



^7Be as a Tracer of Atmospheric Processes in Rainfall in São Paulo: Correlations with Major Ions and Trace Metals.

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1. Introduction

The atmospheric system is governed by emission, transport, and removal of aerosols and gases [1],[2]. Wet deposition is a key removal mechanism, incorporating particulate and dissolved species into precipitation [3],[4].

Among atmospheric tracers, ^7Be stands out due to its cosmogenic origin and short half-life (53,3 days), being produced in the upper atmosphere and transported attached to aerosols. Previous studies in São Paulo [5] have reported its occurrence in air and precipitation. Its removal occurs primarily via precipitation, making it an effective tracer of atmospheric scavenging processes [6-9].

The interpretation of ^7Be in rainwater depends on both aerosol concentration and rainfall volume, introducing dilution effects. Therefore, analyzing ^7Be together with metallic concentrations provides a more complete understanding of atmospheric processes, especially in urban regions with complex emission sources [10].

This work aims to evaluate correlations between ^7Be and major ions and trace metals, assess spatial consistency among sampling sites.

2. Methodology

Rainwater sampling was conducted at six sites distributed across the city of São Paulo representing distinct urban environments (UL, WE, NR, LT, CN and IP). High-density polyethylene (HDPE) collectors with a collection area of 0.19 m² were installed at each site, along with rain gauges. Samples were collected on a weekly basis.

The dataset comprises 321 precipitation samples collected between January 2023 and December 2024.

In the laboratory, samples were concentrated to a final volume of 100 mL prior to chemical analysis. The activity concentration of ^7Be was determined using high-resolution gamma spectrometry with a high-purity germanium (HPGe) detector [11].

The concentrations of Al, Ba, Fe, Mn, Pb, and Zn were determined by inductively coupled plasma optical emission spectrometry (ICP-OES), while Na, K, Mg, and Ca were measured by ion chromatography, both widely used techniques for environmental analysis [12].

Prior to statistical analysis, data were screened for missing values and inconsistencies. Descriptive statistics were based on median and quartiles due to the asymmetric distribution of most variables. Correlation analyses were performed using both Spearman and Pearson coefficients to assess monotonic and linear relationships, respectively. Associations between ^7Be and rainfall volume were also examined in logarithmic scale to evaluate dilution effects.

Hierarchical clustering analysis was applied to investigate the relationships among chemical species and to identify similarities between sampling sites. Clustering of variables was based on Spearman correlation distances using the unweighted pair group method with arithmetic mean (UPGMA), while clustering of sampling sites employed standardized median profiles and Ward's method.

3. Results and Discussion

The distribution of ^7Be activity concentrations in rainwater samples shows a right-skewed pattern, with most values concentrated between approximately 0.93 and 1.82 Bq/L, consistent with typical environmental radionuclide behavior [6]. As illustrated in Figure 1a, the relationship between ^7Be concentration and rainfall volume exhibits a clear inverse trend when plotted on a logarithmic scale, evidencing the dilution effect. This behavior indicates that atmospheric scavenging is accompanied by dilution due to increasing water volume. Seasonal variability further supports this interpretation. As shown in Figure 1b, higher ^7Be concentrations occur during dry periods, particularly in winter months, while lower values coincide with intensified rainfall during late autumn. This pattern reflects reduced atmospheric washout during dry conditions and increased dilution during wetter periods. The spatial distribution, presented in Figure 1c, reveals minimal differences among sampling sites, indicating that the variability of ^7Be is predominantly temporal rather than spatial. This homogeneity is expected given the cosmogenic origin of ^7Be and its production in the upper atmosphere.

