had lowest UV-B radiation and highest 558 cloud cover. This agreement was found for both winter and summer. Circulation anomalies at 559 250 hPa were found to support the observed variability in ozone and cloud cover. In winter, 560 height and circulation anomalies favoring reduced cloudiness, and thus elevated surface ozone, 561 were found on days when the MJO was in phase 2, and height and circulation anomalies favoring 562 enhanced cloudiness, and thus reduced surface ozone, were found on days when the MJO was in 563 phase 8. In summer, monsoon-like 250-hPa circulation patterns that favor enhanced cloudiness, 564 and thus reduced surface ozone, were found on days when the MJO was in phase 1, and 250-hPa 565 circulation patterns opposite to the monsoon, favoring reduced cloudiness and thus elevated 566 surface ozone, were found on days when the MJO was in phase 6. We did not find physically 567 meaningful variability in surface wind direction by MJO phase, despite earlier studies suggesting 568 a relationship between surface wind and surface ozone in Mexico City. This suggests that the

569 intraseasonal variability in both summer and winter surface ozone by MJO phase is driven

570 primarily by variability in cloud cover via modulation of upper-troposphere circulation.

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- 572
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681 Table captions

Table 1: Station names, locations, period of record, and number of observations.

683

684 Table 2: Relative frequency of extreme ozone days in winter (top two rows) and summer (bottom

two rows). <u>A high ozone day was defined as one with a mean afternoon (1200 to 1600 local)</u>
ozone anomaly across the 5 observing stations greater than the long-term (1986-2014) 90th
percentile. Similarly, a low ozone day was defined as one with a mean afternoon anomaly across
the 5 observing stations less than the long-term 10th percentile. Bold values (winter phase 2;
summer phase 6) indicate phases with highest mean ozone concentrations in those seasons;

690 jtalics in italics (winter phase 8; summer phase 1) indicate phases with lowest mean ozone
691 concentrations in those seasons. Number of days (n) in each active phase is given for each
692 season, used to estimate the relative frequency.

693

694 Figure captions

Figure 1: Locations of RAMA surface ozone stations used in this study (colored dots; abbreviations defined in Table 1) and topographic height (shaded, in m) of the Mexico City metropolitan region. State boundaries shown as black contours. Surface meteorology station at Tacubaya (TCBY) also indicated. The inset in the upper right corner shows the location of Mexico City within Mexico.

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Figure 2: (a) Diurnal cycle of surface ozone concentrations (ppb) at five observing stations(colored lines), as well as the mean (black dotted line) for all seasons, 1986-2014. (b) Diurnal

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graciela binimelis d..., 14/10/16 8:16 A.M. Eliminado: An extreme ozone day was defined as one with mean afternoon hourly (1200 to 1600 local) ozone concentrations at average of all 5 stations either greater than the 90th percentile value or less than the 10th percentile value. graciela binimelis d..., 14/10/16 8:16 A.M. Eliminado: values in 709 cycle of surface ozone concentrations for Pedregal (PED; blue lines) and Xalostoc (XAL; red

710 lines) by season from the RAMA network, 1986-2014.

Figure 3: Annual cycles of surface ozone concentrations (ppb) for five observing stations for
hours 1200-1600 (local time) from the RAMA network, 1986-2014. Observations are smoothed
using a 30-day running mean.

714

Figure 4: (a) Hourly observations of surface ozone concentrations (ppb) at Pedregal station (PED in Fig. 1). (b) Relative frequencies (in %) of hourly ozone concentrations (ppb) at five observing stations, 1986-2014. (c) Standard anomalies of hourly surface ozone concentrations at PED. (d) Relative frequencies (in %) of standard anomalies of hourly ozone concentrations at five observing stations from the RAMA network, 1986-2014.

720

721 Figure 5: (a) Height (contoured, in m), height anomalies (shaded, in m), and mean winds 722 (vectors) at 250-hPa for winter (DJF) days with standard anomalies of afternoon (1200 to 1600 local time) surface ozone at the five observing stations (Fig. 1) below the 10th percentile. (b)-(d) 723 724 Anomalies (in %) of total cloud fraction, high cloud fraction, and low cloud fraction, 725 respectively, for the same winter days with standard anomalies of afternoon surface ozone 726 concentrations below the 10th percentile. (e)-(h) Same as in (a)-(d), but for winter days with mean afternoon surface ozone concentrations above the 90th percentile. Percentile calculations 727 728 based on hourly observations from 1986-2014. Height, wind, and cloud fraction data from ERA-729 Interim; ozone concentrations from RAMA stations.

730

731 Figure 6: As in Figure 5, but for summer (JJA) days.

733 Figure 7: Mean standard anomalies of midday (hours 12-16 local time) surface ozone 734 concentrations by active MJO phase for (a) annual, (b) DJF, and (c) JJA. Stations indicated by 735 line color. Error bars indicate largest and smallest standard anomaly values for all stations; 736 dashed black curve indicates mean value. All surface ozone observations from the RAMA 737 network, 1986-2014. (d) Standard anomalies of UV radiation (blue curves) and total cloud 738 fraction (black curves) for each active MJO phase for the entire year. (e) and (f) Same as panel 739 (d) but for DJF and JJA, respectively. UV and cloud fraction data from ERA-Interim reanalysis, 740 1986-2014, for the grid closest to Mexico City.

