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1 Surface ozone climatology of South Eastern Brazil and the impact of biomass burning
2 events

3
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23 **Abstract**

24 In the austral spring, biomass fires affect a vast area of South America each year. We
25 combined *in situ* ozone (O₃) data, measured in the states of São Paulo and Paraná, Brazil,
26 in the period 2014-2017, with aerosol optical depth, co-pollutants (NO_x, PM_{2.5} and PM₁₀)
27 and air backtrajectories to identify sources, transport and geographical patterns in the air
28 pollution data. We applied cluster analysis to hourly O₃ data and split the investigation
29 area of approximately 290,000 km² into five groups with similar features in terms of
30 diurnal, weekly, monthly and seasonal O₃ concentrations. All groups presented a peak in
31 September and October, associated with the fire activities and enhanced photochemistry.
32 The highest mean O₃ concentrations were measured inland whilst, besides having lower
33 concentrations, the coastal group was also associated with the smallest diurnal and
34 seasonal variations. The latter was attributed to lower photochemical activity due to
35 frequently occurring overcast weather situation. The mean annual regional contribution
36 of O₃ over the area was 61 µg/m³, with large seasonal and intersite variabilities (from 35
37 to 84 µg/m³). The long-range transport of smoke contributed with between 23 and 41%
38 of the total O₃ during the pollution events. A pollution outbreak in September 2015 caused
39 many-fold increases in O₃, PM_{2.5} and PM₁₀ across the investigation area, which exceeded
40 the World Health Organisation recommendations. We show that the regional transport of
41 particulates and gas due to biomass burning overlays the local emissions in already highly
42 polluted cities. Such an effect can outweigh local measures to curb anthropogenic air
43 pollution in cities.

44

45 Key words: Short-lived climate forcer; Transboundary pollution; Cluster analysis; Air
46 quality

47 **1. Introduction**

48 Planet Earth is frequently affected by smoke from fires caused by humans (*e.g.*, burning
49 of vegetation and waste, preparation of agriculture fields, conversion of cropland to
50 pasture) and by natural processes (*e.g.*, lightning-induced fires). Australia, California and
51 many other regions of Earth are prone to wildfires, defined as uncontrollable fires caused
52 by the concomitant occurrence of vegetative resources to burn (such as forest, shrub or
53 grass), sustained dry spells and ignition sources. Wildfires are seasonal because the
54 constraints for their occurrence (especially fire-conducive weather patterns) occur in
55 specific periods of the year (Krawchuk *et al.*, 2009). Fires that particularly take place at
56 low temperatures and limited oxygen favour the formation of trace gases, such as VOC,
57 CO and NO_x (NO+NO₂), and particulate matter (PM_{2.5}, PM₁₀ and black carbon) (Akagi
58 *et al.*, 2011; Wevers *et al.*, 2004; Crutzen and Andreae, 1990). The transboundary
59 transport of smoke from wildfires and agricultural burns deteriorates the air quality
60 downstream of the burning areas (McClure and Jaffe, 2018a; Targino and Krecl, 2016;
61 Sarangi *et al.*, 2014; Sillanpää *et al.*, 2005), even at a considerable distances from the
62 sources (over 2,000 km, see Targino *et al.*, 2013 and Witham and Manning, 2007).

63 One aggravating aspect about wildfires is that they are becoming longer and more
64 frequent in some regions of the planet, such as Eurasia and western North America
65 (Riaño *et al.*, 2007), which may be related to anthropogenic climate change (Flannigan *et*
66 *al.*, 2013; 2009). For South America, Riaño *et al.* (2007) showed a consistent fire regime
67 of interannual cycles with no clear trends for any month or annually. The majority of
68 wildfires in Brazil occurs in the dry season (between July and September) in the areas of
69 Amazon, Cerrado (a savanna-like biome of central Brazil) and in the Pampas (grasslands
70 in Southern Brazil). In the Amazon and Cerrado, the wildfires are predominantly man-
71 made, with the purpose of removing brush, accumulated waste and vegetation to install

72 crop cultures or pastures (Ten Hoeve *et al.*, 2012; Pivello, 2011). Moreover, sugar cane
73 field burning to eliminate the sharp-edged leaves and poisonous animals before
74 harvesting also contributes to regional biomass smoke (Allen *et al.*, 2004).

75 Depending on the meteorological setting, the long-range transport of smoke during the
76 dry season affects the air quality of small and large cities downwind of the fire spots,
77 including the megacity of São Paulo (e.g., Lopes *et al.*, 2012; Freitas *et al.*, 2005;
78 Reinhardt, 2001). Freitas *et al.* (2005) observed that the position of the South Atlantic
79 subtropical high pressure plays an important role in the transport of aerosol plumes from
80 the Amazon region to Southern Brazil. This system also prevents rain-bearing cold fronts
81 from penetrating the area, favouring the accumulation of pollutants and deterioration of
82 the air quality (Oliveira *et al.*, 2016; Targino and Krecl, 2016).

83 The hotspot of primary pollutants is found at the fire front, whilst high concentrations of
84 secondary pollutants, such as tropospheric ozone (O₃) are usually detected a few
85 kilometres downwind of the burning area (Wentworth *et al.*, 2018). O₃ is formed via a
86 series of complex, non-linear reactions involving NO_x and non-methane VOC in the
87 presence of sunlight (Monks *et al.*, 2015 and references therein). The O₃ production rate
88 is governed by NO_x- or VOC-limited conditions and possibly aerosol effects on the
89 photochemical production (Baylon *et al.*, 2018; Alvarado *et al.*, 2015).

90 Many countries have targeted the transportation sector as a strategy for abating air
91 pollution and global warming. For example, in 2015, the mayors of eight Latin American
92 cities (Curitiba, Rio de Janeiro, Salvador, Bogotá, Quito, Caracas, Buenos Aires and
93 Mexico City) members of C40 –a network of the world’s megacities committed to tackle
94 climate change (www.c40.org)– signed a declaration of intent in which 35% of the diesel-
95 fuelled public buses will be replaced by hybrid and electric buses by 2020. Although this
96 is an important measure to tackle air pollution in cities, they may not be enough if other

97 sources prevail, such as biomass burning. McClure and Jaffe (2018a) reported maximum
98 daily (8-h average) O₃ increase up to 70 µg/m³ on days affected by smoke in Meridian
99 (USA). Zhou *et al.* (2019) observed a concomitant 2.5-fold increase in O₃ concentrations
100 at three sites in the Sichuan Basin (China) due to biomass burning, whilst Lin *et al.* (2013)
101 reported an increase from 200 ppb to 600 ppb at Mei-Feng (Taiwan) due to the outflow
102 of smoke from South East Asia. Besides affecting air quality and increasing the risk of
103 death from respiratory causes (Jerrett *et al.*, 2009), O₃ is a short-lived climate forcer
104 (residence time of the order of several weeks in the free-troposphere, Monks *et al.*, 2015).
105 Hence, mitigating O₃ levels has two-fold benefits: reducing the impacts on air quality and
106 climate.

107 Atmospheric emission data for Brazil are rare and reliable emission inventories remain
108 elusive. However, the NO_x and non-methane hydrocarbons (NMHC) estimates from
109 biomass burning and the road transport sectors provided by the EDGAR v4.2 database
110 (Crippa *et al.*, 2018) reveal the importance of biomass burning for atmospheric chemistry.
111 The NO_x emissions from savanna, agricultural waste, forest and grassland fires in 2008
112 were 434.14 Gg whilst the road transport sector emitted 1,270 Gg. In terms of NMHC,
113 the figures are 839.4 and 1,250 Gg, respectively. However, considering that the fires in
114 Brazil occur mainly over three months, the emissions from the road transport should be
115 scaled accordingly to make a fair comparison. If we divide the annual road transport NO_x
116 and NMHC emissions by four, we obtain 317.5 and 312.5 Gg, respectively, over three
117 months, which suggests that emissions from biomass burning make up a substantial
118 fraction of the precursors for O₃ formation.

119 In this study, we present a four-year climatology of O₃ for the states of São Paulo and
120 Paraná (Brazil), using ground-based *in situ* observations. We quantify the contribution of
121 long-range transport on the O₃ concentration in cities of different sizes by analysing the

122 coupling between O₃, NO and NO₂. We assess the impact of long-range transported
123 smoke from central Brazil on the air quality by investigating a pollution outbreak within
124 the most polluted months of 2015. We analysed the *in situ* data in combination with co-
125 pollutants (NO_x, PM_{2.5} and PM₁₀), satellite retrieved aerosol optical depth, fire spots and
126 air mass backward trajectories.

