



SEASONAL VARIATION OF TROPICAL PRECIPITATION CHEMISTRY: LA SELVA, COSTA RICA

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Abstract—The chemistry of wet precipitation was measured from February 1992 to February 1995 at La Selva Biological Station, Costa Rica. Sea salt aerosols were the primary contributors to Na^+ , Cl^- , and Mg^{2+} ; however, K^+ , Ca^{2+} , and SO_4^{2-} were derived primarily from non-sea-salt sources. Seasonal patterns, with concentrations inversely proportional to rainfall, were found for marine salts and aerosols (Na^+ , Cl^- , and Mg^{2+}) and inorganic nitrogenous compounds (NO_3^- and NH_4^+). DON accounted for a significant fraction (30%) of total dissolved nitrogen deposition. Terrigenous dust from local agricultural or natural aeolian processes appeared to be the primary influence on concentrations of non-sea-salt cations. High concentrations of non-sea-salt sulfate (SO_4^{2-}) were correlated with both non-sea-salt chloride (Cl^-) and high H^+ concentrations as well as a shift in wind direction from the northeast to the southwest, which may indicate a strong volcanic influence on precipitation chemistry during a few weeks of the year. Annual fluctuations in distribution and amount of rainfall contributed to differences in precipitation chemistry over the course of the study. © 1997 Elsevier Science Ltd.

Key word index: Tropics, precipitation chemistry, wet deposition, marine aerosols, nitrogenous compounds.

INTRODUCTION

The importance of seasonal variation in precipitation chemistry for temperate regions with cold and warm seasons is well established (Buishand *et al.*, 1988; Mossello *et al.*, 1988; Saylor *et al.*, 1992; Driscoll and Dreason, 1993; Albeic-Juretic, 1994; Probst *et al.*, 1995; Blew and Edmonds, 1995). Such changes in precipitation chemistry can have a significant impact on aquatic and terrestrial ecosystems, especially in areas with high rates of acidic deposition (Sellars *et al.*, 1985). Seasonality in precipitation chemistry might be important for tropical water resources as well, especially in regions which are nutrient-poor. Although several studies have noted the apparent effects of wet and dry seasons on precipitation chemistry in tropical ecosystems (Lewis, 1981; Kellman *et al.*, 1982; Hendry, 1984; Talbot *et al.*, 1988, 1990; Andreae *et al.*, 1990; Veneklaas, 1990; Lesack and Melack, 1991; Forti and Moreira-Nordemann, 1991), we are aware of no published studies of long-term seasonal trends in deposition and precipitation chemistry in tropical ecosystems.

Seasonal variation in biogenic emissions, local agricultural practices, long-range transport, marine salts and volcanic activity can all affect precipitation

chemistry. Hendry *et al.* (1984) concluded volcanic activity was one of several possible influences on concentrations of nutrients and acidity at Turrialba, Costa Rica. High volcanic activity was also present in the one-year study of nutrient flux performed by Veneklaas (1990) in Colombia and may have contributed to monthly variation in precipitation chemistry at that site. McDowell *et al.* (1990) observed changes in excess (non-sea-salt) Ca^{2+} and Mg^{2+} in Puerto Rican precipitation which they attributed to seasonal variation in production of Sahara dust.

In this paper, we present data from a three-year study at La Selva, Costa Rica in which we (1) examine seasonal variation in precipitation chemistry for a tropical ecosystem, (2) quantify annual deposition at the site, and (3) attempt to isolate primary sources of the principal ions in a coastal region with considerable agricultural and volcanic activity.

METHODS

Site description

The La Selva Biological Station is located in northern Costa Rica (10°26'N, 84°01'W) at an elevation of

