

## Variation of chemical composition of wet precipitation, using a sequential sampling: urban-rural areas comparison

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(Manuscript received July 13, 1992; accepted in final form Oct. 27, 1992)

### RESUMEN

En este estudio se describen los resultados obtenidos durante dos años originados por el muestreo secuencial de fracciones de lluvia en dos sitios: La Ciudad de México y una área rural. Los resultados indicaron que los constituyentes químicos, determinados en las muestras de lluvia colectadas secuencialmente, decrecieron en su concentración iónica en la porción primera del evento de lluvia, mientras que esta concentración se incrementó, decreció o aun no varió durante la última parte del evento.

La prueba no-paramétrica de Mann-Whitney-Wilcoxon fue aplicada a los datos mostrando claramente que hubo diferencias significativas entre estos dos lugares de muestreo. Este estudio también permitió inferir los mecanismos más importantes de lavado atmosférico que actúan en el evento de lluvia y el posible origen de los principales iones analizados.

### ABSTRACT

This study describes the results obtained during two years of sequential sampling of wet precipitation in two sites: Mexico City and a rural area. The results indicated that the chemical constituents determined in the sequentially collected samples, decreased in ionic concentration in the early portion of the rainfall event, while it increased, decreased or remained the same during the latter part of the event.

The non-parametric Mann-Whitney-Wilcoxon test when applied to data, clearly showed that there were significant differences between these two sampling sites. This study has also permitted to infer the most important scavenging mechanisms acting on the rainfall event and the possible origin of the major ions analyzed.

### Introduction

The chemical composition of wet precipitation is mainly determined by three mechanisms: condensation of water vapor on condensation nuclei, capture of contaminants by cloud (rainout) and the scavenging processes below cloud (washout). The variability of chemical composition of rain depends in the type of precipitation. It is known that the intrastorm variability of precipitation chemistry can be large (Lim *et al.*, 1991). Also the concentration of chemical constituents in rain water is dependent upon the mass of captured particles and gases, the chemical transformation and the liquid content of precipitation. The most important of these features are: the inverse relationship between concentration and intensity of rainfall and a decrease in concentration during the initial stages of precipitation and an increase or even no variation during the final stages (Huff and Stout, 1964; Gatz and Dingle, 1971; Kins, 1982; Colin *et al.*, 1987). Observations

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made in rural areas from frontal and convective storms, using the sequential sampling indicates that this method reflects the different mechanism by which aerosol and gases are incorporated into wet precipitation. The below and within cloud scavenging processes have important effects upon the change of ionic concentration during a rainfall event (Lim *et al.*, 1991). The importance of the scavenging mechanism may differ between urban and rural regions.

This study describes the results obtained during two years of sequential sampling of wet precipitation at two sampling sites, the first a highly polluted urban area and the second a rural zone 80 km away from the city, but under its meteorological influence. This study has also allowed to infer the most important scavenging mechanism upon the precipitation events and the possible origin of the major ions analyzed.

## Methodology

### Sampling sites

The selected urban area was Mexico City, one of the most polluted cities of the world, with around 16 million inhabitants (INEGI, 1990) and around 3 million motor vehicles. More than 30,000 small, medium and large industries located in the valley emit into the atmosphere huge amounts of air pollutants.

