166 The tendency is clearer from 2008 to 2015, where all elevations saw a decrease in precipitation (-
167 70, -120, -90, -168, -225 mm yr^{-1} from LC to UCFL; r^2 = 0.51 – 0.70), accentuated by a severe
168 drought that took place in summer of 2015. The decreasing trend is then interrupted in 2017
169 because of the high amount of precipitation caused by hurricane María. While our dataset is limited
170 for analyzing climate trends, we can combine these observations to gauge how this variable is
171 behaving as a function of time, as well as analyze short-term trends. The short-term trend seen in
172 this study adjust to predictions of decreased precipitation in tropical forests as a consequence of
173 climate change that have not been seen in previous studies for the Luquillo Mountains. While a
174 richer dataset is required to assess changes in climatic patterns, short-term trends can highlight
175 important features that deserves further observation.

176

177 pH of Rainfall Samples

178 The pH had no relationship with elevation or rainfall volume, and in most instances, it remained
179 within 5-6 for all elevation groups. The accepted value of unpolluted rainwater is 5.6 (Manahan,
180 2000), slightly acidic because of the carbon dioxide to carbonic acid equilibrium reaction that takes
181 place in the atmosphere/water interface. A pH lower or higher than this value could be influenced
182 by acidic species from anthropogenic pollution, or by neutralizing species, like those found in
183 mineral dust, respectively.

184

185 Ionic Composition of Rainfall Samples

186 The mean annual weighted total ion concentration was studied as a function of time and grouped
187 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.

Seasonal Variation of Rainfall and Ionic Composition

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 Stated 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

255 of PO_4^{3-} and K^+ did not have a clear pattern with elevation. Still, the deposition of K^+ at the CFL
256 and UCFL decreased, a behavior also seen by Medina et al. (2013). High inputs of K^+ and Mg^{2+}
257 can be attributed to both marine and crustal sources (Valle-Díaz et al., 2016), while PO_4^{3-} can be
258 attributed to crustal sources (Pett-Ridge, 2009). These results show that marine and crustal sources
259 are the main contributors to the ion load and deposition to the Luquillo Mountains and that they
260 are an important source of nutrients to the ecosystem.

261 The annual weighted mean concentration of ions was analyzed as a function of elevation (Fig. 5).
262 This plot shows that the ion concentration at lower stations does not follow a clear trend but rather
263 erratic movements. Similarly, the annual amount of rainfall did not follow a clear pattern. However,
264 while the elevation between these stations is not large, their geographical location and exposure to
265 the northeasterly trade winds are vastly different. The stations CDI, CDII, H, and PDM are located
266 on the southeastern coast, while the stations LCD and LCM are situated in the most northeastern
267 part of the island. This suggests that the trade winds and precipitation will more directly influence
268 the latter two stations from marine cumulus clouds than those in the southeastern region. However,
269 this is not necessarily the case as only the station CDII received less precipitation than those in the
270 northeast. There is a clear difference in the total concentration of ions for these stations, with those
271 located on the northeastern coast receiving more ions than those in the southeastern coast. The
272 higher concentration of sea-salt ions (Na^+, Cl^-, K^+ and Mg^{2+}) in the northeastern coast stations
273 suggests that the influence of the trade winds could be resulting in higher wind speeds that are
274 dragging more marine aerosols with them. Also, these stations had the largest concentrations of
275 nss-SO_4^{2-} because of the nearby mangroves that cause anoxic conditions in the ground and high
276 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 countertrend 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 station 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

346 concentrations of marine aerosols. We also saw an overall higher concentration of all ions than
347 what Lesack and Melack, 1991 reported, which could be due to differences in location and
348 sampling methodology, which can also explain differences with the other studies.

