

NUTRIENT CONTRIBUTION BY BULK PRECIPITATION TO SOILS IN AN AGRICULTURAL AREA

Armando P. BAEZ, Raúl BELMONT, Gabriel P. BELMONT and Hugo PADILLA

Laboratorio de Química Atmosférica y Estudios del Agua, Centro de Ciencias de la Atmósfera, UNAM, Ciudad Universitaria, Coyoacán, 04510 D.F., México.
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ABSTRACT

Systematic study of the chemical composition of precipitation in a given region allows determination of the precipitation contribution of nutrients to soils. The data were obtained from a rain sampling program at Guanajuato Plains, Guanajuato State, Mexico, one of the most important agricultural areas in Mexico, but in a process of rapid industrialization. The total amount of inorganic N deposited on Bajío Plains, ranged from 6 to 17 Kg/Ha, representing 5.7 to 22.8 % of the urea-N applied during the growing season. With respect to sulfate, the most abundant ion in rain water, the amount deposited by rain represented only 5.4 to 22 % of the total SO_4 as $(\text{NH}_4)_2\text{SO}_4$ applied.

RESUMEN

A través del estudio sistemático de la composición química de la precipitación en una región dada, es posible determinar la contribución de nutrientes que son depositados por la lluvia. En este trabajo se describen los resultados que se obtuvieron por medio de una red colectora de lluvia en la zona del Bajío del Estado de Guanajuato, que es una de las áreas agrícolas más importantes del país, pero que se encuentra en un rápido proceso de industrialización. La cantidad total de N inorgánico depositado en el Bajío fue de 6 a 17 Kg/Ha, representando de 5.7 a 22.8 % del N de urea aplicado durante la época de siembra y crecimiento. Por otro lado, a pesar de que el sulfato fue el ión más abundante en el agua de lluvia la cantidad de S depositado fue solamente de 5.4 a 22 % del SO_4 total del $(\text{NH}_4)_2\text{SO}_4$ que se aplicó durante el periodo de siembra.

INTRODUCTION

There have been previous studies of the inorganic content of rain, motivated by interest originally in crop nutrition and, more recently in the cycling of natural and anthropogenic trace constituents of the atmosphere. Presumably, in the past, the reason that precipitation composition generated little sustained interest was because of the lack of appreciation of its potential effects, beneficial and detrimental for fertilization of crops, forests and aquatic ecosystems which can be eutrophied or otherwise massively altered (acid rain).

One of the beneficial effects of precipitation is the contribution of nutrients to agricultural soils and forest (Eriksson 1963, Chan and Kuntz 1982), since it has been considered that the atmosphere is a source of nutrients. Precipitation inputs are small compared to agricultural amendments, but they are significant in the cycling of these elements in natural ecosystems. Since nutrients are water soluble they go directly into the soil surface where root system is, and consequently the potential availability for plant use is much higher than when these nutrients come from soil and/or rock weathering. It is also important to mention that the limited amounts of N and S brought down by precipitation might be useful to meet the requirements of crops for these elements in areas with a deficiency of N and S (Tabatabai and Laflen 1976). The atmospheric nutrient contribution through wet deposition is relatively constant over time at a given place, but due to their low concentration it is necessary to supply fertilizers for growing crops which need more N and P.

When a systematic study of the chemical composition of precipitation in a given region is carried out, it is possible to determine the contribution of nutrients by precipitation and to evaluate how much more of these nutrients have to be added to specific soils to avoid either over-fertilization or soil degradation. With proper management some expenses in fertilizers could be reduced.

This paper reports the results obtained from a rain sampling program to assess the pH, and concentrations of nutrients $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, K, $\text{SO}_4\text{-S}$ and $\text{PO}_4\text{-P}$, plus Ca and Mg in precipitation over the Bajío Plains, Guanajuato State, to determine the quantities of these nutrients added by precipitation during the rainy season to the land surface.

MATERIAL AND METHODS

Sampling site

The agricultural area for this study is located in Guanajuato State, a region commonly called Bajío Plains, that comprises the counties of Celaya, Salamanca, Irapuato, Sal-

