

Organic carbon, total nitrogen, and water-soluble ions in clouds from a tropical montane cloud forest in Puerto Rico

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ABSTRACT

Chemical characterization to determine the organic and nitrogen fractions was performed on cloud water samples collected in a mountaintop site in Puerto Rico. Cloud water samples showed average concentrations of 1.09 mg L⁻¹ of total organic carbon (TOC), of 0.85 mg L⁻¹ for dissolved organic carbon (DOC) and of 1.25 mg L⁻¹ for total nitrogen (TN). Concentrations of organic nitrogen (ON) changed with the origin of the air mass. Changes in their concentrations were observed during periods under the influence of African dust (AD). The ON/TN ratios were 0.26 for the clean and 0.35 for the AD periods. Average concentrations of all these species were similar to those found in remote environments with no anthropogenic contribution. In the AD period, for cloud water the concentrations of TOC were 4 times higher and TN were 3 times higher than during periods of clean air masses associated with the trade winds. These results suggest that a significant fraction of TOC and TN in cloud and rainwater is associated to airborne particulate matter present in dust. Functional groups were identified using proton nuclear magnetic resonance (¹H NMR) spectroscopy. This characterization led to the conclusion that water-soluble organic compounds in these samples are mainly aliphatic oxygenated compounds, with a small amount of aromatics. The ion chromatography results showed that the ionic species were predominantly of marine origin, for air masses with and without African dust influence, with cloud water concentrations of NO₃⁻ and NH₄⁺ much lower than from polluted areas in the US. An increase of such species as SO₄²⁻, Cl⁻, Mg²⁺, K⁺ and Ca²⁺ was seen when air masses originated from northwest Africa. The changes in the chemical composition and physical properties of clouds associated with these different types of aerosol particles could affect on cloud formation and processes.

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1. Introduction

Aerosols interact with radiation and play an important role in climatic processes. They affect the Earth's radiative balance directly by scattering and absorbing of solar radiation, and indirectly by acting as cloud condensation nuclei (CCN), affecting cloud droplets and cloud albedo (NRC, 1996). Clouds provide important removal mechanisms for atmospheric aerosols. Clouds contain a variety of organic and inorganic compounds that can be suspended and dissolved. Large concentrations of various species can accumulate, even in a small volume of cloud water. Little is known about the organic composition of clouds and how clouds process organic

compounds. Therefore, it is important to understand interactions between clouds and carbonaceous aerosol particles.

It is known that organic matter comprises a large fraction of fine particulate matter in some environments, and it is possible that aqueous reactions in cloud drops are important sources of secondary organic aerosol (Herckes et al., 2002; Kerminen et al., 2005; Prenni et al., 2007; Ervens et al., 2008; Wex et al., 2009). Activation of carbonaceous particles to form cloud drops may also significantly alter optical properties of clouds, indicating that these particles can be effective CCN and contributing to the number and size of cloud droplets formed (Rissman et al., 2007). Some organic compounds present in aerosols are surface-active and their presence in CCN can affect the surface tension of cloud droplets (Gill et al., 1983; Capel et al., 1990; Shulman et al., 1996; Facchini et al., 1999a,b, 2000; Svenningsson et al., 2006; Engelhart et al., 2008). The nature of these surface-active compounds in clouds and

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rainwater is not well understood and there is very little information about their content in remote tropical environments.

Organic aerosols can constitute a significant fraction of CCN and in certain environments they may be present in concentrations similar to or even higher than sulfate aerosol (Novakov and Penner, 1993; Rivera-Carpio et al., 1996). Other studies have provided strong evidence of the CCN ability of organic aerosols (Novakov and Corrigan, 1996; Noone et al., 1996; Cruz and Pandis, 1997; Hansson et al., 1998). Therefore, the organic fraction should be taken into account when determining the hygroscopic behavior and CCN ability of atmospheric aerosols.

Nitrogen is another important component of clouds solutes. Total nitrogen (TN) in cloud water can include both be organic and inorganic forms. Organic nitrogen (ON) has been largely ignored for decades (Veneklass, 1990; Eklund et al., 1997; Keene et al., 2002; Cornell et al., 2003). Inorganic nitrogen (IN) has been more extensively studied due to its impact on acid rain. Recently, organic nitrogen (ON) has been shown to influence climate and environment by means of its light absorption properties, photochemical reactivity, and its contribution to the acid buffering capacity of cloud water (Zhang and Anastasio, 2001, 2003; Zhang et al., 2002; Mace et al., 2003; Nakamura et al., 2006).