127

128 **2. Methodology and data analysis**

129 **2.1 Study area**

130 São Paulo is one of the 27 Brazilian federal units, located in the South Eastern region. It
131 is the wealthiest and most populous state, accounting for 33.9% of the country's total
132 GDP (Gandhi *et al.*, 2017) and hosting approximately one fifth of the country's
133 population (45 million inhabitants). The state of São Paulo's economy is diversified and
134 the chemical, sugar and ethanol production, metalworking, machinery, automobile and
135 aviation industries account for 75% of the economic sector (Governo do Estado de São
136 Paulo, 2019). The state has the largest vehicular fleet in the country, with 28.6 million
137 units (DENATRAN, 2018) that emitted 331, 180, 5 and 4.7 Gg of CO, NO_x, PM and SO₂,
138 respectively, in 2016. About 60% of these emissions occurred in the municipalities that
139 form the metropolitan area of São Paulo (MASP), the cities of Campinas, Sorocaba, and
140 urban agglomerations in Baixada Santista and Vale do Paraíba (CETESB, 2017). The
141 vehicular emissions of NO_x and total hydrocarbons (THC) dominate at state level (65 and
142 87%, respectively) and in the MASP (75 and 87%, respectively), which emphasises the
143 effect this sector may have on local air quality.

144

145

146 **2.2 Data**

147 We used a combination of ground-based *in-situ*, remote sensing and modelling data to
148 investigate the O₃ climatology at sites in the states of São Paulo and Paraná from 2014 to
149 2017. The *in situ* data are from 25 sites managed by São Paulo State Environmental
150 Company (CETESB) and from Londrina, a mid-sized city located in the neighbouring
151 state of Paraná (Fig. 2). The CETESB monitors criteria air pollutant with methods that
152 follow closely those of the US Environmental Protection Agency. The data from Londrina
153 were collected at the campus of the Federal University of Technology (UTFPR). A full
154 list of the cities included in this study is provided in Table S1 (Supplementary Material).
155 Note that Brazilian air quality networks are not designed for remote or rural conditions,
156 like the sites in Europe (*e.g.*, Targino *et al.*, 2013; Witham and Manning, 2007). Instead,
157 they are located in the urban core, close to highly-trafficked streets or industrial areas.
158 This means that the analysis of long-range transport of air pollutants is more challenging,
159 since the regional contribution cannot be easily isolated from local urban contributions.
160 The MODerate resolution Imaging Spectroradiometer (MODIS) Aqua and Terra
161 Collection 6.1 Level 2 standard 10-km products were used here for best quality retrievals
162 (quality flag = 3) of aerosol optical depth (AOD) over land. The data were obtained
163 through NASA Goddard Space Flight Center's Atmosphere Archive and Distribution
164 System (<http://ladsweb.nascom.nasa.gov>). Detailed descriptions of the MODIS dark
165 target algorithm for retrievals of AOD over land can be found in Levy *et al.* (2013; 2007).
166 Fire spots were identified by satellite remote sensing furnished by the National Space
167 Research Institute of Brazil (<http://www.inpe.br/queimadas/bdqueimadas>) (INPE, 2018).
168 Infrared radiation at 3.7 and 4.1 μm emitted from the fires is detected by the Advanced
169 very-high-resolution radiometer (AVHRR) on board the polar-orbit satellites NOAA-15,
170 NOAA-18, NOAA-19 and METOP-B, MODIS on board TERRA and AQUA, VIIRS on
171 board NPP-Suomi and the geostationary satellites GOES-13 and MSG-3. The product

172 identifies spots at least 30 m long, occurring on non-cloudy days and with fire outbreaks
173 lasting long enough to be captured between images.

174 To assess influences of atmospheric large-scale circulation on the air quality at the sites,
175 five-day backward trajectories that arrived at 500 m above terrain level were calculated
176 with 1-hour interval, eight times per day (00, 03, 06, 09, 12, 15, 18, 21 h), using the
177 Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) (Stein *et al.*,
178 2015). ERA-Interim reanalysis data of diagnosed boundary layer height, with three-hour
179 time resolution, was taken from the European Centre for Medium-Range Weather
180 Forecasts (ECMWF). We use meteorological data (air temperature, relative humidity,
181 solar irradiance, wind speed and direction and atmospheric pressure) measured at UTFPR
182 campus and at CETESB sites.

183

184 **2.3 Cluster analysis**

185 We applied hierarchical cluster analysis to reduce the number of observations and to find
186 groups of similar stations within the O₃ dataset. We used O₃ concentrations due to the
187 large data availability and its relatively long residence time in the atmosphere, which
188 makes it a good tracer of long-range transported pollution. This technique was
189 successfully used by Lyapina *et al.* (2016) to classify surface O₃ data over 1,400 European
190 monitoring stations.

191 The hourly O₃ concentration for 26 sites in the period 2014-2017 yielded a matrix of
192 34,560 rows and 26 columns. The hierarchical clustering procedure starts with each site
193 in its own group, which is progressively merged with the most similar site until all sites
194 are in a single group. Observations that are as homogeneous as possible are collected into
195 a group (large intra-group similarity), whilst keeping between-group (inter-group)
196 observations as heterogeneous as possible (Hair *et al.*, 1998).

197 We used Ward's minimum variance method as merging criterion, since it has been widely
198 used for climatic classifications with superior performance compared to other methods
199 (e.g, Kalkstein and Corrigan, 1986). Ward's method starts with K groups (in our case, K
200 sites) and at each step it fuses groups based on an error function that leads to a minimal
201 within-group sum of squared distances (W) between the points and the centroids of the
202 merged groups (Wilks, 2011). This means that the pair to be merged must minimise the
203 sum of the squared distances between the data points and the centroids of their respective
204 groups, summed over the resulting groups (Wilks, 2011):

205

$$206 \quad W = \sum_{k=1}^K \sum_{j=1}^J \sum_{i=1}^N (x_{ijk} - \bar{x}_{jk})^2, \quad 1$$

207

208 where x_{ijk} is the i -th O₃ concentration of the j -th site in the k -th group, J is the number of
209 sites, N the number of observations, and \bar{x}_{jk} is the mean O₃ concentration inside this
210 group. Ward's method computes W and W' before and after the merging, respectively,
211 and merges clusters with the smallest $\Delta W = W' - W$.

212 We applied two approaches to decide on the number of clusters: the elbow and silhouette
213 methods. The elbow method consists in running the clustering algorithm for a range of
214 number of clusters (n) and calculating W for each n . W decreases monotonically as the
215 number of n increases, and the W vs. n plot usually shows a bend which can be taken as
216 a cut-off point to determine the number of clusters. From that point on, the W decrease
217 flattens, indicating small changes and exaggerated specificity in the choice of clusters by
218 increasing n (Lyapina *et al.*, 2016). The silhouette method (Rousseeuw, 1987) provides a
219 graphical representation and an index to measure how well each object lies within its
220 cluster. The silhouette value (s) lies between +1 (the object is correctly clustered) and -1
221 (the object belongs to other cluster).

222

223 **2.4 Urban and regional contributions to the O₃ concentration**

224 To estimate the regional contribution of O₃ to the *in situ* O₃ concentration, we calculated
225 the daylight mean mixing ratios (in ppb) of the oxidant ($OX = O_3 + NO_2$) and NO_x
226 (Clapp and Jenkin, 2003). The analysis assumes that the interconversion of O₃, NO₂ and
227 NO occurs in a closed system, where the total mixing ratio of both NO_x and OX is
228 unchanged. This photostationary state is valid during daylight, hence we considered the
229 hours between 08:00 and 18:00.

230 Then, a linear regression analysis was performed between OX and NO_x concentrations,
231 where the offset can be interpreted as NO_x-independent and the slope as NO_x-dependent
232 contributions. The former is attributed to regional background O₃ and the latter accounts
233 for the local contribution, which correlates with the level of primary pollution. Any local
234 change in NO_x concentration will lead to a simultaneous increase or decrease in the
235 concentration of total oxidants (Pancholi *et al.*, 2018; Mazzeo *et al.*, 2005; Clapp and
236 Jenkin, 2003). To investigate this aspect, we chose one city within each cluster with
237 concurrent NO_x, NO₂ and O₃ measurements.

