CHEMICAL COMPOSITION OF PRECIPITATION AT TWO SAMPLING SITES IN MEXICO: A 7-YEAR STUDY

A. P. BAEZ, R. D. BELMONT and H. G. PADILLA

Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México, Ciudad Universitaria, México, D.F., 04510, Mexico

Abstract—This paper describes the results of a study of the chemical composition of bulk and wet precipitation, collected for 7 years in a large urban area and a forested rural site in Central Mexico. In rain samples from both sites, sulfate was the most abundant ion followed by ammonium. Seasonal patterns of monthly volume-weighted concentration show that the highest values of SO_4^{2-}, NO_3^-, Ca^{2+} and NH_4^+ were measured in May, the beginning of the rainy season in Central Mexico. The lowest values were observed from July to September, the months when most thunderstorms occurred. Multiple regression correlation analysis was applied to all data and a hierarchical model was used to select the variables included in the final model. In Rancho Viejo the model showed that SO_4^{2-} contributed with 41% in the H^+ concentration prediction. In Mexico City, despite the high SO_4^{2-} concentration in rain water, this ion only contributed 0.46% whereas Ca^{2+} contributed in wet and bulk precipitation, 61 and 41%, respectively. Finally no long-term trends were noticed. Copyright © 1996 Elsevier Science Ltd

Key word index: Rain chemistry, urban–rural comparison.

INTRODUCTION

Many studies have been made on the chemical composition of precipitation over extended intervals, to detect modifications caused by the increase of human activities, but it has been difficult to show trends due to the wide variations observed in rain water composition (Colin *et al.*, 1990). Precipitation, however, has unique scavenging properties, which makes it a useful indicator of ambient pollution levels. Its analysis yields valuable data concerning inputs of both nutrients and toxic compounds to terrestrial and aquatic systems (Caiazza *et al.*, 1978; Peden and Skowron, 1978; Kins, 1982; Pratt *et al.*, 1983; Baez and Belmont, 1987; Parungo *et al.*, 1990).

Wet deposition for a given area depends on total precipitation and on factors that determine concentration variations of the chemical species of interest in rainfall (Prado-Fiedler, 1990).

In this study we analyzed the composition of daily precipitation during a 7-year period, its annual variation, and determined an annual estimate of wet and bulk precipitation. We also determined the precipitation chemistry in a highly polluted urban area and in a forested rural region.

EXPERIMENTAL METHODS

Sampling sites

Two sampling sites were selected: an urban area and a forested rural region. The selected urban area was Mexico City. The collector was located on the roof of the Atmospheric Sciences Center's building, at the campus of the National University, at an elevation of 2250 m above sea level (ASL). The mean annual temperature is 16°C and the mean annual rainfall is 860 mm at this location. Prevailing winds during the rainy season come from the southeast to northeast and usually the clouds are of the convective type (Jáuregui, 1986). The second sampling site (Rancho Viejo) was located in a forested region, 80 km southwest of Mexico City, in the State of Mexico, at 2700 m (ASL) with a mean annual rainfall of 1440 mm. During the rainy season, easterly winds at 700–600 mb (Servicio Meteorológico Nacional, 1992) transport air pollutants, emitted in Mexico City, to Rancho Viejo, according to the synoptic conditions that prevail during summer. The locations of the sampling sites are shown in Fig. 1.

Sampling methods

From 1987 to 1990, bulk precipitation was collected daily at the Mexico City site using a polyethylene funnel 24 cm in diameter, draining into a 3 ℓ polyethylene bottle inside a sealed polyurethane insulated box to reduce the evaporation and growth of microorganisms. The top of the funnel was placed 1.80 m above ground level to prevent contamination from splashing. Funnel and bottles were rinsed thoroughly with deionized water before exposure. From 1991 to 1993, only wet precipitation samples were collected in Mexico City, on a daily basis, with an automatic wet/dry precipitation collector (Andersen, General Metal Works, Inc.) into a standard high-density polyethylene bucket. After collection, bottles were sealed with polyethylene caps and the buckets were tightly sealed with polyethylene covers. In both cases, bottles and buckets were sent to the Atmospheric Sciences Center's Chemical Laboratories in Mexico City for chemical analysis.

