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


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 $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Cl}^-$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{K}^+$, $\text{Na}^+$, $\text{NH}_4^+$ and $\text{H}^+$ 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 $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Cl}^-$, $\text{NH}_4^+$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{K}^+$, $\text{H}^+$ 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 ($\text{SO}_4^{2-}$) in wet precipitation showed a significant decreasing trend, corresponding to the reduction in $\text{SO}_2$ 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, $\text{NO}_3^-$ did not show a significant increasing trend. The $\text{NH}_4^+/\text{Ca}^{2+}$ ratio showed a nearly significant increasing trend, due mainly to the significant decrease in $\text{Ca}^{2+}$ concentration. This decreasing trend was not as marked as that of $\text{SO}_4^{2-}$. The contribution of $\text{NH}_4^+$ to neutralization was relatively small, showing only a non significant increase in $\text{NH}_4^+$ over the study period, while a considerable decreasing $\text{SO}_4^{2-}$ trend occurred, which could mean that part of the $\text{NH}_4^+$ 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 $\text{SO}_4^{2-}$ concentration was found; this decrease was explained in most of the studies by a reduction in $\text{SO}_2$ emissions. Seto et al. [12] reported a decreasing trend in non-sea-salt (nss) $\text{SO}_4^{2-}$ concentrations with an annual mean change of 3% year$^{-1}$, while no significant trends were detected for $\text{NO}_3^-$ at 59% of study sites. Aherne and Farrell [3], using a least-squares regression analysis, found slight decreasing trends in precipitation concentrations for $\text{SO}_4^{2-}$ (20%), $\text{NO}_3^-$ (13%), $\text{H}^+$ (24%) and $\text{NH}_4^+$ (15%) in Ireland over the period 1991–1998. Jun Tu et al. [10] reported a significant decreasing trend in $\text{SO}_4^{2-}$ due to abatement strategies for $\text{SO}_2$, while a significant increasing trend was found in the concentration of $\text{NO}_3^-$. 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 $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Cl}^-$, $\text{H}^+$, $\text{pH}$, $\text{NH}_4^+$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{K}^+$ and alkalinity trends.

One of the most important objectives was to determine the concentration variation through the years, particularly of the ions $\text{SO}_4^{2-}$, $\text{NO}_3^-$ and $\text{NH}_4^+$ because the first two are responsible for rain acidity, while $\text{NH}_4^+$ 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 closed in order to protect the samples from humidity and temperature changes. After collection, the samples were immediately frozen at $-20^\circ$C and dried in a forced air oven at $100^\circ$C to avoid loss of water and other volatile compounds. After drying, the samples were stored in desiccators until analysis.
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 (NO₃⁻), chloride (Cl⁻) and sulfate (SO₄²⁻) 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 (NH₄⁺) was analyzed by suppressed chromatography with a Hamilton PRPX-200 analytical cation column. Calcium (Ca²⁺), magnesium (Mg²⁺), 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 (HCO₃⁻) 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 SO₄²⁻, Cl⁻, NO₃⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺ and NH₄⁺, 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 SO₄²⁻, Cl⁻, NO₃⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺ and NH₄⁺, 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, NH₄⁺/Ca²⁺, SO₄²⁻/NO₃⁻ ratios, sum of acidifying and the sum of neutralizing components. The linear regressions were evaluated using the analysis of 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 NH₄⁺ concentration occurred, moreover, was the most abundant ion, with a total average of 90.3 μeq l⁻¹ followed by SO₄²⁻ (65.6 μeq l⁻¹), NO₃⁻ (44.6 μeq l⁻¹), Ca²⁺ (38.1 μeq l⁻¹), Cl⁻ (9.4 μeq l⁻¹), Na⁺ (5.6 μeq l⁻¹), Mg²⁺ (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 SO₄²⁻ with NO₃⁻, Ca²⁺, Mg²⁺ and NH₄⁺ and significant correlations (p<0.05) of SO₄²⁻ with Na⁺ and K⁺ were found. High correlations and significant correlations (p<0.05) among NO₃⁻, Na⁺, K⁺, Ca²⁺ and Mg²⁺ were found, suggesting that these ions could have the same anthropogenic origin. The highest correlation was between Ca²⁺ and Mg²⁺ followed by NO₃⁻ and NH₄⁺.

