

# OZONE CHANGE AND ULTRAVIOLET SOLAR VARIATIONS

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The solar electromagnetic radiation is the primary source of energy for the terrestrial environment. The largest fraction of energy associated with the solar spectrum is situated in the visible. The ultraviolet domain for wavelengths shorter than 320 nm represents only a small fraction (2 percent) of the total incident flux. This spectral range is of fundamental importance for aeronomic processes from the troposphere to the thermosphere. It also plays an important role for photobiological processes in the biosphere because of its ability to destroy living cells and its role in initiating photosynthesis, the primary basis for life on Earth. Most of the solar radiation of wavelength larger than 320 nm is reaching the Earth's surface and channelled into heat. About 70 percent of the incident flux is so absorbed. The Earth's radiative budget depends upon the balance between the outgoing infrared radiation and the total solar input.

Because of the complexity of the atmospheric processes and the strong interplay and feedback between chemical composition and radiative budget, climate studies should include observations of visible and ultraviolet solar radiation and its variability, in close relation with the atmospheric constituents which control the penetration of solar radiation and the transfer of the outgoing thermal radiation. The ozone molecule is a key minor constituent for the troposphere, the stratosphere and the mesosphere. It provides the main stratospheric heat source through the absorption of solar ultraviolet radiation and thus determines in large part the temperature profile in the stratosphere and the general circulation. Ozone therefore couples the stratosphere and the tropospheric climate through complex processes involving radiative, chemical and dynamic effects. The study of solar variability with respect to anthropogenic perturbations is of crucial importance to distinguish between the various perturbation expected to affect the terrestrial environment in the future (Brasseur et al, 1988).

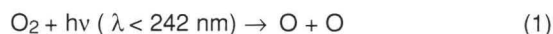
These problems are of major concern for the study of global atmospheric change experienced since decades and more recently with stratospheric ozone depletion. This work will briefly review the current knowledge in solar ultraviolet variations and their impacts on atmospheric processes, with the emphasis on stratospheric ozone change.

## 1. Aeronomic processes

Absorption of solar extreme ultraviolet radiation (EUV) determines the structure of the upper thermosphere and leads to ionization of the major species, namely O<sub>2</sub>, N<sub>2</sub> and O. Consequent reactions involving recombination of ions and electrons produce minor species like NO. Details on nitric oxide photochemistry are given by Barth (1992). In the lower thermosphere (altitudes below 120 km) absorption by molecular oxygen in the Schumann-Runge continuum is responsible for heating and production of atomic oxygen which is transported to the upper mesosphere, together with nitric oxide. The thermal balance in this region is also controlled by infrared radiative losses from CO<sub>2</sub> and NO. More informations on thermospheric aeronomy have been reported, for instance, by Banks and Kockarts (1973) and Roble (1977).

Solar Lyman  $\alpha$  and ultraviolet radiation of wavelengths larger than 180 nm are absorbed in the mesosphere and in the stratosphere. The Lyman  $\alpha$  solar chromospheric line initiates photoionization processes in the D-region, and the photodissociation, for instance, of water vapor in the mesosphere, controlling the ozone budget in the mesosphere through the production of OH radicals.

Ozone, which protects the biosphere from harmful solar ultraviolet radiation, is produced in the upper stratosphere by photodissociation of molecular oxygen by solar irradiance of wavelengths shorter than 242 nm, through the following reactions :



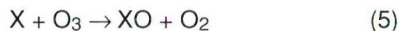
The ozone itself is photodissociated to form atomic oxygen :



Chemical loss of odd oxygen was first attributed by Chapman in 1930 only to the reaction :



Later on, it was realized that this reaction is catalyzed by various radicals, mainly according to the following scheme :



