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ACID RAIN OVER MEXICO CITY VALLEY AND SURROUNDING RURAL AREAS

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RESUMEN

Durante el período de junio a septiembre de 1983, se llevó a cabo la determinación del pH en 173 muestras de lluvia colectadas en forma secuencial por fracciones, en la ciudad de México y áreas circundantes.

Los resultados indican valores ácidos del pH en la mayoría de las muestras colectadas en el área urbana y aun en aquellas muestras que fueron obtenidas en lugares montañosos (valores de pH menores de 4.5).

La variabilidad en los valores del pH pueden deberse a: mecanismos de transporte, las condiciones meteorológicas que prevalecieron, la situación geográfica y el número de la fracción colectada en el evento.

ABSTRACT

173 determinations of pH were made during sequential rain fractions of single rain events in Mexico City and surrounding rural areas from June to September 1983.

Results indicate acidic pH values in the majority of rain samples collected in the urban area, even in those samples taken at mountainous locations (pH values less than 4.5).

The variability in the pH values could be attributed to: transport mechanisms of pollutants, prevailing meteorological conditions, geographic location and the rain fraction sequential number.

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INTRODUCTION

Different authors have reported and discussed the occurrence of acidic rain in the northeastern USA, the southern region of Canada and the Scandinavian countries (Cogbill and Likens, 1974; Barret and Brodin, 1975), and even in Florida (Brezonik *et al.*, 1980). Other studies have shown that the occurrence of acidic rain has spread to many areas of the world, with potential damage to ecosystems (Schofield, 1977; Galloway *et al.*, 1978 and Evans, 1979).

The results of a preliminary study on acidic rain in Mexico City Valley have been reported by Sequeira (1982), using data of Aguilar *et al.* (1980). Their pH measurements at 12 sampling sites were performed from May to October, 1980. The reported pH average values ranged from 6.2 to 6.8.

Mexico City is one of the most polluted cities in the world, with huge emissions of SO_2 from fuel oil consumption, hydrocarbons and NO_x emissions, from more than 2.5 millions of motor vehicles so it seemed reasonable to suppose the existence of acidic rain. Therefore, the authors considered that the rain sample collection from events used by Aguilar *et al.* (1980) did not represent the ideal sampling conditions for the evaluation of the acidic rain for a place like Mexico City Valley with a very high content of suspended coarse particles that are capable of affecting a whole rain event by neutralizing rain acids.

A program to collect rain samples in a sequential mode was undertaken instead of collecting whole rain events, because the sequential mode enables to eliminate coarse particles by the first rain fractions, leaving the subsequent fractions relatively free from this interference and thus allows to obtain an actual rain pH, as it will be discussed later in this paper.

EXPERIMENTAL

Sampling sites

The sampling sites were chosen to cover different topographic and meteorological conditions. The main characteristics of these sites are summarized as follows:

Lomas de Chapultepec. This site is located at one of the residential zones in the northwestern part of Mexico City. down-wind from one of the most important industrial areas in the valley.

The University of Mexico. This site is located in a residential area at the southern part of the city, with no appreciable industrial emissions in the immediate vicinity but with an average transportation of 30 thousand vehicles/day, except on weekends when much less traffic is observed.