At Rancho Viejo only wet precipitation samples were collected from 1987 to 1993. The collection system consisted
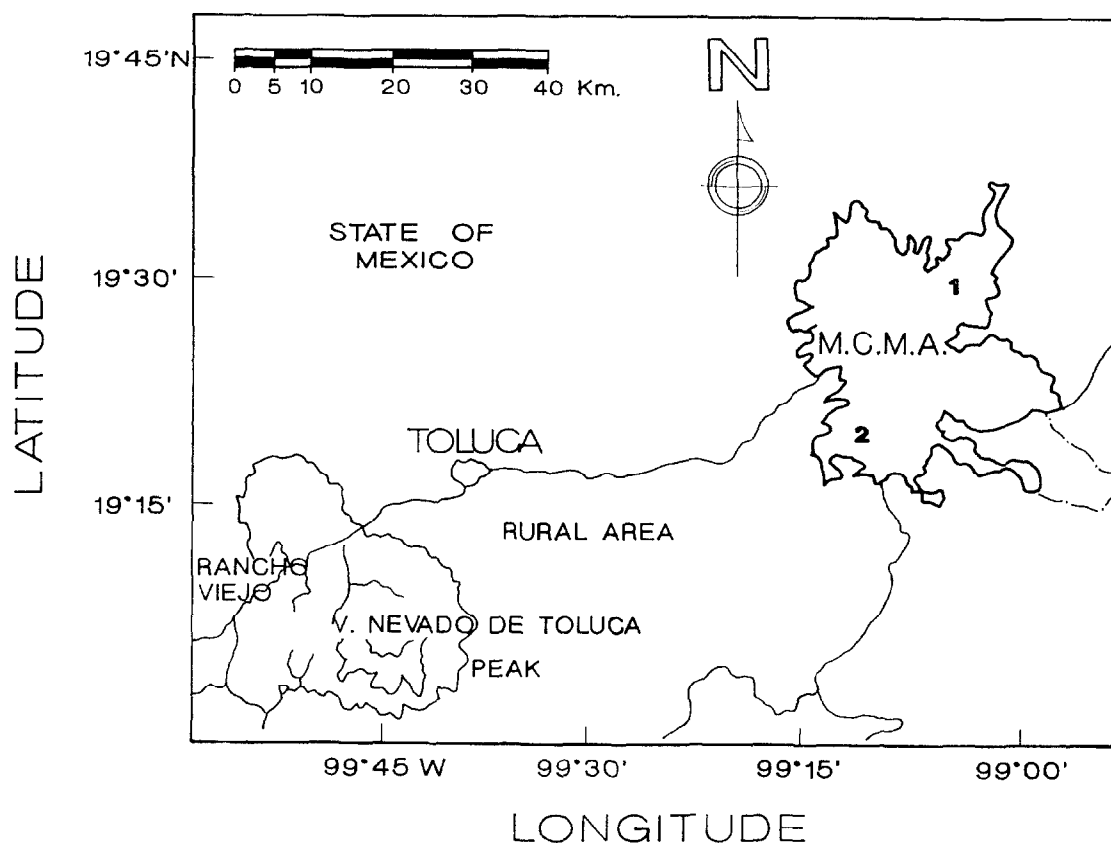
Fig. 1. Monitoring network sampling stations: (1) Xalostoc; (2) Pedregal and University of Mexico (MCMA: Mexico City metropolitan area).

of a 24 cm diameter polyethylene funnel, which was 1.80 m above grass-covered ground. The funnel was attached to a 30 cm long polyethylene tubing inserted into a 3.5 ℓ polyethylene bottle. The funnel was covered between rain events. The funnel and tubing were rinsed with deionized water shortly before the rain started.

Chemical analysis

The samples were analyzed for pH, SO_4^{2-}, NO_3^-, Ca^{2+}, Mg^{2+}, and NH_4^+. For chemical analysis, unfiltered samples were used from 1987 to 1990. From 1991 to 1993, samples were filtered through a 0.45 μm membrane Millipore leached with deionized water before chemical analysis. pH was measured within 24 h upon the arrival of samples to the laboratory. Sulfate, NH_4^+ and NO_3^- were determined by turbidimetric, phenate and salicylate methods, respectively (APHA, 1985; Mészáros, 1978). Since 1992, SO_4^{2-} and NO_3^- were determined by ion chromatography (Perkin-Elmer-Isocratic LC pump 250 with a conductivity detector). Calcium and Mg^{2+} were measured by flame atomic absorption spectrophotometry (Perkin-Elmer 460). The detection limits (DLs) for SO_4^{2-}, turbidimetric and ion chromatography methods, were 1 and 0.2 mg ℓ^{-1}, respectively. The DLs for NO_3^-, salicylate and ion chromatography methods, were 0.1 and 0.09 mg ℓ^{-1}, respectively. The detection limit (DL) for NH_4^+ was 0.013 mg ℓ^{-1}. The DL for Ca^{2+} was 0.01 mg ℓ^{-1} and for Mg^{2+} it was 0.002 mg ℓ^{-1}.

Precision of analysis

Precision was determined by analysis of standards from 10 replicate measurements at different concentrations. The

results showed that the precision for SO_4^{2-}, NH_4^+ and NO_3^- (turbidimetric, phenate and salicylate methods) was < 10% relative standard deviation (RSD) and for SO_4^{2-}, NO_3^- (ion chromatography method), Ca^{2+} and Mg^{2+} it was < 5% RSD.

RESULTS AND DISCUSSION

This study corresponded only to the rainy season in Central Mexico (May to October). For the statistical analysis, whenever a value of a particular ion was below the detection limit, half the detection limit was used for computation purposes.

In the statistical analysis the first step was to plot frequency distributions. Figure 2 shows the frequency distribution for the SO_4^{2-} in Mexico City (wet precipitation, 1991–1993) and Rancho Viejo (only wet precipitation, 1987–1993), which follows approximately a log-normal distribution, but skewed toward higher concentration values. The distribution shown in Fig. 2 is similar for the concentrations of most other ionic species in precipitation samples from Mexico City and Rancho Viejo.