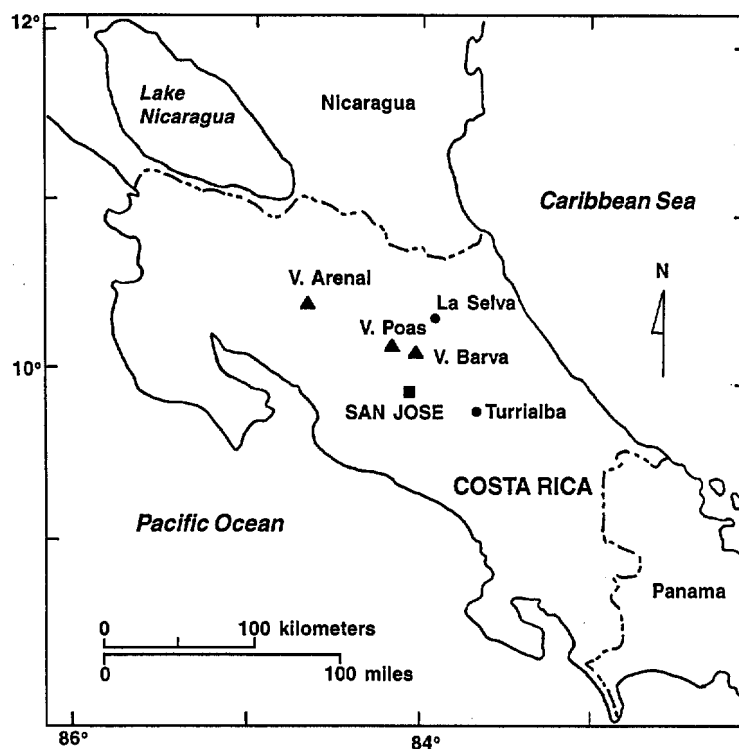


Fig. 1. Map of Costa Rica and study site (La Selva Biological Station).

approximately 35 m above sea level and 50 km from the eastern shore of the Caribbean Sea (Fig. 1). The station is approximately 3300 ha and borders the Parque Nacional Braulio Carrillo, a protected forest of ca. 45,000 ha, to the south and the Puerto Viejo and Sarapiquí Rivers to the north (Pringle, 1991). The precipitation collector was centrally located in a 40 × 50 m clearing to prevent interference from the tree canopy, on the northeast (upwind) side of the field station. Potential local sources of solutes in rainfall include the town of Puerto Viejo de Sarapiquí (population of several thousand at time of the study) and a diesel generator at the field station which was used only during power outages.

Sampling protocol

Wet-only precipitation was sampled at weekly intervals from February 1992 to March 1995 using an Aerochem Metrics automatic precipitation sampler. The sampler was activated Monday mornings, and samples were collected following a storm event or series of storm events resulting in a collection volume of > 1 ℓ. The 1 ℓ volume was necessary for adequate sample volume for all analyses. We chose to sample on an event basis rather than continuously to better describe the relationship between rain chemistry and meteorological conditions. The instrument was subsequently turned off until the following Monday and the sampling bucket was washed with laboratory grade phosphate-free detergent and rinsed copiously with distilled water. Weekly blank samples were collected from the washed bucket prior to its re-installation in the collector. Total rainfall was quantified for the week using a separate meteorological station located at La Selva.

Sampling processing and analysis

pH was measured in the field laboratory immediately following collection, using NADP procedures (unstirred, open vessel, Beckman Model 21 m and gel-filled temper-

ature-compensated combination probe). The pH meter and probe were used solely for analysis of precipitation. Samples were frozen and shipped in dry ice to the University of New Hampshire for chemical analysis. Samples remained frozen until analysis. All samples were filtered with Whatman GF/F 0.45 μm filters. Prior to analysis of Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺, samples were filtered with 0.22 μm Acrodisc filters. All water blanks for each week of sampling were treated as samples and run for all constituents to check for contamination. Starting in March 1993, the weight of the sampling bucket was measured for more accurate determinations of the volume of rain collected per sampling event.

Analytical procedures

Chloride, NO₃⁻, SO₄²⁻, Na⁺, K⁺, Mg²⁺, and Ca²⁺ were analyzed using a Waters HPLC with conductivity and UV-Vis detectors. A Dionex Anion Self-Regenerating Suppressor (4 mm) and Ionpac AS4A (10–32) Analytical Column were used to separate Cl⁻, NO₃⁻, and SO₄²⁻; NO₃⁻ was quantified using UV detection (214 nm), while the other ions were quantified with conductivity detection; Na⁺, K⁺, Mg²⁺ and Ca²⁺ were measured using a Waters IC-Pak cation column. Flow injection analysis colorimetry (Lachat) was used for NH₄⁺ (phenol hypochlorite method with sodium nitroprusside enhancement) and PO₄³⁻ (ascorbic acid method with ammonium molybdate and antimony potassium tartrate). A total organic carbon analyzer (Shimadzu TOC 5000) with acidification and sparging was used for measuring NPOC (non-purgeable organic carbon), hereafter referred to as DOC. High temperature catalytic oxidation (Shimadzu TOC 5000 furnace) with chemiluminescent nitrogen detection (Antek 720) was used to analyze TDN (Merriam *et al.*, 1996); dissolved organic nitrogen (DON) was estimated as the difference between TDN and NH₄⁺ + NO₃⁻.

