

Article

Atmospheric pollution monitoring by water rain analysis

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Abstract: Environmental legislation is moving towards global standards for ease of application and to impose sanctions and penalties when necessary, without compromising human health and biota. International environmental measures for control and monitoring of atmospheric air only monitor emissions of SO_x, NO_x, O₃, and Pb. In general, most research work in air pollution done using the analysis of elements in rainwater show analysis of trace metals such as Na, Mg, Zn, and Mn. In this work, trace metals in the rainwater at the city of Goiânia, capital of the State of Goiás, were analyzed. Goiânia is a large city set in a predominantly agricultural province located in central Brazil. Presence of trace metals in rainwater was detected, indicating atmospheric air pollution levels higher than occupational limits set by WHO.

Keywords: Rainwater; Air pollution emissions; Health; Environmental law, Environmental policy instruments

1. Introduction

Urban development causes deleterious effects on the environment through hydrological cycle modifications caused by the reduction of permeable areas, which, in turn, leads to increased runoff in large urban centers [1].

Soil waterproofing increases rainwater evaporation [2] leading to floods in urban centers, causing an increase in urban chaos and carries contaminants that have been deposited in rooftops, building facades, sidewalks, vacant lots, etc, during the dry season.

These particulates are capable of binding toxic substances either by simple deposition or by adsorption. When leached by rainwater, they reach the soil, bodies of water and atmospheric air through evaporation, especially in countries where the hot climate is predominant, such as Brazil [3-5], or in regions where precipitation has been altered by particle and gas emission from anthropogenic actions and forest fires during the dry season [6].

Rainwater is an important source of diffuse environmental contamination. Trace elements contained in the rain can be carried by long distances, deserving attention by the environmental control bodies [7] because of the high degree of metal toxicity in the rainwater and the short-term environmental impact that metals have on the environment: inability to degrade and bioaccumulation in living organisms [4].

Metals such as Zn, Pb, Ca, Cu, Cd, Cr and Ni, resulting from leaching processes of building materials, atmospheric deposition, brake and rubber tire wear, gasoline and oil car leaks, are examples of trace elements that are released into nature by common sources of emission that make up the routine of urban centres, not counting the industrial waste disposal in cities with industrial production [1,8-11].

The ability to carry trace elements through rainwater is so high that Cd, Cu, Fe, Mn, Ni, Pb, and Zn were found in a remote marine region of the island of Bermuda, about 1,000 km east of the North American continent [11]. This study was carried out by collecting rainwater for one year in regions distant from vehicle traffic, trees and buildings.

Bunio et al. [12], in addition to the cardiovascular and pulmonary diseases that are already widely attributed to the increase in the concentration of atmospheric pollutants in the human metabolism [6,13-15,3,15], correlated the incidence of diseases such as diabetes and obesity and the presence of trace elements in rainwater as an indirect indicator of the existence of airborne dust. They also showed that there was an increase in the frequency of hospitalization caused by the deterioration of the endocrine system of the population of Opole Voivodeship (province in Poland with a population of one million) from 2000 to 2002. In the case of diabetes-related syndromes, there was a strong correlation between the presence of chromium, cadmium, lead and zinc in men and women [12].

The problem of the presence of trace elements in rainwater has been the object of study in several countries due to the health problems it causes. Báez et al. [16] analysed rain in Mexico City, finding several trace metals such as Cd, Cr, Mn, Ni, Pb, V and Al. The latter element appeared in higher concentrations due to anthropogenic emissions.

Trace elements in the atmosphere from artificial and natural emission sources were found in Greece due to Etna Volcano emissions in Naples, Italy, due to the ease of transporting pollutants over long distances, mainly through ocean currents [17]. A similar observation of pollutants from vehicles and natural volcanic sources was made by Gonzáles [18] in a study carried out in a medium size city in Colombia.

Economic development and strong industrial production have also generated particle emissions in the atmosphere, and from the beginning of this century, they began to be the subject of publications demonstrating the presence of particles containing trace elements in critical Brazilian capitals (1998) especially industrialized centers such as Rio de Janeiro, Curitiba, and São Paulo [1,19-20]. De Mello [19] found, at the Rio de Janeiro metropolitan area, more amounts of metal particulates in the atmosphere in the rainy season compared to periods of drought.

The São Paulo metropolitan area, the largest and most polluted Brazilian city, still among the 20 worst cities in the world concerning atmospheric pollution [6], has a population of 20 million and 1/5 of the country's vehicles. The most important Brazilian city presents a substantial variation of particulates during the day, especially during the warmest working hours. The presence of trace elements in the particulates, as well as the compounds CO_x, NO_x, and SO_x, are usually present in the air of the metropolis [21]. Elements Cd, Pb and Cu, suspended in atmospheric air, predominate during the rainy season [22].

A study carried out in Curitiba, a large urban centre located in the temperate southern region of Brazil, simulated the leaching of rainwater on brakes, roofs and in reservoirs containing residues of lubricating oils, which were washed with synthetic rain, applied with a spray gun, to produce wet and dry atmospheric deposition samples collected in one gallon of PET plastic material. This study

was able to detect the release of several metals which would be carried by rainwater, and, in increasing order of abundance, were Zn, Pb, Cu, and Cd [1].