Geometric means, volume-weighted means (VWM), standard deviations of the VWM, and minimum and maximum values for the entire data period 1987–1993
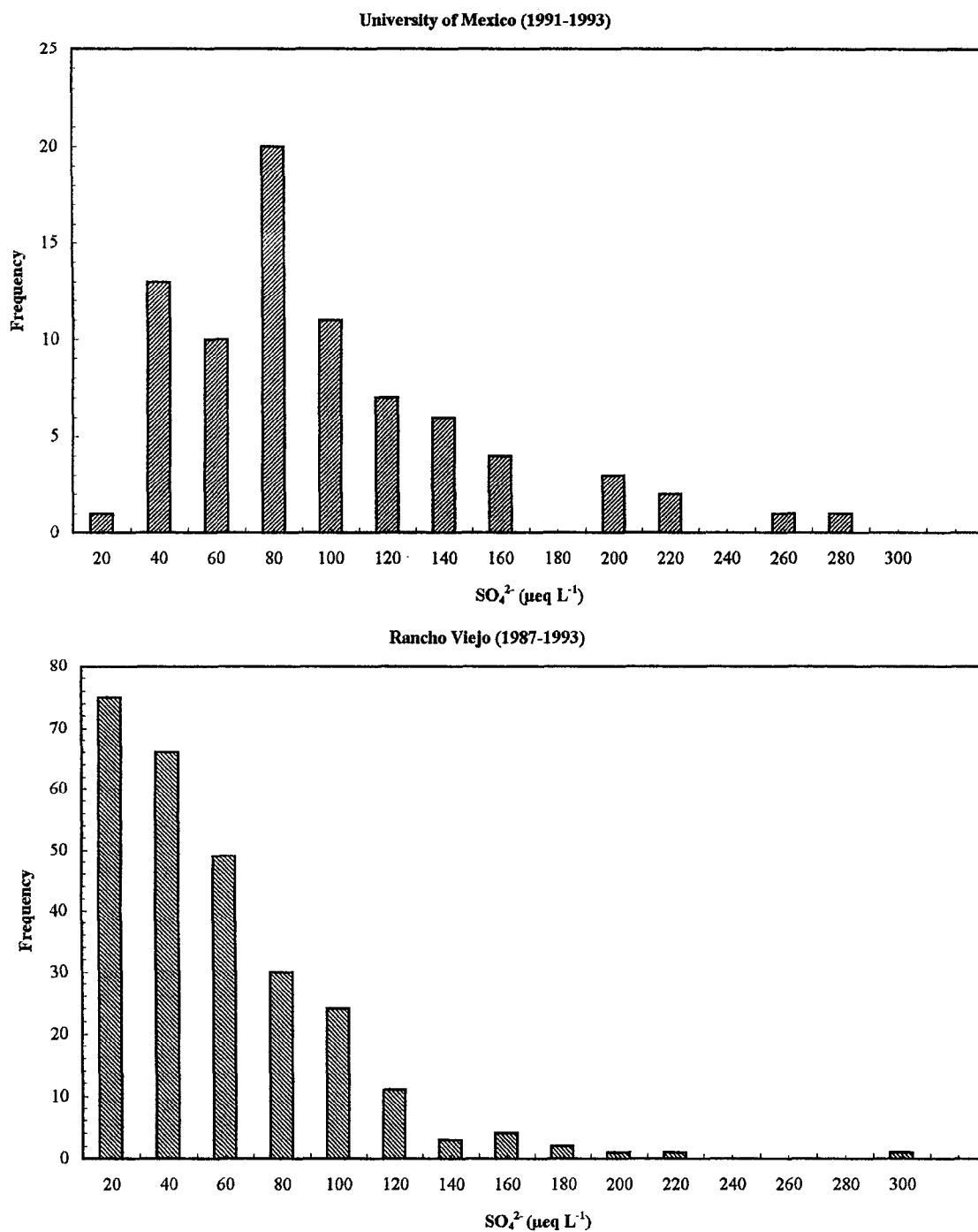
University of Mexico (1991-1993)

Rancho Viejo (1987-1993)

Fig. 2. Frequency distribution plots of SO_4^{2-} for both sampling sites, which follow an approximately log-normal distribution, but skewed toward higher concentration values.

for all analyzed ions are shown in Table 1. The standard deviations of the VWM were calculated using the formula of Galloway et al. (1984).

Figure 3 shows monthly volume-weighted concentrations of rain samples in Mexico City (bulk and wet precipitation) and in Rancho Viejo (only wet precipitation) averaged over the 7-year period. The SO_4^{2-}

monthly concentration in Mexico City was highest in May, while at Rancho Viejo the highest concentration was observed in June. The lowest concentration for this ion was found from July to September at both the sampling sites. The monthly behavior of NO_3^- and alkaline ions Ca^{2+}, Mg^{2+}, NH_4^+ followed similar patterns as those of SO_4^{2-}. The high values found in

Table 1. Volume-weighted means (VWM), standard deviations of the volume-weighted means (SVWM), geometric means, minima and maxima, in $\mu eq\ \ell^{-1}$, for entire data 1987–1993

	SO_4^{2-}	NO_3^-	Ca^{2+}	Mg^{2+}	NH_4^+	H^+
University of Mexico, 1987–1990 (N = 104)						
VWM	131.3	41.45	70.51	9.67	93.51	23.51
SVWM	9.28	3.79	4.57	0.70	7.20	4.28
G. mean	132.6	36.71	70.87	9.28	88.35	5.41
Minimum	34.17	5.29	3.50	0.82	15.71	0.04
Maximum	600	255	344	47.54	498	251
University of Mexico, 1991–1993 (N = 79)						
VWM	75.30	34.82	33.07	3.67	76.16	22.29
SVWM	6.41	3.29	2.82	0.30	5.01	4.00
G. mean	74.61	32.81	31.48	3.63	74.25	4.43
Minimum	17.70	5.50	4.45	0.57	15.00	0.10
Maximum	268	202	363	31.15	264	275
Rancho Viejo, 1987–1993 (N = 267)						
VWM	39.75	15.65	9.26	2.53	26.91	20.50
SVWM	3.17	1.27	0.91	0.32	2.06	1.81
G. mean	32.52	14.19	6.14	1.63	21.96	14.94
Minimum	1.46	1.21	0.50	0.16	0.71	0.11
Maximum	284	179	146	45.90	307	199

N = number of samples.

May for these ions are associated with the beginning of the rainy season. The first rains scavenge the accumulated pollutants resulting in relatively high ionic concentrations.

The increase in Ca^{2+} concentration, observed also in May, reflects the increased amounts of soil particles being blown into the atmosphere by wind action (Galloway and Likens, 1978) and dust from lime and cement plants. The washout of large particulate matter takes place during the early stages of rainfall; this particulate matter settles rapidly due to dry fall out, increasing the Ca^{2+} content in bulk precipitation more than in wet precipitation (Fig. 3). Saylor et al. (1992) have suggested that larger ionic concentrations are due to in-cloud and below-cloud removal of aerosols during brief showers that occur after extended periods of dryness and air stagnation.

