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INFLUENCE OF LAND USE AND OCCUPATION ON AEROSOL CHEMICAL COMPOSITION IN THE EASTERN PART OF SÃO PAULO CITY

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1. INTRODUCTION

In large urban centers, one of the main environmental problems is air pollution, related to industrialization and the urbanization of cities, severely impacting human health (Cohen *et al.*, 2017). There is also the influence of pollution sources that are not considered in official inventories, such as biomass burning, waste burning, and regional transport of pollutants (Kumar *et al.*, 2016). The city of São Paulo, located in southeastern Brazil, with a population of approximately 20 million people and concentrating 8 million vehicles, is an example of a megacity that experiences this environmental problem on daily basis (Brito *et al.*, 2013).

Atmospheric aerosol consists of solid and liquid particles suspended in the atmosphere that can influence the climate and cause respiratory and cardiovascular diseases in the population (Kundu *et al.*, 2010; Newby *et al.*, 2015), depending on its size, chemical composition, and structure. Specific chemical compounds can be used as tracers to identify the sources of the pollutant.

The chemical characterization of particulate matter and its pollutant sources have been studied since the late 1970s in the city of São Paulo (Orsini and Bouéres, 1977). Studies showed influence of vehicular emissions, differences in fuels used, resuspension of soil dust, and industrial emissions (Brito *et al.*, 2013; Miranda*et al.*, 2018; Pereira *et al.*, 2017)

The present study aims to identify the main trace elements in fine particulate matter ($PM_{2.5}$) on days of high concentration of this pollutant and its possible relationship with the use and occupation of land in the eastern region of the city of São Paulo.

2. DATA AND METHOD

For the present study, PM_{10} and $PM_{2.5}$ hourly monitoring data were obtained from São Paulo environmental agency (CETESB) in its open online platform QUALAR (CETESB, 2020), for the year 2015. Ten automatic monitoring stations from CETESB and one manual monitoring station located in the East campus of the University of São Paulo (EACH) were used. At this last location, $PM_{2.5}$ samples were collected over a 24-h period (24:00 to 24:00) onto 47-mm Teflon membrane filters with a sampler (Partisol Model 2025i Sequential Air Sampler; Thermo Scientific) operating at a flow rate of 16.7 $L.min^{-1}$. Complementary techniques were employed: gravimetry to determine $PM_{2.5}$ mass concentrations; energy dispersive X-ray fluorescence (EDXRF) to characterize elemental composition; and ion chromatography to determine the composition and concentrations of anions and cations. Thus, EDXRF can detect the following elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Cd, Sb and Pb.

Data regarding meteorological conditions, including wind speed (WS) and wind direction (WD), collected at Guarulhos International Airport, near the sampling site, were provided by the Aeronautic Meteorological Network (www.redemet.aer.mil.br) and were organized by the Master Laboratory at the Institute of Astronomy, Geophysics, and Atmospheric Science.

The hourly average of pollutants was calculated according to the air quality standards established by WHO for particulate matter: 50 $\mu g/m^3$ for PM_{10} and 25 $\mu g/m^3$ for $PM_{2.5}$ in the 24-hour period. The time series of meteorological variables were also reduced, calculating daily averages.

The following criteria have been used to define and identify persistent exceedance events: i) events that occurred at least in 50% of the air quality monitoring stations chosen for this study (being 10 stations in total) and ii) among the

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events that met the first criterion, those with a duration equal to or greater than 5 days, which correspond to the 80% percentile of the event duration distribution. 2 episodes were selected, with 17 days of high concentration of PM_{10} and $PM_{2.5}$.

For the days of high concentration selected, $PM_{2.5}$ samples collected at EACH were analyzed in order to know chemical composition and possible sources of particulate matter.

3. RESULTS

Considering the 2015 daily database, using the WHO air quality standard and the criteria previously mentioned to identify days of high concentration of PM_{10} and $PM_{2.5}$, 17 days were identified between July and September, the austral winter months, consequence of the meteorological conditions of the season: low relative humidity, low precipitation, and atmospheric stability. For such days the elemental and ionic composition of the $PM_{2.5}$ concentrations were analyzed to identify elements with higher elemental proportion in the $PM_{2.5}$.

