Tethys, 3, 43–53, 2006
www.tethys.cat
ISSN-1139-3394
DOI:10.3369/tethys.2006.3.06

Journal edited by **ACAM**
(Associació Catalana de Meteorologia)

Stratospheric ozone

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Received: 22-V-2006 – Accepted: 23-XI-2006 – **Translated version**

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Abstract

Stratospheric ozone acquired a huge importance two decades ago because of the discovery of strong anomalies above the Antarctica due to gases of anthropogenic origin. From that date, stratosphere has become one of the research lines receiving more funding. A result, an important progress in the development of observational techniques, the understanding of the dynamics of the polar regions and, above all, in understanding of the chemical interactions among the species that influence the chemical-radiative balance of ozone. In this article a general revision is made of the distribution of the ozone in the stratosphere, the mechanisms that determine its equilibrium, the gases that contribute to its destruction, the present situation and the forecast of the health state of the layer.

1 Introduction

The discovery, in 1985, of unexpected massive ozone destructions in the Antarctic stratosphere during the austral spring immediately made this research field a priority. In the presence of the important consequences that the extension of such a phenomenon towards lower latitudes could mean on the ecosystem equilibrium, through the increases of ultraviolet radiations in the B rank (280-320 nm), some measures were adopted, initially towards knowing the origin of the destruction, and, later, towards limiting the production of those species directly involved in the problem.

The research financing organisms, fundamentally NSF in the USA and the EU Frame Programs of R+D+I, dedicated a significant quantity of resources which has become an important impulse for the research of the stratosphere, in observation methods as well as in model development.

Nowadays, we can say that we understand well the chemistry and the dynamics of the region at the macroscale, even though there are still doubts about the microphysical mechanisms on the stratospheric clouds and the stratosphere-troposphere exchange processes.

2 General description of the stratosphere

The vertical structure of the Earth atmosphere is defined, from a thermal point of view, by the changes in the sign of the temperature vertical gradient slope. We call stratosphere the area with positive gradient with height, included between the troposphere and the mesosphere and it extends between heights of 8-15 km and around 50 km. The increasing of temperature with height is due to the presence of ozone in the region through the following exothermic reactions of formation and destruction:

- Formation

$$O_2 + h\nu\ (\lambda < 242\,nm) \rightarrow 2O(^3P)$$
$$O(^3P) + O_2 + M \rightarrow O_3 + M + 25.4\,kcal\,mol^{-1} \quad (1)$$

- Destruction

$$O_3 + h\nu(\lambda = UV + visible) \rightarrow O_2 + O$$
$$O_3 + O \rightarrow 2O_2 + 93.7\,kcal\,mol^{-1} \quad (2)$$

The result is that the stratosphere warms up at the expense of the solar energy absorbed by the reaction cycle called "Just Oxygen Atmosphere" or Chapman's, since this British scientist proposed it in 1930 to explain the existence of an ozone layer in the stratosphere. The temperature of each layer is dependent on the quantity of heat and the air

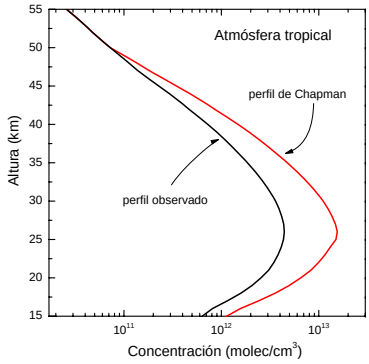

Figure 1. Vertical distribution of ozone according to Chapman equations (dashed line) and observations (solid line).

density.

The Chapman model has been confirmed as valid as far as the ozone production is concerned but it is not satisfactory to explain the destruction mechanisms. According to Chapman, the atmosphere should have 4 times more ozone than what it actually exits (figure 1). In the 60s' and 70s' catalytical cycles of three gas families, OH radicals, nitrogen and halogen oxides, were proposed. The general cycle is the following:

$$\begin{array}{l} O_3 + X \rightarrow XO + O_2 \\ XO + O \rightarrow X + O_2 \\ \hline Net \quad O_3 + O \rightarrow 2O_2 \end{array} \qquad (3)$$

where X can basically be NO, OH, CIO or BrO.

While the production of the two first ones is fundamentally of natural origin, the chlorate compounds did not exist in the stratosphere in concentrations over 1% of the current values before the industrial revolution, or more precisely until 1929, the year in which the commercial production of CFCs (chlorofluorocarbons) began. The contribution of the human activities to the observed concentrations of brome compounds is lesser, by some ten per cent, even though the uncertainty in the dimension of the natural production is high. Later on, we will come back to the halogens.

In terms of absolute concentration, the vertical distribution of ozone in the atmosphere has its maximum at about 25 km, a height where the relation production-destruction is maximum (figure 2). The tropospheric concentration does not exceed 10% of the total column and, furthermore, its variability is small. This is the reason why the total ozone column or TOC (integrated value for all the atmosphere height) for the analysis of the ozone in the stratosphere. From its maximum absolute concentration, the production increases with height, since there is a larger available atomic oxygen concentration, but the photochemical destruction does also, and faster. Below the maximum, the production decreases, but the low radiation and the absence of atomic oxygen turn

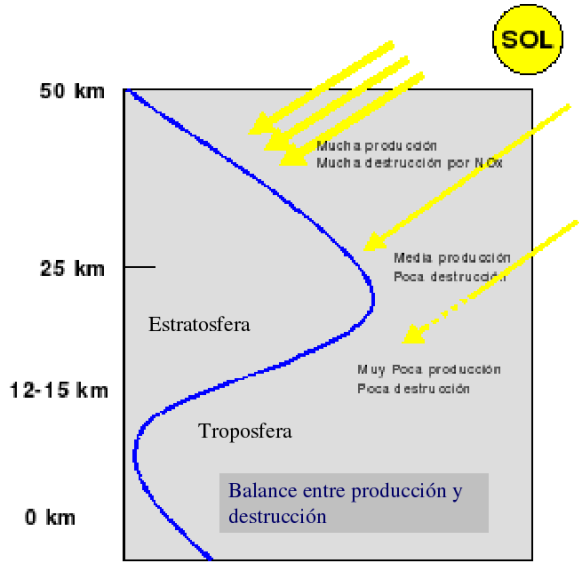

Figure 2. Maximum ozone concentration is located around 25 km. At this height the relation production/destruction is maximum.

