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Air quality in São Paulo – Brazil: temporal evolution and spatial distribution of carbon monoxide, coarse particulate matter and ozone

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1. Introduction

One of the major issues in urban areas is air pollution. Industrialization and transportation that use essentially fossil fuels are responsible for emitting several pollutants in the air, decreasing air quality and menacing the health of urban population. Just in the Metropolitan Region of Sao Paulo 9,700 deaths a year may be attributed to air pollution (Miranda et al., 2012)

The largest conurbation in South America, Metropolitan Region of Sao Paulo (MRSP) is formed by 39 cities, including the city of Sao Paulo (Fig. 1). It has more than 20 million inhabitants and 7 million vehicles, that is 48% of the population and fleet of the state, in approximately 8,000 km^2 of area. Its climate presents a dry winter from June to August and a wet summer from December to February (Oliveira et al., 2003). Stationary and mobile sources of air pollution emit yearly 165,000 tons of carbon monoxide (CO), 46,000 tons of hydrocarbon (HC), 71,000 tons of nitrogen oxides (NOx), 10,000 tons of sulfur oxides (SOx), and 5,000 tons of particulate matter (PM). Vehicular emission are responsible for 97% of CO, 82% of HC, 78% of NOx, 43% of SOx, and 40% of PM (CETESB, 2015).

CO is mainly produced by incomplete combustion processes. It has not exceed the environmental standards of the Environmental Agency of the state of Sao Paulo (CETESB) since 2008, however it is a precursor for ozone (O3) and carbon dioxide (CO2), both greenhouse gases and, since it remains from days to weeks in the atmosphere, it is also an important tracer of pollution sources (Worden et al., 2013). PM is usually classified by the aerodynamic diameter of the particles: particles with diameters equal to or less than 2.5 μm are called fine particulate matter or PM2.5 and particles with diameters equal to or less than 10 μm (including PM2.5) are called PM10. As in this work we are only considering PM10, hereby it will be called PM. This pollutant has several anthropogenic and natural sources, for example, combustion processes from vehicles and industry, dust resuspension, secondary aerosol formation, etc. It is formed by gaseous, liquid or solid particles and its composition varies. Miranda et al. (2012) analyzed the elemental composition of PM2.5 in six capitals of Brazil, including Sao Paulo, and found mainly mineral dust, anthropogenic particles, Sulfur from diesel combustion and Potassium from biomass combustion. PM concentration has decreased in time for the past two decades, however continues to eventually exceed the standard limits determined by the Environmental Agency (CETESB, 2015). This particles, because of their size, may be inhaled, causing a variety of health problems (WHO, 2015).

O3 is a secondary pollutant, which means that it is not emitted, but formed in the atmosphere through several chemical reactions. To form O3 it is necessary: nitrogen oxides (NOx), volatile organic compounds (VOCs), and solar (ultraviolet) radiation. Therefore, when there is solar radiation, it is the content of its precursors (NOx and VOCs) that determines its concentration. Nevertheless, it is not a simple correlation, since high concentrations of nitrogen monoxides destruct O3, limiting its formation: O3 production is determined by a VOCs/NOx ratio and can be VOCs limited, NOx limited, or both. In the MRSP, O3 is mostly VOCs limited (Alvim, 2013; Martins and Andrade, 2008; Sanchez-Ccoyllo et al. 2006). It is the pollutant that has most frequently exceeded the Environmental Agency standards and it also affects the health of the urban population, particularly the respiratory system (WHO, 2015).

One way of decreasing air pollution is controlling emissions. Therefore, the National Environmental Council of Brazil (CONAMA) has develop the Vehicular Air Pollution Control Program (PROCONVE) in 1986. The program established limits for the emissions of some pollutants by motor vehicles, that would gradually decrease (CONAMA 18/86, CONAMA 415/09). This program has proved to effectively decrease air pollution (Carvalho et al., 2015). Nevertheless, the vehicular fleet has been increasing and some pollutants still exceed the air quality standards, demanding new policies to improve air quality in the MRSP.

The goal of the present work is to analyze the spatial distribution and temporal evolution of these three air pollutants in the MRSP, as well as their relation to the meteorological variables, to provide information to

decision making processes in determining the public policies that would efficiently improve air quality in this urban area.

