Ozone Levels in Portugal: the Lisbon Region Assessment

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ABSTRACT

Ozone levels in southern European countries have been particularly high in last Summers. New European legislation will enter into force obliging Member States to develop abatement measures in case of alert thresholds exceedances. Therefore, it is crucial to implement an effective air quality assessment, in order to ensure that abatement measures are successful.

In this context, several diffusive sampling campaigns were performed, aiming both to complement monitoring stations results and to analyze distribution patterns under different meteorological conditions. Different kinds of campaigns took place: two at national level, and two at a regional level. Passive samplers were exposed during one-week period. In the case of the national campaigns samplers were distributed throughout background locations only while in the second set of campaigns tubes were exposed in all kinds of locations.

In parallel with these measurements, 5-years datasets from the official air quality monitoring network were used in order to establish trends and correlations with meteorological parameters such as temperature, global solar radiation, wind directions, and wind velocities. Several statistical analyses such as principal component analysis were performed, particularly for interpreting peak episodes.

Passive samplers results pointed out very high average levels situated far from the coast, where no monitoring network currently exists. The statistical analyses focused particularly for the Lisbon area. Preliminary results show the strongest correlation between temperature and ozone levels.

INTRODUCTION

Ozone is a pollutant with a significant contribution to the degradation of ambient air quality in urban areas. Due to its climate conditions, the Lisbon area in Portugal is an example such an urban area affected high ozone levels, particularly during the Summer.

Ozone is a secondary pollutant. Is not emitted directly from tailpipes or smokestacks, but instead it is formed in the atmosphere as a result of reactions between other emitted pollutants. These primary pollutants (ozone precursors) result from the use of gasoline, other petrochemicals, and fossil fuels, and they are emitted largely by industry and automobiles.

Ozone is one of the main products of tropospheric chemistry. The source of atomic oxygen for ozone formation in the troposphere is nitrogen dioxide through the following basic cycle:

$$NO_2 + h\nu \rightarrow NO + O$$
$$O_2 + O + M \rightarrow O_3 + M$$
$$O_3 + NO \rightarrow NO_2 + O_2$$

M represents a molecule that absorbs vibrational energy and thereby stabilizes the O_3 formed, while hν is the energy from solar radiation necessary for the reaction to take place. In urban areas reactions are more complex: volatile organic compounds (VOCs), nitrogen oxides (NO_x), and hydroxyl radical (OH) play important roles in ozone formation. The ratio between VOCs and NO_x could determine if ozone is either formed or removed. For a given level of VOCs there is a NO_2 concentration correspondent to a maximum amount of ozone produced: an optimum VOC-to-NO_x ratio.[1]

Meteorological conditions also play an important role in the ambient ozone concentrations.[2] The main meteorological variable that influence surface ozone concentrations is the temperature although wind speed, ultra-violet radiation, atmospheric stability, atmospheric moisture and long-range transport could also have a significant role in ozone formation.[3]

METHODOLOGY

Most of the tropospheric ozone assessment in Portugal has been performed by analyzing gathered by air quality monitoring stations located in the coastal area of the country. Until recently, there were no monitoring stations located inland, since the priority was to evaluate the concentrations close to the most populated areas. A few steps were taken in the last few years to provide a better understanding of the ozone levels, from the overall country levels to a close-up through the Lisbon area. A combination of diffusive sampling campaigns performed at different scales and at different time periods combined with the analysis of air quality monitoring stations data enabled a better assessment of tropospheric ozone levels in Portugal. The role of meteorology was also evaluated for this pollutant that presents considerably high concentrations, particularly during hot Summer periods.

The Lisbon regional diffusive sampling campaign

A detailed campaign was promoted by the Commission for Regional Development of Lisbon and Tagus River Valley Region (CCDR-LVT) using the same type of diffusive samplers previously used in the national campaign. The area of this campaign involved the administrative area of Lisbon and the Tagus River Valley.

A total of 560 samplers were distributed over 479 monitoring sites selected taking into account parameters as total population, population density, and territorial area units - the sub-municipalities administrative level (*freguesias*).

A seven day exposure time period was used for both campaigns:

- 2001 Summer campaign (from July, 3rd to July, 10th) and,
- 2002 Winter campaign (from January, 29th to February, 5th).

