AVALIATION OF CONCENTRATION, SIZE DISTRIBUTION AND CHEMICAL CHARACTERISTICS OF FINE ATMOSPHERIC PARTICULATE MATTER IN THE CENTRAL REGION OF THE STATE OF SÃO PAULO

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Abstract: This study presents physical and chemical analysis of particulate matter (PM) smaller than 2.5 µm presented in Araraquara city atmospheric air. Evidenced the relation between the fires places, air trajectory, concentration, size distribution and chemical analysis of particulate matter sampled by a cascade impactor and an optical monitor. The ionic composition of the particulate matter was analyzed for different particles size. The chemical and physical characterization of the pollutant sampled, evidence the harmful effects to health and climate relate to the increase of biomass burning in industrial processes as energy source.

Keywords: particulate matter, air pollution, chemical analysis, sampling, monitoring, sources.

INTRODUCTION
Currently Brazil is the largest producer of sugar cane (635 million tons) and is responsible for one third of the global harvest, with a planted area of 9,0 Mha in 2014/2015, 90% of the cultivated area are in the Mid-South region, with approximately 157 active sugar cane distilleries (CONAB, 2015). The growing demand of ethanol associated with a future projected expansion and the excess of sugar cane bagasse produced is used more often as a biofuel, cause concerns about the potencial of environment impacts in this region. The prospect of increasing use of bioenergy in many countries has brought international debate concerns about environment impacts, poverty, deforestation and biodiversity reduction, and health problems due to water quality and air pollution emission. (Moraes, M.A.F.D. et al. 2015).

According to França et al. (2012) is necessary to expand the scientific knowledge about the impacts of the growth of ethanol production in Brazil and generate inventory of Greenhouse gases and emission of aerosols associated with this activity. Whether biomass burning is in agricultural activities to facilitate harvest with the burning of the external leaves, or the burning of the sugar cane bagasse in industrial processes to generate energy and heat, is one of the most important sources of pollutant gases and particulates for atmosphere (Urban. R.C. et. at., 2016). The use of sugar cane bagasse as a biofuel in distilleries and industries intensified, and the emission from the burning of this fuel extend to the local population, regional and global (Ibrahim Al-Naiema et al., 2015).

In order to evaluate such changes, the characterization of particulate matter emissions has been and will continue to be studied to determinate its size distribution, concentration and its ionic composition (Oliveira, P.L. et al., 2013). Emitted particle from the burning of biomass has variegated composition, including organic, inorganic, as well elemental carbon. According to Oliveira, P.L. et al., (2013) the variation of size range of particulate matter is related with the different emission sources and its chemical composition. Considering the chemical processes that occurs in the atmosphere, in addition to combustion which favor the formation of fine particulate matter. As some of these elements may come from specific sources, knowledge of the particulate matter distribution combined with the concentration of these elements in the different size ranges is relevant because of the possibility of indicating sources and residence time in the atmosphere, in addition to being able to predict effects due to toxicity (Oliveira, P.L. et al., 2013).

The aim of this study was to evaluate the local atmosphere quality of an important agroindustrial region in the countryside of the State of São Paulo through the sampling of particulate pollutants, considering the number of fires places and the air mass trajectories. It was analyzed the
concentration, particulate matter size distribution and the composition of trace elements present in these pollutants, as well how the distribution of these elements as a function of the particulate size.

METHODS
The study was performed out in the city of Araraquara located in the central region of the State of São Paulo, Brazil. It is located at geographic coordinates 21°47' 37" (South latitude) e 48°10' 52" (West longitude). The particulate material sampling was conducted using optical monitor DataRam (DR4) and Impactador sampler of cascade of eight stages. For the comparative study of particle size distribution with the concentrations of ions present in the samples were analyzed the filters of eight stages of the impactador corresponding to the fractional size distribution (0 to 10 μm). The solutions were submitted to chromatographic determination. The ionic species analyzed were: sodium (Na⁺), ammonium (NH₄⁺), potassium (K⁺), magnesium (Mg²⁺), calcium (Ca²⁺), fluoride (F⁻), acetate (H₃COO⁻), Formate (HCOO⁻), chloride (Cl⁻), nitrite (NO₂⁻), nitrate (NO₃⁻), phosphate (PO₄³⁻), sulfate (SO₄²⁻) and oxalate (C₂O₄²⁻). Ionic species concentrations were determined by ion exchange chromatography using the ion chromatograph Thermo Scientific ICS 5000.

FINDINGS AND ARGUMENT
Figure 1 shows the size distribution and composition of particulate matter sampled. The average particle size distribution was 0.1 to 0.4 μm and reached minimum value 0.0473 μm.

The Figure 2 shows the chemical analyses of particle colletcted in filters. The presence of particles in this size range can have as a primary source to burning of biomass used as industrial fuel or even the open burning of biomass near the area sampled or both for transport of air masses of distant regions. The results of concentration and size distribution were obtained with the optical monitor and confirmed by the impactador, which have larger quantities of particles to the smallest diameter ranges in all sampling days.

The concentration reached values close to 90 μg/m³ with 0.085 μm diameter, with the largest concentration for diameters smaller than 0.1 μm. Evaluating the fire of burned (https://prodwww-queimadas.dgi.inpe.br), the presence of sugar distilleries in the State (Unica2017) e trajectories of air masses (www.arl.noaa.gov/HYSPLIT) is possible pick up a relationship between the results with the emission sources. Evaluating the fire places in the central region and the State, it was found that a large number exist in the North and Northeast region in 02/2017. In the 11/2016 period the greatest amount of fires places was in the Northeast and Northwest and Northeast regions 03/2017. The vast majority of
plants that use biomass as fuel are located in the Northwest, North and Northeast of the state. Evaluating the air mass trajectories in the period from 11/2016 these came from the Northeast regions, in 02/2017 from the North and Northeast region passing specifically by some distilleries and regions with large number of industries. To 03/2017 the masses of air from the Northeast region the same regions. From the analysis of anions present in the filters of different stages of impactador showed the highest concentrations of acetate, formate and ammonium to the larger particles T11 (9-10 μm), Figure 1. A greater range of analytes for the smaller particles T18 (0.4 - 0.7μm) and T19 (0-0.4 μm). Nitrate, sulphate and potassium in stages with particles with diameter less than 1 μm. In the study of Souza, M.L. (2016) made in the same region reported that the nitrate and sulfate are important components of aerosols present in the region of study and related to the burning of sugarcane. The same influence was found for potassium, nitrate and sulfate in 0.4 μm size fraction. According to Souza (2016), the concentration of potassium measured on the day influenced by the biomass burning was about four times higher in comparison to the day that it was not affected by the burning, whereas the concentrations of nitrate and sulfate were about 2 Times on the impacted day.

CONCLUSIONS
The high particles concentration with diameter low that 0.05 μm were observed in 25/11/16. In the anions analysis were observed the higher analytes quantity in the low particles diameters. In the low diameters (below 1 μm) were observed high anions concentration of Sulfate, Nitrite, Nitrate and Chlorate. For the cations observed high concentration of Sodium, Potassium and Magnesium. These analyses are important to predict the possible source of emissions of the particle material and changes of chemical atmospheric.

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