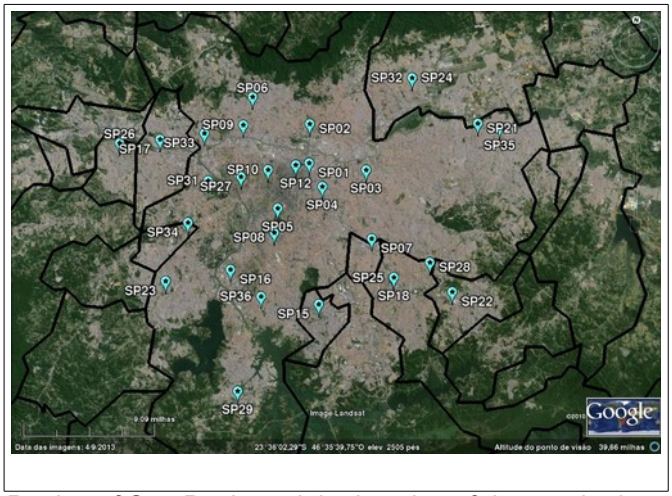

Figure 1: Metropolitan Region of Sao Paulo and the location of the monitoring stations. Black lines are the boundaries of the municipalities and the larger area is Sao Paulo city (23° 32' 51"S and 46° 38' 10"W).

2. Methodology

This work used the monitoring records of 30 stations of the Environmental Agency of the state of Sao Paulo (CETESB) for CO, PM, O3 (air pollutants), temperature, relative humidity, and wind speed (meteorological variables). The stations are described in Table 1 and presented in Fig. 1. The stations record hourly averages of the variables and not all stations record all the variables. A spectral analysis was performed to each station to assess the most significant periods of variation of the pollutants, and diurnal and annual cycles were produced. Then, monthly averages were calculated, a scatter plot was produced, and a trend line analysis was performed by fitting a function to the scatter plot. The best fit was analyzed for each station considering the coefficient of determination (R^2), that indicates the percentage of the variation of the series that is explained by the function. Next, annual averages were calculated and a diagram of the spatial distribution of each pollutant in the MRSP was created interpolating the average concentration for 1997, the first complete year of the series, and 2012 for CO and 2013 for PM and O3, the last year analyzed for each pollutant. Finally, the correlation between each pollutant and each meteorological variable was calculated, when there were simultaneous records of the two parameters, and a statistical test with 95% of confidence was performed.

Station	Location (lat/lon)	CO	MP	O3	Station	Location (lat/lon)	CO	MP	O3
SP01	-23.54454/-46.62759	X	X	X	SP21	-23.498526/-46.444803	-	X	X
SP02	-23.505993/-46.62896	-	X	X	SP22	-23.668549/-46.466	-	X	X
SP03	-23.54940/-46.59838	X	X	X	SP23	-23.668356/-46.780043	-	X	X
SP04	-23.567708/-46.61227	-	X	-	SP24	-23.455228/-46.518456	X	X	-
SP05	-23.5911/-46.66014	X	X	X	SP25	-23.65672/-46.53098	X	X	-
SP06	-23.4801/-46.69205	-	X	X	SP26	-23.53108/-46.83568	X	X	X
SP07	-23.61816/-46.55625	X	X	X	SP27	-23.56075/-46.70157	-	X	X
SP08	-23.61559/-46.66296	X	X	X	SP28	-23.6398/-46.491636	-	X	X
SP09	-23.50865/-46.70114	X	X	X	SP29	-23.77597/-46.69695	X	X	X
SP10	-23.55284/-46.67223	X	X	-	SP31	-23.5659/-46.73737	X	X	X
SP12	-23.547/-46.64217	X	X	-	SP32	-23.455534/-46.51833	-	X	X
SP15	-23.68588/-46.611622	-	X	X	SP33	-23.5184/-46.74332	X	X	-
SP16	-23.65424/-46.70949	X	X	X	SP34	-23.60858/-46.7578	X	X	-
SP17	-23.52602/-46.79156	X	X	X	SP35	-23.501547/-46.420737	-	X	X
SP18	-23.65671/-46.53097	X	X	-	SP36	-23.680508/-46.675043	-	X	X

Table 1: Environmental monitoring station, their locations and pollutants. The X indicates that the pollutant is recorded.

3. Results

3.1 Spectral analysis and diurnal and annual cycles

The spectral analysis presented some differences between the pollutants. PM series presented 1 year as the most significant period, followed by 24 hours, and 7 days (67% of the series). CO most frequent period is 24 hours, followed by 12 hours, and then 1 year, while only 21% of the series presented the 7 days period. For O3, all of the series presented the 24 hours as most significant period, 12 hours was always among the 3 most significant periods, and a period around 1 year was always among the 5 most significant periods (only 7% of the series presented the 7 days period). Therefore, the most significant variation periods for these pollutants are diurnal and annual. Figures 2, 3, and 4 presents the diurnal and annual variations for CO, PM, and O3 respectively.

