P2.19 CHEMICAL CHARACTERIZATION OF CLOUD WATER AT THE EAST PEAK, PUERTO RICO, DURING THE RAIN IN CUMULUS OVER THE OCEAN EXPERIMENT (RICO)

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1. INTRODUCTION

Aerosols interact with radiation and play an important role in climatic processes. They influence the Earth's radiative balance directly by scattering and absorbing solar radiation and indirectly by acting as cloud condensation nuclei (CCN) affecting cloud droplets and cloud albedo (NRC, 1996). Some aerosol particles in the presence of supersaturated water vapor act as cloud condensation nuclei (CCN), which are responsible for the formation of cloud and fog droplets. The constituents in the liquid phase of clouds come from species in aerosol particles scavenged by the droplets, from the dissolution of trace gases within the droplets, or as products of the aqueous phase reaction of precursor species (Fuzzi, 2001). Clouds can accumulate large concentrations of different species in a small volume of cloud water. The concentration in cloud water of a particular species depends on its concentration in the air and on the efficiency by which it is scavenged. Scavenging theories have been used to evaluate the transfer from air to cloud water of a specific species. The first studies of scavenging efficiencies were focused on inorganic constituents, mainly sulfate (Hegg et al., 1984) followed by nitrate and ammonium (Kasper-Giebl et al., 1999). Studies showed that organic aerosols could contribute significantly to the CCN fraction and that they may be present in certain environments in concentrations similar to or even higher than sulfate aerosol (Novakov and Penner, 1993). Nevertheless, few studies have examined scavenging efficiencies to determine organic partitioning between aerosols and cloud water (Facchini et al., 1999: Limbeck and Puxbaum, 2000). Although these studies were not performed in the tropics and/or with marine organic aerosols, they have clearly shown that the organic aerosol composition should be taken into account in determining the hygroscopic behavior and CCN ability of atmospheric aerosols.

This project is part of the international project *Rain In Cumulus over the Ocean Experiment* (RICO) (http://www.ofps.ucar.edu/rico) that seeks to understand the properties of trade wind cumulus with emphasis on the importance of precipitation. It took place during the months of December 2004 and January 2005. Here we determined the inorganic composition of cloud water collected at the East Peak, located at the Caribbean National Forest (the only tropical rainforest that is part of the United States Forest Service) in Puerto Rico. Some measurements of aerosol collected at our reference site (Cape San Juan) were also considered to determine scavenging efficiencies.

2. METHODOLOGY

2.1. Sampling Site

Cloud water samples were collected at the East Peak (EP), in the Caribbean National Rainforest, Puerto Rico (see Figure 1). East Peak is located ~35 km from San Juan and ~20 km from the South Atlantic Ocean at 1020 m.a.s.l. in a tropical rainforest. The area is a humid mountaintop with frequent and abundant cloud coverage fed by high altitude trade winds. The average yearly precipitation and temperature are about 4000 mm per year and 22.2 °C, respectively. Cape San Juan (CSJ), located at the most northeastern part of Puerto Rico, is our reference site used to collect aerosol samples.

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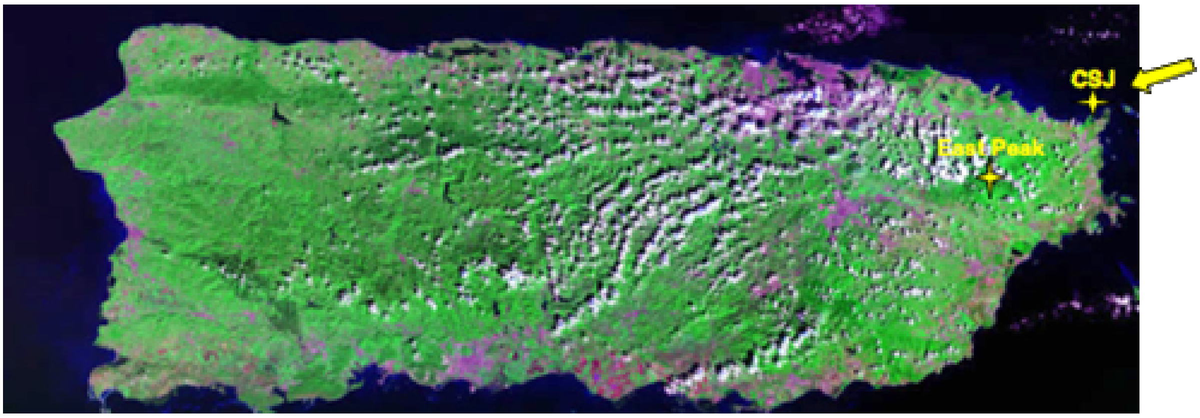


