23 YEARS OF OZONE EPISODES IN PORTUGAL: PHOTOCHEMICAL AND/OR STRATOSPHERIC INTRUSION

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Abstract
Tropospheric ozone is a secondary pollutant having a negative impact in health and environment. To control and minimize ozone concentrations, European Community established regulations, defining in the Directive 2008/50/CE, of May 2008, in order to promote a clear air all over Europe.

The aim of this work is to identify the origin of ozone episodes in Portugal, in particular, the ozone episodes associated to stratospheric intrusions. This paper will present the analysis of ozone data series between 1988 and 2010 by statistical methods and specific criteria. This work allows the identification of 303 ozone episodes with an eventual stratospheric or transboundary advection signature. The majority of these episodes occurred in 1988, 1989, 2005 and 2006.

1. Introduction

Ozone (O_3) is a photochemical pollutant produced in the troposphere by oxidation reactions between certain precursors, mainly non-methane volatile organic compounds (NMVOCs) and nitrogen oxides (NO_x), in the presence of solar radiation (wavelength < 424 nm) (Crutzen *et al.*, 1999; Alvim-Ferraz *et al.*, 2006; Fishman *et al.*, 1978; IPCC, 2007). Another important source for the presence of ozone in the troposphere is the stratospheric ozone brought down through Stratosphere-Troposphere Exchange (STE) processes (e.g.: (Carvalho *et al.*, 2005; Moreira *et al.*, 2005; Stevenson *et al.*, 2006)). This source can contribute to the presence of 552-765 $Tg.yr^{-1}$ of tropospheric ozone whereas the contribution from photochemical reaction is 6.2-6.7 times higher (Wild, 2007).

The production of tropospheric ozone was increasing in Europe between 1960 and 1990. However, in the 90s these concentrations have stabilized (Oltmans *et al.*, 1998; Oltmans *et al.*, 2006; Logan *et al.*, 1999). Since the early of the 80s at high latitudes of the free troposphere over Europe the concentration of tropospheric ozone, has been suffered a reduction but the same didn't happen at low latitudes. One possible explanation for this phenomenon is the reduction of ozone in the stratosphere, leading to smaller amount of ozone in the stratosphere is exchanged into the troposphere (European Comission, 2003).

Due to its oxidative characteristics, it is recognized the negative impact of ozone on human health and in the environment (Parmet *et al.*, 2003; Agrawal *et al.*, 2003). Tropospheric ozone is associated to health damages particularly in the respiratory system, leading to asthma and lung irritations (WHO, 2006; Ebi *et al.*, 2008). Concerning to cardiac problems, several authors (e.g. (Halonen *et al.*, 2010; Hamade *et al.*, 2008)) studied the relation between peaks of ozone and the appearance of cardiac diseases, however there isn't any prove that ozone is the single responsible (Jerrett *et al.*, 2009; Srebot *et al.*, 2009). Ozone also induces a reduction of the photosynthetic process influencing in growth, reproduction, and quality plant's, among others, leading to a minor biodiversity and also a decrease in agriculture activity (EEA, 2011).

Another negative characteristic of tropospheric ozone is that it is also a greenhouse gas, one of the major contributors to the smog, which consequently promotes warming of the atmosphere (EEA, 2011).

For these reasons, there is a global concern for evaluate the ozone trends and implement regulations to decrease and minimize the ozone concentrations and its effects. At European level, the Directive 2008/50/EC, of 21 May 2008, defines the main rules concerning to the ambient air quality in order to promote a cleaner air in Europe. This policy results from the review of European legislation with the idea of reduce pollution to target values and minimize the adverse effects associated with human health and environment as well as disposing information of pollutants concentrations. In Portugal this Directive was transposed in 23 September 2010 to the Decree No. 102/2010. In its objectives were established for the assessment and management of air quality, taking into account guidelines, programs and standards derived from the World Health Organization (WHO).

In Portugal the air quality network has been collecting data since 1988. These data are usually used to analyse the conformity with legislation; however, long time series analysis's and STE identification are unusual. In order to fulfil this gap in the scope of the STRATOZON Project (2002-2004) some possible events of stratospheric intrusion of tropospheric ozone over Portugal were identified and evaluated (Carvalho *et al*., 2005; Moreira *et al*., 2005; Borrego *et al*., 2003). Following this study and in the scope of the DYNOZONE Project (2010-2013) the importance of the STE on some ozone episodes is under investigation. The preliminary results will be present in this work.

2. Material and methods

To perform this work, long data series of ozone collected in 75 stations between 1988 and 2010 in Portugal have been analysed (Fig. 1).