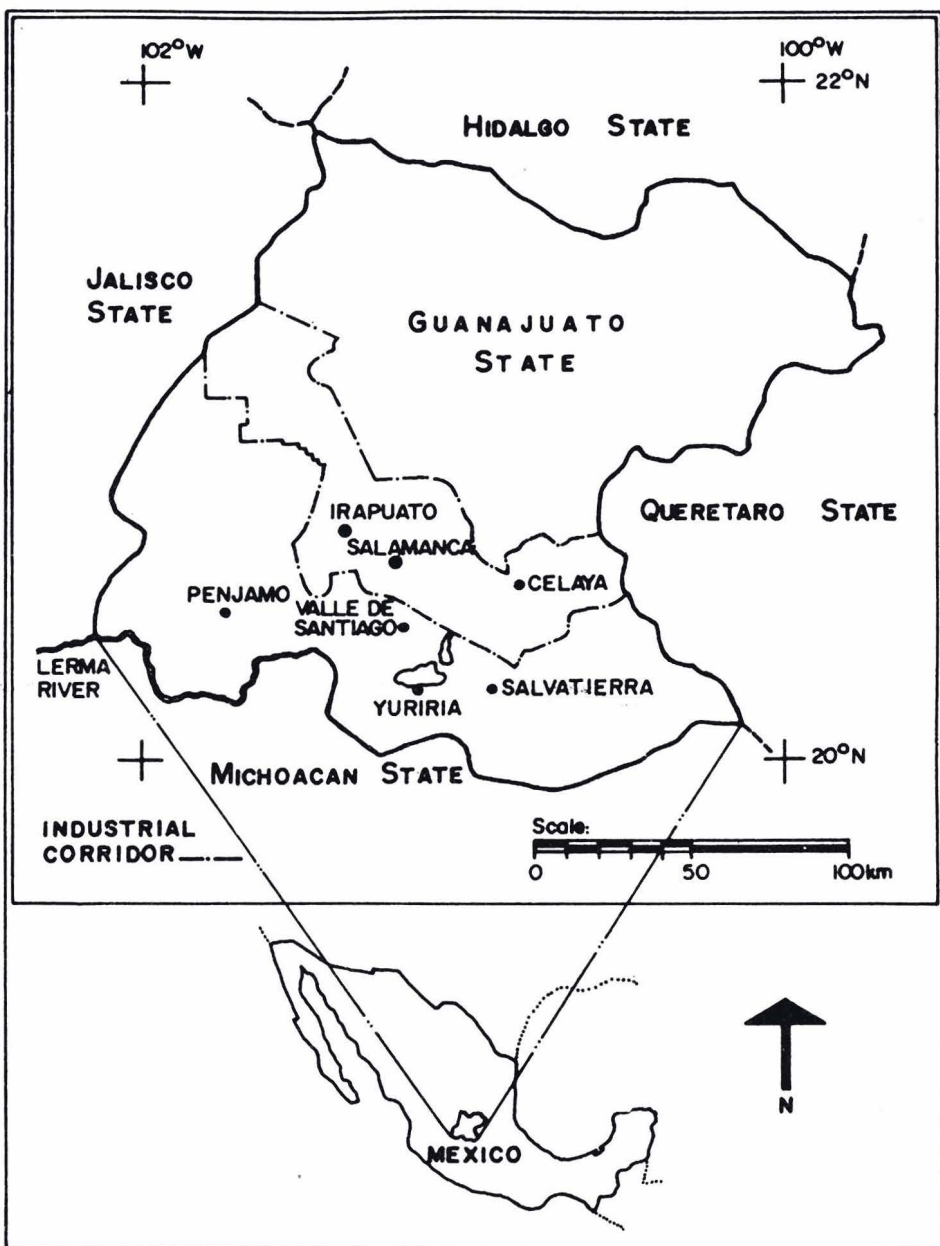


Fig. 1. Sampling site location at Bajio Plains, Guanajuato State, Mexico

vaticerra, Valle de Santiago, Pénjamo and Yuriria, between $100^{\circ} 41' \text{ W}$ and $20^{\circ} 21' \text{ N}$ at 1750 m above sea level (Fig. 1). The climate is subtropical (A_c), with a annual median temperature of 18°C and a median annual rainfall of 640 mm. The rainy season usually begins at the end of May and lasts until the beginning of October. This region is one of the most important agricultural areas of Mexico, but at present is in a process of industrialization. A large industrial corridor has been established between Celaya and Guanajuato cities, that includes a large oil refinery, a fertilizer plant, a fuel-oil-burning thermoelectric power plant (with 3.5 to 4.5 % sulfur content), sulfuric and nitric acid plants, other important petrochemical and chemical industries, and a heavy traffic highway for mainly diesel trucks.

Sample collection

The bulk precipitation samples of this study were collected during May to October 1985, using 24-cm diameter funnels attached to 3-L polyethylene bottles, which were placed inside a polyurethane insulated box, to minimize bacterial growth and evaporation and mounted 1.8 m above ground level at each of the seven sampling sites. Funnels were open to the atmosphere during the collection period.

Before use, all bottles and funnels were thoroughly scrubbed with a brush using detergent and tap water, rinsed with distilled water and finally deionized water. All collectors with the exception of two, were installed in the downtown area on the roofs of buildings, the first of the two others was located at the Meteorological Station of the University of Guanajuato, 6 Km away from Irapuato, on grass covered ground, and the second one on the roof of one of the buildings of an Agricultural School 5 Km from the town of Yuriria. The samples were collected fortnightly, then promptly transported to the laboratory and refrigerated near 4°C until analysis.