Figure 1. Location of East Peak (EP) and Cape San Juan (CSJ). The arrow indicates the predominant wind direction**.**

2.2. Sampling and analysis

Cloud water samples were collected using a single-stage Caltech Active Strand Cloud water Collector (ss-CASCC). Immediately after the samples were collected, pH measurements were performed (at the site). The samples were transported in coolers and stored in a freezer (-18^{o} C) until further analysis. pH measurements were performed again prior to the analysis with ion chromatography (IC). The water-soluble ions analyzed were acetate (Ace), formate (For), oxalate (Ox), methane sulfonic acid (MSA), chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), ammonium (NH_4^+), calcium (Ca^{2+}), hydrogen (H^+), magnesium (Mg^{2+}), potassium (K^+) and sodium (Na^+). The details about the analyses are presented by Gioda et al. (2006). Aerosol filter sampling was conducted with stacked-filter units (SFUs, NILU) during daytime, nighttime, and integrated day and night times. The filters were extracted with high-purity water in order to characterize the soluble fraction. The CSJ aerosol samples were used with these data to determine scavenging efficiencies.

Meteorological data was collected at both sites. To determine the origin of the air masses, backward trajectories (BTs) were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectories (HYSPLIT) computer model (Draxler, 1997).

3. RESULTS AND DISCUSSION

Eight cloud water samples were analyzed with average cloud water collection rate of 1.4 mL/min. Averages and ranges of ion concentrations (µeq/L) in cloud water from East Peak are presented in Table 1.

Table 1. Ionic concentrations (µeq/L) for the cloud water samples taken at East Peak.

Species	**Range**	**Average**
	Conc. (µeq/L)	Conc. (µeq/L)
Acetate (Ace)	0.25-1.23	0.57
Formate (For)	0.06-2.88	0.91
Methane sulfonic acid (MSA)	0.09-0.92	0.25
Oxalate (Ox)	0.23-6.68	1.72
Chloride (Cl^-)	159.45-674.92	426.72
Nitrate (NO_3^3)	2.22-84.89	24.26
Sulfate (SO_4^{2-})	27.86-98.07	59.65
Ammonium (NH_4^+)	1.93-6.01	4.14
Calcium (Ca^{2+})	7.69-27.63	18.23
Hydrogen (H^+)	0.01-0.14	0.04
Magnesium (Mg^{2+})	37.81-153.48	103.11
Potassium (K^+)	2.59-12.42	7.72
Sodium (Na^+)	165.11-675.55	455.29

