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Monitoring the Antarctic Stratosphere after the Montreal Protocol

S. Genco,
ISAC – CNR, Bologna, Italy

D. Bortoli
ISAC – CNR, Bologna, Italy
CGE-UE, Evora, Portugal

I. Kostadinov
ISAC – CNR, Bologna, Italy

M.Premuda
ISAC – CNR, Bologna, Italy

S. Masieri
ISAC – CNR, Bologna, Italy

G. Giovanelli
ISAC – CNR, Bologna, Italy

F. Ravegnani
ISAC – CNR, Bologna, Italy

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President
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D. Bortoli
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G. Giovanelli
ISAC – CNR, Bologna, Italy

F. Ravegnani
ISAC – CNR, Bologna, Italy

Abstract

The use of CFCs, which are the main responsible for the ozone depletion in the upper atmosphere and the formation of the so-called "ozone hole" over Antarctic Region, was phased out by Montreal Protocol (1989). CFC's concentration are recently reported to decrease in the free atmosphere, but severe episodes of ozone depletion in both Arctic and Antarctic region are still present and the complete recovery of the Ozone layer is expected by about 2070, assuming the full compliance with the Montreal Protocol and its amendments and the absence of un-accounted effects.

In order to perform a continuous monitoring of the Antarctic Stratosphere, a spectrometric system named GASCOD was installed in December 1995 in the Italian Antarctic station "Mario Zucchelli" (MZS) at Terra Nova Bay (74"26' S, 164"03' E). The instrument performs continuous measurements of zenith scattered solar radiation. Applying the DOAS methodology to the collected data the total column and vertical profile of trace gases involved into

the ozone chemistry (such as ozone, nitrogen dioxide - NO_2 and bromine oxide - BrO) are retrieved.

The time series of NO_2 vertical columns obtained during more than 15 years with GASCOD at MZS are presented and discussed. The diurnal and seasonal variations of stratospheric NO_2 are highlighted. It's also discussed the behavior of NO_2 data during the spring season due to the position of the station.

Keywords:

Corresponding Author:

Introduction

The "ozone hole" is a great environmental issue arisen in the second part of XX century. The ozone layer was discovered in 1913 by C. Fabry and H. Buisson [1] but its properties were studied in detail by G. Dobson, who developed a spectrophotometer able to measure stratospheric ozone from the ground. Between 1928 and 1958 Dobson constituted a worldwide network of ozone monitoring stations, which is still operating. In 1974 M. Molina and S. Rowland published a study [2] highlighting that chlorofluorocarbons (CFC - non toxic, non inflammable, inert gases, used mostly as refrigerants) in the presence of UV radiation, in the stratosphere, can undergo photolytic decomposition, releasing ozone destroying products.

During the first half of '80s, it became clear that Molina and Rowland's predictions were right: it was observed that during the Antarctic spring the thickness of the stratospheric ozone layer was drastically lower than the summer measurements. The ozonosphere protects biosphere from the harmful effects of UV light (in particular UV-B radiations) so the decrease of the stratospheric ozone concentration can cause effects like higher incidences of skin cancer and alteration of marine ecosystem also.

In 1985 to stem the problem of "ozone hole" in Vienna, Austria, the United Nations delegates enter in a contractual agreement concerning protection of the stratospheric ozone layer for human health and environment safeguard against human activities which can modify the ozonosphere. On 16 September 1987 the Montreal Protocol was signed. It is an agreement aimed to the reduction in emissions of ozone-depleting substances (ODS). That was a great example of cooperation between nations concerning environment. The Montreal Protocol was revisited during periodic controls: in London (1990), and Copenhagen (1992).

In the period 1988-2000 the CFCs production decreased from a million tons to less than 100.000 tons per year.

In spite of those successes and in addition to an increase of UV radiation, recent studies highlighted a close link between climate change and stratospheric ozone loss [3, 4]. One of the main factors underlining this connection is the stratospheric cooling due to ozone depletion. Ozone is a greenhouse gas which radiatively heats the stratosphere contributing to determine its typical temperature profile. The ozone depletion phenomena cause the cooling of the interested atmospheric layer, offering the best conditions for the formation of the Polar Stratospheric Clouds (PSCs) which support the decreasing of inactive chlorine reservoir [5]. Therefore a positive feedback is started in which a cold stratosphere leads to an increasing ozone loss. These processes entail important dynamical and chemical changes in troposphere which are being investigated and make the ozone hole events an up-to-date problem.

