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Rainwater chemistry at the eastern flanks of the Sierra Madre Oriental, Veracruz, Mexico

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Abstract. A rainwater chemistry study was carried out at a single site in Xalapa located at the eastern flanks of the Sierra Madre Oriental, Veracruz, Mexico, during the rainy and dry seasons under the influence of different meteorological conditions. Rain samples were analyzed for the most important ions. The statistical results indicated that there were significant differences at the 95% confidence level between the ionic concentration measured in samples collected in both seasons. The lower concentration values found during the rainy season could be attributed to dilution processes since in this season 79% of the annual precipitation occurs, compared to only 21% in the dry season. High and positive ion-pair correlations were found among the most important ions in both seasons. Although Xalapa is situated at less than 100 km from the coast, marine contribution of SO_4^{2-} and Ca^{2+} is negligible compared with the nonmarine contribution. In the rainy season, enrichment of SO_4^{2-}, NH_4^+, and NO_3^- is due to upwind medium- and long-distance emission sources of Veracruz, as back trajectories of the predominant winds from the southeast indicate. On the other hand, in the dry season this enrichment is due to emission sources situated in Tampico, Madero, and Poza Rica and south-southeastern Texas, as indicated by the predominant winds from the northeast. Finally, wet deposition rates were, as expected, higher during the rainy season in spite of the dilution processes.

1. Introduction

Meteorological conditions such as rainfall rate and amount, cloud base height, and the air mass back trajectories affect the chemical composition of wet precipitation. *Miller* [1980] reported the acidity of Hawaiian precipitation as evidence of long-range transport of pollutants, and *Asman et al.* [1981] showed that air mass back trajectories are the most important meteorological parameters in explaining the variations in the chemical composition of rain. *Pack et al.* [1978] studied thoroughly the long-range transport of pollutants. *Chung* [1978] found a relation between cyclones, anticyclones, and stationary fronts and airborne sulfate in Canada. *Wolff et al.* [1979] classified the rain events according to their origin (mainly cold fronts and low-pressure systems) and to their trajectories. According to *Raynor and Hayes* [1982], the variability in the concentration of chemical species depends not only on precipitation amounts but also on emission rates and atmospheric processes. *Pacyna et al.* [1984] compared emission data with measured air concentrations with the help of trajectory model calculations. *Singh et al.* [1987] correlated wind direction, speed, and temperature, vertical movement of the atmosphere, and other parameters with rainwater. *Samson et al.* [1986] reported a receptor probabilistic model which described the spatial changes in the source-receptor relation steps for both varying meteorological conditions and for varying chemical transformation mechanisms. Sulfur wet deposition demonstrated substantial fluctuations. *Martin et al.* [1990] reported the use of a vertical wind component in their three-dimensional trajectory model using geochemical tracers to validate the model with horizontal and vertical transport considerations. Many factors involved in the atmospheric cycles of the elements, such as the spatial distribution and strength of sources, transport, and chemical transformations and the scavenging processes of chemical components, produce a great variability in the concentration of these components in precipitation [*Colin et al.*, 1989]. It is also important to take into account the specific nature of the receptor site [*Colin et al.*, 1989]. *Smith and Hunt* [1978] reported that slow moving active frontal systems and anticyclones, characterized by the convergence of moist air and by light winds that prevail for several days, respectively, favor the occurrence of episodes of sulfate wet deposition. *Singh and Nobert* [1982] showed that precipitation acidity was inherently related to air masses in Quebec, Canada. *Colin et al.* [1989] reported that two main mechanisms are responsible for the enrichment of rain: the dissolution of gases and the impacting of particles that occur in the air column below the cloud base, when raindrops fall (a local phenomenon), and the incorporation of gases and aerosols to the

