# URBAN INFLUENCE ON INCREASING OZONE CONCENTRATIONS IN A CHARACTERISTIC MEDITERRANEAN AGGLOMERATION

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**Abstract**

Air quality in cities has been extensively studied due to the high population density potentially exposed to high levels of pollutants. The main problems in urban areas have been related to particulate matter ($PM$) and $NO_2$. Less attention has been directed towards $O_3$ because urban levels are generally lower than those recorded in rural areas. The implementation of air quality plans, together with technological improvements, have resulted in reductions of $PM$ and $NO_2$ levels in many European cities. In contrast, urban $O_3$ levels have experimented increases which may respond to declining $NO_x$ emission trends. It is therefore necessary to intensify the study of urban $O_3$ and its potential relation with $NO_x$ variations. In the agglomeration of Zaragoza (NE Spain), traffic circulation through the centre has dropped by 28.3% since 2008 due to several factors such as the implementation of a mobility plan, the completion of major construction projects and the economic crisis in Spain. The study of this case offers a unique opportunity to evaluate the impact of reductions in $NO_x$ emissions on the levels of $O_3$ in a characteristic Mediterranean city. This work analyses the variability and trends of ambient air levels of $O_3$ and $NO_x$ in Zaragoza and the Ebro valley from 2007 to 2012. Results demonstrate that, although the main factor explaining $O_3$ variability is still linked to meteorology, changes in $NO_x$ emissions strongly influence $O_3$ variability and trends, mainly due to interaction with fresh $NO$. Specific analysis of the $O_3$ "weekend effect" show a significant correlation ($r^2 = 0.81$) between the drop of $NO$ concentrations (associated to emissions) and the increment of $O_3$ levels during weekends. Moreover, trend analyses reveal that the decline in $NO_x$ emissions in Zaragoza from 2007 to 2012 can be associated with significant increments in $O_3$ levels.

*Keywords:* Ozone, urban areas, $NO_x$, emission reductions, weekend effect.

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## 1. INTRODUCTION

Ozone ($O_3$) is a trace gas with secondary origin, formed in the troposphere by means of reactions involving nitrogen oxides ($NO_x = NO + NO_2$) and volatile organic compounds ($VOCs$) in the presence of sunlight (see Atkinson (2000) for a complete description). Ozone acts as an important oxidant agent generating negative effects on health such as increased morbidity and mortality and alterations in the respiratory, cardiovascular and cerebrovascular systems (WHO, 2008; Sicard et al., 2011). $O_3$ affects vegetation and ecosystems by, among other impacts, visible leaf symptoms, defoliation, senescence and reduction in crop productivity (Paoletti, 2006; Sicard et al., 2011). Ozone also acts as a corrosive agent for natural and synthetic rubbers, plastic materials, surface coatings and buildings (de Leeuw, 2000; Screpanti and Marco, 2009). Finally, tropospheric ozone also acts as greenhouse gas absorbing earth's outgoing infrared radiation and altering the energy balance (IPCC, 2007).

Although variability and trends of surface $O_3$ in northern Europe have been widely studied (Vingarzan, 2004; Derwent et al., 2007; Sicard et al., 2009; Parrish et al., 2012), it is in the Mediterranean where ozone levels reach the highest levels (Cristofanelli and Bonasoni, 2009; Sicard et al., 2013). Climate-related factors such as high temperatures, intense solar radiation and frequent dry spells favour $O_3$ formation in southern Europe. Additionally, anthropogenic emissions of precursors across the continent have a decisive influence on the elevated levels of $O_3$ in the Mediterranean area. For example, frequent biomass burning mainly under dry summer conditions (Pace et al., 2005; Tressol et al., 2008), have been found to be responsible of the aggravation of $O_3$ (Adame et al., 2012). Furthermore, large emissions of natural and anthropogenic precursors in Central and Eastern Europe generate high concentrations of $O_3$ when continental air masses are transported towards the Mediterranean region (Lelieveld et al., 2002; Duncan et al., 2008). Finally, long-range transport of $O_3$ and its precursors from North America (Auvray and Bey, 2005) and Asia (Lelieveld et al., 2002) over the Mediterranean has also been suggested.

The Iberian Peninsula presents particular conditions associated with atmospheric dynamics which aid to increase $O_3$ levels, especially in spring and summer. The influence of the Azores high in summer establishes low horizontal pressure gradients across the Iberian Peninsula, leading to the predominance of local breeze cycles with limited spatial development and day/night alternating flows. These situations frequently produce recirculation processes on a regional scale, poor renovation of air masses and a dynamically confinement of polluted air layers. Under these circumstances, long residence time (ageing) of air masses and a gradual increase in the levels of $O_3$ and other pollutants especially in rural areas occur (Millan et al., 1996, 2000; Valdenebro et al., 2011). In consequence, most of the studies describing surface variability of $O_3$ in Spain have been oriented to rural or suburban areas (Garcia et al., 2005; Castell et al., 2008, 2012; Ezcurra et al., 2013). There are different reasons to explain this, such as the higher relative levels in natural/rural areas, the prominent negative effects of $O_3$ on vegetation and ecosystems and the need for characterising background contribution (de Leeuw, 2000). Some other works have included data from urban background sites often to make comparisons with rural data (Ribas and Peñuelas, 2004; Adame et al., 2008) although none have simultaneously assessed the differences between $O_3$ levels registered in kerbside, urban background, suburban and rural locations as result of the influence of the different anthropogenic $O_3$-precursor emission patterns (mainly $NO_x$).

The introduction since 1990 of new technologies in vehicles and stringent inspection systems associated to the EURO standards (Vestreng et al., 2009) have been successful in the reduction of global emissions of $NO_x$ in Europe and, in particular, in Western Europe. However, although ambient measurements of $NO_x$ slightly reflect the emissions drop, $NO_2$ levels have increased in cities. This is explained by the increase in $NO_2$ primary emissions related with the use of oxidation catalysts in diesel vehicles which are nowadays dominant in passenger car fleets (Carslaw, 2005; Grice et al., 2009; Anttila et al., 2011). In addition, emissions of total $NO_x$ from diesel vehicles in use have not decreased as expected comparing them with test cycles (Weiss et al., 2011). Finally, the economic crisis being endured in Mediterranean countries since 2008, particularly in Spain, may have resulted in reduced traffic flows in the region.

The elevated ambient air concentrations of $PM$ and $NO_2$ associated with traffic emissions is a common environmental issue in European urban agglomerations. This has motivated the implementation of emissions reduction plans aiming to improve air quality standards for those two pollutants. The question emerges on how the variability in the emissions of precursors ($NO_x$) is reflected on $O_3$ levels, especially in western Mediterranean cities. The possibility of an increment of urban $O_3$ levels associated with $NO_x$ reductions, given the size of population exposed, converts the urban $O_3$ into a highly relevant issue. As demonstrated by Sicard et al. (2013) in an extensive study analyzing the 2000-2010 trends of $O_3$ in urban, suburban and rural monitoring stations in the Mediterranean basin, average levels increased in cities and decreased in rural regions. It is therefore essential to evaluate the relationships between ozone and its precursors in urban areas when implementing environmental policies directed to reduce primary emissions.

