CHEMICAL COMPOSITION OF AIRBORNE PARTICULATE MATTER AND HEALTH RISKS

ABSTRACT:This work reported a research about air pollution in an industrialized city (Volta Redonda – RJ, Brazil). A chemical analysis of atmospheric particulate matter was performed in order to identify and measure the presence of heavy metals. A sample of Total Suspended Particles (TSP) was collected using a HiVol particulate sampler in the period from march until july, 2017. The chemical analysis, made by X-Ray Fluorescence (XRF), showed the majority presence of Iron (79.5 wt.%), followed by Ca (9.54 wt.%), Si (4.8 wt.%), Al (2.34 wt.%) e Mg (2.24 wt.%), the other elements (Cl, Zn, Rb, Pb, Cu Sr, V, Zr) showed contents below 1% in the TSP. The Scanning Electron Microscopy (SEM) showed a predominantly spherical shape of TSP, this shape is typical of metal fumes (iron, zinc and aluminum) generally. The laser granulometry technique showed that 27 wt.% of TSP has 11-58μm of diameter, these particles are usually deposited in the upper respiratory system and may cause respiratory diseases (such as allergies, rhinitis, and sinusitis). 5 wt.% of TSP has<10μm and 2.1 wt.% has<2.5μm of diameter. The large amount of metal in the atmospheric particulate can be harmful because it can be able to cause health risks.

Keywords: Air pollution; heavy metals; X-Ray Fluorescence; health risks

COMPOSIÇÃO QUÍMICA DO MATERIAL PARTICULADO ATMOSFÉRICO E RISCOS À SAÚDE

RESUMO: Este trabalho relatou uma pesquisa sobre poluição do ar em uma cidade industrializada (Volta Redonda - RJ, Brasil). Uma análise química do material particulado atmosférico foi realizada para identificar e medir a presença de metais pesados. Uma amostra de partículas suspensas totais (TSP) foi coletada usando um amostrador de partículas HiVol no período de março a julho de 2017. A análise química, realizada por fluorescência de raios-X (XRF), mostrou a presença maioritária de ferro (79,5% em peso). %), seguido por Ca (9,54% em peso), Si (4,8% em peso), Al (2,34% em peso) e Mg (2,24% em peso), os outros elementos (Cl, Zn, Rb, Pb, Cu Sr, V, Zr) apresentaram conteúdo abaixo de 1% no TSP. A Microscopia Eletrônica de Varredura (MEV) mostrou uma forma predominantemente esférica de TSP; essa forma é típica de vapores metálicos (ferro, zinco e alumínio) em geral. A técnica de granulometria a laser mostrou que 27% em peso de TSP tem 11-58μm de diâmetro, essas partículas geralmente são depositadas no sistema respiratório superior e podem causar doenças respiratórias (como alergias, rinite e sinusite). 5% em peso de TSP tem <10μm e 2,1% em peso tem <2,5μm de diâmetro. A grande quantidade de metal nas partículas atmosféricas pode ser prejudicial, pois pode causar riscos à saúde.

Palavras-chave: Poluição do ar; metais pesados; Fluorescência de Raios-X; Riscos à saúde.

COMPOSICIÓN QUÍMICA DE MATERIAL ATMOSFÉRICO PARTICULADO Y RIESGOS PARA LA SALUD

RESUMEN: Este trabajo reportó una investigación sobre la contaminación del aire en una ciudad industrializada (Volta Redonda - RJ, Brasil). Se realizó un análisis químico del material particulado atmosférico para identificar y medir la presencia de metales pesados. Se recolectó una muestra de partículas suspendidas totales (TSP) usando un muestreador de partículas HiVol de marzo a julio de 2017. El análisis químico, realizado por fluorescencia de rayos X (XRF), mostró la mayoría de hierro (79, 5% en peso). %), seguido de Ca (9,54% en peso), Si (4,8% en peso), Al (2,34% en peso) y Mg (2,24% en peso), los otros elementos (Cl , Zn, Rb, Pb, Cu Sr, V, Zr) presentaron contenido por debajo del 1% en TSP. La microscopía electrónica de barrido (SEM) mostró una forma predominantemente esférica de TSP; Esta forma es típica de los vapores metálicos (hierro, zinc y aluminio) en general. La técnica de granulometría láser mostró que el 27% en peso de TSP tiene un diámetro de 11-58 μm, estas partículas generalmente se depositan en el sistema respiratorio superior y pueden causar enfermedades respiratorias (como alergias, rinitis y sinusitis). El 5% en peso de TSP es <10 μm y el 2,1% en peso es <2.5 μm de diámetro. La gran cantidad de metal en las partículas atmosféricas puede ser dañina, ya que puede causar riesgos para la salud.

