Chemical constituents in clouds and rainwater in the Puerto Rican rainforest: Potential sources and seasonal drivers

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HIGHLIGHTS

► Results of a long-term of monitoring of rain and cloud water in background sites.
► Few places on the Planet are possible to collect cloud water with natural features.
► The results are important for comparison and evaluation of anthropogenic impacts.
► Concentrations, trends, seasonality and correlations are discussed in the paper.
► It is important to understand the effects of nutrients and pollutants on ecosystems.

ARTICLE INFO

ABSTRACT

Cloud- and rain-water samples collected between 1984 and 2007 in the Luquillo Experimental Forest, Puerto Rico, were analyzed in order to understand the main processes and sources that control their chemistry. Three sites were used: El Verde Field Station (380 m asl), Bisley (361 m asl), and East Peak (1051 m asl). Bulk rainwater samples were collected from all sites, and cloud water was also collected on East Peak. All samples were analyzed for pH, conductivity, and concentrations of Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}. Similar patterns in overall chemistry were observed for both cloud- and rain-water samples. The majority of samples had low acidity (average pH of 4.4–5.0), similar to other remote sites. Sea salt (Na^+ and Cl^-) had a large influence on rain and cloud chemistry and accounted for approximately 70% of the total mass of solutes, followed by $SO_4^=$, which controls the acidity of the clouds and rainwater. Calcium accounted for 6–8% of the total cations and dominated neutralization processes. The highest concentrations of Ca^{2+} and NO_3^- in both cloud- and rain-water were observed in the summertime when large amounts of dust from the African continent reached the sites. Enrichment Factor and Principal Component Analyses showed that Na^+, Cl^-, and Mg^{2+} in the cloud- and rain-water were primarily of marine origin, while most of the Ca^{2+} was from crustal sources; and NO_3^- was predominantly anthropogenic, presumably from both local and long-range sources. In general, the results of this study suggested that cloud- and rain-water chemistry in northeastern Puerto Rico is strongly influenced by natural and marine sources rather than local anthropogenic sources. The pollutant species in the samples were mainly derived from long distance transport.

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1. Introduction

The atmosphere is an important pathway by which many gaseous and aerosol species are transported within and between regions. Clouds and precipitation play important roles in removing particles and dissolved gaseous pollutants from the atmosphere (e.g., Al-Khashman, 2005) and wet deposition is a potential source of nutrients in many ecosystems. In addition, precipitation and cloud water also scavenge sulfur dioxide (SO_2), nitrogen oxides (NO_x), and other atmospheric pollutants, which can affect the acidity and chemical composition of precipitation and clouds and in some cases can cause ecological damage to

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ecosystems (e.g., Driscoll et al., 2001; Al-Khashman, 2005; Migliavacca et al., 2005).

The chemical composition of rain- and cloud-water depends on the source constituents and the chemical reactions that occur during both local and long-range transport. Nitrogen oxides, SO_2 and other ions such as NH_4^+, Cl^-, Mg^{2+}, Ca^{2+}, K^+, and Na^+ are commonly present in the aqueous phase or precipitation. Some of these species (Cl^-, Mg^{2+}, Ca^{2+}, K^+, Na^+) originate from natural sources such as sea spray, soils and forest fires (Dordevic et al., 2005). Other species such as ammonium come from anthropogenic activities, including agricultural practices and biomass burning (e.g., Migliavacca et al., 2005). Ammonium, together with calcium, plays an important role in neutralization of acidity (Zunckel et al., 2003; Basak and Alagha, 2004).

The Luquillo Experimental Forest (LEF), which is also referred to as the El Yunque National Forest (EYNF), is a humid sub-tropical forest located in the higher elevations of the Luquillo Mountains of North East Puerto Rico (Fig. 1). The watersheds within this forested landscape drain eleven rivers, which are an essential source of water for the island. Here we discuss and compile data from other studies

(McDowell et al., 1990; Asbury et al., 1994; Gioda et al., 2008, 2009, 2011) performed, mainly at East Peak, and add new data from all sites to get a better interpretation of the results. Unlike previous papers, here was discuss only the major ions, pH and conductivity of cloud water sampled between 1984–1987 and 2004–2007, and rainwater collected from 1984 to 2007. Long-term monitoring is critically important to understanding the potential effects of atmospheric nutrient and pollutant inputs on ecosystems and are needed to develop control strategies and environmental protection (e.g., Driscoll et al., 2001; Weathers and Ponette-Gonzalez, 2011).

2. Methods

2.1. Sampling sites

The LEF is an 11,331 ha rainforest located in the upper elevations of the Luquillo Mountains in Puerto Rico, approximately 49 km from the San Juan metropolitan area and 10 km from the ocean. Elevation ranges from 100 to 1075 m above sea level (asl) and one of the highest and prominent peaks in the Luquillo Mountains is
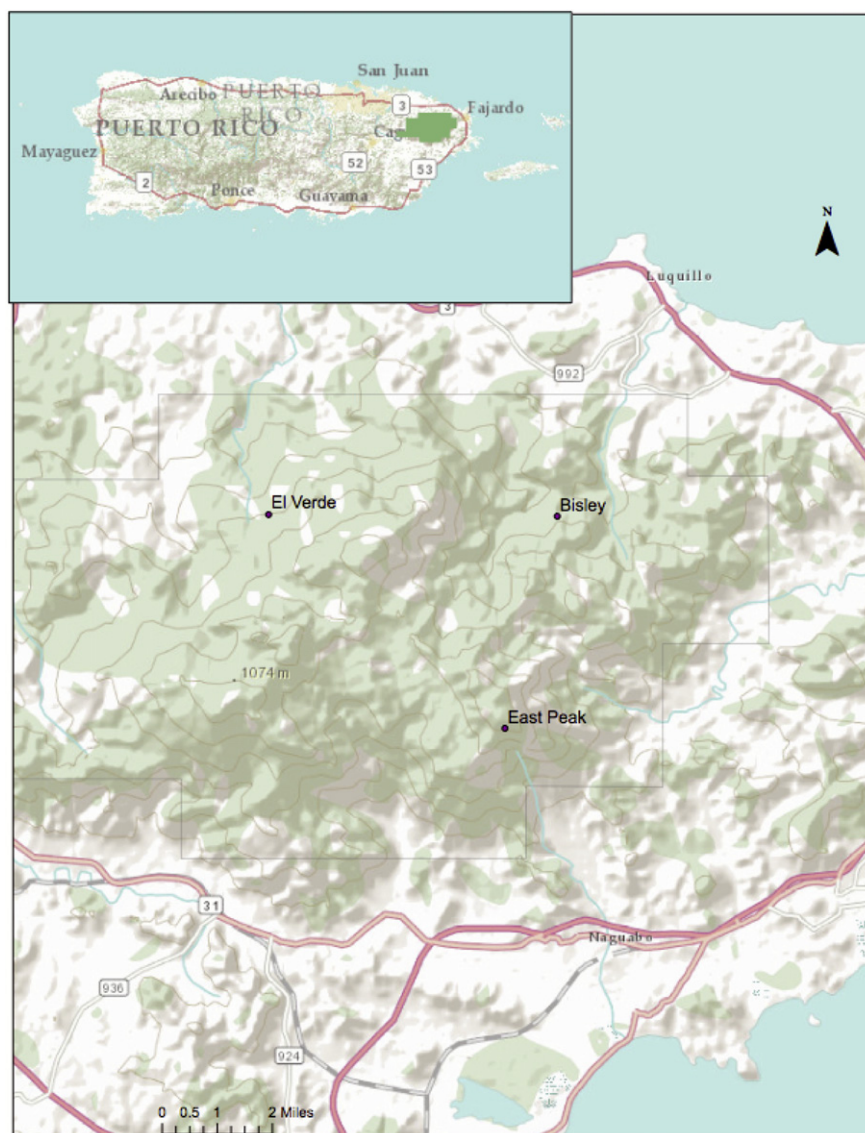
Fig. 1. Location of Luquillo Experiment Forest and the sampling sites Bisley, El Verde Field Station and East Peak, Puerto Rico. Figure provided by the Luquillo Critical Zone Observatory.

