1. Introduction

Surface ozone ($O_3$) concentrations are strongly influenced by meteorological variables (e.g., solar radiation and wind) and photochemical reactions. Previous studies have suggested that meteorological variability has an important role in diurnal, daily, seasonal and annual cycles of $O_3$ levels (2, 5, 9, 11). The solar cycle is statistically significant with $O_3$’s long-term trends, influencing photochemical reactions and vertical transport of $O_3$ precursors (4). The temporal $O_3$ variability is also affected by temporal variations in the intensity of human activities, contributing to the temporal pattern of $O_3$ precursor’s emissions (1).

The pattern cycle of $O_3$ in rural areas is characterized by the presence of a single maximum and minimum. The minimum $O_3$ values are recorded in the period from night until the first hours of morning. During the morning $O_3$ levels increase gradually after the period of higher intensity of $O_3$ precursor’s emissions. The maximum is achieved in the early afternoon due to the period of higher photochemical activity and poor dispersion. In the late afternoon, $O_3$ levels present a marked reduction due to its consumption by titration with nitrogen monoxide (NO) emissions.

In urban areas the daily cycle of $O_3$ presents two relative maximum values. The second peak occurs during the evening, usually, rather than the rush-hour maximum. Studies proved which presence of the second peak indicate that it is a result of poor dispersion conditions and by process of vertical and/or horizontal transport of older air masses with high levels of $O_3$ (1, 2, 5–8).

The knowledge of $O_3$ temporal variability is an important factor that contributes to an adaptation of control policies for $O_3$ concentration peaks in order to protect the population and environment from its exposure.

3. Results

As general characteristics, Fig. 2 shows that in urban type stations the maximum concentration of $O_3$ during the morning appears at around 16:00 during most of the year; a secondary maximum appears during the early morning, at around 4:00; the minimum values of the curves appear at around 8:00. This is also observed for the suburban stations during autumn and winter months, only. These characteristics where not observed for the rural stations, in which the maximum ozone concentration appears as smooth afternoon peaks during spring and summer, and the minimum values have similar values between 0:00 and 8:00.

Fig. 3 shows the daily individualized climatological pattern found for each station present in a certain region (1-6). The black vertical lines group these regions, and are numerated in the top x axis of each graphic. The early morning secondary maximum peak of $O_3$ is expressive in regions 3 and 5. During winter (JFM) and autumn (ONM) the ozone concentrations show higher values in region 5.

When compared to the other regions, the $O_3$ average urban values in region 5 are higher during the daily pattern. This characteristic is visible also in rural background stations over the four seasons for regions 5 and 1.

These patterns indicate that these regions may be under the influence of air masses photochemically active during transport from regions with high emissions of $O_3$ precursors. This may also be supported by the time of the maximum value found over these same regions, which is around 28:00 during spring and summer. For both regions, emission sources may be located in Portugal as well as in Spain.

It is also visible that the early morning secondary peak is more intense during spring (AMJ) over urban background stations. As expected, $O_3$ titration is more intense when the human daily activity starts and radiation is available and at the end of the day.

2. Methods

$O_3$ measurements from urban, suburban and rural background stations (Fig. 1), during several years, were used to compute the $O_3$ concentration climatology. Only stations with 5 or more years of available data were considered.

An inter-annual mean for every hour of the year was calculated and a 30-day moving average was applied to the annual cycle. The daily cycle was filtered using a 3-hour moving average.

The daily cycles for every day of the year were grouped into the months of winter (January to March), spring (April to June), summer (July to September) and autumn (October to December), and average daily cycles were computed for each station.

Daily cycles for each background station are presented, with the median cycle overlaid, in Fig. 2, for each environment type.

Fig. 3 shows the spatial distribution of the daily cycles of $O_3$ concentration, by displaying $O_3$ concentrations, for each hour of the day, for each station, grouped by region code (as shown in Fig. 1).

4. Final Remarks

The present work applies statistical treatment, usually applied on meteorological data, to $O_3$ quality data measured in background environment stations subject to different influences: urban, suburban and rural. Background environment stations were chosen in order to diminish local emission influences on the measured data. Also, the ozone time series analyzed span from 5 to 22 years which was still a lack in literature.

The climatological behavior of the air quality stations shows differences among the annual seasons (as defined in this work) and the type of stations, as expected. The unexpected finding relates with the secondary ozone maximum, which is reported in the literature as occurring in the afternoon whereas the data in Portugal show this secondary maximum in the early morning, at around 4:00, especially in urban background stations. This characteristic may occur when the residual layer above stable surface layers may be at the same level of the stations sensors, which is highly probable during very cold nights. This residual layer may have contribution from local photochemistry, medium distance transport.

References


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