Palabras clave: contaminación del aire; metales pesados; Fluorescencia de rayos X; Riesgos de salud.

1. Introduction

The air is essential for survivor on Earth, not only for the human being but also for other living beings. When the air quality is changed, it becomes inappropriate or harmful to welfare, starting to arise many impacts on human health, environment and economy [1, 2, 3].

Since the Industrial Revolution, the issues associated to atmospheric pollution gained notoriety due to their potential health risks, once this industrial expansion contributed to increase the air quality degradation. The migration processes, during the industrialization, increased the urbanization of industrial cities because many people moved from rural areas to these cities searching for jobs. Such process caused an increse of energetic demand and pollutants emission due to the burning of fossil fuel, emitted by mobile sources such as vehicles and stationary sources such as industries, contributing to the environment degradation [4, 5, 6.]

The air pollution is composed by a mix of many components, harmful to human health. However, the damages caused by exposure to particulate matter (PM) have been shown more dangerous to human health, since PM interacts directly with the human body [7]. The lungs are the primary site of deposition, but the particles can be found in many organs, such as liver, kidneys, heart and brain [8, 9.]

The human exposure to air pollutants increases the risks of morbidity and mortality by respiratory and cardiovascular diseases, adverse pregnancy outcomes (low birth weight and premature birth), lung cancer, sickle cell disease, stroke, high blood pressure. The children, seniors and people with a history of chronic diseases are the most susceptible to the deleterious effects of pollutants [10, 11, 12, 13.]

Many epidemiological studies have reported associations between inhalation of particulate matter with lung inflammation and cardiovascular diseases [14, 15]. There is no standard toxic amount, due to the differences in their chemical and physical compositions, the exposure to particulate matter, even at a concentration below the air quality standards, poses a risk to human health [16], [17].

Atmospheric particulate matter is a complex mixture of solid particles and liquid droplets of different sizes and sources (Han et al., 2017). The chemical composition can vary and depends significantly on the emission source, as well as its interaction with the other pollutants that affect the chemistry of the atmosphere [18, 19]. Due to their nature, carcinogenic effects and non-degradability through the food chain, they have been gaining more attention by researchers [20, 21, 22.]

The municipal economy of Volta Redonda city is based on the industrial activity; however, it shows a variety of service and commerce activities [23]. Volta Redonda is the second city of Rio de Janeiro state with the highest potential pollution, only behind Rio de Janeiro city [24]. The industrialization process, population growth and the fast urbanization contributed to the degradation of air quality over time. Researches about atmospheric pollution on human health are important, considering risk areas, as well as the costs for the public health system associated with this kind of pollution [25, 26, 27, 28.]

The particulate matter can be toxic, affecting the air quality e causing serious health damages due to the exposition to chemical compounds. It is worth to mention the existence of many researches about heavy metals in soil and water, however there are few researches that investigate the atmospheric heavy metal concentrations in the particulate matter [29, 30, 31, 32.]

This research is justified by the need to identify the presence of heavy metals in the airborne particulate matter, due to its deleterious effects on human health [33, 34, 35.] The purpose of this work was the chemical analysis of atmosferic particulate matterin order to evaluate its chemical composition (heavy metals).

2. Methodology

2.1. Particulate matter sample

This research was carried out in Volta Redonda, an industrial city of Rio de Janeiro state, Brazil (Figure 1). The chemical analysis of particulate matter had the purpose to identify the presence of heavy metals. The particulate matter sample was collected in the period from march until july, 2017, in some neighborhoods considered more affected by air pollution (Conforto, Belmonte, Vila Santa Cecília and Retiro). The samples were collected in the winter and fall, with a five-month interval between them, by stations situated in each neighborhood. The samples were unified in order to have sufficient amount to perform the chemical analysis of the material.

Figure 1 – Location of Volta Redonda city, Rio de Janeiro State, Brazil [36].

