Dynamical and temporal characterization of the total ozone column over Spain

Authors: D. Mateos[1,*], M. Antón[1], G. Sáenz[1], M. Bañón[2], J.M. Vilaplana[3], J.A. García[1]

[1] Departamento de Física, Avda. de Elvas s/n, CP 06006, Badajoz, Spain

[2] Departamento de Producción, Agencia Estatal de Meteorología, Madrid, Spain.

[3] Departamento de la Tierra, Teledetección y Atmósfera, Estación de Sondeos Atmosférico El Arenosillo, INTA, Huelva, Spain.

* Corresponding author: D. Mateos, Departamento de Física, Universidad de Extremadura, Avda. Elvas s/n, 06010, Badajoz, Spain. Telephone: 0034-924289300 (ext. 89122). E-mail: davidmv@unex.es

Abstract

As the ozone is one of the most relevant variables in the climate system, to get further in its long-term characterization is a critical issue. In this study, measurements of total ozone column (TOC) from five well-calibrated Brewer spectrophotometers placed in the Iberian Peninsula are analyzed. The ozone recovery is observed for the period 1993-2012, with a significant positive trend of +9.3 DU per decade in Central Iberian Peninsula. However, the low TOC levels during 2011 and 2012 over the study region notably reduce the rate of the TOC temporal trend. Empirical linear relationships are established between TOC and pressure, height, and temperature of the tropopause. The three linear fits showed seasonal and latitudinal dependence, being the relationships stronger during winter and spring months. Events with the presence of a double tropopause (DT) are proved to be characteristic of the study region. The decrease in TOC levels when these anomalous events occur is quantified around 10% in winter and spring with respect to the usual cases with a single tropopause. The total weight of the DT events with respect to the annual values is about 20%, with a negligible occurrence in summer and autumn and being latitudinal-dependent. The North Atlantic Oscillation (NAO) index explains the 30% of the total ozone variability in winter. The DT events are found to be more frequent with a positive phase of NAO index.

1. Introduction

Ozone is a greenhouse gas, with a maximum concentration of 0.0012% of the total of atmospheric constituents (Iqbal 1983). However changes in its abundance may contribute to global climate change (World Meteorological Organization, WMO 2007) with an estimated shortwave radiative efficiency around -0.011 W m^{-2} per Dobson Unit (Antón and Mateos 2013). Between the end of the 1970s and the beginning of the 1990s, a significant decreasing trend in ozone concentration values was observed due to the increase in chlorofluorocarbon (CFC) emission by anthropogenic activity. Successful implementations of the Montreal Protocol on substances that deplete the ozone layer have controlled their levels in the atmosphere, with the corresponding recovery of the ozone layer out of the polar regions (Bais et al. 2007).

Due to the recovery of the ozone layer during the last years, natural variations of ozone caused by the 11-year solar cycle, circulation patterns like North-Atlantic Oscillation (NAO), Artic Oscillation (AO), Quasi-Biennial Oscillation (QBO), or large-scale Brewer-Dobson circulation, together with emission of man-made ozone depleting substances have to be analyzed in detail (e.g., Appenzeller et al. 2000; WMO 2007; Steinbrecht et al. 2011; Rieder et al. 2011). Natural variations caused by dynamical processes are the main responsible for the ozone declines/increases observed during the 20th century in the Northern hemisphere (e.g., Harris et al. 2008; WMO 2007; Hood and Soukharev 2005). Koch et al. (2005) explained the variation of TOC values in the 1980s by the action of a global mechanism, the fast far-range transport of air masses from different regions, but also by a local mechanism of adiabatic vertical displacement of isentropes. For instance, high levels of TOC observed during 2010 in the Northern hemisphere were attributed to a pronounced and persistent negative phase of AO and

NAO, together with the easterly wind-shear phase of the QBO (Steinbrecht et al., 2011). NAO influences TOC values not only in winter (Appenzeller et al. 2000), but also in summer (Ossó et al. 2011). With respect to the ozone radiative effect, Mateos et al. (2013) obtained for thirteen stations in the Iberian Peninsula a maximum impact in spring, being the annual ozone radiative effect less than -1 W m^{-2} in the solar shortwave range.

Changes in ozone profiles in the midlatitude lower stratosphere are linked to changes in vertical transport (e.g., Fortuin and Kelder 1996). Hence, the meteorological influences on TOC have been studied by previous works using tropopause characteristics. This choice is justified since the tropopause forms a boundary between the well-mixed and ozone-poor troposphere, and the stratified and ozone-rich lower stratosphere (Steinbrecht et al. 1998). Therefore, tropopause, somehow, can quantify the dynamical disturbances in the TOC values (Krzyscin et al. 1998). The height of the thermal tropopause is negatively correlated with TOC, i.e., high tropopause cases correspond to low ozone values, and vice versa. Over two central European stations, Hoinka et al. (1996) and Steinbrecht et al. (1998) obtained rates of -13 and -16 DU per kilometer in tropopause height, respectively.