In Mexico City, SO₂ is emitted by ore processing and industrial fuel oil combustion. NO₂ is produced by combustion processes and motor vehicle exhaust. Both pollutants are oxidized to the respective acids in the atmosphere.

More than 98% of SO₄²⁻ 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]:

$$SO_{4}^{2-}_{\text{nss}} = SO_{4}^{2-} - \left( \frac{SO_{2}^{2-}}{Cl^-} \right)_{\text{sw}} \times Cl^-_{\text{rs}}$$

where Cl⁻ was considered the reference species and SO₄²⁻ is the concentration of sulfate due to non-sea-salt sources; SO₄²⁻ is the concentration of sulfate observed in the rainwater sample; (SO₄²⁻/Cl⁻)sw is the ratio of the concentrations of sulfate and chloride in seawater, and Cl⁻ is the concentration of chloride observed in the rainwater sample.

Hydrogen ion concentration correlated positively with SO₄²⁻ and NO₃⁻ and negatively with Ca²⁺. 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 Ca²⁺ and Mg²⁺ 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

<table>
<thead>
<tr>
<th>Year (N =)</th>
<th>SO₄²⁻</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>NH₄⁺</th>
<th>H⁺</th>
<th>Alkalinity</th>
<th>pH</th>
<th>Rain Amount (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1992 (N = 29)</td>
<td>70.2±9.7</td>
<td>NA</td>
<td>26.8±4.6</td>
<td>NA</td>
<td>NA</td>
<td>27.2±3.2</td>
<td>3.1±0.4</td>
<td>60.0±7.0</td>
<td>17.7±5.8</td>
<td>NA</td>
<td>4.75</td>
<td>482.7</td>
</tr>
<tr>
<td>1993 (N = 29)</td>
<td>61.1±8.1</td>
<td>5.7±0.7</td>
<td>35.1±5.7</td>
<td>5.8±0.8</td>
<td>2.5±0.4</td>
<td>43.1±6.9</td>
<td>4.5±0.7</td>
<td>75.6±8.2</td>
<td>7.9±3.6</td>
<td>29.3±5.7</td>
<td>5.10</td>
<td>305.0</td>
</tr>
<tr>
<td>1994 (N = 30)</td>
<td>95.1±17.4</td>
<td>8.1±1.0</td>
<td>45.6±6.5</td>
<td>5.5±0.7</td>
<td>3.0±0.6</td>
<td>35.7±7.3</td>
<td>5.7±0.7</td>
<td>112±17.6</td>
<td>6.5±2.6</td>
<td>19.3±3.9</td>
<td>5.19</td>
<td>337.0</td>
</tr>
<tr>
<td>1995 (N = 36)</td>
<td>68.4±11.8</td>
<td>5.7±0.9</td>
<td>39.3±7.4</td>
<td>3.5±0.5</td>
<td>2.3±0.3</td>
<td>37.0±6.6</td>
<td>3.9±0.8</td>
<td>76.2±10.6</td>
<td>14.4±4.6</td>
<td>17.2±4.5</td>
<td>4.84</td>
<td>535.9</td>
</tr>
<tr>
<td>1996 (N = 28)</td>
<td>96.1±12.7</td>
<td>15.5±4.1</td>
<td>66.4±12.6</td>
<td>8.5±2.0</td>
<td>3.7±0.8</td>
<td>52.2±8.2</td>
<td>6.9±1.2</td>
<td>101±14.8</td>
<td>25.2±10.4</td>
<td>11.6±4.8</td>
<td>4.60</td>
<td>347.6</td>
</tr>
<tr>
<td>1997 (N = 36)</td>
<td>78.5±8.1</td>
<td>14.2±4.0</td>
<td>48.6±6.5</td>
<td>8.3±1.4</td>
<td>4.0±0.5</td>
<td>53.0±7.4</td>
<td>6.1±0.9</td>
<td>96.2±11.6</td>
<td>9.3±3.8</td>
<td>39.3±12.5</td>
<td>5.03</td>
<td>379.8</td>