EPA certified reference standards were used for all analyses in order to insure accuracy of working stock solutions. Check standards and replicate samples were analyzed every 15 samples to check for accuracy throughout each individual

run. Replicate samples were carried over from previous runs, and in conjunction with EPA certified standards, were used to insure consistency between runs.

Data manipulation

Deposition was calculated for each water year (March–February) as the product of weekly rainfall (total) and concentration in the sample collected that week. Sea salt and non-sea salt fractions of Cl^- , SO_4^{2-} , K^+ , Mg^{2+} , and Ca^{2+} were calculated for each sample using Na^+ as a sea salt tracer, which proved to be more appropriate than Mg^{2+} according to the method of Keene *et al.* (1986). The assumptions inherent in this method are that Na^+ was derived solely from sea salt aerosols, and that the other ions did not undergo fractionation during aerosol formation, transport, or scavenging (Keene *et al.*, 1986). Non-sea-salt aerosols will hereafter be referred to as Cl^* , SO_4^* , Ca^* , K^* and Mg^* . Volume weighted means were also calculated for both sea salt and non-sea-salt ions as well as DOC and DON. Concentrations of $\text{PO}_4^{3-}\text{-P}$ in rainfall were below the level of quantification of $10 \mu\text{g l}^{-1}$ for the ascorbic acid method used for analysis.

Seasonal patterns in the data were quantified using regression analysis of all concentrations versus weekly precipitation, and one-way ANOVA with season (wet vs dry) as the treatment. More sophisticated analysis of seasonal trends such as the Kendall Seasonal Test were not performed due to uneven sampling intervals, particularly during the dry season. Regression analysis and principal component analysis were used in order to identify inter-component relationships and aid in locating potential source vectors.

Wind data (magnitude and direction in degrees) was provided by the meteorological station at the La Selva field station. Vector analysis was used to generate the prevailing wind direction on a hourly basis from January 1993 to February 1995.

RESULTS

Deposition and chemistry

Total rainfall was between 3500 and 4500 mm annually; we sampled approximately 35% of this rainfall for chemical analysis. Depositions of all constituents analyzed were highest in 1994, probably due to increased precipitation during that year (Table 1).

Na^+ and Cl^- were the most abundant ions in deposition and had the highest average concentrations (Table 2). Sea-salt aerosols accounted for 97% of Cl^- and 88% of Mg^{2+} ; however, non-sea-salt fractions of SO_4^{2-} , Ca^{2+} and K^+ were 73%, 76% and 62%, respectively. Although both excess sulfate and calcium were enriched with respect to the other major ions, their concentrations were not correlated ($r^2 = 0.01$). There was no particularly strong correlation among any of the non-sea salt species, nor between SO_4^* and NO_3^- ($r^2 = 0.11$; $p < 0.05$). We observed a series of high SO_4^* events throughout the 3 years of the study, with concentrations as high as $56.4 \mu\text{eq l}^{-1}$. When SO_4^* was greater than $20 \mu\text{eq l}^{-1}$, H^+ and SO_4^* were correlated ($r^2 = 0.65$; $p < 0.05$). Principal components analysis was used to indicate inter-component relationships. Factor loading scores for factor 2 show that SO_4^* , Cl^* and H^+ are related, as are K^+ , Ca^{2+} , DOC and DON (Table 3).