The samples were collected using High Volume Sampler (HiVol) AGV PTS Energética. These equipment is based on the standard NBR 9547 (ABNT, 1997). The sampler location meet the requirements of U.S. EPA (United States Environmental Protection Agency): 20 meters away from threes, buildings or another obstacle; the sampler inlet placed at 2-15 meters away from the ground; the air flow around the AGV PTS free of obstructions; the sampler cannot be placed directly on the ground neither near chimneys or exhaust fans; if the sample needs to be chemically analyzed, local potential contamination sources must be considered. The operation of AGV PTS was performed according to the manufacturer's instructions: after the installation at appropriate place, inside a shelter, a certain amount of air was collected during a period of time (24 hours). The flow was 1.1-1.7 m^3/min [37].

The TSP samples were collected using fiberglass filters (Whatman GF/a 8x10 in, category 1820_866, lot 9549816). The filters were stabilized in a desiccator with silica gel for 24 hours in order to remove the humidity before the initial weighing. Such filters are specific for 99% of minimum efficiency for FDO particles (dioctyl phthalate) of 0,3 µm diameter. An analytical balance (Shimadzu, Ay-220, certified by Instituto Nacional de Metrodologia, Qualidade e Tecnologia – INMETRO, by the code 00415653) was used to weigh the filters. In order to avoid filter damage, glove and tweezers were used to handle the filters.

Before the first sample, the AGV PTS was calibrated through the orifice and U-tube water column manometer, according to the ABNT NBR 9547 method. The instrument was calibrated every 7 days. A new filter was used for each new collection. The removed filter was properly stored for later weighing.

2.2. Chemical analysis of heavy metal by X-ray Fluorescence (XRF)

The XRF analysis was performed using a spectrometer (Malvern Panalytical model Epsilon) in order to identify the chemical composition of particulate matter. This technique was used for this purpose in several studies about chemical characterization of particulate matter [38, 39, 40.]

The XRF is mainly used for solid samples, it allows a simultaneous concentration determination of many chemical elements, without the sample destruction. It is not necessary a pretreatment of the samples. This technique measures the intensity of emitted X-Rays by chemical elements present in the sample. There are three stages: electron excitation, typical X-Ray dispersion by the sample and detection [41]. The emitted X-Ray from a source, excite electrons from de elements, ejecting electrons from one energy level to another, through a quantum leap to fill the vacancy. Energy losses occur during the process, they are emitted in the form of an X-Ray photon, with a distinct energy for each element, the intensities are related to their concentration in the sample [42, 43.]

The advantages of the XRF technique are: no sample destructive technique, unnecessary to make an acid digestion of solid samples for metals analysis (which can lead to losses of heavy metal contents), invulnerable to interference by chemical substances during the analysis.

2.3. Scanning Electron Microscopy (SEM)

The SEM analysis was performed using a Scanning Electron Microscope (Carl Zeiss model EVO MA 1). This technique allowed to identify the TSP morphology. The Scanning Electron Microscopy is a type of microscopy that uses a beam of electrons to scan the entire sample. The interaction between the electron beam and the sample produces effects that are monitored. The resulting signals can be collected in synchronization with the position of the electron beam, allowing information about the sample morphology and generating a three-dimensional perspective image [44].

2.4. Laser Granulometry

The Laser Granulometry analysis was performed using a Particle Size Analyzer (Malvern Instrument model Mastersizer 2000) with the GRADISTAT software [45] in order to identify the granulometric distribution of TSP. The use of this technique, with laser light scattering, has been replacing traditional particle size analyzes to characterize the particle size of materials [46, 47, 48.]

The Laser Light Scattering method uses the interaction of a light beam with particles in a fluid, capturing the intensity of the spreading energy and transforming into volumetric distribution [49].

3. Results and discussion

3.1. Chemical analysis of heavy metals by X-Ray Fluorescence (XRF)

According to the XRF results (Table 1), most of TSP composition is Fe (79.5 wt%) followed by Ca (9.5 wt%), Si (4.8 wt%), Al (2.3 wt%) and Mg (2.24 wt%). The other elements (Cl, Zn, Rb, Pb, Cu, Sr. V, Zr) presented contents below 1wt%.