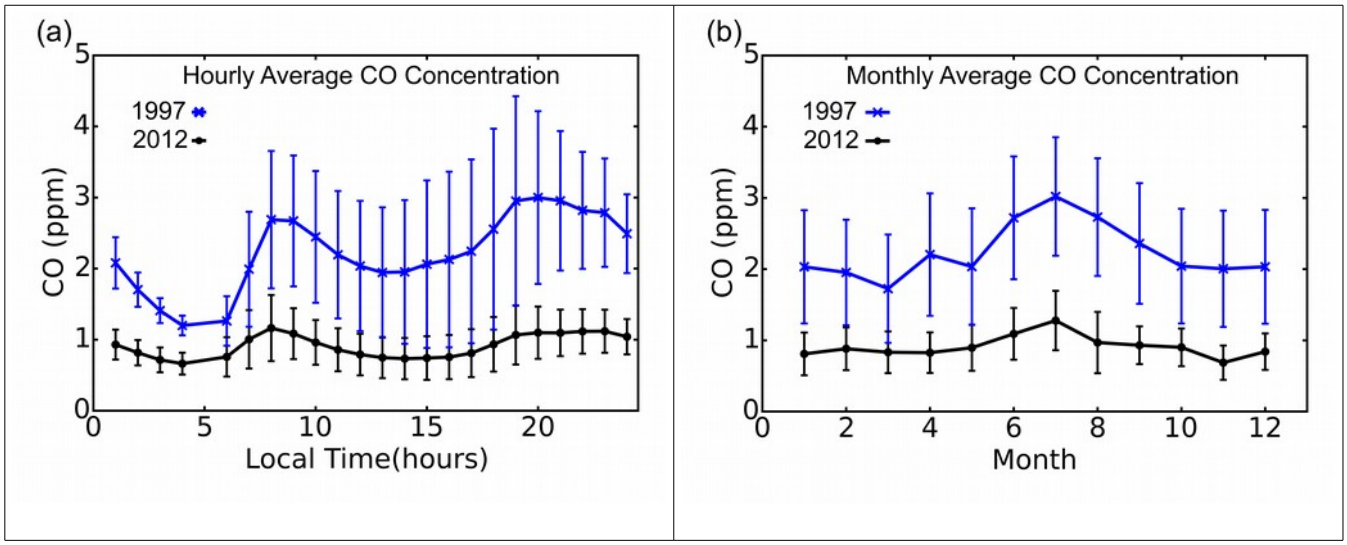

Figure 2: (a) Diurnal and (b) annual evolutions of CO in the MRSP.

Fig. 2 shows that the average concentration of CO has decreased in time. CO diurnal evolution presents 2 peaks, for the morning and the evening rush hours. From 1997 to 2012, the evening peak has decreased in intensity and extended in duration. The annual evolution shows June to August (austral winter) as the most polluted season for both years.

