









An assessment of atmospheric deposition of metals and the physico-chemical parameters of a rainwater harvesting system in Rio de Janeiro Brazil, by means of statistical multivariate analysis

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ABSTRACT

This study evaluates the rainwater harvesting system to determine the chemical quality of the water and allocate it for use. Samples were collected in the city of Rio de Janeiro at the points of Direct Precipitation (DP), First Flush (FF) and Reservoir (RR). The methodology involved carrying out an analysis of Ca, Cd, Cu, Na, Ni, Fe, K, Mg, Pb, Zn, conductivity, turbidity, pH and chloride. The R language was used for the principal component analysis, Pearson coefficient correlation, hierarchical cluster analysis, Tukey test and boxplot. The results show that when there is no interference from the catchment surface (DP), the rainwater has a low concentration of metals, although the first millimeters of rain have a concentration above what is permissible in the guidelines issued by the Ministry of Health (Ordinance n° 05/2017). The disposal system (FF) reduced the concentration of pollutants in the RR, but not enough to comply with legislation. It was noted that Ca, K and Na are the main metals found in rainwater. During the dry period, there were significant correlations between the physico-chemical and meteorological parameters. The high concentration of metals in the wet period suggests that rain assists the cleaning of the atmosphere and that most metals are present in the form of aerosols or fine particles suspended in the air. The findings reveal significant indications of acid rain and pre-treatment is recommended to ensure rainwater can be used safely for more mundane purposes.

Keywords: metals, multivariate statistical analysis, urban environment, water quality.



Avaliação da deposição atmosférica de metais e dos parâmetros físico-químicos de um sistema de captação de águas pluviais no Rio de Janeiro Brasil, por meio de uma análise estatística multivariada

RESUMO

Este estudo avalia o sistema de captação de água da chuva para verificar a qualidade química da água e aloca-la para uso. As amostras foram coletadas na cidade do Rio de Janeiro, Brasil, na Precipitação Direta (DP), *First Flush* (FF) e Reservatório (RR). A metodologia consiste em análises de Ca, Cd, Cu, Na, Ni, Fe, K, Mg, Pb, Zn, condutividade, turbidez, pH e cloreto. A linguagem R foi utilizada através da análise de componentes principais, correlação linear de Pearson, análise hierárquica de agrupamentos, teste de *Tukey* e *boxplot*. Os resultados indicam que a água da chuva sem interferência da superfície de captação (PD) apresenta baixa concentração de metais, porém os primeiros milímetros de chuva apresentam uma concentração acima da permitida pela Portaria nº 05/2017 do Ministério da Saúde. O sistema de descarte (FF) reduziu a concentração dos poluentes no RR, mas não o suficiente para atender a legislação. Observou-se que Ca, K e Na são os principais metais encontrados na água da chuva. O período seco apresentou correlações significativas entre os parâmetros físico-químicos e meteorológicos. A alta concentração de metais no período úmido indica que a chuva promove a limpeza da atmosfera e que a maioria dos metais está presente na forma de aerossóis e em partículas finas suspensas no ar. Os resultados indicam características de chuva ácida e sugere-se o pré-tratamento da água da chuva para uso com segurança em fins menos nobres.

Palavras-chave: ambiente urbano, análise estatística multivariada, metais, qualidade da água.

1. INTRODUCTION

Water is essential for maintaining the life cycle on earth. The demand for water is increasing more rapidly than population growth throughout the world, and this is causing an imbalance between the consumption and availability of water resources. Management failure and a lack of information on the current situation of natural resources, combined with unsustainable development, can have an adverse effect on the availability and quality of water. There are a number of factors that harm the quality of water, such as urbanization, pollution, deforestation and unsuitable agricultural practices (UNESCO, 2015). About 3.6 billion people live in areas where there is likely to be a scarcity of water for at least one month a year, and it is predicted that this number could increase to 4.8 - 5.7 billion by 2050. The population currently affected by land degradation/desertification and drought is estimated to be about 1.8 billion people, which makes this the most significant category of natural disaster (WWAP, 2018).

Rainwater harvesting is a freely available source that can meet the requirements for water in different regions of the world, especially in places where there is a shortage or lack of access to water of a good quality (Alim *et al.*, 2020). In addition, the rainwater system reduces the municipal consumption of water and mitigates the harmful consequences of urban stormwater runoff in extreme events (Ghaffarianhoseini *et al.*, 2015). Despite the large amount of water available in Brazil, many regions suffer from a lack of a supply and distribution of water and long periods of drought, especially in the country's semi-arid regions. In rural areas, rainwater is generally used to meet basic demands, including human consumption, while in urban areas rainwater is used as a supplementary source to serve secondary demands (Gomes *et al.*, 2014).

In developing countries, rapid industrialization and urbanization have increased the problem of metallic air pollutants that damage the environment and are a hazard to human health (Lu and Yu, 2018). Air contaminants can chemically affect rainfall, especially during the dry season (Mimura *et al.*, 2016). Several factors, such as mesoscale circulation, topography

and local sources influence the chemical composition of precipitation (Vieira-Filho *et al.*, 2013). High levels of Zn and Pb have been found in rainwater, which may be caused by metal leaching from roofing, and storage tanks or through atmospheric pollution (WHO, 2008). In a clean atmosphere, the pH of rainwater is around 5.6 (Charlson and Rodhe, 1982) whereas a lower pH is characteristic of acid rain, which is caused by the presence of SO₂ and NO_x oxidation, and leads to the bioavailability and dissolution of trace- and major metals in rainwater (Anil *et al.*, 2017; Oliveira *et al.*, 2012). The main sources of metals in the atmosphere are petroleum refineries, waste incinerators, coal burning power plants, metal treatment services, fuel combustion and road traffic (Connan *et al.*, 2013). The trace metals present in urban areas can be found in the roofing, electronic materials, paintwork and the components of automobiles (Le Pape *et al.*, 2012).

The presence of NO_x and SO₂ in rainwater can be attributed to fossil fuel combustion, mainly vehicular and industrial emissions. Resuspended particles and other contaminants can be carried through the atmosphere and are responsible for various chemical and physical processes (Martins *et al.*, 2014). Particulate matter (PM) and gases present in the atmosphere during rainout and washout are incorporated into the water droplets, which act as a water distiller (Conceição *et al.*, 2011), and reach the surface of the earth and water resources. After this, the pollutants are removed from the atmosphere by wet and dry deposition (Szép *et al.*, 2019). Atmospheric deposition is responsible for the spatial redistribution and continuous cycling of chemical elements through the removal of particles and gases by snow, rain or mist in the wet phase or, in the absence of rainwater, in the dry phase (Ohnuma *et al.*, 2014).

The relative humidity influences the solubilization of water-soluble pollutants in the form of aerosols by means of wet deposition, thus triggering the most effective aqueous phase reaction (Gioda *et al.*, 2017). Thus, urban and, in particular, industrial areas pose a risk to aquatic species owing to the bioaccumulation of elements, such as toxic metals associated with PM that are present in atmospheric emissions (Mateus *et al.*, 2018). The effect of metals on the environment and the atmosphere has become a serious hazard, since the accumulation of toxic metals in human body tissue through inhalation and being passed through the food chain can cause damage to internal organs and the nervous system (Kamani *et al.*, 2014).

The results of revised work on rainwater harvesting systems show an average potential savings of 53% can be made in drinking water (Ghisi *et al.*, 2018). These systems have aroused considerable interest and play an important role in increasing the availability of water, reducing adverse impacts on the environment, improving human health (Diehl de Souza and Ghisi, 2020) and providing economic benefits (Pavolová *et al.*, 2019). In Brazil, there are no monitoring networks for acid precipitation and only a few studies on the subject have been carried out, mainly concentrated in the Southeast and Southern regions (Martins *et al.*, 2019), which are areas at risk owing to intense urbanization and industrial activity.

The physical and chemical characterization of rainwater helps to assess the influence of different sources of pollution and the regional and local dispersion of gases and particles, in addition to their possible impact on the ecosystem (Laouali *et al.*, 2012). Furthermore, it is essential to understand the relationship between air pollution and water and determine the nature of the compounds present in the rain and their concentrations, since the available data are limited (Gasperi *et al.*, 2014).

This study was carried out in the urban area of Rio de Janeiro, Brazil, between November 2017 and October 2018 with the following objectives: (i) to analyze the physico-chemical composition and presence of metals in rainwater; (ii) to apply multivariate statistics using the R language to assess the pattern of behavior of the physico-chemical and meteorological parameters during the dry and rainy season; and (iii) to compare the findings about these parameters with the drinking-water quality standards set by the Ministry of Health (Ordinance n° 05/2017) when deciding on uses for rainwater.

2. MATERIALS AND METHODS

2.1. Study area

The city of Rio de Janeiro has approximately 6.7 million people spread over 1,200 km² (IBGE, 2019); about 36% of this area is covered by vegetation, mainly the Tijuca National Park which comprises 40 km² (Braga *et al.*, 2018). The Tijuca Forest is an area of mountainous tropical forest that forms a natural barrier to air circulation (Silva *et al.*, 2016b), and is regarded as the largest urban secondary forest in the world (Silva *et al.*, 2016a). Its topography, geographic location, the use and the occupation of the soil and proximity of the oceanic region result in a complex rainfall pattern (Brito *et al.*, 2017; Siciliano *et al.*, 2018) (Figure 1).

