

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

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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 (O<sub>3</sub>) data, measured in the states of São Paulo and Paraná, Brazil,  
26 in the period 2014-2017, with aerosol optical depth, co-pollutants (NO<sub>x</sub>, PM<sub>2.5</sub> and PM<sub>10</sub>)  
27 and air backtrajectories to identify sources, transport and geographical patterns in the air  
28 pollution data. We applied cluster analysis to hourly O<sub>3</sub> data and split the investigation  
29 area of approximately 290,000 km<sup>2</sup> into five groups with similar features in terms of  
30 diurnal, weekly, monthly and seasonal O<sub>3</sub> concentrations. All groups presented a peak in  
31 September and October, associated with the fire activities and enhanced photochemistry.  
32 The highest mean O<sub>3</sub> 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 O<sub>3</sub> over the area was 61 µg/m<sup>3</sup>, with large seasonal and intersite variabilities (from 35  
37 to 84 µg/m<sup>3</sup>). The long-range transport of smoke contributed with between 23 and 41%  
38 of the total O<sub>3</sub> during the pollution events. A pollution outbreak in September 2015 caused  
39 many-fold increases in O<sub>3</sub>, PM<sub>2.5</sub> and PM<sub>10</sub> 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<sub>x</sub> (NO+NO<sub>2</sub>), and particulate matter (PM<sub>2.5</sub>, PM<sub>10</sub> 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 (O<sub>3</sub>) are usually detected a few  
85 kilometres downwind of the burning area (Wentworth *et al.*, 2018). O<sub>3</sub> is formed via a  
86 series of complex, non-linear reactions involving NO<sub>x</sub> and non-methane VOC in the  
87 presence of sunlight (Monks *et al.*, 2015 and references therein). The O<sub>3</sub> production rate  
88 is governed by NO<sub>x</sub>- 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](http://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) O<sub>3</sub> increase up to 70 µg/m<sup>3</sup> on days affected by smoke in Meridian  
99 (USA). Zhou *et al.* (2019) observed a concomitant 2.5-fold increase in O<sub>3</sub> 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), O<sub>3</sub> 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 O<sub>3</sub> 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<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub>  
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 O<sub>3</sub> formation.

119 In this study, we present a four-year climatology of O<sub>3</sub> 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 O<sub>3</sub> concentration in cities of different sizes by analysing the

122 coupling between O<sub>3</sub>, NO and NO<sub>2</sub>. 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<sub>x</sub>, PM<sub>2.5</sub> and PM<sub>10</sub>), 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<sub>x</sub>, PM and SO<sub>2</sub>,  
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<sub>x</sub> 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 O<sub>3</sub> 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  $\mu\text{m}$  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 O<sub>3</sub> dataset. We used O<sub>3</sub> 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 O<sub>3</sub> data over 1,400 European  
190 monitoring stations.

191 The hourly O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> concentration**

224 To estimate the regional contribution of O<sub>3</sub> to the *in situ* O<sub>3</sub> concentration, we calculated  
225 the daylight mean mixing ratios (in ppb) of the oxidant ( $OX = O_3 + NO_2$ ) and NO<sub>x</sub>  
226 (Clapp and Jenkin, 2003). The analysis assumes that the interconversion of O<sub>3</sub>, NO<sub>2</sub> and  
227 NO occurs in a closed system, where the total mixing ratio of both NO<sub>x</sub> 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<sub>x</sub> concentrations,  
231 where the offset can be interpreted as NO<sub>x</sub>-independent and the slope as NO<sub>x</sub>-dependent  
232 contributions. The former is attributed to regional background O<sub>3</sub> and the latter accounts  
233 for the local contribution, which correlates with the level of primary pollution. Any local  
234 change in NO<sub>x</sub> 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<sub>x</sub>, NO<sub>2</sub> and O<sub>3</sub> measurements.