Even smaller cities, with strong anthropogenic actions provoked by emissions from cement industries, showed particulates in atmospheric air containing trace elements, as found in the towns of Laranjeiras and Nossa Senhora do Socorro, cities of the state of Sergipe, in north-eastern Brazil, with the presence of Al, Ca, Cu, Fe, K, Mg, S, Sr and Zn in its atmospheric air, whose population is 29,603 and 160,829 respectively [23].

The present study aims to determine the presence of trace elements air of the city of Goiânia, capital of the State of Goiás, located in the center of Brazil. Goiânia, unlike a sizeable industrialized metropolis, has regional economic activity in agriculture.

2. Materials and Methods

The study site was the city of Goiânia (-16.67°L, -49.25°N), capital of the state of Goiás, located in the center of Brazil. Its population is approximately 1,300,000 (2010 Census) distributed in an area of 733 Km². The city has a fleet of more than 1 million vehicles. In 2012, every 1.22 citizens of Goiânia had a vehicle at his disposal. In 2011, this number was 1.27, showing that the car fleet grows more than the local population.

The Goiania's biome is the tropical savannah "Cerrado" and its most important economic activities are within the service sector but it is located in an eminently agricultural state [23].

Five locations were chosen for the collection of rainwater, based on the works carried out by Muro and Antoniosi Filho [24] and by Brait and Antoniosi Filho [25]. Locations were chosen based on the highest concentration of atmospheric pollutants in the city. The positions where the rainwater collectors were allocated are indicated in Figure 1 and the geographical coordinates shown in Table 1.

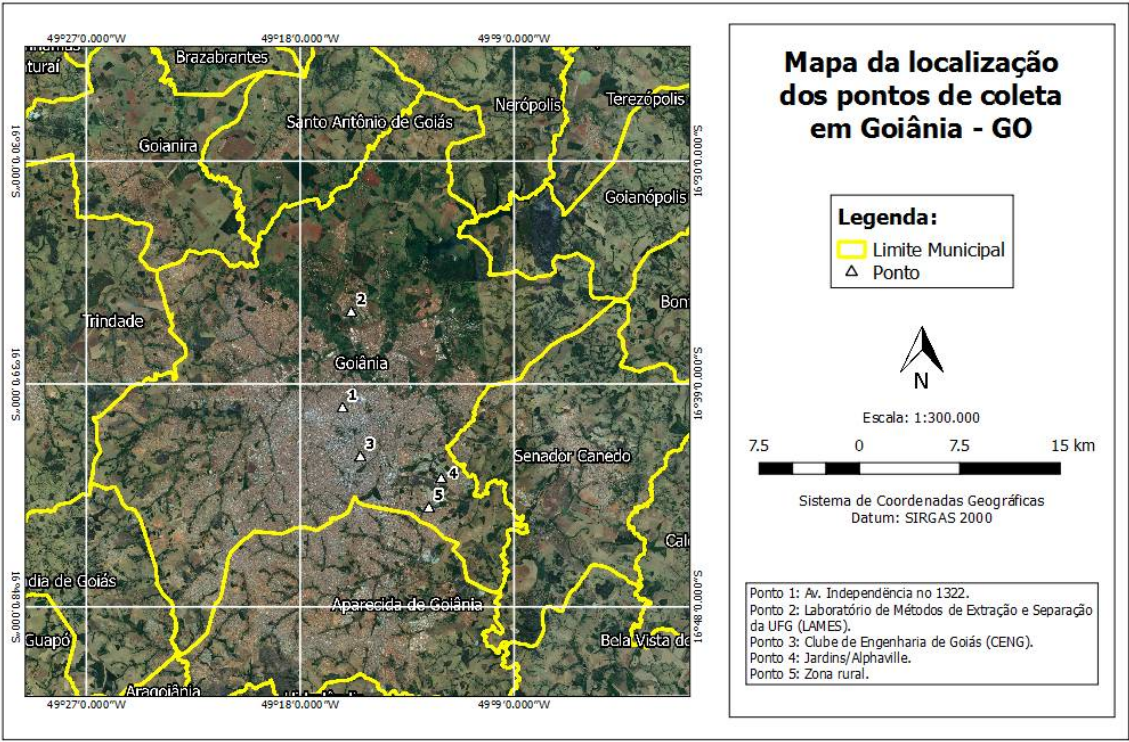


Fig. 1. Five locations used for rainwater collection in the city of Goiânia, Brazil.

Table 1

UTM Coordinates and geographical coordinates of locations for rainwater collection

LOCATION	LOCATION OF				
	SISCO	X (UTM)	Y (UTM)	LATITUDE	LONGITUDE
INSTALLATION					
1	Avenida Independência	684463	8156514	16°40'00"S	49°16'13"O
2	Campus II UFG/ LAMES	685182	8163659	16°36'08"S	49°15'51"O
3	Clube de Engenharia	685783	8152826	16°41'58"S	49°15'28"O
4	Alphaville/Jardins	693259	8150657	16°42'51"S	49°12'04"O
5	Zona Rural	690856	8149018	16°44'02"S	49°12'35"O

Rainwater samples were collected from February 2nd, 2013 to March 18th, 2013.