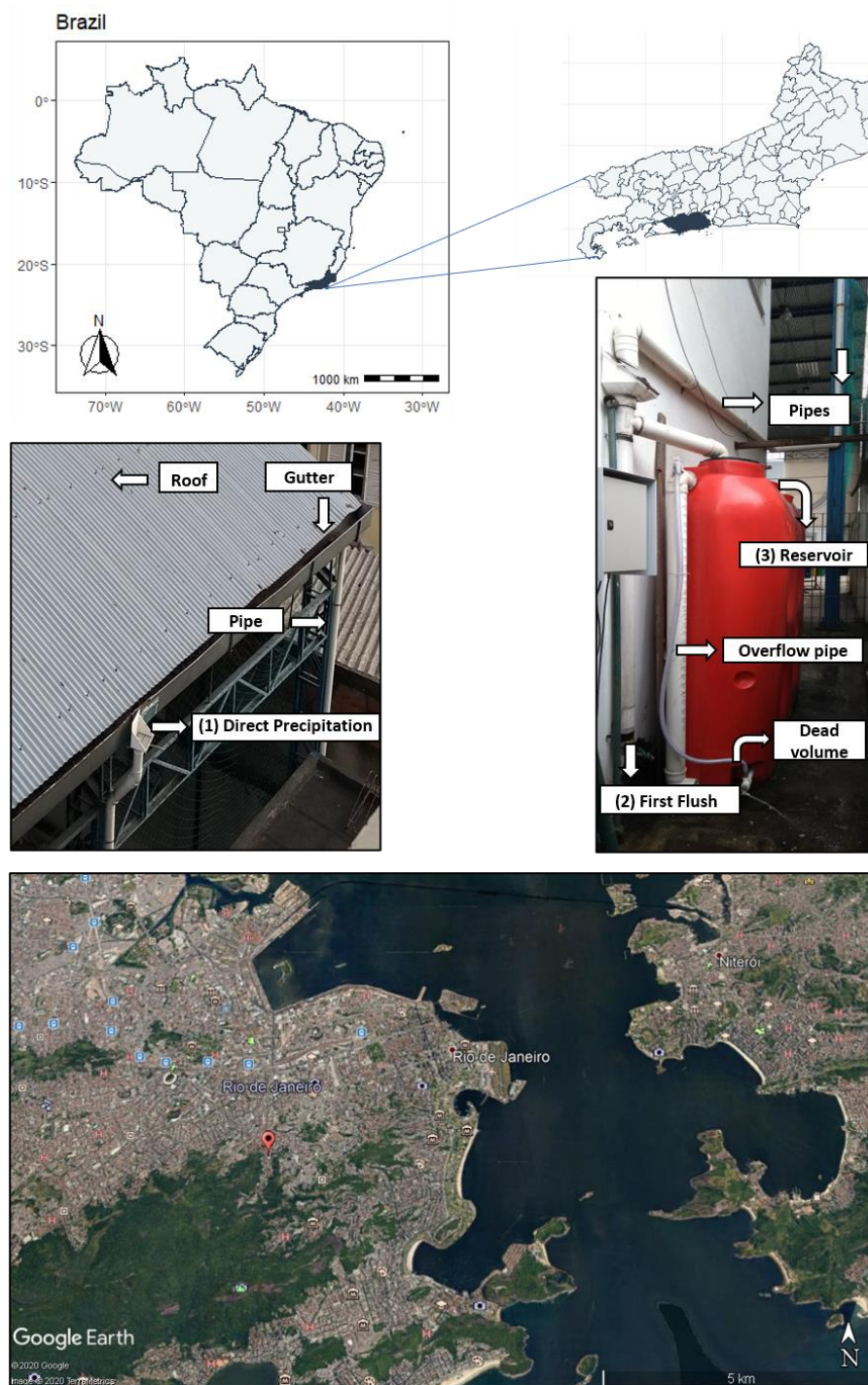


Figure 1. The study area and collection points.

The Geo-Rio Foundation monitors rainfall in the city of Rio de Janeiro - RJ through 33 strategically-located rainfall stations. It is an early-warning system for landslides and heavy rainfall in the city of Rio de Janeiro. According to the historical series from 1997 to 2016, the average annual total for the area is 1,212 mm. The highest rainfall occurs in the month of January, when there is an average rainfall of 176.6 mm, and August is the driest period with 39.8 mm (GEO-RIO, 2018).

The rainwater harvesting system is located on the roof of the multi-sport facility building at the college of the State University of Rio de Janeiro (CAp-UERJ), together with a catchment area of 80 m² (22°55'39.4" S 43°12'30.4" W), in the district of Rio Comprido, in the north-central region of the city of Rio de Janeiro. The location is in one of the main north-south transition zones of the city, where there is heavy road traffic. During a precipitation event, rainwater passes through the roof, flows along conduits to the coarse solid filtration point using a 1.0 mm mesh. Then, the water is sent to the first flush (FF) disposal system, which has an accumulated storage capacity of 0.20 mm of rain. After reaching this, the rainwater goes directly to the 2,460-liter fatboy slim reservoir with polyethylene coating. If the volume of the reservoir reaches full capacity, the overflow system is activated.

2.2. Sampling and chemical analysis

The analysis of the physico-chemical and rainfall data of the collections carried out from November, 2017 to April, 2018 allowed this to be characterized as a wet period (N = 7), and the samples obtained between May and October, 2018 were defined as a dry period (N = 6). The sampling campaign was carried out from three specific points: (1) Direct Precipitation (DP): the collection point without interference from the intake system, that was only influenced by local atmospheric conditions, and had the capacity to store up to 700 mm of accumulated precipitation; (2) First Flush (FF): the initial capture of rain with a mixture of wet and dry deposition. This has the capacity to store 0.2 mm of precipitation and (3) Reservoir (RR): where the quality of the stored water determines the operations of the initial disposal system (FF) and the possible use of water. The RR point is located about 0.40 meters from the bottom level of the reservoir and has a capacity to store up to 23.66 mm of precipitation. This study disregards analyses of samples of the dead volume stored in the reservoir, as it is concerned with its potential use and the operating conditions of the system.

The pluviometric data were obtained from the Rio Early Warning System (Alerta Rio, 2018) operated by the City Hall, and corresponds to the number 4 pluviometer located in the district of Tijuca. The Tijuca station is about 1 Km from the location of this study. Thirteen campaigns were carried out to collect rainwater and the samples were collected monthly in 1 L polyethylene bottles. The stages for the preparation and sample collection were based on the National Sample Collection and Preservation Guidance Manual of the National Water Agency (ANA, 2011). The chemical analysis of the metals involves a special procedure of washing the vials and lids by immersion in a 10% nitric acid solution for 48 h, and then rinsing them with MilliQ water 5 times; after this, they are dried on absorbent paper and stored in a dry and clean place to avoid contamination. After each collection, 1 L of sample was vacuum filtered through a 47 mm glass fiber filter (Merck Millipore) with 0.7 µm porosity and acidified with HNO₃ 1:1 until pH <2.

Greater precision in the quantification of the metals present was achieved by concentrating the samples with the aid of a heating plate at a temperature of 80 to 90°C to reduce the volume from 250 mL to 10 mL. Straight after this, 40 mL of HNO₃ (3 mol L⁻¹) was added, after which the samples were transferred to 50 mL Falcon tubes which were pre-washed with HNO₃ and stored in the refrigerator at a temperature of 4°C until the time of analysis. The cleaning of the flask for the analysis of pH, turbidity, chloride and conductivity entails washing the bottles and lids with distilled water. The samples were kept on ice until they arrived at the laboratory. It was not possible to perform blank in the field due to the difficulty of accessing the area of the

rainwater catchment system. The blank was carried out in the laboratory with the collected rainwater and HNO₃ used to wash the flasks and in the physico-chemical analyses.

The pH buffer solution was used in the pH meter calibration for samples in the acid range of pH 4 solution, and for the basic range of pH 10 solution. The turbidimeter was calibrated to the standards of 0.1 UNT, 8 UNT, 80 UNT and 1000 UNT. The conductivity meter was calibrated in accordance with the Digimed DM-S6A conductivity standard. The chloride was determined by potentiometry in triplicate using 1 mL of the 50 g L⁻¹ potassium chromate solution and 0.013 mol L⁻¹ silver nitrate solution for 50 mL of the sample.

The analytical methodology is based on the Standard Methods for the Examination of Water and Wastewater (APHA *et al.*, 2012). The 10 elements: Calcium (Ca), Cadmium (Cd), Copper (Cu), Iron (Fe), Potassium (K), Manganese (Mn), Sodium (Na), Nickel (Ni), Lead (Pb) and Zinc (Zn) were analyzed by means of the Flame Atomic Absorption Spectroscopy (EAA) method 3-14 with a quantification limit between 0.01 and 0.02 mg L⁻¹, in the PerkinElmer AAnalyst 400 equipment, installed in Resende - RJ, at the Faculty of Technology of the State University of Rio de Janeiro.

Standards were used for the analytical curves, at concentrations of 10, 50, 100, 300, 500 and 1000 µg L⁻¹. An additional standard of 5000 µg L⁻¹ was used for iron. Acetylene was used as a fuel to determine the concentration of metals and compressed air as an oxidizer, with a flame temperature of 2100°C - 2400°C. However, in the case of the most refractory element such as Ca, it was necessary to replace compressed air with nitrous oxide, which has a flame temperature of 2500 to 3100°C. The concentration was determined at room temperature, with deionized water used between the analyses. When the sample reading was above the maximum calibration point, the sample was diluted with HNO₃ solution. The analytical curve was assessed every day before the samples were read.

2.3. Statistical analysis

The result of a chemical experiment involves analyzing several interrelated variables, and for this study Language R version 3.4.4 (R Core Team, 2018) was applied so that the data could be handled with multivariate statistics. The R package called FactorMineR was applied for the multivariate data. This package is characterized by the use of different data structures, and quantitative or categorical variables (Lê *et al.*, 2008). Pearson's correlation coefficient was used to determine the behavior of one variable in relation to another. The Tukey test was also conducted to compare the data subsets.

The Principal Component Analysis (PCA) led to the linear transformation of the data and enabled the values resulting from this transformation to have their key components in the first dimensions (i.e., in the main denominated axes), with the least possible loss of information (Lyra *et al.*, 2010). Hierarchical cluster analysis was carried out with the aim of dividing a set of objects into several groups to ensure that the objects within the same group are more similar to each other (Bratchell, 1989). These are techniques that are considered to be essential in the analysis of chemical data (Luna *et al.*, 2014; Moita Neto and Moita, 1998).

The experiment involved a large number of physico-chemical and meteorological variables and they had to be separated into two groups to understand the relationships between them: one group for metals and another group for the other physico-chemical variables. Meteorological parameters, such as the number of consecutive dry days and the sub-daily rainfall intensity were included in these two groups as a way of determining if there was a possible correlation. In addition, the data were interpreted by dry periods and wet periods and explained in terms of the seasonality of certain parameters.

With regard to descriptive statistics and boxplot, all the results were included, although, in the application of PCA and the linear correlation with a dendrogram, it was necessary to disregard variables that had results below the limit of quantification or that did not have any

significant variation between the points collected. The data obtained from the Tijuca station were used for the selection of rain events, calculation of Consecutive Dry Days (CDD) and sub-daily rainfall intensity. The sub-daily rainfall intensity was calculated for the first rain event ≥ 7 mm that occurred in the period between the collections from the reservoir for analysis of samples. The CDD represents the sum total of successive days with less than 1 mm of rain.

2.4. Legislation

Despite its increasing use for human consumption in areas where rain is the main source of supply, as well as for more mundane purposes, the use of rainwater in Brazil is not subject to legislation. As an alternative, the use of drinking water legislation is applied in several studies to determine possible uses (Alcolea *et al.*, 2015; Despins *et al.*, 2009; Hoseinzadeh *et al.*, 2016; Igbiosa and Aighewi, 2017; Magyar *et al.*, 2008; Olaoye and Olaniyan, 2012; Senevirathna *et al.*, 2019; Yaziz *et al.*, 1989). Although a number of projects for rain-use have been undertaken in many countries, they have been designed for conserving water, without taking note of other benefits that can be derived from the multi-purpose nature of rainwater catchment and storage systems (Campisano *et al.*, 2017).

In Brazil, Ordinance n° 05/2017 of the Ministry of Health (Brasil, 2017) regulates the procedures for controlling and monitoring the quality of water for human consumption and its drinking water quality standards. In addition to the WHO recommendations, the ordinance standardizes the permissible limits for metals, and thus the measures stipulated by the legislation of the Ministry of Health (MS) were selected for the comparison of results.

