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STUDIES OF FOG EVENTS AT TWO CLOUD FORESTS NEAR CARACAS, VENEZUELA—II. CHEMISTRY OF FOG

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Abstract—Atmospheric pollution is generally believed to have played a major role in forest decline in northeastern North America and Europe, particularly at high elevation sites. Recently, acidic fogs have been reported to contribute significant acidic and trace elemental inputs to these montane forests. However, in tropical montane systems, especially in cloud forests, very little is known about fog chemistry.

Fog chemistry was examined in two Venezuelan cloud forests directly adjacent to the Caracas Valley in the wet and dry seasons of 1989–1990. Fog was found to be a very important chemical input in these high altitude forests. Ion concentrations in fog were up to 20-times higher than in precipitation at the same site. Fog at both sites was acidic with a mean pH of 4.6–5.0, while the lowest fog pH recorded was 3.7. Nitrate concentrations reached 30.9 mg ℓ^{-1} and accounted for a large proportion of the acidity. Fog water also contained elevated concentrations of trace metals, particularly Pb and Zn, which reached 0.27 and 1.03 mg ℓ^{-1}, respectively. Major sources are thought to be anthropogenic. The apparent contamination of cloud forest fogs may be deleterious to the cloud forests, particularly in national parks, surrounding the Caracas Valley.

Key word index: Fog chemistry, Venezuela, cloud forest, acid precipitation, South America.

INTRODUCTION

There is a growing body of literature on fog as an important vector of pollutants at high elevation forests in temperate regions of Europe and eastern North America (Falconer and Falconer, 1980; Lovett *et al.*, 1982; Schemenauer, 1986; Sigmon *et al.*, 1989; Mohnen, 1989; Schmitt, 1989; Vong *et al.*, 1991). However, there is a dearth of information in mountainous forested areas of the tropics where fog incidence is often extremely high, and where fog deposition may be a significant wet deposition pathway. The hydrological importance of fog in tropical montane forests (cloud forests) is well-documented (Vogelmann, 1973; Zadroga, 1981; Cavelier, 1986; Stadtmuller, 1987; Cavelier and Goldstein, 1989). None of these studies deals with the chemistry of fogs nor the possibility of fog acting as a source of contaminants in these cloud forests. In northern Venezuela, many of the cloud forests are situated within close proximity to major urban and industrial centres and may therefore be at risk due to atmospheric pollution. There are data (Schemenauer and Cereceda, 1991, 1992a, 1992b) on the chemical composition of high elevation coastal fogs in the arid tropics and subtropics in Chile, Peru and the Sultanate of Oman which provide baseline information for comparison to the work reported here. There is also a small data set (Lazrus *et al.*, 1970) on the chemistry of fog water on Pico del Oeste in Puerto Rico, which is also useful in assessing the quality of fog water in Venezuela.

Recent studies report the existence of acid precipitation in tropical areas, including Venezuela (Steinhardt and Fassbender, 1979; Galloway *et al.*, 1982; Sanhueza *et al.*, 1989). In these studies, organic and nitric acids were shown to account for a large portion of the "natural" acidity in precipitation from these areas (Keene *et al.*, 1983; Crutzen and Andreae, 1990). However, in urban and industrial areas of the humid tropics, anthropogenic emissions may significantly increase the "natural" acidity of precipitation and fog.

It has been established that Caracas air is heavily polluted with trace elements such as Cl, Br, Zn, Pb and Cd in suspended matter (Ishizaki and Sanhueza, 1979; Escalona and Sanhueza, 1981; Lara *et al.*, 1984). Reports by Ishizaki *et al.* (1978) and Ishizaki and Sanhueza (1979) also conclude that high levels of NO_x are emitted from the Caracas Valley. Precipitation studies have shown that organic and nitric acids are important components of acidity of rain in this area and that during vegetation fires, ion concentrations in precipitation increase significantly (Hermoso *et al.*, 1990). Biomass burning, particularly in the dry season can play a major role in tropical atmospheric chemistry (Crutzen and Andreae, 1990). The direct emissions of acetic acid, NO_x, SO_2 and the photochemical formation of formic acid from biomass fires can substantially acidify naturally acidic precipitation to pH values below 4.0 (Crutzen and Andreae, 1990). Nothing is known about the chemical composition of the fogs at cloud forests surrounding the Caracas Valley. However, fog frequency is extremely high in these cloud forests and fog accounts for an important hydrological input (Gordon *et al.*, 1994). It seems important to evaluate the chemical input of fog to these forests.

SITE DESCRIPTION

Fog monitoring sites were established at two cloud forest locations: (1) Pico del Avila at El Avila National Park, Distrito Federal (DF), 10°32′38″N, 66°52′57″W, 2150 m a.s.l.; and (2) Altos de Pipe, Miranda State, 10°20′N, 66°55′W, 1747 m a.s.l. These sites are located in the coastal mountain range of northern Venezuela. Pico del Avila rises 1100 m above and 3 km north of the Caracas Valley, and Altos de Pipe rises 800 m above and 18 km southwest of Caracas (Fig. 1). The Altos de Pipe site has been the site of the Instituto Venezolano de Investigaciones Cientificas (IVIC) since 1959 and covers an area of 832 ha. From 1964 to 1986, annual precipitation averaged 1009 mm and monthly temperatures averaged 16.1°C (average maximum of 22°C, and average minimum of 12°C) (MARNR, 1990). The El Avila site is situated in "El Avila Parque Nacional" which has been a national park since 1954. The park consists of 85,192 ha reaching from sea level to 2765 m. From 1969–1990, the temperature averaged 13.4°C (average maximum 18°C, and average minimum 11.3°C) and annual precipitation averaged 827.5 mm at the Estacion El Avila meteorological station located at 2112 m (Comandancia General de la Marina, 1990). Soils at both sites are inceptisols, clay loam and acidic with a pH of <4.5. Soils from Altos de Pipe have a very high organic matter content, low cation exchange capacity and high Al and Fe content (Cuenca *et al.*, 1990).

GENERAL METEOROLOGICAL CONDITIONS

The local climate in this region is strongly influenced by the NE–ENE tradewinds, and thus much of the surface air is oceanic in origin. These tradewinds are stronger during the dry season in the northern region of Venezuela (Zambrano, 1970; Huber, 1986; Sanhueza *et al.*, 1988). During the summer in the Northern Hemisphere, air masses passing over the warm Atlantic Ocean become moisture-laden and are pushed southwest by the tradewinds where they meet the coastal mountain range. Here they rise up the mountain slopes and deposit water in the form of rain and/or fog. The wet season in northern Venezuela is from May to November, while the dry season usually occurs between December and April (Zambrano, 1970; Huber, 1986). Surface temperature is highly dependent on altitude. The daily variation in surface temperature is more significant than seasonal variation. According to Zambrano (1970), average annual temperature oscillation in this region is 2.5°C while the average daily temperature oscillation can be as high as 14°C. At both sites fog formation is frequent and usually occurs overnight, during the early morning and early evening, with general clearing occurring during midday. This maintains a high relative humidity, favoring the growth of cloud forest vegetation.

FOG WATER COLLECTION

Fog water collection was carried out at Pico del Avila and Altos de Pipe on a continuous basis for approximately six weeks at each site both in the dry and wet seasons of 1989–1990. Fog water samples were collected using a Canadian Teflon fibre passive cloud/fog collector built under the specifications of the Canadian Atmospheric Environment Service (A.E.S.), Environment Canada. These collectors are identical in design to those used in the U.S. Mountain Cloud Chemistry Project and in the Chemistry of High Elevation Fog (CHEF) Program (Schemenauer, 1986). Fog collectors were mounted on wooden supports 3 m above the ground to minimize contamination from soil dust and splash-back. At the Altos de Pipe site, the collector was mounted 3 m above a rooftop to avoid ground contamination and human tampering. To exclude dry deposition from samples, collectors were not uncovered or mounted until immediately prior to a sampling event. In addition, three replicate precipitation collectors were placed at each fog collection site at the onset of each precipitation event. Samples were collected in clean, high density, polyethylene bags, lining 25 cm diameter plastic buckets, placed 1 m above the ground. At these same locations temperature, wind direction, and wind velocity were monitored using a Digitar Weatherpro TWR-3 Station with anemometer. Relative humidity was measured using a Lambrecht Pernix Thermo-hygrometer.