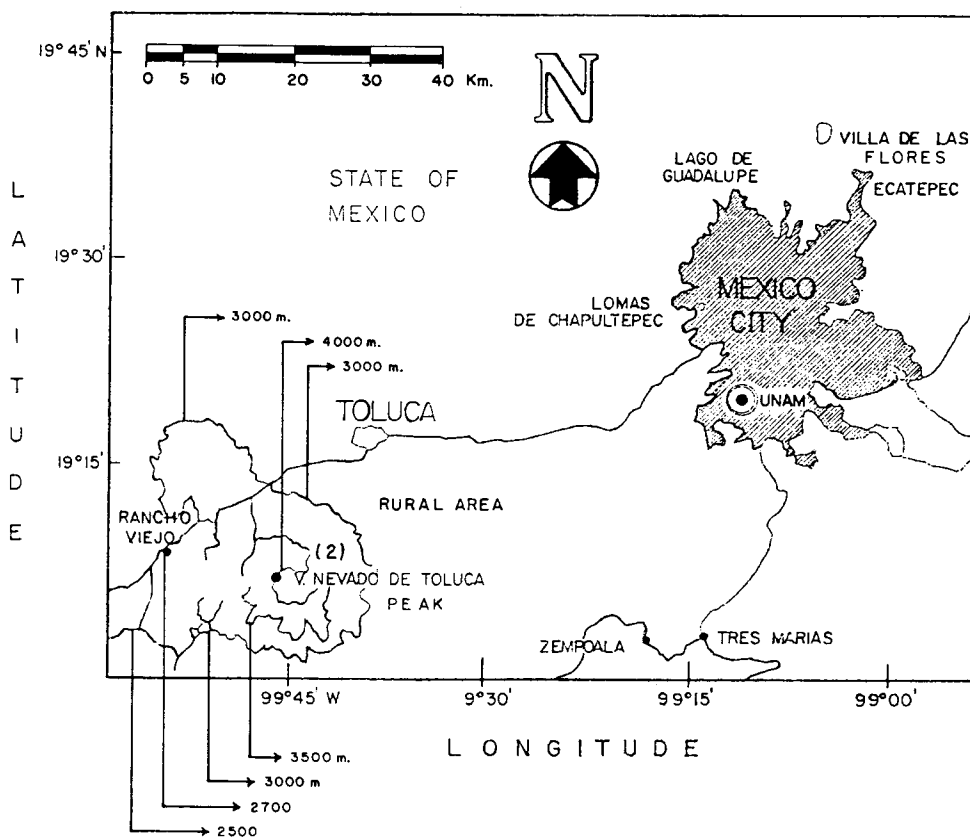


Fig. 1. Sampling stations at Mexico City, University of Mexico campus (UNAM) and Rancho Viejo, State of Mexico.

The City is 2250 m above sea level, with a mean annual temperature of 16.0 °C (Jáuregui, 1992) and a mean annual rainfall of 860 mm. The prevailing winds during the rainy season come from the southeast to northeast and usually the clouds are of the convective type. (Jáuregui, 1986).

The rural area is located around 80 km wsw from the City in a forest region of the state of Mexico at 2760 m above sea level. The place is named Rancho Viejo. During the rainy season, advective winds at 700-600 mb level (Servicio Meteorológico Nacional, 1992) transport part of the air pollutants emitted in the City to Rancho Viejo, according to the synoptic conditions that prevail during the summer, with a mean annual rainfall of 1440 mm. The sampling site locations are shown in Figure 1.

### *Sampling methodology*

Two mm rain fractions were collected through a 66 cm diameter funnel draining into 500 ml bottles. The funnel and the bottles were made out of polyethylene. The funnel was rinsed with deionized water prior to the rain event, the fraction collector was manually operated, as soon as the samples were collected, they were sent to the laboratory and kept under refrigeration at 4 °C. No chemical preservatives were added, since refrigeration hinders microbiological activity.

### *Chemical analysis*

Samples were analyzed for pH,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . Measurements of pH were made immediately at the end of the event using a Philips Model PW 9409 digital pH meter with a combination glass electrode calibrated against 4 and 7 pH buffers. The low ionic strength of rain samples was increased to 0.1 M by the addition of solid KCl (Hansen and Hidy, 1982). The concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were determined by flame atomic absorption spectrophotometry.

Concentrations of  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  were measured by the methods described in the Standard Methods (APHA, 1975).

Ammonium and nitrates were determined by the nessler and brucine methods respectively, and sulfates by turbidimetric method.

Whenever there was enough sample to perform duplicate analysis, the overall precision of data was assessed. Duplicate analysis showed precision withing 10% of mean values.

### **Results and discussion**

Ionic composition and the pH of each sequentially collected samples were measured at the two sampling sites. In Mexico City the pH of individual samples varied from 3.88 to 7.10 in 1986 and between 4.31 to 7.11 in 1987, whereas the variation observed in Rancho Viejo was from 4.05 to 5.40 in 1986 and from 4.46 to 5.40 in 1987. For data discussion pH was calculated as  $\text{H}^+$  concentration. From Figures 2a and 3a, it is observed that in Mexico City the  $\text{H}^+$  concentration increased during the early portion of the rainfall, while small decrease, increase or even no changes occurred during the latter portion of the rain event in 1986, but in 1987 a continuous increase occurred during the entire event.

The chemical constituents determined in the sequentially collected samples in Mexico City, varied in an opposite way to that of the  $\text{H}^+$ . A rapid decrease in ionic concentration occurred

in the early portion of the rainfall, while it increase, decrease or remained the same during the latter part of the event. Diagrams for the 53 rainfall events representing 214 fractions collected in Mexico City are given in Figures 2a to 2f and 3a to 3f. Each fraction representing the average of all individual fractions collected.