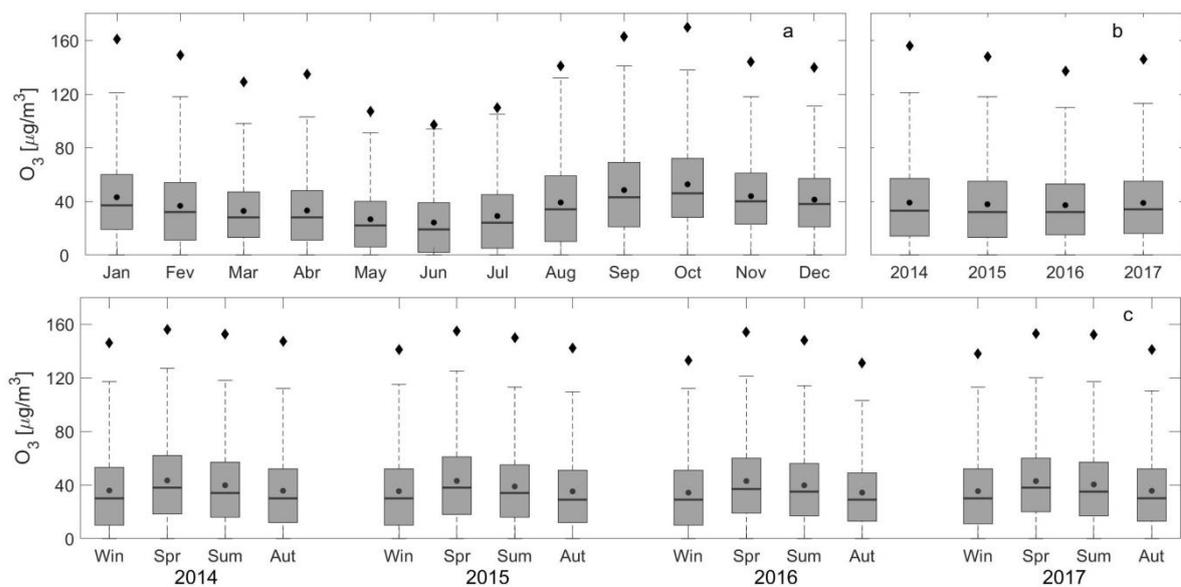
238

239 **3. Results**

240 **3.1 Overall O₃ concentrations in different time domains**

241 Figure 1a depicts a statistical summary of O₃ concentrations at all sites between 2014 and
242 2017. The lowest O₃ concentrations were recorded in June and the highest in September
243 and October. The air quality in South Eastern Brazil is affected by smoke plumes from
244 the Amazon and Cerrado with peak activity in September, caused by the atmospheric
245 transport under the influence of lingering high-pressure systems, which increases air
246 temperatures and enhances photochemistry (Rosário *et al.*, 2013). Another source of air

247 pollution is the interhemispheric transport of plumes from Africa to Eastern South
 248 America, especially in September, October and November, enhancing the tropospheric
 249 O₃ column up to 40 Dobson Units (Ziemke *et al.*, 2011).
 250 The stratosphere-troposphere intrusion is a well-documented phenomenon since the early
 251 1960s (Junge, 1962). However, this mechanism is not common in the Southern
 252 hemisphere, with the exception for some hotspots observed in June, July and August over
 253 the East and West coasts of Australia, and from September to February over the Andes
 254 and the southern tip of Africa (Škerlak *et al.*, 2014). Figure 1b suggests a small variation
 255 in O₃ amongst the years investigated. However, the Krustal-Wallis test applied at the 5%
 256 significance level showed that there are statistically significant differences in O₃ between
 257 the years. These differences may be caused by fumigation of upper air masses that is
 258 influencing the boundary layer and surface O₃ concentrations, the number of fire
 259 outbreaks, regional transport and photochemistry. These mechanisms will not be
 260 addressed in this manuscript. The O₃ concentration was consistently higher in the spring
 261 months (September and October) for all years investigated in the present study (Fig. 1c).



262

263 **Figure 1:** Statistical summary of hourly O₃ concentration from 2014 to 2017 for all sites,
 264 with respect to a) month, b) year and c) season disaggregated per year. The dots indicate

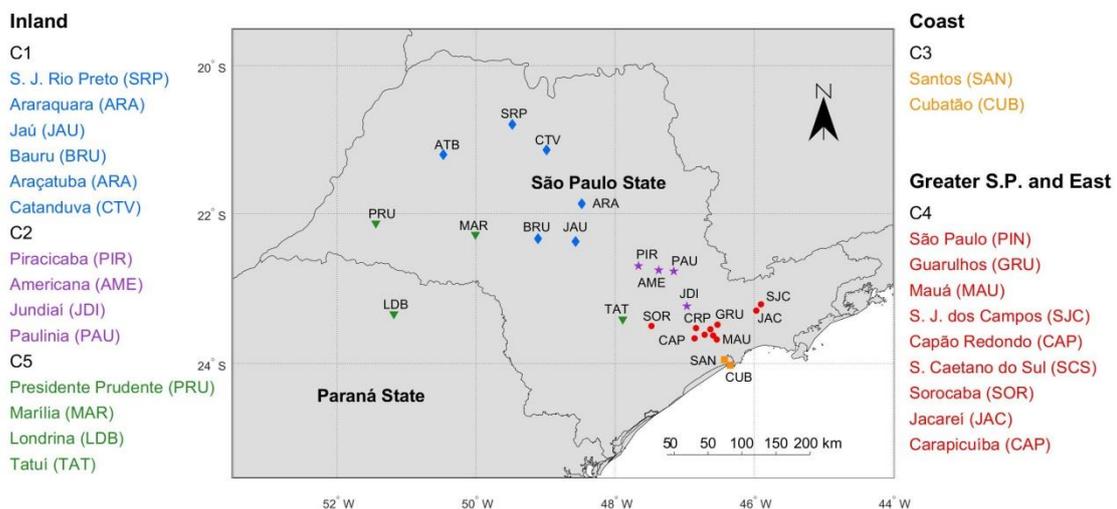
265 the mean values, the diamonds are the 99.5 percentile, the whiskers are the 5th and 95th
 266 percentiles, the box limits are the 25th and 75th percentiles and the black lines across the
 267 boxes are median values.

268

269 3.2 O₃ data reduction based on cluster analysis

270 The elbow method suggested that the O₃ dataset measured at the 26 sites could be divided
 271 into either five or six clusters. However, the silhouette method revealed that choosing six
 272 clusters would yield negative *s* values and an overall decrease in the *s* values (between
 273 0.1336 and 0.4660 for five clusters, and between 0 and 0.4324 for six clusters). Another
 274 aspect that we also considered to maintain five clusters was the consistency in the location
 275 of the stations within each regional area. Figure 2 shows that the stations are distributed
 276 across three main areas **Inland:** clusters 1, 2 and 5 (C1, C2 and C5), **Coast:** C3, and
 277 **Greater São Paulo and East:** C4.

278

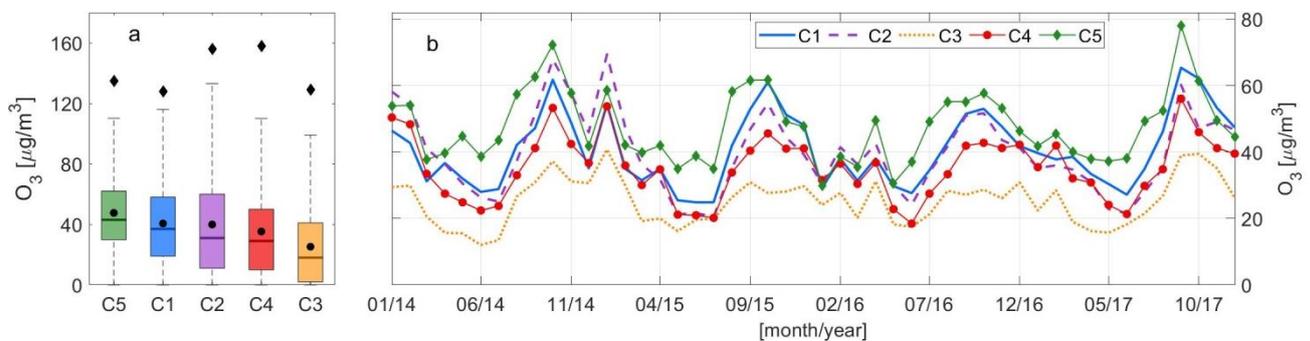


279

280 **Figure 2:** Location of the sites investigated in this study. The colours indicate the groups
 281 as determined by the cluster analysis and the symbols diamond, star, square, circle and
 282 triangle correspond to the groups C1, C2, C3, C4 and C5, respectively.

283

284 Figure 3a shows statistic summaries of O₃ for the individual clusters using the datasets
285 from 2014 to 2017, organised in descending order of median values. Overall, the largest
286 O₃ concentrations were recorded at the inland sites and the lowest concentrations at the
287 coastal sites, with mean values varying from 25.2 to 47.6 µg/m³ and medians from 18.0
288 to 43.0 µg/m³. Even though C2 on average was not the most polluted cluster, the stations
289 in this group had the largest interquartile range and 95th percentile. This suggests that the
290 sites within this group were affected by events causing frequently extreme O₃
291 concentrations. The mean daily O₃ concentrations per cluster (Fig. 3b) showed similar
292 patterns with a large interannual variability along the years investigated. The intercluster
293 correlations using monthly mean O₃ concentrations were statistically significant (*p* values
294 much smaller than 0.05) with Pearson's correlation coefficients (*r*) between 0.75 (C3 and
295 C5) and 0.93 (C2 and C4).