To analyze the chemical composition of rainwater, wide mouth polyethylene flasks with a capacity of 1L were used. They were previously submitted to a decontamination procedure by immersion in 10% nitric acid for 24 hours, triple wash with Mili-Q® grade deionized water and total drying.

Immediately after the onset of rainfall, the plastic beakers for collecting rainwater were placed on a pedestal 1.0 m high (Figure 2) and positioned in an open field. Care was taken so that only rainwater was collected, and the beakers were place at a minimum distance of 50 meter from any source that could cause contamination in the rainwater sample, such as trees, roofs or any type of construction capable of carrying sediments by the wind.



Fig. 2. Pedestal for placement of beakers for rainwater collection.

The eventual contaminations of the collected water by birds or the accumulation of visible sediments in the flasks caused the samples to be discarded.

Six samples were collected at Location 1, two samples at Location 2, four samples at Location 3, four samples at Location 4 and six samples at Location 5.

After collection, the samples were transferred to 100 mL polyethylene bottles, previously submitted to decontamination procedure and acidified with Vetec® 70% Ultra Pure Metal nitric acid.

Metal analysis was performed with ICP-OES from Thermo Fisher Scientific, model iCAP 6300 Duo, with the following accessories: tygon tubes, concentric nebulizer, cyclonic nebulizer chamber and 2 mm central tube.

The wavelengths were chosen to take into account the lines with the highest intensity and the lowest number of interferents: Al (396,152 nm), B (249,773 nm), Ba (455,403 nm), Be (234,861 nm), Bi 223, 666 nm), Cd (214.438 nm), Cu (228.616 nm), Cr (267.716 nm), Cu (324.754 nm), Fe (259.940 nm), K (769.896 nm), Li (670.784 nm) Mn (280.270 nm), Mn (257.610 nm), Mo (202.030 nm), Na (588.995

nm), Ni (231.647 nm), P (178.284 nm), Pb (220.353 nm), Sn (189.989 nm), Sr (421.552 nm), Ti (337.280 nm), Tl (190.856 nm), V (292.402 nm) and Zn (206, 200 nm).

The readings were performed using axial torch vision, pump rotation of 50 RPM, auxiliary argon gas flow of 0.5 L min⁻¹, argon gas pressure of 0.16 M Pa and power source of 1250 Watts.

The quantification limits were calculated by multiplying the standard deviation of 10 blank analyses (Milli-Q acidified water) by 10, divided by the angular coefficient of the respective calibration curve are some examples for citations. Haydar and Khire [1] used this method. Brachman et al. [2] introduced a new method in the conference. Similar materials are used in these studies.

3. Results and discussion

The average concentration of trace elements that were found in rainwater in Goiânia for the five collection locations, following a decreasing quantitative order, were: Ca > Al > Sr > Mg > Fe > Na > Zn > Mn > Ba. The concentrations of trace elements found are listed in Table 2 along with the human exposure limits for occupational environments determined by the World Health Organization [27] and with limits for human consumption as recommended by the Brazilian standard CONAMA Resolution No. 357, amended by CONANA Resolutions No. 410/2009; and 430/2011 [27].

Table 2
Average concentration of trace elements found in Goiânia and occupational limits established by the WHO and CONAMA for water for human consumption. Units: mg m⁻³

<i>Element</i>	<i>Alphaville</i>	<i>Av. Ind.</i>	<i>CENG</i>	<i>LAMES</i>	<i>Rural</i>	<i>WHO⁽¹⁾</i>	<i>CONAMA⁽²⁾</i>
<i>Al</i>	86,11	94,54	55,04	36,16	152,55	0,01	100
<i>Ba</i>	< L. Q.	< L. Q.	< L. Q.	0,48	< L. Q.	- ⁽³⁾	700
<i>Ca</i>	2494,72	3208,20	2001,64	97,41	61,43	0,005	-
<i>Fe</i>	30,83	17,03	13,54	49,93	17,50	-	300
<i>Mg</i>	43,13	52,41	31,66	17,41	13,71	-	-
<i>Mn</i>	0,63	< L. Q.	0,29	0,68	0,80	0,001	100
<i>Na</i>	< L. Q.	0,0241	0,0633	< L. Q.	0,02156	-	-
<i>Sr</i>	13,70	17,98	11,23	< L. Q.	< L. Q.	-	-
<i>Zn</i>	2,83	1,41	1,69	1,98	0,51	0,001	180

(1) Occupational exposure limits.
(2) Emission limits in fresh waters for human consumption.
(3) “-” Absence of limits, both in WHO standards and in Brazilian standards.

