

# [The local and regional oxidants health and social care essay](https://assignbuster.com/the-local-and-regional-oxidants-health-and-social-care-essay/)

Climate Research Group, Division of Environmental Physics and Meteorology, Faculty of Physics, University o f Athens, University Campus Bldg. Phys. V, Athens 15784, GreeceAbstract. A comparison of the local and regional oxidants levels between Athens and Puertollano is attempted in the current study. In more details, we applied the analysis proposed recently by Notario et al. (2013) on the oxidant levels of two monitoring stations of the greater Athens basin, an urban and a background one, during 2001-2011 and 2007-2011, respectively. Total agreement is observed between Athens and Puertollano stations regarding the annual average data of [NO], [NO2], [NOx], [O3], [Ox] at each hour of the day. Studying the variation of NO, NO2 and O3 with the level of NOx for daylight and nighttime, exactly similar results are exhibited between the background station of Athens and both stations of Puertollano. As far as the monthly variation of NOx levels is concerned, the diurnal values are continuously higher (lower) than the nocturnal values at the background (rural) station, whereas at Puertollano stations diurnal [NOx] is observed to be higher than nocturnal one, during only few months of the year. A progressive increase of the daylight and nighttime average [NO2]/[Ox] vs [NOx] is observed for both Athens and Puertollano stations, showing a larger proportion of Ox in the form of NO2 when the level of NOx increases. Similar results are also observed studying the variation of mean values of [NO2]/[NOx] vs [NOx] between Athens and Puertollano stations. Finally, we indicate the differences between Athens and Puertollano as far as the monthly variation of regional and local Ox concentration is concerned (during daylight and nighttime).\*Corresponding author. E-mail address: covar@phys. uoa. gr (C. Varotsos)

## 1 Introduction

Clapp and Jenkin (2001) studied the relationships between ambient concentration of ozone (O3), nitric oxide (NO) and nitrogen dioxide (NO2) as a function of nitrogen oxides (NOx = NO + NO2), using monitoring data from the UK Automatic Urban and Rural Network. They attempted to establish how the level of " oxidant" (Ox = O3 + NO2) varies with the level of NOx, in order to contribute to the knowledge of the atmospheric sources of Ox, particularly at polluted urban locations. They also indicated that Ox concentration consists of NOx-independent ‘ regional’ contribution (corresponds to the regional background O3 level) and NOx-dependent ‘ local’ contribution (correlates with the level of primary pollution). Furthermore, it was proposed that the local oxidant source has probable contributions from direct NO2 emissions, from the thermal reaction of NO with oxygen at high NOx and from common-source emission of species which promote NO to NO2 conversion. Clapp and Jenkin (2001) also tried to define expressions which describe the possible variation of annual mean NO2 versus NOx (at 14 urban and suburban sites) and which can take into consideration possible changes in the regional background of O3. Three years later, Jenkin (2004) examined the diurnal and seasonal dependence of sources of oxidant, and their origins, by using hourly mean concentration data for NO, NO2 and O3 at Marylebone Rd (an urban kerbside site in London). He studied the concentrations of oxidant ([Ox]) as a function of the sum of a NOx-independent regional contribution and a linearly NOx-dependent local contribution. As it was derived, the regional [Ox] display a significant seasonal variation, with an obvious peak in April, giving similar results to those reported for background ozone at low altitude sites in northwest Europe. On the other hand, the local Ox contribution seemed to present a strong diurnal variation, throughout the year, with maximum values at the daytime hours. Han et