This study aims to characterize the trends and variability of $O_3$ and $NO_x$ in a set of monitoring stations including kerbside, urban background, suburban and regional background types in a representative area of the Mediterranean (Zaragoza and the Ebro valley). The conclusions of this work may be extrapolated to other areas of Spain and the Mediterranean basin given the representativity of this area and the orientation of the study.

## 2. MATERIALS AND METHODS

*Study area.* Study area. The Central Ebro valley (NE Spain) is a relatively wide area which runs in the west-east direction. It is delimited by mountain ranges such as the Pyrenees (to the north), the Iberian range (to the south) and the Catalan coastal range (to the south-east). The climate in the central Ebro valley is semi-arid Mediterranean, characterized by extreme temperatures and low precipitation. Compared with other Mediterranean locations, winters are cold with frequent episodes of thermal inversions often associated with the development of dense fogs along the valley. Summers are usually hot, exceeding $35^\circ\ C$ on many days. The scarce precipitation (about 315 $mm/year$) is concentrated in spring and autumn. The characteristic wind regime is influenced by the orientation of the valley so two prevailing directions coexist. The first is a cold, dry north-westerly wind, which is often strong. The second is a hotter/warmer, more irregular, light wind from the south-east.

The main emission sources in the Ebro valley are road traffic with several busy highways crossing the valley longitudinally (the A-2, AP-2, A-68, AP-68 and AP-15) and transversally (the A-2 and A-23). Moreover, water availability and a propitious climate have favoured the development of a strong primary sector (agriculture and farming) with potential associated emissions. Among the industrial sources, there are seven gas power plants located along the valley. Finally, densely populated and industrialized regions with strong potential emissions border the Ebro valley to the east (the coastal metropolitan and industrial areas of Catalonia and Valencia), to the southwest (Madrid metropolis) and to the north-west (the Basque Country).

Located in the central Ebro valley, Zaragoza is a conurbation with $682,000$ inhabitants although the entire population of its metropolitan area may exceed $750,000$ (population density around $\sim$ 700 $inhabitants/km^2$). In recent years, Zaragoza has undergone a major transformation in aspects related with mobility. The completion of the Z-40 ring road around the city along with the introduction of a north-south light rail line has resulted in a 14.5% decrease in traffic of private vehicles on major entrance roads and a 28.3% decrease in the city centre since 2008 (Ayuntamiento de Zaragoza, 2014). Other circumstances that have contributed to this reduction may be the decline in economic activity associated with the economic crisis after 2008 and the completion of large construction projects (Expo 2008 and new residential districts, among others).

*Data.* For this study, hourly mean data of $NO$, $NO_2$ and $O_3$ corresponding to the period 2007-2012 from nine air quality monitoring stations have been used (Figure 1, Table 1). In Zaragoza, six stations from the municipal air quality network have been selected: four urban traffic (UT-CE, UT-JF, UT-PI, UT-RF) and two urban background (UB-LF, UB-RE). Outside Zaragoza, data from three monitoring stations along the Ebro valley have been also employed: a suburban station (SU-AL) and a regional background station (RB-BU), both belonging to the air quality network managed by the Government

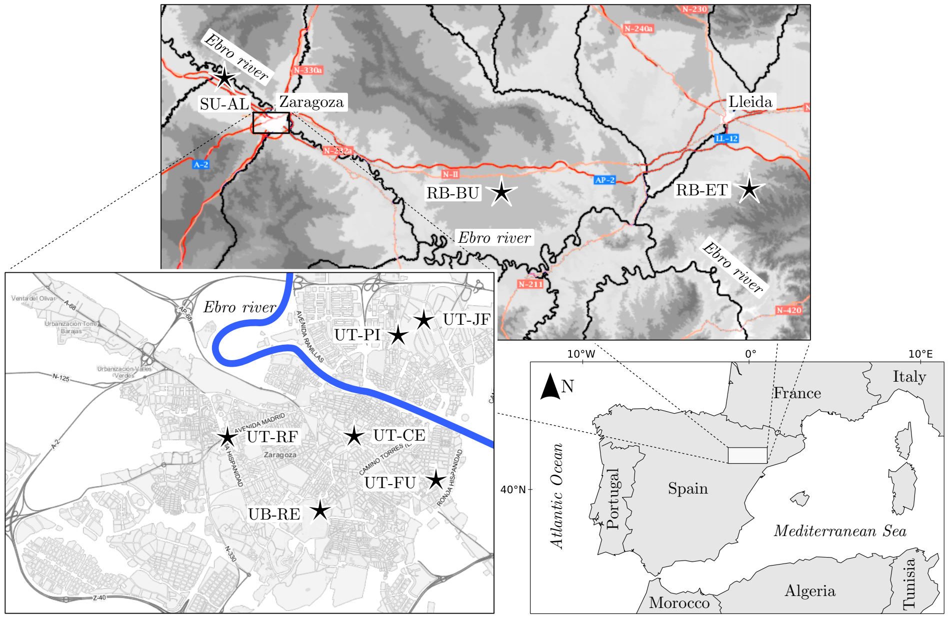



Figure 1: Location of the nine monitoring stations in Zaragoza and the Central Ebro valley providing data series of $O_3$, $NO$ and $NO_2$ used in this study.

of Aragón, and a regional background station from the EMEP network (RB-ET). All stations are equipped with $NO_x$ and $O_3$ automatic monitors based on the standard techniques: chemiluminiscence technique (UNE-EN 14211:2006) for $NO_x$ and UV photometry method (UNE-EN 14625:2005) for $O_3$. Monitors were tested and calibrated periodically according to the manufacturers' guidelines and maintenance planning ensured reliability of the measurements. Finally, wind direction and speed data have been were collected from the meteorological tower located at UT-JF station.