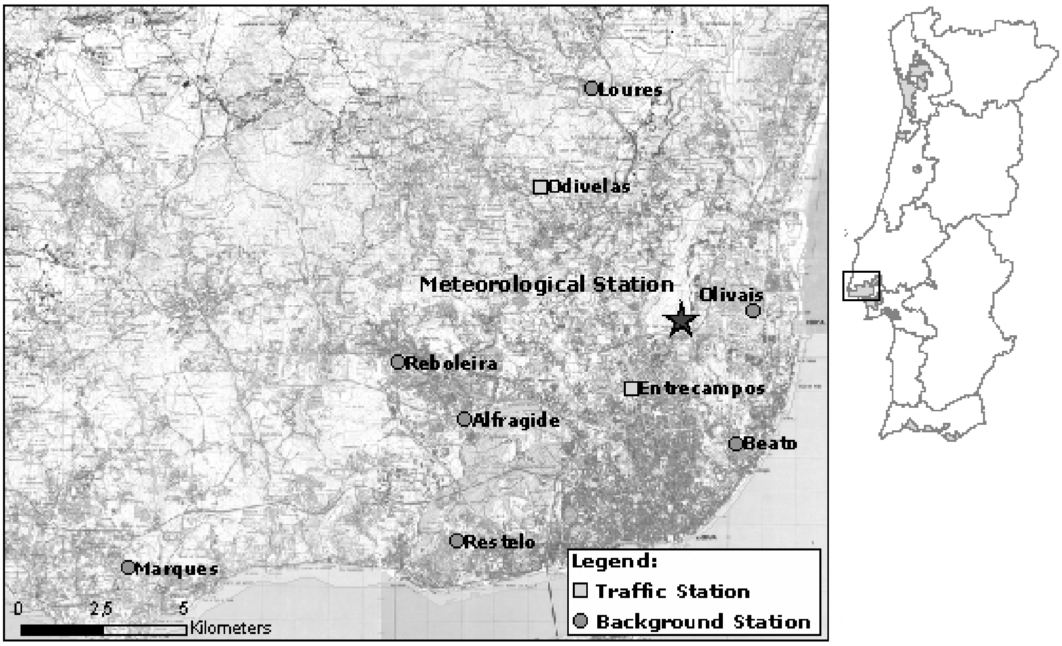
The aim was to evaluate air quality under different meteorological conditions.

In each sub-municipal administrative territorial unit, three types of monitoring sites were classified according to traffic level criteria as: "background", consisting essentially in residential areas and parks with very low traffic; "intermediate", mostly residential/commercial areas with medium/low traffic, and "hot spot" characterized by proximity to busy roads with heavy traffic.

Air Quality Stations Data

Air quality monitoring stations making continuous measurements of several pollutants are spread within the study area as presented in Figure 1. Ozone is measured in nine monitoring stations through an UV generator method. Six stations were selected for data analysis: Alfragide (ALF), Beato (BEA), Entrecampos (ENT), Loures (LOU), Olivais (OLI) and Reboleira (REB). These stations are located in the city of Lisbon, except three of them that are located in the suburban area of the town (Loures, Odivelas and Marques).

Figure 1: Ozone monitoring stations within Lisbon region



A period of three years, from 2001 to 2003, was used for basic statistical analysis of the ozone measured concentrations. All selected stations had at least 75% efficiency of data gathering except Olivais with only 55% (Olivais started to measure ozone in February, 2002).

The number of exceedances of limit values was counted taking into account the new European legislation regulating air quality ozone levels (Directive 2002/3/CE). The limit values selected for comparison were:

- 180 $\mu g.m^{-3}$ (1 hour average): designated as the information threshold;

- 120 µg.m^{-3} (8 hour average): human health protection limit value;

Different time scales were studied in order to evaluate the exceedances occurring during the day, week and month. The same procedure was used to evaluate the concentration pattern under different time scales. Ozone levels were also compared with NO_2 levels, due to the chemical relationship between the two pollutants.

Ozone and relations with meteorological variables

Ozone concentrations measured between 1998 and 2003 by air quality monitoring stations in the Lisbon city and vicinity, and meteorological variables were analyzed in order to develop a multiple regression model that would support forecasting.

Surface meteorological data was obtained in weather station Lisbon – Gago Coutinho managed by Portuguese Meteorological Institute (see Figure 1).

Data was split in different seasons to check for the specific variability of meteorology and the related measured concentrations.

To better understand the role of meteorology in air quality, a classification of weather patterns for a period of two years (January of 2001 to December of 2002) was performed. Meteorological daily reports and synoptic charts at surface and in upper level analysis from ECMWF Model were used for this purpose Daily maximum ozone values calculated by the same method of the Portuguese air quality index were also used. The stations of the air quality monitoring network are shown in Figure 1.

Principal Component Analysis (PCA)

Receptor modeling has been widely used for some years now, especially in the last few years for evaluating the different contributions of sources to particulate matter (PM) levels.[4] Ozone as also been a pollutant evaluated by this kind of approach.[5]. Using meteorological and air quality' datasets (35 different parameters, 1998 to 2003 daily averages, from three monitoring stations located in the Lisbon area), principal component analysis were performed for several periods (using all the data gathered and by season). Nevertheless, analysis was focused mainly in the total and Summer periods, for which results show a clearer pattern.

RESULTS

The Lisbon regional diffusive sampling campaign

The data from the background monitoring sites from both campaigns were interpolated, in order to produce concentrations maps of O_3 for Summer and Winter, using the ordinary krigging geostatistical algorithm.

The two campaigns results agree with what was expected. The highest O_3 concentrations occurred during the Summer, when solar radiation levels and temperature are higher.