EVENT SAMPLING OF FOG WATER

A fog event was defined both by visibility and by volume, and collections were initiated when a stationary object 1000 m away was obscured from view for more than 15 min (A.E.S., 1987). Sample collection was discontinued when (1) the stationary object was clearly in view and/or (2) <40 ml were collected in the minimum sampling period of 1 h. When fog events persisted, collections were made every hour until the end of the event. If fog events continued through the night, a clean collector was placed outside between 2200 h and midnight and the sample was then collected the following morning between 0600 and 0730 h. These "overnight" samples are mixed samples and may contain fog, dew, precipitation and/or dry deposition.

Between fog events, fog collectors were thoroughly washed with distilled deionized water until the final rinsewater and a conductivity $< 1.0\ \mu S\ cm^{-1}$. Fog water samples were collected in 500 ml Nalgene bottles. Collection bottles were acid-

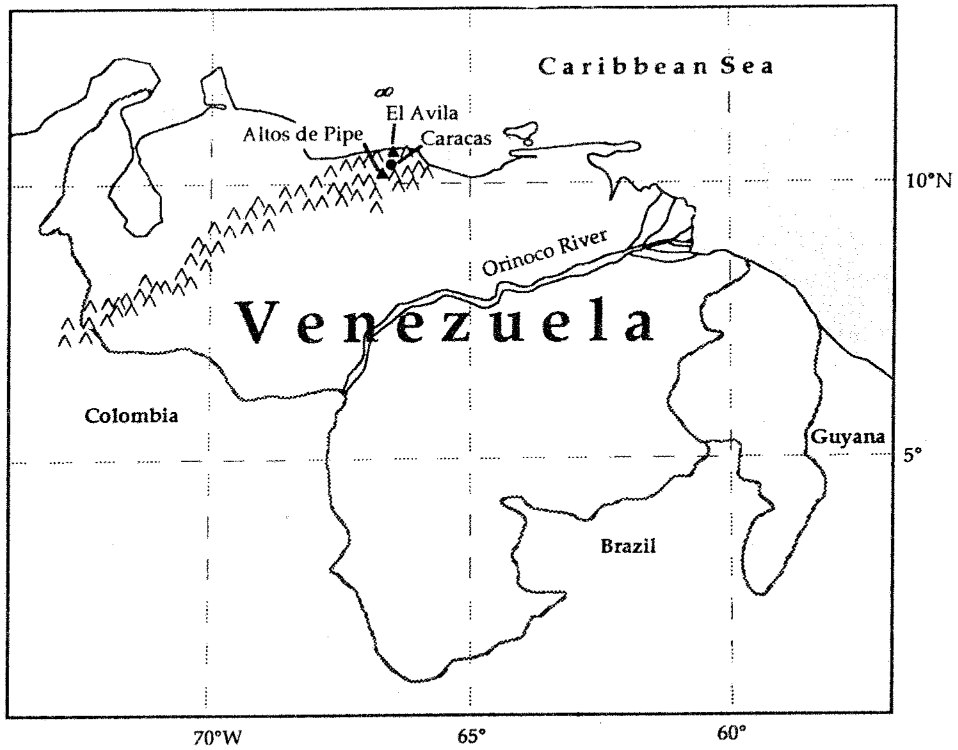

Fig. 1. Locations of study sites.

washed in 5% HNO_3, then rinsed five times with distilled water and five times with distilled deionized water. All collection bottles were stored with distilled deionized water and the storage water was measured for pH and conductivity before each use. The final collector rinsewaters were collected and treated as samples to ensure minimal contamination.

CHEMICAL ANALYSIS

All samples were measured for pH and conductivity within 15 min of collection. Field pH measurements were performed with a Fisher Accumet Model 230A pH/ion meter equipped with a combination glass electrode. Conductivity measurements were performed with a portable Fisher Conductivity Meter Mdl C33. Samples were filtered with 0.45 μm Millipore filters, using a Sartorius SM 165 10/11 polyethylene filtering apparatus (Batley and Gardner, 1977). The soluble fraction was then divided into two aliquots, one was preserved with reagent high grade chloroform: 1 ml/500 ml sample (Andreae *et al.*, 1988; Sanhueza *et al.*, 1989) for the subsequent analysis of organic acids and anions, while the other aliquot was preserved with high grade concentrated nitric acid: 2 ml/500 ml sample (Sanhueza *et al.*, 1989) for the analysis of cations and heavy metals. All samples for chemical analyses were refrigerated at 4°C until chemical analysis could be conducted, approximately one month later. Laboratory blanks were also collected and treated identically.

Anions including F^-, Cl^-, NO_3^- PO_4^{3-}, SO_4^{2-} were measured by ion chromatography using a DIONEX 2010 Ion Chromatograph. Cations including K^+, Na^+, Mg^{2+}, and Ca^{2+} were measured by flame atomic absorption spectrophotometry (AAS) using a Varian Techtron SpectrAA/30/40. Reference material used was National Research Council Canada (NRCC) SLRS-1 Riverine Water Reference Material for Trace Metals. Ammonium was determined by automated colorimetry using a Technicon Autoanalyser II. A subset of samples was analysed for formic and acetic acids. These ions were measured by ion chromatography exclusion with a DIONEX HPLC Module, DIONEX Conductivity Detector, and a Shimadzu C-R5A Chromatopac Plotter.

A subset of fog samples was selected for trace element analysis. These consisted of both overnight fog and "pure" fog samples. Due to low concentrations of trace elements in wet deposition, the subset was based on those samples previously analysed for ion concentrations and found to be at the upper range of ion concentrations. Trace elements were analysed by Inductively Coupled Plasma Emission Spectrometry (ICP) Model Jarrell-Ash 61E at Ortech International Laboratories in Mississauga, Ontario and included the following elements: Al, B, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, S, V and Zn. Reference material and blanks were run simultaneously to ensure quality control.

Means and standard deviations were calculated whenever appropriate, including for H^+ concentrations and conductivity. For all other ion concentrations means and ranges are presented. Since very large variances are common for fog chemistry, ranges rather than standard deviations are reported for ion concentrations. For trace element analyses means and ranges are also given. Ion balances ($\mu eq\ \ell^{-1}$) were calculated and presented as scatter plots to ensure that all the major ions were analysed.

RESULTS

The chemistry of fogs collected during the wet and dry seasons from the two sites is described in Tables 1a and 1b. The pH was highly variable in all sample types, but generally lowest in "pure" fog and highest in overnight fog. At El Avila, pH was generally lower

Table 1a. Fog water chemistry during wet and dry seasons at El Avila Parque Nacional, Distrito Federal. Venezuela, 2150 m a.s.l. Values are means ±S.D.

Type	n	pH	$[H^+]$ (μeq ℓ^{-1})	Conduct. (μS cm^{-1})	$NO_3:SO_4$ ratio
Wet season (June–August, 1989)					
Fog	19	5.03	9.33 ±12.66	41.6 ±24.3	1.50 ±0.57
Overnight*	14	5.81	1.54 ±1.52	84.6 ±66.8	1.17 ±0.30
Precipitation	9	5.26	5.49 ±2.73	5.0 ± 1.6	—†
Fog and precipitation	8	5.49	3.27 ±5.29	17.6 ±17.9	1.13 ±0.32
Dry season (March–May, 1990)					
Fog	51	4.64	23..04 ±32.34	36.2 ±39.3	1.09 ±1.10
Overnight*	10	5.18	6.58 ±3.91	35.7 ±36.4	1.46 ±0.57
Precipitation	8	4.89	12.99 ± 5.13	4.5 ± 2.0	—†
Fog and precipitation	10	4.98	10.43 ±8.12	7.6 ± 5.1	—†

*Overnight samples may include fog/dew/dry deposition/precipitation.
†Sulphate below detection limit of 0.5 mg ℓ^{-1}, therefore no $NO_3:SO_4$ ratio.