296

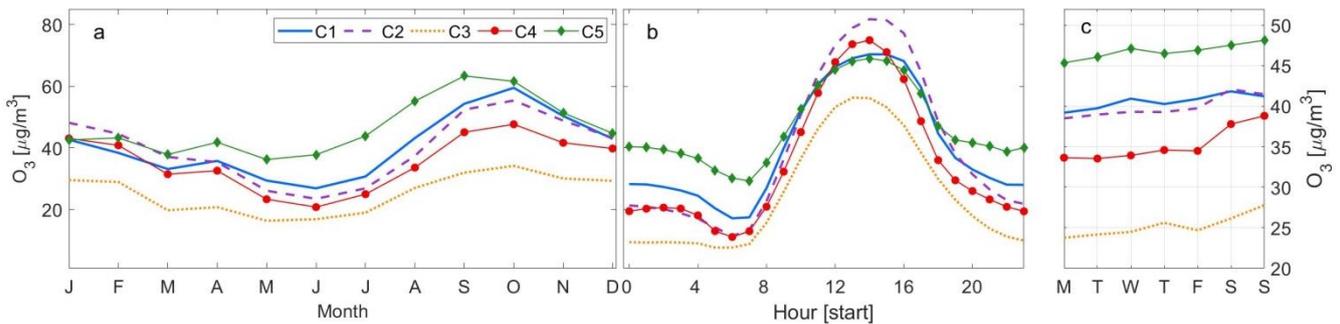
297 **Figure 3:** (a) Statistical summary of O₃ data for the clustered stations. The dots indicate
298 the mean values, the diamonds are the 99.5 percentile, the whiskers are the 5th and 9th
299 percentiles and the box limits are the 25th and 75th percentiles and the black lines across
300 the boxes are median values. (b) Mean monthly O₃ concentrations segregated per cluster
301 in the period 2014 – 2017.

302

303 3.3 Seasonal, weekly and diurnal profiles of O₃ concentrations

304 Figure 4a shows that the monthly mean O₃ concentration vary seasonally for all clusters,
 305 with an increase that begins in July and peaks in September or October. C5 is by far the
 306 most polluted cluster from April to September. The comparison between C5 and C3 is
 307 particularly striking, with differences in O₃ concentrations of 13.0 and 31.3 µg/m³ in
 308 January and September, respectively. Another outstanding feature is that whilst the O₃
 309 concentrations for C1, C2, C3 and C4 show a clear decrease between January and June,
 310 the concentration for C5 remain relatively stable and fluctuate between 36.2 and 43.2
 311 µg/m³. Comparatively, the concentration for C4 more than halved over the same period
 312 (from 43.1 to 20.8 µg/m³).

313



314

315 **Figure 4:** (a) Monthly, (b) diurnal and (c) weekly mean O₃ concentrations for the
 316 clustered stations.

317

318 The clusters show rather similar diurnal patterns, with peak O₃ values in the early
 319 afternoon (13:00-15:00, Fig. 4b), with C2 and C4 having the largest peaks and C3 the
 320 lowest. C2 and C4 consist mostly of mid-sized and large cities, with traffic volumes that
 321 emit large amounts of NO_x. However, the reduction of NO emissions relative to NO₂,
 322 typical in urban environments, decreases the NO titration effect and increases the daytime
 323 O₃ concentration (Querol *et al.*, 2016). This effect was more pronounced for C4, which
 324 contains larger cities (including those that form the MASP) and larger vehicle fleets

325 (Table S1, Supplementary Material). At night, O₃ decreases due to the cease of
326 production, loss mechanisms (dry deposition on the ground) and titration by NO (Monks
327 *et al.*, 2015). C1 and C5 have comparable daytime mean O₃ peak concentration of about
328 70 µg/m³, but diverge at night with concentrations for C5 up to 12 µg/m³ greater than for
329 C1. C5 has an outstanding secondary nocturnal O₃ peak and the smallest diurnal range.
330 Krecl *et al.* (2016) also observed a secondary O₃ maximum at night in Londrina (a site
331 within C5), which they attributed to horizontal and vertical transport of O₃ from other
332 regions.

333 The inspection of the diurnal cycle with respect to month showed that this feature prevails
334 along the year and intensifies in September with a maximum nocturnal peak of 55 µg/m³
335 (Fig. S1, Supplementary Material). Comparatively, the mean maximum diurnal peak was
336 92 µg/m³ at 15:00 in the same month. We hypothesise that two phenomena may control
337 this feature within this group: (i) C5 consists mostly of small cities, Marília (pop.
338 237,000), Presidente Prudente (pop. 208,000) and (Tatuí, pop. 120,000) (except Londrina,
339 pop. 564,000), that have relatively small traffic volumes to furnish NO and to effectively
340 destroy O₃ at night. Although Londrina's fleet amounts to about 387,000, the sampling
341 site was on the city's outskirts, with little influence from direct vehicular emissions. (ii)
342 Persistent transport of aged pollutants from other regions contributes to a rise in the O₃
343 nocturnal base line during the year, which is intensified in the spring months due to
344 pollution outbreaks. One pathway is the advection of O₃ from large urban
345 conglomerations, such as MASP. Boian and Andrade (2012) conducted a study using a
346 photochemical model and pinpointed that a nocturnal O₃ peak of 176 µg/m³ (at 22:00 h)
347 in Campinas (northwest of the city of São Paulo) was due to a plume from the MASP,
348 which still lingered in the early hours. The cities in cluster C5 are all located west of the
349 MASP, and according to INMET (2018) the prevailing wind directions in Presidente

350 Prudente and Londrina (both within C5) are easterly and easterly/southeasterly,
351 respectively. More precisely, Krecl *et al.* (2016) observed easterly components in
352 Londrina between 00:00 and 10:00 h.

353 C3 is the cleanest cluster and although Santos and Cubatão have a relatively large fleet (a
354 combined total of 331,600 vehicles) and Cubatão is an industrial city with a cluster of
355 petrochemical, steel and fertilizer industries, they are located on the coast, where frequent
356 overcast weather reduces the incoming solar radiation and inhibits photochemical
357 processes. The mean annual insolation for Santos is 1,376 h with 70% of cloud coverage.
358 For comparison, Londrina in C5 has mean annual insolation of 2,420 h and 50% of cloud
359 coverage (INMET, 2018).

360 Figure 4c shows that the O₃ concentration tend to increase at weekends, following what
361 has been coined “the ozone weekend effect” (Heuss *et al.*, 2003), attributed to changes in
362 precursors due to the decrease in the traffic volume and travelled distances. Vukovich
363 (2000) and Altshuler *et al.* (1995) showed that the reduction in NO_x at weekends is more
364 pronounced than for VOC, favouring the O₃ formation due to an increase in the
365 VOC:NO_x ratio. The weekend effect was more evident for clusters C3 and C4 (Table 1)
366 that consist of highly urbanised areas and have large vehicle fleets. We did not have VOC
367 measurements in this study; however, we refer to the results by Orlando *et al.* (2010) who
368 measured VOC in the MASP and reported a high VOC:NO_x ratio, especially due to
369 formaldehyde and acetaldehyde. They used model simulations to show that an increase
370 (decrease) in VOCs would result in an increase (decrease) in O₃. Hence, we suggest that
371 this effect combined with the reduction in O₃ loss due to less titration with NO (Atkinson-
372 Palombo *et al.*, 2006; Torres–Jardon and Keener, 2006; Alghamdi *et al.*, 2014) yields
373 higher O₃ concentrations at weekends within these clusters.

374 Other pathways for the O₃ weekend effect include: (i) the shift in the timing of NO_x peak
 375 favours O₃ formation at weekends than on weekdays), (ii) carryover of pollutants with
 376 higher VOC:NO_x ratios from light-duty vehicle traffic on Friday and Saturday evenings
 377 that can generate more O₃ at weekends, (iii) lower aerosol concentrations at weekends
 378 increase incoming solar radiation and photochemistry (Heuss *et al.* (2003).