Northeastern Puerto Rico is a relatively unpolluted marine location because of its proximity to the Atlantic Ocean and distance from upwind land masses with anthropogenic activity. However, the Caribbean region, including Puerto Rico, is influenced by African dust incursions, especially during the summer months (Prospero and Lamb, 2003). Mineral dust has a great impact on visibility, climate forcing and public health. It may even reduce or suppress precipitation (Prospero and Lamb, 2003) and will alter the chemical composition of cloud water.

Chemical characterization of clouds is fundamental to determine the impact of aerosols on cloud chemistry. This study focuses on the chemical characterization of cloud water samples collected in a tropical montane cloud forest in northeastern Puerto Rico. There clouds frequently envelop the mountain peaks facilitating study of the interaction of aerosols with clouds over extended periods of time. We sought to relate the cloud chemical composition to air mass origin, and to determine the organic and nitrogen fraction of aerosols.

2. Sampling and analytical methods

2.1. Cloud sampling

Cloud water samples were collected at East Peak (EP), part of the El Yunque National Forest (EYNF), Puerto Rico (Fig. 1). East Peak is located ~35 km from San Juan and ~20 km from the South Atlantic Ocean at 1051 m.a.s.l. in a tropical rainforest. The area is a humid mountaintop with frequent abundant cloud coverage fed by high altitude trade winds. During the sampling period, the average annual precipitation was 4200 mm and the annual mean temperature was 18 °C. The results presented here are for 9 cloud

interception events sampled during June and July 2007 at the East Peak (EP) site. Samples were collected in periods with air masses arriving from the North Atlantic Ocean in the presence and absence of African dust.

Cloud water samples were collected using an aluminum version of the single-stage Caltech Active Strand Cloud Water Collector Version 2 (AI-CASCC2) that had been previously cleaned with Triton X-100. The AI-CASCC2 is an active collector that uses a fan to draw drop-laden air across a bank of Teflon strands (508 µm diameter), which serve as inertial impaction surfaces (Demoz et al., 1996; Collett et al., 2002). Details about the sampling procedure are presented by Gioda et al. (in press). pH and conductivity were measured on site immediately after the samples were collected. All the samples were divided for different analyses: 25–50 mL of each sample was stored for measurement of total organic carbon (TOC), total nitrogen (TN), dissolved organic carbon (DOC), proton nuclear magnetic resonance (¹H NMR) spectroscopy, and ion chromatography (IC) analyses. Plastic bottles were used to store samples for IC analysis; the other sample fractions were stored in amber glass bottles, which were previously cleaned with Milli Q water, and baked overnight at 450 °C. A volume of 0.5 mL of hydrochloric acid was added to the sample aliquots for TOC, TN and DOC analyses, and chloroform was added to preserve inorganic analysis aliquots. The samples were transported in coolers and stored at –18 °C until analysis. All of the samples were taken during the morning and each sampling period was 3 h long.

2.2. Quality control (QC) of cloud water samples

To control for contamination, laboratory and field blanks were collected and analyzed in the same way as the samples. The cloud water collector (AI-CASCC2) was cleaned using large amounts of Milli Q water between events. Once the collector was cleaned, a blank was taken by spraying about 200 mL of Milli Q water onto the collection strands in the collector.

2.3. AOT satellite images and air mass backward trajectories

For identification of the origins of sampled air masses, back trajectories and satellite images were used. Five-day back trajectories (100 m.a.s.l. ending height) were calculated for each sampling day using the Hybrid Single-Particle Lagrangian Integrated Trajectories (HYSPLOT) computer model (Draxler and Rolph, 2003) and the GDAS meteorological data set produced by the U.S. National Center for Environmental Prediction. 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 Advanced Very High Resolution Radiometer (AVHRR) aerosol optical thickness (AOT) images were used to evaluate African dust events (<http://www.nrlmry.navy.mil/aerosol/satellite/noaa-aer/noaa-daily-images/>).

2.4. Total organic carbon/total nitrogen/dissolved organic carbon (TOC/TN/DOC)

Aliquots of samples were taken for the analysis of carbon and nitrogen fractions. Also, aliquots were taken to be filtered through single-use syringe membrane filters of 0.45 µm diameter (SP15, Sartorius, Germany) and the filtrate was used for the analysis of dissolved organic carbon (DOC). Aliquots for TOC, TN, and DOC were stored and frozen until analysis. To avoid contamination of the cloud water collector, Milli Q water used for cleaning and the filtration procedure was checked regularly using field blanks (QC). Organic carbon concentrations (TOC and DOC) were determined using a total organic carbon analyzer (Shimadzu TOC-V 5500/TNM-1).



