Atmospheric ozone and the greenhouse gases observations: an update

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Abstract

While the presence of stratospheric ozone is known since 1925, a concern for its stability in presence of industrial perturbations was first felt in 1970 to be confirmed by the important seasonal decrease observed during the Antarctic spring since around 1980. After these twenty years of atmospheric studies including extensive dynamic modeling, it is now clear that atmospheric chemistry plays a major role in this process and that the human influence cannot be excluded as the drive to stratospheric ozone decrease. In the meanwhile, tropospheric ozone which was studied since the fifties as an agent of urban pollution has been observed to increase on larger scales. This paper intends to present the situation in terms of the future ozone research and the present political response to this situation. On the contrary, the greenhouse gases and effects are studied since the late nineteenth century, the present situation in the observation and understanding of global warming will be shown.

History: seventy years of stratospheric ozone research.

Ozone (O_3) has been known in the troposphere since its chemical discovery by Schönbein in 1848, at these very early dates, field measurements were performed at various stations and put in correlation with all kinds of environmental phenomena, these observations have unfortunately very little value for us because non standard techniques were used and that the indicated value was more often a function of the total balance of oxidants. This area of research felt into a routine status in the early 20th century, it was at that time that the progresses in UV. instrumentation led to discover that ozone was the absorber limiting the penetration of ultraviolet radiation of wavelengths lower than 300 nm to the ground. The discovery of the stratosphere in 1912 and the progresses of aviation led to a development of all aspects of meteorology and

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almost simultaneously Fabry and Buisson in France, Dobson in England and Götz in Switzerland discovered that the bulk of the absorbing ozone was situated in the stratosphere, the maximum altitude being around 25 km. Accurate routine observations began at the Arosa station in 1926 and were continued since. The intent of the first observers was to use the ozone as a tracer of the atmospheric circulation for direct meteorological uses, we must thank them now of their care in obtaining absolute values so that the total series can still be compared with the present network of "Dobson" instruments. A first theoretical explanation was given by Chapman in 1930: the ozone was formed and destroyed by UV. radiation in the stratosphere:

$$O_2 + h\nu\ (\lambda<242\ nm) \rightarrow O + O$$
$$O_2 + O + M \rightarrow O_3 + M$$

$$O_3 + h\nu\ (\lambda<300\ nm) \rightarrow O_2 + O$$

This simple mechanism leads to a layer which was approximately at the right location, the next progress came from extensive rocket observations made after the war which helped refine the values of ozone and led Bates and Nicolet in 1950 to introduce the hydrogen brought by water vapor and methane in this scheme.

The ozone controversy

Nitrogen oxides had of course been introduced by Nicolet in order to explain the formation of the lower layer of the ionosphere but in the absence of any mechanism to form it in the stratosphere, they had to wait until 1970 to come in the picture; tropospheric nitrous oxide was then found to be a stable source of N_2O in the stratosphere where it dissociates in NO and atomic oxygen. It was also found that NO was an important component of the exhaust of high performance aircrafts and especially the planned fleet of American and Franco-British supersonic aircrafts. NO leads, among other reactions to a catalytic cycle in which ozone and atomic oxygen recombine while NO rebuilds itself:

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$
$$\overline{O_3 + O \rightarrow O_2 + O_2}$$

This mechanism would lead to the destruction of the stratospheric ozone layer by a very small nitrogen oxide injection, this led to a five year accelerated atmospheric program based essentially on balloon and Concorde campaigns on the observational side and one-dimensional atmospheric models on the theoretical side, the final conclusion was quite surprising: nitric oxide was a long-time constituent of the stratosphere and its sink is the wash-out of nitric acid by rain in the troposphere, even, at altitudes below 15 km, the planes should begin to initiate smog reactions and even become (negligible) ozone producers, at the Concorde altitude (18 km.), the planes would be neutral in terms of ozone balance. The conclusion was very moderate compared to the heath of the controversy which was on the background of the failure of the American and Soviet super-sonic transports while Concorde was performing its first commercial flights. It was however stated that a new impact study should be performed before launching a development program for a high altitude (30 km) and heavier plane, this is the present situation.

