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Seasonal variation of atmospheric nutrient deposition in the western part of Rio Grande do Sul, Brazil

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ABSTRACT

The chemical composition of rainfall is influenced by natural or anthropogenic factors; the amount of nutrients deposited is increased by the amount of rainfall. This work sought to estimate the amount of nutrients deposited by precipitation in the Pampa biome, the seasonal variation of the chemical composition of rain water, and the origin of nutrients found in the water. Precipitation collectors were installed in the open area to measure precipitation volumes biweekly over 2 years, and the samples were chemically analyzed. Concentrations of nutrients in the rain water increased over winter; however, since there was less precipitation, the total deposition was similar to the other seasons. Correlation analysis using the Pearson coefficient showed a negative correlation between rain volume and ion contents, indicating a dilution effect. The total amount of nutrients from precipitation during the study was 72.7 kg ha^{-1}, representing an average of 36.3 kg ha^{-1} year^{-1}. The Ca^{2+} and K^+ ions are predominantly of litholical origin, whereas the SO_4^{2-} and NO_3^- ions were of anthropogenic origin. The balance between the sum of cations and the sum of anions was shown to be unitary, indicating excellent data validation. The input of these nutrients occurs gradually, avoiding excessive losses, increasing the stock in the soil.

Keywords: hydrology, nutrient cycling, seasonality, sustainability.

Variação estacional da deposição atmosférica de nutrientes na região central do Rio Grande do Sul, Brasil

RESUMO

A composição química da chuva é influenciada por fatores naturais ou antropogênicos, sendo a quantidade de nutrientes resultante da multiplicação de sua concentração pela quantidade precipitada. O objetivo do presente trabalho foi estimar: a quantidade de nutrientes aportada pela precipitação no bioma Pampa, a variação sazonal da composição química da água da chuva, a origem dos nutrientes encontrados na água. Os coletores de precipitação foram instalados em área aberta e quinzenalmente, durante 2 anos, os volumes foram aferidos e as amostras analisadas quimicamente. A concentração de nutrientes na água da chuva aumentou no inverno, porém, devido às menores precipitações, a deposição total foi semelhante às demais estações do ano. A análise que utiliza o coeficiente de Pearson mostra correlação negativa entre volume de chuva e conteúdo de íons, indicando o efeito de diluição. A quantidade total de nutrientes na precipitação incidente durante o estudo foi de 72,7 kg ha^{-1}, representando uma média de 36,3 kg ha^{-1} ano^{-1}. Os íons Ca^{2+} e K^+ são predominantemente de origem litólica, enquanto os íons SO_4^{2-} e NO^{3-} de origem antropogênica. O equilíbrio entre a soma dos cátions pela soma dos ânions mostrou-se unitário, indicando excelente validação dos dados. A entrada desses nutrientes ocorre gradualmente, evitando perdas excessivas, aumentando o estoque no solo.

Palavras-chave: ciclagem de nutrientes, hidrologia, sazonalidade, sustentabilidade.

1. INTRODUCTION

The southwestern region of the State of Rio Grande do Sul (RS), Brazil is characterized by predominantly sandy soil and low natural fertility, susceptible to erosive processes (Streck *et al.*, 2008). The major problem is associated with the formation of sandstone cores, of a morphogenic nature, intensified by anthropic action such as excessive grazing and inadequate soil management (Bertê, 2004; Souto, 1984). The most affected region is the Arroio Puitã Basin, which includes the municipalities of Itaqui, Maçambará and São Borja (Souza and Pires, 2017).

Sustainable management is the only alternative to reverse the sandstone situation in these areas, and the quantification of inputs deposited by precipitation is essential for understanding the biogeochemical cycling of nutrients (Schumacher and Viera, 2015). The soil of sandstone areas has a low nutrient load, and annual supplementation by precipitation represents an important source of nutritional replacement, indispensable for the development of several ecosystems.

Several factors can determine the chemical composition of rainwater, including maritime influence, biomass burning, litholic and anthropogenic actions (Tiwari *et al.*, 2016). Incident precipitation is the sum of dry and wet depositions, and the identification of the main sources can be determined by enrichment factors which consider Ca^{2+} and Na^+ in their equations to be exclusively of litholic and maritime origin, respectively (Keene *et al.*, 1986, Taylor, 1964).