Origin of Ozone Depletion: Stratospheric Chemistry

In the upper atmosphere the solar radiation below 242 nm can be absorbed by molecular oxygen (O_2), splitting it into two oxygen atoms. Usually, each one of these compounds binds itself to another O_2 using some third molecule to stabilize the final product that is ozone:

$$O_2 + hv \rightarrow O + O$$
$$O + O_2 + M \rightarrow O_3 + M$$
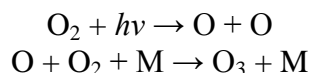
The ozone molecule absorbs UV light splitting into mono-atomic oxygen and bi-atomic oxygen:

$$O_3 + hv \rightarrow O + O_2$$
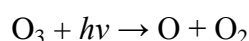
The solar UV energy absorbed by M in this photochemical reaction is converted into heat. In the stratosphere, this exothermal reaction creates a region between 15 and 50 km in which the temperature increases with altitude. The ozone layer thus performs two important physical processes: the removal of the most energetic UV radiation (the shortest wavelengths) and the conversion of this electromagnetic energy into heat.

The solar UV radiation with $\square$<290 nm is absorbed by O_2 and O_3, avoiding that the high energy radiation reaches the lower atmospheric layers.

Laboratory studies conducted by Molina and Rowland [2] defined that CCl_3F molecules are able to absorb UV radiation at wavelengths <220 nm, but to encounter such solar radiation in the atmosphere the molecule has first to lift through it to altitudes higher than most of the O_2 and O_3 molecules (~25 or 30 km). Because more than 98% of the atmosphere and 80% of the ozone lies below 30 km altitude only at this level the CFCs molecules are exposed to a radiation able to decompose them. For example:

$$CCl_3F + hv \rightarrow Cl + CCl_2F$$
$$CCl_2F_2 + hv \rightarrow Cl + CClF_2$$
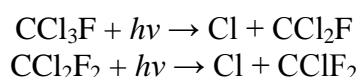
These photochemical reactions release Cl atoms which react with ozone, forming ClO.

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$
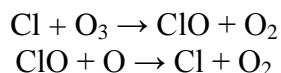
The combination of the two previous reactions constitutes a catalytic chain reaction in which the Cl atom alternates among the chemical species Cl and ClO. The first step removes one O_3 molecule, while the second intercepts an O atom which could have become an O_3 but is instead also converted to O_2. The Cl atom, however, is only a catalyst and can initiate the process once more.

The ClO_x chain has a close analogy with the NO_x free radical catalytic chain of the following reactions

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$
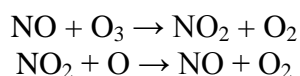
which also combine to convert O_3 into O_2. This chain can be initiated in the stratosphere by the decomposition of the long-lived molecule nitrous oxide, N_2O.

Another catalytic cycle found to be important in depletion of stratospheric ozone during Antarctic spring involves Br radicals produced by photolysis and oxidation of anthropogenic gaseous compounds:

$$Br + O_3 \rightarrow BrO + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$BrO + ClO \rightarrow Br + Cl + O_2$$
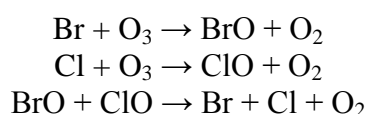
In order to explain Antarctic ozone hole we must also consider heterogeneous chemistry on the surface of Polar Stratospheric Clouds formed by nitric acid trihydrated crystals (NAT PSCs). PSCs are usually present from June to September in polar stratosphere and they are associated with temperature below 195 K and located between 12 km and 25 km [5].

NAT crystals catalyze the conversion of inactive compounds of chlorine, such as HCl and $ClONO_2$ which are naturally present in stratosphere, into their photochemical active form like Cl_2:

$$HCl + ClONO_2 \rightarrow HNO_3 + Cl_2.$$
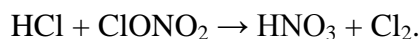
Cl_2 photolyze in sunlit air splitting in two Cl atom which reacts with O forming ClO: this reaction inhibits the concentration of NO_2 by forming nitric acid, and so the ClO released couldn't rapidly reform the $ClONO_2$ reservoir.

