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COMPARATIVE STUDY OF THE CHEMICAL COMPOSITION OF RAIN OF THREE DIFFERENT ZONES IN MEXICO

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RESUMEN

El estudio comparativo de la química de la precipitación pluvial, se llevó a cabo en 3 diferentes zonas del país. La primera correspondió a un área urbana fuertemente contaminada, la segunda fue un lugar preminentemente agrícola y la tercera fue una región costera en donde se encuentra instalado uno de los mayores complejos petroquímicos del país. Los resultados de este estudio regional indicaron que están condicionados a las fuentes locales de contaminación. Las concentraciones de todos los iones determinados variaron de lugar a lugar. La influencia de la atmósfera fuertemente contaminada de la Ciudad de México, se reflejó en la química de la lluvia. Las concentraciones más altas de SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+} y Mg^{2+} se hallaron en este lugar. De igual forma las emisiones industriales en el sitio de muestreo en Salamanca, contribuyeron a tener concentraciones más altas de los iones en el agua de lluvia, que aquellos valores encontrados en la zona predominantemente agrícola y de aquel bajo la influencia de condiciones meteorológicas marítimas.

ABSTRACT

A comparative study of the precipitation chemistry of three different zones in Mexico was undertaken. The first zone corresponded to a highly polluted urban area, the second, was a predominantly agricultural region and the third, was a coastal zone where the biggest petrochemical complex of the country is located. Results of this regional study were shown to be conditioned by local sources. The concentrations of all determined ions varied from site to site. The influence of the highly polluted atmosphere of Mexico City was reflected in the chemistry of rain. The highest concentrations of SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+} and Mg^{2+} were found there. In like manner, the industrial emissions at the Salamanca sampling station contributed to higher concentrations in rain water than those found at the predominantly agricultural area. In general the concentrations of inorganics in rain water in Mexico City and Salamanca were higher than those located at the predominantly agricultural zones and under influence of maritime meteorological conditions.

INTRODUCTION

Studies of precipitation chemistry have been carried out many in countries of the northern hemisphere, mainly highly developed countries, since the turn out of the 20th century. At present these studies are very relevant because a great amount of air pollutants are scavenged by washout and rainout processes and are integrated into the different phases of the environment (Caiazza *et al.* 1978, Pratt *et al.* 1983).

One of the most important results observed through the chemistry of precipitations is the continuous increase in the concentration of sulfates and nitrates in rain water. Junge (1960) estimated that as a global average 30% of atmospheric sulfur comes from anthropogenic sources, locally and regionally important sources may increase this percentage. For example in the NE USA the anthropogenic sulfur may be 80% of the total; however, this amount could be increased due to the huge consumption of carbon fossil fuel during the last two decades. On the other hand, it has been considered that the intervention of man in the nitrogen cycle will reach important proportions in the next 30 years. A great part of the nitrogen compounds (NO_x) are emitted from either industrial or mobile sources in which an annual increase is observed.

It is obvious that industrialization and high population density can change the precipitation chemistry over large areas. Then it is important to consider the study of the chemistry of precipitation as a valuable tool to estimate the degree of atmospheric degradation in polluted areas or those under its meteorological influence.

Few studies about precipitation chemistry have been made to date in Mexico (Báez *et al.* 1980, 1984, 1986). These studies were aimed toward acid rain chemistry and determining levels of heavy metals and formaldehyde in rain water.

This paper deals with a comparative study of precipitation chemistry of three different areas. The first is a highly polluted urban area, the second is an agricultural region with an industrial corridor that includes a large oil refinery, and the third is a coastal zone that comprises two medium-sized cities 20 km apart. The two medium-sized cities share the biggest petrochemical complex of the country, one oil refinery and the most important piers for the shipping of crude oil, refining products and petrochemical compounds.

MATERIAL AND METHODS

Methods and Analysis

Bulk precipitation was collected at each sampling site using a nalgene funnel 24 cm in diameter, draining into a 3 liter polyethylene bottle inside a polyurethane sealed insulated box. In this way evaporation of sample and growth of organism was diminished. The top of the ring funnel was 1.80 m above ground level to prevent contamination from splashing. Funnels and bottles were rinsed throughly with deionized water before exposure. Samples were collected every 15 days, returned to the laboratory and maintained under refrigeration at 4°C until chemical analysis. Determination of pH was usually done upon return to the laboratory.