In Mexico City during winter and early spring, the atmosphere is characterized by almost daily temperature inversions and stagnation conditions. These conditions contribute to the accumulation of air pollutants emitted in huge amounts by small, medium and large industries located in and near Mexico City, and by more than three million motor vehicles. Therefore, it is reasonable to assume that the highest ionic concentrations occur during the first rains in May or after periods of dryness, as Saylor et al. (1992) have also reported. July through September are the months when most thunderstorm activity occurs, easterly winds are well established, and the amounts of precipitation are the highest, resulting in dilution of ionic species.

The annual variations of volume-weighted means for SO_4^{2-}, NO_3^-, NH_4^+ and H^+ are shown in Fig. 4.

Annual trends were not evaluated, because the data sets showed small annual term variations. This may be due to the high variability of annual inputs of the different ionic species, or to the variation of various meteorological factors such as wind direction (trajectories of the precipitation air masses), rainfall rate, total amounts of rainfall, and height of cloud base (Asman et al., 1981). Care must be taken, however, when interpreting these results since analytical methods were not the same throughout the 7-year sampling period.

To test for significant differences among ionic concentrations in wet precipitation between both sampling sites, the Student's t-test (two-tail at 5%) was applied. The results of this statistical test indicate that there were significant differences between these two sampling sites. These variations in ionic concentrations possibly include differences in the meteorological conditions and rain chemistry between events and between locations (Pratt et al., 1983). Additionally, changes in air pollutant concentrations in the atmosphere of Mexico City are important in explaining the variability of rain water chemical composition. Table 2 shows the ion pair $\log_{10}$ correlation from both sampling sites. For the University of Mexico, the highest correlation coefficients corresponded to the pair Ca^{2+}–Mg^{2+} in both sampling periods. This can be attributed to suspended soil dusts (calcareous soils are predominant in this area) and industrial alkaline particle emissions. The high correlation between SO_4^{2-}–NO_3^-, in both sampling periods, is probably due to the coemission of their precursors SO_2 and NO_x, which are emitted in great amounts by the multiple fossil fuel combustion sources in the Mexico City
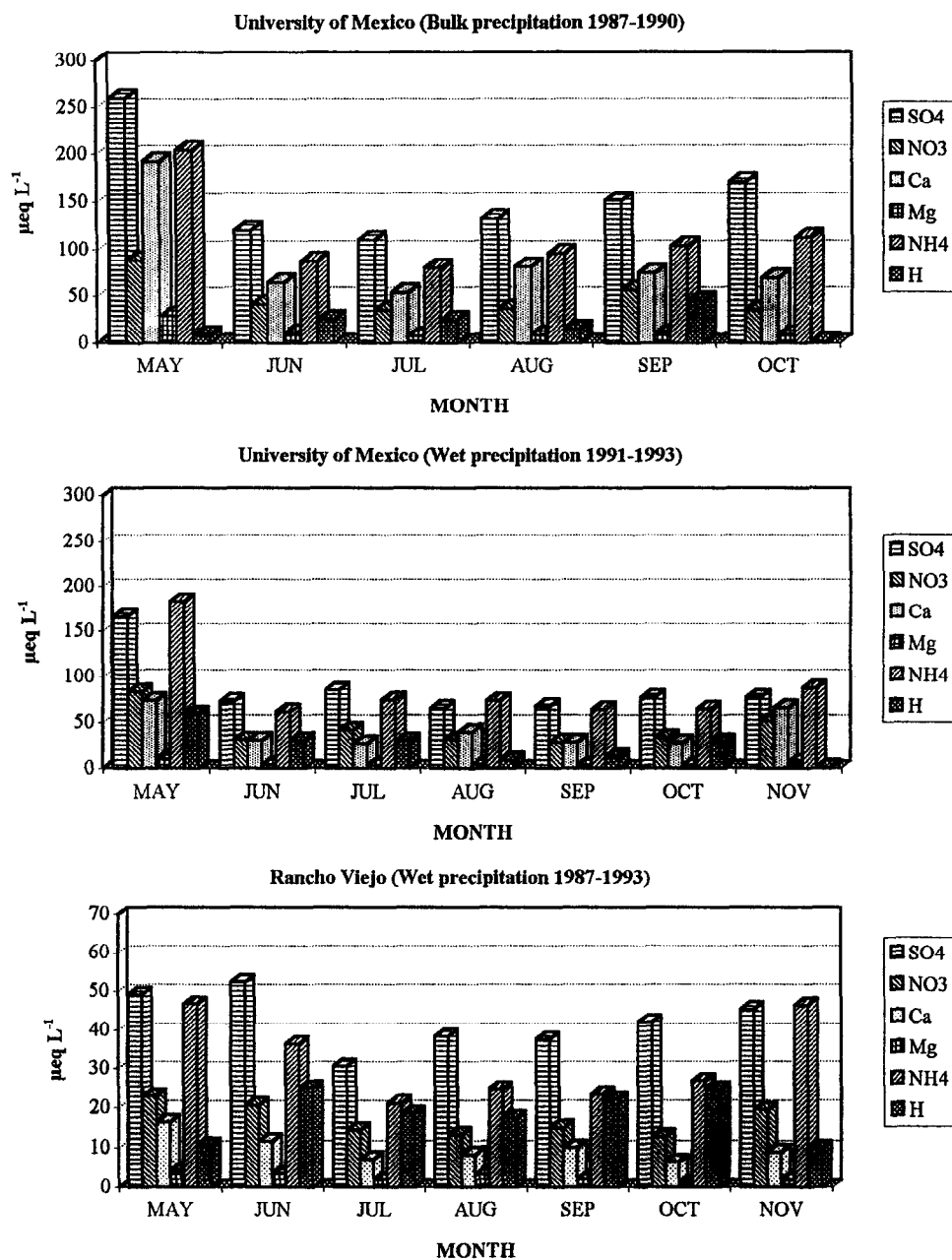
University of Mexico (Bulk precipitation 1987-1990)

