Learning from 24 years of ozone data in Portugal

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Abstract

Ozone (O_3) is a secondary pollutant mainly produced in the troposphere by photochemical reactions with high impact on human health. In this work hourly average O_3 concentrations from the Portuguese air quality network collected during 24 years (1988–2011) were analysed. The background time series were assessed by environment type (urban, suburban and rural) and considering several criteria: the annual mean O_3 concentration, the Directive 2008/50/EC O_3 long-term objective and the 2005 WHO Guideline for protection of human health and, finally, the hourly information threshold exceedances. The trend of annual mean O_3 concentration data and the maximum daily eight-hour mean ozone concentration data were both annually compared using an one-way ANOVA followed by a Tamhane post-hoc comparison test. In both series, although of an instable trend, a tendency for an increase of the mean O_3 concentrations was found. On the other hand, after 2006, for all stations types, the normalized number of exceedances for public O_3 information are significantly decreasing ($p<0.05$). In this paper, the O_3 trend will be analyzed and discussed, contributing to improve knowledge of long time series of O_3 concentrations in Portugal.
Keywords: tropospheric ozone, background stations, time series, trends, exceedances.

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1 Introduction

The importance on the control of surface ozone (O_3) concentrations relies on its oxidative characteristics. O_3 has negative impacts on human health and on the environment [1, 2]. Tropospheric O_3 is responsible for damage particularly in the respiratory system such as asthma and lung irritations [3, 4] for which, were estimated world health costs of $580 billion for 2050 [5]. In the environment it is also known its involvement on the reduction of photosynthetic process activity, with a negative impact in the growth, the reproduction of flora and its quality, leading to a loss in the biodiversity and a reduction of agriculture activity [6].

O_3 is a secondary pollutant with three main distinct sources within the lower atmosphere, which include a low background concentration, probably less than half of the concentration currently encountered in the northern hemisphere, arising from Stratospheric-Tropospheric Exchange – STE and an identical contribution from background chemistry. The third contribution arises as a result of atmospheric chemical and photochemical reactions at regional and local scale.

The production of O_3 can occur on both short and longer timescales. The longer timescales involve reactions in the remote atmosphere, to increase the hemispheric background of O_3, probably to about double that which prevailed in the pre-industrial era [7]. The short timescale, involve reactions in more polluted atmospheres, as large urban areas and its surroundings. Here the anthropogenic emissions introduces a large amount of reactive hydrocarbons (HC) and nitrogen oxides (NO_x) which if enough solar radiation is available, will induce a rapid (hours) formation of high O_3 levels. On the other hand, O_3 concentrations at urban centres are often lower than those in the suburban surroundings or rural areas. In fact, fresh nitric oxide emissions from urban traffic can suppress relatively higher O_3 concentrations entering from the boundary of the urban airshed. At a larger regional scale, such as in Europe, emissions from an intense anthropogenic activity lead to a highly polluted atmosphere, where O_3 can be produced and transported over long distances.

In Portugal other factors play a major role on local or mesoscale O_3 formation, like the prevalence of an important sea breeze circulation system and the importance, not yet fully explained, of a large amount of forest emissions which induce an atmosphere largely NO_x-limited [8].

Ozone is a pollutant of most concern. Due to the characteristics and processes in which O_3 is involved the control of their surface concentration it is not a straight forward task. Moreover, due contributions mentioned above it is of paramount importance to be able to identify them in a time series. As a first approach, on the scope of the DYNOZONE project (Total column and surface ozone variability over the Iberian Peninsula: Dynamical and Chemical atmospheric factors – PTDC/CTE-ATM/105507/2008), 24 years of hourly average O_3 data (1988–2011) from the Portuguese air quality network were statistically analysed.

This paper aims to contribute and improve knowledge of long time series of O_3 concentrations. The main questions of this research are: (i) What are the main trends of O_3 concentration in the last decades?; (ii) What are the environment stations types more affected by O_3 exceedances?; and (iii) If the World Health Organization (WHO) guidelines of O_3 human health protection were applied, what will be the impact?