Selected days of high PM_{10} concentration in the city of São Paulo were usually accompanied by high levels of $PM_{2.5}$ concentration in the eastern region of São Paulo, with an average concentration of approximately 40 µg/m³. The concentrations showed a higher percentage of three main chemical elements, namely: Sulfur, Silicon, and Potassium. Figure 1 shows the percentage of the main chemical elements on the days of these episodes.

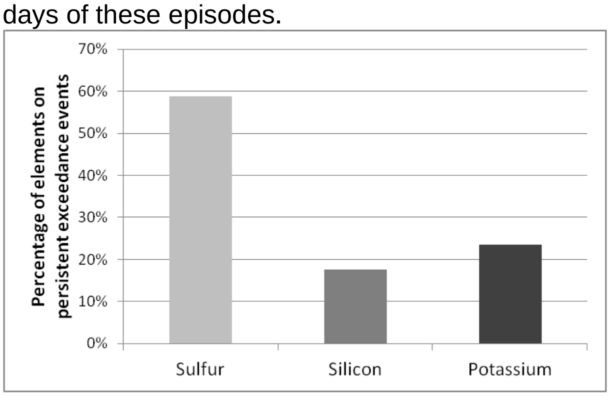

Figure 1: Percentage of the identification of the highest concentration of chemical elements (S, Si, and K) in the 17 days.

The main prominent element was sulfur with an average concentration of 1.73 µg/m³ and presenting the highest mass percentage of the chemical elements in the $PM_{2.5}$ concentration, in 59% of the days of high concentration, possibly associated with vehicular emission. Potassium with an average concentration of 1.02 µg/m³ stood out in 24% of the days and can be associated, for example, with resuspension of road dust and biomass burning. Silicon stood out in 18% of the days with an average concentration of 0.997 µg/m³ and can be associated mainly withs soil resuspension (Miranda, de *et al.*, 2018).

In order to relate land use occupation in the eastern region to possible aerosol sources, wind direction and speed were evaluated in the high-concentration episodes.

Thus, figure 2 shows the WD and WS related to sulfur, with the sampling point location at USP/EACH (23º48'S, 46º49'W). It is observed that the predominant frequency of winds is from the first quadrant (north/east), coming from the highway located north of the university and to the east is an industrial pole, with winds between 0.5 to 5.7 m/s. In this way, the sulfur identified in $PM_{2.5}$ can be associated with vehicular emission from various directions, but mainly from the highway.

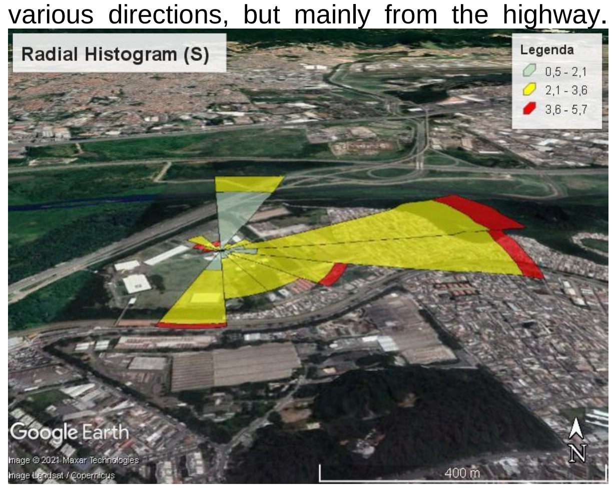

Figure 2: Radial Histogram with the percent frequency of wind direction (WD) and wind speed (WS) for sulfur (S).

Potassium was also a representative element on days of high PM_{10} and $PM_{2.5}$ concentrations. Figure 3 shows that the predominant frequency of the winds is east, an area occupied by the low-income population. Thus, K may be associated with burning waste in the community near USP/EACH.