During this period 607 annual series, on base of hourly average concentrations, have been analysed considering the classification of the stations: rural, urban and suburban, according with the environmental type; and traffic, background and industrial according with the influence type (2008/50/EC). The air quality stations measurements are validated according with the requests mentioned in standard methods ISO/IEC 17025:2005. They are also integrated within a system of quality control and maintenance of the measurements equipments.

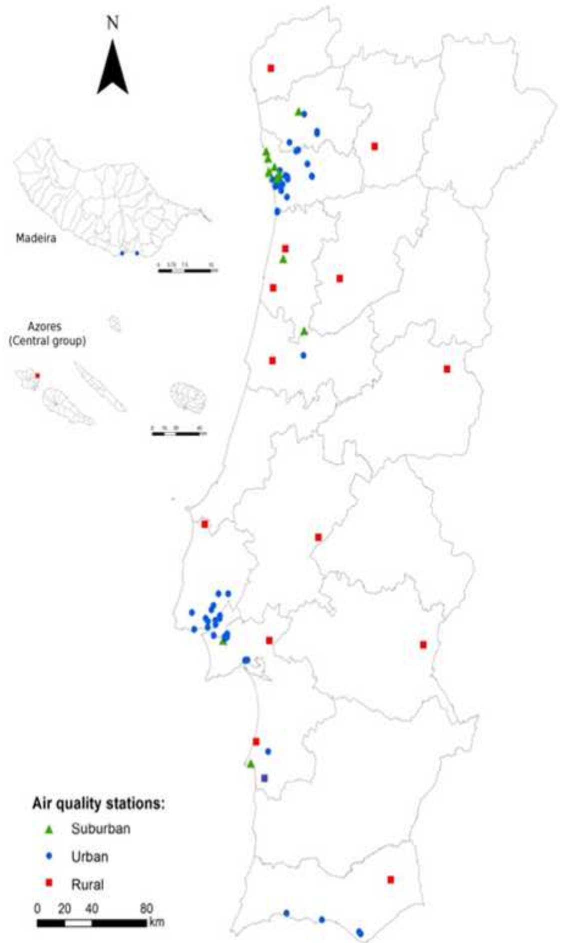

Fig. 1.- Spatial distribution of stations of air quality all over Portugal.

Ozone episodes correspond to time periods where its concentrations exceed a threshold of human protection which may correspond to some days or even two to three weeks (EEA, 2010)**¡Error! Referencia de hipervínculo no válida.**.
In this work the information threshold to the population defined by the Directive 2008/50/EC was used to identify the episodes (180 $\mu g.m^{-3}$).

To analyse and identified episodes, several criteria's were defined. The definition of criteria was set with aim to select episodes with potential origin in stratospheric events. For this purpose, criterion like opposite conditions to promote formation of tropospheric ozone by photochemical reaction was chosen, as nocturnal episodes and autumn-winter episodes. One of criteria corresponds to episodes which are questionable data by the validation method of the World Meteorological Organization (WMO). This questionable data are events that don't satisfy with the requisites imposed, rising doubts about its origin. Last studies over Portugal have proved that the selection of suspicious ozone episodes may be achieved through the application of these criteria (Carvalho *et al*., 2005).

Thus the episodes were selected when measured ozone concentrations were above the defined information threshold and at least one of following criteria was satisfied:

Criterion 1: Data questionable by the method of ozone data validation adopted, i.e. the World Meteorological Organization proposed guidelines (Center, 1994);

Criterion 2: Date of occurrence: autumn - winter episodes (between November and February);

Criterion 3: Time of occurrence: nocturnal episodes (between 21:00 UTC and 7:00 UTC);

Criterion 4: Number of stations with simultaneously episodes: three or more stations;

Criterion 5: Number of regions of simultaneous occurrence of episodes: two or more regions.

Criterion 1 is composed by five requirements for the data to be considered as questionable, namely:

a) Ozone concentration greater than 300 $\mu g.m^{-3}$;

b) Ozone concentration constant (±1%) for over 8 hours;

c) Ozone concentration in excess of 280 $\mu g.m^{-3}$ for more than 8 hours;

d) Ozone concentration in excess of 200 $\mu g.m^{-3}$ for more than 10 hours;

e) Ozone concentration less than 4 $\mu g.m^{-3}$ for more than 6 hours.

However, some of these requirements have been excluded because they had characteristics which cannot be used for the identification of STE episodes. That is the case of the requirement b) and e).