East Peak (Pico del Este − 1051 m asl). This study reviews and contrasts precipitation chemistry at the three sites within the Luquillo Experimental Forest where precipitation chemistry has been repeatedly measured over a series of years: East Peak (EP), El Verde Field Station (EVFS) and Bisley (Fig. 1).

East Peak station (18°16′ N, 65°45′ W, 1051 m asl) is a strategic point to study clouds, because they are present approximately 70% of the time (Brown et al., 1983). As observed in this study, on most days the clouds tend to disappear during the middle of the day and in the early afternoons (Eugster et al., 2006). The cloud droplet size spectrum at East Peak has a characteristic volume-weighted mean diameter of 12−13 μm during very dense clouds and 22−23 μm when dense to light clouds are present (Eugster et al., 2006). Cloud deposition rates at EP were estimated at 0.11 ± 0.05 mm h^{-1} for rain-free periods and 0.24 ± 0.13 mm h^{-1} for periods with rainfall (Holwerda et al., 2006). In this context, the estimated annual cloud deposition for the windy summit cloud forest is 770 mm year^{-1} and for the cloud forest on the lower windward slope was 785 mm year^{-1} (Holwerda et al., 2006). Earlier studies estimated that cloud water input contributed 7−10% of total precipitation in the Luquillo mountains overall (Weaver, 1972; Schellekens et al., 1998). Calculated and measured liquid water content (LWC) for all cloud experiments performed at EP ranged between 0.02 and 0.68 g m^{-3} and averaged 0.17 ± 0.13 g m^{-3} (Novakov and Penner, 1993; Asbury et al., 1994; Eugster et al., 2006; Allan et al., 2008; Reyes-Rodriguez et al., 2009; Gioda et al., 2011). Cloud- and rain-water samples on East Peak were collected from 1984 to 1987 (Weathers et al., 1988; Asbury et al., 1994) and again from 2004 to 2007 (Gioda et al., 2011). A total of 125 and 80 cloud-interceptions and rain-water events, respectively, were sampled during these two time periods.

The Bisley site (18° 20′N, 65° 50′W) is located in the wet forest zone at an elevation of 361 m asl. The EVFS (18°19′16.83″N, 65°49′10.13″W) is located 12 km to the west of Bisley and at 380 m asl. Both EVFS and Bisley sites are on the windward side of the island and vegetation is mature secondary growth of the Tabonuco forest type (Heartsill-Scalley et al., 2007). In Bisley, a total of 940-bulk rainwater samples were collected from 1988 to 2007 by the US Forest Service and the NSF supported Luquillo Long-Term Ecological Research program (LUQ LTER). At EVFS, a total of 1055 bulk rainwater samples were collected between 1984 and 2007.

The influence of local pollution at all the sites is probably minor since the prevailing trade winds at the sites come in from the Atlantic Ocean and there are no local upwind anthropogenic sources of pollution (McDowell et al., 1990). Active volcanism on the island of Montserrat, about 500 km south of PR, may occasionally impact precipitation chemistry (Heartsill-Scalley et al., 2007; Gioda et al., 2008). Convective storms, African dust, winter cold fronts, tropical storms, depressions, and hurricanes can also influence local precipitation patterns and the sources of air masses reaching the island (Heartsill-Scalley et al., 2007; Gioda et al., 2008; 2009).

2.2. Sampling and chemical analyses

At East Peak, cloud water samples (2004−2007) were collected with the compact aluminum version of the Caltech Active Strand Cloud water Collector (Al-CASCC2, Demoz et al., 1996) and bulk rainwater samples were collected using an amber glass bottle with a stainless steel funnel (Gioda et al., 2008). Other cloud water samples (before 2005) were collected using CWP active collector and rainwater in a standard Hubbard Brook type bulk collector described previously (Daube et al., 1987; Weathers et al., 1988; Asbury et al., 1994). The collectors were placed at a height of 2-m in a large open area (~ 300 m^2). Cloud- and rain-water samples at EP were collected on an event basis and the collectors were covered between events to avoid dry deposition. Prior to sample collection,

the collectors were rinsed thoroughly with Milli-Q water and blanks were collected. The samples were filtered (0.45 μm) and stored over ice during transport to the laboratory and then kept at 4 °C until analysis.

Precipitation was collected on a weekly basis at EVFS and Bisley using an HDPE funnel and bottle that collects bulk precipitation (http://luq.lternet.edu/data/luqmetadata174). The samples collected were filtered with pre-combusted Whatman GF/F glass fiber filters, held cool and analyzed at the University of Puerto Rico-Río Piedras campus from 1983 to 1994. After 1994, the samples were analyzed at the University of New Hampshire.

The ionic balance for each sample was checked as following: the samples were discarded when the ion difference was 15−30% for samples having total ion concentrations >100 μeq L^{-1}, and 30−60% for samples having total ion concentrations of 50−100 μeq L^{-1}, respectively.

Conductivity and pH were measured immediately after sampling in the field for both cloud and rainwater samples. Sample analysis for earlier studies has been described elsewhere (Weathers et al., 1988). Cloud- and rain-water samples collected from 2004 to 2007 in East Peak were analyzed by ion chromatography (IC) (Dionex ICS 1000, Dionex Co., USA) for Na$^+$, Ca^{2+}, K$^+$, and Mg^{2+}, NH$_4^+$, Cl$^-$, NO$_3^-$, and SO$_4^{2-}$ using a Dionex AS4A separator column and a micro-membrane suppressor. A gradient (H$_2$O; NaOH 5 mM; NaOH 100 mM) was used for the analysis of anions with a Dionex ION Pac® AS11 column. For the cations, a Dionex CS12A column with an eluent of 20 mM methanesulfonic acid was used. The detection limit for each ion was computed as twice the standard deviation of a blank average (Gioda et al., 2011). The samples collected at EVFS and Bisley through 1994 were analyzed for base cations (Na$^+$, Ca^{2+}, K$^+$, and Mg^{2+}) by flame atomic absorption spectrometry, NH$_4^+$, Cl$^-$, and NO$_3^-$ by colorimetry, and SO$_4^{2-}$ by ion chromatography. From 1994 on, both base cations and anions were measured by ion chromatography (http://luq.lternet.edu/data/luqmetadata174).

2.3. Meteorological data

Meteorological data were obtained from The Southeast Regional Climate Center (http://www.sercc.com/) and the Luq-LTER (http://luq.lternet.edu/) web sites.

2.4. Statistical analyses

Relationships among various ions present in cloud- and rain-water were evaluated by simple linear regression of the two sample types. Principal components analysis (PCA) was used to identify the sources of different constituents and understand the matrix complexity. Principal components analysis is generally applied to measurable variables; only a small number of dichotomous is accepted. Data were normalized prior to statistical analysis using a logarithmic transformation, which reduces heteroscadiscity (sp) and also improves the homogeneity of variance. Factorial rotation is the most important step in factor interpretations. Orthogonal rotation methods (Quartimax, Varimax and Equimax) and oblique rotation methods (Direct Oblimin, Promax, Orthoblique, Dquart and Doblimin) (Hair et al., 2009) can both be used for PCA. The former is preferred for its statistical simplicity and availability, which results in less complex and reliable components. In this study we chose the Varimax method, which is focused on column simplification. This approach results in high factor loadings (near +1 or −1) in some columns and low loadings in others (near 0). In this way, Varimax is analytically easier and more effective in separating factors than other methods (Quartimax, Equimax). Use of Varimax in this study reduced the number of columns of the matrix from 9 to 6, facilitating clearer interpretation of the results.

Moreover, this method minimizes the occurrence of high factor loadings related to variables in different factors. The software used for PCA was Statistica 7.0 (Statsoft) for Windows.

To check statistical similarity among the sample types, analysis of variance (ANOVA) and Tukey Test were applied. The adjusted p-value returned by Tukey Test was used (confidence level: 95%). ANOVA and Tukey Test were performed using R-Console (R, 2009).