The purpose of this study is to provide an exhaustive characterization of TOC over the Iberian Peninsula as a function of different meteorological parameters, such as height, pressure and temperature of the thermal tropopause, the presence of double tropopauses, and the NAO circulation pattern. In this paper, daily values of NAO index and tropopause characteristics are analyzed as a function of long-term ground-based databases of TOC between 1990 and 2012. Furthermore, this article contributes to improve the knowledge about the relationship between TOC and double tropopause events, being the first time, to our knowledge, that ground-based measurements are used to this purpose.

2. Ground-based measurements and reanalysis data

2.1. Ground-based TOC data

Daily values of TOC used in this study were measured by the Spanish Brewer Network which consists of five Brewer spectrophotometers at five ground-based stations, covering most of the Iberian Peninsula geography. This network is managed by the Spanish Agency of Meteorology (AEMET) with nearly 20 years of experience in measuring TOC data with this type of instruments. Table 1 shows information about the geographical situation of these five stations.

Table 1. Geographical locations of the five stations used in this study.

Station	Latitude (ºN)	Longitude (ºE)	Altitude (m a.s.l.)	Time interval	Data coverage (% of total days)
A Coruña	43.33	-8.42	58	Jan/1999 - Dec/2012	75%
Zaragoza	41.01	-1.01	260	Oct/2001 - Dec/2012	87%
Madrid	40.45	-3.72	664	May/1991 - Dec/2012	83%
Murcia	38.03	-1.17	61	Apr/1995 - Dec/2012	75%
El Arenosillo	37.10	-6.73	41	Jan/1998 - Dec/2012	85%

Brewer instruments are type MK-IV (single monocromator), except the Brewer MK-III (double monocromator) located at El Arenosillo. The quality of the TOC data provided by the Spanish Brewer Network is ensured due to the periodic checks and tests. Furthermore, intercomparisons with the traveling references Brewer 017 from the International Ozone Services (IOS) and the Brewer 185 from the Regional Brewer Calibration Centre–Europe (RBCC-E) are performed every 2 years, guarantying that the ozone calibration of all Spanish Brewer spectrophotometers is traceable to both the triad of international reference Brewers maintained by Environment Canada at Toronto (Fioletov et al. 2005) and the AEMet-Izaña instrument. In this sense, the estimated uncertainty of the TOC data obtained through the direct sunlight measurements is about 1%. As these instruments of the Spanish Brewer Network are properly calibrated and regularly maintained, they have the potential to maintain a precision of 1% over long periods of time (WMO 1996). More details about the calibration process and the reliability of the TOC data used in this study were described by, e.g., Antón et al. (2010) and the references there in.

2.2. Reanalysis data and tropopause characteristics

The tropopause temperature (TRO_T), pressure (TRO_P), height (TRO_H) and double tropopause (DT) events used in this study have been calculated from the ERA-Interim reanalysis data. This is the new reanalysis produced by European Centre for Medium-Range Weather Forecasts (ECMWF) and covers the period from 1979 to the present day. ERA-Interim uses 4D-variational analysis on a spectral grid and a hybrid vertical coordinate system with 60 levels. Further details were given by Simmons et al. (2007) and Dee et al. (2011). We have chosen ERA-Interim because its vertical resolution suits better to the analyses of tropopause. The horizontal resolution is a fixed grid of 1.5 by 1.5 degree.

The tropopause is usually located across the abrupt change in the vertical temperature gradient between the troposphere, where temperature decreases with altitude, and the stratosphere, where the temperature is constant or increases with height. Thus, the thermal tropopause is defined from thermal gradient ($\Gamma=-\partial T/\partial z$), applying the standard definition of the World Meteorological Organization (WMO, 1957): the thermal tropopause corresponds to "the lowest level at which the thermal gradient decreases to 2ºC/km or less, provided that the average thermal gradient between this level and all higher levels within 2 km does not exceed 2ºC/km". As the thermal-based criterion is designed to locate transition points in the thermal structure and not quasimaterial surfaces, it also allows for multiple tropopauses. Thus, following the WMO, "if above first tropopause, the average lapse rate between any level and all higher levels within 1 km exceeds 3ºC/km, then a second tropopause is defined by the same criterion than first tropopause. This tropopause may be either within or above the 1 km layer". The requirement of a minimum depth of 2 km in the first tropopause definition and a range of pressure levels below 700 hPa in the thermal gradient for searching the tropopause are demanded to minimize the influence of outliers in the temperature profile and the misinterpretation with lower or mid-troposphere inversions.

The TRO_P is calculated from thermal gradient (Γ), using the methodology proposed by Reichler et al. (2003), especially created for reanalysis data. To obtain the TRO_T, an interpolation of temperature profile to value of $(TRO_P)^{\kappa}$ (where $\kappa=R/C_p$, R denotes the gas constant for dry air and C_p the specific heat capacity of air at constant pressure) is carried out. The TRO_H is calculated by vertically integrating the hydrostatic relation:

$$TRO_H = h_0 - \frac{R}{g}\int_{p_{sfc}}^{p_{TP}} T \ln p \qquad (1)$$

where h_0 is the height of the orography, R is the specific gas constant, g is the acceleration due to gravity, p_{TP} is tropopause pressure, p_{sfc} is surface pressure, T is the temperature calculated from average virtual temperature and p is the pressure in each atmospheric level.

