Speciation of water-soluble inorganic, organic, and total nitrogen in a background marine environment: Cloud water, rainwater, and aerosol particles

Adriana Gioda,[1,2] Gabriel J. Reyes-Rodríguez,[1,3] Gilmarie Santos-Figueroa,[1,3] Jeffrey L. Collett Jr.,[4] Stefano Decesari,[5] Maria da Conceição K. V. Ramos,[6] Heleno J. C. Bezerra Netto,[6] Francisco R. de Aquino Neto,[6] and Olga L. Mayol-Bracero[1]

[1]   Cloud water, rainwater, and aerosol particles were collected in Puerto Rico from December 2004 to March 2007 in order to investigate their chemical composition, relation to sources, and removal processes. The species analyzed were inorganic ions, metals, total and dissolved organic carbon (TOC, DOC), total nitrogen (TN), and organic acids. For all samples, the dominant species were marine (Na^+, Cl^-), representing about 50%–65% of total content. Non-sea-salt fraction was dominated by SO_4^{2-} (17%–25%), followed by water-soluble organic (2%–8%) and total nitrogen (2%–6%) compounds. Organic acids represented contributions to the organic fraction in cloud water of 20% and 6% for aerosol particles. Inorganic species were predominant in total nitrogen portion. The chemical composition of cloud water, rainwater, and aerosol particles were observed to be sensitive to transport patterns. Air masses from northwest Africa showed the highest concentrations of nss-Ca^{2+}, Fe, and Al, suggesting a crustal origin. The pH values for cloud water and rainwater observed under this transport pattern were higher than background conditions, probably due to the alkalinity associated with nss-Ca^{2+}. The highest concentrations of Cl^- and SO_4^{2-}, with lower pH, were measured during periods of influence from Soufriere Hills volcano eruptions, most likely due to emitted SO_2 and HCl. Air masses from North America had an anthropogenic influence, where levels of nss-SO_4^{2-}, TOC, and TN were higher (~4 times) than in clean air masses. These results suggest that long-range transport could be an extra source of metals and organic/nitrogen species to the Caribbean region ecosystems.

1. Introduction

[2]   Since cloud processing and precipitation are important removal mechanisms for aerosol particles, the study of the chemical composition of aerosol particles, cloud water, and rainwater and associated aerosol scavenging efficiencies is essential to understand which compounds are more efficiently removed and which will stay longer in the atmosphere, influencing direct and indirect aerosol climate forcing.

[3]   The size and chemical composition of aerosol particles dictate their role in cloud formation. The water-soluble compounds present in aerosol particles play a central role in determining their cloud condensation nuclei (CCN) activity [*Saxena and Hildemann*, 1996]. Particles of sufficient size and water-soluble content are effective as CCN, and hence play a role in indirect radiative forcing [*Kulmala et al.*, 1996]. The water-soluble organic carbon (WSOC) fraction of the aerosol also constitutes an important fraction of the aerosol organic carbon due to its contribution to CCN activity [*Saxena and Hildemann*, 1996]. Composition data for this fraction is helpful for improving our understanding of the contribution of aerosols to atmospheric chemistry and climate. WSOC is often composed of a highly complex mixture of compounds covering a wide range of molecular structures,

[1]Institute for Tropical Ecosystem Studies, University of Puerto Rico, San Juan, Puerto Rico, USA.
[2]Now at Department of Chemistry, Pontifical Catholic University of Rio de Janeiro, Rio de Janeiro, Brazil.
[3]Department of Chemistry, University of Puerto Rico, San Juan, Puerto Rico, USA.
[4]Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado, USA.
[5]Institute of Atmospheric Sciences and Climate, CNR, Bologna, Italy.
[6]Institute of Chemistry, Federal University of Rio de Janeiro, LADETEC, Rio de Janeiro, Brazil.

physical properties and reactivities. Mono, dicarboxylic and keto-carboxylic acids and nitrogen-containing compounds, such as amines and amino acids, are all important species which can act as possible CCN [*Saxena and Hildemann*, 1996]. Among organic compounds, soluble organic nitrogen (ON) has received little attention, although its importance in precipitation and cloud water has been recognized [*Beem et al.*, 2010]. Based on their solubility and polarity, water-soluble organic nitrogen compounds could be important contributors to particle hygroscopicity and CCN activity.

[4] Significant amounts of pollutants brought from other continents to the Caribbean region have been reported [*Prospero and Nees*, 1986; *Savoie et al.*, 1989; *Jiménez-Vélez et al.*, 2009]. Previous studies in the Caribbean region showed an increase of sulfur compounds during periods under influence of anthropogenic air masses [*Savoie et al.*, 1989]. Sulfur plays an important role in cloud water and rain acidification and also in aerosol CCN activity, too [*Watanabe et al.*, 2001]. Mineral dust particles associated with outbreak storms in the African continent also reach the Caribbean area [*Prospero and Nees*, 1986; *Jiménez-Vélez et al.*, 2009]. These particles have been shown to be rich in $CaCO_3$ causing suppression of precipitation acidification [*Loÿe-Pilot et al.*, 1986]. Other elements such as iron, silicon, and aluminum are also present in significant concentrations in dust particles. Dust particle composition can also change due to reaction with gas phase compounds, especially acidic N and S gases [*Dentener et al.*, 1996]. Non-sea-salt sulfate (nss-SO_4^{2-}) and dust measured in aerosols in Barbados were highly correlated during African mineral dust episodes [*Li-Jones and Prospero*, 1998]. Mineral particles in dust samples were also shown to have an effect on the radiation balance. They contribute to neutralization of acidity and are a source of nutrients to ecosystems [*Loÿe-Pilot et al.*, 1986].

[5] Few studies on cloud water, rainwater, and aerosol particles have been performed in Puerto Rico, an important site in the Caribbean to collect background marine samples [*Weathers et al.*, 1988; *McDowell et al.*, 1990; *Novakov and Penner*, 1993; *Novakov et al.*, 1994; *Asbury et al.*, 1994; *Mayol-Bracero et al.*, 2001; *Allan et al.*, 2008]. Although these studies produced important information on ionic and organic species, none of them presented data on the organic and nitrogen fractions and metals, and in most of them long-range transport was discussed only briefly. Therefore, it was not clear if reported sample compositions were representative of the marine environment or included the influence of long-range transport from continental regions. Few studies have been done in remote marine areas and these are essential to determine the impact of anthropogenic pollution.

[6] The chemical compositions of cloud water, rainwater, and aerosol particles collected at marine background sites in Puerto Rico were studied in order to investigate the influence of air masses of different origin on the concentrations of water-soluble species and the removal processes. In this article we present a complete set of results from an extended period of monitoring (2004 to 2007) of cloud water, rainwater and aerosol particles samples associated with air masses of different origin. These results include organic nitrogen (ON) compounds, metals, organic acids (OA), free amino acids (FAA) and other soluble species that were not presented in our earlier papers [*Gioda et al.*, 2008, 2009].

These data provide a more complete profile of chemical composition for atmospheric liquid and particle phases in Puerto Rico.

2. Methodology

2.1. Sites

2.1.1. East Peak, Luquillo, Puerto Rico

[7] Experimental studies were carried out at East Peak (EP) station (18°16′N 65°45′W, 1051 m a.s.l.), in El Yunque National Forest (EYNF, Puerto Rico), an ecological reserve. East Peak is about 10 km from the Atlantic Ocean and 65 km from San Juan, the capital of the Island. The site is a strategic point for the study of warm cloud water, present around 70% of the year [*Brown et al.*, 1983]. The influence of local pollution on the site is very small since industries or other potential anthropogenic sources are minimal. The most important activity around the forest is the land use for agriculture. Moreover, the site typically receives the trade winds with clean air from the North Atlantic Ocean. Also, access to the site is restricted to authorized personnel, minimizing anthropogenic emissions during sampling periods. Therefore, the most important contribution to the chemical composition of aerosol particles and cloud/rainwater is from natural sources, such as marine bubbles and emissions from the forest. However, an anthropogenic contribution is unequivocal when air masses from North America or other Caribbean islands reach the site.

[8] Cloud water and rainwater sampling was performed between December 2004 and March 2007 during eight intensive campaigns. A total of 45 and 21 cloud interception and rainwater events, respectively, were sampled.

2.1.2. Cape San Juan, Fajardo, Puerto Rico

[9] Due to the high humidity at East Peak most parts of the day/year, it is very difficult to collect aerosol particles samples using stacked-filter units (SFUs). Therefore, aerosol particles were collected at the natural reserve of Cape San Juan (CSJ) (18.38°N, 65.62°W), which is located at the most northeastern part of PR and 20 km from EP. Because of the predominance of trade winds and the absence of significant landmasses with anthropogenic activity upwind, CSJ is well suited to study background marine aerosol particles. Anthropogenic influences are possible when air masses from other continents reach the site. In spite of its proximity to EP, few rain events occur during the year and no cloud events occur since CSJ is located at sea level. 24–48 h aerosol samples were collected at CSJ, with the times chosen to encompass sampling periods of cloud water/rainwater at East Peak. Cloud water samples were collected within the filter sampling intervals, with 1–3 cloud samples collected during each filter collection period. The average solute concentrations in cloud water (1 to 3 samples) were compared with aerosol concentrations collected during the overlapping time interval. A total of 16 aerosol sampling periods were included in the study containing a total of 26 cloud water sampling periods.

2.2. Meteorological Data and Back Trajectories

[10] Meteorological parameters were monitored at both stations including wind speed and direction, temperature, pressure, and relative humidity (RH). High relative humidity (~100%) was measured during sampling period at EP. The

annual value of rainfall was 4300 mm and average temperature was 18°C (maximum of 23°C and minimum of 14°C) for this site. Different conditions were measured for CSJ with lower rainfall (1500 mm annual) and relative humidity (75%) and higher temperatures, average of 26°C, with maximum of 32°C and minimum of 20°C. Trade winds with clean air masses from the North Atlantic (NE) are predominant during the year at both sampling sites, representing meteorological background conditions. In the winter/spring months, the stations frequently received air masses from the North American continent. During the summer, air masses from northern Africa reached the island, carrying mineral dust. Volcanic ash from the Soufriere's Hill volcano located at Montserrat Island, 500 km from Puerto Rico, also arrived at the site during the year. To study air mass origins we completed back trajectory analysis with the Hybrid Single-Particle Lagrangian Integrated Trajectories (HYSPLIT) computer model (D. Draxler and R. Rolph, Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, 2003, access via NOAA ARL READY Web site, http://www.arl.noaa.gov/ready/hysplit4.html). Five day backward trajectories (BTs) were calculated in order to reveal the history of the air masses arriving at the site. The Aerosol Index taken by the Ozone Monitoring Instrument (OMI) onboard NASA's Aura satellite (http://toms.gsfc.nasa.gov/aerosols/aerosols_v8.html) together with aerosol optical thickness (AOT) images from the Naval Research Laboratory (http://www.nrlmry.navy.mil/aerosol/satellite/noaa-aer/noaa-daily-images/) were used to determine the influence of African dust events and of ash plumes from the Soufriére's Hills volcano.