A small anion deficit of $1.9 \mu\text{eq l}^{-1}$ (Table 2) indicates the potential presence of low concentrations of

Table 1. Annual wet deposition rates ($\text{kg ha}^{-1} \text{yr}^{-1}$) for La Selva, Costa Rica

Constituent	1992–1993	1993–1994	1994–1995
Cl	51.5	41.5	63.3
NO_3N	2.4	1.8	3.4
SO_4S	10.6	7.5	11.3
Na	27.9	22.7	32.9
K	2.4	2.2	5.0
Mg	3.9	3.0	4.9
Ca	4.3	3.9	9.0
H	0.2	0.2	0.2
NH_4N	3.6	2.6	5.0
DOC	27.9	21.9	35.6
DON	2.5	1.0	6.6
Rainfall (mm)	3773	3591	4404

Table 2. Average concentrations of major constituents in rainfall collected at La Selva, Costa Rica (all values in $\mu\text{eq l}^{-1}$, except DOC & DON (μM)). Negative values are associated with indirect measures (calculated by difference or sea salt ratios). VWM = volume weighted mean

Constituent	Mean	Maximum	Minimum	VWM
n	107–110			
H^+	5.4	67.6	0.0	4.6
Na^+	38.9	165	2.2	27.2
K^+	2.3	15.3	0.0	1.8
Mg^{2+}	10.1	42.8	0.8	7.4
Ca^{2+}	7.1	25.4	1.5	6.8
NH_4^+	8.7	49.4	0.1	6.0
Cl^-	47.6	203	3.0	33.0
NO_3^-	5.3	21.0	0.0	4.1
SO_4^{2-}	17.7	57.3	4.4	14.8
PO_4^{3-}	< LOQ			
Cations	72.5			53.8
Anions	70.6			51.8
K^*	1.4	11.7	– 0.5	1.2
Mg^*	1.3	5.3	– 0.5	1.3
Ca^*	5.4	18.2	– 1.1	5.6
Cl^*	2.4	20.6	– 4.0	1.5
SO_4^*	12.9	56.4	3.5	11.5
DOC	58.3	233.1	25.0	58.3
DON	7.1	28.6	– 14.3	7.1

organic acids (Keene *et al.*, 1983). DOC values ($58.3 \mu\text{M}$) are consistent with an anion deficit of this magnitude, assuming a charge density of $10 \mu\text{eq mg}^{-1}$ dissolved organic carbon (Oliver *et al.*, 1983). Dissolved organic N accounted for 30% of total N deposition, and concentrations were correlated with DOC concentrations ($r^2 = 0.43$; $p < 0.05$).

Seasonality

La Selva exhibits strong seasonal trends in both the quantity and chemistry of precipitation. During the wet season (June–December), concentrations of almost all ions declined (Fig. 2). Sulfate, K^+ and Ca^{2+} showed the weakest seasonal patterns. No seasonal trends were evident for any of the non sea-salt species. For February through April 1994, a period of prolonged dry weather, high concentrations of all

Table 3. Principal components analysis for all non-sea-salt components and DOC & DON

Constituent	Loadings	
	Factor 1	Factor 2
Cl*	0.500	0.557
SO ₄ *	0.516	0.686
H ⁺	0.088	0.848
NO ₃ ⁻	0.759	-0.001
NH ₄ ⁺	0.843	0.014
Mg*	0.682	0.104
K*	0.796	-0.290
Ca*	0.495	-0.441
DOC	0.777	-0.171
DON	0.637	-0.326

constituents were observed. Dilution during periods of high rainfall appears to be a major factor controlling the precipitation chemistry of this region. The most striking seasonal trends were those associated with marine salts and aerosols (Na⁺, Cl⁻, Mg²⁺), and inorganic nitrogenous compounds. Concentrations of ions showing strong seasonal patterns (Fig. 2) also were significantly correlated with volume of precipitation (Cl⁻, Na⁺, Mg²⁺, NO₃⁻, NH₄⁺; $r^2 > 0.1$ and $p < 0.01$). Moderate seasonal patterns were exhibited for SO₄²⁻ and K⁺ ($r^2 < 0.1$ and $p < 0.01$). For all other ions, DOC and DON, concentrations were not significantly related to rainfall volume ($p > 0.05$). ANOVA showed similar results where season (defined as 1 January – 30 April = dry season, 1 May – 31 December = wet season) had a significant effect on concentrations of Cl⁻, Na⁺, Mg²⁺, NO₃⁻, NH₄⁺, SO₄²⁻, K⁺ and Ca²⁺ ($p < 0.01$), and had no effect on H⁺, DOC, and DON ($p > 0.05$).

Weather patterns

Based on the daily average wind vectors for two of the three years studied, the predominant wind pattern was trade winds blowing in from the northeast off the Caribbean Sea (Fig. 3a). On collection dates for which there were high concentrations of both excess sulfate and hydrogen ions, the wind shifted from predominantly northeasterly to predominantly southwesterly (Fig. 3).

