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Chapter 5

Atmospheric N and S Deposition Fluxes in the Metropolitan Area of Monterrey, Mexico and Its Relation with Criteria Air Pollutants and Meteorological Conditions

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Additional information is available at the end of the chapter

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Abstract

The objective of this study was to assess the spatial and temporal variability of N and S atmospheric deposition and its relation with criteria air pollutants (CAPs) and meteorological conditions (MCs) in the metropolitan area of Monterrey (MAM). Atmospheric deposition was collected in 10 sampling sites during 3 climatic periods by using passive samplers based on ionic exchange resins (IERs); simultaneously, CAP and MC were monitored. Ions were extracted from IER to determine nitrate, ammonium, and sulfate levels, and deposition fluxes were estimated. On the other hand, from CAP and MC, wind and concentration roses were built to identify the exceedances of the current regulations, and relationships between CAP and meteorological conditions. It was found that only S deposition fluxes exceeded critical load values proposed in Europe, suggesting that S deposition could be a serious threat in MAM. It was found that CO in Juárez sampling site and O_3 and PM_{10} in all sampling sites showed exceedances of the current regulatory limits, showing seasonal and spatial patterns similar to N and S deposition fluxes. Deposition fluxes were mapped to identify critical zones or periods in which these fluxes could be higher as a result of the prevailing meteorological conditions.

Keywords: N deposition, S deposition, criteria pollutants, Monterrey, Mexico

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1. Introduction

Atmospheric deposition of nitrogen and sulfur is a growing and significant problem for the environment in many parts of the world. However, in urban areas it has become a concern due to the increase in atmospheric emission of gases and particulate that entails consequences for the environment and for the health of population. Sulfur dioxide (SO_2), nitrogen oxide (NO_x), and ammonia (NH_3) are usually produced by anthropogenic activities. Industrial activities, vehicular emissions, and the burning of biomass are just some of the main sources of these pollutants in the atmosphere. The deposition of S and N occurs as a result of removal processes, either from precipitation (wet deposition) or from the deposit of particulate material or gas adsorption (dry deposition), and is associated with the acidification of soils and surface waters. Deposition of sulfur compounds results in the modification of the chemistry and biology of soil and water bodies such as the decrease in pH. On the other hand, the deposition of nitrogen compounds causes changes through the direct acidification of soils and natural water, or the saturation of nitrogen in vegetation species, which leads to the loss of vitality of diverse ecosystems. In addition, the deposition of N and S can cause deterioration to historical monuments and diverse materials [1]. Despite its importance, in Mexico, the monitoring of the deposition of these compounds, as well as the evaluation of their spatial and temporal distribution, and the estimation of their effects on ecosystems have not been sufficiently studied. Although in Mexican territory there are many cities with significant urban and industrial development, many of which are close to valuable historical heritage or important ecological zones, with the exception of the surrounding areas to the metropolitan zone of the Valley of Mexico, there are few air pollution studies available [2] One of the main reasons that limits the study of wet atmospheric deposition is that their study requires expensive automatic samplers that require compliance with certain specifications for installation and operation; while, in the case of dry deposition, standardized techniques are not available. In this regard, some authors [3] have proposed the use of passive samplers based on ion exchange resins for the monitoring of atmospheric deposition, this type of device allows to study several points simultaneously due to its low cost and simple design.

On the other hand, the state of Nuevo Leon has been characterized by its accelerated urban and industrial growth, which places it within the three main metropolitan areas of the country and the second with the greatest territorial extension. Additionally, the city of Monterrey is the second city in the country with the highest reports of air pollution and subsequent effects not only on public health but also on ecosystems. Previous studies in this region have shown significant correlations between the wind direction and temperature inversions and contaminant transport from regional sources. That is, the pollutants in the MAM have a seasonal component as a result of the influence of these transport processes, resulting in a greater concentration and deposition of pollutants at certain climatic periods of the year. Likewise, in addition to the contribution by regional transport, there are also significant emissions from local industrial sources and vehicular sources that may result in background levels above the reference values considered as acceptable. However, since in the case of atmospheric deposition, it is not a criterion contaminant, that is, there is not a standard or reference value that

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regulates it, it is necessary to carry out monitoring studies at a medium or long term to establish a baseline that allows to perform an environmental diagnosis of the area and infer its possible effects. Notwithstanding, in the MAM, some authors [4–7] have measured wet and dry atmospheric deposition; these studies have been carried out at a short term and systematic measurements that allow a proper diagnosis considering the seasonal and spatial components are not available. Therefore, the present work focuses on the mapping and study of the seasonal and spatial variability of N and S atmospheric deposition in the metropolitan area of Monterrey (MAM), Nuevo Leon, during three climatic seasons (dry, rainy, and cold fronts) using passive samplers based on ionic exchange resin at ten points distributed throughout nine municipalities of MAM.

2. Study area

The metropolitan area of Monterrey (MAM) is located to the northeast of the country in Nuevo Leon (25°42′26.53 N, 100°17′29.36 W). In 2015, it registered a total of 4,437,643 inhabitants within a surface of 6357 km^2, being the third most populated city in Mexico only after Guadalajara and Mexico City; and the second in territorial extension. Worldwide, MAM occupies the 17th place, while in Latin America, it ranks number 10. Also, it was considered by Forbes in 2010 as the fourth most intelligent city in the world, with a great capacity of sustainable growth. MAM is located 913 km from Mexico City. It is known as "The City of the Mountains" due to the orographic formations existing within and in the surroundings of the city and, because of this, MAM exhibits serious air pollution problems. MAM climate

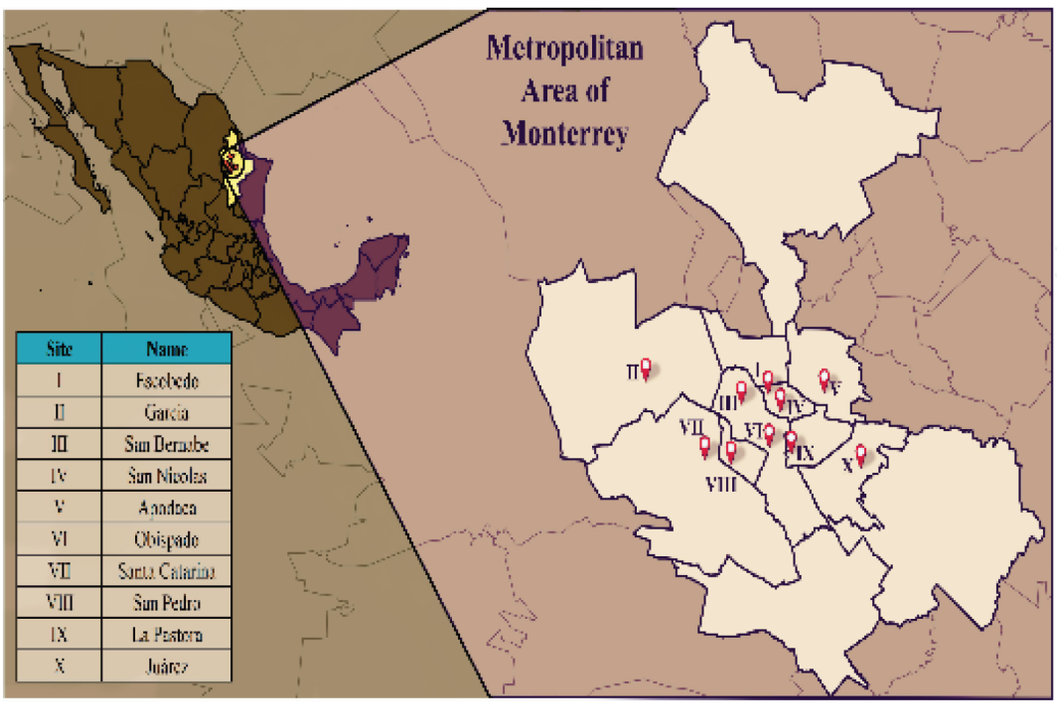


Figure 1. Sampling sites location along MAM.

is considered extreme, and according to Köppen climatic classification, it has warm and semi-arid climate (BSh), with an annual precipitation from 431.1 to 1300 mm. To assess the spatial and temporal distribution of N and S deposition fluxes, ten sampling sites were selected along MAM. The location of these sampling sites corresponds to the location of automatic monitoring stations of SIMA (Integral System of Environmental Monitoring of Monterrey). The specific location of these sampling sites and the name of each automatic monitoring station are presented in **Figure 1**.

3. Methodology

3.1. Sampling

The characterization of complex spatial patterns as atmospheric deposition of N and S in a given area requires simple monitoring equipment, which is cheap, easy to operate, and does not require frequent visits to the field. Throughfall deposition consists of solute collected in atmospheric deposition. This method is widely used to estimate the inputs of atmospheric deposit to the forests ecosystems, since, they include both, dry and wet deposition; therefore, this kind of passive sampler constitutes a good choice to obtain a reliable estimation of atmospheric inputs of N and S in a given ecosystem [8]. Passive samplers type throughfall are based in collectors of ionic exchange resin (IER). They consist of a funnel connected to a column that contains a mixed bed of ionic exchange resin (Amberlite™ IRN150). Deposition falls on the surface of the funnel, washing toward the inside of the column. The main advantage of this type of device is that it can be used during long periods of time (e.g., months) and the equipment has a very low cost, allowing to increase the number of sampling points in a given area. Therefore, with this kind of collector, it is possible to display a great number of them to characterize spatial patterns in deposition with a high resolution [9]. Nitrate, sulfate, and ammonium (NO_3^-, SO_4^{2-} y NH_4^+.) can be exchanged in IER for cations and anions, respectively, and then be trapped by functional groups with opposite electric charges. In this study, a design of a mixed resin bed was chosen, since this kind of resin captures both, anions and cations.

Throughfall deposition was collected in MAM, Nuevo Leon, Mexico, from February 26, 2017, to February 26, 2018, in ten sampling sites (**Figure 1**) which correspond to automatic monitoring stations of SIMA, by using deposition collectors based on IER operated and built according to [3, 10]. IER devices consist of funnels covered with a mesh (to prevent the fall of solid material such as leaves and insects) that are attached to PVC tubes. Inside these tubes, 30 g of IER are placed (where ions of interest are retained). Each tube is sealed with glass fiber at the bottom (as a platform or support for the resin) and at the top (as a filter). The resin tube is placed inside an outer PVC tube (shadow tube), which protects resin from solar radiation and helps avoid changes in its physical and chemical properties due to solar radiation. The lower end of the inner tube (resin tube) is closed or open by using a PVC valve to allow the hydrological flux to drain or not. Finally, resin tubes were placed in open areas at each sampling site within SIMA facilities. This exposition period allowed to obtain a data set for three seasons of 4 months each, corresponding to dry, rainy, and cold fronts or Norths seasons on an annual basis.