Higher ozone concentration values occur in surrounding Lisbon areas. In city center, near the major sources of VOC and NO_x, ozone concentration decreases because of titration of O_3 by NO_x tailpipe

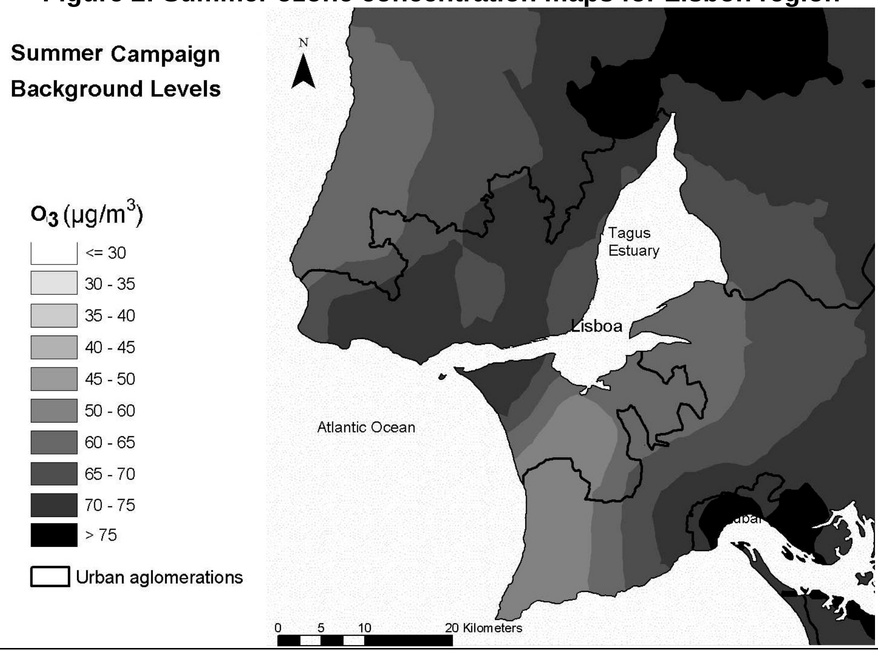


Figure 2: Summer ozone concentration maps for Lisbon region

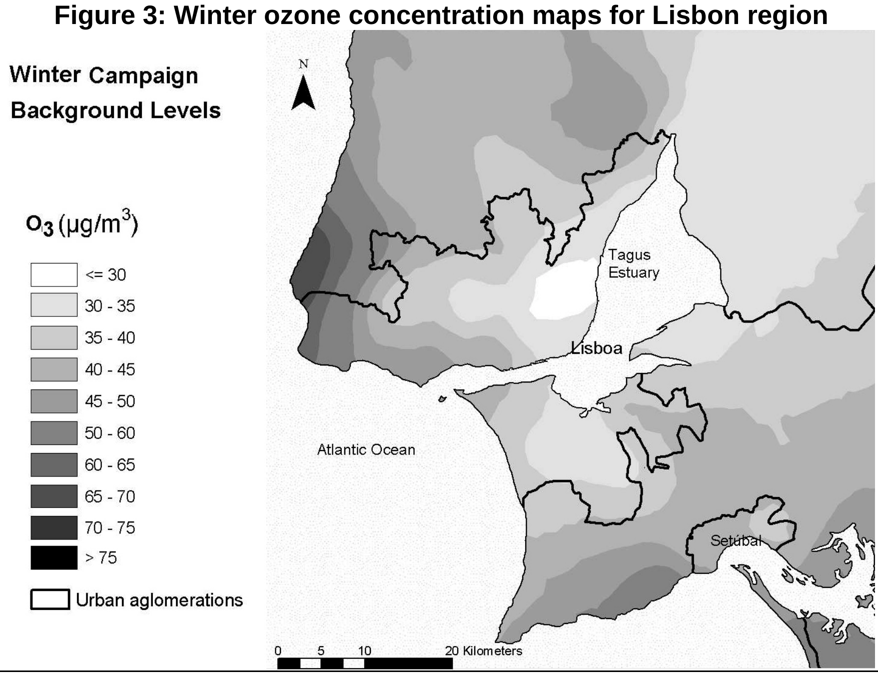
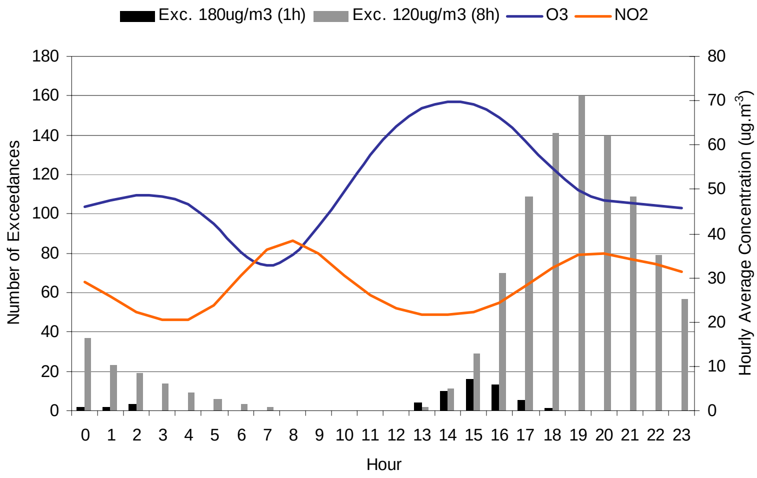