2.3. Sampling and Chemical Analyses

[11] Cloud water samples were collected at a mountain top location, typically located about 300 m above cloud base. The instrument used was the compact aluminum version of the Caltech Active Strand Cloud water Collector (Al-CASCC2) similar to the compact plastic CASCC2 described by *Demoz et al.* [1996]. The Al-CASCC2 is an active collector that uses a fan to draw drop-laden air across a bank of cylinders which serve as inertial impaction surfaces. The collection surface is 508 μm Teflon strands. The theoretical lower 50% size cut for this sampler is 3.5 μm (drop diameter). Rainwater (bulk water) was collected below cloud using an amber glass bottle with a stainless steel funnel. The collectors were placed at about 2 m height in a large open area (~300 m^2) with no nearby trees to avoid splash or throughfall contamination. The samplers were exposed just before an event and removed immediately after. Samples were collected only during the day, monitored by on-site personnel. Prior to sample collection, the collectors were rinsed thoroughly with Milli-Q water. Immediately after collection of each cloud/rainwater sample, a portion was filtered through a 0.45 μm Nuclepore polycarbonate membrane and split in aliquots. The unfiltered part of each sample was used to determine total organic carbon, pH and conductivity. Each aliquot was treated to stabilize reactive species. For trace metal analyses, concentrated HNO$_3$ was added to achieve a pH of <2. Aliquots for total and dissolved organic carbon (TOC and DOC) were preserved by addition of 0.1% H$_2$SO$_4$ (to achieve pH < 2) (U.S. EPA method 415.1). Carboxylic acids were preserved by addition of 0.4% CHCl$_3$. The samples and preserved aliquots were stored over ice during transport to the laboratory and then

kept at 4°C until analysis. The samples of cloud water and rainwater were directly analyzed without treatment, except as described above.

[12] Cloud liquid water content (LWC) was not measured directly but calculated from the cloud water collection rate according to the approach outlined by *Demoz et al.* [1996]. In this approach, CASCC2 collection rate is a function of the cloud LWC, the drop-size-dependent collection efficiency of an individual Teflon collection strand, an empirical drop size distribution (that varies with LWC), the air sampling rate of the CASCC2, and the fraction of air sampled as it crosses the 6 rows of CASCC2 Teflon strands. Separate (unpublished, 2010) comparisons of PVM LWC and cloud water collection rate by collectors in the CASCC family reveal a clear linear relationship and a strong correlation. Based on these comparisons we estimate the uncertainty in LWC calculated from cloud water collection rate at 20%.

[13] Data quality of individual cloud water and rainwater samples was checked by ionic balance. The samples were discarded when the ion difference in the samples was 15%–30% for samples having total ion concentrations > 100 μeq/L, and 30%–60% for samples having total ion concentrations of 50–100 μeq/L, respectively.

[14] Aerosol particles samples were collected using stacked-filter units (SFUs, NILU) with a flow of 50 L/min. The sampling design is as presented by *Mayol-Bracero et al.* [2002]. Here we describe it briefly. Two SFUs, each consisting of two polycarbonate 47 mm diameter serially connected filter holders, were used. A Nuclepore prefilter (PC membrane, Whatman, nominal pore size 8.0 μm) was placed in the first stage of each unit to collect the coarse particle fraction (D$_p$ > 1.7 μm). This filter collected the coarse fraction with particles larger than ca. 1.3 μm and smaller than 3 μm (50% size cut) aerodynamic diameter. In the second stage one unit had two quartz filters (tandem arrangement) and the other had a PTFE Teflon membrane filter (Zeflour Membrane filter, Pall Gelman nominal pore size 2.0 μm) to collect fine aerosol particles (D$_p$ < 1.7 μm). Sampling was performed for 24–48h. Aerosol particle samples from the fine fraction (second stage) were extracted with 3.2 mL Milli-Q water for 30 min with sonication for chemical analyses.

[15] Aerosol particles, cloud water, and rainwater samples were analyzed for soluble inorganic ions (NO$_2^-$, NO$_3^-$, Cl$^-$, SO$_4^{2-}$, Br$^-$, PO$_4^{3-}$, NH$_4^+$, Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}), metals (Al, Fe, Mn), TOC, DOC and TN. A few samples were analyzed for organic acids (acetate, formate, oxalate and methanesulfonic acid (MSA)) and for 17 amino acids.

[16] TOC, DOC and TN concentrations were determined using a TOC analyzer (Shimadzu 5500 with total nitrogen module, Kyoto, Japan). TOC standards were prepared from reagent grade potassium hydrogen phthalate and TN standards from potassium nitrate in Milli-Q water. The coefficient of variation of triplicate injections was always < 2%. The limit of detection was based on three times the standard deviation of blanks (0.06 mg/L of C and 0.08 mg/L of N).

[17] Inorganic ions and organic acids were determined by ion chromatography (IC) (Dionex ICS 1000, Dionex Co., United States) with a Dionex AS4A separator column and a micromembrane 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 a blank average plus twice the blank standard deviation (i.e., 0.30 mg/L for Na^+, Cl^-, and SO_4^{2-}; and 0.01 mg/L for NO_3^-, NH_4^+, Ca^{2+}, Mg^{2+}, and K^+). For both cations and anions, a calibration check with external standards was performed to assure accuracy of ±5%.

[18] Soluble forms of trace metals were determined by Inductive Coupled Plasma (ICP Model Ciros CCD, SPECTRO Analytical Instruments, Germany). All concentrations were checked against quality controls. Accuracy for most analyses was evaluated by running every fourteenth sample against standards of known chemical composition obtained from the National Institutes of Standards and Technology, United States. The coefficient of variation for this comparison was less than 5% and the precision was at least 2%. The limit of detection was based on three times the standard deviation of blanks.

[19] Seventeen free amino acids (FAA) were analyzed by a modified patented method [Hušek, 1999] in which the solution of amino acids was loaded onto a cation bed. The detailed procedure has been described elsewhere [Nozal et al., 2004]. Briefly, the bed was washed with aqueous organic solvent, which displaced the captured amino acids with a medium containing aqueous sodium chloride/hydroxide, alkanol with 1–4 carbon atoms and a pyridine type base. The displaced amino acids were treated directly in the eluate with an alkyl chloroformate of 1 to 4 carbon atoms in the alkali moiety and, after transferring the derivatized compounds into an organic solvent immiscible with water, an aliquot was injected for analysis by gas chromatography. Standards at a concentration of 200 mmol/L and reagents were supplied in the kit of reagents "EZ:faast GC–FID for free amino acid analysis" by Phenomenex (Torrance, California, United States). An HP6890 gas chromatograph equipped with flame ionization detector, (Hewlett-Packard, Avondale, Pennsylvania, United States) and 10m x 0.25mm ZB-PAAC column (Phenomenex- Torrance, California, United States) were used. The carrier gas (H_2) flow rate was kept constant during the run at 1.3 mL/min. The oven temperature program was as follows: initial temperature 110°C, a 32°C/min ramp to 320°C, held for 1 min.

[20] Field blank samples, obtained by spraying the collectors with Milli-Q water, and blank filters yielded low values for all species and the average was subtracted from measured sample concentrations. To determine non-sea-salt (nss), Na^+ was used as the reference species for marine origin [Wilson, 1975]. Non-sea-salt concentrations were calculated for a given species (X) using the following equation:

$$\text{nss-X} = [X] - ([Na^+] \times X/Na^+ \text{ ratio in seawater})$$

where [X] and [Na^+] are the concentrations of the species in the samples.

3. Results and Discussion

3.1. Chemical Composition

[21] The measurements at the mountain station allowed us compare water-soluble species concentrations in cloud water and rainwater samples (Table 1). To improve understanding of the mechanisms affecting cloud water and aerosol particles, measurements of aerosol particles were made across the cloud sampling period, but at CSJ (a site about 20 km upwind

of our cloud water/rain sampler). No rainwater samples were obtained at this time at CSJ. Cloud water samples were evaluated as a function of the measured cloud water composition and liquid water content (LWC). Multiplying the aqueous cloud water concentration of a solute by the cloud LWC yields the concentration of that solute in cloud water per unit volume of air. This concentration can be directly compared to upwind aerosol particle concentrations of the same species. Calculated LWC ranged from 0.07 to 0.68 g/m^3, with an average of 0.17 (±0.13) g/m^3 (Table 2). These values are similar to LWC values measured at EP in previous studies (0.11–0.50 g/m^3) [Novakov and Penner, 1993; Allan et al., 2008; Gioda et al., 2009]. LWC can also help evaluate each species concentrations in the liquid phase. Concentrations can vary inversely to LWC, due to changes in dilution. In this study we observed a moderate inverse correlation (r = −0.4–0.5) for some species (TOC, TN, NH_4^+, NO_3^- and SO_4^{2-}) but no correlations (r ~ −0.1) for others (Na^+, Cl^-, K^+, Mg^{2+} and Ca^{2+}). The same behavior was observed for concentrations and volume in rainwater samples. Weak correlations between solutes and LWC can be related to changes in aerosol activation in clouds of different LWC/supersaturation and contributions from uptake of soluble gases.

[22] Sea salt (Na^+ and Cl^-) and SO_4^{2-} were the dominant species in aerosol particles, cloud water and rainwater, as expected for a marine region (Tables 1 and 2 and Figures 1 to 3). Overall, these species accounted for 50%–65% (Na^+ and Cl^-) and 17%–25% (SO_4^{2-}) of the total measured solute content. The average (std. dev.) concentrations for Na^+, Cl^- and SO_4^{2-} in cloud water were 418 (±288) μeq/L, 433 (±289) μeq/L, and 83 (±57) μeq/L, respectively (Table 1). In a previous study performed at EP, cloud water samples also presented Na^+ (average of 397 μeq/L), Cl^- (384 μeq/L) and SO_4^{2-} (181 μeq/L) as major species [Asbury et al., 1994]. In other studies recently performed at East Peak the same major ions were observed [Allan et al., 2008; Reyes-Rodríguez et al., 2009]. The sea-salt concentrations were similar among studies, however, SO_4^{2-} concentrations were higher in the Asbury study. Probably this increase occurred because more events with anthropogenic air masses reached the site during sampling periods. Increased SO_4^{2-} concentrations under the influence of air masses from the African continent were reported by Reyes-Rodríguez et al. [2009]. In that experiment, the SO_4^{2-} concentrations increased from 68 to 156 μeq/L, with an input of 68 mg/L of nss-SO_4^{2-}. For rainwater the average concentrations were lower than in cloud water by a factor of three: Na^+ (114 ± 56 μeq/L), Cl^- (113 ± 52 μeq/L), $SO_4^=$ (24 ± 17 μeq/L) (Table 1). The same major ions, but in lower average concentrations for bulk rainwater, were observed in previous studies at EP, i.e., Na^+ (71 μeq/L), Cl^- (88 μeq/L), and $SO_4^=$ (31 μeq/L) [McDowell et al., 1990]. In aerosol particles the average amounts of these species were 209 (±94) ng/m^3 for Na^+, 292 (±180) ng/m^3 for Cl^-, and 249 (±100) ng/m^3 for $SO_4^=$ (Table 2). Observed aerosol $SO_4^=$ concentrations were lower than obtained in other studies performed at CSJ, 270 to 840 ng/m^3 [Novakov et al., 1994; Allan et al., 2008]. However, in cloud water at EP these sources measured concentrations from 960 to 1200 ng/m^3, similar to this study (632 to 1200 ng/m^3). As sulfate also comes from anthropogenic sources their concentrations in the samples are likely related to the extent of anthropogenically influenced events during the study period.