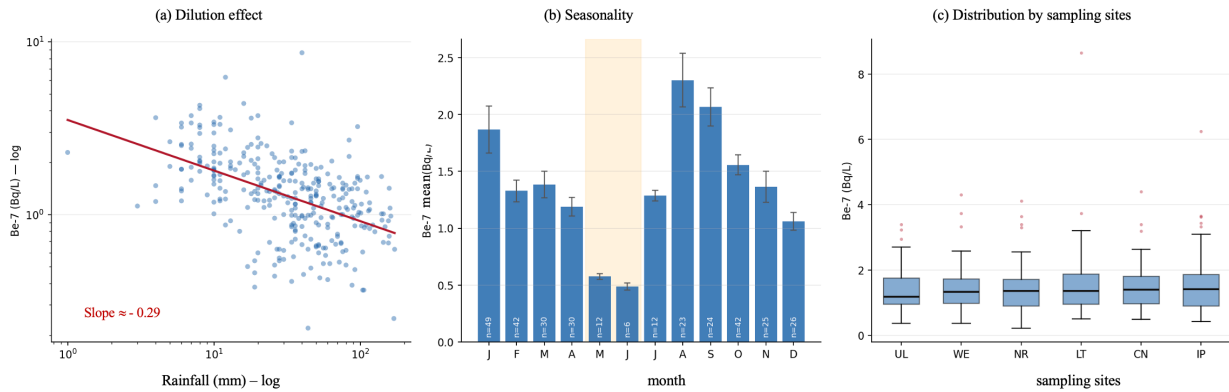


Figure 1: Characterization of ^7Be . (a) Relationship with rainfall depth on a logarithmic scale, highlighting the dilution effect; (b) monthly mean concentrations, emphasizing the minimum period (May–June), with n representing the number of events; (c) distribution by sampling site.

Moderate positive correlations were observed between ^7Be and elements typically associated with crustal material, such as Ba, Mn, Al, and Fe, as well as with soluble ions (Na, K, Mg, and Ca). These associations suggest that ^7Be is transported attached to atmospheric particulate matter and is removed through wet deposition processes.

The correlation with rainfall volume is the strongest and negative, reinforcing the dominant role of dilution. In contrast, correlations with Pb and Zn are weak, indicating that ^7Be is not strongly associated with anthropogenic emissions represented by these elements.

The comparison among sampling sites reveals a consistent pattern for ^7Be but highlights a clear anomaly in the chemical composition at site WE (Figure 2a). The median concentrations of Fe, Ca, Mn, and Al at this site are substantially higher than those observed at the other locations with enrichment factors ranging from approximately 1.9 to 2.4.

This pattern indicates a localized influence affecting mainly mineral-derived elements, while ^7Be concentrations remain uniform across sites (Figure 1c), suggesting that the processes controlling the radionuclide are not affected by the same local factors influencing the chemical composition.

Hierarchical clustering of the sampling sites (Figure 2b) further confirms this behavior, with site WE separating from the remaining sites at an early stage of the clustering process. The other five sites form a cohesive group with similar chemical profiles.

This combined evidence supports the interpretation that site WE reflects a distinct local influence on the chemical composition, while the behavior of ^7Be remains representative of broader atmospheric processes. The clustering approach thus proves effective for identifying atypical patterns and assessing data consistency in environmental monitoring datasets.

To evaluate the impact of the anomalous site on the dataset, the analyses were repeated excluding site WE ($n = 267$; Figure 3). The correlations between ^7Be and the crustal elements remained stable and became slightly more homogeneous, while the negative correlation with rainfall volume was unchanged.

The clustering structure of chemical species was preserved, with only a clearer separation between mineral-derived elements (e.g., Ba, Mn, Al, Fe) and more soluble ions (e.g., Na, Mg, Ca). These results

demonstrate that the exclusion of site WE reduce noise without altering the overall interpretation of the dataset.

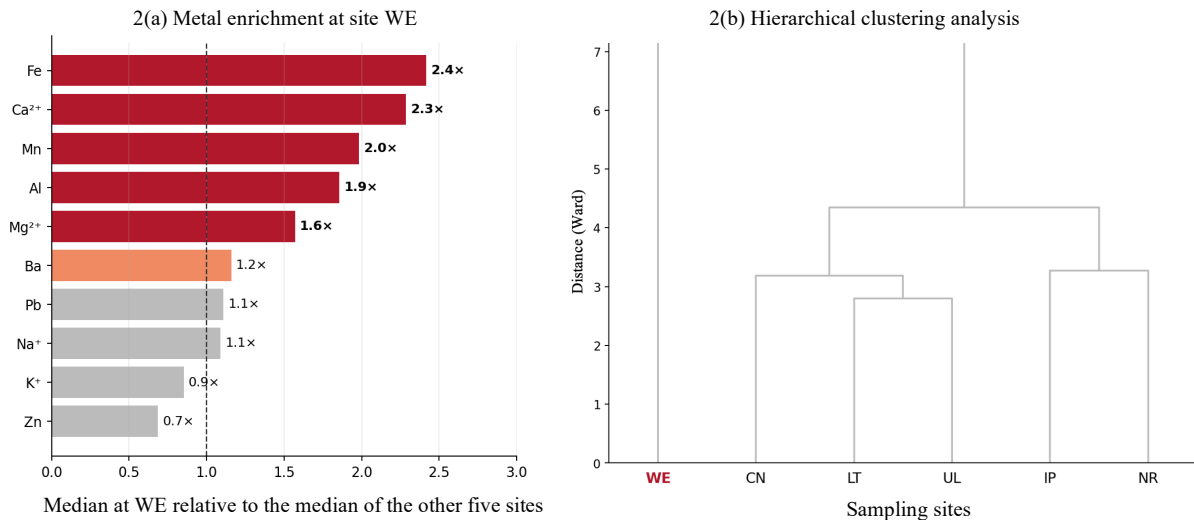


Figure 2: Anomaly at site WE. (a) Ratio between the median concentrations at site WE and the median values of the other sampling sites for each element; (b) Hierarchical clustering analysis. Sampling sites, based on standardized median profiles. Site WE are clearly separated from the remaining sites.