Another important reaction is the so-called stratospheric "denitrification". This process removes gaseous nitric acid, because of the absorbtion due to NAT crystals, and makes it sediment in lower regions of the stratosphere:

$$NO_2 + OH \rightarrow HNO_3$$
$$N_2O_5 + H_2O \rightarrow 2HNO_3.$$
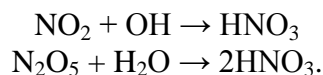
The "denitrification" removing nitrogen promotes the presence of radical chlorine which depletes stratospheric ozone [6, 7].

Historical Data

The first device able to measure atmospheric ozone column was the Dobson spectrophotometer, developed in the late '20s by G. Dobson. In 1956 a

network of those instruments was operating in several regions of the earth, including Antarctica. In 1985 for the first time the Antarctic stratospheric ozone loss was observed [8].

After one year, NASA scientists, using satellite-based data, demonstrated the regional-scale problem of the ozone hole.

Nowadays global data coverage is provided with satellite borne equipments and ground-based observations carried out mainly with remote sensing techniques and systems like Dobson and Brewer spectrometers. The Brewer instrument is the evolution of the Dobson systems allowing for automatic and unattended measurements of direct solar radiation mainly in the UV spectral range. One of the more promising techniques appeared in the last 40 years is the Differential Optical Absorption Spectroscopy (DOAS) methodology [9], that can be applied to spectral measurements of scattered solar radiation obtained in the UV-Visible spectral range. This last technique gave also the opportunity to develop a new series of spectrometric equipments usually called DOAS systems. The ground based equipments are usually well calibrated, more stable in time and cover a wider time span and are used for validation/comparison with the satellite data.

In addition to such devices, balloons and aircraft-based sensors are also used in field campaigns of measurements for limited times.

Such a sensors deployment allows to measure a full set of chemical species involved in the stratospheric ozone chemistry, as well as to characterize the ozonosphere with very good levels of confidence.

The historical data set of the ozone column are necessary to fully understand both the history and the future evolution of the ozone hole phenomenon.

In Figure 1, the total ozone historical data set obtained with the Dobson spectrometer located in Amundsen Scott station, Antarctica (89,9° S-24,8° W), is shown. The plot highlights the beginning of the strong depletion of stratospheric ozone starting on 1980: from 1963 to 1980 the trend is roughly constant; from 1980 to now it's clearly negative.

Similarly, in figure 2, the mean size of the ozone hole over Antarctica is plotted for the period 1980-2012. In both figures the singularity occurred in 2002 is clearly evident. Actually the episode of Sudden Stratospheric Warming (SSW) occurred in that year caused the break-up of the polar vortex, avoiding the formation, persistence and evolution of the ozone hole.

The same phenomena of ozone depletion occur also in Arctic regions. Since very low temperatures do not persist in the Arctic polar vortex during the winter season, the formation of PSCs is limited. Therefore ozone depletion in Arctic winters usually has not the magnitude of Antarctic ozone hole. Anyway, during winter 2010-2011, the unusually long-lasting cold conditions in the Arctic lower stratosphere [10] led to ozone depletion event close to the Antarctic ones [3].

At mid-latitudes, the stratospheric temperature is too high to allow formation of PSCs so the ozone depletion caused by the heterogeneous chemical reactions cannot take place. Nevertheless, detailed studies have

revealed a decreasing trend in total O_3 column of a few percent per decades [11]. This trend can be attributed partially to gas-phase chemical reactions and, more substantially, to the so-called "dilution effect". Large ozone depletion inside the vortex in both hemispheres leads to transport of ozone-poor air masses to mid latitudes after break-up of the vortex.

Due to the long replacing time for the extra-tropical lower stratosphere, the recovery time from ozone depletion is long tens of years [11].

CFCs, which are the main responsible of the Antarctic ozone depletion, are stable compounds in troposphere: it's important to monitor their level because their concentration decreases slowly during time.