Most industrialized regions are responsible for the increase in emissions of some ions, such as SOx and NOx. These pollutants cause rainwater acidification, and soil pH and river and lake waters may as a result cause harm to vegetation and the corrosion of materials (Singh *et al.*, 2007). Thus, rainfall precipitation provides information related to environmental quality (Zhou *et al.*, 2019).

In Brazil, the chemical composition of rainwater has been evaluated over the years, although the information is sparse and comes only from metropolitan regions or areas with greater industrial activity in the southeast and south of the country (Migliavacca *et al.*, 2004, Fontenele *et al.*, 2009, Alves *et al.*, 2018). In the southeastern region of the state of RS, where areas are being sanded, studies are absent. In view of this situation, this study evaluated the chemical composition of rainwater, the nutrient supply in the sandstone area and identified the origin of the main ions.

2. MATERIALS AND METHODS

2.1. Characterization of the experimental area

The work was developed in a sandstone area in the municipality of Maçambará-RS (29º02’32.67" S and 55º19’40.44" W), at an average altitude of 191 m. The 82-hectare sandy area has a perimeter of 6.55 km.

The dystrophic, low fertility, natural soil (SBCS-CQFS, 2016) of the experimental area has an average percentage of 83.4, 3.4, 2.7 and 10.4% for coarse sand, fine sand, silt and clay, respectively. Organic matter in the 2-m-deep soil profile was 0.2%, and base saturation (V) 4.2%.

The climate of the region is classified as being subtropical humid, with no dry season and hot summers (Cfa). The average annual rainfall is 1916 mm, well distributed throughout the months of the year. The driest month presents mean precipitation of > 40 mm. The average temperature of the coldest month is ≥ -3°C and <18°C, and the temperature for the hottest month is ≥ 22°C. (Alvares *et al.*, 2013).

2.2. Measurement of incident precipitation

The quantification of the incident rainfall was performed biweekly over two years by means of 3 collectors with a capture diameter of 20 cm and a storage capacity of 7 liters. The collectors were installed in an open area, 1.5 meters above ground level.

The Equation 1 for quantification of rainfall incidents (in mm) is described as follows:

$$\mathrm{P} = \mathrm{V} / \mathrm{A} \tag{1}$$

Where: P = Incident precipitation; V = volume of water (liters); A = catchment area (0.0314 m²).

2.3. Chemical analysis

The pH of the samples was determined with a pH meter using electrodes (Metrohm 827 pH Lab), with simple prefiltration with 0.45 um pores. The values for NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, SO_4^{2-}, Cl^-, Na^+, K^+, Ca^{2+} and Mg^{2+} were determined by ion chromatography (Metrohm 861 Advanced Compac IC). The methodology proposed by APHA *et al.* (1998) was followed.

2.4. Statistics and Data Analysis

The acidity of the incident precipitation is a result of the balance between the ions with acidifying power against the species with neutralizing capacity. However, a portion of the SO_4^{2-}, Ca^{2+} and Mg^{2+} ions originates in the form of marine salts, which do not play any role in the acid balance (Budhavant *et al.*, 2011), thus requiring their values to be corrected from the subsequent equations. Na^+ is considered purely of marine origin. (Keene *et al.*, 1986). Thus, the concentration of non sea salt (nss) was calculated following the Equation 2:

$$nss = [x]\ incident\ precipitation - [Na^+]\ incident\ precipitation \times \left[\frac{x}{Na^+}\right] seawater \tag{2}$$

Where: nss = non sea salt; [x] represents the concentration of the desired ion; [x / Na^+] seawater is the ratio of the mean concentration of the respective ion to Na^+ of seawater.

To obtain the percentage of marine source in each ion, the following Equation 3 was used:

$$ss\ (\%) = \frac{\left[\frac{x}{Na^+}\right] seawater}{\left[\frac{x}{Na^+}\right] incident\ precipitation} \times 100 \tag{3}$$

Where: ss = sea salt (%); [x / Na^+] = ratio of the mean concentration between the ion of interest and Na^+ in seawater and incident precipitation.

To obtain the percentage of litholic source in each ion, the following Equation 4 was used:

$$c\ (\%) = \frac{\left[\frac{x}{Ca^{2+}}\right] soil}{\left[\frac{x}{Ca^{2+}}\right] incident\ precipitation} \times 100 \quad (4)$$

Where: c (%) = crust (%); [x / Ca^{2+}] = ratio of the mean concentration between the ion of interest and Ca^{2+} in soil and incident precipitation.