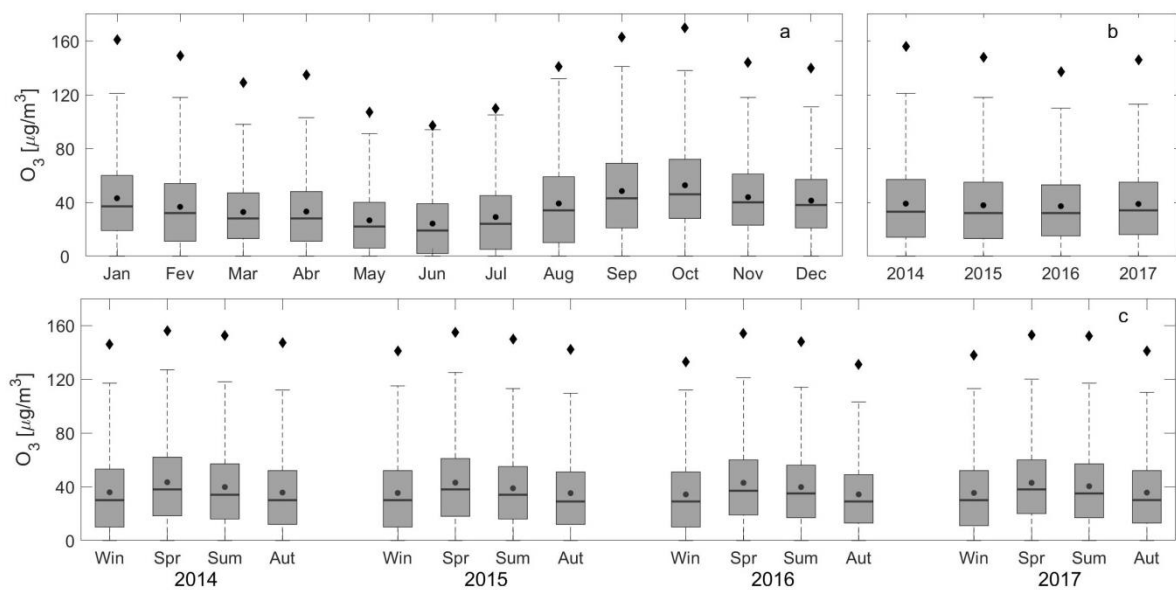
238

## 239 **3. Results**

### 240 **3.1 Overall O<sub>3</sub> concentrations in different time domains**

241 Figure 1a depicts a statistical summary of O<sub>3</sub> concentrations at all sites between 2014 and  
242 2017. The lowest O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> amongst the years investigated. However, the Krustal-Wallis test applied at the 5%  
 256 significance level showed that there are statistically significant differences in O<sub>3</sub> between  
 257 the years. These differences may be caused by fumigation of upper air masses that is  
 258 influencing the boundary layer and surface O<sub>3</sub> concentrations, the number of fire  
 259 outbreaks, regional transport and photochemistry. These mechanisms will not be  
 260 addressed in this manuscript. The O<sub>3</sub> 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 O<sub>3</sub> 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

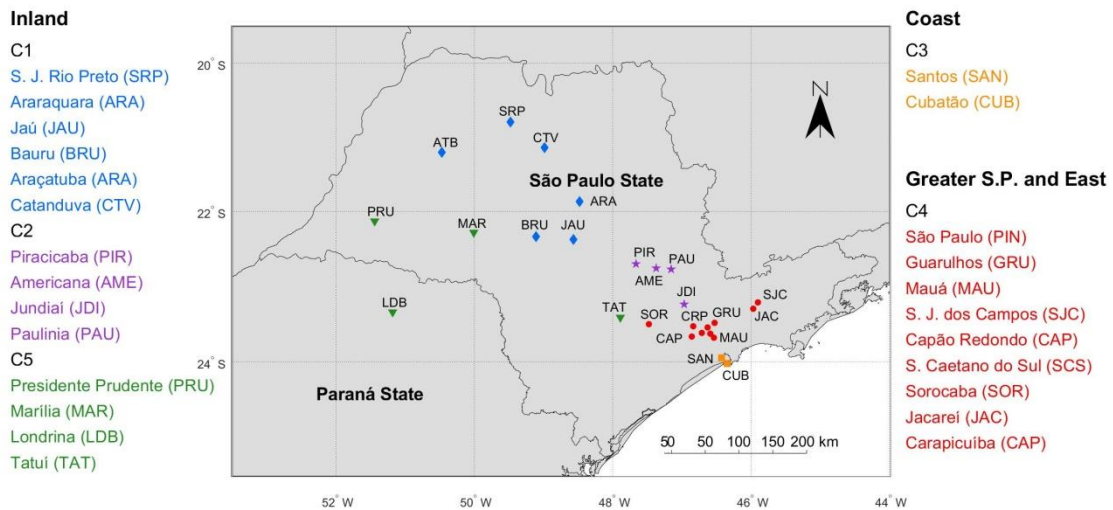
265 the mean values, the diamonds are the 99.5 percentile, the whiskers are the 5<sup>th</sup> and 95<sup>th</sup>  
 266 percentiles, the box limits are the 25<sup>th</sup> and 75<sup>th</sup> percentiles and the black lines across the  
 267 boxes are median values.

