

Trend of total column ozone over Mexico from TOMS and OMI data (1978-2013)

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RESUMEN

En este trabajo se presentan las tendencias de 35 años de mediciones diarias de la columna total de ozono (TCO, por sus siglas en inglés) sobre la República Mexicana y en el estado de Zacatecas, y se describen las variaciones interanuales y su dispersión estadística. Para ello se utilizan mediciones satelitales de la TCO obtenidas con el espectrómetro para mapear ozono total (TOMS, por sus siglas en inglés) y el instrumento para el monitoreo del ozono (OMI, por sus siglas en inglés) versión 8. El comportamiento interanual, así como los niveles de dispersión de la TCO resultan sorprendentemente sistemáticos. A lo largo del año los valores más bajos ocurren en los meses de diciembre y enero, mientras que los más altos entre abril y mayo. Los análisis estadísticos realizados muestran que hubo un deterioro significativo del orden del 2.5% en la TCO entre 1978 y 1994, y que entre 1996 y 2013 hubo una estabilización. Aunque el deterioro es apenas significativo, es un indicio de que estas regiones de estudio, atravesadas por el Trópico de Cáncer, no han escapado al deterioro de la capa de ozono. La caracterización aquí descrita tiene importancia desde el punto de vista de monitoreo, pero sobre todo desde el punto de vista científico, por la correlación que existe entre el TCO y los niveles de radiación ultravioleta.

ABSTRACT

Using satellite measurements from the Total Ozone Mapping Spectrometer (TOMS) and Ozone Monitoring Instrument (OMI) version 8, this work presents the total column ozone (TCO) trends over Mexico and, in particular, over the state of Zacatecas. Interannual variations and their statistical dispersion show a surprisingly systematic behavior. Yearly low values occur during December and January, while high values between April and May. A significant depletion of about 2.5% in TCO between 1978 and 1994 is derived from their statistical analysis, which also shows stabilization from 1996 to 2013. Although the depletion is merely significant, it is a sign that the studied regions, crossed by the Tropic of Cancer, have not escaped to the depletion of the ozone layer. The characterization described herein is important in terms of the correlation of TCO and ultraviolet radiation levels.

Keywords: Total column ozone, interannual variation, TOMS data, OMI data.

1. Introduction

The German scientist Christian Friedrich Schönbein discovered ozone in 1839, naming it after the Greek word ὄζειν meaning “to smell”, as suggested by his colleague W. Vischer, professor of greek in Basel (Schönbein, 1840).

The French physicists Charles Fabry and Henri Buisson discovered the ozone layer in the stratosphere and its capacity to absorb the sun’s ultra-violet rays in 1913 (Stratton, 1946).

Ozone represents only about 0.00001% of the atmosphere by volume (de la Casinière, 2003), which implies that there are about two ozone molecules for every 10 million air molecules. However, atmospheric ozone plays a vital role that contradicts this small proportion. Ozone absorbs most of the UV-B radiation and a major part of the UV-A radiation coming from the sun, allowing only a small part to reach the Earth’s surface.

Ozone is found in two regions of the Earth’s atmosphere: about 90% of the ozone resides in the stratosphere, at about 10-50 km above the Earth’s surface; the remaining 10% of ozone is at the troposphere, which extends itself to an altitude of 10 km. The origin of both is different.

At the stratosphere, ozone is formed by oxygen photolysis, induced by UV-C solar radiation. Upon entering the atmosphere, solar radiation can simply be dispersed, producing diffused radiation, or it can interact selectively, leading to changes in the chemical composition of some constituents of the atmosphere.

The nitrogen and oxygen generally produce dispersion or attenuation of solar radiation. However, the higher energy photons, UV-C or extreme-ultraviolet, interact with oxygen molecules causing its dissociation to form oxygen radicals, which combined with other oxygen molecules produce ozone. At the stratosphere, the oxygen molecules’ density is enough to completely attenuate the UV-C radiation. Since UV-C radiation comprises a very small fraction of the solar spectrum, the number of ozone molecules created cannot be very large.

Ozone plays a dual role at the stratosphere, beneficial for the various forms of life on Earth. On one hand it protects the Earth’s surface against much of the UV-B and UV-A radiation, and on the other hand it plays a structural role in atmospheric temperature.

The formation and destruction sequence reactions of natural ozone in the ozone layer are known as Chapman reactions (Chapman, 1930).

Stratospheric ozone is destroyed by photo-dissociation, by absorbing UV-A and UV-B radiations. The photon’s energy is used to break the link in ozone molecules and the energy excess is converted into kinetic energy of the oxygen molecules and of the atomic oxygen produced and released in the dissociation. The kinetic energy of the photo-dissociation results in an increase of the gaseous stirring, and thus generates a significant temperature gradient at the stratosphere.

At the troposphere, ozone formation comes from reactions produced by combustion, but a small fraction is produced naturally by the atmospheric electrical discharges. Nevertheless, the ozone in the vicinity of the surface of the Earth in contact with life forms has the property to react strongly with a number of molecules and becomes chemically toxic to living organisms.

The global mean total column ozone (TCO) is approximately 300 DU, which could be equivalent to a layer 3 mm thick strictly containing ozone at normal conditions. Typically, the TCO range can vary from 100 to 600 DU.

For hundreds of millions of years, the stratospheric ozone concentration remained stable. Molina and Rowland (1974) predicted that ozone would be destroyed by the action of gradually accumulated chlorofluorocarbons (CFC) released into the atmosphere. Chlorine in these compounds acts as the catalyst in the destruction of the ozone layer.