All calculations were based on an equivalent basis (μeq L^{-1}). Sea salt (ss) and non-sea-salt (nss) fractions of ion concentrations were obtained for each sample using Na$^+$ as the sea-salt tracer (Wilson, 1975). To examine potential sources of elements, an enrichment factor (EF) was calculated by comparing the elemental ratio found in elements collected in precipitation to ratios for elements present in the Earth's crust and seawater (Lide, 2005). This study used Ca^{2+} as the reference element for soil and Na$^+$ as the reference element for marine sources (Zhang et al., 2007):

$$EF_{soil} = \left[X/Ca^{2+}\right]_{sample} \Big/ \left[X/Ca^{2+}\right]_{crust}$$

$$EF_{marine} = \left[X/Na^{+}\right]_{sample} \Big/ \left[X/Na^{+}\right]_{seawater}$$

where, X is the concentration of the ion of interest, X/Na^+ of seawater is the ratio from seawater composition (Keene et al., 1986) and X/Ca^{2+} of crust is the ratio from crustal composition (Taylor, 1964).

3. Results and discussion

3.1. Meteorological trends

Temperature, relative humidity, and precipitation were compared at the different sites (Table 1). On average EP was 5–6 °C cooler than the lower elevation sites. The highest annual mean temperatures for EVFS and Bisley were observed in 1998 (24.8–25.0 °C) and in 2003 at EP (19.8 °C). According to the World Meteorological Organization (WMO), global temperatures in 1998 were some of the warmest on record, together with 2005 and 2010.

Measured average precipitation from 1984 to 2007 in EVFS was 3544 mm (±881), East Peak was 4163 mm (±901), and Bisley was 3678 mm (±725) (Table 1 and Fig. 2). A low precipitation index was observed for all sites during periods of drought such as 1994 (3170 mm for EP, 1323 mm for EV, and 2678 mm in Bisley) (Fig. 2). The lowest average precipitation occurred in March for all sites (236 mm for EP, 196 mm for EV, and 171 mm for Bisley). According to previous studies, orographic rainfall contributes 29% of total rainfall in the Luquillo Mountains due primarily to easterly waves and low-pressure systems (Scholl et al., 2009). Due to orographic effects the largest precipitation totals generally occur on the highest peaks of the Luquillo Mountains. In general, precipitation increased at an average rate of approximately 140% per km elevation (Daly et al., 2003), which explains the differences in precipitation amount for EP, EVFS, and Bisley.

The EP average daily relative humidity is around 100% year round while for EVFS and Bisley the humidity ranged from 60 to 100%. Although all the sites are located in the LEF, the temperature, precipitation, and relative humidity trends were different due to the differences in altitude among the three locations (from 361 m asl to 1050 m asl). At the greater altitudes cooler temperatures prevail. Also, the proximity of EP to sea to land breeze contributes to make this location cooler than the others. The effects of hurricanes may also be significant for some periods. For example, at EVFS temperature was the highest in 1998 probably due to Hurricane Georges that caused deforestation around the sampling tower resulting in higher local air temperatures.

A weak correlation ($r \sim 0.2$) between precipitation (mm) and total ion concentrations (μeq L^{-1}) was observed. However, no other trends between meteorological data and the concentrations of species within precipitation were found.

3.2. pH and conductivity

The average conductivity values of cloud- and rain-water samples range from 21 to 74 μS cm^{-1} (Table 1). The conductivity reflects the total soluble ionic components. Cloud water samples had conductivities higher (13–250 μS cm^{-1}) than precipitation (1–185 μS cm^{-1}) due to dilution factors in the rain, i.e., cloud droplets have lower water content than rain droplets; therefore,

Table 1
Meteorological data, average inorganic ion concentrations, conductivity and pH for cloud water and bulk rainwater collected at El Verde Field Station, Bisley and East Peak stations during the period 1984–2007.

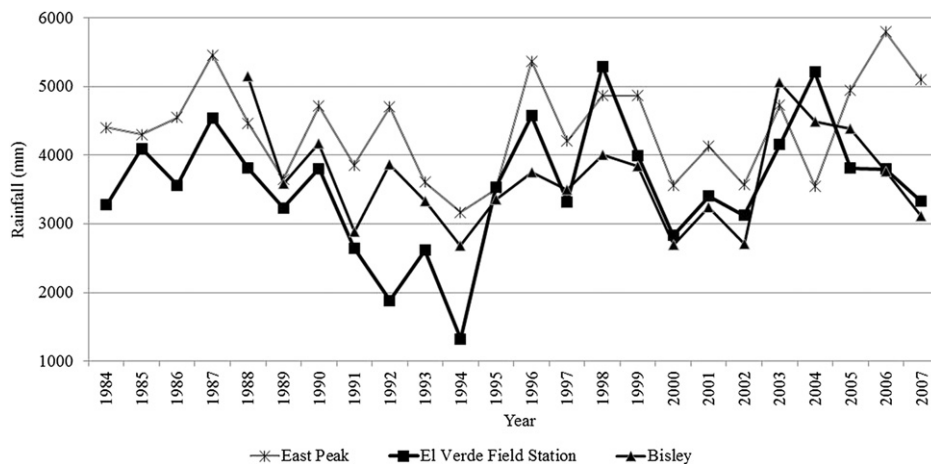|	Rainwater − El Verde Field Station		Rainwater − Bisley		Rainwater − East Peak		Cloud water − East Peak	
m asl	380		361		1051		1051	
Period	1984–2007		1988–2007		1984–1987 and 2004–2007		1984–1987 and 2004–2007	
N	1055		940		80		125	
	Mean ± Sdev	Range	Mean ± Sdev	Range	Mean ± Sdev	Range	Mean ± Sdev	Range
Annual Precipitation (mm)	3544 ± 881	1323–5294	3678 ± 725	2678–5147	4163 ± 901	3170–5793	–	–
Mean daily Temperature (°C)	23.6 ± 0.6	17.0–29.5	24.2 ± 0.5	17.4–33.1	18.6 ± 0.6	16–20	–	–
RH (%)	83.8 ± 2.2	64–100	78.5 ± 6.1	62–100	96.5 ± 0.6	90–100	–	–
Conductivity (uS cm^{-1})	15.3 ± 2.6	3.3–65	25.6 ± 18.6	1.1–185	29.8 ± 18.0	12–54	74.2 ± 41.4	13–250
pH	4.92 ± 0.58	4.7–5.7	4.98 ± 0.83	3.3–7.9	4.76 ± 0.71	3.2–7.0	4.35 ± 0.98	3.3–7.4
Ca^{2+} (μeq L^{-1})	22.4 ± 21.9	0.8–20	26.4 ± 26.8	5.0–310	39.1 ± 38.5	3.6–169	95.9 ± 95.0	7.5–320
Mg^{2+} (μeq L^{-1})	28.4 ± 28.6	2.4–49	34.9 ± 32.0	8.3–308	41.3 ± 57.5	11.0–425	107 ± 99	6.0–405
K$^+$ (μeq L^{-1})	4.72 ± 4.36	0.2–5.3	5.7 ± 6.3	2.6–93	11.8 ± 21.4	1.0–130	31.3 ± 40.8	0.3–144
Na$^+$ (μeq L^{-1})	101 ± 75	7.5–290	129 ± 99	9.6–773	158 ± 169	20–398	532 ± 435	52–1937
NH$_4^+$ (μeq L^{-1})	1.9 ± 1.8	0.5–10	1.6 ± 3.7	0.1–38	5.2 ± 6.7	0.6–42	24.5 ± 26.1	0.2–131
NO$_3^-$ (μeq L^{-1})	3.3 ± 4.6	0.1–27	1.6 ± 3.6	0.1–37	9.1 ± 6.9	0.5–32	44.0 ± 41.9	1.6–200
SO$_4^{2-}$ (μeq L^{-1})	29.4 ± 21.4	5.0–73	30.3 ± 30.0	19–669	43.1 ± 42.3	4.1–240	152 ± 130	22.0–730
Cl$^-$ (μeq L^{-1})	114 ± 89	8.5–321	144 ± 117	4.5–1331	172 ± 166	23–906	618 ± 613	68.0–3066
nss-SO$_4^{2-}$ (μeq L^{-1})	18.5 ± 19.5	3.5–27	19.4 ± 17.7	17.6–573	23.9 ± 28.9	1.7–149	101 ± 98	5.6–301
nss-Ca^{2+} (μeq L^{-1})	18.6 ± 21.2	0.1–13	21.2 ± 22.8	4.6–279	29.3 ± 31.3	0.1–136	74.0 ± 87.0	0.6–29

Fig. 2. Annual precipitation (mm) at East Peak (EP), El Verde Field Station (EVFS), and Bisley sites from 1984 to 2007.

the ionic concentrations were higher in cloud water. Average values (21 and 30 μS cm^{-1}) for rainwater samples for all sites were quite similar in ionic strength.