*Statistical tests.* Where necessary, the significance of the correlation between variables has been studied by means of the Spearman's rank test (Spearman, 1904). Spearman's Rank estimates if two random variables are related by a monotonic function by computing the linear correlation between the associated ranked variables. Moreover, the Wilcoxon's signed-rank test (Wilcoxon, 1945), which can be considered the nonparametric version of the paired Student's t-test, has been used to check the significance of the differences found between variables means. Finally, time trends for the annual means of $O_3$, $NO$ and $NO$ have been analysed in order to determine whether they are statistically significant by the non-parametric Mann–Kendall test. The Mann–Kendall test is applicable for the detection of a monotonic trend of a time series with no seasonal or other cycles. Moreover, the slope of the linear trend has been estimated by the nonparametric Sen's test. These operations have been carried out with MAKASEN'S template (Salmi et al., 2002).

| Station | Name | Lat. (N) | Long. (E) | Alt. (m.a.s.l.) | Network | Classification |
|---|---|---|---|---|---|---|
| UT-CE | Centro | 41° 38’ 54” | −0° 53’ 02” | 210 | Zaragoza | Urban traffic |
| UT-PI | El Picarral | 41° 40’ 13” | −0° 52’ 16” | 195 | Zaragoza | Urban traffic |
| UT-JF | Jaime Ferrán | 41° 38’ 54” | −0° 53’ 02” | 210 | Zaragoza | Urban traffic |
| UT-RF | Roger de Flor | 41° 39’ 05” | −0° 54’ 58” | 212 | Zaragoza | Urban traffic |
| UB-LF | Las Fuentes | 41° 38’ 13” | −0° 52’ 14” | 198 | Zaragoza | Urban background |
| UB-RE | Renovales | 41° 38’ 07” | −0° 53’ 37” | 220 | Zaragoza | Urban background |
| SU-AL | Alagón | 41° 30’ 20” | −0° 09’ 07” | 327 | Aragón | Suburban |
| RB-BU | Bujaraloz | 41° 45’ 46” | −1° 08’ 36” | 235 | Aragón | Regional background |
| RB-ET | Els Torms | 41° 23’ 37” | 0° 44’ 05” | 471 | EMEP | Regional background |

Table 1: Description of the monitoring stations employed in this study.

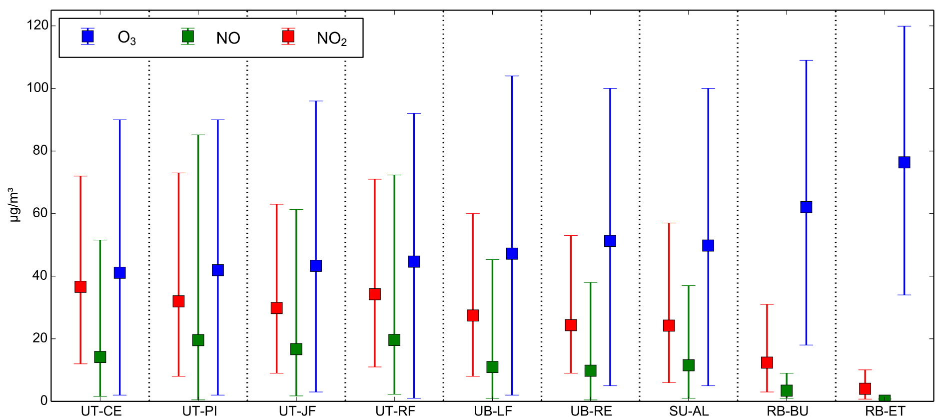



Figure 2: Average concentrations of $O_3$, $NO$ and $NO_2$ in the period 2007-2012 in the nine monitoring stations in Zaragoza and the Central Ebro valley. The bars indicate the range between the $5^{th}$ and $95^{th}$ percentiles.

## 3. RESULTS

Figure 2 shows the average concentrations of $O_3$, $NO$ and $NO_2$ for the period 2007-2012 in the nine stations analysed. Average $O_3$ levels on the studied stations are significantly anticorrelated with mean $NO$ and $NO_2$ levels according to Spearman’s Rank Test with significance levels greater that 99% and 99.5% respectively. Kerbside stations, with strong influence of direct traffic emissions, register the lowest mean levels of ozone and the highest of $NO_x$. In contrast, the lowest nitrogen oxide levels and the highest $O_3$ concentrations are found in rural stations where $O_3$ titration is reduced considerably by the low presence of $NO$. Finally, intermediate $NO_x$ and $O_3$ levels were registered in urban background and suburban sites.

The frequency distributions of $O_3$ (Figure 3) concentrations are a good characterisation of the

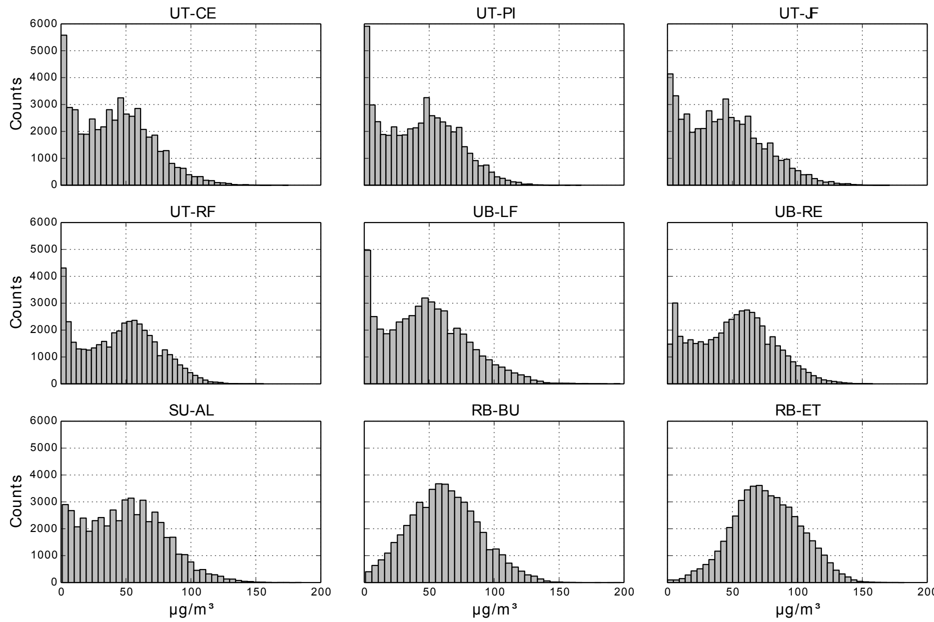



Figure 3: Frequency diagrams of the hourly concentrations of $O_3$ in the period 2007-2012 in nine monitoring stations in Zaragoza and the Central Ebro valley.

nature of the monitoring station because they capture the influence of the distance to $NO_x$ emission sources (mainly traffic). Rural stations present unimodal distributions for ozone (mode around $60-70$ $\mu g/m^3$) with concentrations rarely reaching below 15 $\mu g/m^3$ and a considerable number of cases above 100 $\mu g/m^3$. Urban and suburban stations which are more influenced by traffic, and consequently with higher levels of $NO$ and $NO_2$, show bimodal distributions. Kerbside stations present the main mode for low concentrations (around 5 $\mu g/m^3$), with a significant number of cases registered when ozone is consumed by fresh $NO$ emitted during rush hours, and a secondary mode for concentrations around $40-55$ $\mu g/m^3$. In suburban and urban background stations, the relative importance of the first mode decreases with respect to roadside sites, and the second mode shifts towards higher concentrations ($45-60$ $\mu g/m^3$).