2.3. NAO index data

Atmospheric circulation affects the levels of atmospheric ozone because of the presence of different phenomena and conditions. The North Atlantic Oscillation (NAO) governs the atmospheric circulation mode in the Euro-Atlantic sector. It is defined as the pressure difference at sea level between Iceland and Azores Islands. The NAO controls the direction and intensity of the westerly tropospheric jet stream over the Atlantic (Orsolini and Limpasuvan, 2001). Positive NAO index produces higher tropopause pressure at high latitudes and lower mid-latitudes. During this phase, the enhanced pressure difference between the subtropical area and Iceland produces air masses crossing the Atlantic Ocean northwards. As a consequence, lower ozone values over Europe are produced. The opposite occurs in the NAO negative phase (Appenzeller et al., 2000; Orsolini and Doblas-Reyes 2003).

To evaluate daily values of NAO index we proceed as follow: Empirical Orthogonal Functions (EOF) of the geopotential at 1000 mb over an Atlantic area, from 20ºN to 90ºN and from 60ºW to 40ºE, were calculated using seasonal winter (December, January and February) data, which were weighted by the root squared of the latitude. The first EOF that explained more than 40% of the variability was selected. The projection of the daily field onto the first EOF gives out the sought daily NAO index. (e.g., Blessing et al. 2005; Johansson 2007).

2.4. Methods

From the daily TOC data, monthly averages are calculated when, at least, 10 days of the selected month present ozone data. As was shown by, e.g., Palancar and Toselli (2004), the frequency distribution of the change in TOC between two consecutive days peaks at 0 DU. Hence, with the threshold of 10 days, the monthly mean can be considered as representative. With respect to the yearly TOC averages, analyzing the TOC annual cycle (e.g., de Miguel et al. 2011), they are calculated when daily data is over 70% of whole year.

To establish a relationship between TOC and the different variables used in this study, the linear fits in the form Y = a + b X were used. The correlation coefficients (r) and the 95% confidence intervals are evaluated ($95\%_{CI}$).

In order to homogenize as much as possible the obtained results among the five stations used in this study, the monthly standardized anomalies (SA) of TOC were evaluated by the following expression:

$$SA = \frac{TOC_i - TOC_{month}}{SD_i^{TOC}} \quad (2)$$

where TOC_i is the monthly value, SD_i^{TOC} is the standard deviation for this month, and TOC_{month} is the monthly average over the period between 2002 and 2012. This selection was made attending to the largest common period among the five ground-based stations used in this study. With this selection, the SA values are directly comparable among them.

The Mann-Kendall nonparametric test is used at the 95% confidence interval in order to check the significance level of the linear trends. The criterion to determine the significance of the results obtained in the section dedicated to the double tropopause events is based on a Montecarlo test, and the 95% confidence interval is required to be classified as statistically significant.

3. Long-term TOC evaluation over the Iberian Peninsula

The temporal evolution of the yearly TOC values over the five measuring sites is plotted in Figure 1. As main results, evolution of the maximum and minimum values, and increasing/decreasing trends of yearly TOC seem to be in agreement at the five ground-based stations. Northern and Central stations (A Coruña, Zaragoza, and Madrid) presented larger TOC than the Southern stations (Murcia and El Arenosillo). This difference between Northern and Southern stations was also observed in Portugal by Antón et al. (2011a; 2011b). As was noticed by previous studies mentioned above, 2010 was a year with very high levels of TOC at northern mid-latitudes. Over the Iberian Peninsula, we also observed very high levels of TOC this year, and also in 2003 (particularly at A Coruña station). These maximum TOC values can be understood as the mixed of global circulation effects with a predominant negative phases of NAO and QBO. As regards the absolute minimum values, they were achieved at mid-1990s, the beginning of the analyzed time interval, with annual values <310 DU at Madrid and Murcia stations. For instance, the low TOC levels in 1997 and 2011 can be related to a positive NAO contribution together with the easterly phase of QBO. Krzyscin (2012) also noted an extreme ozone loss at high latitudes of the Northern hemisphere at the beginning of 2011 explained by a low stratospheric temperature and a strong positive phase of the Arctic Oscillation. The linear TOC trends of the five series were determined, and only Madrid station showed a statistically significant trend (>95% of significance level) of +9.3 DU per decade between 1993 and 2012.

