Chemical composition of rainwater in northeastern México

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RESUMEN
En el presente trabajo se investigó la composición química del depósito atmosférico húmedo en Monterrey capital del Estado de Nuevo León la ciudad industrial más importante del noreste de México, y donde la calidad del aire presenta serios problemas debido a las partículas suspendidas. El período de muestreo fue de enero a diciembre de 2007. La estación se localiza en la azotea de la Facultad de Ciencias Químicas de la Universidad Autónoma de Nuevo León la cual está localizada al norte del Área Metropolitana de Monterrey. Treinta y dos muestras de depósito húmedo fueron recolectadas utilizando un muestreador automático analizando concentración de iones (SO$_4^{2-}$,NO$_3^-$,Cl$^-$,Ca$^{2+}$, Na$^+$,K$^+$,NH$_4^+$) y conductividad. Los resultados muestran que el valor de pH promedio ponderado fue de 6.58 debido a la neutralización. La química del agua de lluvia muestra una alta concentración de Ca$^{2+}$ y Mg$^{2+}$ como especies cationicas y de SO$_4^{2-}$ y Cl$^-$ como especies aniónicas. La baja concentración de H$^+$ encontrada en las muestras de agua de lluvia de Monterrey N.L. sugiere que una parte importante de H$_2$SO$_4$ y de HNO$_3$ fue neutralizada por partículas alcalinas presentes en la atmósfera. Para analizar la posible asociación entre los iones en las muestras de lluvia y consecuentemente la correlación con fuentes de emisión se aplicó el programa estadístico SPSS v.12. Se encontró una baja correlación entre los iones H$^+$, SO$_4^{2-}$ y NO$_3^-$ posiblemente debido a la neutralización. Las pedreras ubicadas en la localidad y la composición propia de las montañas pueden estar contribuyendo a las altas concentraciones de Ca$^{2+}$ y Mg$^{2+}$. Los resultados de esta investigación serán utilizados para evaluar la composición de la depositación atmosférica, la calidad del aire y para desarrollar estrategias para implementar medidas de control de las emisiones atmosféricas en el Estado. El presente trabajo representa la primera contribución de la química del agua de lluvia en el noreste de México.
The present study reports the chemical composition of atmospheric wet deposition in Monterrey, capital of the state of Nuevo León and the most important industrial city in northeastern México, where air quality presents a serious problem due to dust particles emitted. The sampling period was from January to December 2007. The station was mounted on the roof of the College of Chemical Sciences at the University of Nuevo León which is located in the north of the Metropolitan Area. Thirty-two samples of rain were collected with an automatic sampler and analyzed for pH, ion concentrations (SO$_4^{2-}$, NO$_3^-$, Cl$^-$, Ca$^{2+}$, Na$^+$, K$^+$, NH$_4^+$) and conductivity. The results show that the average weighted pH value of the rainwater was 6.58 due to neutralization. Rainwater chemistry showed high contribution of Ca$^{2+}$ and Mg$^{2+}$ in cations and SO$_4^{2-}$ and Cl$^-$ in anionic species. Low concentration of H$^+$ found in rainwater samples from Monterrey N.L. suggests that an important portion of H$_2$SO$_4$ and HNO$_3$ have been neutralized by alkaline particles in the atmosphere. In order to find possible association between ions in precipitation, and consequently, the possible sources of pollutants correlation study was applied using the program SPSS v.12. Weak correlations were found between the H$^+$ ions and SO$_4^{2-}$ or NO$_3^-$ because of neutralization. The local dust cement factories and surrounding limestone environment might be causing high concentration of Ca$^{2+}$ and Mg$^{2+}$. The results of this research will be used to evaluate the composition of atmospheric deposition, to evaluate air quality and to develop strategies to implement preventive measures and control of the atmospheric emissions in Nuevo Leon. This work represents the first study of rainwater chemical composition in the northeast of México.