The percentage of anthropogenic fraction was given by the following Equation 5:

$$A\ (\%) = (100 - ss\% - c\%) \quad (5)$$

Where: ss = sea salt (%); c = crust (%).

The sum of ions SO_4^{2-} and NO^{3-} represents the acidification potential of rainwater. The result of the sum of NH_4^+ + $nssCa^{2+}$ + $nssMg^{2+}$ + $nssK^+$ represents the ions with neutralizing capacity. The AP / NP ratio (potential acidity / potential neutralization) greater than 1 indicates that the sums of bases were not capable of neutralization, and the inverse is valid (Equation 6).

$$\frac{AP}{NP} = \frac{[nssSO_4^{2-}] + [NO_3^-]}{[NH_4^+] + [nssCa^{2+}] + [nssMg^{2+}] + [nssK^+]} \quad (6)$$

The enrichment factor is used to obtain information about the origin of a particular element. To obtain these results, reference rates were used. Na^+ serves as a base element of marine origin (Keene *et al.*, 1986). Ca^{2+} is classified as being typically litholytic (Safai *et al.*, 2004; Das *et al.*, 2011) and the relationship was obtained through the study of Taylor (1964) (Equations 7 and 8).

$$EF\ seawater = \frac{\left[\frac{x}{Na^+}\right] incident\ precipitation}{\left[\frac{x}{Na^+}\right] seawater} \quad (7)$$

$$EF\ soil = \frac{\left[\frac{x}{Ca^{2+}}\right] incident\ precipitation}{\left[\frac{x}{Ca^{2+}}\right] soil} \quad (8)$$

Where: EF is the enrichment factor of [x] ion. [x / Na^+] incident precipitation is the relation between the concentrations of the ions of interest by Na^+ in the incident precipitation. [x / Na^+] seawater is the ratio of ions in seawater. [x / Ca^{2+}] incident precipitation is the relationship between the concentrations of ions of interest by Ca^{2+} in incident precipitation. [x / Ca^{2+}] seawater is the ratio of ions in seawater. Values much smaller than 1 or much larger than 1 are considered diluted or enriched according to the reference source.

3. RESULTS AND DISCUSSION

3.1. Relationship of the sum of cations and anions: validation of the data

A correlation between the sum of the cations and the sum of the anions in the rainwater was observed, with a Pearson coefficient r of 0.94. In addition, the relationship between cations and anions can be considered unitary. Through analysis of the regression residuals, it is observed that the points are distributed evenly around the mean 0 (Figure 1).

The balance between the sum of cations and anions is important for understanding the measurements. The relationship between the two groups is expected to be unitary (Al-Monami *et al.*, 1995). In the present study, the results showed a unit balance of 1.01. Caggiano *et al.* (2014), studying the chemical composition of rainwater in western Bulgaria, found a value of

1.5, indicating that some cations were excluded from the measurements. Xiao (2016) found a positive relationship between cations and anions with an adjustment of R^2 0.96 in central China. Under strong sea influence, Das *et al.* (2011) evaluated by means of correlation the sum of cations by anions and also found excellent adjustments with R^2 of 0.98 in the Maldives islands. For Conceição *et al.* (2013), the cations and anions ratio was 1.02, similar to the present study.