379

380 Table 1: O₃ concentrations in different time domains, derived from hourly mean data.

O ₃ [$\mu\text{g}/\text{m}^3$]	C1	C2	C3	C4	C5
Diurnal range ^a	53.1	70.3	48.6	63.8	39.7
Diurnal maximum ^b	70.3	81.7	56.3	74.9	69.0
Seasonal range (October - January) ^c	32.6	31.9	17.8	26.8	23.8
Sunday-Monday difference ^d	2.0	3.0	4.0	5.2	2.8

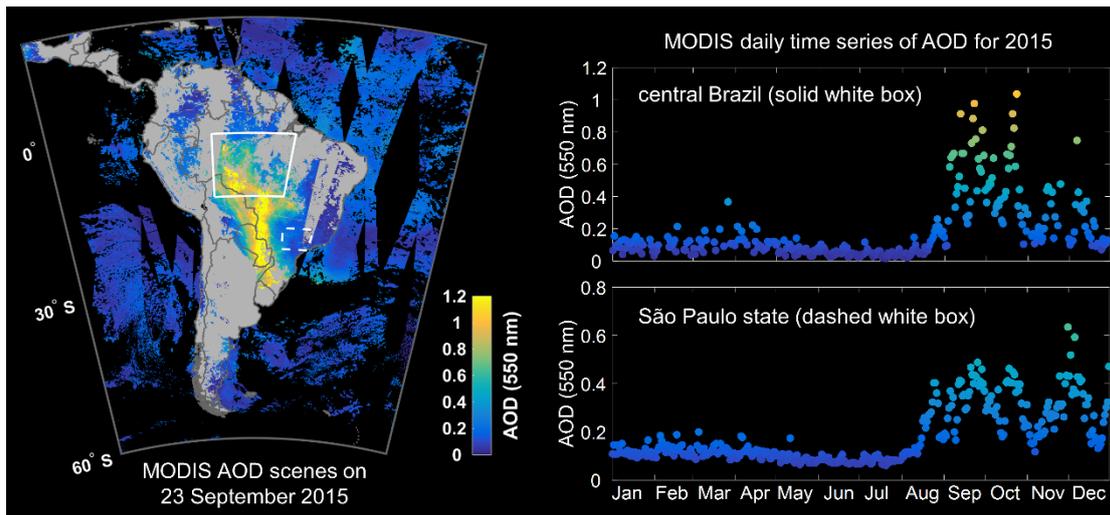
381 ^aBased on the difference between the mean maximum and minimum diurnal O₃ concentrations.

382 ^bMaximum O₃ concentration of the diurnal cycle. ^cBased on the difference between the mean
 383 monthly O₃ concentrations in October and January. ^dBased on the difference between the mean
 384 concentrations for all Sundays and all Mondays.

385

386 **3.4 Pollution outbreak in September 2015**

387 In the austral spring of 2015 an area of about 225,300 km² was burned in Brazil, of which
 388 56.0% and 24.5% comprised Cerrado and Amazon biomes, respectively (INPE, 2018).
 389 Figure 5 shows MODIS AOD scenes for September 23rd 2015 over South America (left)
 390 and daily AOD time series along this year (right). It is clearly discernible that enhanced
 391 levels of aerosols began to influence the central part of Brazil (right, upper panel) and the
 392 state of São Paulo (right, lower panel) in August until the end of the year.



393

394 **Fig. 5:** MODIS Aqua and Terra AOD scenes over South America for September 23rd
 395 2015 (left), and daily time series of AOD for the central Brazil and the state of São Paulo
 396 (right).

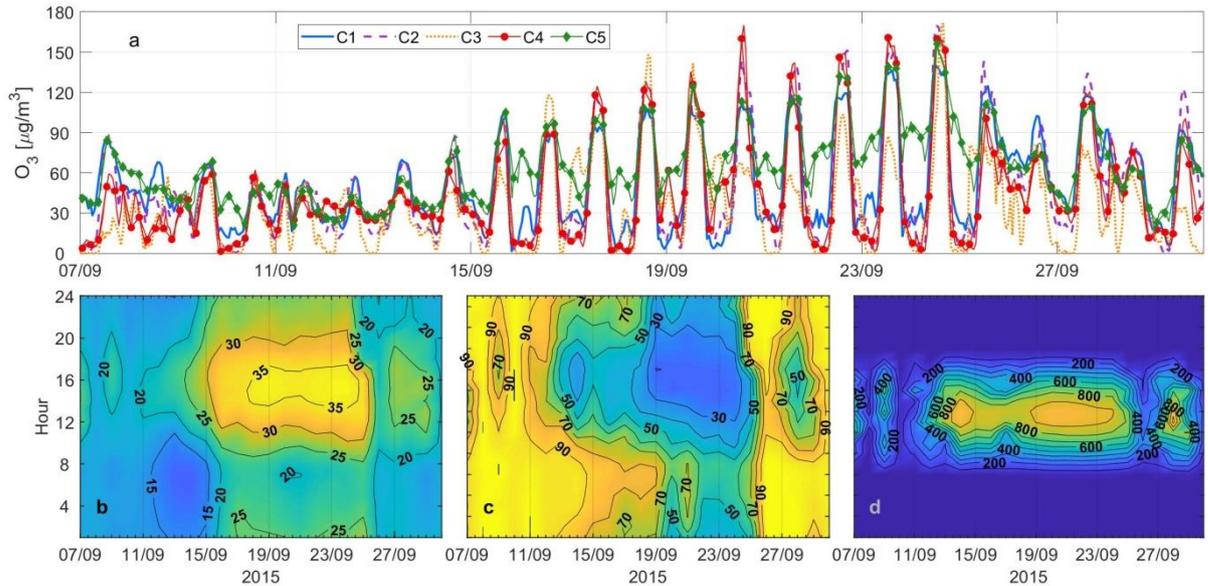
397 We focus here on an air pollution outbreak that led to an enhancement in O₃ concentration
 398 and other co-pollutants over the investigated area during the second half of September
 399 2015. Figure 6a shows that the O₃ concentration started to increase around September
 400 15th for all clusters, with enhancements between two- and four-fold: for example, from
 401 48.0 to 103.5 μg/m³ within C3 and from 38.0 to 169.8 μg/m³ within C4, between
 402 September 11th and 20th. Meteorological data measured at UTFPR campus in Londrina
 403 (C5) show that the substantially higher O₃ concentrations that occurred in the afternoon
 404 during the period September 14th-25th coincide with a high-pressure system that led to
 405 high temperatures, low relative humidity and strong solar irradiance (for example, > 35
 406 °C, < 20% and > 1,000 W/m², respectively, in the afternoon of September 23rd) (Figures
 407 6b-6d). Such a meteorological situation causes subsiding air to warm adiabatically,
 408 inhibits convective mixing and creates a shallow boundary layer where pollutants can
 409 accumulate. This is in line with Pudassainee *et al.* (2006) who showed that O₃ production
 410 is favoured by increase in air temperature and solar irradiance, and with Querol *et al.*

411 (2016) who reported very high O₃ concentrations during heat waves in Spain in the
412 summer of 2015.

413 The surface winds measured at UTFPR campus between September 16th-19th were
414 northerly and larger than 5.0 m/s in the afternoon, which facilitated advection of polluted
415 air. Between September 20th-23rd the mean wind speed dropped to 2.7 m/s (Fig. S2,
416 Supplementary Material), reducing the air pollution dispersion and facilitating their
417 accumulation.

418 Although Figs. 6b-6d illustrate the weather conditions in Londrina, the corresponding
419 meteorological variables correlate well with data from sites within other clusters (see
420 Figs. S3-S8, Supplementary Material). For example, the Pearson's correlation coefficient
421 for hourly air temperature between Londrina and São José do Rio Preto (distance 390 km)
422 and between Londrina and the city of São Paulo (distance 540 km) during the pollution
423 outbreak were 0.95 and 0.91, with linear regression equations of $1.1x-0.29$ and $1.0x-2.9$,
424 respectively, and *p*-values much smaller than 0.05. Only Santos (distance 600 km from
425 Londrina) showed a more modest air temperature increase, yielding weak or moderate
426 correlations with other sites, possibly due to local atmospheric circulations embedded in
427 the large-scale circulation (for example, sea breeze).