Table 1. Concentrations, pH, and Cation/Anion Ratios for Cloud Water and Rainwater Obtained at East Peak[a]

Cloud Water	pH	Cation/Anion	TOC	DOC	TN	ON	H^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	Ace	For	MSA	Oxa
Background (n = 18)																			
Ave (Stdev)	5.8 (±0.5)	1.1 (±0.1)	0.7 (±0.5)	0.5 (±0.4)	0.4 (±0.2)	0.12 (±0.09)	1.5 (±0.5)	532 (±385)	30 (±39)	89 (±78)	60 (±40)	5.8 (±3.5)	473 (±364)	16 (±14)	54 (±18)	3.8 (±2.7)	3.0 (±2.0)	1.0 (±0.5)	1.4 (±0.7)
Anthropogenic (n = 16)																			
Ave (Stdev)	4.5 (±0.4)	0.9 (±0.1)	1.3 (±0.5)	1.0 (±0.5)	1.0 (±0.5)	0.24 (±0.11)	3.9 (±0.5)	370 (±204)	20 (±19)	68 (±44)	23 (±10)	24 (±23)	388 (±243)	40 (±27)	89 (±53)	11.6 (±9.5)	2.0 (±0.5)	4.4 (±2.5)	7.4 (±5.5)
African dust (n = 9)																			
Ave (Stdev)	6.3 (±0.5)	1.2 (±0.1)	1.2 (±0.5)	0.9 (±0.5)	1.5 (±0.6)	0.26 (±0.11)	0.5 (±0.3)	373 (±205)	34 (±25)	129 (±99)	153 (±59)	36 (±40)	476 (±309)	43 (±15)	126 (±41)	5.2 (±3.5)	0.8 (±0.5)	1.2 (±0.5)	0.6 (±0.5)
Volcanic ash (n = 2)																			
Ave (Stdev)	3.5 (±0.2)	0.4 (±0.1)	1.0 (±0.1)	0.7 (±0.2)	1.7 (±0.3)	0.13 (±0.03)	21.9 (±0.5)	203 (±41)	5.4 (±3.5)	61 (±21)	73 (±28)	38 (±20)	652 (±252)	76 (±30)	325 (±150)	18.1 (±5.5)	0.2 (±0.1)	1.8 (±0.5)	0.00
OVERALL (n = 45)																			
Ave (Stdev)	5.5 (±1.0)	1.1 (±0.2)	0.9 (±0.6)	0.7 (±0.4)	0.9 (±0.5)	0.18 (±0.11)	3.4 (±0.8)	418 (±288)	28 (±19)	88 (±71)	69 (±80)	20 (±15)	433 (±289)	29 (±22)	83 (±57)	5.4 (±3.5)	1.0 (±0.5)	2.1 (±1.5)	1.0 (±0.8)

Rainwater	pH	Cation/anion	TOC	DOC	TN	ON	H^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	Ace (n = 1)	For (n = 1)	MSA (n = 1)	Oxa (n = 1)
Background (n = 7)																			
Ave (Stdev)	5.1 (±0.6)	1.1 (±0.1)	0.4 (±0.3)	0.3 (±0.1)	0.2 (±0.1)	0.09 (±0.05)	8.1 (±0.5)	134 (±65)	6.2 (±5.5)	12.9 (±9.5)	13.9 (±8.1)	3.9 (±1.8)	129 (±55)	2.8 (±2.5)	20 (±9)	2.6	0.4	0.49	0.0
Anthropogenic (n = 7)																			
Ave (Stdev)	4.9 (±0.6)	1.0 (±0.1)	1.0 (±0.7)	0.6 (±0.2)	0.4 (±0.2)	0.20 (±0.10)	12.6 (±0.6)	135 (±100)	1.5 (±0.2)	17.4 (±6.2)	4.1 (±0.7)	7.0 (±3.0)	133 (±82)	7.7 (±5.6)	29 (±23)	7.1	0.0	0.36	0.0
African dust (n = 5)																			
Ave (Stdev)	6.2 (±0.6)	1.3 (±0.1)	1.0 (±0.6)	0.8 (±0.6)	0.6 (±0.2)	0.11 (±0.03)	0.6 (±0.6)	106 (±36)	17.9 (±5.6)	8.7 (±5.0)	32.1 (±9.4)	0.7 (±0.3)	97 (±32)	5.7 (±2.4)	22 (±8)	9.5	0.0	0.00	0.0
Volcanic ash (n = 2)																			
Ave (Stdev)	4.1 (±2.6)	0.5 (±0.1)	0.6 (±0.2)	0.5 (±0.1)	0.3 (±0.1)	0.09 (±0.03)	83.2 (±66)	75 (±43)	3.4 (±1.6)	18.4 (±12)	21 (±16)	6.4 (±3.2)	165 (±62)	16.2 (±5.1)	75 (±26)	4.0	0.6	0.65	0.0
OVERALL (n = 21)																			
Ave (Stdev)	5.3 (±0.8)	0.9 (±0.2)	0.5 (±0.1)	0.4 (±0.1)	0.2 (±0.1)	0.10 (±0.03)	5.0 (±0.6)	114 (±56)	7.2 (±6.6)	12.3 (±6.7)	14 (±11)	3.7 (±2.6)	113 (±52)	5.4 (±4.1)	24 (±17)	5.8 (±3.1)	0.2 (±0.2)	0.38 (±0.3)	0.0

[a]TOC, DOC, TN and ON in mg/L. Other species in μeq/L.

Table 2. Aerosol Particles and Cloud Water Species Concentrations Per Unit Volume of Air[a]

Period	LWC (g/m³) CW	WSOC (A)	TOC (CW)	Na⁺ A	Na⁺ CW	K⁺ A	K⁺ CW	Mg²⁺ A	Mg²⁺ CW	Ca²⁺ A	Ca²⁺ CW
Background A(n = 4) CW(n = 8)	0.20 (±0.16)	74 (±12)	144 (±89)	346 (±55)	2202 (±1604)	18.3 (±4.4)	214 (±167)	43.9 (±6.8)	188 (±170)	30.4 (±6.9)	134 (±71)
Anthropogenic A(n = 3) CW(n = 9)	0.10 (±0.01)	105 (±25)	264 (±120)	244 (±124)	1701 (±938)	11.9 (±4.3)	163 (±95)	31.1 (±15.1)	163 (±106)	16.5 (±5.2)	94 (±42)
African dust A(n = 9) CW(n = 9)	0.22 (±0.12)	59 (±12)	232 (±108)	168 (±25)	1718 (±946)	12.6 (±4.1)	266 (±199)	24.8 (±3.7)	311 (±240)	41 (±22)	613 (±239)
Overall A(n = 16) CW(n = 26)	0.17 (±0.13)	81 (±18)	187 (±122)	209 (±94)	1586 (±1364)	11.8 (±4.8)	185 (±136)	27.8 (±11.1)	139 (±78)	25 (±17)	111 (±98)
Efficiency			2.3		7.6		15		4.9		4.5

Period	NH₄⁺ A	NH₄⁺ CW	Cl⁻ A	Cl⁻ CW	NO₃⁻ A	NO₃⁻ CW	SO₄²⁻ A	SO₄²⁻ CW	Ace A	Ace CW	For A	For CW	MSA A	MSA CW	Oxa A	Oxa CW
Background A(n = 4) CW(n = 8)	21 (±9)	43 (±36)	393 (±283)	3245 (±2356)	235 (±203)		186 (±57)	632 (±446)	2.8 (±1.4)	45 (±38)	1.5 (±0.2)	14 (±8)	3.5 (±0.3)	13 (±6)	4.2 (±2.4)	12.2 (±8.8)
Anthropogenic A(n = 3) CW(n = 9)	43 (±32)	88 (±93)	377 (±209)	2758 (±1726)	493 (±343)		259 (±53)	857 (±508)	3.9 (±1.1)	136 (±96)	1.3 (±0.3)	19 (±17)	4.6 (±3.2)	66 (±39)	9.1 (±2.6)	65 (±48)
African dust A(n = 9) CW(n = 9)	57 (±16)	130 (±94)	211 (±53)	3382 (±2196)	528 (±193)		343 (±66)	1209 (±392)	1.6 (±0.8)	61 (±45)	0.1 (±0.1)	7.5 (±3.4)	17 (±10)	24 (±18)	6.2 (±2.1)	5.3 (±1.8)
Overall A(n = 16) CW(n = 26)	41 (±19)	115 (±92)	292 (±180)	3291 (±2192)	432 (±295)		249 (±100)	1200 (±636)	2.8 (±1.5)	63 (±46)	1.0 (±0.5)	8.9 (±3.8)	8.5 (±7.6)	39 (±28)	6.8 (±2.4)	8.9 (±5.8)
Efficiency		2.8		11		10		4.8		22		11		3.5		1.5

[a]Units are ng/m³. Efficiency, [cloud water]/[aerosol]: CW, cloud water; A, aerosol.

[23] Other species commonly present in seawater were also detected in high concentrations, such as K^+, Mg^{2+} and Ca^{2+}. In most of the aerosol particles, cloud water and rainwater samples, the K^+/Na^+, Mg^{2+}/Na^+, and Cl^-/Na^+ ratios were similar to those in seawater, suggesting a marine origin for these ions (Table 3). Other minor species measured in this study were NO_2^- Br^-, Li^+, PO_4^{3-}, and Mn (<0.1%). Since these species were detected in few samples and at low levels, we did not include them in Table 1.

[24] The ion balance between anions (Cl^-, NO_3^-, and $SO_4^=$) and cations (H^+, K^+, Na^+, Ca^{2+}, Mg^{2+} and NH_4^+) for cloud water and rainwater was evaluated through linear regression analysis on the data. An average value of $r^2 = 0.6$ for correlation coefficient for both cloud water and rainwater was obtained. This moderate correlation is due to the high concentrations of SO_4^{2-} and Cl^- for some samples which are influenced by air masses with volcanic ash. When these samples are not considered the coefficient presented a better correlation for both cloud water and rainwater ($r^2 = 0.86$) indicating an acceptable data quality. The cation/anion ratios showed clearly the differences among air masses origin (Table 1). The observed anion deficiency is likely attributable to organic acids that were measured just in a few samples.

[25] Water-soluble organic fraction was less abundant in all kinds of samples than water-soluble inorganic species. Samples collected under background conditions showed an average percentage in mg per liter of TOC ranging from 2% to 6% of all species measured. Average concentrations ranged from 0.5 to 1.3 mg/L for TOC and DOC in cloud water (Table 1), similar to other measurements at EP where average concentrations ranged from 0.4 to 1.6 mg/L [*Reyes-Rodríguez et al.*, 2009]. For rainwater the average TOC and DOC concentrations varied from 0.3 to 1.0 mg/L. Measured DOC in rainwater reported in another study at EP was within this range (0.6 mg/L) [*McDowell et al.*, 1990]. For aerosol particles, the water-soluble organic content ranged from 59 to 105 ng/m³. Measurements taken using Counterflow Virtual Impactor (CVI) and Aerosol Mass Spectrometry in EP showed lower to nondetectable organics in cloud water, suggesting that low amounts of submicron particles from forest or anthropogenic activities are emitted near this site [*Allan et al.*, 2008].

