Chapter

Mapping and Estimation of Nitrogen and Sulfur Atmospheric Deposition Fluxes in Central Region of the Mexican Bajio

Rosa María Cerón Bretón, Julia Griselda Cerón Bretón, Reyna del Carmen Lara Severino, Marcela Rangel Marrón, María de la Luz Espinosa Fuentes, Simón Eduardo Carranco Lozada and Lizbeth Cisneros Rosique

Abstract

The objective of this study was to assess the spatial and temporal distribution of nitrogen and sulfur deposition and its relationship with meteorological conditions in the metropolitan area of León in Guanajuato, México. N and S atmospheric deposition was collected using passive samplers (IER) in 10 sites in León City during three climatic seasons in 2018. Nitrate, ammonium, and sulfate concentrations and deposition fluxes of N and S were determined. From wind and air-mass trajectories analysis, mechanisms and possible sources contributing to N and S deposition in the study area were assessed. Atmospheric deposition fluxes were compared to critical load values reported for sensitive ecosystems in Europe. It was found that mean deposition flux for N (5.82 Kg N ha^{-1} $year^{-1}$) was within the range of values reported for sensitive ecosystems in Nuevo México, Europe, and California. On the other hand, the mean deposition flux for S (13.77 S Kg ha^{-1} $year^{-1}$) exceeded the critical load values proposed for Europe, suggesting that current S deposition could be a risk for ecosystems and water bodies in the region.

Keywords: atmospheric deposition, nitrogen, sulfur, Guanajuato, México

1. Introduction

Air pollution constitutes an important health risk not only for developed countries but also for developing countries. SO_2 and NO_2 are among primary pollutants commonly present in urban and industrial areas, whose main sources are combustion processes, and being both, acid rain precursors. The two main mechanisms responsible for pollutant removal in the atmosphere are dry and wet deposition. Gases and particulate matter are deposited in dry form, while completely soluble components are deposited by the rain action (wet deposition). Dry deposition of gases and particles occurs through complex processes such as sedimentation, impactation, and adsorption and can contribute in a significant way to local deposition of atmospheric components, being particularly important near urban and industrial areas, where particle concentration and dust can be relatively high [1]. On the other hand, wet deposition occurs as rain, fog or snow and plays an important role in the removal processes of soluble wastes in the atmosphere [2]. Some of components of atmospheric deposit (as nitrate and sulfate) are precursors of acidification, being able to harm the aquatic and terrestrial ecosystems not only in the surroundings of sources but also in nearby regions.

Thus, it is necessary to measure the total atmospheric deposition of N and S, to estimate the inflows and outflows, their effects on the balance of biogeochemical cycles, and to assess the biologic and ecologic response to the current atmospheric pollution levels and their relationship with emission patterns. Since the effective design of public politics requires of surveillance and monitoring programs to understand and to quantify the current conditions, by comparison with historical data and reference values, measurement chemical composition, and physical characteristics are required. This will allow to propose environmental politics focused to protect not only public health but also ecosystems and diagnose the real effects of N and S deposition as a result of the current emission patterns [3]. Deposition maps are very useful tools to carry out this kind of assessments, since they allow to analyze the spatial distribution and temporal variability of N and S deposition in a given area; likewise, they allow to visualize those areas in which exceedances to threshold values of critical loads are occurring. In this way, the decision makers can implement control strategies of regionalized emissions to protect different receptors. Several exceedance ranges can be established and be related to sensitivity categories, from which, it is possible to diagnose in a preliminary way, the vulnerability of ecosystems to the inputs of N and S. However, the main problem during this process is to have enough and reliable data of N and S deposition fluxes.

Dry deposition fluxes for ecosystems are obtained from theoretical models, due in part to the lack of monitoring standardized methods. On the other hand, in the case of wet deposition, the estimation depends on the occurrence of rain events, resulting in the case of arid or semiarid regions in insufficient data to study the spatial and temporal variability at long-term. In addition, atmospheric sampling devices for atmospheric deposition comprise manual and automatic collectors. Although the first choice in more economical, it is hard to implement in field in the case of remote sites, while in the case of automatic collectors, these are expensive and must meet specific criteria for installation and operation. Fenn and Bytnerowicz [4] proposed a collector based on ionic exchange resin (IER) to quantify atmospheric deposition in forests. In this regard, comparison between conventional collectors and passive sampling devices of atmospheric deposition have been carried out [5, 6], concluding that passive collectors can be used to quantify total sulfur deposition and report a strong correlation between N Deposition and the presence of nitrate in soils. From combined use of mapping and measurement of N and S deposition fluxes, it is possible to study the spatial and temporal variability of deposition. Therefore, this study was aimed to estimate N and S atmospheric deposition fluxes using passive collectors to assess their spatial distribution and temporal variability in Central Region of México known as “Bajío.”

2. Materials and methods

2.1 Study area

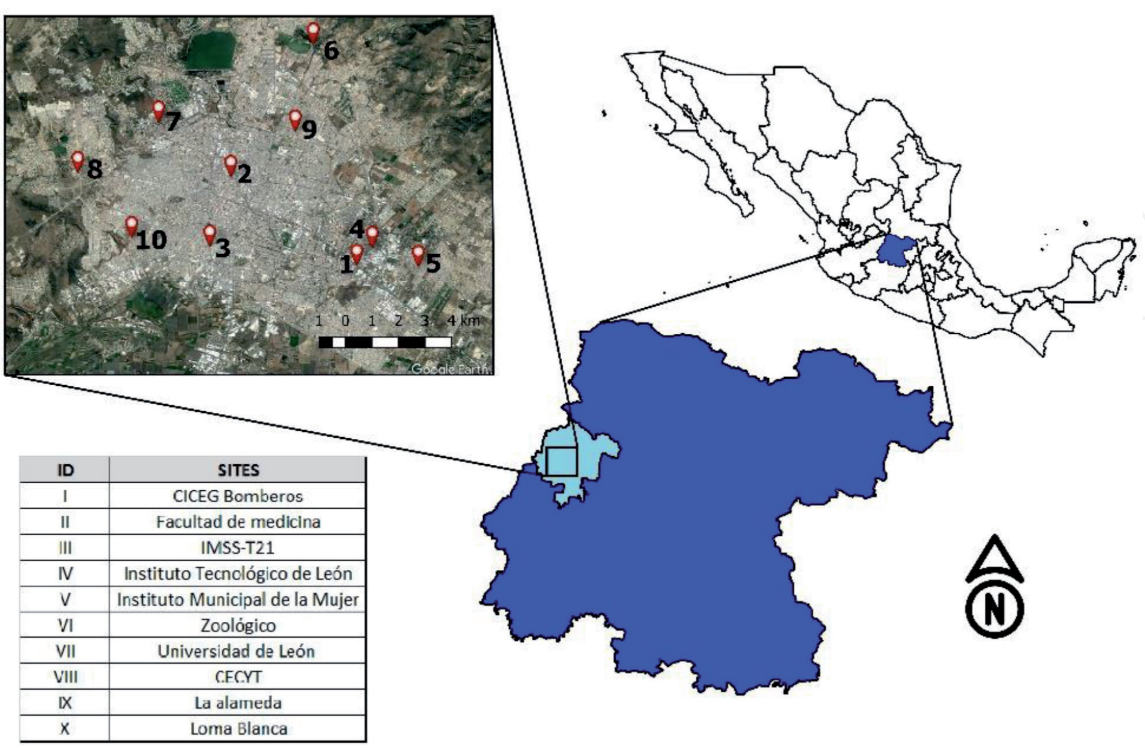
Study area is located in Central México within an area known as "Bajío," in metropolitan area of León, in Guanajuato. León City is the most populated in Guanajuato state with a population of 1,578,626 inhabitants [7]. Climate is semi-dry semi-warm [8].

The main economic activities in this region are shoe manufacturing, tanned skin, cardboard production, and chemical industry; however, economical activities are not only based on these sectors, but also building, plastics, mining, manufacturing, textile, and automotive industries. There were selected a total of 10 sampling sites considering in first place the site accessibility and the land use; as well as safety of sampling devices, preferring public buildings to safely house the equipment. In **Figure 1**, study area and sampling site location are shown.

2.2 Sampling

Since passive sampling is defined as hydrologic flux to soil of ions and other compounds in solution, passive sampling provides a useful estimation of atmospheric inputs to a given site, because of it includes both, wet and dry deposition. Considering the high cost and the difficulty of measuring dry deposition fluxes, passive collectors constitute a useful alternative to measure annual atmospheric inputs at ground level [4, 9]. Additionally, automatic collectors are very expensive, for this reason, passive collectors constitute a good sampling choice in a given area, since they allow to increase the number of sampling sites at a low cost and take samples simultaneously in different locations in a specific region.

Therefore, it is possible to obtain complex spatial patterns of N and S atmospheric deposition in a given area by using monitoring equipment of low cost, easy to operate, and that does not require frequent field visits. Collectors based on IER



ID	SITES
I	CICEG Bomberos
II	Facultad de medicina
III	IMSS-T21
IV	Instituto Tecnológico de León
V	Instituto Municipal de la Mujer
VI	Zoológico
VII	Universidad de León
VIII	CECYT
IX	La alameda
X	Loma Blanca

Figure 1.
Study area location.

beds have been used to measure atmospheric deposition in forest ecosystems with a high spatial resolution [10].