Analytical methods

Upon receipt of the samples at the laboratory, volume and pH were determined. A Philips PW 9409 digital pH meter equipped with a Philips combination electrode was used for the pH determinations after a two point calibration with pH 7.00 and 4.00 buffers. The ionic strength of each sample was increased to 0.1 M by addition of KCl (Hansen and Hidy 1982).

Unfiltered samples were used for chemical analysis. Calcium and Mg^{2+} concentrations were determined by flame atomic absorption spectroscopy using a Perkin-Elmer Model 460 atomic absorption spectrophotometer. The other ions were determined by the procedures described in Standard Methods (APHA 1975).

Sulfate was measured turbidimetrically using the precipitation of sulfate as BaSO_4 in excess BaCl_2 . Phosphate ($\text{PO}_4\text{-P}$) and total phosphorus (T-P) were determined by

colorimetry measuring the intensely colored molybdenum blue produced by reduction of heteropoly acid-phosphomolybdic acid by ascorbic acid, for the total phosphorus, each sample was digested prior to phosphate analysis using the persulfate digestion technique.

Nitrate-N was measured by colorimetric measurement of a yellow color produced by the reaction between nitrate and brucine.

Nitrite-N was determined by diazotation with sulfanilamida under acid conditions and coupling with N-(1-naphthyl)-ethylendiamine dihydrochloride to produce a red-dish-purple azo dye which is measured colorimetrically.

Ammonium-N determination was made by means of a colorimetric method with Nessler's reagent. Potassium was determined by flame photometric method. Conductance was not measured.

Analytical procedures were verified by comparison with the USA Environmental Protection Agency quality assurance samples.

Precision and accuracy at low concentrations were determined by blind analysis of standards prepared by chemists not included in this study. Precision and accuracy were determined from seven replicate measurements at two different concentrations of the constituent of interest. The results of these are summarized in Table I.

TABLE I. SUMMARY OF PRECISION AND ACCURACY DATA FOR NO_2^- -N, TOTAL -P, PO_4^- -P AND K^+

<i>Constituent</i>	<i>Concentration mgL⁻¹</i>	<i>Relative standard deviation, %</i>	<i>Relative error %</i>
NO_2^- -N	0.02	11.1	- 10.0
	0.10	11.4	- 4.0
T - P	0.03	10.3	- 3.3
	0.10	5.9	2.0
PO_4^- -P	0.03	11.1	- 10.0
	0.10	6.1	- 1.0
K^+	0.30	10.3	- 3.3
	0.70	4.8	1.4

Blanks (deionized water rinses) were analyzed for the sample collectors and storage bottles. The results indicated concentrations of blanks below the method detection limits.

Duplicate results are given in terms of the standard deviation in Table II, which gives the precision and accuracy obtained for measurements close to the detection limit for each element. Considering the levels measured the range of precision (1.0 to 10.0 %) seems to be satisfactory.

RESULTS AND DISCUSSION

Only bulk precipitation was collected which displays the combined effects of all water soluble airborne components of precipitation. It is considered the most significant phase in studying the contribution of atmospheric mineralization to the chemical quality of rain water. Whitehead and Feth (1964) have reported that bulk precipitation contains 4 to 10 times more mineralization than rain water. Apparently the major portion of this mineralization is derived from the accumulation of dry fallout on the collector.

TABLE II. PRECISION OF DUPLICATE MEASUREMENTS FOR INDIVIDUAL CONSTITUENTS OF BULK PRECIPITATION

Constituent	No. of samples	Range mgL ⁻¹	Mean mgL ⁻¹	Std. dev. of duplicate analysis	Rel. Std. dev. (%)
Ca ²⁺	54	0.20 – 12.4	2.17	0.08	3.69
Mg ²⁺	54	0.02 – 1.30	0.13	0.0127	9.77
K ⁺	54	0.10 – 0.75	0.24	0.008	3.39
NH ₄ -N	54	0.15 – 4.78	1.64	0.06	3.60
NO ₃ -N	54	0.11 – 0.81	0.39	0.028	7.18
NO ₂ -N	54	0.01 – 0.085	0.021	0.002	11.59
SO ₄ ²⁻	54	1.88 – 24.4	6.69	0.19	2.84
PO ₄ -P	52	0.01 – 0.224	0.047	0.0038	8.09
T-P	52	0.01 – 0.230	0.061	0.005	8.19
pH(a)	54	5.44 – 8.13	6.82	0.019	0.28

(a) in pH units

Vet *et al.* (1988) made a comparison measurements of bulk, wet-only and wet-plus-dry deposition at the Turkey Lakes watershed. The four methods were compared for numerical and statistical differences. They found that The Canadian Forestry Service (CFS) bulk deposition measurements were inconsistent with the two wet-only measurements and the other bulk measurements produced higher deposition of soil- and salt-derived ions and lower deposition of acid-related ions, SO₄²⁻ and NO₃⁻.