268

269 **3.2 O<sub>3</sub> data reduction based on cluster analysis**

270 The elbow method suggested that the O<sub>3</sub> 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

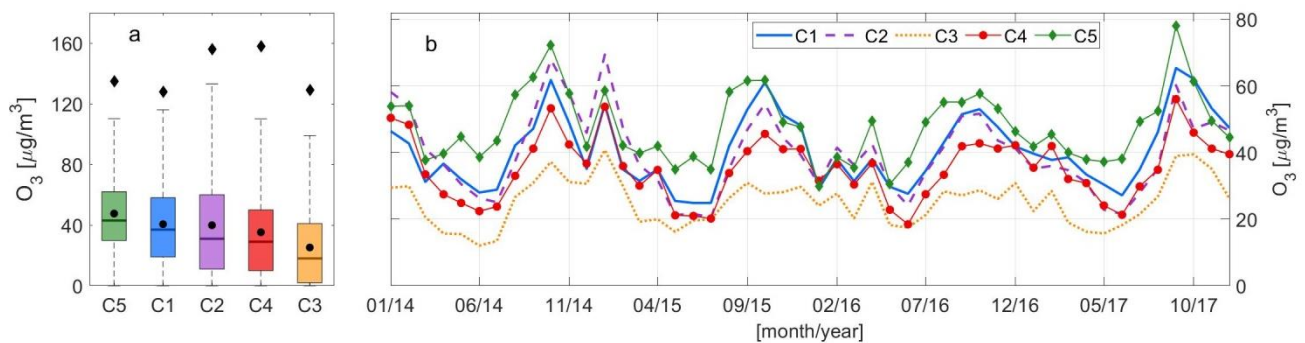


279

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 O<sub>3</sub> for the individual clusters using the datasets  
285 from 2014 to 2017, organised in descending order of median values. Overall, the largest  
286 O<sub>3</sub> 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/m<sup>3</sup> and medians from 18.0  
288 to 43.0 µg/m<sup>3</sup>. Even though C2 on average was not the most polluted cluster, the stations  
289 in this group had the largest interquartile range and 95<sup>th</sup> percentile. This suggests that the  
290 sites within this group were affected by events causing frequently extreme O<sub>3</sub>  
291 concentrations. The mean daily O<sub>3</sub> 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 O<sub>3</sub> 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

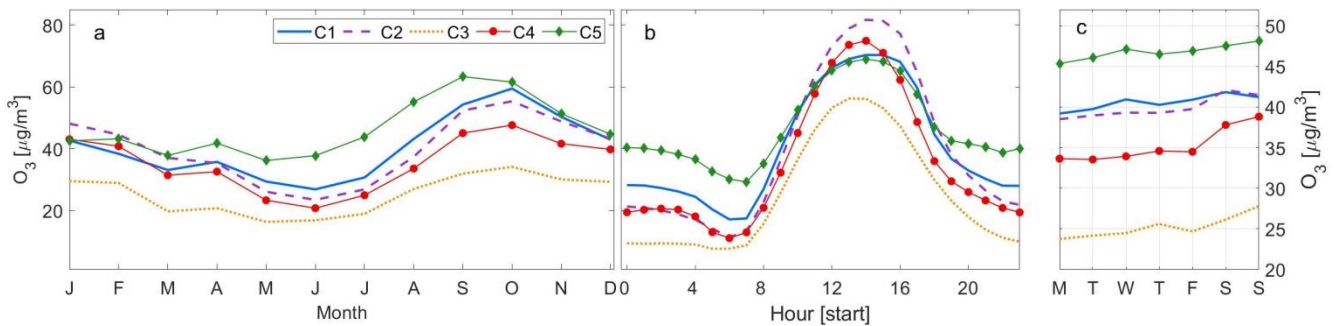
297 **Figure 3:** (a) Statistical summary of O<sub>3</sub> data for the clustered stations. The dots indicate  
298 the mean values, the diamonds are the 99.5 percentile, the whiskers are the 5<sup>th</sup> and 9<sup>th</sup>  
299 percentiles and the box limits are the 25<sup>th</sup> and 75<sup>th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

302

303 **3.3 Seasonal, weekly and diurnal profiles of O<sub>3</sub> concentrations**

304 Figure 4a shows that the monthly mean O<sub>3</sub> 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 O<sub>3</sub> concentrations of 13.0 and 31.3 µg/m<sup>3</sup> in  
 308 January and September, respectively. Another outstanding feature is that whilst the O<sub>3</sub>  
 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/m<sup>3</sup>. Comparatively, the concentration for C4 more than halved over the same period  
 312 (from 43.1 to 20.8 µg/m<sup>3</sup>).

313



314

315 **Figure 4:** (a) Monthly, (b) diurnal and (c) weekly mean O<sub>3</sub> concentrations for the  
 316 clustered stations.

317

318 The clusters show rather similar diurnal patterns, with peak O<sub>3</sub> 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<sub>x</sub>. However, the reduction of NO emissions relative to NO<sub>2</sub>,  
 322 typical in urban environments, decreases the NO titration effect and increases the daytime  
 323 O<sub>3</sub> 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, O<sub>3</sub> 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 O<sub>3</sub> peak concentration of about  
328 70 µg/m<sup>3</sup>, but diverge at night with concentrations for C5 up to 12 µg/m<sup>3</sup> greater than for  
329 C1. C5 has an outstanding secondary nocturnal O<sub>3</sub> peak and the smallest diurnal range.  
330 Krecl *et al.* (2016) also observed a secondary O<sub>3</sub> maximum at night in Londrina (a site  
331 within C5), which they attributed to horizontal and vertical transport of O<sub>3</sub> 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/m<sup>3</sup>  
335 (Fig. S1, Supplementary Material). Comparatively, the mean maximum diurnal peak was  
336 92 µg/m<sup>3</sup> 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 O<sub>3</sub> 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 O<sub>3</sub>  
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 O<sub>3</sub> 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 O<sub>3</sub> peak of 176 µg/m<sup>3</sup> (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 O<sub>3</sub> 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<sub>x</sub> at weekends is more  
364 pronounced than for VOC, favouring the O<sub>3</sub> formation due to an increase in the  
365 VOC:NO<sub>x</sub> 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<sub>x</sub> 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 O<sub>3</sub>. Hence, we suggest that  
371 this effect combined with the reduction in O<sub>3</sub> 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 O<sub>3</sub> concentrations at weekends within these clusters.

