# Composición química de agua de lluvia en Puebla, México.

## Rainfall chemical composition at Puebla, México

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**Resumen**

La evaluación química de 26 muestras de agua de lluvia colectadas durante la estación de lluvia en el año 2009 exhibió un pH promedio de 6.37, los principales iones fueron $CO_3^{-2}$, $Cl^-$, $HCO_3^-$, $SO_4^{-2}$, $NO_3^{-1}$, $PO_4^{-3}$, $Na^+$, $Mg^{+2}$, $Ca^{+2}$, $Co^{+2}$, $Cu^{+2}$, $Ni^{+2}$, $Fe^{+2}$, por análisis de correlación fue establecido su origen marino o disolución, la acidez es debida principalmente a la contribución de $SO_4^{-2}$.

**Abstract**

Chemical evaluation of 26 rainwater samples collected during 2009 rainy season exhibit an average pH of 6.37, the main ions were $CO_3^{-2}$, $Cl^-$, $HCO_3^-$, $SO_4^{-2}$, $NO_3^{-1}$, $PO_4^{-3}$, $Na^+$, $Mg^{+2}$, $Ca^{+2}$, $Co^{+2}$, $Cu^{+2}$, $Ni^{+2}$, $Fe^{+2}$, a marine or soil suspended particles dissolution origin was established from a correlation analysis, main acidity contributor is $SO_4^{-2}$.

*Keywords:* weathering, rainfall quality, urban atmosphere

**Introduction**

The city of Puebla is located in an open Valley (2,095,000-2,145,000 N UTM y 550,000-592,000 E UTM), with a well defined season pattern exhibiting dry weather in winter and spring, rainfall during summer, and a windy stage during fall. Most of economical activities take place at the downtown area, in which a high density of vehicles is involved; also, the heritage architecture is composed of several historical buildings having stone facades; these facts are of concern since it is known that vehicle emissions promote acid rain formation mainly by sulfuric and nitric acids, both of them are in detrimental for old buildings exposed stones (Bogan et al, 2009). Intense air pollution by itself does not affect straightforward the stone, it requires the presence of water to form acid or alkali compounds, in chemical or photochemical processes a temperature gradient acts like a catalyst for reaction rate be increased (Theoulakis et al, 1999).

At Mexico country some authors have tried to assess how chemical composition of the atmosphere affects rainfall quality, one of them (Báez et al. 1987) reported an study, based on three sites with different atmospheres: an urban one (Mexico City), a rural one (Guanajuato State), and a coastal industrial one (Veracruz State); from the three, Mexico City is the one with higher ion contents; another report (Ramírez et al 2010), considered an industrial city (Monterrey, Nuevo León State), with an strong contribution from dust particles, which represents an advantage, since the average rainfall pH was 6.58, non acid condition. Therefore, the main objective in this work is to assess if the urban quality atmosphere at downtown Puebla is defining conditions to develop in an acid rainfall that eventually could accelerated the weathering damage of exposed stones.

**Materials and methods**

Rainfall collection was done with a specially designed container, in which it is avoided both dust penetration and water evaporation, as well as sunlight incidence. Collectors were placed on the roof of St Agustin church, which is located inside the 0.5 km radial area from the geographical center of the city. Physicochemical analysis were run as established in the Standard Methods (Clescerl et al, 2005) for: a) chloride, b) alkalinity (total and phenolphthalein), c) total and calcium hardness. Otherwise, sulfate, nitrate and phosphate ions were detected with Hach reagents in a 2500 Hach spectrophotometer. After getting the above parameters, the water samples were acidified with nitric acid, and cations were determined in a GBC 932 atomic absorption spectrophotometer, calibration curve was prepared using a 1000 ppm atomic absorption standard Baker brand.

**Results and discussion**

The 2009 rainy season at Puebla city was very irregular and of magnitude smaller than rainy seasons from previous years. For this study a total of 26 samples were collected, Figure 1 shows the cumulative precipitation expressed in mm of rainfall ($l\,m^{-2}$). As it can be observed, the season started with scarce precipitations; there was a two weeks period of zero precipitation; also, last month was characterized by abundant precipitations, a windy condition and dust suspension, all these factors made that collected rainfall in the last thirty

