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Environmental Impact Monitoring of a Minero-Chemical Complex in Catalão Urban Area of PTS, PM10 and PM2.5 by EDX Characterization

Lincoln L. Romualdo*[a], Rafaela S. Santos[a], Francielle C. Lima[a], Leonardo S. Andrade[a], Idelvone M. Ferreira[b], Simone A. Pozza[c]

[a] Chemistry Department, Federal University of Goiás / Regional Catalão. Av. Dr Lamartine Pinto de Avelar, 1120, Setor Universitário. CEP: 75704020. Catalão, Goiás, Brazil
[b] Geography Department, Federal University of Goiás / Regional Catalão. Av. Dr Lamartine Pinto de Avelar, 1120, Setor Universitário. CEP: 75704020. Catalão, Goiás, Brazil
[c] State University of Campinas / School of Technology. Rua Paschoal Marmo, 1888, Jd. Nova Itália. CEP: 13484332. Limeira, São Paulo, Brazil
lincolnromualdo@ufg.br

Depending on its nature, particulate matter has very different size, composition and morphology. By the combination of these criteria it is possible to distinguish the emitting sources (primary or secondary). The shape and the dimension of the particles have also a direct interaction with the risk assessment for human health. The minero-chemical complex consists of phosphate fertilizer manufacturing, rock phosphate and niobium mining open pits and it is located northeast of the urban area of the city. Environmental issues associated with it include the following: fugitive emissions which are primarily associated with operational leaks from tubing, valves, connections, flanges, packings, open ended lines, floating roof storage tank and pump seals, gas conveyance systems, compressor seals, pressure relief valves, tanks or open its/containments, and loading and unloading operations of products. Furthermore the area of study is characterized by a predominantly northeast winds direction. The monitoring was performed weekly particulates samples were collected in two seasonal episodes at one representative places in the urban area of Catalão (a Brazilian city located in Goiás state) in the period from August to November of 2014. Suspended particles were sampled on pure fiberglass filters by using a High Volume air sampler and were analyzed via an energy dispersive X-ray microanalysis system (EDX). The airborne particulate matter was characterized from a physico-chemical point of view to supply information on the particle composition and the compounds carried on their surfaces. The microanalysis enables identification of several groups of particles such as: soot, Si-rich, metal-rich and biological particules. These results may help in controlling and preventing fugitive emissions in atmospheric air.

1. Introduction

The air pollution caused by particulate species emission is a serious environmental and health problem (Alfoldy, 2010), especially in less industrialized countries in early stages of industrial growth and that do not present a concern with environmental issues or investments in this field (Xie et al., 2005). In order to understand how these processes influence the processing and contamination of the atmosphere, the monitoring and identification of different chemical species are activities essential. This contaminant species may be present especially in areas where the atmospheric composition is influenced by the presence of anthropogenic sources of gaseous and particulate matter (PM) emissions, such as industrial activities and the increase in local vehicle fleet. (Al-Rajhi et al., 1996). In this sense, the main anthropogenic sources of pollution include any combustion processes and industrial activities, which are more frequently found in

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underdeveloped and in-developing countries that do not have effective policies for monitoring and control of air pollution (Sellitto et al., 2013). Also, it can be highlighted the serious problems concerning air pollution faced by towns and villages that develop economically at the expenses of mining activities. These kinds of activities have caused changes in the original environmental conditions such as environmental pollution, soil erosion and ecological destruction (Liang et al., 2014). Currently the population has become aware on the effects of the anthropic activities mainly due to olfactory disorders caused by pollution (Amodio, 2012). In these places (towns and villages), the major problem is related to the total suspended particles (TSP), PM10 and PM2.5 (Particulate Matter with diameter lower than 10 microns and 2.5, respectively), which can cause the emergence or worsening of pulmonary and cardiovascular diseases. (Huertas et al., 2014). In order to better understand the health effects caused by suspended particles is necessary to know also the physicochemical properties of these pollutants (Singh et al, 2014). The size, composition and origin of these particles vary significantly. For instance, a particulate material sample collected in a city with air pollution problems can contain different types of salts, organic and biological components, iron and/or other metals coming from industrial processes as well as from rock fragments with geological formations nearby (Lu et al, 2006). For this reason, researchers have focused more attention on the effects caused to health taking into account the composition (and sizes) of particulates from different sources than the mass content of these particulates by itself (Vallius et al., 2005). However, some studies have shown a direct connection with the daily hospitalization increasing at people over age 65 diagnosed with asthma, cardiovascular and chronic obstructive pulmonary diseases increase with the increase in the concentration of PM10 (Brunekreef and Holgate, 2002). The possible causes of these effects include the composition of the particulates which may contain, for instance, soluble transition metal such as copper, iron, vanadium, nickel or zinc. Other studies have also reported a correlation between adverse health effects with the particulates in the environment even in concentrations allowed for air quality standards (Lighty et al., 2000).