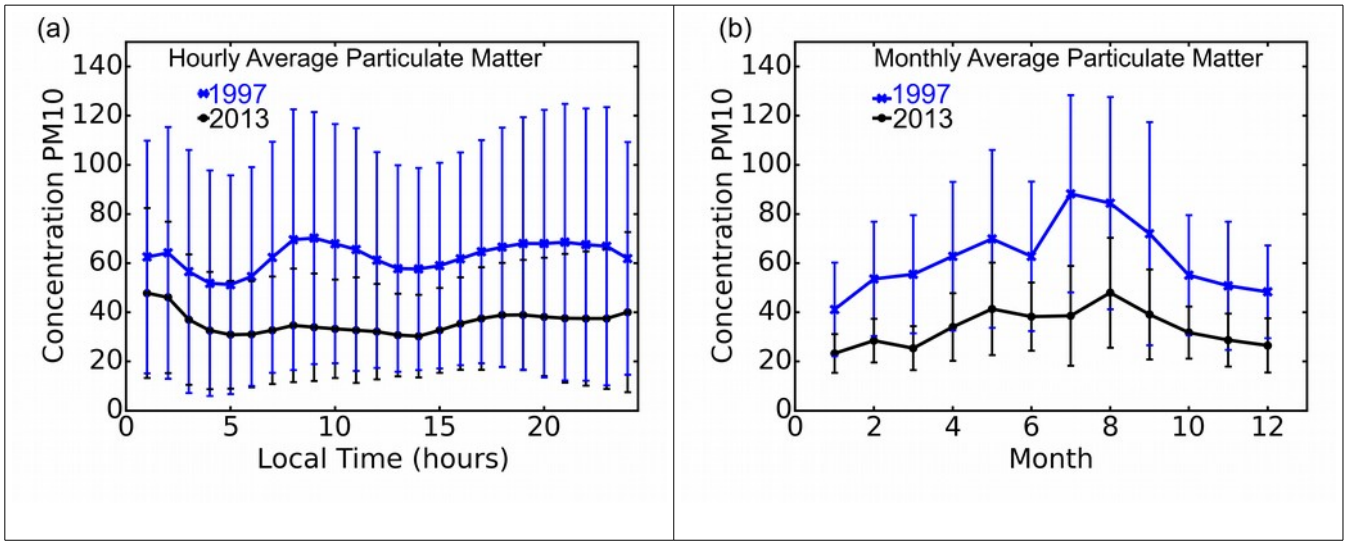

Figure 3: (a) Diurnal and (b) annual evolutions of PM in the MRSP.

PM has also decreased in time (Fig. 3), even though not as drastically as CO. The diurnal evolution shows two peaks during the rush hours and a third one at 0200 LT (Fig. 3a). The latter may be caused by a nocturnal stable boundary-layer. From 1997 to 2012, the rush hour peaks decreased in intensity, particularly the morning peak, and became less intense than the 0100 LT to 0200 LT peak. This change may be caused by the local public policies, that restricted the traffic of heavy-duty vehicles on the center of the city of São Paulo during rush hours and in some strategic motorways during the day (CETSP, 2015). The annual evolution also presents higher concentration during austral fall/winter (May to August), since these are the months with less precipitation.

O3 does not present significant variation in time from 1997 to 2013 (Fig. 4). Nevertheless, 2014 was an anomalous year: during the end of January and beginning of February the presence of an anticyclonic vortex caused subsidence over the MRSP, increasing air temperature near the surface and decreasing precipitation and cloud formation. From October 8th to 19th, the South Atlantic Anticyclone influenced the MRSP, producing again subsidence, decreasing precipitation and cloud formation and increasing air temperature near the

surface. These conditions are favorable to O3 formation and therefore the average concentration of this pollutant was higher than expected for these three months (Fig. 4b). The diurnal evolution shows a peak during the afternoon, since O3 is formed in the presence of solar radiation. There is a subtle peak at 0400 LT, related to a more stable boundary layer and lower inversion height during the night.

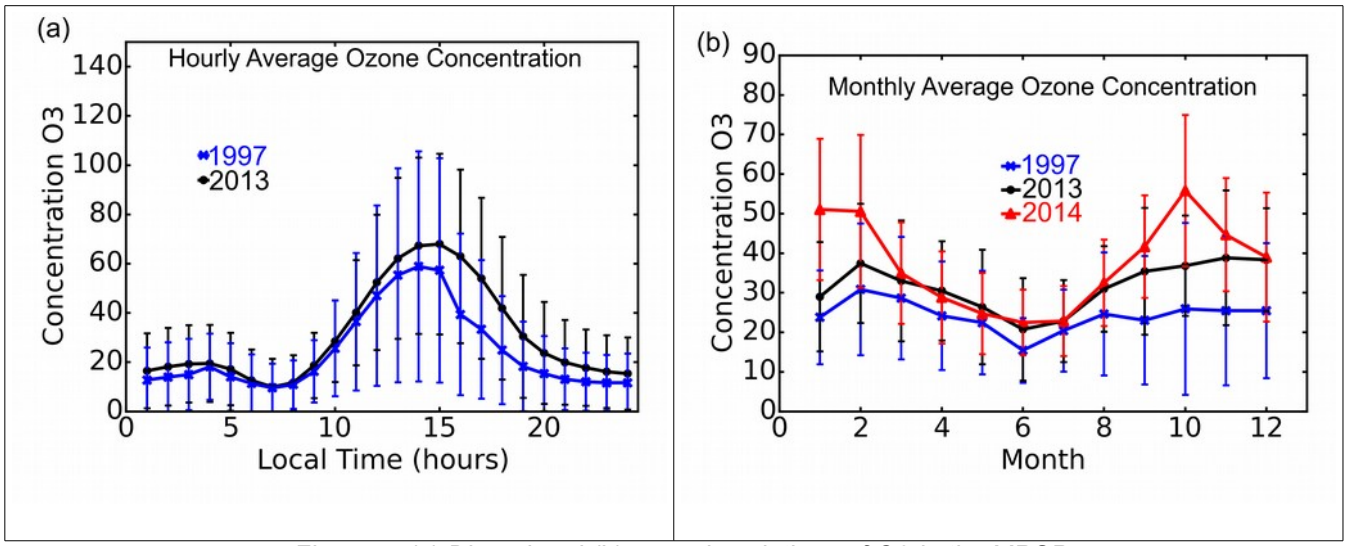

Figure 4: (a) Diurnal and (b) annual evolutions of O3 in the MRSP.

