



CLOUD WATER AND PRECIPITATION CHEMISTRY IN A TROPICAL MONTANE FOREST, MONTEVERDE, COSTA RICA

KENNETH L. CLARK,*† NALINI M. NADKARNI,‡ DOUGLAS SCHAEFER§
and HENRY L. GHOLZ*

*School of Forest Resources and Conservation, University of Florida, Gainesville, FL 32611, U.S.A.; †The Evergreen State College, Olympia, WA 98502, U.S.A. and §Terrestrial Ecology Division, University of Puerto Rico, San Juan, 00936, Puerto Rico

(First received 9 September 1996 and in final form 21 July 1997. Published April 1998)

Abstract— Cloud water, mist and precipitation samples were collected at two sites in a tropical montane forest (TMF), Monteverde, Costa Rica. Cloud water, mist and wind-driven ($u \geq 2 \text{ m s}^{-1}$) precipitation samples were collected with passive cloud water-type collectors, and precipitation at low windspeeds ($u < 2 \text{ m s}^{-1}$) was sampled with a bulk precipitation-type collector. Concentrations of H^+ , NO_3^- , and NH_4^+ in cloud water were 132 ± 150 , 103 ± 82 , and $149 \pm 200 \mu\text{mol l}^{-1}$ (mean ± 1 S.D., $n = 15$), respectively. Concentrations of NO_3^- , NH_4^+ , Ca^{2+} and K^+ in cloud water samples collected at the middle and end of the dry season, which corresponded to biomass burning activities in the region, were significantly greater when compared to those collected early in the dry season. The mean concentration of H^+ in cloud water at Monteverde was lower, but concentrations of NO_3^- and NH_4^+ were within the range of those collected at a number of montane sites in North America ($62\text{--}195 \mu\text{mol NO}_3^- \text{ l}^{-1}$ and $74\text{--}184 \mu\text{mol NH}_4^+ \text{ l}^{-1}$). Ion concentrations in mist were 2–24 times greater than those in both categories of precipitation. Ion concentrations in both categories of precipitation were generally within the range of those reported in bulk precipitation from other tropical premontane and TMF sites. © 1998 Published by Elsevier Science Ltd. All rights reserved.

Key word index: Cloud water chemistry, rainfall chemistry, cloud forest, biomass burning, tropics.

INTRODUCTION

Cloud water and precipitation chemistry has been the focus of considerable research over the last two decades at temperate montane forest sites (e.g. Lovett *et al.*, 1982; Dollard *et al.*, 1983; Fowler *et al.*, 1988; Weathers *et al.*, 1988; Mohnen and Kadlecak, 1989; Johnson and Lindberg, 1992; Mohnen and Vong, 1993). These investigations indicate that ion concentrations in cloud water are typically 3–10 times greater than those in precipitation, and high concentrations of H^+ , NO_3^- , NH_4^+ and SO_4^{2-} in cloud water and precipitation have been linked to anthropogenic emissions of NO_x , NH_3 and SO_2 (Warneck, 1988; Irving, 1991). Because rates of ion deposition are partially a function of cloud exposure, they are often greater in montane forests when compared to forests at lower elevations (Lovett and Kinsman, 1990; Vong *et al.*, 1991; Johnson and Lindberg, 1992; Miller *et al.*, 1993; Asbury *et al.*, 1994). High rates of H^+ , NO_3^- , NH_4^+ and SO_4^{2-} deposition potentially lead to forest

decline, N saturation and acidification of soils, and relatively high concentrations of NO_3^- and H^+ in surface waters (Schulze, 1989; Aber, 1992; Johnson and Lindberg, 1992; Stevens *et al.*, 1994; Dise and Wright, 1995).

Less information is available for cloud water and precipitation chemistry at tropical montane forest (TMF) sites (Steinhardt and Fassbender, 1979; Weathers *et al.*, 1988; Veneklaas, 1990; Asbury *et al.*, 1994; Gordon *et al.*, 1994). However, changes in land use practices and increased combustion of biomass and fossil fuels have led to an increase in the emissions of nitrogen oxides (N_2O and NO) and ammonia (NH_3) at tropical latitudes (Talbot *et al.*, 1988; Crutzen and Andreae, 1990; Keller *et al.*, 1991; Galloway *et al.*, 1994; Galloway, 1996; Thompson, 1996). Reports from lowland sites have indicated regional effects of biomass burning on precipitation chemistry (Lewis, 1981; Kellman *et al.*, 1982; Hendry *et al.*, 1984; Andreae *et al.*, 1990) and on air chemistry (Andreae *et al.*, 1988a; Artaxo *et al.*, 1988, 1990). Conversion of forests to pasture and croplands may also lead to increased emissions of N_2O , NO , and NH_3 , particularly where N fertilizers are used (Davidson *et al.*,

†Author to whom correspondence should be addressed.

1991, 1993; Hutchinson and Brams, 1992; Keller *et al.*, 1993; Hall *et al.*, 1996). These activities potentially lead to greater concentrations of H^+ , NO_3^- and NH_4^+ in cloud water and precipitation in TMFs, but few measurements have been reported. The objective of this study was to characterize the concentrations of H^+ , NO_3^- , NH_4^+ , and other major ions in cloud water, mist, and precipitation at a TMF site at Monteverde, Costa Rica.

METHODS AND MATERIALS

Site description

Cloud water, mist, and precipitation samples were collected at two sites in the Monteverde Cloud Forest Reserve (MVCFR) in the Cordillera de Tilarán, in west central Costa Rica (10°18'N, 84°48'W). Slopes and ridges in the MVCFR are similar to those of other tradewind-dominated montane forests in terms of climate and forest physiognomy (Lawton and Dryer, 1980; Nadkarni *et al.*, 1997). Three distinct seasons are differentiated primarily by the seasonal migration of the intertropical convergence zone: (i) a dry season (mid-January to April), characterized by moderate northeasterly tradewinds and wind-driven cloud and mist, (ii) a wet season (May to October), characterized by convective precipitation, and (iii) a transition season (November to mid-January), characterized by strong tradewinds and wind-driven precipitation and mist. Mean annual precipitation depth measured ca. 2 km NW from the MVCFR headquarters between 1959 and 1995 was 2519 mm, but wind-driven cloud water and precipitation inputs were underestimated (J. Campbell, pers. communication). Mean monthly minimum and maximum temperatures ranged between 13.9 and 16.5°C, and between 17.6 and 21.1°C during October 1991 to September 1992, respectively (Clark, 1994).