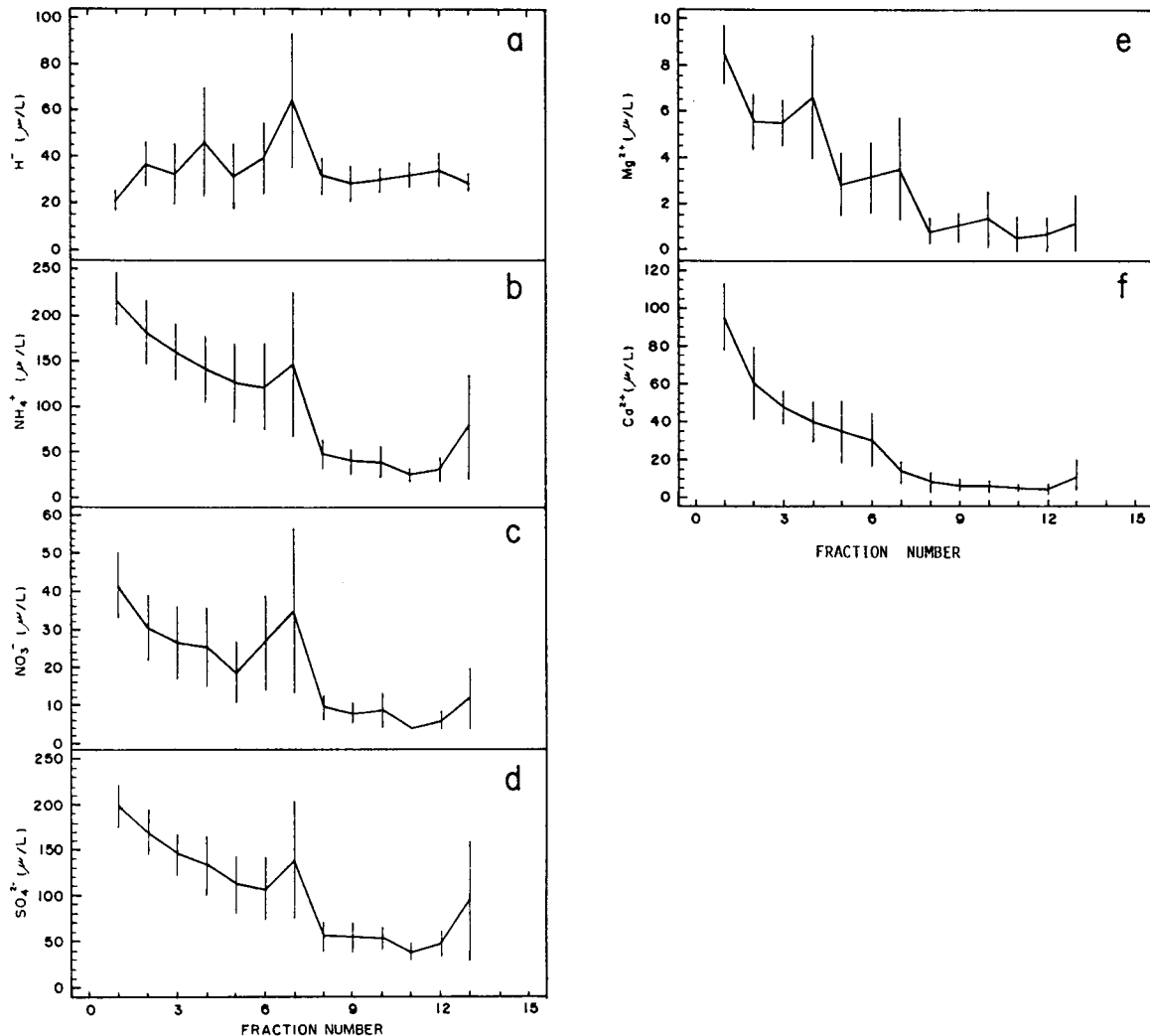


Fig. 2. Scatter plots of average concentrations with standard error bars of (a)  $\text{H}^+$ , (b)  $\text{NH}_4^+$ , (c)  $\text{NO}_3^-$ , (d)  $\text{SO}_4^{2-}$ , (e)  $\text{Mg}^{2+}$ , and (f)  $\text{Ca}^{2+}$ , from rain samples collected at Mexico City in 1986.

Concentrations of chemical constituents in rain water are dependent upon the mass of captured particles and gases, the chemical transformations and the liquid water content of precipitation.

Scavenging processes controlling wet precipitation are determined by the properties of the particulated matter, gas solubility and type of precipitation. These scavenging processes are probably reflected by the changing concentration of the ionic components in rain water measured in this sequential sampling. (Lim *et al.*, 1991). For all the events shown in Figures 2 and 3, the total ion concentration in rain was decreasing; this could be the effect of washout of particulated

material, mainly large soil derived particles which are more rapidly depleted at the early stages of the rainfall (Tanaka *et al.*, 1980). The low concentration of  $H^+$  in the initial fraction of the rain event may be due to neutralization of some strong acids present in wet precipitation by atmospheric alkaline particles, that neutralization would be most effective near the ground (Kasina, 1980).