3. RESULTS AND DISCUSSION

Thirteen rainwater samples were collected during the period 2017-2018. Analyses of pH, chloride, conductivity, turbidity, metals and rainfall were performed at the points of DP, FF and RR. Pearson's correlation coefficient with a dendrogram was applied to define the possible sources of certain elements and to determine the relationships between the physico-chemical parameters of the rain composition. PCA was applied to a set of variables, both to reduce their dimensionality and to investigate the relationship between the elements of rainwater and the possible sources of pollution. The Tukey graph was used to compare the averages obtained between the points of collection of certain parameters. The results are divided into dry and wet periods and the averages are shown with the standard deviation of each series. Ordinance n° 05/2017 of MS was used as a basis for comparing the results obtained.

3.1. Physico-chemical parameters

In general, the results of pH and turbidity are beyond the limits of what is permitted by Ordinance n° 05/2017; chloride meets the standard and conductivity has no limit (Table 1 and Figure 2). The wet deposition obtained by the DP maintained its acidic properties in the dry and wet periods. High turbidity was observed in the dry period. The highest concentrations of chloride were observed in the dry period, although the samples of DP in the wet period obtained the highest average of 10.45 ± 3.41 mg L⁻¹.

The presence of chloride in rainwater samples can be attributed to marine aerosols and the proximity to the sea, as was also reported in a study carried out in the Alto de Sorocaba Basin in Southeast Brazil (Conceição *et al.*, 2011) and in Greece (D'Alessandro *et al.*, 2013), or it might be derived, for example, from the dissolution of evaporated minerals in the form of soil dust (Wu *et al.*, 2012). In addition to natural emissions, Cl⁻ can be attributed to pollution, mainly from human activities such as burning biomass, vehicular traffic and the decomposition of organochlorine compounds (Conceição and Bonotto, 2004; Négrel and Roy, 1998; Pelicho *et al.*, 2006; Sanusi *et al.*, 1996).

Table 1. Descriptive statistics for concentrations of physico-chemical parameters. in the wet period and in the dry period.

| Parameter | Chloride (mg L ⁻¹) | | | Conductivity (µS cm ⁻¹) | | | pH | | | Turbidity (NTU) | | | |
|-----------|--------------------------------|-------|-------|-------------------------------------|--------|--------|-------|------|------|-----------------|-------|--------|------|
| | Ordinance n° 05/2017 | | | | | | | | | | | | |
| | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | |
| Wet | Average | 10.45 | 6.82 | 6.34 | 50.82 | 46.03 | 23.14 | 4.04 | 6.15 | 5.84 | 5.51 | 25.31 | 0.35 |
| | Median | 8.77 | 6.82 | 5.85 | 41.09 | 39.68 | 23.51 | 4.23 | 6.20 | 6.27 | 0.45 | 4.20 | 0.35 |
| | SD | 3.41 | 3.18 | 1.16 | 24.77 | 22.80 | 9.87 | 0.56 | 0.31 | 0.50 | 12.58 | 35.23 | 0.19 |
| | Minimum | 6.82 | 2.92 | 4.87 | 21.14 | 22.88 | 8.85 | 3.68 | 5.86 | 5.14 | 0.14 | 0.60 | 0.10 |
| | Maximum | 15.60 | 11.70 | 7.80 | 93.03 | 84.00 | 35.73 | 5.32 | 6.64 | 6.65 | 34.00 | 96.00 | 0.70 |
| | | Point | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF |
| Dry | Average | 7.38 | 9.42 | 3.83 | 165.90 | 143.77 | 48.92 | 3.58 | 6.35 | 6.17 | 3.18 | 35.96 | 1.34 |
| | Median | 7.80 | 4.73 | 1.61 | 153.85 | 113.25 | 43.10 | 3.63 | 6.33 | 6.16 | 1.12 | 12.10 | 1.13 |
| | SD | 5.47 | 13.23 | 5.52 | 109.18 | 101.29 | 22.47 | 0.22 | 0.12 | 0.23 | 3.51 | 51.41 | 0.69 |
| | Minimum | 0.97 | 0.00 | 0.00 | 48.90 | 68.70 | 27.90 | 3.30 | 6.23 | 5.96 | 0.00 | 0.00 | 0.62 |
| | Maximum | 12.97 | 34.41 | 14.33 | 353.00 | 344.00 | 91.20 | 3.99 | 6.58 | 6.61 | 8.00 | 129.00 | 2.60 |
| | | Point | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF |

Key to initials: DP: Direct Precipitation; FF: First-Flush; RR: Reservoir; SD: Standard Deviation.

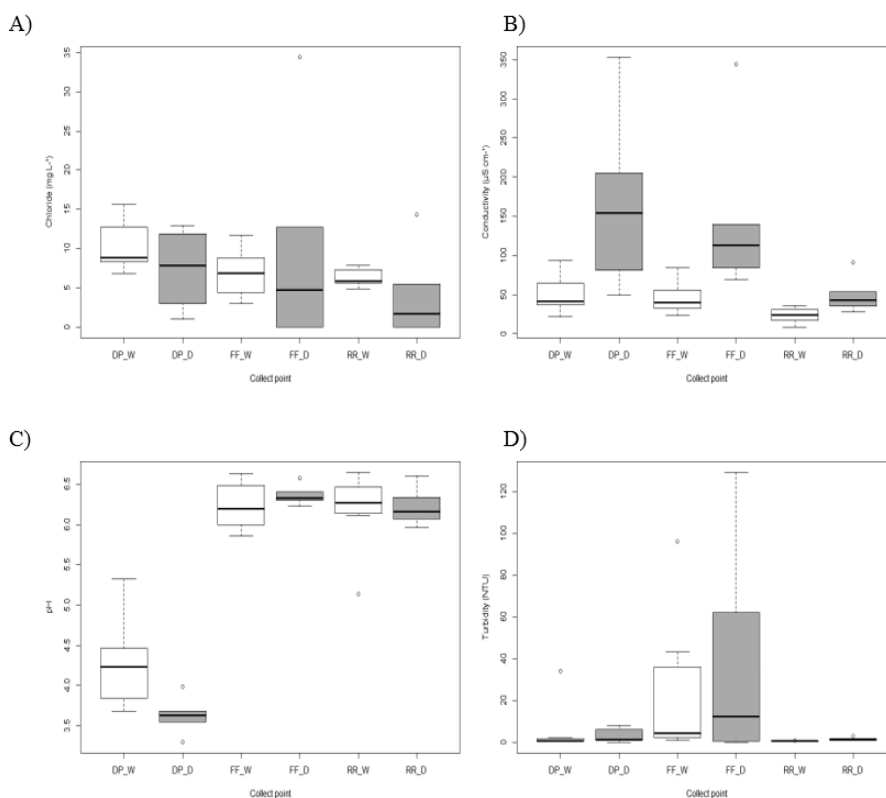


Figure 2. Boxplot for physico-chemical concentrations collected in the wet period (W) – shown in grey and dry (D) – shown in white, at the points of direct precipitation (DP), first flush (FF) and reservoir (RR).

The dry period resulted in a wider variation of concentrations, particularly in the first millimeters of rain or at the FF point, with a minimum of 0 mg L⁻¹ and a maximum of 34.41 mg L⁻¹. At this stage, total deposition occurs, and consists of both wet deposition and dry deposition, which can lead to higher concentrations of chloride. The accumulation and washing of pollutants are extremely dynamic processes, where the variation can be accounted for by the continuous changes of pollutants throughout the dry period and throughout the rain event (Wijesiri *et al.*, 2016).

The legislation does not cover conductivity limits. In the assessment of seasonality, the highest values were recorded in the dry period, with average concentrations of 165.90 ± 109.18 µS cm⁻¹ at the point of DP; 143.77 ± 101.29 µS cm⁻¹ at the FF point and 48.92 ± 22.47 µS cm⁻¹ at the RR point. Despite the high standard deviation for conductivity, especially in the dry period, according to the Tukey test which compares the means two by two, the average means are found to be statistically equal (Figure 3). In light of this, it can be assumed that the characterization of environmental data is subject to intermittent precipitation events and a wide range of meteorological elements and factors, before a greater variability can be found in the results obtained from the physico-chemical parameters. In the drier months, there is a higher concentration of particulate material, much of it in the form of dissolved solids that are deposited and accumulated on the catchment surface and can influence electrical conductivity.

Close values for conductivity were found in a study that was based on different rainwater storage systems in Greece: the first flush located in an industrial area displayed a conductivity of 143 µS cm⁻¹, similar to this study (Gikas and Tsihrintzis, 2012). In the rainy months, the average conductivity found in the DP, FF and RR was 50.82 ± 24.77 µS cm⁻¹, 46.03 ± 22.80 µS cm⁻¹ and 23.14 ± 9.87 µS cm⁻¹, respectively, lower values than those in the period of drought. These results demonstrate that rain assists in cleaning the atmosphere through a greater dilution of the analytes, where the conductivity showed more critical values in the dry period (Mimura

et al., 2016). All the samples analyzed resulted in conductivity below $100 \mu\text{S cm}^{-1}$, with a low level of mineralization (Vialle *et al.*, 2011).

