

Spatial and temporal heterogeneity of rainfall inorganic ion composition in northeastern Puerto Rico

Ernesto Medina, Grizelle González and Maria M. Rivera

We measured the ion composition of rainfall collected in stations located at different elevations in northeastern Puerto Rico to explore relationships between rainfall volume and distribution, and influence of marine aerosols on ion composition. Rainfall collected during the last two weeks of each month between February and December 2009 at different altitudes from sea level to 1000 m a.s.l., was analyzed by ion chromatography for Cl^- , SO_4^{2-} , Br^- , NO_3^- , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and NH_4^+ . Electrical conductivity was inversely related to rainfall volume following a power relationship. Conductivity varied little for rainfall above 100 mm. Upper montane stations showed smaller conductivity and variability than lowland stations. Na^+ and Cl^- accounted for the largest ion fraction in all rainfall stations, and were highly correlated indicating strong influence of marine aerosols. Cl^-/Na^+ and $\text{SO}_4^{2-}/\text{Na}^+$ ratios in rain water did not vary significantly with altitude, but other ion/ Na^+ ratios showed significantly higher values in rainfall stations located below 600 m a.s.l., indicating contributions of different aerosol sources. All stations had several times larger K^+/Na^+ , $\text{Ca}^{2+}/\text{Na}^+$, and $\text{SO}_4^{2-}/\text{Na}^+$ ratios ($\mu\text{eq l}^{-1}$), than the marine reference value, a result requiring confirmation with continued measurements. Comparison with previous studies in the Luquillo Experimental Forest showed that volume-weighted ion concentrations measured in the lower montane stations during 2009 (200–500 m a.s.l.) were similar to those of Bisley watershed and higher than those of El Verde station. Ion concentrations measured in rainfall from seven stations at and above the average cloud formation level (600 m a.s.l.) are much lower than those reported by a previous report from Pico del Este. Results emphasize the need to continue routine analysis of rainfall chemistry as a mean to monitor changes in element supply to terrestrial ecosystems.

E. Medina (medinage@gmail.com), G. González and M. M. Rivera, International Inst. of Tropical Forestry, USDA Forest Service, Jardín Botánico Sur, 1201 Calle Ceiba, Río Piedras, PR 00926, USA. EM also at: Centro de Ecología, Inst. Venezolano de Investigaciones Científicas, Aptdo. 21827, Caracas 1020-A, Venezuela.

The Luquillo Mountains in northeastern Puerto Rico have been the center of intensive ecological research since the middle of last century (Odum 1970). This effort continues as part of the Long Term Ecological Research Program (LTER, <<http://www.ites.upr.edu/>>). Nutrient cycling stands among the main research subjects, and within it nutrient inputs in rainfall play a central role.

Rainfall in northeastern Puerto Rico is mostly orogenic, i.e. it is generated by the elevation of humid air masses transported by the trade winds as they press against the Luquillo mountain range (Martens and Harriss 1973, McDowell et al. 1990, García et al. 1996, Wu et al. 2006). The ionic content of rainfall water is, therefore, strongly determined by the composition of seawater particles transported by the air ascending masses. In this process, the air masses are lifted and their temperature decreases as they ascend reaching the level of water condensation (cloud for-

mation). As the temperature continues to decrease, excess water is precipitated as rainfall (Wu et al. 2006). Rainfall chemistry patterns have been documented in detail for the Luquillo Mountains. At El Verde (ca 400 m) concentrations of most ions were correlated negatively with weekly rainfall measurements (Odum 1970, McDowell et al. 1990). Sea salt aerosols contributed most of the Na^+ , Cl^- , Mg^{2+} and K^+ found in wet and bulk precipitation; SO_4^{2-} and Ca^{2+} , however, were derived primarily from non-sea salt sources. Weathers et al. (1988) showed that both cloud and rainwater in Pico del Este (1020 m), one of the highest points of the Luquillo Mountains, was less acidic and had lower concentrations of SO_4^{2-} and NO_3^- than several sites located in the eastern coast of the United States. The study of Asbury et al. (1994) on the cloud water chemistry in Pico del Este, showed that Na^+ and Cl^- from marine aerosols dominated the ion profile, and confirmed the higher

concentrations of ions in cloud water compared to rainwater reported by Weathers et al. (1988). Heartsill-Scalley et al. (2007) calculated nutrient fluxes in rainfall at the Bisley site (ca 250 m) in the Luquillo Experimental Forest (LEF) measured weekly over a 15-yr period. Mean annual rainfall was 3482 mm yr⁻¹, and average annual rainfall fluxes of K⁺, Ca²⁺, Mg²⁺, Cl⁻, Na⁻, and SO₄²⁻ were somewhat larger than those reported for most tropical forests. Rainfall chemistry has been invoked as one of the potential factors responsible for the ongoing decrease in amphibian populations in the Luquillo Mountains because of potential acidification derived from air pollution (Stallard 2001). Decrease in total rainfall during recent years and pathogens are also involved in this process (Burrowes et al. 2004). Pett-Ridge et al. (2009) showed that Sahara mineral aerosol dust contributes significantly to atmospheric inputs in the Luquillo Mountains, whereas volcanic ash inputs are minor in comparison (Heartsill-Scalley et al. 2007). Jiménez-Vélez et al. (2009) measured during a short period the input of metallic elements in African dust in bulk deposition over Puerto Rico, and showed that K/Na ratios increase with the concentration of PM_{2.5} particles. More recently Goda et al. (2011) published analyses of rain water at Pico del Este and calculated contribution of Saharan dust to dry deposition of minerals and organic compounds.