The discovery of the ozone hole over the Antarctic by Farman *et al.* (1985) confirmed the predictions of Molina and Rowland. After the recognition of the stratospheric ozone’s destruction and mankind’s responsibility for it, international actions were promoted to try to reverse the trend. The Montreal Protocol, signed on September 16th, 1987, promoted the ban of production and use of CFCs and other ozone layer depletion compounds. Although the ban was scheduled to begin by 1996, the actions could not take immediate effect, since CFCs dispersed in the atmosphere have very long lives.

The destruction of the ozone layer did not happen only over the Antarctic. In 2003, the Scientific Assessment of Ozone Depletion revealed a drop in ozone levels of about 4% per decade in mid latitudes (WMO/UNEP, 2003). Newchurch *et al.* (2003), among others, reported stabilization in stratospheric ozone since 1997.

The majority of studies of global ozone trends are simulations founded on ground-based measurements and on zonal means over large latitude bands. Decadal trend changes in ozone are modeled by using a satellite monthly mean of ozone data (WMO/UNEP, 2003; Stolarski and Firth, 2006). Zonal means over large latitude bands have already been used in different studies (Fioletov *et al.*, 2002; Fioletov and Shepherd, 2005).

The interannual variability of TCO has received less attention. Ziemke *et al.* (2005) have exceptionally used a TOMS 25-year record to estimate the seasonal cycle, latitude dependence and long-term trends in ozone average over the Pacific region (120° W to 120° E) for six 5° latitude bands extending from 15° S to 15° N.

The goal of this study is to take advantage of the enormous amount of data provided by the Total Ozone Mapping Spectrometer (TOMS) and the Ozone Monitoring Instrument (OMI) in order to study the interannual variation of the TCO over Mexico and the state of Zacatecas. It is assumed that knowing the behavior in these regions can help to better understand the dependence of the radiation levels, UV, Vis and IR with respect to the TCO.

2. Methods and materials

The central Mexican state of Zacatecas is crossed by the Tropic of Cancer between 21° and 25° latitude north and between 100.5° and 104.5° longitude west. Its area is approximately 75 000 km² (about 3.83% of the country). It has an altitude of 1800 to 2400 masl. Its geographical location makes the local characteristics of the atmosphere and the spectral nature of UV of high concern. Mexico is comprised among 86.5° and 114.5° longitude west and among 14.5° and 32.5° latitude north with an area of approximately two million square kilometers.

For this study, NASA's Total Ozone Mapping Spectrometer (TOMS) and Ozone Monitoring Instrument (OMI) satellite measurements of TCO were used, which are the largest and most detailed sources of total column ozone measurements.

TOMS and OMI provide a daily digital data file potentially useful to develop multiple studies of global, regional or local character. The measurement principle is based on registering the atmospheric absorption of solar radiation reflected by the Earth's surface. Due to lack of visibility, Polar Regions cannot be measured during polar nights, which imply the absence of up to 29° of latitude around the

poles during December and June (near the winter and summer solstices). Similarly, there is a lack of up to 6° of latitude around both Poles during March and September (the spring and fall equinoxes). Each daily file contains close to 48 600 TCO data for March and September, and close to 43 200 TCO data for December and June.

NASA's satellite measurements have 35 years of history. Five satellites have been launched carrying the monitoring instruments: (1) Nimbus-7 collected measurements between November 1, 1978 and May 6, 1993; (2) Meteor-3 covered the period from August 2, 1991 to November 25, 1994; a break of 18 months occurred after the failure of Meteor-3, and then (3) the ADEOS satellite was put in orbit covering from August 17, 1996 until June 29, 1997, but these data could not be validated. Before the failure of ADEOS, on July 2, 1996 a new satellite, (4) Earth Probe, was put in orbit to replace ADEOS. Earth Probe covered from July 1996 until December 14, 2005. Before Earth Probe failed, on July 14, 2004, (5) the Aura satellite was launched, in order to develop the Earth Science Projects Division program, dedicated to monitoring the complex interactions that affect Earth. AURA is equipped with an ozone monitoring system called OMI, which has improved the TOMS functions.

Since the beginning of the TOMS program satellite measurements and up to November 22, 2007 (i.e. from NIMBUS-7 to Earth Probe), the measuring instruments onboard the various satellites have provided coverage in such a way, that every TCO measurement was done in steps of 1.25° longitude × 1° latitude. This implies that each latitude degree was covered by 288 measurements, ranging from 179.375° W to 179.375° E. From the most recent phase of the OMI mission, started in September 2004, the coverage improved substantially. For the OMI stage, there are two ways of collecting data: one of 1° longitude × 1° latitude, and another of 0.25° × 0.25°. This means that data readings differ, since the number of measurements per latitude for 1° × 1° steps is 360, so 15 lines are required to report every latitude, instead of 12 TOMS files. For this work at the OMI phase, only measurements with a step of 1° longitude × 1° latitude were used.

TOMS and OMI satellite measurements have been validated against ground-based measurements and have become a standard long-record reference in many studies (McPeters and Labow, 1996;

Fioletov *et al.*, 1999; Bodeker *et al.*, 2001; Harris *et al.*, 2003; Jaross *et al.*, 2003; McPeters *et al.*, 2008).

In order to take advantage of TOMS and OMI measurements, the understanding of the structure of the digital files is required, as well as facilities in order to read the data of interest. After solving the problem of reading and storing data, the problem lies in its statistical treatment, validation and interpretation.