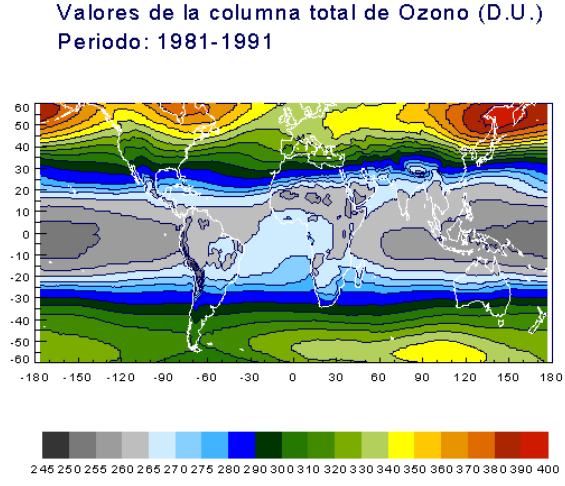

Figure 3. Averaged fields of the ozone column derived from satellite data (TOMS) show the presence of a meridional circulation towards the poles. The transport of the ozone is done from the tropical regions of production towards the polar zones where it is accumulated.

its mean time life (required time to make it possible that, in the absence of production, its concentration decreases) into several months. That is why global scale transport studies are necessary to understand how ozone is spread around the globe.

Taking into account the global spatial distribution (figure 3), it is paradoxical to observe that the total ozone minima are in the tropical belt, where the ultraviolet radiation is larger, and therefore is the atomic oxygen production

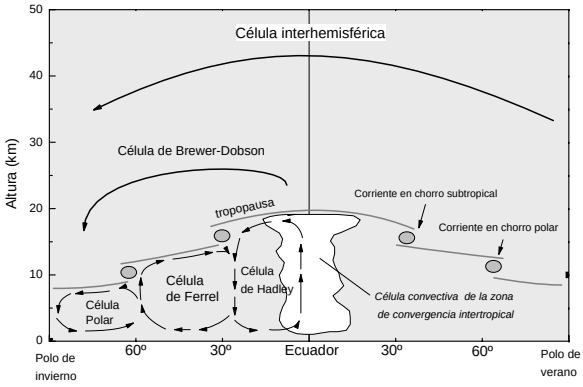

Figure 4. Scheme of the meridional circulation in the atmosphere. In the low stratosphere there is a hemispheric cell radiatively forced (the thermal differences between equator and the poles induce a meridional gradient) known as the Brewer-Dobson cell.

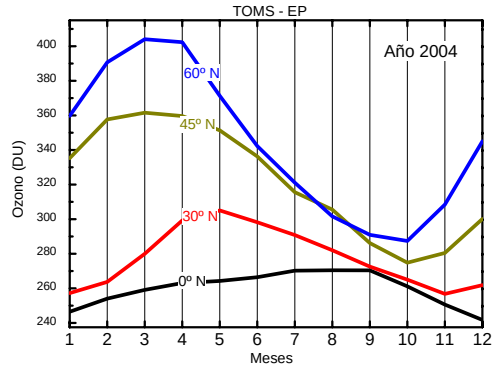

Figure 5. Annual distribution of the column of ozone. In the polar regions there is a strong seasonal difference. However, it is very stable in the tropics during the whole year.

too. Brewer and Dobson postulated in the 50's a conceptual model based on a unique hemispherical meridian cell with ascents in the intertropical convergence zone (ITCZ) and descents in the polar regions during the winter (figure 4). The Brewer-Dobson cell model is accepted currently, even though a detailed explanation of the dynamic mechanisms that produce it is still an open subject.

One of the main difficulties for its study is the small magnitude of the air speed in meridian sense (following the cell). The circulation in the stratosphere is, of course horizontal, since the vertical movements are made difficult by the superadiabatic vertical gradient (increasing of temperature with height), but it is also basically zonal, that is to say following the parallels, with some long period waves activity superimposed on the basic flow. The geostrophic wind approach, where the pressure gradient between the areas of high and low pressure is balanced with the force due to the Coriolis acceleration, fails in the regions near the equator where the equation presents a discontinuity, and where the influence of the friction must be taken into account or the wind rotational is very high, but it is substantially valid in the stratosphere where the disturbances are of planetary scale. The geostrophic wind must be amended taking into account the diabatic effects of the non-considered heat exchanges, but it can be used without rectifications in periods of about 1 or 2 weeks. Compared to the zonal winds, the meridian transport is very slow. While an air particle takes from 7 to 10 days to make a tour of the Earth in the zonal direction (W-E), it needs several months to cover the route between the equator and the pole. What mechanism causes the maximum ozone concentration to be found in the polar regions at the end of the winter, where the solar radiation is minimum?

Traditionally, it has been thought that the engine of the hemispherical stratospheric cellule was the temperature meridian gradient between the equator and the pole. Holton

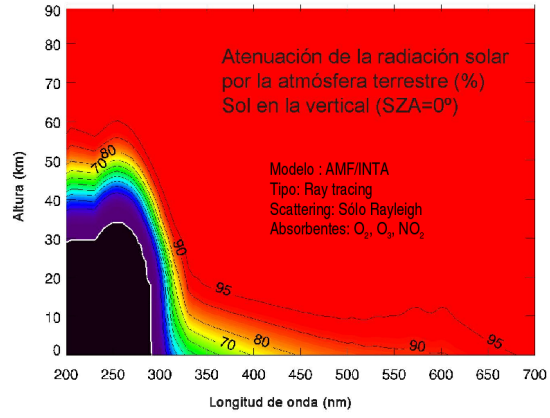

Figure 6. Proportion of zenithal solar radiation that reaches the different atmospheric levels. In the UV-B region (280-320 nm), due to the strong gradient, low variations of ozone are reflected as strong changes in the intensity that is received in the surface (INTATRANS model). The white isoline shows the height in which the 1% of the extraterrestrial radiation is reached.

et al. (1995) proposed that the transport is included by means of "pumping" made by the planetary waves. In any case, the ozone produced in the tropical regions in the high stratosphere is transported to the polar regions during the winter and the spring, while there is a hemispherical gradient and the activity of the planetary waves is intense, and it stops in the summer. For this reason, the maxima in mid and high latitudes occur in spring, and from then on the ozone slowly decreases by chemical processes until the following winter when the "pumping" mechanism towards the pole starts again. This way, a great variability is obtained in the poles, but the entire terrestrial globe is covered by a more or less homogeneous ozone layer during the whole year (figure 5).