Fig. 1. Location of East Peak in the El Yunque National Forest.

Table 1Concentrations (mg L⁻¹) of TOC, DOC, TN and ON, DOC/TOC ratios, and LWC of cloud water samples collected at the East Peak (*n* = 9).

Sample ID	Date	Air mass origin	TOC (mg L ⁻¹)	DOC (mg L ⁻¹)	TN (mg L ⁻¹)	ON (mg L ⁻¹)	DOC/TOC	LWC (g m ⁻³)
Cloud_1	July 5, 2007	Clean	0.44	0.41	0.72	0.08	0.92	0.06
Cloud_2	July 6, 2007	Clean	0.66	0.65	0.97	0.18	0.99	0.06
Cloud_3	July 30, 2007	Clean	0.55	0.44	0.65	0.26	0.81	0.14
Cloud_4	July 31, 2007	Clean	0.15	0.13	0.61	0.24	0.89	0.28
Average	–	–	0.45	0.41	0.74	0.19	0.90	0.14
Std. Dev.	–	–	0.22	0.21	0.16	0.11	0.07	0.11
Cloud_5	June 26, 2007	African dust	1.89	1.81	2.25	0.48	0.96	0.14
Cloud_6	July 3, 2007	African dust	2.88	2.23	2.61	0.64	0.78	0.08
Cloud_7	July 28, 2007	African dust	2.12	1.25	1.11	0.64	0.59	0.28
Cloud_8	August 2, 2007	African dust	0.87	0.62	1.27	0.34	0.72	0.28
Cloud_9	August 3, 2007	African dust	0.29	0.13	1.07	0.84	0.44	0.28
Average	–	–	1.61	1.21	1.66	0.59	0.70	0.21
Std. Dev.	–	–	1.03	0.85	0.72	0.29	0.20	0.12

High temperature catalytic oxidation with chemiluminescent nitrogen detection was used to analyze TN by the same instrument. The TOC/TN analyzer was calibrated using a series of aqueous potassium hydrogen phthalate and potassium nitrate standards. Each sample was injected 3 times with resulting precision of <2%. The limits of detection were based on three times the standard deviation of blanks (0.06 mg L⁻¹ of C and 0.08 mg L⁻¹ of N).

2.5. Ion chromatography (IC)

Ionic concentrations in cloud water samples were determined using an ion chromatograph (model DIONEX series 1000). Anions [sulfate (SO₄²⁻), nitrate (NO₃⁻), and chloride (Cl⁻)] were measured using an ION Pac[®] AS11 column with a gradient elution (H₂O; NaOH 5 mM; NaOH 100 mM). Cations [sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), magnesium (Mg²⁺), and ammonium (NH₄⁺)] were measured with a CS12A column with an eluent of methanesulfonic acid (20 mM). The detection limit for each ion was based on three times the blank standard deviation with a measurement precision of <2% (i.e., 0.30 mg L⁻¹ for Na⁺, Cl⁻, and SO₄²⁻; and 0.01 mg L⁻¹ for NO₃⁻, NH₄⁺, Ca²⁺, Mg²⁺, and K⁺).

2.6. Proton nuclear magnetic resonance (¹H NMR) spectroscopy

Cloud water samples were analyzed using ¹H NMR spectroscopy after the method of Decesari et al. (2000). Cloud samples were first freeze-dried and then redissolved with D₂O, containing 0.05% (by weight) sodium 3-(trimethylsilyl)-2,2,3,3-d₄-propionate (TSPd₄) as an internal standard. The spectra were recorded on a Bruker AV-500 spectrometer at 500 MHz in a 5 mm probe. Approximately 5000 scans were collected for each spectrum. Quantitative analysis of the present functional groups was performed, since the integrated area of the spectra is proportional to the moles of protons present in the sample (Decesari et al., 2000).

3. Results and discussion

3.1. TOC, TN, and DOC

Table 1 presents the concentrations (mg L⁻¹) of TOC, DOC, TN, and the liquid water content (LWC) for cloud samples collected at EP. LWC was calculated using the collection rate (mL min⁻¹) that is then converted to LWC (g m⁻³) according to the approach used by Demoz et al. (1996). They calculated that 2.5 mL min⁻¹ corresponds to an LWC of approximately 0.5 g m⁻³ using a CASCC2.