Reddy and Claassen (1985) made estimates of average major ion concentrations in bulk precipitation at two high-altitude sites, near the continental divide in southwestern Colorado. They found that major ion concentrations for bulk precipitation collected at these sampling sites, showed similar log-normal data distributions, means and standard deviations. Individual concentrations at either site, do not exhibit a systematic deviations from means, with respect to season of ionic components. This uniformity may reflect the absence of significant contributions of local or regional pollutional sources contributing to deposition.

The chemical composition of precipitation is mainly determined by two mechanisms; the capture of contaminants by clouds, condensation of water vapour on condensation nuclei; rainout via cloud liquid water content, and washout via surface volume ratios of rain drops and relation between raindrop size and rainfall rate (Petrenchuck and Selezneva 1970).

The results of distribution and chemical composition of gas-particle aerosol admixtures in various atmospheric layers show that the chemical composition of atmospheric precipitation changes in space and time under the influence of both macrocirculation conditions and local factors that determine air pollution.

Hales (1972) has reported that calculations of precipitation scavenging rate for trace gases in the atmosphere is complicated by a number of factors including reversible sorption behaviour, liquid phase mixing and chemical reactions. The general problem of modelling macrophysical systems in the atmosphere is discussed by Hales and relates this fact to the pertinent microphysical phenomena of droplet-gas interactions.

A model of pollutant scavenging by precipitation applicable to the class substances in which both gaseous and particulate precursors contribute to pollutant's concentrations in precipitation was used by Barrie (1985), as a guidance in regression analysis of several years of observations of daily sulfate and nitrate scavenging ratios (w). The findings of this study were: that w of SO_4^{2-} and NO_3^- bearing particles is inversely proportional to the one third power of the precipitation amount in the event. It includes the effects of location, precipitation amount, precipitation type and in-cloud SO_2 oxidation. These results combined with observations in eastern United States indicated that in eastern North America SO_2 oxidation within a rain storm becomes an increasingly important source of rain SO_4^{2-} as latitude increases.

In Table III are tabulated the volume-weighted mean ionic concentrations and ionic balance for bulk precipitation samples collected at Bajio Plains. In spite of the fact that the zone is relatively small, a variability in the mean concentrations of inorganic components of rain was observed at the seven sampling sites.

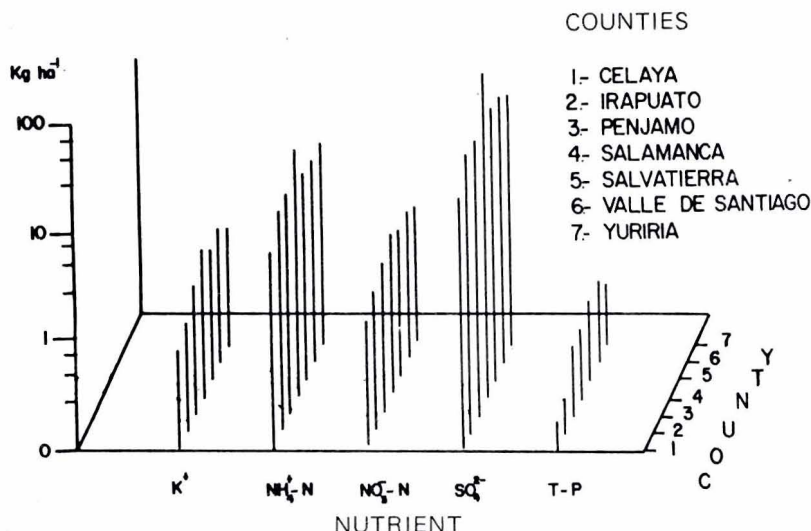


Fig. 2. Comparison of nutrient contribution by bulk precipitation at the seven sampling sites

Correlation coefficients among some bulk precipitation components are given in Table IV. Since statistical analysis indicated that, with a few exceptions, the rain volume was not correlated with concentrations of ions, local emissions are implicated as sources of high concentrations of SO_4^{2-} , $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, Ca^{2+} and Mg^{2+} found in rain water. Figure 2 shows the influence that these local sources have upon the chemistry and variability of precipitation.

Salamanca was precisely the place where the highest contribution of nutrients were brought down by precipitation and it is the zone where more of the most important industries are located, whose main emissions are SO_2 , NH_3 , NO_x , HC and particulate matter. It is possible to infer the contribution that these emissions have upon the chemistry of precipitation in places under the influence of meteorological factors that transport part of these emissions down wind as it was observed in Salvatierra and Valle de Santiago (Fig. 2 and Table III).

