A Multiyear Record of Rainfall and Ionic Composition Along an Elevation Gradient in Northeastern Puerto Rico

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Abstract

Wet deposition is an essential source of nutrients and pollutants for terrestrial ecosystems, such as tropical forests. This article analyses a multiyear record of rainfall and ion composition data for 21 stations along an elevation gradient (0-1045 m a.s.l.) in the Luquillo Mountains. We found the concentration of total ions exponentially inversely correlated with rainfall volume with correlation coefficients ranging from -0.66 to -0.90, and rainfall increased with elevation. Variations in that trend were observed in several stations due to their location and exposure to predominant winds. The ion composition had a clear seasonal pattern with crustal aerosols from Africa present in the summer period and a small influence of anthropogenic aerosols from North America present during winter, while marine aerosols are present year-round. The annual ion load (kg/ha/year) increased from lowland stations up to the cloud formation levels (47-121%) except for PO₄³⁻ and K⁺ and then decreased in the higher stations except for PO₄³⁻ and NO₃⁻.

Keywords: Precipitation chemistry; Luquillo Experimental Forest; Rainforest hydrology; Tropical forest; Nutrient deposition

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INTRODUCTION

Wet deposition is an essential source of nutrients and pollutants for terrestrial ecosystems, such as tropical forests. The Luquillo Experimental Forest (LEF), also known as El Yunque National Forest, is a tropical forest located in the Luquillo Mountains in northeastern Puerto Rico, which elevates from the coast to an elevation of over 1,000 m in a horizontal distance of about 8 km (González et al., 2013; Lugo et al., 2015), creating steep slopes within the mountain range. Due to these topographic characteristics and the trade winds that constantly influence the island, cloud formation is mainly formed through orographic ascension making the Luquillo Mountains the rainiest part of the island (García-Martínó et al., 1996; Murphy et al., 2017). Several rivers and creeks are fed from the rainfall at the Luquillo Mountains and are a vital water supply to people and other organisms.

One of the most interesting features of the Luquillo Mountains is the steep slope from the coast to its highest peak. This steep slope creates an elevation gradient that provides different biotic and abiotic conditions, such as temperature, cloud cover, and rainfall patterns. As air masses move up the slope, the temperature of the air mass decreases until water vapor condenses and falls as precipitation. Precipitation not only provides water but also pushes down atmospheric aerosols via rainout and washout processes that get deposited on the surface, and that can have considerable ecological consequences in the different ecosystems.

Since the mountains are close to the coast, marine aerosols are prominent around the area year-round. However, distinct air masses can reach the island and alter the rain composition at different times. During summer, high concentrations of African dust can be detected in the Caribbean basin.
African dust travels long distances from the African continent due to the movements of the Intertropical Convergence Zone (ITCZ), which moves north toward the Caribbean region during the northern hemisphere summer and south towards the South American region during winter. During winter, Puerto Rico is affected by cold fronts that move from North America towards the Caribbean and drag anthropogenic pollution from the east coast of the United States (Allan et al., 2008; Valle-Díaz et al., 2016).

The Luquillo Mountains have been a place of intense multidisciplinary research for many decades (Odum, 1970; Brokaw et al., 2012). Studies involving rain characteristics and composition have been performed in several places across the mountains, some concerned with climatological patterns of precipitation and others to biogeochemical cycles (Martens and Harriss, 1973; Weathers et al., 1988; McDowell et al., 1990; Asbury et al., 1994; Heartsill-Scalley et al., 2007; Gioda et al., 2009, 2011, 2013; Medina et al., 2013). Studies assessing rain chemical composition coincide with the observation that marine air masses are the primary source of ions. Many of these studies show that crustal and anthropogenic air masses can also influence precipitation (Allan et al., 2008; Gioda et al., 2013; Medina et al., 2013; Valle-Díaz et al., 2016). Gioda et al., (2013) determined that sea salt contributed to 70% of the total ion load, with $\text{Ca}^{2+}$, a proxy for crustal air masses (McClintock et al., 2019; Stallard and Murphy, 2012), accounting for 6-8% of the total load.

While many studies assessing precipitation chemistry at the Luquillo Mountains are available, only the study of Medina et al. (2013) focused on how it changes through the elevation gradient in this mountain range. However, that study was limited to one year of data. The objective of this study is to build on the work of Medina et al. (2013) to answer the question of how do rainfall and ion
composition varies between seasons and in the elevation gradient of the Luquillo Mountains using a multiyear record of rain chemistry.

METHODS

Sampling Sites

The meteorological stations used for this study are located across the elevation gradient of the Luquillo Mountains (Gould et al., 2006), starting from sea level (0 m a.s.l.) to El Yunque Peak, the highest peak of the mountains (1045 m a.s.l.). The stations were grouped in five categories based on their elevation and distance from the coast: Lowland Coastal (0-100 m a.s.l.; LC), Lowland Interior (0-100 m a.s.l.; LI), Lower Montane (200-525 m a.s.l.; LM), Cloud Formation Level (600-800 m a.s.l.; CFL), and Upper Cloud Formation Level (900-1045 m a.s.l.; UCFL) (Medina et al., 2013). Station names, abbreviations, elevation, elevation category, and coordinates are presented in Table 1. A detailed map with the locations of the stations is included in Medina et al. (2013) and Van Beusekom et al. (2015).

