Trends in Chemical Composition of Wet Precipitation in Mexico City, Mexico: 1992–2007

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Abstract: This paper presents the results of a study of variation in the chemical composition of wet precipitation over a 16-year period. The ions SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, Mg^{2+} K^+, Na^+, NH_4^+ and H^+ were analyzed. The correlation analysis showed a high positive correlation among these ions, indicating that anthropogenic emissions were the most important source. Trends in annual concentrations of SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Mg^{2+}, Ca^{2+}, K^+, H^+ and alkalinity as function of time were calculated using a linear least-square regression of the volume weighted mean concentrations of these ions in rainwater collected over a 16-year period. Sulfate (SO_4^{2-}) in wet precipitation showed a significant decreasing trend, corresponding to the reduction in SO_2 emissions in the Mexico City valley due to the change from oil to gas fuel in thermoelectric power plants and heavy and medium sized industries. In spite of the fact that the number of motor vehicles has risen considerably in Mexico City, NO_3^- did not show a significant increasing trend. The NH_4^+/Ca^{2+} ratio showed a nearly significant increasing trend, due mainly to the significant decrease in Ca^{2+} concentration. This decreasing trend was not as marked as that of SO_4^{2-}. The contribution of NH_4^+ to neutralization was relatively small, showing only a non significant increase in NH_4^+ over the study period, while a considerable decreasing SO_4^{2-} trend occurred, which could mean that part of the NH_4^+ ions reacted with other ions, forming ammonium compounds.

Keywords: Chemical composition of rain, Trend analysis, Neutralization, Mexico.

1. INTRODUCTION

Numerous studies have reported on temporal trends in the chemical composition of precipitation in Europe [1-4], North America [5-8], Mexico [9], China [10], Japan [11, 12] and India [13].

In most of these studies, a decreasing trend in SO_4^{2-} concentration was found; this decrease was explained in most of the studies by a reduction in SO_2 emissions. Seto *et al*. [12] reported a decreasing trend in non-sea-salt (nss) SO_4^{2-} concentrations with an annual mean change of 3% year^{-1}, while no significant trends were detected for NO_3^- at 59% of study sites. Aherne and Farrell [3], using a least-squares regression analysis, found slight decreasing trends in precipitation concentrations for SO_4^{2-} (20%), NO_3^- (13%), H^+ (24%) and NH_4^+ (15%) in Ireland over the period 1991–1998. Jun Tu *et al*. [10] reported a significant decreasing trend in SO_4^{2-} due to abatement strategies for SO_2, while a significant increasing trend was found in the concentration of NO_3^-. Studies have been made of the chemical composition of precipitation over extended intervals to detect changes caused by an increase in human activities. Precipitation has unique scavenging properties; in other words, it is one of the most important mechanisms for washing the atmosphere, and analysis has yielded valuable data concerning nutrients and toxic inputs to terrestrial and aquatic systems [14-17].

Studies on the chemical composition of wet precipitation have been carried out in several regions of Mexico [9, 18-20]. These data plus unpublished data from 1992 to 2007 (a total of 16 years) on the chemical composition of rain in Mexico City were used in the present study to determine SO_4^{2-}, NO_3^-, Cl^-, H^+, pH, NH_4^+ Ca^{2+}, Mg^{2+}, K^+ and alkalinity trends.

One of the most important objectives was to determine the concentration variation through the years, particularly of the ions SO_4^{2-}, NO_3^- and NH_4^+ because the first two are responsible for rain acidity, while NH_4^+ is one of the principal neutralizing ions.

2. METHODS

2.1. Sampling Site

Mexico City is one of the largest urban areas of the world with a population of around 22 million in the metropolitan area and some 30 thousand large, medium and small industrial complexes. The city also has one of the most polluted atmospheres in the world in spite of laws and regulations to control air pollution.

Wet-only precipitation samples were collected in Mexico City on the roof of the Centro de Ciencias de la Atmósfera (Atmospheric Science Center) at the Universidad Nacional Autónoma de México on a daily basis from 1992 to 2007 during the rainy season in Mexico City (from May to mid-October), with an automatic wet/dry precipitation collector (Andersen, General Metal Works, Inc) into a standard high-density polyethylene bucket. Only samples above 2 mm were analyzed. After collection, the buckets were tightly

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sealed with polyethylene covers and sent to the Centro de Ciencias de la Atmósfera laboratories for chemical analysis.

