

Water-soluble organic and nitrogen levels in cloud and rainwater in a background marine environment under influence of different air masses

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Abstract Chemical characterization was performed on cloud and rainwater samples collected as part of the *Rain In Cumulus over the Ocean Experiment* (RICO). This experiment took place at a mountaintop site (East Peak) in Puerto Rico from December 2004 to March 2007 in order to determine water-soluble organic and nitrogen fractions in a marine background environment. For cloud water, similar average concentrations of 1.0 (± 0.3) mg/L were found for total organic carbon (TOC) and total nitrogen (TN) and an average concentration of 0.8 (± 0.2) mg/L was found for dissolved organic carbon (DOC). In rainwater, these concentrations were lower, ranging from 0.3 to 0.5 (± 0.1) mg/L. Changes in the concentrations of these species were observed in periods under the influence of anthropogenic, African dust, and volcanic ash air masses. In these periods the concentrations of TOC, DOC, and TN were 2 to 4 times higher than in periods under the influence of trade winds. The insoluble organic material arriving during African dust events showed total carbon (TC) concentrations on averaging 1.5 mg/L for cloud water. The TC was composed mainly of organic carbon with polar compounds from low to high molecular weight (MW). The polar compounds with high MW were probably associated with pollution (e.g., fossil fuel combustion) from other regions. Crustal species (Al and Fe) dominated particles associated with dust episodes, confirming the soil origin. Our results suggested that a fraction (40–80%) of TOC and (<100%) of TN in Puerto Rican

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cloud/rainwater could be originated from long-range transport of dust, ash and/or pollution.

Keywords Saharan dust · Volcanic ash · Air masses · Fogwater · Nutrient flux · Elemental composition · Precipitation

1 Introduction

In the atmosphere, carbon and nitrogen particles influence the earth's radiative budget directly by scattering and absorbing solar radiation and indirectly by modifying cloud properties and persistence through their activity as cloud condensation nuclei (CCN). Interactions of carbon and nitrogen containing species with clouds and precipitation are central to understanding their atmospheric cycling, especially their removal processes and their impacts on climate and ecosystems.

Clouds and precipitation remove atmospheric aerosols and add nutrients to terrestrial and aquatic ecosystems. These substances are found in clouds and rain as organic and inorganic compounds in both dissolved and particle forms. In the past research has concentrated mainly on the inorganic components in clouds and rainwater (Weathers et al. 1988; Watanabe et al. 2001; Collett et al. 2002; Aiuppa et al. 2003), focusing especially on sulfate production and removal. However, the characterization of the organic fraction of cloud water and precipitation remains limited, although it is increasing. Some attention has been given to total organic carbon (TOC) (Collett et al. 1999; Straub et al. 2007) and its constituent phases and dissolved organic carbon (DOC) in cloud and/or rainwater (McDowell et al. 1990; Willey et al. 2000; Kieber et al. 2002; Herckes et al. 2002; Neal et al. 2005). Only few studies have considered the undissolved particulate form (POC) in cloud or rainwater (Hadi et al. 1995; Keene et al. 2002; Blanco et al. 2003).

Most of the studies that deal with the nitrogen content of rain or cloud water have also focused on inorganic species (IN), especially ammonium and nitrate. Some measurements have been made of total nitrogen (TN), which is composed of inorganic and organic forms. The inorganic forms were extensively studied due to their significance for acid rain while organic nitrogen (ON) has been largely ignored for decades. Atmospheric organic nitrogen is an important part of the global nitrogen cycle and, like IN, can influence atmospheric visibility, climate forcing, atmospheric photochemistry, and can be deposited on sensitive ecosystems. ON may also help to buffer acids in fog water (Zhang and Anastasio 2001). The widespread occurrence of organic carbon and nitrogen in the atmosphere and their potentially important effects in cloud and rainwater justify their further study.

Characterization of background levels of organic carbon (OC) and nitrogen compounds is essential to understand the extent of anthropogenic vs. natural influence on cloud and rainwater chemistry. Puerto Rico is a good place to study the influence of anthropogenic and natural sources since throughout the year it is exposed to air masses of different origin. During wintertime the island can be influenced by anthropogenic pollution when air masses from North America reach the Caribbean (Savoie et al. 1989; Asbury et al. 1994; Gioda et al. 2008). During the summer, air masses carrying dust from North Africa reach Puerto Rico (Gioda et al. 2007; Heartsill-Scalley et al. 2007). In Barbados, another island in the Caribbean, the concentrations of particles reached about $100 \mu\text{g}/\text{m}^3$ during African dust events, that is up to ten times

greater than the background levels ($10 \mu\text{g}/\text{m}^3$) (Prospero and Nees 1986). This mineral dust may have an impact on climate, marine biogeochemical processes, water, and air quality (Jickells 1999). Volcanic ash from the Soufriere Hills volcano, on Montserrat island (500 km distant), can also reach PR when winds blow from the southeast (Gioda et al. 2007; Heartsill-Scalley et al. 2007). All these events could change significantly the chemical composition of cloud and rainwater in Puerto Rico.

The objective of this study was to characterize organic and nitrogen species in cloud/rainwater from a tropical marine environment, with minimal local input, in order to improve understanding of the concentrations of these compounds in atmospheric water during periods of varying air mass influence. This project is part of the *Rain In Cumulus over the Ocean Experiment* (RICO, <http://www.eol.ucar.edu/rico/>).