The two study sites are in the tropical lower montane wet-forest zone (Holdridge, 1967), and have been further classified as windward cloud forest (WCF) and leeward cloud forest (LCF) (Lawton and Dryer, 1980). The WCF site is located on the continental divide, ca. 2.2 km southeast of the MVCFR headquarters, and the LCF site is located below

the continental divide, ca. 1.0 km south of the MVCFR headquarters. Elevation of the WCF and LCF sites are 1460 and 1480 m, respectively. Immersion in a hill cap cloud occurs more frequently at the WCF site.

Cloud water, mist and precipitation sampling

Samples collected during non-precipitating cloud immersion conditions, where visibility was reduced to ≤ 0.5 km and there was no deposition to a standard rainfall gauge, were defined as "cloud water" (Table 1). Samples collected during precipitating cloud immersion conditions were defined as "mist". Precipitation samples collected during periods of minimal cloud immersion were separated into two categories; samples where mean windspeed (u) ≥ 2 $m s^{-1}$, and samples where $u < 2$ $m s^{-1}$. Precipitation samples collected when $u \geq 2$ $m s^{-1}$ typically originated from stratus cloud, and those collected when $u < 2$ $m s^{-1}$ typically originated from cumulus or stratocumulus cloud (Table 1). Cloud water, mist, and precipitation events were delimited by at least 12 h without measurable cloud water or precipitation on the basis of meteorological data, corroborated by visual observations.

Cloud water was collected at the WCF site with Atmospheric Sciences Research Center (ASRC) passive cloud water collectors (Falconer and Falconer, 1980). Collectors (30 cm tall, 10 cm dia.) consisted of acrylic plastic frames with ca. 100 Teflon monofilament lines (0.05 cm diameter) strung vertically between the top and base of the frames. Collectors were rinsed with an excess of deionized water and then soaked in deionized water overnight before use. They were transported to the site in new polyethylene bags and connected to clean (washed with 0.1 M HCl and rinsed 5–10 times with deionized water) polypropylene funnels (16 cm or 19.5 cm dia.) and collection bottles. Collectors, funnels, and bottles were mounted on a PVC plastic frame 2.5 m above the floor of an observation deck. Following cloud immersion, polyethylene bags were removed from collectors and the first 10–20 ml of sample was discarded. Samples were transferred to clean polypropylene bottles and stored in a cooler at the site, and transported to the laboratory daily. Samples collected during intermittently dry periods when cloud base lifted were discarded.

Passive cloud water collectors were used to collect mist and precipitation during events where $u \geq 2$ $m s^{-1}$ at both sites (Table 1). At the LCF site, a cloud water collector was

Table 1. Meteorological conditions, collector type, number of events, and number of samples or subsamples collected at the WCF and LCF sites by event category

	Event category			
	Cloud water	Mist	Precipitation	
			$u \geq 2$ $m s^{-1}$	$u < 2$ $m s^{-1}$
Mean windspeed ($m s^{-1}$)	≥ 2	≥ 2	≥ 2	< 2
Cloud immersion	Yes	Yes	No	No
Precipitation	No	Yes	Yes	Yes
Collector type	ASRC cloud collector	ASRC cloud collector	ASRC cloud collector	Bulk precip.
Location	WCF	WCF, LCF	WCF, LCF	LCF
Duration of sampling period (h)	1–12	1–72	1–72	24–72
Number of events	15	32	54	68
Number of samples or subsamples	34	44	76	47

Note: Sampling dates for the WCF site: 15 Apr. 1988 to 20 May 1988, 31 Dec. 1990 to 6 Jan. 1991, 7 Jan. 1992 to 11 Jan. 1992, 17 Feb. 1992 to 21 Feb. 1992, 21 Apr. 1992 to 24 Apr. 1992; "a" indicates sampling during periods of biomass burning activity. Sampling dates for the LCF site: 15 Apr. 1988 to 20 Jun. 1988, 15 Apr. 1989 to 23 Jul. 1989, 11 May 1990 to 25 May 1990, 30 Sep. 1991 to 29 Sep. 1992.

mounted at 17 m height on a 27 m meteorological tower in a large gap in the forest and accessed with a rope and pulley system. Some of the mist and precipitation samples were "bulk" samples because collectors were exposed to dry deposition for up to 72 h before the onset of an event, and samples were collected no later than 72 h after the onset of mist or precipitation. Precipitation during events where $u < 2 \text{ m s}^{-1}$ was sampled with a bulk precipitation-type collector at the LCF site only (Table 1). The collector (16 or 19.5 cm funnel dia.) was mounted 3 m above the forest floor in a large gap in the forest (1988, 1989, 1990) or at 17 m on the meteorological tower (1991, 1992). Some of these samples were also "bulk" samples, and they were collected no later than 48 h after the onset of precipitation. Mist and precipitation samples were transferred to clean polyethylene bottles, and the collectors, funnels and bottles were either rinsed three times with an excess of deionized water or replaced.

Meteorological variables

A tipping bucket rain gauge (Model # 2501, Sierra Misco Environmental Ltd., Victoria, B.C.) mounted at 12 m on the tower was used to determine hourly precipitation depth and event duration at the LCF site in 1991–1992. A 3-cup anemometer (Model # 12-002, R. M. Young Co., Traverse City, Michigan) mounted at the top of the tower was used to measure windspeed. Instruments were recorded with an automated data logger (Easy Logger Model EL824-GP, Omnidata Inc., Ogden, Utah).

Chemical analyses

Within 24 h of collection, pH was determined on unfiltered subsamples (Corning model # 120 pH meter; Orion 915600 probes calibrated with Fisher pH 4.00 and 7.00 standards) in the laboratory. Remaining subsamples were filtered through Gelman AE 0.45 μm pore size filters that had been rinsed with deionized water with a polypropylene syringe and stored at 4°C. Nitrate and NH_4^+ analyses were performed on a Sequoia Turner 340 colorimeter equipped with a semi-automated flowcell assembly within two weeks of collection for most (>90%) samples (Table 2). Potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), and sodium (Na^+) concentrations were determined using standard procedures on a Perkin Elmer Model 603 atomic absorption spectrophotometer at the Analytical Research Laboratory, University of Florida (Table 2). Lanthanum additions (ca. 5 mmol l^{-1}) were used to reduce interferences during Ca^{2+} and Mg^{2+} determinations.