To minimize the impact of the ozone annual cycle, Figure 2 shows the monthly standardized anomalies of TOC values at the five stations. The five curves follow similar pattern, particularly at certain periods. For instance, during 2003 (at the beginning of the year) and 2010, just the same years mentioned above, the SA were positive with monthly values even larger than +1. The five curves also show negative values in 2011. Hence, the events mentioned before in the yearly TOC values can also be seen in the monthly SA. Looking at the SA temporal evolution shown in Figure 2, temporal trends were evaluated for the common period among the five stations, i.e., between 2002 and 2012. The results obtained show three statistically significant temporal trends around -0.5 SA-units per decade for Madrid, Murcia, and A Coruña stations. Analyzing the two longest data series, Madrid and Murcia, the temporal trends obtained for these stations were 0.36 and 0.24 SA-units per decade, respectively, for 1991-2012 and 1995-2012, respectively. The positive trends can be understood because the lowest TOC values at the northern mid-latitudes occurred at the beginning of the 1990s, which are mainly attributed to the effects of the Mt. Pinatubo eruption (e.g., WMO, 2011). All these temporal trends complete those determined over the Iberian Peninsula before 2010 (Antón et al. 2011a, 2011b). The decrease of the TOC levels (negative anomalies) observed at the end of the period (between 2011 and 2012) reduces the values of the trends. For instance, the trend obtained for Madrid station between 1991 and 2012 was 0.36 SA-units per decade, while the one for the period between 1991 and 2010 was 0.6 SA-units per decade. The period following the high TOC levels in 2010 has received much attention due to the severe Arctic polar ozone depletion in spring 2011. The Arctic polar vortex showed low temperatures and high-speed zonal winds, and it was associated with a weak stratospheric wave activity and a strong positive phase of the Arctic Oscillation. All these effects caused an enhanced ozone chemical loss greater than 80% (Arnone et al. 2012; Krzyscin 2012; Hu and Xia 2013).

4. Relationship between TOC and tropopause

In order to look for a relationship between total ozone column and the tropopause characteristics in the last twenty years over the Iberian Peninsula, we performed analyses between daily TOC and tropopause pressure (TRO_P) . The following linear fit is evaluated using all the daily values for each one of the twelve months for the time periods shown in Table 1:

$$TOC = p_1 + p_2\ TRO_P \qquad (3)$$

The results of the monthly linear fits of equation (3) are shown in Figure 3. As it can be seen, the slope of the linear fit, the rate of change in TOC for change in the tropopause pressure, exhibits a clear seasonal pattern: p_2 presents values around 0.6 DU hPa^{-1} in the first five months of the year, beyond this month the influence of the tropopause pressure is weaker with minimum values around 0.2 DU hPa^{-1}. This pattern is linked to the variability of ozone through the year. Antón et al. (2010) studied the day-to-day TOC variations over Madrid finding the maximum rate of change between January and April (~8%) while the minimum (~2.5%) during summer months. This fact is attributed to the pass of synoptic weather systems at middle and high latitudes and the decrease in the planetary wave activity in summer (e.g., Vaughan and Price 1991). In this case, there is not influence of the geographical position on the obtained results.. Analyzing the values of the correlation coefficient (r) for equation (3), Figure 3b, the variations in the tropopause pressure can explain between the 40% and 80% of the variations in TOC values.

The linear fits between TOC and other tropopause characteristics were also analyzed. The results obtained for the linear fits between TOC and tropopause height, and TOC and tropopause temperature are very similar to the TRO_P fit. Tables 2 and 3 shows the statistical estimators for the linear fits with annual values at the five stations.

Table 2. Annual statistics of $TOC = h_1 + h_2\ TRO_H$.

Station	r	$95\%_{CI}$	h_2 (DU km^{-1})	h_1	n
A Coruña	-0.58	(-0.60,-0.56)	-16.2	546.6	3803
Zaragoza	-0.55	(-0.57,-0.53)	-13.1	563.1	3406
Madrid	-0.50	(-0.52,-0.48)	-11.1	540.8	5878
Murcia	-0.47	(-0.49,-0.45)	-8.7	451.0	5630
El Arenosillo	-0.34	(-0.37,-0.31)	-7.7	420.0	4630

Table 3. Annual statistics of TOC = t_1 + t_2 TRO_T.

Station	r	$95\%_{CI}$	t_2 (DU K^{-1})	t_1	n
A Coruña	0.44	(0.41,0.47)	3.10	-336.49	3803
Zaragoza	0.50	(0.47,0.52)	3.69	-464.23	3406
Madrid	0.49	(0.47,0.51)	3.27	-379.60	5878
Murcia	0.50	(0.48,0.52)	3.12	-343.94	5630
El Arenosillo	0.41	(0.39,0.43)	3.08	-338.09	4630

The results obtained in this study (Figure 3 and Table 2) were compared with the reported by earlier studies. For instance, Hoinka et al. (1996) analyzed TOC values over Hohenpeissenberg site against tropopause pressure data above Munich for different subsets in the period 1974-1993. They obtained a seasonal pattern of the correlation coefficients with larger values in spring (between 0.50 and 0.66) and smaller in winter (between 0.38 and 0.49). Analyzing our seasonal results, we obtained r values over 0.63 in spring and below 0.46 in winter. The slopes of the linear fits with the tropopause height obtained by Hoinka et al. (1996) ranged between 13 and 18 DU km^{-1}, around the middle annual value obtained in this study at A Coruña station. Steinbrecht et al. (1998) analyzed the same rate for two different month intervals: May-June-July and November-December-January. They obtained h_2 = -16.3 DU km^{-1}, and h_2 = -15.7 DU km^{-1}, respectively. In our study, for instance, at A Coruña station: h_2 = -22.7, -22.2, -9.0, and -7.4 DU km^{-1} in winter, spring, summer, and autumn, respectively. Our results for the northern stations (A Coruña, Zaragoza, and Madrid) are slightly smaller than the obtained by these authors. Larger differences are obtained with respect to the Southern stations (Murcia and El Arenosillo), with an annual $h_2 < 9$ DU km^{-1}.