The pH was measured at the end of each sampling period (15 days), but the net effect upon the measured pH of dry deposition components in the bulk deposition samples is difficult to determine. Certainly, the dry deposition contribution is geographically and temporally variable, depending on a variety of meteorological and geographically specific factors, yet, certain generalizations can be made. Dry deposition disproportionally contributes alkaline species such as Ca^{2+} , Mg^{2+} and K^+ to bulk deposition. Acidic aerosol particles containing SO_4^{2-} and NO_3^- have a lesser dry contribution. This finding is reasonable since alkaline materials are normally found in

TABLE III. VOLUME-WEIGHTED MEAN CONCENTRATIONS IN mgL^{-1} OF THE CHEMICAL COMPOSITION OF BULK PRECIPITATION COLLECTED AT SEVEN SITES IN GUANAJUATO STATE (BAJO PLAINS) MEXICO

Sampling site		Amount of precipitation (cm)	pH	H^+ ($\times 10^{-3}$)	Ca^{2+}	Mg^{2+}	K^+	NH_4^+N	NO_3^-N	NO_2^-N	SO_4^{2-}	$PO_4^{3-}P$	$T-P$	$\Sigma(+)^{***}$ $\Sigma(-)$	
Celaya (n = 6)	Mean	27.61*	6.16**	0.69	0.71	0.091	0.21	1.68	0.40	0.013	5.79	0.39	0.047	1.09	
	Minimum	2.08	5.75	0.036	0.38	0.050	0.10	0.88	0.33	0.010	3.40	0.010	0.012	-	
	Maximum	8.87	7.44	1.78	1.88	0.330	0.75	4.54	0.56	0.030	13.70	0.214	0.222	-	
Irapuato (n = 8)	Mean	51.45*	6.09**	0.81	0.47	0.046	0.13	1.53	0.29	0.010	5.69	0.022	0.030	0.98	
	Minimum	1.62	5.45	0.20	0.26	0.020	0.10	0.79	0.12	0.010	2.78	0.011	0.014	-	
	Maximum	11.06	6.70	3.55	1.09	0.100	0.25	4.68	0.77	0.020	16.20	0.068	0.070	-	
Salamanca (n = 8)	Mean	52.77*	7.15**	0.071	5.51	0.290	0.32	2.73	0.45	0.040	14.80	0.046	0.057	1.44	
	Minimum	3.51	6.84	0.0078	3.03	0.110	0.16	1.65	0.27	0.020	9.00	0.014	0.024	-	
	Maximum	9.41	8.11	0.14	12.20	1.260	0.56	3.38	0.79	0.080	24.00	0.088	0.095	-	
Salvatierra (n = 8)	Mean	52.36*	6.55**	0.28	1.48	0.074	0.21	1.13	0.32	0.014	4.65	0.028	0.076	1.35	
	Minimum	1.31	6.13	0.040	0.41	0.030	0.10	0.70	0.16	0.010	3.30	0.010	0.034	-	
	Maximum	12.76	7.40	0.74	6.85	0.270	0.65	2.68	0.93	0.060	11.50	0.055	0.160	-	
Valle de Santiago (n = 8)	Mean	56.68*	6.89**	0.13	1.94	0.120	0.22	0.96	0.32	0.015	4.15	0.062	0.072	1.55	
	Minimum	2.00	6.53	0.038	0.86	0.070	0.11	0.15	0.12	0.010	3.24	0.010	0.010	-	
	Maximum	13.26	7.42	0.29	5.60	0.350	0.65	1.99	0.52	0.040	6.40	0.174	0.210	-	
Ponjamo (n = 8)	Mean	51.44*	6.88**	0.13	1.78	0.100	0.21	1.55	0.35	0.016	5.23	0.050	0.060	1.52	
	Minimum	2.99	6.55	0.043	0.42	0.060	0.12	1.04	0.19	0.010	2.93	0.020	0.032	-	
	Maximum	10.64	7.37	0.28	4.49	0.220	0.42	2.16	0.55	0.030	8.50	0.116	0.128	-	
Yuriria (n = 8)	Mean	53.07*	6.40**	0.40	0.41	0.066	0.17	1.01	0.27	0.010	3.04	0.041	0.052	1.18	
	Minimum	1.02	6.12	0.10	0.20	0.030	0.10	0.50	0.13	0.010	1.90	0.019	0.026	-	
	Maximum	17.89	7.00	0.76	0.85	0.130	0.29	1.75	0.63	0.020	4.91	0.130	0.132	-	

* Total amount of precipitation to collected from May to October; ** Calculated from the corresponding H^+ value; *** Calculated from the concentrations in mgL^{-1}

suspended soil dust. These particles are relatively large and are efficiently collected by the bulk deposition samplers.

Acidic species frequently occur in smaller particles which are less efficiently collected and contribute a smaller fraction of total dry deposition mass than the larger particles. Thus the pH of bulk deposition samples is probably normally higher than wet-only samples (Hansen and Hidy 1982, Parkhurst *et al.* 1980, Galloway and Likens 1976).

Hansen and Hidy (1982), reported that precipitation samples of pH values greater than about 4.5 often have very low ionic strengths approaching those of distilled water.