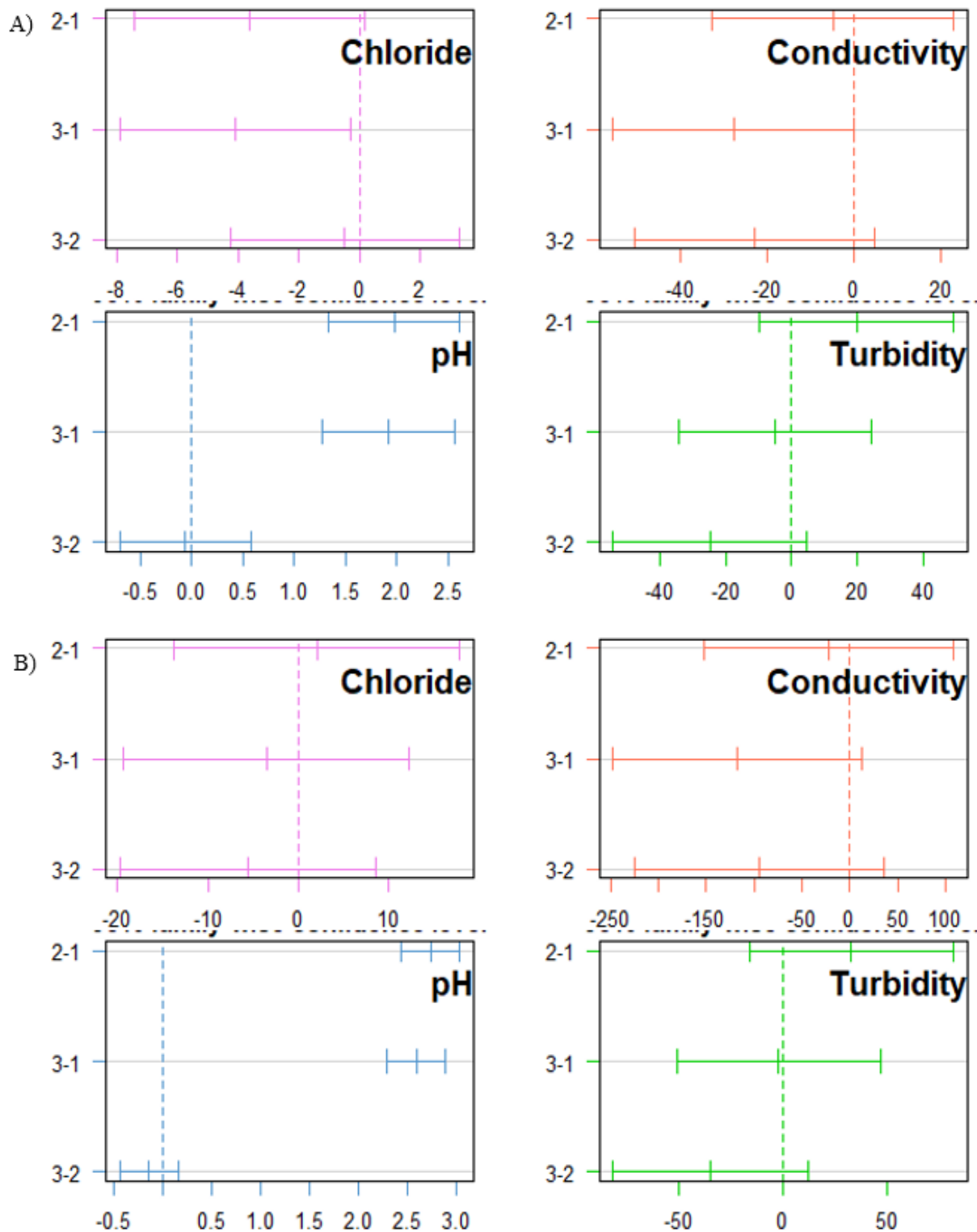


Figure 3. Tukey test for physico-chemical parameters collected in the wet period (A) and dry (B), at the points of direct precipitation (1), first flush (2) and reservoir (3).

Rainwater samples collected directly from the atmosphere in a rural area close to the forest in the city of Guarapuava, Brazil, showed a variation of $4.4 - 24.4 \mu\text{S cm}^{-1}$ (Beló *et al.*, 2009). In Ganhaizi, and in the city of Lijiang in China, where rainwater samples were also analyzed,

the conductivity observed in these locations during the rainy season ranged from 2.14 to 57.2 $\mu\text{S cm}^{-1}$, with an average of 11.5 $\mu\text{S cm}^{-1}$; differences in anthropic activity may be the reason for the different results in each city (Niu *et al.*, 2014). The conductivity found in these studies show fewer variations than in CAP-UERJ, located in an urban area and there was a high concentration of air pollution of vehicular origin.

The pH range of rainwater is generally between 4.0 and 6.0, with NH_x being ionized and the H^+ ion resulting from the acid-base balance in the rain (Souza *et al.*, 2006). Rainwater caused by dissociation of dissolved carbon dioxide (CO_2) has a natural pH of 5.6 (Hoinaski *et al.*, 2014); however, this value can be reduced and the acidity increased in the presence of pollutants originating from human activities (Charlson and Rodhe, 1982). Throughout the period of analysis, the FF and RR points showed a minimum average of 5.84 ± 0.50 in RR (W) and a maximum of 6.35 ± 0.12 in FF (D). The pH has no direct impact on human health, although the low pH value in the water can lead to corrosion in rainwater storage pipes or tanks (Lee *et al.*, 2017).

In the humid period, there is a greater variation in pH than in the dry period; in addition, the rain is more acidic in the less rainy period, as has also been confirmed by research on rainwater in Minas Gerais (Cerqueira *et al.*, 2014). The highest pH values are found at the points where the water traveled through the roof (FF and RR), possibly as a result of the deposition of dissolved solids (Hagemann and Gastaldini, 2016). The feces of birds that are considered to be alkaline and have a high concentration of NH_3 lead to an increase in pH at the points of total deposition. The presence of outliers was observed at the points of DP, FF and RR. These outliers are common in environmental data, especially in rainwater. The Tukey test was carried out to compare whether the data are different from each other and it was found that the PD point is statistically different from the other collection points; however, FF and RR had similar populations in the two study periods.

A study carried out in São Paulo concluded that the use of ethanol as a fuel leads to the emission of several compounds such as acetic acid and acetaldehyde directly into the atmosphere, which means that organic compounds may be responsible for about 44% of the acidity present in the wet deposition (Fornaro and Gutz, 2003). All the samples collected without roof interference (DP) were below the recommended limit for drinking use in both periods ($N = 13$), which may indicate the presence of acidic substances in the atmosphere. During the first flush in the wet period, 28.57% of the samples were slightly below the permissible pH limit of 5.86 and 5.96. In the dry period, all the FF samples were within the permitted range. At the RR reservoir point, only one result was below 6.0 in the wet period, and the same was observed in the dry period.

Turbidity indicates the degree of attenuation that a beam of light undergoes when it passes through water (ANA, 2019). The initial precipitation is stored at the FF point; this consists of gases originating from the atmosphere and dissolved in raindrops and particulate matter found on the roof, which cause a greater incidence of turbidity at this point and considerably reduce the total suspended solids at the RR reservoir point.

Rainwater is affected by surface runoff and storage conditions (Abu-Zreig *et al.*, 2019); the initial 2 mm of rain contains most of the contaminants directed to the FF disposal point (Kus *et al.*, 2010b). In this way, the initial precipitation event removes most of the material deposited on the catchment surface and stored in the FF; this reveals the need to dispose of the first millimeters of rainwater to avoid contaminating the reservoir. The deposition of pollutants from the atmosphere over the roof surface during a certain dry period, influences the quality of rainwater. The longer the dry period between the precipitation events, the greater the probability of pollutants being deposited on the roof surface (Yaziz *et al.*, 1989). Turbidity can be a risk to human health if the suspended particles have adsorbed toxic inorganic or organic compounds, so it is essential to avoid the first volumes of effective precipitation (Kus *et al.*, 2010a). Results

above the limit of 5 UNT were found in the city of Khorramabad in western Iran (Hoseinzadeh *et al.*, 2016), at points FF and DP. FF had a total of 6 non-compliant samples, DP had few events with turbidity levels above the permitted level with $N = 1$ in the wet period and $N = 2$ in the dry period.

PCA in the wet season showed that the first and second components (DIM 1 and 2) represented 32.9% and 29.4% of the total variance, respectively. PCA of data is recommended when the sum of DIM 1 and DIM 2 is greater than 60%. Most of the variables are well represented in the first two components in the wet season, with an emphasis on Conductivity and Chloride in the FF, which make a greater contribution to DIM 1 due to their proximity to the X-axis and have a strong correlation with the vector size. In the first quadrant, the CDD, DP Conductivity, DP Turbidity and FF pH are correlated, although RR Turbidity and RR Chloride have a negative correlation because they are in opposite quadrants. The correlation between the variables in the total dataset was confirmed by the Pearson correlation coefficient, together with the Hierarchical Cluster Analysis (HCA), which were used to visualize the clusters and possible correlations. The search for clusters between the variables was an additional way of studying the structure of the results provided by the PCA with the HCA.

In the wet season, most correlations between physico-chemical parameters are weak, and the highest correlations occurred between the Turbidity in the DP and the CDD and between Conductivity and Chloride in FF, which suggests that Chloride ions may increase the rainwater Conductivity. In this study, the relationship between CDD and Turbidity is directly proportional, i.e., the longer the time interval without rain, the greater the accumulation of suspended particles in the atmosphere that increase turbidity in DP. The correlation is null between the Turbidity in the DP and the Turbidity in the RR. The Turbidity in the RR might be related to the solids deposited in the roof and the DP Turbidity is only influenced by the atmospheric conditions. In the Pearson correlation dendrogram 3 clusters are formed. RR Turbidity, DP pH, FF Chloride and FF Conductivity, form the lowest group and these parameters are not connected to the other clusters, which shows a low correlation (Figure 4).

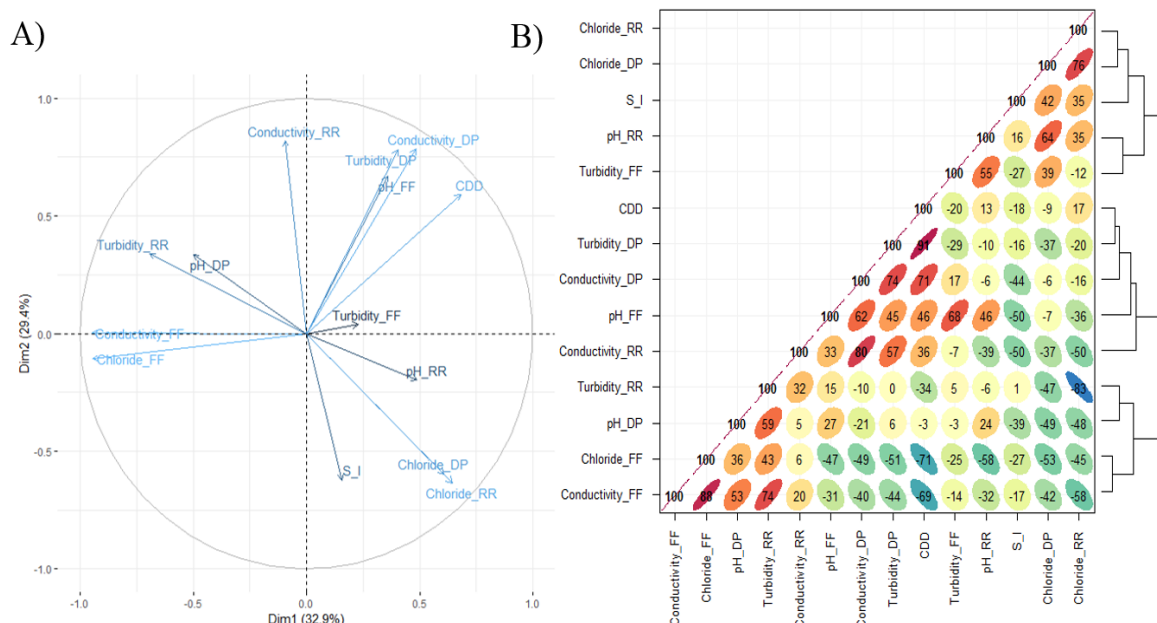


Figure 4. (A) Principal component analysis (PCA) and (B) Pearson correlation matrix, together with the hierarchical cluster analysis (HCA) of physico-chemical and meteorological parameters in the wet period - in direct precipitation (DP), first flush (FF) and reservoir (RR). CDD: Consecutive dry days; S_I: Sub - diurnal rainfall intensity.