2.2. Chemical Analysis

Rain samples were filtered through a 0.45 µm Millipore membrane leached with deionized water before chemical analysis. The pH was measured within 24 h of the arrival of samples to the laboratory. Nitrate (NO_3^-), chloride (Cl^-) and sulfate (SO_4^{2-}) were analyzed by non-suppressed ion chromatography with a Perkin Elmer liquid chromatograph equipped with an isocratic 250 LC pump, and a Conducto-Monitor III conductivity detector and Hamilton PRPX-100 analytical anion column. Ammonium (NH_4^+) was analyzed by suppressed chromatography with a Hamilton PRPX-200 analytical cation column. Calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+) were analyzed by flame atomic absorption spectroscopy with a Perkin Elmer 460 from 1992 to 1993 and a GBC 932AA double beam atomic absorption spectrophotometer at 422.7 nm from 1994 to the end of the study. Deuterium and hollow cathode lamps were used for background correction and analysis. High-purity standards were used as calibration standards for each ion. The analytical methods used are described fully by the authors in previous published papers [9, 18-20]. Alkalinity was determined using the Gran titration method with an Orion 960 autochemistry system, and bicarbonate (HCO_3^-) concentrations were calculated using the equation described by Stumm and Morgan [21].

Calibration standards were prepared from certified standards for each ion (High-Purity Standards traceable from the National Institute of Standards and Technology, NIST). The detection limits in mg l^{-1} were: 0.22, 0.04, 0.31, 0.002, 0.006, 0.01, 0.002, and 0.05 for SO_4^{2-}, Cl^-, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+, respectively.

2.3. Quality Control

Precision and bias of analysis were determined from quality control check samples prepared in the laboratory. Ten replicate measurements of each ion were made. The precisions (standard deviations) were 0.071, 0.026, 0.02, 0.005, 0.014, 0.067, 0.006 and 0.032 mg l^{-1} for SO_4^{2-}, Cl^-, NO_3^-, Na^+, K^+ Ca^{2+}, Mg^{2+} and NH_4^+, respectively. The biases, in the same order, were 0.02, -0.01, -0.007, 0.005, -0.015, 0.04, 0.005 and 0.031 mg l^{-1}.

The quality of analysis of each sample was checked using all ions analyzed for ion balance and specific conductance calculations defined by Peden *et al.* [22].

2.4. Statistical Analysis

The least-squares regression analysis was carried out to estimate the trend from ion concentrations, fractional acidity (FA), NP/AP, NH_4^+/Ca^{2+}, SO_4^{2-}/NO_3^- ratios, sum of acidifying and the sum of neutralizing components. The linear regressions were evaluated using the analysis de variance (ANOVA) and the correlation coefficient r.

3. RESULTS AND DISCUSSION

Table **1** shows the volume weighted mean concentrations (VWMC), standard deviation of VWMC (SDVWMC) and annual rain amounts for 1992–2007. A large variability between years can be observed in rain amounts and H$^+$

values. Concentrations of H$^+$ decreased from 25.2 to 1.40 µeq l^{-1} (pH values increased from 4.60 to 5.85). Small variations in NH_4^+ concentration occurred, moreover, was the most abundant ion, with a total average of 90.3 µeq l^{-1}, followed by SO_4^{2-} (65.6 µeq l^{-1}), NO_3^- (44.6 µeq l^{-1}), Ca^{2+} (38.1 µeq l^{-1}), Cl^- (9.4 µeq l^{-1}), Na^+ (5.6 µeq l^{-1}), Mg^{2+} (3.9 µeq l^{-1}) and K^+ (2.5 µeq l^{-1}).

3.1. Correlation Analysis

Table **2** shows the Pearson matrix of correlation coefficients of the correlations among ion concentrations. High correlations and significant correlations at p<0.05 of SO_4^{2-} with NO_3^-, Ca^{2+}, Mg^{2+} and NH_4^+ and significant correlations (p<0.05) of SO_4^{2-} with Na^+ and K^+ were found. and significant correlations (p<0.05) among NO_3^-, Na^+, K^+, Ca^{2+} and Mg^{2+} were found, suggesting that these ions could have the same anthropogenic origin. The highest correlation was between Ca^{2+} and Mg^{2+} followed by NO_3^- and NH_4^+. Although Ca^{2+} is mainly of crustal origin, it is also emitted in large amounts by lime, cement and brick factories. The correlation coefficient (r), a number between -1 and +1, is used to quantify the strength of the relationship between two variables; p is the probability of being wrong when asserting that a true difference exists. Had been widely accepted that there are difference statically significant when p<0.05 [23].

In Mexico City, SO_2 is emitted by ore processing and industrial fuel oil combustion. NO_2 is produced by combustion processes and motor vehicle exhaust. Both pollutants are oxidized to the respective acids in the atmosphere.

More than 98% of SO_4^{2-} had non-sea-salt (nss) sources, because Mexico City is located 400–450 km from the Gulf of Mexico and the Pacific Ocean coast in a valley at 2200 masl (meters above sea level). The concentration of non-sea-salt sulfate was calculated using the equation defined by Keene et al. [24]:

$$SO_4^{2-}{}_{nss} = SO_4^{2-}{}_{nss} - \left(\frac{SO_4^{2-}}{Cl^-} \right)_{sw} \times Cl^-_{rs}$$

where Cl^- was considered the reference species and $SO_4^{2-}{}_{nss}$ is the concentration of sulfate due to non-sea-salt sources; $SO_4^{2-}{}_{rs}$ is the concentration of sulfate observed in the rainwater sample; $\left(\frac{SO_4^{2-}}{Cl^-} \right)_{sw}$ is the ratio of the concentrations of sulfate and chloride in seawater, and Cl^-_{rs} is the concentration of chloride observed in the rainwater sample.