3. Results

Between 1988 and 2010, 303 of ozone episodes were identified that meet at least one criterion. Accomplish criterion 3 (nocturnal episodes) is the most recurrent situation with 139 episodes (26%), while in the opposite is the criterion 2 (episodes during the autumn - winter period) with an incidence of 78 episodes (14%) (Fig. 2). About 22% of the selected episodes attained simultaneously at least three or more criteria leading to suspicious in eventual events of stratospheric intrusions.

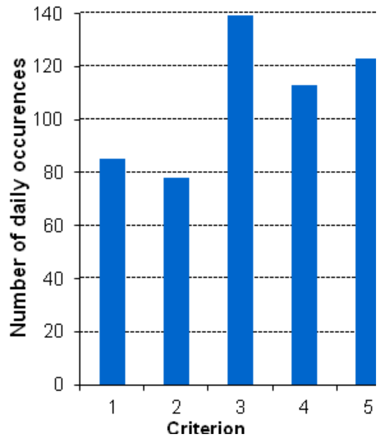

Fig. 2.- Number of daily occurrences for each criterion between 1988 and 2010.

Globally, for the selected episodes, none of them has satisfied simultaneously the five criteria previously defined, while 144 episodes (47.5%) meet only one criterion, being concentrated mostly in 1988 and 2005 (Fig. 3). At the same time 91 episodes (30%) and 60 episodes (19.8%) fulfilled simultaneously two and three criteria, respectively. Only 8 episodes (2.6%) fulfil four criteria, 5 of these episodes have occurred in 2005, whereas 1 episode was recorded in the years of 1988, 1989 and 2001.

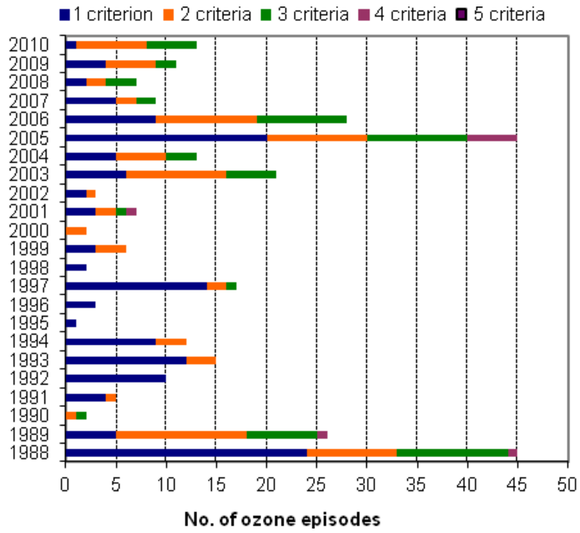

Fig. 3.- Number of ozone episodes with number of criteria satisfied.

The temporal analysis shows that all criteria were verified simultaneously only in 1988 (Fig. 4). There is a tendency of a higher growing prevalence of the criteria 1, 2 and 3 for the time interval from 1988 to 1997 and the criteria 4 and 5 in the case of the period from 1999 to 2010. In the years of 1995 and 1998 are particular cases of the existence of episodes that only fulfil one of the criteria, they being the criterion 1 and criterion 5, respectively. The years of 1988 and 2005 reveal a greater number of episodes that fulfil most of the applied criteria.

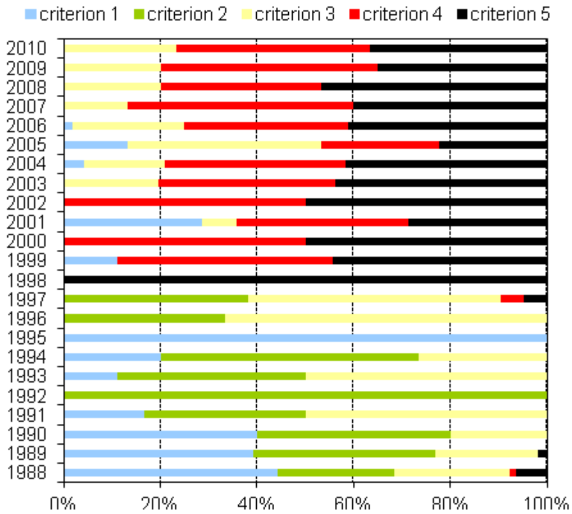

Fig. 4. - Percentage distribution of criteria used for selection the ozone episodes recorded by the active air quality stations between 1988 and 2010 in Portugal.