Keywords: Wet deposition, acid rain, ionic species, conductivity, pH, chemical composition, precipitation chemistry.

1. Introduction

The issue of acid precipitation has received much attention in the international community for the last several decades because of its notable direct adverse effects on ecosystems and indirect effects on human health (Hu et al., 2003).

Recently innumerable efforts have been made to understand the physical and chemical processes responsible for the formation of acid species and their removal from the atmosphere. The chemistry of the rainwater has been subjected to numerous investigations during the last two decades due to the increase of environmental problems caused by acid rain. The composition of rainwater is important in understanding the role of transport of the soluble components of the atmosphere and the contribution of different sources of atmospheric pollutants.

The chemical composition of rainwater varies from site to site and from region to region, due to the influence of local sources. The processes controlling the composition of rain are complex and influenced by both natural and anthropogenic sources. If the source is influenced by increasing made man activities, the rainwater will become acid because the anthropogenic activities contribute acidic gases like SO$_2$ and NO$_x$ and basic gases like NH$_3$ (Kulshrestha et al., 2003). Acidity is mainly due to sulfur and nitrogen oxides emissions from fossil fuel combustion, which after being dispersed and being transported react chemically in the atmosphere before becoming wet or dry deposited as sulfuric and nitric acid or neutralized ammonium salts (Possanzini et al., 1988).

Several studies have reported potential ecological deterioration caused by acid rain, such as deterioration of forests, acidification of lakes and grounds, decay of marble, and degradation of buildings and ancient monuments (Samara et al., 1992; Galloway, 2001). The phenomenon known as acid rain, along with its effects on the deterioration of buildings and monuments, have reached the level of public awareness.

Special attention has been drawn to deterioration of buildings and ancient monuments (Dikaiakos et al., 1990; Samara et al., 1992; Cobourn et al., 1993; Bravo et al., 2006).
Considering the importance of acid rain and the relation that exists with the population growth of large cities, the aim of this paper is to gain an initial understanding of rainwater chemistry, including its composition and possible sources, at an urban locality in northeast México, where these kind of data have not previously been available.

2. Experimental

2.1 Demographic details of the study area

Monterrey, the third largest city in México, is located in Nuevo León State (Lat. 25°40’N; Long 100°18’W). Its average altitude is 537 m above sea level, and has an area of 580.5 km² (Fig. 1).

The Monterrey Metropolitan Area is the third most populous city in México and is considered a high profile center of education, tourism and business, with a population of 4 000 000 inhabitants with 85% in urban areas.

The regional climate is classified as semi-arid, with tropical conditions interspersed with cold air incursions associated with North American frontal systems. Its weather, though reasonably pleasant in spring and autumn, is hot in the summer; the temperature average high reaches 35 °C (95 °F) in August, with an average low of 23 °C (74 °F). Winters are cool with an average January high of 19 °C (67 °F) and low of 8 °C (48 °F). The average annual precipitation is 615 mm, and is more prominent during May through September. Humidity in winter can be high, although snowfall is a very rare event.

Industrial activities and vehicular emissions are common potential pollution sources. More than 60% of the total emissions of NOx, CO, HC and Pb are due to vehicles, and 92% of SO2 emissions are due industrial activities (INEGI, 2002).
2.2 Sample collection

Rainwater samples were collected continuously by event from January to December 2007. An automated wet-dry sampler was used (Anchor International, model TE-78-100), with high-density polyethylene buckets. The sampler was located on the roof of the Ciencias Químicas Building (12.3 m above ground level) of the Universidad Autónoma de Nuevo León, located in the urban municipality of San Nicolás de los Garza. Following rainfall events, the bucket was tightly sealed with a clean plastic lid to avoid contamination during transport to the laboratory (ASTM, 2004).

Upon arrival at the laboratory, samples were immediately measured weight, volume, pH and conductivity (Hanna HI model 255 pH/conductivity/temperatures).