Hydrogen ion concentration correlated positively with SO_4^{2-} and NO_3^- and negatively with Ca^{2+}. The nitric and sulfuric acids are the main H$^+$ donor species, and neutralization reactions between soil particles and acids in rainwater are less significant. Rainfall amounts correlated negatively with all ions except H$^+$, indicating that heavy rains lower the concentrations of ions but raise rainwater acidity. Both Ca^{2+} and Mg^{2+} showed strong correlations with alkalinity, indicating the formation of calcium and magnesium carbonates, possibly originating from fine clay

Table 1.   Volume Weighted Means Concentrations (VWMC) ± Standard Deviation of the VWMC (SDVWMC) in µeq l^{-1} in Rainwater Collected at Mexico City from 1992 to 2007

Year	SO_4^{2-}	Cl^-	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	H^+	Alkalinity	pH	Rain Amount (mm)
1992 (N = 29)	70.2±9.7	NA	26.8±4.6	NA	NA	27.2±3.2	3.1±0.4	60.0±7.0	17.7±5.8	NA	4.75	482.7
1993 (N = 29)	61.1±8.1	5.7±0.7	35.1±5.7	5.8±0.8	2.5±0.4	43.1±6.9	4.5±0.7	75.6±8.2	7.9±3.6	29.3±5.7	5.10	305.0
1994 (N = 30)	95.1±15.4	8.1±1.0	45.6±6.5	5.5±0.7	3.0±0.6	35.7±7.3	5.7±0.7	112±17.6	6.5±2.6	19.3±3.9	5.19	337.0
1995 (N = 36)	68.4±11.8	5.7±0.9	39.3±7.4	3.5±0.5	2.3±0.5	37.0±6.6	3.9±0.8	76.2±10.6	14.4±4.6	17.2±4.5	4.84	535.9
1996 (N = 28)	96.1±12.7	15.5±4.1	66.4±12.6	8.5±2.0	3.7±0.8	52.2±8.2	6.9±1.2	101±14.8	25.2±10.4	11.6±4.8	4.60	347.6
1997 (N = 36)	78.5±8.1	14.2±4.0	48.6±6.5	8.3±1.4	4.0±0.5	53.0±7.4	6.1±0.9	96.2±11.6	9.3±3.8	39.3±12.5	5.03	378.9
1998 (N = 31)	69.7±19.7	12.0±4.0	40.2±12.5	3.9±0.7	2.4±1.0	22.6±4.4	2.3±0.4	90.5±18.6	17.7±7.4	13.9±3.7	4.75	498.8
1999 (N = 20)	57.2±9.8	8.6±1.5	41.8±8.3	10.3±2.4	4.5±1.2	55.5±12.8	6.3±1.8	104±17.2	1.4±0.5	54.6±11.5	5.85	216.7
2000 (N = 39)	53.9±10.2	7.8±1.2	47.8±10.7	4.8±1.1	1.8±0.3	31.6±5.6	3.3±0.5	90.5±15.7	12.8±6.1	26.0±6.2	4.89	465.8
2001 (N = 29)	62.0±11.3	8.6±1.1	41.3±7.3	3.7±1.5	2.8±1.7	30.3±10.5	2.1±0.8	94.3±15.0	8.2±2.3	29.2±13.2	5.09	400.0
2002 (N = 27)	63.1±10.2	7.4±0.9	49.0±8.7	11.6±3.4	1.9±0.5	25.9±9.9	2.9±0.9	92.1±10.4	11.2±3.9	27.3±9.5	4.95	347.8
2003 (N = 35)	47.6±5.7	10.0±1.9	47.8±8.8	4.1±0.7	1.6±0.2	33.6±5.4	2.8±0.4	94.1±11.9	6.1±2.5	25.4±5.0	5.21	448.9
2004 (N = 42)	58.4±6.6	11.7±1.9	58.9±7.2	5.0±0.7	2.1±0.2	38.3±4.5	3.5±0.4	104±11.1	7.9±2.7	24.2±4.6	5.10	386.1
2005 (N = 37)	57.9±15.2	8.3±1.6	39.0±9.1	3.2±0.4	1.4±0.2	23.8±5.1	2.3±0.5	81.0±15.9	12.2±4.7	11.2±2.9	4.91	497.3
2006 (N = 27)	57.1±12.0	7.7±1.5	38.7±5.6	3.4±0.7	1.7±0.3	42.5±11.6	3.4±0.8	90.1±17.5	5.9±2.1	27.0±8.3	5.23	348.3
2007 (N = 37)	53.7±7.0	9.4±1.6	47.5±6.7	2.7±0.6	1.7±0.4	38.6±5.6	3.3±0.6	83.0±8.3	6.0±1.4	16.0±5.4	5.22	528.6
Average 1992-2007	65.6	9.4	44.6	5.6	2.5	38.1	3.9	90.3	10.6	24.8	4.97	408.2

NA: Not analyzed.

particles of calcite and dolomite as reported by Saxena *et al*. [25] and Noguchi and Hara [26]. Significant correlations were observed between Ca^{2+} and all ions except H^+. Due to the geographical location of Mexico City, there are no contributions from marine components; a partial crustal origin is also suggested.

