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**CARACTERIZACIÓN Y VARIACIÓN INTERANUAL DE LA CALIDAD DEL
AIRE EN LA CIUDAD DE BUENOS AIRES EN RELACIÓN A LAS NUEVAS
DIRECTRICES DE LA OMS**

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RESUMEN

La Organización Mundial de la Salud (OMS) actualizó sus directrices de calidad de aire en septiembre de 2021. Las concentraciones medias diarias y anuales de dióxido de nitrógeno (NO₂) y material particulado con diámetro menor a 10 µm (PM₁₀) medidas en las tres estaciones de monitoreo de calidad del aire de la ciudad de Buenos Aires, superan frecuentemente los nuevos niveles guía (NG) de la OMS en el período 2010-2019. Un análisis de tendencias revela una disminución significativa en la concentración media anual de PM₁₀ de 1.6 µg m⁻³ yr⁻¹ y una reducción consistente en la frecuencia de superaciones del NG diario de 1.6 % yr⁻¹ en la estación de fondo urbano. En cambio, las concentraciones de NO₂ muestran ligeras tendencias positivas en los tres sitios de monitoreo que podrían llegar a ser estadísticamente significativas a medida que se disponga de nuevos datos. Para ambos



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contaminantes, las fuertes relaciones lineales entre las concentraciones medias anuales y sus frecuencias de superación diaria sugieren que los nuevos NG anuales son más estrictos que sus correspondientes límites diarios, aunque estos resultados son sensibles al conjunto de datos utilizado. Por otro lado, las concentraciones medias diarias de monóxido de carbono (CO) se encuentran por debajo del nuevo NG, con ligeras tendencias interanuales positivas no-significativas en dos de los sitios. Cuando se utiliza la secuencia horaria diaria del viento como variable de clasificación, se obtienen marcadas diferencias en los niveles de concentración de los tres contaminantes con distintos patrones de viento, las cuales se mantienen a lo largo de los años resaltando el rol de las fuentes locales en las tendencias. En algunos casos, se observan variaciones interanuales pronunciadas con patrones de viento específicos, lo que sugiere el impacto de fuentes nuevas o más intensas procedentes de sectores específicos. Mayores esfuerzos en monitoreo y en desarrollo de inventarios de emisiones de contaminantes de alta resolución contribuirán a comprender las causas de estas variaciones y a evaluar la calidad del aire en toda el área metropolitana.

Palabras clave: datos de calidad del aire, análisis de tendencias, viento, niveles guía de calidad del aire de la OMS.

CHARACTERIZATION AND INTERANNUAL VARIATION OF AIR QUALITY IN THE CITY OF BUENOS AIRES RELATIVE TO THE NEW WHO GUIDELINES

ABSTRACT

The World Health Organization (WHO) updated its air quality guidelines in September 2021. The daily and annual mean concentrations of nitrogen dioxide (NO₂) and particulate matter with a diameter of less than 10 μm (PM₁₀) measured at the three air quality monitoring stations in the city of Buenos Aires frequently exceed the new WHO air quality guideline (AQG) levels in the period 2010-2019. A trend analysis reveals a significant decrease in the annual mean PM₁₀ concentration of 1.6 μg m⁻³ yr⁻¹ and a consistent

reduction in the frequency of exceedances of the daily AQG of 1.6 \% yr^{-1} at the urban background station. In contrast, NO_2 concentrations show slight positive trends at all three monitoring sites that could become statistically significant as new data become available. For both pollutants, the strong linear relationships between annual mean concentrations and their daily exceedance frequencies suggest that the new annual AQG levels are stricter than their corresponding daily limits, although these results are sensitive to the data set used. On the other hand, daily average concentrations of carbon monoxide (CO) are below the new AQG, with slight non-significant positive interannual trends at two of the sites. When the daily hourly wind sequence is used as a classification variable, marked differences in the concentration levels of the three pollutants with different wind patterns are obtained, which are maintained over the years, highlighting the role of local sources in the trends. In some cases, pronounced interannual variations are observed with specific wind patterns, suggesting the impact of new or more intense sources from specific wind sectors. Further efforts in monitoring and in developing high-resolution pollutant emission inventories will contribute to understanding the causes of these variations and to assessing air quality across the metropolitan area.

Key Words: air quality data, trend analysis, wind, WHO air quality guideline levels.

1) INTRODUCTION

Growing knowledge about the effects of air pollution on human health makes air quality an issue of increasing concern worldwide. According to the World Health Organization (WHO), globally, 9 out of 10 people are exposed to levels of pollutant concentrations that put them at increased risk of diseases such as stroke, chronic obstructive pulmonary disease, and cancer (WHO, 2021). In urban areas, where the largest fraction of the world's population lives, emissions and meteorology – which affects the capacity of the atmosphere to transport and dilute pollutants – play a fundamental role on pollutant concentrations. Studying interannual variations in air quality allows understanding how pollutant concentrations change over time and their trends in relation to local emission changes, which can contribute to the design of appropriate policies for mitigating air pollution in a given location (e.g., Barmpadimos et al., 2012). When the interannual variations of air

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pollutant emissions are not available, the analysis of air quality data by wind sector can help to identify the possible role of different sources (e.g., Carslaw and Beevers, 2013).

Works studying the interannual variations of air quality often perform the analysis over large areas where pollutant concentrations are averaged over available monitoring stations (e.g., Munir et al., 2013; Silva et al., 2017; Vu et al., 2019). Such trends give a measure of the air pollution change in a city as a whole and can be useful to summarize the information from large datasets or to compare different urban areas (e.g., Pelaez et al., 2020; Zhao et al., 2020). However, studies analyzing interannual variations by monitoring site (e.g., Carslaw, 2005; EEA, 2020; Mavroidis and Chaloulakou, 2011; Querol et al., 2014; Salvador et al., 2012) show that strong differences in both concentration levels and their trends between different types of sites (urban traffic, urban background, residential, rural, industrial) can exist. For example, while European annual mean concentrations of nitrogen dioxide (NO₂) have fallen, on average, between 18% and 23% in industrial and traffic stations, respectively, over the last decade (2009-2018), larger differences may be found at city level including positive trends at specific sites (EEA, 2020). Such differences are usually attributed to trends in different emissions sectors and need to be considered when a major goal is to contribute to air quality management which in general applies locally.

The city of Buenos Aires (CBA) and the Greater Buenos Aires form the Metropolitan Area of Buenos Aires (3,830 km², 14,967,000 inhabitants), which is considered the third largest mega-city in Latin America (UN, 2019). It is located at 34°38'S and 58°28'W, on the west coast of the La Plata River, on flat terrain approximately 10 m above sea level, and is surrounded by non-urban areas. A few air quality studies were conducted in the city based on short (weeks or months) experimental campaigns and analyzed aspects such as particulate matter composition (e.g., Arkouli et al., 2010; Bogo et al., 2003) or oxidant level (Mazzeo et al., 2005). Recently, Pineda Rojas et al. (2020) studied the first long series (eight years) of hourly concentrations of NO₂, carbon monoxide (CO) and particulate matter with diameter less than 10 μm (PM₁₀) measured at the three air quality stations of the CBA and their relationship with meteorological conditions. Their results show

statistically significant differences in the air quality levels of the three pollutants and their hourly profiles (i.e., the average hourly variation) when days are grouped according to their similarities with respect to the daily sequence of hourly wind (Pineda Rojas et al., 2020). In that work, pollution events were defined according with the previous WHO air quality guideline (AQG) levels (WHO, 2005). Recently, the World Health Organization updated its air quality recommendations, adding a guideline value for the daily NO₂ concentration (13 ppb) and reducing the annual level by a factor of four (from 20 to 5 ppb). In addition, WHO AQG levels for the daily and annual PM₁₀ concentrations were decreased by 10% (from 50 to 45 µg m⁻³) and 25% (from 20 to 15 µg m⁻³), respectively and a daily level for CO was introduced (3.5 ppm). At the three CBA stations, the concentrations of NO₂ and PM₁₀ present a high frequency of exceedances of these new levels on the daily and annual scales. In this work, we study the interannual variations of the annual and daily mean concentrations of NO₂, CO and PM₁₀ at the three monitoring sites in the city of Buenos Aires in the period 2010-2019, using simple trend analysis and the wind classification proposed by Pineda Rojas et al. (2020). The objectives are to determine whether significant trends in air quality over the past decade exist, and to explore the usefulness of the classification at the annual scale.