days became twice the amount observed during the previous 90 days, and some parameters exhibit an increase in their values.
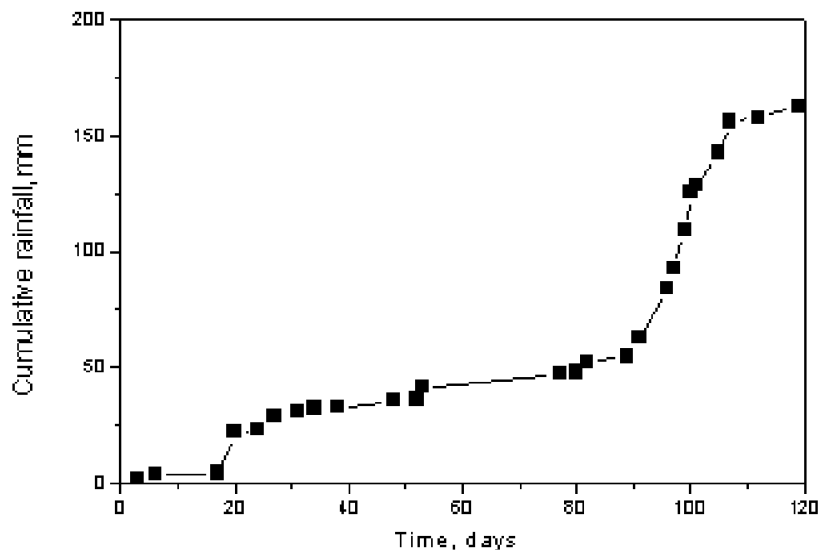


Figure 1. Cumulative rainfall observed during the rainy season, Puebla, 2009.
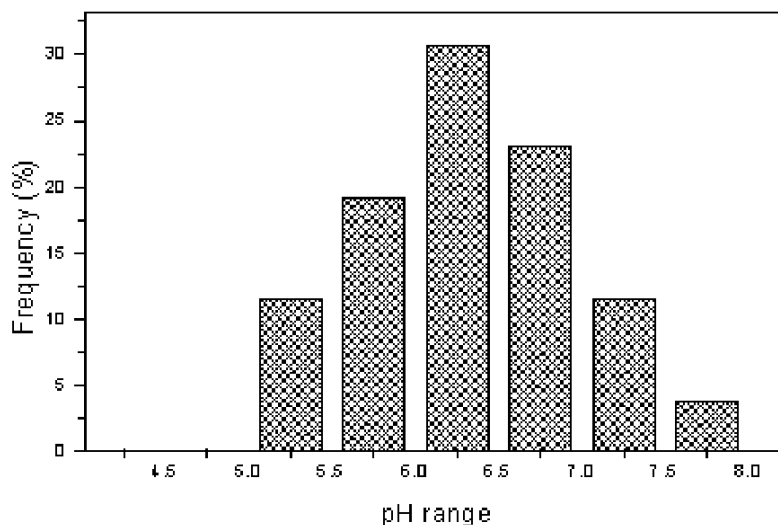


Figure 2. pH distribution in rainwater collected samples,
Puebla, 2009.

In Figure 2 it is presented the pH distribution of the collected samples, as can be observed pH values go from 5 to 8, in detail 31% of the samples fall in the 6-6.5 interval;

also, in the interval from 5.6-7.5, there are 85% of the samples, 4% exhibit a pH higher than 7.5; and 11% of the samples a pH between 5.0-5.5.

Considering that pH of 5.6 is a threshold pH of the cloud water in equilibrium with $CO_2$ (Charlson et al, 1982), then only 11% of the samples can be regarded as acidic.

Higher conductivity values were registered at the beginning of the rainy season, exhibiting a decreasing trend and a slight rise at the final, the last corresponding to the abundant precipitation stage.

Alkalinity determination accounts for hydroxide, carbonate and bicarbonate concentrations, and from titration points can be established the amount of each one. In the Standard Methods (Clescerl et al, 2005) it is mentioned that when phenolphthalein alkalinity is zero, total alkalinity represents the bicarbonate content, this was the case for all collected rain samples.
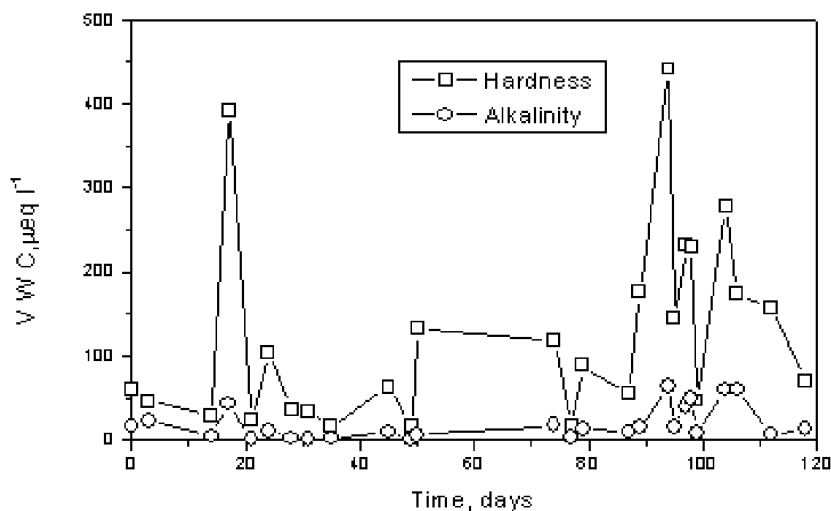