The introduction of chlorine came in 1974 after it was discovered that freons used in aerosol cans and refrigerators had become a permanent component of the atmosphere of cities, other observations aimed at using them as tracers of atmospheric transport showed that they were already present in the entire atmospheric system and it was then published by several authors (e.g. Rowland and Molina, 1974) that these freons would diffuse intact to the stratosphere where they would photo dissociate to release atomic chlorine which would initiate a catalytic cycle in balance with ClO which would destroy the ozone, here also, a very heavy controversy began which is not yet settled. Part of the conflicts which appeared came from the vital importance to industries of the preservation of investments in freon plans made as late as 1974 at a time when every opinion was that these products were perfectly safe. After twenty years of research, it can be stated that no natural source of stratospheric chlorine has been identified and that one has to assume that all the stratospheric chlorine and fluorine compounds observed are of man-made origin, the question of chlorine sinks appears to be much more complicated than the simple wash-out of HCl. The industry and political world slowly responded by searching for freon

substitutes, first for aerosol cans, secondly, for industrial cleaning and now for refrigeration. Several agreements, notably, the Montreal protocol, were passed to reduce production and release of these products and are enforced by national laws. The newest aspect of this study is the role of bromine which is used in the halon fire extinguisher systems, bromine could be much more effective than chlorine in destroying ozone, but halons were not restricted by the Montreal protocol, the American Environmental Protection Agency enforces now a regulatory policy imposing the use of the existing stocks for essential uses.

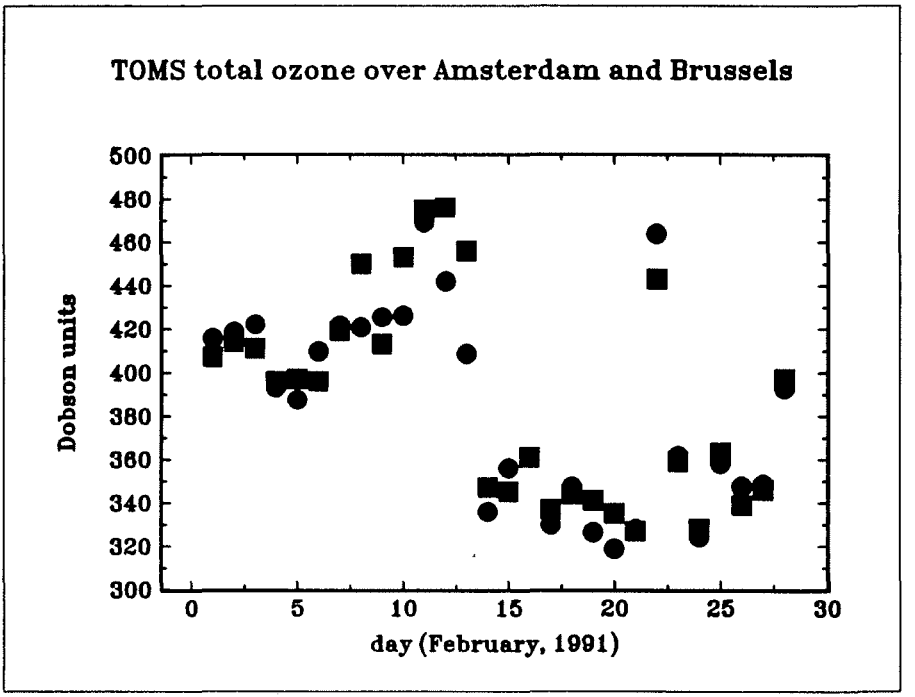

Fig 1: Total daily ozone values expressed in Dobson units obtained from the data of the American TOMS satellite instrument at the vertical of Brussels (squares) and Amsterdam (circles), the Brussels data are validated by the Uccle Royal Meteorological Institute Dobson instrument, this figure indicates normal ozone fluctuation, it also indicates that the Uccle instrument is also representative of the Dutch ozone situation (adapted from TOMS data 1978-1992, NASA).