With respect to the TRO_T, the correlation coefficient exhibits a weak dependence through the year, with slight smaller values during winter season. Overall, its values range between 0.35 and 0.8, with an annual average around 0.5. However, the behavior of the linear fit slopes (t_2) exhibits a seasonal pattern, similar to p_2, being the TRO_T influence stronger in winter and spring.

Once the relationship between the tropopause and TOC values is proved, the connection between global circulation patterns and TOC is searched. Gallego et al. (2005) found the North Atlantic Oscillation as the principal mode of climatic variability modulating the climate of the Iberian Peninsula. Hence, daily values of the NAO index were used in this section. The relationship between daily NAO and TOC were evaluated and seasonally averaged (see Table 4). A Coruña site exhibits the strongest influence of the NAO. At this station, the largest correlation was achieved in winter, being the variability in the TOC explained up to 38% by the NAO. On average over the Iberian Peninsula, NAO can explain up to 30% of the TOC variability in winter. This figure substantially decreases for the other three seasons. These results, obtained using ground-based data, can be compared with previous studies using satellite or reanalysis data. Ossó et al. (2011) found a correlation coefficient around -0.2 during wintertime for the Iberian Peninsula region. These authors reported a positive sign of the relationship using the summer NAO index, however this result is not verified with our database. A weak, but still negative, relationship between NAO and TOC in summer was observed. Appenzeller et al. (2000) obtained a winter correlation less than -0.5 for the Iberian Peninsula. One of the reasons behind the relationship between TOC and NAO index is the effect of this index on the tropopause (see, e.g., Ambaum and Hoskins 2000). Other global phenomena, such as the Polar Vortex, QBO, and ENSO can also affect the TOC levels (e.g., Brönnimann et al., 2004; Barriopedro et al. 2010; Frossard et al. 2013; Rieder et al., 2013).

Table 4. Correlation coefficient (r) between daily NAO and TOC. Only significant r values are shown.

	Winter	Spring	Summer	Autumn	Annual
A Coruña	-0.38	-0.16	-0.10	-0.22	-0.33
Zaragoza	-0.17	-	-0.15	-	-0.19
Madrid	-0.33	-	-0.09	-0.11	-0.24
Murcia	-0.28	-0.11	-0.13	-0.11	-0.28
El Arenosillo	-	-	-0.1	0.09	-0.13

5. Double Tropopause events and TOC

Previous studies (Randel et al. 2007; Pan et al. 2009; Peevey et al. 2012; Castanheira et al. 2012) proved that episodes of subtropical air (with a smaller ozone mixing ratio) intrusions above the extratropical tropopause produce a modification of the vertical profiles of atmospheric ozone. As was noticed by Randel et al. (2007), these episodes with a double tropopause (DT) occur frequently over midlatitude regions of both hemispheres, with a higher likelihood of occurrence during winter in the northern hemisphere (Peevey et al. 2012). Castanheira et al. (2012) found negative correlations between the area covered by DTs and TOC. As our study region is placed in the latitude belt of a high relevance of DT events, we analyzed the effect of the presence of double tropopause in the long-term ground-based measurements of TOC.

For each month, we classified each day of the time period by the presence (2TRO) or absence (1TRO) of double tropopauses in the atmosphere. Hence, each seasonal value can be obtained by

$$TOC_{seasonal} = \frac{n_{2TRO}\ TOC_{2TRO} + n_{1TRO}\ TOC_{1TRO}}{n_{day}} \qquad (4)$$

where $TOC_{seasonal}$ is the seasonal TOC average, TOC_{2TRO} is the ozone average value for the days with DT events (n_{2TRO}), and TOC_{1TRO} is the mean ozone for the days without DTs (n_{1TRO}), and n_{day} is the total number of days with TOC data for each season.