2 Experimental

2.1 Site

Cloud/rainwater samples were collected at East Peak (EP), a mountaintop in Luquillo, PR that is part of the El Yunque National Forest (EYNF). East Peak is located in a tropical rainforest ($18^{\circ}16' \text{ N } 65^{\circ}45' \text{ W}$) at an altitude of 1050 m asl. During the sampling period an average annual precipitation of 4300 mm and annual mean temperature of 19°C were measured. The site is mainly influenced by northeasterly trade winds, bringing clean air from the North Atlantic Ocean, but it is also impacted under certain conditions by the long-range transport of pollutants. Local anthropogenic pollution is minimized, as long as the site is under the influence of the trade winds, because of the proximity to the coast (10 km) and the absence of local industries and other potential sources of anthropogenic pollution upwind.

2.2 Meteorological data, satellite images and back trajectories

Meteorological data, back trajectories, and satellite images were used to identify the origins of the sampled air masses. Five-day back trajectories were calculated for each sampling day using the Hybrid Single-Particle Lagrangian Integrated Trajectories (HYSPLIT) model (Draxler and Rolph 2003). 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 Navy Research Laboratory/ Monterey Aerosol (<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 Soufrière Hills volcano at the island of Montserrat. For volcano eruptions, data from the Montserrat Observatory website (<http://www.mvo.ms>) were also used.

2.3 Sampling

Bulk precipitation and cloud water were collected during 8 intensive field campaigns from December 2004 to March 2007. A total of 45 cloud interception events and 17 precipitation events were sampled during this period. Fog/cloud water was sampled using a compact aluminum version of the Caltech Active Strand Cloudwater Collector (Al-CASCC2); rainwater was collected using an amber glass bottle with a stainless steel funnel. Both collectors were placed at about 2 m height to avoid splash contamination. The collection of

both cloud and rainwater samples was done in a large open area $\sim 300 \text{ m}^2$ with no nearby trees. The cloud sampler was operated in the following way: when the visibility was less than 200 m for 10 min the collector was turned on and a glass amber bottle (500 mL) was installed with the bottle mouth covered with aluminum foil. The first 30–50 mL of sample was discarded. The collector was turned off when rain started or cloud interception ended. The rain sampler was put out just before an event; the first five minutes of rain were discarded and additional rain was collected until the end of event. Samples were collected only during the day, monitored by on-site personnel and were removed just after the end of each event. Cloud and rain collectors were thoroughly cleaned before each event as described below. These procedures minimized contamination by dry deposition or evaporated sample residuals between cloud and rain events. pH and conductivity measurements were performed in the field immediately after sample collection. The samples were split into aliquots in order to analyze total organic carbon, dissolved organic carbon, and total nitrogen (TOC, DOC, and TN). For DOC analyses, the samples were filtered with a $0.45 \text{ }\mu\text{m}$ pore-size membrane (SP15, Sartorius, Germany). All samples were stored in pre-baked glass bottles, immediately preserved (HCl pH<2.0 for TOC, DOC and chloroform for TN), refrigerated to 4°C , and typically analyzed upon arrival at the laboratory. Any samples that were not analyzed immediately were frozen at -18°C until analysis.

2.4 Chemical analysis

TOC, DOC, and TN were analyzed by a high temperature catalytic oxidation (HTCO) method. Analyses were performed using a TOC analyzer coupled to a nitrogen chemiluminescence detector (Shimadzu TOC-V 5500/TNM-1, Kyoto, Japan). TOC standards were prepared from reagent grade potassium hydrogen phthalate and TN standards from potassium nitrate in Milli-Q water. TOC, DOC and TN concentrations were calculated with the instrument software and a 5-point standard calibration curve that ranged from 0.05 to 2 mg/L. 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).

Insoluble particles present in cloud and rainwater were filtered using a pre-baked 25-mm quartz filter, and dried in a dessicator before analysis. The quartz filters containing the extracted particulate matter then underwent thermal/optical analyses (EC/OC Analyzer, Sunset Lab Inc.) in order to determine total carbon (TC), organic carbon (OC) and elemental carbon (EC) (Mayol-Bracero et al. 2002). In an oxygen-free helium atmosphere, the sample is heated increasing temperature steps to remove all organic carbon on the filter. The transition from the third temperature to the fourth (from 500 to 700°C) will quickly decompose inorganic carbonates, producing a sharp, characteristic peak. As the organic compounds are vaporized, they are immediately oxidized to carbon dioxide in an oxidizer oven. The flow of helium, containing the carbon dioxide, then goes to a methanator oven where the CO_2 is reduced to methane. The methane, then, is detected by a flame ionization detector (FID). Selected filters were also qualitatively analyzed using scanning electron microscopy (SEM-JEOL JSM-6480) equipped with an Oxford X-ray energy dispersive detector (Jeol Ltd. Tokyo, Japan) to determine the elemental composition (Blanco et al. 2003).

2.5 Quality control (QC) of samples and statistical analyses

Samplers were cleaned in the laboratory with 1:100 aqueous solution of Triton X-100 surfactant and rinsed with copious quantities of Milli Q water. In the field, the samplers

were cleaned again with Milli Q water before and after the sampling. After sampling, they were also covered with aluminum foil and plastic protection to avoid contamination. Field blanks were collected before each event. After cleaning, approximately 200 mL of water was sprayed onto the collectors to collect the blanks. The blanks were analyzed in the same way as the samples. Average blanks were subtracted from the samples.