The ozone density in the atmosphere is extremely low

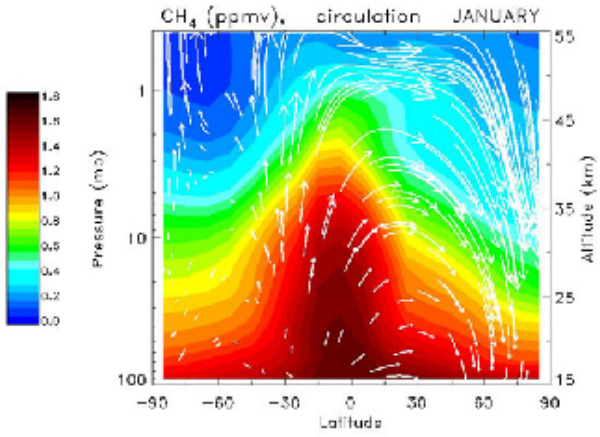

Figure 7. Meridional cross-section of the methane concentration (produced in the surface) obtained from the orbital instrument HALOE. This gives a clear information about the place where entrance of atmospheric pollutants is done and their polarward transportation (http://haloedata.larc.nasa.gov).

($< 4\times10^{-6}$% of the air), but its capacity of absorption of the energetic ultraviolet radiation, of wavelengths smaller than 300 nm (distant UVB and UVC), is so high that it completely filters all the radiation coming from the sun. At 280 nm, for example, with the sun in the zenith, only 1% of the radiation reaches the height of 30 km (figure 6). For this reason, life is possible even in latitudes where the ozone layer is weaker and the solar zenith angles are very low.

The gases which maintain the ozone density in its equilibrium values have their sources in very stable compounds of tropospheric origin. The nitrogen oxides come from the nitrous oxide, the OH radicals from the methane oxidation and the oxides of the CFCs halogenated elements, halocarbons and its substitutes (table 1).

With very long mean lives, the compounds are transported to the stratosphere, where they are taken apart, generally by photolysis in the B and C ultraviolet. The oxides produced enter into the cycles of the ozone chemistry.

Traditionally, the inter-tropical convergence zone (ITCZ) has been considered to be the belt through which the source gases reached the stratosphere. Especially, the Indonesian region where the convective activity is maximum. Holton has proposed as a second option the almost-horizontal transport over isentropic surfaces in the extra-tropical regions, near the subtropical and polar jet streams. Whereas the troposphere-stratosphere exchange proportion in this region can be globally important, mostly in the irreversible entrance of stratospheric air in the troposphere, the data provided by satellites about the global distribution of long-life compounds are conclusive: maxima in the stratosphere are found in the tropical regions indicating that that is the main entrance region of tropospheric air in the stratosphere (figure 7).

Nowadays, we know that the exchanges of matter and

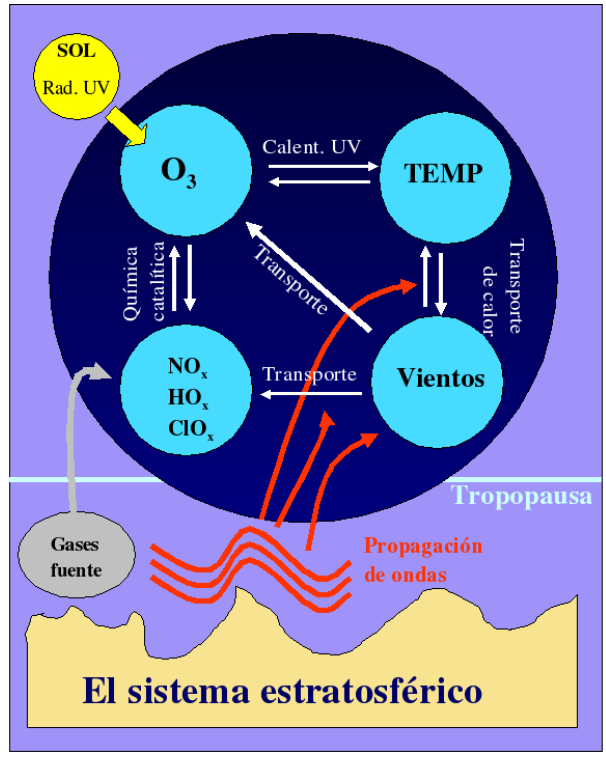

Figure 8. The atmospheric system is regulated by the solar radiation (the stratosphere is basically in radiative equilibrium), the wave-based transport of energy and the photochemistry. The different features are related to strong reinforce mechanisms.

energy with the troposphere control the thermodynamic equilibrium of the region and that the chemistry, and, especially, the ozone concentrations depend fundamentally on emitted gases from the surface, which makes the classical view of the stratosphere as an isolated system, without a significant interaction with other regions of the atmosphere obsolete.