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<tr>
<td>1998 (N = 31)</td>
<td>69.7±19.7</td>
<td>12.0±4.0</td>
<td>40.2±12.5</td>
<td>3.9±0.7</td>
<td>2.4±1.0</td>
<td>22.6±4.4</td>
<td>2.3±0.4</td>
<td>90.5±18.6</td>
<td>17.7±7.4</td>
<td>13.9±3.7</td>
<td>4.75</td>
<td>498.8</td>
</tr>
<tr>
<td>1999 (N = 20)</td>
<td>57.2±9.8</td>
<td>8.6±1.5</td>
<td>41.8±8.3</td>
<td>10.3±2.4</td>
<td>4.5±1.2</td>
<td>55.5±12.8</td>
<td>6.3±1.8</td>
<td>104±17.2</td>
<td>1.4±0.5</td>
<td>54.6±11.5</td>
<td>5.85</td>
<td>216.7</td>
</tr>
<tr>
<td>2000 (N = 39)</td>
<td>53.9±10.2</td>
<td>7.8±1.2</td>
<td>47.8±10.7</td>
<td>4.8±1.1</td>
<td>1.8±0.3</td>
<td>31.6±5.6</td>
<td>3.3±0.5</td>
<td>90.5±15.7</td>
<td>12.8±6.1</td>
<td>26.0±6.2</td>
<td>4.89</td>
<td>465.8</td>
</tr>
<tr>
<td>2001 (N = 29)</td>
<td>62.0±11.3</td>
<td>8.6±1.1</td>
<td>41.3±7.3</td>
<td>3.7±1.5</td>
<td>2.8±1.7</td>
<td>30.3±10.5</td>
<td>2.1±0.8</td>
<td>94.3±15.0</td>
<td>8.2±2.3</td>
<td>29.2±13.2</td>
<td>5.09</td>
<td>400.0</td>
</tr>
<tr>
<td>2002 (N = 27)</td>
<td>63.1±10.2</td>
<td>7.4±0.9</td>
<td>49.0±8.7</td>
<td>11.6±3.4</td>
<td>1.9±0.5</td>
<td>25.9±9.9</td>
<td>2.9±0.9</td>
<td>92.1±10.4</td>
<td>11.2±3.9</td>
<td>27.3±9.5</td>
<td>4.95</td>
<td>347.8</td>
</tr>
<tr>
<td>2003 (N = 35)</td>
<td>47.6±5.7</td>
<td>10.0±1.9</td>
<td>47.8±8.8</td>
<td>4.1±0.7</td>
<td>1.6±0.2</td>
<td>33.6±5.4</td>
<td>2.8±0.4</td>
<td>94.1±11.9</td>
<td>6.1±2.5</td>
<td>25.4±5.0</td>
<td>5.21</td>
<td>448.9</td>
</tr>
<tr>
<td>2004 (N = 42)</td>
<td>58.4±6.6</td>
<td>11.7±1.9</td>
<td>58.9±7.2</td>
<td>5.0±0.7</td>
<td>2.1±0.2</td>
<td>38.3±4.5</td>
<td>3.5±0.4</td>
<td>104±11.1</td>
<td>7.9±2.7</td>
<td>24.2±4.6</td>
<td>5.10</td>
<td>386.1</td>
</tr>
<tr>
<td>2005 (N = 37)</td>
<td>57.9±15.2</td>
<td>8.3±1.6</td>
<td>39.0±9.1</td>
<td>3.2±0.4</td>
<td>1.4±0.2</td>
<td>23.8±5.1</td>
<td>2.3±0.5</td>
<td>81.0±15.9</td>
<td>12.2±4.7</td>
<td>11.2±2.9</td>
<td>4.91</td>
<td>497.3</td>
</tr>
<tr>
<td>2006 (N = 27)</td>
<td>57.1±12.0</td>
<td>7.7±1.5</td>
<td>38.7±5.6</td>
<td>3.4±0.7</td>
<td>1.7±0.3</td>
<td>42.5±11.6</td>
<td>3.4±0.8</td>
<td>90.1±17.5</td>
<td>5.9±2.1</td>
<td>27.0±8.3</td>
<td>5.23</td>
<td>348.3</td>
</tr>
<tr>
<td>2007 (N = 37)</td>
<td>53.7±7.0</td>
<td>9.4±1.6</td>
<td>47.5±6.7</td>
<td>2.7±0.6</td>
<td>1.7±0.4</td>
<td>38.6±5.6</td>
<td>3.3±0.6</td>
<td>83.0±8.3</td>
<td>6.0±1.4</td>
<td>16.0±5.4</td>
<td>5.22</td>
<td>528.6</td>
</tr>
<tr>
<td>Average 1992-2007</td>
<td>65.6</td>
<td>9.4</td>
<td>44.6</td>
<td>5.6</td>
<td>2.5</td>
<td>38.1</td>
<td>3.9</td>
<td>90.3</td>
<td>10.6</td>
<td>24.8</td>
<td>4.97</td>
<td>408.2</td>
</tr>
</tbody>
</table>