Each sample was later filtered through 0.25 mm, 0.22 µm pore diameter cellulose membranes (Millipore) in order to remove particulate matter. All the filtered samples were stored in precleaned polyethylene bottles and refrigerated to 4 ºC while awaiting major inorganic ion analysis by ion chromatography.

2.3 Chemical analysis

After collection and weighing, an unfiltered aliquot of each sample was used for pH and conductivity determination. The pH meter was calibrated before every measurement using standard buffer solutions of pH 4.00 and 7.00 (SCFI, 2000a). For conductivity measurements (25 ºC), a conductivity meter was used after calibration with KCl standard solutions (SCFI, 2000b). Concentrations of H\(^+\) were calculated from the pH values.

A second aliquot of each sample, retrieved from the refrigerated polyethylene bottle, was used for the determination of major ion concentrations. The cations Na\(^+\), K\(^+\), Ca\(^{2+}\) and NH\(_4^+\) were determined by ion chromatography using a Hewlett Packard 1090 with Hamilton PRP –x100 (150 x 4.1 mm) separation column and an Alltech 550 conductivity detector and for the anions Cl\(^-\), NO\(_3^-\) and SO\(_4^{2-}\). All solutions were prepared with deionized water supplied by a Milli-Q-Millipore system, and with standards solutions prepared by dissolution of 99% purity analytical grade salts. In order to check the instrumental errors a quality standard solution of the anions and cations, as well as blank samples, were prepared with different concentrations and given random numbers among real samples. The quality assurance procedures included the routine running of blanks and control samples as well as replicate samples. The column and the other operating conditions employed for analysis of both the ions are reported by Bravo et al. (2006).

3. Results and discussion

3.1 Rain quantity

A total of 32 rainwater samples were collected. The largest number of monthly events occurred in August (7) followed by May (6), June (5) and July (5); no rain events were observed on January, November and December. Monthly rainfall during the study period is presented in Fig. 2. The highest rainfall was during August (93.5 mm), followed by June (88.5 mm) and September (62.8 mm). The months of January, February, March, October, November and December are considered the dry season.
3.2 Variation of pH

The pH of individual precipitation events ranged from 5.44 to 8.5, with both acidic and alkaline values. In this study the volume-weighted mean pH (VWM) value was 6.58, higher value than the widely accepted background rain pH of 5.6 (Charlson and Rhode, 1982). In comparison with other results (pH = 5.6) reported in México by Bravo et al. (2006), the results are quite similar. The pH of natural precipitation is controlled by dissolved CO₂, due the interaction between water droplets and carbon dioxide. Precipitation pH is modified by the addition of both acidic and alkaline components (Topçu et al., 2002; Singh and Mondal, 2008).

Fig. 3 shows the temporal variation of volume weighted pH. The highest precipitation acidity (5.44) was associated with summer samples, especially in the period May to August 2007.

The frequency distribution of pH is shown in Fig. 4. Only 25% of the 32 rain samples showed a pH below 5.6, indicating that rainfall with above-background acidity is not common in Monterrey. Instead, the abundance of pH values above 5.6 indicate the presence of alkaline substance in the rainwater (Hu et al., 2006).
Alkaline precipitation has been reported in different parts of the world. In India, previous studies have recorded pH values ranging from 6.0 to 7.5 (Kemani et al., 1985; Saxena et al., 1996). Chandra Mouli et al. (2005) reported an alkaline VWM of 6.78. Another study, in the urban area of Ankara, Turkey, reported alkaline pH values due to high calcium (CaCO$_3$) loading from alkaline soil (Topçu et al., 2002). Thus, the VWM pH of 6.58 for our Monterrey samples likely reflects a strong impact of alkaline soil dust on rainwater composition.