In summary, the stratosphere is a complex system (figure 8) in a state of critical equilibrium between the UV solar radiation, the input of energy through vertically propagating waves, the thermodynamic balance induced by the ozone itself and the contribution of source gases that, photolysed, react catalytically with the ozone. The concentration of this gas in a planetary scale depends on the available UV radiation, on the volume of source gases emissions and on the planetary scale (Rossby) wave activity. The global ozone concentration also depends strongly on the quantity of aerosols in the stratosphere. After explosive volcanic eruptions during which large quantities of sulphates are injected in the stratosphere, decreases of up to 20% with a duration of 1-2 years have been observed (the last ones due to the Chichón volcano in 1982 and Cerro Pinatubo in 1991). Locally, and in short time scales, the stratospheric ozone also depends on the tropospheric meteorological systems which change the height of the tropopause and the direction of the meridian wind. Global modelling demands the incorporation of all the

Table 1. Mean gases intervening in the ozone chemistry

Compound	Mean life in the atmosphere (in years)	Pre-industrial concentration (1750)	Current concentration (2005)
Nitrous Oxide (N_2O)	114	270 ppb	318 ppb
CFC-12	100	Zero	255 ppt
CFC-113	85	Zero	80/80 ppt
CFC-11	45	Zero	255 ppb
Methane (CH_4)	12	688/730 ppb	1730/1853 ppbv

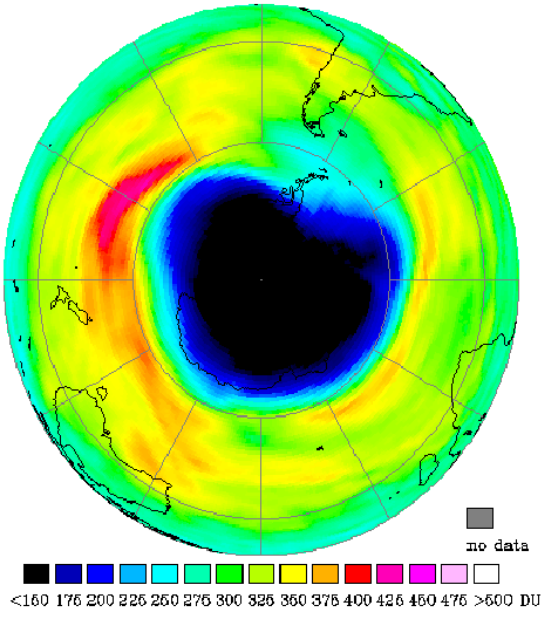

Figure 9. False colour map of the ozone distribution above the Antarctica during the ozone hole. 200 DU value gives the threshold of the hole (data from TOMS/NASA instrument) (http://toms.gsfc.nasa.gov/eptoms/ep_v8.html).

mentioned aspects. The CTM models (Chemistry-Transport Models) that work off-line using meteorological fields of the large predictive models such as ECMWF, UKMO, NCEP have obtained important successes in the last decade, not only at reproducing the global vertical ozone distribution, but also of other minority species that participate in its chemistry.

The reliable forecasts extend to some days, but they still fail for longer time scales.

3 Problems of anthropogenic origin in the ozone equilibrium

3.1 The ozone hole

More than two decades ago, Scientists from the University of California (Molina and Rowland, 1974) put forward the possibility that small stable gas concentrations of anthropogenic origin could disrupt the ozone layer by means of catalytic reactions with halogen radicals photochemically decomposed in the stratosphere. In particular, they suggested chemical potential destructions from liberated halogens of very stable synthetic products, extensively used, already in that time, in many industrial applications. These products, generically called chlorofluorocarbons or CFC have very long lifetimes, centuries in some cases, which allow their diffusion and accumulation in the whole atmosphere. When the CFCs reach the high stratosphere they are photodissociated by short UV radiation present in that region, liberating chlorine. Molina and Rowland propose a catalytic cycle of the type of the explained in 5, alerting about the possible negative consequences on the ozone layer.

Despite the intensification of the observations in following years, until 1985, with the discovery of the "ozone hole" in the Antarctica, there is no evidence of the proposed mechanism efficiency. In fact, the discovery that 99% of the CFC liberated chlorine returned to inactive species substracted credibility to the Rowland and Molina theory. Actually, the most important destructive species for its abundance, chlorine monoxide, immediately deactivates its production by means of the following reactions:

$$\begin{aligned} ClO + NO_2 &\rightarrow ClONO_2 \\ ClO + H_2O &\rightarrow HClO_3 \end{aligned} \qquad (4)$$

That is to say, nitrogen oxides and water are those in charge of inhibiting the ozone destruction. Confronted with this fact, some authors have speculated about the capacity of the Earth, as a living system, of defending itself against external aggressions, somehow relating to the Gaia hypothesis.

The ozone hole is a massive and complete destruction in the whole area covered by the Antarctic polar vortex, of some 35 million km^2 surface in its maximum peak (figure 9) in a height rank between 14-15 and 20-21 km during the austral spring months (figure 10). It was discovered by British Antarctic Survey scientists from the data of a spectrophotometer developed by Dobson and installed in the Halley Bay base on the occasion of the international geophysical year of 1958 (Farman et al., 1985).

The polar vortex is a depressionary structure of planetary scale persistent in winter and spreading from the troposphere to the high stratosphere, caused by the strong

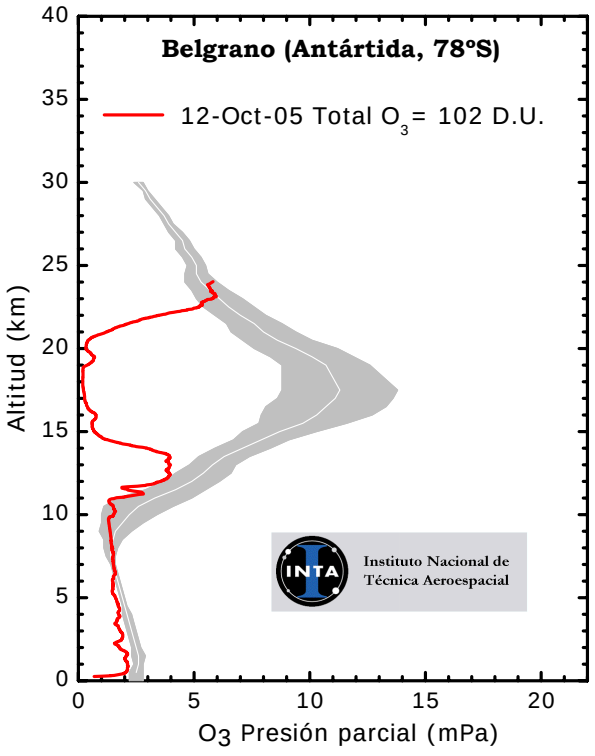

Figure 10. During the months of September-October ozone vanishes in the layer between 14-15 km and 20-21 km (red line). Grey line shows the averaged normal values of winter (August) and its standard deviation.