Data analyses

Volume-weighted mean ion concentrations were calculated for samples collected within each event. Arithmetic means and standard deviations were then calculated for

cloud water events, and volume-weighted mean ion concentrations were calculated for mist and both categories of precipitation. Correlation coefficients (Pearson's product-moment) were calculated for ion concentrations in cloud water, mist and both categories of precipitation. Wilcoxon two-sample nonparametric tests (Sokol and Rohlf, 1981) were used to detect differences in ion concentrations in cloud water among transition season to early dry-season and middle-to-late dry-season sampling periods. Prior to statistical analyses, data were tested for normality and homoscedasticity of group variances. All statistical analyses were performed using SYSTAT statistical packages (SYSTAT, 1992).

RESULTS AND DISCUSSION

Cloud water

Mean concentrations of H^+ , NO_3^- and NH_4^+ in cloud water were 7, 14, and 17 times greater than those in precipitation from events where $u \geq 2 \text{ m s}^{-1}$, and 10, 30, and 45 times greater than those in precipitation from events where $u < 2 \text{ m s}^{-1}$, respectively (Table 3). Mean concentrations of Na^+ and Mg^{2+} were much greater in cloud water when compared to those in both categories of precipitation. The molar ratio of Na^+ and Mg^{2+} in cloud water was similar to that in sea water (0.137 ± 0.015 (mean ± 1 S.D.) vs 0.123), indicating that these ions originated primarily from wind-driven marine aerosol (Blanchard, 1983). In contrast, Ca^{2+} and K^+ were relatively less enriched in cloud water when compared to mist and both categories of precipitation (Table 3). With the exception of H^+ and the other ions, all ion pairs in cloud water were positively correlated ($P < 0.05$ or 0.01; Table 4). There was little relationship between H^+ and NO_3^- , and the relatively high concentrations of NH_4^+ in cloud water suggest that H^+ was partially neutralized by NH_3 . In addition, free acidity in cloud water and precipitation at remote tropical sites may be largely controlled by weak organic acids rather than by mineral acid concentrations (Keene *et al.*, 1983; Andreae *et al.*, 1988b; Weathers *et al.*, 1988; Talbot *et al.*, 1990a; Sanhueza *et al.*, 1992), but we did not measure these. Precipitation acidity may also be locally controlled by vulcanism at remote sites (Kellman *et al.*, 1982; Veneklaas, 1990), although there

Table 2. Analytical methods, detection limits, and precision for ion analyses

Ion	Analytical method	Detection limit ^a ($\mu\text{mol l}^{-1}$)	Analytical precision ^b (%)	Reference
NO_3^-	Cadmium reduction column	0.5	4.3	Mackereth <i>et al.</i> (1978)
NH_4^+	Indophenol blue	1.1	2.4	Harwood and Kuhn (1970)
K^+	Flame Emission	1.3	2.0	Instrument manual
Ca^{2+}	Atomic Absorption	3.0	5.0	Instrument manual
Mg^{2+}	Atomic Absorption	2.1	2.0	Instrument manual
Na^+	Flame Emission	2.2	2.0	Instrument manual

^aDetection limit is two times the standard deviation of the mean of deionized water blanks analyzed throughout the study.

^bAnalytical precision is two times the standard deviation of the mean/mean $\times 100$ of medium concentration standards analyzed throughout the study.

Table 3. Ion concentrations (mean $\mu\text{mol l}^{-1} \pm 1$ S.D.; $n = 15$) in cloud water, and volume-weighted mean ion concentrations in mist ($n = 32$), precipitation where mean windspeed (u) ≥ 2 m s^{-1} ($n = 54$), and precipitation where mean $u < 2$ m s^{-1} ($n = 47$). (ranges are in parentheses; bdl = below detection limits)

Sample type	Ion concentration ($\mu\text{mol l}^{-1}$)						
	H ⁺	NO ₃ ⁻	NH ₄ ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	K ⁺
Cloud water	132.1 \pm 149.8 (2.5–489.8)	102.8 \pm 82.0 (32.1–382.9)	148.9 \pm 199.7 (47.2–739.4)	365.0 \pm 175.7 (144.4–713.4)	63.4 \pm 30.9 (18.1–121.8)	35.2 \pm 20.0 (8.7–70.1)	30.7 \pm 18.4 (7.7–76.5)
Mist	30.8 (0.2–251.2)	37.3 (10.8–106.1)	45.3 (2.8–131.1)	183.0 (45.7–839.5)	21.9 (4.9–137.4)	16.8 (6.0–78.6)	13.5 (2.3–71.4)
Precipitation $u \geq 2$ m s^{-1}	19.0 (3.7–91.2)	7.5 (1.3–47.1)	8.9 (0.6–87.2)	75.4 (7.4–765.6)	8.8 (0.8–104.9)	6.6 (3.0–49.4)	4.1 (1.3–94.6)
Precipitation $u < 2$ m s^{-1}	13.8 (2.8–55.0)	3.4 (bdl–46.8)	3.3 (bdl–127.8)	7.8 (2.6–107.0)	1.2 (bdl–8.2)	3.4 (bdl–11.7)	2.1 (bdl–27.6)

Table 4. Correlation matrices (Pearson's product-moment) for ion concentrations in (i) cloud water ($n = 15$), (ii) mist ($n = 32$), (iii) precipitation where mean windspeed (u) ≥ 2 m s^{-1} ($n = 54$), and (iv) precipitation where $u < 2$ m s^{-1} ($n = 47$)