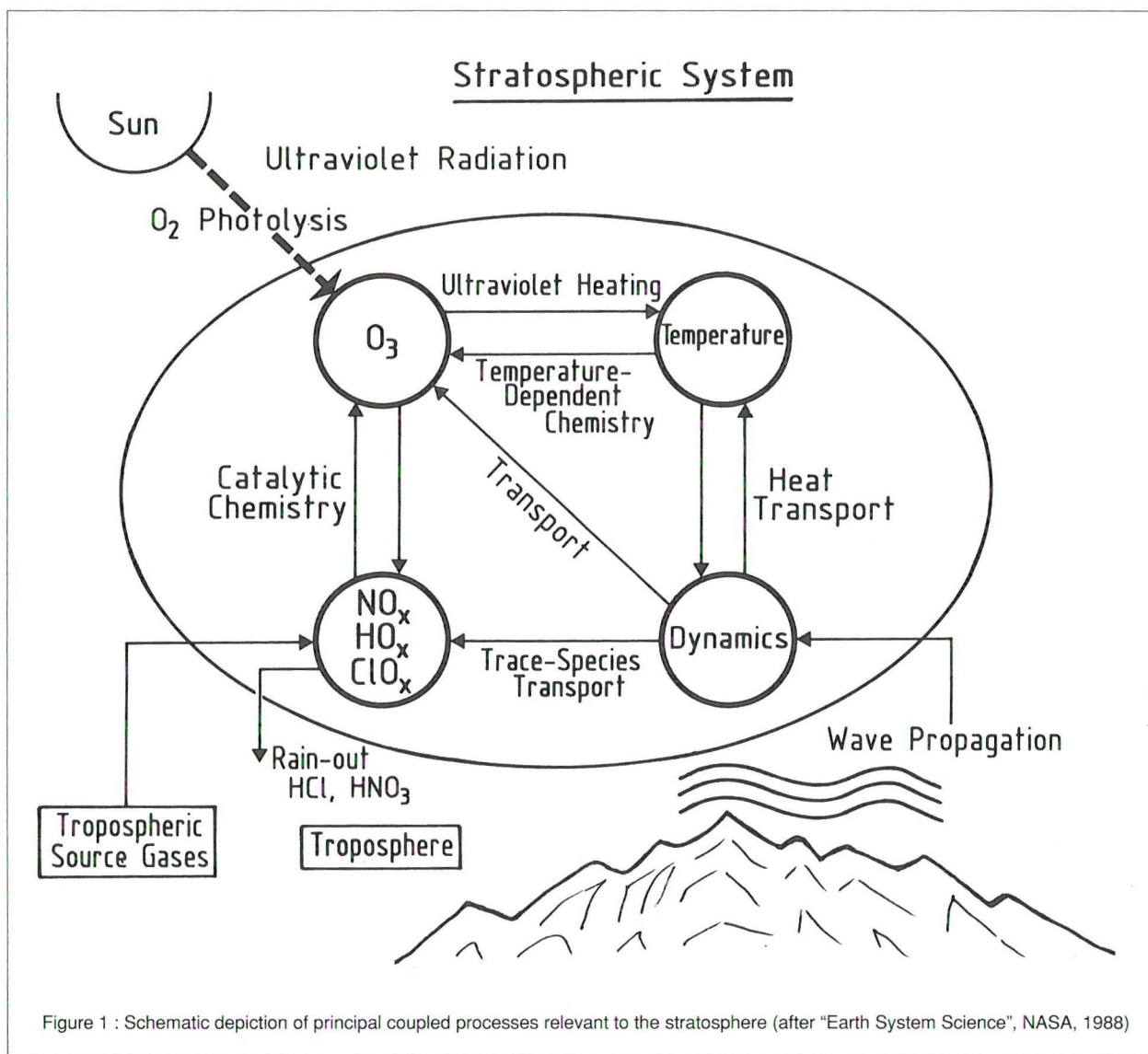
the catalyst X being H, OH, NO, Cl or Br.

The chlorine catalytic cycle mainly occurs in the upper stratosphere, with a maximum efficiency around 40 km altitude.

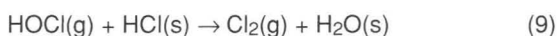
Those radicals result from oxidation processes of constituents of tropospheric origin such as H<sub>2</sub>O, CH<sub>4</sub>, H<sub>2</sub>, N<sub>2</sub>O and photodissociation of halocarbons. Nitrogen oxide can also be supplied by downward transport from the lower thermosphere during the polar night.

More details on gas phase chemical processes in the middle atmosphere are given in Brasseur and Solomon (1986). Figure 1 illustrates the complexity of processes determining the structure of the stratosphere.

Different destruction processes of ozone predominate in the lower stratosphere. Since the discovery of the dramatic seasonal depletion of ozone during austral springs (Farman et al, 1985), additional processes are needed to explain the rapid reduction in ozone concentration between 15 and 20 km altitude.