DISCUSSION

Many authors have described differences in rain chemistry associated with individual wet and dry seasons (Hendry, 1984; Veneklaas, 1990; Andreae *et al.*, 1990; Talbot *et al.*, 1990; Forti and Moreira-Nordemann, 1991). To establish true seasonal patterns, however, several years of observation are required. Our results show that strong, persistent patterns in rain chemistry do occur at this tropical site, and are thus analogous to the persistent seasonal differences in precipitation chemistry observed in more industrialized temperate regions (Saylor *et al.*, 1992; Dris-

coll and Dreason, 1993). It appears that dilution and concentration of marine aerosols, rather than human activity, drive these patterns. Minimal seasonality was observed in the concentration of non-sea-salt cations, which are probably derived from terrigenous dust associated with agriculture or natural aeolian processes.

Unlike most of the elements which we analyzed, concentrations of K⁺ and Ca²⁺ were derived primarily from non-sea-salt sources. In addition, neither K⁺ nor Ca²⁺ was highly correlated with the amount of rainfall per event except during the extreme dry period of February – April 1994 (regression: $r^2 = 0.06$, $p < 0.01$ and $p > 0.05$, respectively). Extreme drought during the dry season does result in high concentrations of K⁺ and Ca²⁺, but these are episodic, rather than seasonal, increases (Fig. 2). Because La Selva is located in an agricultural region, agricultural dust coupled with the lack of dilution during this extremely dry period probably accounts for the high cation concentrations. The effects of agricultural dust may be further supported by the association between K⁺, Ca²⁺, DOC and DON (Table 3) in that high dust events would yield high concentrations of cations and organic matter.

Dissolved organic carbon and nitrogen are rarely measured in studies of precipitation chemistry and deposition. Recent studies of DON in precipitation indicate that it is a quantitatively significant input of N in various regions of the northern hemisphere (Cornell *et al.*, 1995). DON in precipitation was found by Cornell *et al.* (1995) to be higher at continental sites. Our results show that even with primarily marine-derived precipitation, DON accounts for a significant fraction (30%) of total dissolved N deposition. Inclusion of DON in precipitation chemistry surveys thus may be warranted. If our results are representative of tropical maritime precipitation, inputs of fixed nitrogen into the ocean may have been underestimated, with consequences for the global nitrogen budget and human induced climate change (Cornell *et al.*, 1995). The flux of DOC which we have measured at La Selva is similar to that reported by McDowell *et al.* (1990) for El Verde, Puerto Rico, where inputs of DOC in precipitation were approximately 26% of hydrologic losses in stream flow (McDowell and Asbury, 1994), and thus we suspect that deposition of organic C and N at La Selva is typical of tropical maritime precipitation.

Based on concentrations of nitrate and sulfate, precipitation at La Selva is relatively uncontaminated by industrial emissions and is similar to that of remote areas. The overall average concentration of SO₄²⁻ observed in wet precipitation at La Selva (13 $\mu\text{eq } \ell^{-1}$) slightly exceeded the upper limit (10 $\mu\text{eq } \ell^{-1}$) proposed by Galloway *et al.* (1984) as representative of remote regions, but was much lower than the 50 $\mu\text{eq } \ell^{-1}$ typical of industrialized areas. NO₃⁻ was equal to their proposed limit for remote areas (5 $\mu\text{eq } \ell^{-1}$; Galloway *et al.*, 1984), suggesting little