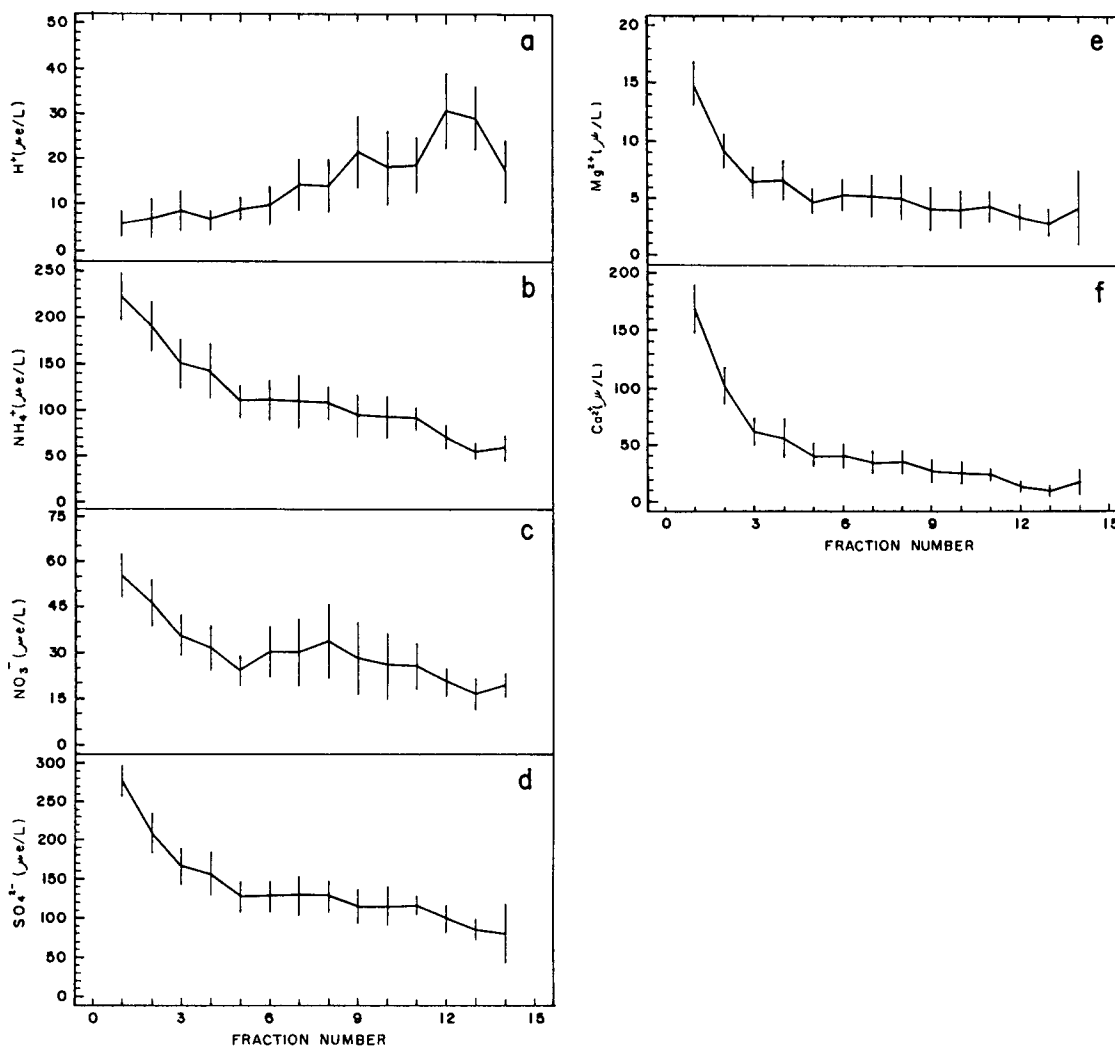


Fig. 3. Scatter plots of average concentrations with standard error bars of (a)  $H^+$ , (b)  $NH_4^+$ , (c)  $NO_3^-$ , (d)  $SO_4^{2-}$ , (e)  $Mg^{2+}$  and (f)  $Ca^{2+}$ , from rain samples collected at Mexico City in 1987.

A decrease in concentration of constituents during a rainfall has also been observed by other researchers working in the sequential sampling of convective precipitation, in continental regimen (Seymour and Stout, 1983; Lim *et al.*, 1991). This behavior has been attributed to several possible effects: within cloud scavenging, dilution with cloud droplet growth, below cloud scavenging, evaporation and evaporation followed by accumulation of aerosol particle aloft and precipitation of these accumulated particles (Lim *et al.*, 1991). Also the dissolution of gases in cloud water is expected to take place concurrently with cloud formation (Warneck, 1986). Most

of the rain events in Mexico City are of convective precipitation type. The rapid decrement of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  during the early portion of the event seems to indicate that below cloud scavenging (washout) is the most important mechanism, while from the small variations observed in the latter portion of the rainfall it is possible to assume within cloud scavenging (rainout) as the predominant mechanism. The similar decrease of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  with those of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  would complement the apparent washout behavior observed in these events. The conjunction of the alkaline cations and the basic anions that were initially present, when they decreased in concentration, this decrease was followed by an increase in acidity of the rain, which was indeed the case observed in this study.