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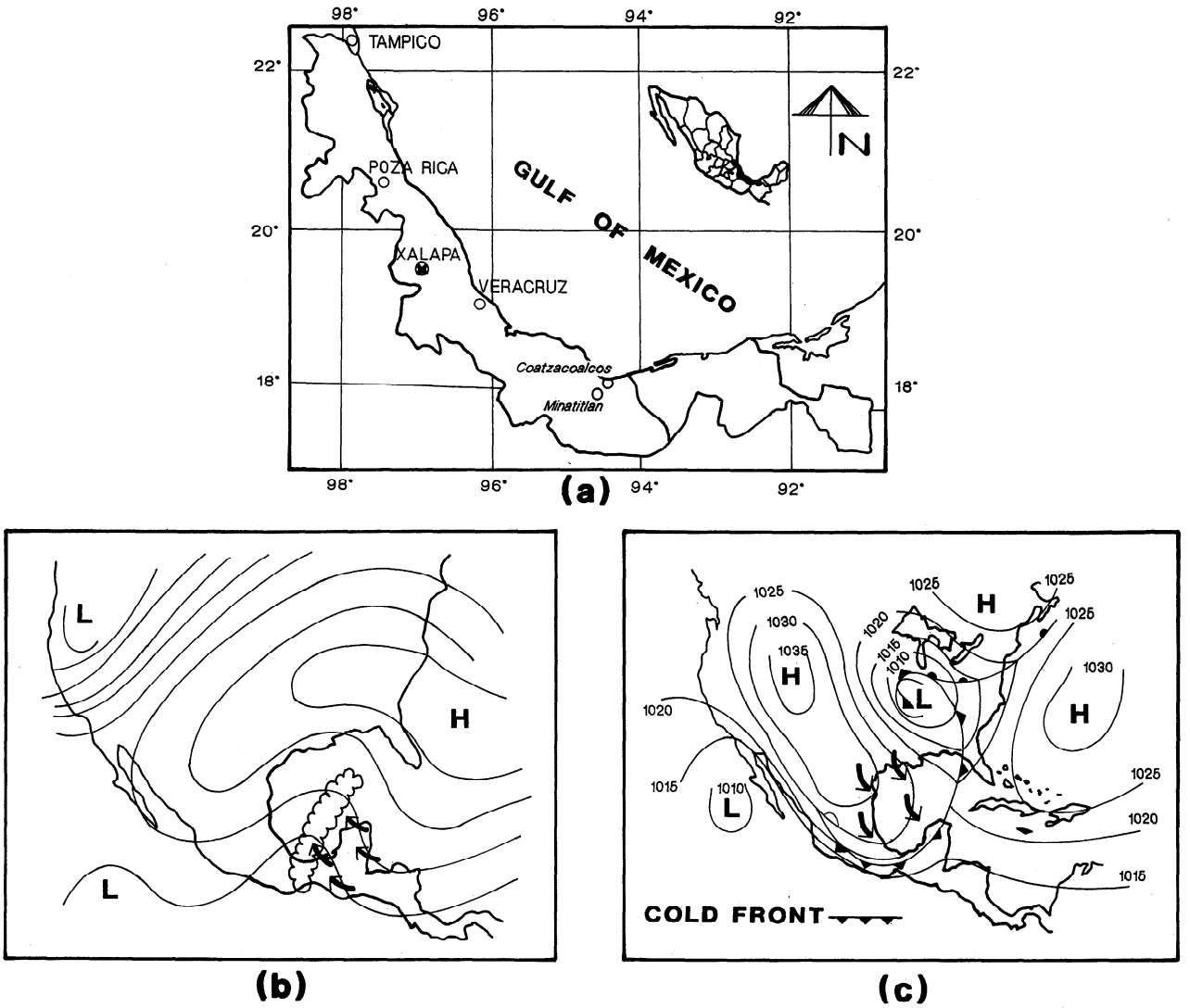

Figure 1. (a) Sampling site location. Despite the fact that Xalapa is near the Gulf of Mexico coast, the topography (1427 meters above sea level (masl)) plays an important role in determining its climate (high-altitude modified tropical climate). (b) Typical summer synoptic conditions in the Gulf of Mexico. The arrows indicate the wind directions that prevail during this situation. An easterly wave is schematically shown. (c) Typical winter synoptic conditions in the Gulf of Mexico. The passage of the cold front produces light rains and/or drizzle for 1–3 days. The arrows indicate the wind directions during this synoptic condition, and the triangles indicate the direction of the cold-front line displacement.

cloud during its formation and motion. Also, the nature of the site is fundamental to determine the relative proportions of the two mechanisms. Local incorporation can be more important in urban areas with important anthropogenic emissions, depending on the relative contributions of Aitken and large particles. That is, Aitken particles have a higher percentage of free acid than particles >0.1 μm radius [*Winkler*, 1980]. *Baez et al.* [1987] reported higher concentrations of alkaline elements and higher *p*H in the first rain fractions of rain events sequentially collected in urban areas. *Pratt et al.* [1984] also found an inverse relationship between alkaline cations and acidity in rainwater. This study is concerned with the chemical variation of rainwater collected at a single sampling station located at the eastern flanks of the Sierra Madre Oriental in Veracruz, Mexico. It also covers the different synoptic conditions that occur during the rainy and dry seasons.

2. Materials and Methods

The rainwater chemistry study was carried out during the rainy and dry seasons from 1993 to 1995.

2.1. Sampling Site

Sampling was performed in Xalapa, Veracruz, at the eastern flanks of the Sierra Madre Oriental facing the coastal prairies of the Gulf of Mexico at 19.5°N latitude and 96.9°W longitude (Figure 1a). The city is located between 1350 and 1550 meters above sea level (masl) and has an average altitude of 1427 masl. Because of its latitude, Xalapa is in the tropical region but with a high-altitude modified tropical climate classified as (A)Cb(fm))w″(i′)g that stands for a moderate climate with rains throughout the year but concentrated in the summer with an annual precipitation of 1454 mm. A relatively dry period

occurs within the rainy season; this period is referred to as the midsummer drought. The summer is long and fresh. The annual temperature oscillation is small (<7°C). The annual temperature variation corresponds to the Ganges type; that is, the highest temperature occurs just before the beginning of the rainy season, which begins before the summer solstice [*García*, 1964]. Two types of air masses dominate the region: the tropical maritime air mass that prevails during the rainy months and the continental polar air mass that prevails during the dry months; however, there are transition periods with alternancy of both air masses between the dry and wet periods.