Ca^{2+} and Mg^{2+}. Detection was made by atomic absorption of solution components aspirated into a flame, using hollow cathode sources of the appropriate metal.

Low level standards were prepared daily, detection limit was 0.001 mg L^{-1} for Mg^{2+} and 0.01 mg L^{-1} for Ca^{2+}.

SO_4^{2+}. The turbidimetric method used the precipitation of $BaSO_4$ in excess of $BaCl_2$, the sensitivity of the turbidimeter was 1 mg L^{-1}.

NH_4^+. Ammonium was determined colorimetrically by absorption at 420 nm from complex formed upon reaction nessler reagent:

FIG. 1. Sampling sites location

NO_3^-. Detection was made by the brucine colorimetric method using absorption at 410 nm. Detection limit was 0.1 mg L^{-1}.

H^+. Conbination Philips electrode and pH meter were used.

Quality Control.

The data, for precision, was quality assured during sample processing, the results were checked by making the same analysis on two separate aliquots of each sample. All analytical techniques were evaluated using quality control samples provided by the Environmental Monitoring and Support Laboratory, US Environmental Protection Agency.

Intrumements Calibration.

For the analytical calibration of the instrumentation, the manufacture's recommended instructions and the procedures given in the Standard Methods for the Examination of Water and Wastewater (APHA 1976), were followed.

Standarizations of pH were made with 4.0 and 7.0 pH buffer solutions.

Sampling Site Descriptions.

Three different sampling sites with different characteristics and activities were chosen for this study (Fig. 1). These regions were: The cities of Minatitlan and Coatzacoalcos (Veracruz State), the Bajio plains (Guanajuato State) and Mexico City.

Minatitlan-Coatzacoalcos. This is coastal area of the Gulf of Mexico, at the southern shore of the Coatzacoalcos River 20 km up from the estuary, 94° 25' W and 18° 00' N.

Coatzacoalcos City is situated at the delta of the Coatzacoalcos River Estuary, 94° 25' W and 18° 10' N. This coastal zone is characterized by a warm-humid climate with only a few degree annual temperature variation and a rainy season almost year around, with a total annual precipitation of 2109 mm (22 year average) associated with upper winds from the northeastern direction but with a maximum precipitation rate in September and October due to tropical storms from the Gulf of Mexico. This zone in which both cities are located is at present one of the most important industrial areas of the country, with more than 20 petrochemical complexes, one big oil refinery and all associated maritime and ground transportation for the shipping of oil and refining products. As a result of this industrial development, water and air have been severely polluted.

In Minatitlan the sampling station was located on the roof of one of the Medicine School buildings, one story high. One of the most important fertilizer plants was about 800 m east from the sampling site. The oil refinery was 2 km south and other petrochemical complexes were between 1 and 3 km northeast from the station.

In Coatzacoalcos City the collector was installed on the roof of the Engineering School building, University of Veracruz, located at the northern suburbs of the city, 1 km from the ocean shore. This was considered as a clean area when it was under the influence of ocean air; however, many times an ammonia mist released from some industries, covered part of the city, sometimes reaching the sampling station mainly during calm meteorological conditions, also when the surface wind blew from land to sea the emissions from the petrochemical complex affected the sampling station.

Bajio plains (Guanajuato State). This area comprises the counties of Celaya, Salamanca, Salvatierra, Irapuato, Valle de Santiago, Penjamo and Yuriria, located in the southern part of Guanajuato State, between 100° 41' W and 20° 21' N, it is 1750 m above sea level. The climate is subtropical $(A)_c$, with an annual median temperature of 18°C and a medium annual rainfall of 640 mm.

The prevailing upper winds associated with precipitation usually come from the southeastern direction.

This region is one of the most important agricultural areas of the country, but at present is in the process of industrialization. A big industrial corridor has been established between Celaya and Irapuato cities, that includes a large oil refinery, a fertilizer plant, a fuel oil-burning thermoelectric power plant (3.5 at 4.5% sulfur content), sulfuric and nitric acid plants, other important chemical and petrochemical industries and heavy highway traffic (mainly diesel trucks).

All sampling sites with the exception of two, were installed in the downtown area on the roofs of building. The other two were located at the Meteorological Station of the University of Guanajuato, around 6 km from Irapuato on grass covered ground, and on the roof of one of the buildings of the Agricultural School 5 km from the town of Yuriria.