The predominant inorganic species were Na^+ (average of 455.3 µeq/L) and Cl^- (426.7 µeq/L), which are the primary components of sea salt. These species are produced by the sea surface activity of the nearby Atlantic Ocean. The ion abundances were: $Na^+ > Cl^- > Mg^{2+} > SO_4^{-2} > NO_3^- > Ca^{2+} > K^+ > NH_4^+ >$ Ox > For > Ace > MSA > H^+ (Table 1). In two previous studies at the same site, similar ion abundances were obtained for the 4 most abundant ions (Asbury et al., 1994; Weathers et al., 1988). On the other hand, the East Peak ion composition varies significantly from that observed in California (Collett et al., 1999). These differences could result from the sources for the ions. In California, anthropogenic sources were dominant, as indicated by the high concentrations of SO_4^{2-}, NO_3^-, and NH_4^+, while in Puerto Rico the sources were basically marine (Na^+, Cl^-). Backward trajectory (BTs) indicated that from January 4-19 the air masses were mainly from the northeast. However, starting on the 20th, the air masses started to come from North America. In this period the highest concentration of sulfate (98 µeq/L) and nitrate (85 µeq/L) were measured. When NO_3^- and SO_4^{2-} were normalized by Na^+ concentrations, SO_4^{2-}/Na^+ (0.17-0.24) and NO_3^-/Na^+ (0.14-0.19) ratios were higher than those found in seawater ($SO_4^{2-}/Na^+ \sim 0.12$ and $NO_3^-/Na^+ \sim 0$), consistent with anthropogenic inputs due to air masses arriving from the US continent.

Conductivity and ion total concentrations were correlated for each sample (Figure 2). In this study the measured conductivity (CM) ranged from 30 to 94 µS/cm (average of 61 µS/cm), while ion total concentrations varied from 420 to 1,656 µeq/L (average of 1,102 µeq/L). A good correlation ($r^2 = 0.87$) was obtained between ion total concentrations and measured conductivity during the sampling period.

We also calculated the conductivity in order to check the results of chemical analyses. To calculate the conductivity was used the following equation (1):

$$CE = \Sigma \lambda_i c_i \qquad \text{Eq. (1)}$$

Where CE is the calculated conductivity; λ_I is the equivalent ionic conductance at infinite dilution and at given temperature, and c_i is the individual ion concentration.

The percentage difference (CD) between conductivities was also determined according to equation 2:

$$CD = 100*(CE-CM)/CM \qquad \text{Eq. (2)}$$

A CD value no more than 2% should be obtained between measured and calculated conductivity for deposition samples (Miles and Yost, 1982). Mosello et al. (2002) in interlaboratorial validation studies for precipitation considered acceptance threshold values of 10% for conductivity higher than 20 µS/cm. In our study, an average CD of 11% was obtained. The most significant difference was observed on January 16 (see Figure 2) reaching 54%. In this date probably losses of more reactive and/or volatile species (NH_4^+ and NO_3^-) could have occurred. Analytical errors also could be a factor. Also contributing could be unidentified ion species including various organic compounds.

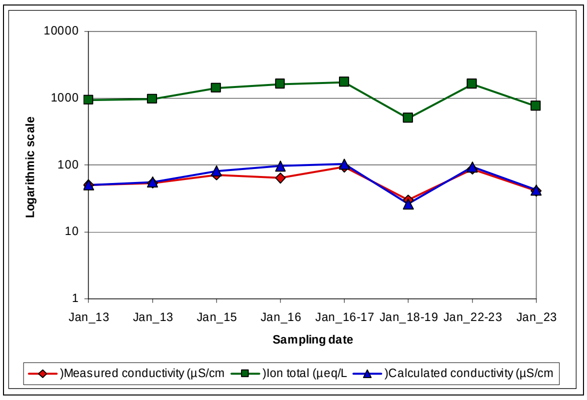
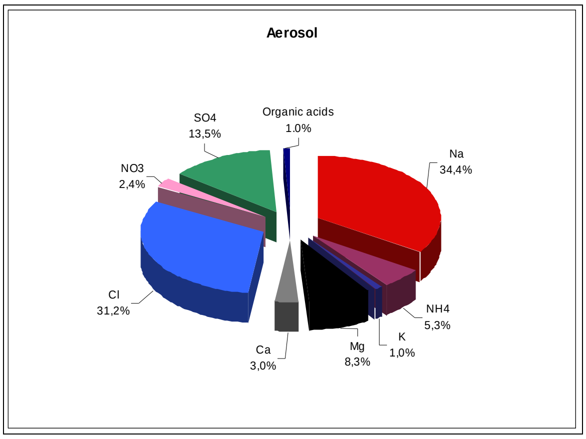


Figure 2. Ion total (µeq/L) and conductivity (µS/cm) variations of cloud water samples collected at the East Peak.