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3.2. Chemical analysis

3.2.1. IER extraction procedure

To carry out this process, an extraction system specially designed for this purpose was built. This system consisted of a PVC tube 5 mm (ID) and 15 cm in length, adapted to each collector with the resin to be extracted. Glass fiber is removed with tweezers to verify that the drain hole was not dirty. After this, each resin tube is labeled and it is verified that the PVC valve is closed. All columns are placed in vertical position, and then, the resin tubes are washed with 100 ml of deionized water, allowing a repose of 20 minutes. Simultaneously, the threaded connections are revised to identify leaks. In the case of one leak identification, the joints are tightened, and if necessary, Teflon™ tape is added. Once, 20 minutes have elapsed, the valve opens so that a drip rate of 2 drops by second is obtained. A continuous drip is maintained during 10 minutes until drainage is completed. This rinse is discarded. Then, it is ensured that the PVC valve is closed, and 100 ml of 2 N KCl extraction solution is added, and allowed to repose for 20 minutes. Again, the PVC valve is open so that a drip rate of 2 drops by second is obtained. This continuous drip is maintained for 10 minutes. Finally, the valve is open to allow the remainder solution to leave the resin tube until the drainage is completed. Once, the extracts of the samples are obtained, they are stored and refrigerated at 4°C until analysis.

3.2.2. Ammonium determination

NH_4^+ was determined by using blue indophenol method, whose color intensity is proportional to the ammonium concentration in the sample. Determination was done by colorimetry at a wave length of 630 nm. Color formation is completed after 10 minutes and remains stable for 24 hours. Once absorbances of the samples are obtained, a quantification process was done to obtain ammonium concentrations by using a calibration curve [11].

3.2.3. Sulfate determination

Sulfate ion precipitates with barium chloride in an acid medium (HCl) forming crystals of barium sulfate. The spectral absorption of the barium sulfate suspension is measured at 420 nm by using a UV-Visible spectrophotometer. Sulfate concentration is determined comparing the absorbance lectures with a calibration curve, by using the turbidimetric method [12].

3.2.4. Nitrate determination

Nitrate anion present in the sample reacts with alkaloid brucine in an acid medium (H_2SO_4), oxidizing it and producing cocoteline, with an unstable red color, which changes quickly to yellow, being determined colorimetrically at 410 nm [13].

3.3. Meteorology analysis, criteria air pollutants and mapping

3.3.1. Meteorology

Speed and wind direction are determining factors in the composition of atmospheric deposition, since depending on the prevailing wind direction, it will have the influence of local continental or regional sources located upwind or the influence of maritime sources. In this study,

the analysis of meteorological parameters at surface level was done by using data obtained from SIMA during the study period to identify possible anthropogenic or natural sources influencing the N and S levels found in the sampling sites. Wind roses were built to identify the prevailing wind direction in the study area. To assess the transport mechanism controlling deposition process in the study area by season, back air mass trajectories were estimated by the Lagrangian hybrid model HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) from US NOAA (National Atmospheric and Oceanic Administration).

3.3.2. Criteria air pollutants concentration

Database for the entire study period for each sampling point was obtained from SIMA of Monterrey for: CO, NO, NO_x, NO_2, SO_2, O_3, PM_{10} y $PM_{2.5}$. From the obtained data, concentration roses were estimated for each air pollutant and for each sampling point by climatic season to identify if daily concentrations exceeded reference values someday. These concentration roses were useful to visualize in which wind direction there were higher concentrations and, then, to identify the possible sources contributing to these levels.

3.3.3. Statistical analysis

A Friedman test was used to determine if atmospheric deposition fluxes were different among sampling sites, according to land use or between climatic seasons. Friedman test is a non-parametric test that can be used with block design, in which the underlying assumptions are not as restrictive as those of an ANOVA procedure (XLStat v.2017). On the other hand, principal components analysis is a technique used to reduce the dimensionality of a data set. The projection according to which data is better represented is least squares. It converts a data set of variables possibly correlated in a data set of variables without lineal correlation called principal components. Descriptive, multivariate, and principal components analysis were carried out by using XLstat-Pro v. 2017.

3.3.4. Deposition fluxes mapping

One of the main uses of geo-statistical mapping consists in predicting new values from variables from the sample in a given area, which is referred as spatial prediction or spatial interpolation. Spatial distribution of a variable can be modeled either using a continuous model or a discrete or mixed model. On the other hand, temporal variability makes geo-statistical mapping expensive and complex. Taking into account that the seasonal periodicity in this work is regular for the studied environmental parameters, in this case, spatial variability was analyzed for each climatic period: Dry, rainy, and cold fronts or Norths seasons. The coordinates of each sampling site and the values for N and S deposition fluxes were the inputs used to derive the specific points in the maps showing the dispersion and the measured concentration for the different studied chemical compounds. In a second step, the concentrations at neighboring sampling points within the grid were averaged to attribute a value to the point. These points were the input for the interpolation procedure [14]. The deposition contours were smoothed by using the kriging method [15]. Kriging weights were estimated from a

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variogram, which measures the correlation grade among sampling values in the area as a function of the distance and direction. Digital images for MAM were obtained from INEGI, and these maps were integrated to build a base map in which concentration isolines obtained from Surfer program v. 10.0 were graphed, obtaining deposition fluxes maps in each studied zone by pollutant and by climatic season.

4. Results and discussion

4.1. Sulfate deposition fluxes

4.1.1. By season

The mean S deposition flux (as sulfate) during the dry season was 27.30 ± 10.34 Kg ha^{-1} $yr.^{-1}$, with a maximum value of 47.69 Kg ha^{-1} $yr.^{-1}$ in the site labeled as VI (Obispado) at the center of MAM. The average value obtained for the rainy season was 23.65 ± 4.14 Kg ha^{-1} $yr.^{-1}$, with a maximum of 28.63 Kg ha^{-1} $yr.^{-1}$ in site I (Escobedo) located to the north of MAM. On the other hand, the mean value for S deposition flux during the Norths season was 24.15 ± 7.39 Kg ha^{-1} $yr.^{-1}$, with a maximum value of 31.48 Kg ha^{-1} $yr.^{-1}$ in the sampling site labeled as V (Apodaca), located at the northeast side of MAM. From **Figure 2a**, it was observed that S deposition fluxes showed an evident seasonality, with the highest values during the dry season, and with the lowest values along the rainy season. However, from Friedman test, since p value is major than significance levels ($\alpha = 0.05$), null hypothesis (H_0) cannot be rejected; therefore, it can be concluded that there were no significant differences among S deposition fluxes by climatic season and that sulfate deposition levels have an evident influence from regional transport during all year.

4.1.2. By sampling site

In the analysis by sampling site, a mean value for S deposition flux of 25.03 ± 7.63 Kg ha^{-1} $yr.^{-1}$ was obtained. According to **Figure 2b**, it can be observed that S deposition fluxes were higher in the sampling sites labeled as VI and V, which correspond to Obispado and Apodaca at the center and northeast of MAM. By applying Friedman test, p value is major than significance level ($\alpha = 0.05$), and null hypothesis cannot be rejected. Therefore, it can be concluded that there were not significant differences in S deposition fluxes among sampling sites, suggesting an evident regional influence on MAM.

4.1.3. By land use

Sampling sites were grouped depending on their land use as: Rural (sites II and VII), Urban (sites I, IV, VI, VIII, IX and X), and Industrial (sites III and V). From **Figure 2c**, it can be observed that S deposition fluxes were higher at sites with an industrial land use (sites III and V), which correspond to San Bernabé and Apodaca, located to the northwest and northeast of MAM. A Friedman test was applied, and since p value is major than