TABLE I. MINIMUM, MAXIMUM, ARITHMETIC MEANS, STANDARD DEVIATION AND VOLUME-WEIGHTED MEANS OF THE CHEMICAL COMPOSITION OF BULK PRECIPITATION COLLECTED AT THREE SITES IN MEXICO

	Amount of precipitation (mm)	pH	μeq L^{-1} H^+	NH_4^+	Ca^{2+}	Mg^{2+}	NO_3^-	SO_4^{2-}	Σ^+/Σ^-
Mexico City, 1984-1985 (n = 29)									
Minimum	2.5	4.59	0.04	92.9	75.3	8.2	30.7	142.0	
Maximum	124.1	7.40	25.7	393.0	468.0	68.9	110.0	476.0	
Arithmetic mean	41.6	5.48*	3.3	211.0	208.0	33.4	62.4	249.0	
Standard deviation	31.6	—	6.0	74.1	102.0	16.9	21.8	79.2	
Volume-weighted mean	—	5.34*	4.6	170.0	157.0	24.5	59.7	220.0	1.27
Bajio Zone (Guanajuato State) 1985 (n = 54)									
Minimum	10.2	5.45	0.008	10.7	10.0	1.6	7.1	39.6	
Maximum	178.9	8.10	3.50	334.0	609.0	104.0	66.4	500.0	
Arithmetic mean	64.0	6.45*	0.35	117.0	108.0	10.9	26.8	139.0	
Standard deviation	32.2	—	0.62	65.5	116.0	14.2	12.4	101.0	
Volume-weighted mean	—	6.48*	0.33	107.0	91.8	9.5	23.7	129.0	1.36
Minatitlan-Coatzacoalcos (Veracruz State) 1984-1985 (n = 26)									
Minimum	23.4	3.75	0.022	9.3	6.0	4.1	7.1	20.8	
Maximum	178.0	7.66	178.0	397.0	135.0	84.7	132.0	362.0	
Arithmetic mean	104.0	4.66	21.7	86.2	33.6	21.9	12.6	119.0	
Standard deviation	41.3	—	38.5	94.1	31.9	20.3	25.6	81.2	
Volume-weighted mean	—	4.60	25.0	80.3	28.9	18.6	10.9	109.0	1.27

* Calculated from the corresponding H^+ value.

Σ^+/Σ^- Ion balance.

Mexico City. The city is one of the most polluted of the world, with 17 million inhabitants in the metropolitan area, 2.7 million automobiles and more than 100 thousand buses and taxicabs. There are at present, located in the valley, around 130 thousand small, medium and big industries, that emit into the atmosphere large amounts of air pollutants, among them SO_2 is the most important, because it is emitted in huge quantities by combustion of fossil fuels. The city is 2200 mm above sea level. The climate is subtropical $(A)_c$, with an annual median temperature of 18°C and a median annual rainfall of 860 mm. The prevailing upper winds during the rainy season come from the southeast direction and usually the clouds are of the convective type.