Figure 3. Total alkalinity and total hardness volume weighted concentration profiles in rainwater collected samples, Puebla, 2009.

In Table 1 it is reported the minimum, maximum, arithmetic mean and standard deviation of main anions using as basis of calculus Volume Weighted Concentration (VWC) expressed in meq $l^{-1}$, they are presented from high to low concentration as follows:

$CO_3^{-2} > Cl^- > HCO_3^{-1} > SO_4^{-2} > NO_3^- > PO_4^{-3}$. In order to get an insight of its behavior based on their concentration range, they are organized in pairs. In Figure 3 it is shown the VWC data for total alkalinity and total hardness, concentrations for these anions are in the range of 0-450 meq $l^{-1}$; it can be observed that for all samples total alkalinity is less than total hardness.

Table 1. Statistical parameters of pH, conductivity and main anions (VWC basis) in rainwater collected samples, Puebla, 2009.

| | pH | Conduct mS cm$^{-1}$ | CO$_3^{-2}$ meq/l | Cl$^-$ meq $l^{-1}$ | HCO3$^-$ meq/l | SO$_4^{-2}$ meq $l^{-1}$ | NO$_3^-$ meq $l^{-1}$ | PO$_4^{-3}$ meq $l^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| **Min** | 5.28 | 30 | 15.75 | 0.94 | 0.39 | 0.48 | 0.00 | 0.00 |
| **Max** | 7.66 | 340 | 441.50 | 154.82 | 64.21 | 25.71 | 6.00 | 9.32 |
| **Arith mean** | 6.35 | 100 | 122.29 | 39.87 | 18.91 | 4.77 | 1.36 | 1.10 |
| **Std dev** | 0.67 | 0.07 | 113.84 | 47.92 | 20.13 | 6.15 | 1.43 | 2.17 |

Figure 4 shows the VWC for chloride and sulfate, this pair has concentrations in the range of 0-150 meq l-1. As it can be seen at the beginning of the season both exhibit similar concentrations, but after a "washout" of the atmosphere, it occurred that sulfate concentration was less or equal to the chloride; finally, during the high precipitation stage, chloride concentration exhibited an important rise in concentration, evidence of its marine origin and consequence of the faster seawater transport; this was not the case for sulfate, which increased its concentration but in lower amounts than chloride.
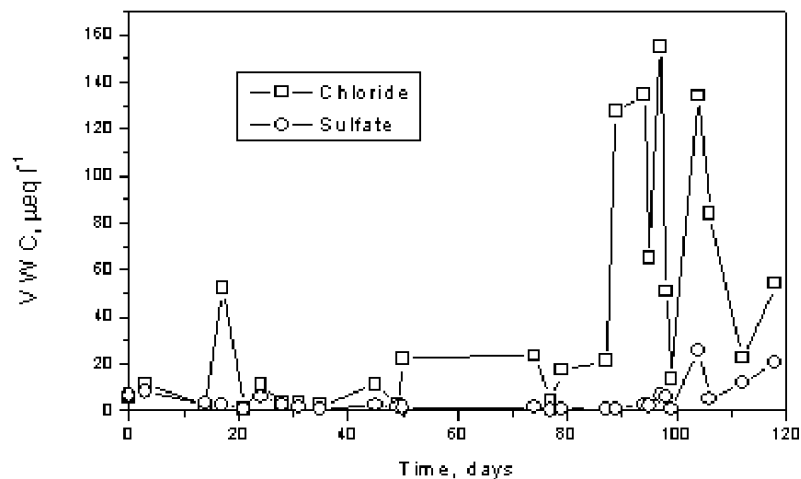
Figure 4. Sulfate and chloride volume weighted concentration profiles in rainwater collected samples, Puebla, 2009.