NA: Not analyzed.

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.

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

<table>
<thead>
<tr>
<th>Variables</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>NH₄⁺</th>
<th>H⁺</th>
<th>Alkalinity</th>
<th>Amount of Rain</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₄²⁻</td>
<td>0.383</td>
<td>0.637</td>
<td>0.377</td>
<td>0.483</td>
<td>0.662</td>
<td>0.654</td>
<td>0.699</td>
<td>0.247</td>
<td>0.113</td>
<td>-0.204</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.288</td>
<td>0.386</td>
<td>0.451</td>
<td>0.373</td>
<td>0.443</td>
<td>0.304</td>
<td>0.048</td>
<td>0.129</td>
<td>-0.166</td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.340</td>
<td>0.339</td>
<td>0.483</td>
<td>0.496</td>
<td>0.763</td>
<td>0.372</td>
<td>0.074</td>
<td>-0.216</td>
<td></td>
<td></td>
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<tr>
<td>Na⁺</td>
<td>0.523</td>
<td>0.558</td>
<td>0.689</td>
<td>0.399</td>
<td>-0.081</td>
<td>0.489</td>
<td>-0.214</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K⁺</td>
<td>0.634</td>
<td>0.736</td>
<td>0.384</td>
<td>-0.092</td>
<td>0.424</td>
<td>-0.192</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ca²⁺</td>
<td>0.898</td>
<td>0.655</td>
<td>-0.159</td>
<td>0.070</td>
<td>-0.249</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Mg²⁺</td>
<td>0.609</td>
<td>-0.113</td>
<td>0.615</td>
<td>-0.262</td>
<td></td>
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</tr>
<tr>
<td>NH₄⁺</td>
<td>0.008</td>
<td>0.426</td>
<td>-0.292</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>H⁺</td>
<td>-0.336</td>
<td>0.073</td>
<td></td>
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<tr>
<td>Alkalinity</td>
<td>-0.188</td>
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</tr>
</tbody>
</table>

It is known that the acidity of rain is controlled mainly by strong acids, e.g. H₂SO₄ and HNO₃ [27]. Sulfates and NO₃⁻ neutralizing components ([Ca²⁺] + [NH₄⁺] + [Mg²⁺] + [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 NH₄⁺ [10].
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. (1). Correlation between the sum of acidifying ions and the sum of neutralizing components.](image)

![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.](image)
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 $[\text{NO}_3^-]/([\text{NO}_3^-] + [\text{SO}_4^{2-}])$, 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 I 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), $\text{NP}/\text{AP} = ([\text{Ca}^{2+}] + [\text{NH}_4^+])/([\text{SO}_4^{2-}] + [\text{NO}_3^-])$, was calculated. Fig. (2b) shows the trend of this ratio, although non significant ($r = 0.483$), indicating that
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 \( \text{SO}_4^{2-}, \text{NO}_3^-, \text{Cl}^-, \text{NH}_4^+, \text{H}^+, \text{Mg}^{2+}, \text{K}^+, \text{Ca}^{2+} \) 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 \( \text{SO}_4^{2-} \) in precipitation indicated a significant decreasing trend \( (r = 0.62, p < 0.05) \), corresponding to the control of \( \text{SO}_2 \) 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 \( \text{SO}_2 \) control strategies which have lowered the emissions of this pollutant since the 1960s \([3, 4, 6, \text{and } 30]\).