The choice of these occupational emissions limits is because these limits usually consider human exposure to the pathogenic substances during a mean time interval of 8 h d⁻¹. Since the exposure to pollutants contained in dry or humid atmospheric air is higher than the time used as an occupational limit, such restrictions were used as a reference for human exposure and compared to trace element pollution levels found in rainwater in Goiânia.

Analysis of the levels of contamination of trace elements in rainwater for Al, Ca, Mn and Zn indicates there was environmental contamination above the limits suggested by WHO [28] as not pathogenic to human health. The trace elements Ba, Fe, Mg, Na and Sr, although detected in rainwater, were not present above limits established by WHO [28]. The representations of the trace element quantitative values compared to the limits defined by the WHO are shown in Figures 3 to 11.

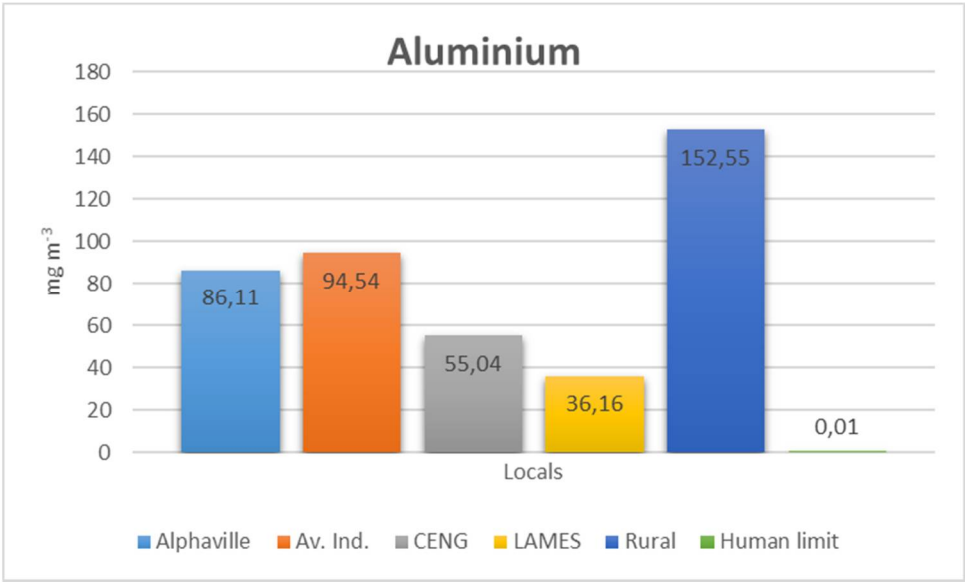


Fig. 3. Aluminium emission levels at the five collection locations and levels considered acceptable by the WHO.

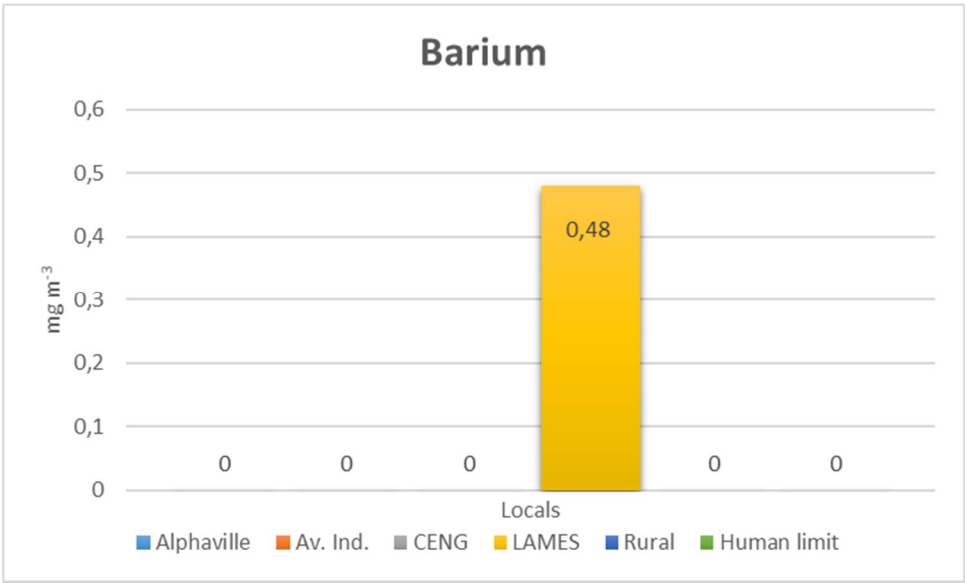


Fig. 4. Barium emission levels at the five collection locations and levels considered acceptable by the WHO.