374 Other pathways for the O<sub>3</sub> weekend effect include: (i) the shift in the timing of NO<sub>x</sub> peak  
 375 favours O<sub>3</sub> formation at weekends than on weekdays), (ii) carryover of pollutants with  
 376 higher VOC:NO<sub>x</sub> ratios from light-duty vehicle traffic on Friday and Saturday evenings  
 377 that can generate more O<sub>3</sub> at weekends, (iii) lower aerosol concentrations at weekends  
 378 increase incoming solar radiation and photochemistry (Heuss *et al.* (2003).

379

380 Table 1: O<sub>3</sub> concentrations in different time domains, derived from hourly mean data.

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

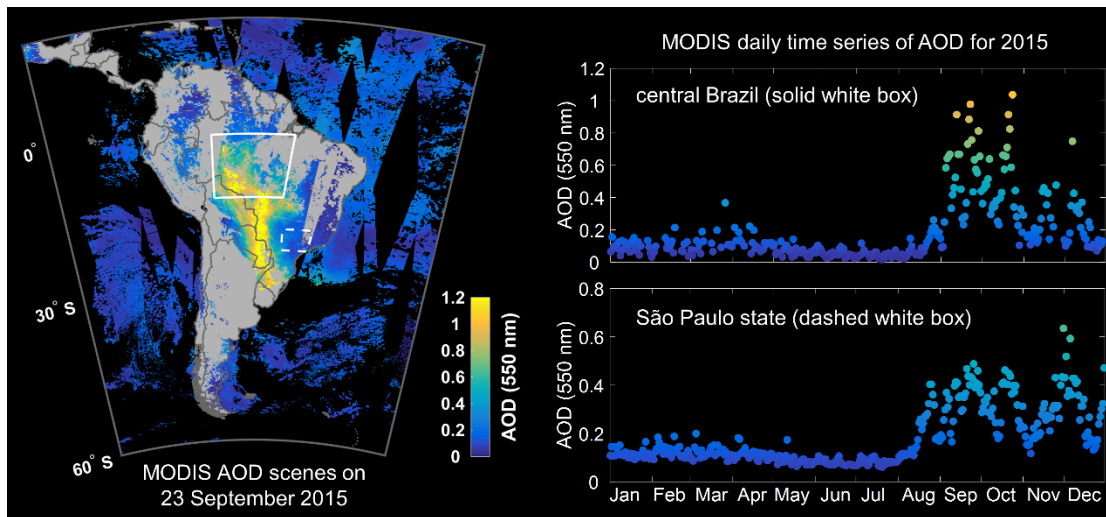
381 <sup>a</sup>Based on the difference between the mean maximum and minimum diurnal O<sub>3</sub> concentrations.

382 <sup>b</sup>Maximum O<sub>3</sub> concentration of the diurnal cycle. <sup>c</sup>Based on the difference between the mean  
 383 monthly O<sub>3</sub> concentrations in October and January. <sup>d</sup>Based 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 km<sup>2</sup> 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 23<sup>rd</sup> 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 23<sup>rd</sup>  
 395 2015 (left), and daily time series of AOD for the central Brazil and the state of São Paulo  
 396 (right).

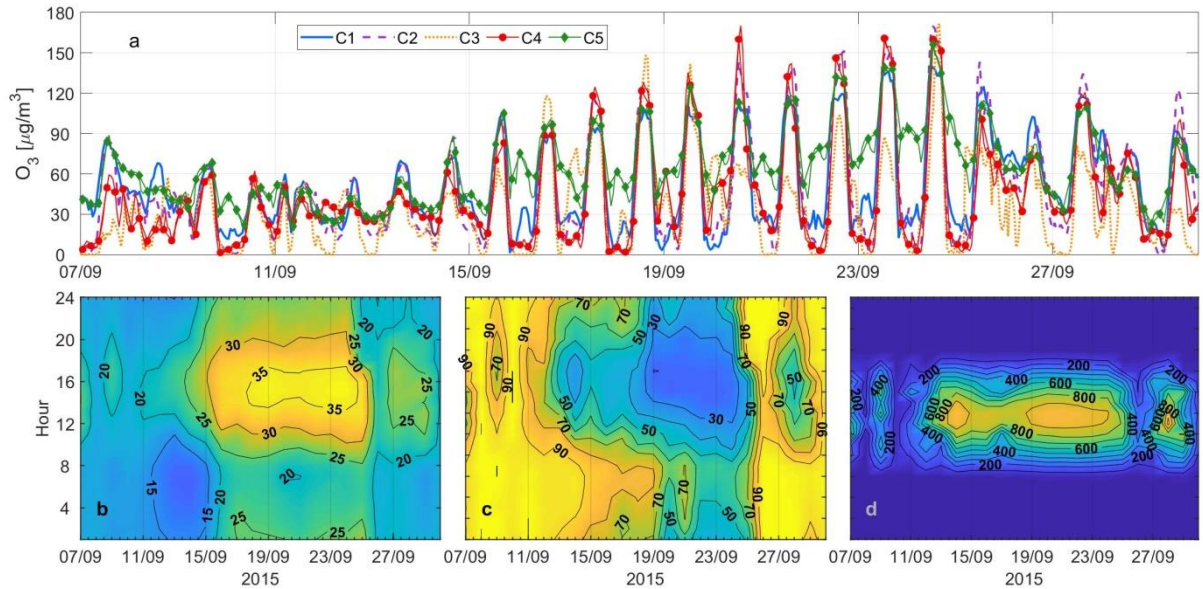
397 We focus here on an air pollution outbreak that led to an enhancement in O<sub>3</sub> concentration  
 398 and other co-pollutants over the investigated area during the second half of September  
 399 2015. Figure 6a shows that the O<sub>3</sub> concentration started to increase around September  
 400 15<sup>th</sup> for all clusters, with enhancements between two- and four-fold: for example, from  
 401 48.0 to 103.5 μg/m<sup>3</sup> within C3 and from 38.0 to 169.8 μg/m<sup>3</sup> within C4, between  
 402 September 11<sup>th</sup> and 20<sup>th</sup>. Meteorological data measured at UTFPR campus in Londrina  
 403 (C5) show that the substantially higher O<sub>3</sub> concentrations that occurred in the afternoon  
 404 during the period September 14<sup>th</sup>-25<sup>th</sup> 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/m<sup>2</sup>, respectively, in the afternoon of September 23<sup>rd</sup>) (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 O<sub>3</sub> production  
 410 is favoured by increase in air temperature and solar irradiance, and with Querol *et al.*

