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

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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<sub>x</sub>), in the presence of solar radiation. Another important source for the presence of ozone in the troposphere is the stratospheric ozone bridged down through Stratosphere-Troposphere Exchange (STE) processes (e.g.: [1, 2, 3]). This source can contribute to the presence of 552-765 Tg.yr<sup>1</sup> of tropospheric ozone whereas the contribution from photochemical reaction is 6.2-6.7 times higher [4].

Due to its oxidative characteristics, is recognized the negative impact of ozone on human health and in the environment [5, 6]. For this reason, at European level, the Directive 2008/50/EC 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. This rule establishes objectives for assess and manage 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 [1, 2, 7]. 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 poster.

To perform this work, long data series of ozone collected between 1988 and 2010 in Portugal have been evaluated. The series 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).

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 [8]. In this work the information threshold to the population defined by the Directive 2008/50/EC was used to identify the episodes (180 µg.m<sup>-3</sup>).

To analyse and identified episodes, several criteria's were defined. Thus the episodes were selected when are above information threshold and at least one of following criteria was satisfied:

**Criterion 1:** Data questionable by the method of validation data for ozone adopted the WMO;

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

**Criterion 3:** Time of occurrence: nocturnal episodes, (between 21h and 7h); **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.

Between 1988 and 2010 were identified 303 ozone episodes that meet at least one criterion. Accomplish Criterion 3 (nocturnal episodes) is the most recurrent situation with 26%, while in the opposite is the criterion 2 (episodes during the autumn - winter period) with 14% of incidence. About 22% of the selected episodes records at least three or more criteria's at time leading to suspicious in eventual events of stratospheric intrusions. Globally, for the selected episodes, none of them has the five criteria defined previously, while 144 episodes (47.5%) meet only one criterion.

The temporal analysis shows that only in 1988 were verified simultaneously all criteria (Fig. 1). 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 an only one criterion, they being the criterion 1 and criterion 5, respectively. The years of 1988 and 2005 reveal a greater number of episodes with diversity of criteria applied.

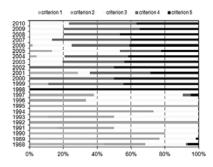


Fig. 1.- Percentage distribution of criteria used for selection the ozone episodes recorded by the active air quality stations between 1988 and 2010 in Portugal.

A high percentage of ozone episodes for the years 1988, 1989, 2005 and 2006, on a daily basis, were recorded. 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<sup>-3</sup> (Fig. 2). This is visible in 1988, when the largest amount of episodes has occurred.

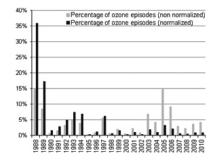


Fig. 2.- Percentage of ozone episodes recorded in Portugal between 1988 and 2010.

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 measures during 1988 and 1989. A long the years there is a tendency of fluctuation in the number of ozone events maybe related to changes in emissions of ozone precursors and variations in meteorological conditions [9].

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