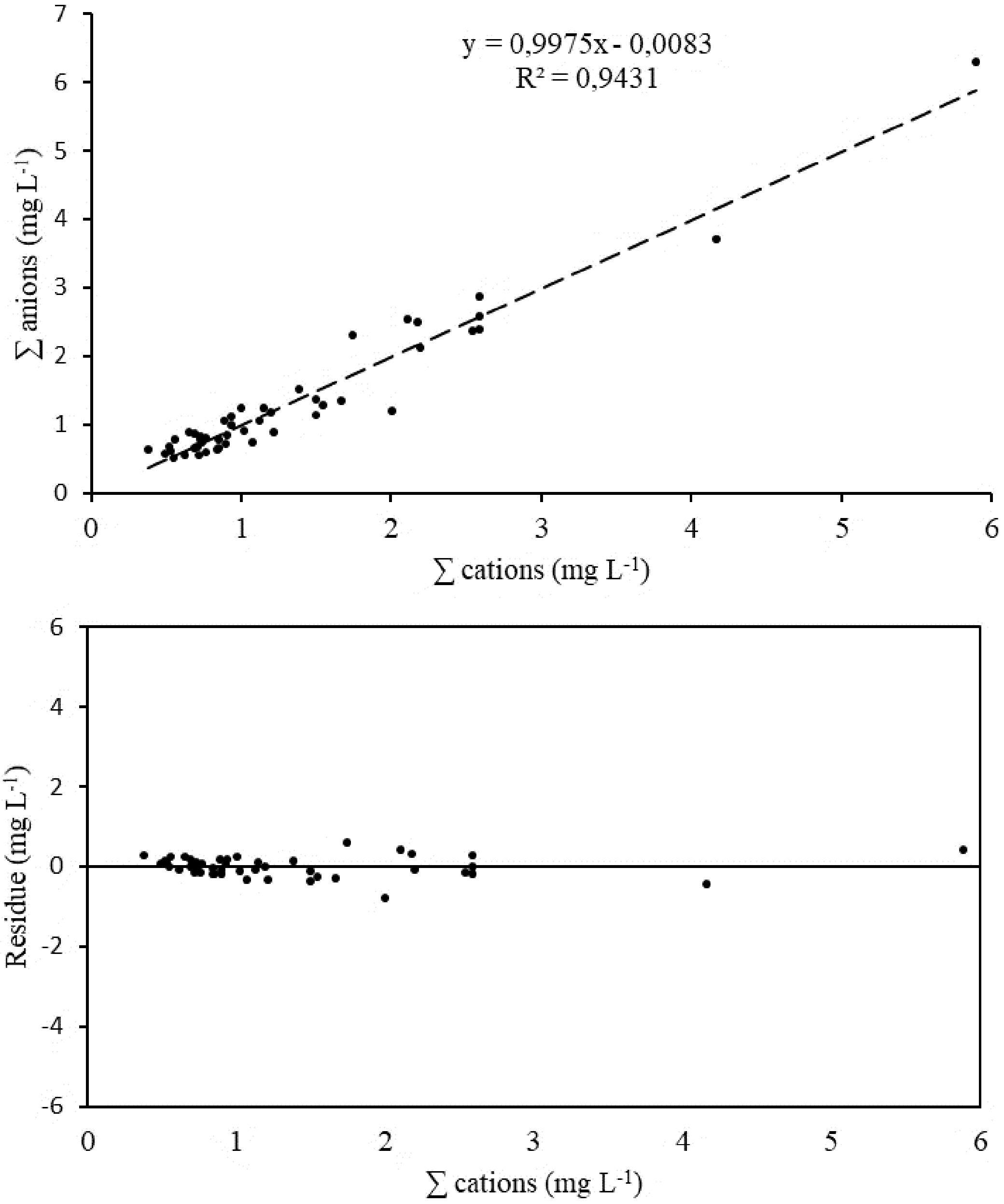

Figure 1. Correlation analysis and residues for sum of cations and anions.

3.2. Seasonal ion concentrations

The concentration of ions in the rainwater changed with the season. There was a strong tendency to increase concentrations during the winter season. The pH reached a mean of 6 and 6.2 for the first and second winter season evaluated. For the other seasons of the monitored period, the pH ranged between 5.3 and 5.9 (Table 1).

By means of the Tukey test, we observed the same trend of increase of the concentrations for the SO_4^{2-} ion in the winter seasons, differing statistically to 5% of probability of error of the other stations. The NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, K^+, Ca^{2+}, Mg^{2+}, Na^+ and Cl^- ions showed the highest levels in the winter season.

Table 1. Seasonal variation in ion concentrations and pH over 2 years in Maçambará-RS.