This type of passive collectors consists in a funnel connected to a column which contains 30 g of ionic exchange resin (IER) [11]. Glass wool is placed in both, bottom (as a support) and top (as a filter) sections. Samples are collected through the funnel, and hydrologic flux is channeled to resin mixed bed through the column where ions are retained. The funnel is connected to IER column by a PVC tube (1.27 cm × 35.6 cm), in addition, a double-wall shadow tube is placed around resin column to avoid that solar radiation damage the resin. Resin used for IER collectors was a mixed bed of polystyrene to exchange both, anions and cations (Amberlite IRN-150™). In the top of sampling devices, a fine mesh is placed to avoid the input of insects, leaves, and so on. The PVC column has a valve which must be open all time to let the pass of hydrologic flux through the collector.

The main advantage of this kind of collector is that can be used during long exposition periods (i.e., months), the equipment has a low cost, and let to display a great number of them to characterize deposition spatial patterns with a high resolution [12].

Sampling was carried out from January 1 to December 31 of 2018, with three sampling sub-periods considering three climatic seasons: cold dry, warm dry, and rains. At the end of each sampling sub-period, resin tubes were changed by tubes containing fresh resin. Later, retained ions (sulfate, nitrate, and ammonium) were extracted from resin tube by using an extraction solution (KCL 2N solution) and analyzed by turbidimetric and colorimetric methods, respectively.

2.3 Chemical analysis

Atmospheric deposition samples were sent and analyzed in Environmental Protection Laboratory of Chemistry Faculty of Autonomous University of Carmen. NH_4^+ was determined by molecular absorption spectrometry by using blue indophenol method [13]. SO_4^{2-} was determined by turbidimetric method [14], whereas NO_3^- was analyzed by colorimetric method using the brucine method [15].

2.4 Meteorological analysis

To identify possible natural and anthropogenic sources and to analyze transport processes which could influence on N and S levels in atmospheric deposition in the study area, a meteorological analysis was carried out at both, surface and altitude. For this, surface meteorological data were obtained from meteorological portable stations (Davies Vantage Pro II). Later, to carry out surface meteorological analysis, wind rose graphs were obtained by using WRPLOT View™ (Lakes Environmental), to identify prevailing wind direction in the study area.

For the altitude meteorological analysis, backward air-masses trajectories for 24 h were obtained from HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory) from NOAA (National Oceanic and Atmospheric Administration of United States) to identify the origin of air masses and to identify the main transport processes contributing to N and S deposition during the study period.

2.5 Statistical analysis

To obtain descriptive measurements, to analyze the morphology and symmetry of data, univariate, bivariate, and multivariate analysis was carried out by using XLSTAT 20016 program. Likewise, non-parametric tests (Friedman test) were applied to establish if, there were significant differences between treatments (sites and sampling seasons) [16].

2.6 Kriging interpolation and mapping deposition fluxes

To obtain deposition maps in the study area, a geo-statistical procedure was applied to interpolate field measurements (kriging interpolation) and to obtain a continuous spatial pattern for the variables (concentration iso-lines) to increase the number of points in the maps.

3. Results and discussion

3.1 Sulfate

3.1.1 Seasonal variability

To assess the seasonal variability, deposition fluxes were analyzed for three climatic periods: cold dry, warm dry, and rainy. During the cold dry season, a mean flux of 10.89 Kg Ha^{-1} $year^{-1}$, with a maximum of 17.14 Kg Ha^{-1} $year^{-1}$ in site VI, which corresponds to Zoológico, located at NE, whereas the minimum value of 6.58 Kg Ha^{-1} $year^{-1}$ was obtained for site VII that corresponds to Universidad de León (**Figure 2**).

On the other hand, the mean value obtained during warm dry season was 13.98 Kg Ha^{-1} $year^{-1}$, with a maximum value of 25.82 Kg Ha^{-1} $year^{-1}$ in site IV (Instituto Tecnológico de León), located at SE, whereas the minimum value (1.81 Kg Ha^{-1} $year^{-1}$) was found in site III, which corresponds to monitoring station IMSS T-21, located at downtown of the city (**Figure 2**).

Finally, during rainy season, the mean value obtained was 15.52 Kg Ha^{-1} $year^{-1}$ with a maximum of 18.43 Kg Ha^{-1} $year^{-1}$ in sites III and VI, located at NE and at downtown of the city, whereas the minimum value (11.77 Kg Ha^{-1} $year^{-1}$) was obtained for site I (monitoring station CICEG-Bomberos) (**Figure 2**).

From **Figure 2**, it can be observed that mean deposition fluxes for sulfate were relatively higher during the rainy season and lower during cold dry season. With respect to extreme values, the highest values were observed during warm dry

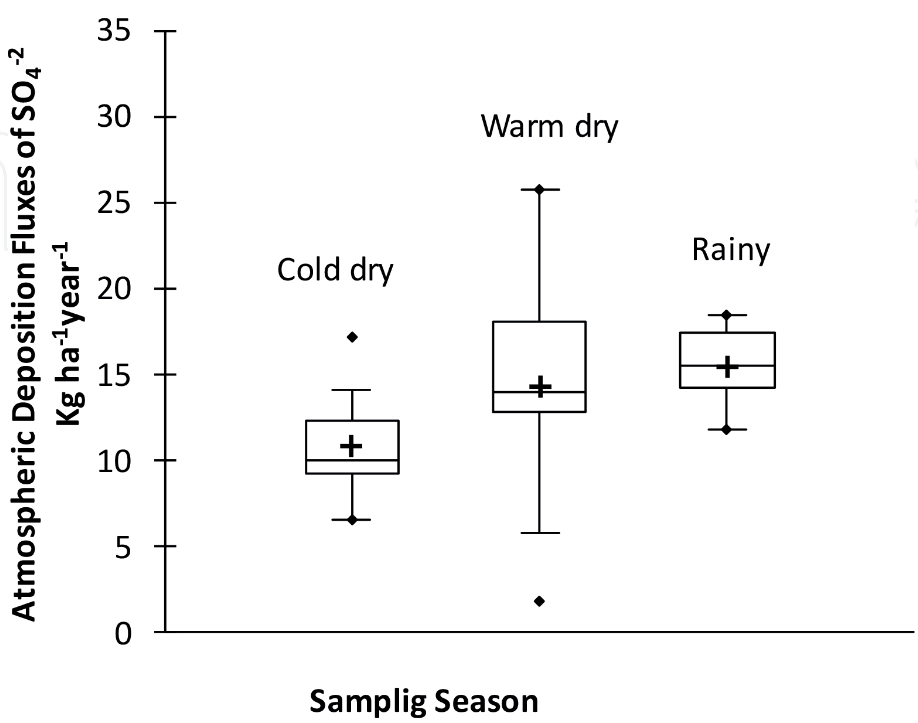


Figure 2.
Sulfate atmospheric deposition fluxes by season.

season, suggesting that the lack of dilution during this season could result in higher values in the region. Applying the Friedman tests, significant differences in sulfate atmospheric deposition fluxes were found between seasons.

3.1.2 Spatial variability

To assess the spatial distribution, sulfate atmospheric deposition fluxes were analyzed by site. A mean value of 13.78 Kg Ha^{-1} $year^{-1}$ was found, with a maximum value of 25.82 Kg Ha^{-1} $year^{-1}$. From **Figure 3**, it can be observed that the highest mean value was found in site IV (Instituto Tecnológico de León) located at SE, whereas the minimum value (1.81 Kg Ha^{-1} $year^{-1}$) was registered for site III, where monitoring station IMSS-T21 is located just at downtown of the city. Considering extreme values, the higher fluxes were found for site IV; however, when Friedman test was applied, significant differences were not found. It suggests a certain homogeneity in sulfate deposition levels in the study region, which confirms the regional character of sulfate precursor (SO_2).

3.1.3 Analysis by land use

To assess the variability of sulfate atmospheric deposition fluxes by land use, sampling sites were grouped according to the prevailing land use as follows:

Industrial land use: Sites I, II, III, IV, V.

Urban land use: Sites VI, VII, VIII, IX, X.

According to **Figure 4**, it can be observed that mean sulfate deposition fluxes were slightly higher in sites with an urban land use; however, sites with an industrial land use showed extreme values. When Friedman tests was applied, significant differences between land use were not found. It demonstrates a spatial homogeneity that suggests the regional origin of sulfate as a result of long-range transport mainly during the rainy season.