349

350 CONCLUSION

351

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

360 A positive correlation was found between elevation and rainfall, although not all stations followed
361 this behavior. This suggests that ecosystems at higher altitudes (CFL and UCFL) could be more
362 affected by changes in precipitation inputs, such as the elfin cloud forest found at the most upper
363 parts of the Luquillo Mountains. There was not a clear pattern of pH with rainfall, but an inverse
364 exponential relationship between the total ion concentration and the total rainfall was found.

365 Ion composition was shown to be dependent on transported aerosols and have a clear seasonal
366 pattern. While marine aerosols are present year-round, crustal aerosols are more abundant during
367 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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DISCLAIMER

Reference to any companies or specific commercial products does not constitute an endorsement from authors.

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497

Table 1: Description and geographical information of collection stations.

Station Name	Station ID	Elevation (m)	Elevation site	Latitude (N)	Longitude (W)
Palmas del Mar	PDM	0	Lowland coastal	18°05'32.63"	65°48'04.64"
Humacao	H	3	Lowland coastal	18°10'42.27"	65°45'53.23"
Sabana Seca #2	SS#2	3	Lowland coastal	18°27'40.45"	66°12'16.65"
Las Cabezas II	LCM	4	Lowland coastal	18°22'40.73"	65°37'08.90"
Ceiba I	CDI	9	Lowland coastal	18°13'59.01"	65°35'59.13"
Ceiba II	CDII	14	Lowland coastal	18°13'15.13"	65°40'13.43"
Las Cabezas I	LCD	31	Lowland coastal	18°22'51.29"	65°37'13.71"
Ford	Ford	13	Lowland interior	18°23'12.23"	65°52'48.04"
Jardín Botánico	JB	26	Lowland interior	18°23'01.35"	66°03'11.30"
Saint Just	SJ	81	Lowland interior	18°23'04.90"	65°59'58.23"
Sabana 4 Bisley	S4	226	Lower Montane	18°19'01.63"	65°44'30.68"
Sabana 4 Bisley #2	S4#2	226	Lower Montane	18°19'01.63"	65°44'30.68"
El Verde	ELV	361	Lower Montane	18°19'10.02"	65°48'58.28"
Rio Grande	RG	525	Lower Montane	18°17'36.83"	65°48'23.47"
UPR (Nido)	NIDO	655	Cloud Formation Level	18°18'00.81"	65°47'00.05"
Pico del Este I - Colorado	CO	778	Cloud Formation Level	18°17'38.58"	65°47'11.46"
El Toro	TORO	792	Cloud Formation Level	18°16'40.06"	65°50'53.26"
Mount Britton	MB	901	Upper Cloud Formation Level	18°18'16.02"	65°47'26.14"
Pico del Oeste	POC	987	Upper Cloud Formation Level	18°16'39.18"	65°45'51.44"
Pico del Este II - Cloud	PEC	1002	Upper Cloud Formation Level	18°16'17.15"	65°45'40.42"
El Yunque	YPC	1045	Upper Cloud Formation Level	18°18'38.23"	65°45'26.14"

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.

	Pearson Correlation Factor			
Station	Na^+ vs Cl^-	Na^+ vs Ca^{2+} (nss-Ca^{2+})	Na^+ vs SO_4^{2-} (nss-SO_4^{2-})	n
PDM	0.49	0.445 (0.599)	0.496 (0.095)	64
H	**0.781**	0.312 (0.424)	**0.745** (0.285)	59
SS#2	**0.948**	0.332 (0.496)	**0.749 (0.759)**	32
LCM	**0.718**	0.358 (0.344)	0.634 (0.154)	63
CDI	**0.949**	**0.784** (0.430)	**0.779** (0.209)	63
CDII	0.693	0.584 (0.469)	**0.703** (0.347)	62
LCD	**0.948**	0.397 (**0.799**)	0.179 (0.126)	61
Ford	0.699	0.187 (0.582)	0.649 (0.194)	65
JB	**0.737**	0.35 (0.260)	0.592 (0.499)	65
SJ	0.569	0.288 (0.210)	**0.792** (0.398)	66
S4	**0.891**	0.021 (-0.031)	**0.712** (-0.027)	70
S4#2	**0.851**	0.113 (-0.108)	0.65 (-0.434)	38
ELV	**0.907**	0.134 (0.090)	**0.732** (-0.044)	70
RG	**0.922**	0.158 (0.231)	0.599 (0.617)	70
NIDO	**0.901**	0.169 (0.181)	**0.778** (0.413)	70
CO	**0.896**	0.144 (0.093)	**0.802** (0.167)	70
TORO	**0.911**	0.564 (0.413)	0.609 (-0.138)	70
MB	**0.895**	0.246 (0.176)	**0.751** (0.188)	70
POC	**0.833**	0.145 (0.036)	**0.757** (0.097)	70
PEC	**0.907**	0.089 (0.028)	**0.785** (0.096)	69
YPC	**0.92**	0.248 (0.157)	**0.768** (0.377)	68

