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Diurnal variability of total ozone column over Madrid (Spain)

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ABSTRACT

In recent years, research on ozone variability has mainly focused on the analysis of its trend. Additionally some studies have analyzed the annual, seasonal and day-to-day ozone variations. However, intra-diurnal total ozone variations are notably less explored. Thus, the main objective of this paper is to analyze the diurnal variability of total ozone column (TOC) as recorded by a Brewer spectrophotometer in Madrid (Spain). The results show that about 90% of days present non-negligible diurnal variability, indicating that, in general, it should not be assumed that TOC remains constant throughout a particular day in urban areas. In addition, this variability has a notable seasonal behavior which should be considered (the spring and summer months show higher diurnal TOC variations than autumn and winter months). This pattern is likely caused by the diurnal photochemical processes in the lower troposphere related to the formation of tropospheric ozone near the earth's surface at populated urban locations. Thus, these diurnal fluctuations in tropospheric ozone could explain part of diurnal TOC variations (between 20% and 70% depending on the mixing layer height).

1. Introduction

About 85–90% of the ozone in the atmosphere is accumulated in the stratosphere, the region from about 10 to 40 km above the earth's surface. Variations in total ozone column (TOC) are mainly due to changes in stratospheric ozone which, at midlatitudes, are caused mostly by transport and photochemical processes (World Meteorological Organization, 2003).

Ozone variability occurs on different time scales. The relationship between TOC changes and time scales are well documented in literature such as day-to-day (i.e. meteorological conditions, ozone mini-holes or mini-highs) (Vaughan and Price, 1991; Barsby and Diab, 1995; Bojkov and Balis, 2001; Wohltmann et al., 2005; Antón et al., 2008), seasonal (i.e. Brewer–Dobson circulation) (Salby and Callaghan, 1993; Nikulin and Karpechko, 2005; Bortoli et al., 2009; Antón et al., 2010), year-to-year (i.e. planetary wave activity, quasi-biennial oscillation) (Tung and Yang, 1994; Fusco and Salby, 1999) and long-term (i.e. photochemical destruction, climate change, solar variability) (Molina and Rowland, 1974; Farman et al., 1985; Zerefos et al., 1997; Rex et al., 2004). In contrast, few results were found in the literature about the diurnal variability of TOC in different locations (none in Spain). Subbaraya et al. (1994) studied the diurnal TOC variation at one Indian location during two months, reporting diurnal changes between 1.6% and 4%. Kerr and McElroy (1995) analyzed the relationship between the ozone concentration at ground-level and the diurnal variability of TOC data recorded by a Brewer instrument during only two weeks at Table Mountain Observatory (USA). Raj et al. (2004) studied the daytime patterns of the TOC series measured during the period 1998–2003 at Pune (India), obtaining a mean variability of 7%. Vasilyev (2004) classified the diurnal trend of the TOC data over two distant stations located at Russia and Cuba by three views: zero, quasi-linear with a monotonous increase or decrease, parabolic with a minimum or maximum during a day.

In this context, the present article analyzes the diurnal variability of the TOC in Madrid (5 million inhabitants) recorded by a well-calibrated Brewer spectrophotometer for the period 1999–2003. In addition, the relationship between the diurnal TOC changes and the tropospheric surface ozone variability is studied in detail. To our knowledge, only the work of Kerr and McElroy (1995) has been focussed on this subject. Therefore, our study will contribute improving knowledge of the processes which drive very short-term variability of TOC over urban areas.

Day-to-day variations in TOC are mainly attributed to dynamical atmospheric transport processes (Wohltmann et al., 2005). This is due to the well known short-term chemical stability of stratospheric ozone which presents no significant diurnal variability.

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However, the troposphere contains between 6% and 20% of the TOC (Kourtidis et al., 2002, see Fig. 9) and ozone contained in this layer actually shows a notable diurnal variability mainly attributed to photochemical processes (primary in the lower troposphere in certain locations and seasons) and to transport processes (in the medium and upper troposphere) (Massambani and Andrade, 1994; Gimeno et al., 1999; Varotsos et al., 2001). Thus, very short-term changes of the tropospheric ozone may result in diurnal variations in TOC values. In addition, the well documented diurnal variability of ozone amount above 40 km altitude could also contribute to diurnal TOC fluctuations. For example, in the work of Schneider et al. (2005) a relative increase in ozone amount between daytime and night-time of about 20% at the 47.5 km layer is reported. However, since the ozone amount above 40 km is less than 3% of TOC, its diurnal variability could hardly have a measurable effect on accumulated TOC values (less than 0.6%).

It is worth to note that in general, the Langley method to retrieve values for the aerosol optical depth (AOD) from spectral UV irradiance measurements assumes that the daily total ozone amount remains constant throughout a particular day (Slusser et al., 2000). This hypothesis is assumed since it greatly simplifies the inversion algorithms. However, in the work of Arola and Koskela (2004) the effect of a diurnal ozone cycle on the Langley method from Brewer measurements is briefly discussed and it is suggested that the systematic diurnal ozone change cannot be overlooked if this method is applied for highly polluted urban stations. Thus, the analysis of diurnal TOC variability in this type of locations is necessary in order to obtain accurate AOD values from the Brewer spectrophotometers.