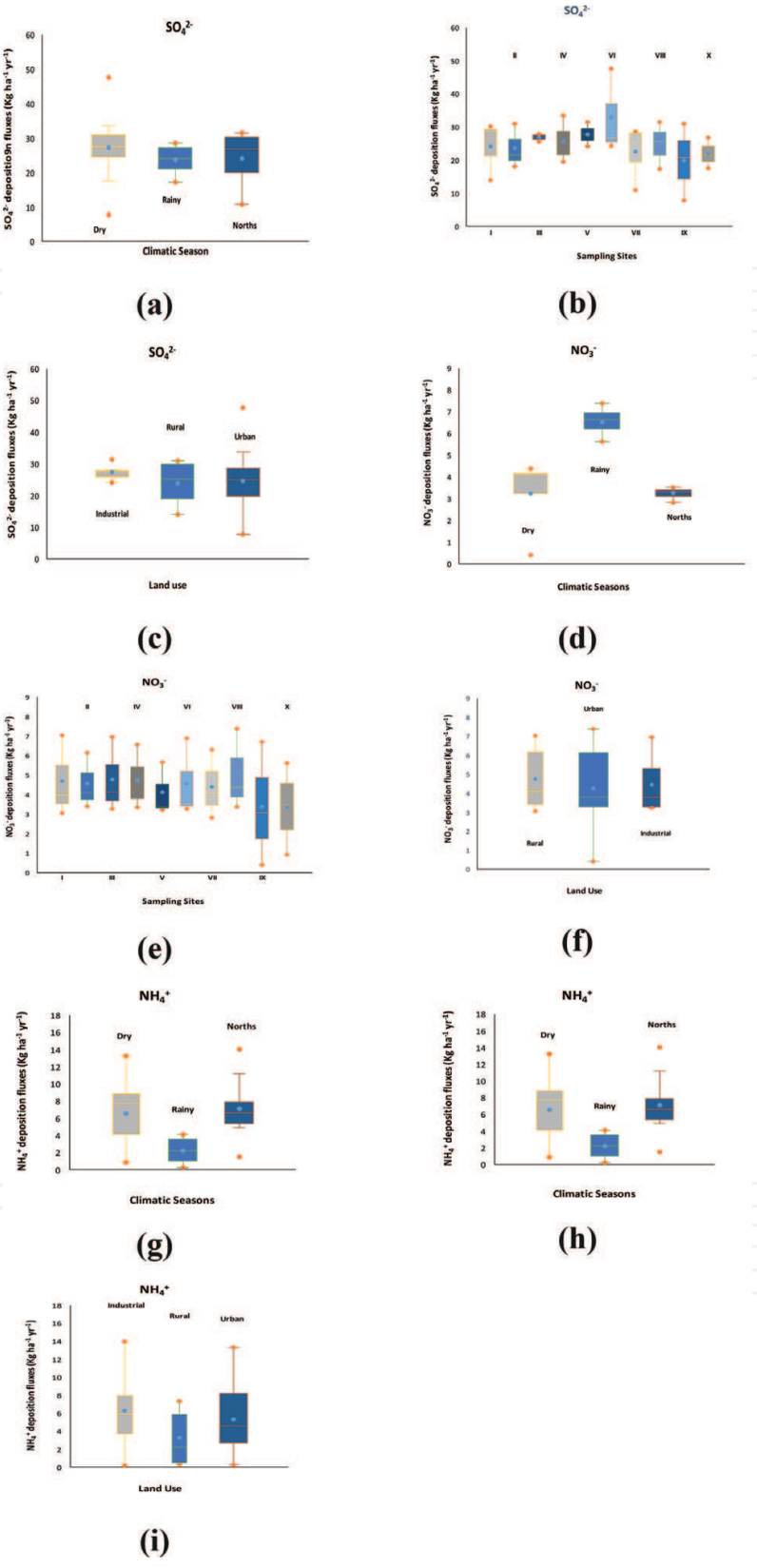


Figure 2. Sulfate deposition fluxes by: (a) climatic season, (b)sampling site, and (c) land use for MAM during the study period; Nitrate deposition fluxes by: (d) climatic season, (e) sampling site, and (f) land use for MAM during the study period; Ammonium deposition fluxes by: (g) climatic season, (h) sampling site, and (i) land use for MAM during the study period.

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significance level (α = 0.05), the null hypothesis cannot be rejected, and it can be concluded that S deposition fluxes did not show significant differences by land use. This fact supports those found in the previous sections, where the regional character of sulfate due to residence time of SO_2 was completely evident.

4.2. Nitrate deposition fluxes

4.2.1. By season

The mean nitrate deposition flux value during the dry season was 3.30 ± 1.43 Kg ha^{-1} $yr.^{-1}$, with a maximum of 4.38 Kg ha^{-1} $yr.^{-1}$ corresponding to the sampling site VIII (San Pedro) located to the southwest of MAM. The average value obtained for rainy season was 6.54 ± 0.58 Kg ha^{-1} $yr.^{-1}$, with the highest value (7.39) at the sampling site VIII (San Pedro). On the other hand, during the cold fronts season, the mean value for nitrate deposition flux was 3.26 ± 0.21 Kg ha^{-1} $yr.^{-1}$, with a maximum value of 3.52 Kg ha^{-1} $yr.^{-1}$ at site X (Juárez) located to the southeast of MAM. From **Figure 2d**, it can be observed that nitrate deposition fluxes were higher along the rainy season. From Friedman test, it was found that p value is minor than significance level (α = 0.05); therefore, it can be concluded that there were significant differences in nitrate deposition fluxes between rainy season and the rest of the year (dry and cold fronts seasons). It suggests that reactions in aqueous phase can be important, at the same time.

4.2.2. By sampling site

From the analysis of results by sampling site, from **Figure 2e**, it was found that nitrate deposition fluxes were higher in the sites VIII and III: San Pedro to the southwest and San Bernabé to the northwest of MAM. By applying a Friedman test, it was found that p value was minor than significance level (α = 0.05); therefore, null hypothesis must be rejected and it is concluded that there were significant differences between sites. It means that the influence of local sources was important. It agrees with the residence time of NO_2 in the atmosphere, since it has been reported that nitrate is a local pollutant.

4.2.3. By land use

Sampling sites were grouped according to their land use as: Rural (sites II and VII), Urban (sites I, IV, VI, VIII, IX and X), and Industrial (sites III and V). From **Figure 2f**, it can be observed that nitrate deposition fluxes were higher in sampling sites with an urban land use (sites VIII and IX: San Pedro and La Pastora, located to the southwest and southeast of MAM). However, considering extreme values, these were found in sites with an industrial land use (most of the sites: IV, VI, VII, IX, and X). From **Figure 2f**, a great variability was observed, suggesting that local urban sources were mixed and emissions presented different magnitudes. It agrees with the different kinds of sources (industrial and urban) coexisting in this great metropolitan area. In spite of this, from Friedman test, it was found that p value was major than the significance level (α = 0.05); thus, the null hypothesis cannot be rejected, and therefore, it can be concluded that there were not significant differences between sampling sites by land use.

4.3. Ammonium deposition fluxes

4.3.1. By season

The mean ammonium deposition flux during the dry season was 6.90 ± 3.88 Kg ha^{-1} $yr.^{-1}$, with a maximum value of 13.31 Kg ha^{-1} $yr.^{-1}$ in the sampling site labeled as VII (Santa Catarina) located to the southwest of MAM. During the rainy season, the average of ammonium deposition flux was 2.21 ± 1.49 Kg ha^{-1} $yr.^{-1}$, with a maximum of 4.08 Kg ha^{-1} $yr.^{-1}$ in site X (Juárez) located to the southeast of MAM. Finally, during the cold fronts season, ammonium deposition fluxes presented a mean value of 7.14 ± 3.49 Kg ha^{-1} $yr.^{-1}$, with a peak value of 14.04 Kg ha^{-1} $yr.^{-1}$ in the sampling site III (San Bernabé) at the northwest side of MAM. From **Figure 2g**, it is observed that, ammonium deposition fluxes were higher during the dry and cold fronts seasons. Ammonium levels were significantly lower during the rainy season, suggesting a washing effect during this season. From Friedman test, it was found that p value was minor than the significance level ($\alpha = 0.05$), and the null hypothesis can be rejected; therefore, it is possible to conclude that there were significant differences between dry and cold fronts seasons and the rainy season. It suggests that, during the rainy season, a dilution effect could influence the ammonium deposition fluxes, considering that during the rest of the year, rains are scarce in MAM.

4.3.2. By sampling site

From **Figure 2h**, analyzing ammonium deposition fluxes by sampling site, the highest value was found in the sites VII and IV (Santa Catarina and San Nicolás), located to the southwest and northeast of MAM. Applying a Friedman test, it was found that p value is major than significance level ($\alpha = 0.05$), and therefore, the null hypothesis cannot be rejected. Then, it can be concluded that there were not significant differences among sampling sites.

4.3.3. By land use

Sampling sites were grouped according to their land use as: Rural (sites II and VII), Urban (sites I, IV, VI, VIII, IX, and X), and Industrial (sites III and V). From **Figure 2i**, it can be observed that ammonium deposition fluxes were higher in sampling sites with an industrial and urban land use. The emission of amines and NH_3 has been reported from vehicles (with the presence of a catalytic convertor that has enough stored hydrogen), where NO is reduced to NH_3, and deposited as NH_4^+. Therefore, vehicular emissions could have an important influence on ammonium deposition in MAM. According to the Friedman test, p value was major than the significance level, thus null hypothesis cannot be rejected, and therefore, it can be concluded that there were not significant differences among sampling sites considering their land use.

4.4. Meteorology and criteria air pollutants

4.4.1. Site I Escobedo

O_3 showed a strong seasonal variation (**Figure 3a**) with the highest values during the dry season, (0.074–0.095 ppm) exceeding the reference value for 8 hours (70 ppb) [16]. Both, O_3 and PM_{10} showed highest values when wind direction came from the East. In the case of PM_{10},

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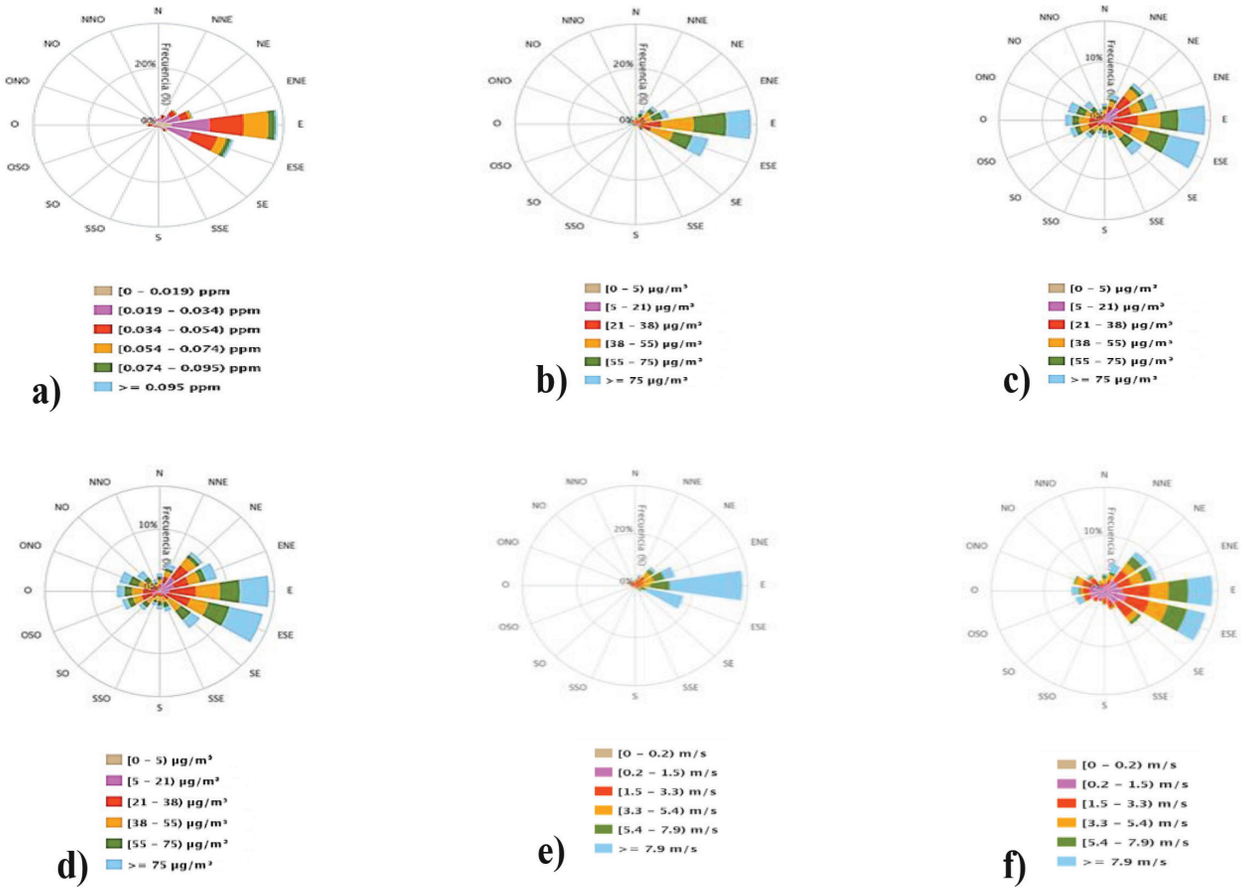


Figure 3. Criteria air pollutants and meteorological conditions for site I (Escobedo) during the study period: (a) O_3 dry season, (b) PM_{10} dry, and rainy seasons, (c) PM_{10} cold fronts season, (d) $PM_{2.5}$ cold fronts season, (e) wind dry and rainy season, (f) wind cold fronts season.