The average rainwater pH (based on average H$^+$ concentrations) was 4.92 ($\pm$0.58) at EVFS, 4.98 ($\pm$0.83) at Bisley, and 4.76 ($\pm$0.71) at EP. Cloud water pH at EP was 4.35 ($\pm$0.98) (Table 1). No statistically significant differences ($p > 0.05$) for mean pH (or H$^+$ concentrations) were observed between the sites.

The mean equivalent NO$_3^-$/SO$_4^{2-}$ ratios ranged from 0.1 to 0.3, suggesting that sulfate exerted a large average influence on acidity on both media across the study period for all sites. The NO$_3^-$ to SO$_4^{2-}$ ratio has been used as a site remoteness indicator (Weathers et al., 1988); the low NO$_3^-$ to SO$_4^{2-}$ ratio was consistent with its identification as a site comparatively remote from pollution sources. On the other hand, the [nss-Ca^{2+}]/[nss-Ca^{2+}]+[NH$_4^+$] ratios showed an average contribution of nss-Ca^{2+} from 75 to 90%, which suggests that the main neutralizing component in rainwater and cloud water is Ca^{2+} and its source is likely to be dust. During the summer months nss-Ca^{2+} contributed up to 95% of the neutralization and the pH values were higher in cloud- and rain-water (Fig. 3) than during other seasons. The high concentration of Ca^{2+} in the summer is probably due to African dust events, which are commonly observed in Puerto Rico from May to September (Gioda et al., 2007; Jiménez-Vélez et al., 2009). These particles are composed mainly of Fe, Al, Si and Ca, which are elements characteristic of soil (Gioda et al., 2008). The similar NO$_3^-$/SO$_4^{2-}$ and [nss-Ca^{2+}]/[nss-Ca^{2+}]+[NH$_4^+$] ratios for all samples indicate that the neutralization processes are the same in these sites, i.e., dominated by sulfate and nss-Ca^{2+}.

3.3. Chemical composition

Average maximum and minimum values obtained for inorganic ions in cloud- and rain-water collected in the LEF from 1984 to 2007 are shown in Table 1. The average concentrations for cloud water ranged from 25 μeq L^{-1} (NH$_4^+$) to 618 μeq L^{-1} (Cl$^-$); while for rainwater ranged from 2 μeq L^{-1} (NH$_4^+$) to 172 μeq L^{-1} (Cl$^-$) (Table 1). Concentrations of major ionic species in all samples were dominated by sea-salt (70%): Cl$^-$ > Na$^+$ > SO$_4^{2-}$ > Mg^{2+} (Fig. 4). Sea-salt also dominated the chemical concentrations of cloud water during a short campaign at EP using real-time measurements (Allan et al., 2008). These results are unsurprising due to the proximity of the site to the ocean and predominance of trade winds. The relative dominance of ions was quite similar among sites (Fig. 4).

The average value of the ratio between total anions to total cations ranged from 0.9 to 1.0 for all sites. In most studies of

precipitation chemistry an excess of cations relative to anions is generally found (e.g., Keene et al., 1983). There was not such a marked difference in this study.

The species present in cloud water were more concentrated than they were in rainwater, which was not unusual (e.g., Weathers, 1999). Comparing cloud- and rain-water from EP for the whole period, the species measured were on average 2–5 times higher in clouds than in rain. The species associated with long-range transport (nss-Ca^{2+}, nss-SO$_4^{2-}$, NO$_3^-$, NH$_4^+$) had higher concentrations. Concentrations were from 3 to 27 times higher in cloud water (EP) than in rainwater from EVFS and Bisley, with NO$_3^-$ and NH$_4^+$ showing the greatest relative enrichment. Previous studies in tropical forests, as well as other remote locations, also found greater concentrations in cloud water than in precipitation, varying from 2 to 126 times for H$^+$, NO$_3^-$, and NH$_4^+$ and between 5 and 50 times greater for Na$^+$ and Mg^{2+} (Weathers et al., 1988, 2000; Clark et al., 1998; Ponette-Gonzalez et al., 2010). Higher concentrations of species from long-range transport are expected at higher elevations, since more moisture and associated species travel at high altitudes and are intercepted by mountains where cloud and rain is deposited at higher rates (Stallard, 2001; Weathers and Ponette-Gonzalez, 2011). This explains why cloud- and rain-water from EP showed higher concentrations than EVFS and Bisley. Comparing the results with other studies, we can observe that the concentrations of NH$_4^+$ and NO$_3^-$ in cloud water in EP were 2–6 times lower than in a tropical site in Costa Rica. However, Ca^{2+} and Na$^+$ were 1.5–3 times higher (Clark et al., 1998). Thus, these Puerto Rican sites are influenced more by marine sources, and less by anthropogenic or terrestrial sources. For precipitation, the average concentrations of NH$_4^+$ and NO$_3^-$ were quite similar in Puerto Rico (2–5 μeq L^{-1} for NH$_4^+$ and 5–9 μeq L^{-1} for NO$_3^-$) and Costa Rica (3–9 μeq L^{-1} for NH$_4^+$ and 3–8 μeq L^{-1} for NO$_3^-$). Interestingly Na$^+$ and Ca^{2+} concentrations in Costa Rica and EVFS were similar, but 2–6 times lower than at EP.