428



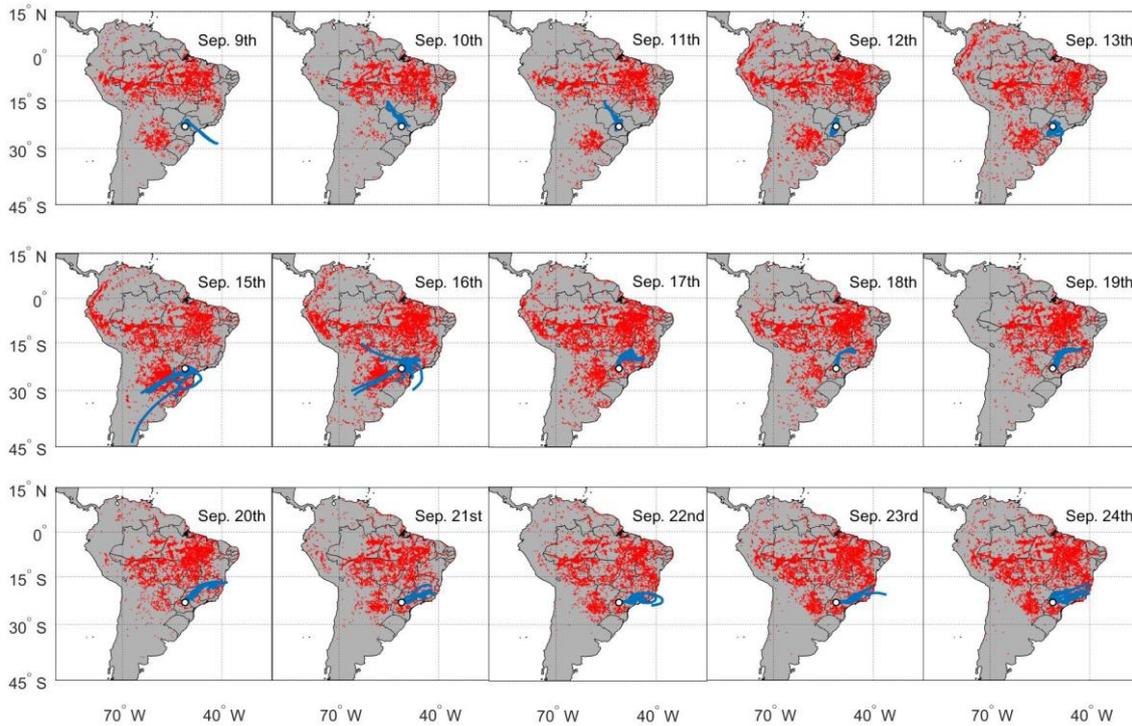
429

430 **Fig. 6:** (a) Hourly mean O₃ concentration segregated per cluster, (b) air temperature, (c)
 431 relative humidity and (d) solar irradiance measured in Londrina (C5) for the case study
 432 in September 2015.

433

434 Figure 7 suggests that air masses that arrived at 500 m above ground level in Londrina
 435 in the period September 9th-13th (prior to the pollution event) had either maritime origin
 436 or mainly passed over land areas unaffected by fire spots (red dots).

437 Areas closer to the receptor point were highly influenced by fires from September 15th
 438 (Fig. 7). Four days prior to and during the pollution events (September 7th-14th and
 439 September 15th-24th, respectively), the mean AOD and corresponding one standard
 440 deviation for the state of São Paulo (20-24°S, 45-52°W) were 0.23 ± 0.07 and 0.39 ± 0.06 ,
 441 respectively. Satellite data provided by INPE indicated an increase of 42% in the
 442 occurrence of fire spots in Brazil in the episode period compared to the non-episode
 443 period. Particularly, the numbers of fire spots in the states of Paraná and São Paulo
 444 increased from 316 to 2,719 and from 68 to 2,302 spots, respectively (Figs. S9 and S10).
 445 Table 2 displays statistics of O₃ concentration within each clusters before and during the
 446 pollution event.



447

448 **Fig. 7:** Fire spots (red dots) over South America and five-day backward trajectories (blue
 449 solid lines) before (first row) and during the pollution outbreak (second and third rows).

450 Table 2: Comparison of mean hourly (\pm one standard deviation) and maximum O_3
 451 concentrations before and during the pollution outbreak in September 2015.

452

O_3	C1	C2	C3	C4	C5
$[\mu\text{g}/\text{m}^3]$	Before the pollution outbreak				
Mean	40.4 ± 17.0	34.1 ± 20.6	24.4 ± 17.6	30.0 ± 15.1	43.9 ± 14.4
Maximum	85.8	87.2	58.0	74.0	88.6
	During the pollution outbreak				
Mean	54.4 ± 40.4	54.2 ± 49.0	43.4 ± 38.2	52.4 ± 49.0	79.8 ± 28.5
Maximum	140.3	169.8	171.5	170.0	156.2

453

454 The pollution outbreak was captured across the state of São Paulo, as shown by the
455 evolution of O₃, NO_x, PM_{2.5} and PM₁₀ at sites representative of each cluster (Fig. 8 and
456 Table 3): São José do Rio Preto (C1), Piracicaba (C2), Santos (C3), São Paulo (C4) and
457 Marília (C5). During this event, a large increase in nocturnal O₃ concentration was
458 observed in Marília and Santos. The results on diurnal cycles (Section 3.3) had already
459 revealed that C5 presented a secondary nocturnal O₃ peak. However, the peak recorded
460 in Marília during this pollution outbreak ($> 100 \mu\text{g m}^{-3}$ on September 23rd) was much
461 larger than observed even in the dirtiest month (Fig. S1, Supplementary Material). The
462 nocturnal peak observed in Santos ($> 60 \mu\text{g m}^{-3}$) was an uncommon feature compared to
463 the diurnal cycle for C4. The enhancement of NO_x was observed at all sites, especially at
464 night, due to the increase in NO₂ via NO-to-O₃ conversion, with mean episode:non-
465 episode NO_x ratios ranging from 1.4 (Santos) to 3.5 (São José do Rio Preto). The
466 particulate concentrations showed a very sharp increase starting on September 15th, with
467 higher concentrations occurring generally in the early morning and late evening hours.
468 The diurnal variation was due to the increase in the boundary layer height in the afternoon
469 –which favours dilution of the pollutants– and by a shallow layer in the evening, as shown
470 by three-hour resolution ERA-Interim reanalysis data taken from the ECMWF (Fig. S11).
471 Pollutant concentrations greatly exceeded the thresholds recommended by the World
472 Health Organisation (WHO), whereas in a few occasions were the Brazilian air quality
473 standards for PM_{2.5} and PM₁₀ (60 and 120 $\mu\text{g}/\text{m}^3$, respectively) exceeded. This occurred
474 only once at Pinheiros in Greater São Paulo and Piracicaba on September 24th (65.5 and
475 134.2 $\mu\text{g}/\text{m}^3$, and 62 and 141 $\mu\text{g}/\text{m}^3$, respectively). However, all clusters exceeded the
476 daily WHO limits for PM_{2.5} or PM₁₀ (25 and 50 $\mu\text{g}/\text{m}^3$, respectively) at least five out of
477 10 days of the duration of the event (São José do Rio Preto exceeded the PM₁₀ limit on
478 10 days). Santos, on the other hand, surpassed the PM₁₀ limit only once (53 $\mu\text{g}/\text{m}^3$ on

479 September 24th). McClure and Jaffe (2018b) found that wildfires caused a significant
480 increase in the 98th quartile PM_{2.5} concentrations at sites in the northwest United States
481 (average $0.21 \pm 0.12 \mu\text{g}/\text{m}^3/\text{year}$), and Targino *et al.* (2013) reported that the
482 concentration of accumulation-mode particles increased by 40 and 340% at urban and
483 rural sites, respectively, in Sweden due to the outflow of wildfire plumes from Eastern
484 Europe.

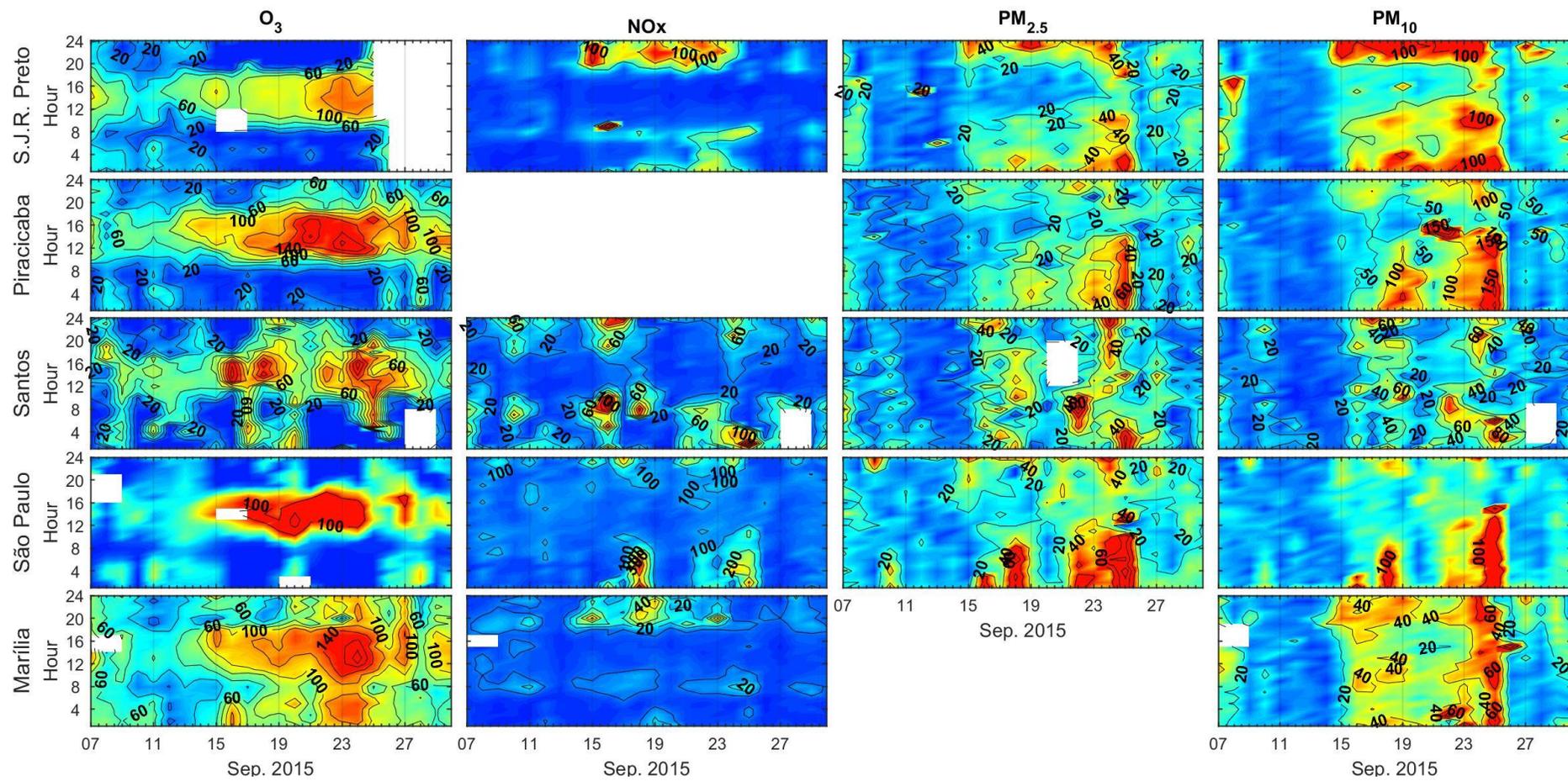
485 The Brazilian standard for O₃ (maximum daily 8-hour moving mean of $140 \mu\text{g}/\text{m}^3$) was
486 exceeded only in Marília (three days), Piracicaba (four days) and São Paulo (one day).
487 However, when considering the WHO guideline of $100 \mu\text{g}/\text{m}^3$, Marília exceeded the
488 limits on all days investigated here, Piracicaba on eight days, São Paulo on four days and
489 São José do Rio Preto on three days. As the increase in O₃ was accompanied by substantial
490 increase in both PM_{2.5} and PM₁₀, it is evident that the long-rang transport of smoke
491 severely deteriorates the air quality in cities of all sizes, and can outweigh measures to
492 curb local air pollution.