For this work, we have used TOMS and OMI files of the TCO measurements taken between November 1978 and March 2013. There is a lack of data for 18 months due to failure of the Meteor-3 satellite. Overall, 11 700 files were available.

Analyses of interannual variations are made by dividing the measurement mission of NASA in two periods: one from 1978 to the interruption of the measurements in 1994 due to the Meteor-3 satellite failure, and the second one from 1996 to 2013. The studied periods nearly coincide with two stages: the first one, associated to the severe depletion of the ozone layer in Antarctica, and the second one, coming from the middle of the 1990s, called the stage of recovery of the ozone layer (WMO, 2007).

The Mexican territory was covered by 461 daily measurements of the TOMS mission and 576 measurements done by OMI. The state of Zacatecas was covered with nine daily measurements during the TOMS mission and 11 daily measurements during the OMI mission.

The dispersion analysis of the measurements for each region was performed using the statistical range, which is defined as the distance between the minimum and maximum daily value for each region. The range expresses the maximum dispersion of the whole data set and has the advantage that, if there is a wrong extreme value among a set of data, the average does not change appreciably.

3. Interannual variation of TCO over Mexico

The calculation of the three types of daily TCO values (minimum, average and maximum) for Mexico was done by reading all ozone column values from TOMS and OMI daily files, covering longitudes between 84.5 and 114.5° W and latitudes between 14.5 and 29.5° N.

Figure 1 shows the behavior of the statistical range for the average TCO in Mexico during the entire TOMS and OMI missions (1978-2013). It can be

observed that the three types of values (maximum, average and minimum) follow a similar though not identical periodic behavior.

Taking into account the maximum spread, or range, it can be observed for Mexico, as Figure 1 shows, that TCO values range from 220 DU to 350 DU. This in itself is a relevant characteristic, which limits the levels of TCO, its interannual variations and their level of dispersion over the entire Mexican territory.

In Figure 1, the maximum values (in blue) have higher dispersion than the minimum values (in black) and than the average values (in red), and this dispersion is more pronounced in the first months of each year. That is, the maximum values have a greater and more frequent overlap than average values and minimum values. Since the scattering is systematically higher early each year, it may indicate the existence of favorable conditions for the stratospheric ozone production at this time, but these conditions are easily changeable.

Contrastingly, the interannual variations of the minimum values have smaller dispersion and are more symmetrical, with the highs in the mid of the year. Meanwhile, the average values have a higher dispersion and a bias towards the first months of the year.

In terms of frequency, the interannual variations of the three categories (maximum, average and minimum TCO values) do not necessarily form a regular sequence but rather a sequence of inverted arches, which account for a relatively sudden change in the processes that characterize the formation and transport of ozone at the stratosphere.

The phases of each sequence, either in maxima or minima, can be located arbitrarily. It can be observed that the phase of the three types of measurement does not match the peaks of the sequences, although they match the minimum points. Furthermore, while the phase changes are abrupt for the maximum values, they are mild for the minimum values.

Little is said in the literature regarding the position of the maxima and minima of interannual variations. According to Bojkov *et al.* (1993), Miller *et al.* (1995), and Jackman *et al.* (1996), the zonal mean ozone trend across the Northern Hemisphere reaches a maximum during February.

In the case of Mexico, the highest levels in Figure 1 in the sequence of maximum values (in blue) appear between March and April; whereas the minimum values (in black) appear between December and

