

## Estimation of atmospheric stability for the city of Zacatecas, Mexico

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Received: August 22, 2022

Accepted: October 5, 2023

Published: November 21, 2022

DOI: <https://doi.org/10.56845/rebs.v4i2.68>

**Abstract:** In the present work, due to the importance of the dispersion of pollutants in the air, the modified Pasquill-Gifford classification was used to determine the classes of atmospheric stability, which serve to indirectly identify the increase or decrease of the existing mechanical and convective turbulence, conditions that at the same time affect the dispersion of pollutants; the above was carried out in the municipality of Zacatecas in the years of 2019 and 2020; the data of concentrations of Carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), PM<sub>10</sub> and PM<sub>2.5</sub> particles, and ozone (O<sub>3</sub>) released from a monitoring station and were contrasted with the estimated atmospheric stability classes in order to observe the influence of these classes on these pollutants; and finally, based on the results obtained, it was identified in which seasons of the year there is a greater and lesser dispersion of pollutants. Once this process was carried out, a series of recommendations were issued about the feasibility of using this classification in the city of Zacatecas. Maximum frequencies of class A were obtained between 9:00 and 12:00 hours, considered the most unstable with 52.22% for spring, 53.57% for summer, 44.87% for autumn, and 40% for winter. When class A increased its frequency, the concentration of particles decreased, and when class F increased, the concentration of particles increased. Therefore, it is recommended to consider different factors that may influence the dispersion of pollutants in the city of Zacatecas and, regarding the results obtained, make use of this classification only in hourly averages. Likewise, the Pasquill-Gifford classification could be combined with atmospheric models to determine the behavior of particles in different periods with greater confidence.

**Keywords:** atmospheric stability; concentration; contaminants; convection

### Introduction

The constant growth of the population in urban areas has brought with it a greater concentration of economic and productive activities, which under certain circumstances exacerbate problems related to poor air quality. The World Health Organization (WHO) published that the air pollution had caused 7 million of deaths, annually, where the main damage to health generated were: pneumonia (21 %), from stroke (20%), ischaemic heart disease (34 %), chronic obstructive pulmonary disease (19%) and lung cancer (7%) (WHO, 2018). On the other hand, for the Metropolitan Zone of Mexican Valley was propose a mortality risk of 1 % for child's with less than a year, and for Zacatecas city was of 0.77%. In both cases these occur for every concentration increment of 10 µg/m<sup>3</sup> of particulate matter PM<sub>10</sub> (SAMA & SEMARNAT, 2018).

In this context, there are regulated pollutants in Mexican standards to which have set a maximum permissible limit of concentration in the air, in order to protect human health and ensure the well-being of the population, which are the criterion contaminants. These pollutants are: ozone (O<sub>3</sub>) (DOF, 2014), carbon monoxide (CO) (DOF, 2021b), sulfur dioxide (SO<sub>2</sub>) (DOF, 2019), nitrogen dioxide (NO<sub>2</sub>) (DOF, 2021c), particulate matter (PM<sub>2.5</sub> and PM<sub>10</sub>) (DOF, 2021a) and lead (Pb) (DOF, 1994).

This classification is due to the fact that SO<sub>2</sub>, NO<sub>2</sub>, suspended particles and O<sub>3</sub> have been detected to have negative impacts on health. Some of them affect the respiratory and cardiovascular systems, both those who suffer from asthma, bronchitis, lung and heart problems, and the population over 30 years, among others (Bromberg, 2016; Koren et al., 2012; Sperber, 1999), in the case of CO, based on evidence from experimental and epidemiological studies documenting adverse effects on human health, especially in oxygen-intensive organs such as the brain and heart (WHO, 2015).

On the other hand, in Mexico, in 2010, the National Institute of Ecology and Climate Change (INECC, 2014) evaluated the economic and health impact of air quality in the metropolitan areas of Mexico, finding that if the limits

recommended by the World Health Organization for the concentration of PM<sub>2.5</sub> particles were met, economic losses of 45,000 million pesos and 2,170 premature deaths would be avoided (SEMARNAT, 2018).

As for the State of Zacatecas, the criteria pollutants (O<sub>3</sub>, SO<sub>2</sub>, CO, NO<sub>2</sub>, PM<sub>10</sub> and PM<sub>2.5</sub>) are continuously measured with only one air quality monitoring station from 2016, which is located at center-south of the Zacatecas capital. A study of premature mortality attributable to PM<sub>2.5</sub> air pollution caused a loss of productivity of around 7.85 million US dollars (SAMA & SEMARNAT, 2018).

One of the methods for estimating atmospheric stability is the Pasquill-Gifford classification, which assigns letters from A to G for increased atmospheric stability, called stability classes. Therefore, in this project, the atmospheric stability of the City of Zacatecas was estimated with the modified Pasquill-Gifford classification (Flores-Jiménez et al., 2021; Essa et al., 2013; Hunter, 2012) as a factor that favors the prevalence or dispersion of criterion pollutants (PM<sub>2.5</sub>, PM<sub>10</sub>, CO, SO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>) in the warm periods of the year and an increase in O<sub>3</sub> concentration in these same periods.

In this context, the dispersion of pollutants plays an essential role in reducing their concentration in the air and that the exposure is lower in people. This is where it comes in atmospheric stability, which describes the trend for horizontal and vertical mixing in the atmosphere. This factor is measured in a zonal way since both the speed conditions of wind, such as solar radiation, temperature and cloudiness vary from area to zone, so there are no official national data. Hence, the purpose of this investigation was to obtain the atmospheric stability classes for the city of Zacatecas during the period 2019-2020, considering the meteorological and satellite data of wind speed and solar radiation for the first, and cloud cover for the second.

## Materials and Methods

To carry out the following points, computer equipment with an Internet connection was used, where an Excel sheet, A C++ language program, geographic information system databases and bibliographic review were used.

### *Description of the study area*

The municipality of Zacatecas is the capital of the State and is located in the southeast center of the State with a population of 149,607 inhabitants in 2020 (INEGI, 2020). It has a temperate arid climate which reaches an average annual temperature between 12 °C and 18 °C; and temperate semi-arid climate with an average annual temperature equal to that mentioned (INEGI, 2017). Because the dispersion of pollutants depends on several factors, including the relief, Figure 1 shows that the monitoring station is located in an urban area and also observes in greater detail the relief in which it is located, where the highest concentration of buildings is from the southeast to the southwest and two peaks at 2,600 m.a.s.l. to the northeast and northwest of the monitoring station.

The data of concentrations of ozone (O<sub>3</sub>), carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>), suspended particles (PM<sub>2.5</sub> and PM<sub>10</sub>) were provided by the Secretariat of Water and Environment (Secretaría del Agua y Medio Ambiente – SAMA, by its acronym in Spanish) with data from 2019 to 2020. These data are obtained with the use of the air quality monitoring station belonging to the air quality monitoring network of the State of Zacatecas "Explanada del congreso", which is geographically located at 22°77" North latitude and 102°57" West longitude, and is located at an approximate altitude of 5 m from ground level and at an altitude of 2,465 m.a.s.l.

Data on radiation, speed, wind direction and relative humidity were obtained directly from the official website of the National Air Quality Information System (SINAICA) for the same years, and cloudiness was obtained from a statistical analysis of historical hourly weather reports and model reconstructions from January 1, 1980 to December 31, 2016. The climatological data, and among them, cloudiness, were obtained from NASA's MERRA-2 Modern-Era Retrospective Analysis (<https://gmao.gsfc.nasa.gov/reanalysis/MERRA-2/>), the spatial resolution is 50 km in the latitudinal direction (Average Weather In Zacatecas, Mexico, All Year Round - Weather Spark, n.d.).