The measured pH of distilled water using a good pH meter can be up to 0.2 units higher than that obtained when ionic strength is increased to 0.1 M by addition of KCl. The lower pH is probably more representative of the true acidity in samples having a pH between 5.5 and 7.0. For the determination of pH all samples were raised to a uniform value by addition of KCl to increase the ionic strength to 0.1 M and pH was measured in quiescent solution to eliminate error due to residual streaming potential.

The main conclusion on the influence of dry fallout on the composition of bulk precipitation is that inclusion of dry fallout introduces a complexity in the investigation of precipitation chemistry. It has a definite effect on the measured composition of rain which be seasonal and varies with each element. Bulk deposition should be used when

TABLE IV. SIMPLE CORRELATION COEFFICIENTS (r) FOR PAIRED RELATIONSHIPS OF SOME CHEMICAL PROPERTIES OF BULK PRECIPITATION AT BAJIO PLAINS, GUANAJUATO STATE MEXICO

Relationship	Celaya ($n=6$)	Irapuato ($n=8$)	Salamanca ($n=8$)	Valle de Santiago ($n=8$)	Salvatierra ($n=8$)	Penjamo ($n=8$)	Yuriria ($n=8$)
SO ₄ : NH ₄ N	0.992 ^a	0.990 ^a	-0.335	0.720 ^b	0.960 ^a	0.927 ^a	0.772 ^b
SO ₄ : K	0.965 ^a	0.690	0.838 ^a	0.924 ^a	0.850 ^a	0.420	0.405
SO ₄ : Ca	0.899 ^b	0.782 ^b	0.833 ^b	0.704	0.871 ^a	-0.141	0.437
SO ₄ : Mg	0.971 ^a	0.524	0.694	0.867 ^a	0.867 ^a	0.120	0.470
SO ₄ : Rain	-0.355	-0.293	-0.564	-0.432	-0.655	-0.447	-0.305
NO ₃ N: NH ₄ N	-0.071	0.699	-0.538	0.854 ^a	0.957 ^a	-0.288	0.617
NO ₃ N: K	-0.138	0.558	0.528	0.712 ^b	0.822 ^b	0.600	0.130
NO ₃ N: Ca	0.225	0.861 ^a	0.181	0.511	0.911 ^a	0.858 ^a	0.088
NO ₃ N: Mg	-0.176	0.888 ^a	0.806 ^b	0.677	0.911 ^a	0.781 ^b	0.696
NO ₃ N: Rain	-0.179	0.857 ^a	-0.025	-0.461	0.854 ^a	-0.589	-0.407
NH ₄ N: Rain	-0.326	0.381	-0.247	-0.385	-0.749 ^b	-0.483	-0.425
Ca : Mg	0.869 ^b	0.790 ^b	0.363	0.925 ^a	0.986 ^a	0.752 ^b	0.325
Ca : Rain	-0.648	-0.767 ^b	-0.663	-0.887 ^a	-0.851 ^a	-0.556	-0.822 ^b
Mg : Rain	-0.368	-0.857 ^a	-0.206	-0.712 ^b	-0.845	-0.663	-0.265

Figures in parenthesis are the number of samples; ^a Significant at 0.01 level; ^b Significant at 0.05 level.

this information is required (Galloway 1978). Bulk deposition is a better indicator of total loading than is wet-only deposition.

Table III shows that ion balance was good in spite of the fact that Na⁺, Cl⁻ and HCO₃⁻ were not considered. These ions were not determined because the object of this study was focused to nutrients.

The correlation coefficients for some paired relationships are shown in Table IV. With the exception of Salamanca, very good correlation was obtained between SO₄²⁻ and NH₄-N. The correlation between SO₄²⁻ and Ca²⁺, Mg²⁺ and K⁺ varied from good to very poor in all sampling sites except Celaya.

NO₃-N was well correlated with NH₄-N in Salvatierra and Valle de Santiago, both

places showed similar means and both are rural areas with not industries in the vicinity. $\text{NO}_3\text{-N}$ also correlated well with Ca^{2+} and Mg^{2+} in Irapuato and Salvatierra, but the correlation of this ion with K^+ , Ca^{2+} , Mg^{2+} and $\text{NH}_4\text{-N}$ also varied from good to very poor in the remaining sampling sites. No correlation or very poor but negative correlation was found between rain amount and the analysed ions in all sampling sites except Salvatierra, but rain amount correlated well with $\text{NO}_3\text{-N}$ and well and negative with Ca^{2+} and Mg^{2+} in Irapuato and Valle de Santiago.

The major ion concentrations for bulk precipitation collected at the seven sampling sites showed deviations from means with respect to ionic components between sampling sites. The lack of uniformity may reflect the significant contribution of local pollution, agricultural or soil sources. The distribution and chemical composition of gas-particle aerosol in the atmospheric layers can change the chemical composition of precipitation in time and space under the influence of both, circulation conditions and local factors that determine air pollution (Petrenchuk and Selezneva 1970).