University of Mexico (Wet precipitation 1991-1993)

Rancho Viejo (Wet precipitation 1987-1993)

Fig. 3. Monthly volume-weighted mean concentrations, in $\mu eq\,\ell^{-1}$, of selected ionic components in Mexico City for bulk precipitation and wet precipitation collected at the University of Mexico during 1987–1990 and 1991–1993, respectively, and wet only precipitation collected at Rancho Viejo during the period 1987–1993.

metropolitan area. At Rancho Viejo the observed high correlations are also probably due to the precursors SO_2 and NO_x, which are transported from Mexico City and the industrial area of Toluca. This assumption is supported by the radiosonde observations made at the Mexico City International Airport and wind data from pilot balloons launched in Rancho Viejo, which showed similar wind directions ranging from north–northeast to south–southwest (Padilla et al., 1993). To support the assumption that

SO_2 and NO_x are important precursors of SO_4^{2-} and NO_3^- due to the coemission of these precursors, a simple linear hourly correlation was calculated between NO_3^-/NO_x and SO_4^{2-}/SO_2, for the period of 1991–1993. The values of NO_x and SO_2 were provided by the Mexico City air quality monitoring network, from two selected sampling stations; one in the northern part of the city (Xalostoc) and one in the southern zone (Pedregal) (Fig. 1). The best correlations found at Xalostoc, between NO_3^-/NO_x were at
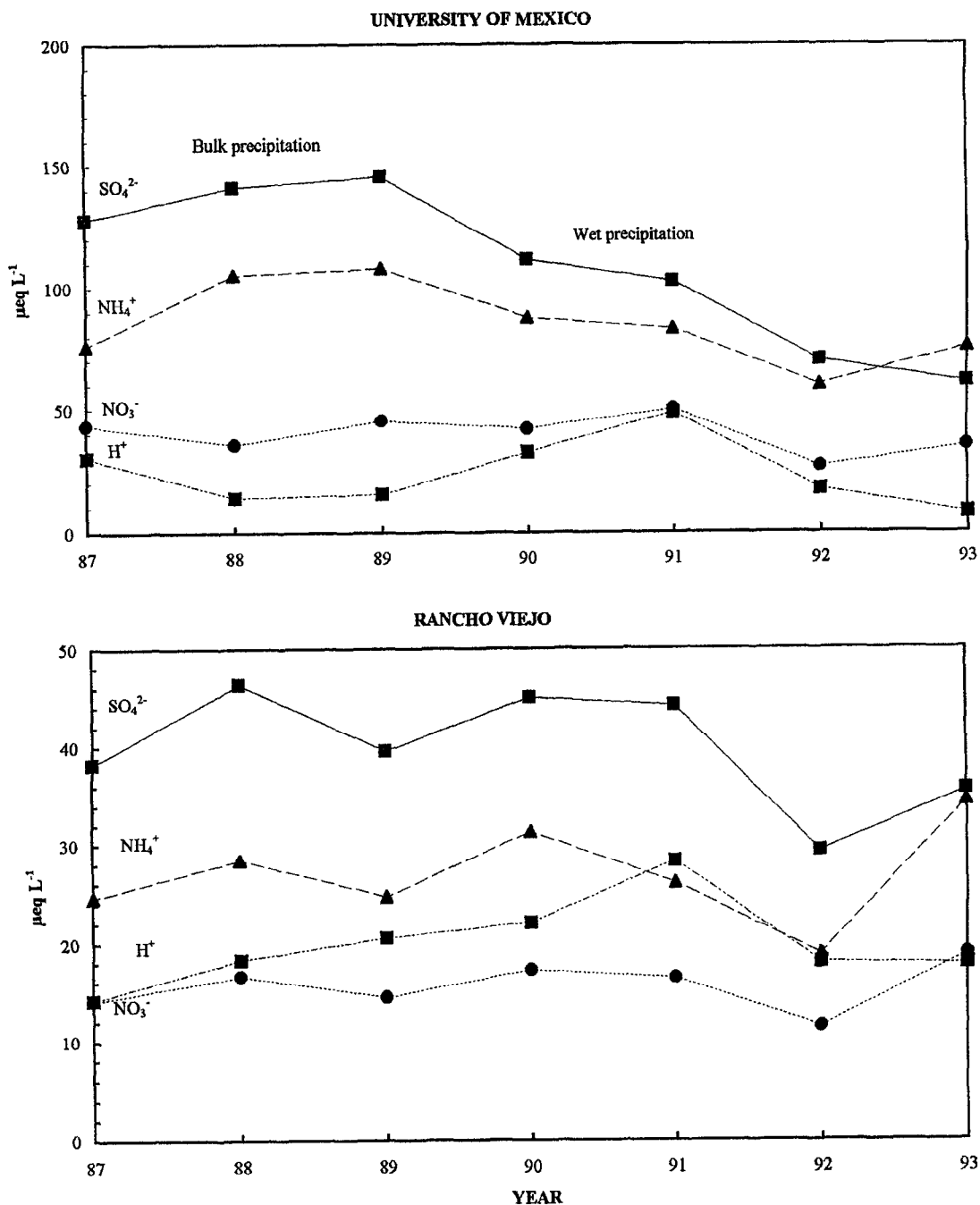
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RANCHO VIEJO

Fig. 4. Annual variations of volume-weighted mean concentrations in μeq ℓ^{-1} for the ionic species SO_4^{2-}, NO_3^-, NH_4^+ and H^+, whose trends could not be evaluated because the data showed small variations.