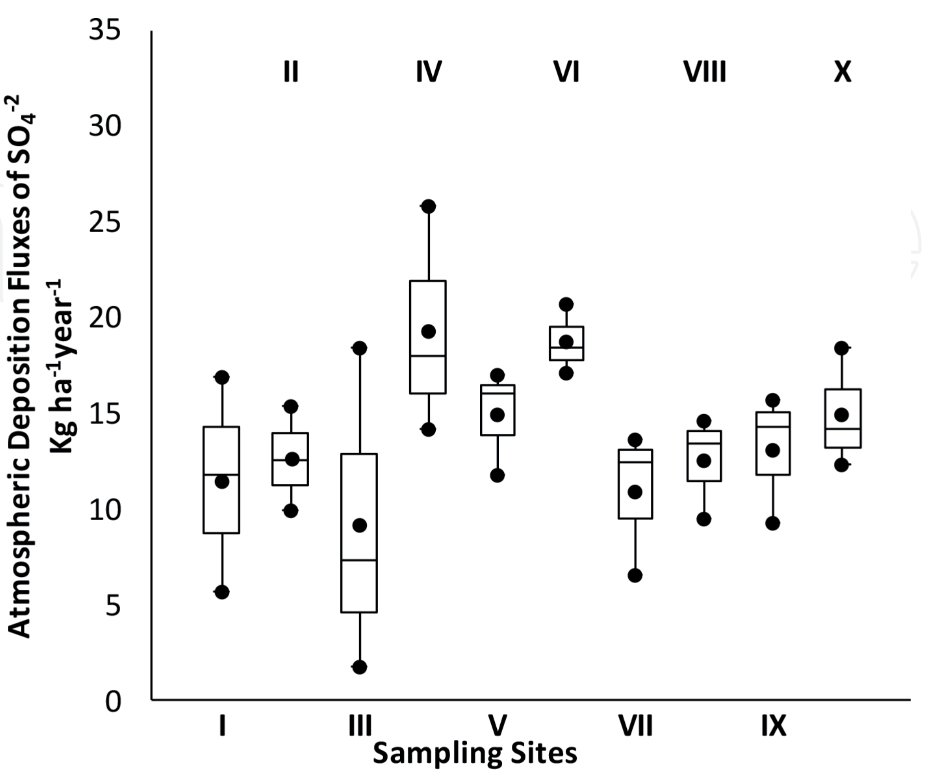


Figure 3.
Sulfate atmospheric deposition fluxes by site.

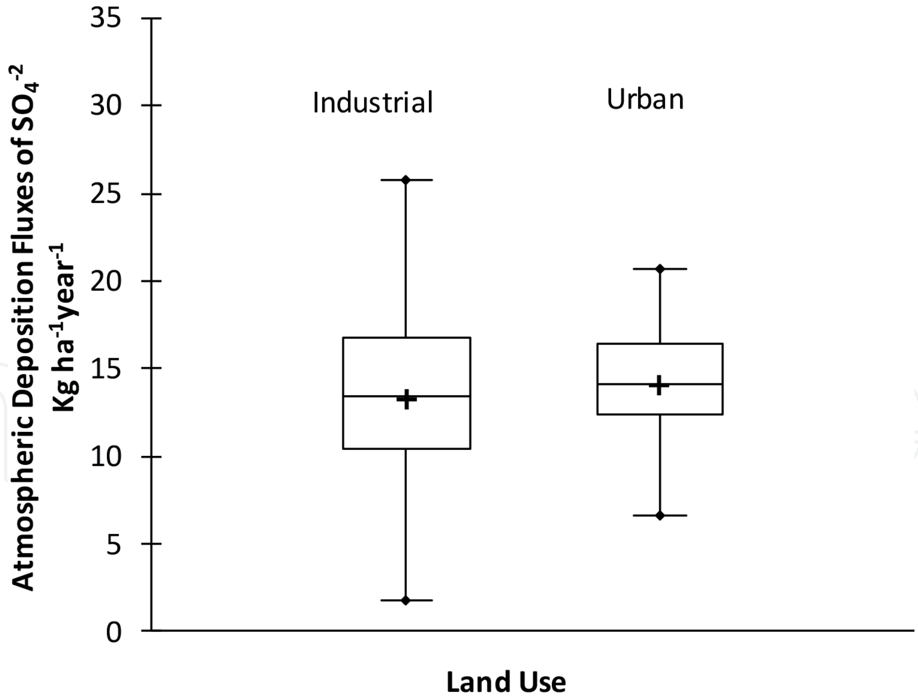


Figure 4.
Sulfate atmospheric deposition fluxes by land use.

In the case of sites grouped with an urban land use, the mean value found was 14.05 Kg Ha^{-1} $year^{-1}$, with a maximum and minimum values of 20.70 and 6.58 Kg Ha^{-1} $year^{-1}$, respectively, observed in sites VI (Zoológico at NE) and site VII (Universidad de León) (**Figure 4**).

On the other hand, in the case of sites grouped with an industrial land use, the mean value found was 13.51 Kg Ha^{-1} $year^{-1}$, with a maximum value of 25.82 Kg Ha^{-1} $year^{-1}$. Considering extreme values, the highest values were found in site IV (Instituto Tecnológico de León at SE), whereas the lowest value (1.81 Kg Ha^{-1} $year^{-1}$) was registered in site III (monitoring station IMSS-T21 at downtown of the city).

3.2 Nitrate

3.2.1 Seasonal variability

From **Figure 5**, it can be observed that the higher nitrate deposition fluxes were obtained during cold dry season, with a mean value of 2.93 Kg Ha^{-1} $year^{-1}$ and a maximum value of 3.93 Kg Ha^{-1} $year^{-1}$, which corresponds to site X (Loma Blanca, at SW). On the other hand, the mean value obtained for warm dry season was 0.78 Kg Ha^{-1} $year^{-1}$ with a maximum of 1.47 Kg Ha^{-1} $year^{-1}$ in site X (Loma Blanca at SW). Finally, during the rainy season, a mean value of 1.13 Kg Ha^{-1} $year^{-1}$ with a maximum value of 2.84 Kg Ha^{-1} $year^{-1}$ in site X (Loma Blanca at SW) and a minimum value of 0.22 Kg Ha^{-1} $year^{-1}$ in site V (Instituto de la Mujer at SE) were found (**Figure 5**).

Applying Friedman tests, significant differences were found between cold dry season and the other two sampling seasons.

3.2.2 Spatial variability

From the analysis by sampling site, a mean nitrate atmospheric deposition flux of 1.61 Kg Ha^{-1} $year^{-1}$ with a maximum value of 3.93 Kg Ha^{-1} $year^{-1}$ was found. The highest value was observed in site X (Loma Blanca at SW) (**Figure 6**).

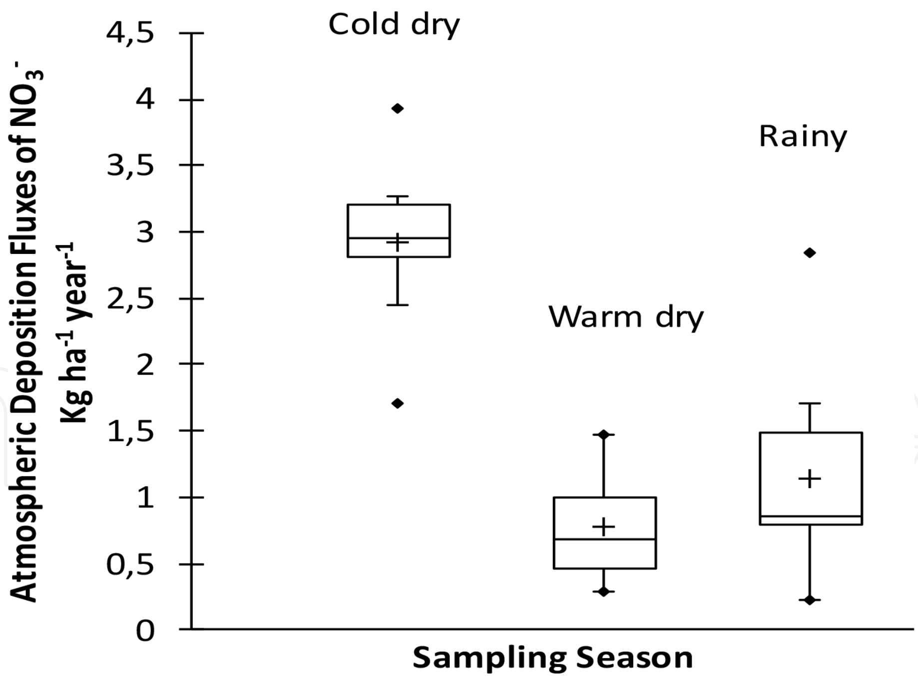


Figure 5.
Nitrate atmospheric deposition fluxes by season.