3.2 Trend line analysis

The stations with the longest data record present a clear decreasing tendency for CO and PM. For CO, the tendency follows a logarithmic or an exponential function, with higher monthly decreasing rates at the beginning of the series and much lower rates at the end, that explains in average 62% of the variation of the series (R^2 = 0.62). For PM, the tendency also presented higher monthly decreasing rates at the beginning of the series, and, since 2009, three stations show a later increasing tendency (SP2, SP6, and SP7). The fitted functions explain in average less than 30% of the variation of PM concentration. This trend was caused by the PROCONVE federal program, that gradually restricted the emission factors of many vehicular pollutants. This program may have been aided by local public policies in the MRSP. Since 97% of CO in the MRSP comes from vehicular emission, it is the pollutant that better responded to the program. However, PM concentrations were also affected. Lately, both pollutants are presenting stabilizing tendencies, since the vehicular fleet is growing. O3 does not present a clear tendency, suggesting a greater correlation to meteorological conditions than to the emission of its precursors.

3.3 Spatial distribution

As for the temporal evolution, O3 presents an inverse pattern of spatial distribution in comparison to the other 2 pollutants (Fig. 5): stations with higher concentrations of CO and PM present lower concentrations of O3, and stations with lower concentrations of CO and PM present higher concentrations of O3. The stations with the highest concentrations of O3 are located inside parks, farther from the vehicular sources, as other researches have already observed (Chiquetto and Silva, 2010). CO and PM present higher concentration near their sources, that, in the MRSP, is heavy traffic roads. For the three pollutants, the spatial distribution show a more homogeneous field lately than in 1997, although a more detailed investigation is necessary, particularly using a numerical model.

3.4 Correlation to meteorological variables

CO presented weak correlation to meteorological variables. The highest correlation was to wind speed, but only for stations with higher average wind speed. PM presented low to moderate coefficients of inverse correlation to humidity (from -0.218 to -0.694) with 95 % of statistical confidence, since precipitation helps decreasing PM concentration. Only half of the stations tested presented significant correlation to wind speed, with coefficients ranging from -0.258 to -0.557, and 7 stations presented inverse moderate correlation to air temperature (-0.373 to -0.627). Inverse correlation of PM to air temperature indicates the influence of the boundary-layer development: from sunset to sunrise the boundary layer tend to be more stable, causing a lower inversion and increasing the pollutants concentration. During the day, the boundary layer grows and the pollutants concentration decreases. O3 is more correlated to meteorological variables: all the 6 stations tested for temperature presented moderate to high correlation coefficients (0.5233 to 0.6993), and all the 6 stations tested for relative humidity presented moderate to high inverse correlation coefficients (-0.556 to -0.69). This is related to the need of solar radiation for O3 to form and to the diurnal evolution of O3 (Fig. 4a), that coincides with the diurnal evolution of temperature, peaking a couple of hours after the peak in solar radiation. The stations tested for wind speed presented low to moderate correlation (0.188 to 0.4).