Rain Collection and Chemical Analyses

Total rainfall was measured in 21 stations located inside and around the LEF from 2009 through 2018. Rainfall collectors were placed at a 1.45 m height and away from any vegetation or structure to avoid interception. The collectors are made from butyrate plastic, have a capacity of 25mm (180 mL), and are covered with a 101 mm diameter funnel. The collector is placed inside a larger capacity cylinder to capture rainwater if it gets overflowed, providing for a total of 300 mm
collection capacity. Overflown conditions over the 300 mm capacity were rare, and for the stations where this happened the most (MB and YPC), this only occurred for 4 out of 124 samples, representing 3% of the data. A more detailed description of the sample collection procedure can be found in Medina et al. (2013).

For all rainwater samples, pH was measured on-site using an EXTECH model ExStik II EC500 meter starting in 2011. Only during September and October of 2017, sampling was interrupted because of the passage of Hurricane María. Means for pH were determined using the concentration of hydronium ion [H+] and later converting it back to pH values. Rainwater was measured bi-weekly, and samples for chemical analysis were collected at the end of the month corresponding to the last two weeks of the month. Samples were stored in 20 mL plastic bottles and transported in ice from the field to the chemistry laboratory at the International Institute of Tropical Forestry in Río Piedras, Puerto Rico, where they were stored at 4°C until analysis. Ion concentrations (Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, PO₄³⁻, Na⁺ K⁺, NH₄⁺, Mg²⁺, Ca²⁺) were determined using a dual column Dionex ICS-3000 ion chromatograph with a conductivity detector. Samples are injected into the system using a low volume 200 µL injection loop to enhance peak sensitivity and avoid saturation in the column, providing and accuracy and precision tolerance of ±5% for each ion with a 0.1 ppm detection limit. The dual column set up allows for both anions and cations to be analyzed in parallel with a separate conductivity detector for each column.

**Statistical Analyses**

Data processing and least-squares fit linear regression statistical analyses for addressing the relationship of ion concentration with the amount of rainfall were performed using Igor Pro 8.0.
Pearson correlation factor table presented for determining the correlation of sodium with chloride, calcium, and sulfate ions was performed using XLSTAT version 19.

RESULTS AND DISCUSSION

Total Rainfall

The amount of rainfall, in general, increased with elevation, but some stations had totals above or below expected (Fig. 1). The stations Ceiba Dry I (CDI), Las Cabeza Dry (LCD), Río Grande (RG), Toro, and El Yunque Peak (YPC) consistently had lower accumulated rain than expected. When stations were grouped and averaged by elevation type, a more explicit relationship between rainfall and elevation unfolds. Through the ten years of measurements, LC stations had the least amount of rainfall, and UCFL stations had the highest amount of precipitation. The ratio of UCFL yearly precipitation over that of LC exhibits a range of 2.94 to 3.44, showing that UCFL stations receive substantially more rainfall (about three times more) that LC stations. In a climate change scenario, where precipitation is expected to decrease, areas that receive large amounts of rainfall can be especially vulnerable to these changes as many species that inhabit these ecosystems are accustomed to these often-saturated conditions. These results also highlight the relative importance of these high-altitude ecosystems in the water budget of the whole ecosystem and human settlements that get their water supply from the precipitation generated there.

The stations with the lowest and highest accumulated rainfall varied during the measuring period. In 2009, 2011 and 2012, CDI was the driest station; in 2010, 2016, and 2018 it was LCD, and from 2013 to 2015 and 2017, it was Las Cabezas Mangle (LCM). Mount Britton (MB) station was the
rainiest from 2009 to 2011 and 2013, Pico del Este (PEC) in 2012, 2015, 2016, and 2018, and Pico del Oeste (POC) in 2014 and 2017. The stations ELV, Toro, and YPC departed from the altitudinal trend, suggesting that slope, distance from the coast, and position of the station regarding the prevailing winds, were the factors responsible for this pattern (Fig. 1). In the case of YPC, which is the highest elevation station, a possible explanation for the deviation from the trend could be that, in some instances, rain develops below the station level. For ELV and Toro, the location could be an important factor as these are the stations further west and more prone to experience the rain shadow effect.

A monthly profile was done for each station to identify seasonal patterns by elevation group (Fig. 2). This profile shows that May is the month with the highest amount of rain followed by a sharp decrease in rainfall in June, while February is the driest month. This pattern was consistent for all elevation categories, but it was more pronounced with increasing elevation. For LC and LI stations, the first four months of the year are the driest ones, but this pattern does not hold in LM, CFL, and UCFL.

