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Surface ozone behaviour at rural sites in Portugal

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A B S T R A C T

Surface ozone (O_3) is one of the most important pollutant in the atmosphere, causing several damages on human health, climate, vegetation and materials. This pollutant presents different behaviours in urban and rural environments. High levels of nitrogen oxides (O_3 precursor) at urban sites have an important role in the photochemical O_3 production in the atmosphere. However, O_3 concentrations tend to be higher in rural areas. To better understand this phenomenon, this study aims to apply statistical methods to evaluate the O_3 behaviour at 13 rural sites in Portugal.

The results showed that: (i) the O_3 concentrations presented the highest values in 2003 and 2005; (ii) the standard values for human health protection was surpassed at almost all monitoring sites; (iii) the maximum concentrations usually occurred at the same time at all monitoring sites (the highest frequency at 16 h), with exception of the monitoring site located in Azores archipelago which had an almost uniform distribution; (iv) three groups of monitoring sites were identified using cluster analysis; and (v) similar daily average profiles of O_3 concentrations were observed at sites belonging to the same group.

1. Introduction

Ozone (O_3) is a natural compound present in different layers of atmosphere. In the troposphere, it is involved in several atmospheric physical and chemical processes. For instance, O_3 is an infrared absorber (greenhouse gas) and it is a precursor to the formation of the hydroxyl radical which affects the oxidising capacity of the atmosphere (Fiore et al., 2002; Fishman, 1991; Oltmans et al., 2006; Rodriguez and Guerra, 2001). Its concentration in any given area is the result of the combination of formation, transport, destruction and deposition. Their sources include: (i) photochemical reactions involving its precursors (volatile organic compounds and nitrogen oxides) with natural or anthropogenic origin; (ii) downward transport from stratosphere; (iii) long-range transport (intercontinental) of ozone from distant pollutant sources (Derwent and Kay, 1988; EPA, 1993).

There are several studies reporting the increase of the surface O_3 (Cartalis and Varotsos, 1994; Lisac and Grubisic, 1991; Nolle et al., 2005; Vingarzan, 2004). The main factors for high ozone level episodes are the increase of temperature, photolysis reactions of nitrogen oxides and the variation in boundary layer as function of temperature during the day and the night times. The increase of surface O_3 concentrations led to the emerging of the public concern about its negative effects on human health, climate, vegetation and materials (Fiore et al., 2002; Fishman, 1991; Fuhrer et al., 1997; Jerrett et al., 2009; Lippmann, 1991). Consequently, the European Union (EU) established limit values for O_3 in ambient air (Directive, 2008). The information threshold (considered to carry health risks for short-time exposure of particularly sensitive groups) is 180 $\mu g\,m^{-3}$ for hourly average concentrations and the alert threshold (considered to carry health risks for short-time exposure of the population in general) is 240 $\mu g\,m^{-3}$. The O_3 target value for the human health protection is 120 $\mu g\,m^{-3}$ concerning maximum daily 8 h average concentrations and should not be exceed more than 25 days per calendar year averaged over 3 years.

To verify if the legislated limits are accomplished and to identify spatial patterns and temporal trends, several air

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quality monitoring networks were established in Europe and other parts of the world. The monitoring sites were generally selected focusing on urban and low-elevation location, aiming the protection of human health in areas of highest population density (the rural areas take less relevance in this selection). However, it is also important to evaluate the background O_3 concentration for protection of the human health and vegetation. Several studies can be found aiming the characterisation of O_3 behaviour in rural areas (Jaffe and Ray, 2007; Kalabokas et al., 2000). Particularly for O_3, the monitoring in rural areas is very important due to the significant differences between its behaviour in urban and rural areas (Duenas et al., 2004; Garcia et al., 2005). The main causes of these differences are the concentration levels of nitrogen oxides that have an important role in O_3 formation.

In this study, the O_3 behaviour was characterised at 13 rural sites in Portugal aiming: (i) the assessment of the tendency and distribution of O_3 concentrations at the rural sites; (ii) the evaluation of the exceedances of the standard values for human health protection; (iii) the analysis of the daily maximum values for O_3 concentrations at all monitoring sites; (iv) the application of cluster analysis (CA) to group the monitoring sites according to their O_3 behaviours; and (v) the analysis of the daily average profiles of O_3 concentrations. The remainder of this paper is outlined as follows: in Section 2 the data are presented and procedure used in CA is described; in Section 3, the achieved results are discussed, and finally; in Section 4 the main conclusions are presented.