Statistical analyses were performed using the computerized software program “Graph-Pad Prism” version 4.0a. The *t*-test and linear regression analyses were performed to establish statistical differences at the 95% confidence interval between TOC, DOC and TN concentrations under influence of different air masses.

3 Results and discussion

3.1 TOC, DOC, and TN concentrations

Concentrations of TOC, DOC, and TN in cloud and rainwater measured in Puerto Rico are presented in Table 1. Average concentrations during 45 cloud events (December 2004 to March 2007) were 1.1 mg/L for TOC, 0.8 mg/L for DOC, and 1.0 mg/L for TN. Concentrations as high as 3.0 mg/L of TOC were measured in these samples. The volume-weighted means (VWM) of 17 rainwater samples collected from July 2006 to March 2007 were 0.3 mg/L for TN, 0.4 mg/L for DOC, and 0.6 mg/L for TOC. Concentrations of TOC and DOC were two times higher, and TN concentrations were 4 times higher, in cloud

Table 1 Monthly concentrations of TOC, DOC, and TN in cloud and rain water collected at East Peak, Puerto Rico from December 2004 to March 2007. Concentrations in mg/L for cloud water and volume-weighted means (VWM) for rainwater

Month	Cloud water (mg/L)		
	TOC	DOC	TN
December 2004 (<i>n</i> =5)	0.60 (±0.31)	0.48 (±0.32)	0.54 (±0.21)
January 2005 (<i>n</i> =14)	0.73 (±0.41)	0.55 (±0.33)	0.40 (±0.10)
July 2006 (<i>n</i> =5)	1.10 (±0.71)	0.98 (±0.54)	1.34 (±0.70)
August 2006 (<i>n</i> =4)	0.79 (±0.26)	0.62 (±0.31)	1.03 (±0.60)
November 2006 (<i>n</i> =4)	1.18 (±0.11)	0.91 (±0.11)	0.92 (±0.20)
December 2006 (<i>n</i> =4)	1.57 (±0.80)	1.52 (±0.91)	1.08 (±0.53)
January 2007 (<i>n</i> =3)	0.72 (±0.32)	0.50 (±0.22)	1.03 (±0.51)
March 2007 (<i>n</i> =6)	1.13 (±0.71)	0.71 (±0.21)	0.76 (±0.31)
Average (<i>n</i>=45)	1.10 (±0.33)	0.79 (±0.42)	1.01 (±0.31)
Month	Rain (VWM)		
	TOC	DOC	TN
July 2006 (<i>n</i> =2)	1.02 (±0.41)	0.80 (±0.20)	0.55 (±0.15)
November 2006 (<i>n</i> =3)	0.64 (±0.32)	0.47 (±0.11)	0.28 (±0.05)
December 2006 (<i>n</i> =3)	0.61 (±0.30)	0.38 (±0.13)	0.22 (±0.10)
January 2007 (<i>n</i> =3)	0.23 (±0.11)	0.15 (±0.03)	0.18 (±0.02)
March 2007 (<i>n</i> =6)	0.76 (±0.23)	0.40 (±0.10)	0.31 (±0.31)
Average (<i>n</i>=17)	0.58 (±0.32)	0.38 (±0.11)	0.27 (±0.12)

water than in rainwater. Cloud solute concentrations are often higher than precipitation solute concentrations. This is due to smaller dilution of collected particles and gases in clouds. The average pH values measured in cloud water (5.8) and rainwater (5.0) collected at East Peak (EP) were similar to those for other remote marine areas (~5.0–5.6) (Collett et al. 1999).

A fraction of the organic matter present in cloud and rain can be insoluble. The amount of insoluble material depends strongly on the composition of aerosol particles scavenged by cloud drops (Herckes et al. 2002). 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%). This could be due to African dust events that were more frequent during the summer (discussed below).

Based on water collection rates from the AI-CASCC2, the calculated liquid water content (LWC) was negatively correlated with TOC and DOC concentrations ($r=-0.4$) and TN ($r=-0.5$), showing that TOC, DOC, and TN concentrations decreased as LWC increased. For rainwater, the volume sampled was also negatively correlated with TOC and DOC ($r=-0.5$) and TN ($r=-0.6$). These inverse correlations were probably the result of dilution. For example, if the same amounts of carbon and nitrogen are scavenged by two clouds, the cloud with higher LWC will have lower aqueous concentrations of the scavenged species. Likewise, if a fixed amount of material is scavenged by two precipitation events, the one that deposits more rain will also have, on average, lower concentrations of these species. Differences in scavenging efficiency, the amount of particles and gases available to be scavenged, or chemical reactions in the cloud water can all mask these simple dilution effects (Marinoni et al. 2004).