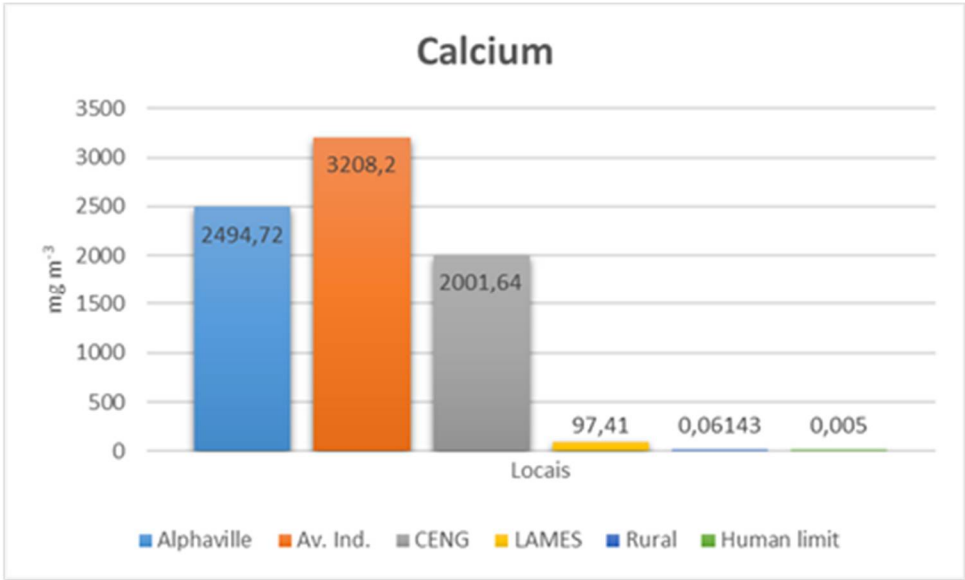


Fig. 5. Calcium emission levels at the five collection locations and levels considered acceptable by the WHO.

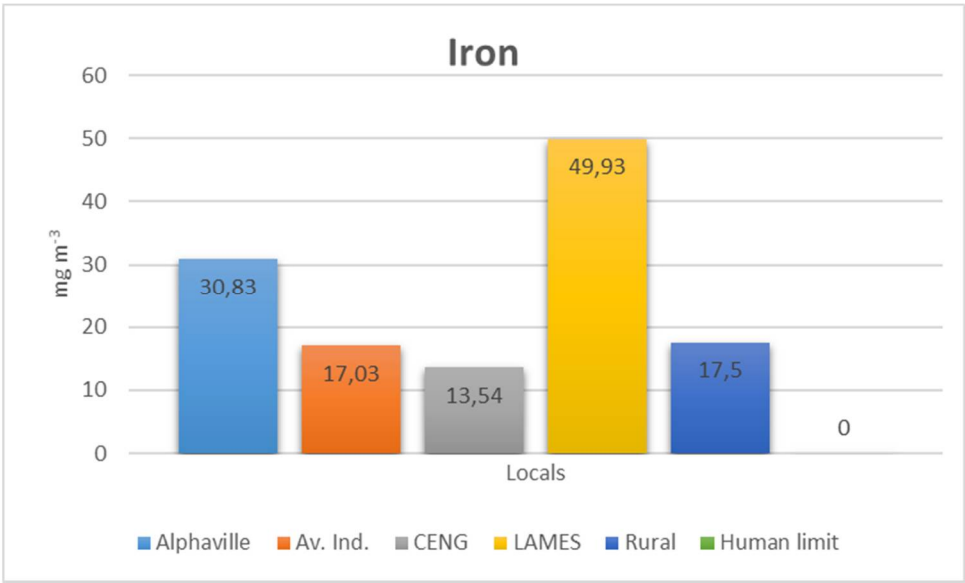


Fig. 6. Iron emission levels at the five collection locations and levels considered acceptable by the WHO.

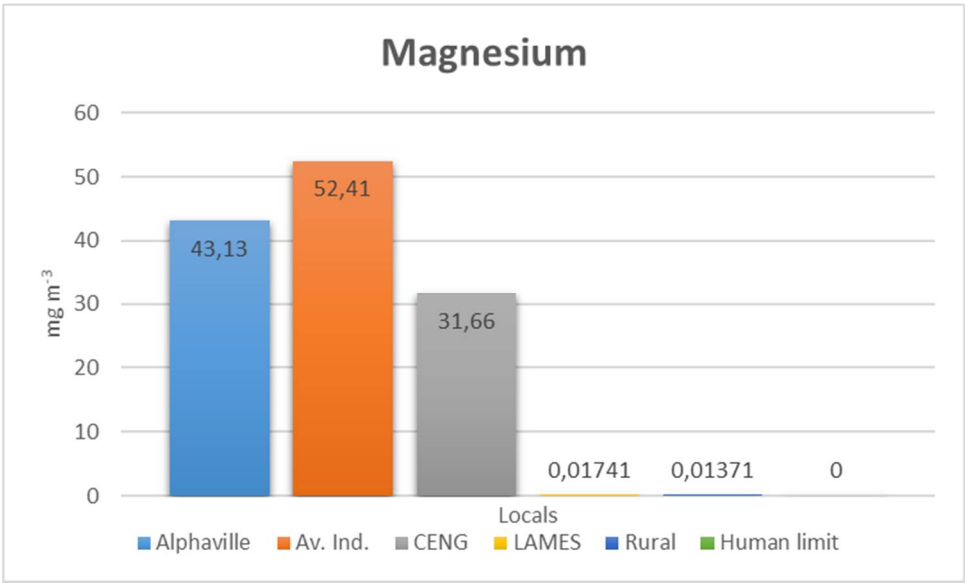


Fig. 7. Magnesium emission levels at the five collection locations and compared to levels considered acceptable by the WHO.