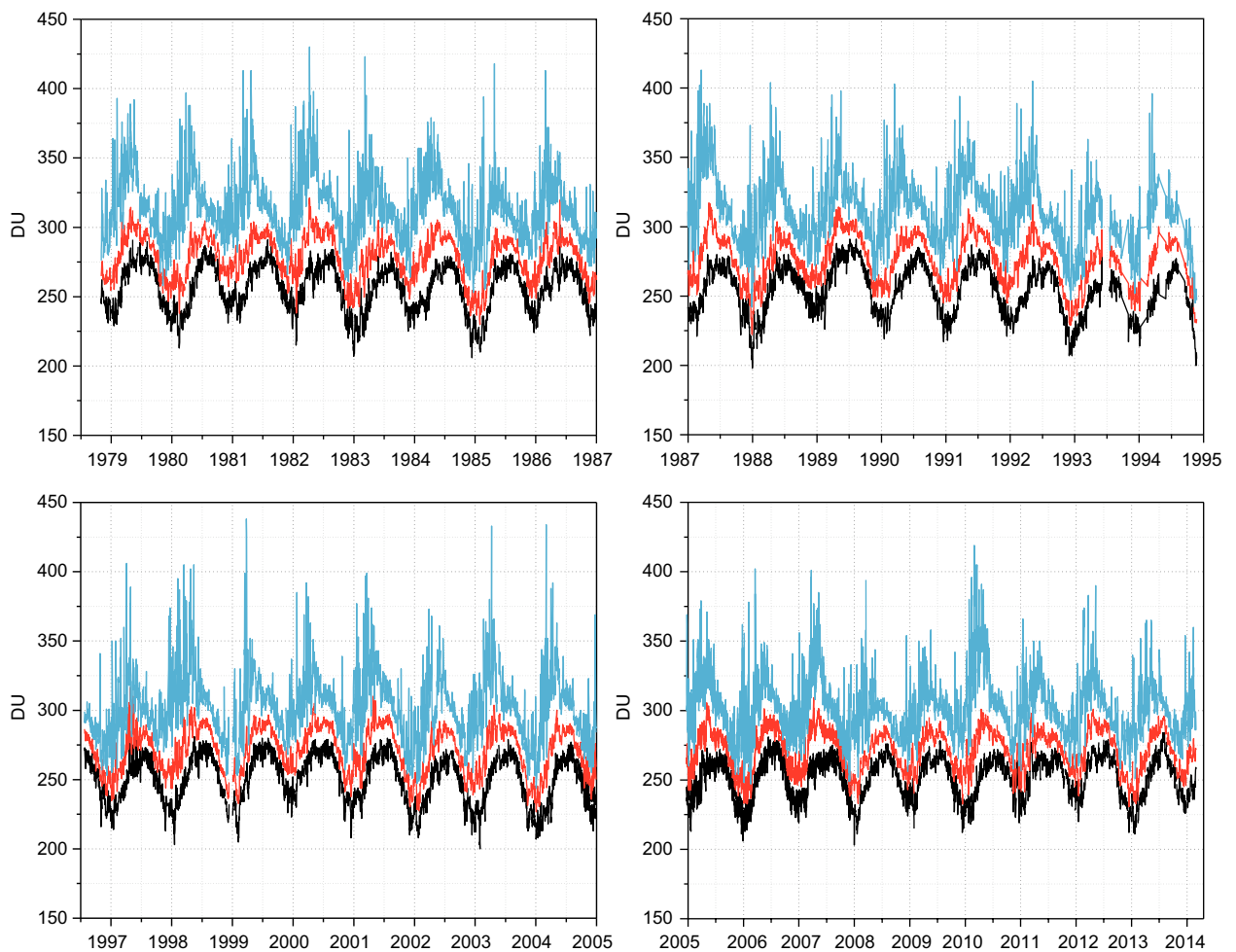


Fig. 1. TCO behavior of the largest (blue), average (red), and smallest (black) daily measurements over the Mexican territory.

January. This results in a slight bias to the left or rather to the first months of each year for the average values. Consequently, a relevant characteristic of the TCO is that higher values do not occur in summer, as it might have been expected.

A consequence of this observation is that in winter the proportion of the UV radiation regarding solar radiation must be greater than in summer, precisely because due to less ozone over the region of the stratosphere, UV radiation attenuation should be lower.

The mean TCO for Mexico in the 35 years of the NASA measurements was 271.1 DU with a standard deviation of 29.8 DU; and the statistical range and its standard deviation was 53.0 ± 23.4 DU. The statistical range is approximately $\pm 9.8\%$ around the mean. Figure 1 shows that the daily average values vary between 275 and 300 DU.

It should be pointed out that the isolated events or incidents can occur during the first few months of each year, which can mean up to around 400 DU. They occur sporadically but are crucial to the interannual TCO behavior modification causing the mentioned bias.

3.1. Comparison of the interannual variations between the periods 1978-1994 and 1996-2013 for Mexico

According to the World Meteorological Organization (WMO), the global TCO decline stopped in 1996 (WMO, 2007). The purpose of this section is to verify whether at the level of Mexico there was also a decline and, if so, it was then followed by stabilization.

It would be desirable to analyze the periods in the same way the WMO does. Due to the lack of data for

the first period, it could only be studied until 1994, as a result of the Meteor-3 satellite failure. It was possible to analyze the second period, which may be called a stabilization period, in a similar way to the WMO, extending it until 2014.

To highlight any differences between the two periods, the calculation of the average values per period was done, and additionally a linear regression of the daily average values per period was performed.

Figure 2 shows the behavior of the average values of TCO for Mexico (red line) and its corresponding linear regression (blue line).

For the period 1978-1994, the average was 276.7 DU with a standard deviation of 16.6 DU, and the statistical range and its standard deviation was 57.3 ± 23.7 DU. The statistical range is $\pm 10.3\%$ around the average per period.

For the period 1996-2013, the average was 270.7 DU with a standard deviation of 16.1 DU, and the statistical range and its standard deviation was 50.6 ± 21.9 DU. The statistical range is $\pm 9.3\%$ around the average per period.

The difference between the two period's average values (6 DU) represents a diminution on the order of 2.2%. This accounts for a significant impact of the depletion of the ozone layer over the entire Mexican territory.

The linear regression analysis (blue line) shows a negative slope of -0.436 DU per year, representing a depletion of 7 DU in the period 1978-1994, which means an order of 2.5%. For the period 1996-2013, there was a slope of -0.033 DU. The negative slope

in the period 1978-1994 indicates a progressive depletion of the ozone column over Mexico, while the slope is virtually zero in the second period, indicating stabilization. This analysis shows that in the period 1978-1994 Mexico experienced a decline in the total column ozone of the order of 2.5%, which is by no means the magnitude observed in Antarctica, but is nevertheless significant.

3.2 *Unsystematic interannual variations*

Figure 2 shows that the interannual variations do not have the same maximum and minimum. To try to elucidate the differences, the TCO average values were calculated per year. The behavior of the annual average values and their standard deviations is shown in Figure 3.

The depletion of the TCO caused by CFCs and ozone-depleting compounds has affected interannual variations, but it should be noted that interannual TCO variations have always existed and have had mainly natural causes. Ozone production depends on UV-C radiation intensity, and natural destruction depends mainly on UV-B radiation intensity, both of which vary throughout the year, which means production and destruction have a stationery character.