As expected, the concentrations of all ions in cloud- and rain-water were statistically different ($p < 0.05$). For rainwater from Bisley, EVFS and EP there were differences for some species. The concentration values obtained for the dataset NO$_3^-$, K$^+$ and NH$_4^+$ were statistically different among all sites ($p < 0.05$). For other ions, the differences were for Cl$^-$, Na$^+$, Mg^{2+}, and Ca^{2+} (EVFS–Bisley), Cl$^-$, SO$_4^{2-}$, Ca^{2+} (EVFS–EP), and SO$_4^{2-}$ (Bisley–EP). The significant differences among concentrations for sites are probably a reflection of the different types of events such as sea-surface activity and the origin of air masses that reach the sampling sites. The elevation of the sites as well as the proximity to anthropogenic sources are other
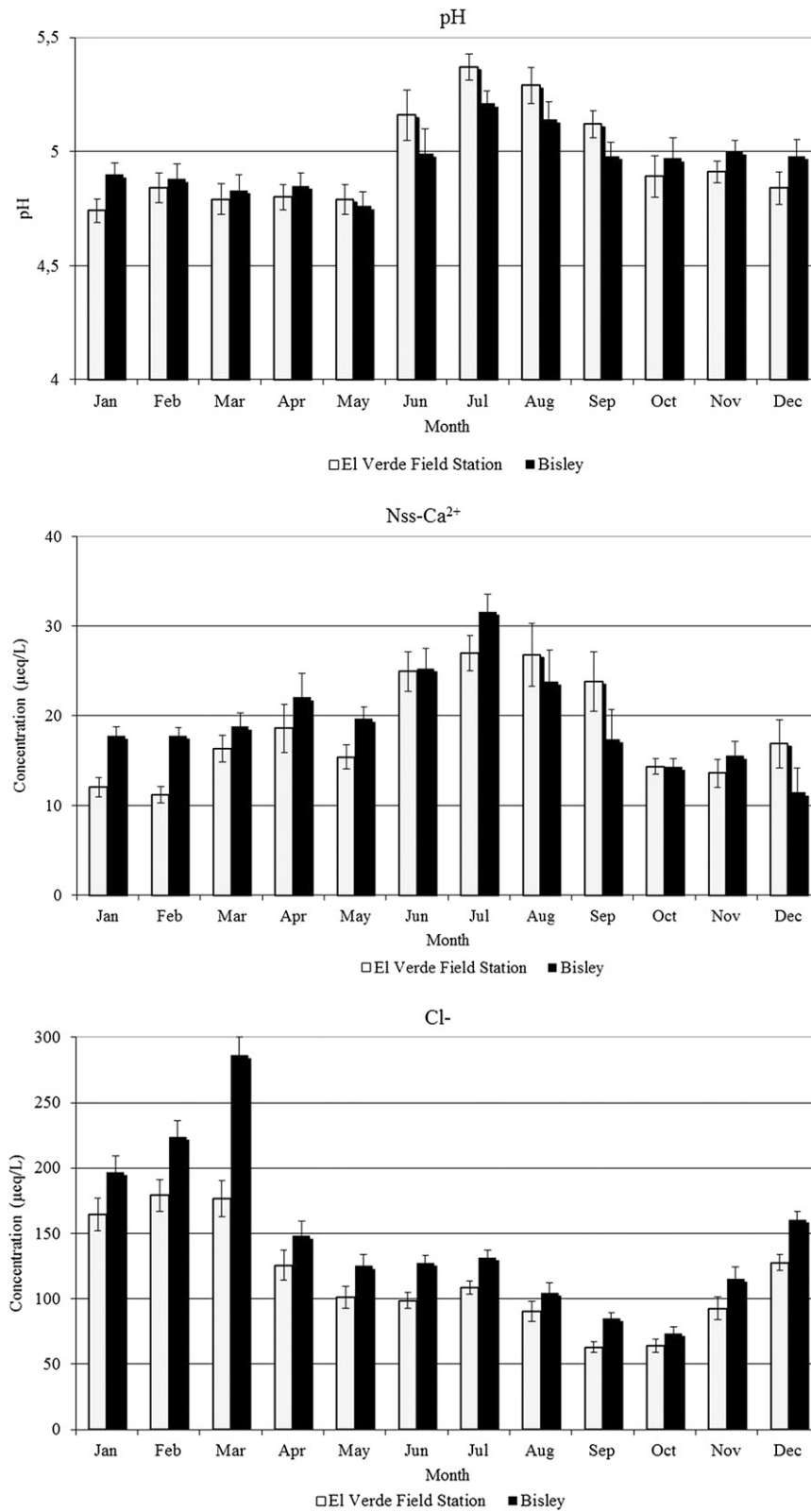
Fig. 3. Monthly average (standard error) of pH and ionic concentrations (μeq L^{-1}) for rainwater sampled at Bisley and EVFS from 1984 to 2007.

possible reasons for those differences. Increased urbanization upwind, deforestation, and periodic use of a backup electrical generator at EVFS could contribute to differences mainly in nitrogen compounds (e.g. NO_3^- and NH_4^+), which are present in the diesel emissions and fertilizers used by homeowners and agricultural operations (Fig. 3). Differences in collection methods (events vs weekly) might also have contributed to differences among the sites. Cloud- and rain-water samples collected at EP were on an event basis, but not all events in a given time period were sampled. In contrast, rainwater at EVFS and Bisley was collected weekly.
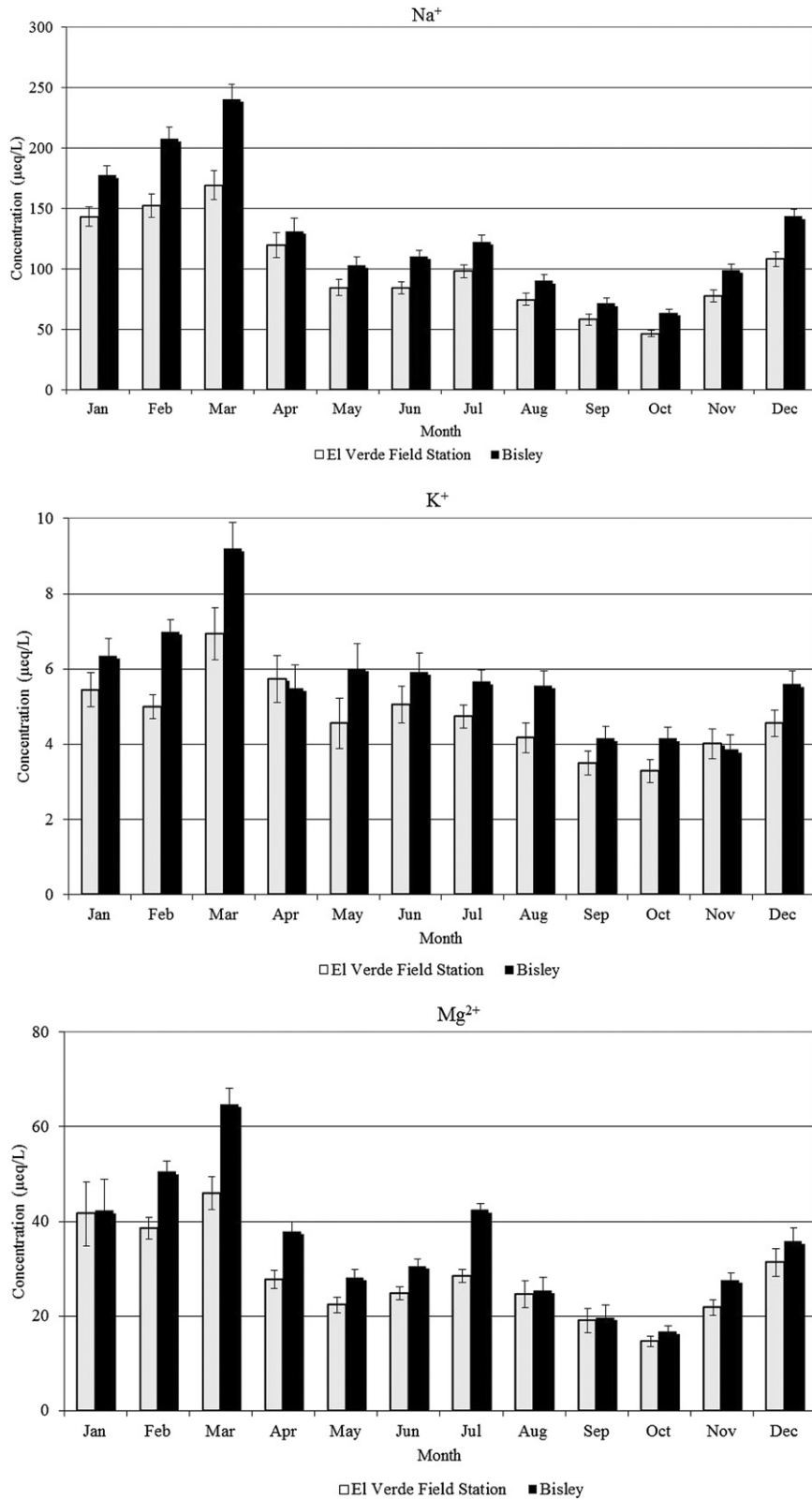
Fig. 3. (continued).