Different pH values were measured at the sampling site and at the laboratory. Values for pH measured at the laboratory ranged from 6.5 to 8.2 while at the site were 4.8 to 6.4. When H^+ concentrations were calculated, a significant reduction (up to 90%) was observed for pH measurements at the field (0.4 to 17.4 µeq/L H^+) and at the laboratory (0.007 to 0.18 µeq/L H^+).

These losses of H^+ probably occurred during the long storage time (about 6 months) since the samples were not preserved with biocide but only kept frozen. Previous studies have attributed losses of H^+ to degradation of organic acids by microbial activity, dissolution of particulate matter, and ion exchange processes involving the walls and/or lid of the shipping container (Bigelow et al., 1989). In our study carboxylic acids also had a small contribution. The percentage of organic acids (3.2%) was much lower when compared to mineral acids (SO_4^{2-} and NO_3^-) (96.8%). In general, the acid concentrations in cloud water and aerosol corresponded only 0.3 to 1% of the total ions, respectively (Figure 3). These low levels could indicate loss of organic acids.

To understand the transfer process of water-soluble ions from aerosols to cloud water we determined aerosol scavenging efficiencies using aerosol samples collected in our upwind background sampling site (CSJ). The comparison between ion concentrations in aerosol and cloud water is shown in Figure 3.



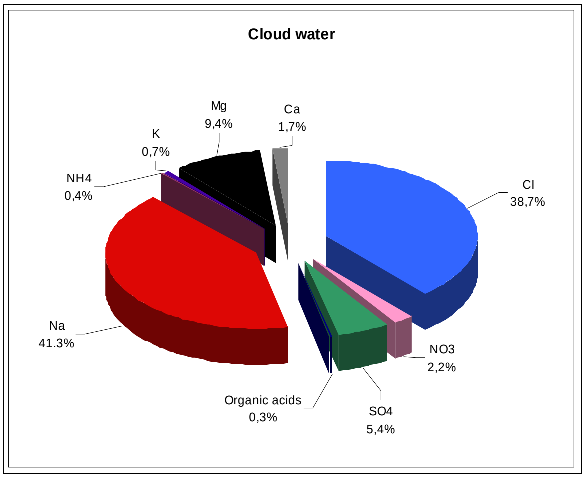


Figure 3. Abundance of ions (in percentage of µeq/L) of East Peak cloud water samples and CSJ aerosol samples. Organic acids = ∑ [Ace, For, MSA and Ox].

For both aerosol and cloud samples the predominant ions were Na$^+$ (34 and 41%), Cl$^-$ (31 and 39%), SO$_4^{2-}$ (5 and 14%), and Mg^{2+} (8 and 9%).

We calculated the scavenging efficiencies for water-soluble ions by the cloud but the values were typically higher than 100%. Possible reasons for these high values could have been the scavenging of gases such as HCl, SO$_2$, HNO$_3$, NH$_3$, HCOOH and CH$_3$COOH, the possibility of having different air masses involved in the scavenging since aerosol samples were not collected at the same location as the cloud samples, and/or problems in an accurate conversion of collection rate to liquid water content. All of these factors could introduce a positive artifact increasing the [cloudwater]/[aerosol] ratios.