Previous studies at the Luquillo Mountains reported that rainfall has been increasing in the last decades. Torres-Valcárcel et al. (2014) found an increase in precipitation for the whole island of Puerto Rico in the 1990-2007 period. This finding is supported by the study presented in Van Beusekom et al. (2015), where they found an increase in precipitation as a function of time from 2001 to 2013. However, our results show a tendency for rainfall to decrease in the period 2009 to 2018, except for LM. The decreasing tendency was mainly driven by reduced precipitation during the 2010 – 2015 period. The LC stations registered the lowest decrease in rainfall (-25 mm yr$^{-1}$; -2.3%; $r^2 = 0.32$) and the UCFL stations had the highest decrease in rainfall (-85 mm yr$^{-1}$; -2.3%; $r^2 = 0.45$), while LM elevation type saw an increase in precipitation (+25 mm yr$^{-1}$, 1.1%; $r^2 = 0.18$).
The tendency is clearer from 2008 to 2015, where all elevations saw a decrease in precipitation (-70, -120, -90, -168, -225 mm yr\(^{-1}\) from LC to UCFL; \(r^2 = 0.51 – 0.70\)), accentuated by a severe drought that took place in summer of 2015. The decreasing trend is then interrupted in 2017 because of the high amount of precipitation caused by hurricane María. While our dataset is limited for analyzing climate trends, we can combine these observations to gauge how this variable is behaving as a function of time, as well as analyze short-term trends. The short-term trend seen in this study adjust to predictions of decreased precipitation in tropical forests as a consequence of climate change that have not been seen in previous studies for the Luquillo Mountains. While a richer dataset is required to assess changes in climatic patterns, short-term trends can highlight important features that deserves further observation.

**pH of Rainfall Samples**

The pH had no relationship with elevation or rainfall volume, and in most instances, it remained within 5-6 for all elevation groups. The accepted value of unpolluted rainwater is 5.6 (Manahan, 2000), slightly acidic because of the carbon dioxide to carbonic acid equilibrium reaction that takes place in the atmosphere/water interface. A pH lower or higher than this value could be influenced by acidic species from anthropogenic pollution, or by neutralizing species, like those found in mineral dust, respectively.

**Ionic Composition of Rainfall Samples**

The mean annual weighted total ion concentration was studied as a function of time and grouped by elevation group. It showed that there was a tendency for higher ion concentrations in the
lowland stations, but it was not consistent through time. This relationship is tied up with increasing rainfall with elevation, which promotes a higher washout rate and a lower concentration of ions in the atmosphere and a more significant dilution caused by a higher volume of rainwater. Charge balance was examined as the slope of anions as a function of cations for all stations. Most stations had a slope higher than 1, which means there was a higher anion concentration than cations. A deviation from one suggests the presence of ions in the samples that the analytical procedure is unable to detect, which could be organic ions. The concentration of hydronium was calculated from pH measurements to identify if this was one of the missing cations. Still, it did not account for the lower concentration of cations relative to anions. The p-value for these regressions with a confidence interval of 95% was smaller than 0.0001 for all stations.

Ion concentration had a negative exponential relationship to rainfall, shown in Fig. 3. Pearson regression coefficient for the yearly values suggests that there is an inverse relationship between these variables for all years ($r^2 = -0.66$ to $-0.86$; $n=159$) except for year 2013 ($r^2 = -0.29$; $n=20$). The poor relationship in 2013 is due to a value with low ion concentrations, that if omitted, improves the linear regression to an $r^2 = -0.90$. The concentration of ions is expected to decrease with an increasing volume of rain due to dilution and increased atmospheric particle washout, which validates the inverse relationship. The dilution effect followed a log-log linear relationship, and the p-values for all the regression coefficients were below 0.005 except for 2013, where it was 0.211. Regression coefficients reveal that the tightness of this relationship is not constant and that large differences can occur. Most of these regression lines fall above the pure dilution line, suggesting that ion concentration is the dominant feature in the dilution process.
The island of Puerto Rico is mainly affected by three aerosol types: marine, crustal, and anthropogenic, being Na\(^+\), Ca\(^{2+}\), and SO\(_4\)\(^{2-}\) the proxy ions used for identifying the influence of these aerosols (McClintock et al., 2019; Stallard and Murphy, 2012). However, the presence of Ca\(^{2+}\), and SO\(_4\)\(^{2-}\) is not constant throughout the year and depends on seasonal patterns that transport aerosols from different sources. Sodium and sulfate ion concentrations were high during the first months of the year (Jan-Apr), which corresponds to the months with generally less rainfall (Fig. 4). The increase in sulfate concentration is considerable during these months, particularly in lowland coastal, lowland interior, and lower montane stations, which could be caused by an enrichment of non-sea salt sulfate transported in anthropogenic aerosols from eastern United States by cold fronts. A bump in concentrations of the three ions is seen during the summer months of Jun-Aug, more drastically seen in the Ca\(^{2+}\) concentration. The cause of this could be an enrichment of non-sea salt calcium transported from the African continent by the trade winds and the position of the Intertropical Convergence Zone (ITCZ).