411 (2016) who reported very high O<sub>3</sub> concentrations during heat waves in Spain in the  
412 summer of 2015.

413 The surface winds measured at UTFPR campus between September 16<sup>th</sup>-19<sup>th</sup> were  
414 northerly and larger than 5.0 m/s in the afternoon, which facilitated advection of polluted  
415 air. Between September 20<sup>th</sup>-23<sup>rd</sup> 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



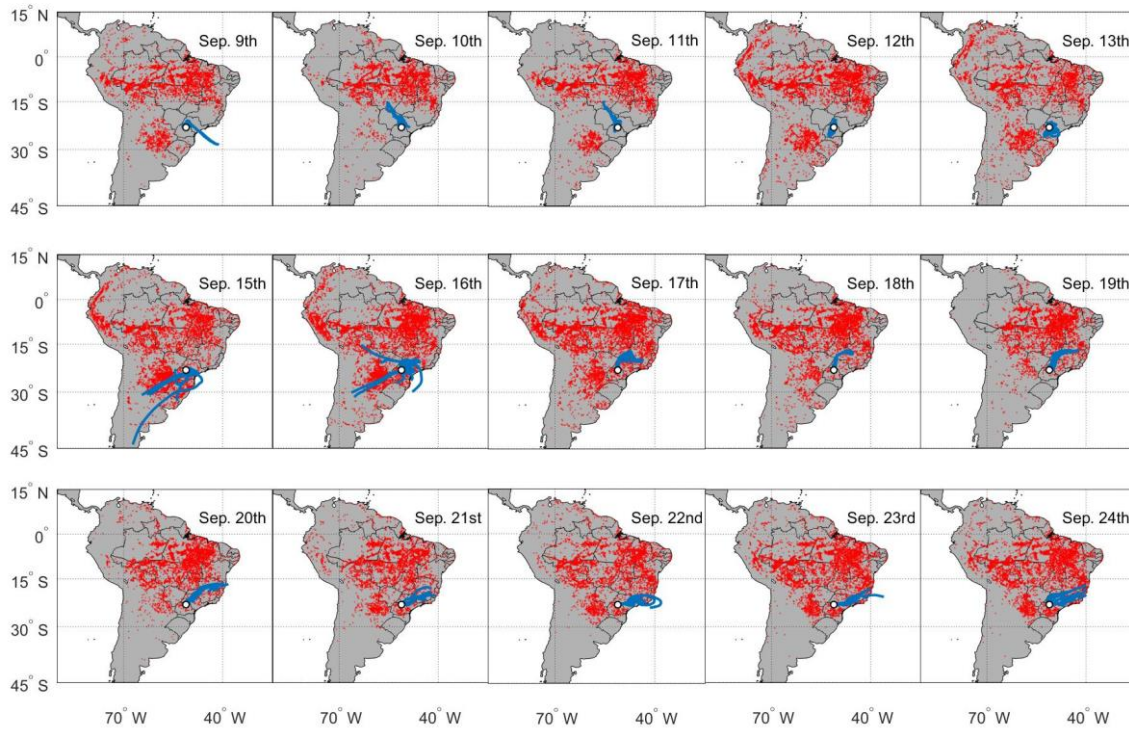
429

430 **Fig. 6:** (a) Hourly mean O<sub>3</sub> 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 9<sup>th</sup>-13<sup>th</sup> (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 15<sup>th</sup>  
 438 (Fig. 7). Four days prior to and during the pollution events (September 7<sup>th</sup>-14<sup>th</sup> and  
 439 September 15<sup>th</sup>-24<sup>th</sup>, respectively), the mean AOD and corresponding one standard  
 440 deviation for the state of São Paulo (20-24°S, 45-52°W) were  $0.23 \pm 0.07$  and  $0.39 \pm 0.06$ ,  
 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 O<sub>3</sub> 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<sub>3</sub>  
 451 concentrations before and during the pollution outbreak in September 2015.