2 Data and methods

On the scope of the DYNOZONE Project, 24 years of background hourly average ozone data (1988–2011) from the Portuguese air quality network were statistically analysed. The analysis was done according with the type of air quality stations, classified in urban, suburban and rural. Firstly, data collections of long data series of O_3 concentrations were done (see Section 2.1). Then, a statistical analysis was performed to evaluate the O_3 concentrations trends and the number of O_3 exceedances relative to the Directive 2008/50/EC (human health protection threshold and public information threshold) and WHO guideline for the human health protection (see Section 2.2).

2.1 Data collection

In this work, the hourly average O_3 concentrations from the Portuguese air quality network were collected during 1988–2011. Air quality stations with background influence were selected because they represent an atmosphere without the direct contribution of local anthropogenic emissions (Figure 1).

At present, the air quality network, as seen in Figure 1, is covering the main urban areas and also the rural background over Portugal. However the number of active stations has changed during the period under consideration. Table 1 presents an overview of the mean number of active stations by hour during the analyzed period.

2.2 Statistical analysis

Even fulfilling the quality criteria referred in standard methods (ISO/IEC 17025:2005) (IPQ, 2005; EC, 2008), the O_3 concentrations time series were validated according to the Directive 2008/50/EC [9] which require 90% of efficiency in the summer season (April–September), and 75% of efficiency for the winter season (January–March and October–December). This efficiency is determined according to the available hourly O_3 concentrations by station in each year. Time series without conformity were rejected for analysis, except regarding to the identification of the number of exceedances to the public information threshold. In that case, all available data were used.

Additionally, the data was normalized by the number of active stations in each year. The analysis was done according with the type of air quality stations (t): urban, suburban and rural. Normalized averages concentrations were obtained in two steps: (i) firstly the hourly average of mean hourly concentrations (C_h) was computed applying the ratio of sum of hourly concentrations (X) by the number of concentration values recorded by a group of active stations in an hour of one station type (n) (see eqn. (1)); (ii) lastly the annual average concentrations (C_y) were obtained through the ratio between

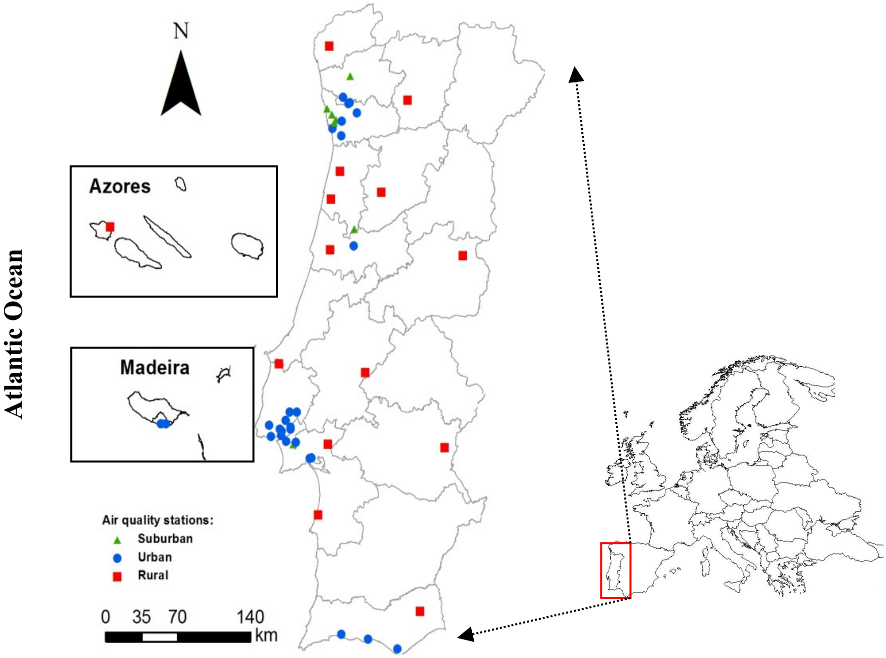

Figure 1: Spatial distribution of background stations of the Portuguese air quality network (1988–2011).

Table 1: Number of active background stations which measure O_3 in Portugal by environment type (1988–2011).

	Number of air quality stations by year																							
	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Urban	-	-	-	-	-	-	-	-	-	1*	1*	2	2	5	8	13	16	15	12	8	17	9	19	16
Suburban	-	-	-	-	-	-	-	-	-	-	-	2	3	4	4	4	7	6	7	7	7	7	8	7
Rural	1*	1	1*	1*	1	1	1*	2	2	2	2	1	2	2	2	4	5	7	7	5	6	9	9	8

*Station which didn't meet the efficiency criteria of the Directive 2008/50/EC.