Cold fronts that affect the Gulf of Mexico originate in southwest Canada or the northwest United States. They advance to the southeast, crossing the United States before entering the Gulf of Mexico. When a cold front reaches the Mexican coasts, it is known in the country as "norte" (north). Commonly, a cold front can sweep the coastal plains in less than 14 hours [*Klaus*, 1973]. Cold fronts reach regions as far south as Central America sometimes; however, their low humidity and temperature are modified as cold air flows over the Gulf of Mexico's warm waters.

According to *Frank* [1969], easterly waves originate over western Africa and travel within the trade winds entering the Caribbean Sea. These systems weaken when they pass over land; however, it is not uncommon that easterly waves cross Central America to the Pacific Ocean. Whereas cold fronts trajectories are meridional over continental regions, the easterly waves are zonal over the sea.

2.2. Sample Collection

Rainwater was collected by events at a suburban area in the east of Xalapa, on the roof of a private house 3 masl, using a polyethylene funnel 24 cm in diameter draining into a 3 L polyethylene bottle. The top of the funnel was placed 1.50 m above roof level to prevent contamination from splashing. Funnel and bottles were rinsed thoroughly with deionized water before exposure. The funnel was covered between rain events, and the collector was rinsed with deionized water and kept covered between events. Generally, rain started in the afternoon; the funnel was uncovered as soon as the rain started. The collector remained open during rainy nights until early morning. Specific conductance (SC) of the final rinse water was 0.081 μS cm^{-1} for bottles and 0.12 μS cm^{-1} for funnels, while the SC for deionized water was 0.055 μS cm^{-1}. After collection, bottles were sealed with polyethylene caps, and refrigerated at 4°C until they were sent to the Atmospheric Sciences Center Laboratories for chemical analysis. The transit from the field site to the laboratory took an average of 6 hours; the chemical analysis was performed within the next 24 hours.

2.3. Chemical Analysis

The samples were analyzed for SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, and H^+. For chemical analysis, samples were filtered through a 0.45 μm membrane Millipore filter leached with deionized water before chemical analysis. The *p*H was measured without stirring, using a Philips Model PW 9409 digital *p*H meter equipped with a combination glass electrode calibrated with standard buffer solutions at *p*H 4 and 7, within 24 hours of the arrival of the samples at the laboratory. Solid KCl was added to correct the low ionic strength [*Hansen and Hidy*, 1982]. Conductance was measured using a YSI model 34 conductance-resistance meter. Chloride, SO_4^{2-}, NO_3^-, and NH_4^+ were analyzed by ion chromatography, with a Perkin Elmer instrument equipped with an Isocratic LC Pump 250 and a Conductivity Detector LDC Analytical conductoMonitor III. The detection limits, in mg L^{-1}, for the anions were as follows: Cl^-, 0.04; NO_3^-, 0.09; and SO_4^{2-}, 0.22. *Munger et al.* [1990] used a Dionex instrument, whose detection limits, also in mg L^{-1}, were Cl^-, 0.22; NO_3^-, 0.17; and SO_4^{2-}, 0.12. The detection limit for NH_4^+ was 0.07 mg L^{-1}. Sodium, K^+, Ca^{2+} and Mg^{2+} were determined by atomic absorption spectrophotometry.

3. Results and Discussion

In the rainy season (May–October), Veracruz is under the influence of trade winds the ascendant motion in the mountainous region of which produces intense rains that mainly occur during afternoon and evening hours. Easterly waves are associated with trade winds from the Atlantic Ocean that produce heavy rains for 3 or 4 days (Figure 1b). Easterly waves are undulate flow lines embedded in the trade winds. On the basis of the wave axis the associated weather with this synoptic condition is as follows: to the west, winds blow from the east-northeast more or less uniformly, and the sky is generally clear with the exception of some isolated cloud banks or small cumulus. As the wave axis advances, the formation of clouds is expedited forming cumulus and cumulonimbus clouds that produce intermittent heavy rains and sometimes storms. Theoretically, this process occurs when the wave axis is passing. Actually, it is observed slightly behind the wave axis. The dominant wind direction is from the southeast with speeds <25 km h^{-1}. Although this synoptic condition can be present during the entire rainy season, in the Gulf of Mexico its maximum frequency occurs in August and September. During this synoptic condition, depressions, tropical storms, and hurricanes can occur [*Tejeda et al.*, 1989]. The rains in the rainy season account for ~79% (1454 mm yearly average) of the annual precipitation. The precipitation is mainly due to cumulonimbus type clouds. In the dry season (November–April), only 21% of the annual precipitation occurs. During both seasons, mountain-valley breezes are frequent. In the dry season, anticyclones produce stagnant conditions. However, this meteorological condition disappears during the frequent outbreaks of cold fronts in the Gulf of Mexico (Figure 1c) that influence greatly the meteorological conditions in Veracruz, including Xalapa. Cold fronts in the Gulf of Mexico commonly produce light rains and/or drizzle for 1–3 days. On the basis of the front line, marked by triangles that indicate the direction of its motion, the associated weather is as follows: when this synoptic condition occurs at the beginning of the dry season, cold air forces maritime air upward producing cumulonimbus clouds with large vertical development. Behind the front, stratiform clouds produce light rains and/or drizzle. These clouds extend from ground level to ~400 m in the Sierra Madre Oriental. This synoptic condition occurs during all the dry season. Under these meteorological conditions the dominant wind is from the north-northwest with gusts up to 70 km h^{-1} in Xalapa and more than 90 km h^{-1} in the coast [*Llanos and Cervantes*, 1996].