	H ⁺	NO ₃ ⁻	NH ₄ ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	K ⁺
i. Cloud water							
H ⁺	—						
NO ₃ ⁻	0.139	—					
NH ₄ ⁺	0.362	0.982 ^b	—				
Na ⁺	-0.250	0.664 ^b	0.607 ^a	—			
Mg ²⁺	-0.266	0.626 ^a	0.574 ^a	0.987 ^b	—		
Ca ²⁺	-0.177	0.786 ^b	0.739 ^b	0.582 ^a	0.568 ^a	—	
K ⁺	-0.038	0.929 ^b	0.880 ^b	0.681 ^b	0.665 ^b	0.933 ^b	—
ii. Mist							
H ⁺	—						
NO ₃ ⁻	-0.151	—					
NH ₄ ⁺	0.048	0.583 ^b	—				
Na ⁺	0.022	0.575 ^b	0.365	—			
Mg ²⁺	0.041	0.673 ^b	0.433 ^a	0.959 ^b	—		
Ca ²⁺	-0.301	0.738 ^b	0.497 ^b	0.670 ^b	0.725 ^b	—	
K ⁺	-0.190	0.723 ^b	0.528 ^b	0.695 ^b	0.737 ^b	0.983 ^b	—
Precipitation, $u \geq 2$ m s^{-1}							
H ⁺	—						
NO ₃ ⁻	-0.086	—					
NH ₄ ⁺	0.102	0.896 ^b	—				
Na ⁺	-0.019	0.683 ^b	0.668 ^b	—			
Mg ²⁺	-0.067	0.705 ^b	0.671 ^b	0.981 ^b	—		
Ca ²⁺	-0.063	0.701 ^b	0.676 ^b	0.673 ^b	0.740 ^b	—	
K ⁺	-0.128	0.845 ^b	0.713 ^b	0.847 ^b	0.862 ^b	0.793 ^b	—
Precipitation, $u < 2$ m s^{-1}							
H ⁺	—						
NO ₃ ⁻	0.411 ^b	—					
NH ₄ ⁺	0.443 ^b	0.950 ^b	—				
Na ⁺	0.072	0.441 ^b	0.574 ^b	—			
Mg ²⁺	0.099	0.584 ^b	0.488 ^b	0.743 ^b	—		
Ca ²⁺	0.196	0.570 ^b	0.527 ^b	0.759 ^b	0.636 ^b	—	
K ⁺	0.362 ^a	0.441 ^b	0.363 ^b	0.872 ^b	0.675 ^b	0.642 ^b	—

Significance levels: ^a $P < 0.05$, ^b $P < 0.01$

are no active volcanic centers directly upwind from the WCF and LCF sites.

Cloud water samples collected during the middle and end of the dry season (late February to mid-May) had greater concentrations of NO₃⁻, NH₄⁺, Ca²⁺, and K⁺ when compared to those collected at the end of

the transition season and in the early dry season (December and January) ($P < 0.05$; Fig. 1). Cloud water sampling periods during the middle and end of the dry season coincided with obvious atmospheric haze layers, presumably due to the burning of agricultural and forest biomass, and grey to black particles

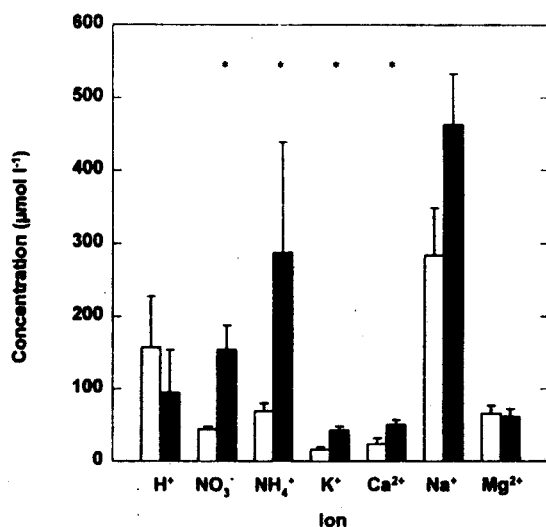


Fig. 1. Ion concentrations (mean $\mu\text{mol l}^{-1} \pm 1 \text{ SE}$) in cloud water collected at the late transition to early dry season (December and January, open bars, $n = 7$ events) and middle to late dry season (late February to May, closed bars, $n = 8$ events). * = $P < 0.05$, Wilcoxon two-sample tests.

were noted on cloud water collectors and on Gelman AE filters following sample filtration. It is likely that ion enrichment in cloud water samples collected during these periods resulted from the incorporation of

gases and particles derived from biomass burning activities (Andreae *et al.*, 1988a; Crutzen and Andreae, 1990; Lobert *et al.*, 1990).

Concentrations of H^+ , NO_3^- , and NH_4^+ in cloud water at Monteverde were 5.5, 1.7, and 4.7 times greater than those in cloud water at Puerto Rico, respectively (Weathers *et al.*, 1988; Asbury *et al.*, 1994; Table 5). Hydrogen ion concentrations in cloud water at Monteverde were generally lower than those in cloud water at temperate montane sites in North America, while NH_4^+ and NO_3^- concentrations were similar. Marine-derived ions also accounted for a majority of the Na^+ and Mg^{2+} in cloud water at Puerto Rico, but were very low at the temperate montane sites in North America (Weathers *et al.*, 1988; Asbury *et al.*, 1994; Table 5).

Mist and precipitation

In general, volume-weighted mean ion concentrations in mist and precipitation were inversely proportional to precipitation intensity; ion concentrations in mist were 1.6 (H^+) to 5.1 (NH_4^+) times greater than those in precipitation from events $u \geq 2 \text{ m s}^{-1}$, and 2.2 (H^+) to 23.5 (Na^+) times greater than those in precipitation from events where $u < 2 \text{ m s}^{-1}$ (Table 3). Concentrations of H^+ , Ca^{2+} and K^+ were relatively less reduced than those of the other ions in precipitation from events where $u < 2 \text{ m s}^{-1}$, suggesting that

Table 5. Cloud water chemistry (mean $\mu\text{mol l}^{-1}$) at montane forest sites in Northern South, Central, and North America

Location	Ion concentration ($\mu\text{mol l}^{-1}$)						
	H^+	NO_3^-	NH_4^+	Na^+	Mg^{2+}	Ca^{2+}	K^+
Tropical sites							
Caracas,	23	94	177	64	9	29	9
Venezuela ^a	9	31	80	62	8	10	5
Pico del Oeste,	20	60	32	650	85	63	25
Puerto Rico ^{b,c}	28	64	32	397	44	31	13
Monteverde,	132	103	149	365	63	35	31
Costa Rica ^d							
Temperate sites							
Whiteface Mountain,	122	62	74	3	3	11	3
New York ^{e,f}	274	115	124	—	—	—	—
Shaver Hollow,	171	94	93	—	—	—	—
Virginia ^{g,h}	205	155	84	13	2	5	3
Mnt. Moosilauke,	263	132	107	—	—	—	—
New Hampshire ^{g,i,j}	270	180	102	32	19	10	11
	288	195	108	30	—	—	10
Mnt. Mitchell,	335	130	175	—	—	—	—
North Carolina ^{g,k}	398	174	184	—	—	—	—

^aGordon *et al.* (1994); Dry season samples collected at Pico del Avila and Altos de Pipe.