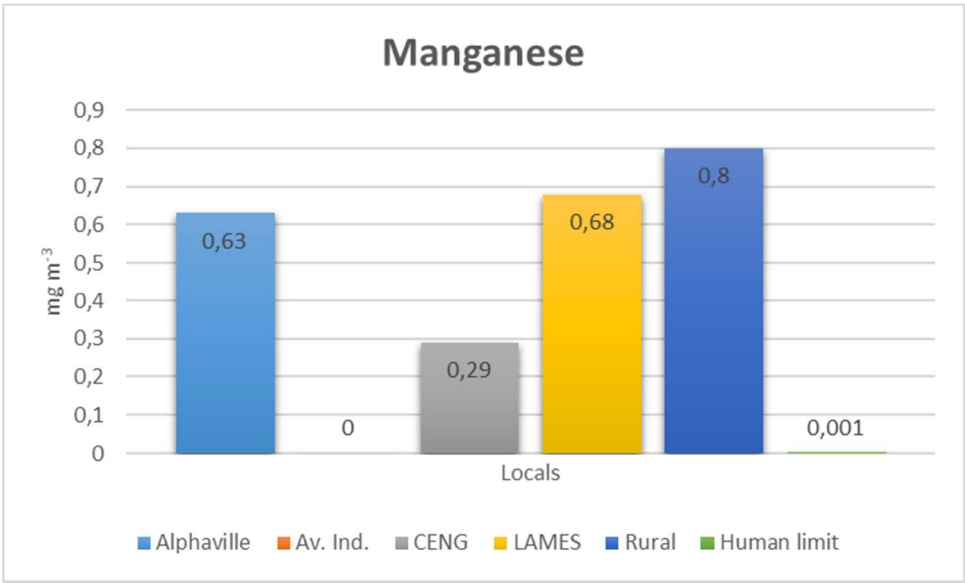


Fig. 8. Manganese emission levels at the five collection locations and levels considered acceptable by WHO.

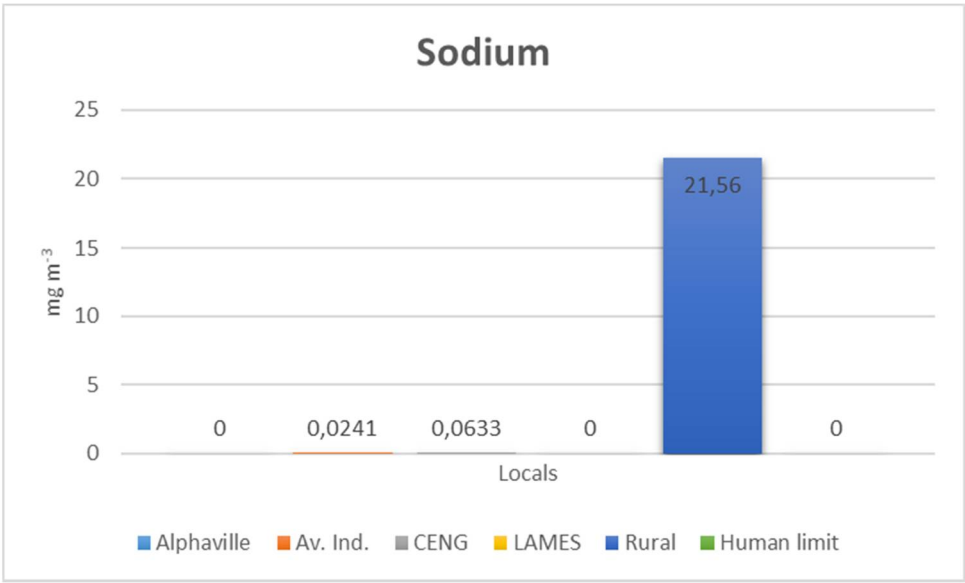


Fig. 9. Sodium emission levels at the five collection locations and to levels considered acceptable by WHO.