The objective of the present investigation was to document changes in chemical profile associated with rainfall distribution and elevation in the northeastern corner of island of Puerto Rico by analyzing rainfall chemistry in a series of rainfall collectors located from sea level, near the coast, to the uppermost peak in the LEF Mountains. Rainwater samples included both wet and dry deposition, therefore element concentrations could be translated in total inputs to the vegetation.

We hypothesized that, 1) in bulk rainfall ion concentration are higher below the level of cloud formation, because of higher dry deposition, 2) variations in total ion input among sites correlate better with differences in bulk rainfall amount, than with differences in element concentration, 3) departures of sea salt ionic ratios in bulk rainfall reveal the influence of other ion sources at altitudes below the average cloud formation level.

Material and methods

The rainfall collection was carried out in stations distributed along the northern and southeastern coasts of Puerto Rico, stations located further inland below 100 m elevation, about 7–10 km from the nearest sea coast, and stations covering the altitudinal gradient of the Luquillo Mountains as well (Fig. 1). The stations were stratified by elevation above sea level for ulterior analyses as lowland coastal (LC) and interior (LI) stations (0–100 m), lower montane (LM) stations (200–500 m), and stations around the average water vapor condensation level (CFL) (600–

800 m) and above it (UCFL) (900–1000 m) (Table 1). Average level of cloud formation in LEF lies around 600 m elevation (Brown et al. 1983, Wu et al. 2006).

Rainfall sampling and analysis

Bulk rain was measured fortnightly; rainfall collectors were containers of rugged butyrate plastic, of 180 ml capacity, covered by a 101 mm diameter funnel, and were located 1.45 m above ground under open sky. After each collection containers were thoroughly cleaned using rainwater. The samples for analysis represented rainfall accumulated during the last two weeks of each month. After measuring the amount of rain (mm), a 20 ml plastic bottle was washed with a small volume of the rain, filled and deposited in a refrigerated container for transportation to the laboratory on the same day of collection. The rainfall collected for chemical analyses corresponding to the last two weeks of each month represented in average 54% of the total monthly rainfall of each station, ranging from 49% for the LM stations to 62% for the CL stations. As the volume of rainfall collected was 50% or more of total rainfall we assumed that comparison in rainfall chemistry among the stations stratified by altitude was reliable.

In the laboratory, conductivity of the raw samples was measured with an Orion meter (Thermo Scientific). The samples were filtered through Millipore Mille-GV Hydrophilic PVDF filters (0.22 microns) and maintained at 4°C until analysis. Storage time varied from 2 to 6 months depending on the availability of the chromatograph. Repeated measurements of the same samples over prolonged periods indicated that they remained stable in ionic composition. Ions (Cl⁻, Br⁻, SO₄²⁻, NO₃⁻, PO₄³⁻, Na⁺, K⁺, Mg²⁺, Ca²⁺, NH₄⁺) were analyzed in a double column Dionex ICS 3000 Ion chromatograph, using an IonPack AS 18 column and a KOH eluent for anions and a CS 12A column and metasilicic acid as eluent for cations. Calibration was conducted with analytic multielement standards from 0.01 to 20 mg l⁻¹.

All the values for conductivity and ion concentrations were weighted by rainfall volume when interstation and regional comparisons were conducted. Absolute ion concentrations were used to calculate ion ratios, and correlations between ions. Ion ratios relative to Na⁺ were calculated to estimate the contributions of non-sea salt aerosols to the chemical composition of the rainwater (Keene et al. 1986, McDowell et al. 1990, Eklund and McDowell 1997, Tiwari et al. 2006, Teixeira et al. 2008).

Statistical analysis

All data sets of ion concentrations had heterogeneous variances (Bartlett test), therefore, significance of differences between stations and dates at p≤0.05, was tested using a