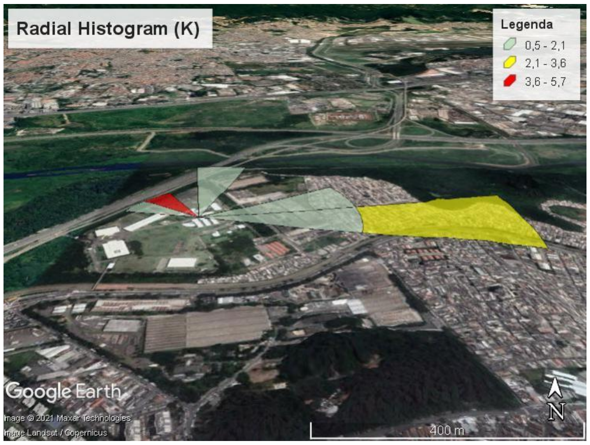

Figure 3: Radial Histogram with the percent frequency of wind direction (WD) and wind speed (WS) for potassium (K).

Figure 4 shows the predominance of wind direction for silicon, it is observed that the winds are mostly from the north (highway) and east(district) and have a more intense wind speed frequency when compared to the other two chemical elements. Silicon for the eastern region of São Paulo may be associated with the resuspension of dust from the soil, road, and pavement.

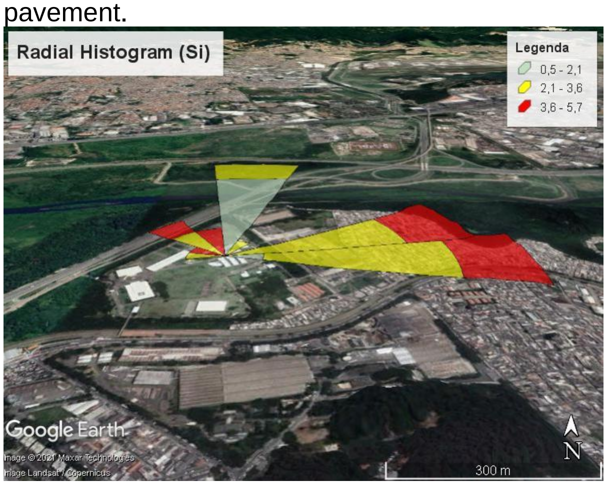

Figure 4: Radial Histogram with the percent frequency of wind direction (WD) and wind speed (WS) for silicon (Si).

For the 17 days studied and analyzed in the present research, it was observed that the prominent ion was SO^{-4} (sulfate), standing out over the other ions on 100% of the days. Wind direction and speed were also analyzed, associating its direction with that of sulfur, possibly being the same pollutant sources, probably influenced by vehicular emissions.

Other chemical elements were also identified on days of high concentration, such as lead (Pb), but their concentration was considered below air quality standards in both Europe and the USA and below the annual lead standards ($0.5 \mu g/m^3$) suggested by CETESB Pb identified in the eastern region of São Paulo can be associated with vehicular emissions and also the international airport, as the wind direction indicates the origin of aircraft influence, as well as previous studies, report the use of Pb in fuels used in small aircraft (Rahim, Pal e Ariya, 2019).

Thus, the influence of land use and occupation in the eastern region of São Paulo is observed through the chemical composition of particulate matter, indicating influences from vehicle emissions, airport, waste and biomass burning emitted by the population of the region, and resuspension of dust from the soil

4. CONCLUSION

Data and sampling of PM_{10} and $PM_{2.5}$ were analyzed throughout 2015 in the eastern region of São Paulo city, a region influenced mainly by vehicular and industrial emissions. 17 days of severe pollution were selected during the winter months, characterized by meteorological conditions unfavorable to pollution dispersion. Considering the trace chemicals obtained through EDXRF analysis, we found that the main contributors were vehicular emissions, resuspension of soil dust, waste burning, and a possible airport influence.

The results presented suggest that local authorities should implement better resolutions regarding vehicular emissions, improve environmental education, sanitation and more sustainable measures to improve air quality and human health.

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