Since, in addition to the predominant Na\(^+\) and Cl- both Ca\(^{2+}\) and SO\(_4\)\(^{2-}\) are found in sea salt particles, we assessed the marine influence of these ions per station calculating their Pearson correlation with Na\(^+\) (Table 2). A high correlation coefficient (>0.7) was found between Na\(^+\) and Cl- in 17 of the 21 stations, suggesting both these ions come from the same source for all stations, which is marine sea-salt particles. On the other hand, Na\(^+\) and Ca\(^{2+}\) were highly correlated in only one station (CDI), suggesting there is an important contribution of calcium from non-marine sources, the most important one being mineral dust from Africa. Na\(^+\) and SO\(_4\)\(^{2-}\) were highly correlated in 13 out of 21 stations, suggesting that there is a substantial contribution of sulfate ions from marine sources. There is also a small but non-negligible contribution from non-marine sources, which
could be the contribution of anthropogenic pollution transported with cold fronts in the winter months.

Pearson correlation factor was analyzed for Na$^{2+}$ and the non-sea salt fraction of Ca$^{2+}$ and SO$_4^{2-}$ (Table 2). In some cases, especially in the lower stations, the correlation of Na$^{2+}$ with nss-Ca$^{2+}$ was stronger than that of Na$^{2+}$ with total Ca$^{2+}$. While Na$^{2+}$ is mainly a marine aerosol, it is important to consider that it is also present in crustal sources, and this can be a possible explanation for this result. For higher elevation stations (LM, CFL, UCFL), the relationship of Na$^{2+}$ with nss-Ca$^{2+}$ was weaker than that of Na$^{2+}$ with total Ca$^{2+}$. The weaker relationship could indicate that air masses containing crustal aerosols are less likely to reach higher elevation stations. The relationship of Na$^{2+}$ with nss-SO$_4^{2-}$ was almost always weaker (19 out of 21 stations) than that of Na$^{2+}$ with total nss-SO$_4^{2-}$ and in cases where it was higher, it was only slightly (less than 3% difference). This shows that Na$^{2+}$ and nss-SO$_4^{2-}$ have very distinct sources and that sources of ss-SO$_4^{2-}$ and nss-SO$_4^{2-}$ can be easily distinguished.

Variations of Rainfall and Ionic Composition with Elevation

The ion mass deposition per unit area for all measured ion was determined for each elevation group, and the yearly average (Table 3). As expected, Cl$^-$ and Na$^+$ had the highest mass deposition for all stations, followed by K$^+$, SO$_4^{2-}$, Ca$^{2+}$, PO$_4^{3-}$, Mg$^{2+}$, and NH$_4^+$. Mass deposition of NO$_3^-$, F$, Br$, and Li$^+$ was almost negligible and thus not further analyzed. Mass deposition of Cl$^-$, SO$_4^{2-}$, Na$^+$ and Mg$^{2+}$ increased with elevation, and that of NH$_4^+$ and Ca$^{2+}$ increased with elevation except for the UCFL elevations. The increase of mass deposition with elevation can be explained by the rise of rain amount, which effectively deposits ions from the atmosphere into the surface. Mass deposition
of $\text{PO}_4^{3-}$ and $\text{K}^+$ did not have a clear pattern with elevation. Still, the deposition of $\text{K}^+$ at the CFL and UCFL decreased, a behavior also seen by Medina et al. (2013). High inputs of $\text{K}^+$ and $\text{Mg}^{2+}$ can be attributed to both marine and crustal sources (Valle-Díaz et al., 2016), while $\text{PO}_4^{3-}$ can be attributed to crustal sources (Pett-Ridge, 2009). These results show that marine and crustal sources are the main contributors to the ion load and deposition to the Luquillo Mountains and that they are an important source of nutrients to the ecosystem.

The annual weighted mean concentration of ions was analyzed as a function of elevation (Fig. 5). This plot shows that the ion concentration at lower stations does not follow a clear trend but rather erratic movements. Similarly, the annual amount of rainfall did not follow a clear pattern. However, while the elevation between these stations is not large, their geographical location and exposure to the northeasterly trade winds are vastly different. The stations CDI, CDII, H, and PDM are located on the southeastern coast, while the stations LCD and LCM are situated in the most northeastern part of the island. This suggests that the trade winds and precipitation will more directly influence the latter two stations from marine cumulus clouds than those in the southeastern region. However, this is not necessarily the case as only the station CDII received less precipitation than those in the northeast. There is a clear difference in the total concentration of ions for these stations, with those located on the northeastern coast receiving more ions than those in the southeastern coast. The higher concentration of sea-salt ions ($\text{Na}^+$, $\text{Cl}^-$, $\text{K}^+$ and $\text{Mg}^{2+}$) in the northeastern coast stations suggests that the influence of the trade winds could be resulting in higher wind speeds that are dragging more marine aerosols with them. Also, these stations had the largest concentrations of nss-$\text{SO}_4^{2-}$ because of the nearby mangroves that cause anoxic conditions in the ground and high sulfur content.
The lowland interior station Ford had the largest concentrations of $K^{+}$, and high concentrations of $PO_4^{3-}$ and $NO_3^-$, suggesting that these could be the results nearby manufacturing facilities and agricultural activity. The station JB had the highest values of nss-$SO_4^{2-}$ from the lowland interior stations, which is expected because this station is in the highly populated metropolitan area and more exposed to the aerosols emitted from anthropogenic activity.