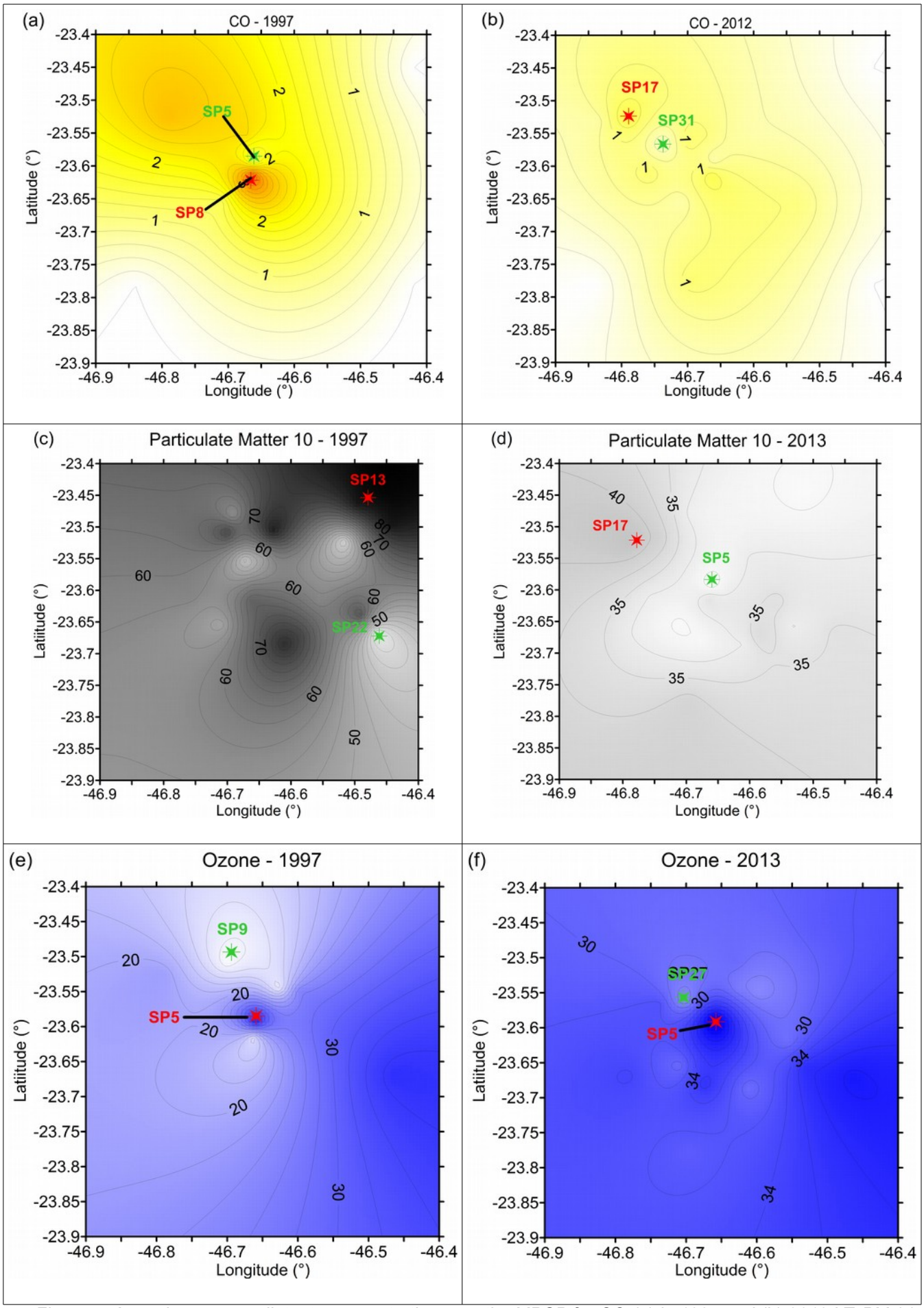

Figure 5: Annual average pollutants concentration over the MRSP for CO (a) in 1997 and (b) 2012 LT, PM (c) in 1997 and (d) in 2013, and O3 (e) in 1997 and (f) in 2013. Stations names in red represent maximum

concentration and in green represent minimum concentration. Contour interval for CO is 0.2 ppm, and for PM and O3 is 2 μg m^{-3}.

4. Conclusions

Public policies are able and should continue to control emissions to provide improved air quality, particularly in high populated areas, although each pollutant requires a different treatment.

1) CO is not currently a great menace to air quality in the MRSP. However, it is a suitable indicator of vehicular emissions and can be a precursor of O3 formation. Therefore, it is an important pollutant to monitor, as it may indicate the efficiency of vehicular emission aimed public policies.
2) PM concentrations have decreased; however, still are a concern for air quality. As PM is only 40% emitted by vehicles and has also natural sources, it is more difficult to control its concentration. Nevertheless, there is still room for public policies that aim to improve air quality.
3) O3 is highly difficult to control, since its formation depends on complex chemical reactions and it is highly dependent on meteorological conditions. It is the pollutant that currently most frequently exceeds the environmental standards, and some public policies are being considered to decrease VOCs emissions.

A next step on the investigation about air pollution in the MRSP may be a numerical study, to better understand the influence of topography and meteorological processes in the pollutants concentration, as well as to have a better description of the spatial distribution of air pollution.

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