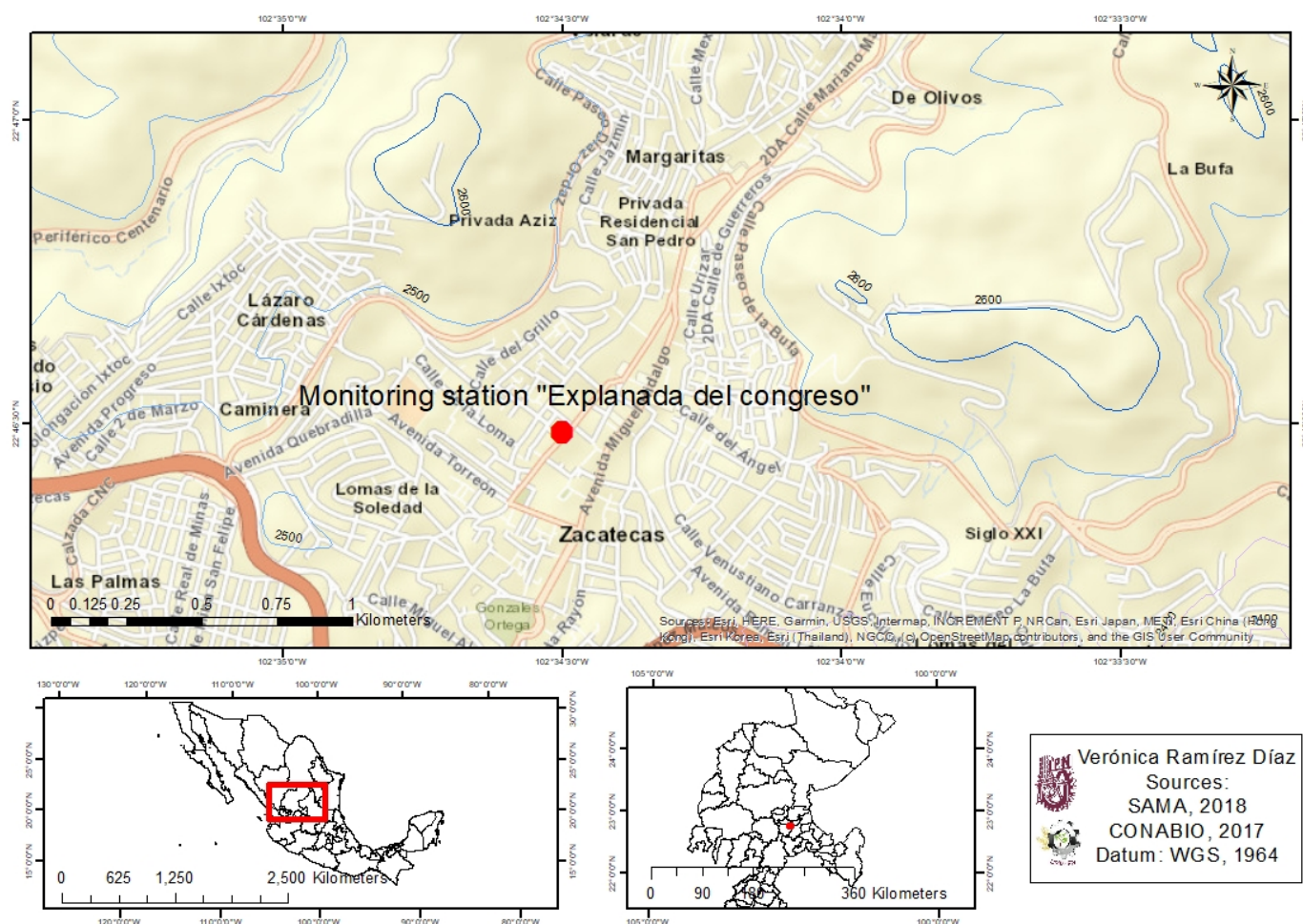


Figure 1. Study area near the monitoring station.

After the data collection, averages of all months were calculated for radiation ( $\text{W/m}^2$ ) and wind speed ( $\text{m/s}$ ) by dividing day and night time, where the first occur in the following hours: 6:00 - 20:00 in spring and summer, 8:00 - 19:00 h in autumn and 8:00 - 18:00 in winter. The night time was assigned when the incidence of radiation was less than  $10 \text{ W/m}^2$ , since through the observation of data it was identified that there were measures of solar radiation at night less than that value, these data were taken as zero, since the incidence of solar radiation in night time is not possible (from 20:00 to 6:00 h in spring and summer, 19:00 to 8:00 h in autumn and 18:00 to 8:00 h in winter).

Also, with these data radial graphs of wind direction and speed were obtained, the wind speed ranges were assigned according to the Beaufort scale (SEMAR, 2001). With the relative humidity data, a graph of monthly averages was obtained to observe their possible relationship with the concentration of contaminants.

#### Air quality monitoring station

The air quality sensors used to measure the criteria pollutants in the monitoring station were, BAM1020 for particulate matter  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$ , whose units are  $\mu\text{g/m}^3$ ; and Serinus for the following gases: ozone ( $\text{O}_3$ ), nitrous oxide ( $\text{NO}_x$ ), sulfur dioxide ( $\text{SO}_2$ ) and carbon monoxide ( $\text{CO}$ ), where in this cases the units are parts per million (ppm). In all cases the concentrations register was every hour (SAMA & SEMARNAT, 2018; Met One Instruments, Inc., 2016; Serinus, 2022, 2013a, 2013b, 2013c).

To measure both particulate matter concentrations, the BAM 1020 sensor provides a constant source of beta rays, that crosses a glass fiber filter before and after a pump pulls a known volume of  $\text{PM}_{10}$  or  $\text{PM}_{2.5}$ . The ratio of the beta ray account that is obtained considering a filter with and without particles is used to determine the mass density of the

sample collected on a filter tape of the sensor. The measuring range of this sensor is dynamic, allowing it to vary from 100 to 10,000  $\mu\text{g}$  per cubic meter (Met One Instruments, Inc., 2021).

The sensor to measure  $\text{O}_3$ , use and absorption technology of non-dispersive ultraviolet rays (UV). To measure  $\text{NO}_2$  and  $\text{NO}_x$ , the standard process in the sensor consist in the detection of gas phase chemiluminescence. For the  $\text{SO}_2$  detection the process is like the ozone sensor, due to the use of UV fluorescent radiation. The monoxide carbon sensor use non-dispersive infrared spectrophotometry (NDIR) to quantify this pollutant. In all the cases, every sensor has their respective measuring range in ppm units: ozone and nitrous dioxide and sulfur dioxide, 0-20; and monoxide carbon, 0-200 (Serinus, 2022, 2013a, 2013b, 2013c).

### Data classification

Data classification was performed using the modified Pasquill-Gifford classification (Davies & Singh, 1985), which has six categories, from very unstable (A) to extremely stable (G). And due to the almost zero or absolute absence of radiation when it does not affect the ground, the classification considers two times, day and night. The first is classified using wind speed in units of meters per second ( $\text{m/s}$ ) and the amount of insolation in units of measurement of watts per square meter ( $\text{W/m}^2$ ).

The insolation at this time, is classified in "Strong" when it is less than  $600 \text{ W/m}^2$ , "Moderate" when it is  $300\text{-}600 \text{ W/m}^2$ , "Light" when the value is less than  $300 \text{ W/m}^2$ ; when there is cloudiness in the day, the values vary between C (slightly unstable) and D (neutral). This classification is shown concisely in Table 1.

Table 1. Modified Pasquill-Gifford classification for daytime.

| Wind speed ( $\text{m/s}$ ) | Insolation in daytime ( $\text{W/m}^2$ ) |          |       | Radiation in cloudy weather |
|-----------------------------|------------------------------------------|----------|-------|-----------------------------|
|                             | Strong                                   | Moderate | Light |                             |
| <2                          | To                                       | A-B      | B     | C                           |
| 2-3                         | A-B                                      | B        | C     | C                           |
| 3-5                         | B                                        | B-C      | C     | C                           |
| 5-6                         | C                                        | C-D      | D     | D                           |
| <6                          | C                                        | D        | D     | D                           |

Source: (Davies & Singh, 1985).

For the night time, the cloud cover with octa measurement unit was taken into account, which indicates in eighths the cloud cover in the sky, that is, if you have a cloudiness of 0 octas, it indicates a clear sky, on the other hand it is a cloudiness of 8 octas, the sky is completely cloudy ([https://web.archive.org/web/20031208161922/http://www.bbc.co.uk/weather/weatherwise/activities/weatherstation/cloud\\_measuring.shtml](https://web.archive.org/web/20031208161922/http://www.bbc.co.uk/weather/weatherwise/activities/weatherstation/cloud_measuring.shtml)) (BBC Weather, 2003). It was also taken into account that one hour before sunset and after sunrise, stability is neutral (D). This classification is shown concisely in Table 2.

Table 2. Modified Pasquill-Gifford classification for night time.

| Wind speed ( $\text{m/s}$ ) | 1 h before sunset or after sunset | Cloud cover (Octas) at night |     |   |
|-----------------------------|-----------------------------------|------------------------------|-----|---|
|                             |                                   | 0-3                          | 4-7 | 8 |
| <2                          | D                                 | F or G                       | F   | D |
| 2-3                         | D                                 | F                            | E   | D |
| 3-5                         | D                                 | E                            | D   | D |
| 5-6                         | D                                 | D                            | D   | D |
| <6                          | D                                 | D                            | D   | D |

Source: (Davies & Singh, 1985).

The way to classify the data of both times was through the elaboration of two programs in CodeBlocks in C++ language.

The frequency of atmospheric stability ratings in each month, as well as by day, was determined and it was identified in which periods the dispersion of pollutants per month could or could not be favored. After observing a relationship of the stability classes of the whole year with the seasons of the year, were made graphs of stability classes per hour for each one.

Finally, the frequency of the stabilities estimated in each month was contrasted with the concentration data of pollutants, determining in which months there is a greater or lesser dispersion of these pollutants.

Once this process was carried out, a series of recommendations were issued about the feasibility of using this classification in the city of Zacatecas.

## Results and Discussion

Air pollutants dispersion depends on several factors, including the relief, wind speed, wind direction, station atmospheric conditions and atmospheric conditions coming from surroundings of the study area. Figure 1 shows that the monitoring station is located in an urban area and also observes in greater detail the relief in which it is located, where the highest concentration of buildings is from the southeast to the southwest and two peaks at 2,600 m.a.s.l. to the northeast and northwest of the monitoring station.

In order to analyze the direction and speed of the wind, radial graphs were made with the Beaufort scale for each month, where three main behaviors can be observed (Figure 2):

- From February to May the direction is from the southeast and southwest to the northwest and northeast respectively.
- From June to October the direction is mostly east, southeast and south to the west, northeast and north.
- From November to January the wind speed and direction is distributed from the southwest, south, southeast, to the northeast, north and northwest.

The Pasquill-Gifford classification is based on the fact that the condition near the ground depends essentially on net solar radiation and wind speed (Rodríguez & Romero K.J., 2018). Where, at a lower wind speed there is greater instability (A) and when there is a higher wind speed, atmospheric stability is designated as neutral (D).

According to the method, increasing wind speed reduces instability during the day (Kahl & Chapman, 2018), and this is because atmospheric stability according to Zoras et al. (2006) can be defined as the atmospheric tendency to resist or improve vertical movement or, alternatively, to suppress or increase existing turbulence (Zoras et al., 2006). And according to Shenelle and Dey (2000), generally, when convective turbulence predominates, the winds are weak and the atmosphere is in unstable conditions (Shenelle & Dey, 2000). Also, according to the method, diurnal clouds have an indirect effect, reducing insolation and thus reducing instability (Moragues, 2002).