Figure 11. Polar stratospheric cloud (PSC) of type II (water) observed in Iceland in 1998. These clouds have a very weak optical thickness that so they can only be seen after the sunset when the troposphere is in the dark.

hemispherical gradient in the stratosphere between the equator and the poles (high branch of the hemispherical cellule known as Brewer-Dobson). Approximately centred on the pole, it extends to a 60° latitude. The strong cyclonic winds of 200 km h^{-1} act as a barrier for the exchange of matter and energy between mid and polar latitudes. Further on, we will see that existence of the vortex is a necessary condition for the production of massive ozone destructions.

Immediately after the discovery of the "hole", the destruction was associated with solar radiation, since the process began with the first sun rays, after the austral winter, but it produced an initial confusion as the destructions occurred during a time in which the radiation is small (the sun is very low in the spring horizon in high latitudes), and, therefore, the atomic oxygen is almost inexistent.

The proposed, and later confirmed, mechanisms are more complex than the simple cycle of two reactions. The process consists of two differentiated phases. Phase one, or preconditioning, takes place in winter, when the stratosphere radiatively cools off until reaching temperatures inferior to those of the troposphere and stratosphere (this fact was observed the first time in 1958, during the campaigns associated with the international geophysical year in which a Catalan scientist took part, [Puigcerver, private communication] reaching minimum values of –95°C never found in any other place in the world. When the temperature decreases below –78°C the nitrous acid present in the air condenses into what has been called PSC – type I (from Polar Stratospheric Clouds). Further on in the winter, with temperatures below –83°C water also passes to a solid state forming PSC of type II. These stratospheric clouds were known in the Scandinavian countries as mother-of-pearl clouds but their constitution had never been studied before (figure 11).

PSC play a decisive dual role in the whole formation process of the ozone hole. On the one hand, they eliminate nitrogen oxides and gaseous phase water, processes known as denoxification and dehydration, respectively. On the other, they act as surfaces on which reactions are produced that liberate molecular chlorine by means of the following reactions:

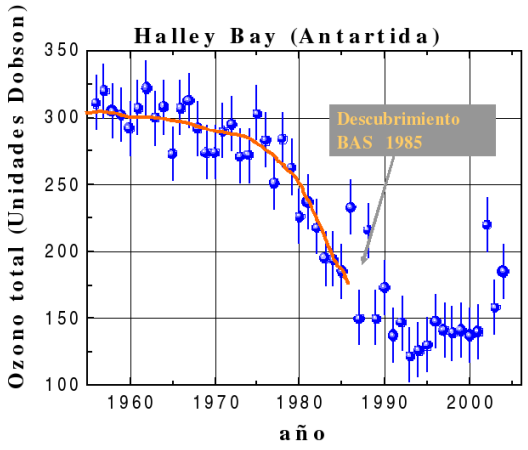

Figure 12. Total October averaged values of ozone measured in the base of Halley Bay by the discoverers of the hole in 1985. The data from 1985 shows that the problem started during the seventies.

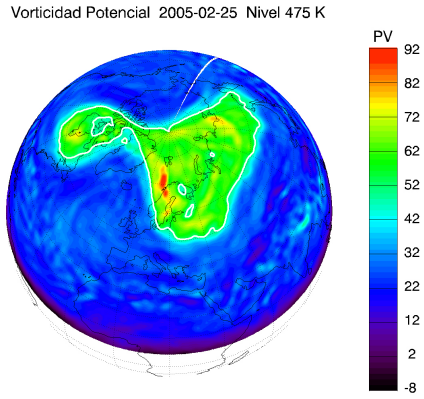

Figure 13. Potential vorticity is used as a way to define the morphology of the polar vortex. The vortex limits are shown with the 42 PVU threshold (white). Shifts respect to the circumpolar antarctic position generate a stronger mixing and refilling of ozone of that zones where a chemical destruction has occurred.

$$
\begin{aligned}
&ClONO_2 + HCl\ (solid) \rightarrow HNO_3\ (solid) \\
&+ Cl_2\ (gas) \\
&ClNO_2 + H_2O\ (solid) \rightarrow HNO_3\ (solid) + \\
&HOCl\ (gas) \\
&HOCl + HCl\ (solid) \rightarrow H_2O\ (solid) + \\
&Cl_2\ (gas) \\
&N_2O_5 + H_2O\ (sòlid) \rightarrow 2HNO_3\ (sòlid)
\end{aligned}
\qquad (5)
$$

Some similar reactions take place with the bromine monoxide, whose concentration in the atmosphere is lesser, but with a larger destructive potential per molecule.

The consequence of this cycle of reactions is the massive molecular chlorine (bromine) liberation. The situation favours a Cl_2 accumulation for two reasons: in the Antarctic winter there is no solar radiation which photodissociates the molecule, and furthermore, the polar vortex acts as a waterproof recipient preventing the Cl_2 escape to medium latitudes. Since the area of temperatures below the PSC formation threshold covers the whole Antarctic continent, the formation of stratospheric clouds takes place in a whole vast area inside the vortex. Therefore, the Cl_2 accumulates in all of the Antarctic stratosphere. On the other hand, PSC gravitationally settle to the stratosphere, where they evaporate. Through this process, the nitrogenated compounds are irreversibly eliminated from the stratosphere. It is said then that the atmosphere is preconditioned.

Phase two begins with the arrival of the first rays of the sun. The chlorine molecule is immediately photodissociated. The chlorine atoms enter in a series of catalytic reactions that do not need atomic oxygen. Several cycles have been described. One of them is the one proposed by the married couple Molina (Molina and Molina, 1987):

$$
\begin{aligned}
&ClO + ClO + M \rightarrow Cl_2O_2 + M \\
&Cl_2O_2 + h\nu \rightarrow Cl + ClO_2 \\
&ClOO + M \rightarrow Cl + O_2 + M \\
&2(Cl + O_3 \rightarrow ClO + O_2) \\
&\overline{Net \quad 2O_3 \rightarrow 3O_2}
\end{aligned}
\qquad (6)
$$

The consequence is a fast ozone destruction, which initially takes place in the most external belt and in the higher layers and it spreads towards the interior as spring advances and the sun reaches higher altitudes. In less than a month the destruction is total in the layer between 13 and 24 km, where the Cl_2 was present. In the 2D maps obtained by the NASA orbital instrument TOMS, the only one with global and diary coverage in 1985, the vortex remained perfectly delimited simply by observing the total ozone field. The medium values of the ozone contents inside the vortex did not overcome 100 DU (basically the remaining ozone in the troposphere and high stratosphere) strongly contrasting with the typical values of medium latitudes of about 300 DU. The image of coloured treated datahelped generating the somehow confusing name of "ozone hole" initially restricted to the media public diffusion but finally also used by the scientific community (Solomon, 1999, see review).

