

Article

Linking Satellite and Ground Observations of NO₂ in Spanish Cities: Influence of Meteorology and O₃

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Abstract: In Spain, several major cities face high rates of avoidable deaths due to NO₂ exposure. Understanding NO₂ atmospheric dynamics is essential to support public health efforts and policymaking. Recent satellite products have proven useful in characterizing urban atmospheric composition in various regions. This study compares NO₂ concentration data from in situ air quality monitoring networks and the Sentinel-5P TROPOMI satellite in Spain's three largest cities (Madrid, Barcelona, and Valencia), alongside O₃ levels—due to its close photochemical relationship with NO_x—wind speed and direction, temperature, relative humidity, and solar radiation. Data from 2022 were analyzed using Pearson correlation coefficients and Principal Component Analysis (PCA) to identify key relationships and patterns. Results showed a consistent negative correlation between NO₂ and O₃, wind speed, temperature, and solar radiation. Differences between in situ and satellite data were more pronounced in coastal cities, influenced by wind patterns and urban morphology (Madrid: $r = 0.86$, $v = 1.34$ m/s; Valencia: $r = 0.68$, $v = 2.97$ m/s; Barcelona: $r = 0.65$, $v = 8.04$ m/s). These insights enhance the understanding of NO₂ behavior in urban environments and support the use of remote sensing to estimate surface-level pollution in areas lacking ground-based monitoring infrastructure. This is the first study in Spain to jointly evaluate NO₂ from satellite and in situ data across multiple cities, linking pollutant concentrations with meteorological and chemical drivers to improve surface-level estimation strategies and support air quality assessment in under-monitored areas.



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1. Introduction

When assessing air quality, nitrogen oxides (NO_x), which encompass nitrogen monoxide (NO) and nitrogen dioxide (NO₂), emerge as undisputed protagonists with a multifaceted impact. These compounds, resulting from the combination of oxygen and nitrogen at high temperatures, can originate naturally (e.g., lightning, volcanic eruptions, biomass burning) [1,2], but their persistence in urban environments stems from the intensive development of activities involving the combustion of fossil fuels (e.g., road transportation, power generation, domestic heating) [3]. Therefore, NO₂ concentration tends to grow with population density.

Once emitted, NO_x rapidly transforms into NO₂, which can have harmful effects on human health by causing diseases of the immune, circulatory, and respiratory systems [4]; on ecosystems, by triggering processes of acidification and eutrophication [5]; and on

historical heritage, by accelerating the corrosion of buildings and monuments [6]. It can further react with other substances and generate secondary pollutants, mainly particulate matter, nitric acid (HNO_3), peroxyacetyl nitrates (PANs), and tropospheric ozone (O_3).

Increasing NO_2 pollution in urban environments raises global concern, as 70% of the world's population will live in cities by 2050 [7]. The European Union has long aimed to tackle this issue. According to current regulations, the annual NO_2 limit value is $40 \mu\text{g}/\text{m}^3$. However, plans are underway to halve this threshold in the near future, with the ultimate goal of eventually meeting the World Health Organization (WHO) recommendation of $10 \mu\text{g}/\text{m}^3$ [8]. In Spain, these efforts involve updating legal frameworks, which advocate for the establishment of low-emission zones in municipalities with over 50,000 inhabitants, and the adoption of more efficient and sustainable transportation models. Yet, Spanish major cities have been identified as some with the highest number of avoidable deaths due to NO_2 in Europe, with Madrid ranking 1st, Barcelona 6th, and Valencia 68th [9]. Out of the 130 air quality zones designated in Spain in 2022, 30 did not meet the annual limits for NO_2 projected by the European Union, and 84 did not meet those recommended by the WHO.

To ensure the ongoing monitoring of air quality and assess the efficacy of new policies, data on pollution levels are gathered via in situ stations. However, in recent years, remote sensing has become an increasingly valuable tool for air quality monitoring, offering spatially continuous data that complement the limited coverage of in situ networks. Satellite-based instruments have been used not only to estimate pollutant concentrations, but also to assess the effectiveness of environmental policies, model emission inventories, and identify pollution hotspots across diverse regions [10–13]. Among the most commonly used sensors for tropospheric NO_2 monitoring are the Ozone Monitoring Instrument (OMI), the Global Ozone Monitoring Experiment-2 (GOME-2), and the TROPospheric Monitoring Instrument (TROPOMI), which is onboard the Sentinel-5 Precursor satellite. TROPOMI represents a major step forward due to its enhanced spatial resolution ($3.5 \times 5.5 \text{ km}^2$ since 2019) and daily global coverage, making it particularly suitable for detecting urban-scale NO_2 variability [14,15].

Despite these advances, the accuracy of satellite-derived NO_2 measurements is influenced by several factors. Retrieval algorithms estimate vertical column densities based on radiative transfer models, which are sensitive to aerosol presence, cloud cover, surface reflectivity, and solar zenith angle [16]. Data may be excluded or flagged under unfavorable conditions, such as high cloud fraction and low-quality pixels, and tropospheric NO_2 can be underestimated in coastal or topographically complex environments due to mixing layer variability and vertical stratification [17,18]. Furthermore, the resolution of satellite data, while improving, still limits the ability to resolve local gradients and street-level pollution peaks captured by ground-based stations. Nevertheless, multiple studies have shown strong correlations between TROPOMI-derived NO_2 values and in situ observations in urban contexts [10,13,17,19–22], confirming its potential for supporting air quality assessments and policymaking strategies in areas lacking dense monitoring infrastructure.

However, the strength of the correlation between satellite and ground-based NO_2 measurements can vary substantially depending on local conditions. To improve surface-level NO_2 estimations in areas where satellite performance is less consistent, it is essential to understand the environmental drivers that influence this relationship. Yet, most studies often neglect how local meteorological and geographical conditions may influence the reliability of satellite-derived NO_2 estimations. Climatic, meteorological, and geographical factors affect the distribution and detectability of NO_2 , both directly (e.g., dispersion, removal, chemical conversion, changes in mean lifetime) [23–27] and indirectly (e.g., boundary layer height) [28–30]. As a result, relying solely on satellite data to estimate surface-level NO_2

concentrations may be insufficient in certain urban settings, unless these local dynamics are properly considered [31–33].

Few studies have aimed to address this gap, which is particularly relevant in countries like Spain, where urban NO₂ pollution is a major concern. This study provides an updated assessment of NO₂ remote sensing performance across three major Spanish cities—Madrid, Barcelona, and Valencia—with distinct meteorological and geographical characteristics. It integrates all available meteorological and air quality data from 2022 and examines their relationship with NO₂ concentrations derived from both ground-based monitoring networks and Sentinel-5P satellite observations. In addition, surface-level O₃ concentration is incorporated due to its strong involvement in NO_x conversion processes. This is the first study to conduct this type of comparative analysis using both in situ and satellite data across multiple cities.

The objective is to improve understanding of air quality dynamics in these locations and to explore the feasibility of using satellite data to estimate surface-level NO₂, particularly in municipalities lacking robust air quality monitoring infrastructure.