al. (2011) investigated the relationship between O3 distribution and its association with ambient concentrations of NO, NO2 and NOx, using the continuous measurement of NO, NO2, NOx and O3 in Tianjin (during 8/9-15/10/2006). The concentrations of the studied pollutants versus the hours of day seemed to be maximized in succession in the daytime, whereas the ground-level ozone concentration peaked in mid-day. Han et al. (2011) also proposed a linear relationship between NO2 and NOx as well as NO and NOx, and a polynomial relationship between O3 and NO2/NO. Furthermore, they certified previous scientific studies, showing that the concentration of Ox at a given location consists of two parts: one independent and the other dependent on NO2 concentration, while the independent part (~20 ppb in Tianjin) was considered as a regional contribution. They also indicated an obvious difference in NO, NOx and O3 concentrations between weekdays and weekends and finally, they tried to analyze the diurnal variation of O3 concentration under different meteorological conditions (Mazzeo et al. 2005). Recently, Notario et al. (2012) studied the concentrations of O3, NO, NO2, NOx and Ox in the southwest of the Iberian Peninsula (Seville, during 2004), an area with frequent photochemical pollution events, mainly in the warm season. They based on observation data obtained at an urban traffic station and a suburban one. Monthly dependence of regional and local [Ox] variation was studied, at both stations, together with the annual variation of the daily mean NOx and Ox. As it was derived, at the suburban station, maximum levels of Ox > 190 μg m−3 with NOx < 70 μg m−3, and Ox < 170 μg m−3 with NOx around 80–90 μg m−3 are expected in summer months and during the daytime. On the other hand, during summer, at the nocturnal hours, more elevated NOx levels are needed in order to achieve maximum Ox values (Ox = 130–150 μg m−3 with NOx ≥ 100 μg m−3 at the suburban station, Ox = 110–130 μg m−3 with NOx ≥ 100 μg m−3 at the urban traffic station). In the present paper, we attempt a comparison of the local and regional oxidants levels between Athens and Puertollano. In other words, we applied the analysis proposed recently by Notario et al. (2013) on the oxidant levels of two monitoring stations of the greater Athens basin, an urban and a background one, during 2001-2011 and 2007-2011, respectively.

## 2. Data and analysis

The present analysis is based on NO, NO2, NOx, O3, Ox observation data, obtained during 2001–2011 at Patission station (38°N, 23. 44°E) located at the central part of the Athens basin, and during 2007-2011 at Aliartos station (38. 22°N, 23. 6°E) located 95 km northwest of Athens. The first station is considered to be the most representative for the air pollution pattern of the Athens basin (urban station). The second one (rural station) is located away from the town emissions and is characterized as a background station. It is well known that air pollution can be released at one location and travel long distances through the atmosphere with prevailing winds. In this way, air pollution can affect air quality locally as well as many miles away (i. e. long-range transboundary air pollution) (Varotsos et al. 2001). The long-range contribution to ozone levels is equivalent to the regional background of ozone, which includes naturally occurring ozone. This contribution is not strongly influenced by single emission sources and should be roughly equivalent to (a) those measured at rural (background) locations and (b) air pollution levels estimated by regional air transport models. To examine the homogeneity of observation data for both Patission and Aliartos station, we applied the non-parametric Friedman test, separately on each time series, comparing several parts to each other to find out if all of them follow the same distribution-law. Friedman test resulted in homogeneity of data for both stations, at 95% confidence level.