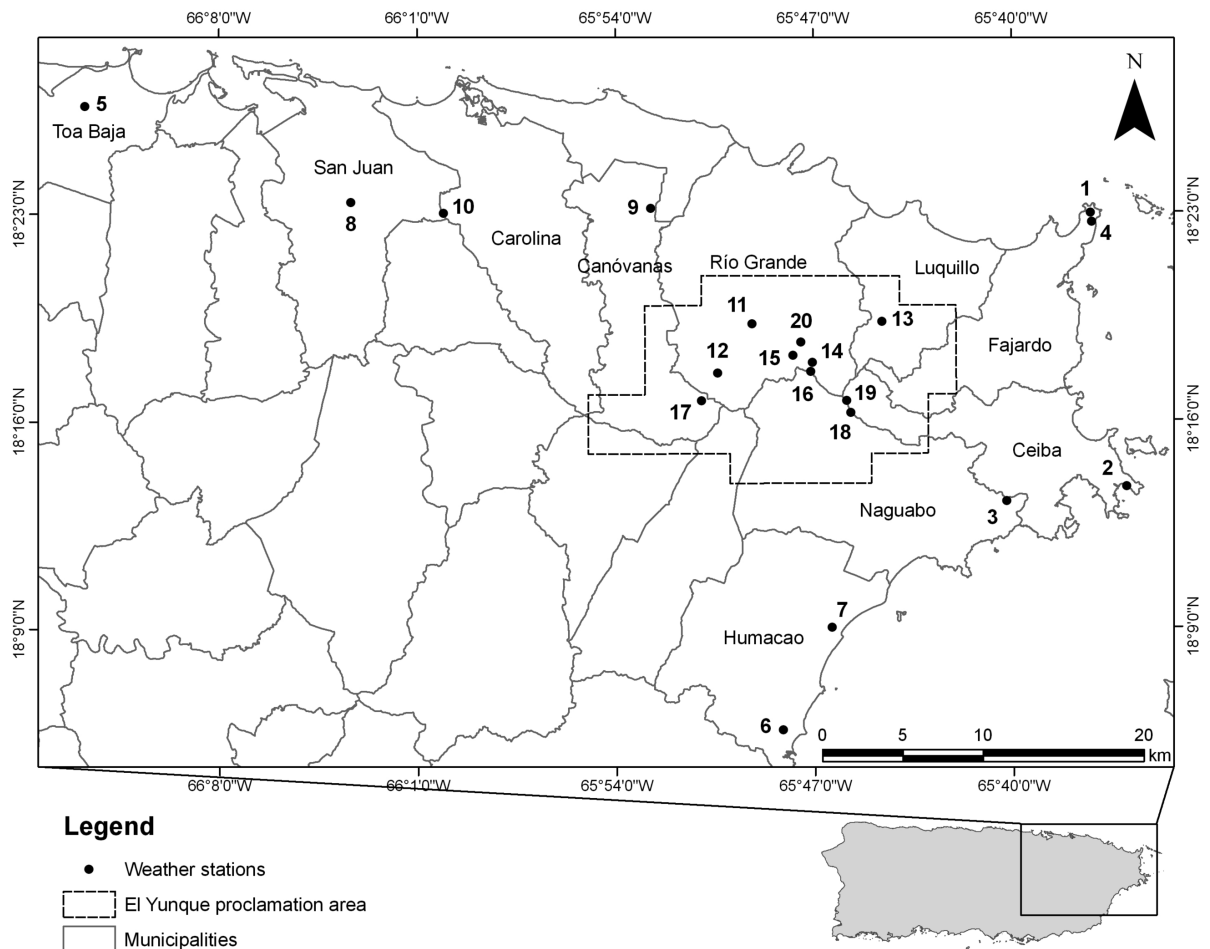


Figure 1. Location of the weather stations in Puerto Rico. Site numbers correspond to the names used in Table 1.

modified analysis of variance allowing the comparison of means with unequal standard deviations (Welsh's test), and a non parametric test (Wilcoxon–Kruskal Wallis rank sum test). All statistical analyses were performed using JMP ver. 8 program (2008).

Results

Total rainfall per station

Total rainfall per station in 2009 followed the general expected pattern of rainfall increase with elevation (Brown et al. 1983, García-Martínó et al. 1996), with the exception of the UPR Nido and El Toro stations (14, 16), showing higher and lower total rainfall than expected. Comparison of data tabulated in García-Martínó et al. (1996) with rainfall measured during 2009 showed that only the stations 13, 14, 17, 18 and 19 followed the same elevation pat-

tern, the rest had lower rainfall values than expected (Fig. 2). This may be caused by differences in wind exposure of those stations (Weaver 1972, Grubb 1977, Asbury et al. 1994). Rainfall distribution showed a certain seasonality in all stations, measured as the proportion of total rainfall in the first quarter of the year (dry season January–April) increasing from lowland stations (LC, LI) with 20%, lower montane station (LM) with 24% and those stations located at or above the cloud formation level (CFL, UCFL) with 30%.

Conductivity of rainfall samples

As volume of rainfall varied among dates and stations we analyzed the volum–conductivity relationship of the samples (Fig. 3). The relationship was fitted by a power function explaining about 24% of the conductivity variance indicating a sharp decrease in conductivity as the volume of rainfall increased up to 75 mm.

Table 1. Altitudinal distribution, total rainfall measured in 2009 and geographical coordinates of the rainfall collection stations.

Site name	Elevation m	Rain mm	Lat N	Long W
Lowland coastal stations (LC)				
1 – Las Cabezas I	0	981	18°22′51.29″	65°37′13.71″
2 – Ceiba I	7	948	18°13′59.01″	65°35′59.13″
3 – Ceiba II	26	1545	18°13′15.13″	65°40′13.43″
4 – Las Cabezas II	0	993	18°22′40.73″	65°37′08.90″
5 – Sabana Seca	2	1709	18°27′40.45″	66°12′16.65″
6 – Palmas del Mar	0	1743	18°05′32.63″	65°48′04.64″
7 – Humacao	0	1664	18°10′42.27″	65°45′53.23″
Lowland interior stations (LI)				
8 – Jardin Botánico	100	2113	18°23′01.35″	66°03′11.30″
9 – Ford	23	1693	18°23′12.23″	65°52′48.04″
10 – Saint Just	81	1600	18°23′04.90″	65°59′58.23″
Lower montane stations (LM)				
11 – El Verde	434	3075	18°19′10.02″	65°48′58.28″
12 – Rio Grande	525	2762	18°17′36.83″	65°48′23.47″
13 – Sabana 4	265	3145	18°19′01.63″	65°44′30.68″
Cloud formation level stations (CFL)				
14 – UPR Nido	634	4087	18°18′00.81″	65°47′00.05″
15 – Pico del Este I	751	3307	18°17′38.58″	65°47′11.46″
16 – El Toro	811	2262	18°16′40.06″	65°50′53.26″
Upper cloud formation level stations (UCFL)				
17 – Mount Britton	902	4338	18°18′16.02″	65°47′26.14″
18 – Pico del Este II	953	4265	18°16′17.15″	65°45′40.42″
19 – Pico del Oeste	954	4229	18°16′39.18″	65°45′51.44″
20 – El Yunque	1000	3742	18°18′38.23″	65°47′26.14″

The volume-weighted conductivity was higher in the LC sites compared to those of the CLF and UCFL sites. LI and LM sites had intermediate and more variable conductivity values (Fig. 4A).

Conductivity did not show a clear seasonal pattern for any station, but there were significant differences among collection dates for all stations pooled together (Fig. 4B). Higher averages in $\mu\text{S cm}^{-1}$ were recorded in March (54), July (38) and October (35), whereas lowest values were those of February (23), August (19) and November (17).