2. Materials and Methods

2.1. Regions of Interest and Study Period

The study regions were the cities of Madrid (3,332,035 inhabitants, Figure 1a), Barcelona (1,660,122, Figure 1b), and Valencia (807,693, Figure 1c) [34]. The study covered the period from 1 January to 31 December 2022.

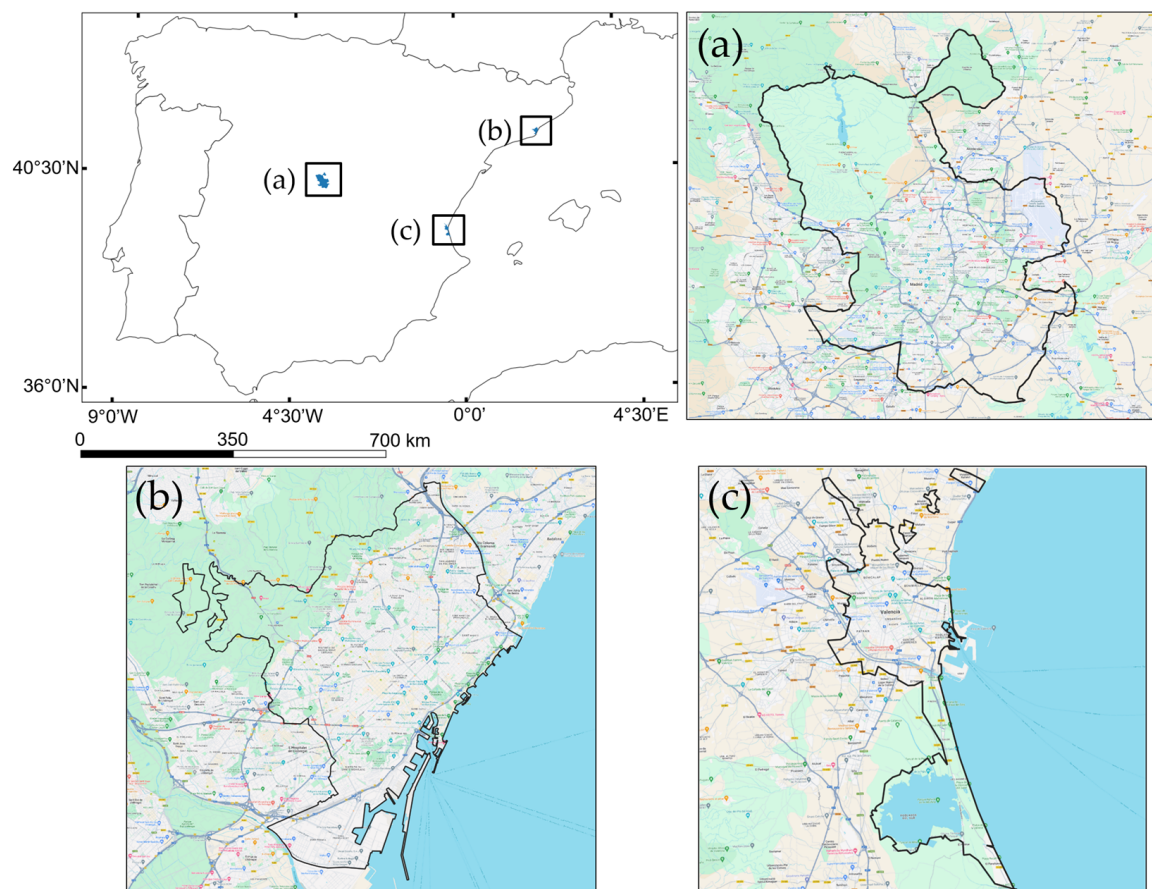


Figure 1. Geographical location of the cities of (a) Madrid, (b) Barcelona, and (c) Valencia in Spain.

2.2. In Situ Data

Surface-level NO₂, O₃, and all meteorological variables information were obtained from the monitoring stations networks located within the city boundaries. Hourly NO₂ and O₃ concentrations are typically measured by chemiluminescence analyzers and ultraviolet photometry devices, respectively, and provide data in mixing ratio units (µg/m³). Hourly wind speed (m/s), wind direction (°), temperature (°C), relative humidity (%), and solar radiation (W/m²) data were simultaneously available in all three cities. Wind direction data, which can be heavily influenced by the sampling location in urban environments [35,36] were instead derived from the ERA5-Land hourly model [37], in line with previous research [12,38]. The geographical location of the stations is presented in Figure S1, and data availability is shown in detail in Table S1.

All this information was openly available in all cases [39–43].

2.3. Satellite NO₂ Data

TROPOMI, developed jointly by the European Space Agency (ESA) and the Netherlands Space Office, is the sensor aboard the Copernicus Sentinel-5P satellite. Launched into orbit in September 2017, its mission is to monitor atmospheric composition and air quality until the future launches of Sentinel-4 [44] and Sentinel-5 [45]. With its capability to measure in the UV (270–500 nm), NIR (675–775 nm) and SWIR (2305–2385 nm) bands, TROPOMI facilitates the observation of a wide range of atmospheric pollutants [46]. Since June 2018, it has provided openly available daily global imagery, initially at a resolution of 3.5×7.5 km², which was subsequently enhanced to 3.5×5.5 km² in August 2019. Sentinel-5P operates on a near-polar, sun-synchronous orbit at an altitude of 824 km. It completes 14 orbits per day, with an ascending node equatorial crossing at 13:30 Mean Local Solar Time [15]. In Madrid, Barcelona, and Valencia (UTC + 1 in winter; UTC + 2 in summer), Sentinel-5P overpasses consistently occurred between 12 PM and 4 PM (local time) in 2022. Occasionally, two consecutive orbits may overlap in some regions, resulting in two readings with a 100 min difference in the same day.

The ESA classifies TROPOMI products into three categories based on the processing level: Level-0, Level-1, and Level-2 [47]. Level-2 images include information on aerosol layer height, absorbing aerosol index, and geolocated total columns of carbon monoxide (CO), sulfur dioxide (SO₂), methane (CH₄), formaldehyde (CH₂O), ozone (O₃), and NO₂. These are primarily derived from a DOAS algorithm, similar to other satellite missions [16,48]. For NO₂, two types of column products are available: the total vertical column and the tropospheric vertical column. In this study, we used the tropospheric column retrievals from the offline (OFFL) processing chain, which offers higher quality and improved post-processing compared to the near-real-time (NRTI) products, albeit with a longer data delivery time.

In previous studies that worked with TROPOMI images and air quality station data simultaneously, additional processing of the images was performed, obtaining Level-3 products [10,19]. The Level-3 images used in this paper stem from Level-2 products that were further processed using the harp-converter drive tool with the bin-spatial operation, obtaining an orthorectified raster layer in a 0.01×0.01 degrees resolution mosaic. High cloud cover, low-quality pixels (<75%), and vertical column density values below -0.001 mol/m² were masked, following the data provider recommendations [49]. Original mol/m² units were converted to Dobson units (DU).