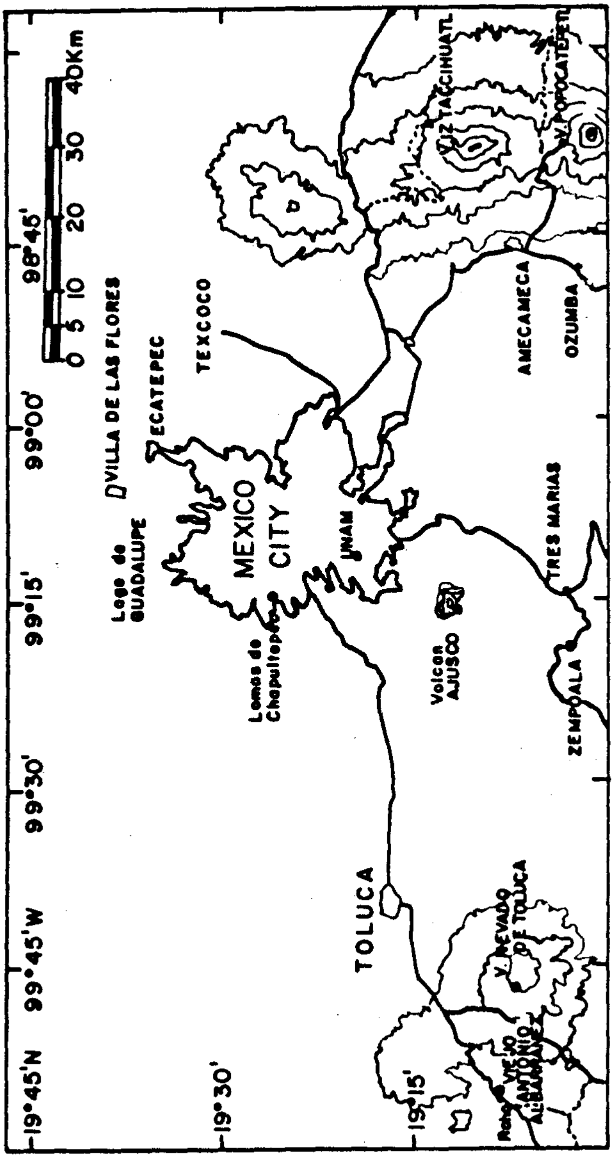

Fig. 1. Location of the sampling sites.

Rancho Viejo. This sampling site is located WSW of Mexico City, in a wooded area 20 km from Toluca, the capital of the State of Mexico. During the rainy season advective winds around 700 - 600 mb transport some part of the air pollutants emitted in Mexico City Valley to Rancho Viejo. This is consistent with the synoptic conditions that prevail during summer.

Zempoala Lagoons. The lagoons are located SSW of Mexico City, in a wooded area 60 km from the city and around 3 000 m above sea level.

Ajusco Station. The sampling site is located at 3 900 m above sea level and 30 km south from Mexico City. Ajusco is an extinct volcano.

Tlamacas. This station is situated in the middle of the Iztaccihuatl and Popocatepetl volcanic area at 4 000 m above sea level and 73 km up-wind from Mexico City in SE direction.

Nevado de Toluca. This station is also situated at about 4 000 m above sea level SW of Mexico City at 70 km of the city.

Figure 1 shows the geographic locations of the sampling sites.

These places were chosen because they represent a set of different conditions mainly geographical and meteorological that allowed us to compare the pH of the rain samples collected in such places and thus to explain the reasons of the substantial differences in the rain pH that were found between some of the stations.

SAMPLING METHODS

Rain samples were collected in nalgene funnels draining into polyethylene bottles mounted on an iron frame 1.5 m above ground to minimize splashing. The apparatus was rinsed with deionized water before sample collection. Each rain event was collected as several subsamples or fractions. The number of fractions depended on the intensity and duration of the rain.

The pH was measured immediately upon sample collection with a portable Corning pH meter. Model 3 D. The instrument was previously field calibrated against buffer solutions of 4 and 7 pH units. Every week each portable pH meter was cross calibrated with a laboratory calibrated pH meter Philips Model PW-9409, with a sensitivity of 0.01 pH units. The difference in the readings never exceeded 0.08 units. Rain samples, buffers and electrodes were always allowed to reach equilibrium at the same temperature, before calibration and measurements.

RESULTS AND DISCUSSION

The mean weighted pH values for each rain fraction collected at each sampling site were tabulated (Table 1).

TABLE I

Sampling site.	Month	Fraction Number 1st (a)	2nd (a)	3rd (a)	4th (a)	5th (a)	6th (a)	7th (a)	8th (a)	Total weighted average for all collected rain fractions. (b)
Lomas de Chapultepec	Jun.	4.49-5	4.62-4	4.57-3	4.39-1	4.45-1				
	Jul.	5.07-8	4.41-7	4.39-5	4.64-3	4.60-2	4.72-1			
	Ag.	5.48-8	5.30-7	4.79-4	4.65-2	4.75-1	5.53-1	5.38-1		
	Sep.	5.16-15	5.59-7	5.69-5	5.11-3	5.51-1	5.77-1	4.53-1	4.65-1	4.97
	(c)	(5.07)	(5.06)	(4.92)	(4.75)	(4.67)	(5.41)	(5.17)	(4.65)	
Rancho Viejo	Jun.	4.73-2	4.10-1	4.38-1						
	Jul.	4.92-6	4.42-5	4.45-5	4.42-5	4.80-1	5.10-1			
	Ag.	4.62-4	4.39-3	4.16-1						
	Sep.	4.54-5	4.55-4	4.70-2						4.53
	(c)	(4.67)	(4.44)	(4.52)	(4.42)	(4.80)	(5.10)			
Tlamacas	Jul.	5.39-2	5.23-2	5.42-2	5.30-2	5.51-1				
Nevado de Toluca	Jul.	3.70-1	3.78-1							
Ajusco	Jul.	4.15-2	4.17-1							
Zempoala Lagoons	Jul.	4.72-1	4.23-1							
University of Mexico	Jun.	4.38-1								
	Jul.	5.16-3	4.60-3	4.58-3	4.45-2					
	(c)	(5.09)	(4.60)	(4.58)	(4.45)					

(a). Number of samples.