*Variability of ozone and nitrogen oxides levels.* In coherence with other studies carried out in the Mediterranean region (Cristofanelli and Bonasoni, 2009), the seasonal pattern of $O_3$ is characterised by summer maxima and winter minima in all stations (Figure 4) due to increased photochemical activity. Average monthly levels of $O_3$ during the warm period (April-September) varied in the range $46-94$ $\mu g/m^3$ while lower levels were found in the remaining months ($15-85$ $\mu g/m^3$). The seasonal variability of nitrogen oxides (Figure 4) is less marked although it is clear that $NO$ and $NO_2$ levels fall in spring and summer ($0.1-14.0$ $\mu g NO/m^3$ and $2.0-36.8$ $\mu g NO_2/m^3$) with respect to autumn and winter ($0.2-41.5$ $\mu g NO/m^3$ and $3.8-46.7$ $\mu g NO_2/m^3$).

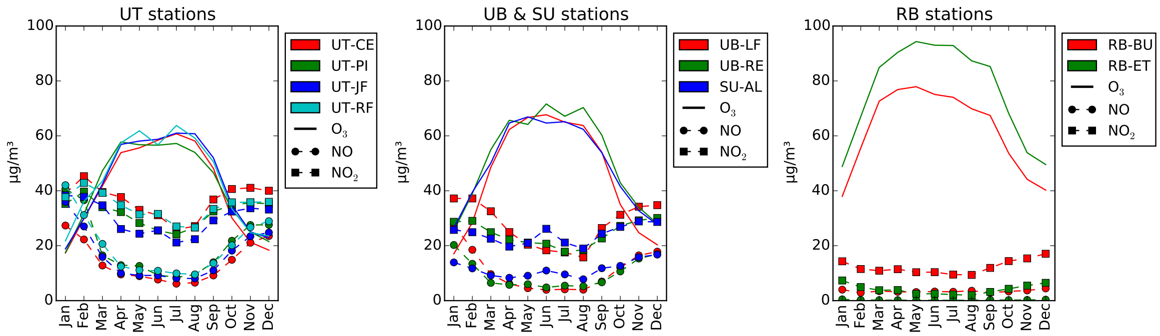



Figure 4: Monthly mean levels of $O_3$, $NO_2$ and $NO$ for the period 2007-2012 in nine monitoring stations in Zaragoza and the Central Ebro valley.

As regards daily variability (Figure 5), photochemical activity determines that $O_3$ concentrations increase during the day reaching the highest levels at around 15 UTC and diminish during the night. The negative correlation between $O_3$ and $NO_x$ throughout the day is also noteworthy (Figure 5). The distributions of $NO$ and $NO_2$ levels present two daily maxima corresponding with the rush hours (at about 7-8 UTC and 19-20 UTC).

Daily cycles of $O_3$, $NO$ and $NO_2$ show seasonal differences (Figure 5). Ozone daily cycles maintain their shape throughout along the year (maximum at around 15 UTC and two relative minima during rush hours) but a considerable increase in magnitude is detectable during spring and summer especially in the highest daily concentrations. With respect to $NO$ and $NO_2$, there are also morphological aspects of the mean daily curves that change throughout the year. $NO_2$ peaks in the evening are more pronounced than in the morning although this difference is greater in winter.

*Relationship between $O_3$, $NO_x$ and wind directions.* Two dominant wind directions prevail in Zaragoza, W-WNW being the most frequent, and SE the secondary. These wind components follow the direction of the Ebro River in Zaragoza and are channelled along the valley. The primary direction (W-WNW) is generally associated with higher wind speeds corresponding to situations when either the Azores High or, on occasions, Atlantic cyclones generate the transport of marine air masses over the Iberian Peninsula. Although the secondary component (SE) can occasionally be linked with transport caused by intense cyclogenesis processes over the Mediterranean (at synoptic scale), the most common meteorological situation inducing this transport over Zaragoza coincides with the establishment of a low pressure horizontal gradient at surface level when anticyclones cover the Iberian Peninsula and prevailing light SE mesoscale winds dominate circulation over Zaragoza and the Ebro basin.

*Trends in concentrations.* The evolution of annual means of the three pollutants along the period from 2007 to 2012 is presented in Figure 6. Urban and suburban stations show increasing $O_3$ concentrations

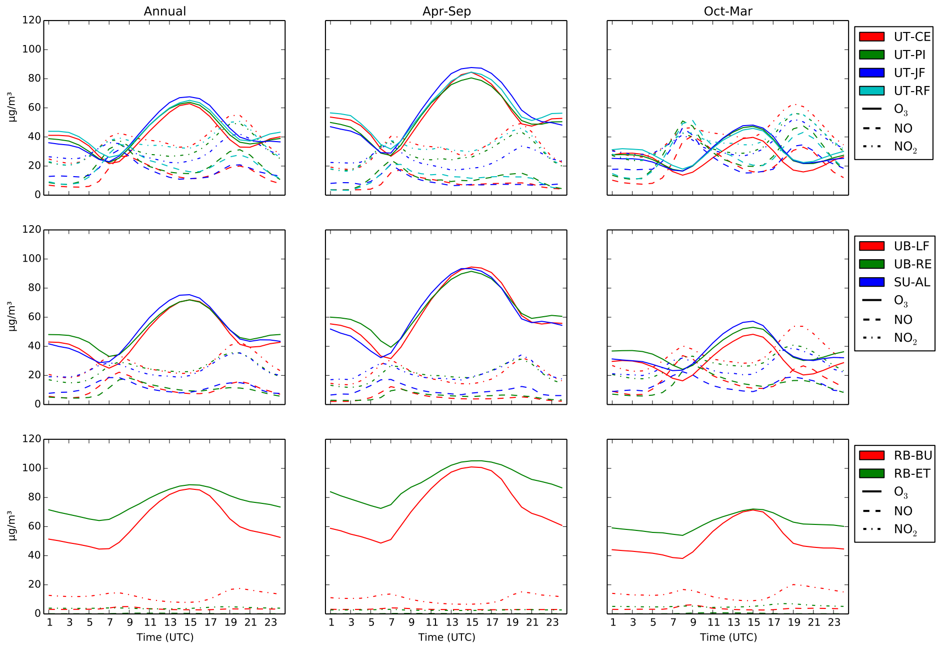



Figure 5: Average $O_3$, $NO_2$ and $NO$ daily cycles for the entire year and for the warm (April-September) and cold (October-March) seasons within the period 2007–2012, at the nine stations analysed in Zaragoza and the Central Ebro valley.

and declining $NO_x$ levels ($NO$ more prominently than $NO_2$) in the six years period while in rural sites, $O_3$, $NO$ and $NO_2$ levels remain stable.

## 4. DISCUSSION

*Variability of ozone and nitrogen oxides levels.* Ozone levels increase in summer and spring with respect to winter and autumn mainly due to photochemical activity. Moreover, the frequent occurrence of meteorological situations favouring strong synoptic stability, which result in recirculation and ageing of air masses in summer, also aid to increase $O_3$ levels. These events occur during a low horizontal pressure gradient at surface level, which allow the development of the Iberian thermal low and activate dynamic mesoscale circulations driven by thermal winds or breezes.

