ASSESSMENT OF THE CHEMICAL COMPOSITION OF TOTAL PRECIPITATION IN PARNASO, RJ

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Palavras-Chave: Ions, Metals, Air Pollution

Introdução

Over the last decades, world society has been experiencing an advance in economic, social and technological development, which can be exemplified in the expansion of the industrial park, in the urbanization process, in the expansion of the productive frontier, in the implementation of the light and heavy fleet, between others. This new reality brings with it new fundamental perspectives, as these new challenges directly affect the environment and human health. In this context, air pollution is highlighted, reflected in the increase in the release of solid and liquid particles from human and natural sources.

The various studies of chemical characterization allow the assessment of human impacts, to produce relevant information on local, regional and global scales, which in the future are the target of comparisons. Thus, atmospheric pollutants are used as gauges of the level of pollution in a given location. These pollutants are classified into primary and secondary according to their origin. The first are those emitted directly by sources, while the other classification encompasses substances formed from chemical reactions in the atmosphere. Thus, the main legislated air pollutants are carbon dioxide (CO_2), ozone (O_3), carbon monoxide (CO), sulfur dioxide (SO_2), volatile organic compounds (VOC), nitrogen (NO_x) and particulate matter (PM).

The particulate matter, in particular, composes a group of solid particles in suspension, of varied sizes, of great importance with regard to atmospheric processes. These inhalable particles can adopt a finer size (diameter less than or equal to 2.5 μm), known as $PM_{2.5}$, or thicker (diameter less than or equal to 10 μm), PM_{10}. These particles come from natural sources, from soil, marine aerosols, the earth's crust and biological material, and from anthropogenic sources, such as vehicular emissions, industrial processes and combustion. However, the presence of these substances in certain amounts can affect different climatic processes, including cloud formation, terrestrial albedo and ocean-troposphere exchanges.

One the ways to follow the impact of these substances in the regions is through studies of the total precipitation, since the particulate material acts as a condensation nucleus during the cloud formation process, leading to pluviometric precipitation. In practice, a total deposition collector is exposed for a certain period of time, both in the presence and in the absence of rain, without differentiating the forms of wet and dry deposition.

The chemical composition of the precipitation, then, is intrinsically related to the composition of the PM, although it cannot be said that both are the same, since the occurrence of parallel reactions and the presence of species in the solid phase of the particulate material transferred to the liquid portion of the drop cannot be disregarded. However, the chemical components that constitute them are generally the same, with variations only in the

concentrations present. The physical-chemical characterization parameters, such as pH and conductivity, are also good indicators of the local atmosphere.

Thus, precipitations are treated as excellent tools for the study of chemical compounds at atmosphere-ecosystem interfaces. Also considered as a sink, rainwater transports organic carbon dissolved in the troposphere air and several species of ions. In addition to toxic metals and organic compounds, such as carboxylic acids, aldehydes and ketones, ions such as Cl^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} and NO_3^- are identified.

It becomes evident, therefore, that the evaluation of the chemical composition of rainwater is of fundamental importance for the understanding of possible impacts of pollution on different locations. The main objective of this work is to study the chemical composition of total precipitation (rain + dry deposition) in the region of PARNASO, as well as to establish comparisons between the results found with those described in the literature.

Material e Métodos

The methodology to be implemented in this project is composed of three main parts: the preparation/installation of the total precipitation collector, the preparation of the samples and, finally, the proper chemical analysis.

First, the plastic funnel is attached directly to the cap of a plastic vial by a silicone ring. This set (funnel + vial) is attached laterally to a rigid PVC tube by a tube connector and supported by an iron base, also fixed to the PVC tube. This installation will be carried out in a reserved area/away from any obstacles and without the influence of contamination in PARNASO.

The decontamination of the funnel and collection bottles follows a specific protocol, which consists of filling a 5.0 or 10 L plastic container with Milli-Q water (deionized or bi-distilled), so that the plastic bottles can emerge, lid and the funnel attached to the lid for 24 h. After this time, the material will be removed, rinsed three times with Milli-Q water and left to dry at 40ºC on a clean tray lined with paper towels in the oven for 6.0 h.

After installation and decontamination of the set (funnel + bottle), the sampling process begins. The system will be exposed for collection for a minimum period of one month. At the end of this period, the samples will be collected, together with the blank, and taken to the laboratory for pretreatment.

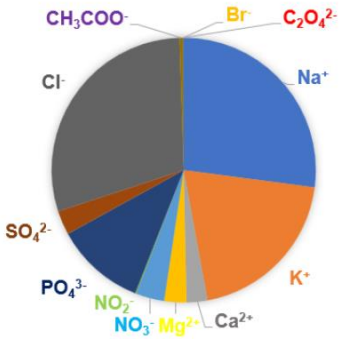
With the aid of a test tube, it is possible to directly measure the volume of rain (mL) collected in that month, which will later be converted into rainfall height (mm).

Then, an unfiltered aliquot (50 mL Falcon tube) is separated for the measurement of physicochemical parameters, such as pH and conductivity. The pH meter and conductivity meter must be calibrated before use.