Figure 3: Winter ozone concentration maps for Lisbon region

Air Quality Stations Data

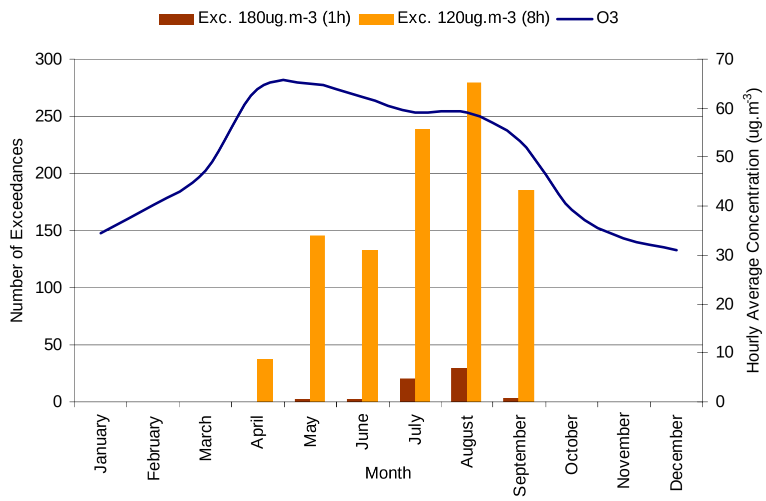
The results show different ozone concentration patterns according to the time scale. The higher number of exceedances occurs during the afternoon as expected, in the hottest period of the day. Around 86% of the exceedances of the 180 μg.m^{-3} (1 hour) information threshold level took place between 13h00 and 17h00. The concentration pattern throughout the day shows an inverse relation between ozone and nitrogen dioxide which demonstrates the influence of traffic in ozone levels (see figure below). Road traffic is indeed the major source of atmospheric pollution in the Lisbon region.[6]

Figure 4: Daily analysis of exceedances and O_3 and NO_2 concentrations.

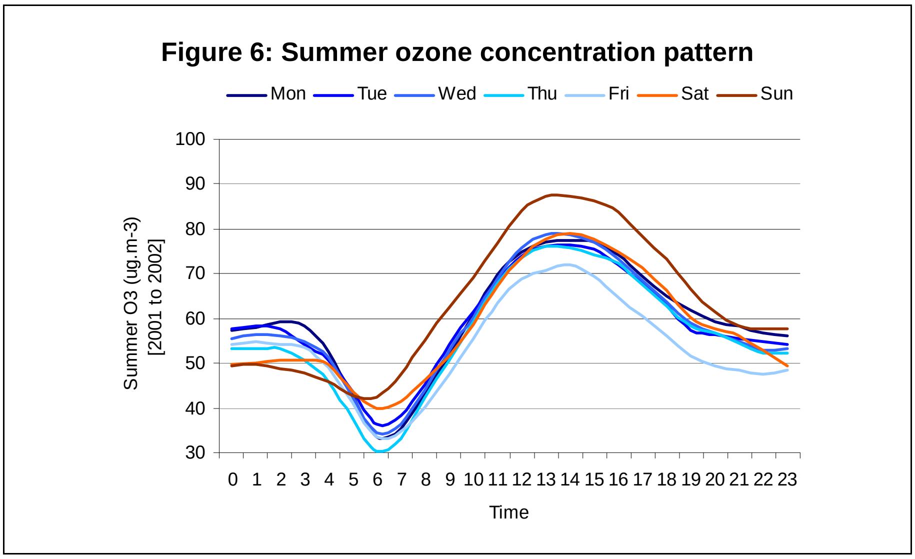


Along the year, the major number of exceedances occurs during the higher temperature months (July, August and September). Exceedances of the information threshold (180 μg.m^{-3} - one hour) are usually registered in July and August. A significant relation between ozone peak and temperature is confirmed. However, highest monthly average ozone concentrations occur in April and May.

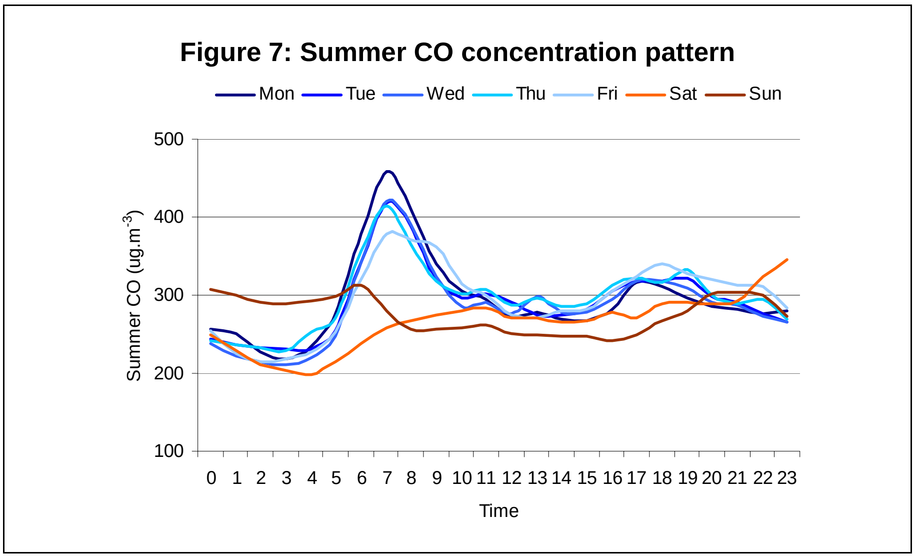
Figure 5: Monthly analysis of O_3 exceedances and concentrations.