Cluster	Site	O ₃			NO _x			PM _{2.5}			PM ₁₀		
		(µg/m ³)									Mean	P5	P95
		Mean	P5	P95	Mean	P5	P95	Mean	P5	P95			
C1	São J. Rio Preto												
	Non-episode	41.2	11.1	79.9	11.1	3.0	27.9	12.3	1.1	30.0	22.9	6.1	58.8
	Pollution outbreak	^a 41.5	^a 1.0	^a 118.9	38.9	4.0	125.0	27.0	9.0	50.5	65.8	29.5	118.5
C2	Piracicaba												
	Non-episode	41.7	4.1	89.0	n.m.	n.m.	n.m.	11.8	3.0	25.0	24.8	9.0	57.8
	Pollution outbreak	61.1	3.0	157.5				25.3	10.0	43.0	78.2	30.0	138.5
C3	Santos												
	Non-episode	24.3	1.0	54.8	24.4	4.0	64.9	11.4	1.0	27.0	15.8	3.0	36.0
	Pollution outbreak	39.0	1.0	91.0	34.7	4.0	110.0	25.3	4.0	51.8	36.4	10.0	74.0
C4	S. Paulo (Pinheiros)												
	Non-episode	23.3	0.9	50.0	41.2	12.6	86.9	11.1	1.0	26.2	16.4	1.0	44.6
	Pollution outbreak	39.7	1.0	131.0	103.2	12.1	284.6	25.3	1.5	66.2	49.0	9.0	84.1
C5	Marília												
	Non-episode	52.7	23.0	83.0	7.2	2.0	17.0	n.m.	n.m.	n.m.	14.7	4.0	37.1
	Pollution outbreak	96.8	41.0	150.0	12.4	3.0	37.5				36.6	19.0	53.0

493 Table 3: Summary of pollutant concentrations during the non-episode (September 7th-14th) and pollution outbreak (and September 15th-24th) periods
494 for sites representative of each cluster.

495

496 ^aThis value may not be representative due to reduced number of observations. n.m. Not measured at this site.



497

498 **Fig. 8:** Hourly O₃, NO_x, PM_{2.5} and PM₁₀ concentrations measured in September 2015 at selected sites in the state of São Paulo.

499 3.5 OX analysis and estimates of local and long-range contribution

500 To disentangle the local and regional contributions of O₃ across the study area, we picked
501 the cities discussed in the previous section due to the availability in NO_x, NO₂ and O₃
502 measurements. Besides analysing the NO_x-OX relationship for all sites and months we
503 split the data into three-month periods, since we observed that August, September and
504 October were the most polluted months (Fig. 4a). We grouped the months as follows: (i)
505 February, March and April, (ii) May, June and July, (iii) August, September and October,
506 and (iv) November, December and January.

507 Figure 9a shows the NO_x-OX relationship for all sites irrespective of the time of the year,
508 and Figs 9b-f subdivided with respect to site and season. Also shown are the linear
509 regression equations and Pearson's correlation coefficient (for all cases, the *p*-values were
510 much smaller than 0.05). We found a positive linear increase of OX with NO_x, with a
511 mean intercept of 31 ppb (60.8 µg/m³), which can be interpreted as the regional O₃
512 contribution. This is in line with previous studies by Pancholi *et al.* (2018), Mazzeo *et al.*
513 (2005) and Clapp and Jenkin (2003) who reported regional contributions of 59, 43 and 70
514 µg/m³ for Jodhpur (India), Buenos Aires (Argentina) and London (UK), respectively.
515 However, when inspecting our results with respect to site and season we found different
516 strengths of the regional contribution (Figs. 9b-f). The largest regional O₃ contribution at
517 all sites was found for the biomass burning season (August-October). Clapp and Jenkin
518 (2001) also found that the regional contribution increased from 76 µg/m³ on non-episode
519 days to 109 µg/m³ on episode days in London (the latter was defined as days in April-
520 September affected by regional-scale photochemical events). We found that during the
521 polluted season in South Eastern Brazil, small cities received a relatively large regional
522 contribution. For example, the mean annual O₃ concentration (± one standard deviation)
523 in Marília was only 26.1±12.6 ppb (51.2±24.6 µg/m³). However, the regional transport

524 may account for as much as 41.4% of the total O₃ in Marília when considering the
525 maximum concentration observed during the biomass burning season (99 ppb). The
526 regional contribution of O₃ for Piracicaba, Santos, São Paulo and São José do Rio Preto,
527 considering the most extreme O₃ concentrations in the same period (117.4, 65.8, 151.5
528 and 98 ppb, respectively) were 36.6, 38.0, 23.1 and 37.8%.

529 We found a large variability in local OX with respect to season, and the largest
530 contribution was observed in summer at all sites (November-January). This term is
531 contributed by primary NO₂ emissions, typically 5-15% of NO_x, and local O₃ formation,
532 which depends on the sources of NO_x. In urban areas, on-road transport are the
533 dominating sources and NO₂ enters the atmosphere mostly via the reaction:

534



536

537 Hence, in most cases the local production will depend on the fleet characteristics, fuel
538 composition and traffic volumes (Carslaw, 2005). However, a source apportionment
539 study for the mega city of São Paulo showed a slightly different scenario in which not
540 only exhaust from on-road transport, but also industrial activities and biomass burning
541 (both local and remote) contributed to the air pollution in the city (Pereira *et al.*, 2017),
542 and, thus, can be sources of NO_x.

543 We found a large variability in local OX with respect to season, and the largest
544 contribution was observed in summer at all sites (November-January). The smallest
545 slopes were observed in São Paulo and Santos (< 1), regardless of the period of the year
546 (see equations in Fig. 9 and S12 for a month-by-month variability). Clapp and Jenkin
547 (2003) and Notario *et al.* (2012) showed that the local contribution at sites in the UK and

548 Spain also peaked in summer, which has been attributed to higher solar irradiance and
 549 enhanced photochemistry.

550 We calculated the NO₂:OX ratios from hourly data and a positive trend was identified
 551 with increasing NO_x concentration (Fig. S13 Supplementary Material). According to the
 552 mean NO₂:OX ratios, the selected sites can be classified within two groups: one with
 553 mean ratios higher than 0.35 (São Paulo and Santos) and the second group with ratios
 554 substantially lower (São José do Rio Preto, Marília and Piracicaba) (Table 4).