3.2 Comparison with other marine remote areas

There has been little research on TOC, DOC, and TN in cloud and rainwater from tropical or remote environments. In Puerto Rico, measurements of TOC, DOC and TN have been done separately for cloud water or rainwater (McDowell et al. 1990; Asbury et al. 1994; Heartsill-Scalley et al. 2007). Bulk precipitation during 4 years (1983–1987) at El Verde, a site at an elevation of 380 m asl EYNF, showed an average rainwater DOC concentration of 0.63 mg/L (McDowell et al. 1990). This was higher than the average DOC measured at EP in this study (0.36 mg/L). More recently, over 1985–2000, higher rainfall concentrations of DOC (3.6 mg/L) and lower concentrations of TN (0.14 mg/L) were found (Heartsill-Scalley et al. 2007). The reduced number of rainwater samples collected in our studies (17 samples), different locations (EYNF 1050 m asl vs 380 m asl) and change in methodologies probably also contributed to the differences between our studies and previous ones. However, an earlier study at EP (Asbury et al. 1994) measured concentrations of TN in cloud water (0.9 mg/L) comparable to our study (1.0 mg/L).

Our results are similar to those from other relatively clean regions. The differences in concentrations of TOC and DOC in cloud water in different regions may be due to variations in LWC, cloud life span, and anthropogenic inputs (Neal et al. 2005). The average DOC concentration in rainwater at EP (0.4 mg/L) was similar to that at the Eneweak Atoll in the western North Pacific (0.3 mg/L) (Zafiriou et al. 1995) which are the lowest averages found in the literature. North of Samoa, New Zealand, and Costa Rica, averages of 0.7 mg/L were measured (Kieber et al. 2002; Eklund et al. 1997). Near a coastal hilltop site in Mid-Wales, the average DOC (1.5 mg/L) in cloud water was substantially

higher than that in bulk precipitation (0.6 mg/L) (Reynolds et al. 1996). Another study in mid-Wales also detected higher DOC concentrations in clouds (2.4 mg/L) than in rainwater (0.7 mg/L) (Neal et al. 2005). Our results for TOC (average of 1.1 mg/L) in cloud water were comparable to those measured in clouds in the NE Pacific Ocean off the coast of southern California (0.85 mg/L) (Straub et al. 2007), a region that could also have anthropogenic influence due to long-range transport of pollutants. In rainwater collected over the open ocean, TOC and DOC concentrations averaged 1.6 mg/L and 1.5 mg/L, respectively, with OC mostly in the dissolved form (Sempere and Kawamura 1996).

The organic fraction (DOC and TOC) of cloud water at human-influenced sites can be much higher than at remote locations. DOC for clouds in rural Scotland averaged 3.6 mg/L (Hadi et al. 1995). DOC at Whiteface mountain (NY) ranges from 5.1 to 11.4 mg/L (Khwaja et al. 1995). At another continental mountain location (Puy de Dôme, France) DOC averaged 5.4 mg/L (Marinoni et al. 2004). Although these sites were in rural areas, the authors suggested that anthropogenic sources were consistent with the higher TOC and DOC levels. In fog water at a rural agricultural site, DOC concentrations were as high as 7.8 mg/L and TOC was as much as 10 mg/L (Herckes et al. 2002). At Davis, Central Valley, CA, anthropogenic influence resulted in levels up to 70 mg/L for TN and 30 mg/L for DOC in fog water (Zhang and Anastasio 2001).

Rainwater TN measured in Puerto Rico (0.3 mg/L) was similar to levels that have been observed in New Guinea and Costa Rica (0.2 mg/L), but lower than in other tropical montane regions influenced by human activity such as Colombia (0.6 mg/L) and Venezuela (0.9 mg/L) (Veneklass 1990; Eklund et al. 1997). The low levels of N at less impacted sites probably reflect a lack of fire, small anthropogenic inputs and clean air masses. Nitrogen at a remote Pacific island (average of 0.7 mg/L) was higher than in East Peak, and the DOC fraction was much higher (8.7 mg/L) (Weathers et al. 2000). In eastern North America lower concentrations of TN were found in precipitation (0.3 to 0.7 mg/L) with visible particles in some samples (Keene et al. 2002). Concentrations of TN in cloud water samples with particles averaged 1.1 mg/L; and those without visible particles had an average TN concentration of 0.65 mg/L (Keene et al. 2002). These higher concentrations were most probably due to the adherence of nitrate compounds to particles.

3.3 Air mass origin

Although the average levels of TOC, DOC, and TN at EP were more similar to those at remote locations than those at places with large anthropogenic influence, the chemical composition of clouds and rainwater samples varied with changes in the origin of the air masses. We assumed that long-range transport affected precipitation/cloud chemistry at EP. Therefore, samples were classified according to the origin of the corresponding air masses. Back trajectories, satellite images (AOT and TOMS) and meteorological data helped to identify the main origin of the air masses. We classified samples according to four observed air mass trajectories: North Atlantic Ocean (NAO) which was considered as clean air; Tropical Atlantic (TA) representing air masses associated with dust events from the African continent; South Atlantic Ocean (SAO) representing air masses associated with ash from the Soufriere Hills volcano on the Caribbean island of Montserrat; and North America (NA) referring to anthropogenically influenced air masses from North America (Fig. 1). “Clean” air masses are defined here as air masses free of major anthropogenic sources, free of African dust, and free of volcanic ash. Levels of organic and nitrogen fractions varied significantly among sampling periods. The clean periods showed the lowest concentrations for both cloud water (0.7 mg/L for TOC; 0.5 mg/L for DOC and 0.4 mg/L for TN) and