The overall data showed that most of the distributions of concentrations in precipitation were approximately lognormal. This type of distribution has been observed at other sites [*Munn and Rodhe*, 1971; *Singh et al.*, 1987; *Colin et al.*, 1989; *Pio et al.*, 1991].

Figure 2a shows the volume-weighted means (VWM) and standard deviations of the VWM (SDVWM) for the most

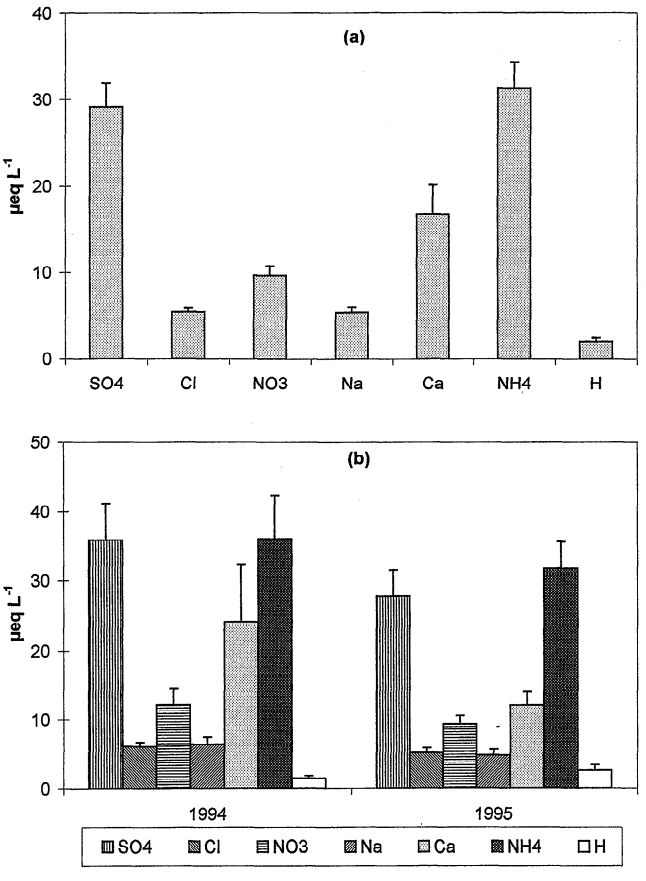

Figure 2. (a) Volume-weighted means (VWM) and standard deviations of the VWM (SDVWM) (lines on the bars) for the most important parameters of the entire wet precipitation data obtained from 1993 to 1995. (b) Same as Figure 2a, except from 1994 to 1995.

important parameters of the entire wet precipitation data obtained from 1993 to 1995. Figure 2b shows the 1994 and 1995 results of wet precipitation. Values for the 1993 dry season are not included because they were not available. Table 1 shows the VWM and SDVWM of the remaining analyzed parameters. The standard deviation of the VWM was calculated by using the formula of *Galloway et al.* [1984]. In Figure 2a it is observed that ammonium was the most abundant ion followed in order by $SO_4^{2-} > HCO_3^- > Ca^{2+} > NO_3^- > Cl^- > Mg^{2+} > K^+ > H^+$. Sea-salt contributions (ss) of $SO_{4\,ss}^{2-}$ and Ca_{ss}^{2+} were subtracted [*Lazrus et al.*, 1970; *Keene et al.*, 1986]. However, the contributions of $SO_{4\,ss}^{-2}$ and Ca_{ss}^{+2} were very small, from <1% to 2.5%, with only a few values ranging from 3% to 9%, compared with nss (non–sea-salt) contributions.

Generally, the overall H^+ volume-weighted mean was very small, varying from 63.10 to 0.15 μeq L^{-1} with a mean of 1.95 μeq L^{-1} (pH = 5.71), around the neutrality of rainwater. This seems to indicate neutralizing processes due mainly to ammonium. However, maximum measured values of H^+ are 2.29 μeq L^{-1} for 1993, 12.3 μeq L^{-1} for 1994, and 63.1 μeq L^{-1} for 1995. The 3 year maximum H^+ average value of 25.8 μeq L^{-1}, which corresponds to a pH of 4.2, is distinctly less acidic than the overall volume-weighted pH of 3.94 reported for eastern France [*Colin et al.*, 1989] but slightly more acidic than the average pH levels (5.3) measured at Coimbra, a town located in the center north of Portugal [*Pio et al.*, 1991]. In a previous study at Mexico City [*Báez et al.*, 1997], during the period from 1991 to 1993, the volume-weighted mean was 22.29 μeq L^{-1} equivalent to a pH of 4.65, which is more acidic than the rainwater collected in Xalapa. Annual weighted means of pH values reported by the National Atmospheric Deposition Program (NADP) were measured at the Beeville station in southern Texas, with values corresponding to 1994 and 1995 of 4.82 and 5.01, respectively, being more acidic than those obtained in Xalapa (5.82 and 5.59 for 1994 and 1995, respectively).