Thirty five rainfall events representing 105 fractions were collected in 1986 and 1987 in Rancho Viejo. Although fewer number of rain samples were collected there, the concentration variations in  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$  and  $\text{H}^+$  were similar to those observed in samples from Mexico City. A rapid decrease in the concentrations of ions occurred in the early portion of the event, while

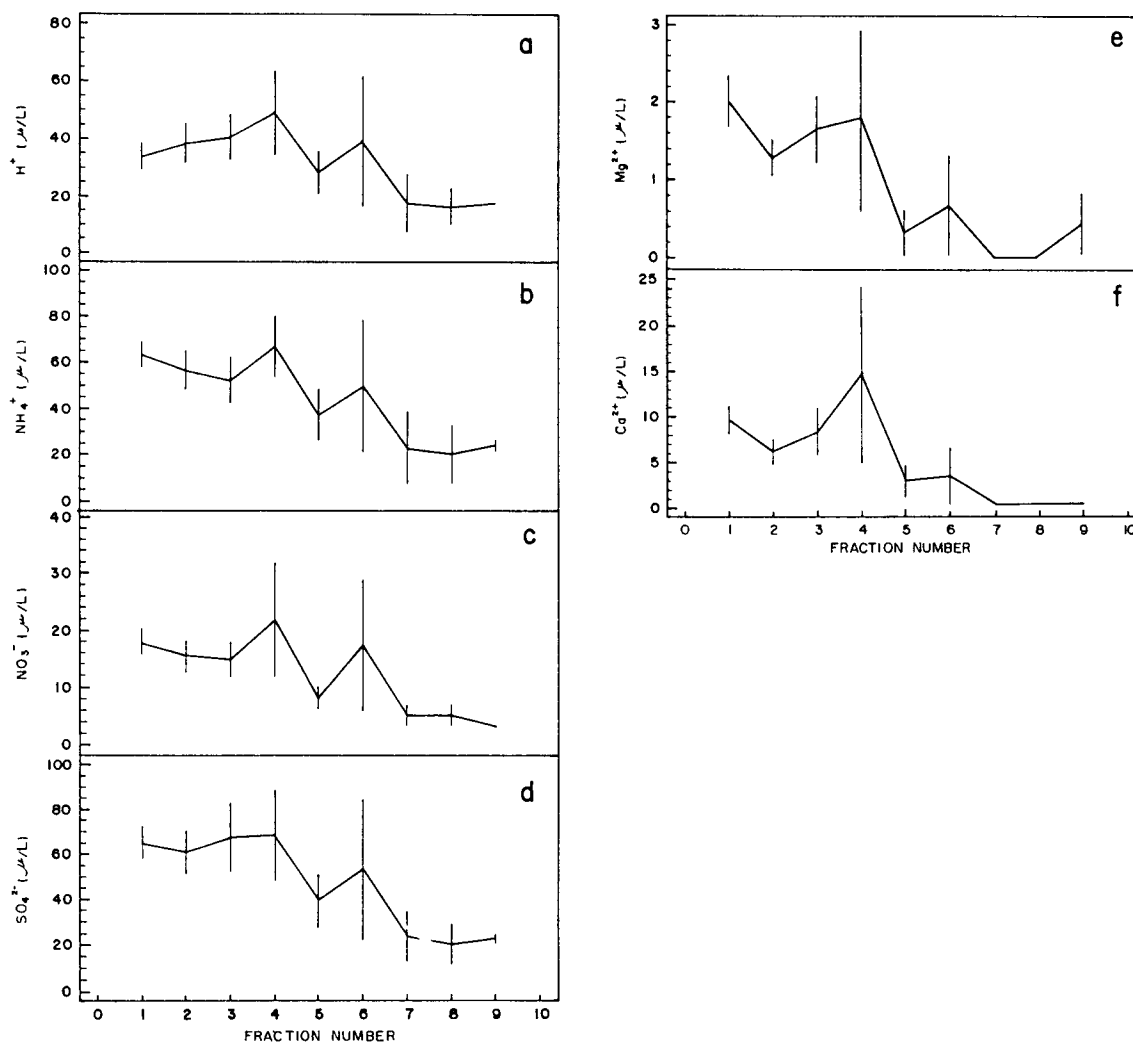


Fig. 4. Scatter plots of average concentrations with standard error bars of (a)  $\text{H}^+$ , (b)  $\text{NH}_4^+$ , (c)  $\text{NO}_3^-$ , (d)  $\text{SO}_4^{2-}$ , (e)  $\text{Mg}^{2+}$  and (f)  $\text{Ca}^{2+}$ , from rain samples collected at Rancho Viejo in 1986.

increased, decreased or remained about the same during the latter part of the rainfall event. Diagrams for the 35 rainfalls, corresponding to 105 fractions are given in Figures 4a to 4f and 5a to 5f. Again each fraction representing the average of individual fractions collected in both years. However for 1987 these variations were much more irregular.