555

Cluster	Site	Feb-Mar-Apr	May-Jun-Jul	Aug-Sep-Oct	Nov-Dec-Jan
C2	Piracicaba	0.17±0.09	0.31±0.17	0.18±0.08	0.12±0.06
C4	São Paulo	0.49±0.19	0.67±0.18	0.51±0.17	0.40±0.17
C1	São José Rio Preto	0.20±0.08	0.28±0.12	0.21±0.13	0.21±0.19
C3	Santos	0.41±0.15	0.51±0.22	0.36±0.14	0.35±0.14
C5	Marília	0.16±0.06	0.23±0.09	0.14±0.06	0.14±0.08

556

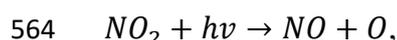
557 Table 4: Summary of mean (± standard deviation) NO₂:OX ratios segregated by site and
 558 season in the period 2014-2017.

559

560 The differences in the partitioning can be partially attributed to:

561 (i) Photochemical processes. The lower insolation in Santos and, to a lesser degree in São
 562 Paulo (1,895 h/year) makes the reaction

563



R2

565

566 less efficient than at the other sites, since the rate of NO₂ photolysis is a function of solar
 567 radiation intensity (actinic flux), which can be attenuated by cloud scattering. This effect

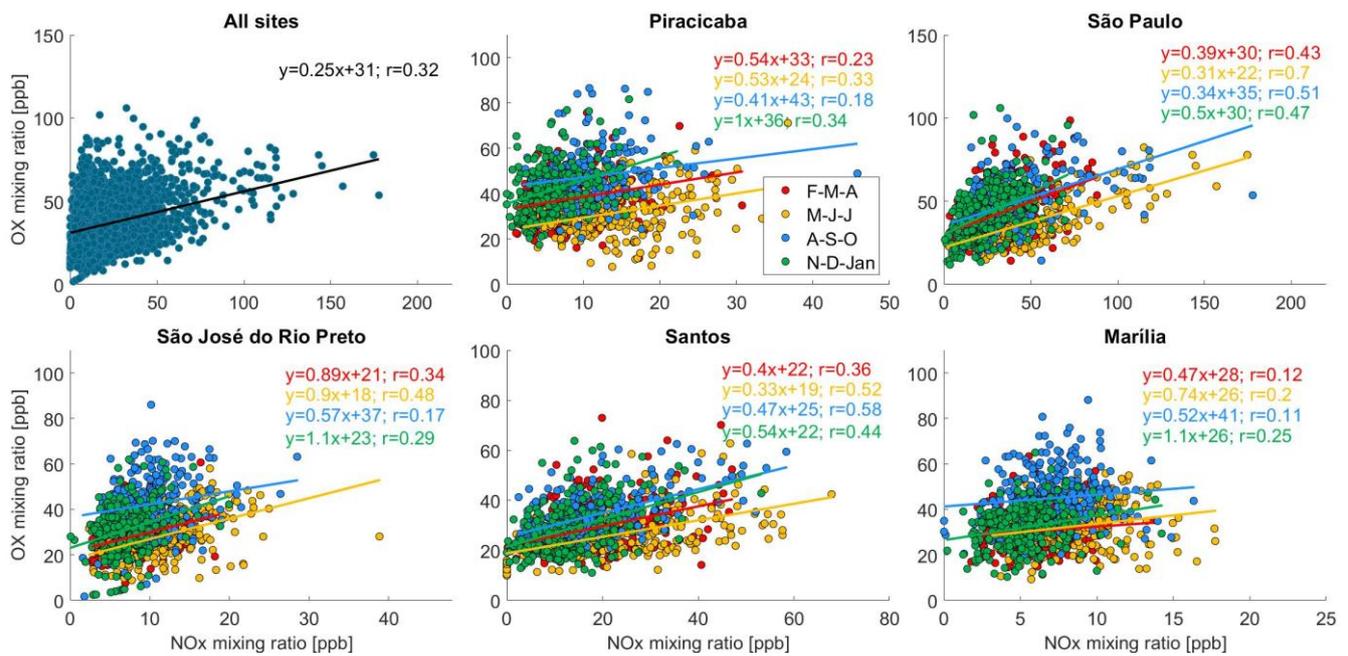
568 preserves NO₂ and increases the NO₂:OX ratio, especially in winter (May, June and July)
569 (Table 4).

570 (ii) Proximity to exhaust emissions from diesel light-duty vehicles. Grange *et al.* (2017)
571 showed a clear positive trend in NO₂ directly emitted by diesel passenger cars in Europe
572 in the period 1995-2010, reaching about 15% of the total NO_x in 2010. Although, current
573 Brazilian regulations prohibit the sales of diesel passenger cars, light-duty vehicles for
574 commercial purposes and sport utility vehicles (SUV) run on diesel and largely penetrated
575 the Brazilian market since 2008. Nowadays, 46% of the sales of light-duty vehicles
576 correspond to diesel-fuelled units and represent 6.8% of the total market sales
577 (ANFAVEA, 2019). These vehicles have emission standards mostly equivalent to Euro
578 3, 4 and 5.

579 Despite the lack of studies on trends in the NO₂:NO_x ratio for Brazil, we hypothesise that
580 direct NO₂ emissions from diesel vehicles increased in recent years. This effect may have
581 been captured by the measurements at São Paulo Pinheiros site, which is located on the
582 kerb of Frederico Hermann street –a eight-lane road used for traffic and kerbside parking.
583 Moreover, the site is only 230 m from the highly trafficked Marginal Pinheiros ring road,
584 where congestion frequently occurs and the proportion of diesel-fuelled vehicles is high.

585

586



587

588 **Fig. 9:** Variation in mean daylight mixing ratios of OX with respect to NOx. The lines
 589 were obtained by linear regression analysis. Also shown are linear regression equations
 590 and the Pearson's correlation coefficient.

591

592 4. Summary and conclusions

593 Applying a hierarchical clustering technique on hourly O₃ data collected in the period
 594 2014-2017 at 26 sites in the states of São Paulo and Paraná, Brazil, enabled us to reduce
 595 the dataset to five homogenous groups with respect to seasonal, monthly, weekly and
 596 diurnal concentrations. The cleanest group was located on the coast whilst the inland sites
 597 showed the highest concentrations. Group C5 (inland) stood out with a pronounced mean
 598 annual nocturnal O₃ peak of 40 μg/m³, which reached 55 μg/m³ in September.
 599 Comparatively, the mean annual diurnal peak was 63 μg/m³. We attributed this peak to
 600 the combined effects of transported smoke from biomass burning and sustained outflow
 601 of aged pollution from the metropolitan area of São Paulo. All groups were associated
 602 with peak O₃ concentrations in September or October, with mean values between 34 and
 603 63 μg/m³, coinciding with the biomass burning season in central and northern Brazil. The

604 overall mean regional O₃ contribution during the polluted period was 61 µg/m³, with a
605 great seasonal and intersite variability, ranging from 35 to 84 µg/m³. We found that the
606 long-range transport of smoke can contribute with between 23 and 41 % of the total O₃.
607 Investigation of a pollution outbreak in September 2015 showed that the smoke caused
608 sharp increases in O₃, PM_{2.5} and PM₁₀ concentrations and exceedances in the levels
609 recommended by the WHO. All cities were affected with between 2.2- and 3.1-fold
610 increases in PM₁₀, 2-fold increase in PM_{2.5}, between 1.5- and 1.8-fold increases in O₃ and
611 between 1.4- and 3.5-fold increases in NO_x concentrations compared to the non-episode
612 period. This indicates that biomass burning, both in remote and proximate areas, increases
613 gas and particulate concentrations and quickly deteriorates the air quality of small and big
614 cities. Depending on the large-scale circulation, the exceedances in air quality standards
615 can last for several days and outweigh the reductions in anthropogenic sources that are
616 promoted to curb air pollution in cities (for example, on-road traffic exhaust emissions).
617 Analysis of the local oxidant sources showed a substantial variability across the study
618 area and a seasonal dependence. More specifically, larger contributions in the period
619 November-January due to enhanced photochemistry. The local oxidant contribution was
620 lower in the cities of São Paulo and Santos, compared to the inland sites.

621 The state of São Paulo has always been at the forefront in terms of progressive measures
622 to curb air pollution, by introducing programs to control sulphur dioxide from industrial
623 sources and by enforcing standards for cleaner vehicles and fuels. However, the present
624 results indicate that policies targeting the reduction of biomass burning is of utmost
625 importance to improve the urban air quality, particularly in densely populated areas where
626 high pollutant concentrations are frequently observed. This can only be achieved with
627 enhanced governance acting at regional, national and international levels to combat
628 biomass burning practices in Brazil and its neighbouring countries. Not only the

629 population health would benefit from such a measure, but also the regional climate, since
630 O₃, BC and PM_{2.5} are short-lived climate forcers (SLCF).
631 This strategy would be well-aligned with the Paris Agreement that aims to limit global
632 warming to below 2 °C compared to pre-industrial, and which must be complemented
633 with the reduction of SLCF emissions.

634

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639

640 **Declaration of interest:** None

641

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