Fig. (**1**) shows a significant correlation between the sum of acidifying ions ([SO_4^{2-}] + [NO_3^-] + [Cl^-]) and the sum of

neutralizing components ([Ca^{2+}] + [NH_4^+] + [Mg^{2+}] + [K^+]). This could explain the fact that pH was higher than in other areas of the world and support the fact that the acidity of the precipitation was neutralized by alkaline particles and NH_4^+ [10].

3.2. Acidifying and Neutralizing Components

It is known that the acidity of rain is controlled mainly by strong acids, e.g. H_2SO_4 and HNO_3 [27]. Sulfates and NO_3^-

Table 2.   Pearson Correlation among Ion Concentrations (µeq l^{-1}) and Amount of Rain (mm) in Wet Precipitation Collected in Mexico City from 1992 to 2007

Variables	Cl^-	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	H^+	Alkalinity	Amount of Rain
SO_4^{2-}	0.383	**0.637**	0.377	**0.483**	**0.662**	**0.654**	**0.699**	0.247	0.113	-0.204
Cl^-		0.288	0.386	**0.451**	0.373	**0.443**	0.304	0.048	0.129	-0.166
NO_3^-			0.340	0.339	**0.483**	**0.496**	**0.763**	0.372	0.074	-0.216
Na^+				**0.523**	**0.558**	**0.689**	**0.399**	-0.081	**0.489**	-0.214
K^+					**0.634**	**0.736**	**0.384**	-0.092	**0.424**	-0.192
Ca^{2+}						**0.898**	**0.655**	-0.159	**0.703**	-0.249
Mg^{2+}							**0.609**	-0.113	**0.615**	-0.262
NH_4^+								-0.008	**0.426**	-0.292
H^+									-0.336	0.073
Alkalinity										-0.188

Marked correlations in bold are significant at p<0.05; Number of samples = 513.
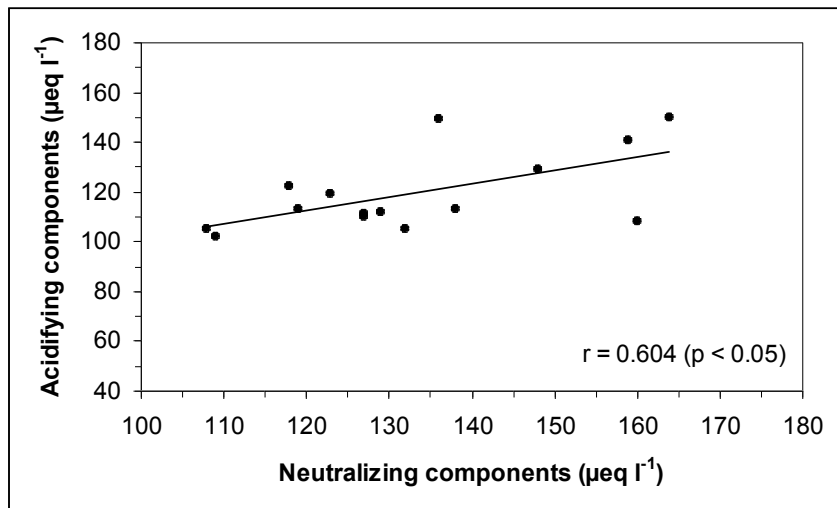N = 483 for correlations of Cl^-, Na^+ and K^+ with the other ions.

Fig. (1). Correlation between the sum of acidifying ions and the sum of neutralizing components.

are the main acidifying components of rain and enable fractional acidity (FA), FA = $[H^+]/([SO_4^{2-}] + [NO_3^-])$ to be calculated [28]. If the ratio is one, it is considered that the