## 3. Discussion and results

Recently, Notario et al. (2013) selected two stations, Barriada 630 and Campo de Fútbol, in order to study the behaviour and variability of local and regional oxidant levels in Puertollano (38. 42°N, 04. 07°W), during 2008-2009. Campo de Fútbol (sited in suburbs to the SE of the town centre) is a suburban station heavily influenced by industrial emissions that is located 60 m from the nearest motorway. Barriada 630 (sited in a residential zone in the north of Puertollano) is an urban station with more elevated traffic emissions (3 m from the nearest). This location is less affected by industrial emissions since it is more shielded and distanced from the industrial sources. The present paper aims to gain some insight into the photochemical air pollution in the greater Athens basin (37. 58-38°N, 23. 43-23. 72°E) by applying the analysis proposed by Notario et al. (2013) on the oxidant levels of the two stations mentioned above, Patission and Aliartos. Fig. 1 shows the annual average data at each hour of the day for [NO], [NO2], [NOx], [O3], [Ox] at Aliartos, during 2007-2011 and at Patission, during 2001-2011. It is obviously seen that the O3 and Ox levels are much higher at Aliartos than at Patission, a fact which is due to the ozone formation and transportation far from the center of Athens. In addition, the O3 and Ox maxima are observed during 14: 00-17: 00, for both monitoring stations, whereas the NO, NO2 and NOx peaks are noted during 7: 00-9: 00 and 21: 00-23: 00. These results are in total agreement with the Notario et al. (2013) analysis, but it is worthy of note that the maximum of [NOx] (observed at Barriada 630 in 2008) was 62μgr m-3, while for Patission is 311 μgr m-3 and for Aliartos is 29. 4 μgr m-3. Fig. 2 depicts variation of NO, NO2 and O3 with the level of NOx at Aliartos and Patission station for daylight and nighttime. The best fit polynomial curves are also shown in Fig. 2, which seem to be statistically significant (according to t-test and F-test) at 95% confidence level. Regarding the O3 levels included in Fig. 2, these are much higher in Aliartos than in Patission, a fact which can be explained due to the long-range transboundary air pollution, at a backaground station such as Aliartos. As far as the values of [NO2], [NOx] and [O3] are concerned, the [O3] seems to decrease as [NOx] increases, while NO and NO2 levels rise along with NOx levels. For Aliartos, it is obviously noted that NO and NO2 levels are very similar at lower mixing ratios, while NO2 dominates at higher NOx levels, mainly in nocturnal. This behavior was also observed in Notario et al. (2013) analysis for both Barriada 630 and Campo de Fútbol station. On the contrary, for Patission station, NO levels are higher than NO2 levels, in both diurnal and nocturnal period. Moreover, inspection of Fig. 2 shows that the [NOx] intersection point during daylight hours (under photostationary state conditions) occurs at ~100 μg m−3 and ~42 μg m−3 for Patission and Aliartos, respectively. Besides, when [NOx] is lower than these values, O3 levels are higher than NO values, whereas NO dominates at higher NOx levels. Regarding the corresponding intersection point in the Notario et al. (2013) analysis, it was observed at ~96 μg m−3 for Campo de Fútbol and ~94 μg m−3 for Barriada 630. at Patission station for daylight, (c) at Aliartos station for nighttime, (d) at Patission station for nighttime. The polynomial fit curves are also shown. Aliartos daylight: NO2: y = -0. 007x2 + 0. 887x - 0. 557 with R² = 0. 94, NO: y = 0. 007x2 + 0. 113x + 0. 556 with R² = 0. 85, O3: y = 0. 017x2 - 2. 305x + 92. 602 with R² = 0. 26. Patission daylight: NO2: y = -0. 0004x2 + 0. 466x + 14. 963 with R² = 0. 71, NO: y = 0. 721x - 33. 541 with R² = 0. 94, O3: y = 0. 0004x2 - 0. 301x + 69. 142 with R² = 0. 54. Aliartos nighttime: NO2: y = -0. 009x2 + 1. 172x - 2. 504 with R² = 0. 