Figure 3 shows the time series of tropospheric concentration for two of the most important ozone depleting substances: CFC-11 (Trichlorofluoromethane - $CFCl_3$) and CFC-12 (Dichlorodifluoromethane - CF_2Cl_2) measured at Mauna Loa, Hawaii, from 1975 to 2012. It is important to highlight the similar trend of both compounds: before the '90s the slope is equally strongly positive, then the CFC-11 concentration remains almost constant for 5 years. Only starting from '96 the CFC-11 presents a slight decrease. The CFC-12 concentrations show diminishing values only since 2005. The 10 years delay in the inversion of the trend for the two CFCs time series is mainly due to their different lifetimes [12]. The observed concentration decrease is a consequence of the application of the Montreal Protocol.

The ozone hole phenomenon involves several gaseous compounds such as bromine, chlorine and nitrogen oxides (BrO, OClO and NO_2). Therefore besides CFCs, the monitoring of NO_2, which have a key role in NO_x catalytic chain reactions involving Cl (see next subsection), has a peculiar importance. Those atmospheric tracers can be measured with satellite borne instruments and also with ground-based DOAS systems.

NO_2 Measurements at "Mario Zucchelli" Station

Since 1996, at the "Mario Zucchelli" Italian Antarctic station (MZS former TNB) (74"26' S, 164"03' E), NO_2 total column data are collected with the DOAS system called GASCOD (Gas Absorption Spectrometer Correlating Optical Differences) [13, 14]. The GASCOD equipment is a ground-based spectrometer measuring zenith-sky scattered radiation. The version installed at MZS was adapted to the Antarctic region and the measuring spectral window is fixed at 400-460nm. The DOAS algorithms are applied to the measured spectra to retrieve the NO2 abundances along the path of measurement [15, 16]. DOAS is a powerful technique for the analysis of many trace gases, especially ozone and nitrogen dioxide. Its main advantages include simultaneous determination of multiple absorbers with high sensitivity. GASCOD NO_2 data sets are available from 1996 until 2012.

The evolution of the daily and seasonal variations for NO_2, O_3 and other tracers have been deeply analyzed and correlated with various parameters such as potential vorticity, temperature and hours of sunlight [17, 18, 19].

Furthermore, the vertical distributions of O_3 and NO_2 have been retrieved [20].Recently the NO2 total column have been used for the validation of results obtained with instruments installed on satellites [21]. In this paper, for the first time the climatology of the observations of NO2 is presented and a preliminary study about trend in recent years is proposed and discussed.

Figure 4 shows the average of the seasonal variation of NO_2 vertical column for the full period of operation (1996-2012) of the GASCOD instrument at MZS. The plotted data sets are the NO_2 columnar values obtained for Solar Zenith Angle (SZA) of 90° at sunrise (morning - AM) and at sunset (evening - PM). As expected, the NO_2 total column values follow the variation of insolation time during the year, with negative slope towards the winter period and with opposite tendency approaching the summer months. Solar radiation photolyzes oxygen molecules creating mono-atomic oxygen which interacts with NO creating NO_2. This aspect can be clarified analyzing the shape of the data plot from 10-12 of February, when the sun crosses for the first time the horizon line after the polar summer, to 8-10 of May, when the last sunrise before the polar night occurs. Actually at the beginning of the considered period, the NO_2 contents are the same for morning and evening, mainly due to the absence of the night time preventing the occurrence of the photochemical reactions affecting NO_2. At the autumnal Equinox, the photochemical reactions can take place at all and the difference between morning and evening NO_2 total column values reaches the maximum. Proceeding towards the winter months, the hours of sunlight decrease systematically and similarly the NO_2 values present the minimum due to the absence of sunlight periods required for the creation of NO_2. Summarizing, this behavior is essentially due to the decrease of solar radiation during the considered period. Similarly, the difference between morning and evening data is due to the duration of the day.