Season	pH	NO_2^-	NO_3^-	NH_4^+	PO_4^{3-}	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Na^+	Cl^-
		mg L^{-1}									
Winter	6.01a	0.03a	0.33ab	0.34ab	0.03a	0.18a	0.99a	0.07ab	1.16ab	0.55a	0.58a
Spring	5.80ab	0.01ab	0.22ab	0.13b	0.00a	0.37a	0.62abc	0.00ab	0.58bc	0.25b	0.37a
Summer	5.54ab	0.01ab	0.11b	0.05b	0.03a	0.36a	0.36c	0.02ab	0.24c	0.25b	0.48a
Autumn	5.61ab	0.00b	0.12b	0.06b	0.00a	0.27a	0.45bc	0.00b	0.34c	0.19b	0.51a
Winter	6.17a	0.00b	0.49a	0.80a	0.00a	0.48a	0.85ab	0.12a	1.40a	0.30ab	0.88a
Spring	5.29b	0.00b	0.25ab	0.26ab	0.00a	0.15a	0.28c	0.01ab	0.39c	0.20b	0.43a
Summer	5.88ab	0.01ab	0.15b	0.12b	0.03a	0.27a	0.24c	0.00b	0.20c	0.34ab	0.40a
Autumn	5.93a	0.01ab	0.12b	0.10b	0.00a	0.12a	0.23c	0.10ab	0.28c	0.14b	0.31a
Mean	5.78	0.01	0.22	0.23	0.01	0.27	0.50	0.04	0.57	0.28	0.50

Equal letters in the same column did not differ statistically at P = 0.05 by means of the Tukey test.

The pH presented seasonal behavior with the highest values during the winter seasons and the lowest value in the second spring. The mean pH during the period evaluated was 5.78. About 33% of the biweekly water samples presented pH values between 4.88 and 5.58 and 20% presented pH between 6 and 6.7. According to Liljestrand (1985), pH <5.6 can be considered as acid rain. Evaluating the chemical composition of rainfall in the Brazilian Southeast, Cerqueira *et al.* (2014) found a similar average pH, 5.77. The authors show that about 36% of the water samples had pH considered as acid and 28% with pH ranging between 6.0 and 7.0. More acidic rains than the one found in the present study are reported by Migliavacca *et al.* (2004) in the region of Candiota, in the extreme south of Brazil. According to the authors, the pH in 87% of the cases was between 5 and 5.5, with an average pH of 5.4. The explanation for such findings is due to anthropogenic action, and the region is important for generating energy through the burning of coal. Alves *et al.* (2018) found 20% of the pH with values below 5.6, with the mean for the period studied being 6.07.

In general, the concentration of ions decreases, whereas it increases with the increase in incident rainfall, the inverse being valid. Pearson's analysis confirms the negative correlation between the volume of precipitation and the concentration of ions, except for the PO_4^{3-}, K^+ and Mg^{2+} ions. The dilution effect was also reported by Zhang *et al.* (2016) in a study developed in northeast China.

3.3. Correlation analysis between ions concentration, pH and rainfall amount

The correlation analysis of Pearson shows a negative correlation between rainfall volume and NO_3^-, NH_4^+, Ca^{2+}, SO_4^{2-}, Na^+ and Cl^- ions, with a significance of 1% of error probability. For pH, there was a significance of 1% of error probability for Ca^{2+} and Mg^{2+} ions. The highest correlations were 0.95 between NH_4^+ and NO^{3-} and 0.90 between NH_4^+ and SO_4^{2-}. Among the ions studied, PO_4^{3-} showed a lower correlation compared to the others (Table 2).

Significant positive correlations were observed between the K^+, Ca^{2+} and Mg^{2+} ions, indicating that they are of litholical origin. Significant correlations were also observed between ions Na^+ and Cl^-. Ions frequently associated with anthropological actions, such as NO_3^- and $SO_4^{2-,}$ presented strong correlations of 0.89. Rao *et al.* (2016), evaluating the chemical composition of precipitation in two megacities of India during the non-monsoon period, found a correlation of 0.91 in both of the cities of Pune and Delhi for NO_3^- and SO_4^{2-} ions. The authors also show a significant correlation between the ions of lithic origin, as well as Na^+ and Cl^-.

Strong correlations were observed between NH_4^+ ions with acidic species of NO_3^- and SO_4^{2-} on the order of 0.95 and 0.90, respectively. Xiao (2016) also found a strong correlation of 0.90 and 0.99 for the respective ions. According to Zhang *et al.* (2012), shares of these ions are derived from anthropogenic actions, such as agricultural activities and biomass burning.

Table 2. Correlation analysis between ion concentrations, pH and volume of precipitation.