Conversely, $NO_x$ levels are lower in the warm seasons due to higher emissions in urban areas during autumn and winter (residential heating, industry and traffic) especially taking into account that traffic circulation is drastically reduced during the summer holidays (July-August). Another factor relates to lower photochemical activity in winter, which diminishes the rate of photolysis of $NO_2$ during the day. Moreover if, as stated before, $O_3$ levels are lower in winter, the destruction of $NO$ is also inhibited for that reason. Owing to all these circumstances, the ratio between the minimum and maximum monthly averages for $NO$ (0.28 as mean value of all stations) is considerably lower than for $NO_2$ (0.55).

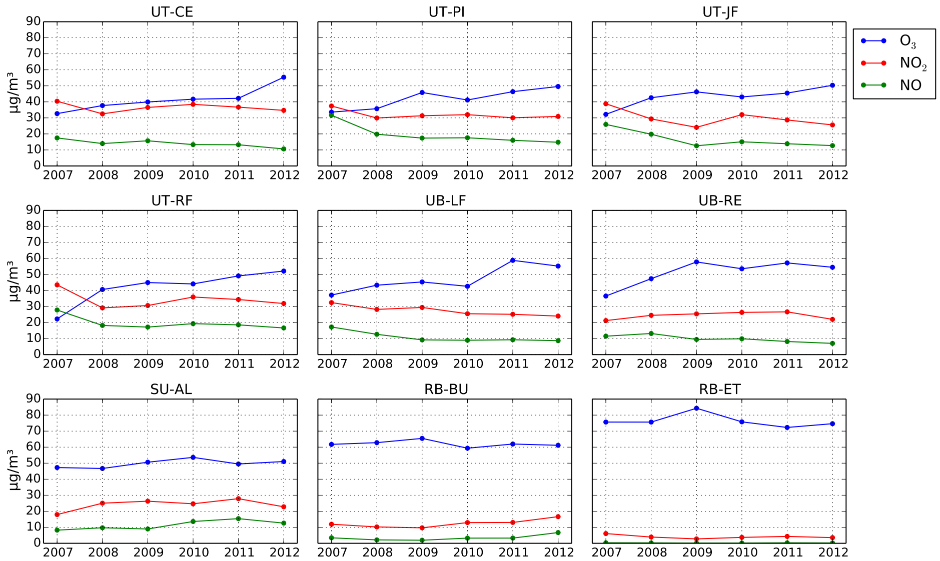



Figure 6: Evolution of annual mean levels of $O_3$, $NO$ and $NO_2$ in 2007-2012 in nine monitoring stations in Zaragoza and the Central Ebro valley.

Daily variability of $O_3$ concentrations is influenced by the solar cycle generating daytime maxima and nightime minima (Figure 5). However, the reduction rate between maximum and night levels of $O_3$ vary between urban and suburban stations ($33 - 45\%$) and regional background sites ($18 - 36\%$). This is mainly due to processes involving air masses, previously loaded with $O_3$ produced locally or regionally during daytime, which undergo recirculation and generate notable ozone concentrations in rural areas at night. Additionally, $O_3$ minima coincide with rush hours reflecting the net destruction effect of ozone by fresh $NO$ emissions. The decline in nitrogen oxides emissions around midday and the increased solar radiation allow $O_3$ to spike at around 15 UTC.

Several aspects related with emission patterns and interactions with ozone can also be highlighted from the daily cycles of $NO$ and $NO_2$ (Figure 5). Traffic emissions begin to increase at around 5-6 UTC coinciding with initial commuting towards work centres. These emissions, dominated by $NO$ versus $NO_2$ (95% $NO$ - 5% $NO_2$), are released into an atmosphere with moderate levels of $O_3$. Rapidly, $NO$ interacts with ozone to generate $NO_2$ and, in consequence, $NO_2$ increases faster (maximum at 7 UTC) than $NO$ (maximum at 8 UTC). This one hour shift between the two peaks is slight but noticeable in practically all the stations. Meanwhile, the $O_3$ morning minimum is recorded at 7 UTC and, in the following hours, concentrations rise when $NO_2$ photolysis is triggered by sunlight.

Seasonal Differences between average daily cycles of $O_3$, $NO$ and $NO_2$ are also observed (Figure 5). The highest summer concentrations of ozone, especially during the middle of the day, can be explained by photochemical factors. Moreover, $NO_2$ evening peaks are more intense than those in the morning, with a greater difference in winter. Morning maximums of $NO_2$ are mostly associated with traffic emissions during the commute to workplaces, schools, and so on, while during the evening peak additional sources of nitrogen oxides, such as domestic heating, also contribute to increased $NO_2$ levels. Heating systems are activated in winter during the evenings when citizens reach their homes, thereby incrementing the magnitude of the evening peak in cold months. The predominance of the evening maximum with respect to the morning one is not observed for $NO$, demonstrating the relative importance of traffic sources in the morning and also the efficient transformation of $NO$ to $NO_2$ in the presence of high $O_3$ concentrations of (considerably higher than in the morning). Finally, another factor to consider is that the evening rush hour in winter occurs after sunset which implies a lack of photochemical activity.

Another feature to outline about $NO$ and $NO_2$ daily cycles is the difference between the time of the evening maximum in summer and winter. While the morning maximum is observed systematically at 9 local time (8 UTC in winter, 7 UTC in summer), the evening peak undergoes a shift in summer compared with winter. $NO_2$ maximizes at 20 UTC (22 local time) in summer, while in winter the evening peak occurs at 19 UTC (20 local time). Finally, the $NO$ evening peak disappears during summer months while in winter it is still notable. Thus, there is a two hour shift that can be interpreted according to social habits of the population. In summer, when the weather is mild and sunlight lasts much longer in the day, people tend to stay out later in the street at sunset delaying the evening commute to 21-22 local time (20 UTC) when nitrogen oxides maxima are recorded. In winter however, with more severe weather predominating, the inhabitants return home earlier in the evening so the peak of $NO$ and $NO_2$ are recorded earlier (19-20 local time or 18-19 UTC).

Finally, the $NO$ evening peak disappears during summer while in winter it is still notable. In addition to higher emission rates and reduced dispersive conditions during winter (poor vertical development of the mixing layer and frequent occurrence of temperature inversions), what determines the reduction of the $NO$ evening peak in summer is the high concentration of $O_3$ which, very efficiently, oxidises $NO$.