For the spring season (end of August - end of October) the slope of the linear function described by the NO_2 total columns data is opposite to the one encountered for the Antarctic fall season, mainly for the increase of the sunlight periods. The data obtained for the first 20-25 days of this second period highlight the occurrence of stratospheric denitrification phenomena since NO_2 data values are lower than last total column observed in May. In addition, it is during the end of August - September that ozone mostly suffers the depletion processes. The geographic position of MZS makes the station, from August to September, alternatively inside and outside the polar vortex and the displacement of the border of the ozone hole can be appreciated. The effect is more clear in Figure 5 where the NO_2 evening-morning ratio (EMR) data set is plotted. EMR is extraordinarily regular during the austral fall, whereas at the beginning of the spring season EMR values are much more spread during the period of austral spring, due to the strong daily variation of the NO_2 data.

Figure 6 shows the seasonal evolution of NO_2 total columns at the "Dumont D'Urville" (DDU) (66°40′ S, 140°01′ E) station. The comparison between the two stations highlights the difference between the observations

performed at two different latitudes. The position of DDU station, located just outside the Antarctic Circle, allow for collection of data all the year round.

In figure 7 the comparison between February-March-April average of total NO_2 over MZS and DDU is drawn. Both time series show a linear positive trend of about 1% per decade. That analysis doesn't consider solar cycle and other climatic oscillations but the confidence of those results is about 75% for MZS and more than 99% for DDU in agreement with the data obtained at the NIWA's research station at Lauder (New Zealand) [22]. That positive trend is due to an increment of N_2O in troposphere, which is the most important source of NO_2, and probably to a change in Brewer-Dobson circulation in stratosphere [23].

Conclusions

The stratospheric ozone is a gas which interacts with several compounds in stratosphere in particular Chlorine, Nitrogen and Bromine. The emission in atmosphere of synthetic Chlorine molecules, known as CFC's, has led to stratospheric ozone depletion. This is a current problem because of the consequences of ozone hole on climate change. In fact CFCs stability in troposphere makes difficult its removal

Recent studies highlight a slow drop of CFCs concentration, as a benefit of Montreal Protocol. The consequence is the first signals of ozonosphere's recovery at mid- and high-latitudes. The decrease of CFCs allows a ozone layer recovery to the pre '80s state but, according to simulations, not before 2070. For that reason it is important to continuously monitoring the ozone layer's recovery to evaluate if undertaken activities and political decisions are suitable for the purpose.

In order to monitor NO_2, which is an important compound involved in ozone layer chemistry and recovery/depletion, a DOAS system called GASCOD was installed at MZS station. The data of NO_2 vertical column collected from 1996 until today have been shown and discussed in this paper. As expected, the seasonal trend of NO_2 vertical column values follows the variation of insolation time during the year, showing a minimum during winter months. Also the difference between morning and evening data is strongly related to the duration of the day.

There is an apparent occurrence of denitrification processes in stratosphere during the first 20-25 days of austral spring, when ozone mostly undergoes depletion processes. The particular position of MZS, alternatively inside and outside the polar vortex in this season, allows to appreciate the displacement of the ozone hole border and causes the spread in evening-morning ratio during spring.

Furthermore the rough seasonal trend of February-March-April average of total NO_2 highlights a positive trend of more than 1% per decade in good agreement with other south hemisphere stations due to an increase in tropospheric N_2O and probably to a change in the Brewer-Dobson circulation.

Acknowledgments

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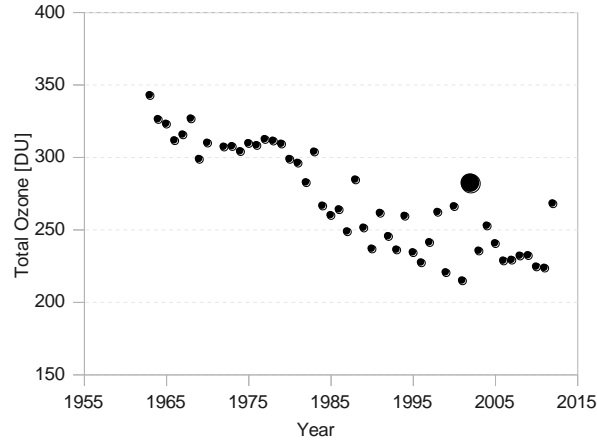**Figure 1.** *Ozone Total Column over Amundsen Scott Station (South Pole)*