The PCA shows most of the variables are close to each other in the dry season; this represents a strong correlation, and suggests a greater contribution is made to the DIM 1 eigenvector (Figure 5). The PCA also includes two main groups: sub-rainfall intensity, RR Turbidity, DP pH and Conductivity and FF Turbidity are in the first cluster and the other parameters in the second cluster. The FF and RR Chloride are closely correlated, as well as the FF Conductivity and RR Conductivity and FF Chloride and Conductivity. Conductivity indirectly measures the presence of ions dissolved in the water, among them the Chloride ion. There are close correlations between FF Conductivity and Chloride ($r = 0.92$), as well as FF pH and Conductivity and between FF and RR pH, as the H^+ ions dissolved in the water also lead to an increase of Conductivity.

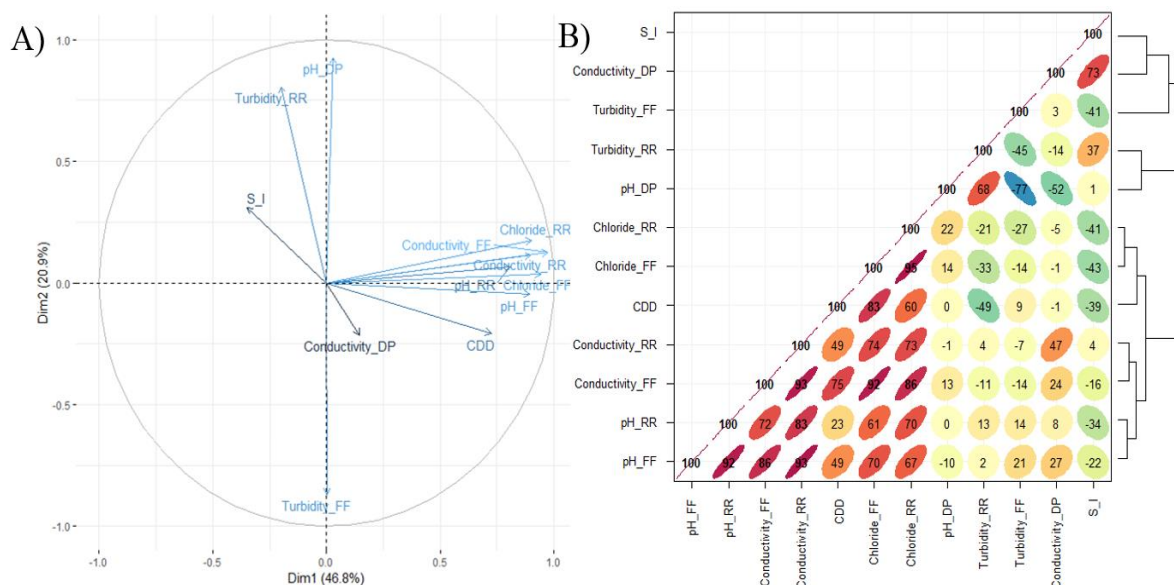


Figure 5. (A) Principal component analysis (PCA) and (B) Pearson correlation matrix, together with a hierarchical cluster analysis (HCA) of physico-chemical and meteorological parameters in the dry period of direct precipitation (DP), first flush (FF) and reservoir (RR). CDD: Consecutive dry days; S_I: Sub - diurnal rainfall intensity.

3.2. Metal

In the wet period, metals (with the exception of Na) are above the permissible limit set by Ordinance n° 05/2017 in at least one sample. The FF can obtain 42.85% of non-compliant results, which assists in reducing the concentration of metals at the RR point; however, it is not effective enough to reduce this concentration to the recommended limit. In the dry period, metals have a lower concentration than in the wet period, and in the case of FF, 22.85% of the samples are above what is permissible (Table 2 and Figure 6 and 7).

The samples collected in the dry season had the highest Ca concentrations and were lower in the wet season. The highest mean Ca value that was obtained for the FF samples was $33.16 \pm 28.4 \text{ mg L}^{-1}$ in the dry season and the lowest mean value which was for the RR samples was $1.12 \pm 0.21 \text{ mg L}^{-1}$ in the wet season. It should be noted that the dominant components were crustal, which increases the alkalinity of the rainwater because it includes components such as Mg and Ca (Kulshrestha *et al.*, 2003). There are many possible sources of Ca, such as marine aerosols, soil particle resuspension and road dust (Ali *et al.*, 2004), and these can neutralize the acidity of rainwater (Han *et al.*, 2011). The legislation does not stipulate if there are any permissible limits for Ca.

Table 2. Descriptive statistics for the metal concentrations and meteorological parameters in the wet period and the dry period.

| Parameter | Ca | | | Cd | | | Cu | | | Fe | | | K | | | Mn | | | Na | | | Ni | | | Pb | | | Zn | | | CDD | S_I | | | | | | |
|------------------|-------|-------|-------|-------|------|------|------|-------|-------|------|-------|------|-------|-------|-------|------|------|------|-------|-------|-------|-------|------|------|------|------|------|------|------|-------|------|------|------|-------|-------|----|--|--|
| Wet | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Ordinance 5/2017 | | | | 0.005 | | | 2 | | | 0.3 | | | | | | 0.1 | | | 200 | | | 0.07 | | | 0.01 | | | 5 | | | | | | | | | | |
| Point | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | | |
| Average | 3.56 | 9.78 | 1.12 | 0.02 | 0.02 | 0.02 | 0.95 | 13.83 | 3.54 | 1.04 | 4.74 | 1.48 | 10.42 | 14.23 | 9.82 | 0.04 | 0.60 | 0.04 | 19.13 | 19.89 | 20.83 | 0.21 | 0.33 | 0.13 | | | | 0.04 | | | 0.91 | 3.71 | 3.02 | 4.00 | 9.37 | | | |
| Median | 2.36 | 6.12 | 1.05 | 0.02 | 0.02 | 0.02 | 0.76 | 13.46 | 1.97 | 0.92 | 3.81 | 0.86 | 9.48 | 14.61 | 10.37 | 0.04 | 0.26 | 0.04 | 18.82 | 20.90 | 19.48 | 0.21 | 0.24 | 0.14 | | | | 0.04 | | | 1.00 | 2.85 | 2.70 | 3.00 | 3.07 | | | |
| SD | 3.28 | 9.69 | 0.21 | 0.00 | 0.02 | 0.00 | 0.39 | 11.71 | 5.12 | 0.53 | 4.33 | 1.37 | 2.35 | 1.52 | 4.44 | 0.02 | 0.78 | 0.03 | 5.28 | 7.01 | 2.78 | 0.05 | 0.34 | 0.04 | | | | 0.04 | | | 0.36 | 2.30 | 0.88 | 3.83 | 11.88 | | | |
| Minimum | 1.00 | 3.44 | 0.89 | 0.02 | 0.01 | 0.01 | 0.59 | 0.04 | 0.36 | 0.38 | 0.39 | 0.26 | 8.29 | 10.90 | 1.06 | 0.01 | 0.16 | 0.01 | 8.77 | 5.02 | 17.80 | 0.17 | 0.08 | 0.09 | | | | 0.01 | | | 0.29 | 2.75 | 2.61 | 1.00 | 1.24 | | | |
| Maximum | 10.56 | 31.11 | 1.53 | 0.02 | 0.06 | 0.02 | 1.57 | 31.34 | 13.78 | 1.91 | 10.59 | 4.23 | 14.61 | 15.46 | 15.67 | 0.06 | 1.98 | 0.09 | 25.74 | 27.16 | 25.22 | 0.25 | 0.92 | 0.17 | | | | 0.06 | | | 1.32 | 8.93 | 5.02 | 12.00 | 30.80 | | | |
| Dry | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Point | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | DP | FF | RR | | |
| Average | 19.25 | 33.16 | 10.31 | 0.02 | 0.02 | 0.02 | | | | 1.85 | 0.16 | 1.64 | 0.08 | 4.17 | 6.98 | 3.88 | 0.28 | 0.39 | 0.22 | 5.99 | 6.49 | 4.58 | 0.25 | 0.30 | 0.60 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 1.41 | 4.05 | 3.57 | 1.67 | 4.19 | | | |
| Median | 18.11 | 19.88 | 10.94 | 0.02 | 0.01 | 0.02 | | | | 0.36 | 0.13 | 0.90 | 0.03 | 2.81 | 6.04 | 2.71 | 0.30 | 0.37 | 0.22 | 1.99 | 2.20 | 1.79 | 0.25 | 0.30 | 0.60 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 1.44 | 2.57 | 2.54 | 0.00 | 0.95 | | | |
| SD | 10.20 | 28.40 | 5.86 | 0.01 | 0.01 | 0.01 | | | | 3.11 | 0.12 | 1.62 | 0.12 | 3.96 | 4.67 | 3.05 | 0.09 | 0.10 | 0.02 | 10.10 | 10.46 | 7.39 | | | | 0.00 | 0.00 | | 0.40 | 3.63 | 2.53 | 2.58 | 6.74 | | | | | |
| Minimum | 7.60 | 16.00 | 1.99 | 0.01 | 0.01 | 0.01 | | | | 0.19 | 0.04 | 0.44 | 0.01 | 1.27 | 2.79 | 2.04 | 0.19 | 0.30 | 0.19 | 1.29 | 1.87 | 0.97 | 0.25 | 0.30 | 0.60 | 0.01 | 0.01 | 0.01 | 0.93 | 2.51 | 2.51 | 0.00 | 0.57 | | | | | |
| Maximum | 33.02 | 89.45 | 16.21 | 0.02 | 0.03 | 0.03 | | | | 6.51 | 0.34 | 4.47 | 0.33 | 11.96 | 15.37 | 9.94 | 0.41 | 0.55 | 0.25 | 26.58 | 27.83 | 19.63 | 0.25 | 0.30 | 0.60 | 0.01 | 0.01 | 0.01 | 1.92 | 11.47 | 8.73 | 5.00 | 17.6 | | | | | |