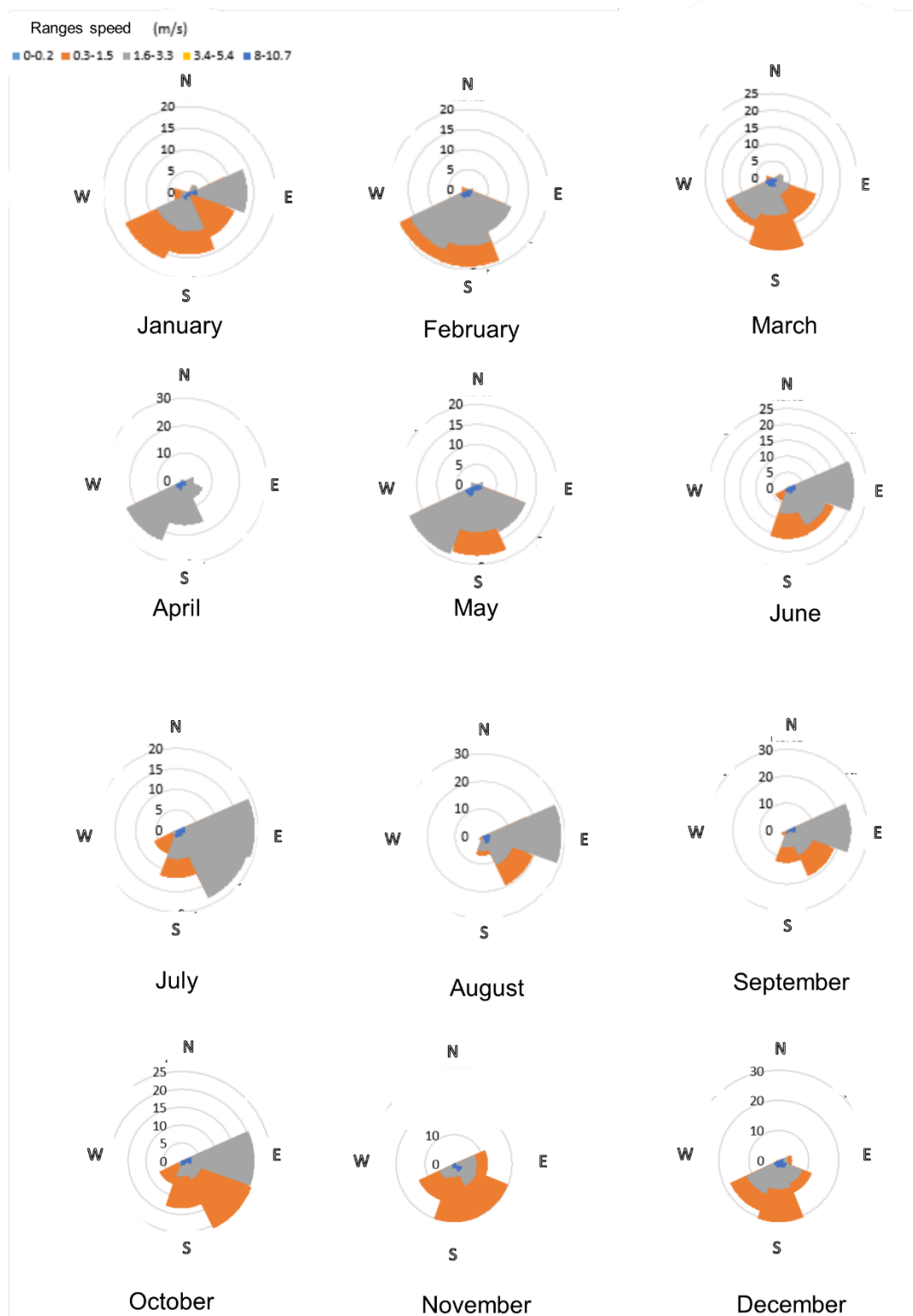


Figure 2. Wind speed and direction averages for every month considering the years 2019 and 2020.

Figure 3 shows the frequencies of atmospheric stabilities obtained with the modified Pasquill-Gifford classification for daytime, where the month with the highest atmospheric instability (A and A-B) is the month of May with a frequency in class A of 50.85%, which has been identified for some years as the month with highest solar radiation levels in the study zone (Contreras Pimentel et al., 2019) or has been selected to make studies of global solar irradiance due to the

clarity of the sky that appears (Pinedo et al., 2006). March also had important conditions of instability with a frequency in this same class (A) of 45.77% indicating an increase in the vertical movement of masses-of air. January presented a lower frequency of this class, with 34.68% due to is one of the months with the lowest incidence of solar radiation as it happened during 2012 and 2019 (Contreras Pimentel et al., 2019; Sigala Valdez, 2020). A small increase in neutral atmospheric stability (C) is observed in the months of January, February, November and December, and a decrease in class A with a frequency of 34.68, 37.28, 35.79 and 33.24%, respectively which are mostly winter months indicating that in those months there is a slight increase in wind speed and there is a light or moderate solar radiation, so neutrality in the atmosphere tends to increase.

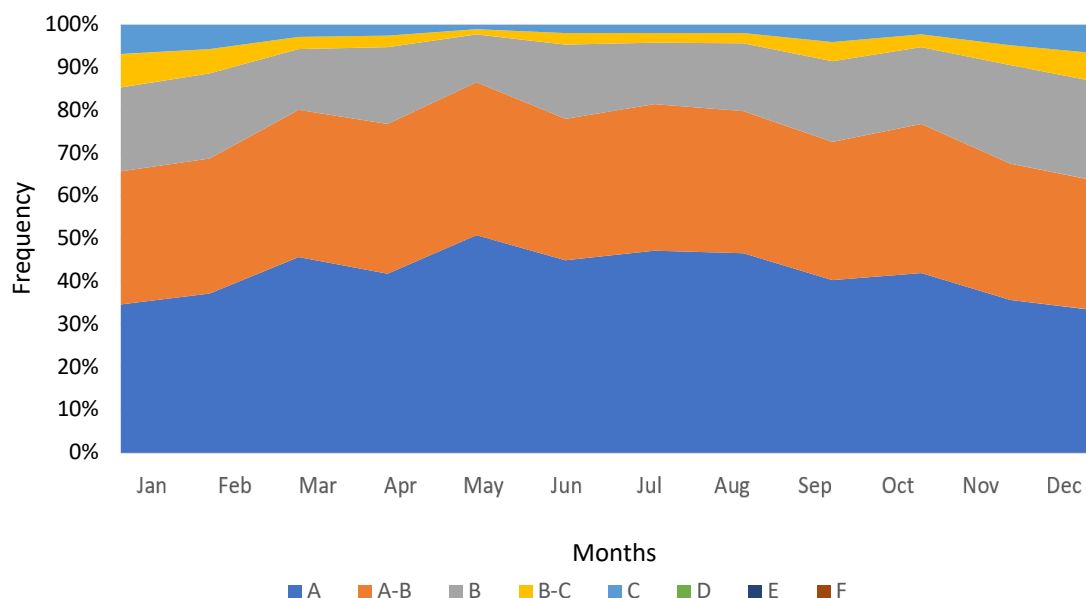


Figure 3. Frequencies of atmospheric stability classes for daytime for the years 2019-2020.

Night time is defined as the period from one hour after sunset, to one hour before sunrise, and cloudiness is measured in octas, that is, 0/8 equals the totally clear sky, 4/8 to half of the covered sky and 8/8 is equivalent to the completely covered sky (Rodríguez & Romero K.J., 2018). Clouds in night time reduce stability (Moragues, 2002), as seen in Table 2, this classification has no effect during day/night transition periods, classifying these hours as neutral (D) (Kahl & Chapman, 2018).

At night, the thermal radiation of the clouds reduces the cooling of the surface (Venkatram, 1996) and in the modified Pasquill-Gifford classification it is assumed that in these conditions there is a neutral class (D), instead when there is no cloudiness, the stability can lead to be extreme (G) (Table 2) where it is assumed that the convective turbulence is almost zero.

Figure 4 presents the frequencies of the stability classes for the time of night for the years 2019-2020 where there is a notorious frequency of neutral class (D) in the months of June to November, these are months of the summer season that is characterized by having greater precipitation per year, which for the state corresponds to the 75% of the annual average amount, that is 510 mm, from June to September (Ortiz Gómez et al., 2018). An increase in frequency of class F is also observed in the month of May with a value of 77.44%, and in the months of February and March it is 70.94% and 68.36% respectively, this increase in stable class (F) is specifically attributed to the fact that the wind speed is most often between 0.5 - 3 m/s and the cloudiness is mostly zero, so being months considered cold and there is little or no cloudiness, there is no reduction of cooling of the surface and therefore the convective movement as well as the turbulent (wind) are affected and drastically decreased.

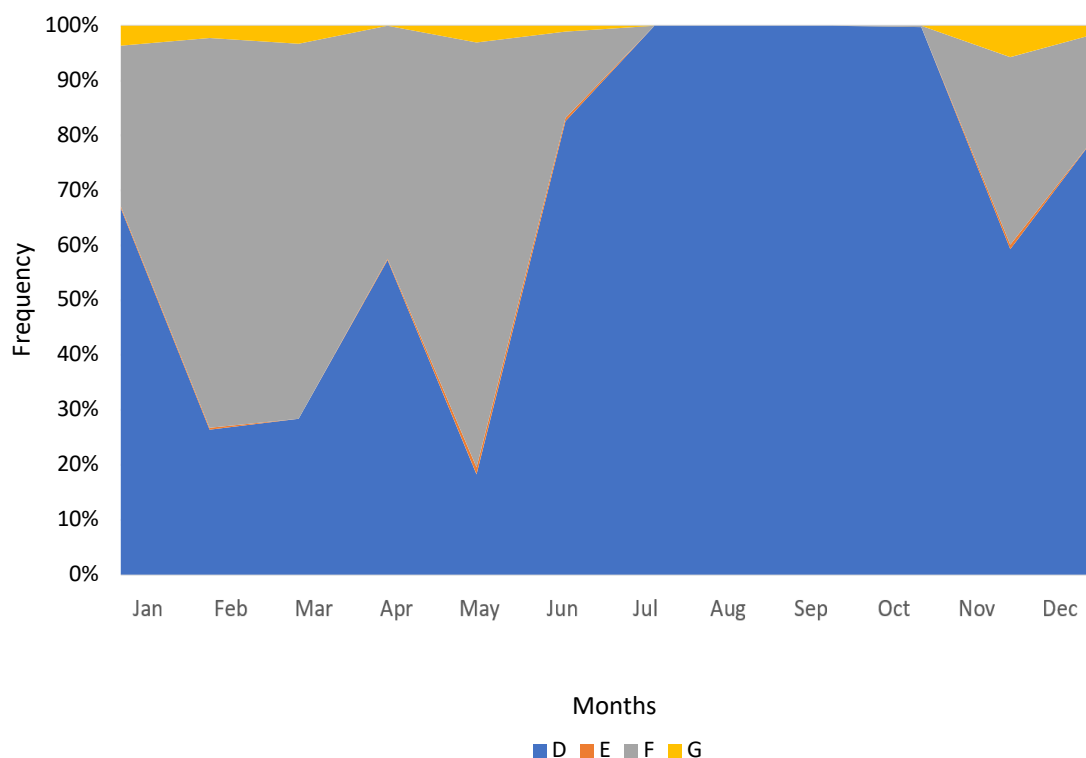


Figure 4. Frequencies of atmospheric stability classes for nighttime for the years 2019-2020.