Thanks to the installation of some earth spectrometers conceived by Dobson especially for the measurement of ozone during the IGY-1958, we know that the hole has not always existed. The monthly mean values of October clearly show how the values in the 60s' were above 300 DU, and how the spring destruction began at the end of the 70s', when the effective chlorine threshold in the stratosphere reached a value of 1.8 ppbv, considered as the threshold and reference to estimate when the total recovery will take place, as we will see later on (figure 12). The effective chlorine is defined as the equivalent in chlorine of all those compounds that destroy ozone, basically chlorine and brome. With a shorter series of data, the TOMS instrument has allowed the realisation of a

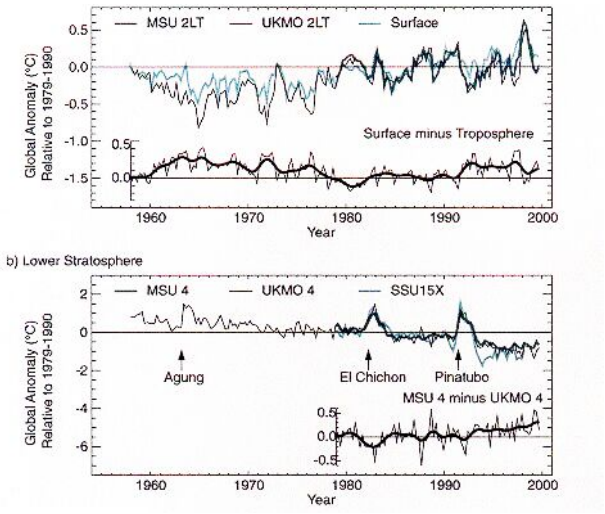

Figure 14. Land surface thermal anomalies (top curve in top panel) and low stratosphere anomalies (top curve in bottom panel). Top panel shows an average increasing about 0.2°C/decade, stratosphere cools four times faster (IPCC, 2001).

2D evolution of the phenomenon since its launch in 1978, coinciding with the beginning of the problem.

3.2 Ozone in the Arctic

The discovery that the necessary reasons for the existence of the hole in the Antarctic were basically astronomical in presence of halogens, caused the scientists, especially European and Canadian, to orientate their research towards the processes in the Arctic vortex. Contrary to the Antarctic, the boreal subpolar region is populated and potential destructions similar to the austral ones could have significant consequences. However, the first observations indicated that, for some reason, presumably related to the highest Arctic temperatures, the contents of ozone barely changed in spring.

Since 1991, Europe has been leading the research in the Arctic with extensive observations and field experiments, with the development of 3D coupled chemical-dynamic models and with laboratory studies on cloud microphysics and studies of reaction constants in stratospheric conditions. The projects have been carried out in a coordinated way from the EORCU (European Ozone Research Coordinating Unit) and they have produced a substantial advance in the knowledge of the processes in the Arctic stratosphere. To summarize the studies, we can say that the processes leading to the Antarctic destruction take place in an identical way in the Arctic (those who are interested can consult WMO-2003). Even more, the year-to-year variability is slightly larger than in the Antarctic, in cold years destructions up to 40% take place, the most recent case has been this last winter 2004-2005. Is it possible that such large destructions were unnoticed by observers for years?

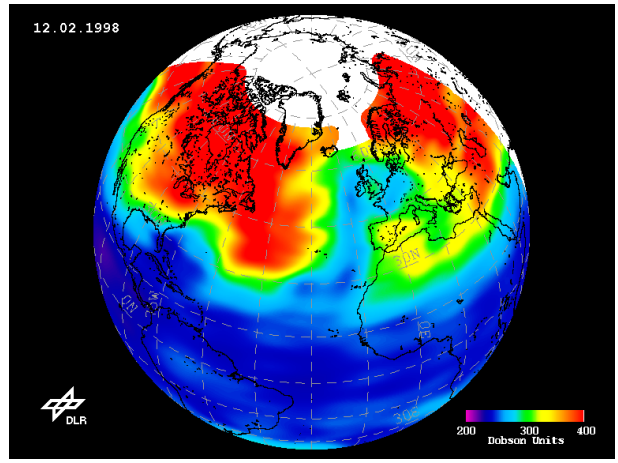

Figure 15. Streamer of low ozone above Europe. These episodes are also known as "mini-holes". They are mainly originated by the dynamics of the region close to the tropopause.

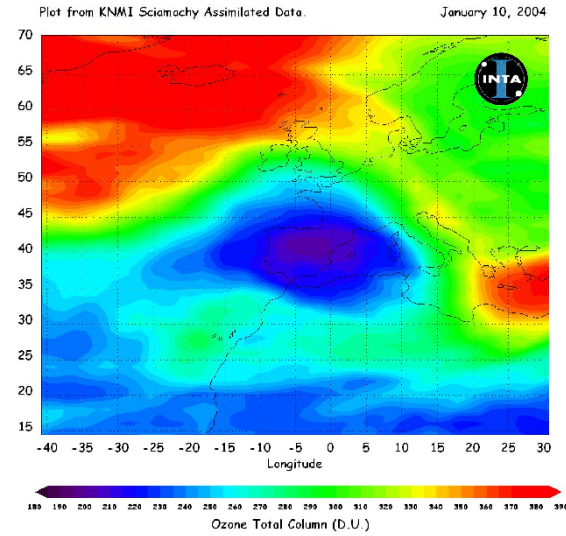

Figure 16. Exceptional "mini-hole" occurred on January 10th of 2004 above the Iberian peninsula. In this case, a closed morphology was produced as a mixing result of tropical air at low levels and chemical destruction at high levels.