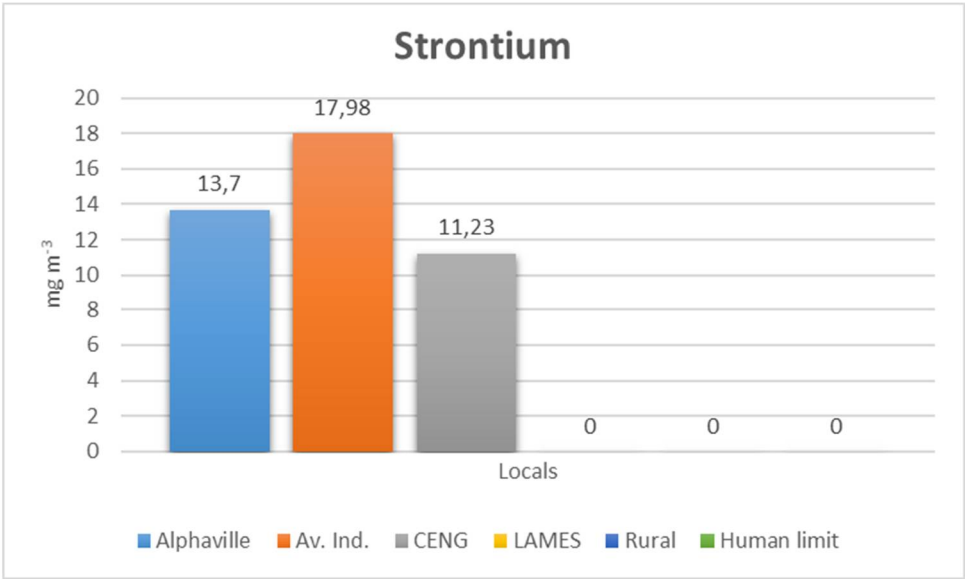


Fig. 10. Strontium emission levels at the five collection locations and levels considered acceptable by WHO.

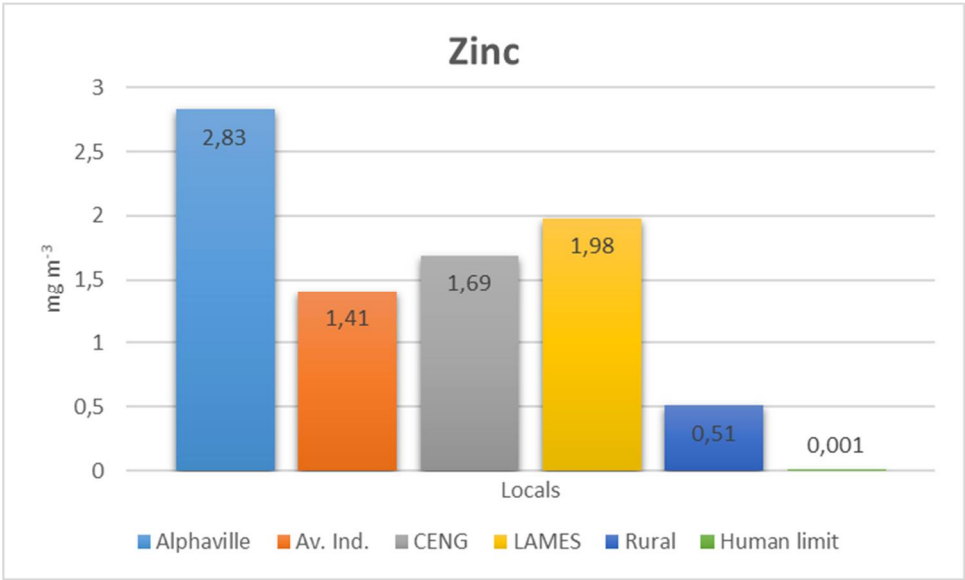


Fig. 11. Zinc emission levels at the five collection locations and levels considered acceptable by the WHO.

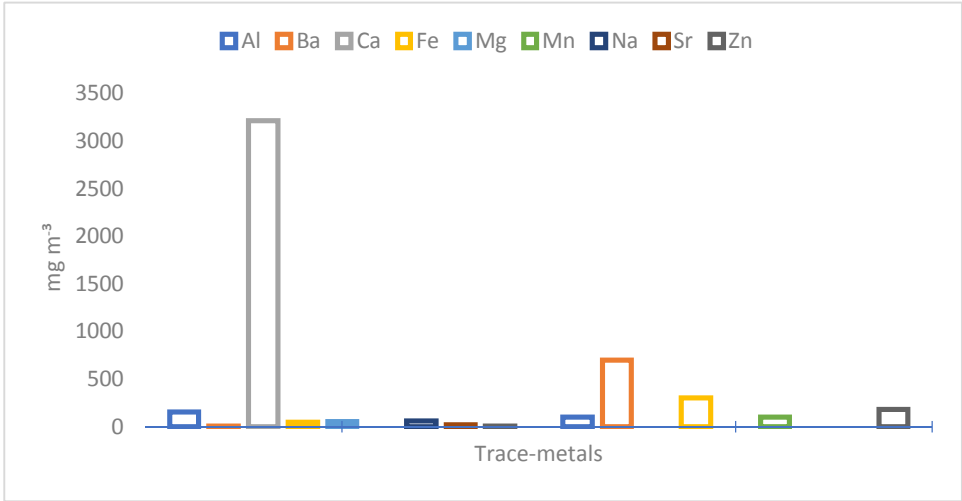


Fig. 11. Zinc emission levels at the five collection locations and levels considered acceptable by the WHO.

The trace elements that were found in rainwater in Goiânia show that there is contamination consistent with the anthropogenic emissions in the city with population of more than one million.