After observing a relationship of the stability classes of the whole year with the seasons of the year, the same was done, but for the hourly conditions for each season of the year (Martínez, 2011).

Figure 5 shows all the seasons of the year and the frequencies obtained for each hour, it can be seen that the maximum peaks of instability (A) are between 9:00 and 12:00 hours with maximum frequencies of 52.22% for spring, 53.57% for summer, 44.87% for autumn and 40% for winter. The first two seasons have the greater atmospheric instability conditions due to during that hours the solar radiation increase their levels as observed Rodríguez Mejía et al. (2022), this favors an increase of the temperature in the air masses and consequently convective processes. For the summer season a marked frequency is observed in class D due to the cloudiness that exists at that time and the high levels of precipitation.

It is also observed that in the winter and spring nights there is a high frequency of the stable class (F), with a maximum frequency of 80.45% in winter between the hours of 18:00-21:00 and a maximum frequency in spring between the hours of 0:00-2:00 of 83.51%, this is attributed to the little cloudiness that exists in those hours, since there is no cloud barrier that reduces surface cooling, consequently, convective turbulence decreases dramatically as mention Li et al. (2018). Although class G (extremely stable) occurs in specific conditions (less than 0.5 m/s and 0 octas), a maximum frequency of 5.8% and 5.6% could be obtained for autumn and winter, respectively. Classes of B-C and E are observed very little because wind speeds of 3-5 m/s are very few throughout the year.

The width of the "bells" of daytime is greater in the spring and summer seasons because the incidence of solar radiation lasts longer in those seasons unlike the width of the "bells" of the autumn and winter seasons. A small peak of class A and A-B is also observed in daytime around 15:00 and 17:00 hours in all seasons of the year, this is because radiation also has a small peak of incidence of solar radiation in those hours according to averages obtained per hour for each season of the year.

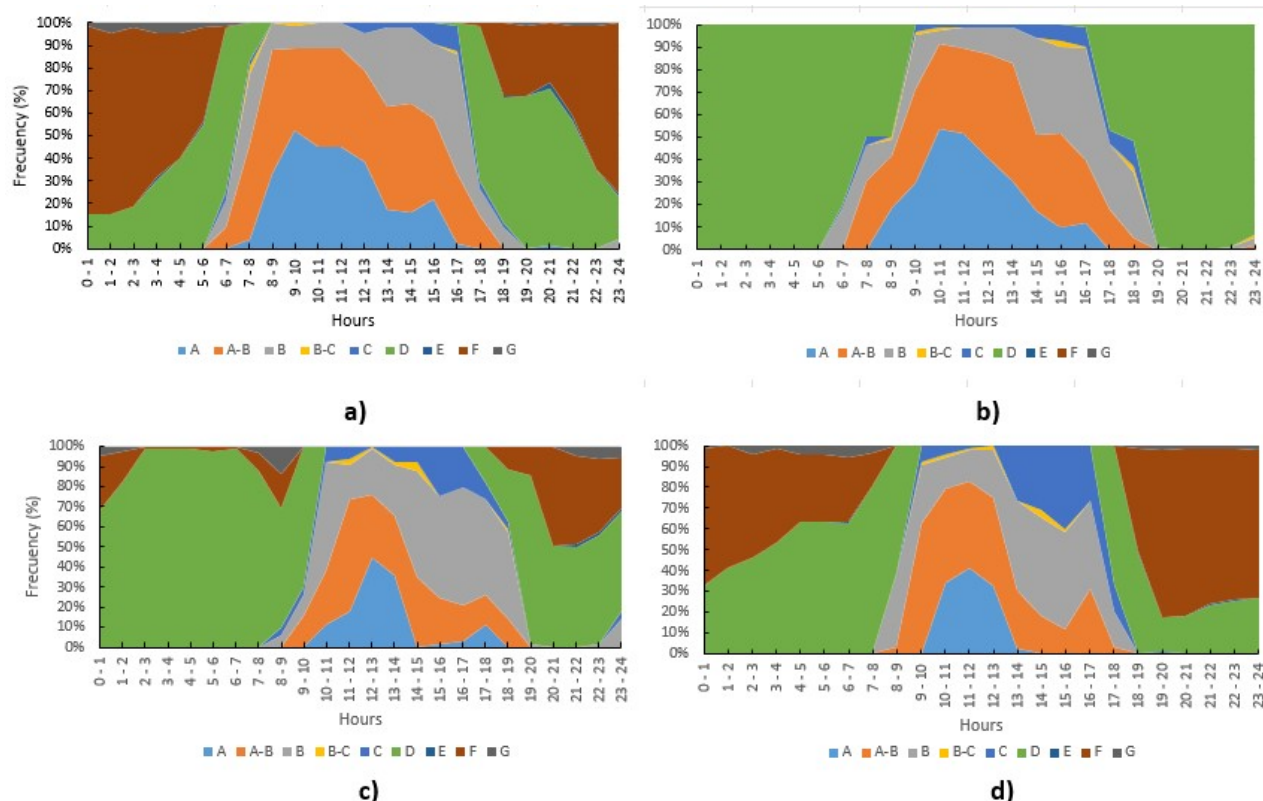


Figure 5. Time frequencies of atmospheric stability classes for the seasons: a) spring b) summer c) autumn d) winter.

### *Pollutants and its relationship to atmospheric stability*

The concentrations of every criteria pollutant shown in the following sections is compared seasonally, for this reason it is important to indicate that said analysis is valid, since the Friedman test, carried out with the R software ([https://rcompanion.org/handbook/F\\_10.html](https://rcompanion.org/handbook/F_10.html)), shows that there are statistically significant differences between the measures obtained in each season of the year, considering that the p-value obtained was less than an established error of 5%. In the supplementary material section, it can find the hypothesis considered for this statistical test.

Table 3. P-value obtained applying Friedman test for every criteria pollutant considering and error of 5%.

| Criteria pollutant | PM <sub>10</sub> | PM <sub>2.5</sub> | CO       | NO <sub>2</sub> | O <sub>3</sub> | SO <sub>2</sub> |
|--------------------|------------------|-------------------|----------|-----------------|----------------|-----------------|
| p-value            | 3.92E-11         | 2.36E-13          | 6.37E-12 | 3.87E-5         | 7.52E-15       | 7.00E-3         |

On the other hand, it is important to show in the Table 4, as a reference, the concentrations ranges obtained seasonally that are compare with the limit values established by the Official Mexican Standards. This will allow us to understand in the following sections the importance of understanding under what atmospheric conditions these levels can be reached. This will allow us to understand in the following sections the importance of understanding under what atmospheric conditions these levels can be reached. It was more convenient to show this type of information in this way because some of the officially established limit values are considered for periods of 8 or 24 hours and not hourly.

Table 4. Ranges of values obtained seasonally per pollutant, compared with their respective maximum permitted limit of concentration.

| Mexican Official Standard<br>(NOM, by its acronym in<br>Spanish) | Pollutant         | Maximum permitted<br>limit (MPL) | Ranges of values<br>obtained<br>seasonally | Exceeded limit value (red);<br>Not exceeded (green) |
|------------------------------------------------------------------|-------------------|----------------------------------|--------------------------------------------|-----------------------------------------------------|
| NOM-021-SSA1-2021                                                | CO                | 1 hr - 26 ppm                    | W: 0 - 14.51                               |                                                     |
|                                                                  |                   |                                  | Sp: 0 - 2.75                               |                                                     |
|                                                                  |                   |                                  | Su: 0 - 1.44                               |                                                     |
|                                                                  |                   |                                  | A: 0.01 - 4.67                             |                                                     |
|                                                                  |                   | 8 hr - 9 ppm                     | W: 0.0675 - 11.53                          |                                                     |
|                                                                  |                   |                                  | Sp: 0.04 - 1.54375                         |                                                     |
|                                                                  |                   |                                  | Su: 0.07 - 0.076125                        |                                                     |
|                                                                  |                   |                                  | A: 0.0575 - 3.41125                        |                                                     |
| NOM-022-SSA1-2019                                                | SO <sub>2</sub>   | 1 hr - 0.075 ppm                 | W: 0 - 0.047                               |                                                     |
|                                                                  |                   |                                  | Sp: 0 - 0.004                              |                                                     |
|                                                                  |                   |                                  | Su: 0 - 0.004                              |                                                     |
|                                                                  |                   |                                  | A: 0 - 0.002086957                         |                                                     |
|                                                                  |                   | 24 hr - 0.04 ppm                 | W: 0 - 0.00130435                          |                                                     |
|                                                                  |                   |                                  | Sp: 0 - 0.002087                           |                                                     |
|                                                                  |                   |                                  | Su: 0 - 0.00113                            |                                                     |
|                                                                  |                   |                                  | A: 0 - 0.029478                            |                                                     |
| NOM-023-SSA1-2021                                                | NO <sub>2</sub>   | 1 hr - 0.106 ppm                 | W: 0.001 - 0.037                           |                                                     |
|                                                                  |                   |                                  | Sp: 0.001 - 0.056                          |                                                     |
|                                                                  |                   |                                  | Su: 0.001 - 0.041                          |                                                     |
|                                                                  |                   |                                  | A: 0.001 - 0.033                           |                                                     |
| NOM-025-SSA1-2021                                                | PM <sub>10</sub>  | 24 hr - 70 ug/m <sup>3</sup>     | W: 0 - 109.54166                           |                                                     |
|                                                                  |                   |                                  | Sp: 0 - 157.23809                          |                                                     |
|                                                                  |                   |                                  | Su: 0 - 44.875                             |                                                     |
|                                                                  |                   |                                  | A: 0 - 38.2083                             |                                                     |
|                                                                  | PM <sub>2.5</sub> | 24 hr - 41 ug/m <sup>3</sup>     | W: 0.71429 - 69.260869                     |                                                     |
|                                                                  |                   |                                  | Sp: 0 - 79.7083                            |                                                     |
|                                                                  |                   |                                  | Su: 0 - 22.9                               |                                                     |
|                                                                  |                   |                                  | A: 0 - 22.18182                            |                                                     |
| NOM-020-SSA1-2014                                                | O <sub>3</sub>    | 1 hr - 0.095 ppm                 | W: 0 - 0.185                               |                                                     |
|                                                                  |                   |                                  | Sp: 0 - 0.198                              |                                                     |
|                                                                  |                   |                                  | Su: 0 - 0.197                              |                                                     |
|                                                                  |                   |                                  | A: 0 - 0.199                               |                                                     |
|                                                                  |                   | 8 hr - 0.070 ppm                 | W: 0.001375 - 0.08487                      |                                                     |
|                                                                  |                   |                                  | Sp: 0.0105 - 0.079875                      |                                                     |
|                                                                  |                   |                                  | Su: 0.004 - 0.09487                        |                                                     |
|                                                                  |                   |                                  | A: 0.005 - 0.088375                        |                                                     |