*Relationship between $O_3$, $NO_x$ and wind directions.* Two prevailing winds dominate circulation in the Ebro valley. Transport from W-WNW was associated with lower pollutant levels because Atlantic transport leads to more dilution and dispersion linked with air mass renewal and, on occasions, periods of rainfall. Weaker winds from the SE sector generate higher residence time of pollutants and, often, rises in concentrations. Nevertheless, in order to interpret any increase in pollutants, the local characteristics of each monitoring site must be considered. Figure 7 shows images of UT-PI and UB-LF stations, highlighting their location relative to adjacent main roads. The influence of traffic emissions from nearby roads are reflected in a rise in pollutants. In particular in UT-PI, where $NO$

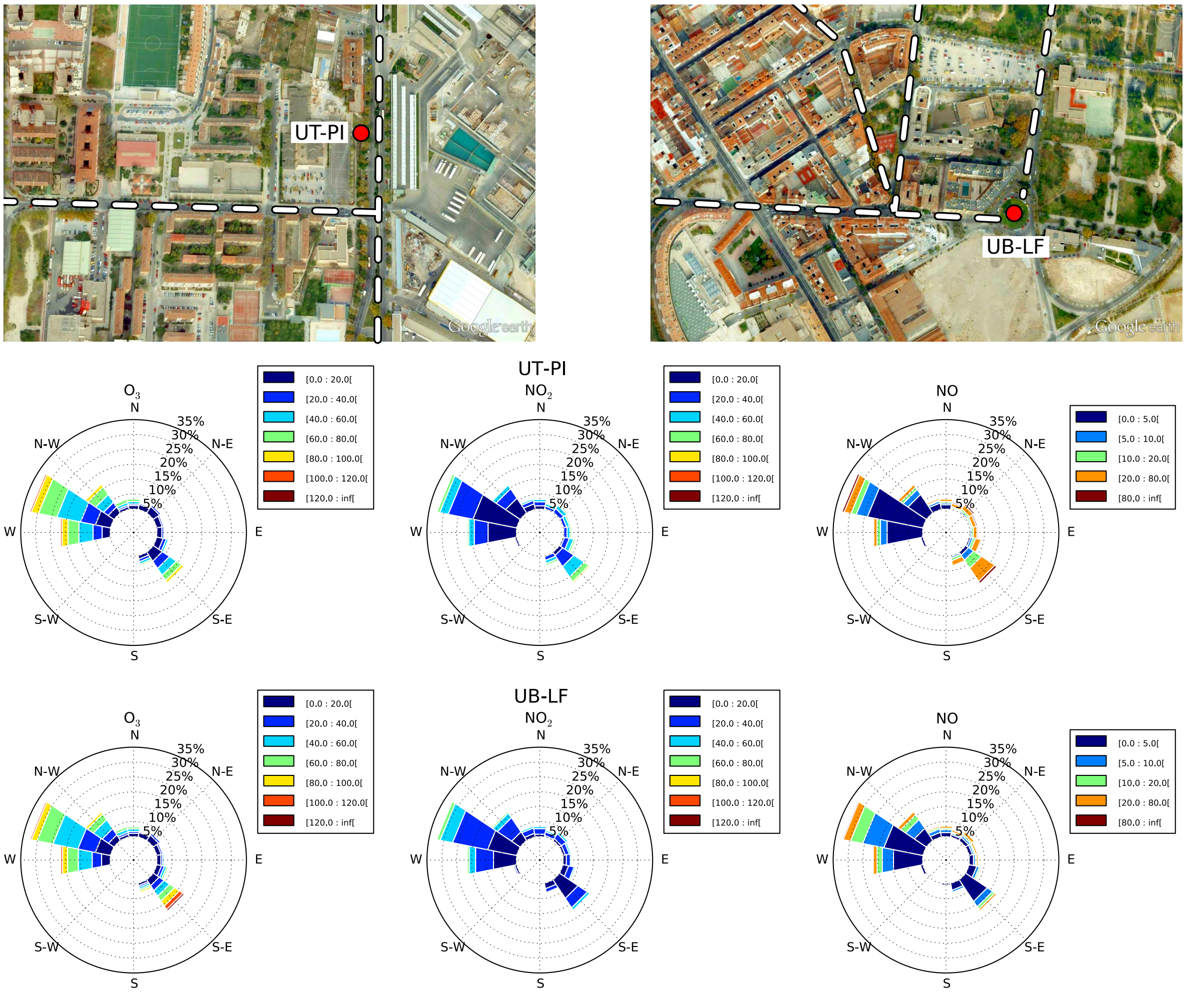



Figure 7: Location of UT-PI and UB-LF monitoring stations with main traffic roads highlited with dashed lines. Pollutant roses for $O_3$, $NO$ and $NO_2$ within the period 2007-2012 are also shown.

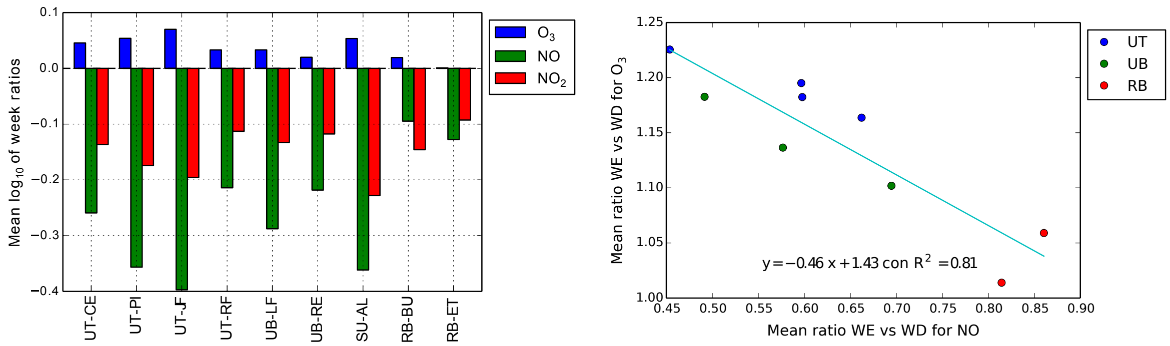
increases during SE transport while in UB-LF, $NO$ levels are often higher during W-WNW transport. $O_3$ concentrations are also influenced by the relative position of monitoring stations with respect to main roads due to N O consumption. In UB-LF, road traffic is more intense to the west of the station and considerable higher $O_3$ records are found with SE transport. In contrast, in UT-PI where the busy roads are located to the east, similar concentrations are found for SE and W-WNW winds.

*The "weekend effect".* The so-called "weekend effect" which consists in an elevation of concentrations during weekends is a particular feature in the time variability of $O_3$ in urban areas (Lebron, 1975). This has been documented in different studies (Altshuler et al., 1995; Jimenez et al., 2005; Atkinson-Palombo et al., 2006; Sadanaga et al., 2008; Castell et al., 2012) which presented several explanations for this effect such as a decrease in $NO_x$ emissions during weekends reducing $O_3$ tritation, a change in the time patterns of $NO_x$ emissions during weekends favouring $O_3$ formation, a shift from $NO_x$-sensitive towards VOC-sensitive conditions due to the reduction of $NO_x$ and increase in incident solar radiation during weekends helped by a reduction in the emission of anthropogenic aerosols.