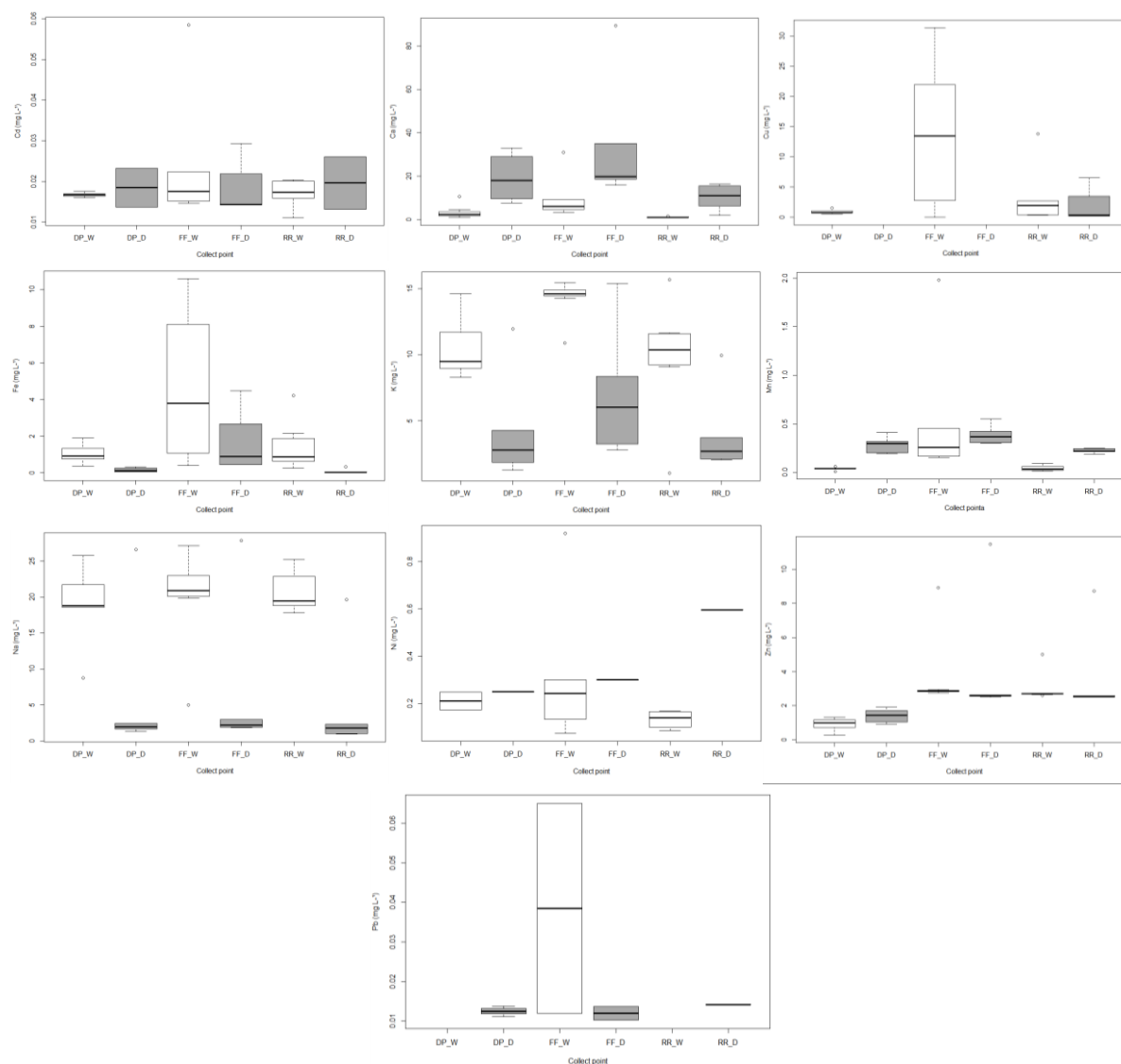


Figure 6. Boxplot for metal concentrations collected in the wet period (W) – shown in grey - and dry (D) – shown in white, at the points of direct precipitation (DP), first flush (FF) and reservoir (RR).

The average for the Cd at DP, FF and RR points, in both periods, was above the maximum permitted value of 0.005 mg L^{-1} . In the dry season, about 61% of the results for the concentration were below the limit of quantification (LQ). Studies have suggested that the corrosion of galvanized metallic structures exposed to the urban atmosphere may be responsible for high concentrations of Cd, as well as the proximity of highways (Van Metre and Mahler, 2003), as well as the presence of this metal in the dust that is carried for distances from buildings being repaired or renovated (Miguel *et al.*, 1997). Results above 0.005 mg L^{-1} have also been found in other rainwater studies (Alcolea *et al.*, 2015), while at the same time there are records of Cd below the limit of quantification (Despins *et al.*, 2009).

The characterization of rainwater in schools in Ghana showed concentrations of Cd above the limit set by the WHO drinking-water quality guidelines (0.003 mg L^{-1}). This can be attributed to sources such as batteries, automobiles and oil-burning furnaces (Cobbina *et al.*, 2015). Analyses of rainwater in Nigeria found that there were anthropogenic impacts on the environment and that these are linked to a high-level of gas flaring and oil refining activities and obtained Cd above the recommended 0.003 mg L^{-1} limit. These are among other factors that can affect these concentrations, such as wind direction and wind speed, pH, the rainfall index and particulate matter concentration (Akintola *et al.*, 2018).

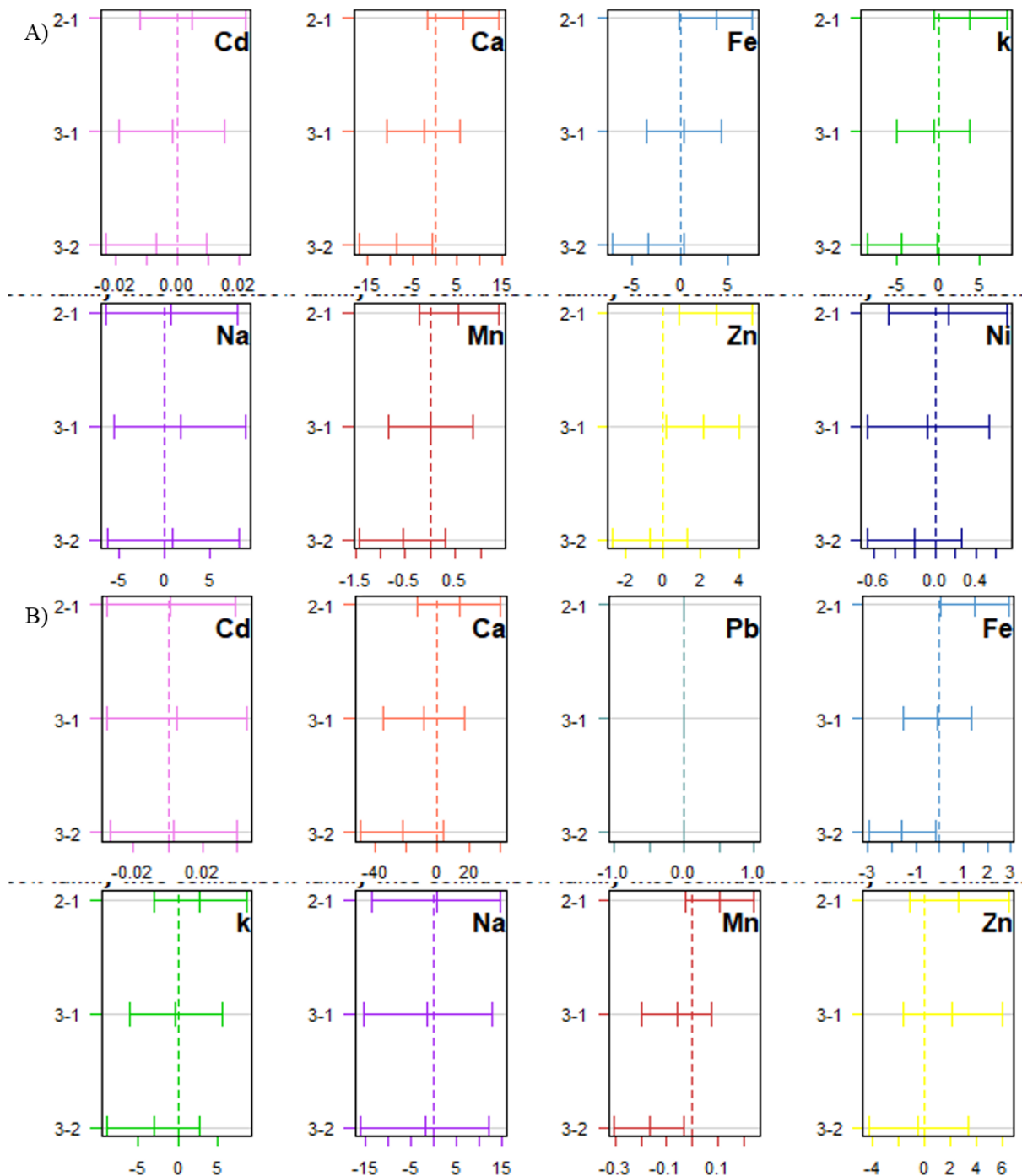


Figure 7. Tukey test metals in the wet period (A) and dry (B), at the points of direct precipitation (1), first flush (2) and reservoir (3).

Cu has a seasonal behavior with higher concentrations in the wet season. In the rainy season, DP had an average value of $0.95 \pm 0.39 \text{ mg L}^{-1}$, unlike the FF samples, where there were high concentrations with a mean value of $13.83 \pm 11.71 \text{ mg L}^{-1}$. The disposal of rainwater (FF) significantly reduced the copper concentration in the water stored in the RR, which had an average of $3.54 \pm 5.12 \text{ mg L}^{-1}$; despite this, in most of the analyzed samples the reduction was not enough to comply with the legislation. Since rainwater is slightly acidic and contains few dissolved minerals, it can dissolve metals and other impurities that can be found in the storage tank, and this causes discoloration, as well as a bad taste and odor in the harvested rainwater (Sánchez *et al.*, 2015). The seasonal variation of Cu can be influenced by local contamination or by sources of air masses that have a pattern of behavior that varies between the seasons (Kim

et al., 2000).

In both periods, the FF showed a high concentration of Fe, which might be influenced by the dry deposition on the roof where there are particles containing Fe that are removed by the first millimeters of rain. Iron is generally classified as an element which naturally originates from the earth's crust (Nadzir *et al.*, 2017). However, in the characterization of rain in a study carried out in Spain, it was concluded that iron was emitted from anthropogenic sources, on the basis of an analysis of retrograde trajectories and the fouling factor that reveals the non-crustal origin of this metal (Moreda-Piñeiro *et al.*, 2014). In fine particles, the presence of iron can be attributed to the corrosion of the internal parts of vehicles and exhaust pipes (Loyola *et al.*, 2012). This is because the study site has an urban profile, which can cause emissions of iron-containing compounds, either anthropogenic or of natural origin, due to its proximity to the Tijuca massif.

Potassium is an element that can be found in the environment and in all-natural waters (WHO, 2008), and the presence of this element was observed during the dry and wet season. In the rainy season, the concentration increased in all the samples. In the rainy season, the K concentration increased at all points. In regions close to the ocean, rainwater has a marine influence on elements such as potassium (Tomaz, 2010; Vázquez *et al.*, 2003). Other studies have shown that K originates from biogenic sources such as aerosols containing leaf fragments, pollen (Forti *et al.*, 2000; Pauliquevis *et al.*, 2012) or air masses containing compounds from biomass burning (Vieira-Filho *et al.*, 2013).