Figures 3a and 3c show the VWM and the SDVWM of the ionic concentrations during the rainy season collected from 1993 to 1995 (entire data) and for 1993, 1994, and 1995, respectively. Figures 3b and 3d show the same parameters for the values obtained during the dry season collected in 1994 and 1995 (entire data) and for 1994 and 1995, respectively. From Figures 3c and 3d it is observed that higher ionic concentrations were measured in rain samples collected during the dry season, as was expected. The high concentrations of all chemicals at low precipitation rates are probably due to the minimum dilution of available atmospheric materials [*Raynor and Hayes*, 1982]. It is generally known that ionic concentrations tend to become lower as rainfall increases [*Asman et al.*, 1981].

Since some ions do not have a lognormal distribution, nonparametric tests were applied. To determine whether there are significant differences between the chemical composition of the wet precipitation of the rainy and dry seasons (1993–1995),

Table 1. Volume-Weighted Means (VWM) and Standard Deviations of the VWM (SDVWM) of the Wet Precipitation Collected at Xalapa, Veracruz, Mexico, 1993–1995

Period	Number of Samples	Year	HCO_3^-	K^+	Mg^{2+}	SC, μS cm^{-1}	IB, %
Three years	149	1993–1995	19.77 (3.45)	1.91 (0.44)	2.41 (0.30)	9.54 (0.87)	−3.46
Annual	58	1994	25.67 (8.48)	2.86 (1.11)	3.20 (0.59)	5.95 (0.76)	−3.63
Annual	67	1995	15.35 (2.40)	1.40 (0.25)	2.06 (0.38)	5.95 (0.89)	−2.58
RS	104	1993–1995	19.57 (4.10)	1.57 (0.52)	1.92 (0.30)	8.30 (0.98)	−4.36
RS	24	1993	19.04 (3.46)	1.12 (0.36)	1.48 (0.25)	7.38 (1.15)	−6.59
RS	32	1994	26.35 (11.74)	2.63 (1.54)	2.87 (0.80)	9.80 (2.57)	−2.94
RS	48	1995	15.30 (2.66)	1.02 (0.22)	1.46 (0.27)	7.65 (0.90)	−5.08
DS	45	1994–1995	20.66 (3.57)	3.43 (0.65)	4.56 (0.86)	15.05 (1.83)	−1.34
DS	26	1994	24.02 (5.13)	3.40 (0.80)	3.99 (0.55)	13.70 (1.41)	−4.88
DS	19	1995	15.63 (4.33)	3.47 (1.12)	5.40 (2.02)	17.06 (4.11)	3.07

The VWM and SDVWM (in parentheses) are measured in μeq L^{-1}. The variables are defined as follows: SC, specific conductance; IB, ion balance [after *Peden et al.*, 1986]; RS, rainy season; and DS, dry season.

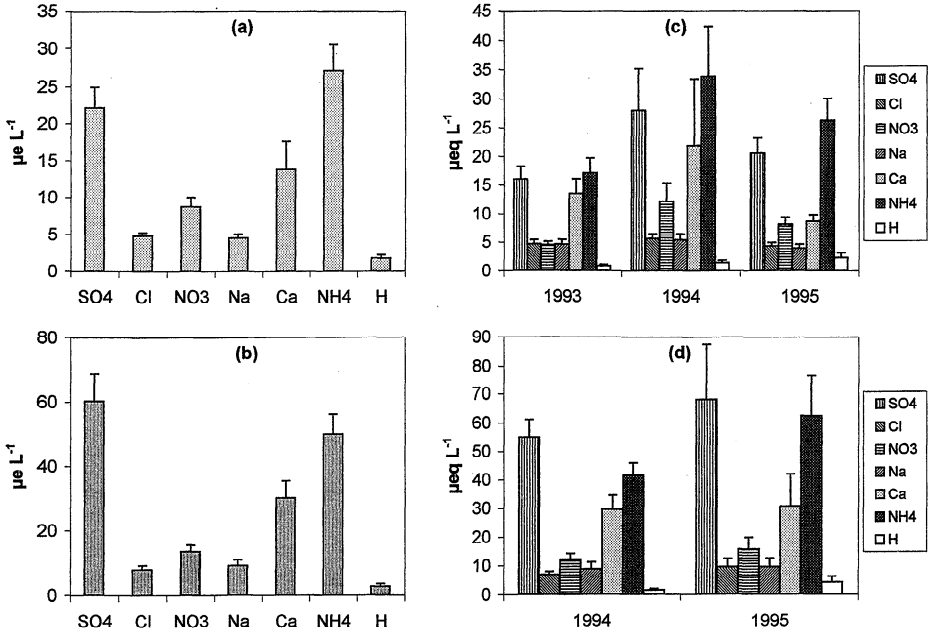

Figure 3. VWM and SDVWM of wet precipitation during (a) the rainy season, collected from 1993 to 1995 (entire data); (b) the dry season, collected from 1994 to 1995; (c) the rainy season, showing 1993, 1994, and 1995 separately; and (d) the dry season, showing 1994 and 1995 separately.