Figure 5 shows the profiles of nitrate and phosphate, these anions are in a lower but no negligible quantity, their concentrations are in the range of 0-9 meq $l^{-1}$. It can be observed that initially both have a similar concentration, during the rainy season both
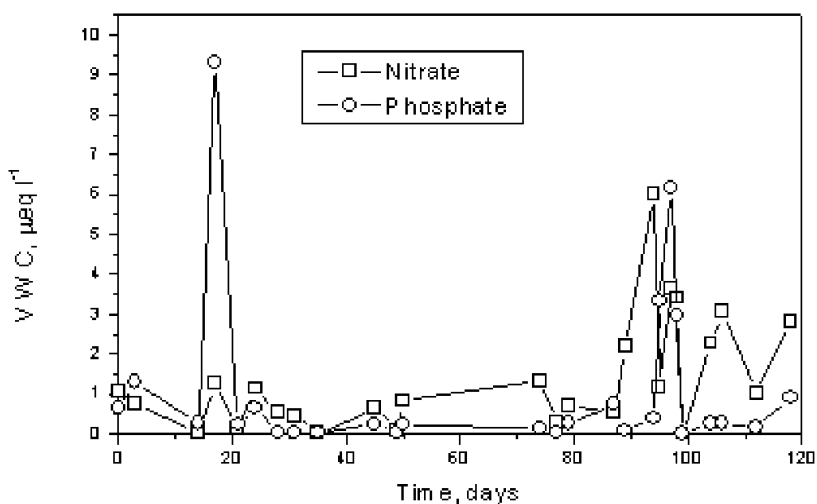


Figure 5. Nitrate and phosphate volume weighted concentration profiles in rainwater collected samples, Puebla, 2009

exhibit an oscillatory behavior, but most of the times being nitrate higher than phosphate. During the last 30 days, nitrate concentration values exhibit an important increase respect to the previous 90 days, corresponding with the period of abundant precipitation and windy conditions, nitrate concentrations became higher than those at the beginning of the season, this was not the case for phosphate which exhibits a slightly rise at the last sample.

Considering that sulfate, nitrate and phosphate are anions providing acidic conditions, then it is important to quantify in which proportion each one contributes to acidity. Fractional acidity (FA) can be calculated as the quotient of protons over the sum of anions; when FA approaches unity, the acidity is not properly neutralized, otherwise values lower than 1, indicate that most of the acidity is neutralized by alkaline constituents like $Ca^{+2}$ (Das et al, 2010). Acidity contributions can be estimated by:

$$X_{A_i} = \frac{A_i}{\sum A_i} \qquad (1)$$

In which $A_i$ stands for a generic denomination of anion $i$, fractional acidity and relative contributions were estimated using reported concentrations from Table 1. It was found that $H^+$ fractional acidity is almost zero, which means acidity is neutralized by alkaline contributors. Also, sulfate ion is the main contributor to acidity with 65.5%, while nitrate contributes with 21.5% and phosphate with 13%.

In Table 2 it is reported the minimum, maximum, arithmetic mean and standard deviation of main cations. They are ordered from high to low concentration, there is evidence of photochemically production of Fe(II) during the greatest sunlight intensity (Willey at al, 2005), and so far this is the specie present in Puebla afternoon rainfall.

Based on sodium concentration, enrichment factors (*EF $X_{marine}$*) are defined as the quotient of the rate ion to sodium in the sample respect to the rate ion in seawater:

$$EF\ X_{marine} = \frac{(X / Na^+)_{sample}}{(X / Na^+)_{marine}} \qquad (2)$$

Table 2. Statistical parameters for cations in rainwater collected samples, Puebla, 2009.

| | $Na^+$ meq $l^{-1}$ | $Mg^{+2}$ meq $l^{-1}$ | $Ca^{+2}$ meq $l^{-1}$ | $Co^{+2}$ meq $l^{-1}$ | $Cu^{+2}$ meq $l^{-1}$ | $Ni^{+2}$ meq $l^{-1}$ | $Fe^{+2}$ meq $l^{-1}$ | $Pb^{+2}$ meq $l^{-1}$ | $Cd^{+2}$ meq $l^{-1}$ | $Zn^{+2}$ meq $l^{-1}$ | $Mn^{+2}$ meq $l^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Min | 3.12 | 6.38 | 2.52 | 0.12 | 0.06 | 0.08 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 |
| Max | 293.05 | 211.68 | 69.40 | 15.48 | 7.97 | 7.95 | 6.47 | 0.86 | 0.16 | 0.30 | 0.05 |
| Arith mean | 81.36 | 55.71 | 18.80 | 3.93 | 2.00 | 2.16 | 1.30 | 0.24 | 0.05 | 0.03 | 0.01 |
| Std dev | 90.02 | 56.77 | 17.68 | 4.60 | 2.38 | 2.46 | 1.63 | 0.28 | 0.05 | 0.06 | 0.02 |