Figure 2. *Mean Ozone Whole Size over Antarctica*

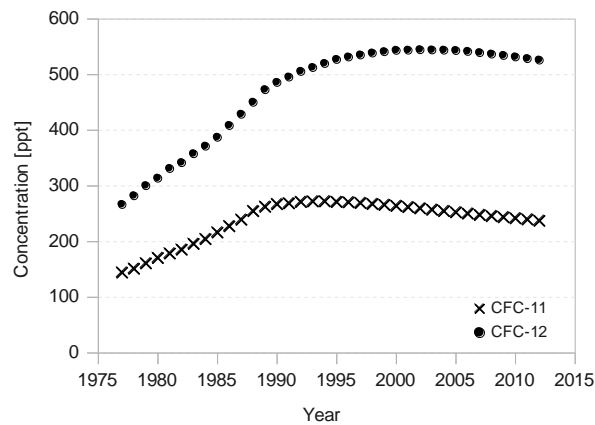**Figure 3.** *CFC-11 and CFC-12 concentration at Mauna-Loa (Hawaii, USA)*

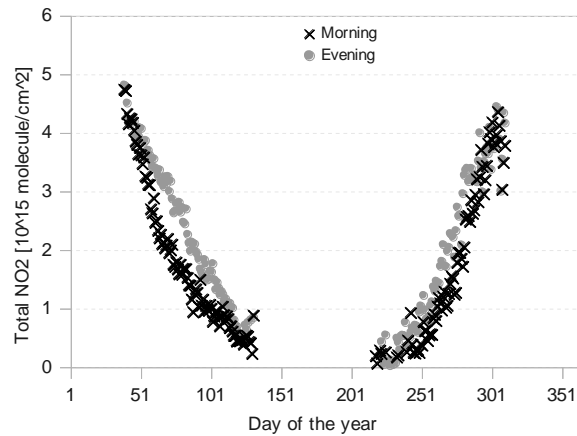**Figure 4.** *Total NO₂ Seasonal average over Mario Zucchelli station Terra Nova Bay (Antarctica)*

Figure 5. *Total NO₂ Evening-morning Ratio over Mario Zucchelli Station (Antarctica)*
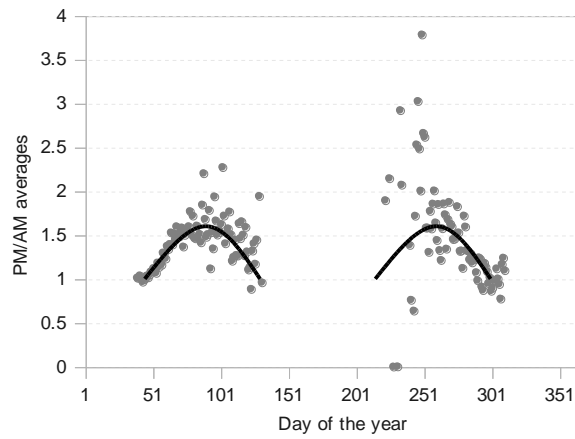

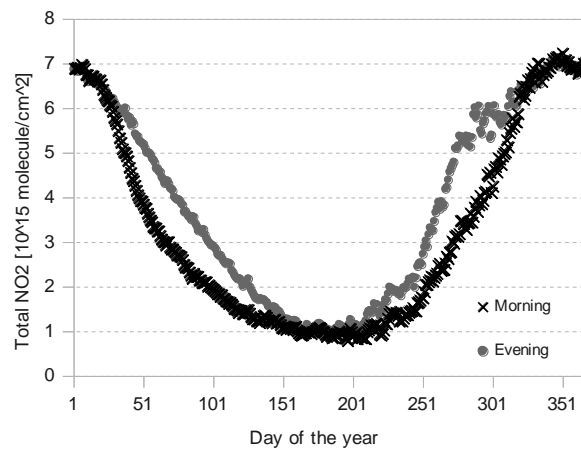**Figure 6.** *Total NO₂ seasonal average over Dumont d'Urville Station (Antarctica)*

Figure 7. *Total NO2 average for February-March-April and Trend over Mario Zucchelli and Dumont D'Urville*