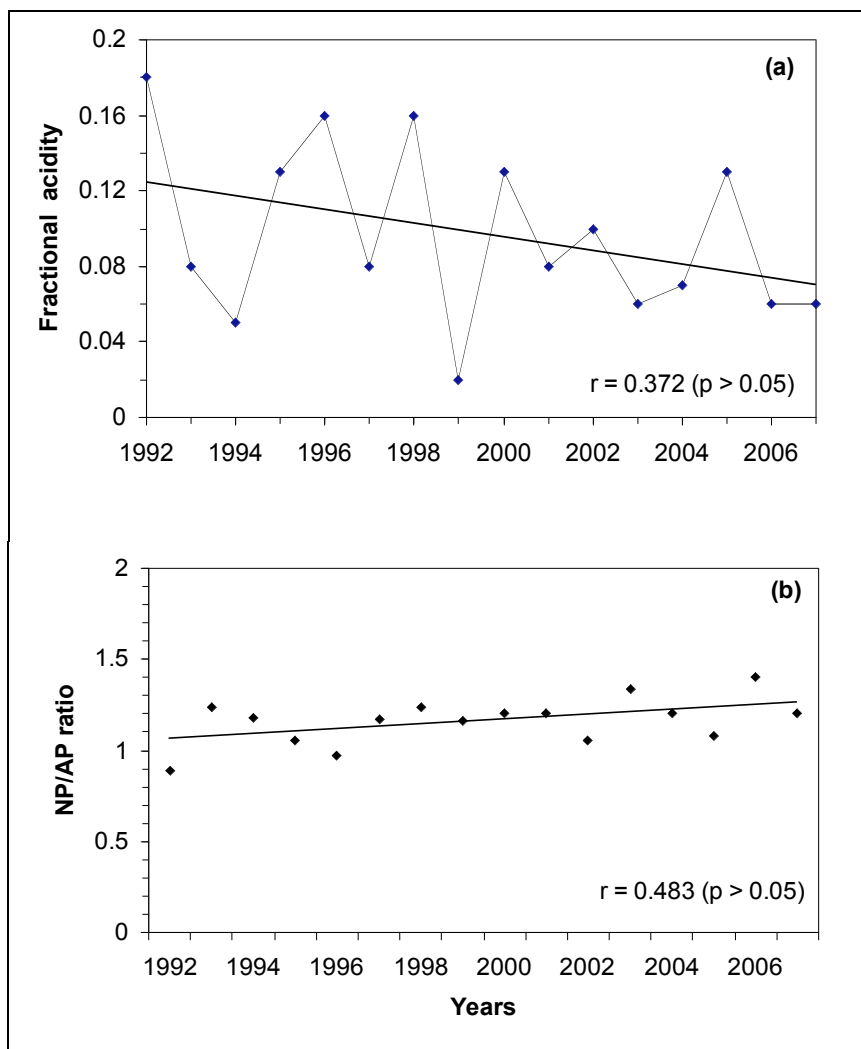acidity generated by these strong acids is not neutralized at all.

Fig. (2). (**a**) Variation in fractional acidity in rainwater collected in Mexico City for the period of 1992-2007, (**b**) Neutralization potential (NP) and acidifying potential (AP) ratio trend.

Fig. (**2a**) shows the variation in FA in rainwater in Mexico City from 1992 to 2007. A non significant decrease in FA (r = 0.37) can be observed, indicating some increase in neutralization of acidification. The average FA value was 0.74, indicating that about 74% of the acidity was neutralized by alkaline constituents. The relative contribution of NO_3^- to acidification was calculated using the ratio $[NO_3^-]/([NO_3^-] + [SO_4^{2-}])$, and the average value of 0.41 indicates that about 41% of the acidity of rain was due to NO_3 and 59% to SO_4^{2-}. Table **1** shows that NO_3^- was the third most abundant ion in Mexico City rainwater after SO_4^{2-} and NH_4^+, representing an important contribution to rain acidity.

Alkalinity concentration (Table **2**) showed great variability over time, which suggests that pH varied between rain events.

To determine the balance between acidity and alkalinity, the ratio of neutralization potential (NP) to acidifying potential (AP), NP/AP = $([Ca^{2+}] + [NH_4^+])/([SO_4^{2-}] + [NO_3^-])$, was calculated. Fig. (**2b**) shows the trend of this ratio, although non significant (r = 0.483), indicating that