Table 1b. Fog water chemistry during wet and dry seasons at Altos de Pipe, Miranda State, Venezuela, 1750 m a.s.l. Values are means ±S.D.

Type	n	pH	$[H^+]$ (μeq ℓ^{-1})	Conduct. (μS cm^{-1})	$NO_3:SO_4$ ratio
Wet season (June–August, 1989)					
Fog	6	4.87	13.22 ±14.92	43.4 ±30.1	0.96 ±0.49
Overnight*	19	5.04	9.04 ±8.28	68.6 ±35.8	0.82 ±0.21
Precipitation	6	4.59	25.32 ±16.56	2.3 ± 0.6	—†
Fog and precipitation	8	4.60	25.26 ±30.28	5.5 ± 1.8	1.05 ±0.11
Dry season (March–May, 1990)					
Fog	10	5.04	9.09 ± 6.56	20.6 ±14.3	0.57 ±0.13
Overnight*	18	5.26	5.48 ±4.91	53.7 ±51.1	0.84 ±0.49
Precipitation	12	5.19	6.49 ± 5.67	10.0 ± 3.4	0.96 ±0.15
Fog and precipitation	3	5.58	2.65 ±2.12	12.6 ± 3.2	—†

*Overnight samples may include fog/dew/dry deposition/precipitation.
†Sulphate below detection limit of 0.5 mg ℓ^{-1}, therefore no $NO_3:SO_4$ ratio.

during the dry season for all sample types. However, the reverse trend was seen at Altos de Pipe with lower pH values during the wet season. Conductivity values were also highly variable with little difference between sites and seasons. Between sample types, the lowest mean values were found in precipitation samples and highest mean values in overnight fog. The values differed by factors of 10–20. The $NO_3:SO_4$ ratios based on equivalents were close to one and were usually higher at El Avila compared to Altos de Pipe.

Figure 2 shows the frequency of fog pH during both wet and dry seasons. Fog at El Avila was considerably more acidic during the dry season compared to the wet season. The pH frequency during the wet season at El Avila was uniformly distributed between 4.0–7.0. Little difference in pH frequency was seen between seasons at Altos de Pipe.

Concentrations of major ions in fog water are shown in Table 2. Great variability in fog chemistry was found. Generally, fog collected from El Avila had

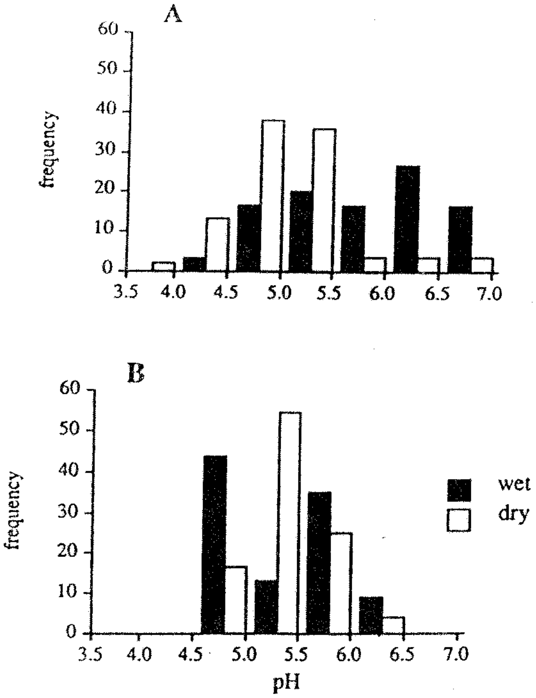

Fig. 2. Frequency of fog pH at (A) El Avila and (B) Altos de Pipe during wet and dry seasons of 1989–1990.

significantly higher mean concentrations of F^-, Cl^-, and NO_3^- compared to Altos de Pipe (Gordon, 1992). Between seasons there were some differences, with significantly higher mean concentrations during the wet seasons for Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-} (Gordon, 1992). The dominant cations in fog collected at El Avila were Ca^{2+} and NH_4^+ during the wet and dry seasons, respectively, followed by Na^+ in both seasons. Dominant anions were NO_3^- and SO_4^{2-} for both wet and dry seasons. At Altos de Pipe the dominant cation in fog was Na^+ followed by Ca^{2+} in the wet season and NH_4^+ followed by Na^+ in the dry season. Dominant anions were Cl^- representing 45 and 37% of all anions during the wet and dry seasons, respectively. The next most dominant anion was SO_4^{2-} in both seasons.

Generally, mean ion concentrations were higher in overnight fog than in "pure" fog (Table 3). Overnight fog collected from Altos de Pipe commonly had lower mean ion concentrations than those collected from El Avila. Dominant ions were the same as in fog samples except for the second most dominant anion at Altos de Pipe which was NO_3^- rather than SO_4^{2-}.

Ion concentrations in precipitation were very low compared to fog ("pure" and overnight), and frequently below detection limits (Table 4). At Altos de Pipe concentrations were higher during the dry season with NH_4^+ and Na^+ as the dominant cations of CH_3COO^- and NO_3^- as the dominant anions. Conversely, at El Avila wet season mean concentrations

Table 2. Mean, maximum and minimum ion concentrations in fog water samples during both dry and wet seasons at Altos de Pipe and El Avila. All values in mg ℓ^{-1}

	Altos de Pipe				El Avila			
	Wet season $n=3$		Dry season $n=10$		Wet season $n=22$		Dry season $n=46$	
Ion	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Ca^{2+}	1.10	0.45–1.74	0.42	0.24–0.72	3.24	0.55–11.10	1.18	<0.10–4.27
K^+	0.34	0.23–0.45	0.18	<0.08–0.51	0.38	0.12–0.86	0.36	<0.08–0.93
Na^+	2.84	0.23–5.44	1.43	0.19–3.04	1.81	0.08–4.35	1.48	0.27–3.90
Mg^{2+}	0.36	0.16–0.56	0.19	0.04–0.57	0.36	0.03–1.12	0.23	0.02–0.65
NH_4^+	na*	na	1.44	0.70–3.60	na	na	3.18	0.20–12.80
F^-	<0.1	<0.1	0.34	0.17–0.74	0.48	<0.1–1.33	0.59	<0.1–1.48
Cl^-	3.99	2.61–5.37	3.43	0.28–8.70	2.71	0.24–5.51	2.70	<0.1–8.36
NO_3^-	1.21	<0.5–1.91	1.95	<0.5–5.97	9.26	1.77–23.15	5.80	0.55–19.49
SO_4^{2-}	3.31	1.87–4.75	2.78	0.99–6.67	5.14	<0.5–12.44	3.92	<0.5–9.65
$HCOO^-$	<0.5†	<0.5	<0.5‡	<0.5	<0.5§	<0.5–1.37	0.54‖	<0.5–3.60
CH_3COO^-	<0.5†	<0.5	<0.5‡	<0.5	<0.5§	<0.5–0.56	0.63‖	<0.5–3.31

* NH_4^+ data not available for wet season samples. PO_4 data all below detection limit of 0.5 mg ℓ^{-1}.
†$n=2$; ‡$n=4$; §$n=9$; ‖$n=27$.