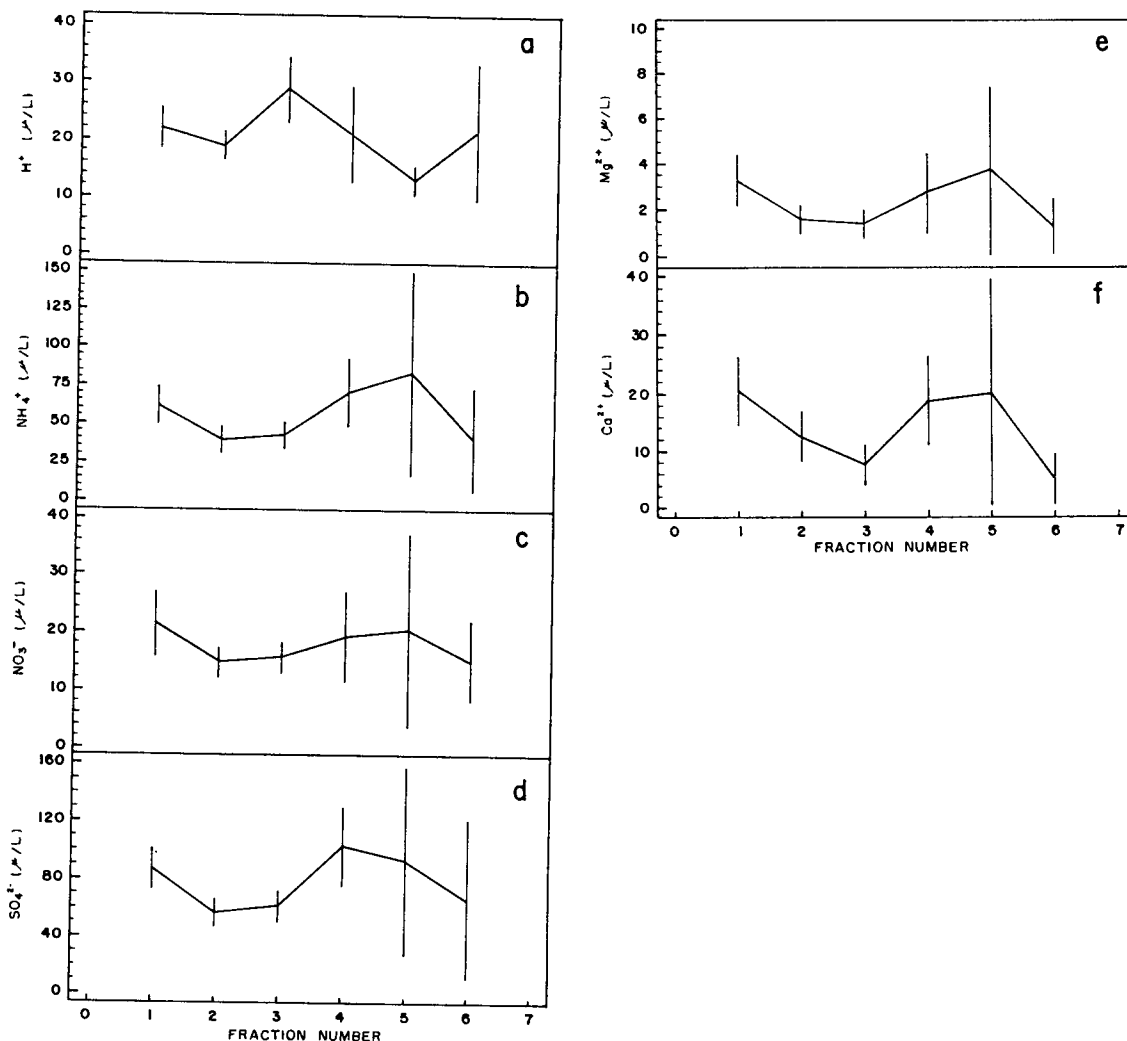


Fig. 5. Scatter plots of average concentrations with standard error bars of (a)  $\text{H}^+$ , (b)  $\text{NH}_4^+$ , (c)  $\text{NO}_3^-$ , (d)  $\text{SO}_4^{2-}$ , (e)  $\text{Mg}^{2+}$  and (f)  $\text{Ca}^{2+}$ , from rain samples collected at Rancho Viejo in 1987.

Although a rapid decrease was observed from the first to the third fractions a rapid decrease or increase were observed in the subsequent fractions. The greater fluctuations in the ion concentrations that occurred in 1987 in Rancho Viejo may be explained by the following fact:

The rain events occurred intermittently, and usually the rain collector, which was manually operated was open to the air during enough time to permit the arrival of different mass clouds of advective origin, from Mexico and Toluca cities, with different concentration of air pollutants and rained out in Rancho Viejo. The higher concentration of  $\text{H}^+$  found in this area suggests that the alkaline inputs of airborne  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are lower than in the city and less neutralization can occur.

In order to determine if there were significant differences between the ionic concentration in rain water collected in Mexico City and Rancho Viejo, the non-parametric Mann-Whitney-Wilcoxon test was applied to data (Sprent, 1989). Table I shows the results of this statistical test, which clearly indicates that there were significant differences between these two sampling sites. The variation in ionic concentration possibly includes differences in below cloud air masses and within cloud air pollutants, in the meteorological conditions and atmospheric chemistry between rain events and between locations (Liljestrand 1979; Pratt *et al.*, 1983). The study of chemical composition of wet precipitation is complicated by the effect of local pollution, particularly in a highly polluted atmosphere as Mexico City has, Báez and Belmont (1987) found that the polluted atmosphere of Mexico City has an important influence upon the chemistry of rain.