452

O <sub>3</sub>	C1	C2	C3	C4	C5
[ $\mu\text{g}/\text{m}^3$ ]	Before the pollution outbreak				
Mean	40.4 $\pm$ 17.0	34.1 $\pm$ 20.6	24.4 $\pm$ 17.6	30.0 $\pm$ 15.1	43.9 $\pm$ 14.4
Maximum	85.8	87.2	58.0	74.0	88.6
	During the pollution outbreak				
Mean	54.4 $\pm$ 40.4	54.2 $\pm$ 49.0	43.4 $\pm$ 38.2	52.4 $\pm$ 49.0	79.8 $\pm$ 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 O<sub>3</sub>, NO<sub>x</sub>, PM<sub>2.5</sub> and PM<sub>10</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> peak. However, the peak recorded  
460 in Marília during this pollution outbreak (> 100 µg m<sup>-3</sup> on September 23<sup>rd</sup>) was much  
461 larger than observed even in the dirtiest month (Fig. S1, Supplementary Material). The  
462 nocturnal peak observed in Santos (> 60 µg m<sup>-3</sup>) was an uncommon feature compared to  
463 the diurnal cycle for C4. The enhancement of NO<sub>x</sub> was observed at all sites, especially at  
464 night, due to the increase in NO<sub>2</sub> via NO-to-O<sub>3</sub> conversion, with mean episode:non-  
465 episode NO<sub>x</sub> 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 15<sup>th</sup>, 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<sub>2.5</sub> and PM<sub>10</sub> (60 and 120 µg/m<sup>3</sup>, respectively) exceeded. This occurred  
474 only once at Pinheiros in Greater São Paulo and Piracicaba on September 24<sup>th</sup> (65.5 and  
475 134.2 µg/m<sup>3</sup>, and 62 and 141 µg/m<sup>3</sup>, respectively). However, all clusters exceeded the  
476 daily WHO limits for PM<sub>2.5</sub> or PM<sub>10</sub> (25 and 50 µg/m<sup>3</sup>, respectively) at least five out of  
477 10 days of the duration of the event (São José do Rio Preto exceeded the PM<sub>10</sub> limit on  
478 10 days). Santos, on the other hand, surpassed the PM<sub>10</sub> limit only once (53 µg/m<sup>3</sup> on

479 September 24<sup>th</sup>). McClure and Jaffe (2018b) found that wildfires caused a significant  
480 increase in the 98<sup>th</sup> quartile PM<sub>2.5</sub> 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 O<sub>3</sub> (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 O<sub>3</sub> was accompanied by substantial  
490 increase in both PM<sub>2.5</sub> and PM<sub>10</sub>, 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.