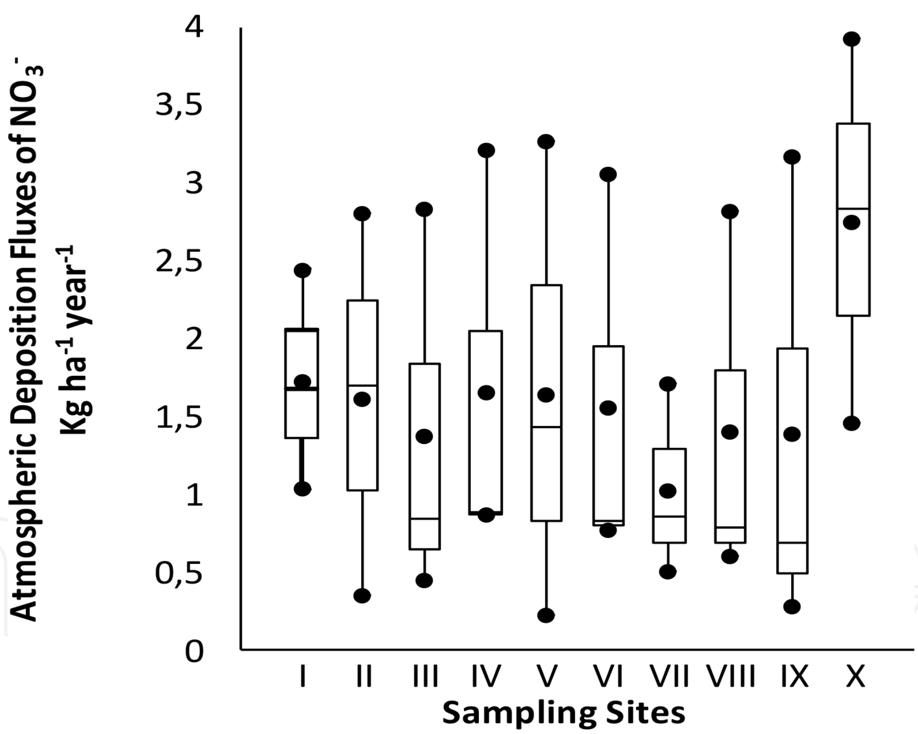


Figure 6.
Nitrate atmospheric deposition fluxes by site.

However, when Friedman test was applied, differences found were not statistically significant, suggesting a certain uniformity in the distribution of sources (especially mobile sources) and nitrate levels around study area.

3.2.3 Analysis by land use

To assess the variability of nitrate atmospheric deposition fluxes by land use, sampling sites were grouped according to the prevailing land use as follows:

Industrial land use: Sites I, II, III, IV, V.

Urban land use: Sites VI, VII, VIII, IX, X.

In the case of sites grouped with an urban land use, it was obtained a mean value of 1.62 Kg Ha^{-1} $year^{-1}$ with a maximum of 3.93 Kg Ha^{-1} $year^{-1}$. Regarding extreme values, the highest nitrate deposition fluxes were found in site X (**Figure 7**). On the other hand, in the case of sites grouped with an industrial land use, the mean value obtained was 1.50 Kg Ha^{-1} $year^{-1}$, with a maximum of 3.26 Kg Ha^{-1} $year^{-1}$. The highest flux was registered in site I, corresponding to monitoring station located at CICEG Bomberos (**Figure 7**).

According to **Figure 7**, it can be observed that nitrate deposition was slightly higher in sites with an urban land use; this agrees with the origin of nitrate, whose main source is mobile sources, which are uniformly distributed along metropolitan area of León. This hypothesis was confirmed by applying Friedman tests which demonstrated that there were not significant differences between sampling sites or land use.

3.3 Ammonium

3.3.1 Seasonal variability

From **Figure 8**, it can be observed that the mean ammonium deposition flux was higher during the cold dry season. During the cold dry season, the mean value obtained was 11.29 Kg Ha^{-1} $year^{-1}$ with a maximum value of 15.78 Kg Ha^{-1} $year^{-1}$ which corresponds to sites I and IV (CICEG Bomberos and Instituto Tecnológico de León, located at SE). On the other hand, during the other two seasons, nitrate deposition fluxes were significantly lower. The mean value obtained during warm dry season was 1.08 Kg Ha^{-1} $year^{-1}$ with a maximum of 6.07 Kg Ha^{-1} $year^{-1}$ in site VI (Zoológico located at NE), whereas the mean value registered for rainy season was 0.25 Kg Ha^{-1} $year^{-1}$ with a maximum value of 1.06 Kg Ha^{-1} $year^{-1}$ in site III (IMSS-T21, at the downtown of the city) (**Figure 8**).

The marked seasonality found in ammonium levels suggests two important aspects: first, the dilution effect is important since ammonium levels during the rainy season were considerably lower as a result of frequent and intense rains

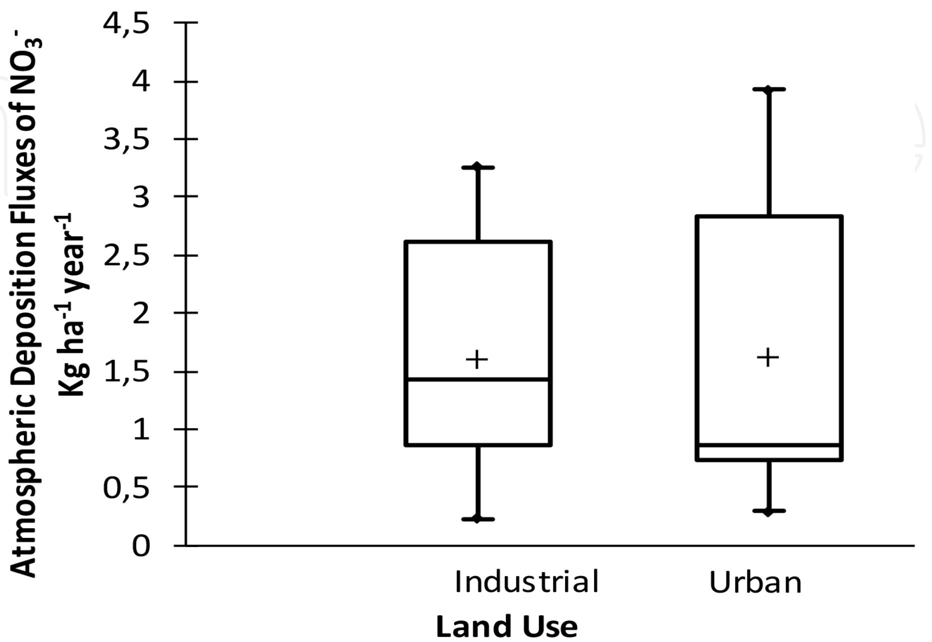


Figure 7.
Nitrate atmospheric deposition fluxes by land use.

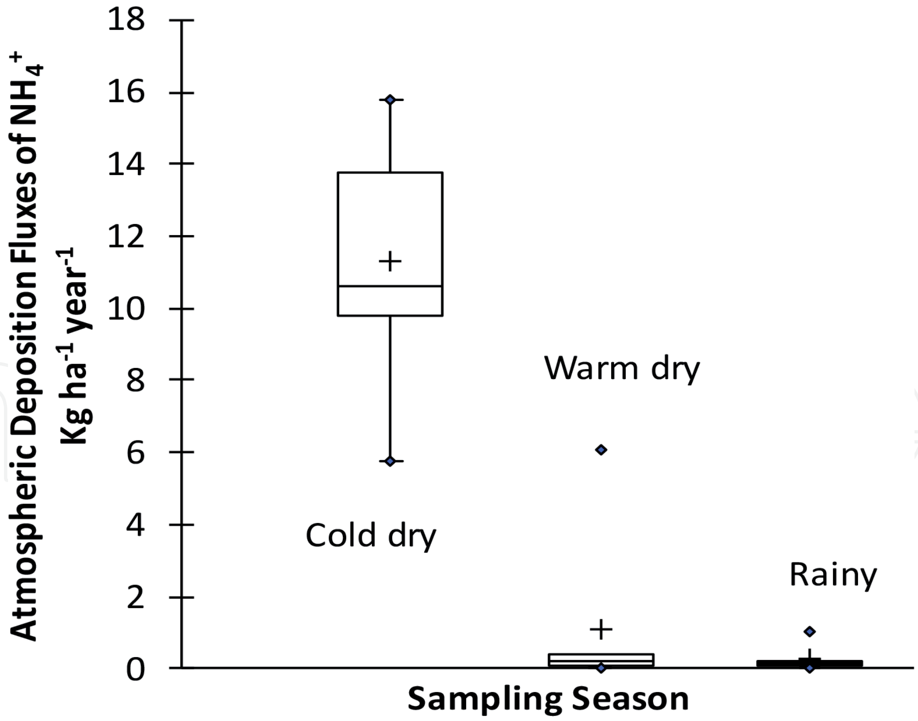


Figure 8.
Ammonium atmospheric deposition fluxes by season.

occurring during this season in comparison with the other two seasons of the year. Second, the temporality of sources could be important, since the use of agrochemicals can be intensive during the cold dry season, resulting in levels considerably high during this season. This was demonstrated applying Friedman test, whose results confirmed that differences between seasons were significant.

3.3.2 Spatial variability

To assess the spatial variability and their distribution, ammonium deposition fluxes were analyzed by sampling site, finding a mean value of 4.29 Kg Ha^{-1} year^{-1}, with the highest value registered in site X (Loma Blanca at SW) (**Figure 9**). However, applying Friedman test, it was concluded that there were not significant differences between sampling sites. It suggests that the differences found could be attributed only to sampling season as a result of agricultural activities and the effect of atmospheric dilution.

3.3.3 Analysis by land use

To assess the variability of ammonium atmospheric deposition fluxes by land use, sampling sites were grouped according to the prevailing land use as follows:

Industrial land use: Sites I, II, III, IV, V.