1:00, 11:00, 12:00, 14:00, 19:00 h (local time) and from 21:00 to 24:00 h, and the correlation coefficient (r) ranged from 0.399 to 0.624 at $p < 0.01$. Between 14:00 and 20:00 h, r was 0.409 and 0.388, respectively, at $p < 0.05$. At Pedregal only the correlation values were found at 1:00, 20:00 and from 22:00 to 24:00 h with r ranging from 0.314 to 0.514 at $p < 0.01$. With respect to SO_2, the best correlation between SO_4^{2-}/SO_2 was found at the Pedregal sampling station

for all hours with the exception of 1:00 and 24:00 h; r ranged from 0.361 to 0.433 at $p < 0.01$, and r ranged from 0.466 to 0.488 at $p < 0.05$. With respect to the Xalostoc station the only correlation between SO_4^{2-}/SO_2 was found at 7:00 h, with $r = 0.470$ at $p < 0.01$, and at 10:00, 17:00, 18:00, 20:00 and 21:00 h, r ranging from 0.363 to 0.470 at $p < 0.05$.

Hydrogen peroxide is an important oxidant of dissolved S(IV) in cloud water and precipitation

(Penkett *et al.*, 1979; Schwartz, 1984; Calvert *et al.*, 1985; Seinfeld, 1986). In addition, observational evidence for the in-cloud reaction of SO_2 and H_2O_2 has been reported from field studies (Daum *et al.*, 1984). However, the solubility of SO_2 in the liquid phase is strongly pH-dependent, since it is governed by the acid–base equilibria; under acidic conditions the solubility of SO_2 is very low, while it is strongly increased at higher pH (Seinfeld, 1986). Thus, the aqueous concentration of S(IV) depends on the presence of acidic and basic components that establish pH in atmospheric water (Seinfeld, 1986). On the other hand, at pH > 5 the oxidation by ozone is more efficient than by H_2O_2 (Penkett *et al.*, 1979; Seinfeld, 1986). Measurements of H_2O_2 were not made during this study; for this reason it is not possible to ascertain the

contribution of H_2O_2 to the oxidation of the SO_2 and NO_x, despite the fact that the average pH of the rain water was less than 5. However, we must consider the inputs of NH_4^+, Ca^{2+} and Mg^{2+} to the neutralization of the acidity of rain water, which in many cases had a pH > 7. In Mexico City the air quality standard for ozone (0.11 ppm) is exceeded on more than 80% of the days per year; thus, it is possible to assume that there are substantial amounts of ozone for the oxidation of the SO_2 and NO_x that account for the presence of SO_4^{2-} and NO_3^- in the precipitation.

A multiple regression correlation (MRC) analysis was performed on the rain chemistry data. The data followed an approximately log-normal distribution; therefore, a $\log_{10}$ transformation was applied to all data and the hierarchical model (Cohen and Cohen, 1975) was used to select the variables included in the final model. Table 3 shows the model with the best-fit coefficients for Mexico City (1987–1990 and 1991–1993 periods) and for Rancho Viejo (1987–1993 period).

At Rancho Viejo, the model shows that SO_4^{2-} contributed by far the most (41%) to the H^+ concentration prediction. This result is expected from the geographic characteristics of the location, which is downwind from Mexico City with neither nearby local industry nor significant soil particle emission sources.

On the other hand, Ca^{2+} contributes with 9%, while Mg^{2+}, NH_4^+ and NO_3^-, combined, account for approximately 7%.

Despite the high SO_4^{2-} concentrations found in bulk precipitation collected in Mexico City from 1987 to 1990, this ion is not important in the regression equation. In fact, calcium is the most relevant and important parameter, with a contribution of 38%, whereas sulfate contributes as little as 0.46%. Note the contrast with Rancho Viejo where Ca^{2+} and SO_4^{2-} contribute 9 and 41%, respectively. We interpret this to indicate that rain chemistry in Mexico

Table 2. Simple ion-pair $\log_{10}$ correlation coefficients (r)

	NO_3^-	Ca^{2+}	Mg^{2+}	NH_4^+	H^+
University of Mexico, 1987–1990 (N = 104)					
SO_4^{2-}	0.760[a]	0.738[a]	0.664	0.789[a]	− 0.068[a]
NO_3^-		0.575[a]	0.551[a]	0.621[a]	0.163
Ca^{2+}			0.810[a]	0.507[a]	− 0.458[a]
Mg^{2+}				0.515[a]	− 0.398
NH_4^+					0.036
University of Mexico, 1991–1993 (N = 79)					
SO_4^{2-}	0.840[a]	0.655[a]	0.702[a]	0.778[a]	0.234[b]
NO_3^-		0.621[a]	0.684[a]	0.764[a]	0.272[b]
Ca^{2+}			0.919[a]	0.817[a]	− 0.408[a]
Mg^{2+}				0.811[a]	− 0.289[a]
NH_4^+					− 0.204
Rancho Viejo, 1987–1993 (N = 267)					
SO_4^{2-}	0.864[a]	0.594[a]	0.505[a]	0.795[a]	0.641[a]
NO_3^-		0.660[a]	0.518[a]	0.828[a]	0.602[a]
Ca^{2+}			0.744[a]	0.587[a]	0.188[a]
Mg^{2+}				0.490[a]	0.062
NH_4^+					0.430[a]

[a] Significant at $p < 0.001$.
[b] Significant at $p < 0.05$.
N: number of samples.