Levels of the TCO may have decreased *inter alia* due to the destruction of the ozone produced by volcanic eruptions. A grandiose volcanic eruption influences the atmosphere seriously and causes many climatic effects globally: it impacts radiation, atmospheric temperature and stratospheric ozone depletion. The main cause of volcanic influence depends on stratospheric

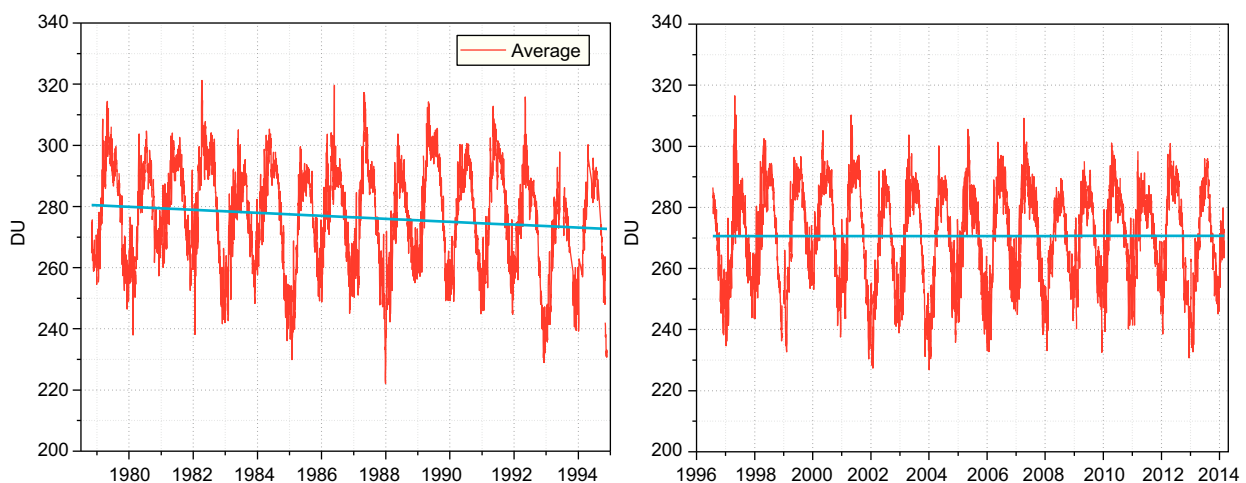


Fig. 2. Behavior of average daily TCO over Mexico.

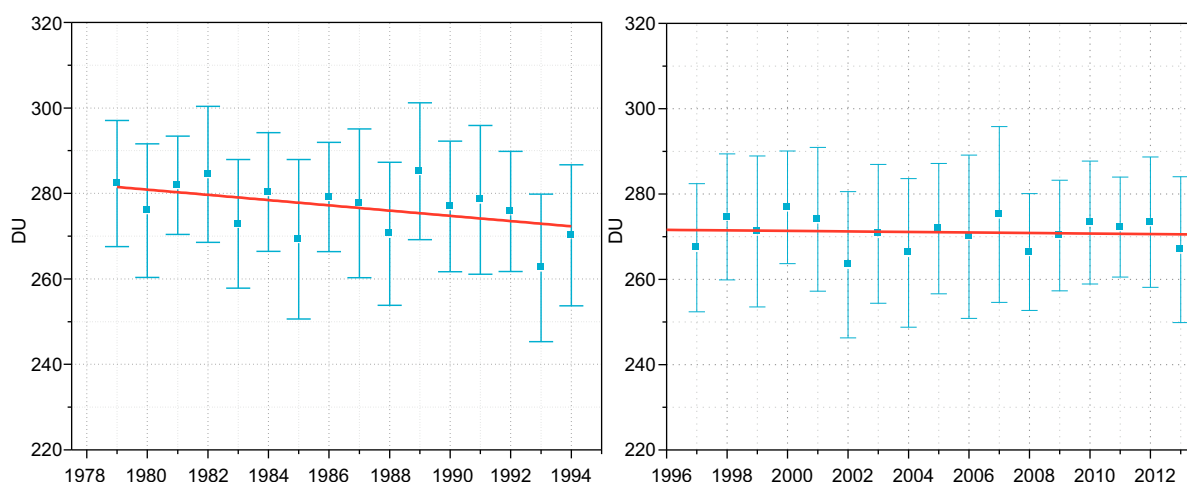


Fig. 3. Behavior of annual average TCO over Mexico.

aerosols, which stay long enough to change the weather, meteorological conditions and ozone depletion. The aerosols injected into the stratosphere can provide a surface where ozone destruction reactions take place very rapidly. Aerosols only have an effect because of the currently high levels of stratospheric chlorine released from ozone-depleting substances: chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), halons, methylbromide, carbon tetrachloride, hydrobromofluorocarbons, chlorobromomethane, methyl chloroform, and the chlorine from HCl, injected into the stratosphere by volcanic eruptions.

Among the major volcanic eruptions since the mid-twentieth century the following are included:

The eruption of Mount St. Helens in the United States in 1980, which had a volcanic explosivity index (VEI) of 5 and released 55 million tons of aerosols into the atmosphere, including 5.5 tons of HCl.

The Chichonal eruption in Mexico, which occurred between March and April 1982 and had a VEI of 4+, expelling 12 million tons of aerosols and 120 tons of HCl.

The Philippine Pinatubo, which erupted between April and June 1991, had a VEI of 5 or 6, and released 30 million tons of aerosols and 310 tons of HCl.