W: Winter; Sp: Spring; Su: Summer; A: Autumn; SSA: Secretariat of Health (SSA by its acronym in spanish)

*PM<sub>2.5</sub> particles*

In Figure 6 it can be seen that the station with the highest concentration of particles PM<sub>2.5</sub> is spring followed by winter, with peak concentrations of 11.73 and 8.17  $\mu\text{g}/\text{m}^3$ , respectively. These results may be due to the direction and speed of wind that is taken in those months (Figure 2), since the wind comes from a more built area, and observing the topography of the place, which it's influenced by the Sierra de Zacatecas and the Cerro de la Bufa (Escalona-Alcázar et al., 2012), can favor the Venturi effect when the wind passes between the areas of mountainous relief, due to can cause an accumulation and / or recirculation to the sampling area of these particulate matter (Figure 1). Similarly, there is the possible resuspension of pollutants caused by wind speed. According to García Lozada (2006), the services found when emitting gases and particles at ground level, pollutants tend to be concentrated. The official standard in Mexico establishes a daily limit value of 41  $\mu\text{g}/\text{m}^3$  (Table 4), in this study the daily averages were in a range of 0.7-69.2  $\mu\text{g}/\text{m}^3$  and 0-79.7  $\mu\text{g}/\text{m}^3$  in winter and spring respectively, for which the maximum allowed limit was exceeded (DOF, 2021a).

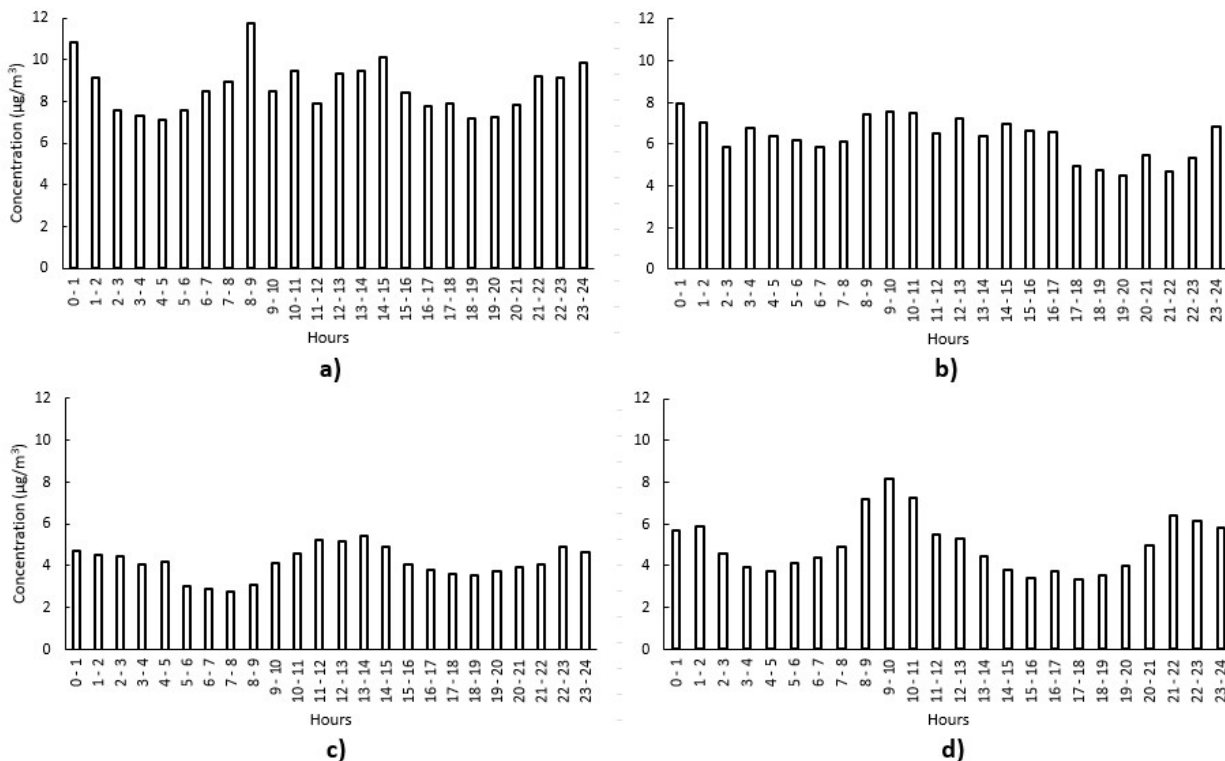


Figure 6. Hourly averages of PM<sub>2.5</sub> particles in the seasons of the years 2019-2020; (a) spring, (b) summer, (c) autumn, (d) winter.

In all seasons there is an increase in the concentration levels between 8:00 and 9:00 hours, due to an increase in vehicle emissions because this schedule coincides with a peak schedule, in which most of the population travels to their workplaces. Observing Figure 5, class A and A-B are barely present, that is, vertical turbulence is just taking place and, at 10:00 a.m., a decrease is observed that continues until 7:00 p.m., which corresponds to the increase in the frequency of stability A (Figure 4). When the concentration begins to increase again, it is precisely where class F takes place (Figures 4 and 5), that is, a relationship between the concentration of PM<sub>2.5</sub> and atmospheric stability is observed, having the other seasons of the year a similar behavior, but not as noticeable as in this season. The highest concentration levels at the mentioned hours occur in spring and winter.

On the other hand, it is also important to emphasize that March and April (spring) are the months with the lowest rainfall and according to Fonseca et al. (2013), rainfall events make it possible to wash away pollutants, giving way to the phenomenon called wet deposition, where substances present in the atmosphere are dragged and return to the ground. As there is little or no precipitation in those months, there is no drag of particles by precipitation. In the Figure 5 can be observed that summer has a decreased of particles compared to spring. Hence, because of the end of the spring and during the summer season occur the main precipitation events in the city (Ortiz Gómez et al., 2018), the

particulate matter levels decrease. These phenomena have an important relation with the atmospheric conditions of stability (F), however, during the autumn, these low concentration levels persist, due to the presence of stability D, which favor a major wind speed level (Table 1). The neutral (D) and stability conditions (F) presented during winter season, favor winds with low velocities (0.3 to 1.5 m/s) (Figure 2) and thermal inversion conditions during the night and before noon, where the hourly concentration levels increase (Figure 5).

### *PM<sub>10</sub> particles*

The behavior of this particulate matter is similar to PM<sub>2.5</sub>, inclusive the concentrations variability is similar; however, their size generates a major deposition during the wet periods (Cheng et al., 2021). In Figure 7, the season with the highest concentration of particles PM<sub>10</sub> is spring, due in the same way both to the direction and speed of wind that is taken in those months, as well as to the Venturi effect and the emission height explained above, due to the topography conditions of the study zone (Escalona-Alcázar et al., 2012). Similarly, it is observed that the concentrations of particles increase in the hours of activity and vehicular flow. Only in the winter season is an increase in concentration in nighttime observed, which can be related to the increase in class F (high stability conditions) in Figure 4, related to the decrease in vertical turbulence and, therefore, the concentration increases at 20:00 hours. The official standard in Mexico establishes a daily limit value of 70 µg/m<sup>3</sup> (Table 4), in this study the daily averages were in a range of 0-109.5 µg/m<sup>3</sup> and 0-157.2 µg/m<sup>3</sup> in winter and spring respectively, for which the maximum allowed limit was exceeded (DOF, 2021a).