Table 3. Mean, maximum and minimum ion concentrations in overnight fog water samples during both dry and wet seasons at Altos de Pipe and El Avila. All values in mg ℓ^{-1}

	Altos de Pipe				El Avila			
	Wet season $n=19$		Dry season $n=18$		Wet season $n=13$		Dry season $n=7$	
Ion	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Ca^{2+}	4.47	0.47–7.20	2.61	0.30–16.70	7.54	<0.1–17.94	2.94	0.42–11.30
K^+	0.68	0.25–1.31	0.64	0.10–1.62	0.70	<0.08–1.62	0.75	0.27–2.41
Na^+	4.19	0.48–7.70	6.19	0.32–26.41	4.28	<0.03–9.97	3.87	0.70–11.95
Mg^{2+}	1.13	<0.01–2.84	0.87	0.06–3.03	1.00	<0.01–2.52	0.57	0.11–1.88
NH_4^+	na*	na	2.43	<0.1–15.70	na	na	5.32	<0.1–16.30
F^-	0.20	0.12–0.38	0.46	<0.1–1.31	1.25	<0.1–3.41	0.94	0.23–2.16
Cl^-	8.88	1.89–15.96	5.58	0.21–17.26	4.89	<0.1–9.72	4.00	1.39–6.87
NO_3^-	5.56	1.77–9.84	5.22	0.76–25.74	14.24	<0.5–30.93	9.09	3.11–24.89
SO_4^{2-}	5.48	1.49–9.95	4.65	<0.5–15.13	9.49	<0.5–25.93	4.57	2.58–10.36
$HCOO^-$	<0.5†	<0.5	<0.5‡	<0.5–1.72	1.68§	<0.5–7.88	0.52‖	<0.5–1.22
CH_3COO^-	<0.5†	<0.5	0.54‡	<0.5–3.13	0.88§	<0.5–3.26	<0.5‖	<0.5–0.76

*NH_4^+ data not available for wet season. PO_4 data all below detection limit of 0.5 mg ℓ^{-1}.
†$n=6$; ‡$n=15$; §$n=7$; ‖$n=6$.

Table 4. Mean, maximum and minimum ion concentrations in precipitation samples during both dry and wet seasons at Altos de Pipe and El Avila. All values in mg ℓ^{-1}

	Altos de Pipe				El Avila			
	Wet season $n=6$		Dry season $n=12$		Wet season $n=5$		Dry season $n=5$	
Ion	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Ca^{2+}	<0.1	<0.1	0.47	0.23–0.86	0.45	0.37–0.53	0.17	<0.1–0.31
K^+	<0.08	<0.08	0.26	<0.08–0.71	0.28	0.19–0.38	0.16	<0.08–0.46
Na^+	<0.03	<0.03	0.53	0.10–1.10	0.32	0.16–0.56	0.09	<0.03–0.33
Mg^{2+}	<0.01	<0.01	0.06	0.02–0.11	<0.01	<0.01	<0.01	<0.01–0.02
NH_4^+	na*	na	0.88	<0.1–7.20	na	na	0.22	0.20–0.30
F^-	<0.1	<0.1	0.21	<0.1–0.32	<0.1	<0.1	0.11	<0.1–0.13
Cl^-	0.40	<0.1–0.87	0.85	<0.1–2.28	0.18	<0.1–0.24	<0.1	<0.1–0.12
NO_3^-	0.90	<0.5–1.91	0.91	<0.5–1.44	<0.5	<0.5	0.66	<0.5–1.31
SO_4^{2-}	<0.5	<0.5–0.52	0.69	<0.5–1.27	<0.5	<0.5	<0.5	<0.5
$HCOO^-$	—	—	<0.5†	<0.5	—	—	<0.5‡	<0.5
CH_3COO^-	—	—	0.98†	<0.5–2.40	—	—	<0.5‡	<0.5–0.98

*NH_4^+ data not available for wet season. PO_4 data all below detection limit of 0.5 mg ℓ^{-1}.
†$n=6$; ‡$n=5$.

Table 5. Blanks and detection limits in mg ℓ$^{-1}$ in atmospheric wet deposition samples

Ion	Detection limit*	Collector rinse $n = 15$	Bag rinse $n = 5$	Field blanks $n = 21$
Ca^{2+}	0.1	<0.1	<0.1	0.1
K^+	0.08	<0.08	0.10	0.09
Na^+	0.03	<0.03	<0.03	0.04
Mg^{2+}	0.01	<0.01	<0.01	<0.01
NH_4^+	0.1	<0.1	<0.1	0.18
F^-	0.1	<0.1	<0.1	<0.1
Cl^-	0.1	0.1	<0.1	0.1
NO_3^-	0.5	<0.5	<0.5	0.52
SO_4^{2-}	0.5	0.52	<0.5	0.53
$HCOO^-$	0.5	<0.5	<0.5	<0.5
CH_3COO^-	0.5	<0.5	<0.5	<0.5

*Detection limits for Ca^{2+}, K^+, Na^+ and Mg^{2+} are calculated from the mean value of 10 blanks + 2 standard deviations using atomic absorption spectrophotometry. Detection limits for F^-, Cl^-, NO_3^-, SO_4^-, $HCOO^-$ and CH_3COO^- are the lowest value within the working range of ion chromatography. The detection limit for NH_4^+ is the lowest value within the working range, using automated colorimetry.

were higher. Dominant cations were NH_4^+ and Ca^{2+} in the dry season and Ca^{2+} and Na^+ in the wet season. The dominant anion was NO_3^- in the dry season changing to Cl^- in the wet season.

Ionic balances for fog and overnight fog were good for data with low ion concentrations (Fig. 3). However, samples with higher ion concentrations often showed a poor ion balance. Those samples which were analysed for all ions, including organic acids, showed a better balance. In most cases where ion balances were poor, the sum of cations was larger than the sum of anions, suggesting that organic acids were the missing ions. Another anion which may be missing is HCO_3^- which has been shown to be an important ion in some tropical fogs, particularly at high pHs (Schemenauer and Cereceda, 1992b).

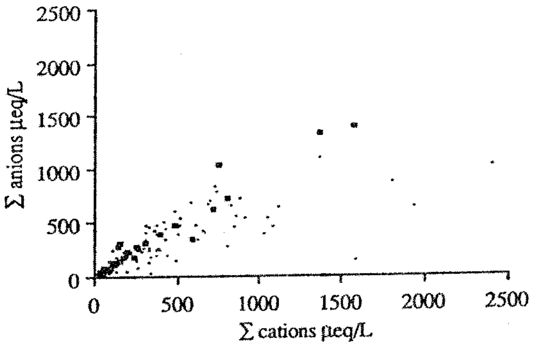

Fig. 3. Total anion vs cation concentrations for fog water samples. ● represent samples without organic acid analysis, ■ represent samples with organic acid analysis.

Detection limits and blank ion concentrations are presented in Table 5. In most cases blanks, which include fog collector rinsewater, precipitation collector rinse water, and field blanks, were close to or below detection limits, suggesting that collectors were adequately free of contamination.

Concentrations of trace elements in fog samples showed that for all elements tested only Al, B, Fe, Mn, Pb and Zn were above detection limits (Table 6). Field blanks were below the detection limit for all 13 elements except for Al which was slightly elevated above the detection limit of 0.02 mg ℓ$^{-1}$. In fog samples Al had highest concentrations of up to 1.56 mg ℓ$^{-1}$ during the wet season at Altos de Pipe. Mean B levels ranged from 0.12–0.14 mg ℓ$^{-1}$. Iron concentrations were very close to the detection limit of 0.02 mg ℓ$^{-1}$ and only elevated at Altos de Pipe during the wet season. Manganese showed similar patterns with highest concentrations (0.236 mg ℓ$^{-1}$) again at Altos de Pipe in the wet season. Lead, on the other hand showed the highest maximum concentration of 0.27 mg ℓ$^{-1}$ at El Avila in the dry season. This value is over 5-times the maximum allowable WHO drinking water standards (Schemenauer and Cereceda, 1992a). Finally, Zn was elevated at both sites during both seasons with highest mean concentrations and the highest maximum value (1.03 mg ℓ$^{-1}$) at Altos de Pipe in the dry season. Six precipitation samples were also analysed for trace elements. However, all of these samples were below detection limits for all elements tested.