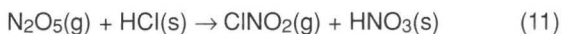


They involve heterogeneous reactions of reservoir (inactive) species at the surface of solid particles, the so-called Polar Stratospheric Clouds (PSCs). These particles are a mixture of nitric acid and water vapor or only pure water, depending on the temperature prevailing inside the polar vortex during the polar night. The chlorine reservoirs like  $\text{ClONO}_2$  and  $\text{HOCl}$  are converted into active chlorine according to the following reactions :

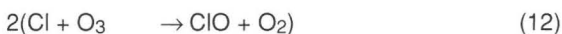


The letter g stands for gas phase and s for solid phase.

In addition,  $\text{N}_2\text{O}_5$  is converted in  $\text{HNO}_3$  :



When the sunlight is coming back after the polar night, photodissociation reactions of  $\text{Cl}_2$ ,  $\text{HOCl}$  and  $\text{ClONO}_2$  are producing  $\text{Cl}$  and  $\text{ClO}$  radicals. Because the concentration  $\text{NO}_2$  is lower than usual due to  $\text{N}_2\text{O}_5$  conversion into  $\text{HNO}_3$  (reactions 10 et 11), a large amount of  $\text{ClO}$  remains available to react with ozone. The predominant destruction cycle is the following



These photolysis processes are initiated by ultraviolet solar radiation of wavelength larger than 300 nm.

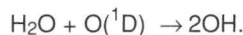
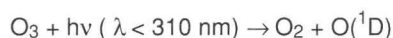
Similar heterogeneous reactions on the surface of acid sulfuric aerosol droplets present at all latitude play an important role in the ozone reduction observed at mid-latitudes :



The role of these two reactions are enhanced after major volcanic eruptions like the Mount Pinatubo eruption in June 1991, leading to significant  $\text{NO}_2$  reductions at all latitudes (Van Roozendaal et al., 1994).

In the troposphere, the central role is played by  $\text{OH}$  radicals which oxidize various organic compounds like, for instance, methane and hydrochlorofluorocarbons and, consequently, control their tropospheric lifetime and their fluxes into the stratosphere.

This radical is of photochemical origin and depends upon the level of UV-B radiation (280-320 nm) in the troposphere and, consequently, upon the amount of ozone in the stratosphere. It is produced by the following reactions :