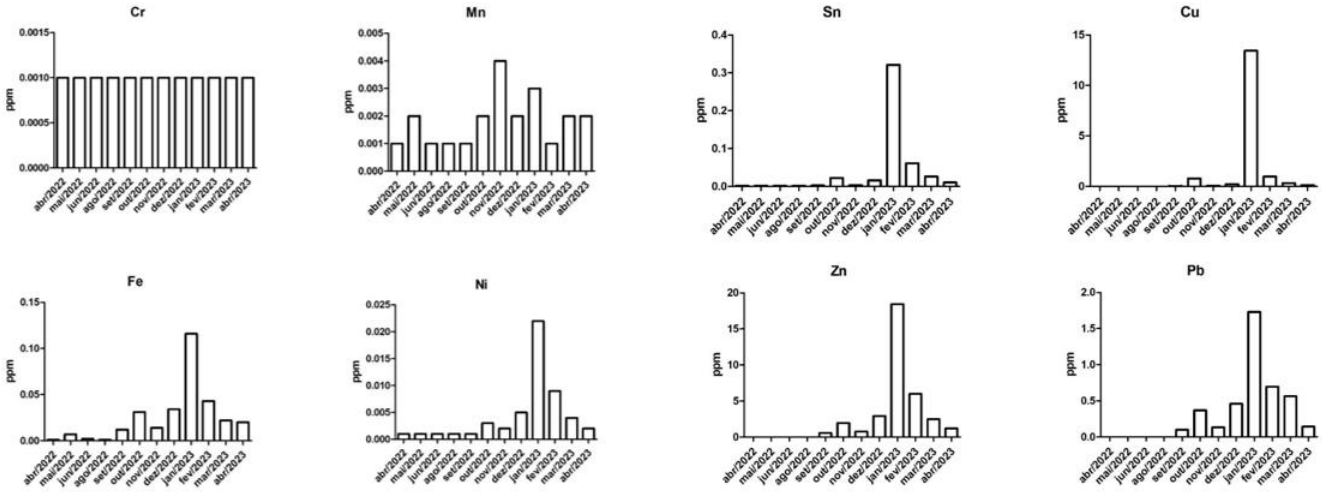
In addition, an aliquot (50 mL Falcon tube) must be separated for ion chemical analysis. For this, it is necessary to filter the collected samples with a 0.22 μm cellulose acetate membrane. The filtrate that will be directed to the ion analysis must be frozen at -22ºC. Finally, the filtered aliquot is subjected to ion chromatography and/or ICP OES. Metal analysis in IPC-MS requires pre-acidification of samples with 1 mL of HNO_3. The concentrations of the chemical species determined will be extrapolated by an analytical curve and interpreted in the form of tables and graphs. Statistical analyses were performed.

Resultados e Discussão

The ion concentration (μeq L^{-1}) of the PARNASO samples was $Br^-<C_2O_4^{2-}<CH_3COO^-<Ca^{2+}<Mg^{2+}<SO_4^{2-}<NO_3^-<PO_4^{3-}<K^+<Na^+<Cl^-$. The concentration (mg L^{-1}) of the trace elements in PARNASO was Cr < Mn < Ni < Fe < Sn < Pb < Cu < Zn. The samples from this region had an average pH of 6.05 and an average conductivity of 21.4 μS cm^{-1}. Na^+ e Cl^- were the most abundant ions in precipitation, having their origin strongly associated with sea spray. The preserved region of PARNASO suffered a greater impact from natural sources (62 %). Sn and Pb have been linked to wear on vehicle components, fuel additives, and traffic. The increases in Fe, Ni and Zn in PARNASO suggested the contribution, respectively, of soil, liquid fuels/coal and geological plant materials/micronutrients. The results are presented below in the form of tables and graphs.



	Cl^-/Na^+	K^+/Na^+	Ca^{2+}/Na^+	Mg^{2+}/Na^+	SO_4^{2-}/Na^+
Sea water ratio	1,16	0,02	0,04	0,22	0,12
Rainwater sample	1,09	0,74	0,09	0,098	0,11
FE $_{sea\ water}$	0,94	36,9	2,35	0,45	0,91
$[X]_{sea}$ %	49,8	58,2	14,8	85,8	51,6
$[X]_{excess}$ %	50,2	41,8	85,2	14,2	48,4
	Cl^-/Ca^{+2}	K^+/Ca^{+2}	Na^+/Ca^{+2}	Mg^{2+}/Ca^{+2}	SO_4^{2-}/Ca^{+2}
Soil ratio	0,0031	0,504	0,569	0,561	0,0188
Rainwater sample	11,6	7,86	10,6	1,05	1,16
FE $_{soil}$	>100	15,6	18,7	1,88	61,8
Source fractionation					
FSM	FC	FA			
62,3	4,52	33,2			



Conclusões

Based on a minimum sampling period of one year, a total of twelve representative samples of the region were collected. Thus, it was possible to understand the behavior of the rainfall dynamics, by the height calculated from the volume collected, the acidity over the months, by the pH values and the conduction of electric current, by the conductivity values referring to the ions present in solution.

Regarding the results of the ionic concentrations, it was possible to observe the great marine influence, characterized by the predominance of sodium, chloride and magnesium, in addition to the contribution of the local vegetation, which emits potassium and calcium, for example, and of anthropogenic emissions, since the region is close to areas with high vehicular traffic and construction activities. Thus, the quantities found were correlated with the respective natural and/or anthropogenic sources. The ionic balance of the system, the correlation coefficients between all the determined chemical species, the calculation of the excesses and deposition fluxes, the correlation graphs and the statistical analyses confirmed the origin of the emissions by source and enriched the discussion of the results.

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