ELEMENTAL ENRICHMENT FACTORS AND RATIOS IN FOG

In order to compartmentalize the sources of major ions and trace elements in fog, enrichment factors (EF_{Cl}, EF_{Al}) were calculated and are shown in Tables 7a,b and 8a,b respectively. Enrichment factors (for element X) were calculated using Cl^- as the tracer element for sea water (EF_{Cl}) and Al as the tracer element for the Earth's crust (EF_{Al}) following Schemenauer and Cereceda (1992a)

$$EF_{Cl}[X] = \frac{[X/Cl]_{Fog}}{[X/Cl]_{Sea}} \quad (1)$$

$$EF_{Al}[X] = \frac{[X/Al]_{Fog}}{[X/Al]_{Crust}} \quad (2)$$

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*NH_4^+ data not available for wet season. PO_4 data all below detection limit of 0.5 mg ℓ$^{-1}$.
†$n = 6$; ‡$n = 5$.

Table 6. Concentrations of trace elements in fog water samples during wet and dry seasons at Altos de Pipe and El Avila. All values in mg ℓ^{-1}. Means and ranges given

Element	Field blanks* $n=8$	Altos de Pipe Wet season $n=8$	Altos de Pipe Dry season $n=21$	El Avila Wet season $n=8$	El Avila Dry season $n=20$
Al	0.05	0.34 (0.02–1.56)	0.10 (0.06–0.20)	0.13 (0.10–0.15)	0.14 (0.08–0.24)
B	<0.07	0.12 (<0.07–0.22)	0.13 (0.08–0.19)	0.14 (0.10–0.18)	0.12 (0.08–0.16)
Cd	<0.002	<0.002	<0.002	<0.002	<0.002
Cr	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	<0.01	<0.01	<0.01	<0.01	<0.01
Fe	<0.02	0.23 (<0.02–0.60)	<0.02	0.03 (<0.02–0.06)	0.03 (<0.02–0.85)
Mn	<0.003	0.076 (<0.003–0.236)	0.017 (<0.003–0.064)	0.039 (0.005–0.183)	0.028 (<0.003–0.112)
Mo	<0.004	<0.004	<0.004	<0.004	<0.004
Ni	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	<0.03	0.03 (<0.03–0.10)	<0.03 (<0.03–0.16)	0.04 (<0.03–0.18)	0.07 (<0.03–0.27)
S	<0.05	1.68 (0.25–3.51)	1.44 (0.32–5.56)	1.86 (0.26–4.72)	1.45 (0.25–3.61)
V	<0.01	<0.01	<0.01	<0.01	<0.01
Zn	<0.01	0.05 (<0.01–0.15)	0.14 (0.01–1.03)	0.10 (0.02–0.24)	0.05 (0.03–0.14)

* Field blanks consist of 4 collector rinse samples and 4 field blank samples.

All ions measured showed some enrichment with respect to sea water except for Na^{+} and Mg^{2+} (Cl^{-} by definition is equal to 1) (Tables 7a and 7b). The largest enrichment factor was F^{-} followed by Ca^{2+} at both sites. For EF_{Al}, highest enrichment factors were found to be with Cl^{-}, F^{-}, Na^{+} and Ca^{2+}, suggesting that soils are probably not a significant source of these ions. However, it must be noted here that EF_{Al} is based on average Earth crustal concentrations and is not specific to this area. Sea salt (SSF) and crustal (CRF) fractions were calculated to give an estimate of the apportionment of each of these ions:

$$\mathrm{SSF}(\%) = 1/\mathrm{EF}_{\mathrm{Cl}} \times 100 \qquad (3)$$

$$\mathrm{CRF}(\%) = 1/\mathrm{EF}_{\mathrm{Al}} \times 100. \qquad (4)$$

The residual fraction (NSSCRF) is calculated as the remaining percentage and is assumed to be from anthropogenic sources. It is clear that the sea salt source accounts for a large portion of Na^{+} (77–100%) and Mg^{2+} (52–100%) at both sites during both seasons. The sea salt fraction (SSF) is always higher in the dry season compared with the wet season for these ions and accounts for a larger portion of Na^{+} and Mg^{2+} at El Avila compared with Altos de Pipe. Similarly K^{+}, SO_4^{2-} and Ca^{2+} had a lower SSF at Altos de Pipe.

Crustal fractions were lower than sea salt fractions for all ions except for F^{-}. Again CRF were higher in the dry season at El Avila, but the reverse was true at Altos de Pipe. Ions with a significant crustal contribution include Mg^{2+}, K^{+} and Ca^{2+}, especially at Altos de Pipe. Anthropogenic or residual fractions were very high for F^{-}, SO_4^{2-}, Ca^{2+} and K^{+} at both sites.

Mean Na^{+}/Cl^{-} ratios were calculated for fog samples and found to be 0.60 (0.42–0.71) which is slightly higher than the value of 0.53 observed by Lazrus *et al.* (1970) in fog collected from Puerto Rico but lower than the 0.64 observed by Schemenauer and Cereceda (1992a) for Chilean fog. The Na^{+}/Cl^{-} ratio for sea water is 0.55 (Schemenauer and Cereceda, 1992a).

Trace elements found to be highly enriched with reference to the Earth's crust and sea salt include B, Pb, Mn and Zn (Tables 8a,b).

DISCUSSION

Fog pH and acidic precursors

From the data obtained in this study, it is unlikely that strongly acidic fog events occur at the two cloud forest sites of El Avila and Altos de Pipe. However, H^{+} data were highly variable, the pH was often slightly acidic and within the upper pH range of fog collected from high elevation sites in northeastern North America (Hileman, 1983; Schemenauer and Winston, 1988). The lowest pH recorded (3.7) was collected from El Avila following 14 days without precipitation.

Overall, El Avila is affected by lower fog pHs compared to Altos de Pipe, especially in the dry season

Table 7a. Mean enrichment factors for fog collected from El Avila based on sea water Cl (EF_{Cl}) and crustal Al (EF_{Al}) values. Sea salt (SSF), crustal (CRF) and residual fractions (NSSCRF) of the ions in the fog water are also given. Values given include wet and **dry** season data

Element	X/Cl Sea	X/Cl Fog	EF_{Cl}	X/Al Crust	X/Al Fog	EF_{Al}	SSF (%)	CRF (%)	NSSCRF (%)
Ca^{2+}	0.021	1.20	57.1	0.50	24.92	49.8	2	2	96
		0.44	**21.0**		**8.43**	**16.8**	**5**	**6**	**89**
K^+	0.021	0.14	6.7	0.25	2.92	11.6	15	9	75
		0.13	**6.2**		**2.57**	**10.4**	**16**	**10**	**74**
Na^+	0.55	0.67	1.2	0.28	13.92	49.6	82	2	6
		0.55	**1.0**		**10.57**	**37.9**	**100**	**3**	**0**
Mg^{2+}	0.067	0.13	1.9	0.28	2.77	10.0	52	10	38
		0.085	**1.3**		**1.64**	**5.7**	**79**	**18**	**3**
NH_4^+	—	—	—	—	—	—	—	—	—
		1.18	—	—	**22.71**	—	—	—	—
F^-	0.00007	0.18	2647	0.00075	3.69	493	0	0.2	100
		0.22	**3235**		**4.21**	**560**	**0**	**0.2**	**100**
Cl^-	1.00	1.00	1.0	0.0016	20.85	13,000	100	0	0
		1.00	**1.0**		**19.29**	**12,063**	**100**	**0**	**0**
NO_3^-	—	3.42	—	—	71.23	—	0	—	—
		2.15	—		**41.43**	—	**0**	—	—
SO_4^{2-}	0.14	1.90	13.6	—	39.54	—	14	0	86
		1.45	**10.4**		**28.00**	—	**10**	**0**	**90**