Stations in the LM, CFL and UCFL areas showed a more consistent trend of increasing precipitation and decreasing ion concentration. The clearest exceptions to this trend were the ELV and Toro stations that had a noticeably lower amount of rainfall that the rest of the stations in its altitude classification. Interestingly, these stations are in the western part of the mountains. Since the mountain formation is close to the coast and has a steep elevation slope, they are prone to form precipitation due to orographic lifting of air masses moved by the trade winds. Those stations in the western part of the mountain will experience the rain shadow effect, where most of the precipitation forms in the eastern face of the mountain. The Toro station is further west than the rest of the mountain stations and thus experiences this effect more, reflected in the reduced precipitation and increased ion concentration compared to the rest of the stations at comparable altitudes. This station also presented higher nss-$SO_4^{2-}$ and $PO_4^{3-}$ than the rest of the mountain stations, suggesting that there could be emissions from primary biogenically aerosols being emitted in the forest and reaching this station. Anthropogenic activity in this area is unlikely since it is part of a protected area where no development is allowed. Another exception to this trend is the UCFL stations, where the concentration of aerosols exponentially increased for the MB, PEC and POC stations and drops for the YPC station. The ions that followed this countetrend were the marine aerosols $Na^+$, $Cl^-$ and $Mg^{2+}$, along with $NO_3^-$ and $PO_4^{3+}$. An explanation for this behavior was not found. A possible reason for the decrease in precipitation at the YPC station relative to the trend
that the other stations in its altitude range follow could be that this station is slightly higher than
where most precipitation forms and being excluded from some of the rain events.

The ion concentration results from this study where higher for all species than those reported in
Medina et al. (2013). However, our dataset comprises a more extended period and is more
representative of the average yearly deposition at the different locations, as well as including
periods of abnormally low rainfall, as in the case of 2015, where concentrations increase. Asbury
et al. (1994) determined ion concentrations at Pico del Este that were 2.5 to 5.5 times higher than
the concentration determined in this study for UCFL stations, like the observation made in Medina
et al. (2013). The results from Gioda et al. (2011) from seven rain events at Pico del Este agree
well with ours, although slightly lower for most ions except NO$_3^-$ and SO$_4^{2-}$, which we attribute is
because this sampling took place during the winter period where cold fronts carrying
anthropogenic pollution are common. Gioda et al. (2013) analyzed ions in rainwater at three
locations of the Luquillo Mountain: El Verde, Bisley, and Pico del Este. Our results of ELV agree
well with their results for the same El Verde area, except for the case of K$^+$ and NH$_4^+$, for which
we got an average concentration about a factor 4 and 10 higher, respectively, and NO$_3^-$ where we
got an about a factor 12 lower concentration. In Pico del Este (PEC), for Ca$^{2+}$, Mg$^{2+}$, K$^+$, and SO$_4^{2-}$
we got about a factor 2 lower concentrations, slightly lower concentrations for Na$^+$ and Cl$^-$, drastically lower concentration for NO$_3^-$ and only NH$_4^+$ agreed well in both studies. Differences in
concentrations determined at PEC may have arisen from not being in the same location and being
possibly exposed to different weather conditions, as well as by different sample collection and
analysis methodology. A more recent study of a 20-yr record of rain chemistry at Bisley and El
Verde by McClintock et al. (2019) showed concentrations of nss-Ca$^{2+}$ lower than those presented
here.
A considerable difference from our work is that most of these studies collected one-week samples or samples by rain events for their analysis, while our samples were from two weeks. The additional time in the field can cause differences in the ion concentrations as they are exposed to daily changes in temperature, and as redox reactions take place. We expect this effect to be higher in lower elevation stations as temperatures decrease with elevation. Also, these samples are more prone to have enhanced concentration of ions due to dry deposition of aerosol particles, which would explain the higher concentration of specific ions in this study in comparison to those who have a shorter hold time in the field. Medina et al. (2013) estimated an enhancement of up to 40% in Na\(^+\) and Cl\(^-\) concentrations and up to 60% in Mg\(^{2+}\) and Ca\(^{2+}\) concentration in comparison to the National Atmospheric Deposition Program (NADP) samples collected at lower montane stations.

When the results from this study are compared with those of other rainforest, the effect of the air mass influence on the rain chemistry becomes more apparent. A study done in West Africa by Sigha-Nkamdjou et al., 2003 reported that their most abundant inorganic ions were NH\(_4\)\(^+\) and NO\(_3\)\(^-\) corresponding to biomass burning aerosols and low abundance of Na\(^+\) and Cl\(^-\), that were the most abundant ions in our study. Concentrations of NH\(_4\)\(^+\) and NO\(_3\)\(^-\) were about 3 times larger and 6 times lower, respectively in our study while concentrations of Na\(^+\) and Cl\(^-\) were substantially higher. A study done in a tropical forest in eastern China influenced by emissions from motor vehicles by Niu et al., 2017 found that SO\(_4^{2-}\) and NO\(_3^-\) accounted for about 88% of their inorganic ion composition. The volume weighted mean values for both of this species were 49.8 and 32.6 μeq L\(^{-1}\), respectively, that where 25 and 97% larger than the maximum concentration seen in this study.