### 3.3 Chemical composition

The variation of monthly mean concentration of major inorganic ions in rain water is illustrated in Table I. Volume weighted mean concentrations of cations can be ordered in descending order as Ca$^{2+} >$ Mg$^{2+} >$ Na$^+ >$ NH$_4^+ >$ K$^+$, with values ranging from 1150 to 93.1 µeq/L. The corresponding order of anions volume VWM concentration was Cl$^-$, SO$_4^{2-}$, and NO$_3^-$, with values ranging from 344 to 154 µeq/L.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Min (µeq/L)</th>
<th>Max (µeq/L)</th>
<th>SD (µeq/L)</th>
<th>VWM (µeq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.44</td>
<td>8.5</td>
<td>0.99</td>
<td>6.58</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>3.91</td>
<td>288.26</td>
<td>96.35</td>
<td>51.77</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>4.28</td>
<td>167</td>
<td>53.13</td>
<td>44.11</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.24</td>
<td>93.1</td>
<td>30.5</td>
<td>18.17</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>38.9</td>
<td>1150</td>
<td>370.81</td>
<td>243.26</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>5.02</td>
<td>329</td>
<td>108.93</td>
<td>61.14</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>2.99</td>
<td>344</td>
<td>118.1</td>
<td>52.01</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>7.58</td>
<td>154</td>
<td>48.96</td>
<td>34.76</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>7.38</td>
<td>269</td>
<td>83.15</td>
<td>71.64</td>
</tr>
</tbody>
</table>

The variation of monthly mean concentration of major ions in rain water is illustrated in Fig 5. Ca$^{2+}$ and SO$_4^{2-}$ concentrations are large because the Monterrey Metropolitan Area is surrounded by several mountains with numerous quarries and associated factories. The rock is composed...
basically of calcium carbonate. Aggregation operations are installed around those hills and represent a significant source of airborne particulate matter.

Fig. 5. Temporal variation of major inorganic ions in rainwater (µeq/L).
The high concentration of cations observed in March may be due to the small volume of rainfall. (Recall, from Fig. 2, March rainfall was only 8.2 mm compared with 93.5 mm in August.) Only one rain event was present in this month.

The smaller amount of rainwater is expected to produce higher concentrations of chemical species in rainwater due to reduced removal of suspended particles by wet deposition (Chandra et al., 2005).

During January, February, November and December no rain events were present in Monterrey’s Metropolitan Area.

On the other hand, the increased anion concentrations during October may be due to the prevailing meteorological conditions in Monterrey that do not allow complete dispersion of NO$_2$ and SO$_2$ (INEGI, 2002).

### 3.4 Comparison with other selected sites

Table II shows volume-weighted mean concentrations in rainwater for this study and other results reported for different regions of México and selected sites worldwide. The pH of the present study (6.58) is higher than the other Mexican regions like El Tajín, Veracruz (4.58) (Bravo et al., 2006) and Estado de México (4.54) (García et al., 2006), but is similar to Tirupati, India (6.78) (Chandra et al., 2005). This may be due to the latter region having a high load of suspended alkaline atmospheric particles.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Cl$^-$</th>
<th>NO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>NH$_4^+$</th>
<th>Ca$^{2+}$</th>
<th>K$^+$</th>
<th>Mg$^{2+}$</th>
<th>Na$^+$</th>
</tr>
</thead>
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<tr>
<td>This study</td>
<td></td>
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<td></td>
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<tr>
<td>Monterrey, N.L., México</td>
<td>6.58</td>
<td>17.61</td>
<td>19.36</td>
<td>44.73</td>
<td>44.11</td>
<td>243.26</td>
<td>28.67</td>
<td>60.58</td>
<td>98.46</td>
</tr>
<tr>
<td>García et al., 2006</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Estado de México</td>
<td>4.54</td>
<td>10.2</td>
<td>26.8</td>
<td>56</td>
<td>46.36</td>
<td>7.67</td>
<td>5.27</td>
<td>3.53</td>
<td>1.84</td>
</tr>
<tr>
<td>Bravo et al., 2006</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>El Tajín, Veracruz, México</td>
<td>4.58</td>
<td>13.82</td>
<td>11.61</td>
<td>6.87</td>
<td>16.6</td>
<td>5.98</td>
<td>3.08</td>
<td>.039</td>
<td>12.17</td>
</tr>
<tr>
<td>Nastos et al., 2007</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Athens, Greece</td>
<td>7.2</td>
<td>342.5</td>
<td>45.2</td>
<td>173.2</td>
<td>a</td>
<td>342.5</td>
<td>24.2</td>
<td>34.1</td>
<td>108.1</td>
</tr>
<tr>
<td>Chandra et al., 2005</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tirupati, India</td>
<td>6.78</td>
<td>34.45</td>
<td>42.33</td>
<td>135.12</td>
<td>21.05</td>
<td>156.521</td>
<td>38.05</td>
<td>60.85</td>
<td>36.39</td>
</tr>
</tbody>
</table>