Average concentrations of TOC, DOC, and TN were 1.09, 0.85, and 1.25 mg L⁻¹, respectively. Concentrations of TOC as high as 2.88 mg L⁻¹ were measured in these samples. TOC, DOC, and TN

average concentrations in EP were more similar to remote sites than to locations with anthropogenic influence (Gioda et al., in press). A difference in chemical composition was observed with changes in the origin of the air mass. This might have been due to differences in dust inputs and some anthropogenic pollution from local sources during the sampling periods, but also due to the volatility of the material under study, where losses of more volatile species could have occurred. Long-range transport of AD influenced cloud chemistry at EP. Based on back trajectories and AOT satellite images, samples were grouped into two periods according to the main origin of the air masses: clean (C) and African Dust (AD). The clean period refers to air masses from the North Atlantic Ocean without the influence of AD; and the AD period represents samples with dust events from northwest Africa, specifically from the Sahara/Sahel regions (Fig. 2). As the main focus of this article is to contrast the chemical composition of clouds under the influence of two different types of air masses, the assignment of the latter is reliable since all samples were taken under the same wind direction, which was monitored constantly. Fig. 2 shows the trajectories for the 9 samples collected during the two different types of air masses. Organic and nitrogen fractions varied for each sampling period. The clean period showed the lowest concentrations of TOC (0.45 mg L⁻¹), while the highest TOC values (1.61 mg L⁻¹) were in clouds from the period of AD air masses (Fig. 3). TOC and TN concentrations for AD periods were 4 and 3 times, respectively, higher than in clean periods. Previous study of chemical characterization of cloud water at EP also showed similar patterns for TN and TOC for AD and clean periods (Gioda et al., in press). Concentrations of organic nitrogen (ON) determined as TN minus the concentrations of ammonium and nitrate (there was no nitrite), were also determined in this study for the cloud samples collected, where a difference was also observed with changes in the origin of the air mass. The average ON/TN ratios for clean and AD periods were 0.26 and 0.35, respectively.

Two carbonaceous fractions can be scavenged by clouds: one fraction is insoluble, while the other one may contain a mixture of organic compounds that can be entirely, or partially soluble. The size of each fraction depends on the composition of aerosol particles scavenged by cloud drops and the uptake of water soluble volatile organic compounds (Herckes et al., 2002). Water-soluble organic compounds may comprise a large portion of cloud condensation nuclei (Collett et al., 1993). That is why we are interested in determining how much of the organic fraction is mainly composed of water-soluble compounds.

Cloud samples were filtered to determine the fraction of TOC dissolved inside cloud drops. The average DOC/TOC ratio was 0.79, suggesting that TOC is mainly composed of water-soluble organics (Table 1). DOC/TOC ratios for clean and AD periods were 0.90 and

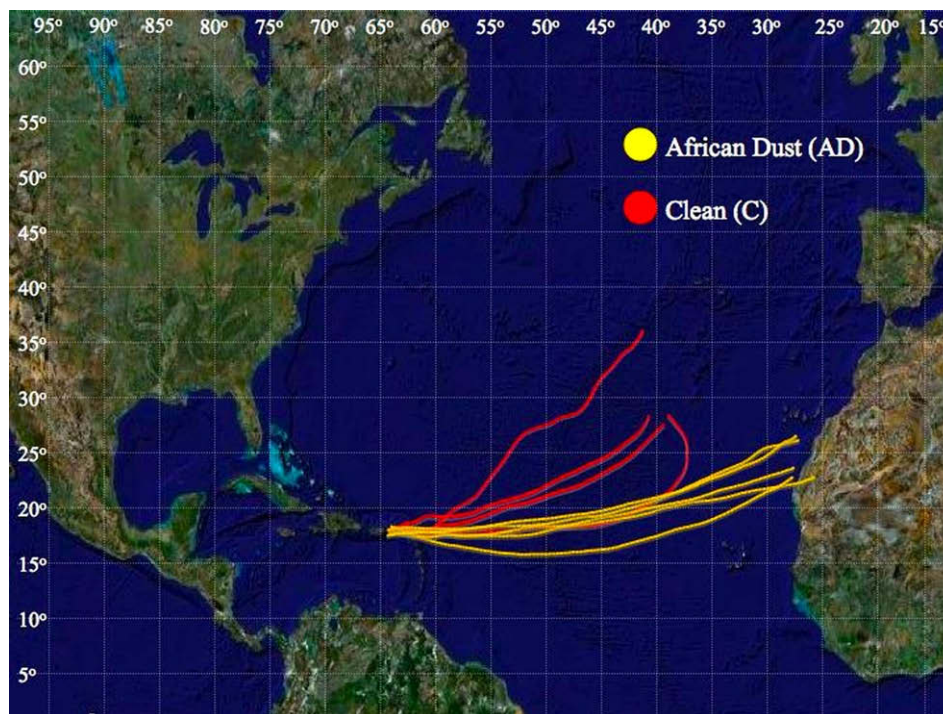


Fig. 2. Air mass backward trajectories for the cloud water samples ($n = 9$): “Clean” air refers to air masses from the Atlantic Ocean without the influence of African dust and “African dust” refers to air masses from outbreak of dust from northwest Africa.