The net effects of a given volcanic eruption depend strongly on the amount of injection and the maximum elevation that emissions reach, as well as the latitude of the volcano itself (Oman *et al.*, 2005; Schneider *et al.*, 2009).

Certainly, in the last 40 years, the eruption that had the biggest effect on stratospheric ozone was that of the Pinatubo. Because of the amount of HCl released

and the intensity of the eruptions, more HCl was further injected into the stratosphere.

The most intense recent volcanic eruptions have been that of the Eyjafjöll in Finland, which occurred between March and April 2010, the Puyehue volcano in Chile in June 2011, and the Nabro, a previously dormant volcano in Northeast Africa that also began to erupt violently in June 2011. The Nabro eruption had substantial ash plumes for the first 48 h, rising to a 9–14 km altitude, and carrying at least 1.3–1.5 Tg of SO₂ (Krotkov *et al.*, 2011). This was probably the largest sulfur yield from an explosive eruption since Pinatubo in 1991 (Pyle, 2012).

In Figure 3, the most drastic annual reduction in TCO during 1993 can be located. The annual average was below 250 DU due to the eruptions of the Pinatubo. This reflects that volcanic effects upon the TCO can persist for up to two years. The Pinatubo eruption generated a decrease on the annual average TCO of the order of 25 DU over the Mexican territory.

Figure 3 shows other significant declines in 1983, 1985, 1988, 1997, 2002, 2008, and 2013. The decline in 1983 may be due to the effect of the eruption of Mount St. Helens in the United States, in 1985 due to the Chichonal effect, in 1997 it can be associated to the minima in the solar activity, and in 2013 it may be due to the eruptions of Nabro and Puyehue. The maximum height reached by the eruption of Eyjafjöll was of approximately 6 km. Thus, this event did not perturb the stratosphere in any way (Thomas and Prata, 2011; Walker, 2012).

Other variations in the levels of the TCO can be due to disturbances in the transport mechanisms of

stratospheric ozone, and to solar activity changes that may induce changes in the ozone production. The 1997 depressions can be associated to the minima in the solar activity.

TCO levels are a kind of radiograph of the phenomena associated with ozone processing in the atmosphere, i.e. production, destruction and transport. However, like all radiographs, they also require interpretation. In any case, the detailed elucidation of the interannual variations of TCO is open to further research.

Figure 3 also corroborates the destruction levels of TCO in latitudes corresponding to Mexico. A linear fit allows us to display a negative slope of -0.6135 DU in the period from 1978-1994, implying 6.1 DU per decade, equivalent to 2.2% per decade or 3.5% per period.

3.3 Inter annual variations of TCO for the state of Zacatecas

In order to study the consistency in the behavior of TCO for the state of Zacatecas, we repeated the methodology applied to the entire Mexican territory.

Figure 4 presents the average daily values of TCO on Zacatecas. It was found, obviously, that the levels of TCO are similar to those of Mexico.

The mean TCO for Zacatecas in the 35 years of the NASA measurements was 264.2 DU with a standard deviation of 39.0 DU; and the statistical range and its standard deviation was 10.4 ± 5.3 DU. The statistical range is approximately $\pm 2\%$ around the mean. TCO values for Zacatecas have a relatively well defined performance; its dispersion is < 5 , and vice versa for Mexico (10.4 vs. 53.0 DU).

No plots are presented for the maximum and minimum values, since the range was found to be very small and the graphics overlap indecipherably.

For the period 1978-1994, the average value of TCO over Zacatecas was 271.8 ± 19.4 DU, and the statistical range and its standard deviation was 11.4 ± 5.12 DU. The statistical range is $\pm 2.2\%$ around the average per period.

For the period 1996-2013 the average value was 266.5 ± 17.4 DU, and the statistical range and its standard deviation was 9.9 ± 5.0 DU. The statistical range is $\pm 1.8\%$ around the average per period.

Between the two periods of study, there is a difference of 5.3 DU, which confirms a depletion of about 2%. Line regression analysis confirms these observations: there is a negative slope of -0.4068 DU per year for the period 1978-1994 (representing 6.5 DU), whereas the period 1996-2013 has a positive slope of 0.169 DU (representing 2.7 DU).

Similar to Figure 2, Figure 4 shows that lowest values of TCO occur in December and January, and the highest are observed in April and May. However, the decline for the whole of Mexico is about 2.5%, whereas for the state of Zacatecas is on the order of 2%.

4. Discussion and conclusions

This study evaluates the TCO interannual variation over Mexico and the state of Zacatecas using the daily files of 35 years of measurements by satellites, conducted by the NASA missions TOMS and OMI.