Urban land use: Sites VI, VII, VIII, IX, X.

In the case of sites grouped with an urban land use, the mean value obtained was 3.97 Kg Ha^{-1} year^{-1}, with a maximum of 14.04 Kg Ha^{-1} year^{-1}. Regarding extreme values, the highest values were found in site VI (Zoológico at NE), whereas in the case of sites grouped with an industrial land use, the mean value obtained was 4.45 Kg Ha^{-1} year^{-1}, with a maximum of 15.78 Kg Ha^{-1} year^{-1}. The highest mean value was registered in site IV (Instituto Tecnológico de León at SE) (**Figure 10**). From **Figure 10**, it can be observed that the mean ammonium deposition flux did not

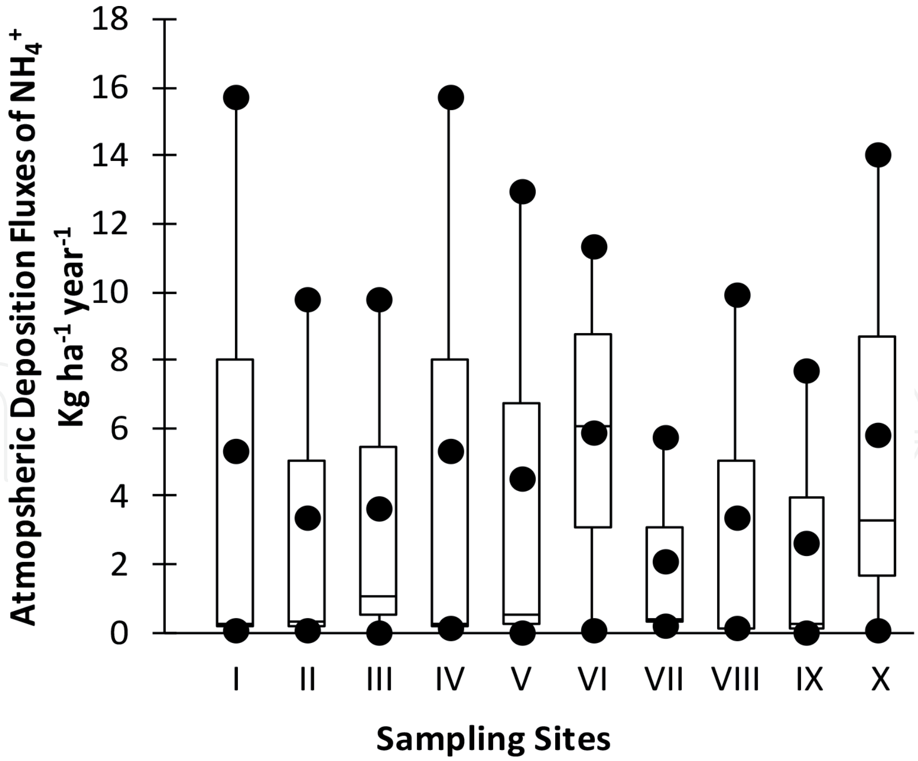


Figure 9.
Ammonium atmospheric deposition fluxes by site.

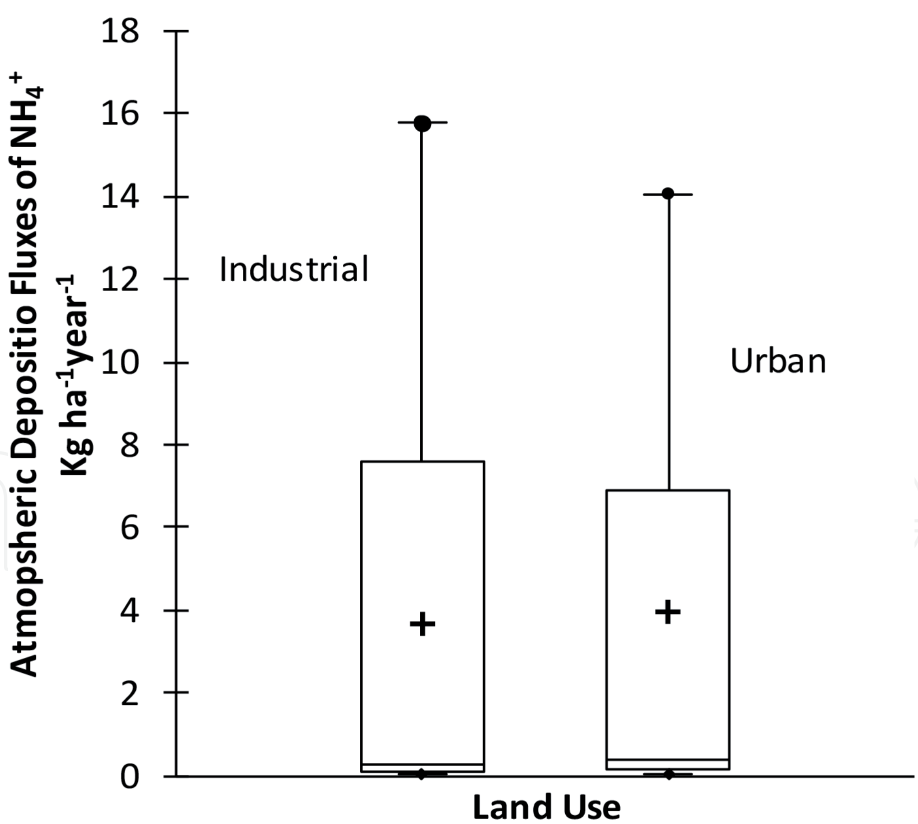


Figure 10.
Ammonium atmospheric deposition fluxes by land use.

show any variability or trend with respect to land use; however, the extreme values were higher in those sites with an industrial land use; however, when Friedman test was applied, any significant difference was found.

3.4 Meteorological analysis

To carry out the meteorological analysis at regional level, 24-h backward air-masses trajectories at 500, 1000, and 1500 m of altitude were obtained (a total of 85 trajectories) from HYSPLIT Model (National Oceanic and Atmospheric Administration), and choosing as representative site to CICEG-BOMBEROS, located at SE of the metropolitan area. In addition, meteorological surface data were obtained from SINAICA (National System of Air Quality Information) to estimate wind roses to identify the prevailing wind direction during the study period.

From surface analysis, it could be observed that wind direction showed a great variability between climatic seasons, for example, the prevailing wind direction during cold dry season was from SW (**Figure 11a**), during warm dry season was from NE (**Figure 11b**), and during rainy season was from E-NE (**Figure 11c**).

3.5 Mapping and reference values

3.5.1 Mapping

3.5.1.1 NH_4^+

In **Figure 12**, it can be observed that during warm dry and rainy seasons, the lowest ammonium deposition fluxes were registered, unlike cold dry season, when the highest levels were observed. During all study period, the highest ammonium