Figure 3b shows that PM_{10} levels (≥75 μg m^{-3}) exceeded the reference value for 24 hours (75 μg m^{-3}) [17]. In **Figure 3c**, it can be observed that PM_{10} levels during the cold fronts season exceeded the reference value but winds also showed a great variability. In the case of $PM_{2.5}$ (**Figure 3d**), its levels (≥75 μg m^{-3}) exceeded the reference value (45 μg m^{-3}) [17] for 24 hours during the cold fronts season when winds showed a great variability. Finally, winds came from the East during dry and rainy seasons (**Figure 3e**), showing a great variability during the cold fronts season (**Figure 3f**) with maximum wind speeds >7.9 m s^{-1} along the year.

4.4.2. Site II Garcia

From **Figure 4a** and **b**, it can be observed that O_3 levels (0.074–0.095 ppm) were higher during the dry and rainy seasons, exceeding the reference value for 8 hours (70 ppb) [16] when wind came from the East. PM_{10} levels (≥75 μg m^{-3}) were high during all year, exceeding reference value for 24 hours (75 μg m^{-3}) [17], mainly when winds came from Northeast (**Figure 4c** and **d**). Finally, winds came from the East-Northeast during dry and rainy seasons (**Figure 4e**), showing a great variability during the cold fronts season (**Figure 4f**) with maximum wind speeds >7.9 m s^{-1} along the year. Both O_3 and PM_{10} showed highest levels when winds had an East-Northeast component.

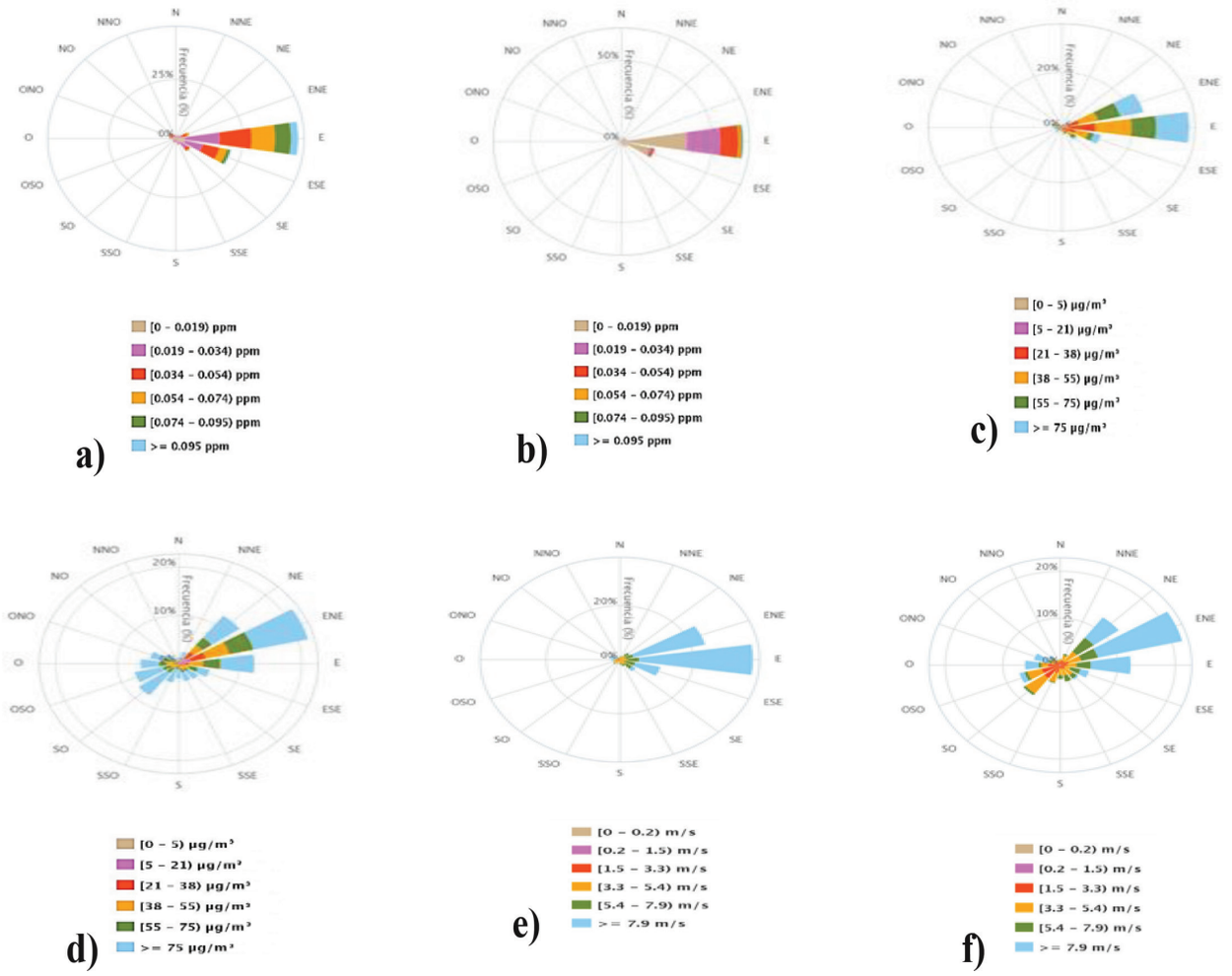


Figure 4. Criteria air pollutants and meteorological conditions for site II (García) during the study period: (a) O_3 dry season, (b) O_3 rainy season, (c) PM_{10} dry and rainy seasons, (d) PM_{10} cold fronts season, (e) wind dry and rainy season, (f) wind cold fronts season.

4.4.3. Site III San Bernabe

O_3 levels (0.074–0.095 ppm) were higher during all year, exceeding the reference value for 8 hours (70 ppb) [16] when winds came from East-Southeast (**Figure 5a** and **b**). In addition, PM_{10} levels (≥75 µg m^{-3}) also exceeded the reference value for 24 hours (75 µg m^{-3}) [17] during all year, but showing highest values and a great variability in wind direction during the cold fronts season (**Figure 5c** and **d**). Finally, winds came from the East-Southeast during dry and rainy seasons (**Figure 5e**), showing a great variability during the cold fronts season (**Figure 5f**) with maximum wind speeds >7.9 m s^{-1} along the year. Both O_3 and PM_{10} showed highest levels when winds had an East-Southeast component.

4.4.4. Site IV San Nicolas

O_3 levels (0.074–0.095 ppm) were high during all year, exceeding the reference value for 8 hours (70 ppb) [16] when winds came from North and East (**Figure 6a–c**). In addition, PM_{10} levels

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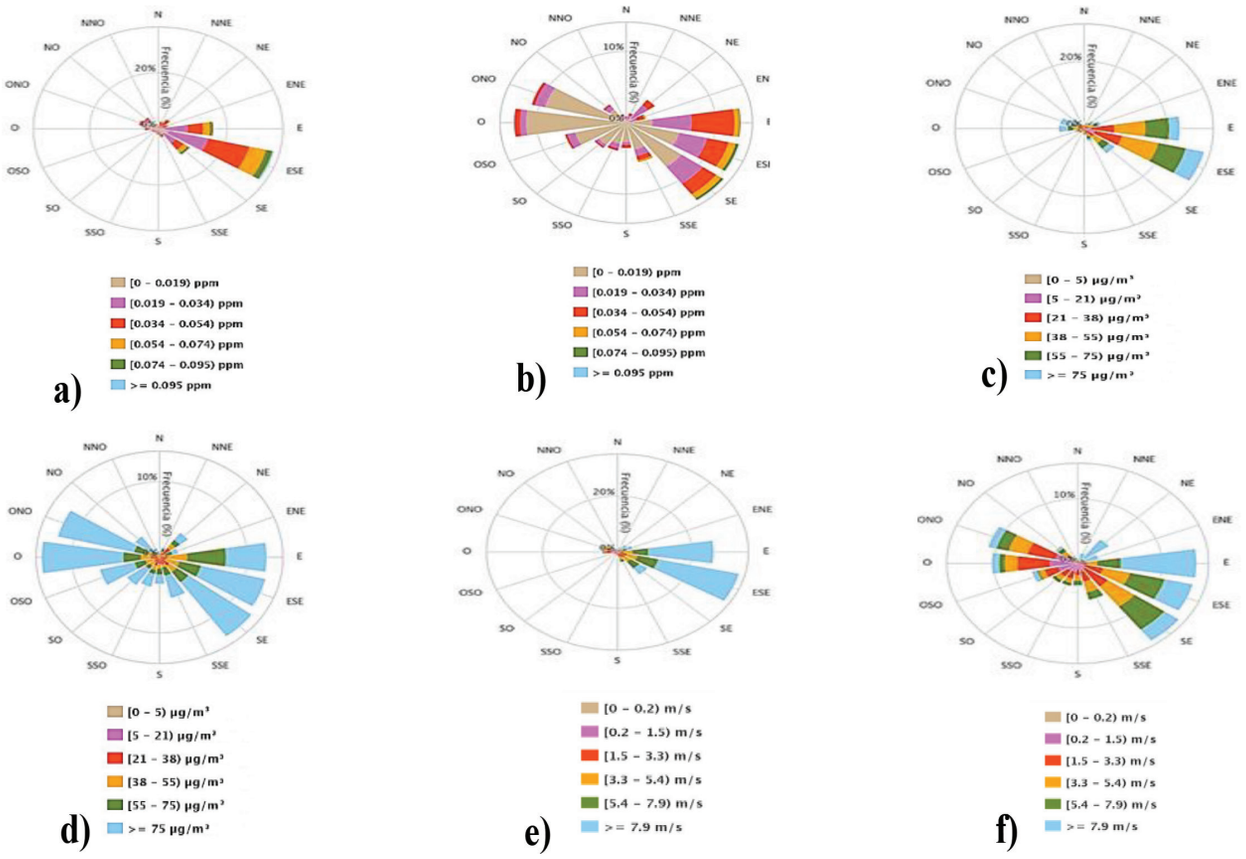


Figure 5. Criteria air pollutants and meteorological conditions for site III (San Bernabé) during the study period: (a) O_3 dry and rainy season, (b) O_3 cold fronts season, (c) PM_{10} dry and rainy seasons, (d) PM_{10} cold fronts season, (e) wind dry and rainy seasons, (f) wind cold fronts season.