Tables II and III show the correlation coefficients among major cations and anions present in the fractions within rain events. Different correlation values were found between the two years and the two sampling sites.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  correlated well but negatively with  $\text{H}^+$  in samples from Mexico City in 1987, but in 1986 only  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  correlated well with  $\text{H}^+$ .

Positive and significant correlation between the major anions and cations was obtained in both years at Mexico City and Rancho Viejo. This not necessarily means that all ions have a common origin, since  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  come mainly from soil dust and alkaline particle emissions. This fact is supported by the high correlation between these two cations, determined in rain water samples collected at both places.

With respect to Mexico City the high values of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  can be attributed to soil erosion, calcareous soils are predominant in this area, since these cations are common constituents of these soils, and to anthropogenic sources as industrial emissions of alkaline metals from cement, lime and ceramic plants, among others. The high and positive correlation between  $\text{NH}_4^+$  and  $\text{NO}_3^-$  (0.897,  $p = 0.01$ ) and with  $\text{SO}_4^{2-}$  (0.924,  $p = 0.01$ ) suggests anthropogenic contribution for these ions.

The high concentration of  $\text{NO}_3^-$  in precipitation has been attributed to increased combustion of fuel oil, natural gas and motor fuels (Tabatabai and Lafen, 1976), then in Mexico City motor vehicles and industrial fuel combustion may represent an important source of inorganic nitrogen, whereas the great  $\text{SO}_2$  emissions from coal and fuel oil industrial combustion may contribute for the high concentration of  $\text{SO}_4^{2-}$  measured in rain water from the city (Báez and Belmont, 1987).

TABLE I MANN-WHITNEY-WILCOXON TEST ( LARGE SAMPLE TEST STATISTIC Z )

	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{NH}_4^+$	$\text{H}^+$
1986	-6.54	-1.19 <sup>a</sup>	-7.20	-5.41	-6.47	2.70
1987	-7.25	-5.32	-7.08	-6.99	-7.50	5.32

<sup>a</sup>

The null hypothesis is accepted at two-tailed test at 5% significance level  $H_0$



TABLE II CORRELATION COEFFICIENTS ( r ) FOR 1986 AND 1987  
RAIN FRACTIONS ANALYZED IN MEXICO CITY

Relationship	1986	1987
	All fractions ( n = 123 )	All fractions ( n = 98 )
H <sup>+</sup> : NH <sub>4</sub> <sup>+</sup>	0.396 <sup>a</sup>	-0.177
H <sup>+</sup> : Ca <sup>2+</sup>	-0.064	-0.418 <sup>a</sup>
H <sup>+</sup> : Mg <sup>2+</sup>	0.029	-0.358 <sup>a</sup>
H <sup>+</sup> : NO <sub>3</sub> <sup>-</sup>	0.525 <sup>a</sup>	0.007
H <sup>+</sup> : SO <sub>4</sub> <sup>2-</sup>	0.382 <sup>a</sup>	-0.286 <sup>a</sup>
H <sup>+</sup> : Rain	-0.348 <sup>a</sup>	-0.274 <sup>a</sup>
NH <sub>4</sub> <sup>+</sup> : NO <sub>3</sub> <sup>-</sup>	0.897 <sup>a</sup>	0.888 <sup>a</sup>
NH <sub>4</sub> <sup>+</sup> : SO <sub>4</sub> <sup>2-</sup>	0.924 <sup>a</sup>	0.904 <sup>a</sup>
NH <sub>4</sub> <sup>+</sup> : Rain	-0.087	-0.226 <sup>b</sup>
Ca <sup>2+</sup> : NO <sub>3</sub> <sup>-</sup>	0.635 <sup>a</sup>	0.599 <sup>a</sup>
Ca <sup>2+</sup> : SO <sub>4</sub> <sup>2-</sup>	0.750 <sup>a</sup>	0.822 <sup>a</sup>
Ca <sup>2+</sup> : Rain	0.032	-0.192
Mg <sup>2+</sup> : NO <sub>3</sub> <sup>-</sup>	0.592 <sup>a</sup>	0.646 <sup>a</sup>
Mg <sup>2+</sup> : SO <sub>4</sub> <sup>2-</sup>	0.681 <sup>a</sup>	0.855 <sup>a</sup>
Mg <sup>2+</sup> : Rain	-0.140	-0.114
NO <sub>3</sub> <sup>-</sup> : Rain	-0.135	-0.195
SO <sub>4</sub> <sup>2-</sup> : Rain	-0.137	-0.179
Ca <sup>2+</sup> : Mg <sup>2+</sup>	0.806 <sup>a</sup>	0.825 <sup>a</sup>

<sup>a</sup> p = 0.01

<sup>b</sup> p = 0.05

The chemical reactions of NO<sub>x</sub> and SO<sub>2</sub> in the atmosphere are producing HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, then NH<sub>4</sub><sup>+</sup> may be formed by the neutralization of these acids contributing to the levels of NH<sub>4</sub><sup>+</sup> found in rain water samples collected at both places. However the natural origin of NH<sub>4</sub><sup>+</sup> may be also an important source for this ion in Rancho Viejo.