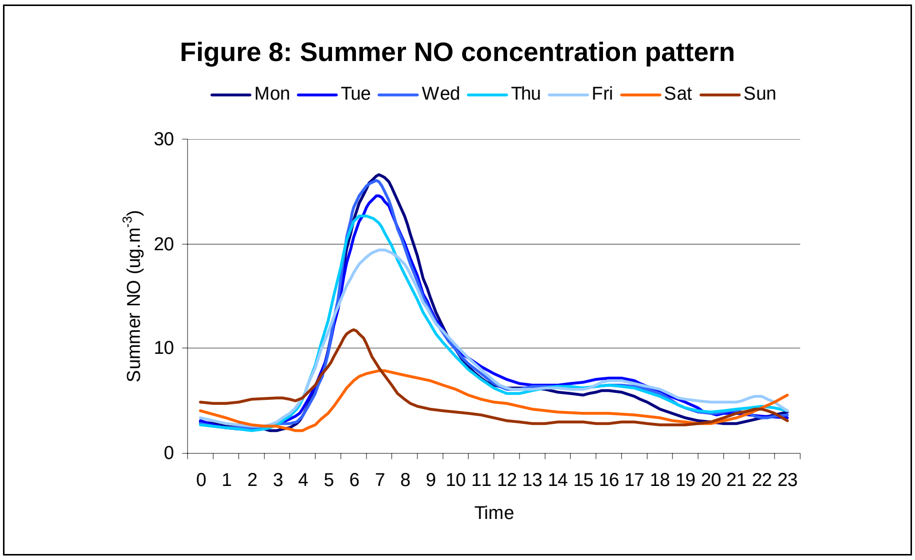


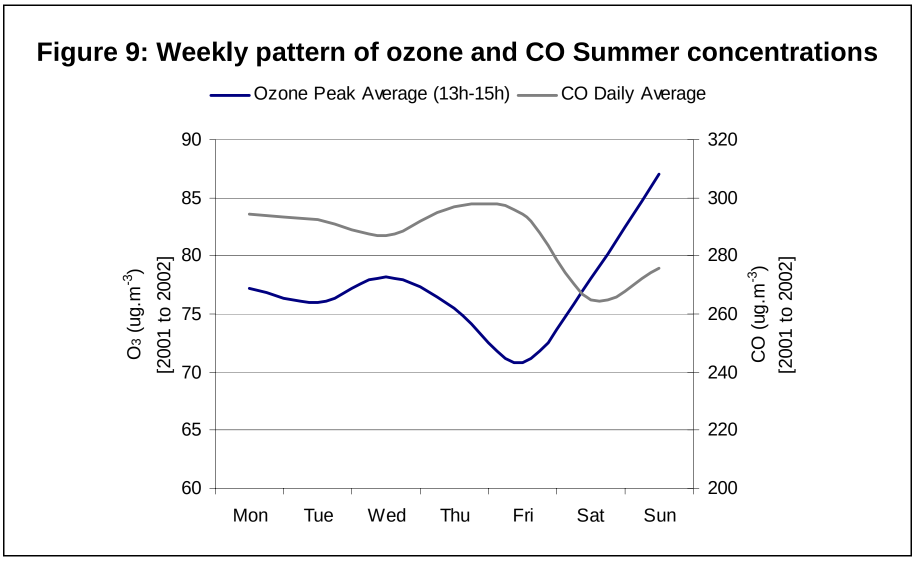
In respect to the weekly pattern, ozone shows an high inverse relationship with traffic volume, measured indirectly through carbon monoxide concentrations. An analysis of the average summer ozone - between May and September of 2001 and 2002 - shows that higher concentrations occur on Sundays. Lower concentrations are observed on Fridays. Ozone concentrations are similar in the remaining days.



Carbon monoxide concentrations measured at monitoring stations (Figure 1) during Summers of 2001 and 2002, follow the traffic volume. Figure 9 shows a consistent relationship between traffic peak and ozone decrease during the morning weekdays. On weekends, traffic pattern in the morning is completely different. On weekend dawn/morning, the lack of a traffic peak leads to higher ozone concentrations. During Sunday dawn high carbon monoxide concentrations are measured. This is related with Lisbon night life activity that begins on Saturdays, around 10 p.m. The increase of road traffic observed on Sundays only takes place during night and dawn, therefore titration of ozone by NO_x tailpipe decreases, leading to higher ozone concentrations values during daylight. Owing to the chemical coupling of O_3 and NO_x, the levels of O_3 and NO_2 are inextricably link. Consequently, any resultant reduction in the level of NO_2 is invariably followed by an increase in the level of O_3.[7]







The year 2003 was excluded from this analysis due atypical high registered temperatures.