Considering that the pollution caused by these activities can achieve global levels, the knowledge of the process as well as the impact of these contaminants in the environment can provide important data which can be used in future actions of pollution control by mining activities. Another concern is the possible damage to the natural ecosystem, including soil, fauna and flora degradations (Thornton, 1995). The combustion of coal, biomass and oil fuels are also examples of potential sources of release of particulate matter into the atmosphere, which can vary from millimeter particles to ultrafine particles aggregates with few nanometers in diameter (Lighty et al., 2000). The soil dust present in urban and industrial environments is another common material which represents an important source of toxic metals. Depending on several factors including climate conditions, traffic density, industrial activities and the proximity to the ground, the composition and accumulation of dust can vary significantly.

In Brazil, the current law provides the standards of air quality for total suspended particles, smoke, inhalable particles, sulfur dioxide, carbon monoxide, ozone and nitrogen dioxide (BRAZIL, 1990). Since then, numerous studies have been conducted in order to assess the environment air quality in accordance with the parameters set out in that legislation.

Around the Catalão (a Brazilian city located in Goiás state with a population of about one hundred thousand) are located two alkaline-carbonatite complexes, Catalão Mine I and Catalão Mine II (see the aerial view in Figure 1). Catalão Mine I is located about 20 km to northeast of the city and is a multiphase intrusion with phosphate, niobium, rare earth metals, titanium and vermiculite deposits. Catalão Mine II is located 10 km to north-northwest of Catalão I and is a complex with multiple intrusions. There are, at least, two magmatic systems in this complex: one to the north dominated by phoscorites and carbonatites, and another to the south with nelsonites and carbonatites. Both systems rely on the presence of sulfides in nelsonites and carbonatites (Gomide et al., 2013).

Thus, in light of the aforementioned, the main goal of this work is to describe and discuss the results obtained regarding the investigation of the air quality in Catalão city by monitoring and characterization of the suspended particulate matter in this atmosphere.

2. Methods

Solid particles, known as TPS and PM10 (particulate matter, smaller than 50 or 10 μm), transported by wind have been studied. They have been collected at University Campus, located in urban area of city. There are about 10 km northwest of the site are installed two mining companies that rely on open-pit mining that explore the complexes Catalão Mine I and Catalão Mine II, and its location favors the entry of fugitive emissions in the urban area of the city, as the winds in region are predominantly northwest. Also phosphate fertilizer plants and intensive chemical industry are concentrated at northeast and additionally a high traffic road for trucks pass along. Samples were taken from 24 h using a high volume sampler of Energética® Company, every six days, for a total period of 12 weeks during the winter and fall. One day classified as critical by the air quality national agency (BRASIL, 1990) was also sampled. All filters (glass fiber), were gravimetrically analyzed before and after sampling with a ±2.700 mg microbalance in order to determine the amount of collected particulate matter. Sampling conditions and mass concentrations are shown in Figure 2. The filters were stored under sterile Petri dishes dried in 50 ºC for two hours before characterization. Following an integrated procedure of characterization and identification of the particulate matter using non-destructive analytical techniques. Characterization of the particles (chemistry) was performed using a fluorescence spectrometer for energy dispersive X-ray (EDX 7000, Shimadzu). Because there is no Brazilian legislation on air quality for particulate matter size less than 2.5 µm, we opted to keep all the discussion of this work only for the relevant parameters present in the current legislation.