The significant differences in ionic concentration found at both sampling places, is supported by the Mann-Whitney-Wilcoxon test (Table I). With the exception of H<sup>+</sup>, the concentration of the major analyzed ions were higher in rain samples from Mexico City than those from Rancho Viejo (Figs. 2 to 5) whose ratios between the two sampling sites were: NH<sub>4</sub><sup>+</sup> = 2.9, Ca<sup>2+</sup> = 8.0, Mg<sup>2+</sup> = 4.0, NO<sub>3</sub><sup>-</sup> = 1.8 and SO<sub>4</sub><sup>2-</sup> = 2.5. From these ratios it is observed the influence of the erosion of calcareous soils and the industrial alkaline particle emissions upon the concentration

TABLE III CORRELATION COEFFICIENTS ( *r* ) FOR 1986 AND 1987 RAIN FRACTIONS ANALYZED IN RANCHO VIEJO

Relationship	1986	1987
	All fractions ( n = 76 )	All fractions ( n = 47 )
H <sup>+</sup> : NH <sub>4</sub> <sup>+</sup>	0.697 <sup>a</sup>	0.011
H <sup>+</sup> : Ca <sup>2+</sup>	0.601 <sup>a</sup>	-0.184
H <sup>+</sup> : Mg <sup>2+</sup>	0.510 <sup>a</sup>	-0.171
H <sup>+</sup> : NO <sub>3</sub> <sup>-</sup>	0.770 <sup>a</sup>	0.026
H <sup>+</sup> : SO <sub>4</sub> <sup>2-</sup>	0.812 <sup>a</sup>	0.024
H <sup>+</sup> : RR	-0.395 <sup>a</sup>	-0.392 <sup>a</sup>
NH <sub>4</sub> <sup>+</sup> : NO <sub>3</sub> <sup>-</sup>	0.741 <sup>a</sup>	0.765 <sup>a</sup>
NH <sub>4</sub> <sup>+</sup> : SO <sub>4</sub> <sup>2-</sup>	0.856 <sup>a</sup>	0.951 <sup>a</sup>
NH <sub>4</sub> <sup>+</sup> : RR	-0.388 <sup>a</sup>	0.011
Ca <sup>2+</sup> : NO <sub>3</sub> <sup>-</sup>	0.833 <sup>a</sup>	0.798 <sup>a</sup>
Ca <sup>2+</sup> : SO <sub>4</sub> <sup>2-</sup>	0.783 <sup>a</sup>	0.882 <sup>a</sup>
Ca <sup>2+</sup> : RR	-0.550 <sup>a</sup>	0.057
Mg <sup>2+</sup> : NO <sub>3</sub> <sup>-</sup>	0.728 <sup>a</sup>	0.834 <sup>a</sup>
Mg <sup>2+</sup> : SO <sub>4</sub> <sup>2-</sup>	0.737 <sup>a</sup>	0.882 <sup>a</sup>
Mg <sup>2+</sup> : RR	-0.415 <sup>a</sup>	0.041
NO <sub>3</sub> <sup>-</sup> : RR	-0.545 <sup>a</sup>	-0.021
SO <sub>4</sub> <sup>2-</sup> : RR	-0.398 <sup>a</sup>	0.053
Ca <sup>2+</sup> : Mg <sup>2+</sup>	0.865 <sup>a</sup>	0.943 <sup>a</sup>

<sup>a</sup> p = 0.01

of these ions in wet precipitation. With respect to NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ratios, these were smaller than the ratios of Ca<sup>2+</sup> and Mg<sup>2+</sup>. These lower ratios probably are due to the transport of gaseous emissions of NO<sub>x</sub> and SO<sub>2</sub> from Mexico City and the industrial zone of Toluca city to Rancho Viejo, since these gaseous pollutants can travel greater distance and are more widely dispersed in the atmosphere.

The relative low ratio of NH<sub>4</sub><sup>+</sup> with respect to Ca<sup>2+</sup> and Mg<sup>2+</sup> ratios, seems to support the important contribution of NH<sub>4</sub><sup>+</sup> in Rancho Viejo possibly by the use of agricultural fertilizers and the decomposition of animal wastes in Toluca Valley. These sources have been reported by Genfa *et al.* (1989) as major contribution of ammonia in both United States and Europe.

In conclusion, sequential sampling of the type used in this study offers information that may be used to infer the relationships between Ca<sup>2+</sup>, Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>, as well the possibly origin of the major constituents in wet precipitation, of the most importance is the inverse relationship between Ca<sup>2+</sup> and Mg<sup>2+</sup> with H<sup>+</sup>, since acidity is mainly neutralized by these alkaline cations.

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