^bWeathers *et al.* (1988).

^cAsbury *et al.* (1994).

^dThis study.

^eMiller *et al.* (1993); 4-yr liquid water content-weighted means.

^fMohnen and Kladekek (1989); 5-yr mean of summer values.

^gMohnen and Vong (1993); 3-yr mean of warm clouds.

^hSigmon *et al.* (1989).

ⁱSchaefer and Reiners (1990).

^jLovett *et al.* (1982)

^kAneja *et al.* (1992).

sources of these ions exist through the wet season. Buffering of H^+ concentrations in precipitation by weak organic acids is probable. Calcium and K^+ in precipitation from events where $u < 2 \text{ ms}^{-1}$ were possibly due to the release of particles from the forest canopy, and/or from soil (Croizat, 1979; Artaxo *et al.*, 1990; Talbot *et al.*, 1990b). With the exception of H^+ and the other ions, all ion pairs in mist and precipitation from events where $u \geq 2 \text{ ms}^{-1}$ were positively correlated (Table 4). In contrast, H^+ was positively correlated with NO_3^- , NH_4^+ , and K^+ in precipitation from events where $u < 2 \text{ ms}^{-1}$. Concentrations of NO_3^- , NH_4^+ , and to a lesser extent Ca^{2+} and K^+ in precipitation from events where $u < 2 \text{ ms}^{-1}$ declined rapidly through the three wet seasons monitored, which is similar to patterns reported for other tropical sites (Lewis, 1981; Kellman *et al.*, 1982; Hendry *et al.*, 1984). Decreases in ion concentrations are presumably due to the washout of atmospheric gases and particles, and reduced agricultural burning activity as the wet season progresses (Lewis, 1981; Andreae *et al.*, 1990; Crutzen and Andreae, 1990).

Most volume-weighted mean ion concentrations in both categories of precipitation were intermediate when compared to values from other tropical premontane and TMF sites in Central and Northern South America (Table 6). Nitrate and NH_4^+ concentrations in precipitation from events where $u \geq 2 \text{ ms}^{-1}$ were greater at Monteverde when compared to those in wet deposition in El Verde, Puerto Rico, and in bulk precipitation in Turrialba, Costa Rica, but were similar to those collected in bulk precipitation in Pico del Oeste, Puerto Rico. Ammonium concentrations were much greater in bulk precipitation in Santa Rosa de Cabal, Colombia (Table 6).

The relatively high concentrations of NO_3^- and NH_4^+ in cloud water and mist reported here suggest that emissions of NO_x , NH_3 , and particles containing NO_3^- and NH_4^+ are considerable upwind from Monteverde during the dry season. Because no major urban areas or industrial sources of NO_x or NH_3 exist in the predominant wind direction, emissions likely originated primarily from forest and agricultural ecosystems. The burning of vegetation typically results in considerable loss of N and other ions from the site (Ewel *et al.*, 1981; Crutzen and Andreae, 1990; Kauffmann *et al.*, 1993, 1994). Plant tissue N is volatilized as NO, NH_3 , HCN, and other organic N compounds, and released as particles containing N and other ions (Lobert *et al.*, 1990; Kauffman *et al.*, 1993, 1994). High concentrations of NO, HNO_3 , PAN, and plant-derived organic particles containing NH_4^+ , NO_3^- , K^+ , and other ions have been associated with haze layers over the Amazon basin during the dry season (Crutzen *et al.*, 1985; Andreae *et al.*, 1988a; Artaxo *et al.*, 1988; Talbot *et al.*, 1988). In addition, NO emissions from soils may be stimulated for some period following burning activities by undefined mechanisms (Anderson *et al.*, 1988). The interactive effects of fertilizer use, cultural treatments and soil moisture levels on the emissions of NO and NH_3 from agricultural ecosystems are less well known (Whitehead and Raistrick, 1990; Davidson *et al.*, 1991, 1993; Hutchinson and Bram, 1992; Keller *et al.*, 1993; Hall *et al.*, 1996). Long-distance transport may also be a minor source of NO_3^- in cloud water and precipitation at this site during the dry season (Savoie *et al.*, 1989, 1992).

Rates of forest clearing in Costa Rica have increased over the period from 1941 to 1983 (Sader and Joyce, 1988), primarily for conversion to pasture and

Table 6. Volume weighted mean ion concentrations ($\mu\text{mol } \ell^{-1}$) in bulk precipitation at tropical premontane and TMF sites in Central and Northern South America

Location	Ion concentration ($\mu\text{mol } \ell^{-1}$)						
	H^+	NO_3^-	NH_4^+	Na^+	Mg^{2+}	Ca^{2+}	K^+
Turrialba, Costa Rica ^a	4.6	1.4	3.6	10.9	1.6	1.5	2.8
Pico del Este, Puerto Rico ^b	6.4	7.6	9.9	214.9	24.7	23.5	13.8
El Verde, Puerto Rico ^c	7.3	4.3	2.9	70.8	9.0	8.0	2.4
Monteverde, Costa Rica ^d	19.0	7.5	8.9	75.4	8.8	6.6	4.1
San Eusebio, Venezuela ^e	13.8	3.4	3.3	7.8	1.2	3.4	2.1
Santa Rosa de Cabal, Colombia ^f	28.2	—	—	9.1	13.6	9.0	4.3
	39.8	—	61	49.6	6.2	12.0	9.7
	40.7	—	55	47.8	7.0	12.7	12.3

^aHendry *et al.* (1984); 650 m elevation.