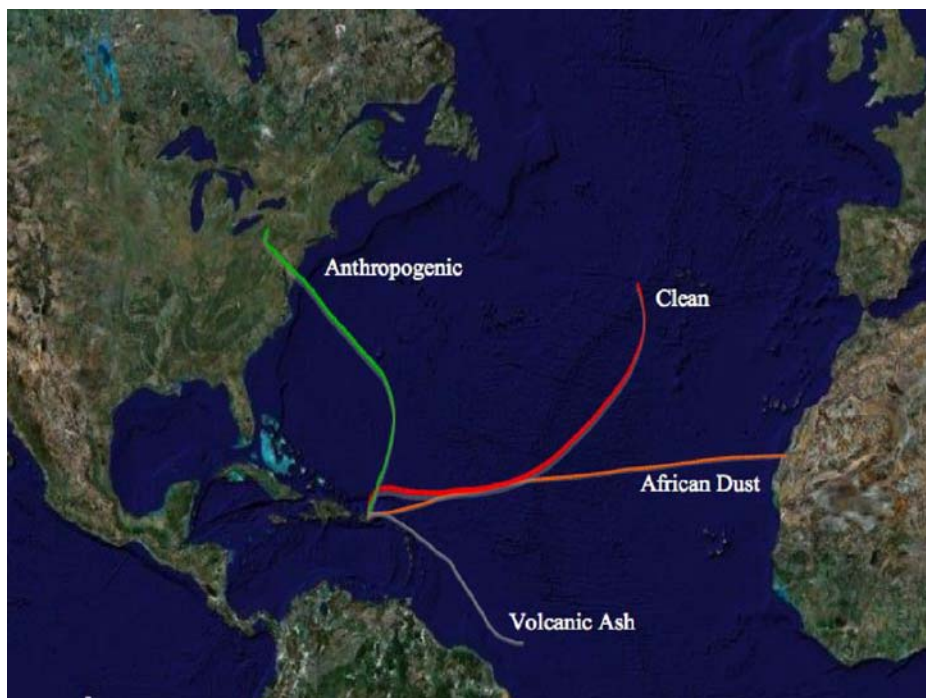


Fig. 1 Representation of the main air mass backward trajectories: North Atlantic Ocean was considered as clean air *C*; Tropical Atlantic represents air masses associated with African dust events *AD*; South Atlantic Ocean represents air masses associated with volcanic ash from the Soufriere Hills volcano *VA*; and North America refers to anthropogenic air masses *A*

rainwater (0.4 mg/L for TOC; 0.3 mg/L for DOC and 0.2 mg/L for TN). On the other hand, the highest levels of TOC, DOC, and TN were found in clouds and rainwater from the periods with anthropogenic and/or dust air masses (Table 2).

Anthropogenic influence in northeast Puerto Rico was mainly observed in winter on days when air masses arrived from North America to the island. Influence from upwind Caribbean islands was also possible. The back trajectories indicated that on some days in January 2005 and November/December 2006, air masses arrived from North America or other Caribbean Islands. During January 2005, the concentrations of ions of potentially anthropogenic origin (H^+ , NO_3^- , nss-SO_4^{2-} and organic acids) were significantly higher for air masses from the NW than for air masses from the NE (Gioda et al. 2008). For both cloud and rainwater the highest average concentrations of TOC, DOC, and TN were observed during the anthropogenic period (Table 2), when these concentrations were 2 to 3 times higher than for the clean period. These species differed significantly between the clean and anthropogenic periods, with *P* values lower than 0.05 (Table 2). The main origin of OC and N was probably pollution (e.g., industry, fossil fuel use) from North America or from upwind Caribbean Islands.

TOC and TN in cloud and rainwater were also higher during dust events (Table 2). TN was higher than TOC in cloud water samples when air masses brought mineral dust from Africa (Jul/Aug 2006) or volcanic ash (Jan 2007) from the Soufriere Hills. *T*-testing confirmed a significant difference between concentrations, with *P* values <0.05 (Table 2). At the same sampling location, we carried out another study in which the same patterns for

Table 2 *T*-test for TOC, DOC and TN in cloud (mg/L) and rainwater (volume-weighted means) for different periods: *C* clean; *A* anthropogenic; and *AD* African dust

Parameter	Cloud water					
	TOC	TOC	DOC	DOC	TN	TN
	C vs. A	C vs. AD	C vs. A	C vs. AD	C vs. A	C vs. AD
<i>P</i> value	0.0022	0.0053	0.0054	0.0073	0.0001	0.0001
Means signif. different ($P < 0.05$)	Yes	Yes	Yes	Yes	Yes	Yes
Mean \pm Stdev	0.72 \pm 0.11	0.72 \pm 0.11	0.48 \pm 0.09	0.48 \pm 0.09	0.36 \pm 0.06	0.36 \pm 0.06
- (n) - clean	(n=18)	(n=18)	(n=18)	(n=18)	(n=18)	(n=18)
Mean \pm Stdev	A	AD	A	AD	A	AD
- (n) -	1.3 \pm 0.15	1.2 \pm 0.14	1.03 \pm 0.16	1.2 \pm 0.29	1.0 \pm 0.13	1.5 \pm 0.26
A or AD	(n=16)	(n=9)	(n=16)	(n=9)	(n=16)	(n=9)
R ²	0.256	0.219	0.253	0.296	0.407	0.617
Rainwater						
<i>P</i> value	0.0051	0.0041	0.0031	0.0073	0.0055	0.0074
Means signif. different ($P < 0.05$)	Yes	Yes	Yes	Yes	Yes	Yes
Mean \pm Stdev	0.38 \pm 0.06	0.38 \pm 0.06	0.26 \pm 0.06	0.26 \pm 0.06	0.19 \pm 0.02	0.19 \pm 0.02
- (n) - clean	(n=6)	(n=6)	(n=6)	(n=6)	(n=6)	(n=6)
Mean \pm Stdev	A	AD	A	AD	A	AD
- (n) -	1.0 \pm 0.16	1.2 \pm 0.28	0.64 \pm 0.08	1.1 \pm 0.26	0.43 \pm 0.06	0.52 \pm 0.12
A or AD	(n=7)	(n=3)	(n=7)	(n=3)	(n=7)	(n=3)
R ²	0.256	0.714	0.563	0.296	0.518	0.665