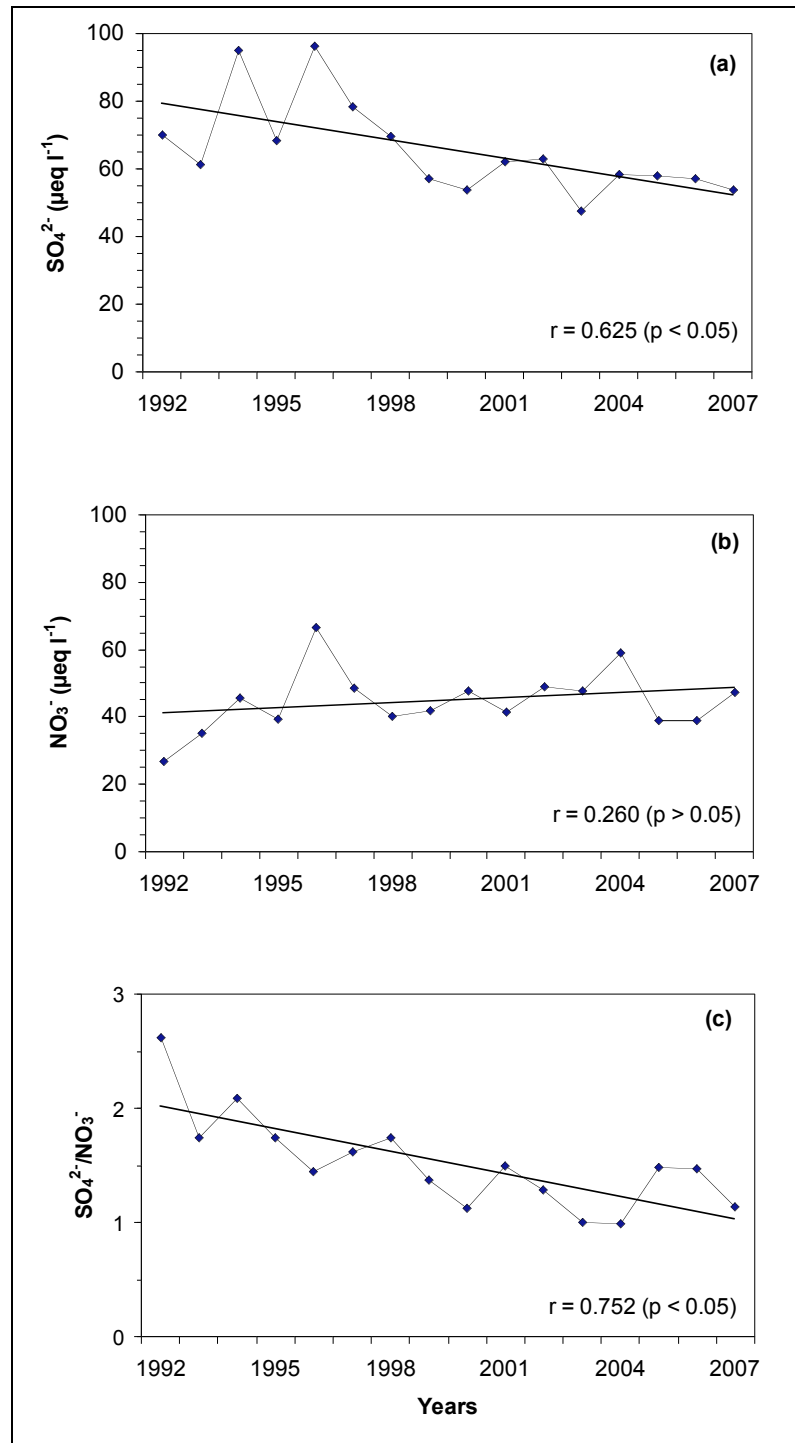**Fig. (3).** Long-term trend for (**a**) SO_4^{2-}, (**b**) NO_3^- and (**c**) SO_4^{2-}/NO_3^- ratio.

neutralization capacity is increasing and acidification is decreasing, which is consistent with the average FA value reported above.

3.3. Annual Trends

Trends in annual concentrations of SO_4^2, NO_3^-, Cl^-, NH_4^+, $H^+ + Mg^{2+}$, K^+, Ca^{2+} and alkalinity as function of time were calculated by means of a linear least-squares regression of volume weighted mean concentrations of these ions in rainwater collected during the 16-year study period. Fig. (**3a**) shows that SO_4^{2-} in precipitation indicated a significant decreasing trend (r = 0.62, p<0.05), corresponding to the control of SO_2 emissions by law in the Mexico City valley [29] due to the change from oil to gas as a fuel in thermoelectric power plants and heavy and medium-sized industries. Urban residents also use gas as a fuel. Similar trends have been observed in Europe and USA due to SO_2 control strategies which have lowered the emissions of this pollutant since the 1960s [3, 4, 6, and 30].

Despite the large number of automobiles in the metropolitan area, which increased from 1.51 million in 1988 to 2.70 million in 2005 (55%) plus buses and trucks (29,900), NO_3^- concentration did not show a significant increasing trend (r = 0.26, p>0.05) over time (Fig. **3b**). However, the SO_4^{2-}/NO_3^- ratio (Fig. **3c**) showed a significant downward trend (r = 0.75), indicating a marked decrease in

the concentration of SO_4^{2-}, possibly as a consequence of the decreasing trend in SO_4^{2-} concentration (Fig. **3a**).

Calcium, Mg^{2+} and NH_4^+ showed a non significant trend. Regarding to Ca^{2+} it can be due to the fact that crustal contributions have become relatively less important over the years because of the rapid urbanization of rural areas surrounding Mexico City and control of industrial emission of particles. Calcium has also anthropogenic sources such as the manufacture of lime and other products containing calcium salts.

The atmospheric content of NH_4^+ could originate from industrial and domestic emissions and seems to be constant over the years, as no notable changes in concentration occurred.

Hydrogen ion (Fig. **4a**) showed a non significant decreasing trend (r = 0.40, p>0.05), which could also indicate decreased acidification.

Potassium (Fig. **4b**) showed a significant decreasing trend (r = 0.58, p < 0.05), probably due to the fact that there were no important anthropogenic emissions and little contribution by crustal materials, because most soil in the Metropolitan Area is paved over.