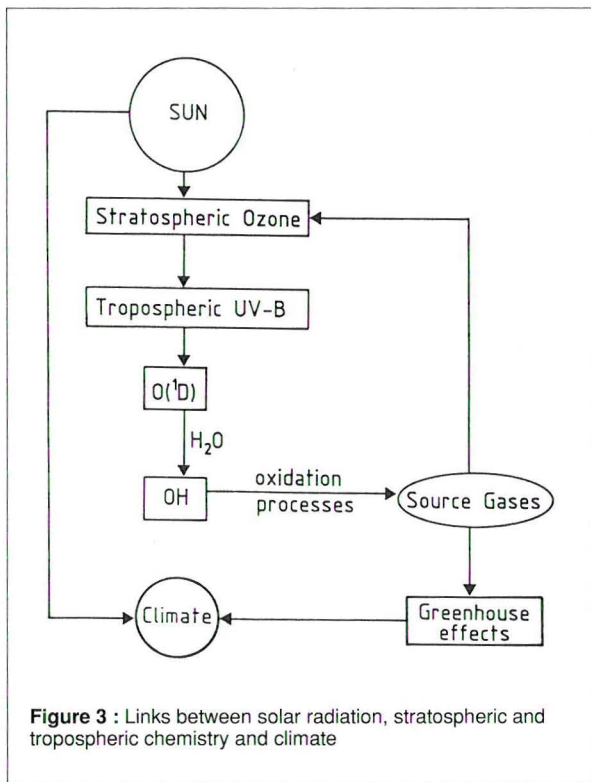
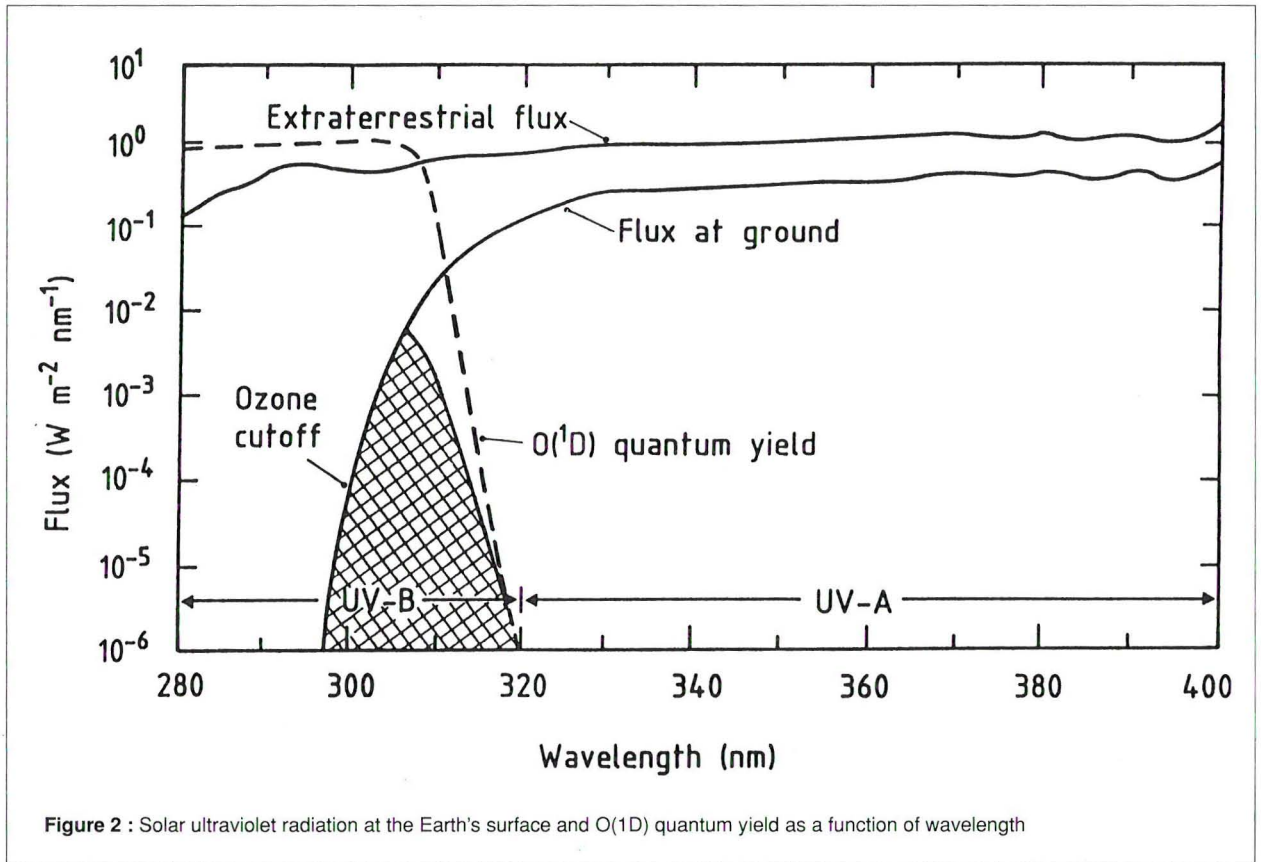
The oxidation processes in the lower stratosphere and the troposphere are actually initiated by a small wavelength range limited on one side by the ozone cutoff of solar radiation and on the other side by the quantum yield values of  $\text{O}(^1\text{D})$  production (Figure 2). Links between solar radiation, stratospheric and tropospheric chemistry and climate are illustrated in figure 3.

This brief survey is intended to demonstrate that the solar ultraviolet radiation is of fundamental importance in aeronomical processes; it illustrates the complexity of the solar-terrestrial interactions, the ozone molecules being involved in coupling phenomena between chemical, radiative and dynamic processes needed to understand our atmospheric environment.

## 2. The ultraviolet solar radiation

The ultraviolet range of the solar electromagnetic spectrum is characterized by its temporal variations which directly affect the atmosphere. Two time scales are generally considered in relation with atmospheric studies : the 11-year activity cycle and the 27-day rotation period of the Sun.

Our knowledge of solar ultraviolet irradiance made an important step forward in the 1980's with the rocket measurements reported by Mount and Rottman (1983a, 1983b, 1985) and the Spacelab 1 and 2 observations reported by Labs et al. (1987) and Van Hoosier et al. (1988). This progress is mainly due to improvements in calibration procedures used in the laboratory but also in orbit, when properly using the space shuttle advantages (Simon and Hilsenrath, 1988). In the 1990's, corresponding to the declining phase of solar cycle 22, two instruments on the Upper Atmosphere Research Satellite (UARS), namely the Solar Stellar Irradiance Comparison Experiment (SOLSTICE) and the Solar Ultraviolet Spectral Irradiance Monitor (SUSIM), are measuring the UV since October 1991, from Lyman  $\alpha$  to 400 nm, with uncertainties from 3 to 5%. Correlative measurements were



made by SUSIM and SOLSPEC (Solar Spectrum Experiment) during the Atmospheric and Terrestrial Laboratory for Application and Science (ATLAS) missions using the space shuttle.