In this area of study, concentrations of $NO$ and $NO_2$ on weekdays are clearly higher than during weekends due to traffic emissions associated with daily commuting. This has a direct impact on $O_3$ concentrations in urban and suburban stations reflected by higher relative levels of ozone during weekends. At regional background stations, with low exposure to direct traffic emissions, the difference between the levels of $O_3$ in weekend and weekdays is negligible (Figure 8(a)).

In order to quantify the magnitude of the "weekend effect" on levels of $O_3$ and nitrogen oxides in the study area, the differences between mean levels during weekdays and weekends have been computed weekly. Each weekend mean level has been compared with the average levels of the five adjacent weekdays (the previous Wednesday to Friday, and the following Monday and Tuesday) calculating the ratio of those two magnitudes. The differences between weekends and weekdays can thus be mainly attributed to variations in emissions and not to meteorological related factors. Finally, the values obtained for each week have been averaged (Figure 8(a)). Increases in $O_3$ concentrations during weekends are common for all the stations although the magnitude differs depending of the station type (increments of $16-23\%$ in traffic stations, $10-18\%$ in urban background and suburban sites, and $1-6\%$ in regional background stations). These differences are significant with a confidence level of 99.99%, following the Wilcoxon Signed Rank test, except in RB-ET where differences are not significant due to the limited influence of traffic sources. Regarding $NO$ and $NO_2$, the decrease in traffic emissions during weekends result in lower levels than on work days. Although $NO_2$ reductions are observed, the dominance of $NO$ in traffic primary emissions explain the greater decline of $NO$ during weekends. Traffic sites register the most prominent reduction during weekends ($34-55\%$ in $NO$ and $20-34\%$ in $NO_2$), with a lesser impact on urban background ($31-42\%$ in $NO$ and $21-24\%$ in $NO_2$) and in regional background ($14-19\%$ in $NO$ and $15-24\%$ in $NO_2$) stations. The influence of traffic emissions from the A-68 motorway, a primary access route into Zaragoza, on the suburban station SU-AL is critical to understand the considerable reduction in nitrogen oxides during weekends (51% in $NO$ and 38% in $NO_2$). High levels of significance (grater than 99.99% in all cases) are found by means of the Wilcoxon test for the differences between weekday and weekend mean levels for $NO$ and $NO_2$ nitrogen oxides.

The connection between reductions in traffic emissions (traced by $NO$ concentrations) and $O_3$ intensification during weekends is evaluated in Figure 8(b). A linear relationship with a high degree of correlation ($r^2 = 0.81$) is established between the rates of reduction of $O_3$ and increment of $NO$ in the nine stations studied. This finding is relevant because it highlights the impact of $NO$ reductions associated, or not, with emissions control on the increment of $O_3$ levels especially in urban areas.




(a) (b)

Figure 8: (a) Logarithm of the ratio between mean levels of $O_3$, $NO_2$ and $NO$ during weekends and during weekdays (b) Correlation between the mean weekends/weekdays ratios of $O_3$ and $NO$ concentrations within the period 2007-2012 at the nine stations analysed in Zaragoza and the Central Ebro valley.

*Concentration trends.* Table 2 illustrates the results of the application of the Mann-Kendall test to determine the significance of time trends. In the study period, ozone increased significantly (to a level of 95% in all cases) in traffic stations with slopes of $3.0 - 4.1$ $\mu g/m^3$ per year. In urban background, suburban and rural stations, $O_3$ trends in the period 2007-2012 were not statistically significant although urban background and suburban sites showed a clear positive trend while rural stations presented a slight negative drift. Annual levels of $NO$ showed significant downward trends (95% significance in all cases) in urban background sites and two kerbside stations (TR-CE and TR-PI) with falls varying between $-1.0$ and $-1.4$ $\mu g/m^3$ per year. In the other two traffic sites (TR-RF and TR-JF), high absolute values for the S-test statistic have been obtained. Suburban and rural sites show non-significant trends for $NO$, positive for SU-AL and RB-BU and weakly negative for RB-ET. Finally, $NO_2$ levels do not show statistically significant trends. UB-LF is the exception with a decrease of $-1.6$ $\mu g/m^3$ per year with a 95% significance level.

The considerable reduction of $NO$ and the associated increase in ozone levels in urban stations, may be partly explained by the execution of a mobility plan in Zaragoza. This plan included the implementation of a north-south light rail line and a limitation of private vehicle flows through the city centre in virtue of a reevaluation of the circulation in that area. This plan has resulted in a 28.3% decrease of private vehicles circulating through the city centre since 2008 and a decrease of 14.5% along the roads entering the city. Additional factors that may have contributed to the decline in $NO_x$ levels after 2007 are the completion of major construction projects (Expo 2008 international exhibition, Z-40 ring road and the Valdespartera suburb in the south of the city) or the reduction in traffic and industrial emissions associated with the economic crisis.

Another factor to consider is the overall reduction in Europe of $NO$ emissions associated with new vehicle technologies according to EURO standards, which have not been so successful for $NO_2$ due to

| | $O_3$ | | | $NO$ | | | $NO_2$ | | |
|---|---|---|---|---|---|---|---|---|---|
| Station | S | Signific. | Slope ($\mu g/m^3$ per yr) | S | Signific. | Slope ($\mu g/m^3$ per yr) | S | Signific. | Slope ($\mu g/m^3$ per yr) |
| UT-CE | 15 | $\alpha = 0.01$ | 3.0 | $-13$ | $\alpha = 0.05$ | $-1.3$ | $-3$ | ns | $-0.6$ |
| UT-PI | 13 | $\alpha = 0.05$ | 3.2 | $-13$ | $\alpha = 0.05$ | $-1.4$ | $-3$ | ns | $-0.6$ |
| UT-JF | 11 | $\alpha = 0.05$ | 3.3 | $-9$ | ns | $-2.0$ | $-7$ | ns | $-2.5$ |
| UT-RF | 13 | $\alpha = 0.05$ | 4.1 | $-7$ | ns | $-1.0$ | $-1$ | ns | $-1.6$ |
| UB-LF | 9 | ns | 3.6 | $-11$ | $\alpha = 0.05$ | $-1.1$ | $-13$ | $\alpha = 0.05$ | $-1.6$ |
| UB-RE | 7 | ns | 3.3 | $-11$ | $\alpha = 0.05$ | $-1.0$ | 7 | ns | 0.7 |
| SU-AL | 7 | ns | 0.9 | 9 | ns | 1.5 | 3 | ns | 0.9 |
| RB-BU | $-3$ | ns | $-0.3$ | 4 | ns | 0.6 | 9 | ns | 0.9 |
| RB-ET | $-4$ | ns | $-0.3$ | $-3$ | ns | 0.0 | $-5$ | ns | $-0.1$ |

Table 2: Results of the application of the Mann-Kendall trend test and of the Sen's test for the estimation of the slope trend for the 2007-2012 mean annual concentrations of $O_3$, $NO_2$ and $NO$ in nine monitoring station in Zaragoza and the Central Ebro valley. ns: $\alpha < 0.05$.

an increase in emissions of primary $NO_2$, particularly in diesel vehicles (Carslaw, 2005; Grice et al., 2009; Anttila et al., 2011). This would aid to explain why the significant reduction of $NO$ levels found in the urban sites of Zaragoza is not associated with a significant reduction in $NO_2$ levels.