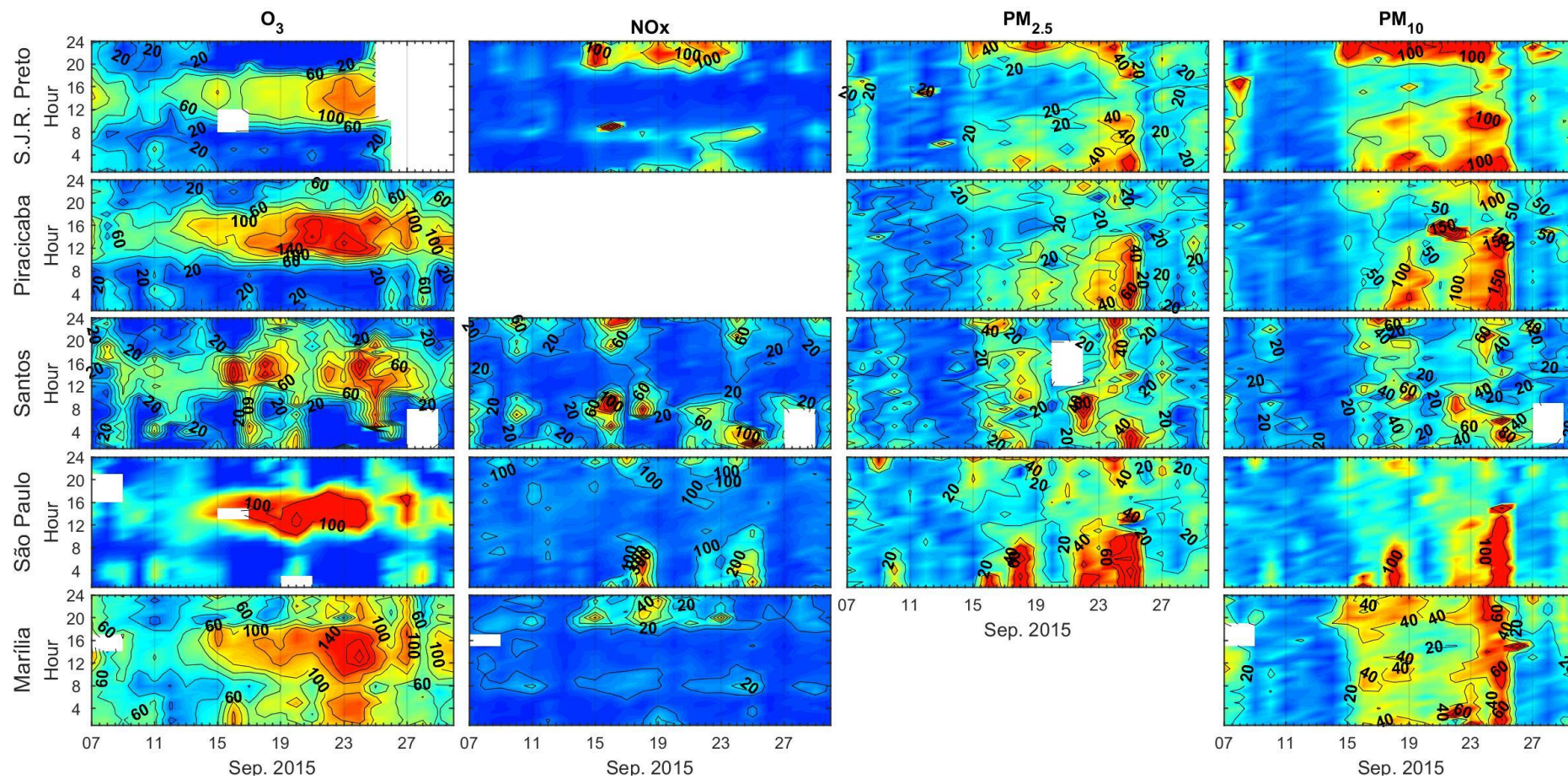


Cluster	Site	O <sub>3</sub>			NO <sub>x</sub>			PM <sub>2.5</sub>			PM <sub>10</sub>		
		(µg/m <sup>3</sup> )									Mean	P5	P95
		Mean	P5	P95	Mean	P5	P95	Mean	P5	P95			
<b>C1</b>	<b>São J. Rio Preto</b>												
	Non-episode	41.2	11.1	79.9	11.1	3.0	27.9	12.3	1.1	30.0	22.9	6.1	58.8
	Pollution outbreak	<sup>a</sup> 41.5	<sup>a</sup> 1.0	<sup>a</sup> 118.9	38.9	4.0	125.0	27.0	9.0	50.5	65.8	29.5	118.5
<b>C2</b>	<b>Piracicaba</b>												
	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
<b>C3</b>	<b>Santos</b>												
	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
<b>C4</b>	<b>S. Paulo (Pinheiros)</b>												
	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
<b>C5</b>	<b>Marília</b>												
	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 7<sup>th</sup>-14<sup>th</sup>) and pollution outbreak (and September 15<sup>th</sup>-24<sup>th</sup>) periods  
494 for sites representative of each cluster.

495

496 <sup>a</sup>This value may not be representative due to reduced number of observations. n.m. Not measured at this site.



497

498 **Fig. 8:** Hourly O<sub>3</sub>, NO<sub>x</sub>, PM<sub>2.5</sub> and PM<sub>10</sub> 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

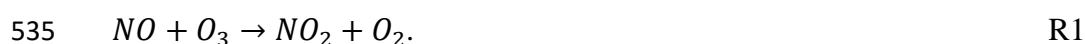
500 To disentangle the local and regional contributions of O<sub>3</sub> across the study area, we picked  
501 the cities discussed in the previous section due to the availability in NO<sub>x</sub>, NO<sub>2</sub> and O<sub>3</sub>  
502 measurements. Besides analysing the NO<sub>x</sub>-OX relationship 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<sub>x</sub>-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<sub>x</sub>, with a  
511 mean intercept of 31 ppb (60.8 µg/m<sup>3</sup>), which can be interpreted as the regional O<sub>3</sub>  
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/m<sup>3</sup> 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 O<sub>3</sub> 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/m<sup>3</sup> on non-episode  
519 days to 109 µg/m<sup>3</sup> 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 O<sub>3</sub> concentration (± one standard deviation)  
523 in Marília was only 26.1±12.6 ppb (51.2±24.6 µg/m<sup>3</sup>). However, the regional transport

524 may account for as much as 41.4% of the total O<sub>3</sub> in Marília when considering the  
525 maximum concentration observed during the biomass burning season (99 ppb). The  
526 regional contribution of O<sub>3</sub> for Piracicaba, Santos, São Paulo and São José do Rio Preto,  
527 considering the most extreme O<sub>3</sub> 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 NO<sub>2</sub> emissions, typically 5-15% of NO<sub>x</sub>, and local O<sub>3</sub> formation,  
532 which depends on the sources of NO<sub>x</sub>. In urban areas, on-road transport are the  
533 dominating sources and NO<sub>2</sub> 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<sub>x</sub>.

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 NO<sub>2</sub>:OX ratios from hourly data and a positive trend was identified  
 551 with increasing NO<sub>x</sub> concentration (Fig. S13 Supplementary Material). According to the  
 552 mean NO<sub>2</sub>: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

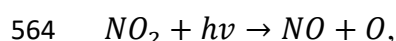
557 Table 4: Summary of mean (± standard deviation) NO<sub>2</sub>:OX ratios segregated by site and  
 558 season in the period 2014-2017.