2) METHODOLOGY

2.1) AIR QUALITY DATA

The environmental protection agency of the CBA (APRA, in Spanish) monitors ambient concentrations of NO₂, CO and PM₁₀ at three stations (**Figure 1**): Parque Centenario (CEN: urban background) since 2006 and in Córdoba (COR: urban traffic) and La Boca (LB: residential industrial) since 2009. These are EPA monitoring stations which have standardized protocols of calibration. CEN is located in the geographic center of the city, in a residential-commercial area, 60 m from a large park. COR is placed in a commercial area surrounded by buildings of different heights (up to 80 m) on the South side of Córdoba Ave., where 38,000 vehicles/day circulate in the East-West direction (Mazzeo and Venegas, 2012). Finally, the LB site is surrounded by two highways and placed near the coast where three thermal power plants operate.

Ten years (2010-2019) of hourly concentrations of NO₂, CO and PM₁₀ measured at the

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three sites are used. For the treatment of air quality data, if an hourly value is missing, it is filled by linearly interpolating the data from the hours before and after, while if more than two consecutive hourly values are missing, the day is discarded to avoid biases. On the other hand, days corresponding to two episodes (October 14-17 and November 22-27, 2011) in which PM_{10} concentrations were considerably higher due to the impact of a volcanic ash plume produced by the Puyehue-Cordón Caulle volcano (Ulke et al., 2016) are eliminated. The basic statistics of daily mean concentrations of NO_2 , CO and PM_{10} used in this study are included in **Table A.I**. A detailed analysis of the temporal variation of these concentration series over shorter time scales (hourly, daily, and seasonal) can be found in Pineda Rojas et al. (2020).

A commonly used criterion in the calculation of air quality trends is to consider years with at least 75 % of the available records (e.g., EEA, 2020; Lang et al., 2019). Considering the large amount of missing data in the first years of monitoring (see **Table A.II**), in this work a limit of 70 % is considered in order to include at least five consecutive years at all stations. In those periods, annual average NO_2 concentrations are in the ranges 16-18 ppb at CEN, 17-22 ppb in COR, and 10-21 ppb in LB, exceeding the WHO guideline (AQG) level (5 ppb) in all cases. Annual CO levels vary between 0.5-0.6 ppm in CEN, 0.5-0.8 ppm in COR, and 0.3-0.6 ppm in LB. Mean annual PM_{10} concentrations are in the ranges 21-31 $\mu g m^{-3}$ at CEN, 25-28 $\mu g m^{-3}$ at COR, and 24-33 $\mu g m^{-3}$ at LB, exceeding the AQG level (15 $\mu g m^{-3}$) in all cases. On the other hand, the frequencies of daily average NO_2 concentrations exceeding the WHO guideline level (13 ppb) are in the ranges 67-81 % at CEN, 69-96 % at COR, and 22-93 % at LB. Daily CO concentrations are below 2.9 ppm at all three sites (**Table A.I**) and, therefore, there are no exceedances of the limit recommended by the WHO for this pollutant (3.5 ppm). Finally, the frequencies of daily PM_{10} concentrations above the guideline level (45 $\mu g m^{-3}$) vary between 0-13 % at CEN, 1-6 % at COR, and 3-15 % at LB.

2.2) ANALYSIS OF INTERANNUAL VARIATION

Interannual variations of annual mean concentrations and frequencies of daily concentration exceedances of the WHO guideline levels are analyzed. For trends in concentrations, the Theil-Sen slope is calculated (Sen, 1968; Theil, 1950), and Kendall's tau test is applied to assess the significance of a monotonic trend in the time series (Mann, 1945). Sen's method evaluates the slopes for all pairs of ordinal points and calculates the slope as the median of all such slopes. For each pollutant and site, the trend is calculated over the shaded periods in **Table A.II**, using the `MannKen()` function of the R package 'wq' (<https://cran.r-project.org/src/contrib/Archive/wq/>). This statistical approach is widely used in air quality studies (e.g., Lang et al., 2019; Querol et al., 2014; Silva et al., 2017; Vu et al., 2019), since it is applicable to non-normally distributed data and is not sensitive to outliers, thus it is suitable for trend detection in time series of a variable (Carslaw and Ropkins, 2012). Trends are also computed for each season considering that emissions may have a more pronounced interannual variation in certain time of the year (for example, the central power plants may change not only consumption but also the fuel type used).

On the other hand, to analyze the interannual variation and potential trends in air quality when the wind comes from different sectors, the wind classification proposed by Pineda Rojas et al. (2020) is used. Using hourly surface wind data from the Aeroparque meteorological station and air quality data measured at the three stations in the city (see **Figure 1**), these authors show that by grouping days with similar hourly wind sequences, five clusters are obtained (see Figure 5 of Pineda Rojas et al., 2020) for which NO₂, CO and PM₁₀ concentration levels are different. Also, differences among sites in the pollutants concentration levels and profiles suggest the potential role of different emission sources (Pineda Rojas et al., 2020). Therefore, the analysis of interannual variation by wind clusters can help to identify whether a given change in concentration occurs to a greater extent under certain wind conditions. To study the interannual variation of pollutant concentrations using this classification on the annual scale, all days in years highlighted in **Table A.II** are included; while for the daily scale, the upper quartile of the daily mean concentrations over the entire period (**Table A.III**) are considered in order to obtain similar numbers of values to distribute among the five wind patterns for the three pollutants.

3) RESULTS

3.1) ANNUAL AVERAGE CONCENTRATIONS

Applying a Mann-Kendall test to the annual mean concentrations in the years of the period with more than 70% of data, a statistically significant negative trend of $-1.62 \mu\text{g m}^{-3} \text{yr}^{-1}$ is obtained for PM_{10} levels at CEN. For other pollutants, the trend values found in the last years of the period suggest a decrease in CO concentrations at CEN and PM_{10} at COR, and an increase in NO_2 concentrations at the three stations, CO at COR and LB, and PM_{10} at LB (see **Table A.IV**). **Figure 2** shows the interannual variation of the averaged concentrations for each wind cluster over the entire decade for each pollutant and monitoring station. While the trend calculation is performed on a part of the series, visual inspection of the values over the whole period can help to interpret the trends obtained. For example, the positive trend in NO_2 annual concentration at LB appears to be dominated by its increase between 2016 and 2019, despite the marked reduction observed between 2012 and 2013. These rapid changes are likely attributable to changes in emission from local sources since regional sources or meteorological factors would have produced similar effects at all stations.