2.3

the hourly average of mean hourly concentrations (C_h) by the number of working hours during this year (h) (see eqn. (2)).

$$C_h = \left(\frac{\sum_{i=1}^{h} X}{n}\right)_t \tag{1}$$

$$C_y = \left(\frac{\sum_{i=1}^{h} C_h}{h}\right)_t \quad (2)$$

A similar procedure was followed for the determination of the maximum daily eight-hour mean concentration, considering the highest daily value of active station.

Statistical analysis was performed using IBM© SPSS© Statistics vs.21. All inferential analysis was done with a significance level of 0.05.

To assess the differences in the annual trend of mean O_3 concentration in each environment type, a one-way ANOVA was applied. Upon detection of significant differences in the trend, the Tamhane post-hoc comparison test was performed (due to variance heterogeneity – Levene test) in order to identify which years were significantly different. The same procedure was used for the analysis of the temporal trend of the maximum daily eight-hour mean concentration for human health protection.

The annual number of exceedances to the current long-term objective for the protection of human health (120 $\mu g.m^{-3}$) and guideline recommended by WHO (100 $\mu g.m^{-3}$) was performed based in the maximum daily eight-hour mean concentration. Their trends were analyzed after being normalized using the number of working days of active stations according with station type. To perform a peak analysis, as opposed to the daily eight-hour mean concentration, the information threshold (180 $\mu g.m^{-3}$) defined by the Directive 2008/50/EC was used. The number of exceedances was normalized by the number of working hours of active stations according with the station type and multiplied by a factor of 10^4 in order to facilitate their handling.

For these three trend analysis, 95% confidence intervals (CI) were calculated considering a Bonferroni correction to make possible direct comparisons using those CI.

3 Results and discussion

In this section the main results are presented and discussed. First the mean O_3 concentrations are presented and then an analysis of the exceedances to the protection of human health threshold value is done (maximum daily eight-hour mean concentration over 120 $\mu g.m^{-3}$ and 100 $\mu g.m^{-3}$, the Directive 2008/50/EC long-term objective and the 2005 WHO guideline, respectively). Finally, the temporal trends of O_3 exceedances to public information threshold (180 $\mu g.m^{-3}$), as a reference of the behavior of peak O_3 concentrations, is presented and discussed.

3.1 Temporal trends

Figure 2 shows the annual mean value of O_3 concentration by environmental type between 1988 and 2011 in Portugal. The trend of this series is characterized by relatively large variations, but a similar pattern for the different type of stations is observed. There is inter-annual variability, on the normalized O_3 mean concentrations in the three types of environmental influences.

Rural stations present an increase tendency between 1999 and 2005. Between 2006 and 2011 its normalized mean concentration values show inter-annual variability without an upward or downward tendency. Rural background stations also show the greatest variability on the data. The suburban stations presented higher oscillations all over the years but is not visible a remarkable increase in its trend. For urban stations, the highest mean annual O_3 concentration was obtained in 2010; except for 2008 (lower concentrations) and 2003 (higher concentrations), from 2005 onwards the values are higher than in the previous periods. Regarding suburban stations, the highest mean annual O_3 concentration was obtained in 2003, followed by the 2005–2007 period were the mean O_3 concentrations were significant lower than in 2003. A decreasing pattern is detected (with fluctuations), although mean O_3 concentration values are still significantly higher than in the period prior to 2003.