	L ha	pH	NO_2^-	NO_3^-	NH_4^+	PO_4^{3-}	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Na^+	Cl^-
L ha	1.00											
pH	-0.17	1.00										
NO_2^-	-0.34*	0.10	1.00									
NO_3^-	-0.47**	0.24	0.30*	1.00								
NH_4^+	-0.44**	0.24	0.23	$\mathbf{0.95}^{**}$	1.00							
PO_4^{3-}	-0.09	0.04	0.29*	-0.10	-0.11	1.00						
K^+	-0.20	0.09	0.03	0.50**	0.54**	0.02	1.00					
Ca^{2+}	-0.46**	0.40**	0.37**	$\mathbf{0.79^{**}}$	$\mathbf{0.68^{**}}$	0.03	0.34*	1.00				
Mg^{2+}	-0.21	0.43**	0.18	$\mathbf{0.73^{**}}$	$\mathbf{0.68^{**}}$	0.03	0.35*	$\mathbf{0.68}^{**}$	1.00			
SO_4^{2-}	-0.43**	0.35*	0.26	$\mathbf{0.89^{**}}$	$\mathbf{0.90}^{**}$	-0.03	0.50**	$\mathbf{0.85^{**}}$	$\mathbf{0.70^{**}}$	1.00		
Na^+	-0.42**	0.23	0.41**	0.48**	0.39**	0.34*	0.48**	0.50**	0.33*	0.51**	1.00	
Cl^-	-0.40**	0.23	0.08	$\mathbf{0.75^{**}}$	$\mathbf{0.75^{**}}$	-0.09	$\mathbf{0.85^{**}}$	$\mathbf{0.60^{**}}$	0.59**	$\mathbf{0.73^{**}}$	0.54**	1.00

Bold text shows high correlations.
*Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed). 0.60–1.00 = strong correlation; 0.50–0.59 = moderate; 0.40–0.49 = weak; 0.00–0.39 = little or no association.

3.4. Enrichment ratio

As can be observed in Table 3, the values of EF seawater and EF soil for SO_4^{2-} and NO_3^- were considered to be greater than 1. This shows that the marine and littoral contributions are too small to serve as a reference for these ions, and suggests that they originated from anthropogenic sources. The possible factor is due to the burning often practiced in the region (Prathibha *et al.*, 2010). Alves *et al.* (2018) also identified that 57% of the origin of SO_4^{2-} comes from the industrialization or burning of fossil fuels, leaving only a 9% marine contribution, a 21% litholic contribution and 13% contribution of agriculture or livestock. With regard to nitrate, 62% of the same was attributed to litholic origin according to the authors above.

Table 3. Ion enrichment factors of seawater and soil.

Variable	K^+	Na^+	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-	Ca^{2+}	Author
Sea water ratio[a]	0.022	-	0.227	1.160	0.125	0.00002	0.044	Present study
Rainwater ratio	1.107	-	0.495	2.104	2.102	0.9	2.026	
EF seawater	**50.3**	**-**	**2.3**	**1.8**	**17.2**	**45.000**	**46.0**	
Soil ratio[b]	0.504	0.57	0.561	0.0031	0.019	0.0021	-	
Rainwater ratio	0.903	0.82	0.209	1.4056	1.199	0.6026	-	
EF soil	**1.6**	**1.4**	**0.4**	**453.4**	**63.8**	**287.0**	**-**	
Sea water ratio	0.022	-	0.227	1.160	0.125	-	0.044	Caggiano *et al.* (2014)
Rainwater ratio	0.918	-	0.939	4.727	6.728	-	4.876	
EF seawater	**42.0**	**-**	**4.0**	**4.0**	**54.0**	**-**	**111.0**	
Soil ratio	0.504	0.57	0.561	0.0031	0.019	0.0021	-	
Rainwater ratio	0.188	0.21	0.193	0.97	1.38	1.523	-	
EF soil	**0.4**	**0.4**	**0.3**	**312.9**	**73.4**	**725.2**	**-**	
Sea water ratio	0.022	-	0.227	1.160	0.125	0.00002	0.044	Xiao (2016)
Rainwater ratio	0.78	-	0.86	1.34	6.03	1.6	6.53	
EF seawater	**35.5**	**-**	**3.7**	**1.2**	**50.3**	**80.000**	**148.4**	
Soil ratio	0.504	0.57	0.561	0.0031	0.019	0.0021	-	
Rainwater ratio	0.12	0.21	0.13	0.21	0.92	0.21	-	
EF soil	**0.2**	**0.4**	**0.2**	**66.5**	**49.2**	**98.1**	**-**	

Note: a Keene *et al.* (1986), b Taylor (1964)

The enrichment factor was calculated for the ionic species. Values found much smaller or much larger than 1 are considered diluted or enriched according to the reference source. The EF seawater of the present study is similar to the results found by Alves *et al.* (2018) evaluating the deposition of ions via pluviometric precipitation in 3 different points at the, base of the river of the state of Rio Grande do Sul. The seawater EF for those authors was 25.5; 31.3 and 6.2 for K^+, Ca^{2+} and SO_4^{2-}. According to researchers 96, 97 and 88% of these ions are not from the ocean. In the present study, 97, 96 and 73% do not originate from oceanic sources.