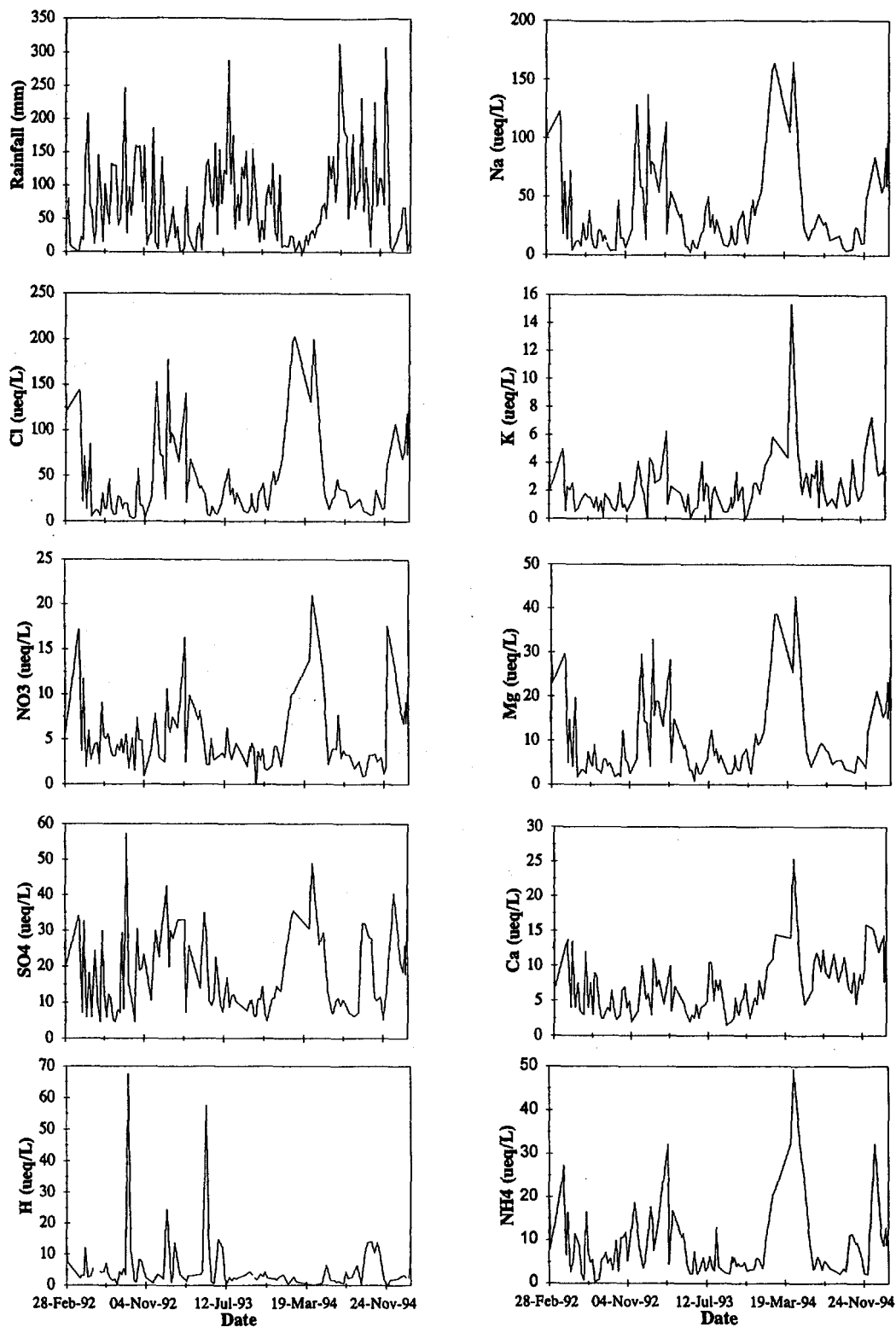


Fig. 2. Concentrations of major cations, anions, and organic C and N in rainfall (wet-only, event) collected at La Selva, Costa Rica.

human influence on nitrogen deposition in this region. The observation that SO_4^{2-} and NO_3^- were uncorrelated supports the contention that anthropogenic sources of sulfuric and nitric acids are minimal in this

region (Table 3). In Puerto Rico, where long-range transport of polluted air masses appears to occur, strong correlations were observed between SO_4^{2-} and NO_3^- ($r^2 = 0.79$; McDowell *et al.*, 1990).