741

Figure 8: Composites of 250-hPa height (in m), height anomaly (in m), and mean wind (a), and total cloud fraction (in %; b), high cloud fraction (in %; c), and low cloud fraction (in %; d) for winter days in active MJO phase 8. (e)-(h) Same as (a)-(d) but for winter days in active MJO phase 2. Phases 8 and 2 were the phases with lowest and highest respective winter ozone concentrations in Mexico City.

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Figure 9: As in Figure 8, but for summer days in active MJO phase 1 (a-d) and active MJO phase
6 (e-h). Phases 1 and 6 were the phases with lowest and highest respective summer ozone
concentrations in Mexico City.

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Figure 10: Mean 10-m winds at Tacubaya station (TCBY in Fig. 1) at 1800 UTC (1200 local time). Mean surface wind vectors for each season, D₄J<u>F</u> and JJA, are on row one and indicated by red arrows. Mean (black arrows) and anomaly (blue arrows) vectors for the MJO phases

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associated with lowest surface ozone (phase 8 in DJF and phase 1 in JJA) are on the middle row. Mean (black arrows) and anomaly (blue arrows) vectors for the MJO phases associated with highest surface ozone (phase 2 in DJF and phase 6 in JJA) are on the bottom row. Note that the mean winds for low ozone in DJF and high ozone in JJA are very similar to the seasonal mean winds, so the anomaly (blue) vector is very small. All wind data are from NOAA National Centers from Environmental Information, 1986-2014.

Table 1: Station nan	nes, locations, p	eriod of rec	ord, and nun	nber and typ	pe of observati	ons.		
Station name	Abbreviation	Latitutde (°N)	Longitude (°W)	Elevation (m)	Period of record	Variable	Number of observations	Frequency of observation
Xalostoc	XAL	19.3	-99.2	2326	1986 to 2014	Surface O ₃	221472	Hourly
Tlalnepantla	TLA	19.4	-99.1	2245	1986 to 2014	Surface O ₃	230992	Hourly
Merced	MER	19.5	-99.1	2160	1986 to 2014	Surface O ₃	219404	Hourly
Pedregal	PED	19.5	-99.2	2311	1986 to 2014	Surface O ₃	217009	Hourly
UAM-Iztapalapa	UIZ	19.4	-99.1	2221	1986 to 2014	Surface O ₃	194224	Hourly
Tacubaya	TCBY	19.4	-99.2	2313	1986 to 2014	Surface wind	7398	Daily (at 1200 local)

Table 2. Relative frequency of extreme (high or low) ozone days in winter (top two rows) and summer (bottom two rows). A high ozone day was defined as one with a mean afternoon (1200 to 1600 local) ozone anomaly across the 5 observing stations greater than the long-term (1986-2014) 90th percentile. Similarly, a low ozone day was defined as one with a mean afternoon anomaly across the 5 observing stations less than the long-term 10th percentile. Bold values (winter phase 2; summer phase 6) indicate phases with highest mean O3 concentrations in those seasons; italics values (winter phase 8; summer phase 1) indicate phases with lowest mean O3 concentrations in those seasons. Number of days (n) in each active phase is given for each season, used to estimate the relative frequency.

Winter (DJF)	Phase 1 n=134	Phase 2 n=169	Phase 3 n=249	Phase 4 n=222	Phase 5 n=226	Phase 6 n=254	Phase 7 n=282	Phase 8 n=187
Relative frequency of days with O_3 concentration greater than the 90th percentile	9.7%	10.1%	7.6%	8.1%	12.8%	9.8%	12.4%	8.6%
Relative requency of days with O ₃ concentration less than the 10th percentile	9.0%	7.1%	7.2%	8.1%	7.5%	9.8%	12.4%	13.9%
	Phase 1	Phase 2	Phase 3	Phase 4	Phase 5	Phase 6	Phase 7	Phase 8
Summer (JJA)	Phase 1 n=351	Phase 2 n=267	Phase 3 n=112	Phase 4 n=114	Phase 5 n=165	Phase 6 n=137	Phase 7 n=121	Phase 8 n=161
$Summer (JJA) \\ Relative frequency of days with O_3 \\ concentration greater than the 90th percentile \\$	Phase 1 n=351 8.6%	Phase 2 n=267 6.7%	Phase 3 n=112 3.6%	Phase 4 n=114 10.5%	Phase 5 n=165 9.7%	Phase 6 n=137 11.7%	Phase 7 n=121 11.6%	Phase 8 n=161 8.7%

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Table 2: Relative frequency of e ozone day was defined as one w stations either greater than the 90 summer phase 6) indicate phases summer phase 1) indicate phases active phase is given for each se

Winter (DJF)

Relative frequency of days with concentration greater than the 90

Relative requency of days with (concentration less than the 10th J

Summer (JJA)

Relative frequency of days with concentration greater than the 90

Relative frequency of days with concentration less than the 10th p





Figure 1: Locations of RAMA surface ozone stations used in this study (colored dots; abbreviations defined in Table 1) and topographic height (shaded, in m) of the Mexico City metropolitan region. State boundaries shown as black contours. Surface meteorology station at Tacubaya (TCBY) also indicated. The inset in the upper right corner shows the location of Mexico City within Mexico.