Table 1 – Chemical composition of TSP by XRF

Element	**Concentration**	**Unit**
Fe	79.5	%
Ca	9.54	%
Si	4.8	%
Al	2.34	%
Mg	2.24	%
Mn	0.52	%
S	0.31	%
K	0.119	%
Ti	0.11	%
Cl	676.1	ppm
Zn	529.1	ppm

Rb	398.2	ppm
Pb	382.3	ppm
Cu	317.7	ppm
Sr	177.6	ppm
V	62.3	ppm
Zr	49.2	ppm

Due to the deleterious effects of heavy metals on human health, researches have been developed in order to study the presence of these metals in atmospheric dust. Vasconcellos et al. (2007) [50] studied the presence of metals in the dust of São Paulo city and found Fe, Al, Cu and Zn, as well as the water soluble metals (K, Na and Mg). The mainly sources of these pollutants were the resuspension of dust, fuel combustion and industrial activities. Pereira et al. (2007) [51] evaluated the presence of metals in atmospheric dust of Salvador city, Bahia state, and found higher amounts of Fe, Zn and Cu, which were attributed to mining and vehicular emissions. The particulate matter toxicity is associated with cardiovascular and respiratory diseases [52].

The XRF results showed the majority presence of Iron (79.5 wt%) in the particulate matter of Volta Redonda (Table 1). The iron presence may be associated to the industrial activity. The basic inputs of steel industry are coal, iron oxide and fluxes, which are the main raw materials used in the steelmaking plants [53] (Mourão, 2007). The exposition to metal iron, by respiratory inhalation, can cause damage to the heart, liver, endocrine, nervous and respiratory system [54, 55, 56, 57.]

Usually, traffic is one of the major source of PM, mainly originating from the wear of vehicle components (brakes and tires) as well as suspension of road dust. The inorganic particles of crystal material from pavement abrasion may contain minerals such as silicon (Si), aluminum (Al), potassium (K), sodium (Na), and calcium (Ca), while brake and tire wear particles may contain metals such as copper (Cu), antimony (Sb), lead (Pb), cadmium (Cd), and zinc (Zn) [58, 59, 60, 61.] Volta Redonda city has currently a car fleet of 143,980 vehicles [62].

Ogundele et al. (2017) [63] used X-ray fluorescence (XRF) to study the contents of Pb, Cr, Cd, Zn, Mn, As, Fe, Cu, and Ni in the size-segregated PM samples and found that heavy metals in the airborne PM pose a severe health risk to people living in vicinity of secondary smelting operations. The diminished air quality with the associated health risks directly depends on the industrial emissions from steel production and control measures are recommended to mitigate the likely risks.

The respiratory system is one of the most affected in the human organism because it is the main point of entry of airborne particles, the effects depend on the chemical composition of the particles, the time of exposure and individual susceptibility. Metal particles of smaller particle size can be absorbed by the human lung during respiration, causing serious risks to human health. Among the main anthropogenic sources of atmospheric emissions of metals are the fossil fuel and wood combustion industries, incineration of waste and industrial processes, as well as vehicular emissions and the resuspension of dust associated with road traffic [64].

The effect of airborne particulate matter in the human organism depends on the chemical composition of the particles, exposure time and individual susceptibility. The respiratory system is the major route of entry for airborne particulate matter. The vehicular emissions and dust resuspension associated to the road traffic are the most important manmade source in urban areas. The presence of metals in the airborne particulate matter is considered a health hazard because they may be adsorbed into human lung tissues during breathing. The main anthropic sources of metals to the atmosphere are: fossil fuel and wood combustion, waste incineration and industrial processes [65], [66], [67], [68].

The XRF results (Table 1) showed 62.3 ppm of vanadium. Among the transition metals, it is worth mentioning the DNA damage caused by vanadium due to its oxidative potential. Their presence in $PM_{2.5}$ has an effect on oxidative DNA damage that is independent of the particle mass or other possible toxic compounds contained in this mixture of particles [69]. The fossil fuel (petroleum and coal) combustion is normally the main source of vanadium in the atmosphere [70, 71.]

Due to the Fenton reaction, the transition metals contained in the particulate material induce airway injury and inflammation. Iron increases the production of reactive oxygen species in vivo (ROS) resulting in cellular and tissue damage, initiating or exacerbating an inflammation [72, 73, 74, 75, 76, 77.] The particulate matter genotoxic effects at the same time can be explained by the presence of such metals. A study with an animal model showed a direct connection between the in vivo role of soluble transition metals in a PM-induced lung injury [78, 79, 80.]