[26] The water-soluble organic fraction contained a significant contribution of organic acids. The contribution of carboxylic acids (CA) to the measured organic carbon was 3.4% (mg of C per L) for cloud water, 18% (mg of C per L) for rainwater, and 4.3% (ng C per m³) for aerosol particles. On the other hand, the contribution of organic acids to the total solute content under background conditions remains low compared to that of major ions, varying from 0.5% to 1.1% (Figures 1 to 3). Among organic acids, MSA was the most abundant in the aerosol phase (8.5 ng/m³ or 45% of total CA), followed by oxalate (6.8 ng/m³) and acetate (2.8 ng/m³) (Table 2). Acetate was the dominant short chain monocarboxylic acid, with average concentrations of 5.4–5.8 µeq/L (about 80% of total organic acids) for cloud water and rainwater (Table 1). This is in agreement with the findings of *Chebbi and Carlier* [1996] that showed that formic and acetic acids are the predominant carboxylic acids in the tropospheric aqueous phase.
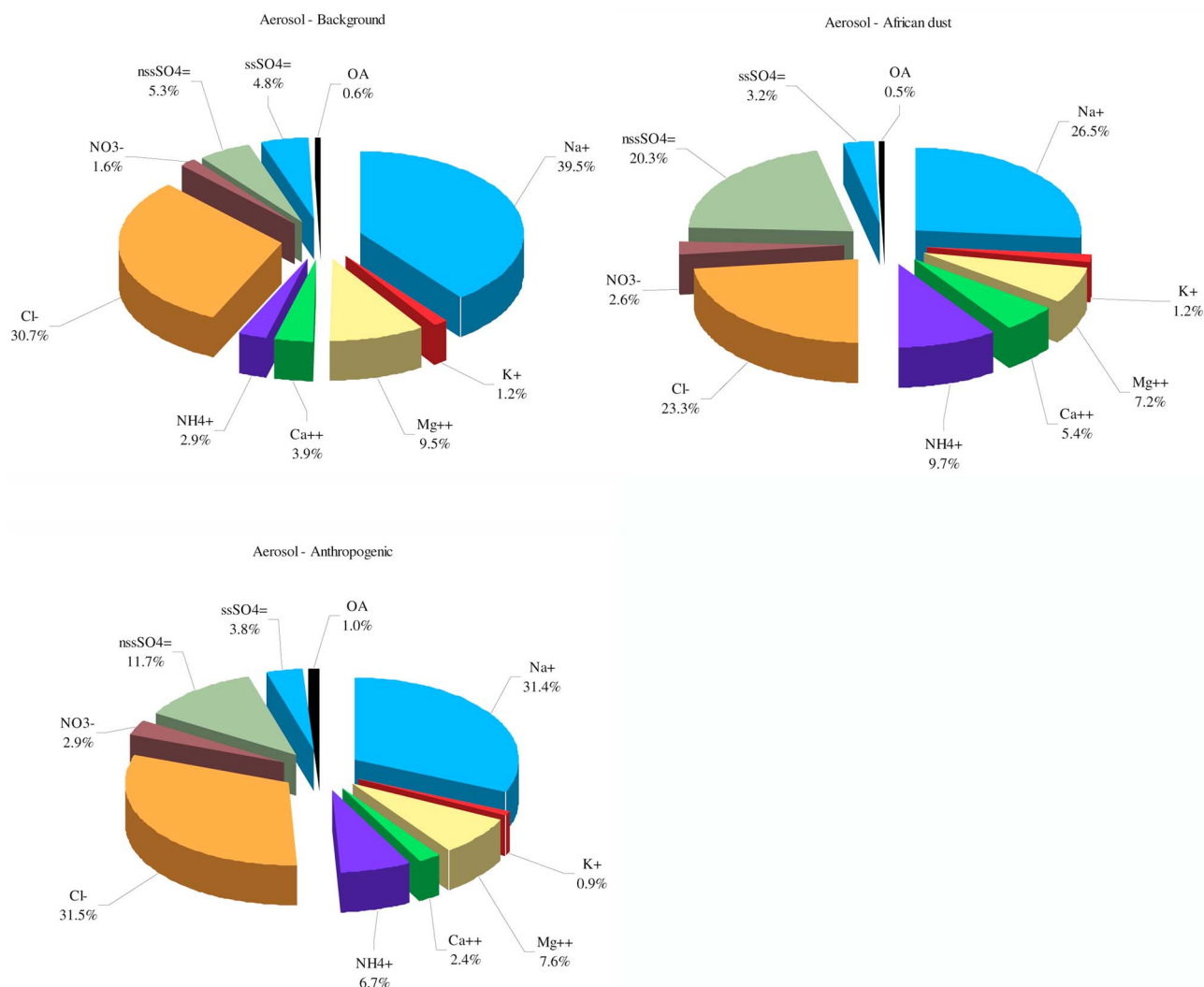
Figure 1. Percentage of main ion concentrations (ng/m^3) of aerosol particles in different air masses.

[27] Total nitrogen fractions represented about 6%–8% of the concentrations (mg/L) of all species measured. Averages in cloud water (0.9 ± 0.5 mg/L) and rainwater (0.2 ± 0.1 mg/L) found in the samples (Table 1) were similar to previous levels reported for remote sites [Eklund et al., 1997]. An average of 0.9 to 1.2 mg/L in cloud water was also obtained in previous studies in Puerto Rico [Asbury et al., 1994; Reyes-Rodríguez et al., 2009], similar to our findings. Total nitrogen in aerosol particles was analyzed only in few samples. The concentrations found in these samples ranged from 2 to 18 ng/m^3 (avg. Seven ng/m^3). The largest contribution to total nitrogen is due to inorganic species (55%–70%) with smaller contributions for organic nitrogen (30%–45%). Average concentrations of water-soluble inorganic nitrogen for cloud water samples were 20 (±15) μeq/L for NH$_4^+$, and 29 (±22) μeq/L for NO$_3^-$ (Table 1). For rainwater, the concentrations were lower than in cloud water with an average of 3.7 (±2.6) μeq/L for NH$_4^+$ and 5.4 (±4.1) μeq/L for NO$_3^-$. Previous studies at EP registered average concentrations of NH$_4^+$ and NO$_3^-$ in cloud water of 32 and 64 μeq/L, respectively, and 2.9 and 4.3 μeq/L for rainwater [Weathers et al., 1988; Asbury et al., 1994]. The

average concentration of NO$_3^-$ and NH$_4^+$ in aerosol particles (n = 16) was 41 (±20) ng/m^3. It was about 3 to 5 times lower than the concentrations found for remote Pacific Ocean areas (105–198 ng/m^3) [Prospero and Savoie, 1989], but similar to marine background concentrations (43 ng/m^3) measured in the northwest Pacific Ocean [Matsumoto et al., 1998]. For organic nitrogen the average concentration in cloud water was 0.18 (±0.11) mg/L and 0.10 (±0.03) mg/L for rainwater. ON was detected only in two of six aerosol particles samples collected during AD periods with a concentration of 2.1 ng/m^3 (representing 11% of TN) and 3.4 ng/m^3 (representing 45% of TN). In rainwater, ON made up 40% of TN, higher than results found in similar regions in Mediterranean rainwater (0.21 mg/L–17% TN) [Mace et al., 2003a] and Cape Grim (0.1 mg/L–19%TN) [Mace et al., 2003b]. In other studies, ON concentrations in rainwater at remote sites (Bermuda, Tahiti and North Atlantic) have been found to range from 0.08 to 0.22 mg/L and contributed 60% to 80% of measured TN [Cornell et al., 1995]. For rural sites (North Carolina and Brazil) ON concentrations have been smaller ranging from
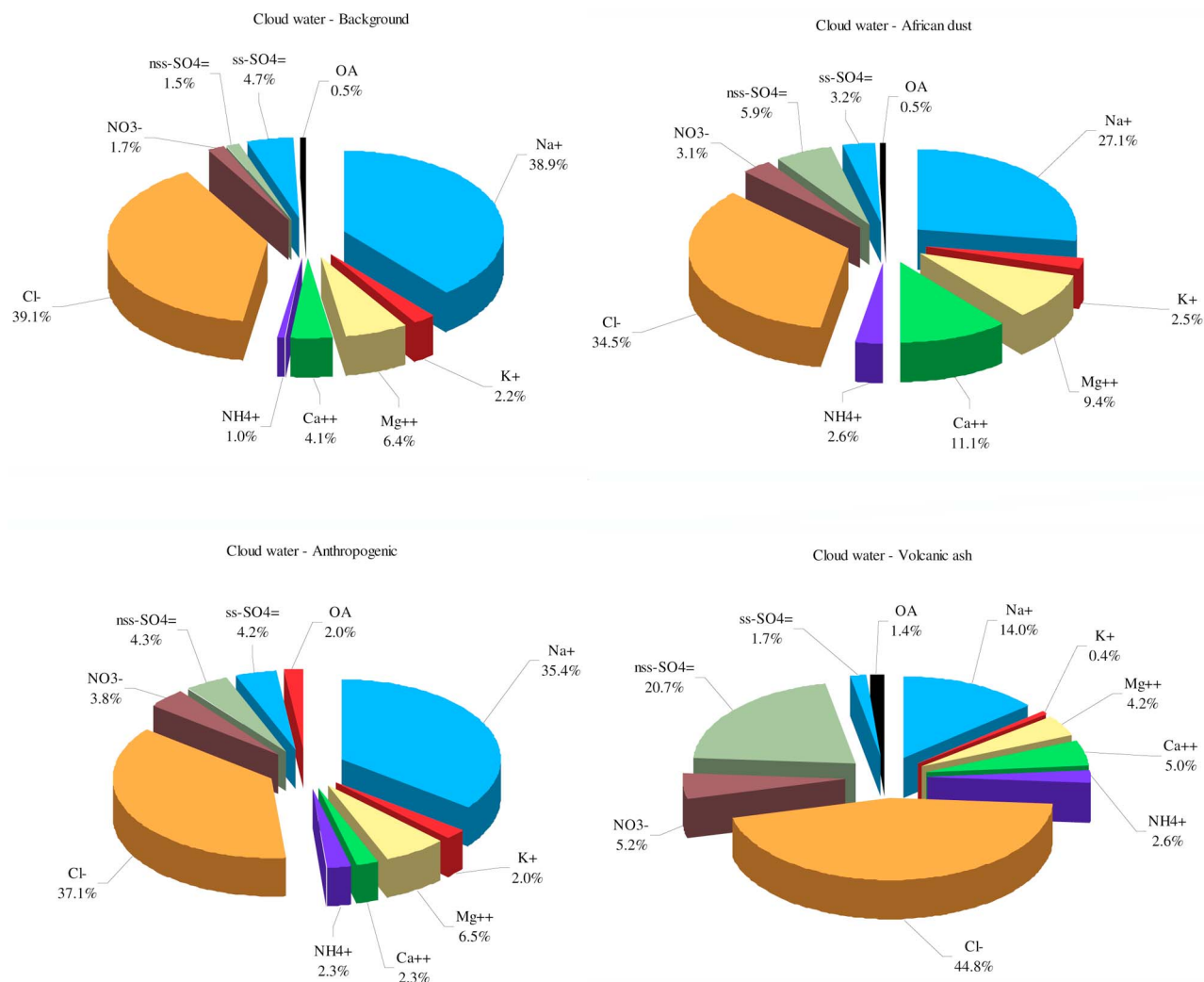
Figure 2. Percentage (μeq/L) of the main ions measured in cloud water for different air masses. OA, organic acids.

0.04 to 0.12 mg/L and representing 20%–25% of the TN [*Cornell et al.*, 1995]. Overall, the ON concentrations measured in this study (0.09 to 0.20 mg/L) were within the range found at other remote sites (0.04 to 0.22 mg/L). However, the percentage of TN varied largely among sites. On the other hand, sites influenced anthropogenically presented higher ON concentrations. An example was fog water samples collected in Fresno, CA whose concentrations of ON ranging from 1.7 to 4.5 mg/L, corresponding to 10%–17% of TN [*Collett et al.*, 2008]. While those absolute concentrations were much higher than reported here for EP cloud water (avg. 0.18 mg/L and 20% of TN), the percentage contribution is somewhat lower. Both in Fresno fog water and EP cloud water, the major contribution to total nitrogen comes from nitrate and ammonium species.

[28] Six cloud water, rainwater and filter samples were analyzed to determine concentrations of free amino acids (FAA). Only two samples of each contained detectable FAA including aspartic acid, alanine, glycine, ornitine, and tyrosine. The FAA in these samples represented up to 60% of ON. High proportions of FAA in rainwater collected in a marine environment were also observed in Cape Grim,

Australia (50% of ON) [*Mace et al.*, 2003b]. Glycine, proline, and valine may be from bacterial or other biological sources, since bacteria contain high concentrations of FAA (up to 10^9/L in surface ocean water) [*Mace et al.*, 2003b]. FAA could also be due to the decomposition of proteins (peptides), forest pollen or bacteria and viruses from the ocean surface [*Mace et al.*, 2003b]. The limited data set of samples together with the implementation of this new methodology to analyze FAA makes difficult an in-depth interpretation of the data.