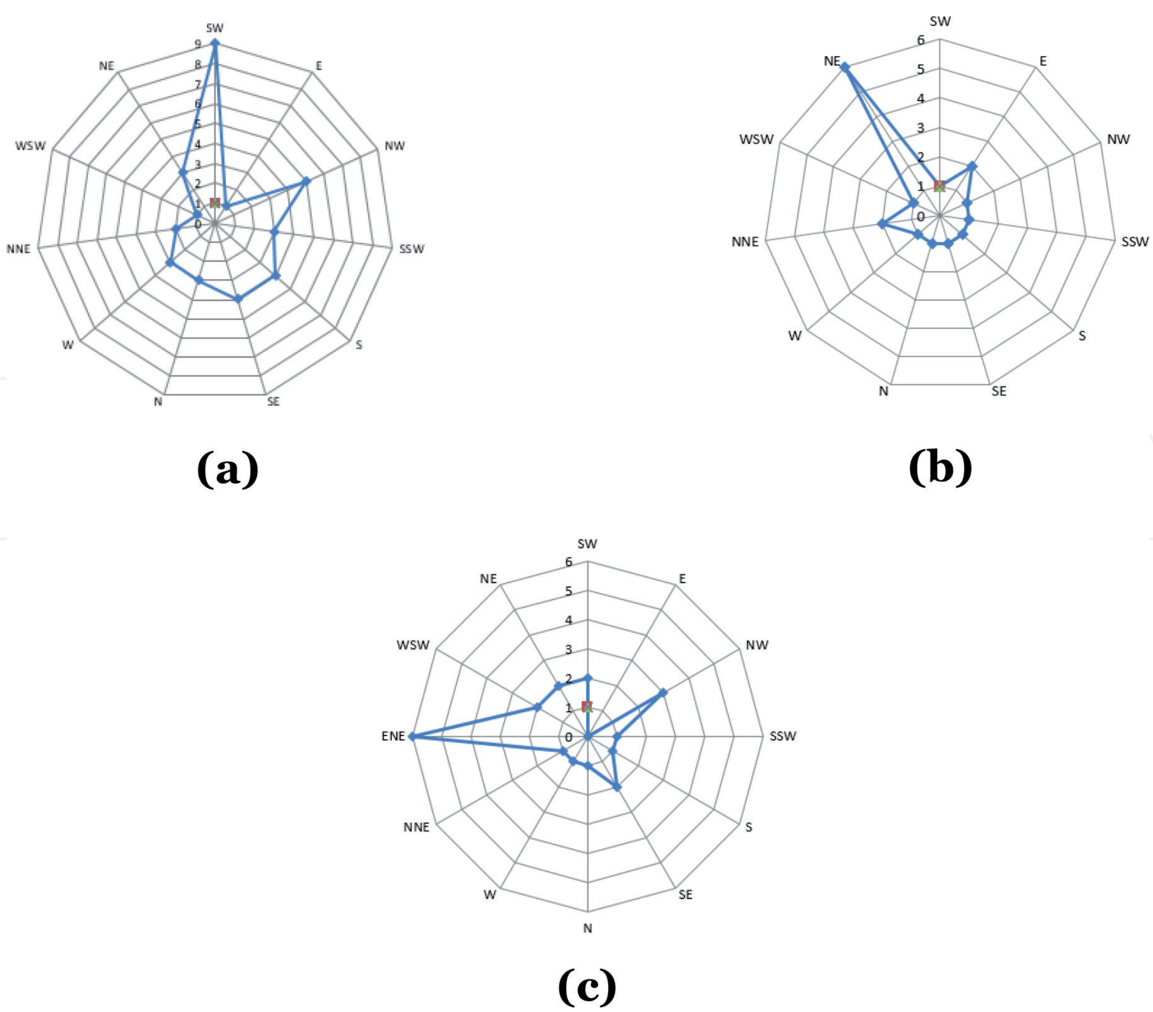


Figure 11.
Frequency histogram for (a) cold dry season, (b) for warm dry season, and (c) for rainy season.

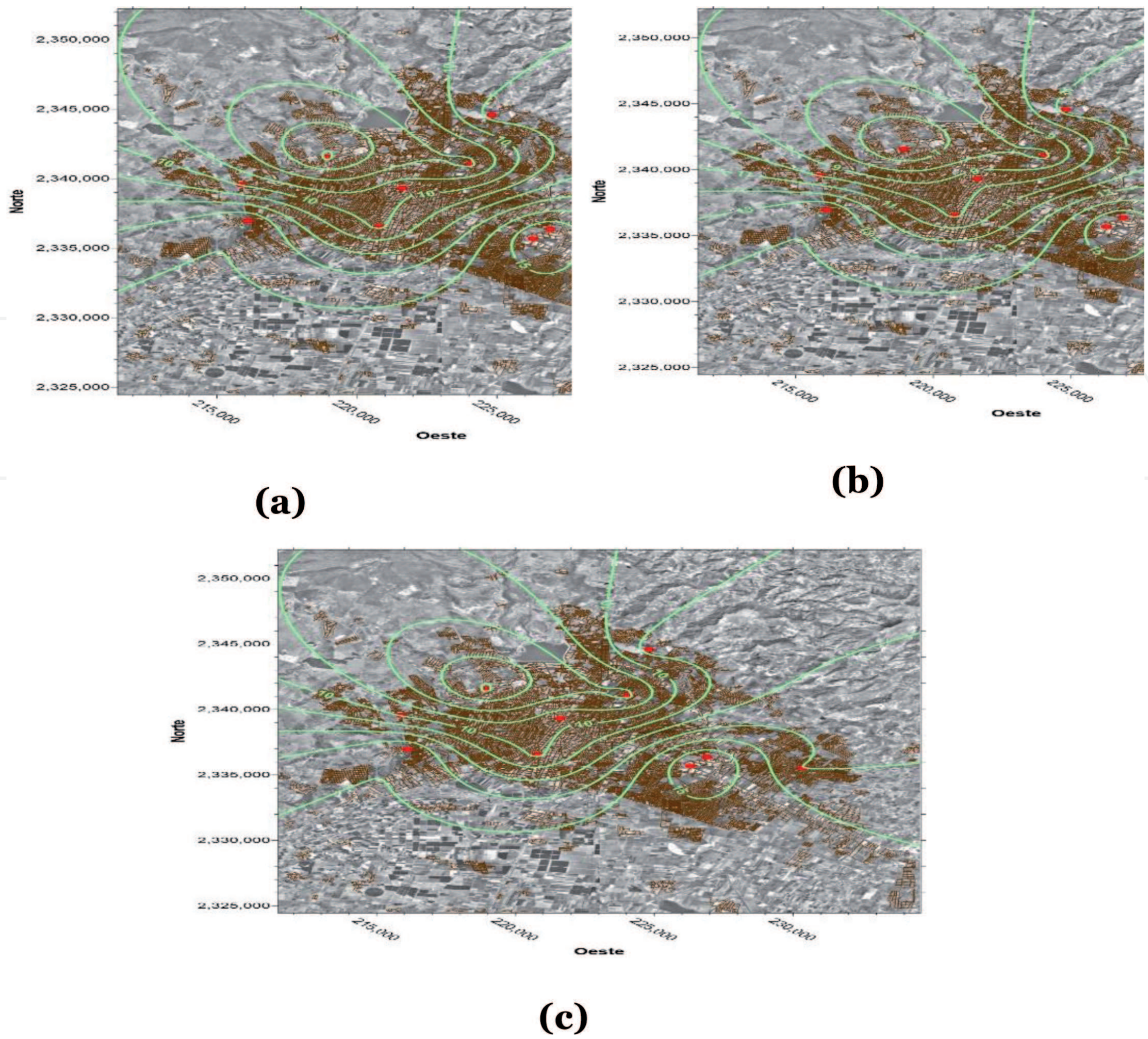


Figure 12.
Deposition map of NH_4^+ (kg ha^{-1} year^{-1}) in León City, (a) cold dry season, (b) warm dry season, and (c) rainy season.

atmospheric deposition fluxes were found at the southeast of the city (CICEG-Bomberos and Instituto Tecnológico de León, both with an industrial land use). It is worth mentioning that both sites are influenced by the emissions released by a great vehicular fleet that circulates daily on the streets, especially near monitoring station CICEG-Bomberos which is located on the main route of entry to the city from Guanajuato and Silao.

3.5.1.2 NO_3^-

In the case of nitrate, from **Figure 13**, it can be observed that the highest nitrate deposition fluxes were found during the cold dry season. Regarding seasonal patterns, it can be observed that the highest nitrate deposition fluxes were registered at de Southwest of the city, specifically in site X, which corresponds to site of Loma Blanca. This zone has an urban land use with the highest altitude in the city (elevation of 1874 m), in which, there are many commercial areas and avenues with high vehicular traffic such as Miguel de Cervantes Av., Miguel Torres Landa Oriente Blvd. and Mariano Escobedo Oriente Blvd.

Since nitrate deposition fluxes were higher during the cold dry season, it suggests the origin of nitrate and its precursor in local sources. In addition, wind velocities are lower during the cold dry season in comparison with the other two seasons; therefore, there is a minor dispersion of pollutants in the region.

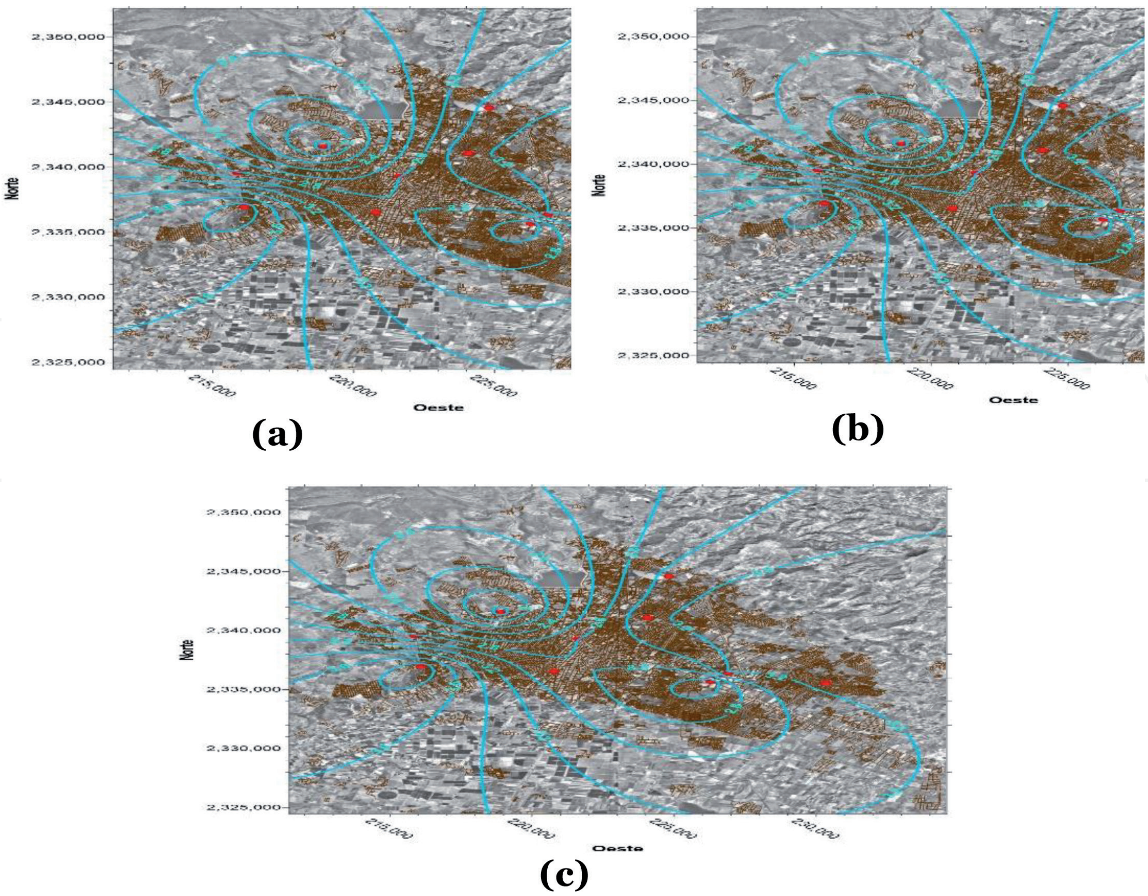


Figure 13.
Deposition map of NO_3^- (kg ha^{-1} $year^{-1}$) in León City, (a) cold dry season, (b) warm dry season, and (c) rainy season.