Despite of considerable effort during the last two solar cycles, the amplitude of solar variation associated with its 11-year activity cycle is still uncertain. The Solar Backscatter Ultraviolet (SBUV) spectrometer data were analyzed by Heath and Schlesinger (1986). They deduced long-term variation from an empirical relation based on temporal variation of ratios between core and wings irradiances of the Mg II lines at 280 nm. The variation in solar irradiance at 205 nm during solar cycle 21 were estimated between 5-8% (Schlesinger and Cebula, 1992). More recently, DeLand and Cebula (1993) have combined Mg II index data from Nimbus 7, NOAA 9 and NOAA 11 instrument, covering the period from November 1978 to January 1992. Scaling factors were developed to derive solar variation during the current activity cycle (nr 22). The estimated change in solar irradiance at 205 nm is approximately 10%. Further work is still needed to improve this value. The variations deduced from the Solar Mesospheric Explorer (SME) during the declining phase of solar cycle 21 (since 1982) lead to similar values around 6% at 205 nm (Rottman, 1988).

These observed cycle variations are supported by the variations recently inferred from four months of observation by the SUSIM instrument on board UARS (Lean et al., 1992) by scaling the observed 27-day modulation to proxy indicators of solar activity at 200 nm. A 11-year variation of 7% was deduced. The validity of such method remains nevertheless to be demonstrated by means of the long term observations made on-board UARS by SOLSTICE and SUSIM and by the sequence of SSBUV flights and the ATLAS missions with SOLSPEC and SUSIM.

The solar cycle variations near 300 nm are negligible, lower than 1%, according to the available solar irradiance time series.

The 27-day solar rotation variations is well documented with the SBUV and SBUV/2 instruments, the SME data base and the current SOLSTICE measurements on-board UARS. This short-term variation has been more extensively studied because it is much less affected by sensitivity drifts of spectrometers. The agreement between SBUV and SME during the overlapping period of time is very good for the major rotation variation on August 1982, the average during the declining phase of the solar cycle shows some appreciable differences beyond 240 nm where SBUV data are less noisy than those of SME and below 190 nm where SME data are of better quality and give higher 27-day variations than SBUV, especially at the Si II line lying in the 180-182 nm interval.

The 27-day variations during the current solar cycle (nr 22) have been by reported from SBUV/2 observations by Chandra and McPeters (1994), based upon the composite Mg II solar UV index, and from SOLSTICE observations from November 1991 to December 1992 (London et al, 1993).

### 3. Atmospheric response to solar ultraviolet variations

Since stratosphere ozone production is primarily controlled by molecular oxygen photodissociation by ultraviolet solar irradiance, there is an obvious relationship between the rate of ozone production and the solar ultraviolet variations. Other constituents photodissociated by solar irradiance around 200 nm and below also respond to solar variations like for instance  $\text{HNO}_3$  (Keating et al, 1986) and  $\text{NO}$  (Barth et al, 1988).

Responses of the middle atmosphere to solar ultraviolet variations are summarized in figure 4.

At present, effects of long-term variation of solar ultraviolet irradiance on ozone have been demonstrated. The first two-dimensional (altitude and latitude) study based upon reasonable but empirical solar ultraviolet variation

related to the 11-year activity cycle was published by Brasseur and Simon (1981).