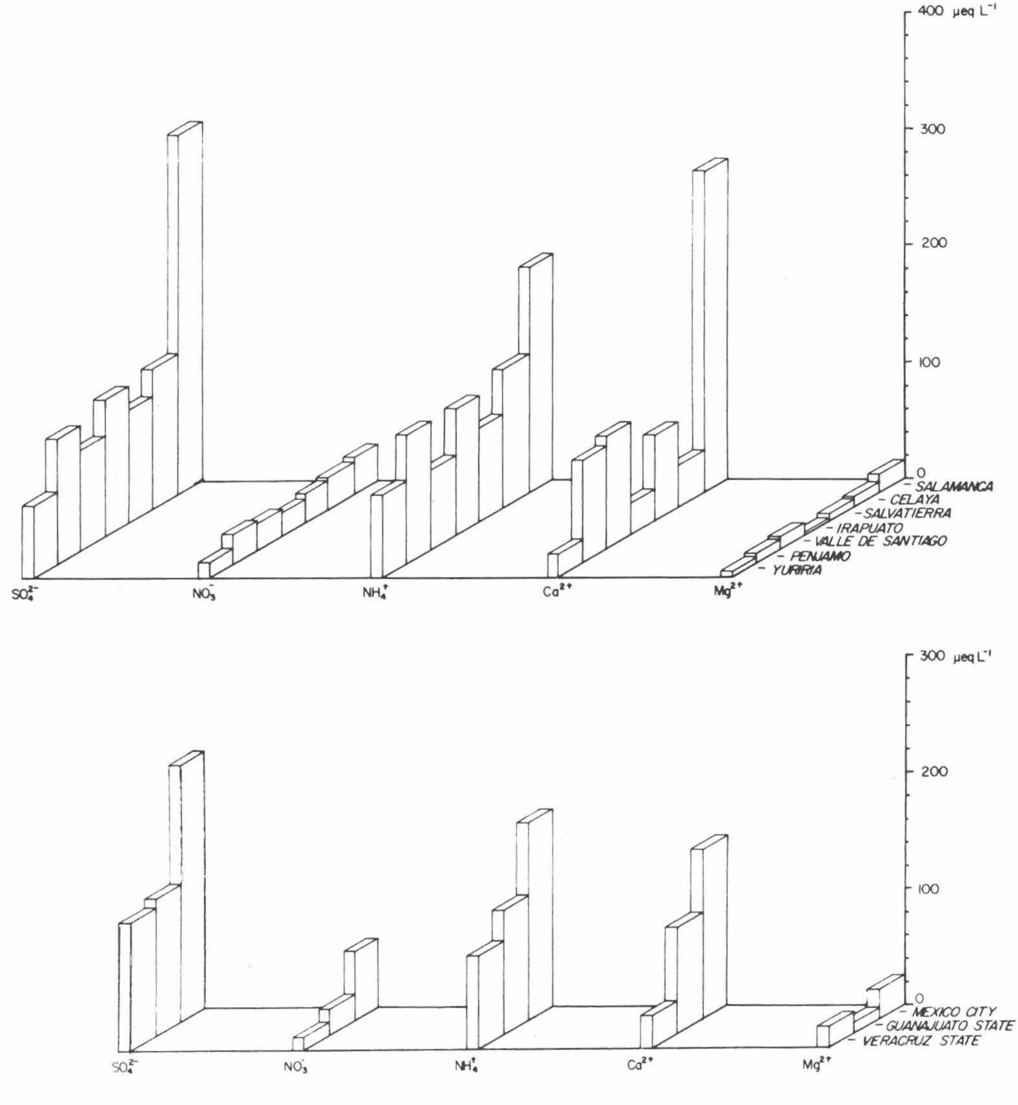

FIG. 2. Comparison diagrams of the weighted average ions concentration found in the different sampling sites

RESULTS AND DISCUSSION

One hundred and nine bulk precipitation samples were collected at eleven sampling sites, three in Mexico City, seven in Guanajuato State and two Minatitlan-Coatzacoalcos region (Veracruz State) from the rainy season of 1984-85, with the exception of Guanajuato State that only the rainy season of 1985 was covered.

The volume-weighted mean pH and ion concentrations are given in Table I. The volume-weighted mean pH was calculated from the corresponding H^+ concentrations. Whenever a nitrate ion was below the detection limit, half of this detection limit was used for computation purposes.

Results of this regional study are shown to be conditioned by local sources as can be seen from Fig. 2 which shows that the concentration of all determined ions varied from site to site.

Sulfate and ammonium were the predominant ions representing the 35.1 and 27.4% respectively of the measured ions (on μeq L^{-1} basis). Hydrogen ion accounted for only 4.2% of the cations.

The concentrations of sulfate, ammonium and calcium were higher at Salamanca City. The pH was lowest at Veracruz and highest at Guanajuato State (Table I). But, when the whole areas are considered, then sulfate, nitrate, ammonium, calcium and magnesium were higher at Mexico City (Table I). On the other hand, lower ion concentrations were observed in the Minatitlan Coatzacoalcos region.

Some of the possible sources of alkaline cations. Animal urine, fuel combustion, fertilizer production and use and soil biological reactions are the major sources of atmospheric ammonia (Galbally 1975), as for the alkaline earth cations according to Winkler (1976) particulate matter of natural terrestrial origin comprises the major portion of atmospheric "dust" and may reflect the soil components for distances of 240 km. This distance is considerably less than the distance over which S emissions are known to influence atmospheric chemistry (Barnes 1979). The alkaline earth cations are usually components of the coarse fraction of the atmospheric aerosol and their impact more localized.