Variation in the correlation coefficients may be attributed to the variability in ionic concentrations between the sampling sites. The very good correlation between SO_4^{2-} and $\text{NH}_4\text{-N}$ indicates the probability that SO_4^{2-} is mainly associated with ammonium, but this probability does not exclude the possibility that SO_4^{2-} could be also associated in a lesser or major degree with K, Ca and Mg.

Fertilizer production and use, animal urine, and soil biological reactions are the sources of atmospheric ammonia in the Bajío Plains. Sulfur dioxide emissions from fuel-oil combustion and H_2SO_4 production are the major sources of SO_4^{2-} in this area. The distance over which SO_2 emission influence the atmospheric chemistry is great (several hundreds of Km, Barnes 1979). The high correlation between Ca and Mg supports the role of agricultural "dust" as a major source of these cations.

Table V shows the amount of nutrients deposited by bulk precipitation. In order to calculate the contribution of these nutrients the rainfall rate for the studied period was used.

The total amount of inorganic N ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N} + \text{NO}_2\text{-N}$) deposited by rain ranged from 6 Kg/Ha in Celaya to 17 Kg/Ha in Salamanca. The contribution of $\text{NO}_2\text{-N}$ was negligible in the whole area and ranged from 0.04 to 0.21 Kg/Ha (average 0.08 Kg/Ha). The data indicates that the predominant form of inorganic N deposited in the seven sampling sites, was $\text{NH}_4\text{-N}$ that averaged 7.37 Kg/Ha. On the other hand, the amount of inorganic N deposited by precipitation represented 5.7 % to 22.8 % of the urea-N applied during the growing season and for the type of crops (Table VI).

The T-P and K^+ deposited was relatively small; 0.13 to 0.41 Kg/Ha and 0.58 to 1.69 Kg/Ha respectively. Although SO_4^{2-} was the most abundant ion in rain water the amount

TABLE V. TOTAL CONTRIBUTION OF NUTRIENTS (Kg ha^{-1}) BY BULK PRECIPITATION IN THE BAJIO PLAINS DURING THE RAINY SEASON OF 1985

Sampling site	K	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	$\text{NO}_2\text{-N}$	SO_4	TOTAL P
Celaya	0.58	4.64	1.10	0.04	16.0	0.13
Irapuato	0.67	7.87	1.49	0.05	29.3	0.15
Salamanca	1.69	14.41	2.37	0.21	78.1	0.30
Salvatierra	1.10	5.92	1.68	0.07	24.3	0.40
Valle de Santiago	1.25	5.44	1.81	0.09	23.5	0.41
Penjamo	1.08	7.97	1.80	0.08	26.9	0.31
Yuriria	0.90	5.36	1.43	0.05	16.1	0.28
TOTAL	7.27	51.61	11.68	0.59	214.2	1.98
AVERAGE	1.04	7.37	1.67	0.08	30.6	0.28

of S brought down by precipitation represented only 5.4 to 22 % of the total S as $(\text{NH}_4)_2\text{SO}_4$ applied as fertilizer to specific crops and averaged in the whole area 10.12 Kg/Ha during the rainy season.

If these percentages are considered it seems possible to assume that for crops such as beans, sorghum and maize some reduction in the application of urea and $(\text{NH}_4)_2\text{SO}_4$, could be made. For beans 2.3 % of N and 2 % of S are deposited by rain and for sorghum and maize 11.4 % N and 10.9 % S are the amounts deposited, these contributions are smaller but even they could be taken into account.

It is necessary to emphasize that the input of nutrients reported in this study corresponds only to bulk precipitation collected during four and half months, the rainy season in the region. Dry deposition was only measured to the extent that it was collected in the bulk samples, and deposition was not measured at all during the remaining months. It has been reported that the importance of dry fallout of inorganic compounds contribute significantly to the total percentage of N, S, T-P and K deposited annually (Tabatabai and Lafen 1976).

In a comparative study of the chemical composition of the wet precipitation in three different zones of Mexico, Baez and Belmont (1987) have shown the influence that atmospheric pollution has upon the chemistry of rain. The results indicated that the highest concentrations of ions were found in samples collected in Mexico City, which is