2.4. Data Processing

The study employed a multi-step statistical approach to explore the relationship between NO₂ concentrations and environmental variables. First, the temporal evolution of

pollutant and meteorological data was assessed using 30-day moving averages to smooth short-term fluctuations. Pearson correlation coefficients were then calculated to evaluate linear associations between variables. To complement this, extreme pollution events were identified by isolating the upper and lower 10% of NO₂ values, allowing for comparative analysis of meteorological conditions under different pollution regimes. Finally, Principal Component Analysis (PCA) was used to reduce dimensionality and detect underlying structures among the variables, offering a synthetic view of the dominant patterns influencing air quality in each city [50]. The analysis included NO₂ concentrations (from both in situ and satellite sources), O₃, wind speed and direction, temperature, relative humidity, and solar radiation. A PCA was performed using statistical software with built-in multivariate analysis functions [51], following standard procedures for component extraction based on the Kaiser criterion (eigenvalues > 1) and scree plot interpretation.

To enable a direct comparison between both NO₂ datasets, satellite observations were obtained at the precise locations of each air quality monitoring station. Following a similar approach to previous studies [22,52], regional daily values were calculated by averaging data falling between Sentinel-5P overpass times (12 p.m. to 4 p.m.) and removing outliers using a 3 σ (standard deviation) limit. Scalar averaging was applied for NO₂ and O₃ concentrations, temperature, relative humidity, and solar radiation, while vector averaging was performed for wind speed and wind direction. The temporal evolution of all variables was represented using 30-day moving averages.

Given the heavy influence of wind on the transport of atmospheric pollution, monthly tropospheric NO₂ spatial distributions observed by TROPOMI were compared with wind speed (measured by the meteorological stations) and wind direction (derived from the ERA5 model) data.

3. Results

3.1. Data Overview

Table 1 presents the key statistics of all variables in each city. A daily record was available for each dataset, except for the TROPOMI images, which did not always meet quality criteria. NO₂ data from ground stations placed Madrid as the city with the highest pollution levels, with concentrations 1.4% higher than those in Barcelona and 22.2% higher than those in Valencia. In the case of TROPOMI observations, the differences were 12.8% and 61.8%, respectively.

O₃ concentration values were similar in all three cities, with Madrid presenting the highest average level (72.8 $\mu\text{g}/\text{m}^3$), followed by Valencia (72.2 $\mu\text{g}/\text{m}^3$) and Barcelona (68 $\mu\text{g}/\text{m}^3$). However, the differences between maximum values were larger, being 147 $\mu\text{g}/\text{m}^3$ in Madrid, 129 $\mu\text{g}/\text{m}^3$ in Barcelona, and 113 $\mu\text{g}/\text{m}^3$ in Valencia.

The highest average wind speed was recorded in Barcelona (8.04 m/s), as were both extreme values (2.15 m/s and 29.6 m/s). The highest average temperature was observed in Valencia (22 °C), while the annual minimum (6.3 °C) and maximum (37.8 °C) occurred in Madrid. The highest average solar radiation (595 W/m²) and extreme values (49.3 W/m² and 977 W/m²) were also recorded in the capital. Mean relative humidity values were similar across the cities, with slightly higher levels observed in the coastal areas, where they exceeded 50%.

Table 1. Statistical summary of the study variables.

		NO ₂ AQ [µg/m ³]	NO ₂ TROPOMI [DU]	O ₃ AQ [µg/m ³]	WS [m/s]	T [°C]	RH [%]	SR [W/m ²]
Madrid	Average	21.4	0.246	72.8	1.34	20.4	45.5	595
	Min	5.5	0.044	5.3	0.119	6.3	12.5	49.3
	Median	17.7	0.18	72.3	1.21	19.6	41.3	604
	Max	73.1	1.06	147	3.73	37.8	99	977
	Count	365	289	365	365	365	365	365
Barcelona	Average	21.1	0.218	68	8.04	21	57.5	542
	Min	6	0.034	10.3	2.15	6.57	17	22.7
	Median	19.3	0.178	68	7.16	21.2	56.8	497
	Max	72.7	0.881	129	29.6	33.8	98.3	927
	Count	365	286	365	365	365	365	365
Valencia	Average	17.5	0.152	72.2	2.97	22	52.2	522
	Min	2.38	0.026	8.63	0.424	10.1	19.8	16.2
	Median	15.8	0.116	75.1	2.82	22.4	53.2	505
	Max	51.5	0.493	113	10.1	36.1	81.1	900
	Count	365	277	365	365	365	365	365

NO₂ AQ represents the average NO₂ concentration measured by the air quality monitoring stations in each city; O₃ AQ represents the average O₃ concentration measured by the air quality monitoring stations in each city; NO₂ TROPOMI represents the average NO₂ concentration observed by TROPOMI at the location of the air quality monitoring stations in each city; and WS, T, RH, and SR represent the average wind speed, temperature, relative humidity, and solar radiation measured by the meteorological stations in each city, respectively. Data were gathered between Sentinel–5P overpass times.

3.2. Temporal Evolution of Study Variables

The temporal evolution of in situ and satellite NO₂ concentration data were compared first. The analysis was limited to those cases where both types of observations could be retrieved simultaneously. Tropospheric column density data from TROPOMI displayed a more evident seasonal pattern in all three cities, with higher mean values in autumn and winter. In Madrid, both datasets aligned closely. However, measurements from air quality monitoring stations showed significant spikes in Barcelona and Valencia during warmer months, which were not clearly observed through satellite remote sensing (Figure 2).

The temporal evolution of the rest of the variables is depicted in Figure 3.

O₃ surface concentration developed similarly in the three cities. It decreased during colder months and spiked in summer, although this enhancement was more significant in Madrid (Figure 3a).

Wind speed (Figure 3b) and relative humidity (Figure 3d) showed similar patterns in the coastal cities. Wind speed was more intense during spring, and relative humidity maintained a relatively constant distribution, with slight increases in spring and autumn. In contrast, opposite trends were observed in Madrid. Wind speed remained more uniform throughout the year, while relative humidity experienced a significant decrease during the summer.

Temperature (Figure 3c) and solar radiation (Figure 3e) followed similar trends in all three cities, increasing from early spring until August, when the seasonal decline began.

Wind distribution is represented separately in Figure 4. In Madrid, 54.5% of wind observations (Figure 4a) were recorded in the N and NE directions, with an average speed of 1.44 m/s. In Barcelona (Figure 4b), 61.1% of observations were recorded between NW and NE directions, with an average speed of 8.63 m/s. In Valencia (Figure 4c), 54.2% of observations were recorded between the W and NW directions, with an average speed of 2.73 m/s.