All the trace elements that were the object of study: Aluminum, Barium, Calcium, Iron, Magnesium, Manganese, Sodium, Strontium and Zinc presented limits above what the WHO prescribes as pathogens, indicating air pollution exists, since article 3, III, of Law no. 31, August, 1981 - Law of National Environmental Policy [26], defines pollution as the advanced stage of environmental degradation, that is, when levels of environmental contaminants are already harming the health, safety and well-being of the population, as well as negatively affecting biota, and the disposal of materials or energies are in disagreement with established environmental standards.

The presence of trace elements Aluminum, Calcium and Zinc in rainwater in Goiânia (Figures 3, 5 and 11) can be justified by the fact that these metals are relatively abundant in the earth's crust. They are usually found in air and water in all cities of the world with anthropogenic emissions from both fixed and mobile sources [27] as the primary cause for their increase in the environment.

The high Calcium content (shown in Table 2 and Figure 5) in rainwater samples at Alphaville, CENG and Av. Independência locations probably occurred due to the high construction activity at these localities due to the building construction boom the city has seen in recent years. It has been demonstrated that the waste from the construction industry usually is carried into the air and, consequently, to the rainwater, with particulates containing the trace element Calcium (MAY, 2004), found in high concentrations in marine and inland regions (1998).

The presence of trace elements Ba, Fe, Mg, Na and Sr, as shown in Figures 4, 6, 7, 9 and 10, show the influence of anthropogenic emissions on air pollution.

Barium is present in rocks, minerals, soil, and air, and its primary source of emission is the evaporation of paints and varnishes, glass and agricultural pesticides. Table 2 and Figure 4 shown that the trace element was only found at location LAMES. It is believed that the presence of such element at that location is due to the local massive transit of buses and other vehicles and the emissions made by the exhaust hoods of the laboratories at the Federal University of Goiás. It eventually contaminated local rainwater since the metal only appeared in a single sample.

Iron, an essential element for the maintenance of all life forms, especially in mammals, due to its function of oxygen transport, must be controlled in the environment. WHO considers the amount of 0.8 mg kg⁻¹ of body weight as the maximum limit for the presence of the metal in the organism human [28]. The iron trace metal contamination was found in all five locations where rainwater was collected in Goiânia (see Table 2 and Figure 6), which was expected due to the high dust emission containing the suspended metal from the activities of metal-mechanics industry.

Magnesium was found at all locations (Table 2 and Figure 7). However, highest concentrations occurred at locations with nearby higher industrial activity. Attention should be given to the trace element Magnesium, due to degenerative brain diseases and osteoporosis that causes and mainly because it is an indirect indicator of vehicular pollution, when present in air or rainwater [28].

Sodium is also present abundantly in the earth's crust, especially in marine regions. However, the presence of these trace elements in the atmosphere can cause diseases of the nervous and respiratory system, as well as eye irritation [28]. The highest concentration of sodium in the rainwaters in Goiania occurred at location LAMES (Table 2 and Figure 9), probably for the same reasons as with Barium, that is, vehicular and laboratories emissions.

Strontium is usually found near open mining activities and fields where fertilizer sprays are used. The highest concentrations of strontium in rainwater, in Goiânia, occurred at the locations of Av. Independência and Alphaville / Jardins. It is believed that the mining activity in the county of Senador Canedo, adjacent to the southern part of Goiânia, was the cause of the emission of such metal-trace, being carried by the winds to CENG and Av. Independência (Table 2, Figure 10).

The trace elements Ba, Fe, Mg, Na and Sr, although detected in rainwater, are not present above limits established by WHO [28].

The concentration levels of inorganic pollutants in water systems prescribed by Brazilian standards are much higher than those predicted for atmospheric air (Table 2, Figure 12). However, the control of atmospheric pollution is important, since continuous precipitation process that occurs in the water cycle, with the presence of trace elements already in quantities exceeding the limits hazardous to human health, will cause the deposition of rainwater in the soil, evaporation and discharge in water bodies, reaching levels high standards of pollution foreseen for water for human consumption, confirming the thesis that the natural resource "air" is the first to be achieved by anthropogenic and physical.

5. Conclusions

Monitoring ambient air quality through the analysis of rainwater can provide reliable indication of air pollution. The average concentration of trace elements that were found in rainwater in Goiânia, - Brazil -, at five collection locations, were (following a decreasing quantitative order): Ca > Al > Sr > Mg > Fe > Na > Zn > Mn > Ba.

The city of Goiânia - Brazil -, presents environmental pollution by the trace elements: Al, Ca and Zn, all harmful to human health, according to the limits established by the World Health Organization (WHO).

The trace elements Ba, Fe, Mg, Na and Sr, found in rainwater, can cause human health pathogens, although they do not have their emission limits defined by the WHO.

It is necessary to elaborate a standard capable of compelling the Public Authority to monitor and control the trace elements, and not include them within the limits of particulate matter, since even in small concentrations, these elements are harmful to human health.

Acknowledgments: The author wish to thank the Foundation for Support of Research of the State of Goiás - FAPEG

Conflicts of Interest: "The authors declare no conflict of interest."

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