The Cl^- has EF seawater and EF soil of 1.8 and 453.4, indicating to be 70% of clearly marine origin 70%. Alves *et al.* (2018) presented similar values, at 57%. The K^+ ion presented higher enrichment in the seawater EF, which indicates that it is mainly of 97% litholiferous origin Table 4. In an evaluation by Xiao (2016), SO_4^{2-} and NO_3^- recorded EF seawater and EF soil much higher than 1. According to the authors, 96 and 99% of SO_4^{2-} and NO_3^- are attributed to anthropogenic actions; therefore, the results agree with the present study. In southwest China, Zhou *et al.* (2019) monitored the chemical composition of rainwater in Shenzhen. This city is characterized by intense industrial activity and has an estimated population of 12.5 million. For the ionic species SO_4^{2-} and $NO_3^{-,}$ the contribution of anthropogenic activities was 67 and 76%, respectively.

The Mg^{2+} and Cl^- ions are mostly of marine origin, 62 and 70% respectively. The cations K^+ and Ca^{2+} and the anion SO_4^{2-} are predominantly of litholic origin, with values of 97, 96 and 73% respectively.

Table 4. Percentage origin of ions.

Source	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-	NO_3^-
	%					
Seasalt	3.23	3.59	61.99	26.90	69.61	-
Soil	96.77	96.41	38.01	2.00	0.44	0.20
Anthropogenic	-	-	-	71.10	29.95	99.80
Total	100.00	100.00	100.00	100.00	100.00	100.00

During the 2 years, the nutrient intake was 72.7 kg ha^{-1}, which represents 36.3 kg ha^{-1} year^{-1} Figure 2. An increase is observed in the first season of the winter, with a total deposition of 17.3 kg ha^{-1}, that is, 24%. The deposition order was as follows: $Cl^- > SO_4^{2-} > Ca^{2+} > N^* > K^+ > Na^+ > Mg^{2+} > PO_4^{3-}$. The contribution of $Cl^- + SO_4^2$ amounts to 41% of the total contributed.

The highest percentage contributions were given for Cl^-, SO_4^{2-} and Ca^{2+} ions, representing 21, 20 and 19% of the total, that is, 21.9 kg ha^{-1}. For Zhou *et al.* (2019) the percentages were 17, 22 and 6% respectively. Xiao (2016) found percentages of 7.6, 26 and 28% respectively. For these authors, the deposition of sulfate, total nitrogen and calcium was 39, 15 and 42 kg ha^{-1}. These values are well above those found for the present study, or 7.2, 5.4 and 7.1 kg ha$^{-1,}$ respectively. Dick *et al.* (2018) found a mean intake of 6.5, 6.8, 1.4, 9.4, 2.5, 0.13, 0.9 and 0.14 kg ha^{-1} for Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, PO_4^{3-}, NO_3^-, $NO_2^{-,}$ respectively.

It is evident that in regions with marked industrial activity and a high fleet of vehicles, atmospheric deposition, mainly of SO_4^{2-}, is increased. Work developed over 2 years by Shen *et al.* (2013) in the city of Heshan, Southeast China showed an average contribution of 110 kg ha^{-1}representing about 15 times more than for the present study. Evaluating nutrient uptake via precipitation incident in Bulgaria over 15 years, Caggiano *et al.* (2014) found an average deposition of 11.5; 3.6; 3.0; 21.3; 1.4; 23.1 and 39.5 kg ha^{-1} for Ca^{2+}, K^+, Na^+, total N, Mg^{2+}, Cl^- and SO_4^{3-} respectively. The values found by these authors represent almost triple the quantities found in the present study.