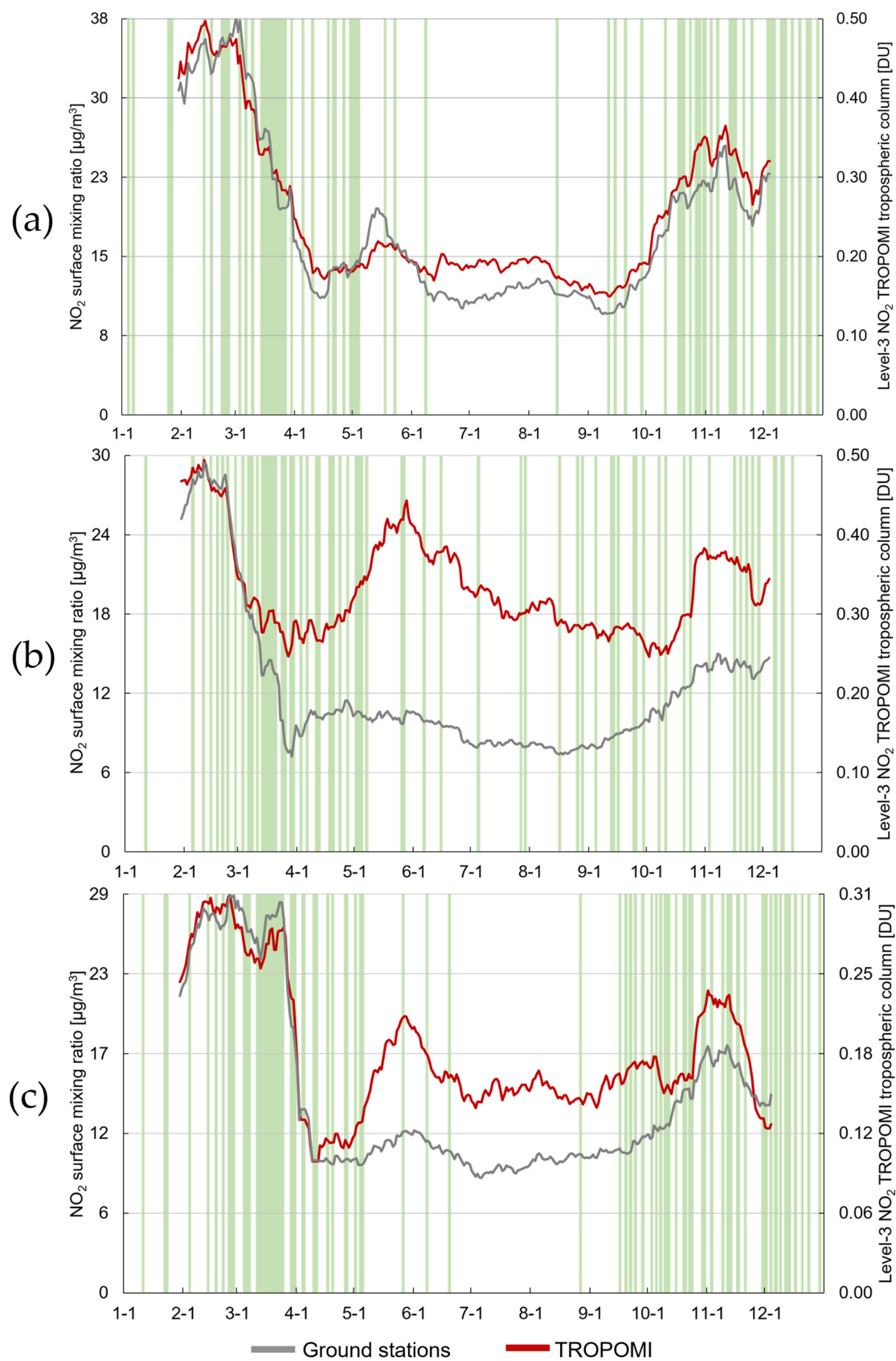


Figure 2. The 30-day moving average of NO₂ concentration measured by the air quality monitoring stations networks and by TROPOMI in (a) Madrid, (b) Barcelona, and (c) Valencia in 2022. Green background highlights the days for which no valid satellite observations were available due to quality constraints.

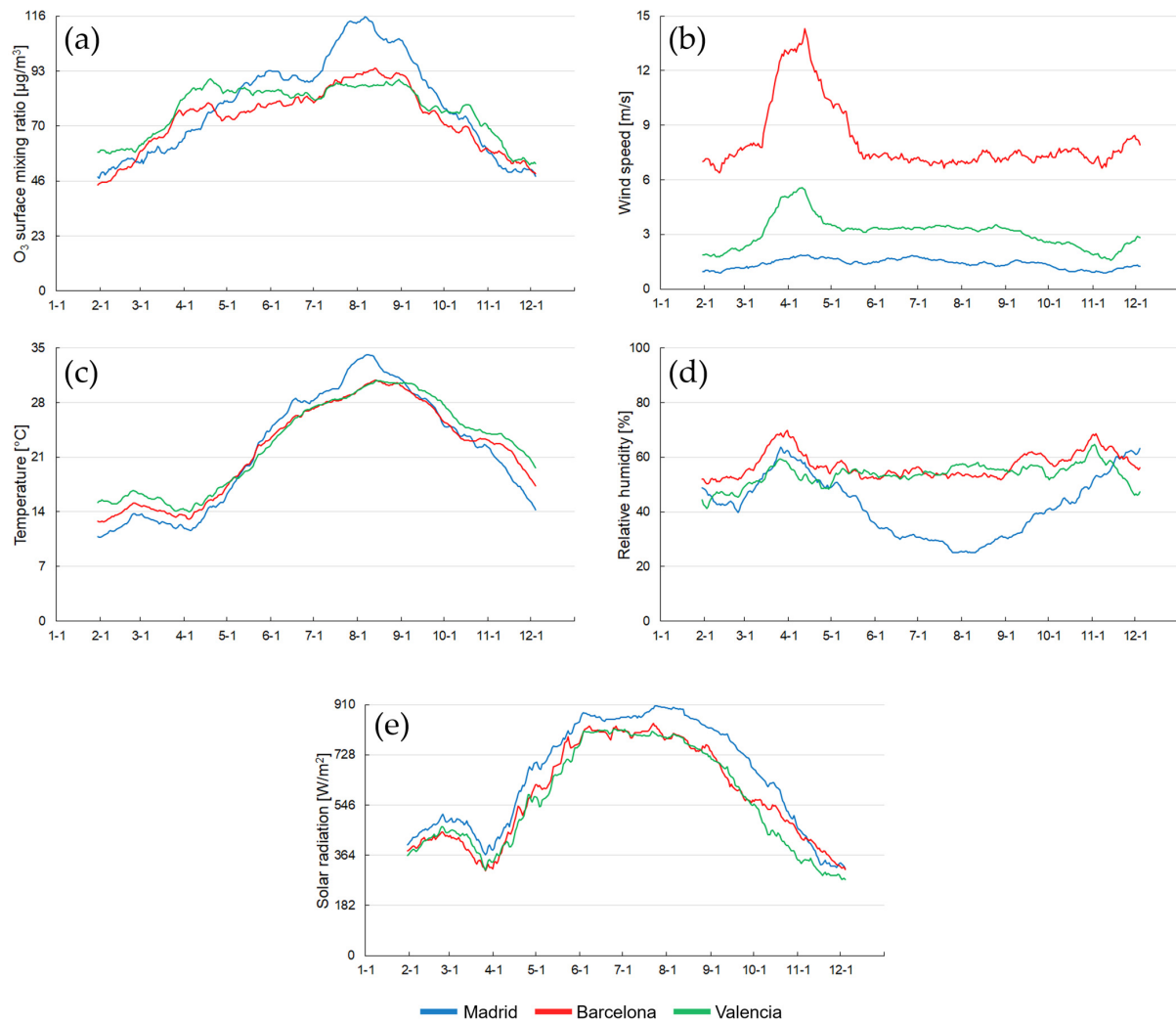


Figure 3. The 30-day moving average of (a) O_3 surface concentration, (b) wind speed, (c) temperature, (d) relative humidity, and (e) solar radiation in (blue) Madrid, (red) Barcelona, and (green) Valencia in 2022.