In this formula, X stands for the ion object of analysis. Also, excess concentrations (EC X*) can be calculated taking as a basis ion concentration difference between the sample and the marine spray, considering the following equation (Sanhueza et al, 2005):

$$EC\ X^* = X_{sample} - Na^+_{sample}\left(\frac{X_{marine}}{Na^+_{marine}}\right)$$ (3)

This non-marine proportion, has a secondary origin, and corresponds to the acid fraction of ions contributing to the acid-base equilibrium. Calculus of EF and EC are limited to the quotients reported by Das et al (2010), results of both EF $X_{marine}$ and EC X* are reported in Table 3. The average quotients respect to sodium show that sulfate is 96% of the value from marine contributions, and so far its excess concentration is zero. Otherwise, calcium and magnesium average coefficients, as well as their enrichment factors are higher than the standard marine values, which indicate that they come from suspended soil particles.

Correlation between variables (X,Y) can be estimated by the correlation coefficient of the sample ($r_{XY}$), expressed as:

$$r_{xy} = \frac{s_{xy}}{s_x s_y}$$ (4)

Table 3. Enrichment Factor (EF) and Excess Concentrations (EC) in rainwater collected samples, Puebla, 2009.

| | $Cl^-$ | $SO_4^{-2}$ | $Mg^{+2}$ | $Ca^{+2}$ |
|---|---|---|---|---|
| Average quotients $X/Na^+_{marine}$ (Das et al, 2010) | 1.167 | 0.125 | 0.022 | 0.044 |
| Average Quotients $X/Na^+_{sample}$ | 0.50 | 0.12 | 1.17 | 0.38 |
| EF $X_{marine}$ (eq 1) | 0.43 | 0.99 | 53.04 | 8.67 |
| EC $X^*$ (eq 2) | -1.51 | 0.00 | 1.86 | 0.61 |

In which $s_{XY}$ is the sample covariance, and $s_X$, $s_Y$ are the standard deviation for variable X an Y. Results of ion correlation analysis are shown in Table 4. As can be observed, ions with a common origin exhibit an strong correlation between them, that is the case: $Na^+$, $Co^{+2}$, $Pb^{+2}$, $Ni^{+2}$, $Cl^-$ corresponding to marine origin, this affirmation is corroborated with the last 30 days rainfall registers, in which all of them exhibited an important concentration rise as the abundant precipitation took place. Also, the same phenomena occurs for: $SO_4^{-2}$ and $CO_3^{-2}$ with either $Ca^{+2}$, $Mg^{+2}$, as well as the pair $Ca^{+2}$-$Mg^{+2}$, therefore they have a common origin, which must be different from marine sources since either $Mg^{+2}$ or $Ca^{+2}$ correlate in a weak ($-0.1 < r_{XY} < 0.1$) or negative form with $Na^+$, $Co^{+2}$, $Pb^{+2}$, $Ni^{+2}$, $Cu^{+2}$, $Mn^{+2}$, $Cd^{+2}$, $Zn^{+2}$; presence of these ions can be attributed to dissolution processes from suspended particles, this argument is reinforced by the strong correlation between $SO_4^{-2}$ and $CO_3^{-2}$, as well as the $PO_4^{-3}$ with $HCO_3^-$. Also, iron presence in rainwater can be attributed to soil origin since exhibit medium and strong correlations with $SO_4^{-2}$, $HCO_3^-$, $CO_3^{-2}$, $NO_3^-$, $PO_4^{-3}$, and a negative correlation with marine ions.