Figure 2 shows that the interannual variations of the mean concentrations of the wind clusters are generally similar. For a given pollutant, a change that is observed at one site and not at others highlights the influence of local emission changes. Thus, the increase in annual CO concentration (black curve) observed at COR and not at CEN appears to be due to an increase in emissions at that site. The fact that, in addition, all clusters vary together reinforces this hypothesis (since the local contribution is present in all clusters). On the other hand, this implies that the differences in concentration levels between clusters remain approximately constant over time. **Figure 2** also shows marked differences in pollutant concentrations with different wind patterns: in CEN, the levels of the three pollutants are the highest with clusters 4 (NNW winds) and 5 (light winds) and the lowest with clusters 1 (NE winds) and 2 (SE winds). At COR, concentrations are higher with clusters 3 (SW winds) and 5 (light winds) and lower with cluster 1; while in LB, they are higher with cluster 4 and lower with clusters 2 and 3. The relative differences between the

highest/lowest air pollutant concentrations and annual averages are in the ranges 9-26 % at CEN, 5-22 % at COR, and reach larger differences (up to 40 %) at LB (**Table I**). The fact that these differences are repeated year after year supports the robustness of the classification proposed by Pineda Rojas et al. (2020).

Although, in general, cluster concentrations vary together, some differences are evident. For example, for NO₂ and PM₁₀ in LB, the ratios between cluster concentrations change from 2017 onwards. For both pollutants, a greater increase in the concentration of cluster 4 (yellow) compared to that of other clusters is observed, which could be due to a greater contribution from sources located to the NNW of the site such as Av. 9 de Julio, as suggested by Pineda Rojas et al. (2020). Likewise, it is observed that the decrease in the annual concentration of CO and PM₁₀ after 2017 at LB, is higher with cluster 2 (green). This could be indicating a lower contribution from the thermal power plant closest to the site (Costanera). However, these changes are observed in a period of a few years and longer series are needed to verify whether these trends are maintained.

Analyzing the interannual changes in the surface meteorological variables measured at the AEP station relevant to air quality (e.g., temperature, relative humidity, wind speed, cloud cover and precipitation), statistically significant variations in wind intensity and cloud cover are obtained (not shown). In the study period, wind speed shows a statistically significant decrease of $-0.07 \text{ m s}^{-1} \text{ yr}^{-1}$. This result is consistent with that obtained by Merino and Gassmann (2021), who analyzed the wind series measured at the EZE station ($34^{\circ}49'S$, $58^{\circ}32'W$) in the period 1990-2020 and found a deceleration in the mean wind speed. Applying the wind classification used by Pineda Rojas et al. (2020) to the 2010-2019 AEP data, it is obtained that the largest decrease occurs with cluster 3 (SW winds, $-0.23 \text{ m s}^{-1} \text{ yr}^{-1}$) and is more pronounced in the period 2015-2017 (**Figure 3**). However, this decrease in wind speed does not result in a larger increase (or smaller decrease) in cluster 3-related concentrations relative to that of other clusters in that period (see **Figure 2**).

Therefore, changes in annual concentrations over the last years appear to be dominated by those in emissions and differences among sites point to role of local sources.

3.2) DAILY MEAN CONCENTRATIONS

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Trends in the frequency of daily exceedances over the WHO AQG levels

As shown in Section 2.1, daily mean NO₂ and PM₁₀ concentrations frequently exceed their WHO AQG levels (13 ppb and 45 µg m⁻³, respectively) at the three AQ monitoring sites. A linear regression test to the daily exceedance frequencies showed that the only significant trend is that of PM₁₀ at CEN (-1.6 % yr⁻¹) (see **Table A.IV**). This could be due to the small amount of annual data available. A way to test this is to analyze a proxy for annual exceedance frequency that is obtained on a daily- rather than yearly basis. Daily mean concentrations have the advantage that they represent a larger database on which statistical tests have greater power. **Table II** shows the correlation between daily mean concentrations and the date index (number of the day since the beginning of the series) in years with more than 70 % of data. The signs of the correlations are similar to those obtained for the annual mean concentration and for the frequency of daily exceedances (**Table A.IV**), but the larger amount of data results in higher statistical power in this case. All correlations are statistically significant (except for PM₁₀ at COR), supporting the idea that non-significant correlations obtained for the frequency of exceedances are mostly related to the size of the dataset rather than to the absence of an effect. The highest correlations are those obtained for NO₂ (0.38) and CO (0.33) at LB, although, as mentioned in Section 3.1, they are largely due to the decrease observed in the 2013-2016 period. This is followed by PM₁₀ in CEN (-0.20) and finally PM₁₀ at LB (0.15). In all these cases, the correlation is higher in June-July-August (see **Table II**) indicating that, in winter, the increase of NO₂, CO and PM₁₀ concentrations at LB is higher, while the decrease of PM₁₀ at CEN is lower. On the other hand, relevant meteorological variables (wind speed, ventilation potential, mixing layer height and temperature) do not present significant interannual changes during these months (not shown), which points to emissions as the main potential driver of interannual variations in pollutant concentrations observed in winter (**Table II**).

Relationship between frequency of daily exceedances and the annual mean concentration

The interannual variations of daily exceedances and annual mean concentrations are linearly related for each pollutant and site (**Figures A.1-A.2**). For PM₁₀, the parameters obtained from the fit (intercept, slope and R²) are similar at the three sites; while for NO₂, the fit is somewhat worse due to the saturation of exceedance frequency values close to 100 %. The parameters obtained for NO₂ suggest that its daily guideline is more restrictive than the recommended annual level. Nevertheless, when the analysis is performed over a period with enough daily concentration data, these parameters change (see **Table III**) so that for both pollutants, the annual WHO AQG value is more stringent than the daily one, highlighting the sensitivity of these results to the dataset used.

Trends in wind-cluster distribution of upper quartile daily concentrations

When analyzing the interannual variation of the frequency of daily concentrations in the upper quartile (**Table A.III**) by wind cluster (**Figures 4-6**), clear patterns and consistent with those of **Figure 2**, are observed. At CEN, in recent years, relatively high daily mean concentrations of the three pollutants occur mainly with clusters 4 and 5. As observed with the annual values (**Figure 2**, left column), a slight increase in NO₂ and a decrease in CO and PM₁₀ is found. At COR (**Figure 5**), high daily NO₂ concentrations occur almost exclusively with cluster 5; while higher CO and PM₁₀ levels occur more frequently with clusters 3 and 5. The street canyon effect (evidenced through cluster 3, SW winds) is more pronounced in CO concentration, as expected due to its highest contribution from local traffic sources. At LB (**Figure 6**), cluster 4 is the most frequent for all three pollutants; although a great contribution is also observed with clusters 5 for NO₂, and clusters 1 and 5 for CO and PM₁₀. At this station, an increase in the frequency of high concentrations with cluster 4 is observed in recent years as in the annual concentrations (**Figure 2**, right column). The higher percentage of upper quartile concentrations with winds from the river (clusters 1 and 2) at LB compared to the other sites suggests an important role of the thermoelectric power plants in the coastal zone.

3.3) NO₂ simulations in the MABA

Given the relatively high annual and daily NO₂ concentrations in relation to the limits

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suggested by the WHO at the three AQ monitoring sites of the city, and that a slight increase in their levels in recent years could be significant as longer series will become available, we applied the last version of the urban scale atmospheric dispersion model DAUMOD-GRS (Pineda Rojas et al., 2022) to explore the estimated annual NO₂ concentrations in the whole metropolitan area due to NO_x and VOCs area emission sources (**Figure 7**). A brief description of the model and the conditions of the simulations can be found in Pineda Rojas et al. (2022). As observed in large urban areas, higher annual concentrations (up to 30 ppb) are found in high traffic avenues and in the downtown. Our estimates provide urban background values with a horizontal resolution of 1 km x 1 km and suggest that the area of NO₂ concentration values above 5 ppb is large and covers most of the MABA.