the Wilcoxon-Mann-Whitney large-sample normal approximation test with continuity correction [*Sprent*, 1989] was used (Table 2). Table 2 shows that there were significant differences at the 5% level in a two-tailed test between both sampling seasons. The difference in concentrations found between the rainy and dry seasons could be attributed to dilution phenomena (see above) since 79% of the annual precipitation occurs during the rainy season. On the other hand, the contribution of $SO_4^{2-}{}_{ss}$ and Ca_{ss}^{2+} is very small. Therefore the enrichment of SO_4^{2-}, NH_4^+, and NO_3^- observed in the rainy season is due to the transport of upwind medium and long-distance emissions of Veracruz's oil refineries, petrochemical complexes, and industrial zones by winds, as was observed in other regions [*Raynor and Hayes*, 1982; *Singh et al.*, 1987; *Colin et al.*, 1989]. This is supported by the predominant winds from the southeast observed during this season. During the dry season the predominant wind direction is from the north-northwest, passing over the oil refineries and petrochemical complexes of Tampico, Madero, and Poza Rica and south-southeastern Texas. Thus, in agreement with previous studies, SO_4^{2-} seems to trace the passage of air masses over industrial regions at medium and long distances from the receptor site. Nitrates play an important role since their precursors are produced mainly by anthropogenic sources [*Colin et al.*, 1989; *Lee*, 1993]. However, most of the pollution observed in rainwater collected in Xalapa seems to originate between southern Texas and Xalapa, as data from the NADP strongly suggest. A station situated at Beeville, Texas, which is situated closest to the border among the NADP stations in Texas, was selected. Annual VWM of sulfate concentration in rainwater at Beeville was lower than in rainwater in Xalapa (Table 3), especially in the winter (Beeville, Texas, 35.0 and 40.9 μeq L^{-1} for 1994 and 1995, respectively, and Xalapa, 55.1 and 68.2 μeq L^{-1} for 1994 and 1995, respectively). Although the dry season in Xalapa is approximately from October to April, it is interesting to compare sulfate concentrations observed in this season with those observed at Beeville in the winter, which at least lies within the dry period in Xalapa (the NADP considered the period from the end of November to the beginning of March as winter). This means that air coming from Texas was relatively clean. Therefore the cold air masses that moved southward over pollution sources in Tamaulipas and Veracruz must have "picked up" air pollutants during the passage of cold fronts. The effect of this process was more important than that of the

Table 2. Comparison of Two Samples (Rainy and Dry Seasons) Using the Wilcoxon-Mann-Whitney Test (a Large-Sample Normal Approximation) in Wet Precipitation Collected at Xalapa, Veracruz, Mexico (1993–1995)

Parameter	SO_4^{2-}	Cl^-	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	H^+
Z	5.92*	1.48	2.53*	1.54	4.15*	3.64*	3.99*	4.02*	−0.17
Average rank of rainy season (104 values)	61.22	71.56	69.11	71.40	65.36	66.52	65.72	65.63	75.40
Average rank of dry season (45 values)	106.84	82.95	88.61	83.31	97.27	94.60	96.45	96.64	74.07

*Significant at the 5% level in a two-tailed test.

Table 3. Comparison of VWM (in μeq L^{-1}) for Annual, Dry, and Winter Seasons Between Xalapa, Veracruz, and Beeville, Texas, During 1994 and 1995

Site	Period	Year	SO_4^{2-}	Cl^-	NO_3^-	NH_4^+
Xalapa, Veracruz	annual	1994	35.88	6.06	12.17	36.08
Beeville, Texas	annual	1994	28.58	24.20	14.18	16.58
Xalapa, Veracruz	dry	1994	55.09	6.92	12.18	41.62
Beeville, Texas	winter	1994	35.06	29.25	15.63	17.13
Xalapa, Veracruz	annual	1995	27.80	5.15	9.28	31.77
Beeville, Texas	annual	1995	25.37	28.92	13.48	17.57
Xalapa, Veracruz	dry	1995	68.18	9.61	15.72	62.61
Beeville, Texas	winter	1995	40.89	35.66	22.76	20.40

dilution of air pollutants from Texas when air masses move southward. Ammonium concentrations presented a larger difference than sulfate between Xalapa and Beeville, meaning that ammonium sources are also important.

In conclusion, the comparison of southern Texas and Xalapa rainwater chemistry for the winter (dry season) allows us to conclude that the main pollution sources are situated to the north of Xalapa, not far away from this city. On the other hand, since in the summer, sulfate and ammonium concentrations in rainwater are also higher in Xalapa than in southern Texas, the pollution sources to the southeast of Xalapa are more important than those of southern Texas. It is also interesting to note that the annual volume-weighted mean NO_3^- concentration was consistently higher in rainwater collected at Beeville than in rainwater collected at Xalapa (Table 3); this could be due to the fact that the vehicle traffic is more intense in Texas.