a not reported

In this study Ca$^{2+}$ is the most abundant cation. The relative high concentration of this ion suggests the effect of local anthropogenic emissions. The Monterrey Metropolitan Area is a major industrial city which has a serious atmospheric pollution problem due principally to the surrounding mountains, quarry hills and factories. These are composed basically of calcium carbonate and the excess calcium is believed to be due to particles originating from these sources (INEGI, 2002). India soils have also been considered to be a major contributor of particulate matter in the atmosphere and to alkalinity in the rainwater (Chandra et al., 2005).
The $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ concentrations in Monterrey are higher than concentrations reported by Bravo et al. (2006) for the El Tajín archeological zone in Veracruz, México and by García (2006) for Rancho Viejo, a rural zone close to México City, but lower than the concentrations reported by Nastos (2007) for Athens, Greece.

### 3.5 Source contribution

In order to find association between ions in precipitation, and consequently, the possible sources of pollutants and the gaseous reaction occurring in the atmosphere, the correlation between ions was calculated for all samples and presented in Table III. The acidic ions $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ present high correlation ($r = 0.817$) indicating their origin from similar sources, because of the similarity in their behavior in rain water and the co-emissions of their precursors $\text{SO}_2$ and $\text{NOx}$ (Chandra et al., 2005; Singh and Mondal, 2008). A significant correlation was observed between $\text{NO}_3^-$ and $\text{Cl}^-$ ($r = 0.648$). On the other hand a strong correlation was observed between $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ ($r > 0.9$), $\text{Ca}^{2+}$ and $\text{NH}_4^+$ ($r = 0.895$) and $\text{Ca}^{2+}$ and $\text{K}^+$ ($r = 0.984$), suggesting the common origin of these ions from natural sources associated with crustal rather than anthropogenic or marine origin (Singh and Mondal, 2008). The high loading of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ and the negative correlation between $\text{NH}_4^+$ and $\text{NO}_3^-$ ($r = -0.439$) and $\text{NH}_4^+$ and $\text{SO}_4^{2-}$ ($r = -0.405$) suggests a buffering factor for the acidity of the rainwater.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>$\text{H}^+$</th>
<th>$\text{P}$</th>
<th>$\text{Na}^+$</th>
<th>$\text{NH}_4^+$</th>
<th>$\text{Mg}^{2+}$</th>
<th>$\text{K}^+$</th>
<th>$\text{Ca}^{2+}$</th>
<th>$\text{Cl}^-$</th>
<th>$\text{NO}_3^-$</th>
<th>$\text{SO}_4^{2-}$</th>
<th>Cond.</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1</td>
<td>$-0.764$</td>
<td>$-0.711$</td>
<td>0.371</td>
<td>0.174</td>
<td>0.388</td>
<td>0.293</td>
<td>0.329</td>
<td>0.719</td>
<td>0.038</td>
<td>$-0.322$</td>
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<td>$\text{H}^+$</td>
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<td>$0.59$</td>
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<tr>
<td>$\text{P}$</td>
<td>1</td>
<td></td>
<td></td>
<td>$-0.459$</td>
<td>$-0.477$</td>
<td>$-0.487$</td>
<td>$-0.47$</td>
<td>$-0.397$</td>
<td>$-0.479$</td>
<td>$-0.101$</td>
<td>0.135</td>
<td>$-0.722$</td>
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<tr>
<td>$\text{Na}^+$</td>
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<td>0.911</td>
<td>0.996</td>
<td>0.991</td>
<td>0.994</td>
<td>$-0.004$</td>
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<td>$\text{NH}_4^+$</td>
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<td>0.914</td>
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<td>0.895</td>
<td>$-0.284$</td>
<td>$-0.439$</td>
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<td>$\text{Mg}^{2+}$</td>
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<td></td>
<td>0.991</td>
<td>$-0.013$</td>
<td>$-0.224$</td>
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<td>$\text{K}^+$</td>
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<td></td>
<td>0.984</td>
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<tr>
<td>$\text{Ca}^{2+}$</td>
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<td>$-0.036$</td>
<td>$-0.206$</td>
<td>$-0.254$</td>
<td>0.632</td>
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<tr>
<td>$\text{Cl}^-$</td>
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<td></td>
<td>0.648</td>
<td>0.321</td>
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<tr>
<td>$\text{NO}_3^-$</td>
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<td>$-0.204$</td>
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<tr>
<td>Cond.</td>
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</tr>
</tbody>
</table>