The XRF results showed the presence of 382.3 ppm of Pb in the TSP. Lead is a naturally occurring bluish-gray metal found in small amounts in the earth's crust. Most of

Lead comes from human activities including burning fossil fuels, mining, and manufacturing. Lead can affect the following Organ Systems: Cardiovascular (Heart and Blood Vessels), Developmental (effects during periods when organs are developing), Gastrointestinal (Digestive), Hematological (Blood Forming), Musculoskeletal (Muscles and Skeleton), Neurological (Nervous System), Ocular (Eyes), Renal (Urinary System or Kidneys), Reproductive (Producing Children) [81].

Young children are particularly vulnerable to the toxic effects of lead and can suffer profound and permanent adverse health effects, particularly affecting the development of the brain and nervous system. Lead also causes long-term harm in adults, including increased risk of high blood pressure and kidney damage. Exposure of pregnant women to high levels of lead can cause miscarriage, stillbirth, premature birth and low birth weight, as well as minor malformations [82].

Even a small amount of lead in the particular matter, is harmful to human health. This heavy metal is 90 % absorbed when inhaled, affecting the proper functioning of enzymes and cell membranes. Studies have shown that, for children, the absorption and retention of the inhaled metal is higher than adults (41.5 and 31.8% respectively). Lead contributes to the physical, mental and cognitive delay in children. Adults are affected by hypertension, renal damage, reproductive and digestive system, as well as the nervous system as a whole. Among the effects of this metal, the most serious is encephalopathy, which affects everyone (adults and children) [83, 84, 85, 86, 87, 88, 89, 90, 91].

Due to their metallic state, the heavy metals Fe, Al, Zn and Mn are introduced in the human organism by respiratory system. They are bioaccumulative and, therefore, do not present health benefits, because the organism cannot excrete them. These elements may be considered micronutrients when consumed in the form of food, but when inhaled they may cause adverse effects to humans [92, 93, 94, 95, 96].

Many studies in urban cities worldwide reported the risk of trace metals from airborne particulate matter on human health. Besides its mutagenic effect, epidemiological studies have shown the association between airborne particulate matter and impaired lung, heart disfunction and higher mortality rates [97, 98, 99, 100, 101, 102.]

According to the Global Burden of Disease, in 2015 there were 4.2 million deaths due to the adverse effects of PM on health. The effects vary with the chemical composition, however, evidences about the most harmful elements are still limited. Individual chemicals may play an important role on PM toxicity [103, 104, 105, 106, 107].

According to Valenti (2016) [108], there is a correlation between pulmonary disease and air pollution in industrialized areas. The lack of health and environmental policies about industrial production may result in severe impact on the population health conditions. The inhabitants that reside in close proximity to processing plants tied to the steel industry are the most affected. It is necessary to advocate for more severe environmental and health policies aimed at limiting the hazards associated with the steel industry.

The particular size and chemical composition will influence on the kind of damage caused by the particulate matter on human health. PM usually has inorganic compounds (sulfates, nitrates, transition metals, soluble salts) organic compounds, such as aromatic polycyclic hydrocarbons, and also biological material [109, 110].

According to Milanez (2008) [111], the pollutants emitted from the steel production process are: hydrogen sulfide (H_2S), sulfur oxides (SOx), carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6), nitrogen oxides (NOx), carbon monoxide (CO), different organic hydrocarbons such as benzene and particulate matter (dust, soot, ore fines). The movement of the motor vehicles also contribute to the resuspension of inhalable particles [112, 113].

Quality standards play a key role in air quality management. In Brazil, such standards are provided by CONAMA Nº 491/2018. The Brazilian environmental legislation (CONAMA 491/2018) only quantifies the maximum amount of particulate matter in the atmosphere, however the chemical compounds in this particulate matter is not specified. The presence of heavy metals in the atmospheric particulate matter can be dangerous to the health of those people residing in the region, increasing the number of diseases and the health expenditures. Depending on the kind of chemicals present in the particulate matter, the population may be exposed to a higher risk of diseases.