It is also important to consider that rainwater in southern Texas presents a much more pronounced marine influence, as can be observed from the annual VWM of Cl^- concentrations (Table 3). Beeville is at 83 masl on a flat terrain, whereas Xalapa is between 1350 and 1550 masl with high mountains from northwest to south.

The Kruskal-Wallis test was applied to the 3 year data to find whether there were significant differences in the wet precipitation collected during these years (Table 4). The results indicate that the only significant differences at the 5% level corresponded to H^+ and NO_3^-. Although significant differences were only found in these two ions, some annual variations are observed among the most important ionic species. These variations may be due to the influence of various meteorological factors such as wind directions, air mass trajectories, rainfall rate, rainfall total amount, and cloud base height [*Asman et al.*, 1981]. Additionally, changes in air pollutant concentrations in the atmosphere are important in explaining the variability of rainwater chemical composition.

Table 4. Comparison of Three Samples (years 1993, 1994, and 1995) Using the Kruskal-Wallis Test in Wet Precipitation Collected at Xalapa, Veracruz, Mexico

Ion	*H* Statistic
SO_4^{2-}	1.1045
Cl^-	0.4236
NO_3^-	7.7424*
Na^+	1.3042
K^+	0.7570
Ca^{2+}	1.2286
Mg^{2+}	2.2373
NH_4^+	2.8772
H^+	8.3698*

Sample sizes are 24 in 1993, 32 in 1994, and 48 in 1995.
*Significant difference at the 5% level.

Figures 4a and 4b show the graphs of the time series of SO_4^{2-} and NH_4^+, respectively. Corresponding to the 1994 and 1995 rainy and dry seasons, these graphs show seasonal variations indicating a marked decrease in ionic concentration during the rainy season due mainly to dilution processes. The time series shown in Figures 4a and 4b are similar to those for the concentrations of the other ions.

Correlation coefficients were calculated by using the Spearman rank correlation procedure for the data obtained during the rainy and dry seasons (Tables 5 and 6). In these correlations, only $SO_{4\,nss}^{2-}$ and Ca_{nss}^{2+} were considered. These tables show that in the rainy and dry seasons, high and positive correlations were found among the most important chemical species, although a little better correlation was observed during the rainy season for sulfate ion pairs. A good but negative correlation among the rain amount (in millimeters) and most of the ions was also found. In most cases the concentrations of SO_4^{2-} and NO_3^- show significant correlations, indicating their relationship to common anthropogenic sources and transport processes rather than to chemical reactions between precursor

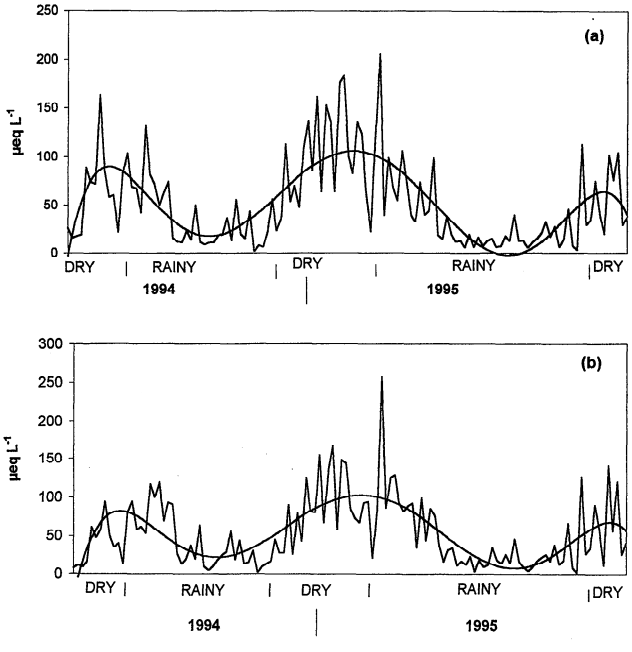

Figure 4. Graphs of the time series corresponding to 1994 and 1995 rainy and dry seasons. These graphs show seasonal variations indicating a marked decrease in ionic concentration during the rainy season.