0.70, respectively, suggesting an increase of insoluble organic material when air masses come from the African continent. The average DOC fraction measured here (79%) was lower than that observed in Duebendorf, Switzerland (93–97%) (Capel et al., 1990).

3.2. Water – soluble ions

Ion concentrations (mg L^{-1} and $\mu\text{eq L}^{-1}$) of all species and pH for cloud water samples collected at EP are presented in Table 2. The most abundant anions were Cl^{-} (average of $489 \mu\text{eq L}^{-1}$) and SO_4^{2-} ($117 \mu\text{eq L}^{-1}$), and the most abundant cations were Na^{+} (average of $457 \mu\text{eq L}^{-1}$) and Ca^{2+} ($131 \mu\text{eq L}^{-1}$). High concentrations of sea salt (Na^{+} , Cl^{-}) and other ions (i.e., Mg^{2+} , SO_4^{2-}) also present in seawater were observed.

The ionic composition of cloud water determined at EP was similar to previous results from this site (Weathers et al., 1988;

Asbury et al., 1994; Gioda et al., 2008) and different from that of polluted environments. The chemical composition of cloud water at EP reflected marine influence, with concentrations of NH_4^{+} , NO_3^{-} , and SO_4^{2-} much lower than for cloud water from polluted areas in the US. For example, clouds in San Joaquin Valley, CA had higher concentrations of NH_4^{+} , NO_3^{-} , and SO_4^{2-} (144 times, 9 times, and 3 times higher, respectively) than at EP (Collett et al., 1999), as well as from the Sacramento Valley and Mount Mitchell (Collett et al., 2002). Concentrations at southern California coastal sites were also higher (73 times, 13 times, and 5 times higher, respectively).

Water-soluble inorganic ions were also influenced by the origin of the air masses. As expected, the lowest concentrations of ionic species occurred in the clean period (see Table 2). Na^{+} and Cl^{-} ions were slightly reduced from the clean to the AD period, but the concentrations of Na^{+} , Cl^{-} , Mg^{2+} , K^{+} and Ca^{2+} did not change significantly between these periods. These ions were probably mainly from seawater due to the proximity of the site to the ocean.

Correlations between the different species in cloud water reflected their marine origin. The predominant species, Na^{+} and Cl^{-} , are sea spray markers, and they were highly correlated ($r^2 = 0.99$). Significant differences in the $\text{Cl}^{-}/\text{Na}^{+}$ ratios were not observed between periods with and without AD influence ($\text{Cl}^{-}/\text{Na}^{+} = 0.99$ for clean and 0.92 for AD). The $\text{Cl}^{-}/\text{Na}^{+}$ ratio for AD periods reflected some Cl^{-} loss from the aerosol. This loss can be attributed to HNO_3 and/or H_2SO_4 uptake onto the sea salt particles (Gioda et al., 2008). Other ions present in our samples and in seawater (Mg^{2+} and K^{+}) correlated well with Na^{+} ($r^2 = 0.99$ and 0.96, respectively). The $\text{Cl}^{-}/\text{Na}^{+}$ ratios were similar to those for seawater (1.10 and 1.16, respectively), showing that the source for these ions was mainly scavenged sea salt aerosol.

There was a low correlation between Ca^{2+} and Na^{+} ($r^2 = 0.20$) during the AD period, when the nss- Ca^{2+} concentrations were much higher than for the clean period (C: $34 \mu\text{eq L}^{-1}$; AD: $173 \mu\text{eq L}^{-1}$). African dust was most likely the source of this nss- Ca^{2+} . The pH values were also higher during AD period (pH = 6.47)

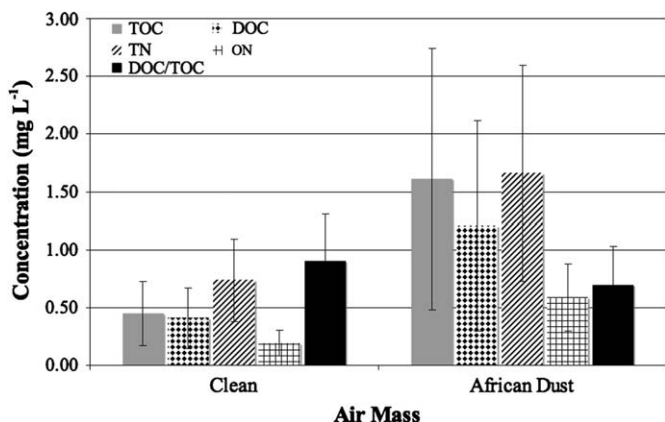


Fig. 3. Distribution of cloud water concentration (mg L^{-1}) among periods with different air masses origin ($n = 4$ for C period, and $n = 5$ for AD period).