4) CONCLUSIONS

Annual NO₂ and PM₁₀ concentrations are above the air quality guideline (AQG) levels recommended by the World Health Organization (WHO) to protect human health (5 ppb and 15 µg m⁻³, respectively) at the three air quality monitoring stations in the city of Buenos Aires (CEN: urban background, COR: urban traffic and LB: residential-industrial) during the past decade. Their daily concentration values are frequently higher than the new WHO AQG level (13 ppb and 45 µg m⁻³, respectively), while daily CO concentrations do not exceed the level suggested by the WHO (3.9 ppm). The trend analysis performed for each pollutant and monitoring station, in years including more than 70% daily data, suggests that:

- NO₂ increases slightly at all three stations,
- CO decreases at CEN and increases at COR and LB,
- PM₁₀ decreases at CEN and increases at LB.

The only statistically significant trend is the decrease in PM₁₀ concentration at CEN whose annual mean decreases at a rate of -1.6 µg m⁻³ yr⁻¹ while the frequency of daily exceedances

shows a trend of -1.6 \% yr^{-1} in the period 2013-2019. However, when the analysis is performed using daily concentration values, statistically significant trends are obtained, with the signs and magnitudes being consistent with those found with the annual series. This suggests that the lack of statistical significance in the trends of annual concentrations or frequencies of daily exceedances could be due to the length of the air quality series (which vary between 5 and 8 years depending on the pollutant and the monitoring site). Also, the correlation analysis of the daily averages shows that the decrease of PM_{10} in CEN is lower and the positive trends of the three pollutants in LB are higher in winter months, which could be due to an interannual change in emissions during cold months.

When the daily hourly wind sequence is used as a classification variable, clear patterns are obtained in both annual concentrations and frequency of high daily concentrations. At CEN, the highest concentration levels of NO_2 , CO and PM_{10} occur with clusters 4 (winds from the NNW) and 5 (low intensity winds) and the lowest with clusters 1 and 2 (winds from the La Plata River). At COR, clusters 1 and 5 separate the low and high concentrations, respectively, although equally high values are observed with cluster 3 (S-SW winds) for CO, highlighting a greater effect of the street canyon for this pollutant. At LB, the lowest concentrations occur with clusters 2 and 3 and the highest with cluster 4, whose relative importance increases in recent years, especially for NO_2 and PM_{10} . Overall, differences in the concentration levels among clusters are observed both in the annual concentrations and in the frequencies of occurrence of high daily concentrations (those corresponding to the upper quartiles) and the fact that they are maintained over the years highlights the robustness of the classification for analyzing long air quality series.

The different variations in annual mean concentrations of CO and PM_{10} at the three stations highlight an important/dominant role of changes in local emission sources. The fact that such variations are observed in the concentrations of all clusters supports this hypothesis since in high emission sites, the local contribution generally dominates under all wind conditions. The cluster analysis also suggests a greater contribution from sources located to the NNW of the most coastal site in the last three years of the decade. These hypotheses may be confirmed or refuted with future analyses that include data on changes in activity that are not currently available.

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Finally, the high frequency of exceedances of daily and annual NO₂ concentrations according to the new WHO recommended limits and the potential large area of exceedances according to our simulations, call for further efforts in both monitoring and modeling. These results show that the new WHO AQG levels change the paradigm of urban air quality in the city of Buenos Aires. Note that as NO₂ also contributes to the formation of fine particulate matter, reducing its concentration may also contribute to lower PM levels. The analysis of possible air pollution mitigation strategies in the city of Buenos Aires will require not only sustaining and expanding the current monitoring to other sites and pollutants (such as PM_{2.5}), but also the development of a high-resolution emission inventory for the Metropolitan Area of Buenos Aires which can also contribute to verify the hypotheses put forward.

ANNEX A

Statistics

	NO ₂ (ppb)			CO (ppm)			PM ₁₀ (µg m ⁻³)		
	CEN	COR	LB	CEN	COR	LB	CEN	COR	LB
Min	3	2	2	0.0	0.1	0.1	6	8	7
Mean	18	25	19	0.5	0.6	0.4	27	28	30
Max	54	103	75	2.6	2.6	2.9	134	140	134
N	2,464	2,258	2,638	2,560	2,203	1,843	2,634	2,431	2,760
%	67	62	72	70	60	50	72	67	76

Table A.I: Basic statistics of daily concentrations of NO₂ (ppb), CO (ppm) and PM₁₀ (µg m⁻³) at each monitoring site (CEN: Parque Centenario, COR: Córdoba, LB: La Boca) during the period 2010-2019, after removing days with very high concentration resulting from Puyehue-Cordón Caulle volcano eruption. [The number of observations (N) and data availability (%) at each site is indicated].

		2010	2011	2012	2013	2014	2015	2016	2017	2018	2019
NO ₂	CEN	32	54	68	51	80	79	76	75	83	76
	COR	16	61	77	27	25	73	90	84	73	94
	LB	53	87	56	69	66	75	84	74	83	76
CO	CEN	0	42	77	74	90	84	75	81	88	91
	COR	26	36	36	12	71	78	89	80	83	91
	LB	19	16	25	7	45	81	80	71	81	80
PM ₁₀	CEN	18	54	63	73	85	89	77	71	94	94
	COR	47	70	56	40	41	78	83	80	85	86
	LB	49	73	87	67	67	76	90	80	92	74

Table A.II: Annual percentage of days having complete 24-hourly values air quality data for each pollutant and monitoring site. Values greater than or equal to 70 are indicated with shading.

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	CEN	COR	LB	Units
NO ₂	22	30	24	ppb
CO	0.7	0.8	0.5	ppm
PM ₁₀	31	33	36	µg m ⁻³

Table A.III: 75th percentile of the daily mean concentrations of each pollutant at each station over the entire period.

	Trend	CEN	COR	LB	Units
NO ₂	Annual concentration	0.22	0.49	2.53	ppb yr ⁻¹
	Daily exceedances	1.7	1.2	16.8	% yr ⁻¹
CO	Annual concentration	-0.01	0.05	0.07	ppm yr ⁻¹
	Daily exceedances	-	-	-	% yr ⁻¹
PM ₁₀	Annual concentration	-1.62	-0.63	1.77	µg m ⁻³ yr ⁻¹
	Daily exceedances	-1.6	-0.8	1.4	% yr ⁻¹

Table A.IV: Trends in annual mean concentrations and annual frequency of daily mean concentration exceeding the WHO guideline for years with more than 70% of data. Significant values are indicated in bold numbers.