Our results are much more comparable to those found in Lesack and Melack, 1991 where rain chemistry was studied in the tropical forest of La Selva, Costa Rica. This study found that the largest ion influence in rainwater was from marine sources, although our study reported larger
concentrations of marine aerosols. We also saw an overall higher concentration of all ions than what Lesack and Melack, 1991 reported, which could be due to differences in location and sampling methodology, which can also explain differences with the other studies.

CONCLUSION

A rich multiyear dataset of rainfall amount and chemical composition along the elevation gradient of the Luquillo Mountains was analyzed. Contrary to what other studies report (Torres-Valcárcel et al., 2014; Van Beusekom et al., 2015), we found that for most stations, the amount of rainfall has been decreasing over the past years up until 2015 and then increased for the last three years. A decrease in precipitation could mean a future negative outcome for the ecosystem that depends on high water inputs yearlong. However, the present is a short-term study and unable to assess any climatic pattern, but these results can help forest managers make timely decisions to preserve biodiversity in the most vulnerable ecosystems.

A positive correlation was found between elevation and rainfall, although not all stations followed this behavior. This suggests that ecosystems at higher altitudes (CFL and UCFL) could be more affected by changes in precipitation inputs, such as the elfin cloud forest found at the most upper parts of the Luquillo Mountains. There was not a clear pattern of pH with rainfall, but an inverse exponential relationship between the total ion concentration and the total rainfall was found. Ion composition was shown to be dependent on transported aerosols and have a clear seasonal pattern. While marine aerosols are present year-round, crustal aerosols are more abundant during the summer period and anthropogenic aerosols during the winter period. Particularly, crustal
aerosols from the influence of African dust are an important source of micro and macronutrients, providing calcium, phosphate, and other nutrients along the gradient.

While it is expected that rainfall would increase and ion concentration would decrease with elevation, this was not always the case. The Luquillo Mountains have a complex topography that largely influences cloud formation and precipitation patterns. Because of this, the elevation is not a sole predictor of these variables, but location along the mountain proved to be important. Montane stations located to the west of the mountain range usually experienced lower rainfall amounts and higher ion concentration that stations in its elevation range, but that where further east because of the rain shadow effect. Ion deposition usually increased with elevation for most ions, indicating that rainfall is an essential source of both water and nutrients to montane ecosystems.

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Table 1: Description and geographical information of collection stations.

<table>
<thead>
<tr>
<th>Station Name</th>
<th>Station ID</th>
<th>Elevation (m)</th>
<th>Elevation site</th>
<th>Latitude (N)</th>
<th>Longitude (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmas del Mar</td>
<td>PDM</td>
<td>0</td>
<td>Lowland coastal</td>
<td>18°05'32.63&quot;</td>
<td>65°48'04.64&quot;</td>
</tr>
<tr>
<td>Humacao</td>
<td>H</td>
<td>3</td>
<td>Lowland coastal</td>
<td>18°10'42.27&quot;</td>
<td>65°45'53.23&quot;</td>
</tr>
<tr>
<td>Sabana Seca #2</td>
<td>SS#2</td>
<td>3</td>
<td>Lowland coastal</td>
<td>18°27'40.45&quot;</td>
<td>66°12'16.65&quot;</td>
</tr>
<tr>
<td>Las Cabezas II</td>
<td>LCM</td>
<td>4</td>
<td>Lowland coastal</td>
<td>18°22'40.73&quot;</td>
<td>65°37'08.90&quot;</td>
</tr>
<tr>
<td>Ceiba I</td>
<td>CDI</td>
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<td>Lowland coastal</td>
<td>18°13'59.01&quot;</td>
<td>65°35'59.13&quot;</td>
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<tr>
<td>Las Cabezas I</td>
<td>LCD</td>
<td>31</td>
<td>Lowland coastal</td>
<td>18°22'51.29&quot;</td>
<td>65°37'13.71&quot;</td>
</tr>
<tr>
<td>Ford</td>
<td>Ford</td>
<td>13</td>
<td>Lowland interior</td>
<td>18°23'12.23&quot;</td>
<td>65°52'48.04&quot;</td>
</tr>
<tr>
<td>Jardín Botánico</td>
<td>JB</td>
<td>26</td>
<td>Lowland interior</td>
<td>18°23'04.90&quot;</td>
<td>66°03'11.30&quot;</td>
</tr>
<tr>
<td>Saint Just</td>
<td>SJ</td>
<td>81</td>
<td>Lowland interior</td>
<td>18°23'01.35&quot;</td>
<td>65°59'58.23&quot;</td>
</tr>
<tr>
<td>Sabana 4 Bisley</td>
<td>S4</td>
<td>226</td>
<td>Lower Montane</td>
<td>18°19'01.63&quot;</td>
<td>65°44'30.68&quot;</td>
</tr>
<tr>
<td>Sabana 4 Bisley #2</td>
<td>S4#2</td>
<td>226</td>
<td>Lower Montane</td>
<td>18°19'01.63&quot;</td>
<td>65°44'30.68&quot;</td>
</tr>
<tr>
<td>El Verde</td>
<td>ELV</td>
<td>361</td>
<td>Lower Montane</td>
<td>18°17'36.83&quot;</td>
<td>65°48'23.47&quot;</td>
</tr>
<tr>
<td>Rio Grande</td>
<td>RG</td>
<td>525</td>
<td>Lower Montane</td>
<td>18°19'10.02&quot;</td>
<td>65°48'58.28&quot;</td>
</tr>
<tr>
<td>UPR (Nido)</td>
<td>NIDO</td>
<td>655</td>
<td>Cloud Formation Level</td>
<td>18°18'00.81&quot;</td>
<td>65°47'00.05&quot;</td>
</tr>
<tr>
<td>Pico del Este I - Colorado</td>
<td>CO</td>
<td>778</td>
<td>Cloud Formation Level</td>
<td>18°17'38.58&quot;</td>
<td>65°47'11.46&quot;</td>
</tr>
<tr>
<td>El Toro</td>
<td>TORO</td>
<td>792</td>
<td>Cloud Formation Level</td>
<td>18°16'40.06&quot;</td>
<td>65°50'53.26&quot;</td>
</tr>
<tr>
<td>Mount Britton</td>
<td>MB</td>
<td>901</td>
<td>Cloud Formation Level</td>
<td>18°18'16.02&quot;</td>
<td>65°47'26.14&quot;</td>
</tr>
<tr>
<td>Pico del Oeste</td>
<td>POC</td>
<td>987</td>
<td>Cloud Formation Level</td>
<td>18°16'39.18&quot;</td>
<td>65°45'11.44&quot;</td>
</tr>
<tr>
<td>Pico del Este II - Cloud</td>
<td>PEC</td>
<td>1002</td>
<td>Cloud Formation Level</td>
<td>18°16'17.15&quot;</td>
<td>65°45'40.42&quot;</td>
</tr>
<tr>
<td>El Yunque</td>
<td>YPC</td>
<td>1045</td>
<td>Cloud Formation Level</td>
<td>18°18'38.23&quot;</td>
<td>65°45'25.14&quot;</td>
</tr>
</tbody>
</table>
Table 2: Pearson correlation factor for different ions. Values in bold represent highly significant correlation (>0.7). Values in parenthesis represents correlation with non-sea salt fraction of the species.