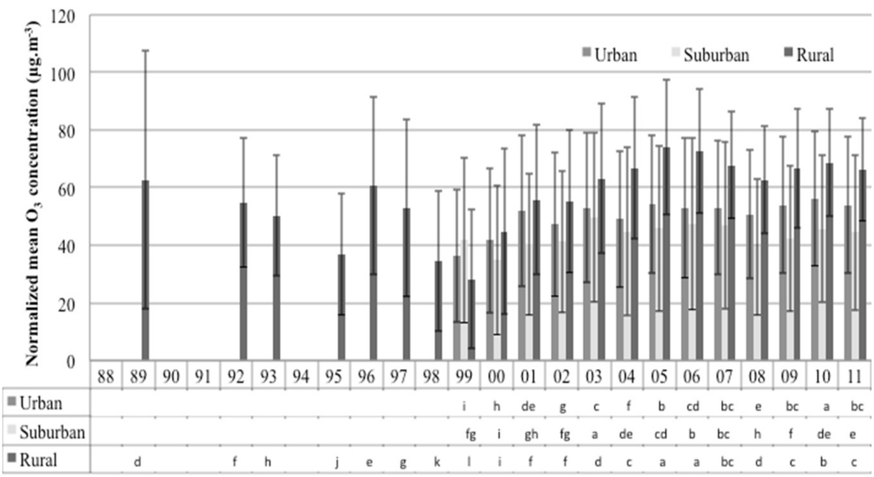

Figure 2: Annual mean and standard deviation value of O_3 concentration amongst all the air quality stations of background influence between 1988 and 2011. Different small cap letters stand for significant mean O_3 concentration differences in the year trend ("a" stands for the highest mean value, and so forward).

For rural stations, a significant higher ($p<0.05$) mean annual O_3 concentration (with relation to the other two types of stations) was obtained, and with the exception of 1989, there is an increase in mean concentrations until the highest are obtained for the 2005–2006 period and then a slight (significant) decrease is steadily observed onward (this information is associated to the small cap letters placed below the year trend in Figure 2).

As can be seen in Figure 2, the highest values of mean O_3 concentrations were recorded for different years according with each type of environment. The higher mean values for suburban and rural stations were recorded in 2003 and 2005–2006, respectively, while in urban stations were recorded more recently, in 2010.

The overall mean of O_3 concentration to rural stations was 58.0 μg.m^{-3}, while in urban and suburban stations was 50.3 μg.m^{-3} and 43.5 μg.m^{-3}, respectively. During the period of 1990 to 2000 the mean values were lower than the overall time series means: -42% to rural stations, -21% in urban stations and -14% to suburban stations. It should be noted that for this period there is a lack of data due to the low representativeness of the existent air quality station at the time (located near the Portuguese coast line) and to the low number of stations which presented efficiency according with the legislation, as presented in Table 2.

Concerning the maximum daily eight-hour mean concentration for human health protection for the Directive 2008/50/EC (120 μg.m^{-3}), the rural station shows the highest number of exceedances, with 17.3% of the available data above to this threshold. The suburban station, on the other hand, shows the lowest number of exceedances, with only 7.5% of the data above the maximum daily eight-hour mean concentration for human health protection (Table 2).

A similar analysis, but considering the WHO 2005 guidelines of 100 μg.m^{-3} for the maximum daily eight-hour mean concentration for human health protection, shows a significant increase of exceedances (Table 2), meaning that a significant part of the Portuguese population is exposed to an unsafe atmosphere and important effort should be done in order to control the situation.

In either scenario (Directive 2008/50/EC or the WHO guideline) rural stations show significantly higher percentage exceedances than urban and suburban stations (Table 2).

Table 2: Number of O_3 concentration exceedances to the maximum daily eight-hour mean concentration values regarding Directive 2008/50/EC and the WHO 2005 guidelines. Values recorded in Portugal between 1989 and 2011 by background air quality stations.

Station type	Directive 2008/50/EC				WHO guideline			
	Threshold (μg.m^{-3})	N*	%	CI** (%)	Threshold (μg.m^{-3})	N*	%	CI**(%)
Urban	≥ 120	563	11.5	10.4-12.6	≥ 100	1455	29.6	28.0-31.2
Suburban		356	7.5	6.6-8.4		863	18.2	16.9-19.5
Rural		1478	17.3	16.3-18.3		2889	33.8	32.6-35.0

*Total N: Urban=4914, Suburban=4741, Rural=8547;
**Confidence intervals according to the exact method allowing for comparisons between Directive 2008/50/EC and WHO proposal with 98.3% confidence degree, and between station type with 95% confidence level (Bonferroni correction, α=0.0167).

The annual highest maximum daily eight-hour mean O_3 concentration (Figure 3) follows trends that resembles, although not completely, the mean annual O_3 concentration (Figure 2).