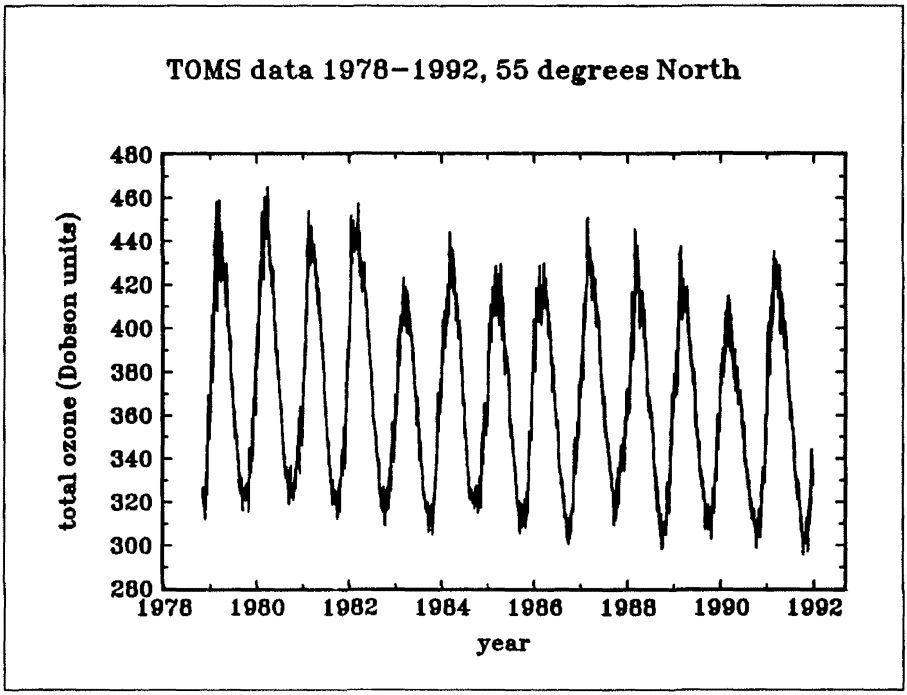

Fig 2: Zonal average of total ozone at 55° North, showing the seasonal variations of ozone, this variation is much more important than the ozone trend and shows the importance of highly accurate observations in order to evaluate these trends. (adapted from TOMS data 1978-1992, NASA).

The unexpected challenge from Antarctica.

Ozone has been measured in Antarctica since the International Geophysical year of 1957-1958. Its annual variation was showing some specificities: a November maximum corresponding to a sudden atmospheric warming and a comparably lower October plateau, in the average, the ozone column was always higher than the middle latitude values corresponding to an extrapolation of the latitudinal ozone increase observed on a world scale. An observation of the total ozone column was even performed by Dutch KNMI meteorologists during the 1965-1967 Belgo-Dutch expedition to 'Base Roi-Baudouin', the meteorologists came at the time to a dynamical explanation of the temporal ozone variations. However in the early 1980's, two sets of observations began to show repetitively low values of October ozone: the Japanese Syowa station and the British Halley Bay station, the Japanese observers were first to

publish this results both in Japanese journals and at the quadrennial ozone symposium in 1984. The British publication in NATURE in 1985 made this phenomenon internationally known, especially after the authors had drawn curves where the ozone decrease paralleled the freon increase in the same period. The ozone hole was then found also in the satellite data of the TOMS back scattering instrument where it had been interpreted as an artifact of the technique before. Two extensive American campaigns in 1987 and 1988 confirmed the existence of the hole and its extent, in 1987, on the fourth of October, the lowest ozone values ever recorded were obtained, since then these values around 100 Dobson units have been matched almost every year and especially in 1991 and 1992.