We can evaluate the weight with respect to the seasonal average TOC of the DTs events using the following scheme:

$$W_{2TRO}\ (\%) = 100\ \frac{n_{2TRO}}{n_{day}}\ \frac{TOC_{2TRO}}{TOC_{seasonal}} \qquad (5)$$

In addition, to quantify the effect that the second tropopause introduces in the TOC value, the relative difference between TOC_{2TRO} and TOC_{1TRO} ($\Delta_{2\text{-}1TRO}$) was calculated by:

$$\Delta_{2-1TRO}\,(\%) = 100\,\frac{TOC_{2TRO} - TOC_{1TRO}}{TOC_{1TRO}} \qquad (6)$$

With equations (5) and (6), the weight and the contribution of the DT events can be determined and quantified for the five stations used in this study. Figure 4 shows the seasonal values of W_{2TRO}, $\Delta_{2\text{-}1TRO}$, and n_{2TRO}. Firstly, the number of cases of DT events among the five stations differ notably. Northern stations (A Coruña and Zaragoza) present less number of DT cases. One of the reasons, but not the mainly one, behind this difference in the number of data is the different time periods analyzed in this study (see Table 1). In addition, the non continuous dataset in each station can produce discrepancies in n_{2TRO}. In spite of that, this fact does not produce false estimations of the impact of the DT events since W_{2TRO} and $\Delta_{2\text{-}1TRO}$ are relative values. The weight of the DT events in the seasonal TOC averages can reach 12% and 10% in winter at El Arenosillo and Murcia stations, respectively, being the most Southern sites considered in this study. In addition, the points shown in the figure in winter exhibit a clear latitudinal pattern with the smallest contribution (~ 4%) at A Coruña station. W_{2TRO} shows values around 5% at Madrid, Murcia, and El Arenosillo stations in spring. Beyond this point, in summer and autumn, the number of cases drastically diminishes and the influence is almost negligible. For instance, the larger amount of DT events in autumn is 12 at Murcia station, and the minimum is 3 at Zaragoza station. The statistical significance of these results was analyzed by a Montercalo test (see section 2). The five stations exhibited significance for the results of winter and spring, just the months with a higher occurrence of these events. With respect to $\Delta_{2\text{-}1TRO}$, the negative values of this variable during winter and spring point out the smaller amount of ozone in the DT events. The TOC average value in the cases with DTs is 10% lower than the cases with only one tropopause. In summer and autumn the difference between the two scenarios decreases, reaching some positive cases at A Coruña and El Arenosillo. Hence, we verified using ground-based data, the decrease in TOC values when a DT event occurs described by previous studies (see references above). We identify this impact as important at seasonal (and monthly, not shown in this study) scale being more relevant during winter, and clearly latitudinal-dependent also in small belts (in our study, around 8º of latitude).

Due to the relationship between NAO and tropopause, the occurrence of DT events and the daily NAO value was analyzed. Figure 5 shows the geographical distribution of the histograms in the DT events presenting positive and negative NAO index. At the five stations, most of the DT events occur during a NAO positive phase. On average for the five ground-based stations, 60% of the DT events occurred with positive NAO and the other 40% with a negative value. During the positive phase, the ozone levels over Europe decrease and the intrusion of the tropical jet over mid-latitudes can occur. The relationship between DT and NAO is still under research, and this will be the issue for further research.

6. Conclusions

Long-term TOC data series between 1991 and 2012 are analyzed in this study. Five ground-based stations placed in a mid-latitude region at the Eastern Atlantic and the Western Mediterranean areas were used. With Brewer spectroradiometer measurements, daily, monthly and yearly TOC values are analyzed in detail. Furthermore, reanalysis data from ERA-Interim are employed to characterize daily NAO, the tropopause by means of its pressure, height, and temperature, and the events with a double tropopause. The main conclusions obtained through this study are the following:

- TOC exhibits a positive significant trend in the period 1993-2012 of +9.3 DU per decade at Madrid station. The last years of the studied period (2011 and 2012) presented low TOC levels, leading to a negative trend in the period 2003-2012 for Murcia and A Coruña stations. - Empirical relationships between TOC and characteristics of the tropopause (TRO_P, TRO_H, and TRO_T) are established. The linear fits show clear seasonal and latitudinal dependences. For instance, annual values of the slope in the correlation between TOC and TRO_H ranges between -16.2 DU km^{-1} at A Coruña and -8.5 DU km^{-1} at El Arenosillo. The results obtained for TRO_P and TRO_H are in line with previous studies.

- The North Atlantic Oscillation pattern can explain more than 20% of the annual TOC variability over the Iberian Peninsula. This relationship can be understood because of the effect of NAO on the tropopause.

- The influence of the events with a double tropopause is studied in the Iberian Peninsula. The contribution of these winter events with respect to the annual TOC average is around 12% (at the most Southern station, El Arenosillo) and 3% (at the most Northern station, A Coruña). Spring season shows a maximum contribution ~5% for the northern stations, while the DT events are scarce during summer and autumn. Results for winter and spring are statistically significant by a Montecarlo test. The difference on the TOC values in a DT event and a 'normal' scenario with a single tropopause achieves the 10% in winter and spring. Hence, the DT events show a clear latitudinal pattern even on a belt of 8º of latitude as the Iberian Peninsula.

- The DT events are found to be more frequent with a positive phase of NAO index. This situation provides better conditions to the intrusion of tropical air above the extratropical tropopause.

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Figure captions

Fig 1 Temporal evolution of yearly TOC values at the five Spanish stations.

Fig 2 Monthly SA values at the five stations used in this study.