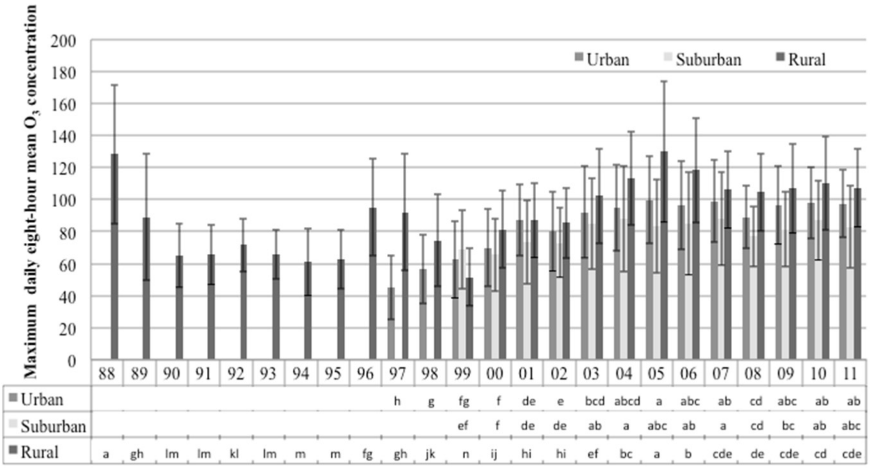

Figure 3: Maximum daily eight-hour mean annual O_3 concentration from the background air quality Portuguese stations (1988–2011). Different small cap letters stand for significant mean O_3 concentration differences in the year trend ("a" stands for the highest mean value, and so forward).

For urban stations, the annual highest maximum daily eight-hour mean O_3 concentration was obtained in 2005, and did not differ significantly from 2006–2007 and 2009–2011 periods (Figure 3). Since 2005 (with the exception of 2008 (lower concentrations)) higher means than in the previous period are observed. Regarding suburban stations, the annual highest maximum daily eight-hour mean O_3 concentrations were obtained in 2003–2007 and 2010–2011. Before 2003 the mean values were significantly lower. Finally, for rural stations this indicator decreases from more than 125 to 65 $\mu g.m^{-3}$ during 1988–1990 period, followed by a stable low annual maximum daily eight-hour mean O_3 concentration, a significant increase in 1996–1997. After this, a decrease in 1998–1999 and a subsequent significant increase up till 2005 (to values that do not differ from the ones obtained in 1988), followed by a slight decrease and stabilization from 2007 onwards is observed.

As can be seen in Figure 4, three peaks can be observed in 1988, 1996 and 2005 for rural stations which is not detected on the other station types. This pattern might be associated to years with large heat waves, which are characterized by a strong photochemical production at rural sites. Forest fires may also explain part of this trend. Nevertheless, after 2000, a consistent increase of the maximum daily eight-hour mean O_3 concentration is portrayed in all stations.

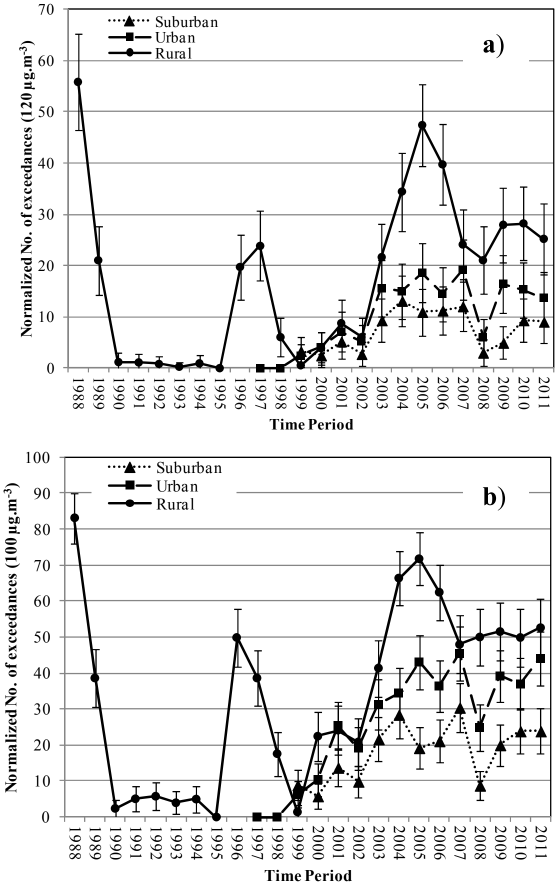

Figure 4: Annual number of exceedances of O_3 concentration to maximum daily eight-hour mean concentration recorded in Portugal between 1988 and 2011 for: a) human health protection (120 μg.m^{-3}); and b) guideline for human health protection (100 μg.m^{-3}). The error bars represent 95% confidence intervals. Values recorded only by background air quality stations.