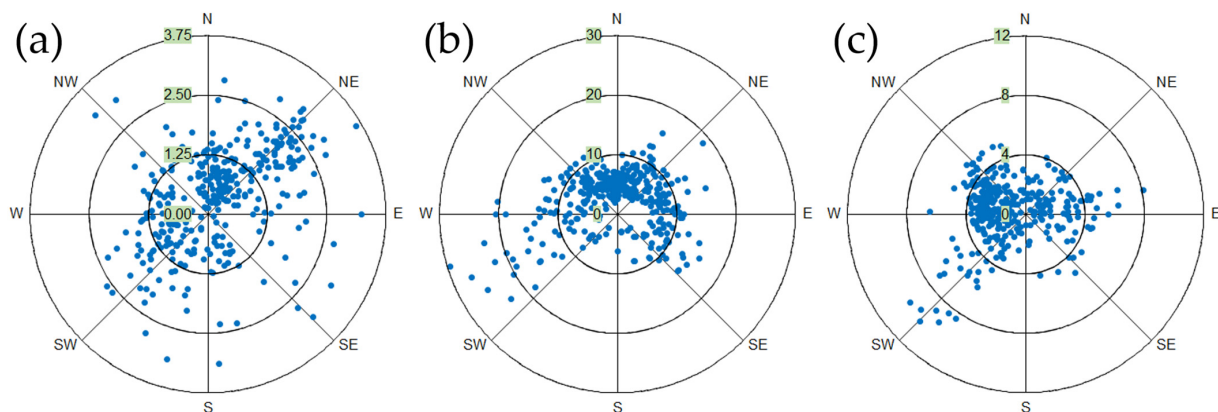


Figure 4. Distribution of wind speed and direction in 2022 in (a) Madrid, (b) Barcelona, and (c) Valencia, where N stands for north ($337.5\text{--}22.5^\circ$), NE for northeast ($22.5\text{--}67.5^\circ$), E for east ($67.5\text{--}112.5^\circ$), SE for southeast ($112.5\text{--}157.5^\circ$), S for south ($157.5\text{--}202.5^\circ$), SW for southwest ($202.5\text{--}247.5^\circ$), W for west ($247.5\text{--}292.5^\circ$), and NW for northwest ($292.5\text{--}337.5^\circ$). Each dot represents average wind speed and direction in a day between Sentinel-5P overpass times. The distance to the center corresponds to the speed magnitude, and the angle with respect to the N represents the direction.

3.3. Correlation Between NO₂ and Meteorological Variables

Table 2 shows the correlation coefficient matrix. The first column displays the relationship between both NO₂ datasets, which align with the graphics in Figure 2.

Table 2. Linear correlation coefficients (*r*) between NO₂ data from air quality monitoring stations and TROPOMI and between the studied meteorological variables in each city. Values marked with an asterisk (*) are not statistically significant at $p < 0.05$.

		NO ₂	O ₃	WS	T	SR	RH
Madrid	AQ stations	0.86	−0.68	−0.57	−0.40	−0.50	0.30
	TROPOMI		−0.56	−0.58	−0.36	−0.37	0.18
Barcelona	AQ stations	0.65	−0.43	−0.38	−0.10 *	−0.17	0.02 *
	TROPOMI		−0.57	−0.33	−0.46	−0.41	−0.01 *
Valencia	AQ stations	0.68	−0.44	−0.40	−0.17	−0.18	0.12 *
	TROPOMI		−0.50	−0.45	−0.48	−0.40	−0.06 *

In all three cities, O₃ had the strongest correlation with both NO₂ datasets. Wind speed coefficients were close to those of O₃, and very similar within each location. Temperature results showed greater discrepancies between ground and satellite data in the coastal cities ($r = -0.10$ vs. $r = -0.46$ in Barcelona; $r = -0.17$ vs. $r = -0.48$ in Valencia). This was also the case for solar radiation ($r = -0.17$ vs. $r = -0.41$ in Barcelona; $r = -0.18$ vs. $r = -0.40$ in Valencia). Relative humidity was the only variable that showed positive correlation coefficients, which did not exceed $r = 0.3$ in any case.

All correlation coefficients presented in Table 2 were tested for statistical significance using Pearson's correlation test. In all three cities, most correlations between NO₂ and meteorological variables—including O₃, wind speed, temperature (except for AQ stations data in Barcelona), and solar radiation—were statistically significant ($p < 0.05$). Only correlations involving relative humidity showed non-significant values ($p > 0.05$), indicating that the weak relationships observed may not result from consistent patterns.

Figure 5 displays the distribution of NO₂ concentration according to wind direction.

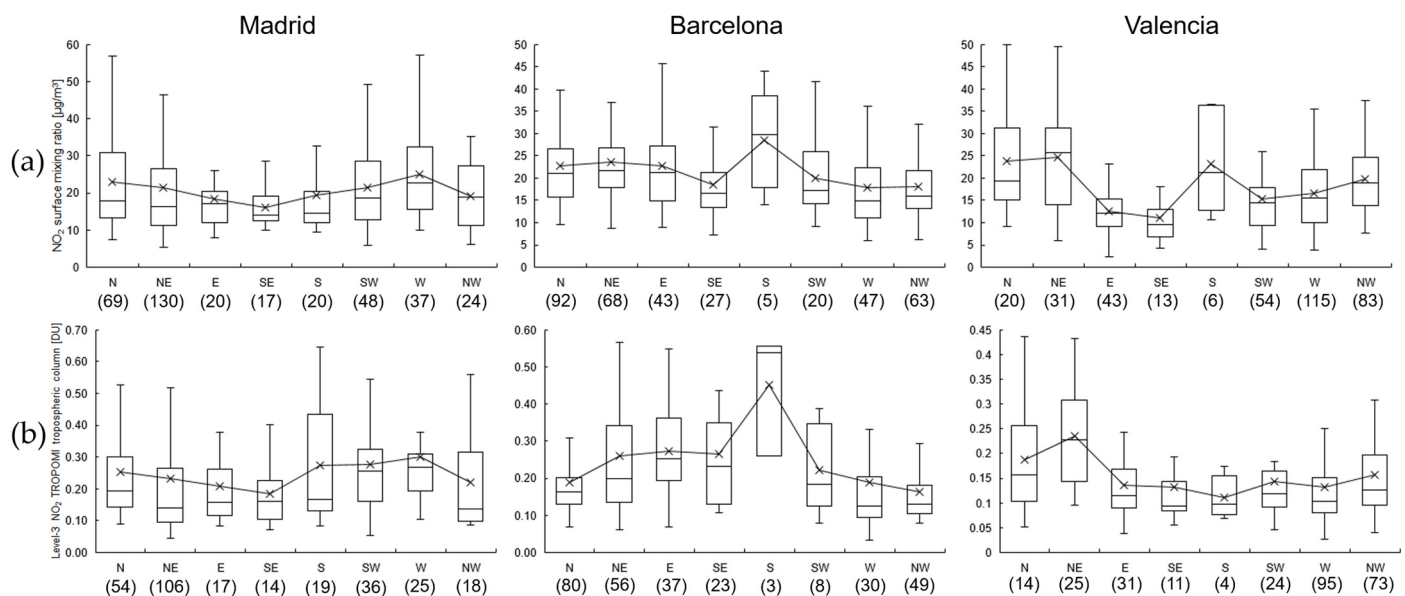


Figure 5. Boxplot of NO₂ concentration data measured by (a) air quality monitoring stations and (b) TROPOMI depending on wind direction in each city in 2022. The number of cases for each direction is indicated in parentheses.