TOC and TN were observed. In that study, TOC (1.61 mg/L) and TN (1.66 mg/L) were higher during African dust period than during the clean period (0.45 mg/L TOC and 0.75 mg/L TN) (Reyes-Rodriguez et al. 2009) also suggesting that African dust affected cloud/rain composition. Previous studies in Puerto Rico showed that Ca^{2+} increased in rainwater during African events, but no increase was observed for DOC (Heartsill-Scalley et al. 2007). Higher emissions and scavenging efficiencies of particles by cloud/rain drops may have raised OC and N during this period. Higher emissions of TN and OC could also be due to agriculture and combustion of fossil fuel on the African continent. These human activities generate ammonia and nitrogen oxides, which can interact with dust (Raes et al. 2000). Some of these air masses from Africa passed over other Caribbean islands and could have trapped additional human generated nitrogen. Secondary sources of N can also be produced from reactions between gaseous nitrogen species and particulate matter (Zhang and Anastasio 2001). Strong interactions between alkaline dust particles and gases (NO_x and N_2O_5) from anthropogenic sources increase HNO_3 levels during dust episodes (Formenti et al. 2003). The uptake of nitrate on mineral dust can be an important sink of NO_x from anthropogenic sources and contribute to the high levels of TN found during dust episodes. Like OC, ON is predominantly in the fine fraction of the aerosol and, therefore, can have long atmospheric lifetimes. Our results indicated an additional input of N and OC in Puerto Rican ecosystems during African storms, which could impact cloud formation as well as be a source of nutrients to the ecosystem.

The Soufriere Hills' volcano is the only active volcano in the Caribbean region and some eruptions occurred during the sampling period. During January 2007, SE winds brought

volcanic ash to Puerto Rico. Large amounts of ash were seen and collected during our sampling period. Since, we collected just one sample for rainwater and two for cloud water during this period; in these cases we could not apply statistical analyses. For this period, the concentrations in cloud water were 1.0 mg/L for TOC; 0.7 mg/L for DOC and 1.5 mg/L for TN and in rainwater were 0.6 mg/L for TOC; 0.5 mg/L for DOC and 0.3 mg/L for TN. We found higher concentrations of TN in cloud water (1.5 mg/L) during volcanic ash events than during clean periods (0.4 mg/L). Heartsill-Scalley et al. (2007) also found increased DOC and TN in rainfall fluxes in Puerto Rico when the Soufriere Hills volcano was active. Volcano fluids expelled from the Dvurechenskii mud volcano in the Black Sea have shown high concentrations of dissolved inorganic nitrogen (DIN) (22 mM) (Aloisi et al. 2004). DIN was also bound to particles expelled by a volcano (Aloisi et al. 2004). NO_3^- was also measured in volcanic ash in New Zealand (Cronin et al. 1998). Other studies have shown high concentrations of Ca^{2+} , Mg^{2+} , SO_4^{2-} and Al in volcanic ash, but no increase in nitrogen (Kellman et al. 1982; Veneklass 1990). Perhaps part of the nitrogen we measured was from volcano gases and part from anthropogenic emissions generated on Montserrat Island or on other upwind islands.

Variations in pH were also observed depending on the origin of the air masses. Cloud water pH averaged 5.8, 4.5, 6.2, and 3.5 for the clean, anthropogenic, African dust and volcanic ash influences, respectively. The high pH measured during the African dust period was probably due to the presence of alkalinity in the Ca^{2+} rich dust particles. The lowest pH during the volcanic ash and anthropogenic periods could be due to higher concentrations of species such as SO_2 and Cl^- and other acidic gases emitted from the volcano (Veneklass 1990; Eklund et al. 1997; Cronin et al. 1998). Similar pH trends were seen in rainwater.

3.4 Nutrient fluxes in rainwater

In tropical montane forests passing clouds and precipitation may constitute an important source of nutrients, since the supply of N and P is poor in these environments (Veneklass 1990). We calculated the nutrient flux for our rainwater samples based on the average concentrations (mg/L) and rainwater annual volume (4300 mm). Average nutrient fluxes based on our sampling period were 21 kg/ha.yr for TOC, 15 kg/ha.yr for DOC and 11 kg/ha.yr for TN. Larger inputs of OC and nitrogen occurred during the period influenced by anthropogenic emissions, as a result of higher concentrations in precipitation. Heartsill-Scalley et al. (2007) estimated lower annual rainfall inputs of nitrogen (4.75 kg/ha.yr) in the lower EYNF, but higher inputs for DOC (121 kg/ha.yr). Our estimates for DOC deposition were similar to those of McDowell et al. (1990) for the lower EYNF (19 kg/ha.yr). In all these studies, rainwater was a considerable source of N to the EYNF. In a tropical forest in Costa Rica, the levels of TOC estimated ranged from 22 to 36 kg/ha.yr and 8 to 9 kg/ha.yr for TN (Eklund et al. 1997), similar to our estimates (21 kg/ha.yr for TOC and 11 kg/ha.yr for TN). Nitrogen fluxes determined from bulk precipitation in other montane tropical forests include 17.9 kg/ha.yr (Colombia), 6.5 kg/ha.yr (New Guinea) and 9.9 kg/ha.yr (Venezuela) (Veneklass 1990; Eklund et al. 1997). The differences in nutrient fluxes may be attributable to precipitation volumes.