The mechanism of the ozone hole is different from the catalytic cycle of chlorine and nitric oxide, it is strongly related to the formation of stratospheric clouds in the Antarctic vortex during the polar night, these clouds condense almost a large number of gases including HCl and HNO_3, at the return of the sun, these ice particles begin to release these gases and build a photochemical haze which is highly reactive and which leads to ozone destruction. The precise mechanism is not known, several chemical schemes based on heterogeneous chemistry are proposed and seem to explain the observation. Reported searches in the pre-seventies Antarctic records have shown the November maximum associated with the breakup of the vortex, they however failed to show the anomalously low October values observed since the eighties. It is unfortunate that the observation series did not start before 1957-1958. One non-standard ozone measurement of 1959 in the French station "Dumont d' Urville" shows very strange relative spectral intensities received on the ground which could be interpreted in terms of low ozone, but in this case, the observation itself could be contaminated by the polar stratospheric clouds themselves and, 35 years later, straylight internal to the instrument cannot be ruled out. The most direct evidence of chemical origin was the anti correlation of ClO and ozone at early spring during a meridian flight of the NASA U2 in 1987.

Since 1990, at each Arctic spring, campaigns are now conducted in order to study the Northern ozone behavior, up to now, no clear ozone holes have been seen, one reason is that due to the distribution of land masses around the North pole, the vortex does not form in a stable form and also, even with high ClO as in 1992, the temperature is too high to allow the formation of long lived polar stratospheric clouds. A ozone spring phenomena in the Northern hemisphere would have of course important economical consequences as important population centers are above 50° North in Europe.

Present situation

The UARS observations of January 1982 have shown high ClO concentrations over Europe which did not materialize in an ozone hole, however, the ozone column was lower than average over Belgium in February for the two consecutive years of 1992 and 1993. If this trend would continue for around five years, serious concern about a Northern ozone depletion could be voiced. In Antarctica, the size of the ozone hole increases each year and now covers the entire continent, its persistence is also longer as the break-up of the vortex happens later in the latest years. A recent NASA report has found this same ozone decrease in the Northern hemisphere and attributes it to the Pinatubo volcanic cloud.

The total ozone depletion is still not well known, a 5% decrease around 40 km altitude is generally advanced, however, the present ozone results, in this bracket of sensitivity could be instrument dependent and a whole new generation of space borne precise monitors is expected to monitor accurately ozone and its parent gases. One of these instruments is the ESA GOME ozone and aerosol monitor due to fly in 1994 on the ESA ERS2 satellite; this instrument is partly designed in the Netherlands and should achieve an accuracy of better than 1% of the total ozone column together with observations of aerosols and several other constituents, most notably NO_2. The polar orbit and the frequency of observation will efficiently address the problems of trends and regional variations, it is hoped that after a few years of observation, this new data base will permit to assess the climatic impact of new ozone threats.

Greenhouse phenomena.

The greenhouse theory was first introduced in the nineteenth century by Arrhenius when it was found that the surface temperature of the earth would be around 246 K in the absence of an atmosphere, it was accepted that the much warmer surface temperature were due to the reabsorption by the atmosphere at wavelength above 4 microns of the radiation reemitted by the earth, the polyatomic minor constituents H_2O, CO_2, O_3, N_2O and CH_4 were rapidly found to be the main cause of this radiative effect and very early, the increase of CO_2 was put in relation with the increase in temperature observed since the very cold winters of the early 18th century. This warming trend lasted certainly from 1830 to 1938 and was followed by a relative cooling which had its minimum in