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 NO<sub>2</sub> photolysis is a function of solar  
 567 radiation intensity (actinic flux), which can be attenuated by cloud scattering. This effect

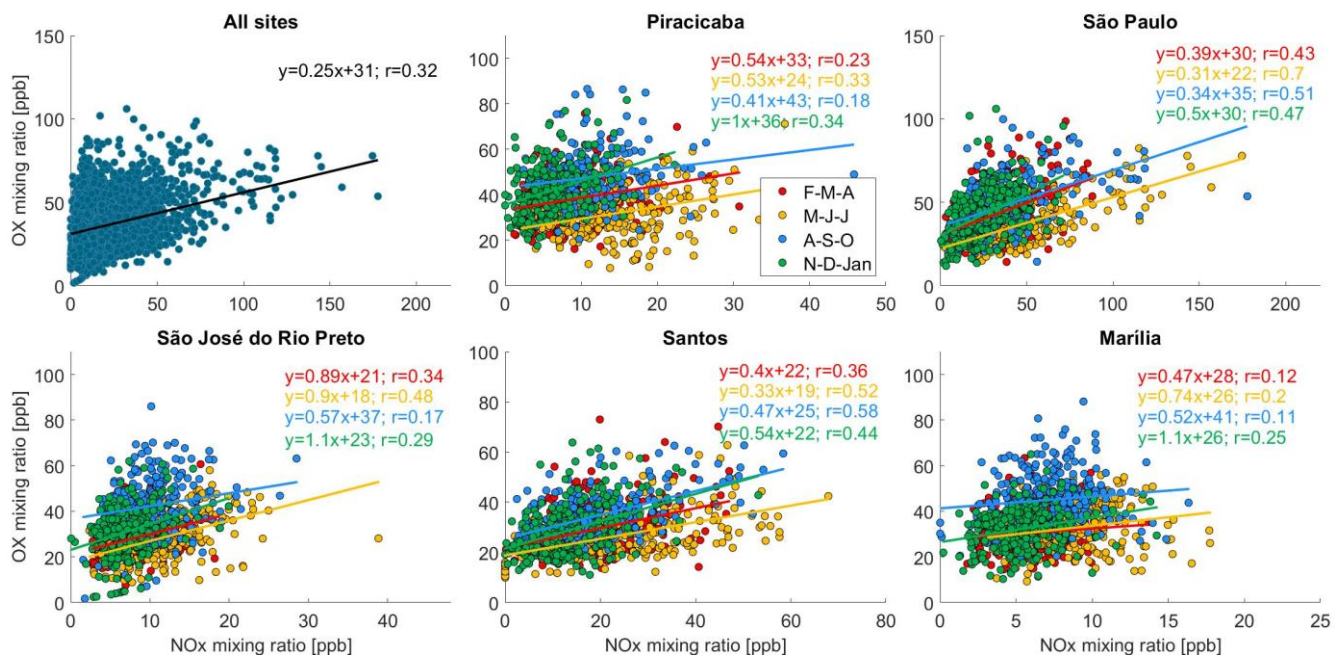
568 preserves NO<sub>2</sub> and increases the NO<sub>2</sub>:OX ratio, especially in winter (May, June and July)  
569 (Table 4).

570 (ii) Proximity to exhaust emissions from diesel light-duty vehicles. Grange *et al.* (2017)  
571 showed a clear positive trend in NO<sub>2</sub> directly emitted by diesel passenger cars in Europe  
572 in the period 1995-2010, reaching about 15% of the total NO<sub>x</sub> 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 NO<sub>2</sub>:NO<sub>x</sub> ratio for Brazil, we hypothesise that  
580 direct NO<sub>2</sub> 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 NO<sub>x</sub>. 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 O<sub>3</sub> 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 O<sub>3</sub> peak of 40 μg/m<sup>3</sup>, which reached 55 μg/m<sup>3</sup> in September.  
 599 Comparatively, the mean annual diurnal peak was 63 μg/m<sup>3</sup>. 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 O<sub>3</sub> concentrations in September or October, with mean values between 34 and  
 603 63 μg/m<sup>3</sup>, coinciding with the biomass burning season in central and northern Brazil. The

604 overall mean regional O<sub>3</sub> contribution during the polluted period was 61 µg/m<sup>3</sup>, with a  
605 great seasonal and intersite variability, ranging from 35 to 84 µg/m<sup>3</sup>. We found that the  
606 long-range transport of smoke can contribute with between 23 and 41 % of the total O<sub>3</sub>.  
607 Investigation of a pollution outbreak in September 2015 showed that the smoke caused  
608 sharp increases in O<sub>3</sub>, PM<sub>2.5</sub> and PM<sub>10</sub> 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 PM<sub>10</sub>, 2-fold increase in PM<sub>2.5</sub>, between 1.5- and 1.8-fold increases in O<sub>3</sub> and  
611 between 1.4- and 3.5-fold increases in NO<sub>x</sub> 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 O<sub>3</sub>, BC and PM<sub>2.5</sub> 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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