Ionic composition and conductivity

As expected conductivity ($\mu\text{S cm}^{-1}$) and Σions ($\mu\text{eq l}^{-1}$) were significantly and linearly correlated but adjusted better to a log–log relationship ($R^2=0.53$, $F_{\text{ratio}}=222$,

$p<0.0001$, $n=196$), probably a result of the highly asymmetrical distribution of concentration values. The sums of cations and anions were also highly correlated throughout the year, adjusting also better to a log–log function (Fig. 5). Most data fell on the 1:1 ratio line, but about 20% of samples showed anion/cation ratios below 1 (Fig. 5). This indicates the presence of additional anions at some stations and sampling times that were not measured in this work.

Volume weighted average concentrations for all ions measured, except NO_3^- , showed consistently lower values in the CFL and UCFL stations compared to the LC and LM stations (Table 2). The Σ of anions and cations showed the same pattern. The stations grouped as LI were characterized by similar ion concentrations as the LM stations except for Na^+ and Cl^- . Their low elevation and their distance from the coast may be the cause of this apparent discrepancy from the overall pattern.

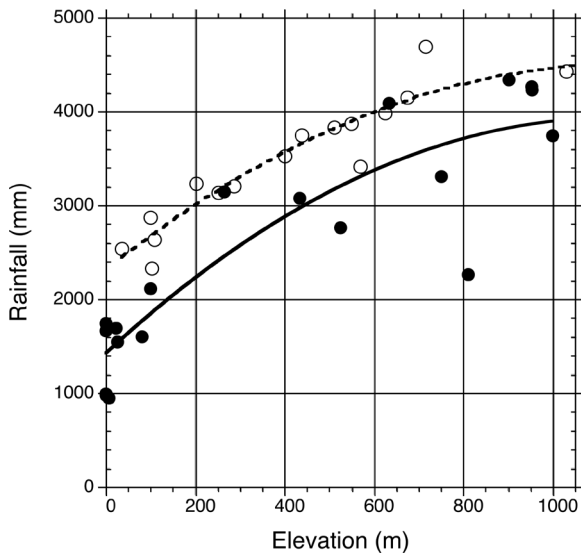


Figure 2. Comparison of multiyear averages for the altitudinal variations in rainfall reported by García-Martínó et al. (1996) (circles, $R^2_{adj}=0.89$; $F=62.9$, $p<0.0001$) compared to 2009 rainfall (dots, $R^2_{adj}=0.89$; $F=76.8$, $p<0.0001$). Lines represent quadratic polynomials fitting, the point surrounded by a circle was considered an outlier and excluded from the calculation for 2009.

The sequence of anion volume weighted concentration in $\mu\text{mol l}^{-1}$ was $\text{Cl}^- > \text{SO}_4^{2-} > \text{PO}_4^{3-} > \text{Br}^- > \text{NO}_3^-$ for all stations. The sequence of cation concentrations was $\text{Na}^+ > \text{NH}_4^+ > \text{K}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$ in all stations clustered in the LC, LM and CFL stations, whereas K^+ occupied the sec-

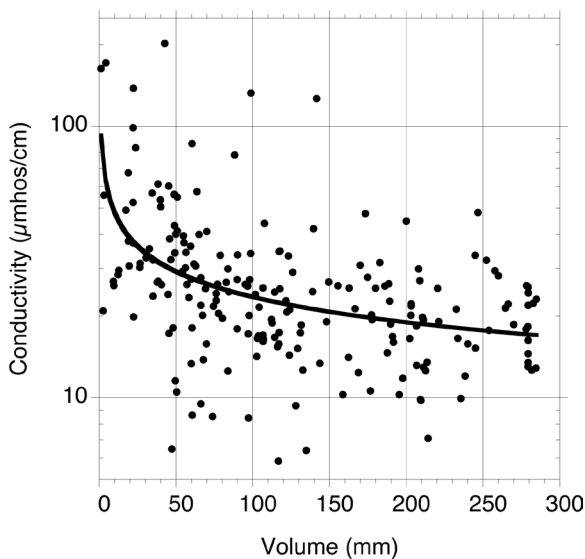


Figure 3. Volume–conductivity relationship observed in rainfall samples collected in 2009. Conductivity $\mu\text{S cm}^{-1} = 98.11 \times \text{Vol}^{-0.31}$; $R^2=0.24$, $n=209$; $F=58.8$, $p<0.0001$.

ond position in LI stations, and Mg^{2+} occupied the third position in the UCFL stations.

The fraction of Cl^- from the Σanions ($\mu\text{mol l}^{-1}$) ranged from 83 to 95%, whereas the fraction of Na^+ from the $\Sigma\text{cations}$ was more variable and ranged from 34 to 83%, as a consequence of the strong contribution of NH_4^+ and K^+ in some stations. The volume weighted $\Sigma\text{anions}/\Sigma\text{cations}$ ratios ranged from 0.5 to 1.1, with a tendency to higher values in CFL and UCFL stations.