3.2. Air Masses

[29] We observed that species of anthropogenic and soil origin, such as NO_3^-, NH_4^+, SO_4^{2-}, and Ca^{2+}, presented higher concentrations in aerosol particles, cloud water and rainwater during some periods. To gain a better understanding of the sources of these species, we classified the results according to the origins of the air masses. To achieve this goal we used meteorological data, HYSPLIT trajectories, observations of the National Weather Service (NOAA NWS San Juan), and the chemical information to group the samples. The predominant air direction from northeast (NE) is
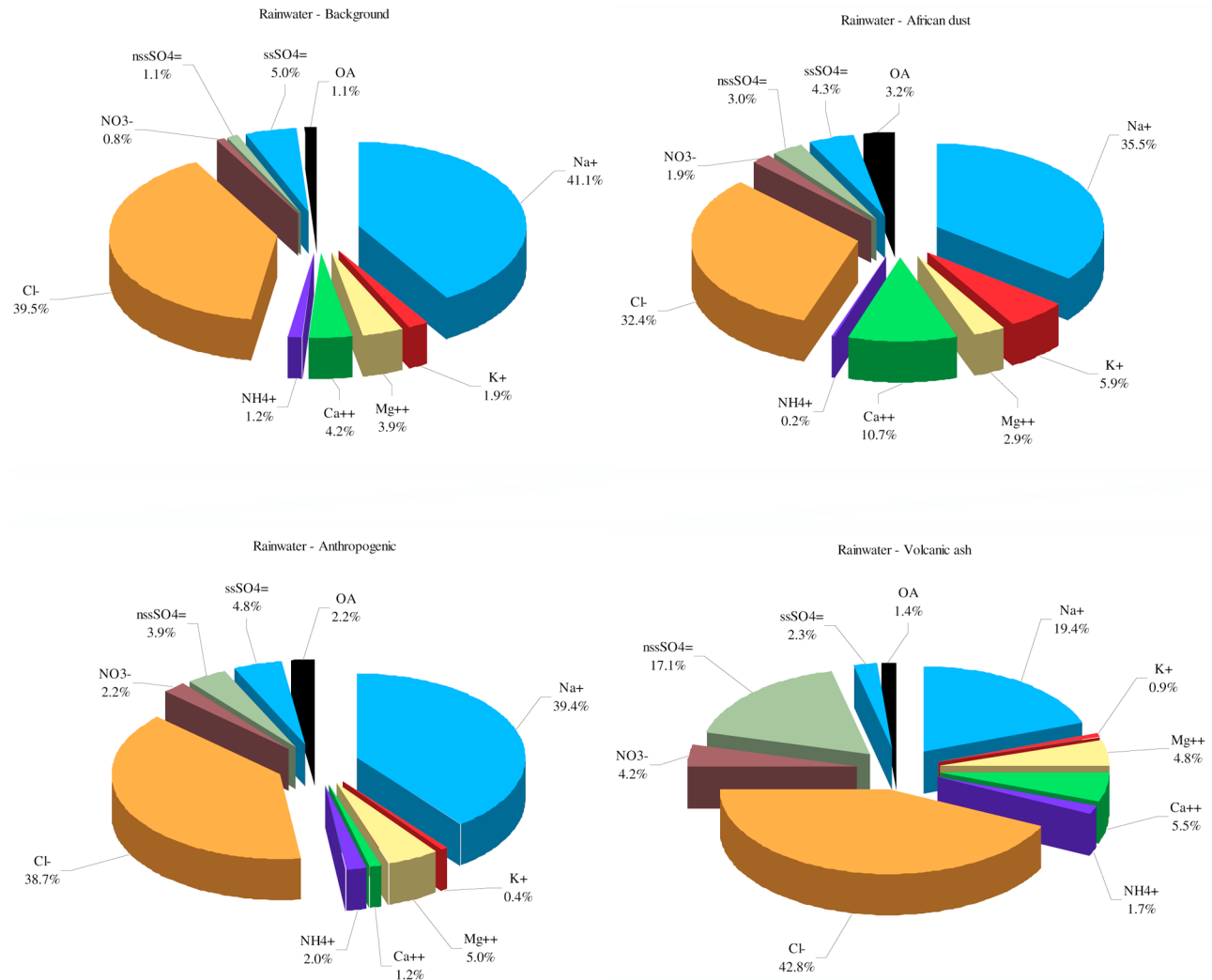
Figure 3. Percentage (μeq/L) of main ions measured in rainwater for different air masses. OA, organic acids.

Table 3. Non-Sea-Salt Concentrations (μeq/L) and Ratios for Ions in Cloud Water, Rainwater, and Aerosol

|	Background			Anthropogenic			African Dust			Volcanic Ash	
	Cloud	Rain	Aerosol	Cloud	Rain	Aerosol	Cloud	Rain	Aerosol	Cloud	Rain
Non-Sea-Salt											
Nss-K^+	30	1.0	3.1	28	0.0	11	29	16	6.9	0.9	1.7
Nss-Mg^{2+}	10	0.0	80	25	7.8	56	86	0.0	76	0.0	1.4
Nss-Ca^{2+}	15	0.0	8.7	8.6	0.9	7.6	137	27	44	64	18
Nss-SO_4^{2-}	17	6.6	45	50	14	87	81	9.1	215	301	66
Ratios											
K^+/Na^+	0.06	0.04	0.03	0.06	0.02	0.03	0.08	0.2	0.04	0.03	0.04
Mg^{2+}/Na^+	0.2	0.09	0.2	0.2	0.2	0.2	0.5	0.08	0.3	0.3	0.3
Ca^{2+}/Na^+	0.1	0.1	0.1	0.07	0.04	0.08	0.6	0.3	0.3	0.4	0.3
Cl^-/Na^+	0.9	0.9	0.8	1.0	1.0	1.0	1.6	0.9	0.9	3.2	2.2
SO_4^{2-}/Na^+	0.1	0.1	0.3	0.2	0.2	0.6	0.5	0.2	1.0	0.8	1.0
Nss-SO_4^{2-}/Na^+	0.03	0.05	0.1	0.1	0.1	0.5	0.2	0.09	0.9	1.5	0.9
NO_3^-/Na^+	0.03	0.02	0.04	0.1	0.06	0.1	0.1	0.05	0.1	0.4	0.2
NH_4^+/Na^+	0.01	0.03	0.07	0.07	0.05	0.2	0.1	0.01	0.4	0.2	0.09
$NO_3^-/$nss-SO_4^{2-}	0.9	0.4	0.3	0.8	0.6	0.2	0.5	0.6	0.1	0.3	0.3
NO_3^-/SO_4^{2-}	0.3	0.1	0.2	0.5	0.3	0.2	0.3	0.3	0.1	0.2	0.2
$NH_4^+/$nss-Ca^{2+}	0.4	4.0	1.3	2.9	7.8	6.5	0.3	0.03	2.3	0.6	0.4
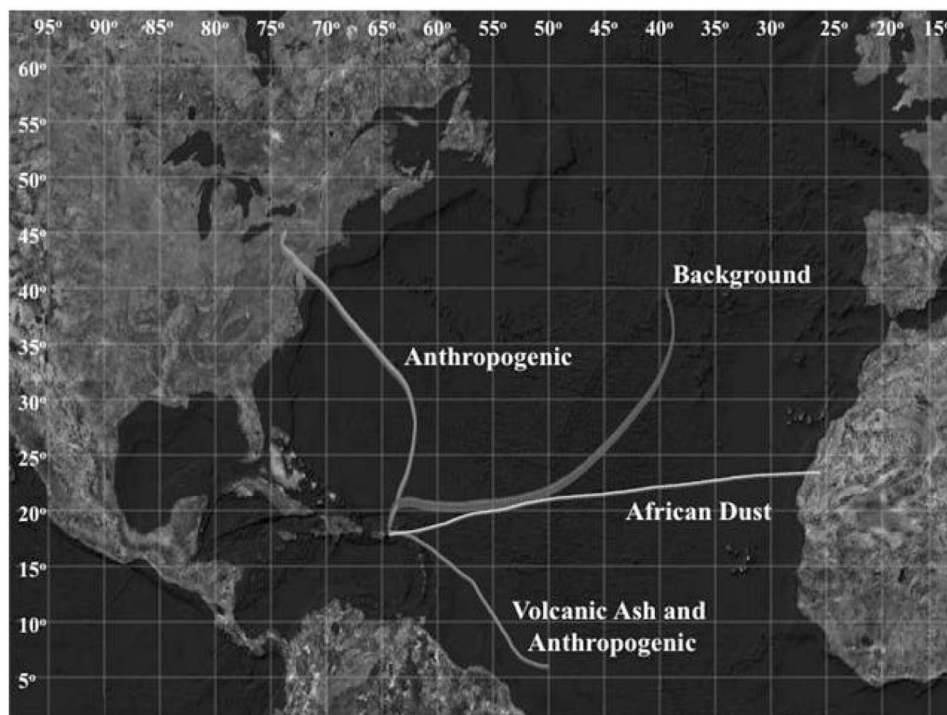
Figure 4. Representation of the main air mass backward trajectories: North Atlantic Ocean was considered as background conditions; tropical Atlantic represents air masses associated with African dust events; South Atlantic Ocean represents air masses associated with volcanic ash from the Soufriere Hills volcano and anthropogenic; and North America refers to anthropogenic air masses [*Gioda et al.*, 2008].

free of dust and anthropogenic influences, and considered as the background condition. In contrast, air from the east-southeast (ESE) and north-northeast (NNE) is influenced by anthropogenic emissions. Similar trends were observed in previous studies in Puerto Rico [*Allan et al.*, 2008]. Overall, we identified three types of air masses differing from the background conditions: African dust (AD), volcanic ash (VA) and anthropogenic (A) (Figure 4) [*Gioda et al.*, 2008]. African dust represents air masses associated with dust events transported from the African continent; volcanic ash represents air masses transported from the Soufriere Hills volcano on the Caribbean island of Montserrat; and anthropogenic refers to polluted air masses transported from North America or from upwind Caribbean Islands.

[30] Observations of aerosol particles, cloud water and rainwater samples for the different periods are summarized in Tables 1 and 2. Variations in concentration of all soluble components measured in aerosol particles, cloud water and rainwater samples are depicted in Figures 5, 6, and 7.

[31] Samples collected under background conditions had Na^+ and Cl^- as the main ion species in aerosol particles, cloud water and rainwater with an average contribution for the sum of both ions of 70%–80% (mg/L) to measured composition (Figures 1, 2, and 3). Overall, the mole equivalent ratios of Cl^-/Na^+ (0.9–1.1) were similar to seawater (1.16) (Table 3). Lower ratios occurred probably due to reactions of sea salt with H_2SO_4, SO_2, or HNO_3, resulting in Cl^- depletion from sea-salt particles [*Collett et al.*, 2002; *Lee et al.*, 2008a, 2008b]. During dust and volcanic ash periods (AD and VA), contributions of Na^+ and Cl^- were reduced (total percentage contribution of 50%–

65% in mg/L) (Figures 1, 2, and 3), due to the enhanced input of other aerosol types. Increases in Cl^-/Na^+ ratios were very high for rainwater (2.2) and cloud water (3.2) when ash from the Soufriere Hills volcano reached PR. In the same air masses, the SO_4^{2-}/Na^+ ratios in cloud water (0.8) and rainwater (1.0) were also much higher than observed in sea salt (0.121) (see Table 3). The nss-SO_4^{2-} calculated for cloud water (301 μeq/L) and for rainwater (66 μeq/L) indicated a substantial input of SO_4^{2-} to these samples during volcanic ash event (Figures 5 and 6 and Table 3). The high Cl^-/Na^+ ratios and nss-SO_4^{2-} suggest a volcanic origin for these species, probably being derived from the interactions between ash particles and volcanic emissions of sulfur dioxide, sulfuric acid, and hydrochloric acid. Increased inputs of SO_4^{2-} were also observed during AD and anthropogenic events for aerosol particles, cloud water and rainwater with an increase of nss-SO_4^{2-} concentrations ranging from 2 to 5 times compare to the background conditions (Table 3).