As seen in Fig. (**5a**), the sum of acidifying components $[SO_4^{2-}] + [NO_3^-] + [Cl^-]$ showed a non significant trend (r = 0.326, p > 0.05); also the trend in the sum of neutralizing
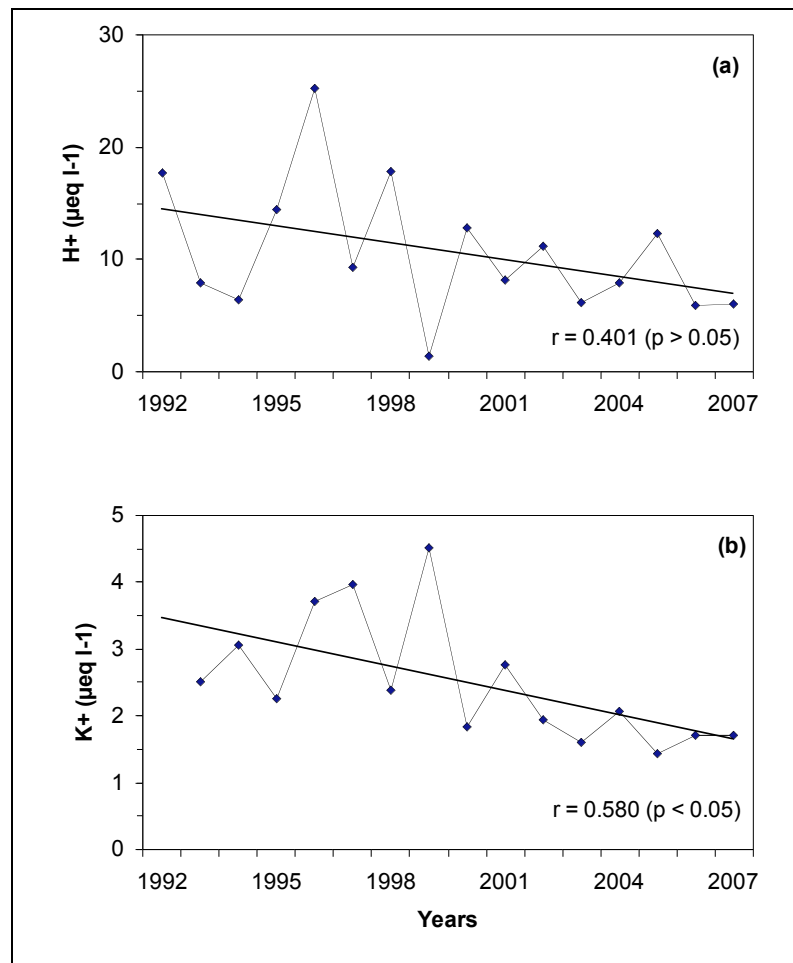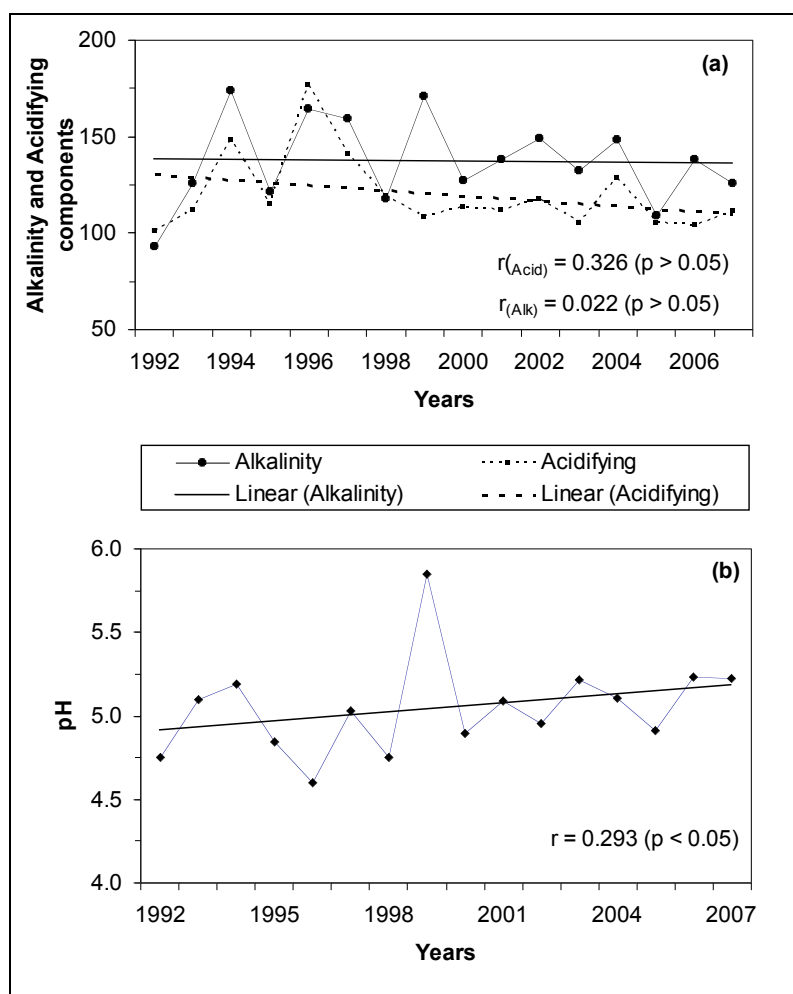

Fig. (4). Long-term trend for (**a**) H^+ and (**b**) K^+.