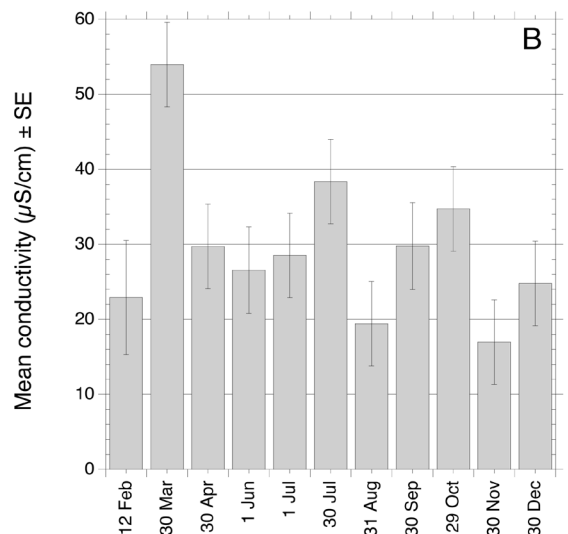
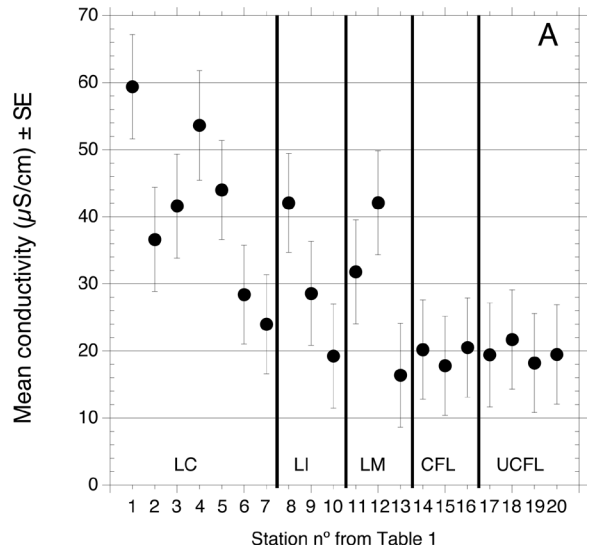


Figure 4. (A) Average volume-weighted conductivity of rainfall from collection stations stratified by elevation: Coastal Lowlands (LC); Lowlands Interior (LI); Lower Montane (LM); Cloud Formation Level (CFL+UCFL) Bartlett $F=10.48$, $p<0.0001$; Welch's $F=2.65$, $p=0.0017$; Wilcoxon–Kruskal Wallis $\chi^2=67.06$, $p<0.0001$. (B) Conductivity of rainwater samples averaged for all stations through 2009.

Table 2. Volume-weighted conductivity ($\mu\text{S cm}^{-1}$) and ion concentrations ($\mu\text{mol l}^{-1}$) average for each station sampled through 2009. Capitals LC to UCFL correspond to location designations as in Table 1.

Station no.	Conduct.	Cl	SO ₄	Br	PO ₄	NO ₃	Σ anion	Na	NH ₄	K	Mg	Ca	Σ cation
1	38.5	137.1	13.3	0.1	4.5	0.0	154.7	117.9	5.4	9.0	15.0	7.9	155.1
2	33.6	150.3	14.9	0.3	14.7	0.1	171.1	123.6	44.7	22.8	21.1	15.6	227.8
3	37.8	112.6	13.9	0.5	14.6	0.0	140.5	85.7	45.4	53.9	39.3	30.7	253.2
4	41.5	176.8	15.3	0.2	8.4	0.1	200.4	153.3	6.5	7.1	17.3	7.8	192.1
5	24.6	95.8	13.3	0.1	8.6	0.0	117.8	77.5	5.1	8.0	9.2	9.2	109.0
6	25.3	128.4	16.3	0.1	12.4	0.2	152.8	100.9	107.1	43.0	13.1	27.8	291.9
7	24.6	123.3	9.6	0.1	11.9	0.0	139.7	95.8	0.9	7.5	13.5	7.9	125.6
8	31.4	106.6	23.7	0.2	8.6	0.0	133.8	70.0	22.0	26.4	11.9	11.0	141.4
9	23.4	117.4	10.5	0.1	5.1	0.3	126.3	102.6	20.3	5.9	12.6	8.0	149.5
10	16.5	79.9	7.9	0.1	4.5	0.1	92.5	65.7	14.4	10.3	8.1	7.9	106.5
11	27.1	101.5	12.7	0.2	0.6	0.2	103.8	100.0	61.9	39.5	11.9	8.6	221.8
12	40.4	141.1	22.4	0.4	4.1	0.2	168.1	121.9	59.5	35.8	21.8	13.3	252.3
13	16.5	80.5	8.5	0.1	3.4	0.0	86.9	86.4	9.5	4.3	9.7	4.4	114.2
14	20.4	87.4	9.5	0.0	1.9	0.0	98.5	72.0	7.5	3.6	8.6	4.5	95.7
15	20.8	108.3	10.8	0.1	1.1	0.0	120.4	89.3	11.3	3.6	9.7	4.4	118.3
16	17.9	100.2	10.6	0.2	1.2	0.6	112.7	80.5	40.6	13.4	9.9	6.4	150.8
17	18.9	78.8	13.5	0.0	3.0	0.1	95.4	66.5	4.2	2.5	9.1	6.5	88.8
18	20.8	97.7	11.0	0.1	6.6	0.1	115.6	81.8	1.4	3.0	9.3	4.8	100.3
19	18.2	94.7	9.4	0.1	1.6	0.1	105.9	81.0	10.2	3.2	8.7	6.0	109.0
20	19.1	93.7	9.7	0.1	4.7	0.0	108.3	77.8	0.1	2.7	8.9	4.6	94.1
Averages													
LC	32.3	132.0	13.8	0.2	10.7	0.1	153.8	107.8	30.7	21.6	18.4	15.3	193.5
LI	23.8	101.3	14.1	0.1	6.1	0.1	117.5	79.5	18.9	14.2	10.9	9.0	132.4
LM	28.0	107.7	14.5	0.2	2.7	0.1	119.6	102.8	43.6	26.6	14.4	8.7	196.1
CFL	19.7	98.7	10.3	0.1	1.4	0.2	110.5	80.6	19.8	6.9	9.4	5.1	121.6
UCFL	19.2	91.2	10.9	0.1	4.0	0.1	106.3	76.8	4.0	2.8	9.0	5.5	98.0