The results were similar for both air quality monitoring stations (Figure 5a) and TROPOMI (Figure 5b) data. In Madrid, the lowest and highest NO₂ concentrations were observed for the SE (16 µg/m³ and 0.184 DU) and W (25.1 µg/m³ and 0.302 DU) directions, respectively, although with very slight differences. In Barcelona, these cases were observed for the NW (18.2 µg/m³ and 0.162 DU) and S (28.4 µg/m³ and 0.451 DU) directions, although S was the least frequent direction. Valencia showed more discrepancies than the other cities, although the highest concentrations were detected for the NE (24.6 µg/m³ and 0.235 DU).

A side-by-side comparison between Figures S2 and S3, Figures S4–S7 provides a more in-depth analysis of the influence of the wind on the spatial distribution of NO₂ concentration. In periods of higher speeds and more persistent directions, pollution hotspots tended to shift accordingly. This is particularly noticeable in Barcelona and Valencia, where wind speeds were consistently higher than in Madrid.

3.4. Study Variables Under Extreme NO₂ Conditions

Table 3 shows the average conditions in the top 10% and bottom 10% cases of NO₂ pollution.

Table 3. Average value of all study variables in the top 10% and bottom 10% (in parentheses) NO₂ concentration scenarios observed by air quality monitoring stations and TROPOMI in each city in 2022.

		O ₃ AQ [µg/m ³]	WS [m/s]	T [°C]	RH [%]	SR [W/m ²]
Madrid	AQ stations	31.5 (91.1)	0.57 (1.95)	14.3 (24.4)	56.6 (34.7)	356 (831)
	TROPOMI	40.6 (78.4)	0.6 (2.15)	14.8 (21.9)	46 (45.1)	488 (663)
Barcelona	AQ stations	46 (74.6)	5.31 (11)	18.7 (20.3)	59.2 (56.8)	411 (589)
	TROPOMI	47.3 (80.2)	6.05 (10.9)	15.7 (23.8)	55.6 (61)	454 (657)
Valencia	AQ stations	50.7 (79.8)	1.7 (3.99)	18.7 (22.8)	51.8 (46.5)	412 (576)
	TROPOMI	54.1 (82.8)	1.74 (3.23)	17.2 (24.6)	49.5 (52.8)	440 (666)

In all three cities, top and bottom NO₂ and O₃ concentrations were inversely related. The same pattern was observed for wind speed, temperature, and solar radiation, but not for relative humidity.

Extreme NO₂ data according to wind records are shown in Figure 6. In Madrid, most results accumulated in the NE direction, with wind speed being a determining factor.

Barcelona presented a more scattered distribution: air quality stations (Figure 6a) observed top NO₂ episodes accumulating between the NW and E, while bottom cases depended on wind speed. TROPOMI (Figure 6b) detected most top NO₂ episodes when the wind blew towards the sea, and bottom cases occurred for opposite directions. In Valencia, top NO₂ episodes frequently gathered between the W and NE, while most bottom cases took place towards the W direction.

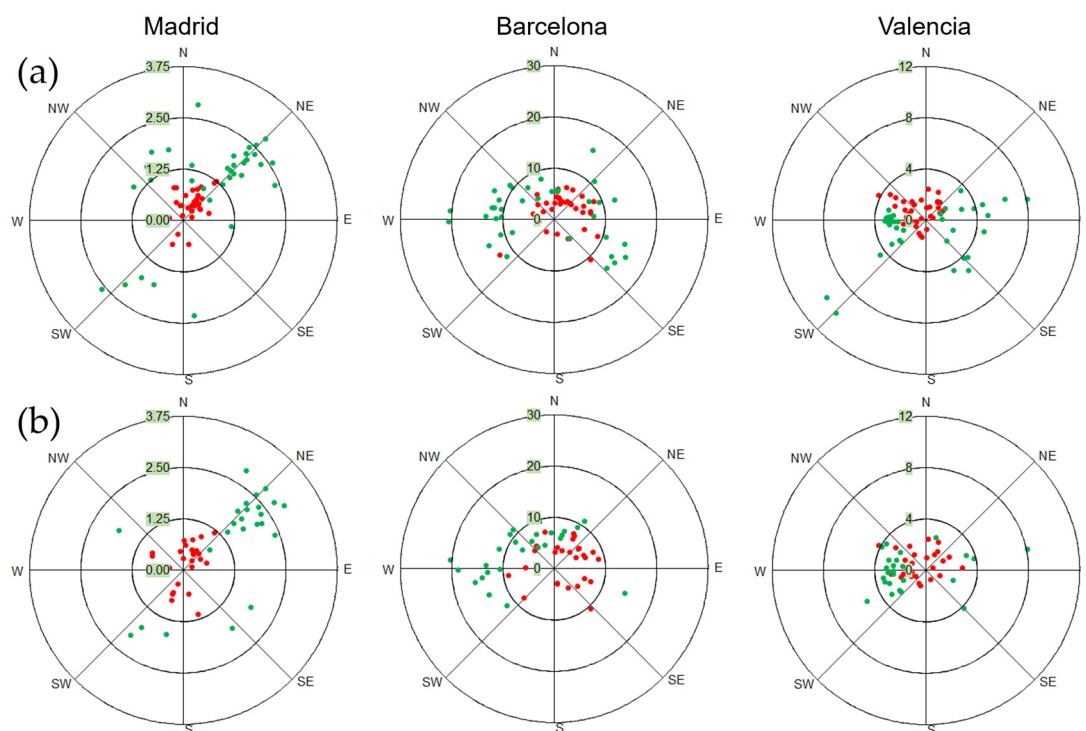


Figure 6. Wind speed and wind direction records in the top 10% (red) and bottom 10% (green) NO₂ concentration scenarios observed (a) by air quality monitoring stations and (b) by TROPOMI in each city in 2022.

3.5. Principal Component Analysis

PCAs were conducted in all cases to further analyze patterns between NO₂ concentration and all study variables. Table 4 shows the main results, with the original variables clustered in each principal component.