Figure 1: Aerial view of Catalão area. Urban area (a), Phosphates fertilizer plants (b), Catalão Mine I (c) and Catalão Mine II (d). (Adapted from Google Earth, 2014)

3. Results and Discussion

The concentration data for total particulate matter and fine particles are in Figures 1 and 2, respectively. The Brazilian legislation, by following the international air quality guidelines provides two air quality standards for the air pollutants. The primary standard is the maximum concentration allowed, and the secondary standard is the concentration of pollutants below which the adverse health effect is considered minimum. Besides, the TSP and PM10 concentrations allowed in a 24 h sampling is 240 $\mu g/m^3$ and 150 $\mu g/m^3$, respectively. So, according Figures 2 and 3 it can be observed that during the sampling the TSP and PM10 values were exceeded only once for PM10, in August 20, when the concentration of these particles was 255 $\mu g/m^3$. This high concentration can be attributed to the launch of fireworks, because the city's birthday party. Fireworks are a source of atmospheric pollution that generates large quantities of particulate matter in a short span of time (Sarkar et al., 2010). The secondary standard was exceeded only once for each particle, i.e., in August 20 and September 25 for PM10 and TSP, respectively. Regarding the elemental analysis, Tables 1 and 2 show the results of Energy Dispersive X-ray Fluorescence Spectrometry obtained for TSP and PM10 samples, respectively. Based on the elements identified and showed in Tables 1 and 2, two main sources of emission characteristics could be identified: vehicular and soil emissions. Due to interference of the filter composition used, the elements Si and Ba were excluded from these analyses. The elements Fe, Cu and Zn are related to vehicular emissions, and are identified mainly when the sampling is performed near busy roads. The vehicular emissions include the combustion in light vehicles and the burning diesel in heavy vehicles (Vallius et al., 2005). The elements S and P can be emitted from combustion in heavy vehicles and comprise the fraction of secondary particles. These particles in the air arise from reactions between primary particles, which are released to environmental directly of their source emissions, with the natural constituent of the atmosphere, as occurs for oxygen, for instance (WHO, 2005). Most of these secondary particles are constituted by nitrates, sulphates and ammonia. The soil emissions constitute a majority emission source in the local where the sampling was performed. Added the soil dust, the wind action can resuspend particles coming other particulate emission sources which were deposited by rain or decantation. The elements Al, K, Ca, Ti, Fe, Sr and Zr represent resuspended soil particles, most of which consist of the coarse particles (aerodynamic diameter higher than 10 µm) (Andrade et al, 1994).