Concerning the peak analysis, it is possible to see on Figure 5 that temporal trends of O_3 exceedances to the public information threshold (180 μg.m^{-3}), records for rural stations a high value in 1988. Moreover, two extremely high peaks for 2003 and 2006, were recorded for all stations types, after which the normalized number of exceedances are decreasing significantly ($p<0.05$).

This trend behavior points in a reverse direction to that observed in the previous analysis of the maximum daily eight-hour mean O_3 concentration, which may indicate that the average values of O_3 concentration are increasing, but the peak values are in the opposite direction.

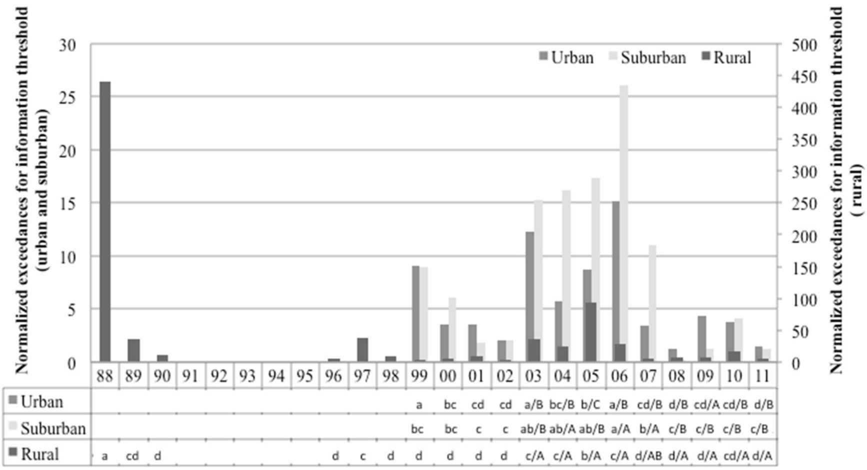

Figure 5: Annual number of exceedances to the O_3 information threshold ($180\ \mu g.m^{-3}$) normalized by the number of working hours of active stations (normalized exceedances) according with station type, multiplied by a factor of 10^4. Values to the Portuguese background air quality stations recorded between 1988 and 2011.

4 Conclusions

At this time, the Portuguese air quality network covers all the territory (not only the coastal regions, as in the past), giving the possibility to study O_3 time series and their behavior over the different regions and influences. This fact results in the first challenge in the analysis. In order to minimize local emissions influences on the O_3 concentrations, only background influenced air quality stations were analyzed, after the validation process according to the criteria stated in the Directive 2008/50/EC. The annual hourly mean concentrations were calculated and normalized according to the number of stations available each year and station type.

Results point to a higher than normal O_3 annual hourly mean concentration during 2003 and 2005 over suburban and rural background stations. This fact may be related to the higher burned area verified over Portugal in those years [10]. The higher than average values verified during 2010 over the urban stations needs to be clarified.

Rural background station are showing the higher number of station with maximum daily eight-hour mean concentration values higher than the threshold of $120\mu g.m^{-3}$ imposed by the Directive 2008/50/EC, which is related to human health protection. However, it must be noted that over the areas they are representing the number of inhabitants significantly less than in suburban and urban area. Around 11.5% of the analyzed urban backgrounds are showing above threshold values for this indicator.

The temporal trends for the normalized public information threshold has shown high values in 2003 and 2006 for all type of environments, however this value has decreased with time.

The last years of the time series the number of exceedances to the O_3 concentration threshold regarding to human health protection have been normalized to a similar number of active stations, it is possible to say that these values have decreased since 2008, regarding previous period of the series.

If one takes into account the WHO 2005 guidelines, measures to diminish exceedances to thresholds value must be considered over, in particular, rural and suburban areas. That will be a challenge in face of the low titration from NO_x emitters, due to anthropogenic emission control by the implementation of the Directive 2001/81/EC (National Emissions Ceilings). Another factor to be considered is the high O_3 production from forest fires, which may play also a major rule in all this process.

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