Fig 3 a) Slope (p_2), and b) correlation coefficient (r) of the relationship between TOC and tropopause pressure, equation (3).

Fig 4 Characterization of the DT events influence through the year: a) W_{2TRO} (equation 7), b) $\Delta_{2\text{-}1TRO}$ (equation 8), and c) number of DT events (n_{2TRO}).

Fig 5 Frequency of NAO positive ('POS' in red) and negative ('NEG' in green) index during DT events.

Figures + Figure captions

Figure 1

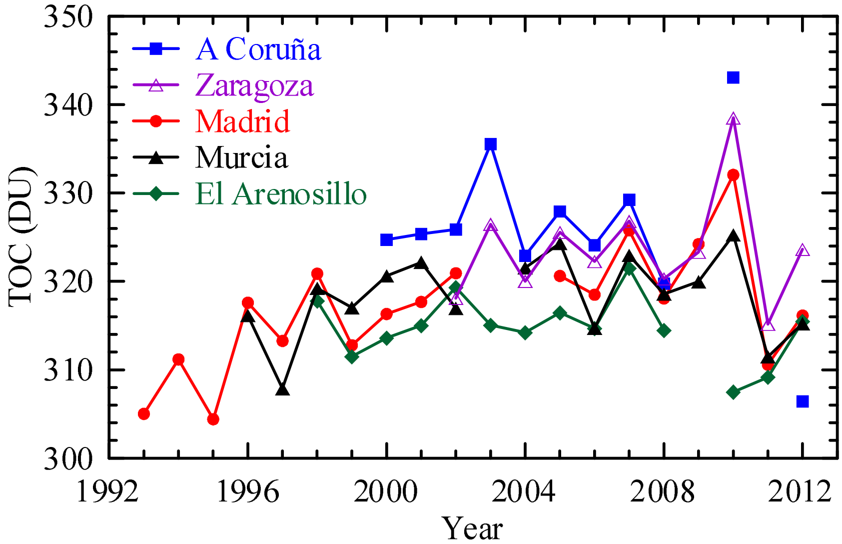

