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Stratospheric Ozone layer: formation and destruction

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KEYWORDS :

Introduction

Ozone (O_3) is the triatomic form of oxygen. It is a key atmospheric trace gas with maximum volume mixing ratio of about 10 to 12 molecules per million air molecules. O_3 abundance is largest in the region that is roughly between 15 and 35 km height above the Earth's surface, referred as the stratospheric ozone layer. O_3 plays a unique role in absorbing certain wavelengths of incoming solar ultraviolet light, as recognized in the latter part of the nineteenth century by Cornu (1876) and Hartley (1880). Interest in ozone stems from the fact that such absorption of solar radiation is important in determining not only the thermal structure of the stratosphere (Andrews et al., 1987), but also the ecological framework for life on the Earth's surface.

1.1. Formation and destruction of ozone layer

Under the normal conditions, the production and destruction of O_3 are in balance and hence the concentration of O_3 remains constant with time. Sidney Chapman (1930) postulated that O_3 is formed by the photolysis of O_2 at wavelengths shorter than 240 nm.

$O_2+h\upsilon \longrightarrow 2O_2$ R1

This is immediately followed by the recombination reaction

$O+O_2+M \longrightarrow O_3 + M$ R2

Where M is any mediating air molecule, in practice N_2 and O_2. To balance the production of O_3, Chapman proposed the following reactions:

$O_3+ h\upsilon \longrightarrow O+O_2$ (λ<1140 nm) R3

$O+O_3 \longrightarrow 2O_2$ R4

In 1930, although no direct atmospheric measurements of O_3 were available, Chapman based his theory a) on ground-based optical measurements, showing that most O_3 was located in the stratosphere, and b) optical night time air glow measurements in the upper atmosphere of vibrationally excited OH, which is produced by the reaction $H+O_3 \longrightarrow OH+ O_2$.

Until the middle of 1960s, it was believed that reactions R1 to R4 were sufficient to explain the O_3 distribution in the stratosphere. These reactions cannot be influenced by human activities. Improved measurements of the rate coefficients of the reactions R2 and R4, using greater care and better techniques, proved that an imbalance existed between O_3 production and destruction and showed that additional reactions are needed to complete the photochemical scheme. In particular, two reactions were proposed

$O_3+OH \longrightarrow HO_2+O_2$ R5

$O_3+HO_2 \longrightarrow OH+2O_2$ R6

With the net result $2O_3 \longrightarrow 3O_2$ were postulated to provide the additional ozone loss in the stratosphere. OH is mainly produced by photolysis of ozone

O_3+h ($\leq$400 nm) $O^{\cdot} + O_2$,

followed by $O+H_2O \longrightarrow 2OH$

Where $O^{\cdot}$ is an electronically excited O atom with sufficient energy to break H_2O bond. Chapman noted that O_3 and atomic oxygen rapidly interchange with each other, while the sum of two is linked to much slower chemical processes.

Ozone formation and destruction require UV radiation, both proceed fastest in the upper stratosphere and in the tropics, so the largest quantity of O_3 would not necessarily be found there. Chapman's theory also provided the first explanation for the temperature inversion of the stratosphere. Absorption by molecular oxygen effectively screens the shortest wavelength (highest energy) UV radiation so it doesn't penetrate below altitudes of about 80 km. O_3 is less tightly bound than O_2 and absorbs lower energy UV radiation with wavelengths up to about 310 nm. The stratosphere is warmer at higher altitudes because it is heated from above by ozone's absorption of UV radiation. Explanation of ozone's distribution was provided by Brewer (1949) and Dobson (1956), who proposed a stratospheric circulation scheme by which O_3 formed in the tropics is transported downward and toward the poles, accumulating in the lower stratosphere at high latitudes.

The short wavelengths needed in reaction $O_2+h\upsilon \longrightarrow O+O$ are available mainly in the upper stratosphere in low latitude regions and therefore the production of O_3 is largest over the equator. However, the highest O_3 columns are found at high latitudes in winter and spring and the lowest are normally found in tropics. This is due to a meridional circulation in the stratosphere termed the Brewer-Dobson circulation. It is characterized by rising motion in the tropical atmosphere and descending motion at high and mid-latitudes (Dobson, 1930; Brewer, 1949). This transport is strongest towards the winter/spring in southern hemisphere and explains the seasonal behaviour of total ozone amount at high and mid latitudes. The large day-to-day variations observed at mid and high latitudes, particularly in winter and spring, are caused by a complicated dynamic active stratosphere and by a large number of photochemical reactions involving numerous compounds and reaction not taken into account in Chapman's oxygen reactions. Since the beginning of 1970s, there has been a discussion about atmospheric ozone depletion due to human activities. Theories about O_3 depletion caused by exhaust gases from supersonic aircrafts were introduced. The ozone discussion was further intensified after Molina and Rowland (1974) and Stolarski and Cicerone (1974) suggested the possibility of O_3 destruction based on chlorine and bromine chemistry.

1.2. Perturbations to stratospheric ozone layer

Stratospheric O_3 can be decreased by any process that leads to increased stratospheric amounts of O_3 destroying catalysts. Many possible catalysts have been proposed such as NO_x from nuclear explosions (Johnston et al., 1973), hypothetical fleets of supersonic aircraft (Johnston, 1971; Crutzen, 1971), solar proton events (Crutzen et al., 1975), increased atmospheric N_2O (McElroy et al., 1976; Liu et al., 1976), chlorine from continued use of CFCs (Molina and Rowland, 1974), volcanoes and space shuttle rocket exhaust (Stolarski and Cicerone, 1974). The synthetic chlorofluorocarbons, dichlorodifluoromethane and trichloromonoflouromethane are sweft upward into the middle stratosphere where UV photolysis dissociates them to yield chlorine atoms. There are no known tropospheric sinks for CCl_2F_2 and CCl_3F, so nearly 100% of the molecules released at the Earth's surface reach the stratosphere. CFCs themselves are not involved in the catalytic process upon reaching the stratosphere, but the higher levels of ultraviolet radiations break CFCs and release atomic chlorine. Reactions involved in the depletion of stratospheric O_3 is given in Fig. 1. In an effort to recover the stratospheric O_3 loss, schedules for the global phase-out of man-made O_3-depleting substances (ODSs) were set by Montreal Protocol in 1987, a sequel to Vienna Convention on

substances that deplete the O_3 layer and its amendments and adjustments.