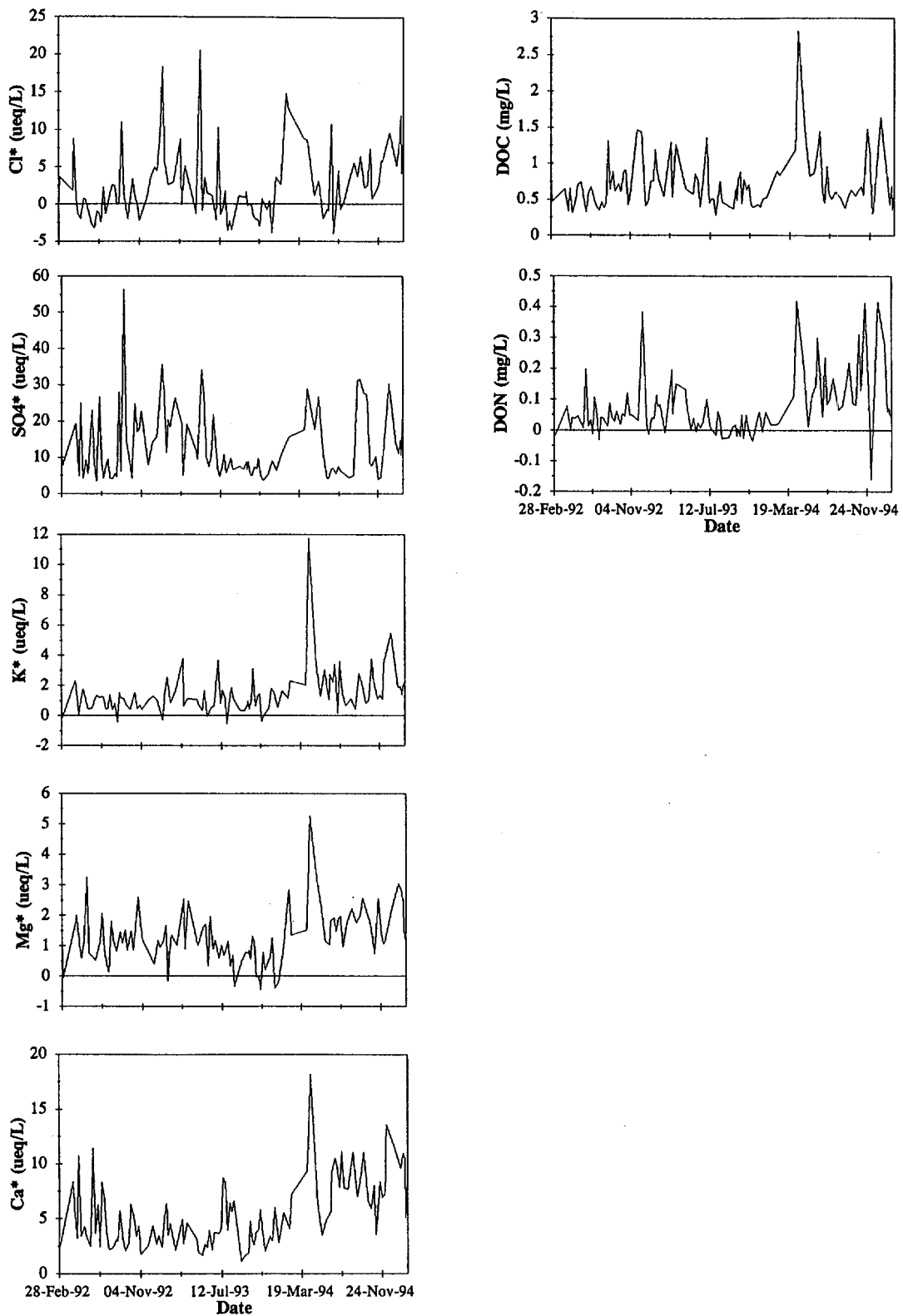


Fig. 2. (continued).

Veneklaas (1990) found that volcanic activity adjacent to a tropical forest in Colombia led to a correlation between high concentrations of SO_4 and acidity in precipitation. In a study of the Masaya Caldera in

Nicaragua, Johnson and Parnell (1986) showed that venting of volcanic gases resulted in contamination of precipitation with both HCl and H_2SO_4 . The high percentage of sulfate composed of non-sea-salt