(≥75 µg m^{-3}) also exceeded the reference value for 24 hours (75 µg m^{-3}) [17] during all year when winds came from East and North, but showing highest values and a great variability in wind direction during the cold fronts season (**Figure 6d–f**). Finally, winds came from the North during dry season and from East during the rainy season (**Figure 6g** and **h**), showing a great variability during the cold fronts season (**Figure 6i**) with maximum wind speeds >7.9 m s^{-1} along the year. Both O_3 and PM_{10} showed highest levels when winds had a North and East component.

4.4.5. Site V Apodaca

From **Figure 7a**, it can be observed that O_3 levels (≥0.095 ppm) were higher during the dry season when winds came from Northeast, exceeding the reference value for 8 hours (70 ppb) [16]. PM_{10} levels (≥75 µg m^{-3}) were high during all year, exceeding reference value for 24 hours (75 µg m^{-3}) [17]; mainly when winds came from North and Northwest (**Figure 7b** and **c**). $PM_{2.5}$ levels (≥44 µg m^{-3}) were high during rainy and cold fronts seasons when wind direction was from North, exceeding the reference value (45 µg m^{-3}) [17] for 24 hours (**Figure 7d**). Winds came from the Northwest and North during dry and wet (rainy and cold fronts) seasons, respectively (**Figure 7e** and **f**), with maximum wind speeds >7.9 m s^{-1} along these seasons. O_3, $PM_{10,}$ and $PM_{2.5}$ showed highest levels when winds had a North-Northwest component.

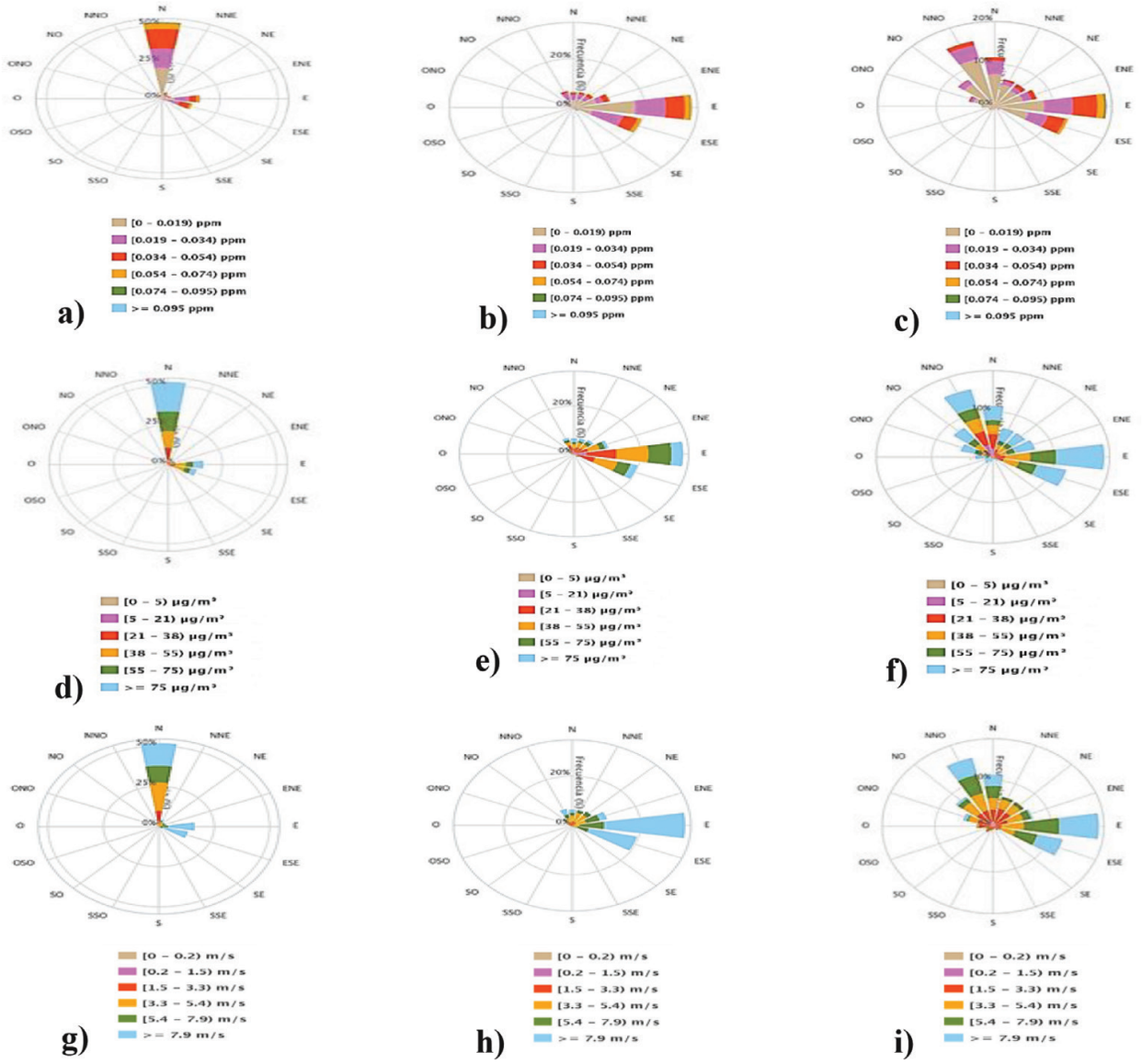


Figure 6. Criteria air pollutants and meteorological conditions for site IV (San Nicolás) during the study period: (a) O_3 dry season, (b) O_3 rainy season, (c) O_3 cold fronts season, (d) PM_{10} dry season, (e) PM_{10} rainy season, (f) PM_{10} cold fronts season, (g) wind dry season, (h) wind rainy season, (i) wind cold fronts season.

4.4.6. Site VI Obispado

From **Figure 8a**, it can be observed that O_3 levels (≥0.095 ppm) were higher during the dry season when winds came from Northeast, exceeding the reference value for 8 hours (70 ppb) [16]. PM_{10} levels (≥75 µg m^{-3}) were high during all year, exceeding reference value for 24 hours (75 µg m^{-3}) [17], mainly when winds came from Northeast and Southwest (**Figure 8b**). $PM_{2.5}$ levels were ≥44 µg m^{-3} during all year when wind direction was from Northeast, exceeding the reference value (45 µg m^{-3}) [17] for 24 hours (**Figure 8c** and **d**). In addition, winds came from the Northeast during all year, showing a great variability during cold fronts season (**Figure 8e** and **f**), with maximum wind speeds >7.9 m s^{-1} along this season. O_3, PM_{10}, and $PM_{2.5}$ showed highest levels when winds had a Northeast component.

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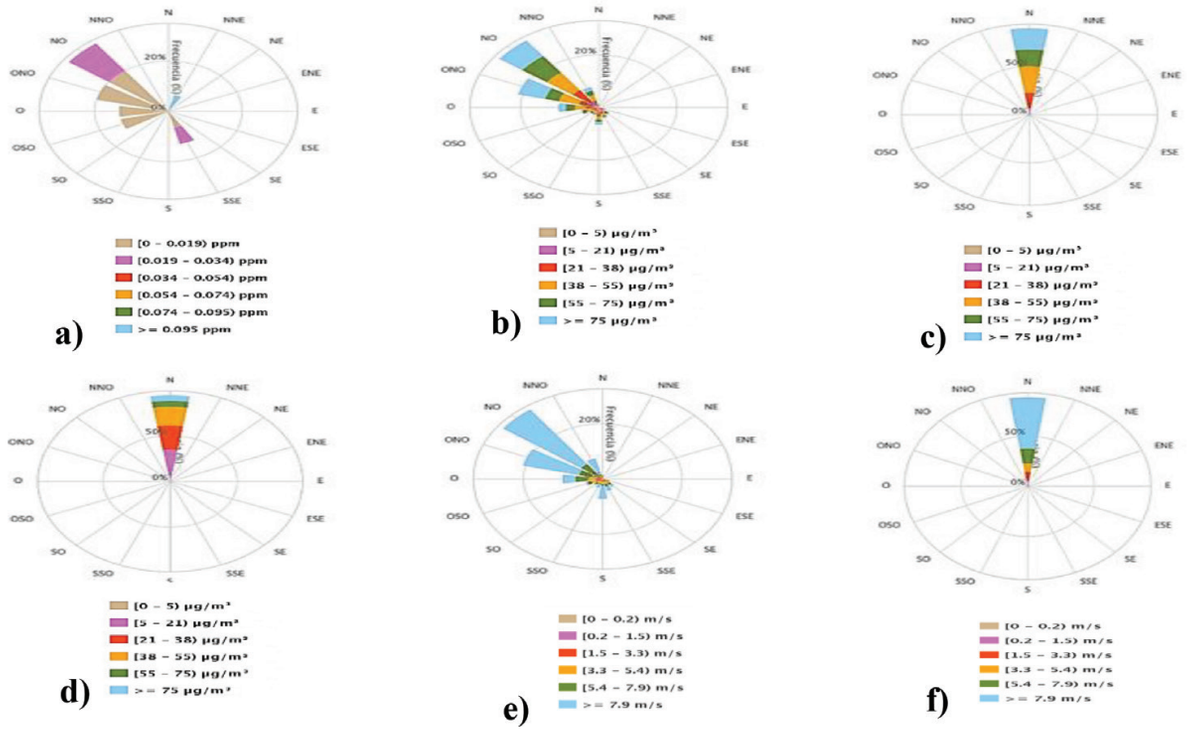


Figure 7. Criteria air pollutants and meteorological conditions for site V (Apodaca) during the study period: (a) O_3 dry season, (b) PM_{10} dry season, (c) PM_{10} rainy and cold fronts seasons, (d) $PM_{2.5}$ rainy and cold fronts seasons, (e) wind dry season, (f) wind rainy and cold fronts seasons.