Table 4. Correlation analysis of ions in rainwater collected samples, Puebla, 2009.

| | Cond | H | Na | Fe | Co | Pb | Ni | Cu | Mn | Cd | Zn | Mg | Ca | Cl | SO4 | NO3 | PO4 | HCO3 | CO3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cond | 1 | | | | | | | | | | | | | | | | | | |
| H | -0.25 | 1 | | | | | | | | | | | | | | | | | |
| Na | 0.48 | 0.01 | 1 | | | | | | | | | | | | | | | | |
| Fe | -0.22 | -0.29 | -0.13 | 1 | | | | | | | | | | | | | | | |
| Co | 0.55 | 0.24 | 0.67 | -0.72 | 1 | | | | | | | | | | | | | | |
| Pb | 0.46 | 0.40 | 0.60 | -0.65 | 0.86 | 1 | | | | | | | | | | | | | |
| Ni | 0.57 | 0.20 | 0.65 | -0.70 | 0.99 | 0.83 | 1 | | | | | | | | | | | | |
| Cu | -0.30 | 0.45 | 0.08 | -0.57 | 0.38 | 0.46 | 0.36 | 1 | | | | | | | | | | | |
| Mn | -0.10 | 0.27 | 0.07 | -0.13 | 0.19 | 0.29 | 0.18 | 0.31 | 1 | | | | | | | | | | |
| Cd | 0.16 | 0.06 | 0.09 | -0.12 | 0.17 | 0.15 | 0.17 | 0.05 | 0.74 | 1 | | | | | | | | | |
| Zn | -0.09 | 0.48 | 0.02 | -0.11 | 0.14 | 0.15 | 0.15 | 0.24 | 0.40 | 0.27 | 1 | | | | | | | | |
| Mg | 0.38 | -0.21 | -0.05 | 0.24 | 0.04 | -0.10 | 0.09 | -0.49 | -0.23 | -0.09 | -0.03 | 1 | | | | | | | |
| Ca | 0.26 | -0.33 | 0.09 | 0.43 | -0.02 | -0.28 | 0.05 | -0.46 | -0.26 | -0.08 | -0.09 | 0.71 | 1 | | | | | | |
| Cl | 0.46 | 0.30 | 0.60 | -0.29 | 0.65 | 0.62 | 0.65 | -0.02 | 0.08 | -0.06 | 0.00 | 0.29 | 0.21 | 1 | | | | | |
| SO4 | 0.37 | -0.32 | 0.27 | 0.72 | -0.16 | -0.25 | -0.13 | -0.73 | -0.26 | -0.13 | -0.10 | 0.63 | 0.70 | 0.24 | 1 | | | | |
| NO3 | 0.36 | -0.25 | 0.46 | 0.30 | 0.02 | 0.04 | -0.02 | -0.59 | -0.13 | 0.06 | -0.19 | 0.14 | 0.04 | 0.31 | 0.50 | 1 | | | |
| PO4 | -0.28 | -0.09 | -0.14 | 0.52 | -0.47 | -0.29 | -0.47 | -0.29 | -0.27 | -0.43 | -0.22 | 0.06 | 0.09 | -0.03 | 0.35 | 0.12 | 1 | | |
| HCO3 | -0.22 | -0.18 | 0.16 | 0.62 | -0.26 | -0.32 | -0.23 | -0.23 | -0.25 | -0.38 | -0.18 | 0.20 | 0.41 | 0.13 | 0.56 | 0.23 | 0.61 | 1 | |
| CO3 | 0.37 | -0.27 | -0.02 | 0.33 | 0.01 | -0.17 | 0.07 | -0.53 | -0.26 | -0.10 | -0.06 | 0.98 | 0.83 | 0.28 | 0.69 | 0.13 | 0.07 | 0.29 | 1 |

## Conclusions

Obtained results allows to affirm that most of the rainwater at Puebla does not exhibit acid characteristics since the average pH is higher than 5.6; Suspended soil particles exert a neutralization effect through the alkaline ions ($CO_3^{-2}$, $HCO_3^{-}$, $Ca^{+2}$, $Mg^{+2}$) considering that the average pH is higher than the threshold for marine sprays. Main acidity contribution corresponds to sulfate ions with a 65.5% followed by nitrate and phosphate, the sum of the last two is about 50% of the sulfate.

Rainfall does an atmospheric washout since the maximum conductivity was registered at the beginning of the rainy season (350 mS cm$^{-1}$), and it drops to values between 50 y 150 mS cm$^{-1}$, except at the end of the season in which it exhibits a rise up to 200 mS cm$^{-1}$.

Considering that a strong correlation between ions occurs when they have a common origin, then $Na^{+}$, $Co^{+2}$, $Pb^{+2}$, $Ni^{+2}$, $Cl^{-}$ can be classified as marine ions. While $CO_3^{-2}$, $HCO_3^{-}$, $SO_4^{-2}$, $PO_4^{-3}$, $Ca^{+2}$, $Mg^{+2}$ can be classified as soil ions.

## Acknowledgements

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