Table 2
pH, and water-soluble ions concentrations ($\mu\text{eq L}^{-1}$) of the cloud water samples collected at East Peak ($n = 9$).

Sample ID	Date	Air mass origin	pH	NO_3^- $\mu\text{eq L}^{-1}$	ss-SO_4^{2-} $\mu\text{eq L}^{-1}$	nss-SO_4^{2-} $\mu\text{eq L}^{-1}$	Cl^- $\mu\text{eq L}^{-1}$	Na^+ $\mu\text{eq L}^{-1}$	NH_4^+ $\mu\text{eq L}^{-1}$	K^+ $\mu\text{eq L}^{-1}$	Mg^{2+} $\mu\text{eq L}^{-1}$	ss-Ca^{2+} $\mu\text{eq L}^{-1}$	nss-Ca^{2+} $\mu\text{eq L}^{-1}$
Cloud_1	July 5, 2007	Clean	5.15	37	38	24	314	312	9	46	11	14	31
Cloud_2	July 6, 2007	Clean	5.54	34	89	12	841	738	1	116	17	32	12
Cloud_3	July 30, 2007	Clean	7.37	21	29	34	231	239	13	37	8	11	50
Cloud_4	July 31, 2007	Clean	5.94	19	19	27	151	158	7	27	6	7	41
Average	–	–	6.00	28	44	24	384	362	7	56	10	16	34
Std. Dev.	–	–	0.97	9	31	9	311	258	5	40	5	11	16
Cloud_5	June 26, 2007	African dust	7.02	115	112	125	1050	925	11	144	50	41	268
Cloud_6	July 3, 2007	African dust	7.17	133	62	141	544	510	7	97	27	22	297
Cloud_7	July 28, 2007	African dust	6.74	34	40	79	334	333	0	57	16	15	163
Cloud_8	August 2, 2007	African dust	4.98	66	63	91	566	522	16	77	27	23	104
Cloud_9	August 3, 2007	African dust	6.45	16	45	24	366	372	1	61	14	16	34
Average	–	–	6.47	73	64	92	572	532	7	87	27	23	173
Std. Dev.	–	–	0.88	50	28	46	286	234	6	35	14	10	110

than the clean period ($\text{pH} = 6.00$), due probably to the excess of Ca^{2+} and alkalinity of the scavenged dust.

The $\text{SO}_4^{2-}/\text{Na}^+$ ratio (0.29) for cloud water during AD period was higher than for seawater (0.19). The average nss-SO_4^{2-} concentration was $92 \mu\text{eq L}^{-1}$ during AD periods and $24 \mu\text{eq L}^{-1}$ during the clean periods. Correlations of NO_3^- and nss-SO_4^{2-} were much lower during the C period than the AD periods ($r^2 = 0.49$ and 0.90 , respectively), suggesting long-range transport of anthropogenic pollution containing both SO_4^{2-} and NO_3^- in AD periods.

Fig. 4 illustrates the relative contributions of the major compounds to the cloud water composition for the C and AD periods. The predominant species in cloud water were Na^+ and Cl^- for both periods. The TN and TOC contributions were also low (about 3%) for both periods. When air masses arrived from northwest Africa, Na^+ and Cl^- concentrations decreased and TOC, TN, nss-SO_4^{2-} , Ca^{2+} , Fe^{2+} and Al^{3+} concentrations increased, suggesting an influence by air masses with input from anthropogenic sources and crustal influence.