3.4. Seasonal variations

Seasonal variations in concentrations were found for some species. For summer (June to August) the highest concentrations of Ca^{2+} (nss-Ca^{2+}) and NO_3^- as well as the highest pH values were observed (Figs. 3 and 5). High concentrations of Ca^{2+} are related to incursions of African dust, which are frequent in summer. High concentrations of NO_3^- can also be associated with the dust and may
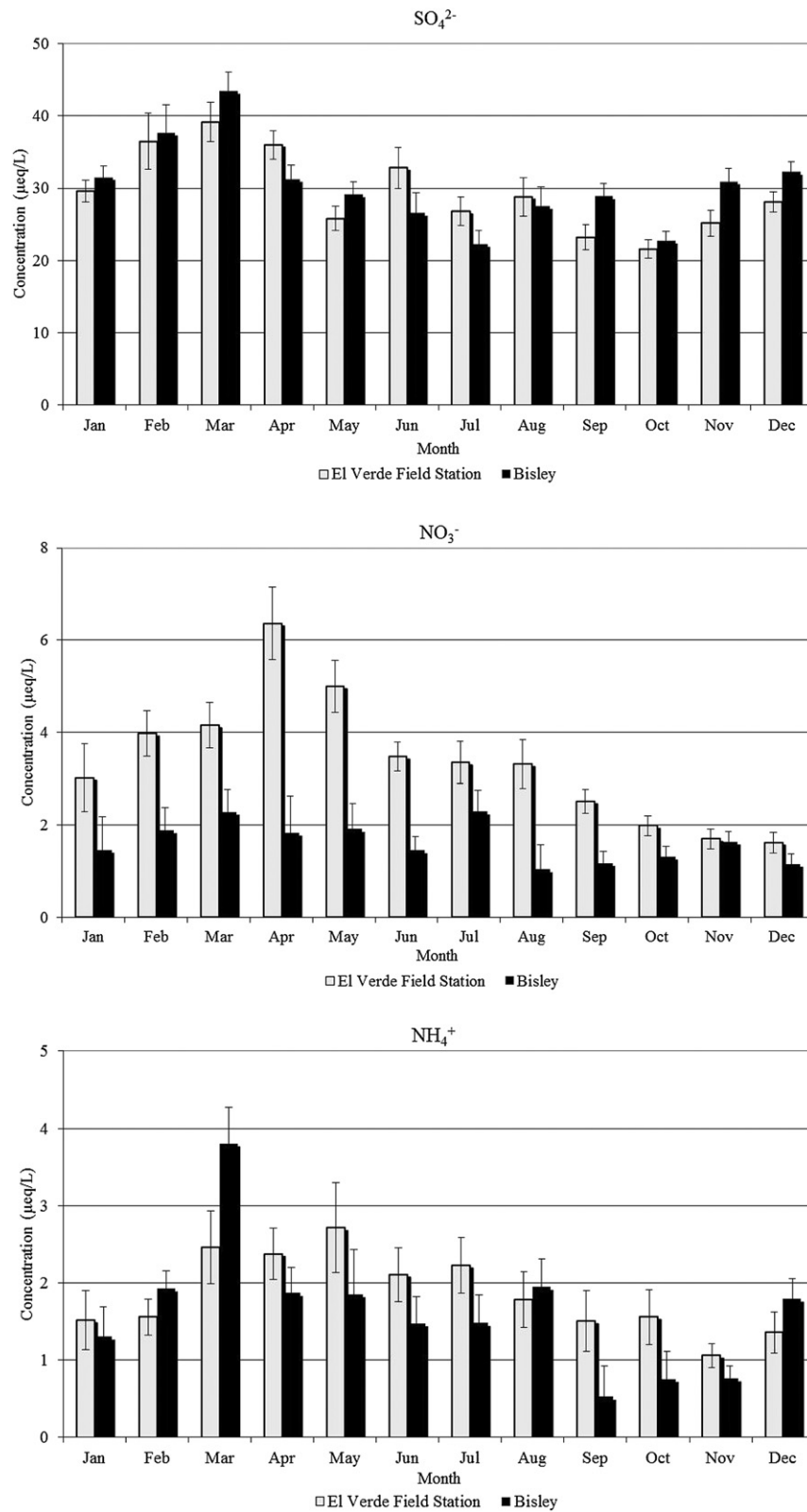
Fig. 3. (continued).

be linked to particles, since particles travel long distances and could trap this species from anthropogenic sources (Savoie et al., 1989). Although NO_3^- is elevated, it is in lower concentrations than nss-Ca^{2+} and insufficient to increase rainwater acidity, as pH was highest in summer. On the other hand, Na^+, Cl^-, Mg^{2+}, and SO_4^{2-} were slightly higher in winter (December to February), suggesting a small seasonal variation of different source strengths (Fig. 5). Sulfate was also detected in higher concentrations in the winter,
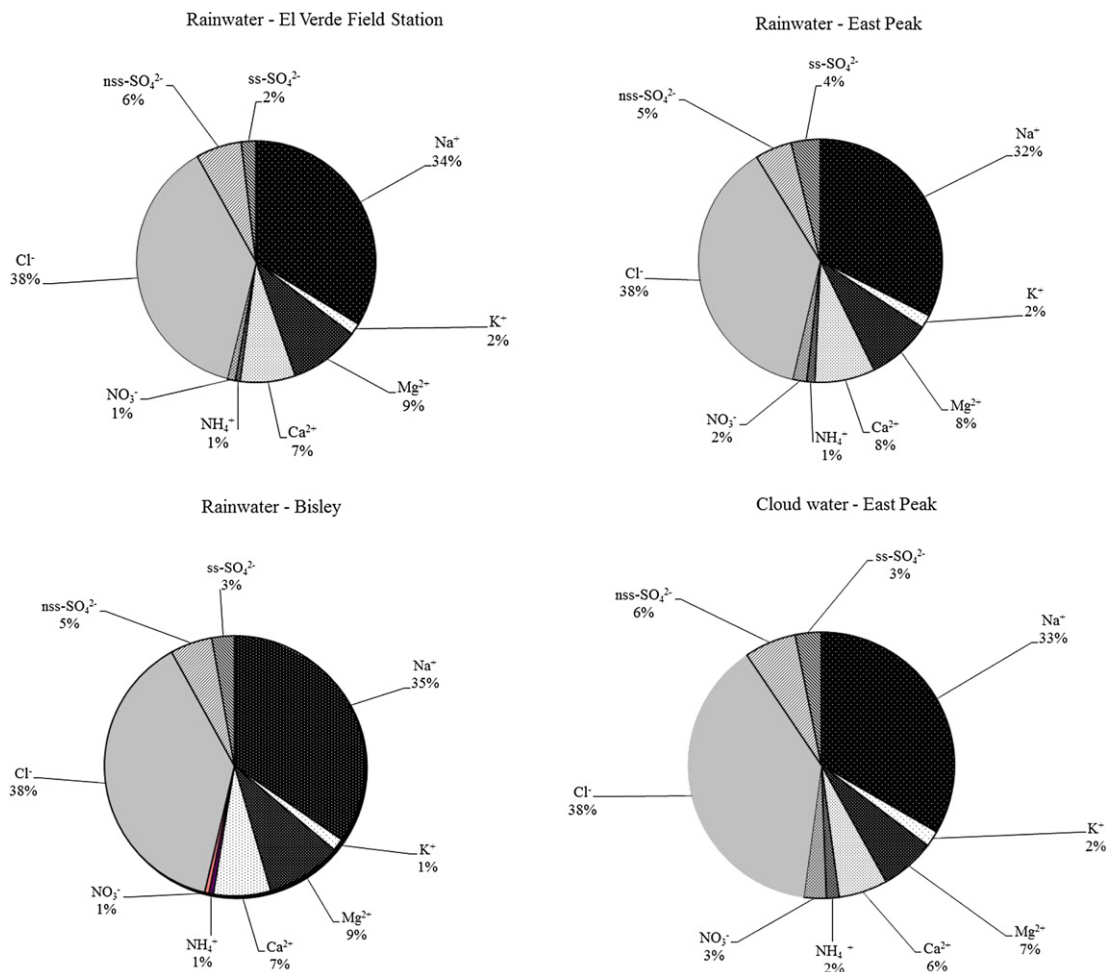
Rainwater - El Verde Field Station

Rainwater - East Peak

Rainwater - Bisley

Cloud water - East Peak

Fig. 4. Percentages of chemical composition of cloud- and rain-water at Luquillo Experimental Forest from 1984 to 2007.

when cold air masses from the North American continent arrive in the Caribbean region as reported by Gioda et al. (2009). These air masses are rich in anthropogenic compounds such as SO_2 and NO_3^- from industrial sources and fuel combustion. Changes in concentrations can be better observed through the monthly distribution of rainwater obtained in Bisley and EVFS (Fig. 3). Overall, concentrations are similarly distributed in both sites.