Table 3. Multiple regression analysis between H^+ and SO_4^{2-}, NO_3^-, Ca^{2+}, Mg^{2+} and NH_4^+ concentrations in Mexico City (1987–1990 and 1991–1993) and Rancho Viejo (1987–1993)

	Coefficient	t-value	Significant level	F-ratio ANOVA[a]	Significant level	R
Mexico City, 1987–1990 (N = 104)						
Constant	11.5166	3.0246	0.0032	64.2412	0.0000	0.748
Ca^{2+}	− 0.2689	− 7.2256	0.0000			
NO_3^-	0.7368	11.2900	0.0000			
Mexico City, 1991–1993 (N = 79)						
Constant	− 0.8666	− 1.5239	0.1317	43.9656	0.0000	0.798
Ca^{2+}	− 1.8211	− 6.5139	0.0000			
NH_4^{2-}	− 1.3530	− 2.5254	0.0137			
SO_4^{2-}	3.6161	9.3308	0.0000			
Rancho Viejo, 1987–1993 (N = 267)						
Constant	− 0.0869	− 1.0114	0.3128	116.378	0.0000	0.684
SO_4^{2-}	0.9674	14.6707	0.0000			
Ca^{2+}	− 0.2545	− 5.3508	0.0000			

[a] Analysis of variance for the full regression.

City is largely affected by dust particle emission sources. Magnesium and SO_4^{2-} only contribute 3%, and NO_3^- only 11%.

The above conclusions are strengthened by the results of chemical analyses performed on wet precipitation samples, also collected in Mexico City in 1991–1993. In this case, the SO_4^{2-} contribution increases to 5.5%. However, Ca^{2+} still has the strongest influence on H^+ concentration (61%). Magnesium plus NO_3^- account for 2% and NH_4^+ for 7%.

In summary, calcium is the most important ion in wet and bulk precipitation collected in Mexico City from 1991 to 1993 and from 1987 to 1990, respectively. This result strongly suggests that storm downdrafts blow off soil particles that are washed out by raindrops affecting their chemistry, and large soil particles are more rapidly scavenged during rainfall early stages (Tanaka et al., 1980; Vong, 1990; Baez et al., 1993; Camarero and Catalan, 1993). This explains why alkaline rainwater pHs are so common, despite the huge SO_2 and NO_x emissions emitted in the Mexico City metropolitan area.

In this study carboxylic acids were not determined; however, one must consider the importance of their contribution in the acidity of precipitation.

Advances in sampling and analytical techniques have revealed that formic acid (HCOOH) and acetic acid (CH_3COOH) are major vapor (Dawson et al., 1980) and aqueous (Keene et al., 1983) phase constituents of the troposphere. Evidence based on direct measurements (Norton, 1985) and indirect estimates (Keene and Galloway, 1984) suggests that anthropogenic activities may represent important local sources for carboxylic acid distribution and origin. We believe that organic acids play an important role in precipitation acidity, since it is a well-known fact that Mexico City has one of the most photochemically polluted atmospheres in the world. Measurements of carboxylic acids are presently underway.

The ionic concentrations measured in rain water collected in Mexico City and Rancho Viejo can be compared with the results reported for other locations (Table 4). This table shows that sulfate concentrations measured at Rancho Viejo were the lowest. This result

Table 4. Comparison of wet and bulk precipitation ionic concentrations collected in two sites in Mexico with those reported in other locations

Site	SO_4^{2-}	NO_3^-	Ca^{2+}	Mg^{2+}	NH_4^+	H^+	References
	(μeq ℓ^{-1})						References
Wet precipitation Minnesota, U.S.A. (seven sites average) (volume-weighted mean)	56.0	33.3	52.8	27.4	50.0	3.91	Pratt et al. (1983)
Warren, Michigan, U.S.A. (urban site, 42 weekly (average) data)	93.0	53.0	69.0	12.0	35.0	62.0	Dash and Cadle (1984)
South Western Europe (volume-weighted mean)	56.1	14.8	—	—	27.9	3.8	Pio et al. (1991)
Athens, Greece (year mean) (volume-weighted mean)	100	23.6	137	31.0	21.9	4.0	Dikaiakos et al. (1990)
Lower Ohio river, Kentucky, U.S.A. (all sites) (volume-weighted mean)	67.2	23.4	9.7	2.9	14.8	52.3	Saylor et al. (1992)
Mexico City, Mexico (all data) (volume-weighted mean)	75.3	34.8	33.1	3.7	76.1	22.3	This paper
Rancho Viejo, Mexico (all data) (volume-weighted mean)	39.7	15.6	9.3	5.5	26.9	20.5	This paper
Bulk precipitation Red Mountain Pass, Colorado (high altitude U.S.A. (geometric mean) sites, all data)	20.6	5.2	39.9	4.7	—	—	Reddy and Claassen (1985)
Greater Manchester, U.K. (volume-weighted mean)	85.4	29.3	49.5	26.5	31.4	43.0	Lee (1993)
Mexico City, Mexico (volume-weighted mean)	131	41.5	70.5	9.6	93.5	23.5	This paper

Table 5. Annual loading for rainfall collected at Mexico City and Rancho Viejo from 1987 to 1993

Year	SO_4^{2-}	NO_3^-	Ca^{2+}	Mg^{2+}	NH_4^+	H^+	Rainfall (mm)
				$g\,m^{-2}\,yr^{-1}$			
University of Mexico							
1987	2.061	0.902	0.500	0.037	0.459	0.010	334.89
1988	2.080	0.680	0.449	0.036	0.582	0.004	306.93
1989	1.854	0.745	0.490	0.044	0.517	0.004	265.71
1990	1.545	0.755	0.248	0.024	0.455	0.009	288.58
1991	1.228	0.775	0.161	0.012	0.373	0.012	249.44
1992	1.626	0.802	0.262	0.018	0.521	0.0085	482.71
1993	0.895	0.663	0.263	0.017	0.415	0.0024	305.02
Rancho Viejo							
1987	0.266	0.127	0.038	0.007	0.064	0.0021	145.08
1988	0.417	0.193	0.068	0.012	0.096	0.0034	187.12
1989	0.639	0.303	0.058	0.013	0.150	0.0069	336.15
1990	0.584	0.290	0.035	0.006	0.153	0.0060	270.21
1991	0.526	0.254	0.037	0.005	0.117	0.0070	248.08
1992	0.352	0.179	0.029	0.003	0.085	0.0045	249.51
1933	0.381	0.262	0.043	0.005	0.139	0.0040	222.98

is expected since the sampling site is located in a rural wooded area with no near pollution sources and scarce road traffic; this fact is also valid for the NO_3^- concentration measured there.