93, NO: y = 0. 0085x2 - 0. 172x + 2. 502 with R² = 0. 66, O3: y = 0. 005x2 - 1. 262x + 64. 983 with R² = 0. 27. Patission nighttime: NO2: y = -0. 0007x2 + 0. 513x + 15. 239 with R² = 0. 63, NO: y = 0. 816x - 46. 69 with R² = 0. 95, O3: y = 0. 0004x2 - 0. 331x + 61. 064 with R² = 0. 63. In the following, we depicted the variation of Ox concentration with the level of NOx during daylight and nighttime at Aliartos and Patission station, in order to show the local and regional contribution of Ox (Fig. 3). The slope obtained from the regression analysis of the [Ox] versus [NOx] plot represents the local Ox contribution, while the intercept represents the NOx-independent regional contribution. The latter is equivalent to the O3 background concentration and the former is a local contribution that depends on the primary pollution. Local contribution to the formation of Ox is a linear function of the local emissions. Total Ox concentration seems to decrease (increase) linearly with NOx levels in Aliartos (Patission) and generally fits well to a linear regression (during both the diurnal and nocturnal period). It is worthy of note that the statistical significance of all the above mentioned linear fits were confirmed by using t-test and F-test, at 95% confidence level. Studying the corresponding figure in Notario et al. (2013) analysis, the slope of the [Ox] vs [NOx] plot was observed to be higher for daytime than nighttime, being close to zero during the night in both stations. Fig. 3 Variation of hourly mean Ox concentration with NOx during daylight and nighttime (a) at Aliartos station and (b) at Patission station. Regression analysis yields, Aliartos daylight: y = -1. 112x + 90. 25 with R² = 0. 13. Patission daylight: y = 0. 154x + 85. 28 with R² = 0. 26. Aliartos nighttime: y = -0. 286x + 64. 3 with R² = 0. 025. Patission nighttime: y = 0. 061x + 87. 9 with R² = 0. 073. Fig. 4 shows the monthly variation of NOx levels at Aliartos and Patission during daylight and nighttime hours. At Aliartos, the diurnal values are continuously higher than the nocturnal values, whereas the exact opposite applies to Patission station. From the other hand, at Barriada 630 and Campo de Fútbol station, diurnal [NOx] was observed to be higher than nocturnal one, during only few months of the year (Notario et al., 2013). Furthermore, studying Fig. 4, a parallel change of [NOx] is observed during the diurnal and nocturnal period, especially in Patission. Regarding the trend of the diurnal and nocturnal curves, a continuous decrease from January until August (May-June) is observed for Patission (Aliartos), and then rising until November. This is clearly observed in Patission, while there is an exception in Aliartos, where maximum NOx levels were measured in February, August and November, for nighttime. Similar results were observed in Notario et al. (2013) analysis, where monthly variation of [NOx] showed a continuous decrease from January until June or July, and then rising until November or December. This was clearly observed in Barriada 630, whereas in Campo de Fútbol there was any exception in the mentioned tendency: March, July and August. To know the proportion of Ox in the form of NO2, the variation of daylight and nighttime average [NO2]/[Ox] with [NOx] was represented in Fig. 5(a, c) and Fig. 5(b, d) for Aliartos and Patission, respectively. A progressive increase of this ratio was observed, showing a larger proportion of Ox in the form of NO2 when the level of NOx increases. This is the expected behaviour during daylight where the photo-stationary state operates. Besides, a well-mixed layer allows smaller proportion of NO2 because of the time for conversion of emitted NO to NO2 is less. At nighttime, as it is shown in Fig. 5(c, d), the proportion of Ox in the form of NO2 is large due to the reaction NO+O3. The corresponding analysis at Barriada 630 and Campo de Fútbol stations gave exactly the same results (Notario et al., 2013). Fig. 5 Variation of mean values of [NO2]/[Ox] versus [NOx] (a) for Aliartos during daylight (b) for Patission during daylight, (c) for Aliartos during nighttime and (d) for Patission during nighttime. Fitted empirical expressions are: 5(a): [NO2]/[Ox] = -3∙10-6[NOx]3 + 0. 