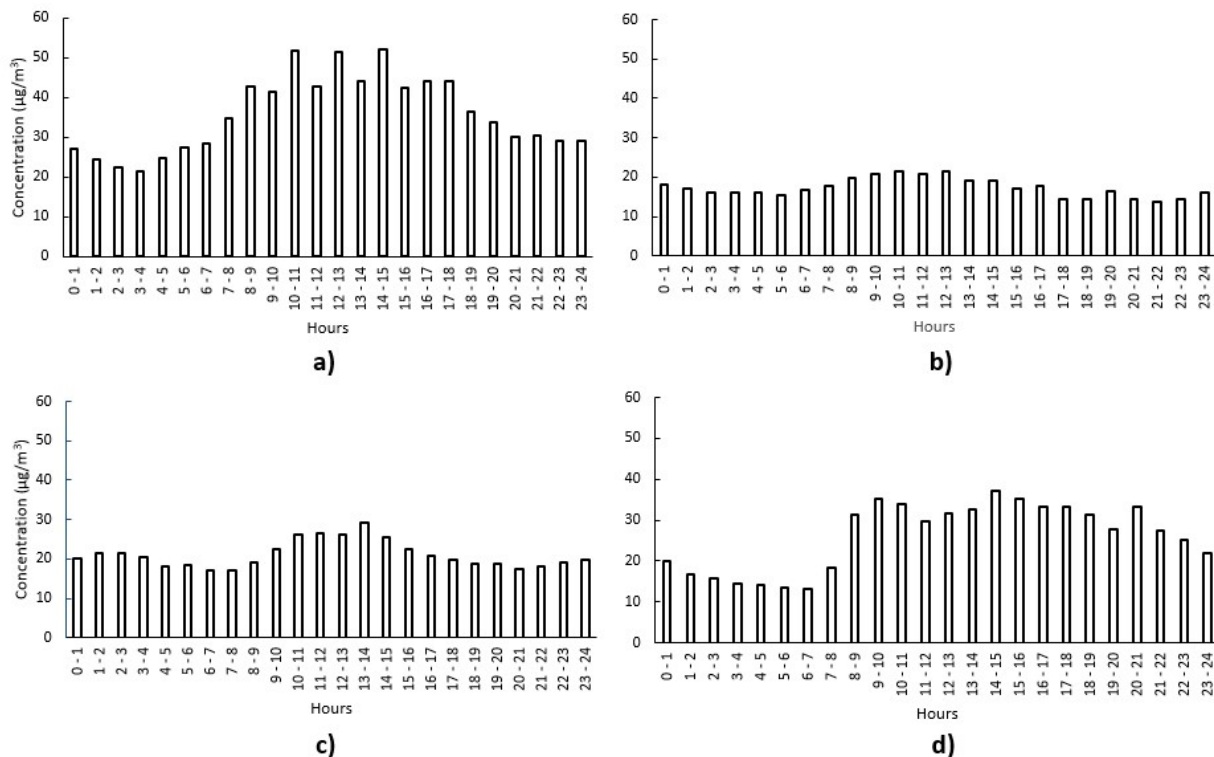


Figure 7. Hourly averages of PM<sub>10</sub> particles in the seasons of the years 2019-2020; (a) spring, (b) summer, (c) autumn, (d) winter.

### *Monoxide carbon*

Figure 8 shows the hourly concentrations of CO. The major hourly concentrations occurred in winter, and relating this result to Figure 4, it can be observed that winter has a higher frequency of class F considered stable between 9:00 and 1:00 hours. On the other hand, class A reaches a maximum percentage of 40% at 11:00 am, where the concentration decreases drastically and increases again after that hour. At 15:00 winter an increase in concentration is observed (Figure 7), which can be associated with the increase in frequency of class C (slightly unstable) of this station, the null appearance of class A (extremely unstable) (Figure 4) and a possible increase in vehicular flow at this time. At 7:00 a.m., the highest concentration of particles is observed, associated with the morning vehicular increase and the atmospheric

condition that is mostly neutral at this time. The highest concentrations are in daytime hours from 7:00 a.m. to 4:00 p.m. as it was mentioned.

The scientific bases of this phenomena are firstly the dynamic relation of the pollutant with the atmospheric stability conditions already explained; and secondly to the CO atmospheric oxidation, due to, when this gas interact with NO<sub>2</sub>, hydroxyls (OH) and solar radiation is dissociated causing a reduction in their concentration levels, mostly in summer and in the hours of greatest intensity in radiation, but in winter and during the morning and evening of the other seasons of the year it can prevail for a longer period of time and increase its levels in the atmosphere again (Seinfeld and Pandis, 2016).

On the other hand, the official standard in Mexico establishes a limit on concentrations for averages every 8 hours of 9 ppm (Table 4), in this study the corresponding averages of winter have values above said limit value allowed (0.06-11.53 ppm) (DOF, 2021b), the other seasons presented ranges of values well below this official value.

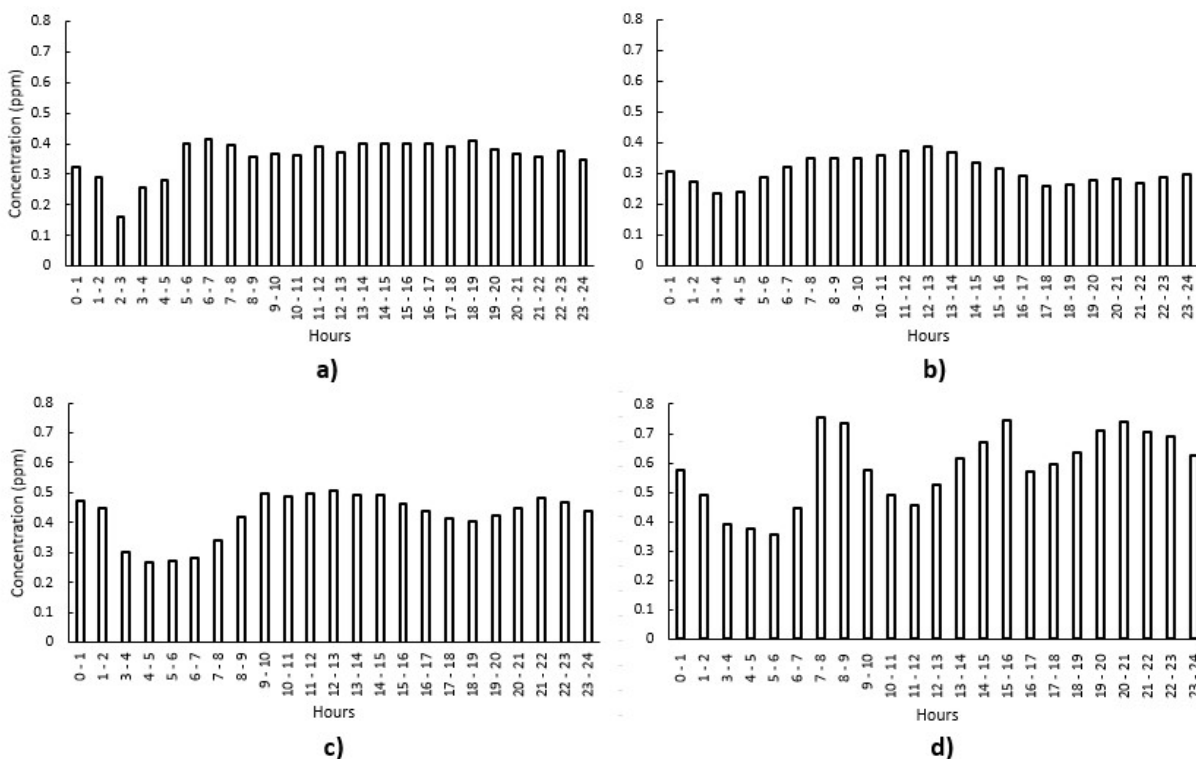


Figure 8. Hourly averages of CO in the seasons of the years 2019-2020; (a) spring, (b) summer, (c) autumn, (d) winter.

### Sulfur dioxide

Figure 9 shows the hourly behavior of SO<sub>2</sub>, which has a higher concentration in the morning in all seasons of the year (7:00-9:00 hours). These phenomena can be related to the high atmospheric stability conditions, that occur mainly during the spring season (F), and with the neutral conditions (D) during the summer and autumn. Winter season has both kind of atmospheric conditions during the morning. Because of this, during the first season, the low wind speed (Table 1 and 2), and the dry conditions favor, consequently, a dry deposition of the SO<sub>2</sub>, however in winter the cloud cover and the presence of humidity, favor a wet deposition. During the second and third seasons of the year, the presence of ozone increase and is more probably that their dissociation favor the presence of O<sub>2</sub> in the environment, hence, an oxidation process reduce the SO<sub>2</sub> levels (Long et al., 2017; Seinfeld & Pandis, 2016). The combustion process generated by vehicles that use fuel with high content of sulfur (diesel) can exacerbate additionally the concentration levels of this pollutant.

The maximum values allowed for this pollutant correspond to periods of one hour (0.075 ppm) and 24 hours (0.04 ppm) (Table 4), so that in both cases the concentrations measured in the four seasons of the year did not exceed these reference levels (DOF, 2019).