A great similarity was found between the interannual behaviors in the TCO in both study regions. Ignoring the significant ozone depletion, the average

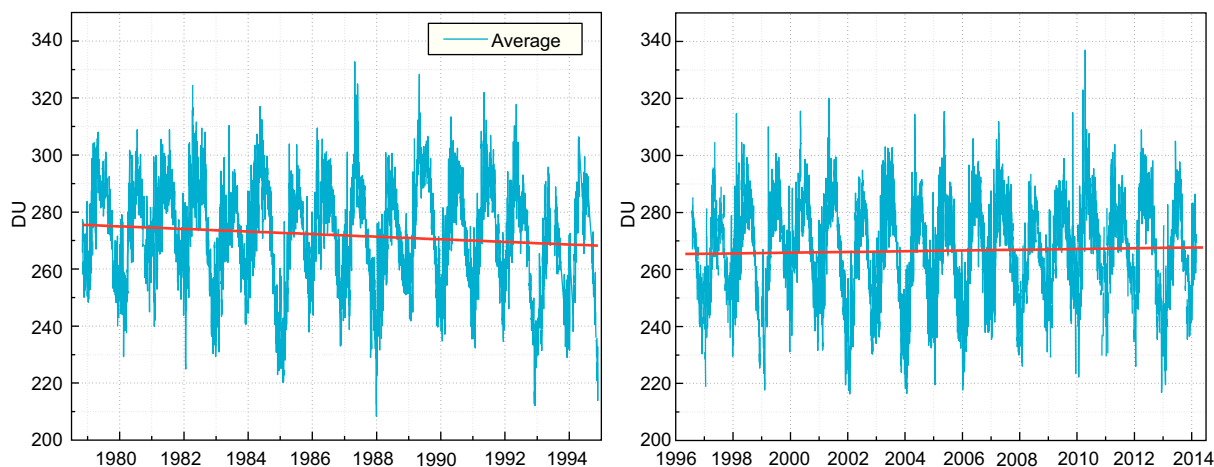


Fig. 4. Behavior of average TCO daily measurements over the state of Zacatecas.

TCO value during the TOMS and OMI measurement missions (1978–2013) for Mexico was 271.1 DU with a standard deviation of 29.8 DU, and a statistical range of 53.0 ± 23.4 DU; while for Zacatecas it was 264.2 DU with a standard deviation of 39.0 DU and a statistical range of 10.4 ± 5.3 DU. That is, the Zacatecas average value was 6.8 DU lower, which represents an order of 2.5 %. This is explained under the very broad range of latitudes in which Mexico is inscribed, since it encompasses 19° of latitude. Previous studies have shown that the TCO dependence on latitude is very important, being greater at mid-latitudes (Pinedo *et al.*, 2013).

It is relevant that the three ways of TCO depletion calculation—difference of average per period (2.2 %); linear regression analysis for the daily measurements (2.5 %); and linear regression analysis of the average annual values (3.5 %)—corroborate significant ozone depletion over Mexico.

These decreases have been calculated with the available measurements. TCO levels before the start of satellite measurements are not really known, and indeed satellite measurements began when the destruction of stratospheric ozone had decades of progress.

It may be noted in Figure 3 that in 1979, before the accentuation of the stratospheric ozone depletion, the TCO annual average value was 283 DU. It can be assumed that the level of TCO before the presence of pollution in the atmosphere, responsible for the destruction of ozone, should be on this order of magnitude or even higher. In such case, given that currently the average levels of TCO are around 270 DU, the decrease (–13 DU) is equivalent to 4.6% per period.

According to the WMO (2003), ozone depletion that occurred in mid-latitudes was around 4%, so it is likely that the decline in the level of destruction in neighboring regions to the Tropic of Cancer has been of the same order as that established by the WMO for mid-latitudes.

The depletion estimated in this work for Mexico is likely an underestimate of what occurred sparsely, but is strictly based on satellite measurements.

Additionally, the different tests carried out show that since the mid-1990s levels have been stabilized. However, the fact that average levels are about 6.4 DU lower from one period to another and that there is no upward trend does not mean that there has been a recovery.

These studies showed that there was indeed a significant depletion in the TCO between the period 1978–1994 and stabilization between 1996–2013, which can be verified separately in Mexico and the state of Zacatecas.

The results comprise a complete characterization, which accounts for the TCO levels in these two studied regions.

References

- Bodeker G. E., J. C. Scott, K. Kreher and R. L. McKenzie, 2001. Global ozone trends in potential vorticity coordinates using TOMS and GOME intercompared against the Dobson network: 1978–1998. *J. Geophys. Res.* **106**, 23029–23042.
- Bojkov R. D., C. S. Cerefos, D. S. Balls, I. C. Ziomas and A. F. Bais, 1993. Record low total ozone during northern winters of 1992 and 1993. *Geophys Res Lett* **20**, 1351–1354.
- Chapman S., 1930. A theory of upper-atmosphere ozone. *Mem. R. Meteorol. Soc.* **3**, 103–125.
- De la Casinière A., 2003. *Le rayonnement solaire dans l'environnement terrestre*. Éditions Publibook, Paris, 264 pp.
- Farman J. C., B. G. Gardiner, and J. D. Shanklin, 1985. Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction. *Nature* **315**, 207–210.
- Fioletov V. E., J. B. Kerr, E. W. Hare, G. J. Labow and R. D. McPeters, 1999. An assessment of the world ground-based total ozone network performance from the comparison with satellite data. *J. Geophys. Res.* **104**, 1737–1747.
- Fioletov V. E., G. E. Bodeker, A. J. Miller, R. D. McPeters and R. Stolarski, 2002. Global and zonal total ozone variations estimated from ground-based and satellite measurements: 1964–2000. *J. Geophys. Res.* **107**, doi:10.1029/2001JD001350.
- Fioletov V. E. and T. G. Shepherd, 2005. Summer-time total ozone variations over middle and polar latitudes. *Geophys Res. Lett.* **32**, L04807, doi:10.1029/2004GL022080.
- Harris M., S. J. Oltmans, G. E. Bodeker, R. Stolarski, R. D. Evans and D. M. Quincy, 2003. Long-term variations in total ozone derived from Dobson and satellite data. *Atmosph. Environ.* **37**, 3167–3175.
- Jackman C. H., E. L. Fleming, S. Chandra, D. V. Considine and J. E. Rosenfield, 1996. Past, present, and future modelled ozone trends with comparisons to observed trends. *J. Geophys. Res.* **101**, 28753–28767.