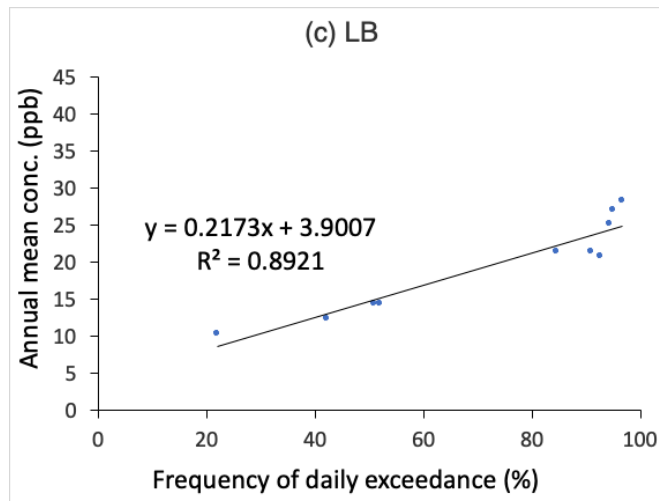
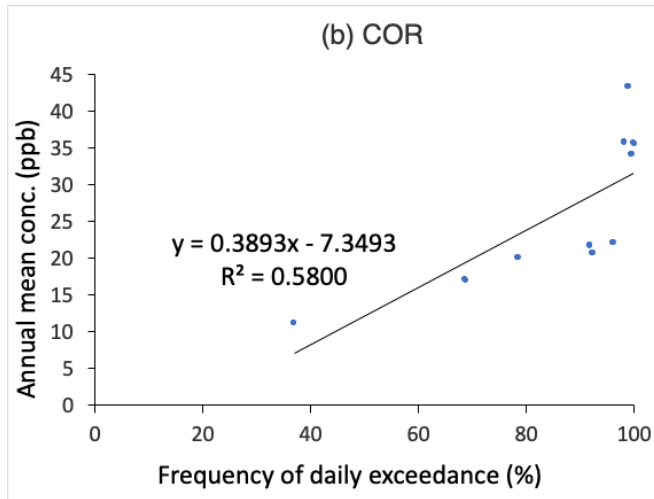
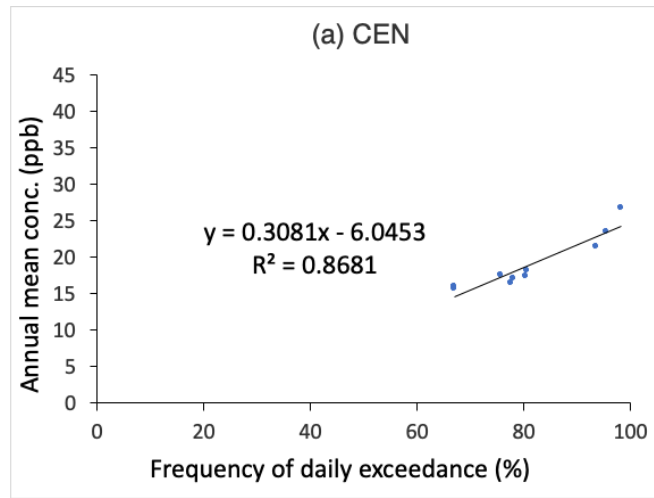


Figure A.1: Scatter plot of annual mean NO₂ concentration vs frequency of daily mean NO₂ concentration exceeding the WHO guideline level (13 ppb) at: a) CEN, b) COR and c) LB. The linear fit is included.

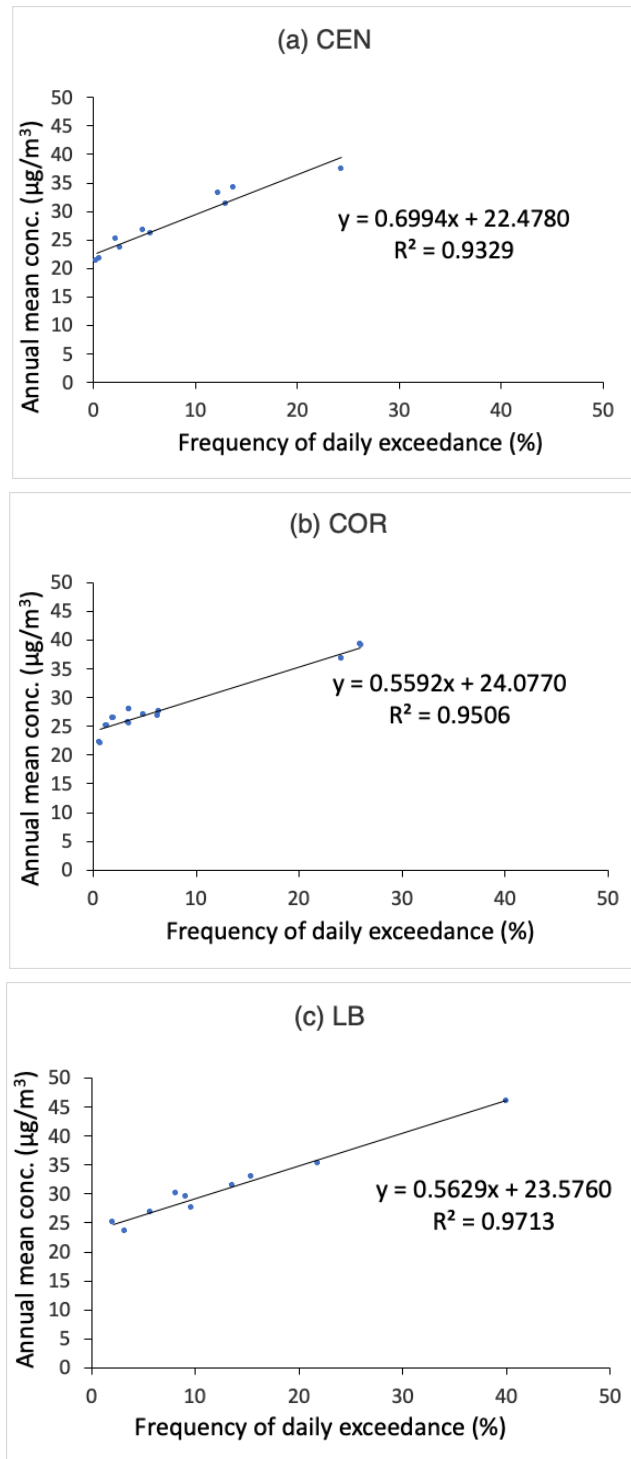


Figure A.2: Scatter plot of annual mean PM_{10} concentration vs frequency of daily mean PM_{10} concentration exceeding the WHO guideline level ($45 \mu\text{g m}^{-3}$) at: a) CEN, b) COR

and c) LB. The linear fit is included.

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FIGURES AND TABLES

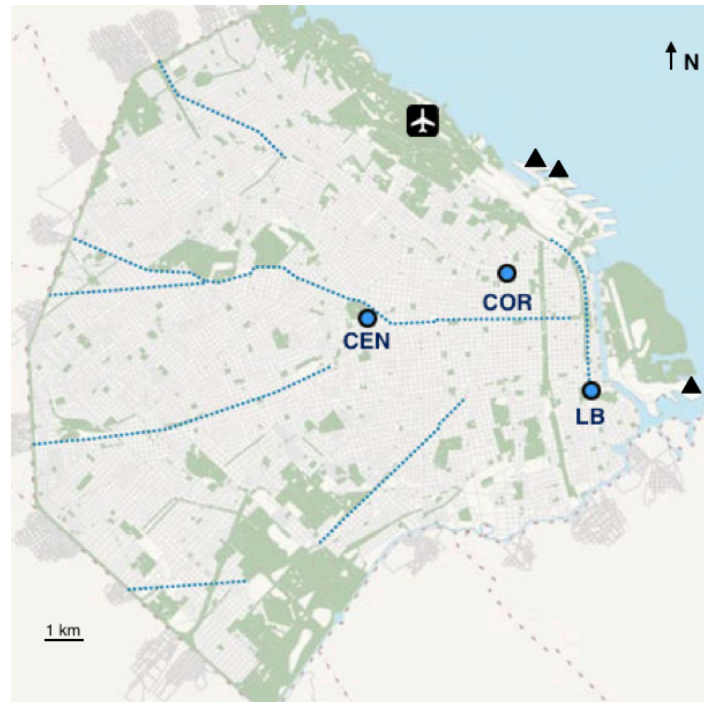


Figure 1: City of Buenos Aires (CBA) and location of the three air quality monitoring stations (CEN: Parque Centenario, COR: Córdoba, LB: La Boca). The locations of the AEP meteorological station at the Domestic Airport and three thermal power plants (triangles) are also indicated. [Source: https://www.buenosaires.gob.ar/areas/med_ambiente/apra/calidad_amb/red_monitoreo/mapa.php?menu_id=32434]