[32] Metals present in dust from African deserts have been reported as an important source of nutrients to ocean [*Jickells*, 1999] and also could catalyze S(IV) oxidation by O_2 [*Watanabe et al.*, 2001]. Iron, together with Al and Ca^{++}, can be important markers for African dust that reaches the Caribbean region, in addition to being a source of nutrients for local ecosystems. Al and Fe were detected in cloud water samples collected during African dust events and also detected in the insoluble particles present in the cloud water [*Gioda et al.*, 2008]. The concentrations of Al and Fe in cloud water were 4–125 μM and 4–37 μM, respectively. For background conditions and anthropogenic air masses, the lowest concentrations were detected for both metals, 4–7 μM.
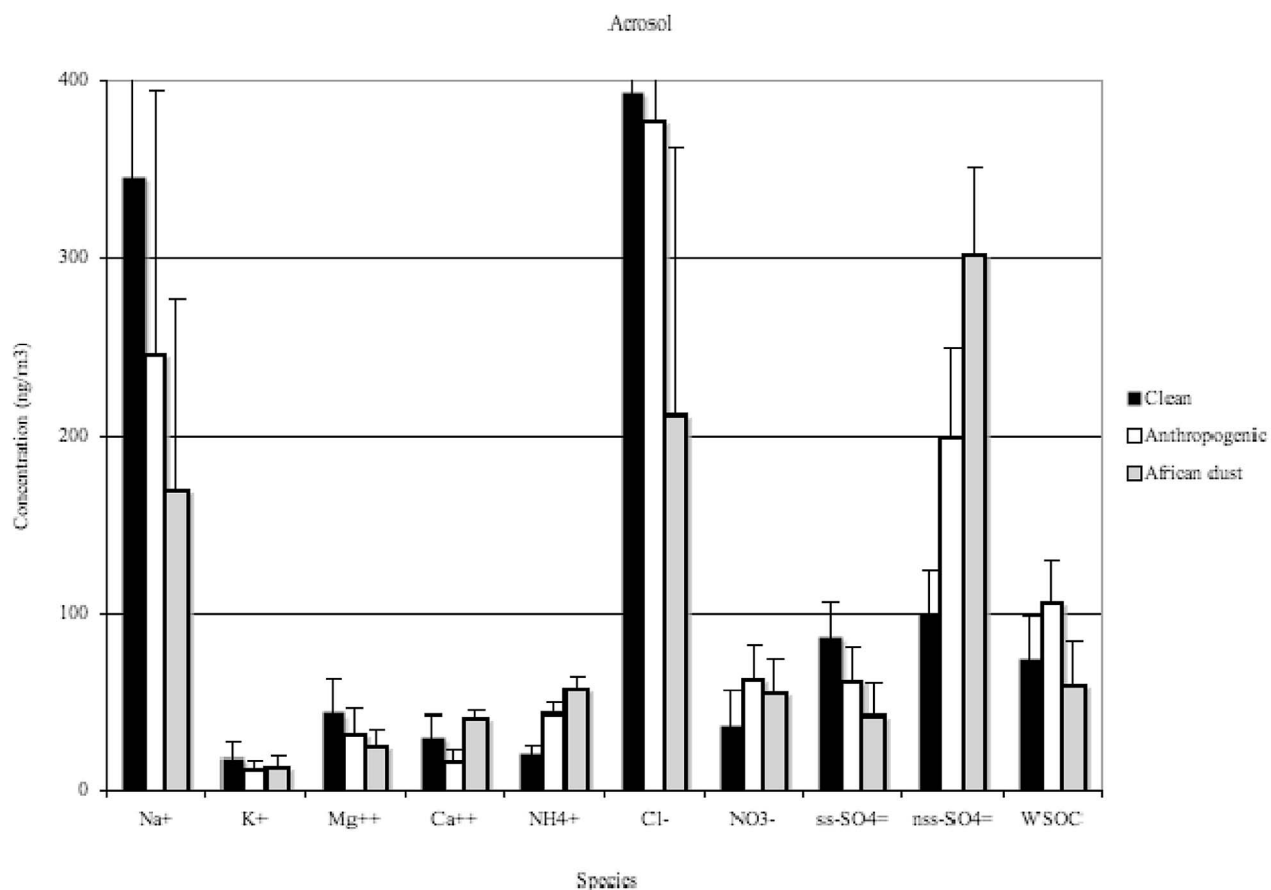
Figure 5. Average concentrations (ng/m^3) of aerosol particles in different air masses. WSOC, water-soluble organic compounds.
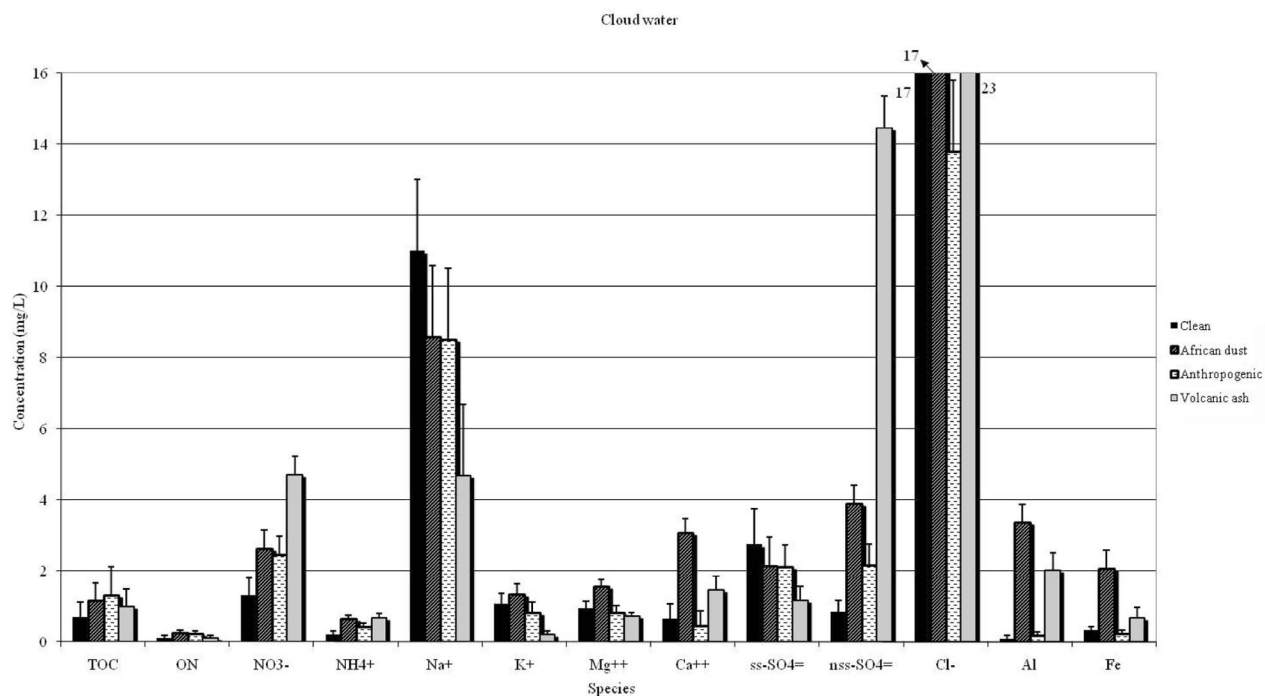

Figure 6. Representation of cloud water concentrations (mg/L) for different air masses. OA, organic acids; TOC, total organic carbon; ON, organic nitrogen.
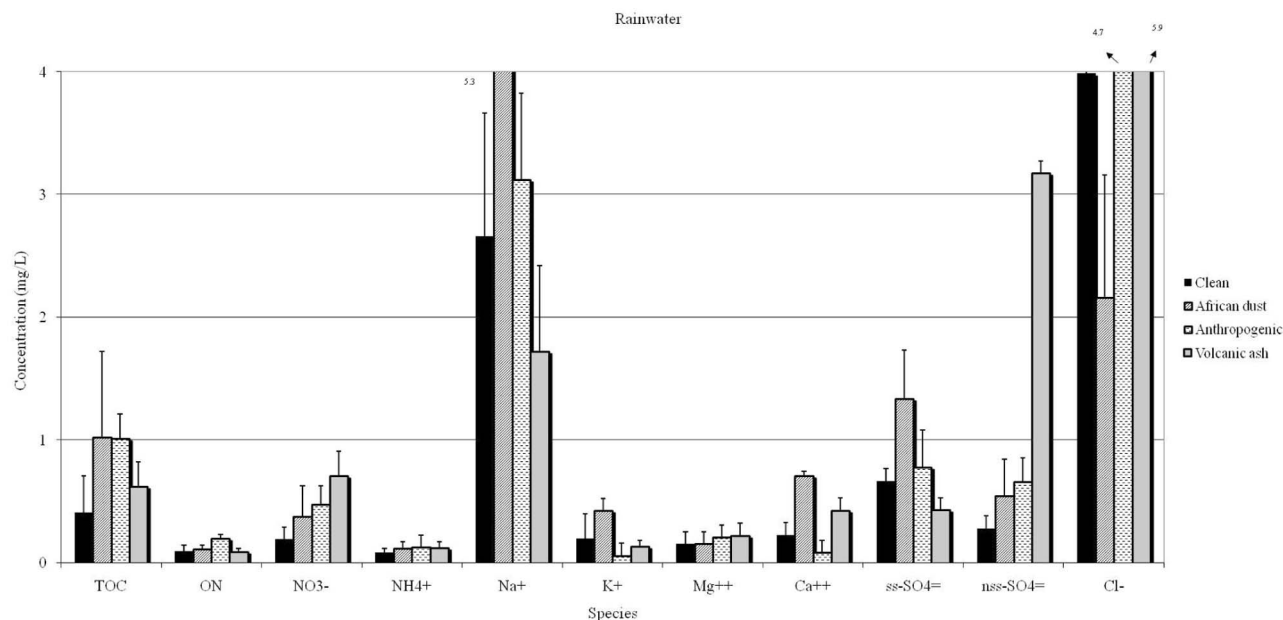
Figure 7. Representation of rainwater concentrations (mg/L) for different air masses. OA, organic acids; TOC, total organic carbon; ON, organic nitrogen.

Highest concentrations were measured during African dust episodes where the average Al concentration was 125 μM and the average Fe concentration was 37 μM (Figure 6). *Fuzzi et al.* [1992] reported Fe concentrations in fog water in the Po Valley, a region influenced by anthropogenic emissions, ranging from 0.5 to 42 μM while *Watanabe et al.* [2001] measured in cloud water over remotes sites of the Pacific Ocean concentrations of 1.2 to 13 μM. *Straub et al.* [2007] found average Fe concentrations of 0.4 μM, with a maximum of 1.5 μM, in cloud water samples collected in a relatively clean region in the eastern Pacific Ocean. Comparing the results obtained in other experiments with different air mass types with observations from this study, one could infer that higher concentrations of Fe are related crustal input during African dust periods. On the other hand, no Fe or Al were detected in rainwater or in fine-mode aerosol particles. It is possible that the reason these elements are detected only in cloud water and not in rainwater is due to dilution. Trace elements, Al and Fe, were measured just in their water-soluble forms so that differences in solubility (e.g., Fe solubility increases at lower pH) might also play some role in making these compounds more detectable in cloud water. In aerosol particles these elements were practically undetectable, because they are present mainly in the coarse fraction, which was not analyzed. Calcium also had the highest concentration measured during AD events for all kind of samples. It is clearly observed in the input of nss-Ca^{2+} that ranged from 3 to 30 times higher than background periods (Table 3). The increase in abundance of nss-Ca^{2+} during AD periods supports the presence of dust particles from African soil, discussed above, in the samples collected (Figure 8). Nss-Ca^{2+} is rarely detected in remote areas without dust influence, therefore these significant nss-Ca^{2+} concentrations probably come from long-range transport from desert dust particles.

[33] The water-soluble organic carbon fraction also varied by air mass type. The most significant variations for aerosol particles, cloud water and rainwater were observed during anthropogenic air mass periods when the concentrations increased 60% to 110% compared to background periods. Smaller increments were observed for African dust events (13% to 50%) and volcanic ash (25% to 40%) (Figures 5, 6, and 7). An increase of water-soluble organic species during these periods suggested that both anthropogenic pollution and dust can be important sources of organic matter to the Caribbean atmosphere [*Gioda et al.*, 2008]. Higher contributions of carboxylic acids to DOC were observed during periods of anthropogenic influence. However, the limited number of samples analyzed for organic acids for each air mass type makes difficult a better interpretation of the data. A fraction of the organic matter present in cloud and rain was also insoluble. In this study DOC/TOC ratios were on average 0.78 for cloud water and 0.73 for rainwater. This suggested that while the main portion of the organic carbon was in the dissolved form, a significant portion was present as undissolved particulate organic carbon (POC). The contribution of POC to the TOC in cloud water was higher in summer (26%) than in winter (18%) when dust from African storms reached the sampling sites.