(b). Total pH weighted average were only computed for the sites regularly sampled.

(c). The values between brackets are pH weighted averaged for each rain fraction.

The Chapultepec station represented an area most affected by air pollution generated in the industrial zones, and by intensive motor vehicle emissions. The pH values varied according to the fractions collected. The first fractions (36 events) averaged 5.07 pH units and decreased in the subsequent fractions down to 4.65. The variability of the pH values observed at this sampling site may be explained by the fact that there are several cement and lime industries in the vicinity that emit large amounts of alkaline coarse particles capable of neutralizing to varying degrees the first fractions of rain precipitation by scavenging. Pratt *et al.* (1984) reported similar results and found that "the higher rainwater acidity at the northern sites of Minnesota and west central Wisconsin appeared to be a function of the lower concentration of alkaline cations such as Ca^{+2} and ammonium". Pratt *et al.* (1983) in studies made also in Minnesota found that "the $[H]^{+}$ tend to increase throughout the events".

In Rancho Viejo, the pH values for the first fraction averaged 4.67 and decreased in the subsequent fractions down to 4.42. Balloon sounding indicated the presence of advective and convective winds (around 700 - 600 mb). These winds transported air pollutants from the city into the Rancho Viejo area. From the results it was assumed that the acidity observed in the rain water collected in Rancho Viejo was poorly affected by a washout process and that rainout process was the most important mechanism in acidic rain formation at the Rancho Viejo sampling site.

It is interesting to note that the pH values obtained with samples collected at Tlamacas station ranged from 5.23 to 5.51, close to the value of pure rain water in equilibrium with 300 ppm of CO_2. These results indicate a slight possibility that this rain water could be contaminated by air pollutants emitted in the city. It was observed during the sampling time that the station was up-wind from Mexico City. However, care must be taken in order not to misunderstand this concept since, in natural rain water it is possible to find naturally occurring substances capable of modifying this pH (Charlson and Rodhe, 1982); also Sequeira (1982) reported the presence of acidic rain in Mauna Loa Observatory, Hawaii due to volcanic emissions of sulfuric acid.

With respect to the remaining stations, the pH values were always significantly acidic (<5.00 pH units) suggesting the possible role of air pollutants on the rain composition.

In order to examine the pH variations with respect to the intensity and duration of the rain and the collection time of the different fractions, four events were selected from the Chapultepec sampling station. This station was selected because it was easier to collect rain samples there; furthermore, it is a suitable place, because it has no immediate industrial areas that could profoundly affect, in a local manner, the rain chemistry. However, if another place had been chosen away from such industrial areas but also downwind from them, similar pH variations with collection time would probably have been obtained.

Figures 2, 3, 4 and 5 are illustrative of these individual rain events. From these figures the pH variations can be observed in the different fractions collected. Cooper *et al.*, 1976 found similar pH changes in rain samples in Texas. Figure 5 shows the pH variations obtained during the rain event of September 12th. A pH decrease from the first fraction down to the 4th of about 2.5 pH units was observed. After the fourth fraction was collected, the rain stopped for about one and a half hour and again resumed for a short period of time. This second rain period was long enough to collect another two fractions, the 5th and the 6th. Then another interruption occurred for four and a half hours. Afterwards, raining started again and two more samples were collected (the 7th and the 8th). In this particular event a pH increase in the 5th and 6th fractions was observed (from 5.5 to 5.75) followed by a decrease in the two remaining fractions (7th and 8th) to 4.5 and 4.75 respectively.