TABLE VI. AMOUNTS OF FERTILIZERS APPLIED IN BAJIO PLAINS GUANAJUATO STATE, DURING THE GROWING SEASON

<i>Crop</i>	<i>Fertilizer</i>	<i>Quantity of applied fertilizer KgHa⁻¹</i>	<i>Equivalents N</i>	<i>amounts P</i>	<i>KgHa⁻¹ K</i>	<i>S*</i>
Bean	a) Urea - TSP	87 - 130	40	26	0	—
	b) (NH ₄) ₂ SO ₄ -OSP	195 - 300	40	26	0	47
Sorghum	a) Urea - TSP	174 - 87	80	17	0	—
	b) (NH ₄) ₂ SO ₄ -OSP	390 - 200	80	17	0	94
	c) Anhydrous ammonia - TSP	87 - 98	80	17	0	—
Maize	a) Urea - TSP	174 - 87	80	17	0	—
	b) (NH ₄) ₂ SO ₄ -OSP	390 - 200	80	17	0	94
Oat and barley	a) Urea - TSP	217 - 109	100	22	0	—
	b) (NH ₄) ₂ SO ₄ -OSP	488 - 256	100	22	0	118
Strawberry	a) Urea - TSP - KCI	348 - 174 - 100	160	35	50	—
	b) (NH ₄) ₂ SO ₄ -OSP-K ₂ SO ₄	780 - 410 - 120	160	35	50	189
	c) Urea -TSP-C, 17	217 - 43 - 353	160	35	50	—

TSP - Triple superphosphate; OSP - Ordinary superphosphate; C, 17 - Complex 17%N, 17% P₂ O₅ 17% K; * Sulfur from (NH₄)₂ SO₄

characterized by a highly polluted atmosphere. The volume-weighted mean SO₄²⁻ concentrations was 220 µeq/L in comparison with 63.3 µeq/L found in Yuriria (rural area), in Bajio Plains, Guanajuato State and 109 µeq/L in Minatitlan-Coatzacoalcos area, Veracruz State, zone although affected by emissions from the petrochemical complex and the oil refinery, is under the influence of maritime meteorological conditions.

It is possible to assume that with greater emissions of SO₂ and NO_x an increase of nutrients S and N brought down by precipitation could be expected, although the total input of nutrients from this source are small compared to agricultural amendments.

The authors have considered the need to evaluate the total nutrient input of both wet and dry deposition during the entire year.

It is important to consider the possibility that the input of the nutrients S and N could be decreased if the industrial control of the emissions of SO₂ and NO_x takes place, since at present laws and regulations have been enacted by the Mexican Government.

Future evaluations of dry and wet deposition have to be made in order to estimate an appropriate management of fertilizers in the studied zone.

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REFERENCES

- APHA (1975). Standard Methods for the Examination of Water and Wastewater. 14th Ed. Am. Public. Health Assoc. Washington, D. C.
- Báez P. A. and Belmont D. R. (1987). Comparative study of the chemical composition of rain of three different zones in Mexico. *Contam. Ambient.* 3, 25-36.
- Barnes S. D. (1979). The Lagrange transport of air pollution. A review of the European experience. *J. Air Pollut. Control Assoc.* 29, 1219-1235.
- Barrie L. A. (1985). Scavenging ratios, wet deposition, and in-cloud oxidation: an application to oxides of sulphur and nitrogen. *J. Geophys. Res.* 90, 5789-5799.
- Chan C. H. and Kuntz K. W. (1982). Lake Ontario, atmospheric deposition 1969-1978. *Water, Air, Soil Pollut.* 18, 83-99.
- Eriksson E. (1963). The yearly circulation of sulfur in nature. *J. Geophys. Res.* 68, 4001-4008.
- Galloway J. N. and Likens G. E. (1976). Calibration of procedures for determination of precipitation chemistry. *Water, Air, Soil Pollut.* 16, 2107-2126.
- Galloway J. N. (1978). The collection of precipitation for chemical analysis. *Tellus* 30, 71-82.
- Hales J. M. (1972). Fundamentals of the theory of gas scavenging by rain. *Atmos. Environ.* 6, 635-659.
- Hansen D. A. and Hidy G. M. (1982). Review of questions regarding rain acidity data. *Atmos. Environ.* 16, 2102-2126.
- Parkhurst W. J., Bittman R. M. and Kelly J. M. (1980). Atmospheric wet/dry deposition measurements and variability. Meeting of Air Pollut. Control Assoc. Montreal. Paper 80-712.
- Petrenchuk O. P. and Selezneva E. S. (1970). Chemical composition of precipitation in regions of the Soviet Union. *J. Geophys. Res.* 75, 3629-3633.
- Reddy M. M. and Claassen C. H. (1985). Estimates of average major ion concentrations in bulk precipitation at two high-altitude sites near the Continental Divide in southwestern Colorado. *Atmos. Environ.* 19, 1199-1203.
- Tabatabai M. A. and Laflen J. M. (1976). Nutrient content of precipitation over Iowa. *Water, Air, Soil Pollut.* 6, 361-373.
- Vet J. R., Sirois A., Jeffries S. D., Semkin R. G., Foster W. N., Haslett P. and Chan C. H. (1988). Comparison of bulk wet-only, and wet-plus-dry deposition measurements at the Turkey Lakes watershed. *Can. J. Fish. Aquat. Sci.* 45, 26-37.
- Whitehead H. C. and Feth J. H. (1964). Chemical composition of rain, dry fall-out and bulk precipitation at Menlo Park, California 1957-1959. *J. Geophys. Res.* 69, 3319-3333.