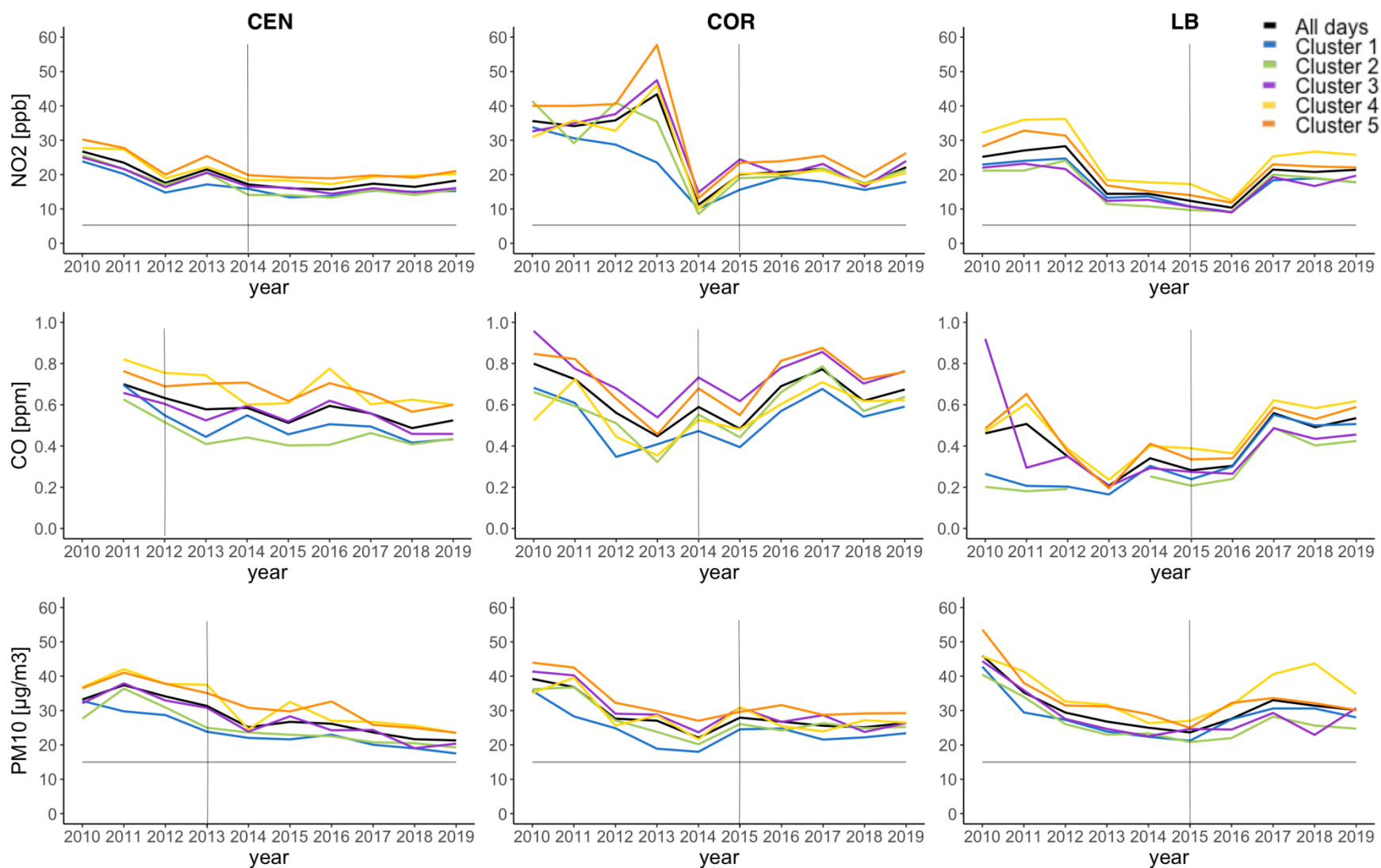


Figure 2: Interannual variation of air pollutant concentrations at each monitoring site (CEN: Parque Centenario, COR: Córdoba, LB: La Boca), by cluster. The horizontal lines indicate the WHO air quality guideline levels and the vertical lines the year since 70% of data is available.

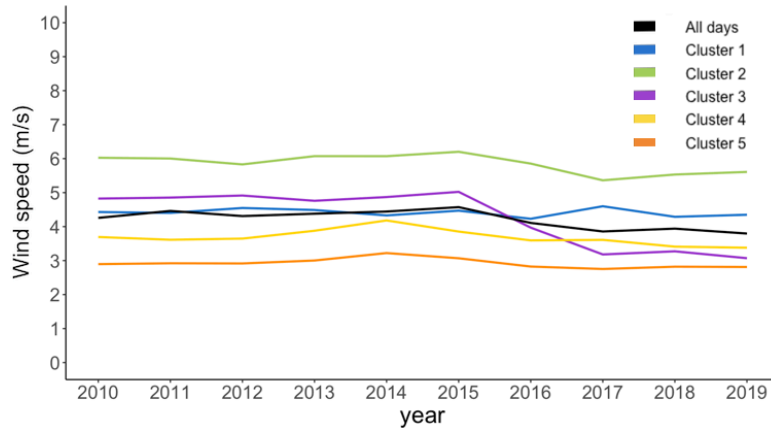


Figure 3: Interannual variation of mean wind speed measured at the AEP meteorological station, considering all data (black) and grouping days by wind cluster (color code).