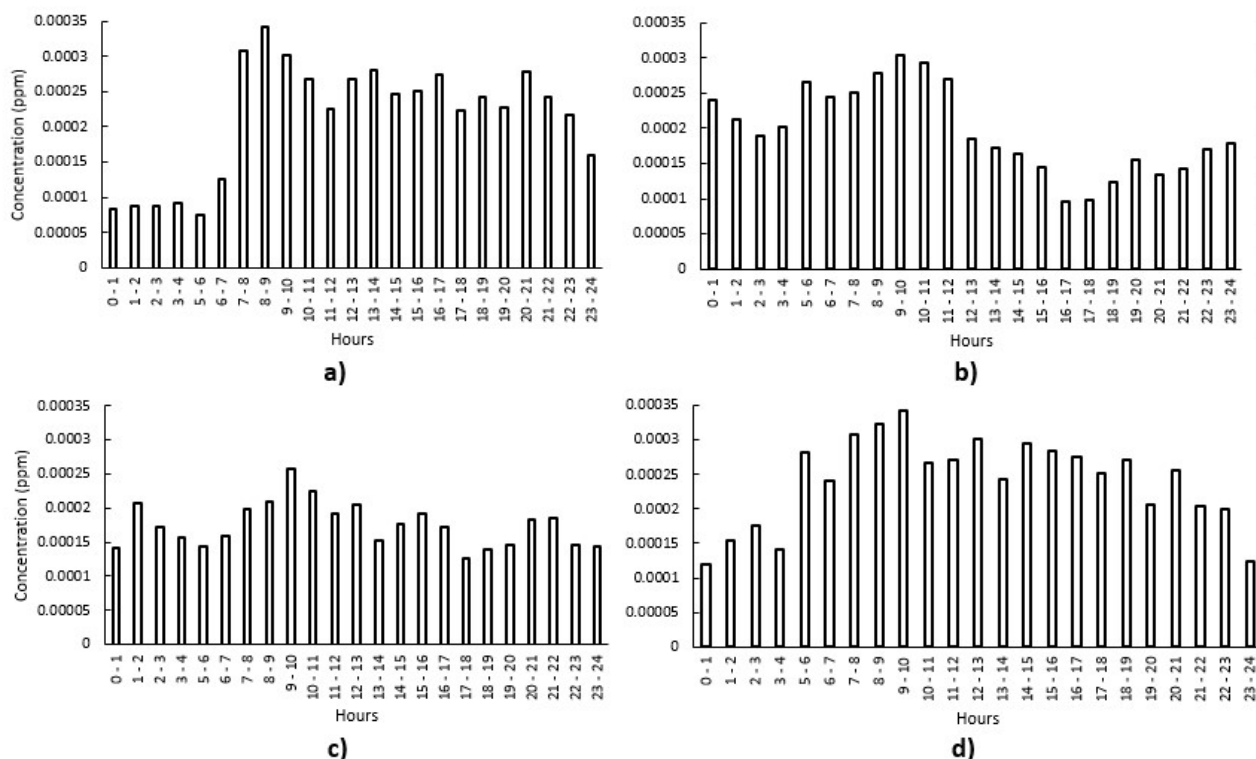


Figure 9. Hourly averages of  $\text{SO}_2$  in the seasons of the years 2019-2020; (a) spring, (b) summer, (c) autumn, (d) winter.

### Nitrogen dioxide

Figure 10 shows the hourly behavior of  $\text{NO}_2$  where winter has the greater concentration and, in general, it is observed in this same station that, between 7:00 and 8:00 hours, there is an increase around 0.017 ppm, corresponding to hours of increased vehicular flow and a neutral atmospheric condition (D) (Figure 4), in the same way, between 19:00 and 20:00 hours, where there is a stable condition (F). The solar radiation reduction in the morning and during the afternoon plays an important role in the atmospheric stability conditions mentioned, due to favors a lower photo-dissociation or destruction of this contaminant increasing their levels in the atmosphere (Seinfeld & Pandis, 2016; Jacob, 2000). In the spring season the same behavior is observed with lower concentrations (0.012 ppm maximum). In summer, such a marked behavior is not observed since it is associated with the washing of particles and relative humidity, which can facilitate the formation of the different fashions described above. The maximum value allowed for this pollutant corresponds to periods of one hour (0.106 ppm) (Table 4), so the concentrations measured in the four seasons of the year did not exceed this reference level (DOF, 2021c).

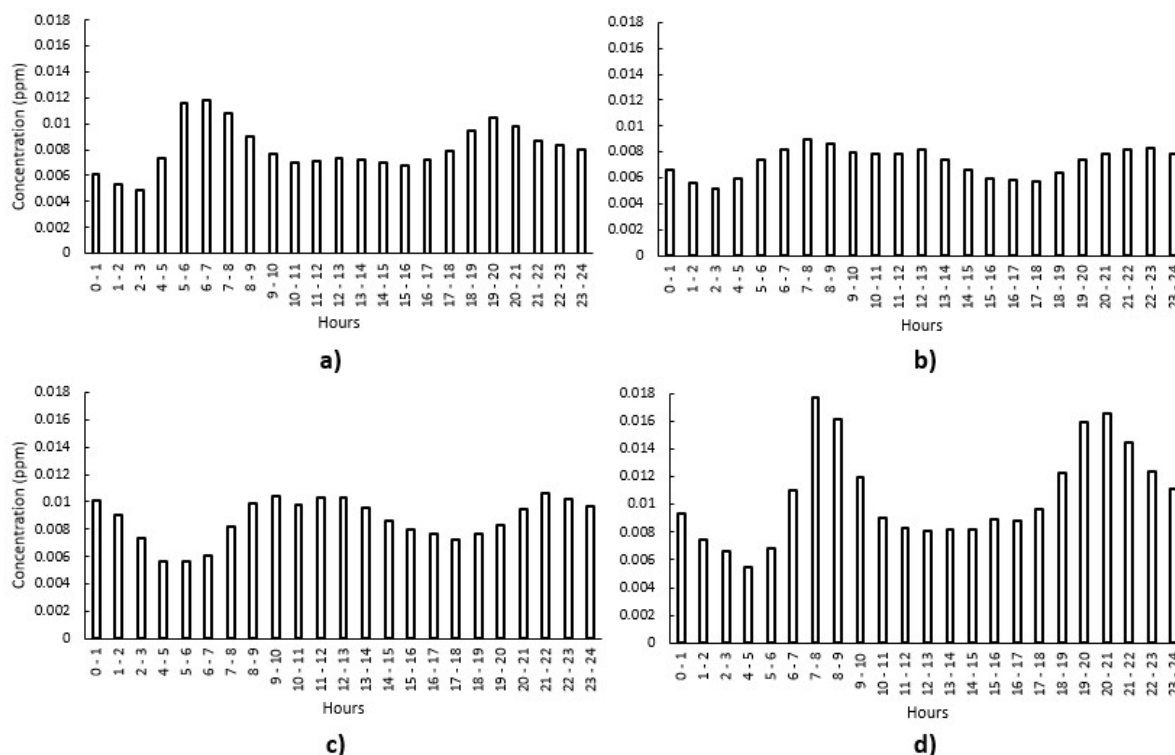


Figure 10. Hourly averages of NO<sub>2</sub> in the seasons of the years 2019-2020; (a) spring, (b) summer, (c) autumn, (d) winter.

### Ozone

Figure 11 shows an outline of the chemistry of gas-phase O<sub>3</sub> in the troposphere that emphasizes the coupling between the O<sub>3</sub>, HO<sub>x</sub>, and NO<sub>x</sub> cycles. Ozone is supplied to the troposphere by transport from the stratosphere, removed by deposition to the surface, and chemically produced and consumed within the troposphere. The production and loss of chemicals are the dominant terms in most of the troposphere sphere (Wang et al., 1998).

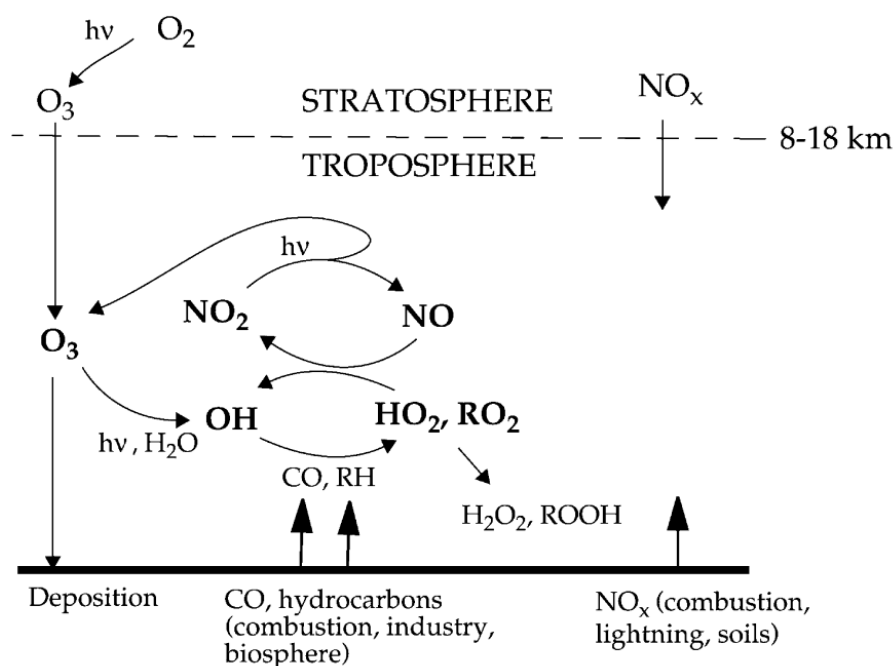


Figure 11. Schematic of tropospheric O<sub>3</sub> chemistry illustrating the coupling between the chemical cycles of ozone, HO<sub>x</sub>, and NO<sub>x</sub> (Jacob, 2000).

Figure 12 shows the hourly behavior of the  $O_3$ , where the largest concentrations occur in daytime, in spring and summer the highest concentration occurs between 11:00 and 13:00 hours, also at times with the highest solar incidence. In winter, the highest concentrations of  $O_3$  occur between 10:00 and 16:00 hours, among this time is the highest solar incidence (11:00-12:00 hours). In this same season of the year, a high concentration of  $NO_2$  is observed (Figure 10), an important molecule for the formation of ozone and for different reactions in the troposphere.

However,  $O_3$  production at this station remains low. This behavior is related to the fact that the formation of  $NO + O$  continues to be affected by solar radiation and if the incidence of solar radiation is low, it is also the dissociation from  $NO_2$  to  $NO + O$ , therefore, the formation of  $O_3$  by  $NO_2$  is also decreased. During this process exist a competition between  $NO_x$  and volatile organic compounds (VOC) to react with the hydroxyl radical (OH), when the ratio of  $VOC/NO_x$  is greater than 5.5, VOC reacts predominantly with OH to form  $O_3$  through an oxidation sequence (Seinfeld & Pandis, 2016), this phenomenon could happen mainly during winter, when the solar radiation presents the lowest values due to the thermal inversion process. Although historically the area, fixed and mobile sources had emitted more VOC's than  $NO_x$  during the years 1999, 2005 and 2008, in the last year reported (2016), both area and mobile sources emitted mainly  $NO_x$  (SAMA & SEMARNAT, 2018), and for that reason is important measure in a constant way the role of this pollutants in the formation of ozone.