Table 5. Spearman Rank Correlations Between Some Ion Concentrations at Xalapa, Veracruz, Mexico, for the Rainy Season 1993–1995

	SO_4^{2-}	Cl^-	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	H^+
Cl^-	0.674*								
NO_3^-	0.886*	0.730*							
Na^+	0.661*	0.968*	0.704*						
K^+	0.803*	0.773*	0.774*	0.812*					
Ca^{2+}	0.703*	0.694*	0.619*	0.707*	0.765*				
Mg^{2+}	0.772*	0.906*	0.806*	0.901*	0.834*	0.815*			
NH_4^+	0.929*	0.653*	0.889*	0.647*	0.800*	0.596*	0.726*		
H^+	0.029	−0.156	0.071	−0.216	−0.191	−0.425*	−0.177	−0.013	
millimeters	−0.549*	−0.601*	−0.450*	−0.607*	−0.573*	−0.677*	−0.559*	−0.480*	0.318*

*Significant at $p \leq 0.01$.

species [*Lee*, 1993]. The sea-salt contribution of sulfates is very small, from 9% to <1%. Nitrates originate from the oxidation of NO_x (products of fuel combustion and vehicle exhaust) and from the formation of nitric acid and its salts. Because nitrates do not have a marine component, it is believed that their sources are anthropogenic and continental [*Colin et al.*, 1989]. On the other hand, SO_4^{2-} and NO_3^- are positively well correlated with NH_4^+, indicating the existence of $(NH_4)_2SO_4$ and NH_4NO_3 compounds in rain [*Pio et al.*, 1991]. The high correlation between Cl^- and Na^+ suggests a marine origin since Cl^- is typically marine. However, there is a slight anthropogenic and continental enrichment [*Colin et al.*, 1989].

If Xalapa is considered an agricultural zone surrounded by mountain forests, then the origin of ammonium seems to be a product of agricultural practices, forest and soil decay, and petrochemical industrial emissions. Calcium content in Xalapa rainwater is mainly of crustal origin because the sea-salt contribution is also negligible.

Table 7 shows the annual ionic loading (g m^{-2}) corresponding to the years 1993–1995. As was expected, SO_4^{2-}, NO_3^-, and NH_4^+ deposition was higher than deposition of the other chemicals. Wet deposition rates are more meaningful than measurements of concentrations because of the impact on ground surface and vegetation [*Raynor and Hayes*, 1982]. It is noteworthy that the contribution of the acidity due to H^+ is negligible. Table 7 also shows that there are differences in the amount of deposition of ionic species between the years and between the seasons. It is observed that in spite of the ionic concentration dilution during the rainy season the deposition was higher than that observed in the dry season.

4. Summary and Conclusions

In this paper the results of a 3 year study of the chemistry of rainwater related to meteorological factors at a single site in Xalapa, located at the eastern flanks of the Sierra Madre Oriental, Veracruz, are reported. The dry and rainy seasons were selected because of the well-marked different meteorological conditions that prevail between them. To find whether there were significant differences in the chemical composition of rainwater between both seasons, the Wilcoxon-Mann-Whitney test was applied to the entire data collected during the 3 years. The test indicated that the significant differences corresponded to the most important chemical species. These differences are attributed to dilution processes since 79% of the annual precipitation occurs in the rainy season. It was also found that the contributions of $SO_{4\,ss}^{2-}$ and Ca_{ss}^{2+} were negligible. So, an enrichment of SO_4^{2-}, NO_3^-, and NH_4^+ is due to upwind medium distance and long-distance emissions from industries located along the wind trajectories in both seasons. On the other hand, the Kruskal-Wallis test was applied to wet precipitation collected during the 3 year period. This test indicated that only significant differences at the 5% level corresponded to H^+ and NO_3^-, although some variations were observed among the most important ionic species. High and positive correlations were found among the most important ionic species. However, poor and negative correlations between SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, and Mg^{2+} and millimeters of precipitation were observed. These correlations seem to indicate common sources, but significant associations between variables must be interpreted with care. Finally, as was ex-

Table 6. Spearman Rank Correlations Between Some Ion Concentrations at Xalapa, Veracruz, Mexico, for Dry Season 1993–1995

	SO_4^{2-}	Cl^-	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	H^+
Cl^-	0.743*								
NO_3^-	0.904*	0.723*							
Na^+	0.593*	0.846*	0.557*						
K^+	0.760*	0.768*	0.741*	0.811*					
Ca^{2+}	0.743*	0.711*	0.726*	0.545*	0.730*				
Mg^{2+}	0.760*	0.870*	0.706*	0.755*	0.774*	0.869*			
NH_4^+	0.925*	0.752*	0.888*	0.590*	0.735*	0.633*	0.650*		
H^+	0.054	−0.172	0.005	−0.127	−0.212	−0.306	−0.205	0.005	
millimeter	−0.512*	−0.519*	−0.435*	−0.321	−0.350	−0.396*	−0.395*	−0.625*	0.295

*Significant at $p \leq 0.01$.

Table 7. Annual Loading (g m^{-2}) for Rainfall Collected at Xalapa, Veracruz, Mexico, 1993–1995

Year	SO_4^{2-}	Cl^-	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	H^+
Rainy season									
1993	0.26	0.06	0.09	0.04	0.01	0.09	0.01	0.10	0.0003
1994	0.85	0.13	0.48	0.08	0.06	0.28	0.02	0.38	0.0009
1995	0.95	0.15	0.48	0.09	0.04	0.17	0.02	0.45	0.0022
Dry season									
1994	0.69	0.06	0.20	0.05	0.03	0.15	0.01	0.19	0.0004
1995	0.57	0.06	0.17	0.04	0.02	0.11	0.01	0.20	0.0007

pected, a higher deposition of chemical compounds was found during the rainy season in spite of the dilution processes.

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