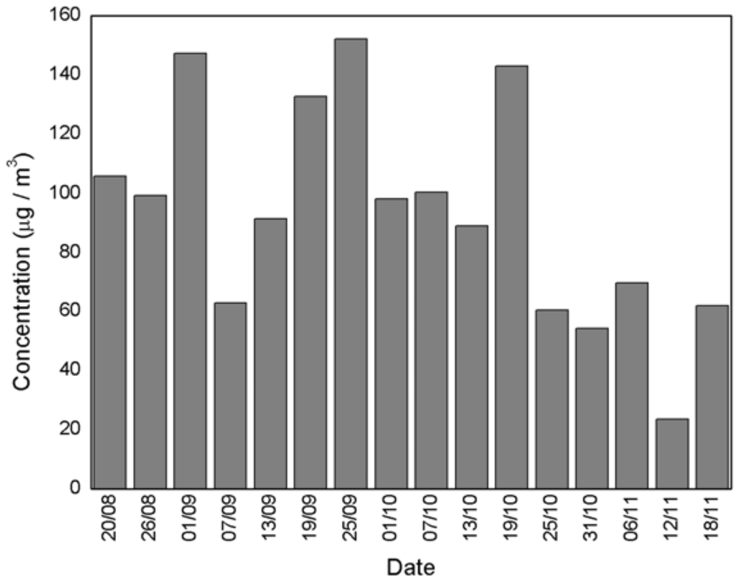

Figure 2: Total suspended particulates concentration

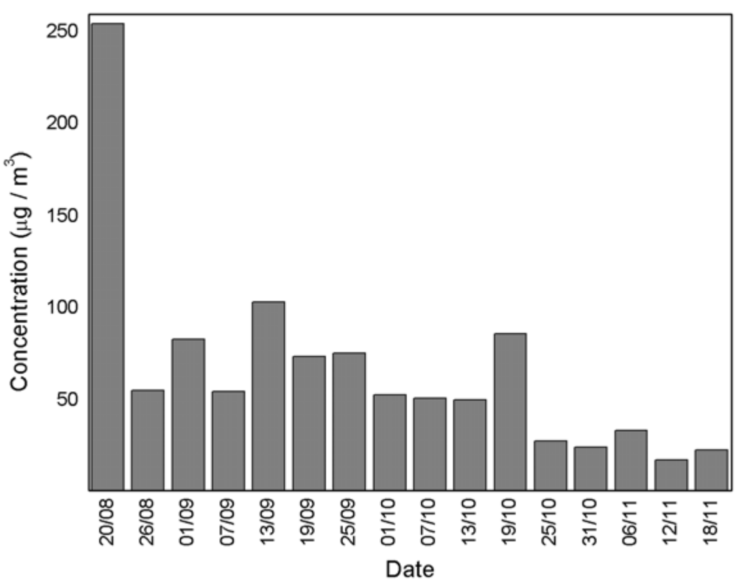

Figure 3: PM10 concentration

Table 1: Elemental analysis of the TSP sample by Energy Dispersive X-ray Fluorescence Spectrometry. The presence or not of elements are checked as "X" or "--" symbols, respectively

Element	Total Suspended Particulates			
	Aug	Sep	Oct	Nov
Al	X	X	X	X
Ca	X	X	X	X
Cu	X	X	X	X
Fe	X	X	X	X
K	X	X	X	X
P	X	X	X	X
S	X	X	X	X
Sc	X	X	X	--
Sr	X	X	X	X
Ti	X	X	X	X
Zn	X	X	X	X
Zr	--	X	X	X

Table 2: Elemental Analysis of the PM10 sample by Energy Dispersive X-ray Fluorescence Spectrometry. The presence or not of elements are checked as "X" or "--" symbols, respectively.

Element	Particulate Matter > 10 μm			
	Aug	Sep	Oct	Nov
Al	X	X	X	X
Ca	X	X	X	X
Cu	X	X	X	X
Fe	X	X	X	X
K	X	X	X	X
P	X	X	X	X
S	X	X	X	X
Sc	--	X	X	--
Sr	X	X	X	X
Ti	--	X	--	--
Zn	X	X	X	X
Zr	X	X	X	X

4. Conclusions

EDX was proved to be an effective method for analysis of airborne particles. This preliminary study focussed on some major element chemistry and particle identification showed that this tool, even if imperfect, yield valuable information on the solid particles and chemical elements present in the air of Catalão. However, accurate data on metal concentrations are needed to obtain a clearer insight into the cause of questions related to respiratory problems in relation to chemical components in the airborne composition. Indeed, it should be kept in mind that once particles can transport (through adsorption or reaction processes) chemicals, including toxic metals. Summary, this contribution indicates that the major sources of pollution by particulate matter in the Catalão city are mainly vehicle emissions and soil dust resuspension. The elements found in the analyses of particulate matter carried further enhance the contribution of these sources, and is a major contribution of soil dust resuspension. For the identification of the elements present in the samples, it can be stated that air quality does not suffer consequences of the intense mining activity around the city. Verification of the real assessment impact of these constituents to the degradation of the natural quality of the atmosphere must be performed by an ongoing study to compare results obtained in the medium and long term. Nevertheless, preliminary studies are needed in order to direct the best way forward.

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