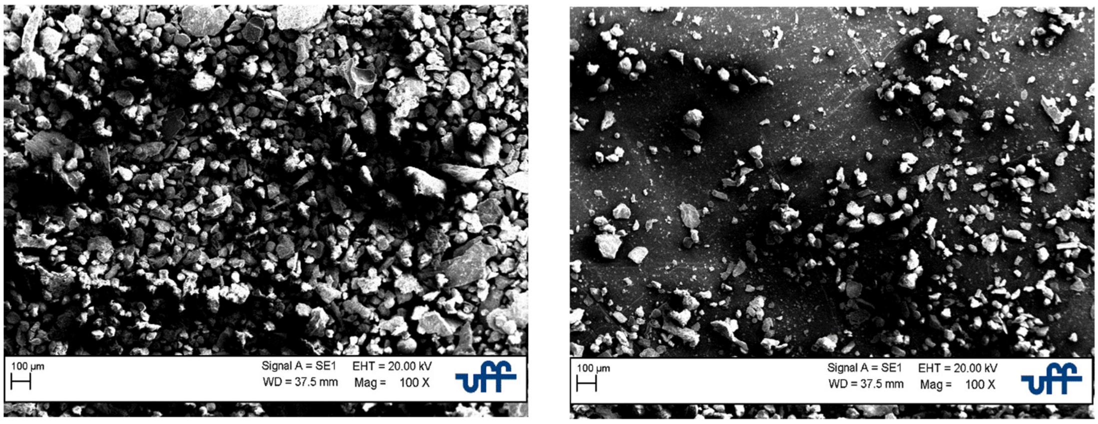
Particulate matter is one of the most efficient carriers of pollutants to the human organism. It can cause irritation of the respiratory tract, inflammation and increased bronchial reactivity. Moreover, it can reduce the transport of ciliary mucus, with exacerbation of bronchial asthma attacks, increased respiratory infections and worsening of wheezing. Continuous exposure to PM may contribute to increased risk of respiratory diseases, arteriosclerosis and lung cancer. In a short period of time the exposure to PM may lead to increase the number of diseases, such as asthma, bronchitis and heart rate changes [114, 115, 116, 117, 118, 119].

3.2. Scanning Electron Microscopy (SEM)

The microscopic analysis of TSP (Figure 1) by SEM showed a predominantly spherical shape. Generally, this shape is typical of metal fumes of iron, zinc and aluminum [120].

The inhalation of dust and fumes containing iron oxides may cause pneumoconiosis called pulmonary siderosis, which may lead to an increased incidence of lung cancer [121].

Figure 1 – Scanning Electron Microscopy (SEM) image from Total Suspended Particles (TSP)



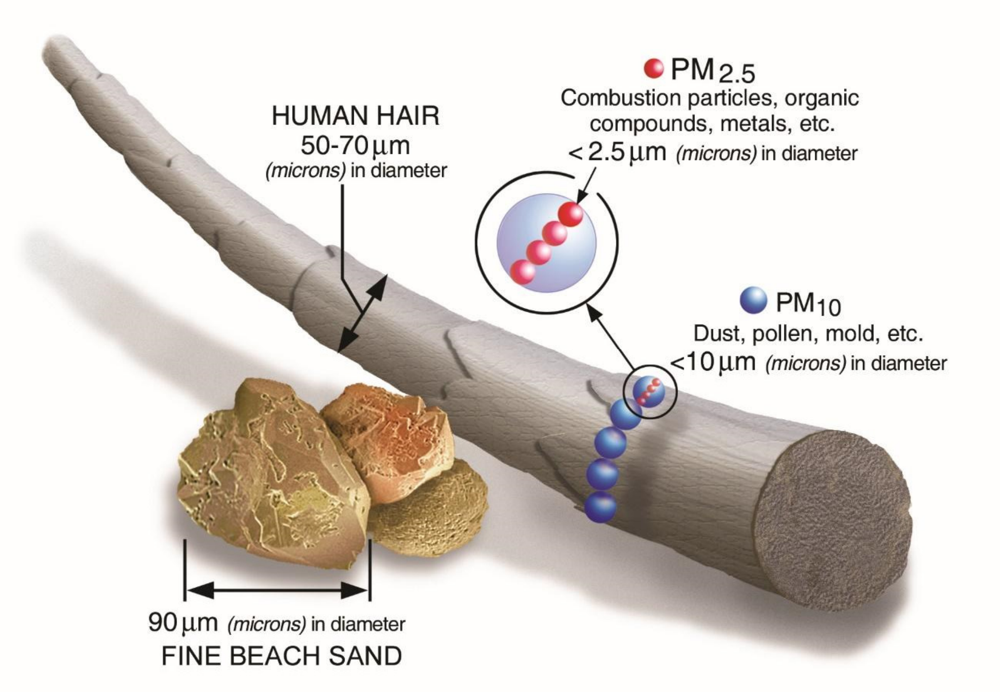
3.3. Laser granulometry

The laser granulometry analysis showed that 27 (wt%) of TSP has 11-58µm of diameter, 5 (wt%) has <10µm and 2.1 (wt%) has <2.5µm of diameter.