## 5. SUMMARY AND CONCLUSIONS

This paper focusses on the study of $O_3$ level variations in response to $NO_x$ emissions changes in urban environments. With this objective, 2007-2012 data from monitoring stations located in the agglomeration of Zaragoza and rural areas along the Ebro valley have been analysed. Major reduction of traffic in the city centre (28.3%) has occurred in Zaragoza since 2008 responding to three main factors: the implementation of a mobility plan, the effects of the economic crisis and the completion of large construction projects. Both Zaragoza and the Ebro valley can be considered representative areas of the Mediterranean region so the results could be extrapolated to other areas of Spain and the Mediterranean region, referring the potential impact of reductions in $NO_x$ emissions on $O_3$ levels in the urban context.

Two main factors influence ozone variability: meteorology and $NO_x$ emission patterns. Firstly, meteorological factors such as photochemical activity and atmospheric stability (the frequent occurrence in summer of meteorological conditions favouring strong synoptic stability which give rise to air mass recirculation and ageing) explain the maximum $O_3$ levels recorded in spring and summer and, along the day, the increment during the daytime.

The influence of $NO_x$ emission patterns (mainly from traffic although other combustion sources can be considered) is basic to understand certain aspects of the ozone variability and concentration trends in the period 2007-2012. The results in Zaragoza and the Ebro valley show the impact of titration caused by $NO$, which results in $O_3$ destruction within the photochemical cycle involving $NO_x$ and $O_3$. At the average level, traffic stations showed higher $NO_x$ and lower $O_3$ levels than urban background and suburban sites, while regional background stations, located far from combustion sources, presented the lowest $NO_x$ and the highest $O_3$ concentrations. $O_3$ daily variability is also influenced by $NO_x$ emission patterns. The mean daily cycle shows two minima during rush hours (at around 9 h LT and 21 h LT) reflecting the $O_3$ destruction by titration in the presence of elevated levels of $NO$ in urban sites.

As mentioned above, the reduction of traffic circulation through the city centre is reflected by significant reductions of $NO$ concentrations throughout the study period in urban sites. With a net reduction of $NO$, and the associated weakening of titration processes, average $O_3$ levels significantly increased in urban sites in Zaragoza in the same period.

The ozone "Weekend effect" consists in an increment of $O_3$ levels during weekends which different authors have explained as being caused by different reasons such as a decrease in $NO_x$ emissions reducing $O_3$ tritation, a change in the time patterns of $NO_x$ emissions during weekends, a shift from $NO_x$-sensitive towards VOC-sensitive conditions or an increase in incident solar radiation during weekends caused by a reduction in aerosols emissions. In urban stations of Zaragoza, mean levels of $O_3$ during weekends are $9 - 17\%$ higher than during weekdays coincident with significant reductions in mean $NO$ $(35 - 66\%)$ and $NO_2$ $(21 - 34\%)$ average concentrations as a result of the reduction of traffic emissions during weekends. In regional background sites, $O_3$ increments and $NO_x$ reductions are more moderate than in Zaragoza. There is a significant correlation between increments of average $O_3$ levels and decrease of mean NO levels during weekends. This result demonstrates the important impact of traffic emissions reductions on increasing $O_3$ in Mediterranean cities.

The results presented in this work are relevant in order to evaluate environmental policies oriented to the reduction of primary emissions in the Mediterranean area, providing the demonstrated risk of incrementing $O_3$ levels in cities where population exposure is greater than in rural regions. It is therefore essential to continue collecting data on $NO_x$ and $O_3$ in urban areas and incorporate $VOCs$ for continuous monitorisation. In particular, the characterisation of the spatial variability of all these parameters in complex urban environments is essential. Moreover, there are still open issues regarding aspects such as determining the dominating chemical or physical factors in the production of the effect of $NO_x$ reduction in $O_3$ growth. To this aim, efforts should be directed towards developing detailed urban emissions inventories with a particular focus on traffic sources and the use of modeling tools, such as box photochemical models, in order to provide some guidance on the most effective means of emissions reduction in a specific area.

## 6. ACKNOWLEDGEMENTS

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## 7. SUPPORTING INFORMATION

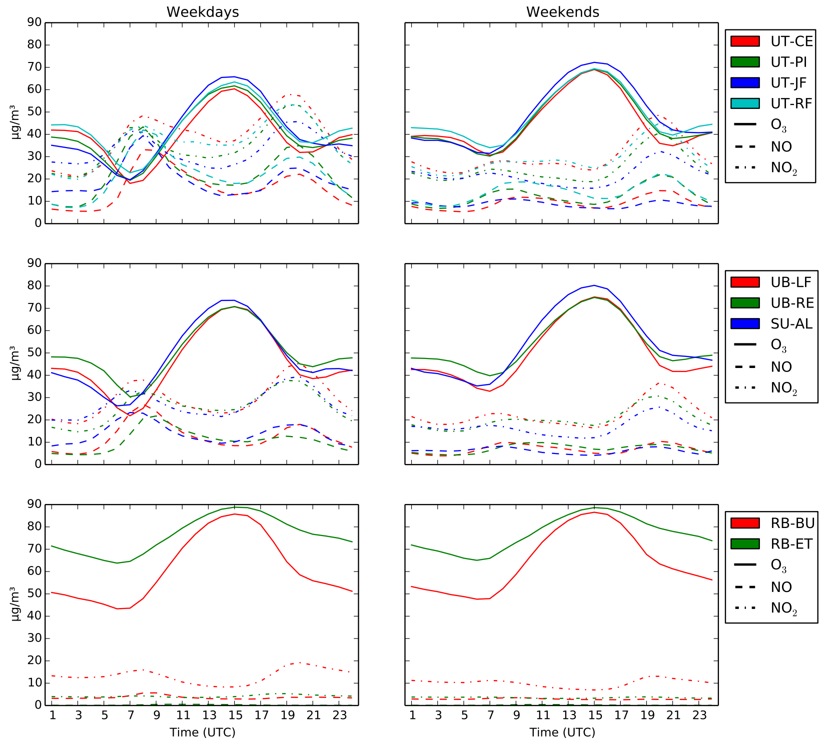


Figure 9: Differences between weekend and weekday mean $O_3$, $NO$ and $NO_2$ levels within the period 2007-2012 at the nine stations analysed in Zaragoza and the Central Ebro valley.