Table 3: Yearly ion mass deposition per unit area for the different elevation groups.

	Ion Deposition (kg/ha/year)											
Elevation Group	Fl^-	Cl^-	$SO4^{--}$	Br^-	$NO3^-$	$PO4^{--}$	Li^+	Na^+	$NH4^+$	K^+	Mg^{++}	Ca^{++}
LC	0.290	34.0	7.64	0.280	0.140	3.33	0.070	17.8	2.06	8.10	2.91	4.38
LI	0.200	32.9	8.73	0.180	0.240	3.49	0.077	16.2	3.07	12.9	2.55	5.84
LM	0.238	44.0	10.6	0.198	0.238	2.69	0.188	25.9	3.39	7.22	3.40	5.19
CFL	0.237	61.2	16.6	0.263	0.310	5.50	0.173	31.9	4.44	7.05	4.28	7.01
UCFL	0.200	70.4	18.8	0.218	0.515	4.74	0.225	40.0	2.38	3.47	4.90	5.93

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.

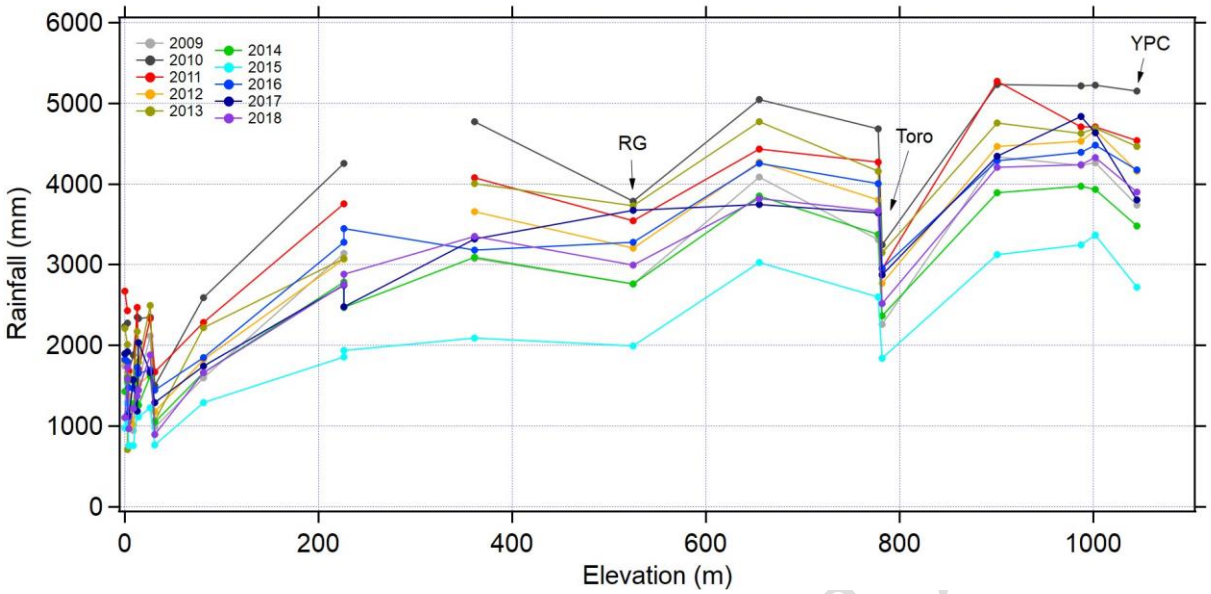


Fig 1: Annual averages of rainfall as a function of elevation for all sampling sites.

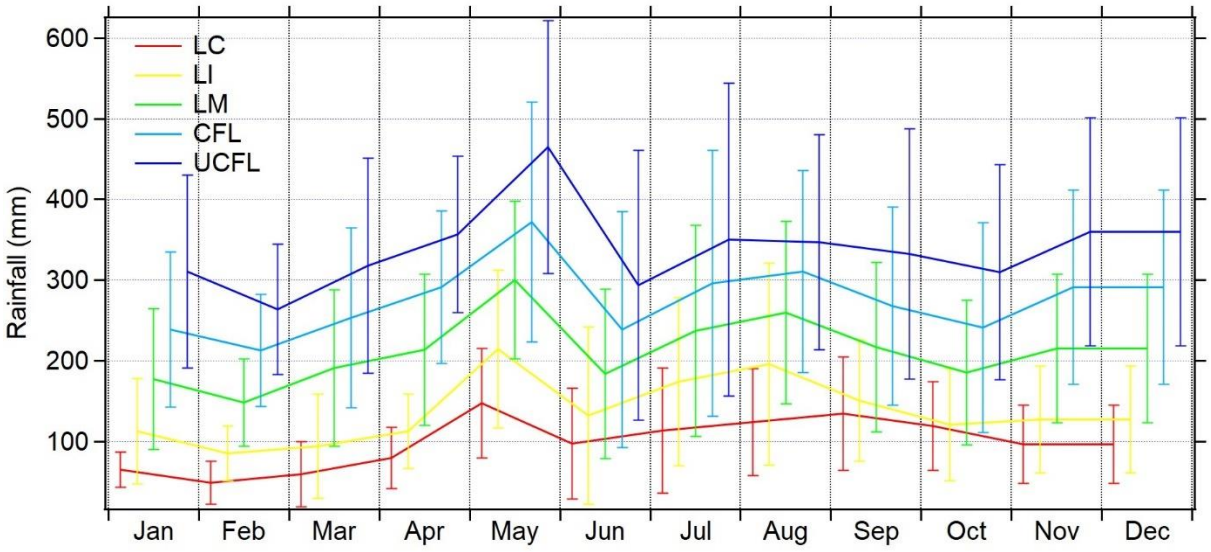
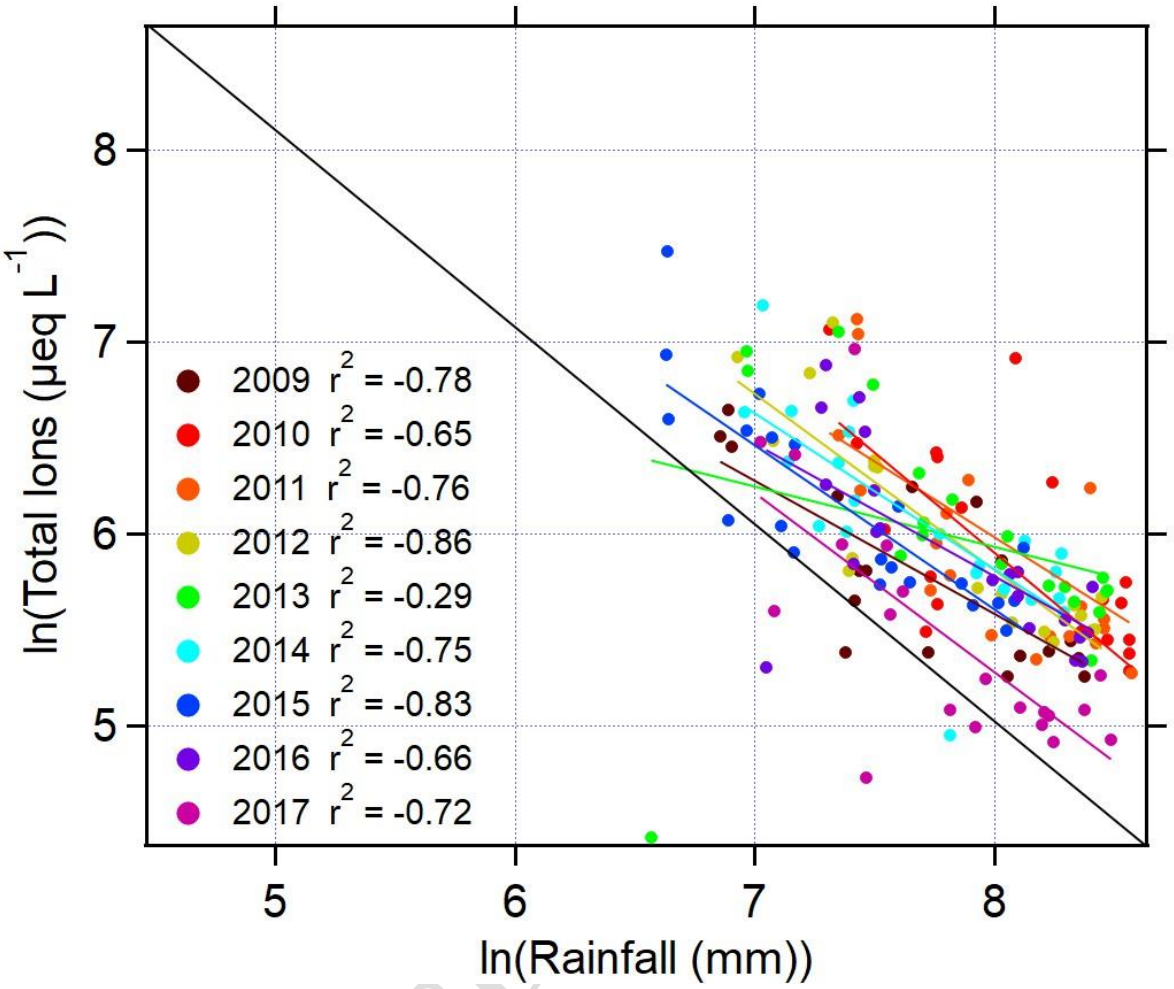