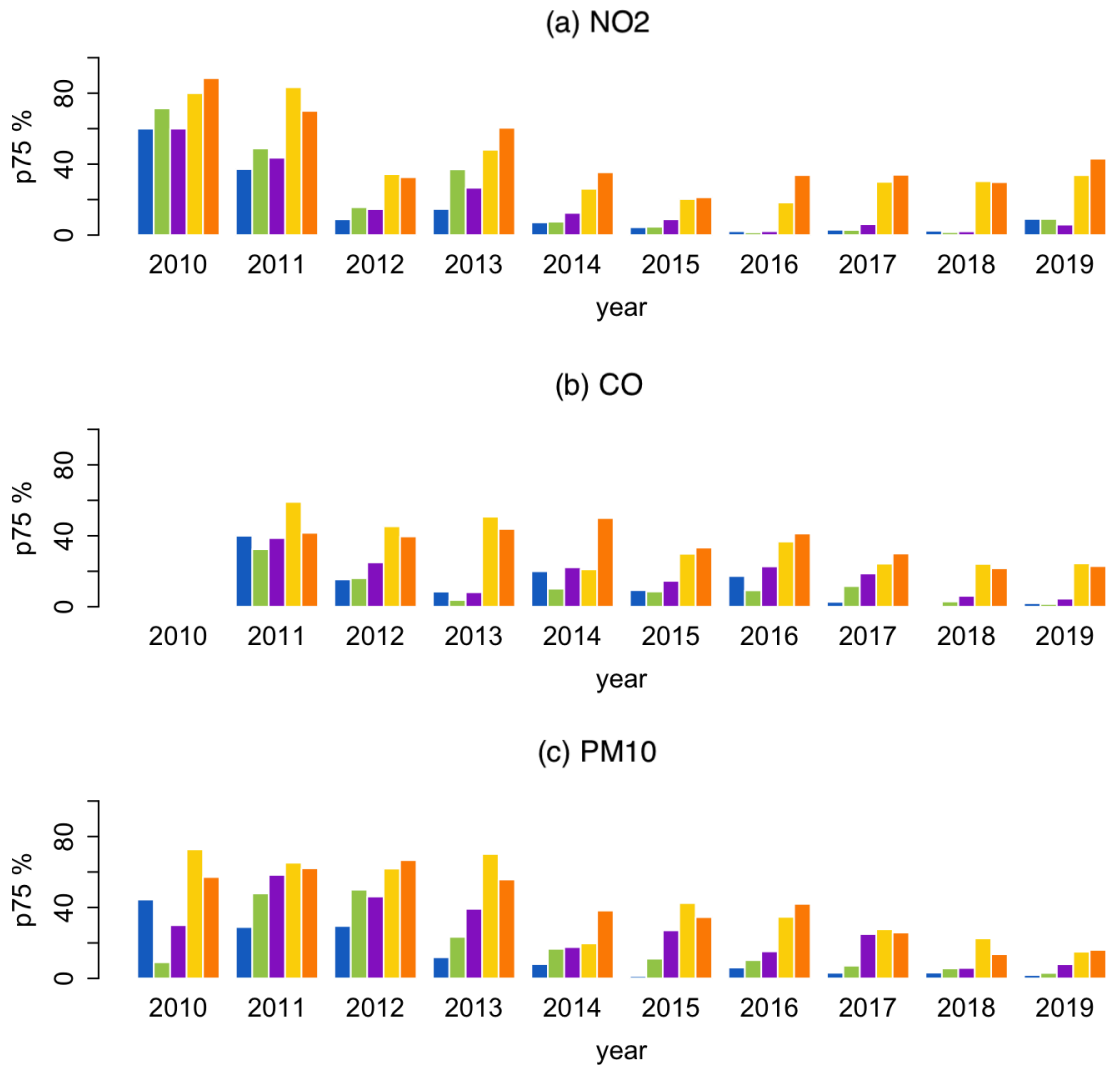


Figure 4: Interannual variation of the cluster-distribution of percentage of days with daily mean concentration exceeding the 75th percentile of: a) NO₂ (p75: 22 ppb), b) CO (p75: 0.7 ppm) and c) PM₁₀ (p75: 31 μg m⁻³) at CEN.

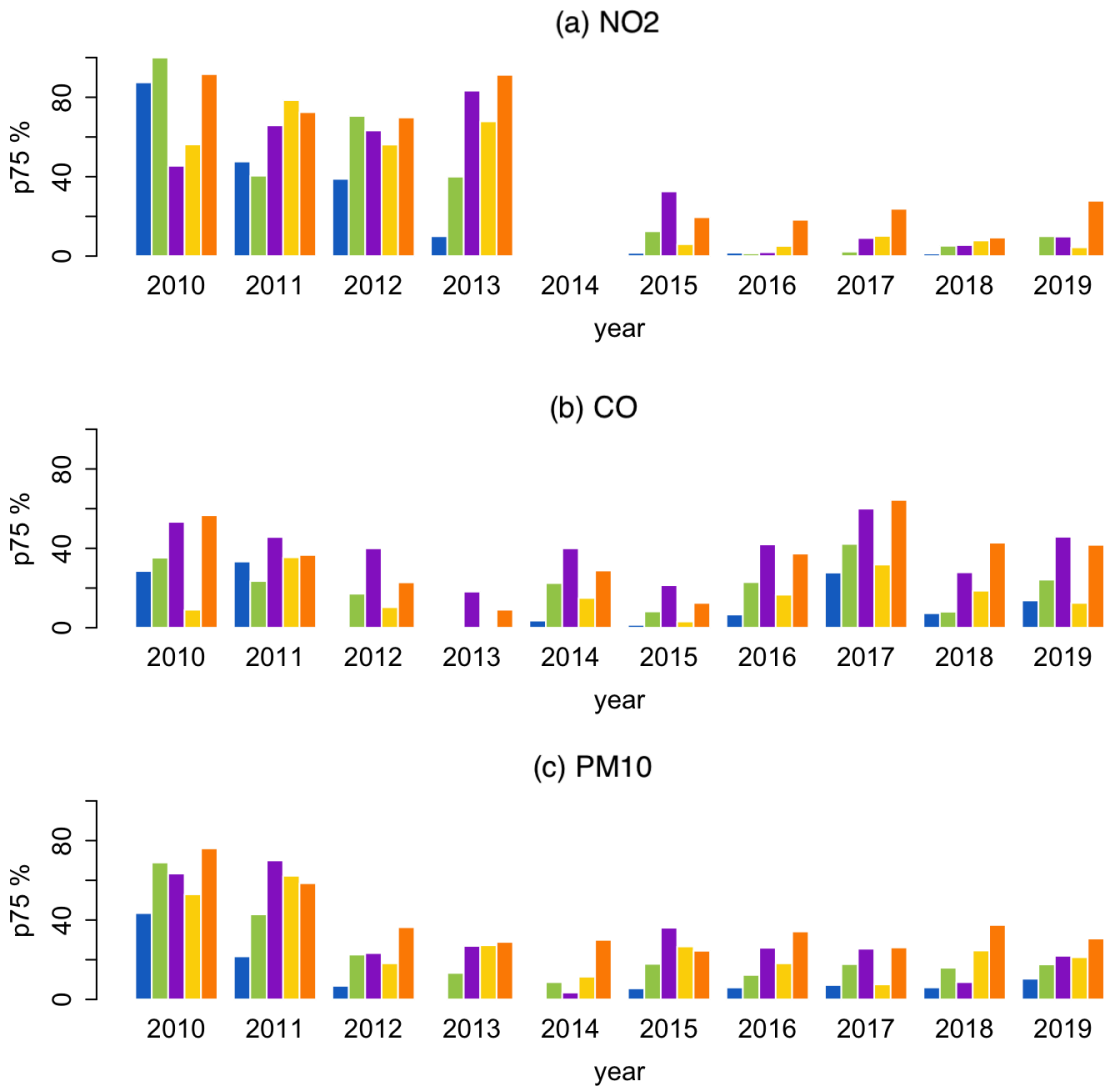


Figure 5: Interannual variation of the cluster-distribution of percentage of days with daily mean concentration exceeding the 75th percentile of: a) NO₂ (p75: 30 ppb), b) CO (p75: 0.8 ppm) and c) PM₁₀ (p75: 33 μg m⁻³) at COR.