Ozone and relations with meteorological variables

Multiple regression

As expected, a very good correlation was found between the average daily ozone concentration and the measurement from the day before. In fact, the persistence method is one of the simplest prediction methods used.[8] Maximum and average temperature and relative humidity show as good predictor variables for ozone. The day of week is also very important. The total variance explained by the best regression models area is only around 70% and still not sufficient for forecasting. Therefore, further developments will include meteorological variables in upper levels, variables dependent on the time of the day, and the use of natural logarithms to increase the consistence of the results.[9]

Table 1: Multiple Regression Parameters

Variables		Total Period	Summer	Fall	Winter	Spring
Day of week (0: weekdays; 1: weekends and holidays)	DW	0,18	0,15	0,18	**0,37**	**0,31**
Daily sea level medium pressure	SLP	-0,13	-0,01	-0,15	-0,04	-0,13
Daily medium temperature	TPM	**-0,40**	**-0,45**	-0,15	0,01	**-0,33**
Daily maximum temperature	TPX	**0,51**	**0,53**	**0,24**	0,13	**0,37**
Daily medium relative humidity	RHM	**-0,22**	**-0,53**	**-0,29**	-0,04	**-0,25**
Daily predominant wind direction	DDD	0,05	-0,06	0,16	0,15	-0,06
Daily medium wind speed	FF	0,02	-0,06	-0,04	**0,25**	0,03
Daily precipitation amount	PQ	0,07	0,01	0,08	0,21	0,06
Daily global radiation	GR	0,01	-0,10	0,04	0,03	0,08
Yesterday daily medium PM10 calculated by the AQI	PM10-1	0,07	0,07	**0,32**	0,19	0,01
Yesterday daily maximum O_3 calculated by the AQI method	O3-1	**0,48**	0,19	**0,24**	**0,49**	**0,50**
Yesterday daily medium NO	NO-1	0,04	**-0,23**	-0,17	0,11	0,16
Yesterday daily medium NO_2	NO2-1	-0,06	0,19	-0,08	-0,03	-0,17
Yesterday daily medium CO	CO-1	-0,10	-0,08	-0,10	-0,19	-0,08

Synoptic surface analysis

After analyzing the reports and charts and grouping all days in different synoptic classes 14 synoptic classes as presented in Table 2.

Table 2: Synoptic Classes

Synoptic Classes	Description
1 Frontal systems	The movement of an Atlantic front through the Iberian Peninsula (PI) gives place to a cloudy sky, rain, and moderate to strong surface winds. Its influence is determined by its activity. A moderate frontal system with significant precipitation and strong winds helps the atmosphere cleaning.
1a Passage of a frontal surface	In the warm air of the front, the wind is predominantly from SW with some intensity. This situation disperses pollution. The adjacent precipitation is a removal mechanism for particles.
1b Influence of a frontal surface	It is applicable for a weak activity front or when the frontal system is approaching or the front is moving in far North. In these cases occurs light winds, some clouds, and sometimes drizzle. It favors stability conditions.
1c Post frontal air	After a cold front, normally the air is unstable and produces showers and north-westerly or westerly moderate to strong winds. This system transports cleaner and colder air. Instable
2 Low pressure systems	In a general way they are associated to instability with showers and winds. They enable pollution dispersion. The instability, mixing layer, and dispersion are positively correlated.
2a	Low in Atlantic or over PI with a low aloft. The winds are predominantly

Deepening low pressure (instability)	southerly, sometimes strong with gusts. Moderate to heavy showers occur. Such as 1A, this situation is favorable to disperse pollution.
2b Low pressure in the south of PI	Centered in the South of Portugal the low leads to Easterly winds, weak to moderate. It can originate circulation from the North Africa, bringing sometimes desert dust. This situation can also originate precipitation in the South
2c Low pressure in the SW of PI	Low centered in the SW of Portugal transports warm and moist air circulation from Atlantic. The winds are predominantly south quadrant light or moderate. It improves the air quality when this situation is followed by showers
2d Low pressure influence	It can be included in this class low filling up pressure (with light activity) or low pressure moved away from the PI, but still influencing weather. These lows are sometimes centered in the W of PI with a High centered in the Central Europe developing in ridge to PI. This situation is expected to be the less favorable for dispersion of all the low pressure systems.
3 Synoptic situations associated to high pressure systems	These situations are in general way unfavorable to the dispersion of pollutants due the formation of thermal inversions (subsidence and radiation) and the weak barometric gradient. Of all these situations, the one that occur the most in Portugal is 3B, associated with the entrance of an Atlantic air mass. This will be the most favorable for pollution dispersion, not only for being a cleaner air mass as for the development of local circulations in the Summer (sea breezes).
3a Surface calm	The PI is under a high pressure region where the gradient is weak. This situation is associated to light winds or calm and sometimes to strong stability when the pressure gradient in altitude is also low or null. This scenario is worse in the Winter because the existence of breezes in the Summer induces circulation. The persistence of fog is a characteristic of this situation.
3b N/NW circulation	High located frequently in the Azores region, that induces in its N/NW circulation the entrance of an air mass from the Atlantic to the Occidental Coast. These situations can originate sometimes showers
3c NE/E circulation	The high is localized in the Atlantic and extended in ridge to the Biscay Gulf or to midland Europe or exactly localized in the Center of the Europe. The air quality can depend on the distance of circulation in the continental territory and wind speed. This situation is associated to high concentration of ozone in the Summer and Spring due to advection of a warm air mass and the transport of the ozone precursors
3d Presence of a high pressure and a thermal low pressure in PI	The weather is conditioned by air masses carried in the joint of high circulation located in the Atlantic and thermal low formed in PI. These situations favor the breeze circulation with moderate to strong north-westerly winds, during the afternoon in the western coast. This situation is frequently in the Summer
3e High pressure and thermal through from the north of Africa	The weather is influenced by the joint of an anticyclone located in the Atlantic develops in ridge to the Biscay Gulf and an inverted thermal through that extends since the North of Africa trough the PI. This synoptic situation carries to the Continent a dry and warm air mass (in the Summer). Situation associated essentially the high particle concentrations of mineral origin
3f High pressure originating a circulation of west	Circulation of West with light winds generally associated to a high located in Madeira or South of the Azores developing in ridge to the South of PI and low moving in the North. This situation is normally associated to cloudy sky, light wind, and light rain or drizzle.