^bAsbury *et al.* (1994); 1015 m elevation.

^cMcDowell *et al.* (1990); 400 m elevation, NO_3^- -N and NH_4^+ -N for wet-only deposition.

^dThis study; 1480 m elevation, precipitation values for $u \geq 2 \text{ ms}^{-1}$ and $u < 2 \text{ ms}^{-1}$.

^eSteinhardt and Fassbender (1979); 2300 m elevation.

^fVeneklaas (1990); sites at 2550 and 3370 m elevation.

other agricultural uses (Veldkamp *et al.*, 1992; Reiners *et al.*, 1994). Although land use changes have been predicted to increase N emissions in the tropics (Keller *et al.*, 1991; Galloway *et al.*, 1994; Galloway 1996), regional emission inventories are limited and subject to a number of uncertainties (Logan, 1983; Crutzen and Andreae, 1990; Schlesinger and Hartley, 1992). Our research suggests that biomass burning activities substantially increased inorganic N concentrations in cloud water towards the end of the dry season. Therefore, it is important to evaluate the effects of deforestation, land use change, and agricultural practices on rates of N emission before we can estimate the contribution of anthropogenic activities to cloud water and precipitation chemistry, and potentially to long-term increased N deposition to TMFs.

CONCLUSIONS

Ion concentrations were highest in cloud water and lowest in bulk precipitation.

Cloud water, mist, and precipitation samples collected when mean wind speeds $\geq 2 \text{ m s}^{-1}$ were strongly influenced by marine aerosols. Agricultural and forest burning activities during the end of the dry season increased the concentrations of NO_3^- , NH_4^+ , K^+ , and Ca^{2+} in cloud water. Mean concentrations of H^+ in cloud water were lower, but NO_3^- and NH_4^+ concentrations were similar to those at a number of North American sites. Following the onset of the wet season, ion concentrations in bulk precipitation decreased, particularly for precipitation events where mean wind speeds were less than 2 m s^{-1} . Ion concentrations in precipitation were similar to those at a number of other tropical premontane and montane cloud forest sites. Further investigation of the controls over the production, transport, and deposition of H^+ vs. NO_3^- and NH_4^+ will be important in the developing tropics.

Acknowledgments—We thank the Tropical Science Center and the Monteverde Cloud Forest Reserve for access to the field sites and logistical support. R. Solano, N. Barbour, and students from Youth Challenge International assisted with fieldwork. Jim Bartose at the Analytical Research Laboratory and Mary Mcleod at the Forest Soils Laboratory, University of Florida, assisted with chemical analyses. This research was partially supported by NSF (BSR 86-14935 and 90-18006), the Whitehall Foundation, and the National Geographic Society Committee for Research and Exploration.

REFERENCES

- Aber, J. D. (1992) Nitrogen cycling and nitrogen saturation in temperate forest ecosystems. *Tree* 7, 220–224.
- Anderson, I. C., Levine, J. S., Poth, M. A. and Riggan, P. J. (1988) Enhanced biogenic emissions of nitric oxide and nitrous oxide following surface biomass burning. *Journal of Geophysical Research* 93, 3893–3898.
- Andreae, M. O., Browell, E. V., Garstang, M., Gregory, G. L., Harriss, R. C., Hill, G. F., Jacob, D. J., Pereira, M. C., Sachse, G. W., Setzer, A. W., Silva Dias, P. L., Talbot, T. W., Torres, A. L. and Wofsy, S. C. (1988a) Biomass-burning emissions and associated haze layers over Amazonia. *Journal of Geophysical Research* 93, 1509–1527.
- Andreae, M. O., Talbot, R. W., Andreae, T. W. and Harriss, R. C. (1988b) Formic and acetic acids over the Central Amazon region, Brazil. *Journal of Geophysical Research* 93, 1616–1624.
- Andreae, M. O., Talbot, R. W., Berresheim, H. and Beecher, K. M. (1990) Precipitation chemistry in Central Amazonia. *Journal of Geophysical Research* 95, 16,987–16,999.
- Aneja, V. P., Robarge, W. P., Claiborn, C. S., Murthy, A., Soo-Kim, D. and Li Z. (1992) Chemical climatology of high elevation spruce-fir forests in the southern Appalachian mountains. *Environmental Pollution* 75, 89–96.
- Artaxo, P., Maenhaut, W., Storms, H. and van Grieken, R. (1990) Aerosol characteristics and sources for the Amazon basin during the wet season. *Journal of Geophysical Research* 95, 16,971–16,985.
- Artaxo, P., Storms, H., Bruynseels, F., van Grieken, R. and Maenhaut, W. (1988) Composition and sources of aerosols from the Amazon basin. *Journal of Geophysical Research* 93, 1605–1615.
- Asbury, C. E., McDowell, W. H., Trinidad-Pizarro, R. and Berrios, S. (1994) Solute deposition from cloud water to the canopy of a Puerto Rican montane forest. *Atmospheric Environment* 28, 1773–1780.
- Blanchard, D. C. (1983) The production, distribution and bacterial enrichment of the sea-salt aerosol. In *Air-Sea Exchange of Gases and Particles*, eds P. S. Liss and W. G. N. Slinn, pp. 407–454. D. Reidel, Dordrecht, Netherlands.
- Clark, K. L. (1994) The role of epiphytic bryophytes in the net accumulation and cycling of nitrogen in a tropical montane cloud forest. Ph.D. dissertation, University of Florida, Gainesville, Florida.
- Crozat, G. (1979) Sur l'émission d'un aerosol riche en potassium par la forêt tropicale. *Tellus* 31, 52–57.
- Crutzen, P. J. and Andreae, M. O. (1990) Biomass burning in the tropics: impacts on atmospheric chemistry and biogeochemical cycles. *Science* 250, 1669–1678.
- Crutzen, P. J., Delany, A. C., Greenberg, J., Haagenson, P., Heidt, L., Lueb, R., Polloc, W., Seiler, W., Wartburg, A. and Zimmerman, P. (1985) Tropospheric chemical composition measurements in Brazil during the dry season. *Journal of Atmospheric Chemistry* 2, 233–256.
- Davidson, E. A., Matson, P. A., Vitousek, P. M., Riley, R., Dunkin, K., Garcia-Mendez, G. and Maass, J. M. (1993) Processes regulating soil emissions of NO and N₂O in a seasonally dry tropical forest. *Ecology* 74, 130–139.
- Davidson, E. A., Vitousek, P. M., Matson, P. A., Riley, R., Garcia-Mendez, G. and Maass, J. M. (1991) Soil emissions of nitric oxide in a seasonally dry tropical forest of Mexico. *Journal of Geophysical Research* 96, 15,439–15,445.
- Dise, N. B. and Wright, R. F. (1995) Nitrogen leaching from European forests in relation to nitrogen deposition. *Forest Ecology Management* 71, 153–161.
- Dollard, G. J., Unsworth, M. H. and Harve, M. J. (1983) Pollutant transfer in upland regions by occult deposition. *Nature* 302, 241–243.
- Ewel, J., Barish, C., Brown, B., Price, N. and Raich, J. (1981) Slash and burn impacts on a Costa Rican wet forest site. *Ecology* 62, 816–829.
- Falconer, R. E. and Falconer, P. D. (1980) Determination of cloud water acidity at a mountain observatory in the Adirondack Mountains of New York State. *Journal of Geophysical Research* 85, 7465–7470.