Table 7b. Mean enrichment factors for fog collected from Altos de Pipe based on sea water Cl (EF_{Cl}) and crustal Al (EF_{Al}) values. Sea salt (SSF), crustal (CRF) and residual fractions (NSSCRF) of the ions in the fog water are also given. Values include wet and **dry** season data

Element	X/Cl Sea	X/Cl Fog	EF_{Cl}	X/Al Crust	X/Al Fog	EF_{Al}	SSF (%)	CRF (%)	NSSCRF (%)
Ca^{2+}	0.021	0.28	13.3	0.50	3.24	6.5	8	15	77
		0.12	**5.7**		**4.20**	**8.4**	**18**	**12**	**70**
K^+	0.021	0.085	4.0	0.25	1.00	4.0	25	25	50
		0.052	**2.5**		**1.80**	**7.2**	**40**	**14**	**46**
Na^+	0.55	0.71	1.3	0.28	8.35	29.8	77	3	20
		0.42	**0.8**		**14.30**	**51.1**	**125**	**2**	**0**
Mg^{2+}	0.067	0.09	1.3	0.28	1.06	3.8	77	26	0
		0.055	**0.8**		**1.90**	**6.8**	**125**	**15**	**0**
NH_4^+	—	—	—	—	—	—	—	—	—
		0.42	—	—	**14.40**	—	—	—	—
F^-	0.00007	0.013	179	0.00075	0.50	66.7	0	1.5	99
		0.099	**1414**		**3.40**	**453**	**0**	**0.2**	**100**
Cl^-	1.00	1.00	1.0	0.0016	11.74	7338	100	0	0
		1.00	**1.0**		**34.30**	**21,438**	**100**	**0**	**0**
NO_3^-	—	0.30	—	—	3.56	—	0	—	—
		0.57	—		**19.50**	—	**0**	—	—
SO_4^{2-}	0.14	0.83	5.9	—	9.74	—	17	0	83
		0.81	**5.8**		**27.80**	—	**17**	**0**	**83**

Table 8a. Mean enrichment factors for fog collected from El Avila based on sea water Cl (EF_{Cl}) and crustal Al (EF_{Al}) values. Sea salt (SSF), crustal (CRF) and residual fractions (NSSCRF) of the ions in the fog water are also given. Values include dry season data only

Element	X/Cl Sea	X/Cl Fog	EF_{Cl}	X/Al Crust	X/Al Fog	EF_{Al}	SSF (%)	CRF (%)	NSSCRF (%)
B	2.42×10^{-4}	0.029	119.8	0.0012	0.86	7167	0.8	<0.01	99.2
Fe	5.26×10^{-7}	0.0074	14,068	0.677	0.0021	0.003	<0.01	100.0	0.0
Mn	1.05×10^{-7}	0.0069	65,714	0.0014	0.20	17.54	<0.01	5.7	94.3
Pb	1.58×10^{-9}	0.017	1.13×10^{7}	0.00015	0.50	3333	0.0	0.03	100.0
S	4.66×10^{-2}	0.356	7.64	0.00313	10.36	3310	13.1	0.03	86.9
Zn	5.26×10^{-7}	0.0123	23,384	0.00084	0.36	428	<0.01	0.2	99.8

Table 8b. Mean enrichment factors for fog collected from Altos de Pipe based on sea water Cl (EF_{Cl}) and crustal Al (EF_{Al}) values. Sea salt (SSF), crustal (CRF) and residual fractions (NSSCRF) of the ions in the fog water are also given. Values include dry season data only

Element	X/Cl Sea	X/Cl Fog	EF_{Cl}	X/Al Crust	X/Al Fog	EF_{Al}	SSF (%)	CRF (%)	NSSCRF (%)
B	2.42×10^{-4}	0.024	99.20	0.0012	1.30	10,833	1.0	<0.01	99.0
Fe	5.26×10^{-7}	—	—	0.677	—	—	—	—	—
Mn	1.05×10^{-7}	0.0032	30,000	0.0014	0.17	14.91	<0.01	6.7	93.3
Pb	1.58×10^{-9}	0.0056	3.48×10^{6}	0.00015	0.09	600*	<0.01	0.2	99.8
S	4.66×10^{-2}	0.267	5.73	0.00313	14.40	4600	17.5	0.02	82.0
Zn	5.26×10^{-7}	0.026	49,430	0.00084	1.40	1665	<0.01	0.06	100.0

*Based on wet season data.

(Fig. 2). This is most likely due to acidic precursors originating from the adjacent Caracas Valley, namely NO_x and SO_2 and organic acids (HCOOH and CH_3COOH). Compared to all other ions analysed, nitrate had highest concentrations in fog and precipitation collected from El Avila. This suggests that NO_x emitted from traffic and industry in the Caracas Valley is being oxidized and converted to NO_3^- in clouds. In contrast, on the north coast of Chile which experiences a persistent daytime onshore flow, Schemenauer and Cereceda (1992a) have shown that SO_4^{2-} is the dominant acidic anion in fog. This was also shown to be the case in Oman (Schemenauer and Cereceda, 1992b) with air masses off the northern Indian Ocean during the southwest monsoon. These two areas are relatively free of anthropogenic emissions and natural sulphur emissions from the oceans seem to dominate the acidifying processes in the fog water.

Caracas air has been shown to contain very high levels of NO_x; Ishizaki and Sanhueza (1979) have reported the NO_2 daily mean hourly average as 62 ppb, with a maximum of 165 ppb. In downtown Caracas, the emission of NO by automobiles, in competition with its conversion to NO_2, make atmospheric levels of NO (53 ppb) as high as NO_2 levels all day long. In Caracas the maximum NO_2/NO ratio is low (< 3) and there is a very rapid NO_2 disappearance, probably due to photolysis and vertical dispersion (Ishizaki and Sanhueza, 1979). These air masses contain a high proportion of NO_x aerosols which may be incorporated into fog as NO_3 at the high elevation cloud forest sites. The Caracas Valley exhibits a daily inversion layer during the morning hours which breaks up usually between 9–10 a.m. (Sanhueza and Romero, 1978). Natural biogenic emissions of NO may also contribute to total NO_x levels at the cloud forest sites: Johansson *et al.* (1988) measured NO emissions from savanna and cloud forest soils in northern Venezuela, and found emissions to range from 2.5×10^{-9} to 14×10^{-9} g NO-N $m^{-2} s^{-1}$.

In comparison to NO_3^- levels, sulphate concentrations in this study were lower in fog and precipitation. This was also reflected in high NO_3:SO_4 ratios (0.57–1.50). This is quite different to the situation at high elevation sites in northeastern North America fogs where NO_3:SO_4 ratios are generally much lower and can range from 0.18–0.67 (Schemenauer and Winston, 1988). Sulphur dioxide emissions have been decreasing in Venezuela since 1980 due to the commercial exploitation of large amounts of natural gas and the need to reserve oil for export. Thus, power plants are changing back to natural gas as a principal source of fuel (Sanhueza *et al.*, 1988).

Sulphur dioxide levels in Caracas were measured by Genatios (1973) and he reported the SO_2 annual average of nine months as 5 ppb. However, SO_2 is rapidly oxidized to SO_4^{2-} in this region. The concentration of SO_4^{2-} was found to be 5.6 $\mu g\, m^{-3}$ (Ishizaki and Sanhueza, 1979). Studies performed by Sanhueza *et al.* (1988) show that SO_4^{2-} levels in precipitation from Caracas were 1.23 and 1.7 mg ℓ^{-1} at Altos de Pipe. These values are higher than values found in this study for precipitation but approximately half the concentrations found for fog (Tables 2 and 4).