3.5. Trends

An analysis of annual average data showed both positive and negative trends over time. The behavior was similar between rainwater from EVFS and Bisley for many constituents. In those samples Na^+ and Cl^- did not show a trend over time ($r = -0.01-0.05$) while a slight decreasing trend was observed for K^+ and Mg^{2+} concentrations ($r = -0.2$ to -0.4). On the other hand, for cloud and rainwater samples from EP a moderate to strong decreasing trend was observed for these same ions (Na^+, Cl^-, K^+, and Mg^{2+}) ($r = -0.2$ to -0.8). A different behavior was observed for the other ions. For Bisley decreases in NO_3^-, nss-SO_4^{2-}, and NH_4^+ concentrations ($r = -0.4$ to -0.8) in rainwater were observed along the decades; while no trends were observed for nss-Ca^+ concentrations ($r = 0.05$). On the other hand, the trends for concentrations in EVFS rainwater were in the opposite direction, i.e., NO_3^-, nss-SO_4^{2-}, and NH_4^+ concentrations increased ($r = 0.3-0.5$) while nss-Ca^+ concentrations decreased ($r = -0.5$). Cloud water and rainwater from EP presented the same behavior as EVFS with moderate

decreases in these species ($r = -0.5$ to -0.7). Although the sites are located in the same region, they receive species in different ways and in different amounts.

Some special events such as hurricanes, droughts, and volcanic eruptions occurred during the sampling periods. However, these episodic events did not seem to impact overall rainwater chemistry trends. Three hurricanes did reach Puerto Rico during the sampling period: 1989 (Hugo); 1997 (Hortense); 1998 (Georges). All occurred in month of September and all had some impacts on the vegetation of the sites (Canham et al., 2010). Ash from Soufriere Hills volcano, located in Montserrat Island, sometimes reached Puerto Rico increasing the concentrations mainly of SO_4^{2-} and Cl^-, and also Ca^{2+} and NO_3^- (Gioda et al., 2011). In fact, an increase in K^+, Ca^{2+}, Mg^{2+}, Cl^-, and Na^+ was observed in throughfall during periods of volcanic activity (Heartsill-Scalley et al., 2007).

3.6. Sources

The geographical location of Puerto Rico is such that it receives marine as well as continental air masses from long-range transport during different seasons, including African dust fallout. Puerto Rico also has the influence of local sources such as traffic and land use. In this study, a correlation analysis, PCA, and EF were used to assess the pollutant sources in cloud- and rain-water.

The average EF values for marine sources ranged from 0.9 to 5.6 and for soil sources 0.4 to 2081 (Table 2) in cloud water, rainwater at EP, and rainwater at EVFS and Bisley. The EF values are in the
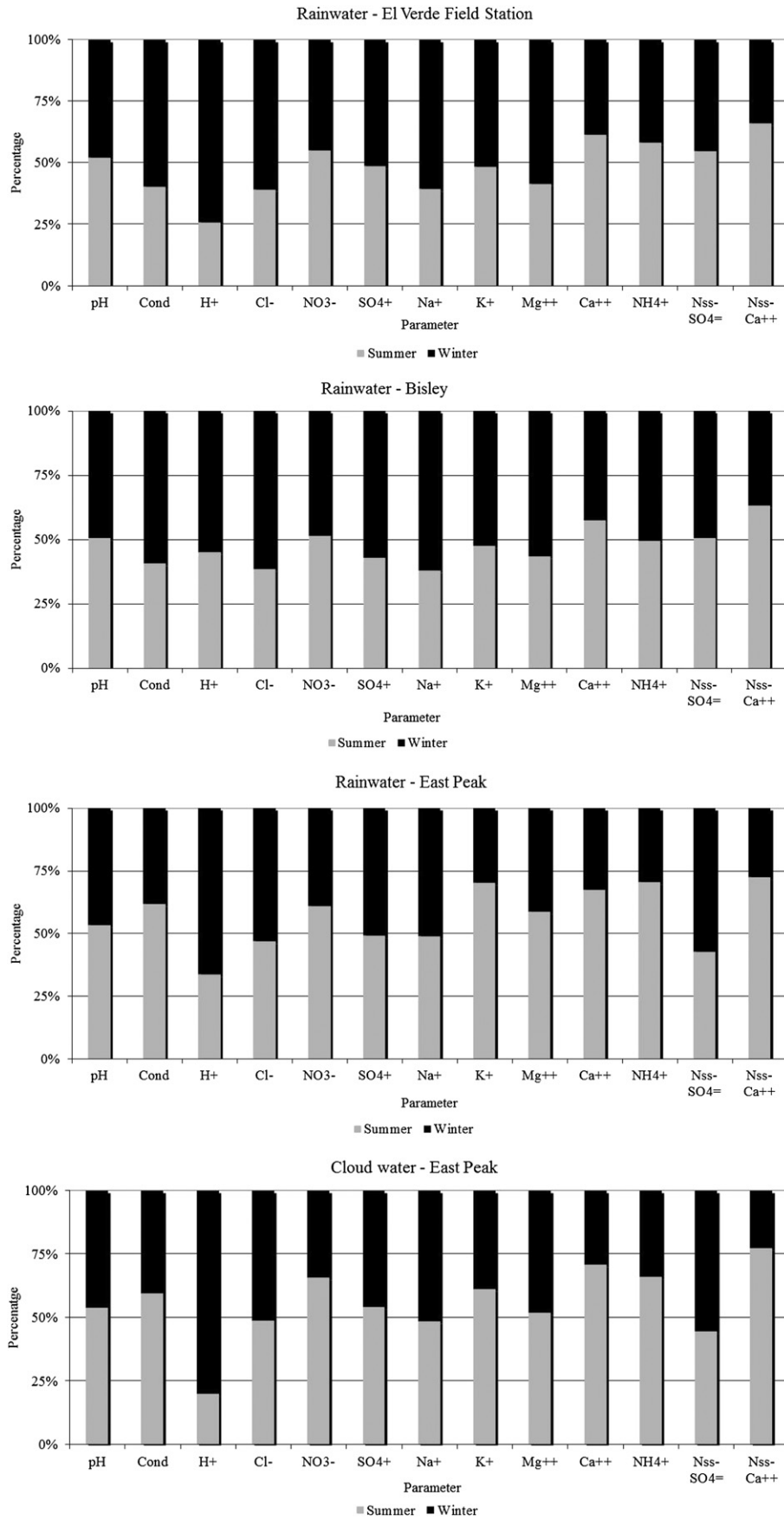
Fig. 5. Distribution of species during summer and winter.

Table 2
Enrichment factors for cloud- and rain-water components relative to soil or sea-salt origin.

	EF_{soil}						EF_{marine}				
	K^+	Na^+	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}
El Verde Field Station − rainwater	0.4	7.9	2.3	1645	70	71	2.1	5.0	1.2	1.0	2.3
Bisley − rainwater	0.4	8.6	2.4	1760	61	29	2.0	4.7	1.2	1.0	1.9
East Peak − rainwater	0.6	7.1	1.9	1413	59	111	3.4	5.6	1.2	0.9	2.2
East Peak − cloud water	0.6	9.8	2.0	2081	85	219	2.7	4.1	0.9	1.0	2.3