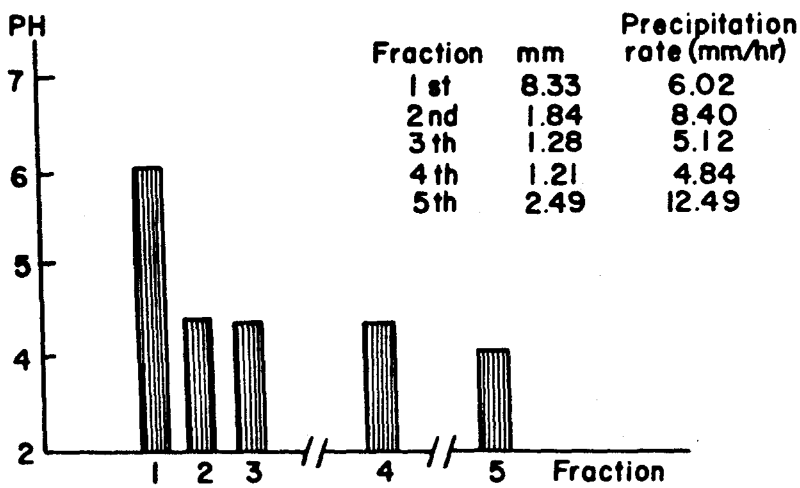

Fig. 2. pH variations during a rain event of July 1st, 1983 at Chapultepec station.

Similar fluctuations were observed for July 1st (Figure 2) and August 22th (Figure 3) rain events. But on September 1st (Figure 4) when four fractions were collected, the pH variations were similar to those observed in all individual rain events sampled previously.

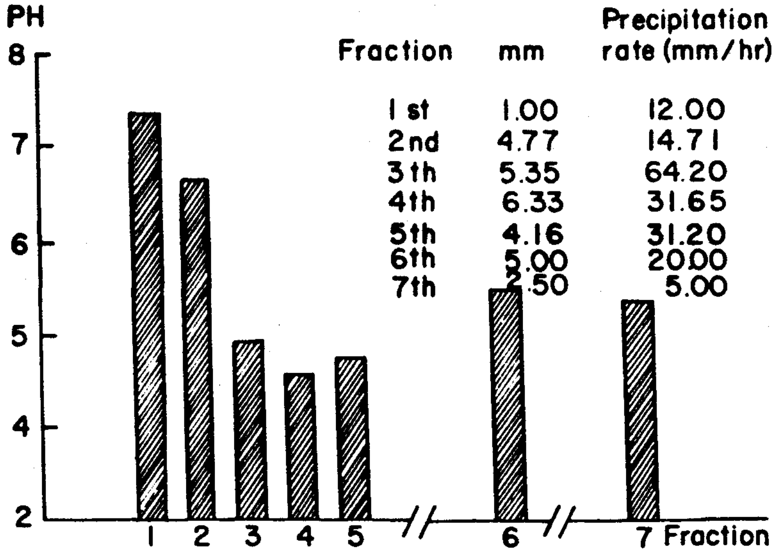

Fig. 3. pH variations during a rain event of August 22nd, 1983 at Chapultepec station.

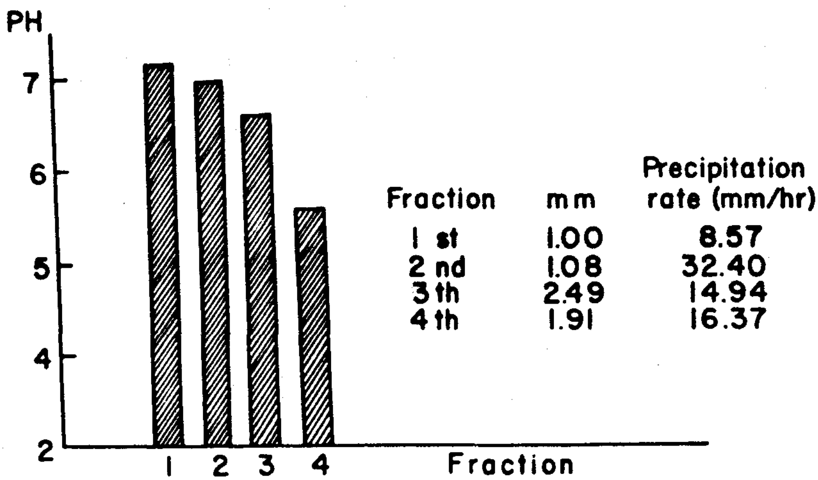

Fig. 4. pH variations during a rain event of September 1st, 1983 at Chapultepec station.