[34] As with many other measured species, total nitrogen concentrations in cloud water and rainwater showed the lowest concentrations during background conditions with an average in cloud water of 0.4 mg/L and rainwater of 0.2 mg/L (Table 1). An increase in the levels from 2 to 4 times was observed during periods with air masses influenced by dust or anthropogenic emissions. These results are in agreement with other observations at EP by *Reyes-Rodríguez et al.* [2009]. Similarly to TN, organic nitrogen concentrations increased in anthropogenic and dust periods. ON was similar during AD and anthropogenic periods (0.26 versus 0.24 mg/L); while in rainwater, the highest ON concentration was detected during
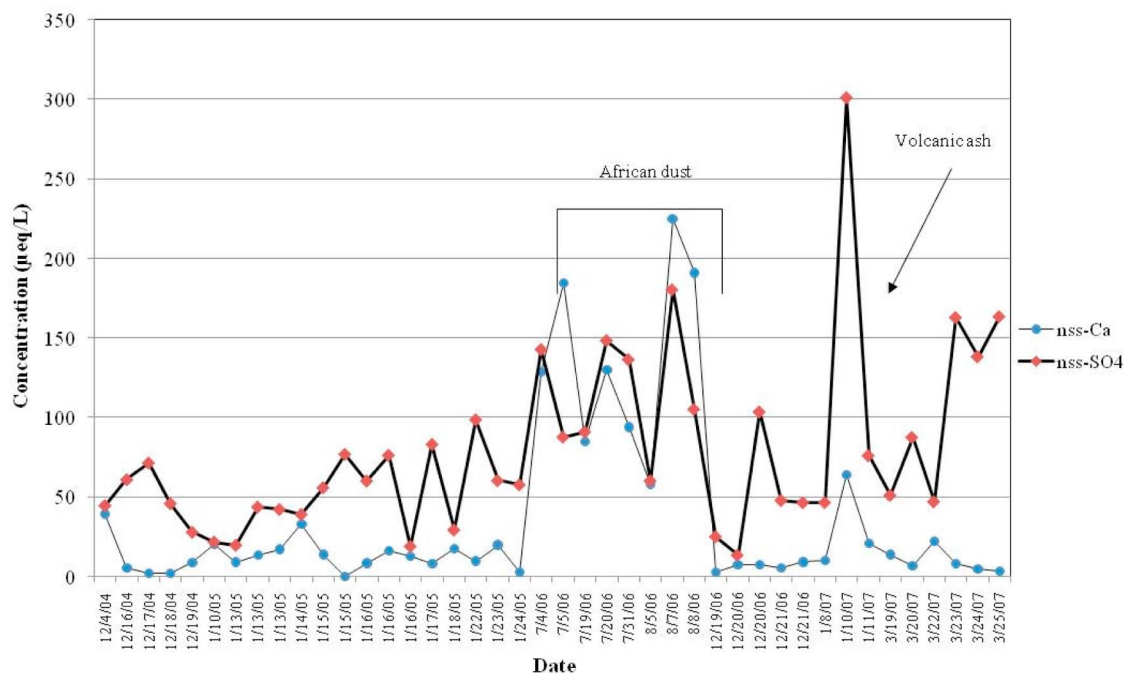
Figure 8. Variation of nss-Ca^{2+} and nss-SO$_4^{2-}$ concentrations in cloud water during the complete sampling period (2004–2007).

the anthropogenic period, 0.20 mg/L. Although in both studies the ON concentrations were higher during AD events compared to background, ON concentrations were lower in this study compared to the previous report (0.24 mg/L versus 0.59 mg/L) by *Reyes-Rodríguez et al.* [2009]. These different concentrations may be related to the intensity of AD events during sampled periods, which may be an important source of nitrogen-containing organic compounds. Although the highest EP concentrations of ON and Ca^{2+} were found during AD for both cloud water and rainwater, these species were not highly correlated, as previously reported during African dust episodes [*Mace et al.*, 2003b]. This suggests that ON does not derive only from soil, but could partially result from bubble bursting and gas-phase adsorption of organics onto dust particles [*Dentener et al.*, 1996] or uptake of gas phase organic nitrogen species by cloud drops and precipitation.

[35] Concentrations of NO$_3^-$ and NH$_4^+$ also increased in cloud water, rainwater and aerosol particles during periods with anthropogenic influence and in African dust air masses (Tables 1 and 2 and Figures 5, 6, and 7). The concentrations of NO$_3^-$ and NH$_4^+$ in African dust and anthropogenic periods were approximately two times higher than in background periods. Previous measurements of aerosol particles at CSJ revealed a concentration of 30–40 ng/m^3 of NO$_3^-$ during polluted periods and 20 ng/m^3 under clean conditions [*Allan et al.*, 2008]. For NH$_4^+$, the concentrations ranged from 140 ng/m^3 (background) to 180 ng/m^3 (polluted). While NO$_3^-$ concentrations were within the range observed in this study, NH$_4^+$ was much higher. This may simply be due to varying degrees of pollution in air masses classified as anthropogenically influenced. *Allan et al.* [2008] classified two periods as polluted; however, the concentrations of

species differ between the periods. We can also compare our observations with those from remote marine areas of the Pacific Ocean. The average NO$_3^-$ concentration in aerosol particles was 45 (±15) ng/m^3, about 3 to 5 times lower than the concentrations found for remote Pacific Ocean areas (105–198 ng/m^3) [*Prospero and Savoie*, 1989]. On the other hand, our average concentration of NH$_4^+$ was 41 (±19) ng/m^3, similar to marine background concentrations (43 ng/m^3) measured in the Northwest Pacific Ocean [*Matsumoto et al.*, 1998]. Although these Pacific areas are considered remote, it seems that anthropogenic substances were transported to these regions as in our study. Regarding African dust, studies performed in different sites also observed this influence. Previous studies in Barbados also showed elevated NO$_3^-$ and nss-SO$_4^{2-}$ concentrations in aerosol particles during African dust storms, probably derived from sources in Europe and North Africa [*Savoie et al.*, 1989]. In another study performed in the Canary Islands bulk aerosol particles were measured [*Díaz et al.*, 2006]. Higher concentrations were detected for NO$_3^-$ (1 to1.2 μg/m^3) and NH$_4^+$ (0.3–0.4 μg/m^3) during influence of African dust compared to periods dominated by marine aerosol particles (0.6 μg/m^3 for NO$_3^-$ and 0.2 μg/m^3 for NH$_4^+$) [*Díaz et al.*, 2006]. A mixing of aged European emissions with African dust could also explain the high levels of NO$_3^-$ and SO$_4^{2-}$ during AD air masses, since N and S gases from fossil fuel combustion can react with mineral dust. The high concentrations of NO$_3^-$ associated with dust, for example, may have resulted from HNO$_3$ reacting with soil. EP concentrations of NO$_3^-$ and NH$_4^+$ measured in our study also increased in aerosol particles during periods with anthropogenic influence and in African dust air masses (Table 2 and Figure 5).

Table 4. Cloud Water/Rainwater and Cloud Water/Aerosol Particles Ratios in Terms of Concentrations (μeq/L)

Cloud Water/Rainwater	Na$^+$	K$^+$	Mg^{++}	Ca^{++}	NH$_4^+$	Cl$^-$	NO$_3^-$	SO$_4^=$	OA	TOC	ON	TN
Background	3.6	4.4	6.1	3.7	3.0	3.7	7.6	8.3	1.9	1.7	1.3	1.8
African dust	3.5	1.9	14.9	4.8	48.8	4.9	7.5	8.7	0.8	1.1	1.3	2.5
Anthropogenic	2.7	14.0	3.9	5.7	3.5	2.9	5.2	8.4	2.8	1.3	2.1	2.5
Volcanic ash	2.7	1.6	3.3	3.4	6.0	3.9	4.7	7.2	3.8	1.6	1.5	5.7
Overall	3	5	7	4	15	4	6	8	2	1	2	3

Cloud Water/Aerosol	Na$^+$	K$^+$	Mg^{++}	Ca^{++}	NH$_4^+$	Cl$^-$	NO$_3^-$	SO$_4^=$	OA	WSOC
Background	1.4	2.6	1.0	1.5	0.5	1.8	1.6	1.8	1.4	0.4
African dust	1.3	2.6	1.7	2.7	0.4	1.9	1.5	1.7	1.5	0.5
Anthropogenic	1.6	3.1	1.2	1.3	0.5	1.7	1.8	2.1	2.8	0.9
Overall	1.4	2.8	1.3	1.8	0.4	1.8	1.6	1.9	1.9	0.6

3.3. Scavenging Process

[36] Ion concentrations in the cloud and rainwater samples were different even though the samples were collected at the same sampling point. Overall, the cloud water ion concentrations were two to fifteen times higher than in the rainwater (Table 4), similar to ratios observed in other studies [*Decesari et al.*, 2005; *Allan et al.*, 2008]. The highest ratios were obtained for NH$_4^+$ (15 times), NO$_3^-$ (6 times) and SO$_4^{2-}$ (8 times), which are all species that exist (or have precursors that exist) in the gas phase and therefore can be more effectively scavenged by cloud drops with their higher surface-to-volume ratios and longer atmospheric residence times. The average solute concentrations measured in cloud water and rainwater changed by approximately the same amount between periods influenced by long-range transport (Table 5). These comparable changes suggest that aerosol particles from the boundary layer exert a broadly similar effect on mountain cloud water and precipitation composition.

[37] The individual solute concentrations derived from cloud water were generally higher than in the corresponding aerosol particle samples (Tables 2 and 4). This could be due to a significant contribution from soluble gases. For example, uptake of gaseous nitric acid increases concentrations of nitrate measured in the cloud water. Likewise, uptake of gaseous sulfur dioxide followed by aqueous phase oxidation can increase cloud sulfate loadings. Furthermore, due to elevation variations the air masses could have different compositions. It should also be considered that only fine particles were analyzed, while the cloud water analysis included fine and coarse modes that could increase the concentrations of species in the aqueous phase.