Fig 2: Monthly profile of rainfall by elevation type. Error bars correspond to standard deviation. Lines are slightly offset for easier viewing.



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

594 of the natural logarithm of rainfall.

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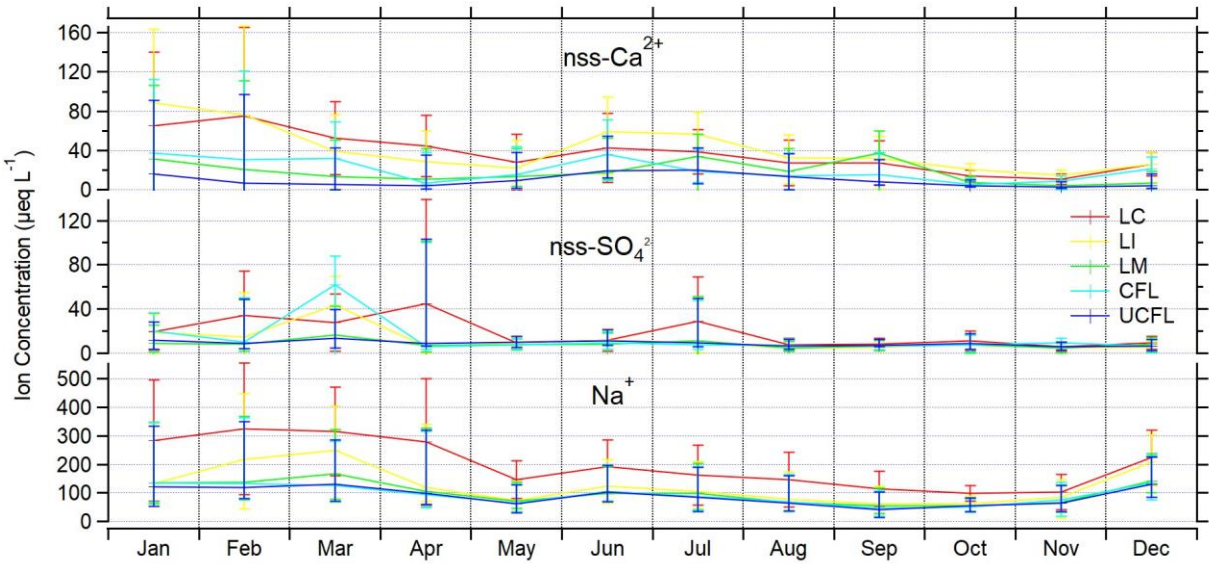
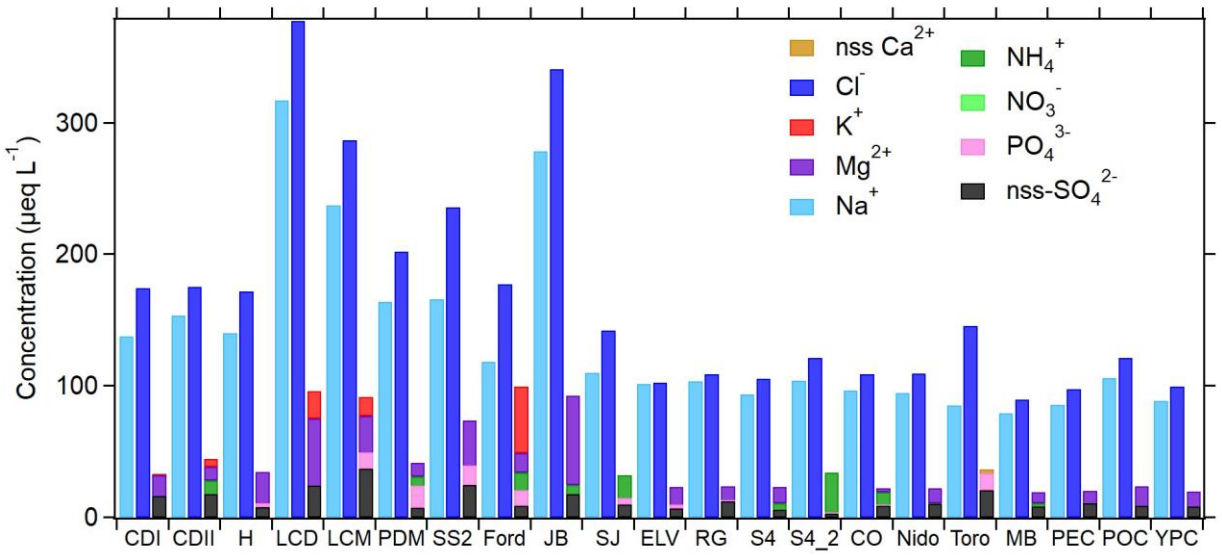


Fig 4: Monthly profile of non-sea salt calcium, non-sea salt sulfate, and sodium concentration at different elevation types.



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613 **Fig 5**: Yearly weighted means ion concentration for each station.