The mean Mn values in the wet season were 0.04 ± 0.02 mg L⁻¹ for DP, 0.60 ± 0.78 mg L⁻¹ for FF and 0.04 ± 0.03 mg L⁻¹ for RR. A similar concentration of Mn in wet deposition was found in rainwater samples in Santa Maria, Rio Grande do Sul and Greece (Hagemann and Gastaldini, 2016; Melidis *et al.*, 2007). In the dry season, only the samples of May 2018 were below the limit of quantification (LQ). The other samples had high concentrations for DP, FF and RR with average values of 0.28 ± 0.09 mg L⁻¹, 0.39 ± 0.10 mg L⁻¹ and 0.22 ± 0.02 mg L⁻¹, respectively.

The Mn concentrations in the rainfall are higher in the spring and winter, but lower in the summer and may be caused by changes in the source of pollutants that can be attributed to the wind direction, which has a seasonal effect (Cheng *et al.*, 2011). An evaluation of total suspended particulates in urban areas in South-East Brazil concluded that Mn concentrations were significantly higher in the dry season and may have resulted from changes in the rainfall pattern (Machado *et al.*, 2018).

A study carried out in Rio de Janeiro for PM_{2.5} samples showed that Mn usually originates from traffic, soil-related sources or raw material in the steel industry (Mateus and Gioda, 2017). The initial disposal system proved to be effective in reducing the concentration of this compound in the reservoir to a level below that recommended by the guidelines of Ordinance n° 05/2017 (0.1 mg L⁻¹). During the whole sampling campaign, Na had the highest concentration in the rainy season, ranging from 5.02 to 27.16 mg L⁻¹ for FF samples and a mean average of 19.13 ± 5.28 mg L⁻¹ for DP and 20.83 ± 2.78 mg L⁻¹ for RR. There was a lower variation for Na results in the dry season, with the highest observed mean average of 6.49 ± 10.56 mg L⁻¹ for FF, while the other samples had a mean of 5.99 ± 10.10 mg L⁻¹ for DP and 4.58 ± 7.39 mg L⁻¹ for RR. The system for the capture and storage of rainwater located near the coast of Rio de Janeiro can lead to higher Na levels, since it is present in the composition of marine aerosols (Al-Momani, 2003). All the points showed results within the 200 mg L⁻¹ limit. Water-soluble Na content results in marine spray (Singh *et al.*, 2007; Soluri *et al.*, 2007; Szép *et al.*, 2019), and leads to the highest concentrations in the rainy season, when it is transported over long distances and via dry or wet deposition (Silva *et al.*, 2017). Studies on PM in Rio de Janeiro have shown that there is a higher Na concentration during March and April, which was also observed in this study (Quiterio *et al.*, 2004).

A reduction in Ni concentration was observed at the reservoir point (unlike the first-flush), but it was not enough to comply with the legislation. The highest mean average for Ni samples found in the wet season was $0.33 \pm 0.34 \text{ mg L}^{-1}$ for FF, and the lowest in the RR with $0.13 \pm 0.04 \text{ mg L}^{-1}$. Ni can appear as the result of the leaching of tubes, connections, taps and steel, but its presence decreases over a period of time (WHO, 2008). In the dry season, only concentrations of 0.25 mg L^{-1} in DP, 0.30 mg L^{-1} in FF and 0.60 mg L^{-1} in RR were determined in the first collection. Ni has been correlated with anthropogenic activities in several studies (Kim *et al.*, 2000), and also with traffic emissions (Nadzir *et al.*, 2017) and fuel combustion (Gunawardena *et al.*, 2013).

DP and FF Pb samples in the wet season were below the limit of quantification (LQ). In the FF, Pb could only be detected in 2 samples with results of 0.01 mg L^{-1} and 0.06 mg L^{-1} . Rainwater systems in Canada also showed levels of Pb lower than 0.01 mg L^{-1} in the RR (Despins *et al.*, 2009). In the dry season, samples were also observed below LQ (N = 12). The cause of Pb emissions is generally attributed to anthropogenic sources (Azimi *et al.*, 2003; Moreda-Piñero *et al.*, 2014), such as factors leading to the wear and tear of vehicles (Egodawatta *et al.*, 2013). In addition, Pb is also linked to the effects of roadside deposition caused by the accumulation of soil residues, fuel additives (Thorpe and Harrison, 2008) and by emission of exhaust fumes into the atmosphere (Gunawardena *et al.*, 2012; 2015; Zhang *et al.*, 2015).

The Zn in the FF season showed a sample with high concentration of 11.47 mg L^{-1} and RR followed the same pattern with a result of 8.73 mg L^{-1} . Zn was found to be the most abundant ion among the metals detected in rainwater (Vlastos *et al.*, 2019); concentrations below 5 mg L^{-1} were reported in urban areas and in areas of heavy traffic (Angrill *et al.*, 2017; Gispert *et al.*, 2018). Higher levels of Zn were detected in rainwater collected from galvanized zinc roofs (Belghazi *et al.*, 2002; Förster, 1996; Simmons *et al.*, 2001) Although the roof of the rainwater catchment system is made of aluminum and zinc, these levels were not found in this study. The Zn can perhaps be attributed to the traffic of nearby avenues. This metal is generally found on the roads as an organometallic compound used in diesel engine lubricants and in tire wear particles (Ball *et al.*, 1998; Davis *et al.*, 2001; Helmreich *et al.*, 2010; Mangani *et al.*, 2005). Other studies advocate the use of porous pavements to reduce the number of metal pollutants originating from roads (Yu and Zhao, 2012).

Any metals that had a low variation or led to results below the LQ were not selected for the multivariate statistical analysis. In the PCA for DP during the wet season, it was found that Fe and the S_I have a negative correlation with the other parameters. The formation of 3 clusters was noted in the dendrogram: the first consisted of CDD, Cu, Zn and Na correlated with the second cluster formed by Ca, K and Mn and the third cluster with IN_SUB and Fe.

Pearson's linear correlation matrix used for the wet season for DP, shows that K and Ca have the highest correlation ($r = 0.98$). Na and Zn ($r = 0.94$), Mn and Ca ($r = 0.88$) and Mn and K ($r = 0.79$) also have high correlations and may have the same natural and / or anthropogenic origin. Cu has negative correlations with most metals, which suggests it is of a different origin from the others; the same pattern of behavior was evident for Fe. Zn has moderate correlation with Cu, which suggests that Zn might be of a natural and anthropogenic origin. In the case of the dry season, Ca and S_I in the PCA showed a low correlation with the other parameters. In the dendrogram, there are 3 clusters and the most significant correlations in the dry season were found to be between Fe, K, Na, Zn and Mn, which probably originate from natural sources. Ca had low correlations with most of the parameters which suggests a different source of emission (Figure 8).

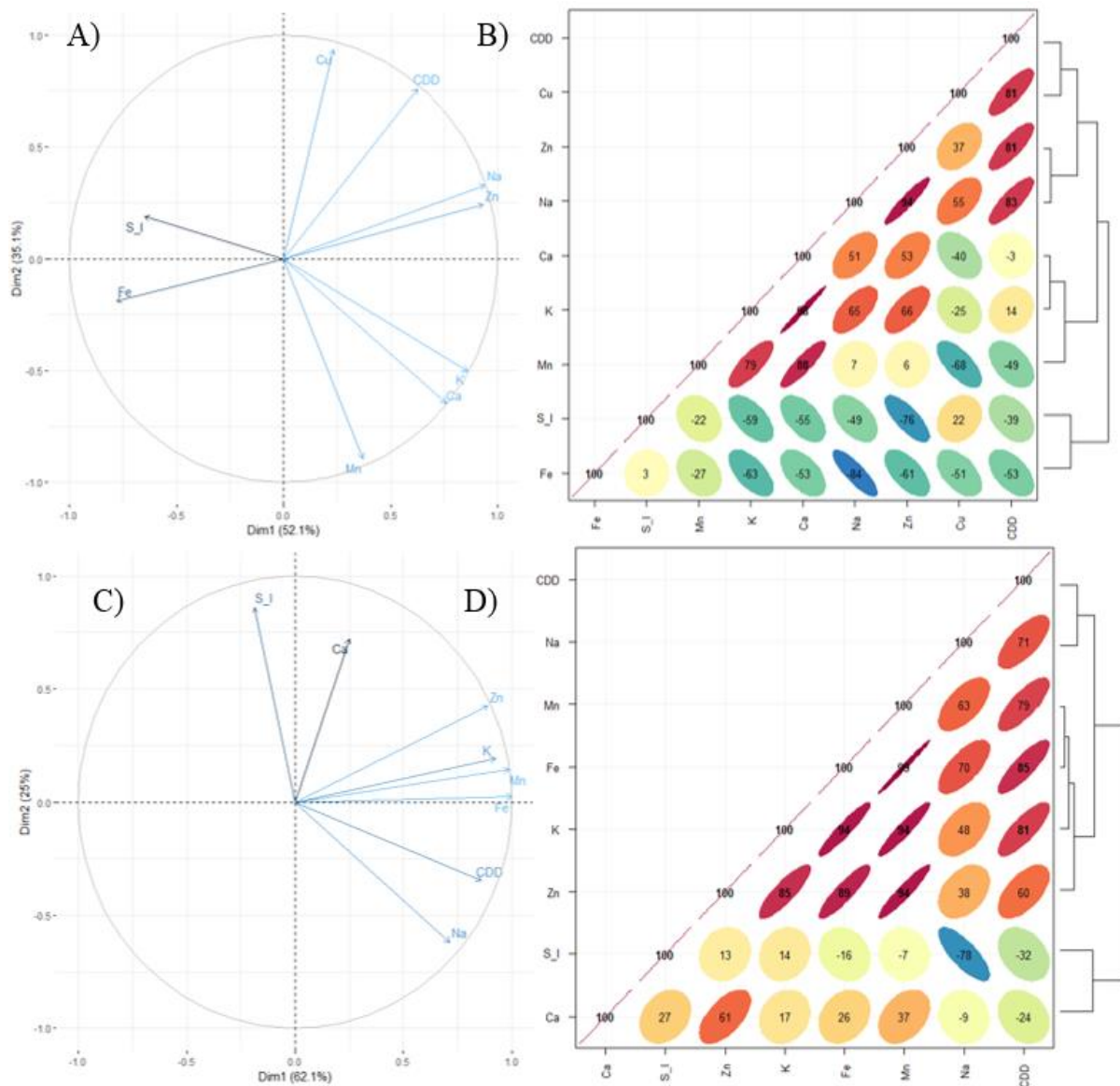


Figure 8. Principal component analysis (PCA) and Pearson correlation matrix, together with the hierarchical cluster analysis (HCA) of physico-chemical and meteorological parameters in direct precipitation (DP): (A, B) in the wet period; (C, D) in the dry period. CDD: Consecutive dry days; S_I: Sub - diurnal rainfall intensity.