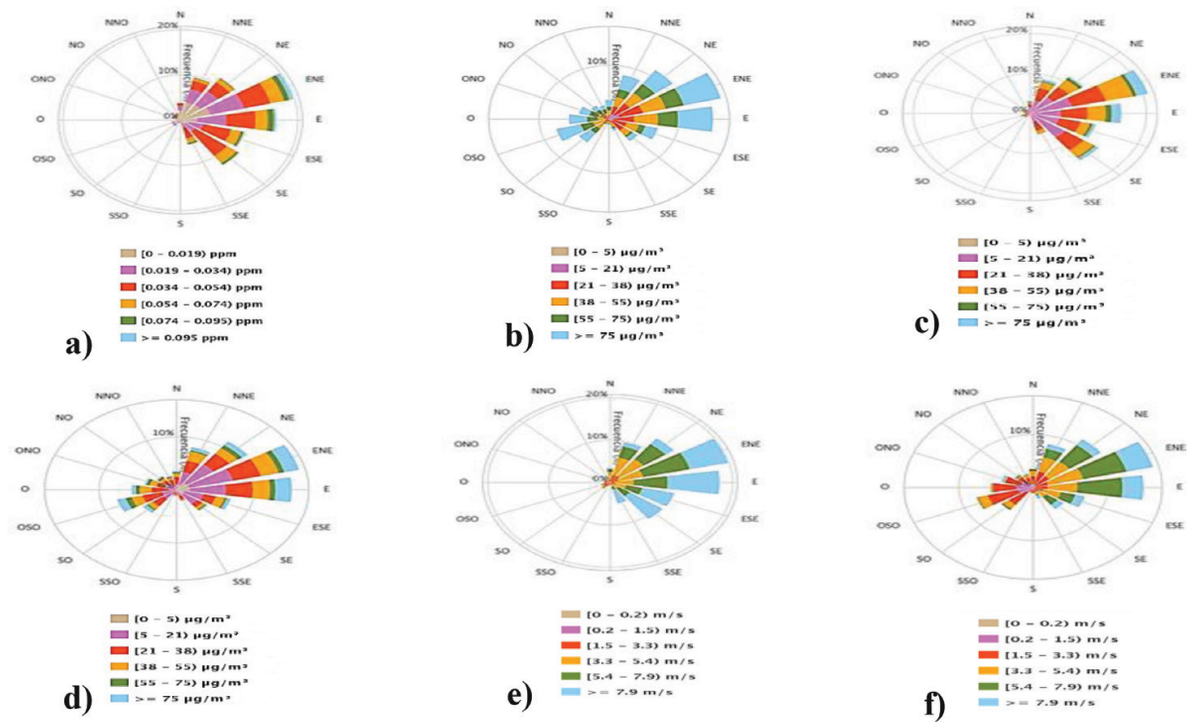


Figure 8. Criteria air pollutants and meteorological conditions for site VI (Obispado) during the study period: (a) O_3 dry, rainy and cold fronts seasons, (b) PM_{10} dry, rainy and cold fronts seasons, (c) $PM_{2.5}$ dry and rainy seasons, (d) $PM_{2.5}$ cold fronts season, (e) wind dry and rainy season, (f) wind cold fronts season.

4.4.7. Site VII Santa Catarina

O_3 levels (≥0.095 ppm) were high during all year, being higher during the dry and rainy seasons, exceeding the reference value for 8 hours (70 ppb) [16] when winds came from North (**Figure 9a** and **b**). In addition, PM_{10} levels (≥75 μg m^{-3}) also exceeded the reference value for 24 hours (75 μg m^{-3}) [17] during all year and mainly when winds came from North (**Figure 9c**). $PM_{2.5}$ levels were ≥44 μg m^{-3} during dry season when wind direction was from North, exceeding the reference value (45 μg m^{-3}) [17] for 24 hours (**Figure 9d**). According to **Figure 9e**, O_3 levels decreased significantly during the rainy season without showing exceedances to reference value. Finally, winds came from the North during all year (**Figure 9f**), with maximum wind speeds >7.9 m s^{-1} along the year. O_3, PM_{10}, and $PM_{2.5}$ showed highest levels when winds had a North component.

4.4.8. Site VIII San Pedro

From **Figure 10a** and **b**, it can be observed that O_3 levels (0.074–0.095 ppm) were higher during the dry season when winds came from East-Northeast, exceeding the reference value for 8 hours (70 ppb) [16]. PM_{10} levels (≥75 μg m^{-3}) were high during all year, exceeding reference value for 24 hours (75 μg m^{-3}) [17]; mainly when winds came from East-Northeast (**Figure 10c** and **d**). Finally, winds came from the Northeast during all year, showing a great variability during cold fronts season (**Figure 10e** and **f**), with maximum wind speeds >7.9 m s^{-1} along this season. Both O_3 and PM_{10} showed highest levels when winds had a Northeast component.

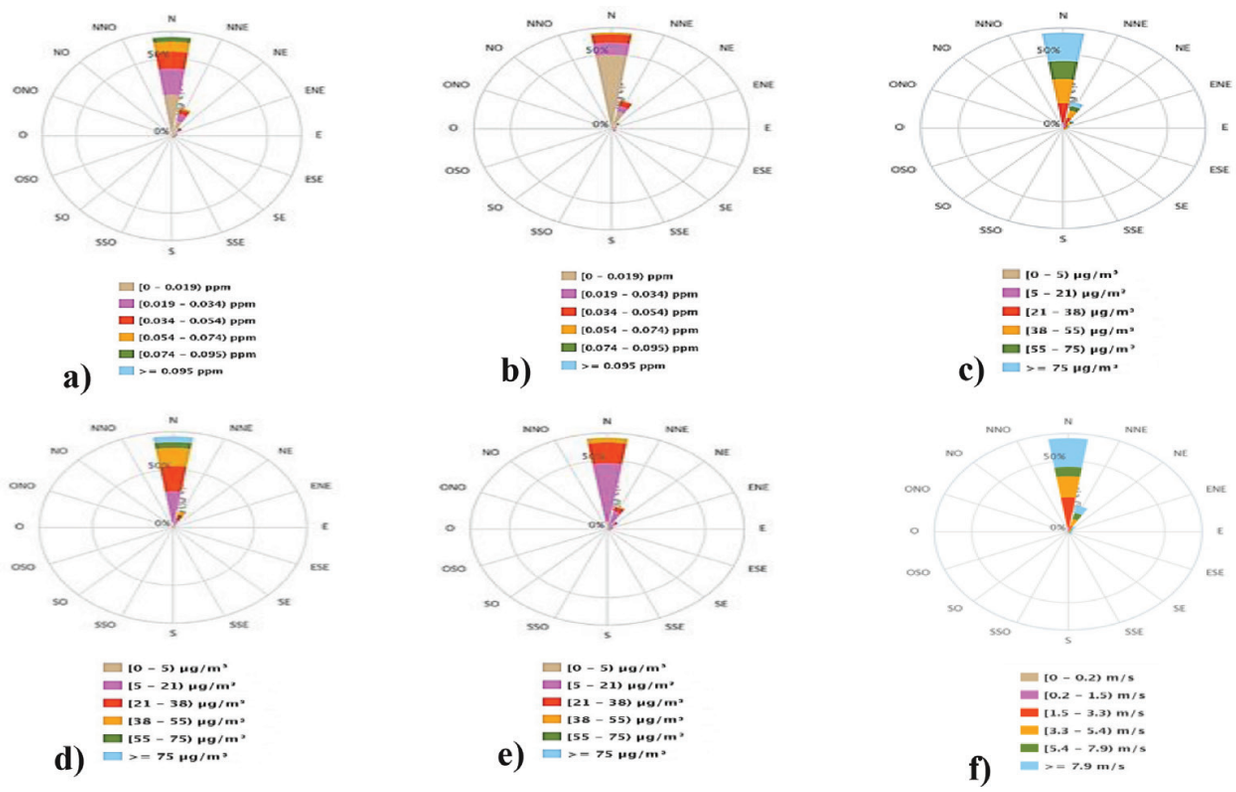


Figure 9. Criteria air pollutants and meteorological conditions for Site VII (Santa Catarina) during the study period: (a) O_3 dry and rainy seasons, (b) O_3 cold fronts season, (c) PM_{10} dry, rainy and cold fronts seasons, (d) $PM_{2.5}$ dry season, (e) $PM_{2.5}$ rainy season, (f) wind all year.

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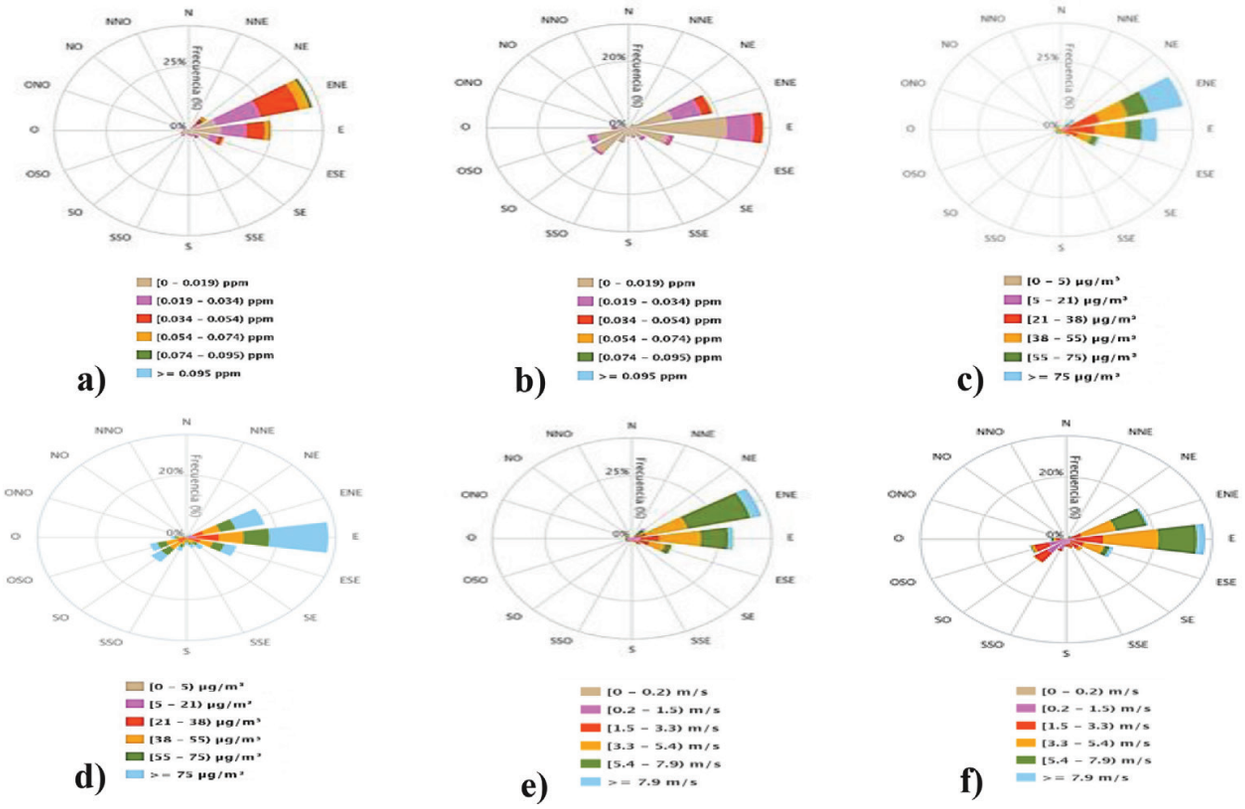