There are several possible sources of alkaline cations in the studied areas. In Guanajuato State it was found that the major possible sources of atmospheric ammonia were fertilizer production and agriculturally related emissions. Maximum pH values were measured in rain water at the time liquid ammonia was being applied to soils and in the vicinity of the fertilizer plant (Salamanca sampling station) where the values ranged from 6.85 to 8.10 with and arithmetic mean of 7.22 (Table II).

In Minatitlan-Coatzacoalcos sampling area high values of ammonia in precipitation were related to industrial emissions and fuel combustion. In fact the highest pH values were measured when accidental industrial releases of ammonia mists occurred. With respect to the Mexico City area. Ammonia concentrations may be related mainly to fuel combustion because the Mexico City Valley contains more than 30 000 small, medium and large industries and more then 2.8 million motor vehicles.

Calcium and magnesium are common constituents of soil and thus are more enhanced in bulk precipitation. This is caused by soil particles being blown into the atmosphere by wind action (Galloway and Likens 1978). The high values measured in rain water over Mexico City sampling stations can ben attributed to soil erosion (calca-

TABLE II — MINIMUM, MAXIMUM, ARITHMETIC MEANS, STANDAR DEVIATION AND VOLUME WEIGHTED MEANS OF THE CHEMICAL COMPOSITION OF BULK PRECIPITATION COLLECTED AT SEVEN STATIONS AT GUANAJUATO STATE MEXICO (1985)

	Amount of precipitation (mm)	pH	H^+	NH_4^+	Ca^{2+}	Mg^{2+}	NO_3^-	SO_4^{2-}	Σ^+/Σ^-
				$\mu eq\ L^{-1}$					
				Valle de Santiago (n=8)					
Minimum	20.0	6.54	0.04	10.7	42.9	5.8	8.6	67.5	
Maximum	132.6	7.40	0.29	142.0	279.0	28.8	37.1	133.0	
Arithmetic mean	70.9	7.00	0.10	76.0	126.0	12.1	25.5	90.6	
Standar deviation	36.7	-------	0.08	41.2	71.7	7.5	10.8	21.6	
Volume-weighted mean	---------	6.89	0.13	68.8	96.9	9.7	23.3	86.4	1.59
				Penjamo (n=8)					
Minimum	29.9	6.55	0.04	74.3	21.0	4.9	13.6	61.0	
Maximum	106.4	7.40	0.28	154.0	224.0	18.1	39.3	177.0	
Arithmetic mean	64.3	6.92	0.12	115.0	105.0	9.8	27.0	115.0	
Standar deviation	26.0	-------	0.09	26.7	82.8	5.0	10.2	36.3	
Volume-weighted mean	---------	6.89	0.13	111.0	88.9	8.6	24.9	109.0	1.55
				Yuriria (n=8)					
Minimum	10.2	6.12	0.10	35.7	10.0	2.5	7.1	39.6	
Maximum	178.9	7.00	0.76	125.0	42.4	10.7	26.4	102.0	
Arithmetic mean	66.3	6.57	0.27	82.7	26.3	5.8	16.8	67.0	
Standar deviation	49.6	-------	0.21	36.5	10.7	2.6	7.4	18.4	
Volume-weighted mean	---------	6.41	0.39	72.5	20.5	5.4	15.4	63.3	1.25
				Celaya (n=6)					
Minimum	20.8	5.74	0.04	62.9	19.0	4.1	23.6	70.8	
Maximum	88.7	7.40	1.8	324.0	93.8	27.1	40.0	285.0	
Arithmetic mean	46.0	6.14	0.72	135.0	45.0	9.0	28.7	134.0	
Standar deviation	25.8	-------	0.76	97.8	31.5	9.0	6.0	79.0	
Volume-weighted mean	---------	6.16	0.69	120.0	35.4	7.5	28.2	121.0	1.09
				Salamanca (n=8)					
Minimum	35.1	6.85	0.008	118.0	151.0	9.0	19.3	187.0	
Maximum	94.1	8.10	0.14	241.0	609.0	104.0	56.4	500.0	
Arithmetic mean	66.0	7.22	0.06	197.0	297.0	25.6	32.6	323.0	
Standar deviation	17.7	-------	0.04	38.3	143.0	32.3	11.9	109.0	
Volume-weighted mean	---------	7.15	0.07	195.0	275.0	24.0	32.5	309.0	1.44
				Salvatierra (n=8)					
Minimum	13.1	6.13	0.04	50.0	20.5	2.5	11.4	68.7	
Maximum	127.6	7.40	0.74	191.0	342.0	22.2	66.4	239.0	
Arithmetic mean	65.5	6.72	0.19	96.0	116.0	8.6	30.3	114.0	
Standar deviation	36.6	-------	0.23	42.0	102.0	6.2	17.0	52.8	
Volume-weighted mean	---------	6.55	0.28	80.6	73.7	6.1	23.2	96.9	1.33
				Irapuato (n=8)					
Minimum	16.2	5.45	0.20	56.4	13.0	1.6	8.6	57.9	
Maximum	110.6	6.70	3.5	334.0	54.4	8.2	55.0	337.0	
Arithmetic mean	64.3	5.96	1.1	124.0	27.8	4.7	27.2	130.0	
Standar deviation	32.3	-------	1.2	88.7	13.2	2.4	16.9	89.0	
Volume-weighted mean	---------	6.09	0.82	109.0	23.3	3.8	20.9	118.0	0.98