A high percentage of daily ozone episodes were recorded during the years 1988, 1989, 2005 and 2006. The normalisation of the annual number of episodes by the annual number of active stations has shown a tendency of decreasing of the occurrence of ozone episodes, where the concentration exceeds 180 $\mu g.m^{-3}$ (Fig. 5). This is visible in 1988, when the largest amount of episodes has occurred, corresponding to 35.9% of ozone episodes. However there is a great inter-annual variability in the number of episodes. In the years of 1995, 1998, 2000 and 2002 the percentage of ozone episodes was lesser than 1% of the 303 total ozone episodes occurred along the period in study. This low percentage has been recorded also since 2007, being expected a continuous decrease of ozone episodes.

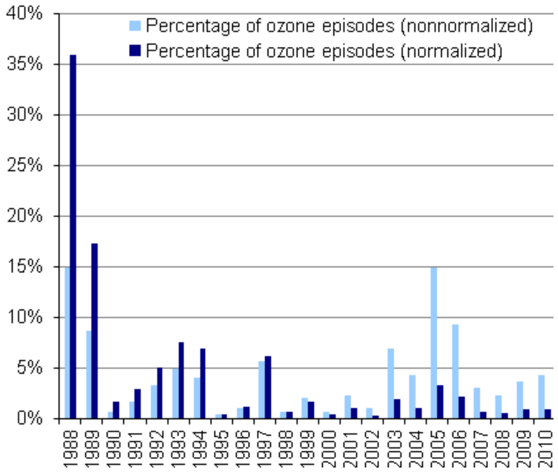

Fig. 5. - Percentage of ozone episodes recorded in Portugal between 1988 and 2010.

4. Discussion

According with our study was possible identified 303 ozone episodes. Part of these episodes may be related with STE conditions. The identification of these ozone episodes fulfilled a selected group of criteria (§2).

The criteria with more relief are the first three criteria, which are not associated to local photochemical production and/or are doubtful occurrences according with its origin by WMO.

Figure 2 presents a higher number of ozone episodes for criterion 3 (nocturnal episodes) having a doubtful for the origin of these ozone episodes because didn´t have total conditions to be ozone episodes with origin from a photochemical reactions. Latest studies (e.g. (Evtyugina *et al*., 2009; Monteiro *et al*., 2012)) demonstrate an occurrence of nocturnal ozone episodes all over Portugal what can be related with some of these selected nocturnal episodes. Criterion 2 show the least number of occurrences, this criterion is not fulfill since 1997 (Fig. 4). However measurements show that winter ozone is increasing, corroborating by EMEP (European Monitoring and Evaluation Programme) model for the year of 1990 and during the time period of 1995-2002 (Jonson *et al*., 2006).

The years with a higher number of possible ozone episodes correspond to 1988 and 2005 (Fig. 5) being years with intense solar radiation, low humidity, meteorological conditions favorable to ozone production by photochemical reactions (IM, 2009; Miranda *et al*., 2006). Although, it is visible that criterion 1 is the most satisfied in 1988, which correspond to suspicious episodes of stratospheric intrusions (Figure 3).

Along the years there is a tendency of fluctuation in the number of ozone events may be related to changes in emissions of ozone precursors and variations in meteorological conditions (Vingarzan *et al*., 2003).

5. Conclusions

The selection of the events, according with the applied set of criteria, allows the identification of 303 possible events caused by stratospheric intrusions.

Mostly of these episodes occurred in the years of 1988 and 2005, which recorded 45 episodes in each year (15% of the 303 episodes).

The analysis of results shows that most of the ozone episodes occur at night (26%) (criterion 3) which suggest stratospheric intrusions or photochemical ozone transport. The majority of the episodes (23%) were measured during 1988 and 1989.

While there has been a fluctuation in the number of ozone episodes, there is a decrease tendency in ozone episodes recorded since 1988, especially since 2007, with stabilization of low number in ozone episodes.

Beside this work, in order to establish ozone background levels and ozone tendencies backward and forward time correlations between the ozone tendencies and the total ozone column from the *Total Ozone Mapping Spectrometer* will be also done. The future work will also include ozone data analysis throughout the application of *Kolmogorov-Zurbenko* (KZ) filters, in order to separate the components involved on the different dynamic processes included on the ozone time series. Furthermore, the future work will include correlations with ground based long term data of natural radionuclides (beryllium 7) with ozone data in order to analyse the influence of stratospheric intrusions on surface ozone concentrations.

The DYNOZONE Project aims to evaluate what are the optimal conditions to originate tropospheric ozone by stratospheric intrusions and create a tool capable to evaluate and preview events of tropospheric ozone by STE.

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