There was a consistent pattern in all performed PCAs. O₃ concentration, temperature, and solar radiation were always placed in the same group. Wind speed was also closely related to NO₂ concentration, in agreement with the correlation matrix in Table 2. Relative humidity was not associated with other variables.

In summary, the results show that NO₂ concentrations were highest in Madrid, followed by Valencia and Barcelona, both in satellite-based and in situ datasets. Temporal trends and 30-day moving averages showed similar seasonal patterns across data sources, with higher values during colder months. Correlation analysis indicated a consistent negative association between NO₂ and O₃, temperature, wind speed, and solar radiation in all three cities. The strongest linear correlation between satellite and surface NO₂ data was observed in Madrid ($r = 0.86$), followed by Valencia ($r = 0.68$) and Barcelona ($r = 0.65$). The PCAs grouped related meteorological and pollution variables into distinct components, which varied by city.

Table 4. Main results of the PCA application for the study variables at Madrid, Barcelona, and Valencia for each NO₂ dataset. Values in bold indicate the variables grouped in each principal component.

City	Parameter	AQ Stations			TROPOMI		
		PC1	PC2		PC1	PC2	
Madrid	NO ₂	−0.68	−0.60		−0.59	−0.67	
	O ₃	0.94	0.03		0.93	−0.02	
	Wind Speed	0.29	0.88		0.32	0.84	
	Temperature	0.85	−0.29		0.86	−0.25	
	Relative humidity	−0.84	0.35		−0.81	0.37	
	Solar radiation	0.92	−0.16		0.91	−0.15	
	Eigenvalue	3.70	1.36		3.54	1.39	
	Variance (%)	0.62	0.22		0.59	0.23	
	Cumulative variance (%)	0.62	0.84		0.59	0.82	
Barcelona							
Valencia							

4. Discussion

The results of this research are based on the officially available meteorological and air quality information in each study region. The most accurate approach to this study was to have simultaneous measurements of NO₂ and meteorological variables at the same locations. However, air quality and meteorological devices are not usually installed at the same points (Figure S2); thus, regional average values were obtained.

It should be noted that this study establishes a comparison between NO₂ observations of different natures. Ground stations measure surface-level mixing ratio, while satellites provide atmospheric column density data. Due to the origin and nature of NO₂, which has a short lifetime and mostly accumulates in the troposphere [18,53,54], both data groups show strong correlations in urban environments.

The linear correlation coefficients between in situ stations and TROPOMI NO₂ data were stronger in Madrid ($r = 0.86$) than in Barcelona ($r = 0.65$) and Valencia ($r = 0.68$). The temporal evolution of NO₂ pollution observed by satellite in all three cities followed a similar seasonal pattern. However, ground stations in Valencia and Barcelona detected an increase during spring that could not be entirely captured by TROPOMI. This discrepancy may partially be due not only to the influence of meteorological conditions on the NO₂ vertical profile but also to data availability (Table S1). Madrid has a larger in situ data series because its monitoring infrastructure is more extensive and has been active for a long time. On the other hand, Sentinel-5P always provides at least one daily observation (Table 1), which sometimes does not meet the pixel quality criteria. The proximity to emission sources must also be considered. Previous studies have found that TROPOMI encounters limitations in detecting spatial gradients of NO₂ concentration at smaller scales, particularly when compared to ground stations influenced by heavily trafficked roads or industrial plants [10,22]. These discrepancies could be more evident in cities with more limited air quality networks, such as Barcelona and Valencia (8 and 10 stations, respectively, compared to 24 in Madrid).

The geographical location and topography of each settlement can definitely play an important role as well. Madrid is placed in a mountain basin that limits movements between air layers during thermal inversion processes [55]. These conditions facilitate the retrieval of high quality pixel satellite images, resulting in a wider availability of TROPOMI data. Barcelona and Valencia are set at sea level on the Mediterranean coast, and experience more heterogeneous climatic conditions due to their proximity to the coastline. Wind speed data are the most evident case (Figure 4), as stronger winds induce air transport (Figures S2–S7) and mixing phenomena that hinder the immediate identification of surface-level pollution hotspots the emission sources. This may be the main reason why in Madrid, where the average wind speed is lower, in situ and satellite NO₂ datasets align more closely compared to the coastal cities. At the same time, this influence on the dispersion of air pollutants is reflected in the correlation coefficients in Table 2. In fact, wind speed was the only meteorological variable that yielded similar results across all cases.

The correlation coefficients of temperature and solar radiation with NO₂ data were equivalent, as they are highly related variables. Once emitted, the mean NO₂ lifetime is longer in winter than in summer. This difference is attributed to higher exposure to UV radiation during summer months, which triggers photolysis processes and chemical conversion into other substances [56]. The photolysis rate depends on the presence of aerosols, solar zenith angle, cloud cover, and temperature itself [57,58]. This seasonality is emphasized by the use of domestic heating during cold periods, which adds to the usual road transport activities [11,59].

This is consistent with O₃ concentration results, which presented the strongest negative correlation with both NO₂ datasets. As a photochemical pollutant, tropospheric O₃ is formed secondarily from reactions involving high solar radiation and temperature as well as other precursor gases, primarily NO_x and volatile organic compounds (VOCs). Thus, tropospheric O₃ levels rise in spring and summer, as opposed to NO₂ (Figure 3a) [60,61]. Furthermore, O₃ can undergo titration processes by NO, leading to an increase in NO₂ concentration.

The correlation between temperature and solar radiation with both NO₂ datasets was consistent in Madrid. In Barcelona and Valencia, a stronger correlation was only observed with TROPOMI observations. Notably, the highest average solar radiations were recorded in Madrid (Table 1), with the bottom 10% of NO₂ pollution cases taking place under 831 W/m² (Table 3).

Relative humidity showed no significant relationships with NO₂ pollution levels. In Madrid, a correlation coefficient of $r = 0.30$ was observed with air quality stations data (Table 2). Although humidity contributes to atmospheric transport processes through the formation of aerosol particles or wet deposition of pollutants, this value might result from a combination of the seasonal nature of emissions in Madrid and the prevalence of drier weather in the city during summer.

PCA results were coherent with these findings. Two main groups, or principal components, were constantly differentiated: one included O₃ levels, temperature, and solar radiation; and the other, wind speed (Table 4). NO₂ concentration always fell into one of these two clusters, meaning that to understand its variability and make accurate estimations, their information will be the most important.

Wind direction also plays a key role, but requires a separate analysis for each case. It determines how air masses are distributed away from or towards the sampling points and can significantly influence atmospheric composition, as shown in Figures S2–S7. Figure 5 depicts a similar distribution of NO₂ levels across wind directions for both data groups. In Madrid, the wind regime (Figure 4a) is shaped by its geographical location, set at the base of one of the main mountain chains of the Iberian Peninsula, the Central System, which divide its core from NE to SW. This is the cause of such persistent directions, leading to pollution being more dependent on wind speed (Figure 6). In Barcelona and particularly Valencia, where winds are consistently stronger, these patterns are influenced by their proximity to the coastline. In Barcelona, scenarios of higher pollution were more frequently observed between the NW and E, albeit with a widely scattered distribution. In Valencia, the worst air quality cases gathered between the NW and NE directions, whereas cleaner air events were associated with W winds. This means that information on wind direction is essential for characterizing changes in air quality in these locations but not so much in Madrid.