same order of magnitude for all samples, suggesting similarities among sources of each species. An EF value much less than 1, or much higher than 1 is considered to dilute or enrich relative to the reference source (Zhang et al., 2007). For example, Cl^- has an EF_{marine} value between 0.9 and 1.0, but has an EF_{soil} value that ranged from 1645 to 2081. Therefore, Cl^- can be considered a species from marine origin. The other ions had marine EFs near the unit; therefore, they came mostly from seawater. Strong correlations between Na^+ and other ions such as: Na^+ and Cl^- ($r = 0.8–0.9$); Na^+ and Mg^{2+} ($r = 0.8–0.9$); Na^+ and K^+ ($r = 0.5–0.8$); Na^+ and SO_4^{2-} ($r = 0.3–0.8$) also suggest a marine origin.
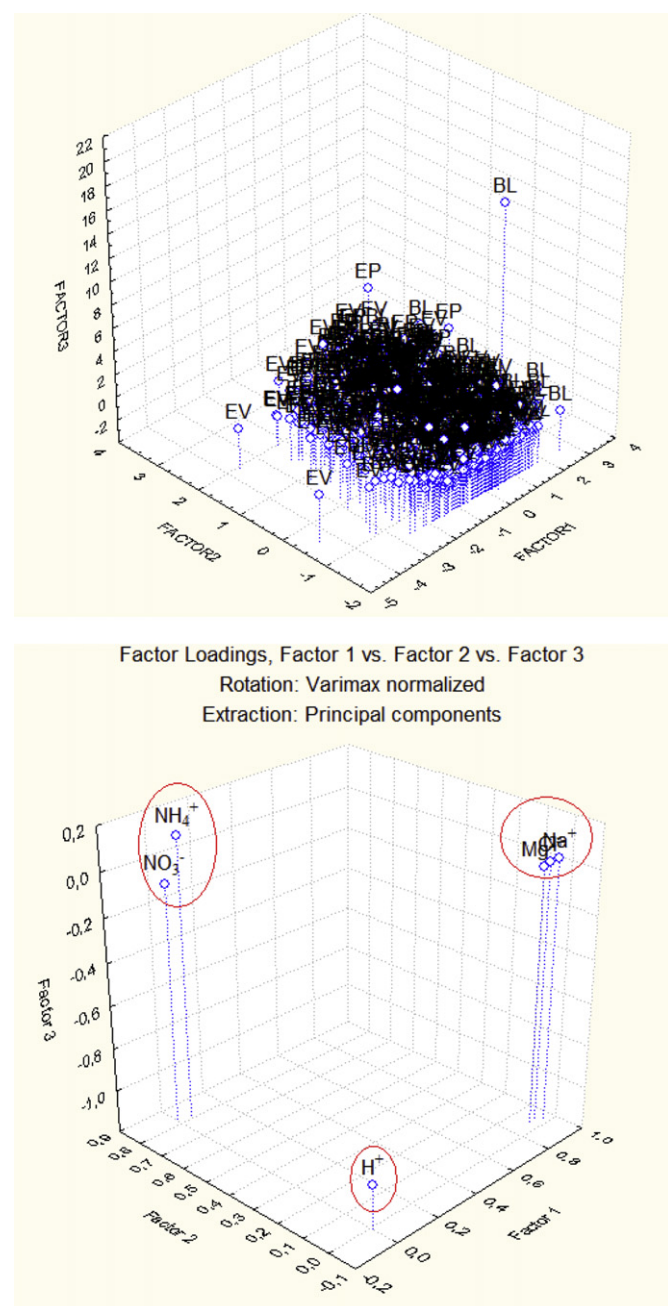
To estimate the approximate contribution of marine sources for each ion, the sea-salt fraction was calculated considering the $[X/Na^+]_{seawater}/[X/Na^+]_{rainwater}$ ratios for each species and multiplying by 100 to convert to percentage. From these calculations, about 100% of Cl^-, 83–110% of Mg^{2+}, 29–50% of K^+, and 18–25% of Ca^{2+} came from the sea. For SO_4^{2-}, about 50% came from the sea, 0.3–0.7% from soil and 49% from anthropogenic sources. On the other hand, just 0.1–0.3% of NO_3^- came from soil sources; therefore, the most important source for this species is anthropogenic. A moderate correlation was found between $nss-SO_4^{2-}$ and NO_3^- ($r = 0.5–0.6$) for all samples in the winter, but no correlations were found in the summer ($r = 0.1$). These correlations indicate that part of the SO_4^{2-} comes from sources similar to the NO_3^- that came from the emissions of their precursors SO_2 and NO_x. In the winter, cold fronts from the North American continent reach the island bringing pollutants, as originally suggested by McDowell et al. (1990).

Factor analysis was applied for all sites together and individually in order to evaluate the distribution of the rainwater samples. PCA resulted in three components (eigenvalue > 1), which explain 83% of rainwater data for Bisley, EVFS and EP (Table 3 and Fig. 6). Factor 1 showed significant loadings for Cl^-, Na^+, and Mg^{2+} that ranged from 0.90 to 0.96. About 44% of variance was explained by this factor, which is clearly related to marine aerosols. Factor 2, which reflects anthropogenic sources, had significant loadings, 0.82 and 0.83, for NH_4^+ and NO_3^- and explaining 22% of their variance. Factor 3 is related to acidity and had significant negative loadings (-0.99) for H^+ and contributed 17% of the total variance. Ammonium acts as a basic agent neutralizing HNO_3, then the differences between component 2 and 3 agree with the chemical reactions of this

species in the atmosphere. There was small dispersion of the rainwater samples through the three factors suggesting similar chemical composition in terms of species related with the factors (Fig. 6).

Factor Loadings, Factor 1 vs. Factor 2 vs. Factor 3
Rotation: Varimax normalized
Extraction: Principal components

Fig. 6. Dispersion of samples among the three factors and the three sampling sites (represented here as: BL = Bisley, EV = El Verde Field Station and EP = East Peak).

Table 3
Factor loadings obtained from chemical variables.

Chemical species	Component		
	1	2	3
H^+	0.01	−0.01	−0.99
Cl^-	0.93	0.04	0.00
NO_3^-	0.01	0.83	−0.09
Na^+	0.96	0.02	0.02
Mg^{2+}	0.90	0.04	−0.01
NH_4^+	0.06	0.82	0.10
Eigen value	2.63	1.34	1.01
Variance (%)	43.8	22.3	16.8

4. Conclusions

This study of cloud- and rain-water chemical composition was carried out at three sites in the Luquillo Experimental Forest in Puerto Rico from 1984 to 2007. The three sites are located at LEF, but have different aspects and elevation, resulting in some different characteristics. The highest precipitation index (mm year^{-1}), lowest temperatures, highest relative humidity and highest ionic content were obtained at EP. These characteristics are related to the height of the site (1051 m asl) and its high frequency of cloud cover. On the other hand, Bisley and EVFS are at a similar altitude (361 and 380 m asl) and presented some significant differences in the concentrations in rainwater, although they had similarities in precipitation levels, relative humidity, and temperature. Bisley had higher concentrations for most of the species in rainwater, with exception of NO_3^- and NH_4^+, compared to EVFS probably due to the different air masses that reach each site and the local sources. Similarities among all sites were observed in terms of the contribution of the different species to the total mass concentrations in the cloud- and rain-water.

The average pH of cloud- and rain-water ranged from 4.35 to 4.98, and was dominated by acidic species, mainly sulfate. The neutralizing agent in these samples appeared to be nss-Ca^{2+}, at higher concentrations during the summer months due to African dust incursions.

Ionic concentrations were higher in cloud than in rainwater due to dilution effects. Rainwater from EP had higher ionic concentrations than EVFS and Bisley, probably due to species from long-range transport that are more prevalent at higher elevations.

Both cloud water and rainwater at the site are strongly influenced by marine aerosols. This evidence is supported with the calculated EF and PCA that suggests that seawater was the main source of Na^+, Cl^-, and Mg^{2+}; while NO_3^- was basically anthropogenic.

Regarding trends in concentrations over time, Na^+ and Cl^- in rainwater from EVFS and Bisley did not showed temporal trends. There was a slight decrease in K^+ and Mg^{2+} concentrations. Rainwater from Bisley showed a decrease in NO_3^-, nss-SO_4^{2-}, and NH_4^+ concentrations while for EVFS rainwater the opposite was observed, i.e., an increase in NO_3^-, nss-SO_4^{2-}, and NH_4^+ concentrations. Apparently for cloud- and rain-water from EP a decrease in average concentrations was observed for most of the species measured (Na^+, Cl^-, K^+, and Mg^{2+}).

Cloud and precipitation chemistry are influenced by air masses from other continents (e.g. Africa and North America), which increase the concentrations of Ca^{2+}, NO_3^- and SO_4^{2-}. The long-range transport has made significant contributions to pollutants in the cloud and rainwater chemistry of the Luquillo Mountains in Puerto Rico.

Acknowledgments

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