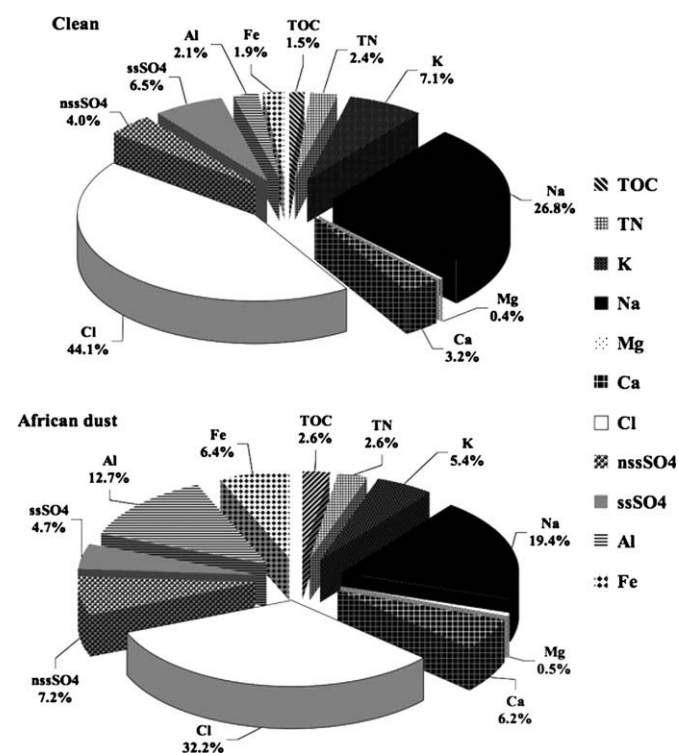


Fig. 4. Percentage of the major compounds identified in cloud water collected at EP during: (a) clean air masses and (b) African dust incursions ($n = 4$ for C period, and $n = 5$ for AD period).

3.3. ^1H NMR spectroscopy

^1H NMR spectroscopy was used to identify the major organic functional groups in the cloud water organic fraction. The samples collected at the EP site were analyzed by this method. Fig. 5 shows the ^1H NMR spectra of deuterated water extracts of cloud water samples collected at EP during African dust activity, during the clean period, and a field blank. Some portions of the spectra appear as continuous distributions of unresolved signals, suggesting a possible mixture of substances at very low concentrations. Some distinct peaks could be attributed to a few main categories of functional groups. The signals were integrated and attributed to principal functional groups on the basis of the main intervals of chemical shift. Some individual compounds seen in both C and AD samples are reported in Table 3.

Low concentrations of aromatic protons are suggested by the weak sharp signals in the spectral region between 6.9 and 7.5 ppm. Aromatics only appeared in cloud water samples influenced by AD events, probably due to the influence of biomass burning in Africa. The intense resonance at 1.3 ppm in the AD sample may reflect the presence of fatty acid-like compounds. Relatively intense sharp signals for aliphatic protons seen between 0.7 and 4.2 ppm indicate several functional groups: methyl groups (0.7–1.0 ppm), chain

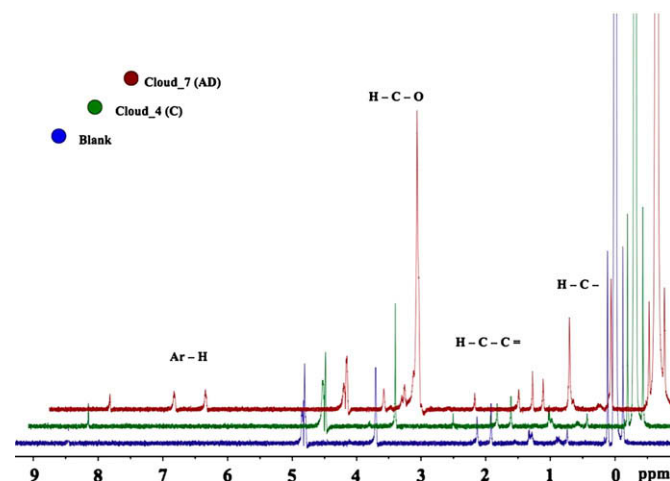


Fig. 5. ^1H NMR spectra of two cloud water samples collected at EP site during AD activity and during a C period. The horizontal axes show the chemical shift in ppm. The peak at 0 ppm corresponds to the internal standard TSPd4. H-C: purely aliphatic hydrogen atoms; H-C-C: hydrogen atoms in alpha position to $\text{C}=\text{C}$ or $\text{C}=\text{O}$ groups; H-C-O: aliphatic C-H directly bound to an oxygen atom; H-Ar: aromatic hydrogen atoms. The signals at ca. 4.8 ppm are artifacts due to the suppression of the water peak.

Table 3

Individual compounds detected by ^1H NMR analysis in cloud water samples collected at the EP site.

Compound	Chemical Shift (ppm)
Acetate	1.91
Methanesulphonate	2.80
Formate	8.46

methylene groups (1.3–1.9 ppm), adjacent to carbonyl/aromatic functionalities (2.1–2.8 ppm), and alcohols and ethers (3.7–4.2 ppm). Aliphatic protons were seen in both the C and AD periods, but more intense signals were seen in samples influenced by AD events.