Organic acids

Formic and acetic acids were not highly significant constituents of the chemistry of fog at these two cloud forest sites. In this study, concentrations of these organic acids were highest in overnight fog samples, with maximum values of 7.88 mg ℓ^{-1} formic acid and 3.26 mg ℓ^{-1} acetic acid. However, fog and precipitation showed concentrations close to or below the detection limit of 0.5 mg ℓ^{-1}. Other studies conducted in this region have shown that organic acids play a major role in the acidity of precipitation (Sanhueza *et al.*, 1989; Hermoso *et al.*, 1990). Precipitation collected by Hermoso *et al.* (1990) from Altos de Pipe and downtown Caracas showed the former site to have mean concentrations of 0.2 and 0.3 mg ℓ^{-1} for formic and acetic acids, respectively. Theses values, however, are both below the present study's detection limits. For precipitation samples in the same study collected from downtown Caracas, mean concentrations were 2.2 and 1.8 mg ℓ^{-1} for formic and acetic acids, respectively. Evidently, these elevated levels are not seen in the present study at the El Avila site. One would expect levels in fog to be higher than in precipitation and therefore higher than observed in the present study. There are several explanations for the low concentrations of formic and acetic acids in fog. Due to difficulties in analysis, a subset of samples was analysed for organic acids in fog. Due to difficulties in analysis, a subset of samples was analysed for organic acids which may not have been representative, and samples with concentrations < 0.5 mg ℓ^{-1} were non-detectable. In addition, organic acids are very unstable and begin to break-down very quickly without very specific sample preservation. Although chloroform was added as a preservative, samples were brought to Canada for analysis and there was a considerable length of storage time before analysis took place. During this time there may have been a loss or chemical transformation of formic and acetic acids within these samples. However, it is evident that these acids are still present in substantial concentrations in some overnight fog samples.

Sources of formic and acetic acids include incomplete products of fuel combustion, especially from automobile emissions, and may also originate from fuel additives (Talbot *et al.*, 1988; Grosjean, 1989). During the dry season, biomass burning has been shown to emit these acids from hydrocarbon precursors (Andreae *et al.*, 1988) and atmospheric concentrations of these compounds are often substantially elevated in comparison with levels in the wet season (Sanhueza *et al.*, 1989; Hermoso *et al.*, 1990). Andreae *et al.* (1987) report that isoprene from biogenic emissions in the Amazon basin is a precursor to formic acid. In industrial or urban areas automobile emissions are the principal source of formic and acetic acids (Talbot *et al.*, 1988) and this is probably the most important source for levels found in this study.

Ion concentrations in fog were often higher in the wet season than in the dry season, particularly for Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-}. This is contradictory to most literature dealing with precipitation and may, in part be explained by the unusual climate during the wet season of 1989 and the following dry season of 1990 in this region. Although beginning in May, the wet season unseasonably dry during June and July. Furthermore, the following dry season was unseasonably wet, compared to long term averages. Differences in ion concentrations in fog water may be due to changes in liquid water content. However, measurements of liquid water content were not made in this study.

Enrichment factors

Mean enrichment factors show that there was general enrichment for all ions with reference to the earth's crust, while enrichment with reference to sea salt included Ca^{2+}, K^+, F^-, and SO_4^{2-}. Sea salt fractions (SSF) account for a large portion of Na^+ and Mg^{2+} and levels of these ions were always higher during the dry season. This suggests that marine aerosols are mainly responsible for these ions. El Avila showed larger SSF for Na^+, K^+, SO_4^{2-} and Ca^{2+}, which we assume to be due to its close proximity to the sea.

The crustal fraction (CRF) accounts for a large portion of K^+, Mg^{2+}, and Ca^{2+} at Altos de Pipe. This "suburban" region is surrounded by bare hills with large scale housing developments ("*urbanizaciones*") taking place. Many of the hills are being excavated and the soils are exposed to erosion. Fine soil particles may become wind-entrained and then scavenged by fog. Soluble portions could then dissolve in the fog droplets. Crustal fractions are much lower at the El Avila site, Mg^{2+} and K^+ being the most significant. This difference may reflect the lower percentage of exposed soil at El Avila.

Anthropogenic sources (NSSCRF) are especially high for Ca^{2+}, K^+, F^- and SO_4^{2-}. At El Avila anthropogenic sources account for between 74–100% of these ions in fog water. Altos de Pipe shows similar but somewhat lower values. These sources may be due to the incorporation of terrestrial aerosols and the soluble fraction of suspended particulates into fog water. Major sources of Ca^{2+} and K^+ may be from urban dust and cement works. It is known that during biomass burning, Ca^{2+} and K^+ are emitted in particulate form (Crutzen and Andreae, 1990). However, this does not seem to be playing a major role in this study, as anthropogenic fractions do not change substantially between wet and dry seasons. The source of F^- is most probably from small industry in the Caracas Valley, such as the brick works. The source of SO_4^{2-} is most probably from the oxidization of SO_2 being emitted in the Caracas Valley. Electric power generation, transport (especially of diesel vehicles), and small industries are the most likely source of SO_2 (Sanhueza *et al.*, 1988; Hermoso *et al.*, 1990).

Chloride in fog showed a loss compared to Cl^-/Na^+ ratios in marine aerosols (Gordon, 1992). This phenomenon has been previously reported by Munger *et al.* (1983), Jacob *et al.* (1985), Sanhueza and Rondon (1988), and Moller (1990). The release of HCl from sea salt aerosols due to its reaction with strong acids such as HNO_3 and H_2SO_4 is the probable explanation. This results in a lowered pH and the volatilization of HCl (Munger *et al.*, 1983). Another possibility is an augmentation of Na^+ from soil dust sources.

Ammonium, which was only measured during the dry season and is not apportioned into sources, shows higher concentrations at the El Avila site. Sources may be anthropogenic, from the decomposition of large amounts of urban wastes within the Caracas Valley. In addition, during the dry season, NH_3 may be emitted through biomass burning, which commonly occurs in areas surrounding both fog collection sites. With further chemical reactions in the atmosphere, this could produce NH_4^+ (Crutzen and Andreae, 1990; Hermoso *et al.*, 1990). Unfortunately, no comparison of NH_4^+ concentrations can be made between seasons, as NH_4^+ was determined for dry season data only due to equipment problems.

Nitrate levels at the El Avila site were significantly higher (by 2–7-times) than at Altos de Pipe in the fog and overnight fog samples. El Avila is located only 3 km from Caracas whereas Altos de Pipe is 18 km away and is situated at the southern base of the Caracas Valley. Here the valley widens rapidly and there may be a large mixing of air coming from the "cleaner" sparsely populated southern region.