- Jaross G., S. L. Taylor, C. G. Wellemeyer, R. P. Cebula, L.-K. Huang, R. S. Stolarski and R. D. McPeters, 2003. An assessment of long-term ozone trend uncertainties using Total Ozone Mapping Spectrometers (TOMS). *Int. J. Remote Sens.* **24**, 329-338.
- Krotkov N., K. Yang and S. Carn, 2011. A-train observations of Nabro (Eritrea) eruption on June 13-16, 2011. National Aeronautics and Space Administration, Goddard Space Flight Center. Available at: <http://aura.gsfc.nasa.gov/science/feature-20120305b.html> (last accessed on July 23, 2012).
- McPeters R. D. and G. J. Labow, 1996. An assessment of the accuracy of 14.5 years of Nimbus 7 TOMS version 7 ozone data by comparison with the Dobson network. *Geophys. Res. Lett.* **23**, 3695-3698.
- McPeters R. D., M. Kroon, G. Labow, E. J. Brinkman, D. Balis, I. Petropavlovskikh, J. P. Veefkind, P. K. Bhartia and P. F. Levelt, 2008. Validation of the Aura Ozone Monitoring Instrument Total Column Ozone Product. *J. Geophys. Res.* **113**, doi:10.1029/2007JD008802.
- Miller A. J., G. C. Tiao, G. C. Reinse, D. Wuebbles, L. Bishop, J. Kerr, R. M. Nagatani, J. J. DeLuisi and C. L. Mateer, 1995. Comparisons of observed ozone trends in the stratosphere through examinations of Umkehr and balloon ozonesonde data. *J. Geophys. Res.* **100**, 11209-11211.
- Molina M. J. and F. S. Rowland, 1974. Stratospheric sink for chlorofluoromethanes: chlorine atom-catalyzed destruction of ozone. *Nature* **249**, 810-812, doi:10.1038/249810a0.
- Newchurch M. J., E.-S. Yang, D. M. Cunnold, G. C. Reinsel, J. M. Zawodny and J. M. Russell III, 2003. Evidence for slowdown in stratospheric ozone loss: First stage of ozone recovery. *J. Geophys. Res.* **108**, doi:10.1029/2003JD003471.
- Oman L., A. Robock, G. Stenchikov, G. A. Schmidt and R. Ruedy, 2005. Climatic response to high-altitude volcanic eruptions. *J. Geophys. Res.* **110**, D13103, doi:10.1029/2004JD005487.
- Pinedo J. L., F. Mireles, C. Ríos, V. M. García, J. I. Davila and J. R. Espinosa, 2013. Assessment of the latitudinal behavior of total column ozone at nine discrete 1°-wide latitude bands, from TOMS and OMI data. *The Open Atmospheric Science Journal* **7**, 92-109.
- Pyle D. M., 2012. Small volcanic eruptions and the stratospheric sulfate aerosol burden. *Environ. Res. Lett.* **7**, 031001 doi:10.1088/1748-9326/7/3/031001
- Schneider D. P., C. M. Ammann, B. L. Otto-Bliesner and D. S. Kaufman, 2009. Climate response to large, high-latitude and low-altitude volcanic eruptions in the Community Climate System Model. *J. Geophys. Res.* **114**, D15101, doi:10.1029/2008JD011222.
- Schönbein C. F., 1840. On the odour accompanying electricity and on the probability of its dependence on the presence of a new substance. *Philos. Mag.* **17**, 293-294.
- Stolarski R. S. and S. M. Frith, 2006. Search for evidence of trend slow-down in the long-term TOMS/SBUV total ozone data record: the importance of instrument drift uncertainty. *Atmos. Chem. Phys.* **6**, 4057-4065.
- Stratton F. J. M., 1946. Prof. Charles Fabry, Foreign Member of the Royal Society. *Nature* **157**, 362, doi:10.1038/157362a0.
- Thomas H. E. and A. J. Prata, 2011. Sulphur dioxide as a volcanic ash proxy during the April–May 2010 eruption of Eyjafjallajökull volcano, Iceland. *Atmos. Chem. Phys.* **11**, 6871-6880.
- Walker J. C., E. Carboni, A. Dudhia and R. G. Grainger, 2012. Improved detection of sulphur dioxide in volcanic plumes using satellite-based hyperspectral infra-red measurements: application to the Eyjafjallajökull 2010 eruption. *J. Geophys. Res.* **117**, D00U16, doi:10.1029/2011JD016810.
- WMO, 2003. *Scientific assessment of ozone depletion: 2002. Global ozone research and monitoring project.* Report No. 47. World Meteorological Organization, Geneva, 498 pp.
- WMO, 2007. *Scientific assessment of ozone depletion: 2006. Global ozone research and monitoring project.* Report No. 50. World Meteorological Organization, Geneva, 572 pp.
- Ziemke J. R., S. Chandra and P. K. Bhartia, 2005. A 25-year data record of atmospheric ozone in the Pacific from Total Ozone Mapping Stratospheric (TOMS) cloud slicing: Implications for ozone trends in the stratosphere and troposphere. *J. Geophys. Res.* **110**, D15105, doi:10.1029/2004JD005687.