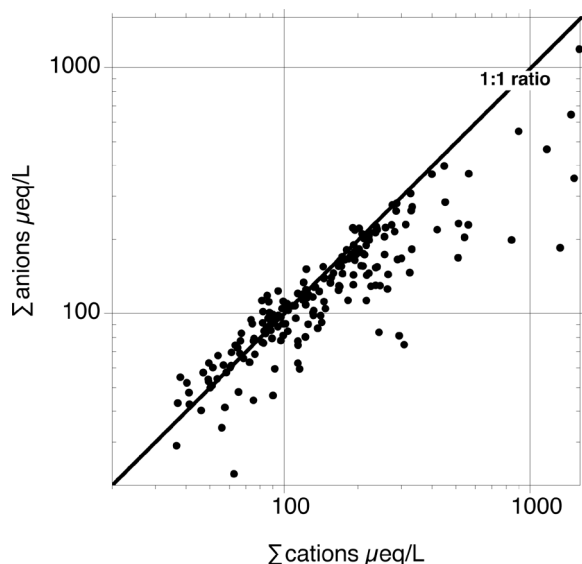


Figure 5. Cation–anion relationship fitted to a log–log line. Depicted the 1:1 ratio line. $\log(\Sigma \text{anions}) = 1.123 + 0.744 \log(\Sigma \text{cations})$; $R^2_{\text{adj}}=0.783$; $F=755$, $p<0.0001$; $n=210$.

All ions showed large variations in volume weighted concentrations during the year 2009 (data not shown). The general tendency was for the higher volume weighted concentrations to be recorded during March and April, corresponding to the drier period of the year, when also the variability of the samples was higher. This pattern corresponds with that of the volume weighted conductivity presented above.

Correlations between ions and ion ratios

Conductivity of rainwater was correlated ($r \geq 0.6$) with Cl^- , SO_4^{2-} , Na^+ , and the Σions . Most ions were significantly correlated to each other when all samples are analyzed together (Table 3). The largest coefficients ($r \geq 0.7$) explaining about 50% of the variance corresponded to Cl^- vs Na^+ and Mg^{2+} ; Mg^{2+} vs Na^+ , Ca^{2+} and Br^- .

The average ion ratios of K^+ , Mg^{2+} and Ca^{2+} relative to Na^+ , decreased significantly with the altitude of the rainfall station ($p < 0.0001$), the tendency was to have lower ratios in the stations located above the 600 m elevation (Table 4). The Cl^-/Na^+ and $\text{SO}_4^{2-}/\text{Na}^+$ ratios did not differ significantly among stations (at $p < 0.01$). The average ion/ Na^+ ratios were slightly higher than the reference values for standard seawater (Keene et al. 1986) for Cl^-/Na^+ (1.1) and $\text{Mg}^{2+}/\text{Na}^+$ (1.3), but much higher for the K^+/Na^+ (9.1) and the $\text{Ca}^{2+}/\text{Na}^+$ (5.0) ratio. This indicates additional sources of K^+ and Ca^{2+} particularly in the stations below 600 m. The ratio $\text{SO}_4^{2-}/\text{Na}^+$ was about twice as high than the reference value for all stations and we do not have an explanation for it.

Annual input of ions

With annual volume weighted average ion concentrations and total rainfall we calculated the load of ions deposited in bulk rainfall along the elevational gradient during 2009 (Table 5). Cl^- and Na^+ were by far the dominant ions, with average Cl^-/Na^+ ratios averaging around 1.2 as expected for areas where aerosols derived from sea water dominate

Table 3. Significant pair-wise correlations ($p < 0.001$) calculated from absolute ion concentrations ($\mu\text{mol l}^{-1}$) in rainfall samples from all stations during 2009. Highlighted significant correlations coefficients ≥ 0.7 explaining about 50% of the variance. ($n=199-207$).

	Cond.	Cl^-	SO_4^{2-}	Br^-	NO_3^-	PO_4^{3-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Σan^-
Cl^-	0.62											
SO_4^{2-}	0.61	0.68										
Br^-	0.33	0.41	0.38									
NO_3^-	0.26	0.44										
PO_4^{3-}	0.20	0.02		0.27								
Na^+	0.64	0.99	0.67	0.43	0.37							
NH_4^+	0.26	0.38	0.61	0.58	0.27	0.35	0.34					
K^+	0.45	0.53	0.59	0.57	0.27	0.32	0.48	0.68				
Mg^{2+}	0.58	0.70	0.39	0.72	0.27	0.37	0.71	0.49	0.67			
Ca^{2+}	0.42	0.61	0.37	0.63	0.28	0.41	0.57	0.64	0.69	0.79		
Σan^-	0.68	0.99	0.70	0.35	0.46	0.12	–	–	–	–	–	
Σcat^+	0.57	–	–	–	–	–	0.76	0.84	0.83	0.82	0.83	0.80

Table 4. Ion ratios referred to Na and stratified by elevations according to Table 1, averaged from absolute concentrations measured throughout 2009 ($\mu\text{eq ion}/\mu\text{eq Na}^+$). Calculated means ($\pm\text{SE}$).