Figure 10. Criteria air pollutants and meteorological conditions for Site VIII (San Pedro) during the study period: (a) O_3 dry and rainy seasons, (b) O_3 cold fronts season, (c) PM_{10} dry and rainy seasons, (d) PM_{10} cold fronts season, (e) wind dry and rainy seasons, (f) wind cold fronts season.

4.4.9. Site IX La Pastora

O_3 levels (0.074–0.095 ppm) were high during dry and rainy seasons, exceeding the reference value for 8 hours (70 ppb) [16] when winds came from North-Northeast (**Figure 11a**). In addition, PM_{10} levels (≥75 µg m^{-3}) were high during all year and also exceeded the reference value for 24 hours (75 µg m^{-3}) [17], when winds came from North-Northeast (**Figure 11b**). $PM_{2.5}$ levels were ≥44 µg m^{-3} during all year, being higher during cold fronts season, and when wind direction was from North-Northeast, exceeding the reference value (45 µg m^{-3}) [17] for 24 hours (**Figure 11c**). Finally, winds came from the North-Northeast during all year (**Figure 11d–f**) with maximum wind speeds >7.9 m s^{-1} along the year, and showing a greater variability in wind direction during cold fronts season. O_3, $PM_{10,}$ and $PM_{2.5}$ showed highest levels when winds had a Northeast component.

4.4.10. Site X Juarez

Figure 12a shows that CO levels (8.5–11 ppm) were higher during cold fronts season, reaching the upper limit value established in the air quality standard (11 ppm) for 8 hours [18]. From **Figure 12b** and **c**, it can be observed that O_3 levels (≥0.095 ppm) were high during dry season when winds came from Southeast, exceeding in both cases, the reference value for 8 hours (70 ppb) [16]. PM_{10} levels (≥75 µg m^{-3}) were high during all year, exceeding

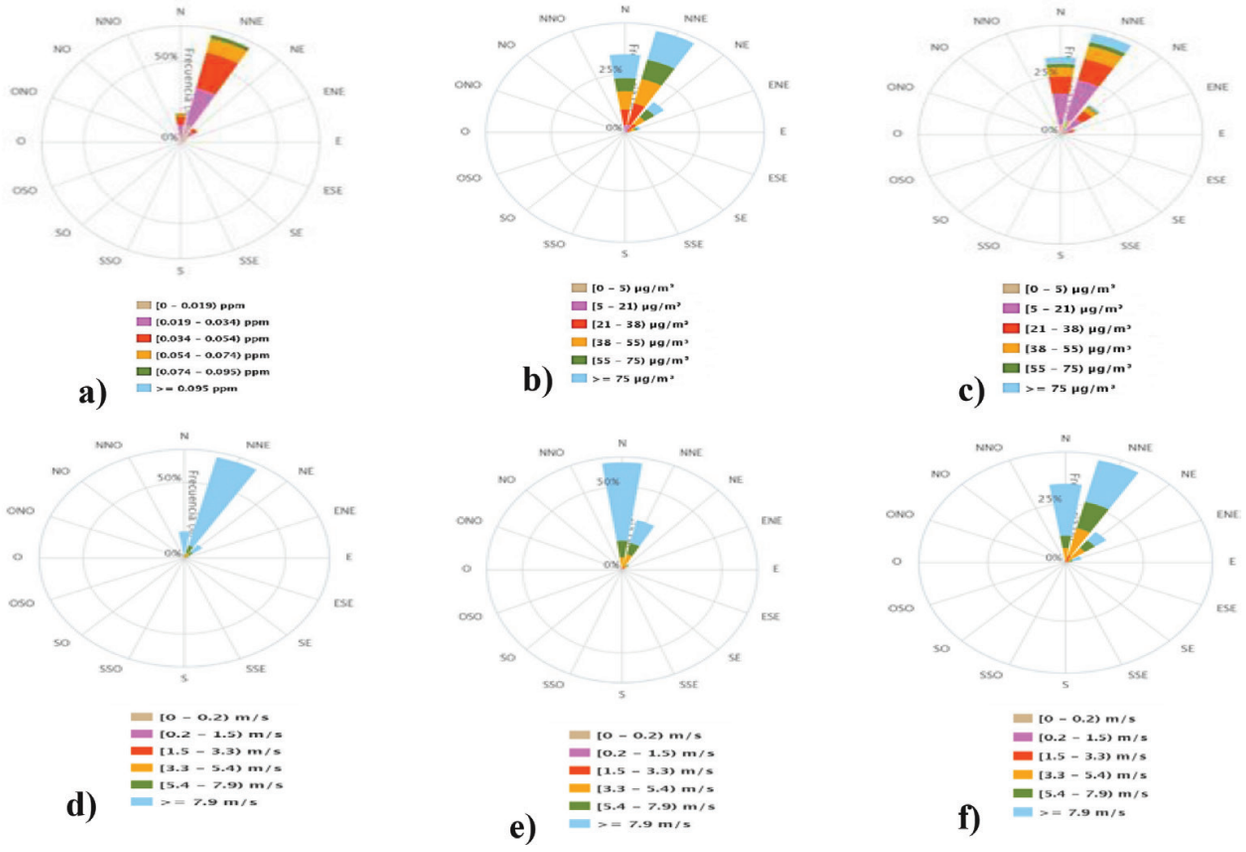


Figure 11. Criteria air pollutants and meteorological conditions for site IX (La Pastora) during the study period: (a) O_3 dry, rainy and cold fronts seasons, (b) PM_{10} dry, rainy, and cold fronts seasons, (c) $PM_{2.5}$ dry, rainy, and cold fronts seasons, (d) wind dry season, (e) wind rainy season, (f) wind cold fronts season.

reference value for 24 hours (75 µg m^{-3}) [17], when winds came from Southeast during dry and rainy season (**Figure 12d**) and from Northwest and Southeast during cold fronts season, showing a greater variability in wind direction (**Figure 12e**). Finally, winds came from the Southeast during dry and rainy seasons, and from Northwest during cold fronts season (**Figure 12f**), with maximum wind speeds >7.9 m s^{-1} along the year. O_3 and PM_{10} showed highest levels when winds had a Southeast component most part of the year and a Northwest component during cold fronts season, suggesting a seasonal behavior for these pollutants. However, in the case of CO behavior, it was completely different, with the highest levels (even exceeding the air quality standard) during cold fronts season with winds coming from Southeast and Northwest.

4.5. Mapping N and S deposition fluxes and reference values

In Mexico, reference values to compare the current deposition fluxes of N and S are not available. However, critical loads have been estimated for European ecosystems and some sites in the United States. A critical load value of 5 Kg N ha^{-1} $yr.^{-1}$ has been proposed for alpine ecosystems [19], whereas for some sites in North America, values of 3–8 Kg N ha^{-1} $yr.^{-1}$ for New Mexico and 4–7 Kg N ha^{-1} $yr.^{-1}$ for California have been proposed [20].

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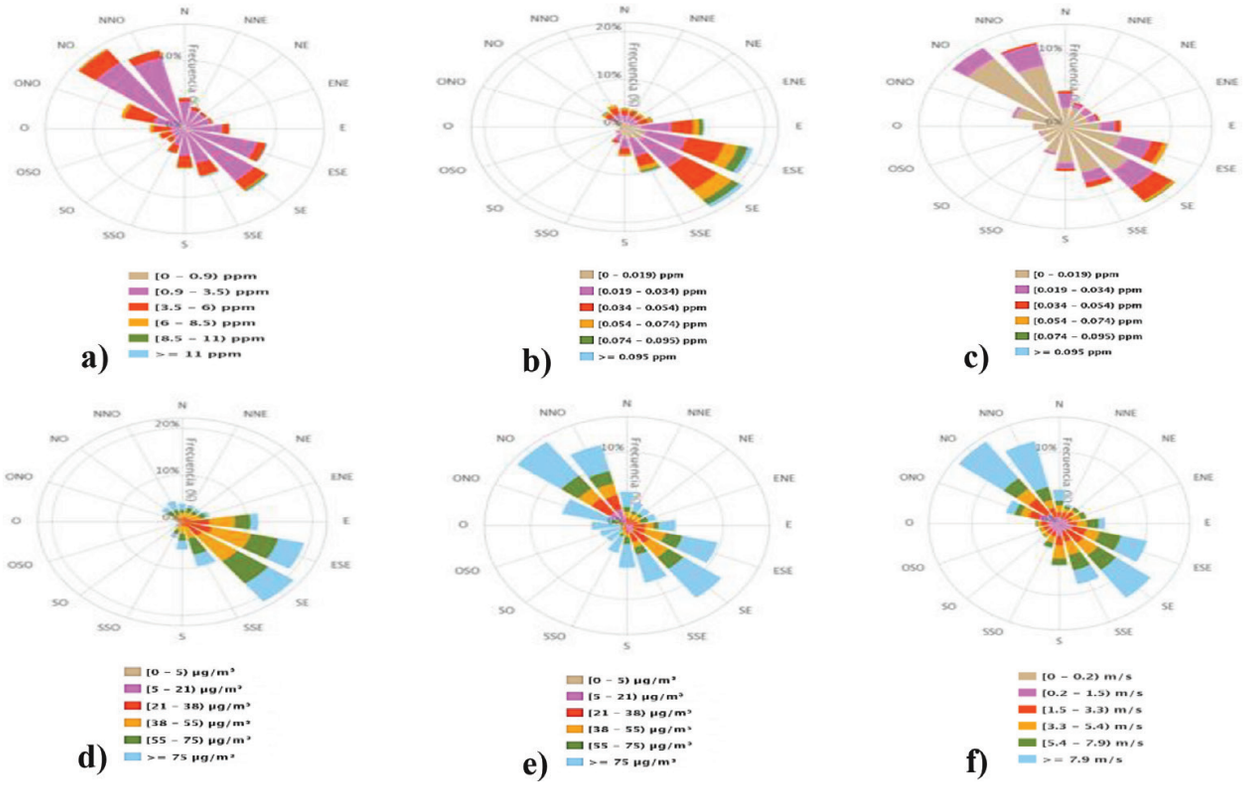


Figure 12. Criteria air pollutants and meteorological conditions for site X (Juarez) during the study period: (a) CO cold fronts season, (b) O_3 dry season, (c) O_3 rainy and cold fronts seasons, (d) PM_{10} dry and rainy seasons, (e) PM_{10} cold fronts season, (f) wind all year.