2. Methodology

2.1. Ozone measurements

This study focuses the analysis of O_3 concentrations at the following rural sites: (i) *Lamas de Olo* and *Senhora do Minho* (managed by *Comissão de Coordenação e Desenvolvimento Regional*—CCDR-*do Norte*); (ii) *Ervedeira*, *Fornelo do Monte*, *Fundão* and *Montemor-o-Velho* (managed by CCDR *do Centro*); (iii) *Chamusca* and *Fernando Pó* (managed by CCDR *de Lisboa e Vale do Tejo*); (iv) *Monte Velho*, *Sonega* and *Terena* (managed by CCDR *do Alentejo*); (v) *Cerro* (managed by CCDR *do Algarve*); and (vi) *Faial* (managed by *Direcção Regional do Ambiente dos Açores*). The study period was from January 2001 to December 2008. However, only two monitoring sites had O_3 measurements for all period. Table 1 presents the geographical coordinates and altitude of the monitoring sites and their starting date of O_3 measurements. Fig. 1 shows a map with the spatial distribution of the monitoring sites. The analysis of O_3 data was performed for each year of the study period.

Hourly averaged O_3 concentrations recorded at monitoring sites were extracted from the Portuguese Environmental Agency database website (http://www.qualar.org, accessed on August 2010). A minimum value of monitoring efficiency (50%) was used to select the monitoring sites for each sub-period corresponding to 1 year. O_3 measurements, according to the EU Directive 2008/50/EC (Directive, 2008), were performed through UV-photometry using the equipment 41 M UV Photometric Ozone Analyser from Environment S.A. (operated on a full scale range of 0–500 ppb/1000 μg m^{-3}, at any temperature in the range of 15 °C to 35 °C, with the response time set to 50 s). Measurements were continuously made and hourly average concentrations (in μg m^{-3}) were recorded. The equipment was submitted to a rigid maintenance programme, being calibrated each month, according the *Laboratório de Referência do Ambiente* (LRA) procedure (LRA, 2010). The calibration procedure consists in the introduction of air without ozone in the analyser, which follows the introduction of standard concentrations of ozone. For each O_3 concentration, the value given by the analyser is registered. The comparison between the reference values and the values given by the O_3 analyser led to create a calibration curve and calculate the corrective factors.

Table 1
Geographical coordinates and altitude of the monitoring sites and their starting date (SD) of O_3 measurements.

	Site	Geographical coordinates	Altitude (m)	SD
CE	Cerro	37° N; 07° W	300	15-10-2004
CH	Chamusca	39° N; 08° W	43	01-11-2002
ER	Ervedeira	39° N; 08° W	32	01-01-2003
FA	Faial	38° N; 28° W	310	06-04-2006
FP	Fernando Pó	38° N; 08° W	57	18-04-2007
FM	Fornelo do Monte	40° N; 08° W	741	04-11-2005
FU	Fundão	40° N; 07° W	473	05-06-2003
LO	Lamas de Olo	41° N; 07° W	1086	03-02-2004
MV	Monte Velho	38° N; 08° W	53	01-01-1987
MO	Montemor-o-Velho	40° N; 08° W	96	24-10-2007
SM	Senhora do Minho	41° N; 08° W	777	11-03-2005
SO	Sonega	37° N; 08° W	235	01-01-1987
TR	Terena	38° N; 07° W	187	15-02-2005

2.2. Statistical methods

CA is a classification method used to divide the data in classes or clusters. The objects grouped in the same class are similar to each other and different from the ones belonging to other classes (Manly, 1994). Recently, CA was applied to the management of air quality monitoring networks, grouping the monitoring sites with air pollution behaviour in urban areas (Gramsch et al., 2006; Pires et al., 2008a, 2008b). As far as it is known, no study was performed aiming the CA application for characterisation of O_3 behaviour in different rural areas.

For cluster analysis, O_3 concentrations were Z standardised to have zero mean and unit standard deviation. Euclidean distance was used to compute the distance between the O_3 standardised concentrations measured at the different monitoring sites and the cluster procedure was the ward linkage method (Manly, 1994). The complete procedure is presented as follows: (i) determination of the distance between all objects; (ii) linkage of the two objects that correspond to the lowest distance to form a new class; (iii) evaluation of the distance between the other objects and the new class; (iv) repetition of the last two steps until all objects belong to one class. The result of this procedure is usually presented by a tree diagram, the dendrogram. This diagram is useful for evaluation of the adequate number of classes.