- Fowler, D., Cape, J. N., Leith, I. D., Choullarton, T. W., Gay, M. J. and Jones, A. (1988) The influence of altitude on rainfall composition at Great Dun Fell. *Atmospheric Environment* **22**, 1355–1362.
- Galloway, J. N. (1996) Anthropogenic mobilization of sulphur and nitrogen: immediate and delayed consequences. *Annual Reviews of Energy Environment* **21**, 261–292.
- Galloway, J. N., Levy, II H. and Kasibhatla, P. S. (1994) Year 2020: consequences of population growth and development on deposition of oxidized nitrogen. *Ambio* **23**, 120–123.
- Gordon, C. A., Herrera, R. and Hutchinson, T. C. (1994) Studies of fog events at two cloud forests near Caracas, Venezuela. II. Chemistry of fog. *Atmospheric Environment* **28**, 323–337.
- Hall, S. J., Matson, P. A. and Roth, P. M. (1996) NO_x emissions from soil: implications for air quality modeling in agricultural regions. *Annual Reviews of Energy Environment* **21**, 311–346.
- Harwood, J. E. and Kuhn, A. L. (1970) A colorimetric method for ammonia in natural waters. *Water Resources Research* **4**, 805–811.
- Hendry, C. D., Barrish, C. W. and Edgerton, E. S. (1984) Precipitation chemistry at Turrialba, Costa Rica. *Water Resources Research* **20**, 1677–1684.
- Holdridge, L. R. (1967) *Life Zone Ecology*. Tropical Science Center, San Jose, Costa Rica.
- Hutchinson, G. L. and Brams, E. A. (1992) NO versus N₂O emissions from an NH₄⁺-amended Bermuda grass pasture. *Journal of Geophysical Research* **97**, 9889–9896.
- Irving, P. M. (Ed.) (1991) *Acidic Deposition: State of the Science and Technology. Vol. 1. Emissions, Atmospheric Processes and Deposition*. The U.S. National Acid Precipitation Assessment Program.
- Johnson, D. W. and Lindberg, S. E. (Eds) (1992) *Atmospheric Deposition and Nutrient Cycling in Forest Ecosystems*. Springer, New York.
- Kauffman, J. B., Cummings, D. L. and Ward, D. E. (1994) Relationships of fire, biomass and nutrient dynamics along a vegetation gradient in the Brazilian cerrado. *Journal of Ecology* **82**, 519–531.
- Kauffman, J. B., Sanford, R. L. Jr., Cummings, D. L., Salcedo, I. H. and Sampaio, E. V. S. B. (1993) Biomass and nutrient dynamics associated with slash fires in neotropical dry forests. *Ecology* **74**, 140–151.
- Keene, W. C., Galloway, J. N. and Holden, J. D. Jr. (1983) Measurement of weak organic acidity in precipitation from remote areas of the world. *Journal of Geophysical Research* **88**, 5122–5130.
- Keller, M. E., Jacob, D. J., Wofsy, S. C. and Harriss, R. C. (1991) Effects of tropical deforestation on global and regional atmospheric chemistry. *Climatic Change* **19**, 139–158.
- Keller, M. E., Veldkamp, E., Weitz, A. M. and Reiners, W. A. (1993) Pasture age effects on soil-atmosphere trace gas exchange in a deforested area of Costa Rica. *Nature* **365**, 244–246.
- Kellman, M., Hudson, J. and Sanmugadas, K. (1982) Temporal variability in atmospheric nutrient influx to a tropical ecosystem. *Biotropica* **14**, 1–9.
- Lawton, R. O. and Dryer, V. (1980) The vegetation of the Monteverde Cloud Forest Reserve. *Brenesia* **18**, 101–116.
- Lewis, W. M. Jr. (1981) Precipitation chemistry and nutrient loading by precipitation in a tropical watershed. *Water Resources Research* **17**, 169–181.
- Lobert, J. M., Scharffe, D. H., Hao, W. M., and Crutzen, P. J. (1990) Importance of biomass burning in the atmospheric budgets of nitrogen-containing gases. *Nature* **346**, 552–554.
- Logan, J. A. (1983) Nitrogen oxides in the troposphere: global and regional budgets. *Journal of Geophysical Research* **88**, 10,785–10,807.
- Lovett, G. M. and Kinsman, J. D. (1990) Atmospheric pollutant deposition to high-elevation ecosystems. *Atmospheric Environment* **24A**, 2767–2786.
- Lovett, G. M., Reiners, W. A. and Olson, R. K. (1982) Cloud droplet deposition in a subalpine balsam fir forest: hydrological and chemical inputs. *Science* **218**, 1303–1304.
- Mackereth, F. J. H., Heron, J. and Talling, J. F. (1978) *Water Analysis*. Scient. Publ. Freshwat. Biol. Assoc. No. 36.
- McDowell, W. H., Sanchez, C. G., Asbury, C. E. and Ramos Perez, C. R. (1990) Influence of sea salt aerosols and long range transport on precipitation chemistry at El Verde, Puerto Rico. *Atmospheric Environment* **24A**, 2813–2821.
- Miller, E. K., Friedland, A. J., Arons, E. A., Mohnen, V. A., Battles, J. J., Panek, J. A., Kadlecek, J. and Johnson, A. H. (1993) Atmospheric deposition to forests along an elevational gradient at Whiteface Mountain, NY, U.S.A. *Atmospheric Environment* **27A**, 2121–2136.
- Mohnen, V. A. and Kadkecek, J. A. (1989) Cloud chemistry research at Whiteface Mountain. *Tellus* **41B**, 79–91.
- Mohnen, V. A. and Vong, R. J. (1993) A climatology of cloud chemistry for the eastern United States derived from the mountain cloud chemistry project. *Environment Review* **1**, 38–54.
- Nadkarni, N. M., Matelson, T. J. and Haber, W. A. (1996) Structural characteristics and floristic composition of a neotropical cloud forest, Monteverde, Costa Rica. *Journal of Tropical Ecology* (in press).
- Reiners, W. A., Bouwman, A. F., Parsons, W. F. J. and Keller, M. (1994) Tropical rain forest conversion to pasture: changes in vegetation and soil properties. *Ecology Applications* **4**, 363–377.
- Sader, S. A. and Joyce, A. T. (1988) Deforestation rates and trends in Costa Rica, 1940 to 1983. *Biotropica* **20**, 11–19.
- Sanhueza, E., Santana, M. and Hermosa, M. (1992) Gas- and aqueous-phase formic and acetic acids at a tropical cloud forest site. *Atmospheric Environment* **26a**, 1421–1426.
- Savoie, D. L., Prospero, J. M., Oltmans, S. J., Graustein, W. C., Turekian, K. K., Merrill, J. T. and Levy, H. II. (1992) Sources of nitrate and ozone in the marine boundary layer on the tropical North Atlantic. *Journal of Geophysical Research* **97**, 11,575–11,589.
- Savoie, D. L., Prospero, J. M. and Saltzman, E. S. (1989) Non-sea-salt sulfate and nitrate in trade wind aerosols at Barbados: evidence for long-range transport. *Journal of Geophysical Research* **94**, 5069–5080.
- Schaefer, D. A. and Reiners, W. A. (1990) Throughfall chemistry and canopy processing mechanisms. In *Acid Precipitation, Vol. 3. Sources, Deposition and Canopy Interactions*, eds S. E. Lindberg, L. A. Page and S. A. Norton, pp. 241–284. Springer, Berlin.
- Schlesinger, W. H. and Hartley, A. E. (1992) A global budget for atmospheric NH₃. *Biogeochemistry* **15**, 191–211.
- Schulze, E.-D. (1989) Air pollution and forest decline in a spruce (*Picea abies*) forest. *Science* **244**, 776–783.
- Sigmon, J. T., Gilliam, F. S. and Partin, M. E. (1989) Precipitation and throughfall chemistry for a montane hardwood forest ecosystem: potential contributions from cloud water. *Canadian Journal of Forest Research* **19**, 1240–1247.
- Sokol, R. R. and Rohlf, F. J. (1981) *Biometry*, 2nd edn. Freeman, San Francisco.
- Steinhardt, U. and Fassbender, H. W. (1979) Características y composición química de las lluvias de los Andes occidentales de Venezuela. *Turrialba* **29**, 175–182.
- Stevens, P. A., Norris, D. A., Sparks, T. H. and Hodgson, A. L. (1994) The impacts of atmospheric nitrogen inputs on throughfall, soil and stream water interactions for different aged forest and moorland catchments in Wales. *Water, Air, Soil Pollution* **73**, 297–317.
- SYSTAT (1992) *SYSTAT: the System for Statistics*. Systat, Inc., Evanston, Illinois.
- Talbot, R. W., Andreae, M. O., Andreae, T. W. and Harriss, R. C. (1988) Regional aerosol chemistry of the Amazon basin during the dry season. *Journal of Geophysical Research* **93**, 1499–1508.