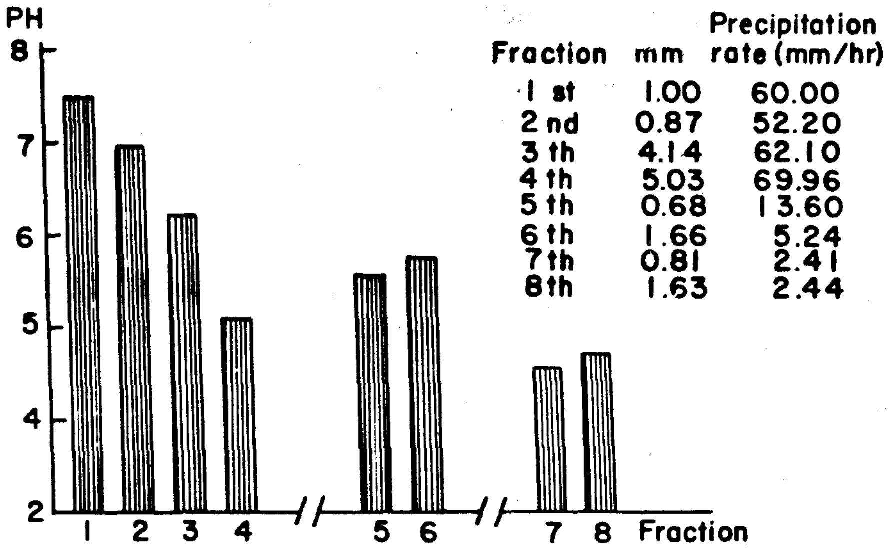

Fig. 5. pH variations during a rain event of September 12th, at Chapultepec station.

The pH changes in rain are likely a result of several complex mechanisms but some of them are suggested here to explain the observed pH fluctuations in the rain samples collected at the sampling sites at Mexico City and surrounding rural areas:

- The effect of meteorological parameters upon dispersion and interaction between pollutants and clouds.

- The vertical and horizontal air motions within and below the clouds and their interaction with the surrounding air masses.

- The physico-chemical characteristics of soil, suspended and other coarse particles and their concentrations.

One mechanism that could explain the rain acidity in Mexico City Valley and surrounding rural areas is that Mexico City has been considered as a heat island because the valley is under a strong solar radiation with enough energy to produce vertical air mass motions that interact with the synoptic winds which transport the air pollutants to rural areas down wind from the valley (Ajusco, Zempoala Lagoons, Nevado de Toluca and Rancho Viejo). Martin and Barber (1978) also found acidic rain in rural sites in Central England and Wales, probably due to contributions from distant and local sources; however, as in our case, this pollution transport is yet to be resolved. It was observed that in spite of the fact that Rancho Viejo is located in an unpollutant area, that is with no industrial emissions to count and a very low traffic density, the pH values of rain samples were similar to those found at Mexico City. On the other hand, at Tlamacas station, samples were gathered when synoptic trade winds blew toward the Mexico City Valley, that is toward the west as it normally happens in tropical latitudes, specially during the summer; unfortunately, there are no concise meteorological data available for the sampling period due to the lack of a meteorological network equipped with sounding devises.

The pH values of these samples were close to the pH of pure rain water (5.7), in equilibrium with atmospheric CO_2, indicating the low probability of cloud contamination by pollutants emitted in the city. The variation of pH values with time at the stations down wind from the city shows that at these stations the scavenging of coarse particles by washout processes is smaller compared to that occurring in Mexico City in the first rain fractions and consequently, for the stations down wind from the city, the washout processes of soil particles contribute a lesser degree to the final chemical composition of rain water, so at these stations the rainout process contributes the most to the chemistry of rain water. Similar conclusions for sulphur were obtained by Garland (1978) where he stated that the "sulphur in precipitation results chiefly from the rainout of cloud condensation nuclei" but the scavenging of large particles by the first few millimeters of rain may account for the increase of sulfate concentration at the beginning of some events.

CONCLUSIONS

No definitive correlation between rainfall amount and pH values was observed, similar results have been reported by Hansen and Hidy (1982). It is well worth emphasizing that there must be a complex relationship between pH and rain intensity rather than rain amount, as was reported by De Pena *et al.* (1984) who found such a relation between rain intensity and SO_4 and NO_3 concentrations.

The rain sampling method used in Mexico City Valley and surrounding rural areas, as described in this paper proved to be very valuable in regions like Mexico City with large emissions of alkaline particles from cement and lime processing plants and with calcareous wind blown dust from the soil.

The data obtained suggest that vertical diffusion of pollutants and their horizontal transport, together with acid-base balance, are the most probable mechanisms to account for the formation and presence of acidic rain in rural areas via a rainout process.

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