4. CONCLUSIONS

This study provides important information about the chemical composition of cloud water in a background tropical marine region where few studies have been conducted. Here we are presenting the water-soluble ions in cloud water collected at the East Peak as part of the RICO project. Preliminary findings showed a considerable variation in pH average values measured at the site (5.8) and at the laboratory (7.4). Losses of organic acids due to microbiological degradation could be the main factor in pH unit increases. The conductivity was directly related to the concentrations of ions, showing that the conductivity index was determined by the ions present in the samples. The most abundant species were sodium and chloride. This is supported by the proximity of the site to the ocean and the NE predominant wind direction. The origin of the air masses had an effect in the ion concentrations, as shown by the differences between the air masses coming from NE and those coming from the continental US. According to our investigation, both sea salt ions and sulfate are incorporated efficiently into cloud drops. Changes in sea salt or sulfate aerosol concentrations,, consequently, could alter regional cloud formation processes.

Presently, aerosol and cloud samples are being collected at the East Peak location, and aerosol samples are collected at the CSJ station. The new results that will be generated here together with the information that we have already produced will contribute to a better understanding of what species in the aerosol phase are more efficiently removed by clouds. This will provide information in terms of the residence times of these aerosol species in the atmosphere and will, therefore, contribute to a better understanding of how aerosols impact the microphysics of trade wind cumuli.

5. REFERENCES

Asbury, C. E., McDowell, W. H., Trinidad-Pizarro, R., Berrios, S., 1994: Solute deposition from cloud water to the canopy of a Puerto

Rican montane forest. Atmos. Environ**.**, **28**, 1773-1780.

Bigelow, D. S., Sisterson, D. L., Schroder, L. J., 1989: An interpretation of differences between field and laboratory pH values reported by the National Atmospheric Deposition Program/National Trends Network Monitoring Program. Environ. Sci. Technol., **23**, 881-887.

Collett, Jr., J. L., Hoag, K. J., Sherman, D. E., Bator, A and Richards, L. W., 1999: Spatial and temporal variations in San Joaquin Valley fog chemistry. Atmos. Environ., **33**, 129-140.

Draxler, 1997: HYSPLIT (HYbridSingle-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD.

Facchini, M. C., Fuzzi, S., Zappoli, S., et al., 1999: Partitioning of the organic aerosol component between fog droplets and interstitial air. J. Geophys. Res., **104D**, 26821-26832.

Fuzzi, S., 2001: IGAC Newsletter, http://www.igac.noaa.gov/newsletter/23

Gioda, A., Rodríguez, A. I., Morales, F., Morales, R., Decesari, S., Emblico, L., Collett, J., Mayol-Bracero, O. L., 2006: Chemical composition of clouds in the Caribbean National forest during the RICO project. J. Geophys. Res.: Atmos. To be submitted in May/2006.

Hegg, D. A., P. V. Hobbs and L. F. Radke L. F., 1984: Measurements of the scavenging of sulfate and nitrate in clouds. Atmos. Environ., ***18***, 1939-1946.

Kasper-Giebl, A., Kalina, M. F., Puxbaum, H., 1999: Scavenging ratios for sulfate, ammonium and nitrate determined at Mt. Sonnblick (3106 m a.s.l.), Austria, Atmos. Environ., **33**, 2647-2659.

Limbeck, A., Puxbaum, H., 2000: Dependence of in-cloud scavenging of polar organic aerosol compounds on the water solubility. J. Geophys. Res., **105**, 19857-19867.

Miles, L. J., Yost, K. J., 1982: Quality analysis of USGS precipitation chemistry data for New York., Atmos. Environ., **16**, 2889-2898.

Mosello, R., J. Derome, K. Derome, E. Ulrich, T. Dahlin, A. Marchetto & G. Tartari. 2002: Atmospheric deposition and soil solution Working Ring Test 2002. E.U. Technical Report, Fontainebleau, France.

National Research Council (NRC), 1996: Aerosol radiative forcing and climate change, National Academic Press, Washington, D.C.

Novakov, T., Penner, J. E., 1993: Large contribution of organic aerosols to cloud-condensation-nuclei concentrations. Nature, **365**, 823-826.

Weathers, K. C., Likens, G. H., Borman, F. B. et al., 1988: Cloud chemistry from ten sites in North America. Atmos. Environ., **22**, 1018-1026.