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), \( \text{NO}_3^- \) concentration did not show a significant increasing trend \( (r = 0.26, p > 0.05) \) over time (Fig. 3b). However, the \( \text{SO}_4^{2-}/\text{NO}_3^- \) ratio (Fig. 3c) showed a significant downward trend \( (r = 0.75) \), indicating a marked decrease in the concentration of \( \text{SO}_4^{2-} \), possibly as a consequence of the decreasing trend in \( \text{SO}_4^{2-} \) concentration (Fig. 3a).

Calcium, \( \text{Mg}^{2+} \) and \( \text{NH}_4^+ \) showed a non significant trend. Regarding to \( \text{Ca}^{2+} \) 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 \( \text{NH}_4^+ \) 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 \( [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] \) showed a non significant trend \( (r = 0.326, p > 0.05) \); also the trend in the sum of neutralizing

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![Fig. (4). Long-term trend for (a) H\(^+\) and (b) K\(^+\).](image-url)
components \([\text{NH}_4^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}]\) 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 \(\text{NH}_4^+/\text{Ca}^{2+}\) 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 \(\text{Ca}^{2+}\) was the most important factor. The decreasing trend in the concentration of \(\text{Ca}^{2+}\) is not as important as that of \(\text{SO}_4^{2-}\) in determining the decreasing trend of \(\text{H}^+\).

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 \(\text{NH}_4^+\) had a higher concentration than \(\text{SO}_4^{2-}\) was unexpected; however the decrease in \(\text{SO}_4^{2-}\) concentration is consistent with the decrease in \(\text{SO}_2\) concentration from 1992 to 2007 which has resulted from the strict air pollution control policies enforced in Mexico.

Significant variations in the concentration of \(\text{NO}_3^-\) were not observed, even though there are some 4 million motor vehicles in the Mexico City valley.

The contribution of \(\text{NH}_4^+\) to neutralization was relatively small, showing only a non significant increase in \(\text{NH}_4^+\) over the study period. There was a sizeable decrease in \(\text{SO}_4^{2-}\), which could mean that part of the \(\text{NH}_4^+\) ions reacted with other ions, forming ammonium compounds.

High correlations between \(\text{SO}_4^{2-}\) and \(\text{NO}_3^-\), \(\text{Ca}^{2+}\), \(\text{Mg}^{2+}\), \(\text{NH}_4^+\) and significant correlations between \(\text{SO}_4^{2-}\) and \(\text{Na}^+\) and \(\text{K}^+\) were found. The highest correlation was between \(\text{Ca}^{2+}\) and \(\text{Mg}^{2+}\) and significant correlations of \(\text{NO}_3^-\) with \(\text{Na}^+, \text{K}^+, \text{Ca}^{2+}, \text{Mg}^{2+}\) and \(\text{H}^+\) were found, suggesting that these ions could have the
same anthropogenic origin. Rainfall amounts correlated negatively with all ions except \( \text{H}^+ \), 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 \( \text{SO}_4^{2-} \), \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \) and \( \text{H}^+ \).

The \( \text{SO}_4^{2-}/\text{NO}_3^- \) ratio showed a significant decreasing trend, mainly because of the decreasing trend in the concentration of \( \text{SO}_4^{2-} \).

The decreasing trend in the concentration of \( \text{Ca}^{2+} \) is not as important as that of \( \text{SO}_4^{2-} \) in determining the decreasing trend of \( \text{H}^+ \).

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

REFERENCES


Fig. (6). Trend of the \( \text{NH}_4^+/\text{Ca}^{2+} \) ratio.
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