In the case of S deposition, a critical value of 3 Kg S ha^{-1} $yr.^{-1}$ has been reported for very sensitive areas in Europe, whereas for natural forests, a reference value of 2–5 Kg S ha^{-1} $yr.^{-1}$ has been proposed [21]. In this study, mean N and S throughfall deposition fluxes were 4.88 and 25.03 Kg ha^{-1} $yr.^{-1}$, respectively. N deposition fluxes did not exceed the reference value reported for alpine ecosystems; however, they are almost in the upper limit of this reference value and similar to those found in New Mexico and California. In addition, N deposition levels found in MAM (**Figure 13**) are almost twice those reported by Escoffie [22] in Carmen Island (2.15 Kg N ha^{-1} $yr.^{-1}$), Campeche; by Sánchez [23] in Orizaba Valley, Veracruz (1.44 Kg N ha^{-1} $yr.^{-1}$); and by López [24] in Mérida, Yucatán (2.7 Kg N ha^{-1} $yr.^{-1}$) and are almost four times those reported by García [25] in Atasta-Xicalango, Campeche (1.15 Kg N ha^{-1} $yr.^{-1}$). On the other hand, S deposition fluxes in MAM exceeded almost eight times the critical load proposed for sensitive areas, and five times the upper reference value for natural forests in Europe. S deposition fluxes found in MAM were almost six times higher than those reported by Escoffie [22] in Carmen Island, Campeche (4.7 Kg S ha^{-1} $yr.^{-1}$); and by López [24] in Mérida, Yucatán (4.07 Kg S ha^{-1} $yr.^{-1}$), and almost three times higher than those reported by García [25] in Atasta-Xicalango, Campeche (8.57 Kg S ha^{-1} $yr.^{-1}$). In spite of S levels in MAM being half of those reported by Sánchez [23] in Orizaba Valley (55.16 Kg S ha^{-1} $yr.^{-1}$), the current S deposition fluxes in MAM represent a risk potential of acidification and impact on ecosystems in this region.

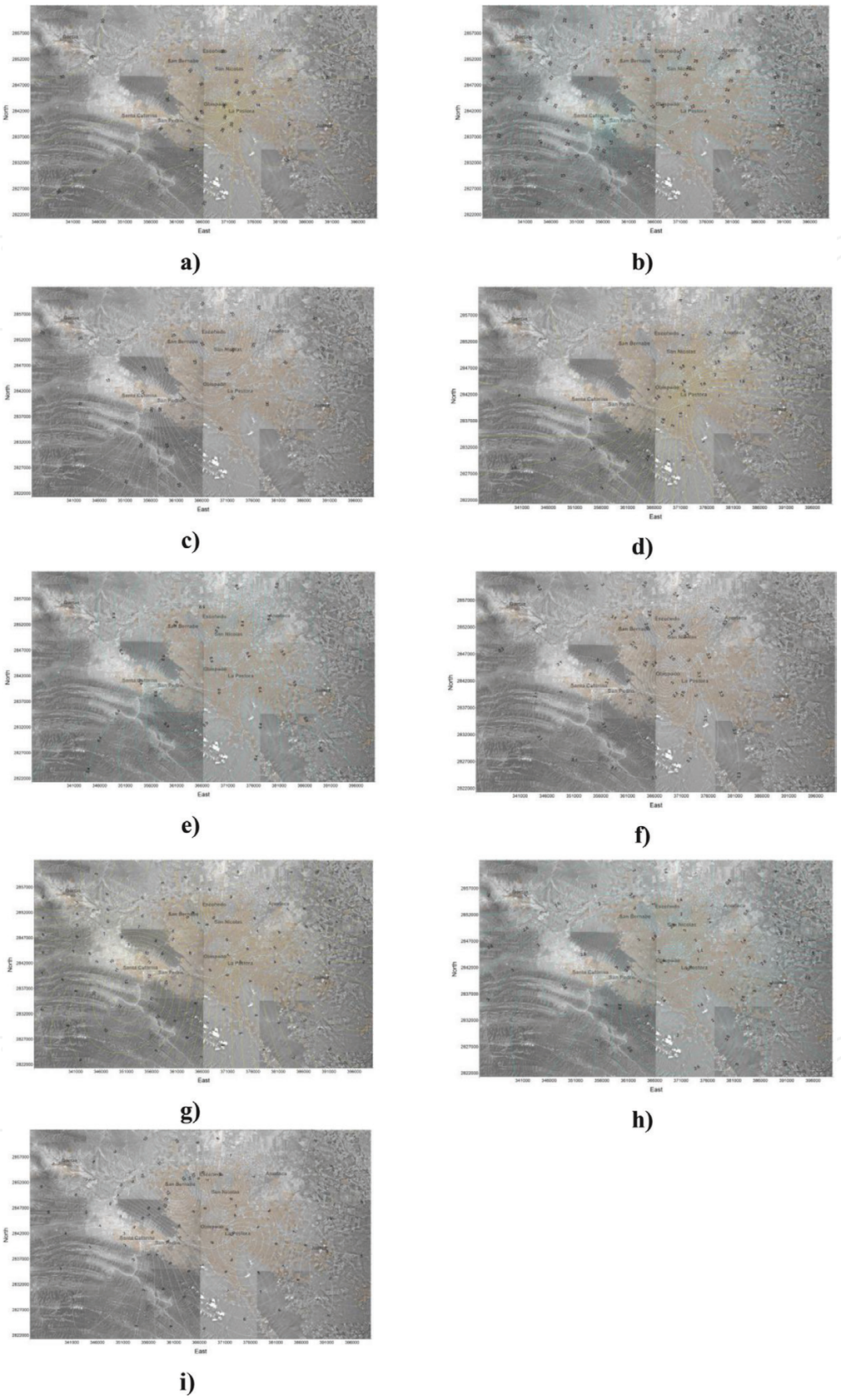


Figure 13. Spatial and temporal patterns for throughfall deposition fluxes of SO_4^{2-} for (a) dry season, (b) rainy season, (c) cold fronts season; of NO_3^- for (d) dry season, (e) rainy season, (f) cold fronts season; and of NH_4^+ for (g) dry season, (h) rainy season, (i) cold fronts season in MAM during the study period.

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5. Conclusions

This chapter presents an overview of atmospheric pollution and its spatial and temporal variability in MAM, and from results, we can conclude that:

N deposition fluxes: Nitrate deposition showed a seasonal pattern with the highest levels during the rainy season (suggesting that atmospheric reactions in aqueous phase play an important role in the removal process). In the case of ammonium, its deposition also presented a seasonal variation, with higher levels during the dry and cold fronts season in Santa Catarina municipality. N deposition fluxes did not exceed the critical load values reported for Europe and USA; however, these levels were higher than those reported for the southeast region of Mexico.

S deposition fluxes: Sulfate deposition did not show significant differences between seasons and sampling points, suggesting that levels found probably correspond to background levels in MAM. Sulfate levels were relatively high in Obispado, Santa Catarina, and Escobedo municipalities. S deposition fluxes exceeded the limit values proposed for sensitive areas and natural forests in Europe, and were higher than those reported at the southeast (SE) of the country, but lower than those found at the center of Mexico. It suggests that S deposition could be a potential risk for ecosystems and historical heritage in MAM.

CO: Juárez municipality was the only sampling site that showed exceedances to the reference value established in the current regulation, this municipality is located to the east of MAM, and its levels were higher when wind came from N.

O_3: Ozone levels exceeded the reference value of the current regulation in all sampling sites during the dry season when wind had an east component (E-SE-NE).

PM_{10}: PM_{10} levels exceeded the threshold value of the current regulation in all sites and during all year, its levels being higher when wind came from East (E-SE-NE).

$PM_{2.5}$: Obispado and La Pastora municipalities (center of MAM) showed the highest levels during all year, whereas in Escobedo and Apodaca (at the northern side of MAM), its levels were higher during the cold fronts season.

In spite of the time scale in which deposition fluxes (by season) and criteria pollutants (by day) were different, we could identify an evident association between CO and nitrate, since both analysis showed that their levels were higher in Juarez municipality during cold fronts season (CO levels exceeded the regulation's reference values and exhibited a different pattern regarding to the remaining sampling sites in MAM). It suggests that both, CO and nitrate had their origin in vehicular sources in this urbane zone highly polluted. On the other hand, a similarity was observed between deposition patterns of S and PM_{10}-$PM_{2.5}$ levels in MAM, since sulfate did not present significant differences in its spatial and seasonal variability; it suggests that levels found in this study remained constant all year, and correspond to the background levels for MAM. The same finding was obtained for PM_{10} and $PM_{2.5}$ levels, since their levels exceeded the reference value established in the current regulation in all sampling sites. Regarding wind direction, an evident association with criteria pollutants was found, PM_{10} and O_3 showed their highest levels when wind had an east component (E-SE-NE), which corresponds to the

prevailing wind direction during all year in MAM. In addition, $PM_{2.5}$ levels were higher when wind came from north. It suggests that sources located at north (N) and east (E) from MAM contributed significantly to pollution in MAM. Finally, this study suggests that, since O_3 and PM_{10} levels exceeded the allowable maximum limit during all year and in all sampling sites, the implications that this fact may have on the population health in MAM could be serious.

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