Σ^+/Σ^- Ion balance.

reous soils are predominant in this city) and to anthropogenic sources. Industrial emissions are the atmospheric sources of the earth alkaline metals Ca and Mg (Granat 1972). In like manner the high values of Ca^{2+} and Mg^{2+} found in Guanajuato State are related mainly to soil erosion and agriculture manipulation of soils. From Fig. 2 it can be observed that the lowest Ca^{2+} value was measured in the Minatitlan-Coatzacoalcos region. This is in agreement with the suspended particulate matter measurements carried out by Báez (1986) in this area, in which the average concentrations of suspended particulate matter was 86.5 μug m^{-3} below the Mexican Air Quality Standard of 275 μgm^{-3}. This was expected because more of the air pollution is of organic nature, product of the emissions from the petrochemical complex and the oil refinery, and in addittion soils are covered by grass and tropical vegetation with practically no soil erosion.

In can be assumed that a great part of atmospheric calcium and magnesium come from sea spray. This assumption is also supported by the high concentration of magnesium measured in rain water over this region, with a Ca/Mg ratio of 1.54 in comparison with the ratios of 9.66 and 6.4 found in Guanajuato State and Mexico City respectively.

Sulfates. Rainout or removal by cloud processes has a high overall efficiency for the removal of gaseous pollutants such as SO_2 which becomes widely dispersed in the atmosphere during long range transport. Sulfate and nitrate contained in bulk precipitation in Mexico City arise primarily from rainout-washout.

Volume-weighted mean concentration of sulfate in rain samples collected over Mexico City, of 220 μeq L^{-1}, was much higher than that reported for the northeastern United States (60.42 μeq L^{-1}) for the period of 1964-1974 (Likens and Bormann 1974). The high SO_4^{2-} value detected in rain water showed that the most common source of atmospheric sulfates and their precursor SO_2 were emissions from combustion of sulfur containing fuels and the refining operations (Friend 1973). This fact was consistent with the high ammounts of SO_2 emitted into the atmosphere by the combustion of fuel-oil with around 3.5 to 4.0% of sulfur content that are daily burned in the Mexico City Valley.

With respect to Minatitlan-Coatzacoalcos region, the most probable source of sulfates in rain can also be attributed to SO_2 emissions from combustion of sulfur containing fuels and industrial operations. In spite of the fact that this zone is heavily industrialized, the influence of the winds blowing from the Gulf of Mexico plays an important role in the diffusion of air pollutants because in general the lowest ion concentrations were found in this area. Since emissions from a point source must travel a great distance before intersecting the cloud layers the washout process is expected to dominate as the primary mechanism in the vicinity of the source (Boyce and Butcher 1976). From Fig. 2 it can be observed that the point sources influenced the chemistry of precipitation at the Salamanca sampling site where the highest concentrations of ions in rain water, in this agricultural area, were found. These results were expected because in Salamanca, an oil refinery, a fertilizer production, a thermoelectric plant and other industries are in operation.