Location	n	$\Sigma\text{cations}/\Sigma\text{anions}$	Cl^-/Na^+	$\text{SO}_4^{2-}/\text{Na}^+$	K^+/Na^+	$\text{Mg}^{2+}/\text{Na}^+$	$\text{Ca}^{2+}/\text{Na}^+$
Coastal Lowlands (LC)							
0–25 m	73	1.31 (0.11)	1.28 (0.02)	0.26 (0.02)	0.21 (0.04)	0.35 (0.06)	0.29 (0.04)
Interior Lowlands (LI)							
25–100 m	31	1.33 (0.08)	1.36 (0.10)	0.23 (0.02)	0.28 (0.11)	0.29 (0.02)	0.29 (0.04)
Lower Montane (LM)							
250–550 m	30	1.71 (0.15)	1.17 (0.06)	0.30 (0.04)	0.43 (0.11)	0.29 (0.02)	0.19 (0.02)
Montane (CFL)							
600–800 m	32	1.27 (0.12)	1.24 (0.03)	0.27 (0.02)	0.10 (0.02)	0.23 (0.01)	0.12 (0.01)
Upper Montane (UCFL)							
900–1000 m	44	1.04 (0.04)	1.22 (0.01)	0.30 (0.02)	0.04 (0.00)	0.23 (0.01)	0.14 (0.02)
Bartlett		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Welch		<0.0001	0.028	0.175	<0.0001	0.006	<0.0001
Wilcoxon–KW		<0.0001	0.056	0.05	<0.0001	<0.0001	<0.0001
Average		1.31 (0.05)	1.26 (0.02)	0.27 (0.01)	0.20 (0.03)	0.29 (0.02)	0.22 (0.02)
n		198	200	206	207	207	207
Reference value (Keene et al. 1986)			1.16	0.121	0.022	0.227	0.044
% sea water			0.92	0.45	0.11	0.78	0.22

the ion input in rainfall (Keene et al. 1986). Inputs of total K^+ were remarkably high, particularly at the LM stations, showing a pronounced decrease at the CFL and UCFL stations. We did not estimate total input of inorganic N as the individual values of NH_4^+ varied erratically within stations and months. Inter-group comparisons showed that rainfall amounts determine the higher inputs of Cl^- , SO_4^{2-} , Na^+ and Mg^{2+} in UCFL stations and lower input of these elements in LC stations in spite of their coastal location. Only data for LM stations could be compared with previous long-term estimations reported by Heartsill-Scalley et al. (2007) for the El Verde and Bisley sites. Load of all ions, except K^+ , calculated in Table 5 for LM sites were 11 to 36 % lower than the long-term averages, but K^+ was 3.8 times higher than the long-term average. This large departure of K^+ can only be related to non-marine inputs, such as the Saharan dust.

Discussion and conclusions

Annual and seasonal distribution of rainfall during 2009 followed the pattern described repeatedly in the literature (Brown et al. 1983, García-Martínó et al. 1996). Based on bulk rainfall and inorganic ion profiles we discriminated three distinct groups of stations related to altitude above sea level, 1) the lowland stations that included coastal and interior locations, 2) the lower montane stations, and 3)

the stations located at or above the level of cloud formation at LEF.

Conductivity was inversely related to rainfall volume and it was fitted by a power function. Our measurements indicate that for volumes above 100 mm collected in periods of two weeks, variations in conductivity are small. The CFL and UCFL stations showed consistently smaller conductivity and variability than the lowland stations. There was no clear-cut seasonality of average volume weighted conductivity during the year, but March and July showed higher and more variable averages.

As expected conductivity was well correlated with the total amount of ions, and the Σ of anions and cations were also strongly correlated to each other and both fitted a log–log relationship. Most ions were significant correlated to each other but the highest coefficients of determination corresponded to Cl^- , Na^+ , and Mg^{2+} (Table 3).

Na^+ and Cl^- accounted for the largest ion fraction in all rainfall stations. They were also highly correlated to each other indicating the strong influence of marine aerosols on rain ion composition at all altitudes.

Comparison of our results with other studies on rainfall chemistry conducted in several sites at LEF reveals similarities and some strong differences that deserve detailed analysis. We compared the volume-weighted molar concentrations of bulk rainfall estimated in this paper for the LM stations with those of McDowell et al. (1990) for El Verde, and Heartsill-Scalley et al. (2007) at the Bis-

Table 5. Input of elements (mol ha⁻¹ yr⁻¹) and total rainfall (mm) calculated for 2009, stratified by elevation as designated in Table 1.

Site no.		Cl	SO ₄	Na	K	Mg	Ca	Rainfall mm
		mol ha ⁻¹ yr ⁻¹						
1		1345	130	1157	88	147	78	981
2		1425	141	1172	216	200	147	948
3		1740	215	1323	832	608	475	1545
4	LC	1756	152	1522	71	172	77	993
5		1638	228	1324	136	158	157	1709
6		2238	283	1758	750	228	485	1743
7		2051	159	1594	125	225	131	1664
8		2251	501	1480	559	251	233	2113
9	LI	1988	178	1737	100	214	136	1693
10		1279	127	1052	165	130	127	1600
11		3122	392	3073	1216	366	263	3075
12	LM	3897	618	3368	989	602	367	2762
13		2532	267	2718	135	304	138	3145
14		3574	389	2945	149	352	184	4087
15	CFL	3583	359	2954	118	321	146	3307
16		2267	239	1821	304	224	144	2262
17		3418	585	2883	109	395	282	4338
18	UCFL	4168	470	3490	127	395	205	4265
19		4004	399	3425	134	367	252	4229
20		3508	364	2912	101	333	174	3742
Averages								
	LC	1742	187	1407	317	248	221	1369
	LI	1839	269	1423	275	198	165	1802
	LM	3184	426	3053	780	424	256	2994
	CFL	3141	329	2573	190	299	158	3219
	UCFL	3774	455	3177	118	373	228	4144

ley watershed, and our UCFL stations with the studies of Asbury et al. (1994) (Table 6). Additional sources of information were the studies on wet deposition conducted routinely by the National Atmospheric Deposition Program (NADP) at El Verde and the study of Gioda et al. (2011) at Pico del Este. Wet deposition values provide a basis to estimate the levels of dry deposition on those stations where both wet deposition and bulk rainfall are measured simultaneously.