In the FF wet season, the PCA analysis showed a high correlation and a link between Zn and Na as contributory factors. The S_I is inversely correlated to the other parameters, as in DP, whereas the S_I is negatively correlated with the metals. Fe has a high correlation with other metals, except for Na and S_I, which shows a low correlation. Despite being correlated with Mn, Fe is also correlated with the Cu and may have natural soil and anthropogenic sources like the vehicular emissions (Loyola *et al.*, 2012). Cu and Zn can be attributed to traffic emissions (Gunawardena *et al.*, 2013). In the case of the dry season, the components (Dim 1 and Dim 2) together represent 88.7% of the data. Fe is the only element in the 3rd quadrant that shows a negative correlation with the other PCA components. According to the dendrogram, two clusters were formed: the first by S_I and Fe and the second by CDD, Zn, Mn, Ca, Na and K. Apart from Fe, the other metals have strong and positive correlations with each other. Fe has negative correlations with other metals and probably does not have the same source. The S_I did not influence the concentrations of FF metal data (Figure 9).

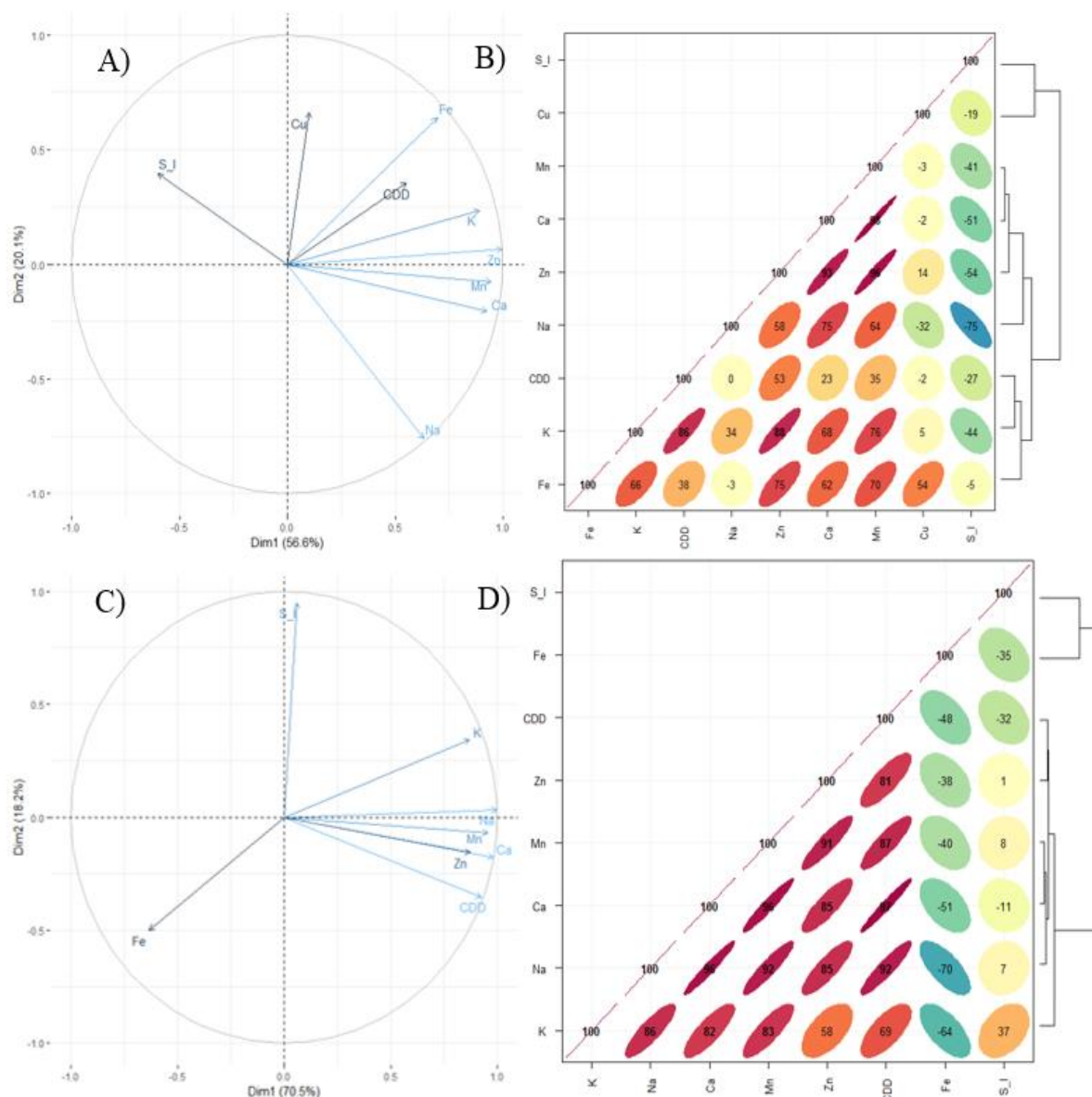


Figure 9. Principal component analysis (PCA) and Pearson correlation matrix, together with the hierarchical cluster analysis (HCA) of physico-chemical and meteorological parameters in first flush (FF): (A, B) in the wet period; (C, D) in the dry period. CDD: Consecutive dry days; S_I: Sub-diurnal rainfall intensity.

In the reservoir for the wet period, the PCA analysis shows a dispersion of the parameters that represent weaker correlations. In general, Fe has negative correlations and probably originates from a different source from the other metals. The most significant correlations were: K and Cu, Na and Cd and S_I and Ca.

There was no variance or contribution made by the CDD vector in the dry period, as there were no consecutive dry days on the dates selected for PCA analysis. It can be seen that the metals are more correlated than in the wet period. The closest correlations occurred between: Ca and Cu, K and Cu and Ca and K, probably from the same natural and / or anthropogenic source. The metals that may have had different sources were: Mn and Fe ($r = -0.94$) and Mn and Na ($r = -0.80$) (Figure 10).

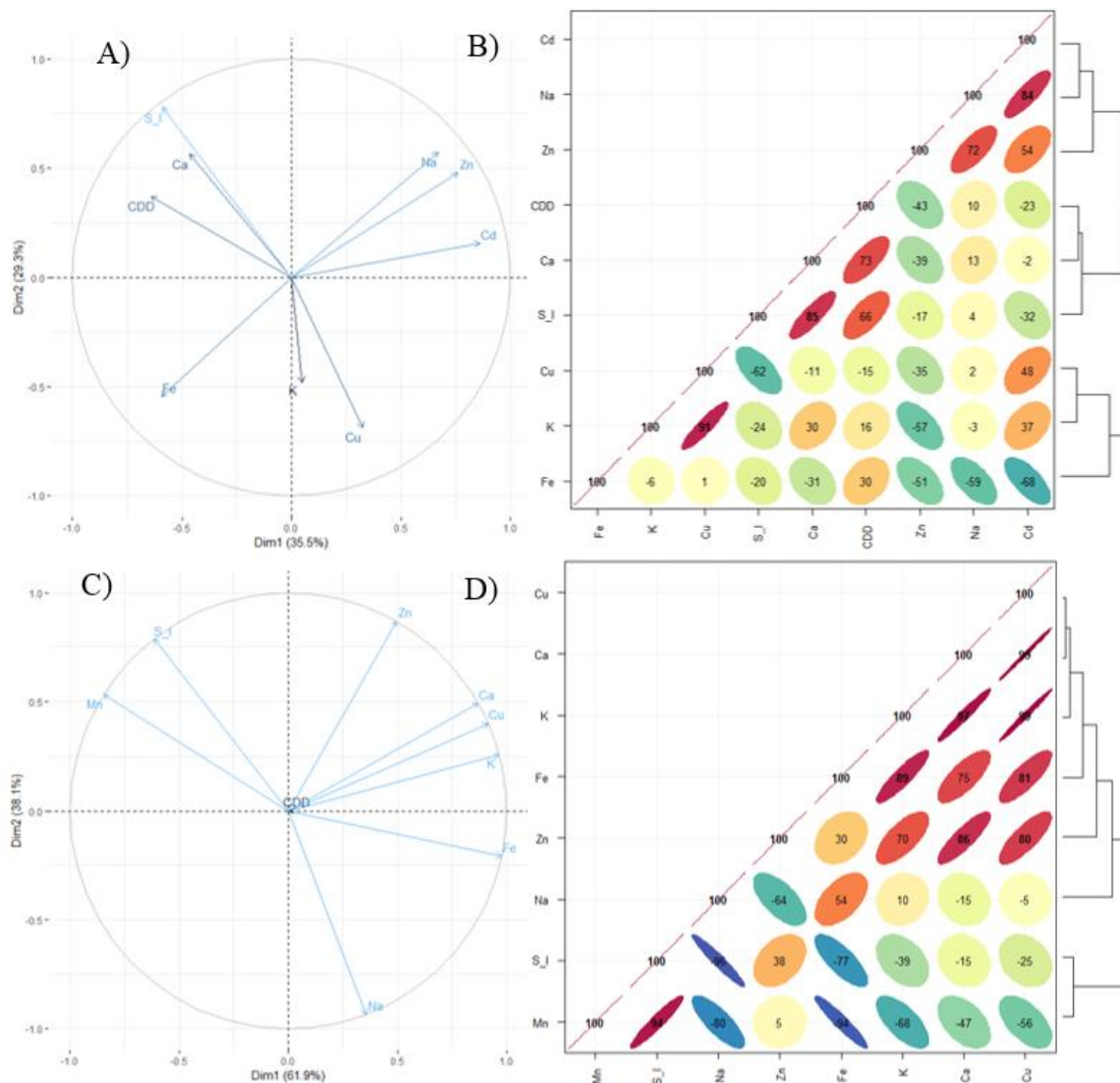


Figure 10. Principal component analysis (PCA) and Pearson correlation matrix, together with the hierarchical cluster analysis (HCA) of physico-chemical and meteorological parameters in reservoir (RR): (A, B) in the wet period; (C, D) in the dry period. CDD: Consecutive dry days; S_I: Sub - diurnal rainfall intensity.

4. CONCLUSION

This study carried out a research project into the chemical composition of rainwater at different points of a rainwater capture and storage system. After 1 year of monitoring, the results revealed that Ca, K and Na are the main metals found in rainwater. The R language was important to evaluate the possible sources and the visualization of groups between the physical-chemical and meteorological parameters. The findings suggest an anthropogenic origin linked to traffic emissions for Cu, Zn and Fe. It was found that Na, K, Ca, Mn and Fe may have a natural origin. Wet deposition is characterized by a low concentration of metals. However, when it comes into contact with the catchment surface, rainwater has a high concentration of pollutants, demonstrating the impact of urbanization on the quality of rainwater. It is suggested that the volume of discard be increased to decrease pollutants that reach the reservoir. The high concentration of metals in the wet period suggests that rain assists the cleaning of the atmosphere and that most metals are present in the form of aerosols and fine particles suspended

in the air. It was thus concluded that rainwater is not suitable for drinking purposes; pre-treatment is essential to ensure rainwater can be used safely for more mundane purposes. In future studies, it is recommended that the cations and anions of metals in rainwater be investigated to determine the existence of long-term volatile organic compounds, in addition to investigating the potential impact of metal contamination on human health.

5. ACKNOWLEDGMENTS

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