Trace elements

Fog water showed elevated concentrations for the following trace elements; Al, B, Fe, Mn, Pb and Zn. Trace elements in precipitation were all below detection limits; however, sample size was very small ($n = 6$) and many of the detection limits were quite high. In fog, aluminium showed the highest maximum concentration (1.56 mg ℓ^{-1}) of all elements tested. The main source could be airborne soil, perhaps with additions from industrial activity. Both sites show high exchangeable Al^{3+} levels in the soil (Cuenca *et al.*, 1990). Iron is also probably largely soil derived. Mean Mn levels were one order of magnitude higher than mean values from high elevation sites in Germany (Kroll and Winkler, 1989), but within the range found at Pasadena and other urban sites in the Los Angeles basin (Munger *et al.*, 1983). Only Schemenauer and Cereceda (1992b) have reported boron levels of fog water. They found B concentrations of 0.035–0.142 mg ℓ^{-1} in fog samples collected from the mountains in southern Oman. These are similar or slightly lower values than those from this study (Table 9). Hendry *et al.* (1984) measured B levels in precipitation

Table 9. Comparison of fog water chemistry from this study* with fog water collected from El Tofo, Chile†, Dhofar Mtns, Sultanate of Oman‡, Pico del Oeste, Puerto Rico§, and Kleiner Feldberg/Taunus Mtns, Germany‖. Concentrations are means expressed in mgℓ^{-1}

Ion/element	This study (wet) (2150 m)	This study (dry) (2150 m)	El Tofo, Chile (780 m)	Dhofar Mtns, Oman (900 m)	Pico del Oeste, Puerto Rico (1020 m)	Taunus Mts, Germany (800 m)
Ca^{2+}	3.24	1.18	0.95	15.1	0.86	2.24
K^{+}	0.38	0.36	0.30	1.09	—	0.84
Na^{+}	1.81	1.48	4.33	24.1	12.3¶	2.46
Mg^{2+}	0.36	0.23	0.52	2.92	1.63	0.61
NH_4^{+}	—	3.18	1.10	0.22	—	21.60
F^{-}	0.47	0.59	—	0.02	—	—
Cl^{-}	2.71	2.70	7.14	44.1	23.2	8.60
NO_3^{-}	9.23	5.80	2.39	4.66	—	10.90
SO_4^{2-}	5.11	3.92	6.30	3.40	5.2	13.30
$HCOO^{-}$	<0.5	<0.5	—	—	—	—
CH_3COO^{-}	0.54	0.63	—	—	—	—
Al	0.13	0.14	0.024	0.009	—	—
Cd	<0.002	<0.002	<0.0005	<0.0005	—	0.0041
Fe	0.03	0.03	<0.05	<0.06	—	0.513
Mn	0.039	0.028	0.012	0.014	—	—
Pb	0.04	0.07	0.0076	<0.0005	—	0.214
Zn	0.10	0.05	0.021	0.0087	—	—
pH	4.89	4.71	4.52	7.37	4.9–5.4	3.8

* Data from this study at the El Avila site during both wet and dry seasons.

† Data compiled from Schemenauer and Cereceda, 1992a.

‡ Data compiled from Schemenauer and Cereceda, 1992b.

§ Data compiled from Lazrus *et al.*, 1970.

‖ Data from Schmitt, 1989. Site located at a forest stand, 25 km northwest of Frankfurt.

¶ Na^{+} concentration calculated from Na/Cl ratio, i.e. 0.53 [Cl].

from Turrialba, Costa Rica (650 m) to be 0.0004–0.0071 mgℓ^{-1}. The Costa Rican levels are one hundred-fold less than boron levels found in fog from this study. Boron is associated with industrial activities and oil refining. There are oil refineries both east and west of the Caracas Valley.

Lead and Zn levels were found to be very high in fog water with maximum values of 0.27 and 1.03 mgℓ^{-1}, respectively. These values are much greater compared with fog collected from Chile and Oman (Schemenauer and Cereceda (1992a, 1992b) (Table 9). Schemenauer and Cereceda (1992a) found maximum Pb and Zn levels in fog from Chile to be 0.036 and 0.078 mgℓ^{-1}, respectively. In the Oman study, these authors found Pb to be below the detection limit of 0.005 mgℓ^{-1} and mean zinc levels to be 0.0087 mgℓ^{-1} (Schemenauer and Cereceda, 1992b). Lead in precipitation from an Andean cloud forest in northwestern Venezuela was measured to be 0.00283 mgℓ^{-1} (Steinhardt and Fassbender, 1979). In the present study, Pb in precipitation was below the detection limit of 0.03 mgℓ^{-1}. Zinc measured in precipitation from a high elevation pine forest in India showed mean concentrations of 0.014 mgℓ^{-1} (Mahadevan *et al.*, 1989) and Hendry *et al.* (1984) reports Zn in precipitation from Costa Rica to be 0.0058–0.037 mgℓ^{-1}.

Lead values in this study are within the range seen in the Los Angeles basin, 0.038–2.5 mgℓ^{-1} (Waldman *et al.*, 1985), an area known for its very high automobile density and use. Lead levels in fog appear to be decreasing in North America where legislation either markedly decreased allowable Pb levels in gasoline, or as in Canada, banned its use as a fuel additive. Estimated Pb concentrations cloud water reaching high elevation forests of Whiteface Mtn (northeastern U.S.A.) were 0.15 mgℓ^{-1} in 1966–1967. Today cloud water values are estimated to be 0.0054 mgℓ^{-1} (Miller and Friedland, 1991). Weathers *et al.* (1988) measured Pb concentrations in fog collected from Mt Washington, N.H., to be 0.0031–0.062 mgℓ^{-1}. Current values in northeastern U.S.A. are thus considerably lower than those found in the present Venezuelan study. Notably, unleaded gasoline is not yet in use in Venezuela, so that combustion of leaded gasoline is most probably the major reason for the high values found in these montane fogs. Automobile emitted lead is generally in fine particulate form, as lead halides, with a mean diameter of $<2\,\mu$. Such fine particles travel readily in the atmosphere.

Elemental enrichment factors were extremely high for B, Pb, Mn, S and Zn. Calculations show anthropogenic sources accounted for between 82 and 100% of these elements in fog collected from both sites and were close to 100% for B, Pb and Zn. The chemical inputs in fogs being intercepted in these cloud forests are clearly markedly affected by anthropogenic emissions, most probably originating from the Caracas Valley.

Studies by Escalona and Sanhueza (1981) have shown that suspended particulates in Caracas air are heavily polluted with compounds containing Zn and

Pb. Lead is still used widely as a gasoline additive in Venezuela and thus motor vehicles are considered to be the major source of this element. Zinc from motor vehicle tire dust and urban refuse incineration are suggested to be the major sources of this element (Escalona and Sanhueza, 1981).

Major ions and trace elements in fog water collected in this study are compared to fog data from other studies (Table 9). Mean Ca^{2+} concentrations were higher during both seasons in this study compared to data from Chile and Puerto Rico. Other ions generally showed mean concentrations to be lower in our study compared with other studies, especially compared with Oman, where major cations and Cl^- showed much higher concentrations than all other studies. The exception to this trend was NO_3^- in the present study which showed elevated levels, close to those from the German study. Mean fog pH values are in agreement with those from both South American studies and are an order of magnitude higher than values from the German study.

Fog pH, although not as low as temperate fog collected from highly polluted areas such as Western Europe and Northeastern North America was, on average, more acidic than precipitation collected from the same area. "Pure" fog showed ion concentrations up to 10-times greater, and conductivity values up to 20-times greater than in precipitation. This is in agreement with the findings of Munger *et al.* (1983), Jacob *et al.* (1985), and Waldman *et al.* (1985). Ion concentrations in overnight fog are even higher than in pure fog and could be attributed to the addition of dry deposition to the fog sample during the long hours (up to 9.5 h) of exposure.

CONCLUSIONS

Fog from both Venezuelan sites is generally acidic with a mean pH between 4.6–5.0. Nitrate concentrations were very high in fog, and nitric acid seems to be the most significant factor in its acidity. Analysis of trace elements show that fog from both cloud forests contained high concentrations of lead, manganese and zinc, which are most likely from anthropogenic sources, and also high concentrations of aluminium and iron, which most likely originate from soil dust. Little difference was seen in fog chemistry between sites, but surprisingly, major ions showed higher mean concentrations during the wet season than the dry season. Generally, fog arriving at El Avila was more polluted than at Altos de Pipe. Fog consistently showed much higher ion concentrations compared with precipitation collected from the same site. Overall, fog was also more acidic than precipitation. Due to the extremely high frequency and duration of fog (Gordon *et al.*, 1994), its acidity, and the elevated concentrations of trace metals there is major cause for concern for the health of these cloud forests in the future. Monitoring would be in order both for the chemistry of fog and precipitation in the future for Central and South America, and for the most sensitive indicator biota of the montane fog forests, such as the epiphytic lichens, bryophytes and bromeliads.

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