These findings are consistent with comparable research using air quality monitoring stations [26] and satellite imagery [27], which emphasize the importance of conducting individual analyses for each study region. In urban settings specifically, atmospheric composition is shaped by a multitude of interconnected drivers. In the cases referred to here, the most defining variables differ between inland and coastal cities. However, this information is not often considered for activating action protocols under high pollution episodes, and can definitely be used for making surface-level estimations.

This methodology could potentially be adapted to smaller municipalities by incorporating proxy variables such as land use, traffic density, and emission sources. Future satellite missions like Sentinel-4 may also enhance data availability for urban areas with more complex topography or limited monitoring infrastructure.

Certain methodological considerations should be acknowledged. The spatial resolution of Sentinel-5P, though improved, is still insufficient to capture fine-scale variability in NO₂ concentrations at the street level, particularly in dense urban areas. Satellite data availability is also subject to quality constraints due to factors such as cloud cover or low-quality retrievals. Additionally, the statistical approach followed here focused on identifying linear associations between variables. While this method is appropriate for exploring dominant patterns, non-linear interactions may require alternative analytical frameworks and could be addressed in future research.

5. Conclusions

Current Spanish action protocols for high-NO₂ pollution episodes do not consider meteorological scenarios for the assessment of severity and duration. Understanding the atmospheric dynamics of NO₂ in urban environments is key to policymaking and compli-

ance with air quality guidelines. This study explored the relationship between O₃ levels, five meteorological variables (wind speed, wind direction, temperature, relative humidity, and solar radiation), and the average NO₂ concentration from air quality stations and the TROPOMI sensor in the cities of Madrid, Barcelona, and Valencia during 2022. These locations were chosen due to significant NO₂ exposure concerns, which have not been previously addressed by comparing in situ and satellite data. The outcome helps identify the similarities and discrepancies between both datasets for making surface-level estimations.

Regional daily mean values were obtained between Sentinel-5P overpass times, which consistently occur between 12 p.m. and 4 p.m. TROPOMI data were obtained at the geographical position of the air quality monitoring stations. This methodology aligns with previous similar research [53,62].

In Madrid, NO₂ satellite measurements followed a similar trend to in situ data, yielding a high linear correlation coefficient ($r = 0.86$). In Barcelona ($r = 0.65$) and Valencia ($r = 0.68$), most discrepancies were found during warmer months. A preliminary statistical analysis revealed that Madrid's meteorological profile was also more stable than that of coastal cities, especially regarding wind speed and direction, which are heavily influenced by geographical location and orographic configuration. Their effect on the NO₂ formation, removal, mixing, or transport affects the relationship between atmospheric column and surface concentrations. As average wind speed increased, the correlation between NO₂ datasets decreased. The emissions profile of each location (which depends on the activity and time of year) and data availability must also be considered. Madrid has a network of 24 air quality stations for NO₂, compared to 8 in Barcelona and 10 in Valencia. Their proximity to emission sources can limit the comparison, since small spatial gradients are hardly noticeable via satellite. In addition, the availability of Sentinel-5P images varied across locations due to pixel quality criteria.

A correlation analysis showed that increased O₃ pollution and wind speed were linked to lower NO₂ concentrations in all three cities for both datasets. This is due to O₃ and NO₂ being involved in opposite formation processes, and wind speed promoting their dispersion. Temperature and solar radiation also presented an inverse relationship, as they trigger NO₂ photolysis (and hence O₃ formation). However, the results using in situ and satellite data were only comparable in Madrid. The distribution of NO₂ concentration based on wind direction showed an overall good agreement, although air quality in Madrid was more dependent on wind speed. Relative humidity did not show significant correlations in any case. The PCAs identified and confirmed these connections, with slight differences across cities and datasets. NO₂ was consistently associated with two clusters: one formed by O₃ concentration, temperature and solar radiation, and the other by wind speed.

These variations emphasize the need to study each location in order to evaluate the impact of meteorology on atmospheric pollution. According to the above results, the most influential study variables in air quality are O₃, wind speed, temperature, and solar radiation in Madrid; and O₃, wind speed, and wind direction in Barcelona and Valencia. Due to their consistency with in situ and satellite NO₂ datasets, this information is of great value to make accurate surface-level estimations, which will be the target of further research.

Future efforts should also focus on studying land cover, land use, and other existing features to better describe the role of anthropogenic factors in the regional distribution of NO₂. Surface-level data from other pollutants (e.g., particulate matter, SO₂, CO), could be of interest to gain insight into atmospheric conversion and removal processes. Eventually, air quality studies conducted via remote sensing will be particularly valuable in regions lacking monitoring infrastructure and for assessing the effectiveness of impact and mitigation policies from a regional perspective. This is especially relevant in Spain's current context, where legislation is being adapted to the European 2030 climate and energy framework.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nitrogen6020032/s1>, Figure S1: Geographical location of air quality monitoring stations (red circles) and meteorological stations (blue triangles) in the cities of (a) Madrid, (b) Barcelona, and (c) Valencia. Numbers correspond to those displayed in Table S1. Figure S2: Monthly maps of mean tropospheric TROPOMI NO₂ column (DU) over Madrid and its surroundings in (a) January, (b) February, (c) March, (d) April, (e) May, (f) June, (g) July, (h) August, (i) September, (j) October, (k) November, and (l) December of 2022. Black lines represent the city limits. Figure S3: Monthly distribution of wind distribution in Madrid in 2022: January (a), February (b), March (c), April (d), May (e), June (f), July (g), August (h), September (i), October (j), November (k), and December (l). Blue dots represent average wind speed and direction in a day between Sentinel-5P overpass times. Figure S4: Monthly maps of mean tropospheric TROPOMI NO₂ column (DU) over Barcelona and its surroundings in (a) January, (b) February, (c) March, (d) April, (e) May, (f) June, (g) July, (h) August, (i) September, (j) October, (k) November, and (l) December of 2022. Black lines represent the city limits. White lines represent the coastline. Figure S5: Monthly distribution of wind distribution in Barcelona in 2022: January (a), February (b), March (c), April (d), May (e), June (f), July (g), August (h), September (i), October (j), November (k), and December (l). Blue dots represent average wind speed and direction in a day between Sentinel-5P overpass times. Figure S6: Monthly maps of mean tropospheric TROPOMI NO₂ column (DU) over Valencia and its surroundings in (a) January, (b) February, (c) March, (d) April, (e) May, (f) June, (g) July, (h) August, (i) September, (j) October, (k) November, and (l) December of 2022. Black lines represent the city limits. White lines represent the coastline. Figure S7: Monthly distribution of wind distribution in Valencia in 2022: January (a), February (b), March (c), April (d), May (e), June (f), July (g), August (h), September (i), October (j), November (k), and December (l). Blue dots represent average wind speed and direction in a day between Sentinel-5P overpass times. Table S1: Air quality monitoring stations, meteorological stations, and data availability in each city under study. Station numbers correspond to those displayed in Figure S1.

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