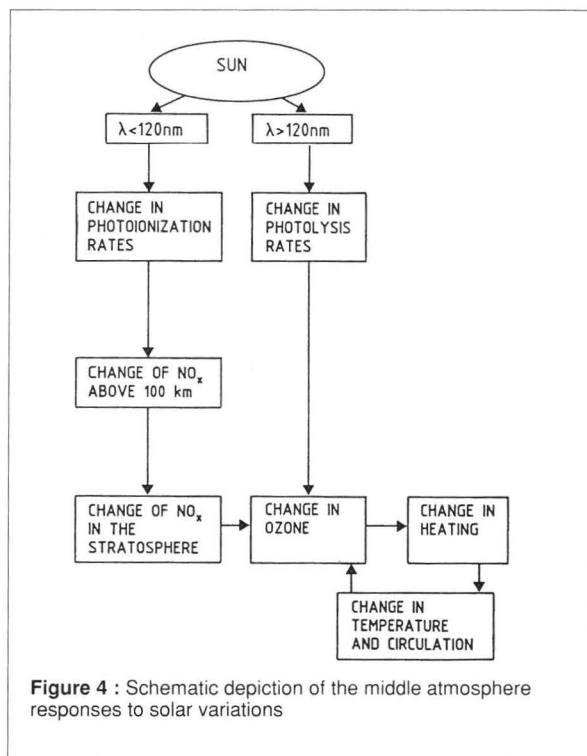


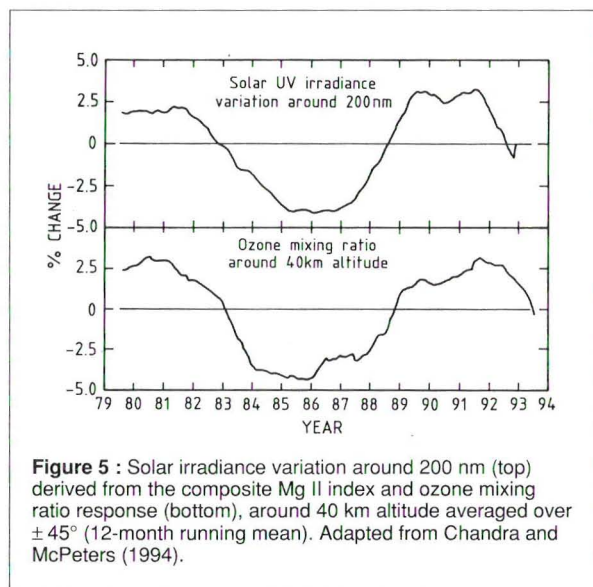
Figure 4 : Schematic depiction of the middle atmosphere responses to solar variations

Recent studies, based upon two-dimensional model (Brasseur, 1993) and upon combined satellite data (Chandra and McPeters, 1994; Keating et al., 1994) or SBUV only (Hood et al., 1993) have inferred total column ozone amount change in correlation with 11-year cycle variation of solar ultraviolet irradiance.

The most pronounced ozone change is situated, as predicted by models, in the upper stratosphere around 2 hPa. The comparison of solar cycle variation with ozone mixing ratio at this pressure level, deduced from the Nimbus 7 SBUV and NOAA 11 SBUV/2 spectrometers (Figure 5) suggest a change of about 6-8% in ozone for solar irradiance variation near 200 nm of about 7-8% (Chandra and McPeters, 1994).

Keating et al. (1994) from the Nimbus 7 TOMS and SAGE II data quoted a 1.9% ozone change between 40°N to 40°S related to the 11-year solar cycle. These ozone trends are already taking into account a reduction by a factor of 2 in the trend analysis by including solar cycle effects.

This ozone trend value is in good agreement with the 2% change in total ozone amount deduced by Chandra and McPeters (1994) for a similar latitude range of 45°. Nevertheless, these ozone responses to the 11-year solar variation are significantly larger than those inferred from two-dimensional atmospheric model.



Brasseur (1993) reported a calculated total ozone amount change in the tropics of the order of 1.1 - 1.3%, with higher values, to 1.5 - 1.7%, in the polar region. In addition, in the upper stratosphere, the model results give lower ozone response to solar ultraviolet changes, by more than a factor 2, than those deduced from satellite observations.

Similar studies have been performed using the 27-day variations in solar ultraviolet irradiance. The estimated ozone changes deduced by Brasseur (1993) from this short term solar variation are about a factor 2-3 lower than the change inferred at 2 hPa by Chandra and McPeters (1994). The agreement with the 2-D model calculation is good.

#### 4. Conclusions

They are theoretical and experimental evidences that the 11-year solar cycle variation of ultraviolet irradiance near 200 nm has an influence on stratospheric total ozone amounts. Both theoretical models and observational studies of satellite ozone data have shown that the variation is likely around 1 to 2% for the amplitude of ultraviolet solar irradiance variation deduced from solar data obtained since the end of the 1970's. Ozone trends reported in international science assessments and in the open literature are much larger than these solar induced changes and have been corrected for solar cycle influence. It remains important to quantify accurately the ultraviolet solar irradiance and variations the ozone over solar cycles to understand discrepancies between model calculations and ozone response inferred from satellite observations. The current solar observations performed

by SOLSTICE and SUSIM spectrometers on board UARS accompanied with differential ozone measurements with improved retrieval methods or new generation of instrument, namely the Global Ozone Monitoring Experiment (GOME) launched in April 1995, will help in resolving this issue.

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