1972. The trend reversed then again and greenhouse theories came back rapidly into favor for two reasons, the first is that the carbon dioxide growth was proved, the second is that the apparition of the CFC's as strong infrared absorbers in former atmospheric windows would increase the positive forcing in radiative models. The observed increase in tropospheric ozone would also lead to a tropospheric warming. Also, the growth of methane was established from Antarctic fossil ice, while the increase of nitrous oxide is still far from established. Negative forcing related to the back-scattering of solar radiation by dust and droplets originating from local pollutions and volcanoes is still in the beginning of its study despite work by prominent scientists on both the problems of 'nuclear winter' ,where soots from the fires of a nuclear war prevent all radiation from reaching the ground and the meteoric dust cloud explaining the disappearance of the dinosaurs. A recent paper indicates that smokestack industries could offset the positive forcing of the temperature in Summer in both the Northeastern United States and Eastern Europe, cooling has also been clearly observed following the Loki eruption of 1786 and the Tambora eruption of 1815, the oil fires of Koweit in 1982 gave also a verification on a very local scale of the nuclear winter theory. The weaknesses of the present models are in the difficulty of introducing the feedbacks which are important and especially the ocean gas absorption and evaporation properties as well as clouds and biomass responses. A recent compilation of Northern hemispheric American and Chinese observations (Boden et al, 1992) seems to indicate a decrease in daytime maximum temperature while nighttime minima are increasing , this could be related to the greenhouse effect, warmer temperature leading to more humidity and more clouds. However, despite the high quality of the research involved, the quantitative assessment of the greenhouse effect is still almost at the same point than at the time of Arrhenius first theories, this being related essentially to the poor modeling of the ocean's role, both as a sink for greenhouse gases and as the main component of the biosphere energy balance.

However, the present consensus is that a doubling of greenhouse gases and especially carbon dioxide would lead to an increase of the air temperature of around two degrees, with unknown consequences on climate and on ocean surface levels, it seems thus evident that the emissions of infrared absorbing gases will soon be regulated even in the absence of validated models.

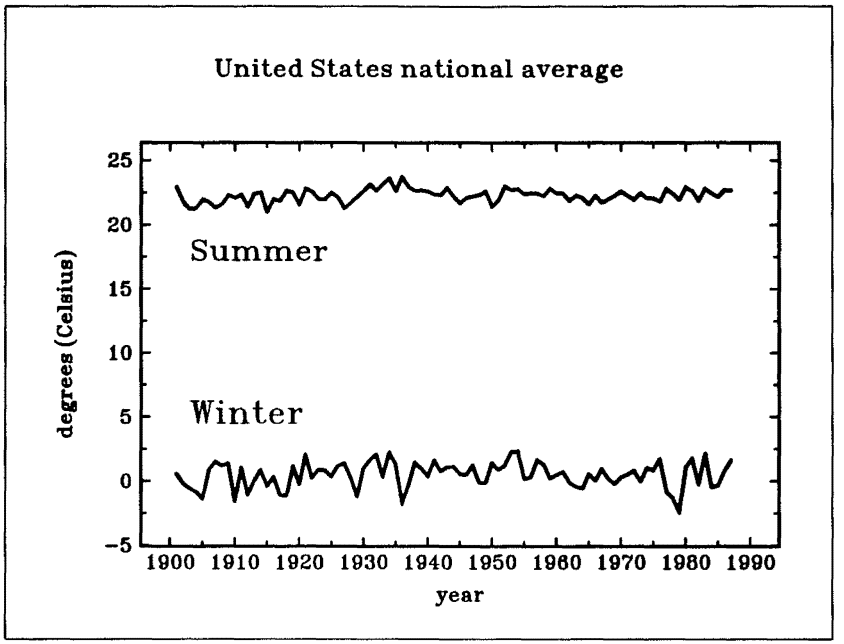

Fig 3: Temperature series of the continental United States meteorological stations between 1900 and 1990, the total series show a negligible decrease (-0.06 °C) during this period, in contradiction with the other Northern hemisphere series. These American stations are essentially rural and continental at mid-latitudes while the other stations are at Northerner latitudes and closer to urban centers. This shows the importance of a complete statistical analysis of all possible situations before concluding to the beginning of the predicted effects of the greenhouse gases (adapted from Boden, Trends91, Oak Ridge National Laboratory, Tennessee).

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