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# 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.

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## 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.



## 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.