Another important factor is the lack of rain, contributing to a minor dilution or washing of the atmosphere. Levels found were homogeneously distributed as a result of local sources, and it agrees with residence time in the atmosphere of NO_2.

3.5.1.3 SO_4^{2-}

In the case of SO_4^{2-}, its deposition fluxes were uniformly distributed in the metropolitan area of León (**Figure 14a**–**c**). In all seasons, the highest levels were found at NE (Site VI: Zoológico) and at SE (Sites I and IV corresponding to CICEG Bomberos and Instituto Tecnológico de León), all of them, with an industrial land use. On the other hand, the lowest sulfate deposition fluxes were found at North of the city.

The highest value for sulfate atmospheric deposition flux was found during the rainy season; however, this difference was not statistically significant in comparison with the other two seasons. Some hot spots were identified: at NE (Site VI), at SE (sites I and IV), and at SW (Site X).

3.5.2 Reference values

It has been proposed a critical load value of 5 Kg N ha^{-1} year $^{-1}$ for alpine ecosystems, which are more sensitive than ecosystems in lowlands [17], whereas in Nuevo México and California, a critical load value of 3–8 and 4–7 Kg N ha^{-1} $year^{-1}$, respectively, has been proposed [18]. Regarding to Mexico, reference values to compare N and S atmospheric deposition fluxes are not available. On the other hand, for S, it has been proposed a critical load value of 3 Kg S ha^{-1} year^{-1} for sensitive areas in Europe, whereas for natural forests, values between 2 and 5 Kg S ha^{-1} year^{-1} have been proposed [18].

In this study, mean deposition fluxes for N (as N-NH_4^+ + N-NO_3^-) and S (as SO_4^{2-}) in metropolitan area of León were 5.82 N and 13.77 Kg S ha^{-1} year^{-1}, respectively. In the case of N, exceeds the value reported for alpine ecosystems, but is near the reference values for Nuevo México and California. N deposition levels found in metropolitan area of León were twice as that reported by Cerón et al. [19] in Carmen Island, Campeche (2.15 N Kg ha^{-1} year^{-1}); by Cerón et al. [20] in Orizaba Valley, Veracruz (1.44 N Kg ha^{-1} year^{-1}); and by López [21] in Mérida, Yucatán (2.7 N Kg ha^{-1} year^{-1}); also exceeding those values reported by Cerón et al. [22] in metropolitan area of Monterrey (4.88 N Kg ha^{-1} year^{-1}) and five times as that reported by Cerón et al. [23] in Atasta-Xicalango, Campeche (1.15 Kg ha^{-1} year^{-1}).

With respect to S, deposition fluxes exceeded almost 4.5 times the critical load value proposed for sensitive areas in Europe, whereas for natural forests, reference value was exceeded almost three times those values reported by Cerón et al. [19] in Carmen Island, Campeche (4.7 S Kg ha^{-1} year^{-1}) and by López [21] in Mérida, Yucatán (4.07 S Kg ha^{-1} year^{-1}), and twice the value reported by Cerón et al. [23] in Atasta-Xicalango, Campeche (8.57 S Kg ha^{-1} year^{-1}). However, values reported by Cerón et al. [20] in Orizaba Valley (55.16 S Kg ha^{-1} year^{-}1) and by Cerón et al. [22] in metropolitan area of Monterrey (25.03 Kg ha^{-1} year^{-1}) were not exceeded. Therefore, it can be inferred that, N and S atmospheric deposition fluxes constitute a potential risk of acidification for ecosystems in the region.

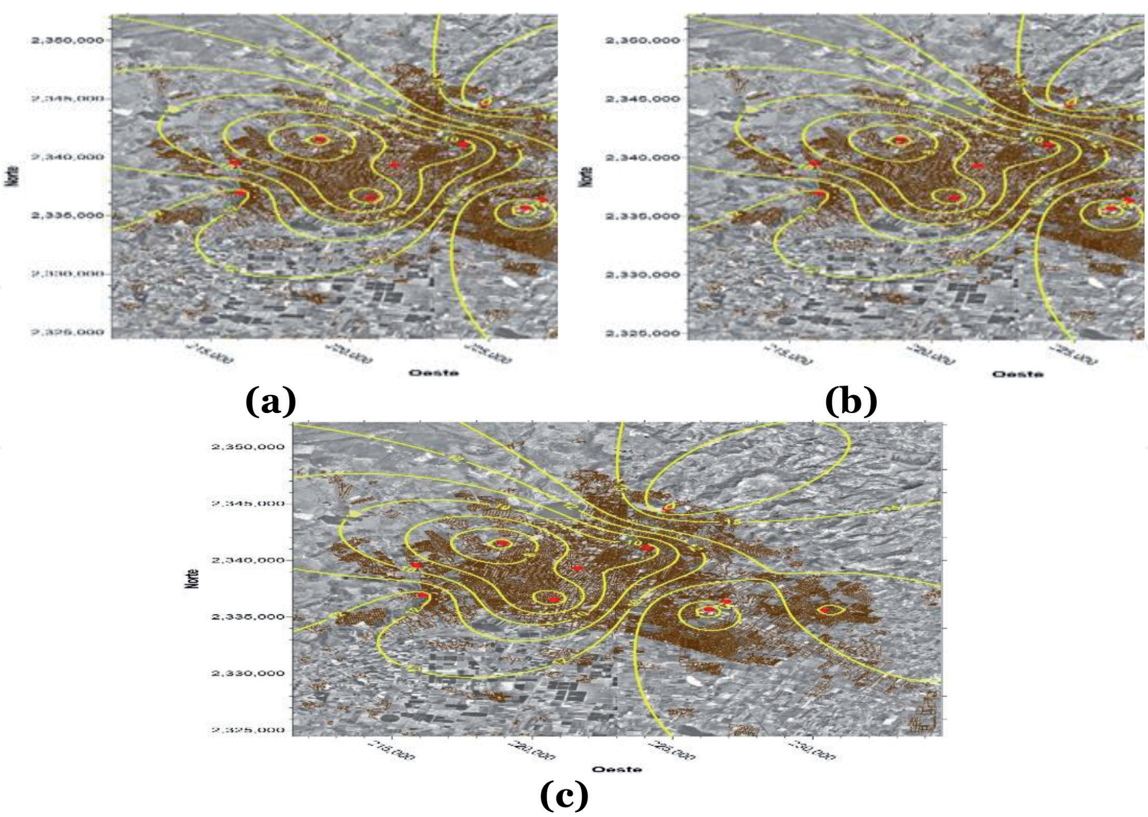


Figure 14.
Deposition map of SO_4^{2-} (kg ha^{-1} year^{-1}) in León city, (a) cold dry season, (b) warm dry season, and (c) rainy season.

4. Conclusions

In general, a strong seasonality in both, N and S atmospheric deposition fluxes was observed. Regarding to spatial variability, it was found that, in each climatic season, fluxes stayed homogeneous and uniformly distributed as a result of meteorological conditions prevailing in each season, having a regional origin during the rainy season and a local origin during the rest of the year. NH_4^+ and NO_3^- showed a similar spatial and temporal pattern in their deposition fluxes. According to the analysis by season, the highest N deposition flux was found during the cold dry season, followed by warm dry season and rainy season, respectively. It could be explained due to the occurrence of a minor dispersion of pollutants resulting from lower wind velocities, and the frequent occurrence of thermal inversions during the cold dry season. On the other hand, dilution phenomena could play an important role during the rainy season, resulting in lower fluxes during this season. From spatial analysis of N deposition fluxes, it can be concluded that the site with the highest N deposition was Loma Blanca (Site X). In general, all sites where the highest N deposition fluxes were found are urban sites located in the suburbs of the city, with high vehicular traffic, where some agricultural sites are located. It suggests that the main sources of NO_3^- are vehicular emissions, whereas the main source of NH_4^+ is the intensive use of fertilizers in these agricultural zones. However, since significant differences were not found between sampling sites by land use, it can be concluded that fluxes could be uniformly distributed, confirming their local origin. It agrees with the residence time of NO_2 in the atmosphere of 1 day, time in which, it is deposited as NO_3^- or NH_4^+ at ground level, being their concentrations higher in the surroundings of the emission point. Since in León city, there was not a territorial ecological order in the past, the city growth and development along the years was not planned, resulting in the coexistence of different type of land use in a given zone.