With respect to Mexico City, the SO_4^{2-} levels in rain water are 1.46, 1.34 and 1.1 times higher than in Minnesota, South Western Europe and the Lower Ohio River, respectively, but only 0.75 and 0.80 times that in Athens, Greece and Warren, Michigan, respectively. It is interesting to note that the highest SO_4^{2-} values correspond to urban areas affected by polluted air masses, like Warren (close to Detroit), Athens and Mexico City. Gatz (1980) has suggested that primary emissions may be the dominant source of SO_4^{2-} in precipitation near or in large cities.

On the other hand, calcium is the ion that probably has the most important influence in rain acidity neutralization (Minnesota, 52.8 μeq ℓ^{-1}; Warren 69 μeq ℓ^{-1}), specially Athens (137 μeq ℓ^{-1}) and Mexico City with values 0.62, 0.48, 0.24 times lower than in Minnesota, Warren and Athens, respectively.

The Ca^{2+} concentration reported in these locations comes from different sources. In Minnesota, Pratt *et al.* (1983) reported that the sampling location may be the recipient of alkaline dust from the west. Calcium in Athens comes from soil dust (Dikaiakos *et al.*, 1990). Limestone is a predominant constituent of Greece's soils, and in Mexico City the Ca^{2+} contribution to rain is from industrial particle alkaline emissions and soil erosion. It is very difficult to compare bulk precipitation results from other sites with those obtained in Mexico City, due mainly to the differences in sampling protocols between sampling locations. Reddy and Claassen (1985) collected bulk precipitation for seasonal periods, while Lee (1993) collected bulk samples on a weekly basis. The collectors were located in Greater Manchester, which covers an area of 1300 km² and with a wide range of activities such

as agriculture, industry, heavy traffic and a large power plant (2000 MW). In Mexico City, bulk precipitation was collected on a daily basis at the University of Mexico Campus 15 km south of Mexico City downtown and under the influence of the heavily polluted atmosphere of the city. Sulfate and Ca^{2+} concentrations, 131.4 and 70.5 μeq ℓ^{-1}, respectively, were higher than the values reported for Southwestern Europe and Greater Manchester. The high SO_4^{2-} values found in Mexico City reflect the contribution of the SO_2 precursor that is emitted in huge quantities in Mexico City metropolitan area. The high calcium concentration seems to be due to the soil-derived compounds associated with wind-blown soil dust and from industrial alkaline particle emissions.

A summary of the rainy season annual deposition for rainfall collected in Mexico City and Rancho Viejo is presented in Table 5. As expected, higher deposition values correspond to bulk precipitation (Mexico City, from 1987 to 1990), since these values comprise dry and wet precipitation. The higher rainy season annual deposition in Mexico City possibly corresponds to high air pollution levels. In spite of the ionic concentration dilution by heavy rains, higher rainy season annual loading values correspond to higher rainfall amounts.

CONCLUSIONS

A study of precipitation chemistry has been carried out for rain samples collected at two sampling sites in Central Mexico, over a 7-year period. The major conclusions are: The precipitation chemistry distribution was approximately log-normal but skewed toward higher values. Sulfate was the most abundant ion in all rain samples, followed by NH_4^+ and NO_3^-. The monthly volume-weighted concentrations showed

that the highest ionic values were measured in May, when the rainy season usually begins in Central Mexico. The lowest concentrations were found from July to September, when most thunderstorms occur. The $\log_{10}$ ion-pair correlations for the entire data set showed that the highest correlation corresponded to the ion pairs Ca^{2+}–Mg^{2+}, which can be attributed to suspended soil dusts. The well-correlated pairs SO_4^{2-}–NO_3^-, SO_4^{2-}–NH_4^+, and NO_3^-–NH_4^+ seem to occur in precipitation because of common sources.

A multiple regression correlation analysis was performed after a $\log_{10}$ transformation was applied to all data. The hierarchical model was used to select variables inserted into the final model. At Rancho Viejo, SO_4^{2-} was the largest contributor to the H^+ concentration prediction. This result is consistent with the geographical characteristics and near-surface wind climatology of the sampling site. In contrast, in bulk precipitation collected in Mexico City, Ca^{2+} is the most important parameter, with a contribution of 38%, reflecting the influence of calcium compound emissions from industrial sources and wind-blown soil dust, in spite of high atmospheric SO_2 levels. Even in wet precipitation collected in the city, Ca^{2+} still had the strongest influence on H^+ ion concentration prediction. This fact suggests the strong influence of alkaline emissions and soil dust on H^+ concentration.

Annual trends were not definitely discerned due to the high variability of the rainy season annual inputs of different ionic species.

The authors have considered the need to continue the study of precipitation chemistry in both Mexico City and a rural region downwind from the city, to determine whether the magnitudes of ionic inputs are increasing or decreasing and thus to assess present emission control effectiveness. In this research, Cl^-, Na^+, K^+ and conductivity determinations will also be included to better understand the rain chemistry of the region.

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