The bulk of the total organic hydrogen atom (proton) distribution presented above can be summarized by the identification of four main categories: 1) Ar-H: aromatic protons (6.9–7.5 ppm); 2) H-C-O: protons attached to carbon atoms singly-bonded to oxygen (3.7–4.2 ppm); 3) H-C-C = : aliphatic protons attached to carbon atoms adjacent to a carbonyl or aromatic group (2.1–2.8 ppm); and 4) H-C: aliphatic protons in extended alkyl chains (0.7–1.9 ppm).

For both C and AD periods, ^1H NMR characterization indicated that alkyl groups and oxygenated aliphatic compounds dominated the organic fraction, with a minor input of aromatics. Oxygenated aliphatics in the form of alcohols (H-C-O) may have come from biomass burning during the AD periods. Because of the low anthropogenic influence when EP is exposed to the trade winds, organic matter was reduced during the C period, resulting in sharp signals rather than continuous spectral signals. The average organic concentrations were more similar to remote sites, such as Jeju Island than to locations with greater anthropogenic influence (Decesari et al., 2004).

Chemical composition changed with the origin of the air mass. An example of this is the presence of aromatics in cloud samples influenced by AD, reflecting long-range transport from a continental source. Peak intensities varied significantly among sampling periods. The C period showed the lowest concentrations for most moieties; the highest peak intensities were found in clouds from the AD periods.

The abundance of non-exchangeable protons in these four functional group categories can be estimated from the area of the observed ^1H NMR signals for both C and AD samples presented (Fig. 6). Fig. 6 shows that the normalized distribution of functional

groups differs between C and AD periods. The AD sample presents a much higher content of H-C-O groups. In summary, the characterization of the cloud water by ^1H NMR leads to the conclusion that water-soluble organic compounds in these samples are mainly aliphatic oxygenated compounds.

4. Conclusions

The chemical composition of cloud water samples at EP was investigated to determine the influence of the origin of sampled air masses on the concentrations of organic, inorganic, and nitrogen species. Cloud chemical composition was influenced by African dust, anthropogenic pollution, and sea salt. Concentrations of TOC, DOC, and TN were similar to those measured at other remote sites. Concentrations of TOC and TN increased during AD events, suggesting that concentrations of organic compounds and nitrogen were related to the dust events themselves or to the transport patterns bringing dust to EP. A significant fraction of TOC was composed of water-soluble organics (mean DOC/TOC = 0.79). DOC/TOC ratios for AD periods were lower, suggesting that air masses from northwest Africa brought more insoluble carbonaceous particles or a lower abundance of water-soluble volatile organic compounds. ^1H NMR spectroscopy indicated that oxygenated aliphatic compounds dominated the organic fraction, with a minor input of aromatics. Aromatics were only present in the AD samples and were probably due to long-range transport pollutants resulting from biomass burning in Africa. Ionic species were predominantly of marine origin, with NH_4^+ and NO_3^- concentrations much lower than in cloud water from polluted areas in the US. These changes in cloud chemical composition and the associated changes in physical properties could influence cloud formation and processes. Continued study of cloud composition at varying sites will improve our understanding of the impact of aerosols and clouds on climate.

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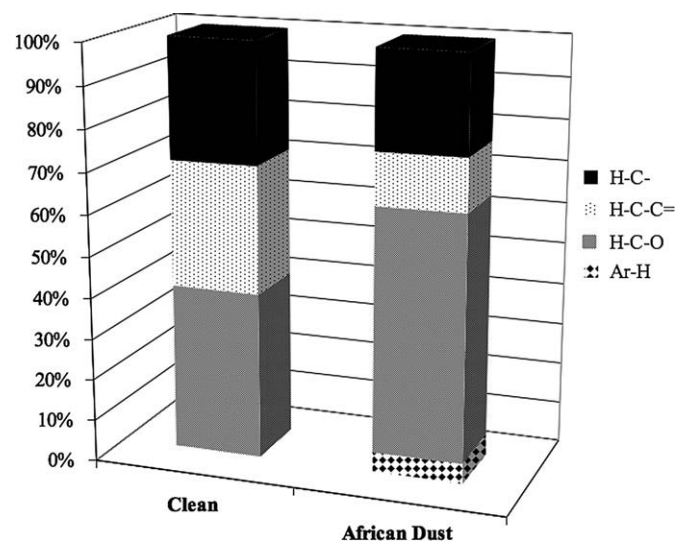


Fig. 6. Normalized abundance in the cloud water samples of non-exchangeable protons in the four categories described in the text.

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