[38] Under the assumption that the aerosol particles and cloud water samples were drawn from the same air masses, a relationship between the aerosol particles and cloud water composition can be expected since cloud droplets are formed on a subset of the aerosol particles which act as CCN, the soluble components of which determine the initial cloud drop composition. In order to compare cloud water and aerosol particles, their mole equivalent ratios were averaged. It is assumed that aerosol particles exert the primary influence, as cloud condensation nuclei, on cloud composition if there is no difference in the mole equivalent ratios between the aerosol particles and cloud water. The average mole equivalent ratios of NH$_4^+$/Na$^+$ and nss-SO$_4^{2-}$/Na$^+$ in cloud water and rainwater for all periods were lower than those in aerosol particles (Table 3). This suggests that sea-salt particles exert a greater influence on cloud water composition than NH$_4^+$ and nss-SO$_4^{2-}$. Ammonium and sulfate are generally present in fine particles (Dp < 1 μm) while sea salts are present in a more coarse fraction in marine environments making it easier for the latter to act as cloud condensation nuclei. Previous studies showed that condensation occurred preferably on coarse particles such as sea salt and mineral dust, than on fine particles [*Sasakawa and Uematsu*, 2002]. Although, coarse particles were not analyzed in this study, it is expected that sea salt, and aged mineral dust from the African continent, are probably most important species that act as CCN due to their abundance in the atmosphere. A previous study performed at EP substantiates these results [*Allan et al.*, 2008]. As the ratios of ammonium and sulfur species to Na$^+$ were lower in cloud water than in the fine aerosol particle samples, it appears that the enhanced scavenging of coarse-mode sea-salt par-

Table 5. Ratios Among Concentrations (μeq/L) Obtained for Different Air Masses and Background Conditions

Cloud Water	Na$^+$	K$^+$	Mg^{++}	Ca^{++}	NH$_4^+$	Cl$^-$	NO$_3^-$	SO$_4^=$	OA	TOC	ON	TN
African dust/background	0.8	1.2	1.7	3.0	3.0	1.0	2.0	5.3	1.1	1.6	2.2	4.2
Anthropogenic/background	0.8	0.8	0.9	0.5	2.1	0.8	1.9	3.3	3.1	1.8	2.0	2.8
Volcanic ash/background	0.4	0.2	0.8	1.4	3.2	1.4	3.6	17	3.0	1.4	1.1	4.7

Rainwater	Na$^+$	K$^+$	Mg^{++}	Ca^{++}	NH$_4^+$	Cl$^-$	NO$_3^-$	SO$_4^=$	OA	TOC	ON	TN
African dust/background	0.8	2.9	0.7	2.3	0.2	0.8	2.1	4.6	1.7	2.5	2.1	3.0
Anthropogenic/background	1.0	0.2	1.3	0.3	1.8	1.0	2.8	3.2	2.1	2.5	2.2	2.0
Volcanic ash/background	0.6	0.5	1.4	1.5	1.6	1.3	5.8	18	1.5	1.5	0.9	1.5

Aerosol	Na$^+$	K$^+$	Mg^{++}	Ca^{++}	NH$_4^+$	Cl$^-$	NO$_3^-$	SO$_4^=$	OA	WSOC	ON	TN
African dust/background	0.8	1.3	1.0	1.7	4.1	0.9	2.1	5.6	1.1	1.3	-	-
Anthropogenic/background	0.7	0.6	0.7	0.5	2.0	0.9	1.6	2.6	1.6	0.9	-	-

ticles may have exerted a larger influence (on the ratios) than the uptake of the gas phase nitrogen and sulfur species. Of course, it must also be borne in mind that differences in sampling location, including elevation, could also have influenced relative aerosol particle concentrations at the aerosol particles and cloud sampling sites.

[39] The mole equivalent ratios of NO_3^-/Na^+ were quite similar between cloud water and the aerosol particles (Table 3) suggesting that an important source of nitrate may be $NaNO_3$ present on the sea-salt particle surface. These findings are similar to results obtained using AMS measurements at EP [*Allan et al.*, 2008]. Consequently, the cloud water nitrate concentration might actually have relatively little to do with the fine-mode aerosol nitrate concentrations. Also, it should be considered that nitrate does not appear together with acid compounds, such as sulfates.

[40] Water-soluble organic carbon differed between aerosol particles and cloud water samples. On average, this fraction represented 8% of the total mass in the aerosol particles, while it accounted for 2%–6% in the aqueous phase. The cloud water/aerosol particle ratios for WSOC (Table 4) was low, suggesting that the organic aerosol fraction may not have been scavenged as efficiently by clouds as inorganic compounds like nitrate and sulfate and coarse-mode sea-salt particles (which are present in the cloud water samples but largely excluded from the fine-mode aerosol samples analyzed). Organic acids seem to be more efficiently scavenged than other organic compounds (not determined in this study) present in the WSOC (Table 4). Higher concentrations of organic acids in cloud water than in aerosol particles suggest significant scavenging of gas phase material by the droplets and/or enhanced organic acid concentrations in the tropical rain forest that covers the hillside of EP. A previous experiment in Puerto Rico reported considerable organic fractions in aerosol particles derived from marine sources that could influence significantly cloud properties [*Novakov and Penner*, 1993; *Novakov et al.*, 1994]. In that study, the average organic carbon concentrations was $1.00 \pm 0.14 \ \mu g/m^3$, while in this study it was $0.06 \pm 0.03 \ \mu g/m^3$ for background conditions; $0.05 \pm 0.01 \ \mu g/m^3$ for African dust and $0.16 \pm 0.10 \ \mu g/m^3$ for anthropogenic influence. More recently, *Allan et al.* [2008] reported results similar to ours, where the organic carbon fraction was not high with an average concentration of $0.17 \pm 0.35 \ \mu g/m^3$. They concluded that under background conditions the aerosol was mostly inorganic, and the marine organic fraction was not as ubiquitous as reported in the earlier studies. As elemental carbon was not detected and no polycyclic aromatic hydrocarbon was found during background conditions, it appears that the organic carbon came from natural sources [*Mayol-Bracero et al.*, 2001]. As in this experiment, they observed a variation in organic fractions related to the degree of air mass pollution. The CCN number (0.6% supersaturation) concentrations measured in CSJ in background conditions ($<200 \ cm^{-3}$) were two times lower than under polluted air masses [*Allan et al.*, 2008]. It was suggested that polluted periods with higher organic carbon fractions reduced the growth factors of aerosols due to lower-solubility material [*Allan et al.*, 2008]. In other words, particulate organic matter is less hygroscopic than inorganic particles, therefore the latter are more important to CCN than organic compounds.

[41] Regarding $nss-Ca^{2+}$, concentrations are higher in cloud water than in aerosols when African dust is present. This may mean that crustal material is not transported by MBL aerosols [*Decesari et al.*, 2005], although it could be that coarse-mode dust was present at CSJ but excluded from the fine-mode aerosol fraction that was analyzed.

3.4. The pH

[42] The average pH value measured in cloud water at East Peak during background conditions was 5.8 (±0.3) and for rainwater was 5.1 (±0.2), similar to values expected for remote sites (~5.0–5.6). Changes in pH were observed with air masses during dust or anthropogenic influences (Table 1). For cloud water, an increase of acidity was measured during anthropogenically influenced periods (pH = 4.5 ± 0.4) and volcanic ash (pH = 3.5 ± 0.2) events. Decreases in acidity were observed during African dust periods (pH = 6.3 ± 0.4). A similar trend was observed for rainwater (Table 1). These changes in pH relative to background conditions reflect cloud and rain scavenging of anthropogenic and crustal substances, since acidic species are present in volcanic ash and anthropogenic emissions (SO_4^{2-}, Cl^- and NO_3^-) and basic species in soil dust (especially Ca^{2+}). This can be better seen in Figure 8, where excess $nss-Ca^{2+}$ is observed during African dust episodes to be higher than $nss-SO_4^{2-}$. A previous study also showed an increase in rainwater pH values during Saharan dust episodes [*Loÿe-Pilot et al.*, 1986].

[43] The acidity of cloud water and rainwater is affected by both NO_3^- and SO_4^{2-}. The mean mole equivalent ratio of NO_3^-/SO_4^{2-} for background periods was 0.1 and 0.3 for rainwater and cloud water, respectively, meaning that sulfate exerted a larger average influence on acidity in both media. The NO_3^- to SO_4^{2-} ratio has been used as an indicator of the remoteness of a location [*Weathers et al.*, 1988]; the low NO_3^- to SO_4^{2-} ratio for EP is consistent with its identification as a remote site. High concentrations of NO_3^- and $nss-SO_4^{2-}$ decreased pH values during volcanic ash periods. The acidity in the VA period was again dominated by $nss-SO_4^{2-}$ since the mole equivalent ratio $NO_3^-/nss-SO_4^{2-}$ was lower than unity (0.3) for both cloud water and rainwater (Table 3).

[44] Since NH_4^+ concentrations were low in many samples, Ca^{2+}, Mg^{2+} and K^+ often had significant roles in acid neutralization. For most periods the mole equivalent ratio of $NH_4^+/nss-Ca^{2+}$ was lower than 1 meaning that $nss-Ca^{2+}$ contributed more, on average, to acid neutralization (Table 3). As expected, during AD events the $nss-Ca^{2+}$ made the highest contribution to acid neutralization. However, during the anthropogenic period, NH_4^+ was predominant, presumably being associated with neutralized anthropogenic acidic products (e.g., ammonium sulfate or ammonium nitrate) that may have been transported from other continents. The same patterns were observed for rainwater.

4. Conclusions

[45] Concentrations of water-soluble organic and inorganic species were measured in cloud water, rainwater and aerosol particles collected in Puerto Rico during eight intensive campaigns from December 2004 to March 2007. Overall, the main species detected in cloud water, rainwater,

and aerosol particles were predominantly marine (Na^+, Cl^-) which represented about 70% of total content. The non-sea-salt fraction was dominated by sulfate (17%–25%) with significant contribution of organic carbon (2%–8%) and nitrogen (6%–8%) fractions. Concentrations of organic and inorganic species exhibited a clear dependence on air mass origin for cloud waters, rainwater and aerosol particles. Marine species (Na^+ and Cl^-) show the highest contributions to measured composition marine background air mass (~70% by mass) in both liquid and aerosol particle samples. The concentrations of TOC, TN, NO_3^-, NH_4^+, nss-SO_4^{2-} and nss-Ca^{2+} were largely affected by continental air masses. Increases in sulfate, nitrate and ammonium were observed for all kinds of samples, which is consistent with anthropogenic emissions. Nss-Ca^{2+} is a marker for soil and it was found in high levels during African dust episodes. The levels of the organic fraction also increase during polluted periods corresponding an increase of 60%–110% in the concentrations. The organic fraction, as other species, depends on the seasonal biological activities and long-range transport. The variations among concentrations of species influenced by polluted periods depend on the degree and number of the events that reach the sites. Based on this, the concentrations found in this study are different from the previous ones. pH was clearly dependent on the air mass origins the most important species being nss-SO_4^{2-} and nss-Ca^{2+} in the neutralization process.

[46] Chemical species in cloud water generally exhibited higher concentrations (per unit air volume) than in the aerosol phase. On average, concentrations in cloud water were 2 to 10 times higher than those observed in the aerosol phase. The variations between aerosol particles and cloud water ratios may be affected by the cloud drop uptake of species from the gas phase and cloud drop scavenging of species (e.g., sea salt) that are in coarse mode (aerosol particles not analyzed in this experiment). In agreement with recent studies at EP, the organic fractions were measured in lower concentration than sea salt. The sea salt was more efficiently scavenged into cloud droplets than organic, ammonium and sulfate species. Therefore, coarse particles (e.g., sea salt and mineral dust) would appear to be the most important species that act as cloud condensation nuclei in this marine atmosphere. However, CCN measurements should be taken to confirm this hypothesis.

[47] Although this study was carried out for approximately 3 years, a limited number of samples were taken due to the difficult access to East Peak. For this reason, for some kinds of analyses few samples were available (FAA, OA,) that could induce a misleading interpretation. The major limitation of the work is the fact that LWC and CCN were not measured and the coarse aerosol particles were not analyzed. With this lack of information it was not possible to examine the dependence of pollutants concentrations with dilution factor and also confirm the sea salt as mainly responsible for CCN. New experiments are being planned with more reliable instruments to gather more data that would assist to understand the importance of air masses in the cloud condensation nuclei.

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H. J. C. Bezerra Netto, F. R. de Aquino Neto, and M. da C. K. V. Ramos, Institute of Chemistry, Federal University of Rio de Janeiro, LADETEC, 21941-901 Rio de Janeiro, RJ, Brazil. (radler@iq.ufrj.br)

J. L. Collett Jr., Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523-1371, USA. (collett@atmos.colostate.edu)

S. Decesari, Institute of Atmospheric Sciences and Climate, CNR, I-40121 Bologna, Italy. (s.decesari@isac.cnr.it)

A. Gioda, Department of Chemistry, PUC-Rio, I-22453-900 Rio de Janeiro, RJ, Brazil. (agioda@puc-rio.br)

O. L. Mayol-Bracero and G. J. Reyes-Rodríguez, Institute for Tropical Ecosystem Studies, University of Puerto Rico, San Juan, PR 00936-8377, USA. (omayol@ites.upr.edu)

G. Santos-Figueroa, Department of Chemistry, University of Puerto Rico, San Juan, PR 00931-3346, USA. (gilmarie17@hotmail.com)