In general, in the hourly behavior of the seasons a consistent behavior is not observed, this can be associated with the fact that  $O_3$  is formed in the daytime mostly and the most stable class (F) takes place at night decreasing its dispersion, adding that the chemical lifetime of the OXs oscillates from a week in the lower layer of the troposphere. The maximum values allowed for this pollutant correspond to periods of one hour (0.095 ppm) and 8 hours (0.070 ppm) (Table 4), so that in both cases the concentrations measured in the four seasons of the year exceed these reference levels (DOF, 2014). For the hourly averages, the following ranges of values, in ppm units, were measured: spring, summer and autumn 0-0.19 ppm, while in winter 0-0.18. For the averages every 8 hours, the following were obtained in the same units of measurement: spring 0.01-0.07, summer 0.004-0.09, autumn 0.005-0.08 and winter 0.0013-0.08.

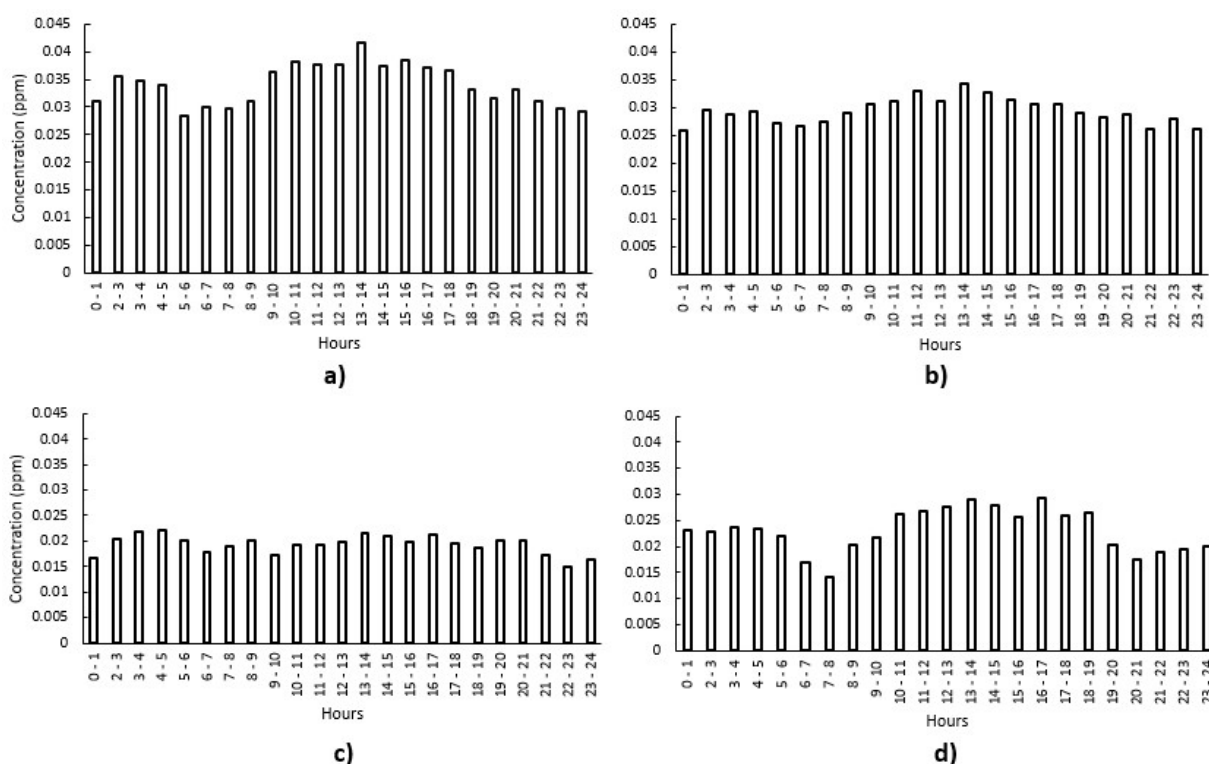


Figure 12. Hourly averages of  $O_3$  in the seasons of the years 2019-2020; (a) spring, (b) summer, (c) autumn, (d) winter.

## Conclusions

The aim of this research was to obtain the atmospheric stability classes for the city of Zacatecas during the period 2019-2020. The Pasquill-Gifford classification was used to accomplish it, due to available information was limited to one air quality monitoring station and one meteorological station, it was analyzed, as a first approximation the variability of pollutants concentrations for this kind of stability classes.

Applying this methodology for the four seasons of the year, the maximum frequencies of class A were found between 9:00 and 12:00 hours, considered the most unstable with values of 52.22% for spring, 53.57% for summer, 44.87% for autumn and 40% for winter. This is directly associated with the particular wind and solar radiation speeds of each season. In the winter and spring nights there is a high frequency of class F, with a maximum of 80.45% in winter between the hours of 18:00-21:00 and in the early morning between the hours of 0:00-2:00 of 83.51%, this is attributed to the little cloudiness that exists in those hours, since there is no cloud barrier that reduces the cooling of the surface therefore, convective turbulence decreases dramatically. The topography conditions of the Zacatecas plays and important role in the stability classes explained, due to the convective process in the air masses is more turbulent than on a flat surface, generating the high frequencies in the instability class A mentioned, also the high-altitude level above sea level, hinders further interaction with cloud cover most of the year.

On the other hand, it was determined that in the spring and summer seasons there is a higher hourly concentration of  $PM_{2.5}$  and  $PM_{10}$  particles, this is attributed to the speed, direction of the wind, topography of the place, as well as the height of emission of pollutants, also that spring is a time with little or no precipitation so the deposition of particles does not occur in an important way, and can be kept longer suspended in the air. The influence of  $NO_x$  on ozone generation was of great importance during the last year reported in the emissions inventory (2016), due to the role played by area and mobile sources. The atmospheric conditions during the hottest months (spring and summer) favored the  $NO_x$  emissions, while in winter, the reduction in the incidence of solar radiation caused that volatile organic compound (VOC) had a greater contribution in the formation of  $O_3$ . A timely behavior of dispersion of  $PM_{2.5}$  particles related to the estimated stability classes was observed, that is, when class A increased, its frequency, the concentration of particles decreased and when class F increased, the concentration of particles increased. The hourly fluctuations of  $PM_{10}$  are attributed to the vehicular flow. Obtaining that the highest concentrations were between 9:00 and 16:00 hours.

In almost all cases, atmospheric stability and/or instability conditions favored exceedances in the maximum permissible limits of criteria pollutants concentrations established by the Official Mexican Standards, except for  $SO_2$  and  $NO_2$ . The  $O_3$  was the pollutant that exceeded the limit levels in all seasons of the years considered, followed by particulate matter ( $PM_{2.5}$  and  $PM_{10}$ ), which exceeded the limits during winter and spring.

The results obtained in this study prove the importance to relate the air quality with the stability classes, due to this atmospheric phenomenon is an indicator of the good or bad dispersion of the pollutants in the air. As a first approximation, it has been shown that the pollution is not an isolated phenomena but requires additional information to interpretate their behavior properly. For future studies in the city of Zacatecas of these pollutants it is recommended to consider measures in additional places of the city and consider different factors that can influence the dispersion of pollutants and regarding the results obtained as the kind of sources emission, finally it is recommended to make use of this classification only in hourly averages.

**Acknowledgments and Funding:** The authors would like to thank the “Secretaria del Agua y Medio Ambiente” of Zacatecas, México for facility the database for analysis of this work.

**Author contributions:** V.R.-D. and D.E.F.-J.: Writing, Analysis and interpretation of data, Provide materials, Data collection; M.M.A.-F.: Design and Editing; V.A.-V.: Conceptualization, Supervision, and Project Administration.

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## Supplementary material

To identify if exist statistical differences for hourly average concentrations estimated stationary, it was applied the Friedman test for every pollutant. The hypothesis considered in every case was as follow:

Null hypothesis ( $H_0$ ): None of four seasons of the year have different concentrations levels. Or the average hourly concentrations are equal for the four seasons.

Alternate hypothesis ( $H_a$ ): The four seasons of the year have different concentrations levels. Or the average hourly concentrations are different for the four seasons.

After applying the Friedman test in R software, it was obtained the p-values showed previously in Table 3. Next, the table is placed again to identify the p values obtained considering a significance level of 5% ( $\alpha=0.05$ ). In the table it can be seen that in all cases the p-value was less than  $\alpha$ , therefore the alternate hypothesis ( $H_a$ ) is approved.

Table S-1. P-value obtained applying Friedman test for every criteria pollutant considering and error of 5% ( $\alpha=0.05$ ).

| Criteria pollutant | PM <sub>10</sub> | PM <sub>2.5</sub> | CO       | NO <sub>2</sub> | O <sub>3</sub> | SO <sub>2</sub> |
|--------------------|------------------|-------------------|----------|-----------------|----------------|-----------------|
| p-value            | 3.92E-11         | 2.36E-13          | 6.37E-12 | 3.87E-5         | 7.52E-15       | 7.00E-3         |

Due to that for every case the sample size is greater than 15, the Friedman test can be approximated to chi-squared distribution. The software R automatically estimate this value at the moment to apply the Friedman test. In the next table are shown the values obtained.

Table S-2. Chi-square values obtained simulataneously at the moment to apply Friedman tes in R software for every criteria pollutant, considering and error of 5% ( $\alpha=0.05$ ). The null and alternate hypothesis are the same.

| Criteria pollutant         | PM <sub>10</sub> | PM <sub>2.5</sub> | CO    | NO <sub>2</sub> | O <sub>3</sub> | SO <sub>2</sub> |
|----------------------------|------------------|-------------------|-------|-----------------|----------------|-----------------|
| chi-square value estimated | 51.45            | 61.85             | 55.15 | 23.08           | 68.85          | 11.85           |

The degrees of freedom are equal to 3. Hence the theoretical value of chi-square is 7.81. It means that chi-square estimated is the greatest value for all criteria pollutants and the alternate hypothesis ( $H_a$ ) continues being approved.