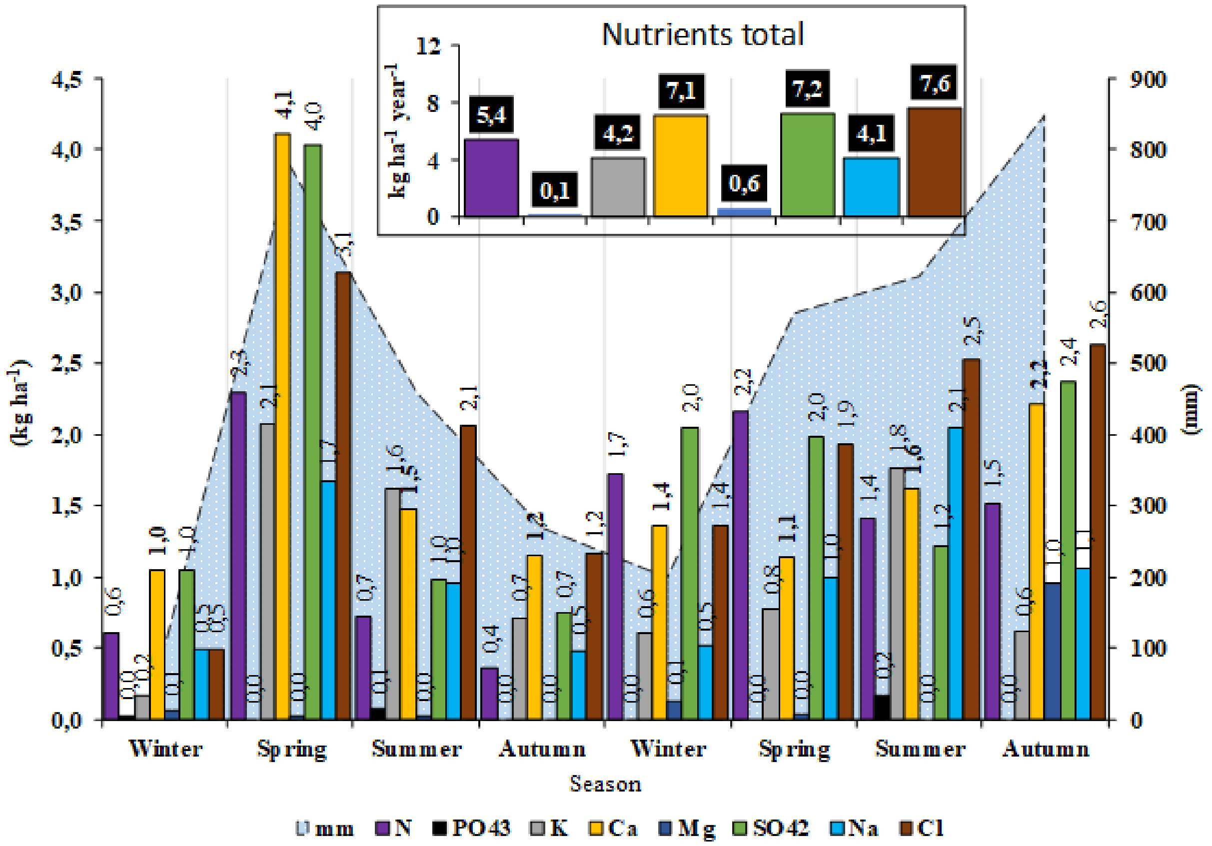

Figure 2. Amount of nutrients input seasonally.

4. CONCLUSIONS

The input of nutrients was 72.3 kg ha^{-1} over 2 years and an average deposition of 36.3 kg ha^{-1} year^{-1}. The incident precipitation represents an important source of nutrients in function of the annual quantity supplied and its distribution throughout the seasons.

The balance between the sum of cations by the sum of anions can be explained by means of linear regression of unit relation. The regression residuals and the R² adjustment confirm the excellent adjustments.

Based on the analysis of the enrichment factor, the K^+ and Ca^{2+} ions are of litholical origin, while Mg^{2+} and Cl^- are of marine origin. Only the SO_4^{2-} and NO_3^- ions did not present natural sources, thus being classified as anthropogenic.

The Pearson analysis shows a negative correlation for all the ions with respect to the volume of precipitation, indicating a dilution effect. Significant correlation was verified between Ca^{2+} and Mg^{2+} ions, indicating that they are of litholical origin.

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6. DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available on request from the corresponding author.

The data are not publicly available due to privacy or ethical restrictions.

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