3.5 Insoluble particles

Particles from volcano and African inputs were observed suspended in both cloud and rainwater samples. The suspended particle composition of cloud water was therefore analyzed for all sampling periods. TC was over 95% OC and little EC was detected. The

average OC concentration in suspended particles in cloud water was 0.3 mg/L for clean air masses; 0.6 mg/L for the anthropogenic; 0.8 mg/L for volcanic ash, and 1.5 mg/L for African dust influences. Previously, EC has been detected in significant concentrations in precipitation particles in urban (2.4–17.3 mg/L) and rural areas (0.02–0.6 mg/L) (Ogren et al. 1984). Hadi et al. (1995) reported rural site values that ranged from 0.03 to 6.9 mg/L (average of 1.05 mg/L) for TC in rainwater particles.

As can be seen in the thermograms obtained from thermal/optical analyses of cloud water samples for all periods (Fig. 2), the carbon content varied with time and evolved at different temperatures. Each peak is for a mixture of compounds with similar characteristics. The first 3 to 4 peaks for more volatile compounds were obtained at temperatures ranging between 300 and 850°C. The other 3 peaks were obtained in He/O₂ and represent the more refractory material (Fig. 2). Organic carbon compounds with higher volatility or low molecular weight (MW) polar organics are associated with the evolution of carbon at lower temperatures (Yu et al. 2004). For samples from the clean period, a small amount of particles was present probably consisting of more volatile organic compounds with low MW (peaks 1–4). During the periods of African dust, the more volatile organic compounds in these early peaks were detected at much higher concentrations. Less volatile, and likely higher MW, organic compounds (peaks 5–7) were also detected in the presence of African dust. During clean periods, the POC may have been derived from the ocean, plants, pollen and microorganisms; while during African dust events, POC may have been derived in part from anthropogenic inputs or from soil emissions. As the measured particles represent material insoluble in the cloud water, we can assume that they probably represent the insoluble residue of partially soluble particles that served as cloud condensation nuclei. As pointed out earlier, the fraction of insoluble organic matter in the cloud water was considerably lower than the soluble organic fraction.

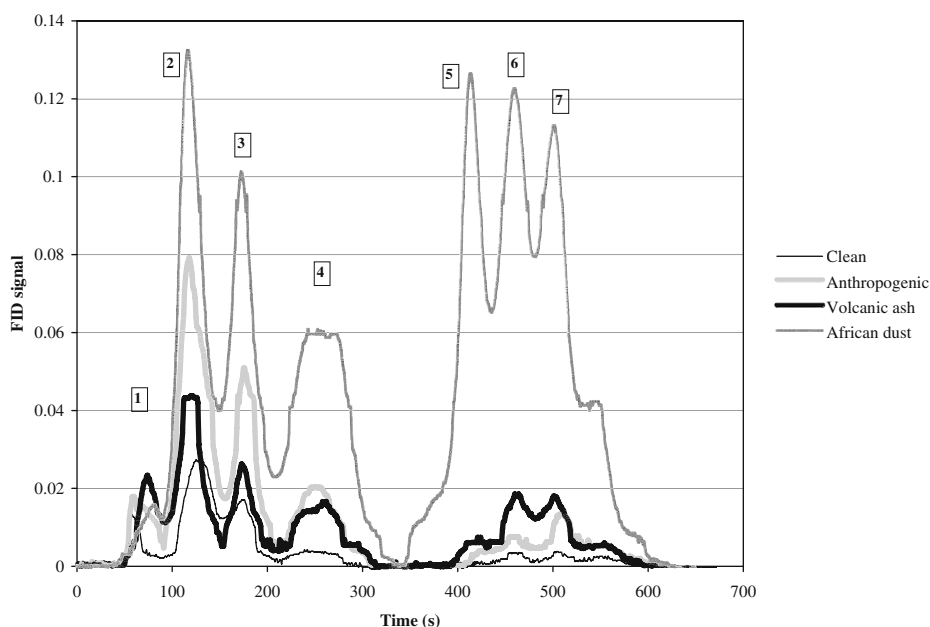


Fig. 2 Thermograms of average EC/OC analysis for suspended particles from cloud water during clean, anthropogenic, volcanic ash and African dust periods