<table>
<thead>
<tr>
<th>Station</th>
<th>Na⁺ vs Cl⁻</th>
<th>Na⁺ vs Ca²⁺ (nss-Ca²⁺)</th>
<th>Na⁺ vs SO₄²⁻ (nss-SO₄²⁻)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDM</td>
<td>0.49</td>
<td>0.445 (0.599)</td>
<td>0.496 (0.095)</td>
<td>64</td>
</tr>
<tr>
<td>H</td>
<td><strong>0.781</strong></td>
<td>0.312 (0.424)</td>
<td><strong>0.745</strong> (0.285)</td>
<td>59</td>
</tr>
<tr>
<td>SS#2</td>
<td><strong>0.948</strong></td>
<td>0.332 (0.496)</td>
<td><strong>0.749</strong> (0.759)</td>
<td>32</td>
</tr>
<tr>
<td>LCM</td>
<td><strong>0.718</strong></td>
<td>0.358 (0.344)</td>
<td>0.634 (0.154)</td>
<td>63</td>
</tr>
<tr>
<td>CDI</td>
<td><strong>0.949</strong></td>
<td><strong>0.784</strong> (0.430)</td>
<td><strong>0.779</strong> (0.209)</td>
<td>63</td>
</tr>
<tr>
<td>CDII</td>
<td>0.693</td>
<td>0.584 (0.469)</td>
<td><strong>0.703</strong> (0.347)</td>
<td>62</td>
</tr>
<tr>
<td>LCD</td>
<td><strong>0.948</strong></td>
<td>0.397 (0.799)</td>
<td>0.179 (0.126)</td>
<td>61</td>
</tr>
<tr>
<td>Ford</td>
<td>0.699</td>
<td>0.187 (0.582)</td>
<td>0.649 (0.194)</td>
<td>65</td>
</tr>
<tr>
<td>JB</td>
<td><strong>0.737</strong></td>
<td>0.35 (0.260)</td>
<td>0.592 (0.499)</td>
<td>65</td>
</tr>
<tr>
<td>SJ</td>
<td>0.569</td>
<td>0.288 (0.210)</td>
<td><strong>0.792</strong> (0.398)</td>
<td>66</td>
</tr>
<tr>
<td>S4</td>
<td><strong>0.891</strong></td>
<td>0.021 (-0.031)</td>
<td><strong>0.712</strong> (-0.027)</td>
<td>70</td>
</tr>
<tr>
<td>S4#2</td>
<td><strong>0.851</strong></td>
<td>0.113 (-0.108)</td>
<td>0.65 (-0.434)</td>
<td>38</td>
</tr>
<tr>
<td>ELV</td>
<td><strong>0.907</strong></td>
<td>0.134 (0.090)</td>
<td><strong>0.732</strong> (-0.044)</td>
<td>70</td>
</tr>
<tr>
<td>RG</td>
<td><strong>0.922</strong></td>
<td>0.158 (0.231)</td>
<td>0.599 (0.617)</td>
<td>70</td>
</tr>
<tr>
<td>NIDO</td>
<td><strong>0.901</strong></td>
<td>0.169 (0.181)</td>
<td><strong>0.778</strong> (0.413)</td>
<td>70</td>
</tr>
<tr>
<td>CO</td>
<td><strong>0.896</strong></td>
<td>0.144 (0.093)</td>
<td><strong>0.802</strong> (0.167)</td>
<td>70</td>
</tr>
<tr>
<td>TORO</td>
<td><strong>0.911</strong></td>
<td>0.564 (0.413)</td>
<td>0.609 (-0.138)</td>
<td>70</td>
</tr>
<tr>
<td>MB</td>
<td><strong>0.895</strong></td>
<td>0.246 (0.176)</td>
<td><strong>0.751</strong> (0.188)</td>
<td>70</td>
</tr>
<tr>
<td>POC</td>
<td><strong>0.833</strong></td>
<td>0.145 (0.036)</td>
<td><strong>0.757</strong> (0.097)</td>
<td>70</td>
</tr>
<tr>
<td>PEC</td>
<td><strong>0.907</strong></td>
<td>0.089 (0.028)</td>
<td><strong>0.785</strong> (0.096)</td>
<td>69</td>
</tr>
<tr>
<td>YPC</td>
<td><strong>0.92</strong></td>
<td>0.248 (0.157)</td>
<td><strong>0.768</strong> (0.377)</td>
<td>68</td>
</tr>
</tbody>
</table>
Table 3: Yearly ion mass deposition per unit area for the different elevation groups.