For each season a box plot describes the variability of the ozone values relative to each synoptic class. Some weather patterns do not occur in certain seasons: 2c, 3a and 3f in Summer, 2b in fall, 3d and 3e in Winter, and, 3d and 3e in Spring.

Figure 10: Box plot analysis of synoptic classes in Winter

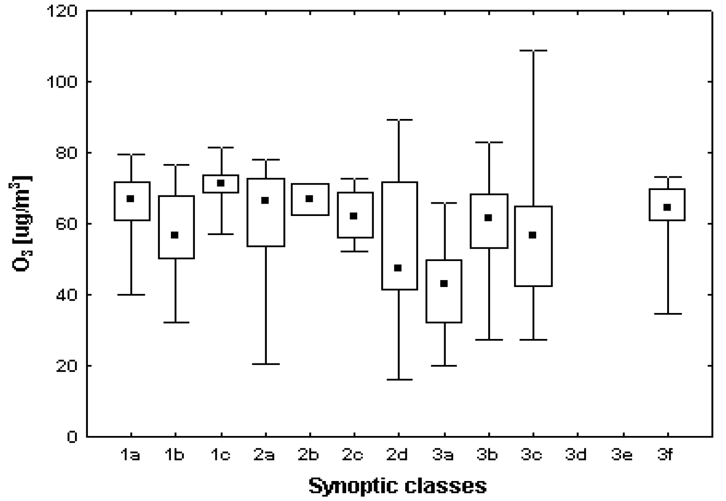


Figure 11: Box plot analysis of synoptic classes in Spring

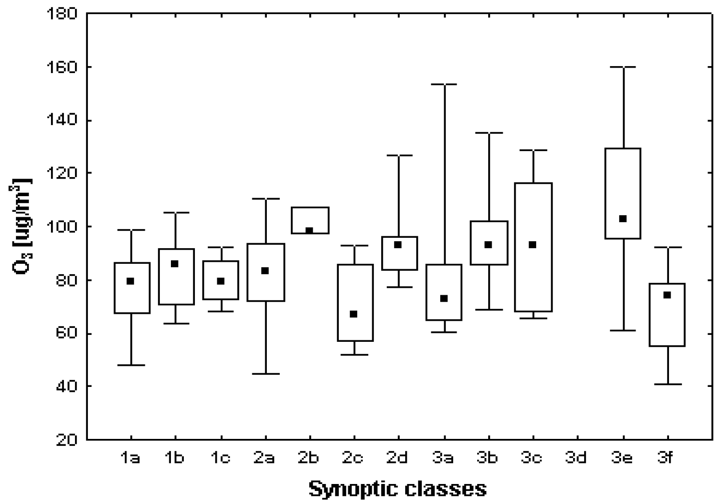


Figure 12: Box plot analysis of synoptic classes in Summer

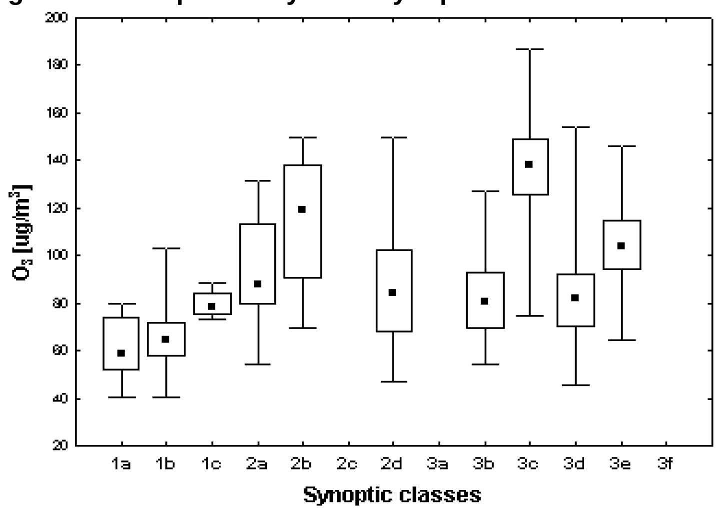
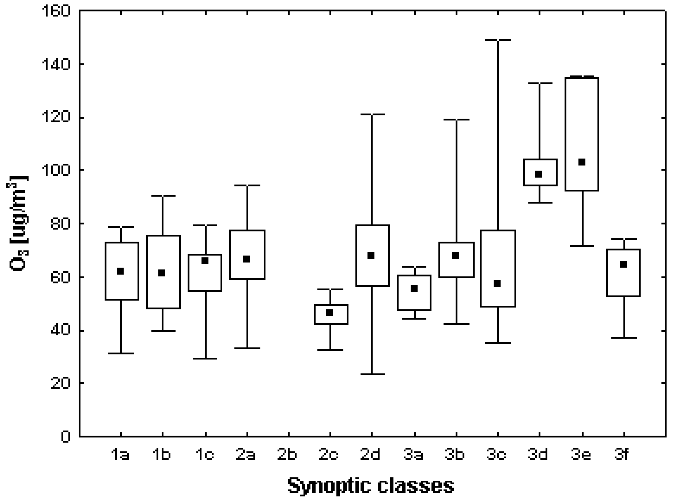