Fig. (5). (**a**) The sum of acidifying components $[SO_4^{2-}] + [NO_3^-] + [Cl^-]$ and the sum of neutralizing components $[NH_4^+] + [Ca^{2+}] + [Mg^{2+}]$ and (**b**) pH variation during the studied period.

components $[NH_4^+] + [Ca^{2+}] + [Mg^{2+}]$ indicated that neutralization has not decreased significantly but remained almost constant ($r = 0.022$, $p>0.05$). The pH trend showed a non significant increasing trend during the period ($r = 0.29$, $p>0.05$) (Fig. **5b**).

The NH_4^+/Ca^{2+} ratio (Fig. **6**) did show a small increasing trend although not significant ($r = 0.37$, $p>0.05$). The decreasing trend in the concentration of Ca^{2+} was the most important factor. The decreasing trend in the concentration of Ca^{2+} is not as important as that of SO_4^{2-} in determining the decreasing trend of H^+.

Weather conditions are the most important factor in explaining the large variations in daily rainwater chemical composition. However, as expected, the annual trend of the concentration of most ionic species in rainwater showed small variations because meteorological conditions do not change abruptly over the years. On the other hand, changes in anthropogenic activities became an important factor in the annual trend of the concentration of sulfate in rainwater, as was clearly shown by its decrease as a result of a decrease in the sulfur content of fossil fuels.

4. CONCLUSIONS

The finding that NH_4^+ had a higher concentration than SO_4^{2-} was unexpected; however the decrease in SO_4^{2-} concentration is consistent with the decrease in SO_2 concentration from 1992 to 2007 which has resulted from the strict air pollution control policies enforced in Mexico.

Significant variations in the concentration of NO_3^- were not observed, even though there are some 4 million motor vehicles in the Mexico City valley.

The contribution of NH_4^+ to neutralization was relatively small, showing only a non significant increase in NH_4^+ over the study period. There was a sizeable decrease in SO_4^{2-}, which could mean that part of the NH_4^+ ions reacted with other ions, forming ammonium compounds.

High correlations between SO_4^{2-} and NO_3^-, Ca^{2+}, Mg^{2+}, NH_4^+ and significant correlations between SO_4^{2-} and Na^+ and K^+ were found. The highest correlation was between The highest correlation was between Ca^{2+} and Mg^{2+} and significant correlations of NO_3^- with Na^+, K^+, Ca^{2+}, Mg^{2+} and H^+ were found, suggesting that these ions could have the
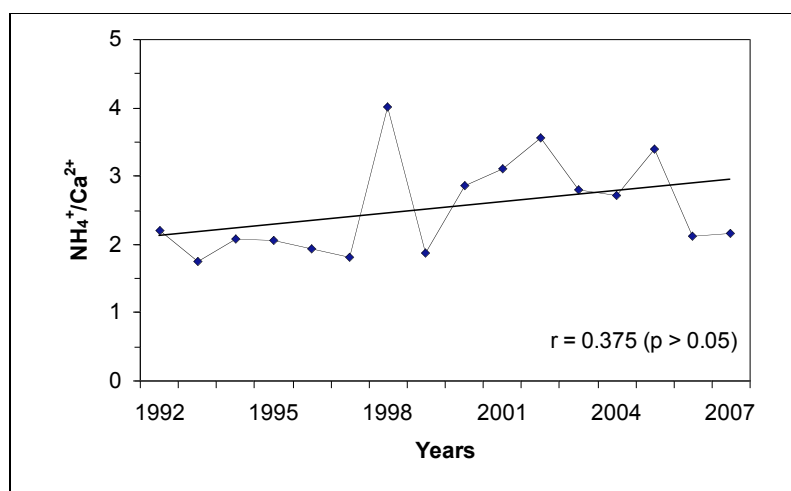
Fig. (6). Trend of the NH_4^+/Ca^{2+} ratio.

same anthropogenic origin. Rainfall amounts correlated negatively with all ions except H^+, indicating that heavy rains lower ion concentrations but raise rainwater acidity.

The results of the linear least-squares regression analysis indicated a decreasing trend in the mean concentrations of SO_4^{2-}, Ca^{2+}, Mg^{2+} and H^+.

The SO_4^{2-}/NO_3^- ratio showed a significant decreasing trend, mainly because of the decreasing trend in the concentration of SO_4^{2-}.

The decreasing trend in the concentration of Ca^{2+} is not as important as that of SO_4^{2-} in determining the decreasing trend of H^+.

It is notable that a decrease in acidification was observed during the study period.

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