To understand this, it is necessary to consider the differences between the Antarctic and the Arctic vortex. In the northern hemisphere, the irregular distribution of the continents and oceans induce a stronger planetary wave activity with two decisive consequences. On one hand, the planetary waves in the stratosphere are responsible for the polar transport of the ozone generated in the equator, on the other, the waves act as energy carrierts from the troposphere, which results in the temperature increases. Since the wave activity is very irregular the temperature fields in the Arctic are very variable. Scherhag (1952) discovered the existence of sudden

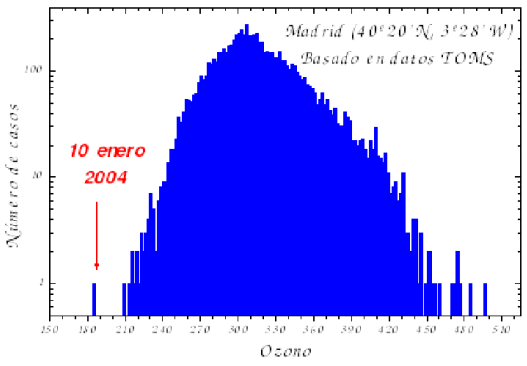

Figure 17. The ozone content on January 10th of 2004 was by far the lowest value since measurements are made (1978). These values are more characteristic of the Antarctica during the ozone hole.

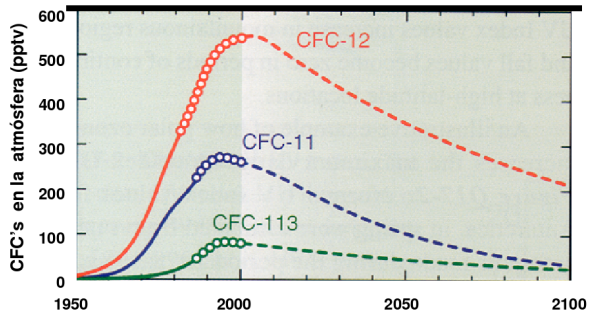

Figure 18. Concentration of chlorofluorocarbon in the atmosphere (circles: observations) and forecasted evolution according to models (WMO, 2003).

warmings that increased the temperature in the stratosphere up to 40°C in less than a week. These warmings deform the vortex to even make it disappear (figure 13). The result is the stagnation of chemical destruction by the disappearance of PSC and, above all, the contribution of "fresh" ozone to the pole. In other words, ozone is destroyed during the winter and the beginning of spring as in the other pole, but this is not seen in the observations because the polar region "refills" it with new ozone coming from the tropical production areas.

To solve this problem, it has been necessary to call upon indirect techniques which escape the aim of this paper, but which are based on the discrimination between the ozone variations due to dynamics and chemistry, calling upon 3D models and observations in different times of the same air mass (lagrangian trajectories) (Rex et al., 2002).

The observation that the mechanisms of preconditioning and even reaction cycles in the Antarctic and Arctic are the same and the level of destruction only depends on the evolution of the temperature in each winter, impels a surveillance year-by-year of the process, even more when the formation of topographical PSC by local cooling not seen by the global model forecasts are frequent. Some authors have predicted negative future tendencies in ozone, even for the same halogen quantities, as a result of cooling by the greenhouse effect (0.8°C/decade at 25 km), a 4 times more intense than the warming at ground level (figure 14).

3.3 Ozone in medium latitudes

The processes of destruction do not only take place in polar regions. Even though in a much lesser way, we also observe statistically significant negative tendencies in spring in medium latitudes. Taking into account that the polar mechanisms do not work in other regions, several alternatives have been proposed. A) The air inside the vortex dilutes in lower latitudes when the vortex breaks at the end of winter, thus contributing to the decrease of the ozone column in medium latitudes. B) Remains of the activated halogens during the period of low temperatures inside the vortex are spread to medium latitudes destroying ozone "in situ". C) The heterogeneous reactions also take place outside the vortex.

The possibility of a dynamic contribution to the observed destruction has strengthened in the last years, after a period in which the field has been dominated by a purely chemical view of the stratosphere. Since the ozone density in the polar regions depends on the intensity of the meridian transport, tendencies of this intensity will necessarily cause tendencies in ozone. If the magnitude of the meridian transport depends, ultimately, on the global field of temperatures, it seems evident that the increase of CO_2 can play a role in the meridian transport modulation. A different approach to the same problem has been proposed by scientists of the German DWD (Steinbrecht et al., 1998), who assure that they can justify almost half of the ozone decreases observed in Baveria simply as a consequence of an elevation of the tropopause in the last two decades. They attribute this elevation of the tropopause to the troposphere warming, linking the problems of global warming to the ozone destruction.

4 Streamers and ozone mini-holes

In the European mid-latitudes it is relatively frequent to find bands with an orientation more or less following the parallels containing much lower concentrations of ozone than what is usual. These episodes take place in winter and are associated with deformities and breakings of the planetary wave ridges in medium latitudes. These structures are known as ozone "Streamers", though they have also been called ozone "mini-holes" (see figure 15). In Europe there is an ozone sub-community which dedicates its research efforts in this field to study its origins (Orsolini and Limpasuvan, 2001) as well as spatial and temporal statistics (Bojkov and Balis, 2001; Erbertseder, 2004). The maximum number of events take place in central Europe even though the frequencies strongly depend on the years and the months taken