This article is structured as follows. Section 2 describes the measuring sites and instrumentation used in this work. Section 3 summarizes the methodology applied to the data. The results and discussion are presented in Section 4 and, finally, Section 5 summarizes the main conclusions.

2. Measuring sites and instrumentation

Madrid is located at the center of the Iberian Peninsula and its metropolitan area has a population of five million inhabitants, involving a car fleet of almost 2.5 million vehicles. This heavy road traffic is the main source of surface ozone precursors in Madrid. Moreover, other anthropogenic emission caused by heating equipment and industries could be a secondary source of surface ozone. The weather in this city is typical of a continental area, characterized by hot dry summers and cold winters.

The instrument used in this work to measure TOC values is the Brewer spectrophotometer MK-IV #070. This fully automated instrument belongs to the Spanish National Weather Service (called the Spanish Agency of Meteorology, AEMET) and it is located in the Complutense University Campus (40.45°N, 3.72°W, 680 m a.s.l.) inside the urban area. A detailed description of the methodology used by the Brewer spectrophotometer to measure the TOC values from direct sunlight can be found in the work of Kerr et al. (1984). The Brewer calibration methodology provides a relative accuracy of measurement of ~1%. The reliability of calibration of Brewer located in Madrid is highly guaranteed. In addition to everyday tests performed with the internal lamps, Brewer #070 is periodically calibrated by comparison with a standard lamp, with calibration traceable to the National Institute of Standards and Technology (NIST). Moreover, this spectrophotometer is intercompared every two years against a Brewer travelling standard (Brewer #017) from International Ozone Services (IOS, Canada), previously calibrated against the triad of Brewer spectrophotometers located at the Meteorological Service of Canada (international world reference of Brewer instruments) (Fioletov et al., 2005). In this work, only the most accurate Brewer ozone data obtained through direct sunlight (DS) measurements were used.

The Madrid Air Pollution Network has made measurements of the surface ozone since January 1999 at the "Barrio del Pilar" monitoring station (40.48°N, 3.71°W, 673 m a.s.l.), also inside the urban area. The surface ozone was measured using an automatic UV-absorption analyzer (Horiba monitor, model APOA-360, Horiba Europe, Langenfeld, Germany) installed in a temperature-controlled room. The continuous surface ozone measurements were hourly averaged and recorded on a data-logger. This ozone analyzer is calibrated every month by means of a reference ozone generator (secondary transfer standard) which was previously verified using the NIST Reference UV Photometer, SRP-22, (Spanish National Standard) located at Instituto de Salud Carlos III (Madrid) (Fernández et al., 2005). Relative expanded uncertainty ($k = 2$, level of confidence 95%) of surface ozone measurements were estimated to be less than ±10%.

The distance between the surface ozone station and the Brewer station is about 3 km. Since both instruments are located at spatially representative stations this distance does not play a significant role in the analysis performed in this work.

3. Methodology

The diurnal TOC variability is quantified by means of the coefficient of relative variation (CRV) defined in this paper as:

$$\mathrm{CRV} = 100\frac{\mathrm{P_{90}} - \mathrm{P_{10}}}{\mathrm{P_{50}}}, \quad (1)$$

where P_{90}, P_{50} and P_{10} are the daily TOC percentiles 90, 50 and 10, respectively. Thus, CRV is a useful descriptive measurement of relative daily dispersion. The percentiles 90 and 10 (robust parameters) are used instead of maximum and minimum values in order to remove possible extreme anomalous values. In this work, the diurnal ozone variability is considered negligible when CRV is lower than 1% (precision of DS total ozone data from the Brewer spectrophotometer). In addition, when the CRV is higher than 5%, the diurnal ozone variability is considered as notable.

The other interesting variable used in this work to characterize the diurnal TOC variability is the mean rate of the diurnal ozone change as calculated by the following definition (Vasilyev, 2004):

$$V_s = \frac{1}{n-1}\sum_{i=1}^{n-1}\frac{\Delta X_i}{\Delta t_i}, \quad (2)$$

where ΔX_i is the difference between two consecutive Brewer total ozone measurements during the period Δt_i and n is the total daily Brewer records. This variable has been calculated only when n is higher than 10 to guarantee the statistical significance. The mean rate of the diurnal ozone change gives an estimation of the net intra-daily trend in TOC.

In order to quantify the day-to-day variability in TOC, the following relative variable was calculated as:

$$\mathrm{DDV}_i = 100 \times \frac{[\mathrm{TOC}_{i+1} - \mathrm{TOC}_i]}{\mathrm{TOC}_i}, \quad (3)$$

where TOC_i and TOC_{i+1} are the daily mean values of the total ozone column for the two consecutive days i and $i + 1$.

The period of Brewer measurements extended from January 1999 to December 2003, sampling a wide representative range of atmospheric conditions. The total number of the days for analysing the TOC diurnal variability is 1499. Within this data set, the month of December has the smallest number of days (89) and July (153) has the most.