0002[NOx]2 + 0. 0093[NOx] - 0. 0033 with R² = 0. 73. 5(b): [NO2]/[Ox] = 1∙10-8[NOx]3  1∙10-5[NOx]2 + 0. 0055[NOx] + 0. 162 with R² = 0. 82. 5(c): [NO2]/[Ox] = -3∙10-6[NOx]3 + 0. 0002[NOx]2 + 0. 0128[NOx] + 0. 0153 with R² = 0. 66. 5(d): [NO2]/[Ox] = 1∙10-8[NOx]3  2∙10-5[NOx]2 + 0. 0063[NOx] + 0. 172 with R² = 0. 85. In order to know the possible source of the local NOx-dependent contribution, we depicted the variation of mean values of [NO2]/[NOx] versus [NOx] for Aliartos and Patission, during the respective measurement periods (Fig. 6a, b). High concentrations of NO2 within the PBL are directly related to anthropogenic NOx emission. The largest NOx emission sources come from combustion and industry processes followed by road transport (Baldasano et al. 2008; Baldasano et al. 2011). Figure 6(a) shows that, in Aliartos (a background station), from [NOx] ≈ 15 μg m−3, the [NO2]/[NOx] ratio decreases when the NOx levels increase, while in Patission (an urban station), the [NO2]/[NOx] ratio presents a continuous decreasing change (Fig. 6b). It is worthy of note that, in the corresponding figure of Notario et al. (2013) analysis, the data from both the selected stations were shown together and the [NO2]/[NOx] ratio was observed to decrease after [NOx] ≈ 20 μg m−3. Fig. 6 Variation of mean values of [NO2]/[NOx] versus [NOx] (a) for Aliartos and (b) for Patission. Fitted empirical expressions are: 6(a): [NO2]/[NOx] = 2∙10-5[NOx]3  0. 0015[NOx]2 + 0. 036[NOx] + 0. 578 with R² = 0. 29. 6(b): [NO2]/[NOx] = -5∙10-9[NOx]3 + 5∙10-6[NOx]2  0. 0024[NOx] + 0. 78 with R² = 0. 60. Fig. 7 depicts the monthly variation of regional and local Ox concentration for daylight and nighttime in both Aliartos and Patission. The vertical bars included in the picture represent the error, ±σ. According to that figure, the regional Ox concentration is higher (lower) for daylight than nighttime, at Aliartos (Patission) station. However, there is an exception in the above mentioned comparison, regarding April at Patission, where the regional [Ox] is lower during the nocturnal period. For both stations, the peaks of the regional Ox concentration are observed in March or April and in July or August. Studying the local Ox concentration at Aliartos, it seems to be maximized in July and October, for both daylight and nighttime, while at Patission, the two maxima are observed in June and September. Comparing these last results with the Notario et al. (2013) study (where the data from both the selected stations were once more shown together), a same trend was observed in both the diurnal and nocturnal curves with higher local Ox concentrations during daylight hours. Furthermore, maximum Ox levels were obtained in June and July, whereas the minimum daytime Ox concentrations were measured in January and November. Finally, the minimum nighttime Ox concentrations were measured from January to April, and September to December. All the above mentioned results can be used as an approximation to estimate the oxidant concentrations in Athens and Puertollano, as a function of the NOx measured, as well as to improve in the atmospheric photochemical dynamic in the Mediterranean area where there are undeniable air quality problems (Millan et al. 1997; Polymenakou et al., 2008; Varotsos et al., 2012; 2005; 2003). of regional Ox concentration for daylight and nighttime (a) in Aliartos and (b) in Patission. Monthly variation of local Ox concentration for daylight and nighttime (c) in Aliartos and (d) in Patission. The vertical bars included in the picture represent the error, ±σ.