An important source of inorganic nitrogen may be automobile exhaust in urban areas. Data of bulk precipitation from sampling stations in Mexico City showed the highest NO_3^-, concentration. Automobile exhaust and industry are implicated as sources. In like manner the high concentration of NO_3^-, found in rain water in Sala-

TABLE III. CORRELATION COEFFICIENTS (r) OF SOME PROPERTIES OF BULK PRECIPITATION AT THREE SITES IN MEXICO

Relationship	Sites Mexico City 1984-1985 (n = 29)	Guanajuato 1985 (n = 54)	Veracruz 1984-1985 (n = 26)
$H^+ : SO_4^{2-}$	− 0.391 [b]	− 0.192	0.094
$H^+ : NO_3^-$	− 0.230	0.054	− 0.150
$H^+ : NH_4^+$	− 0.299	− 0.181	− 0.115
$H^+ : Ca^{2+}$	− 0.516 [a]	− 0.328 [b]	− 0.019
$H^+ : Mg^{2+}$	− 0.437 [b]	0.201	− 0.090
H^+ : Rain	0.289	− 0.049	0.227
$SO_4^{2-} : NH_4^+$	0.475 [a]	0.757 [a]	0.709 [a]
$SO_4^{2-} : Ca^{2-}$	0.738 [a]	0.750 [a]	0.352
$SO_4^{2-} : Mg^{2+}$	0.627 [a]	0.645 [a]	0.289
SO_4^{2-} : Rain	− 0.495 [a]	− 0.195	− 0.339
$NO_3^- : NH_4^+$	0.395 [b]	0.442 [a]	0.323
$NO_3^- : Ca^{2+}$	0.287	0.478 [a]	0.737 [a]
$NO_3^- : Mg^{2+}$	0.228	0.482 [a]	− 0.078
NO_3^- : Rain	− 0.166	− 0.489 [a]	− 0.169

Figures in parentheses are the number of samples.

[a] Significant at 0.01 level. [b] Significant at 0.05 level.

manca may be attributed to the combustion processes and the emissions from the fertilizer plant and the oil refinery.

In general, the concentrations of inorganic ions in rain water in Mexico and Salamanca cities were higher than those found in the predominantly agricultural zones and those located under the influence of maritime meteorological conditions.

Statistical Analysis

In Table III correlation coefficients among the major anions, cations and parameters of rain events are shown. SO_4^{2-}, Mg^{2+}, and Ca^{2+} were all negatively correlated with H^+ in samples from Mexico City, whereas in samples from Guanajuato State only Ca^{2+} was negative correlated with H^+. No correlation between rain volumen and H^+ was found. NH_4^+ was well correlated with SO_4^{2-} at each individual site whereas SO_4^{2-} only correlated well with Ca^{2+} and Mg^{2+} in samples from Mexico City and Guanajuato State.

Nitrate was significantly correlated with NH_4^+, Ca^{2+} and Mg^{2+} in Guanajuato State, but a better correlation with Ca^{2+} was found in Veracruz State and only a positive correlation between NO_3^- and NH_4^- was found in Mexico City.

CONCLUSIONS

The data presented in this paper must be interpreted with caution because we are dealing with bulk precipitation. Samples allowed to remain in the field without cooling or sealing from ambient air, can be expected to undergo significant alterations in their chemical nature (Pratt *et al.* 1984).

Although from these data it is not possible to assume with certainty the sources of the major ions, nevertheless when the rain chemistry data from different ecosystems were compared, it was possible to infer the influence of the emission sources and atmospheric contaminants on the chemical composition of rain.

The high correlation between NH_4^+ and SO_4^{2-} in Veracruz State and Guanajuato State sampling sites may be attributed, at the first site, to the frequent release of ammonia mist from the petrochemical industries and fertilizer production and the SO_2 emissions from fuel-oil combustion, and in the second place to fertilizer production and use, SO_2 emission also from fuel-oil combustion and H_2SO_4 production.

The high correlation found between SO_4^{2+}, Ca^{2+} and Mg^{2+} supports the role of agricultural "dust" as a major source of these cations at the Guanajuato State sampling site while the alkaline particles emitted from cement and lime plants together with the calcareous characteristics of soils in Mexico City Valley may account for the major sources of Ca^{2+} and Mg^{2+} in this area.

The highly polluted atmosphere of Mexico City has an influence upon the chemistry of the rain, because here, the highest concentrations of the ions were found. In like manner the industrial emissions in the vicinity of the sampling site in Salamanca City, contributed to the higher concentrations of SO_4^{2-} and NH_4^{2-} found in rain water respect to the predominantly agricultural areas (Fig. 3) and the zone under the influence of maritime meteorological conditions.

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