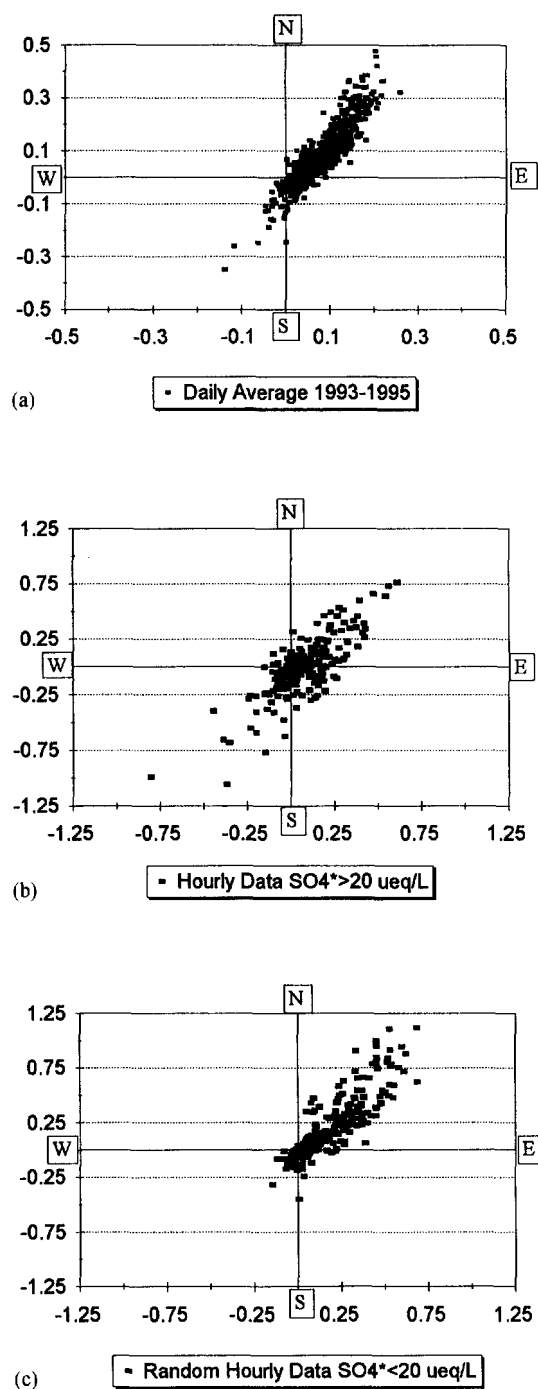


Fig. 3. Wind patterns at La Selva, Costa Rica: (a) daily average wind vector (January 1993–February 1995); (b) hourly wind vector for all collection dates when $\text{SO}_4^* > 20 \mu\text{eq l}^{-1}$ in wet-only precipitation events; (c) hourly wind vector for randomly chosen collection dates when $\text{SO}_4^* < 20 \mu\text{eq l}^{-1}$ in wet-only precipitation events.

sources (73%) at La Selva and the various volcanoes in the vicinity of the collection site, suggest that volcanic activity may affect precipitation chemistry. The association between Cl^* , SO_4^* and H^+ (Table 3) and the correlation between high concentrations of SO_4^*

and H^+ further supports the possible influence of volcanic venting on rain chemistry at La Selva.

Analysis of wind vectors during individual rainfall collections with high SO_4^* shows that these events are associated with winds from the SW, rather than the NE as is typically observed (Fig 3). Volcan Poas, which is located southwest of La Selva, has a history of frequent phreatic eruptions of steam and water and frequent fumarolic activity causing the release of volcanic gases (Pringle *et al.*, 1993). Because the field station (back-up generator only) and possible local sources are also located SW of the collector, however, we cannot be certain that volcanic sources are responsible for the episodes of high SO_4^* which we have observed.

Our observations of predictable seasonal increases in the marine aerosol and nutrient content of precipitation during the dry season at La Selva support the conclusions of earlier workers that increases in concentration during individual dry seasons in Venezuela (Lewis, 1981), Turrialba, Costa Rica (Hendry, 1984), Honduras (Kellman *et al.*, 1982), Colombia (Veneklaas, 1990) and Central Amazonia (Forti and Moreira-Nordemann, 1991) are in fact indicative of seasonal patterns. Annual variation in amounts of rainfall is also important in determining the overall composition of precipitation. Likens *et al.* (1987) found in Katherine, Australia that dilution contributed to lower concentrations in wet years and higher concentrations in dry years. Comparing Turrialba (Hendry, 1984) to La Selva, we can see that sometimes seasonal patterns are only present when conditions become extreme, such as during severe dry periods. Thus, it appears that the amplitude of seasonal fluctuations may be highly influenced by annual fluctuations in total precipitation. Long-term studies such as this one provide a better understanding of the true seasonal patterns in a region because fluctuations due to other factors are more easily recognized.

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