## 4. Conclusions

We applied the analysis proposed recently by Notario et al. (2013) on the oxidant levels of two monitoring stations of the greater Athens basin, Patission (during 2001-2011) and Aliartos (during 2007-2011), in order to study the photochemical air pollution in Athens. According to the analysis and discussion presented above the following findings may be drawn: The annual average data of [O3] and [Ox] are much higher at Aliartos than at Patission, a fact which is due to the ozone formation and transportation far from the center of Athens. In addition, the [O3] and [Ox] maxima are observed during 14: 00-17: 00, for both monitoring stations, whereas the [NO], [NO2] and [NOx] peaks are noted during 7: 00-9: 00 and 21: 00-23: 00. These results are in total agreement with the Notario et al. (2013) analysis, but it is worthy of note that the maximum of [NOx] (observed at Barriada 630 in 2008) was 62μgr m-3, while for Patission is 311 μgr m-3 and for Aliartos is 29. 4 μgr m-3. Studying the variation of NO, NO2 and O3 with the level of NOx at Aliartos and Patission station for daylight and nighttime, the O3 levels are much higher in Aliartos than in Patission, a fact which can be explained due to the long-range transboundary air pollution, at a backaground station such as Aliartos. As far as the values of [NO2], [NOx] and [O3] are concerned, the [O3] seems to decrease as [NOx] increases, while NO and NO2 levels rise along with NOx levels. For Aliartos, it is obviously noted that NO and NO2 levels are very similar at lower mixing ratios, while NO2 dominates at higher NOx levels, mainly in nocturnal. This behavior was also observed in Notario et al. (2013) analysis for both Barriada 630 and Campo de Fútbol station. On the contrary, for Patission station, NO levels are higher than NO2 levels, in both diurnal and nocturnal period. Total Ox concentration seems to decrease (increase) linearly with NOx levels in Aliartos (Patission) and generally fits well to a linear regression (during both the diurnal and nocturnal period). Studying the corresponding figure in Notario et al. (2013) analysis, the slope of the [Ox] vs [NOx] plot was observed to be higher for daytime than nighttime, being close to zero during the night in both stations. As far as the monthly variation of NOx levels is concerned at Aliartos and Patission (during daylight and nighttime hours), it was derived that, at Aliartos, the diurnal values are continuously higher than the nocturnal values, whereas the exact opposite applies to Patission station. From the other hand, at Barriada 630 and Campo de Fútbol station, diurnal [NOx] was observed to be higher than nocturnal one, during only few months of the year (Notario et al., 2013). Furthermore, a parallel change of [NOx] is observed during the diurnal and nocturnal period, especially in Patission. Regarding the trend of the diurnal and nocturnal curves, a continuous decrease from January until August (May-June) is observed for Patission (Aliartos), and then rising until November. This is clearly observed in Patission, while there is an exception in Aliartos, where maximum NOx levels were measured in February, August and November, for nighttime. Similar results were observed in Notario et al. (2013) analysis, where monthly variation of [NOx] showed a continuous decrease from January until June or July, and then rising until November or December. This was clearly observed in Barriada 630, whereas in Campo de Fútbol there was any exception in the mentioned tendency: March, July and August. A progressive increase of the daylight and nighttime average [NO2]/[Ox] vs [NOx] is observed, showing a larger proportion of Ox in the form of NO2 when the level of NOx increases. The corresponding analysis at Barriada 630 and Campo de Fútbol stations gave exactly the same results (Notario et al., 2013). Studying the variation of mean values of [NO2]/[NOx] vs [NOx] for Aliartos and Patission (during the respective measurement periods), it was derived that, in Aliartos, from [NOx] ≈ 15 μg m−3, the [NO2]/[NOx] ratio decreases when the NOx levels increase, while in Patission, the [NO2]/[NOx] ratio presents a continuous decreasing change. It is worthy of note that, in the corresponding figure of Notario et al. (2013) analysis, the data from both the selected stations were shown together and the [NO2]/[NOx] ratio was observed to decrease after [NOx] ≈ 20 μg m−3. Regarding the monthly variation of regional and local Ox concentration for daylight and nighttime in both Aliartos and Patission, the regional Ox concentration is higher (lower) for daylight than nighttime, at Aliartos (Patission) station. However, there is an exception in the above mentioned comparison, regarding April at Patission, where the regional [Ox] is lower during the nocturnal period. For both stations, the peaks of the regional Ox concentration are observed in March or April and in July or August. Studying the local Ox concentration at Aliartos, it seems to be maximized in July and October, for both daylight and nighttime, while at Patission, the two maxima are observed in June and September. Comparing these last results with the Notario et al. (2013) study (where the data from both the selected stations were once more shown together), a same trend was observed in both the diurnal and nocturnal curves with higher local Ox concentrations during daylight hours. Furthermore, maximum Ox levels were obtained in June and July, whereas the minimum daytime Ox concentrations were measured in January and November.