The results indicate that the concentration of ⁷Be in precipitation is primarily controlled by two processes: dilution by rainfall volume and association with atmospheric particulate matter. The consistent behavior across sampling sites reinforces the role of ⁷Be as a tracer of large-scale atmospheric processes rather than local sources. The identification and exclusion of the anomalous site improve the robustness of the analysis and highlight the importance of combined statistical and geochemical approaches for quality control in environmental datasets.

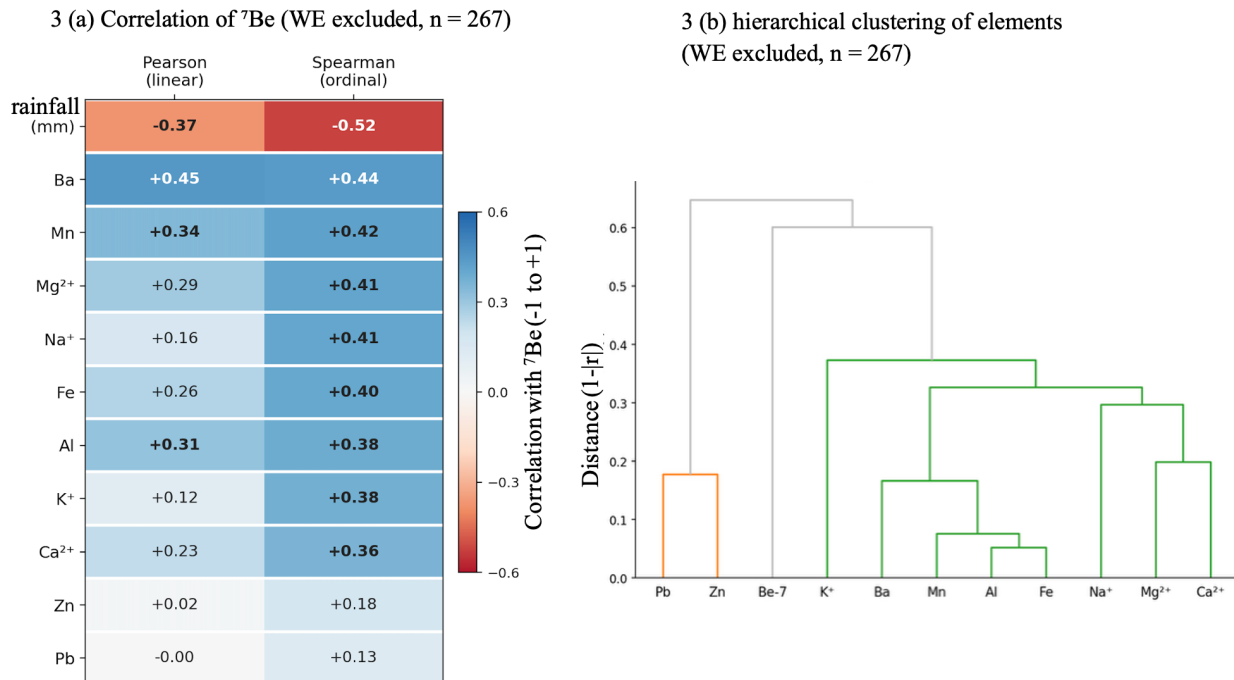


Figure 3: Effect of excluding site WE. (a) Correlation of ⁷Be (WE excluded, n = 267), with preserved and more homogeneous associations with the crustal group; (b) hierarchical clustering of elements (WE excluded, n = 267), showing a preserved structure and improved separation within the crustal group.

4. Conclusions

The results confirm that ^7Be is a robust tracer of atmospheric scavenging, with variability predominantly controlled by rainfall. Its variability is predominantly temporal and related to rainfall intensity. However, ^7Be alone does not discriminate local sources, making complementary spatial and chemical analyses essential. The combined approach adopted in this work proved effective in distinguishing between atmospheric washout effects and local anthropogenic influences in a complex urban environment.

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