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Figure 2

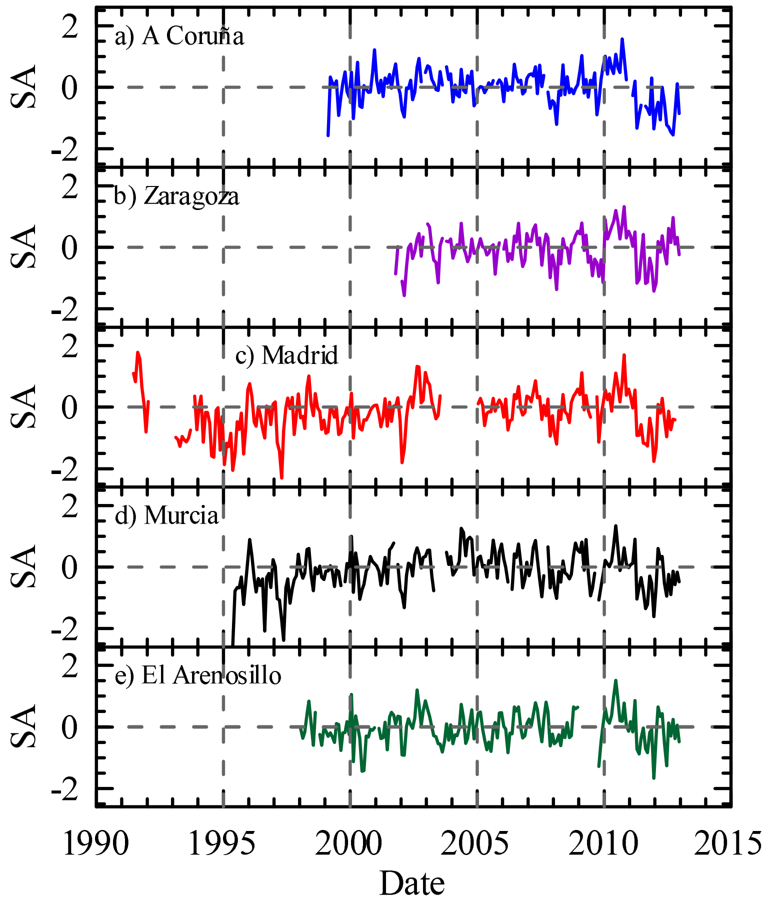

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Figure 3

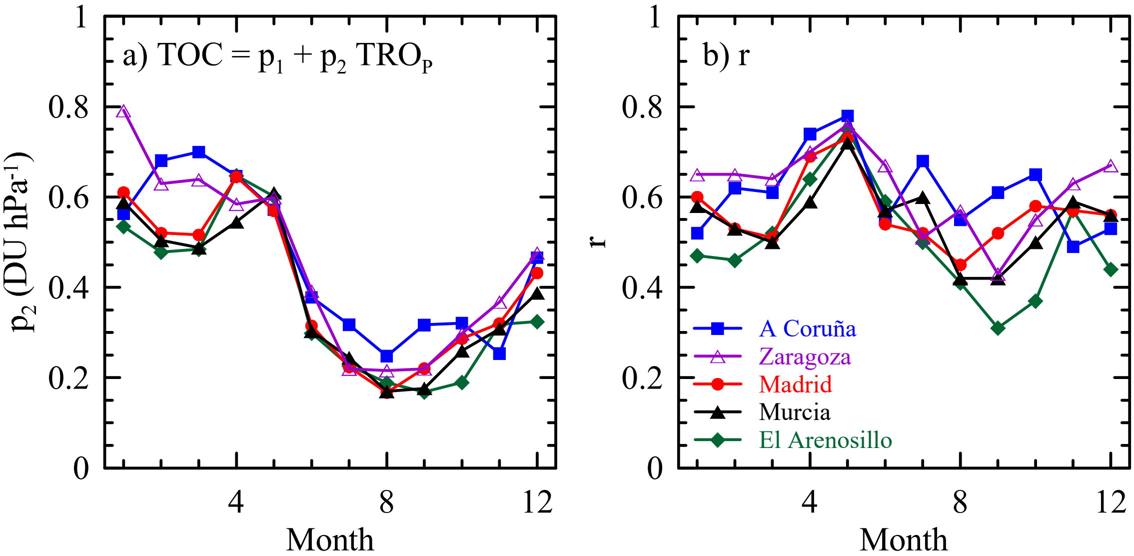

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Figure 4

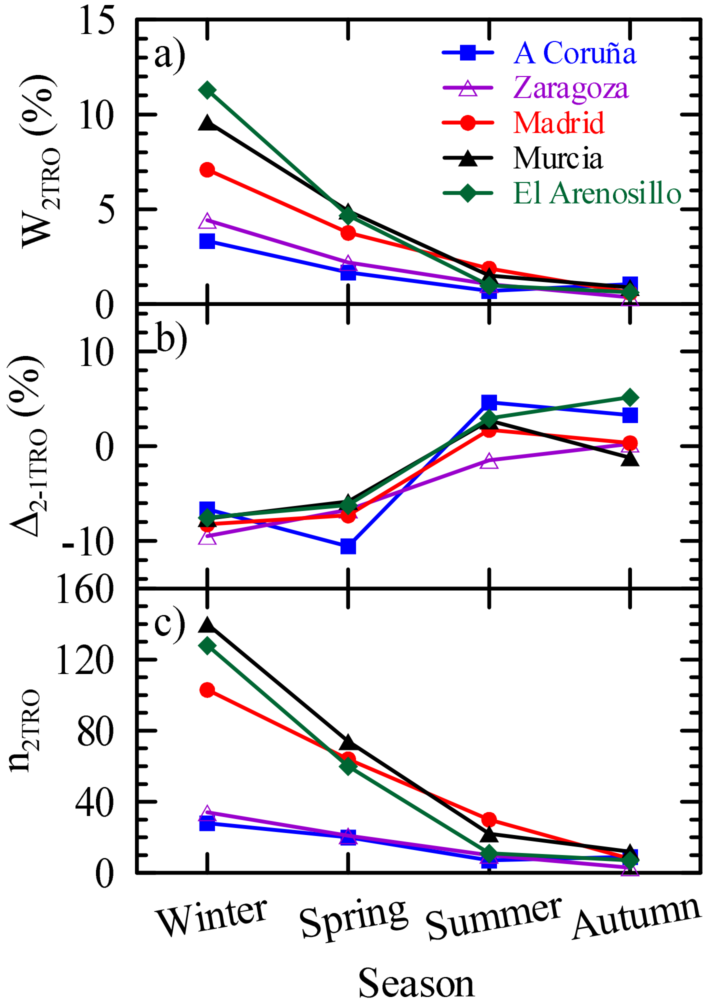

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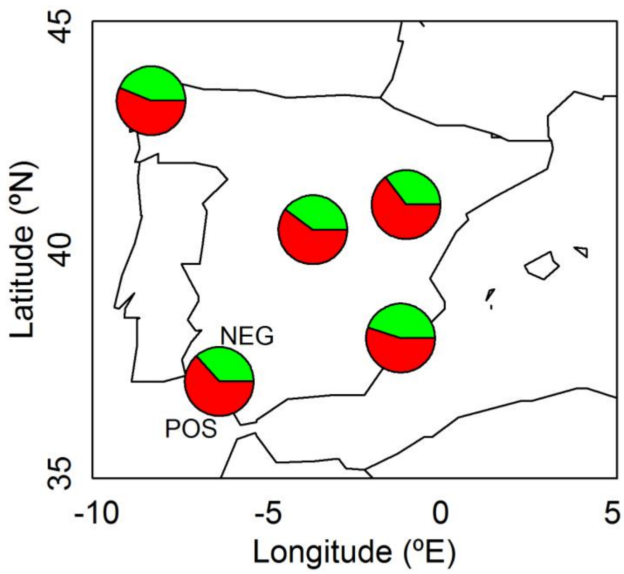
Figure 5



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