- Talbot, R. W., Andreae, M. O., Berresheim, H., Artaxo, P., Garstang, M., Harriss, R. C., Beecher, K. M. and Li, S. M. (1990b) Aerosol chemistry during the wet season in central Amazonia: the influence of long-range transport. *Journal of Geophysical Research* **95**, 16,955–16,969.
- Talbot, R. W., Andreae, M. O., Berresheim, H., Jacob, D. J. and Beecher, K. M. (1990a) Sources and sinks of formic, acetic, and pyruvic acids over Central Amazonia: 2. Wet season. *Journal of Geophysical Research* **95**, 16,799–16,811.
- Thompson, A. M. (1996) Biomass burning and the atmosphere-accomplishments and research opportunities. *Atmospheric Environment* **30**, i–ii.
- Veldkamp, E., Weitz, A. M., Staritsky, I. G. and Huising, E. J. (1992) Deforestation trends in the Atlantic zone of Costa Rica: a case study. *Land Degredation and Rehabilitation* **3**, 71–84.
- Veneklaas, E. V. (1990) Rainfall interception and above-ground nutrient fluxes in Colombian montane tropical rain forest. Ph.D. thesis, University of Utrecht, Utrecht, The Netherlands.
- Vong, R. J., Sigmon, J. T. and Mueller, S. F. (1991) Cloud water deposition to Appalachian forests. *Environmental Science and Technology* **25**, 1014–1021.
- Warneck, P. (1988) *Chemistry of the Natural Atmosphere*. Academic Press, San Diego, California.
- Weathers, K. C., Likens, G. E., Bormann, F. H., Bicknell, S. H., Bormann, H. T., Daube, B. C., Eaton, J. S., Galloway, J. N., Keene, W. C., Kimball, K. D., McDowell, W. H., Siccama, T. G., Smiley, D. and Tarrant, R. A. (1988) Cloud water chemistry from ten sites in North America. *Environmental Science and Technology* **22**, 1018–1026.
- Whitehead, D. C. and Raistrick, N. (1990) Ammonia volatilization from five nitrogen compounds used as fertilizers following surface application to soils. *Journal of Soil Science* **41**, 378–394.