Table III. Pearson correlation coefficients for concentrations of major ions.

P = vol. precipitation
Cond. = Conductivity

There is also a significant correlation between ion components and conductivity, except for the $\text{H}^+$, $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ ions. Because of the significant neutralizing effect of calcium ions, $\text{H}^+$ was not expected to have a good correlation with $\text{SO}_4^{2-}$ and $\text{NO}_3^-$. Topçu et al. (2002) found similar results in Ankara, Turkey.
As can be seen in Table III, all ionic species except sulfate correlate negatively with rainfall amount (P), indicating an atmospheric washout process.

4. Conclusions
A study of the chemical composition of rainwater was carried out over a one-year period at Monterrey, Nuevo León, México the most important industrial state in northeastern México. This represents the first contribution to the literature of rainwater chemistry in the region.

The study reveals the following principal conclusions:
1. The rainwater is typically alkaline, with strong correlations between Ca\(^{2+}\) and other ionic species, revealing that the acidity is being neutralized.
2. The average pH of the rainwater was 6.58, perhaps due to neutralization. Only 25% of the rain samples had a pH below 5.6. This shows strong inputs of alkaline species to rainwater samples in this region. The average pH of samples higher than 5.6 is due to high loadings of calcium ions in the form of CaCO\(_3\). This may be due to a high load of alkaline dust particle by numerous quarry hills and factories. These are composed basically of calcium carbonate.
3. The rainwater chemistry is dominated by Ca\(^{2+}\), Mg\(^{2+}\) and SO\(_4^{2-}\). The principal cations and anions, in decreasing order, are Ca\(^{2+}\) > Mg\(^{2+}\) > Na\(^+\) > NH\(_4^+\) > K\(^+\) and Cl\(^-\) > SO\(_4^{2-}\) > NO\(_3^-\).
4. The cations Mg\(^{2+}\), NH\(_4^+\), Na\(^+\) and K\(^+\) correlated strongly with Ca\(^{2+}\), suggesting a common natural source of crustal origin.
5. The low concentrations of H\(^+\) found in Monterrey rainwater samples suggest that an important portion of H\(_2\)SO\(_4\) and HNO\(_3\) has been neutralized by alkaline particles in the atmosphere.
6. Due to neutralization by alkaline particles, the anions SO\(_4^{2-}\) or NO\(_3^-\) are only weakly correlated with H\(^+\).
7. The monthly variation in ionic deposition is influenced by rainfall rate and ionic species concentration.
8. The correlation study and the comparison of major ion composition with other sites revealed that rainwater ion composition is strongly influenced by anthropogenic sources rather than terrestrial and marine sources.

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References