Concentrations of Na⁺, Mg²⁺, and Cl⁻ of LM and Bisley are similar, and higher than those of El Verde. SO₄²⁻ concentrations overlap in the three lower montane studies. However, the concentrations of K⁺ and NH₄⁺ are several times higher in LM sites of the present study. Although we cannot discard possible contamination, it should be

noticed that in the case of K⁺ the values from our CFL and UCFL stations are similar to those of Bisley and El Verde, whereas all values for the lowland stations are similar to those of LM. The comparison of our LM data with wet deposition reports of the National Atmospheric Deposition Program (NADP) for 2009 reveals that dry deposition constitutes a large fraction of the deposition measured in bulk rainfall. It accounts for about 40% in the case of Na and Cl, and about 60% in the case of Mg and Ca. Our value for K⁺ appears to be too high.

The ion concentration profile of the UCFL stations compared to the values reported by Asbury et al. (1994) reveals strong divergences. Pico del Este data are higher by a factor of 2–3 in the case of Cl⁻, SO₄²⁻, NH₄⁺, Mg²⁺, and Na⁺, and a factor of 4–5 in the case of Ca²⁺ and K⁺.

Table 6. Comparison of volume-weighted ion concentrations ($\mu\text{mol l}^{-1}$) of the wet deposition measurements conducted within the NADP program (<nadp.sws.uiuc.edu/>) at El Verde station and Gioda et al. (2011) at Pico del Este (2) with analyses of bulk rainfall of the present paper and the studies of McDowell et al. (1990) (El Verde), Heartsill-Scalley et al. (2007) (Bisley), Asbury et al. (1994) Pico del Este (1).

Ion	NADP 2009	LM 2009	Bisley 1998–2003	El Verde 1984–1987	UCFL 2009	Pico Este 1 1984–1985	Pico Este 2 2004–2007
	Wet dep.	Bulk rainfall		Bulk rainfall		Wet dep.	
Na ⁺	59.1	103	106	71	77	215	134
K ⁺	1.5	26.6	5.6	2.4	2.8	13.6	6.2
Mg ²⁺	6.6	14.4	15.1	9.0	9.0	24.6	6.5
Ca ²⁺	3.0	8.7	11.0	8.5	5.5	23.5	7.0
NH ₄ ⁺	1.1	43.6	1.8	1.7	4.0	9.9	3.9
Cl ⁻	68.6	108	114	88	91	175	129
SO ₄ ²⁻	7.9	14.5	13.5	15.5	10.9	23.5	10

Moreover, the Cl⁻/Na⁺ ratio is 1.2 in our samples against 0.8 in the Asbury et al. paper. As the ion concentrations in Pico del Este are also higher than the values reported by McDowell et al. (1990) and Heartsill-Scalley et al. (2007) they contradict the pattern reported in the present paper of concentrations decreasing with altitude. The report by Gioda et al. (2011) on the ion concentration for seven events at Pico del Este during the period 2004–2007 indicate that concentrations of K⁺, Mg²⁺, Ca²⁺, NH₄⁺ and SO₄²⁻ are similar to the average found in our study for 2009. Na⁺ and Cl⁻ are intermediate between values reported here and those of Asbury et al. (1994). Comparison of studies at Pico del Este indicate that there are important variations in concentrations over the years, and that differences between wet deposition and bulk rainfall tend to be smaller than at stations located at lower altitudes.

Our results support hypothesis 1 and 2 showing a decrease in conductivity and volume weighted concentrations of the most abundant ions in bulk rainfall with elevation that appears more associated to rainfall volumes than to differences in chemical composition (Table 2, 5).

Precipitation chemistry at the Luquillo Mountains, and probably in most Caribbean islands, is affected by long-range transportation of inorganic salts. Saharan dusts contribute during summers a significant portion of the excess Ca²⁺, K⁺ and Mg²⁺ (Jiménez-Vélez et al. 2009, Pett-Ridge et al. 2009) whereas during winter months, cold fronts may transport SO₄²⁻ and NO₃⁻ from North America and the western part of Puerto Rico to the mountains in the east of the island (McDowell et al. 1990). In addition, occurrence of tropical storms and hurricanes can further change the patterns of chemical composition between years (Heartsill-Scalley et al. 2007). Therefore, comparison between sites taken during different periods may be difficult.

The lack of significant differences among Cl⁻/Na⁺ and SO₄²⁻/Na⁺ ratios in rainwater at different elevations in-

dicates that the influence of marine aerosols was equally distributed from sea level to the upper most cloud forests. The rest of the ion ratios showed clearly higher values in rainfall stations located below 600 m a.s.l., indicating contributions of different aerosols sources at those altitudes. However, all stations showed several times larger K⁺/Na⁺, Ca²⁺/Na⁺, and SO₄²⁻/Na⁺ ratios ($\mu\text{eq l}^{-1}$) than the marine reference value. These large departures certainly require confirmation.

These patterns relate to our third hypothesis, and reveal a complex interaction of different aerosol sources that cannot be definitively elucidated without additional information on atmospheric events such as Saharan dust or volcanic ashes deposition. A recent report on the composition of Saharan dust particles by Jiménez-Vélez et al. (2009) shows that dust transport over Puerto Rico may increase supply of heavy elements and K to both dry and wet depositions. Gioda et al. (2011) analyzed aerosols samples collected during events of Saharan dust deposition (5). Their analyses show that Saharan dust contains amounts of K⁺ and Ca²⁺ capable of influencing strongly the ion ratios relative to Na⁺ to levels similar to those reported here. Unfortunately we do not have continuous records of Saharan dust deposition in Puerto Rico. The correlation between dust deposition and ion composition in bulk rainfall remains to be established. Heartsill-Scalley et al. (2007) argue that its contribution to inorganic ion inputs, although detectable, may be minor.

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