Figure 13: Box plot analysis of synoptic classes in Fall



The analysis of the box plot shows that the variability of ozone concentrations associated with frontal systems is low for all seasons. Pattern 3c has a great variability presenting the maximum values of concentrations in all seasons except for Spring. This result would be expected since it is associated with NE/E circulations. Situation 2d presents great variability and also high maximum ozone levels because it results from the influence of a low system and does not have a defined circulation. In Summer, situations 2b and 3c have the highest median values. In Fall, situations 3d and 3e show the highest median values. In Winter, situation 3a presents the lower median concentrations. In the Spring it is difficult to identify a behavior. The weather forecast is more difficult during this season. The same happens with air quality prediction.

Principal Component Analysis (PCA)

Seven factors were extracted in both cases with a cumulative explained variance of 81.1% and 81.5%, respectively. In order to obtain a more clear distinction between factors, a *varimax* rotation method was applied to the samples. This method resulted in a slight decrease in explained variance. The objective was to calculate factor loadings helpful for interpretation of the results. In Table 3 only the most important three factors are presented since these are the ones who explain most of the variability. Some components (or variables) were also removed.

Table 3: Factor loadings for Principal Component Analysis using varimax rotation for all data and only for Summer periods.

Components	Factor 1	Factor 2	Factor 3
O_3avg_ENT*	-0,352	**0,809**	0,037
O_3max_ENT	-0,209	**0,805**	0,314
NOavg_ENT	**0,719**	-0,290	0,321
NOmax_ENT	**0,748**	-0,192	0,368
NO_2avg_ENT	0,137	0,042	**0,882**
NO_2max_ENT	0,188	0,140	**0,832**
COavg_ENT	**0,737**	-0,201	0,255
COmax_ENT	**0,851**	-0,191	0,122
PM_{10}avg_ENT	0,528	0,240	0,291
PM_{10}max_ENT	**0,724**	0,095	0,225
O_3avg_ALF**	-0,116	**0,862**	-0,293
O_3max_ALF	0,103	**0,833**	0,152
NOavg_ALF	**0,783**	-0,213	0,113
NOmax_ALF	**0,780**	-0,173	0,276
NO_2avg_ALF	0,382	0,004	0,384
NO_2max_ALF	0,422	0,048	0,366
COavg_ALF	0,618	-0,069	-0,154
COmax_ALF	**0,776**	-0,127	-0,042
O_3avg_BEA***	-0,314	**0,882**	-0,039
O_3max_BEA	-0,077	**0,815**	0,218
NOavg_BEA	**0,905**	-0,215	0,113
NOmax_BEA	**0,895**	-0,161	0,202
NO_2avg_BEA	0,281	0,034	**0,821**
NO_2max_BEA	0,384	0,056	**0,845**
COavg_BEA	0,617	0,057	0,477
COmax_BEA	**0,808**	0,020	0,189
Explained variance	9,347	5,178	4,519
Total variance explained (%)	26,7	14,8	12,9

Note: In bold are presented factor loadings above 0,7 in absolute values, taken as acceptable

In PCA analysis, the variables (components) that have the highest loadings are, normally, highly correlated. The factor name is then the result of that combination. In Table 3 there are some factors whose relationship is easily identifiable. Factor 1 is related with road traffic, since it shows strong correlations between CO, NO, and NO_2 in the three stations (maximum concentration for PM_{10} – PM10max) is also in this group, but since it is measured only in Entrecampos that is not so clear. Nevertheless, factor 2 is the most interesting for this evaluation since it shows a strong association between ozone levels measured in the three monitoring stations. This result point out the small spatial variability of ozone in the city and could well indicate that no more monitoring stations will be needed in this area. The existing stations cover different types of areas (traffic and background) and all three show the same kind of behavior for the time period studied. This kind of analysis is helpful for air quality management and will help the use of multi-linear regression for forecast based in the relationships between variables.

CONCLUSIONS

Higher ozone concentration values occur, in general, in surrounding Lisbon areas. In city center, near the major sources of VOCs and NO_x, ozone concentration decreases. An high inverse relation between road traffic (measured indirectly through carbon monoxide) and ozone was found.

Around 86% of the exceedances of information one hour threshold (180 $\mu g.m^{-3}$) took place between 13h00 and 17h00, and are usually registered in July and August (for the period between 2001 and 2003).

As expected, a very good correlation was found between the average daily ozone concentration and the measurement from the day before. Maximum and average temperature and relative humidity show as good predictor variables for ozone. For higher maximum temperatures, as those in Summer, better model responses were found.

PCA analysis point out the small spatial variability of ozone in the Lisbon area indicating that one background monitoring station could be enough to evaluate adequately the area.

ACKNOWLEDGMENTS

The work developed was supported by Instituto do Ambiente and by Instituto de Meteorologia. The authors also wish to acknowledge the Comissão de Coordenação e Desenvolvimento Regional de Lisboa e Vale do Tejo for the data provided, and particularly for the help provided by Luísa Nogueira.

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KEY WORDS

Ozone, meteorological patterns, diffusive sampling, Lisbon, air quality.