<table>
<thead>
<tr>
<th>Elevation Group</th>
<th>F^-</th>
<th>Cl^-</th>
<th>SO4^-</th>
<th>Br^-</th>
<th>NO3^-</th>
<th>PO4^-</th>
<th>Li+</th>
<th>Na+</th>
<th>NH4+</th>
<th>K+</th>
<th>Mg++</th>
<th>Ca++</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC</td>
<td>0.290</td>
<td>34.0</td>
<td>7.64</td>
<td>0.280</td>
<td>0.140</td>
<td>3.33</td>
<td>0.070</td>
<td>17.8</td>
<td>2.06</td>
<td>8.10</td>
<td>2.91</td>
<td>4.38</td>
</tr>
<tr>
<td>LI</td>
<td>0.200</td>
<td>32.9</td>
<td>8.73</td>
<td>0.180</td>
<td>0.240</td>
<td>3.49</td>
<td>0.077</td>
<td>16.2</td>
<td>3.07</td>
<td>12.9</td>
<td>2.55</td>
<td>5.84</td>
</tr>
<tr>
<td>LM</td>
<td>0.238</td>
<td>44.0</td>
<td>10.6</td>
<td>0.198</td>
<td>0.238</td>
<td>2.69</td>
<td>0.188</td>
<td>25.9</td>
<td>3.39</td>
<td>7.22</td>
<td>3.40</td>
<td>5.19</td>
</tr>
<tr>
<td>CFL</td>
<td>0.237</td>
<td>61.2</td>
<td>16.6</td>
<td>0.263</td>
<td>0.310</td>
<td>5.50</td>
<td>0.173</td>
<td>31.9</td>
<td>4.44</td>
<td>7.05</td>
<td>4.28</td>
<td>7.01</td>
</tr>
<tr>
<td>UCFL</td>
<td>0.200</td>
<td>70.4</td>
<td>18.8</td>
<td>0.218</td>
<td>0.515</td>
<td>4.74</td>
<td>0.225</td>
<td>40.0</td>
<td>2.38</td>
<td>3.47</td>
<td>4.90</td>
<td>5.93</td>
</tr>
</tbody>
</table>
Figure Captions

Fig 1: Annual averages of rainfall as a function of elevation for all sampling sites.

Fig 2: Monthly profile of rainfall by elevation type. Error bars correspond to standard deviation. Lines are slightly offset for easier viewing.

Fig 3: Linear regression analysis of the natural logarithm of total ion concentration as a function of the natural logarithm of rainfall.

Fig 4: Monthly profile of calcium, sulfate, and sodium concentration at different elevation types.

Fig 5: Yearly weighted means ion concentration for each station.
Fig 1: Annual averages of rainfall as a function of elevation for all sampling sites.
Fig 2: Monthly profile of rainfall by elevation type. Error bars correspond to standard deviation. Lines are slightly offset for easier viewing.
Fig 3: Linear regression analysis of the natural logarithm of total ion concentration as a function of the natural logarithm of rainfall.
Figure 4: Monthly profile of non-sea salt calcium, non-sea salt sulfate, and sodium concentration at different elevation types.
Fig 5: Yearly weighted means ion concentration for each station.