On the other hand, S deposition fluxes showed a different pattern, suggesting their regional origin. From seasonal analysis, it was found that the highest atmospheric deposition flux occurred during the rainy season, followed by warm dry and cold dry seasons. It agrees with the regional character of SO_2 (sulfate precursor) which has a residence time in the atmosphere of 1–5 days [24, 25], being able to transport long distances before to be deposited finally at ground level. From air masses trajectories analysis, it could be concluded that, during the rainy season, this pollutant is long-range transported from the South of United States and from the North of Gulf of Mexico, explaining in this way, why during this season, a relative sulfate enrichment is observed in comparison with the other two seasons.

From analysis by sampling site, the site with the highest S atmospheric deposition flux was Instituto Tecnológico de León followed by Zoológico (sites IV and VI), these sites have an industrial and urban land use, suggesting that both vehicular and industrial emissions could contribute to background sulfate levels, which in turn were temporarily increased during the rainy season due to the long-range transport of air masses from distant sources (South of United States and North of Gulf of Mexico).

Author details

Rosa María Cerón Bretón[1*], Julia Griselda Cerón Bretón[1],
Reyna del Carmen Lara Severino[1], Marcela Rangel Marrón[1],
María de la Luz Espinosa Fuentes[2], Simón Eduardo Carranco Lozada[3]
and Lizbeth Cisneros Rosique[1]

1 Facultad de Química, Universidad Autónoma del Carmen, Ciudad del Carmen, Campeche, México

2 Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México, Ciudad de México, México

3 Instituto Politécnico Nacional, Guanajuato, México

*Address all correspondence to: rosabreton1970@gmail.com

References

[1] Shahin U, Lu J, Yi SM, Paode RD, Holsen TM. Long-term elemental dry deposition fluxes measured around Lake Michigan with an automated dry deposition sampler. Environmental Science and Technology. 2000;**34**: 1887-1892. DOI: 10.1021/es9907562

[2] Kulshrestha UC, Kulshrestha MJ, Sekar R, Sastry GSR, Vairamani M. Chemical characteristics of rainwater at an urban site of south-Central India. Atmospheric Environment. 2003;**37**:3019-3069. DOI: 10.1016/S1352-2310(03)00266-8

[3] Laj P, Klousen J, Bilde M, Plab C, Pappalardo G, Clerbaux C, et al. Measuring atmospheric composition change. Atmospheric Environment. 2009;**43**:5351-5414. DOI: 10.1016/j.atmosenv.2009.08.020

[4] Fenn ME, Bytnerowicz A. Summer throughfall and winter deposition in the San Bernardino Mountains in southern California. Atmospheric Environment. 1997;**31**:673-683. DOI: 10.1016/S1352-2310(96)00238-5

[5] Warfvinge P. Integrating modeling. In: Heij GJ, Erisman JW, editors. Acid Atmospheric Deposition and Its Effects on Terrestrial Ecosystems in the Netherlands: The Third and Final Phase. Elsevier; 1997

[6] Lovland G, Andersen B, Joffre S, Pedersen U, Hormand M, Reissell A. Mapping deposition of sulphur, nitrogen, and base cations in the Nordic Countries. Swedish Environmental Research Institute. Report B 1055. 1992-06-25; 1992

[7] INEGI Prontuario de información geográfica municipal de los Estados Unidos Mexicanos León, Guanajuato. Clave Geoestadística. 2009; 11020:2

[8] INEGI, Población Total en Viviendas de la Ciudad de León, Guanajuato. 2015. Available from: https://www.inegi.org.mx/app/areasgeograficas/?ag=11

[9] Garten CT, Schwab AB, Shirshac TL. Foliar retention of ^{15}N tracers: Implications for net canopy exchange in low- and high-elevation forest ecosystems. Forest Ecology and Management. 1998;**103**:211-216

[10] Fenn ME, de Bauer LI, Quevedo-Nolasco A, Rodríguez-Frausto C. Nitrogen and sulfur deposition and forest nutrient status in the valley of Mexico. Water, Air, and Soil Pollution. 1999;**113**:155-174

[11] Fenn ME, Poth MA. Monitoring nitrogen deposition in throughfall using ion exchange resin columns: A field test in the San Bernardino Mountains. Journal of Environmental Quality. 2004;**30**:2007-2014. DOI: 10.2134/jeq2004.2007

[12] Clow D, Roop H, Nanus L, Fenn M, Sexstone G. Spatial patterns of atmospheric deposition of nitrogen and sulfur using ion-exchange resin collectors in Rocky Mountain National Park, USA. Atmospheric Environment. 2015;**101**:149-157. DOI: 10.1016/j.atmosenv.2014.11.027

[13] Fresenius W, Quentin KE, Schneider W. Water Analysis: A Practical Guide to Physico-Chemical, Chemical and Microbiological Water Examination and Quality Assurance. New York, NY: Springer-Verlag; 1992. pp. 420-421

[14] Secretaría de Economía. Norma Mexicana. NMX-AA-074-SCFI-2014. Medición del ión sulfato en aguas naturales, residuales y residuales tratadas. Método de prueba. Dirección General de Normas. 2015

[15] Secretaría de Economía. Norma Mexicana. NMX-AA-079-SCFI-2001.

Análisis de Aguas. Determinación de nitratos en aguas naturales, potables, residuales y residuales tratadas. Método de prueba. Dirección General de Normas. 2000

[16] Sáez J. Investigación Educativa, Fundamentos teóricos, Procesos y Elementos prácticos, Enfoque práctico Con Ejemplos [thesis]. Madrid: Universidad Nacional de Educación a distancia; 2017

[17] Fenn ME, Geiser LH. Temperate Sierra. In: Pardo LH, Robin-Abbot MJ, Driscoll CT, editors. Assessment of Nitrogen Deposition Effects and Empirical Critical Loads of Nitrogen for Ecoregions of the United States. General Technical Report NRS-80. Delaware, OH: United States Department of Agriculture; 2011. pp. 175-180

[18] Grennfelt O, Nilsson J. Critical Loads for Sulfur and Nitrogen. Report from a Workshop held at Skokloster, Sweden; 19-24 March 1988. Copenhagen, Denmark: The Nordic Council of Ministers Report; 1988. p. 15. ISBN: 87-7303-248-4

[19] Cerón R, Cerón JG, Muriel M, Anguebes F, Ramírez M, Zavala JC, et al. Spatial and temporal distribution of throughfall deposition of nitrogen and sulfur in the mangrove forests associated to Terminos lagoon. In: Farhad N, editor. Current Air Quality Issues. IntechOpen, Rijeka, Croatia; 2015. pp. 147-164. DOI: 10.5772/59726

[20] Cerón R, Cerón J, Kahl J, Lara R, Rangel M, Rustrián E. Influencia potencial de las emisiones y el transporte de N y S en el Valle de Orizaba, Veracruz, México. Agrociencia. 2018;**52**:653-670

[21] López D, Cerón J, Cerón R, Rangel M, Uc M, Salvaño Y, Lara R. Mapeo del depósito atmosférico de azufre y nitrógeno durante la primavera de 2017 en la Zona Metropolitana de la Ciudad de Mérida. In: Proceedings of VII Congreso Nacional de Investigación en Cambio Climático. Centro de Ciencias de la Atmósfera. UNAM; 3-4 October 2017; Mexico City

[22] Cerón RM, Cerón JG, Kahl J, Ramírez E, Córdova A, Espinosa A, et al. Atmospheric N and S deposition fluxes in the metropolitan area of Monterrey, Mexico and its relation with criteria air pollutants and meteorological conditions. In: Jorge Del Real Olvera, editor. Air Pollution-Monitoring, Quantification, and Removal of Gases and Particles. London, UK: IntechOpen; 2018. pp. 75-98. DOI: 10.5772/intechopen.79484

[23] Cerón J, Cerón R, Aguilar C, Montalvo C, García A, Muriel M, et al. Mapping temporal and spatial variation of sulphur and nitrogen deposition to a complex ecosystem in Campeche, Mexico. Transactions on the Ecology and the Environment. 2016;**203**:113-123. Environmental Impact II. UK: WIT Press. DOI: 10.2495/EID160111

[24] Kahl J, Bravo A, Soto A, Sosa E, Sánchez A, Alarcón A. Characterization of atmospheric transport to the El Tajín archeological zone in Veracruz, México. Atmosfera. 2007;**20**(4):359-371

[25] Cerón R, Kahl J, Cerón J, Solís JA. The influence of meteorology and atmospheric transport patterns on the sulfate levels in rainwater in Orizaba Valley, Veracruz, Mexico. Journal of Environmental Protection. 2019;**10**(6):1-17. DOI: 10.4236/JEP.2019.106049