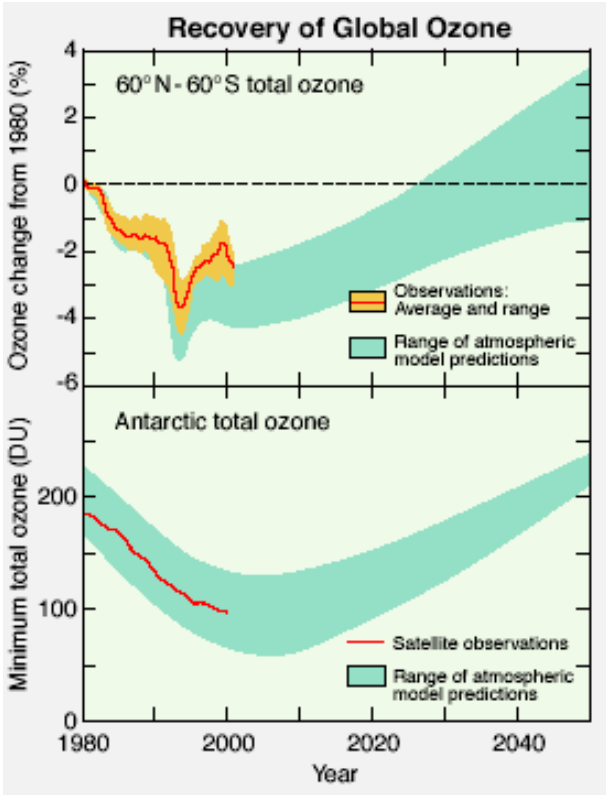

Figure 19. Forecasted recovery of the global ozone (top panel) and the hole (bottom panel). Predictions to long periods show uncertainties due to the model and also to the elected scenarios of the future evolution of the pollutants (WMO, 2003).

into account. The low values of ozone measured coincide with intrusions of tropical air and very high tropopauses, and therefore these episodes do not have a chemical component. An increase in the number of events with time would consequently lead to a decrease of ozone levels over Europe, even though at the moment the series of data do not allow us to have conclusive results.

An especially interesting case for its intensity, structure, origins and location took place on January, 10^{th} 2004 on the Iberian Peninsula (Gil et al., 2004). On that day, the lowest historical values were reached since the measurement were taken (1980). Madrid registered a 181 DU value, typical of Antarctic regions during the ozone hole (figure 16). Morphologically, we can define it as a "mini-hole" since, as opposed to streamers, it is a spatially closed minimum. In this case, three effects combined to give cause to the exceptional registered values. Below the 80 hPa level, the situation is typical of streamers: a ridge breaking of a very deformed intense wave in the Atlantic, which introduces a tropical air mass in the peninsula. Following the retro-trajectories we observe that the air masses come from the Caribbean, where the tropopause temperatures were abnormally low (3°C below the mean temperature 1978-2003 for the season). When it reaches the vertical in Madrid, the temperature at 80 hPa was 11°C inferior to the mean temperature of the month. That is to say, on the 10^{th} the air above the Madrid vertical, in addition to being tropical, contained less ozone because of the low temperatures of the tropical belt. The sounding of Madrid registers the tropopause of medium latitudes and a second tropopause, tropical, higher and colder than the first one. A third phenomenon coincided with the ones explained already. During those days, the polar vortex and the field temperature suffered an elongation on the European continent, thus spreading the low temperatures and the ozone low levels, typical of the vortex up to the north of Africa. To sum up, low ozone up to 18 km because of the entrance of tropical air and low ozone above 20 km because of the presence of polar air. The exceptional nature of the event is clear when we observe the episode frequency diagram (figure 17).

5 Future prospects

The main request of the public opinion to scientists working on stratospheric ozone, made through the international organisations involved in the protection of the ozone layer and through the political structures with environmental responsibilities, is to know if the agreement adopted in the Viena Convention and materialised in the adopted measures in the Montreal Protocol and its consecutive amendments are being effective. The emission data provided by the producers of destructive substances, the inventories compiled by the international organs (OMM, UNEP, etc) and the global observations of the last years have been able to create a perception among politicians in charge, and even those in charge of scientific politics, that the problem of the ozone layer decrease is a resolved problem, up to the point that the funds in this field, and in the stratosphere field in general, are already suffering the consequences. Many scientists incorporated to this field in past decades are taking their interests to lower heights looking for better funding areas.

This situation finds its explanation in the decoupling between scientific and political time scales. In figure 18 we can see the observations of CFC in the air and the predictable decrease, taking into account its mean lifetime. Even though they are all in their descendent branch, the total cleansing of the atmosphere will take decades. The situation concerning halogens is even worse. Most of them are regulated but their concentration in the atmosphere is still increasing. Even in the hypothesis that no new elements are involved, the situation is not going to be normal until halfway through this current century. Unfortunately, the uncertainties of the models in the long term do not make it possible to accurately establish a date (figure 19). The uncertainty is associated to different scenarios of aerosols in the stratosphere caused by unpredictable volcanic eruptions, degree decrease of the temperature or efficiency in the removal of bromine products, among others.

This uncertainty is creating a movement among the institutions with monitoring responsibilities (i.e. meteorological centres) and among scientists with sophisticated

instrumentation that study the stratosphere (i.e. NDSC net, atmospheric satellites community, etc) to alert the people responsible for scientific politics about the need of long-term observation programmes, traditionally considered routine activities with no right to funds by the R+D funding actions. In this sense, the European Program GMES (Global Monitoring for Environment and Security) has been useful to establish a Frame under which large projects will probably be developed and internationally coordinated for the monitoring of the ozone layer.

6 Conclusions

The ozone layer is in a chemical-dynamic-radiative equilibrium, so any alteration in one of these three areas will have an influence on the measured density. In the last decades all the efforts have been orientated in this direction because of the increase of halogen species in the atmosphere. However, the possible dynamic effects on the layer have recently been taken into account. In particular, the tendencies on temperature can: a) modify the equilibrium by means of warming in the lower layers that heighten the tropopause, b) change the stratospheric meridian gradient that, c) disrupts the wave activity and the meridian transport to the poles and, d) the frequency of wave breaking in mid-latitudes that consequently have a larger contribution of tropical air with little ozone in medium latitudes (especially in the European sector). Some chemical-dynamic mixed effects would be the changes in the constants of reactions, and the increase of PSC caused by a cooling of the stratosphere associated to the over-emission of IR radiation because of CO_2 and other greenhouse-effect gases.

The adopted measures for the elimination of gases that destroy the ozone layer seem to be providing good results, even though it is still too soon to establish that the problem is resolved in a conclusive way. The continuous observations in the decades to come, not only of ozone itself, but also of gases intervening in its chemistry, and the temperature evolution of the stratosphere are necessary to confirm if ozone recovers the values measured in the 70s' and before that decade. The observations are also necessary to detect other possible unpredicted interferences and to move on in the research of stratosphere.

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