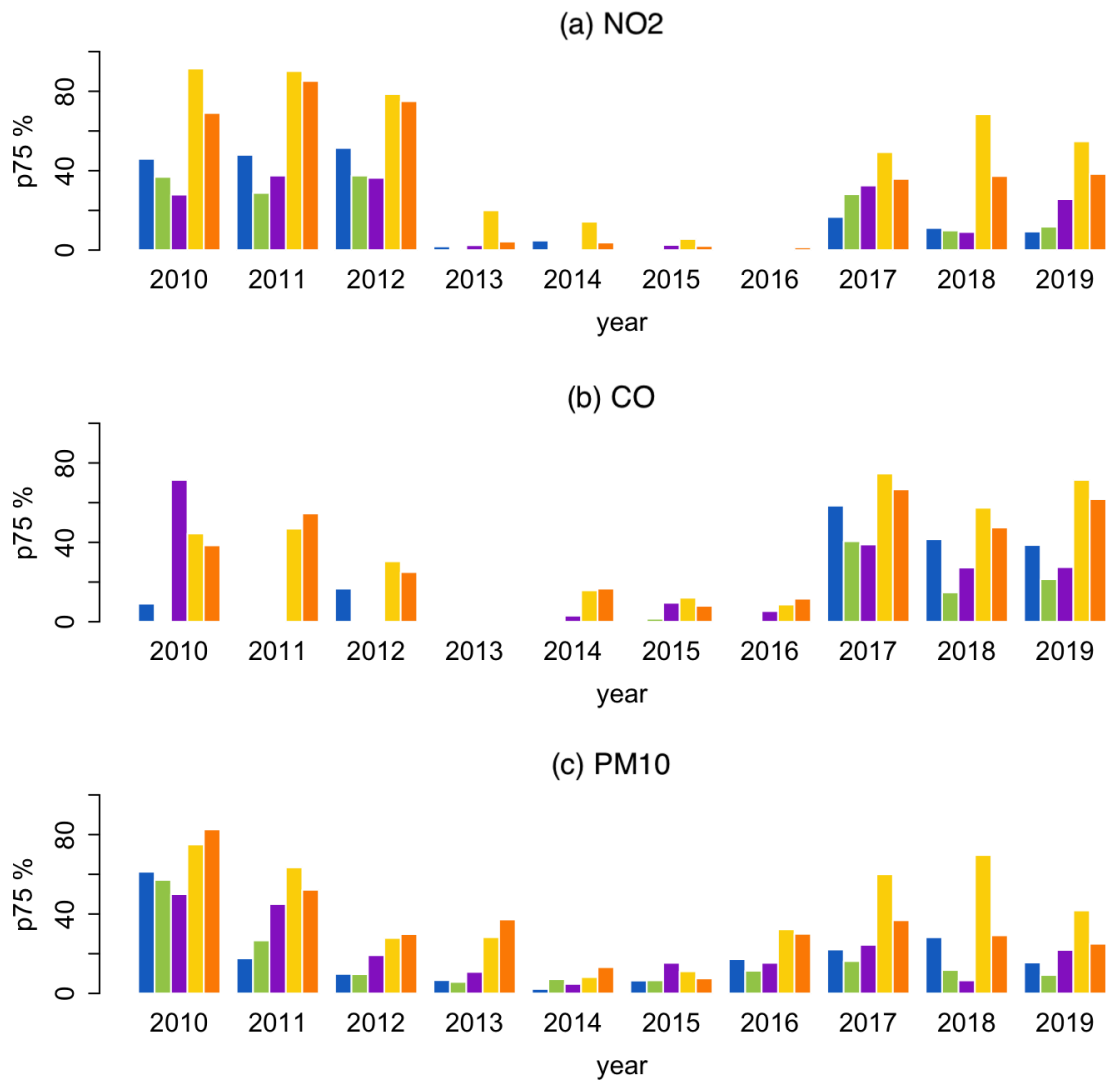


Figure 6: Interannual variation of the cluster-distribution of percentage of days with daily mean concentration exceeding the 75th percentile of: a) NO₂ (p75: 24 ppb), b) CO (p75: 0.5 ppm) and c) PM₁₀ (p75: 36 μgm⁻³) at LB.

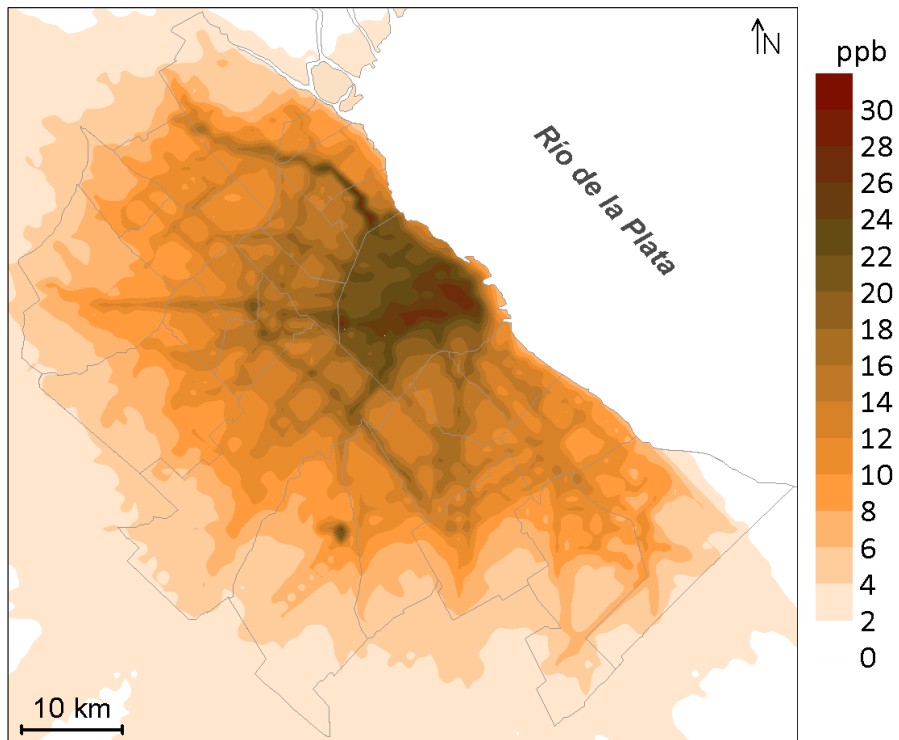


Figure 7: Annual NO₂ concentration (ppb) in the Metropolitan Area of Buenos Aires (MABA), resulting from NO_x and VOCs area emission sources, estimated with the DAUMOD-GRS model.

CEN	NO ₂ (ppb)	dif w/Ca	CO (ppm)	dif w/Ca	PM ₁₀ (µg/m ³)	dif w/Ca
Ca	16-18		0.49-0.63		21-31	
C _{1,2}	14-15	11-15%	0.41-0.53	14-26%	18-24	9-22%
C _{4,5}	18-21	12-18%	0.60-0.74	12-25%	24-36	10-17%
COR						
Ca	17-22		0.48-0.77		25-28	
C ₁	16-19	8-22%	0.39-0.68	12-20%	22-25	7-16%
C _{3,5}	18-25	5-19%	0.58-0.87	12-21%	26-30	5-12%
LB						
Ca	10-21		0.28-0.56		24-33	
C _{2,3}	9-20	8-18%	0.24-0.49	13-18%	23-29	4-23%
C ₄	12-27	18-40%	0.36-0.62	11-38%	27-44	14-39%

Table I: Ranges of annual pollutant concentrations (Ca) and wind-cluster average concentrations (Cx) of the groups with the lowest (blue) and highest (red) concentration values, for each pollutant and monitoring site, since the years highlighted in Figure 2. The percentages indicate their differences with respect to Ca (dif w/Ca): blue values indicate percentages lower than Ca and red those that are higher.

		N	All days	DJF	MAM	JJA	SON
NO ₂	CEN	1,714	0.05	0.05	0.10	0.08	-0.01
	COR	1,507	0.07	0.21	0.08	0.21	-0.17
	LB	1,432	0.38	0.42	0.38	0.44	0.27
CO	CEN	2,406	-0.06	-0.12	-0.01	0.02	-0.17
	COR	1,797	0.12	0.30	0.12	0.15	0.03
	LB	1,436	0.33	0.35	0.26	0.44	0.33
PM ₁₀	CEN	2,130	-0.20	-0.23	-0.20	-0.10	-0.25
	COR	1,503	-0.03	-0.07	-0.04	0.03	-0.06
	LB	1,508	0.15	0.08	0.18	0.24	0.01

Table II: Kendall's rank correlation between daily mean concentrations and day number considering all days in the series highlighted in Table A.II and by season. Significant values ($p < 0.0125$) are indicated in bold numbers.

site	NO ₂			PM ₁₀		
	Slope	Intercept	R ²	Slope	Intercept	R ²
CEN	0.13	7.05	0.76	0.76	21.96	0.93
COR	0.16	6.25	0.89	0.26	25.50	0.21
LB	0.17	6.24	0.97	0.71	22.05	0.86

Table III: Parameters obtained from the linear regression between the mean annual concentration and the frequency of daily concentrations that exceed the AQG level, for NO₂ (Figure A.1) and PM₁₀ (Figure A.2).