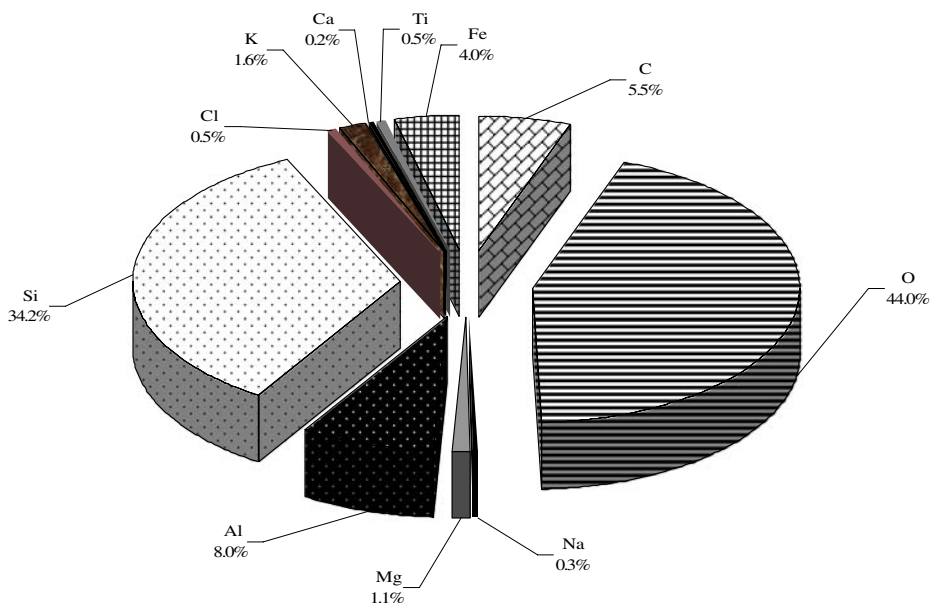


Fig. 3 Elemental composition (%) of particles collected in cloud water during African dust events

The suspended particle samples analyzed using SEM/EDS contained O, C, Si, Al, Fe, K, Mg and traces of Na, Cl, Ti and Ca (Fig. 3). The samples with suspended particles from African dust were rich in Al (8%) and Fe (4%), which originated from soil. The dust composition was very similar among analyzed samples ($n=8$). Most soluble species such as Na^+ and Cl^- in suspended particles had low concentrations; their concentrations were higher in the dissolved fraction of liquid cloud water samples (Gioda et al. 2008). To confirm the origin of the particles, we calculated the Al/Si ratio, which is sometimes used to distinguish between anthropogenic and Saharan sources. Six out of eight samples presented Al/Si ratios higher than 0.3, indicative of desert origin (Blanco et al. 2003). Our results presented similar trends to those observed by Blanco et al. (2003) in particles suspended in rainwater samples collected in southern Italy during an AD event (Table 3). In the same samples higher K/Si, Fe/Si and Mg/Si ratios (Table 3) were observed, suggesting that the soil was composed of smectite, kaolinite, and quartz (Blanco et al. 2003). Also, the same

Table 3 Ratios obtained from SEM/EDS analyses

Samples	Al/Si	Mg/Si	K/Si	Fe/Si	Ca/Al	Fe/Ca	K/Ca	Si/Al
CW#1	0.32	0.03	0.05	0.14	0.01	37.6	12.9	2.8
CW#2	0.41	0.07	0.09	0.24	0.06	9.2	3.5	9.6
CW#3	0.22	0.02	0.03	0.05	0.07	6.5	3.2	10.6
CW#4	0.13	0.01	0.02	0.05	0.05	10.6	4.2	7.8
CW#5	0.31	0.03	0.05	0.13	0.01	37.6	12.9	3.1
CW#6	0.37	0.06	0.07	0.21	0.02	24.0	8.6	3.0
CW#7	0.34	0.01	0.03	0.05	0.04	13.3	6.9	6.6
CW#8	0.32	0.04	0.06	0.14	0.03	17.9	7.4	3.7

samples appeared to have a larger content of quartz calcite and dolomite as per the larger Ca/Al and Si/Al ratios and lower Fe/Ca and K/Ca ratios observed (Avila et al. 1997). These ratios suggest the mineral rocks characteristic of the Saharan region (Blanco et al. 2003) as one of the possible sources.

The SEM/EDS analyses for other periods did not show significant differences in composition. The predominant species were the same as for African dust samples, but with lower percentages of Al (3.5%) and Fe (2%). Slightly higher percentages of Al (4.8%) and Si (23%) were observed for particles from volcanic ash consistent with a volcanic influence on these samples (Cronin et al. 1998).

4 Conclusions

Concentrations of TOC, DOC, and TN were measured in cloud and rainwater collected on a mountaintop in Puerto Rico during 8 intensive campaigns from December 2004 to March 2007. Concentrations of these species were influenced by the origin of air masses. Overall, concentrations and deposition fluxes of TOC/DOC and TN were typical of what has been observed at other remote locations. Higher concentrations of TOC and TN, with consequently higher deposition fluxes, were observed during African dust and volcanic ash events. Higher levels of N and organic compounds in insoluble particles suspended in cloud water may reflect influence from combustion sources from Africa and/or from upwind Caribbean islands. The particles from African dust events contained Al and Fe, suggesting soil dust as the source.

The highest concentrations of TOC and TN occurred during periods where back trajectories indicated a likely anthropogenic influence. These inputs might be due to emissions from agriculture and fossil fuel combustion in North America and upwind Caribbean islands. Long-range transport appears to represent an important extra source of TOC and TN for Puerto Rican ecosystems.

Our results provide further evidence for the influence of long-range transport on the chemical composition of atmospheric particles in marine or unpolluted regions. These results also contribute to our understanding of carbon and nitrogen deposition in a tropical marine environment.

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