Figure 2: (a) Diurnal cycle of surface ozone concentrations (ppb) at five observing stations (colored lines), as well as the mean (black dotted line) for all seasons, 1986-2014. (b) Diurnal cycle of surface ozone concentrations for Pedregal (PED; blue lines) and Xalostoc (XAL; red lines) by season from the RAMA network, 1986-2014.





Figure 3: Annual cycles of surface ozone concentrations (ppb) for five observing stations for
hours 1200-1600 (local time) from the RAMA network, 1986-2014. Observations are smoothed
using a 30-day running mean.



Figure 4: (a) Hourly observations of surface ozone concentrations (ppb) at Pedregal station (PED in Fig. 1). (b) Relative frequencies (in %) of hourly ozone concentrations (ppb) at five observing stations, 1986-2014. (c) Standard anomalies of hourly surface ozone concentrations at PED. (d) Relative frequencies (in %) of standard anomalies of hourly ozone concentrations at five observing stations from the RAMA network, 1986-2014.







789 Figure 5: (a) Height (contoured, in m), height anomalies (shaded, in m), and mean winds 790 (vectors) at 250-hPa for winter (DJF) days with standard anomalies of afternoon (1200 to 1600 791 local time) surface ozone at the five observing stations (Fig. 1) below the 10th percentile. (b)-(d) 792 Anomalies (in %) of total cloud fraction, high cloud fraction, and low cloud fraction, 793 respectively, for the same winter days with standard anomalies of afternoon surface ozone 794 concentrations below the 10th percentile. (e)-(h) Same as in (a)-(d), but for winter days with 795 mean afternoon surface ozone concentrations above the 90th percentile. Percentile calculations 796 based on hourly observations from 1986-2014. Maximum wind speed (in m s⁻¹) is given in 797 lower-right corner of (a) and (e). Height, wind, and cloud fraction data are from ERA-Interim 798 reanalysis.

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Figure 6: As in Figure 5, but for summer (JJA) days.



Figure 7: Mean standard anomalies of midday (hours 12-16 local time) surface ozone concentrations by active MJO phase for (a) annual, (b) DJF, and (c) JJA. Stations indicated by line color. Error bars indicate largest and smallest standard anomaly values for all stations; dashed black curves in (a)-(c) indicate mean values of all 5 observing stations. All surface ozone

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- 808 observations from the RAMA network, 1986-2014. (d) Standard anomalies of UV radiation (blue
- 809 curves) and total cloud fraction (black curves) for each active MJO phase for the entire year. (e)
- 810 and (f): same as panel (d) but for DJF and JJA, respectively. UV and cloud fraction data from

811 ERA-Interim reanalysis, 1986-2014, for the grid closest to Mexico City.





Figure 8: Composites of 250-hPa height (in m), height anomaly (in m), and mean wind (a), and total cloud fraction (in %; b), high cloud fraction (in %; c), and low cloud fraction (in %; d) for winter days in active MJO phase 8. (e)-(h) Same as (a)-(d) but for winter days in active MJO phase 2. Maximum wind speed (in m s⁻¹) is given in lower-right corner of (a) and (e). Phases 8 and 2 were the phases with lowest and highest respective winter ozone concentrations in Mexico City. Height, wind, and cloud fraction data are from ERA-Interim reanalysis.





Figure 9: As in Figure 8, but for summer days in active MJO phase 1 (a-d) and active MJO
phase 6 (e-h). Phases 1 and 6 were the phases with lowest and highest respective summer ozone
concentrations in Mexico City.



827 Figure 10: Mean 10-m winds at Tacubaya station (TCBY in Fig. 1) at 1800 UTC (1200 local 828 time). Mean surface wind vectors for each season, DJF and JJA, are on row one and indicated by 829 red arrows. Mean (black arrows) and anomaly (blue arrows) vectors for the MJO phases 830 associated with lowest surface ozone (phase 8 in DJF and phase 1 in JJA) are on the middle row. 831 Mean (black arrows) and anomaly (blue arrows) vectors for the MJO phases associated with 832 highest surface ozone (phase 2 in DJF and phase 6 in JJA) are on the bottom row. Note that the 833 mean winds for low ozone in DJF and high ozone in JJA are very similar to the seasonal mean 834 winds, so the anomaly (blue) vector is very small. All wind data are from NOAA National 835 Centers from Environmental Information, 1986-2014.

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