The effects and health risks of particulate matter emitted by industrial activities and automotive vehicles can vary depending on both chemical composition and particle size. Thick particles, i.e., larger than 10µm, are usually deposited in the upper respiratory system and may cause allergies, rhinitis, and sinusitis.Small particles can reach the pulmonary alveoli and accumulate in the lungs, the inhalation of dust causes lung diseases (such as pneumoconiosis and cancers) [122, 123].

Figure 2 [124] shows a comparison between fine and coarse particle size with human hair and grain of sand. Some particles, such as dust, dirt, soot or smokeare large or dark enough to be seen with the naked eye. Others are so small that can only be detected using an electron microscope. PM_{10} are inhalable particles, with diameters generally smaller than 10 micrometers. $PM_{2.5}$ are inhalable fine particles, with diameters generally smaller than 2.5 micrometers.

Figure 2 –Size comparisons for PM particles [121]



Particulate matter can cause several diseases, leading to a significant reduction of human life. It can be suspended for a long period of time and travel for long distances in the atmosphere. The particle size plays as important role in thecause of human health damages. Inhalable particles are those with 2.5 to 10 µmin diameter and fine particles are those smaller than 2.5 µm in diameter (KIM, KABIR and KABIR, 2015). The smaller particles can penetrate more deeply on the respiratory tract. The coarse PM, larger than 10 µm in diameter, can be filtered by the cilia and the mucus in nasal-breathing. It tends do lodge in the trachea or in the bronchi because the coarse PM settles quickly. This kind of PM is initially collected in the nose and throat. Then, the human body will react in order to eliminate the intruding PM through process like sneezing and coughing [125], [126], [127]. Damage to the lungs and the respiratory system due to the air pollution is responsible for more than two million deaths worldwide each year [128, 129, 124].

The exposure to PM can directly influence the mortality by cardiopulmonary disease and ischemic heart disease [130, 131, 132, 133, 124]. Approximately 5% of lung cancer and 3% of cardiopulmonary deaths worldwide are attributable to PM exposure. Also, the exposure to PM2.5 [134, 124].

The toxic effects of heavy metals are associated with their amount. They are able to reach different organs, modifying biochemical processes and cell membranes. These metals enter the human body through digestive, cutaneous and respiratory tract. They are reactive and bioaccumulative [135, 136, 137, 138].

4. Conclusions

The XRF analysis of Total Suspensed Particles (TSP), from Volta Redonda city, showed the predominance of Fe (79.5 wt.%) and the SEM analysis showed a predominantly spherical shape, typical of metal fumes. The Laser Granulometry showed that 5 (wt%) of all suspended particulate matter has inlatable size.

This high iron content may be associated to the industrial activity in the city. The traffic also contributes to the emission of PM, mainly originating from the wear of vehicle components (brakes and tires) as well as suspension of road dust.

The lack of health and environmental policies about human activities such as industrial processes may result in severe impact on the population health conditions. More effective public environmental policies are necessary for an appropriate management of air quality.

Acknowledgments

To Profª. Ana Carolina Callegario Pereira, Prof. Cesar Marcelo CajazeiraVidal and Prof. Anderson Gomes from Centro Universitário de Volta Redonda (UNIFOA), by providing the particulate matter sample.

To Prof. Emmanoel Vieira da Silva Filho from Departamento de Geogiências of Universidade Federal Fluminense (UFF), by the X-Ray Fluorescence and Laser Granulometry analysis.

To Prof. Gláucio Soares da Fonseca from Laboratório Multiusuário de Microscopia Eletrônica (LMME) of Universidade Federal Fluminense (UFF), by the Scanning Electron Microscopy analysis.

To Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) by the master studentship for Jéssica Guerra Inácio de Oliveira.

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