1.3. Polar ozone loss

The first evidence of anthropogenic O_3 depletion came dramatically with the discovery of the Antarctic ozone hole (Farman et al., 1985). The study of O_3 column at Halley Bay (76 ˚S) beginning in 1957 showed a rapid decline in the average O_3 column amounts during late 1970s and early 1980s. O_3 had decreased from values of around 300 DU during 1960s to about 150 DU in early 1980s. It was shown that the loss of polar O_3 was rapid, occurring over just several weeks from late August to mid-October. The loss was largest between about 12 and 20 km. During the winter, strong westerly winds circulate around the Antarctica lower stratosphere, isolating the air over Antarctica where temperature falls to below 190 K. At these low temperatures, polar stratospheric clouds (PSCs) form, as a co-condensate of water and nitric acid. It was realized that reaction on the surface of PSCs could turn chlorine into active forms:

$$HCl + ClONO_2 \longrightarrow Cl_2 + HNO_3$$

The Cl_2 is easily photolysed to liberate Cl atoms. Molina and Molina (1987) showed that a cycle involving the chlorine monoxide dimer, Cl_2O_2, was particularly efficient at low temperature. The reactions are given below:

$$ClO + ClO + M \quad Cl_2O_2 + M$$

$$Cl_2O_2 + h\upsilon \quad Cl + ClO_2 + M$$

$$ClO_2 + M \quad Cl + O_2 + M$$

$$2Cl + 2O_3 \quad 2ClO + 2O_2$$

Net: $2O_3 + h\upsilon \quad 3O_2$

The above reactions and a cycle involving ClO and BrO are now believed to explain the majority of the polar O_3 loss. A complex interaction of chemistry, dynamics and radiation leads to conditions suitable for significant ozone loss in the polar regions. The sequence of events leading to the springtime depletion of ozone is initiated by the onset of polar night, when high latitude regions receive no sunlight. The inclination of the Earth's orbit at about 23.5 degree causes the polar regions to experience continued darkness during the winter season. The air above the pole cools and a vortex is formed that isolates the colder region from the lower latitudes. Schoeberl and Hartman (1991) provided a detailed description on the formation and evolution of the polar vortex. It is now accepted that Cl and Br compounds in the atmosphere cause the O_3 depletion observed as 'Ozone Hole' over the Antarctica and the North Pole. The key chemical reactions involved in the chemistry of O_3 hole are unusual. The detailed figure showing the ozone loss at poles is shown in Fig. 1.1.

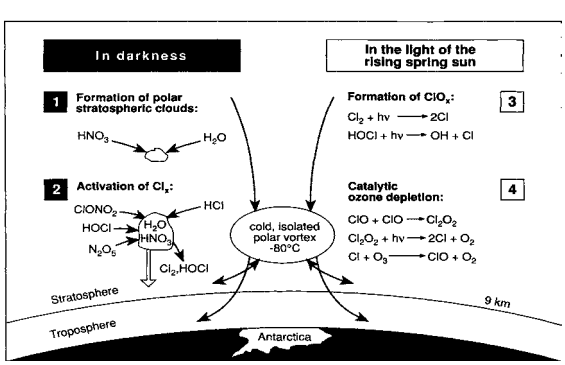

Fig. 1.1 Catalytic destruction of stratospheric O¬3 layer

. Global ozone loss

Studies conducted by the International Ozone Trends Panel under the auspices of the World Meteorological Organization confirmed that O_3 depletion was a global phenomenon. Numerous studies based on ground and satellite measurements have shown the declining trend of total ozone content globally during 1979-1993 (Stolarski et al., 1992; Varotsos et al., 2000, 2004; Ziemke et al., 2000; Varotsos and Kirk-Davidoff, 2006). A decreasing trend of total O_3 content with a large magnitude has been found in the northern Indian region as compared to other parts of India for the period 1978-1993 (Singh et al., 2002). In india, which is a tropical country, the total O_3 amounts are decreasing particularly over the northern parts, during the winter season. Moreover, there were two strong volcanic eruptions, El Chichon (1982) and Mount Pinatubo (1991) during the last century that injected ashes and gases in the form of aerosols into the atmosphere. These reach the stratosphere and remain there for a long period, causing reduction in the total O_3 amounts. It is also seen that Varanasi had big spikes in frequency of low O_3 days in 1985, three years after the El Chichon eruption in 1982 (Fig. 1.2). Similarly, Varanasi station showed large spikes in 1993, 2 years after the Mount Pinatubo eruption in 1991 (Fig 1.2). During the winter season, large number of western disturbances was observed over the northern parts of India which significantly affect the inflow pattern through the inputs of CFCs, aerosols and chlorine loading due to human activities and volcanic eruptions. These may disturb O_3- rich air in the lower stratosphere and ultimately reduce the total O_3 amounts. The transport mechanism which is affected by western disturbances may be responsible for the decrease in total O_3 over the northern India (Patil and Revadekar, 2009).

1.5. Solar UV-B radiation

It is well established that depletion of the stratospheric O_3 layer is increasing the level of ultraviolet-B (UV-B) reaching the Earth's surface. UV-B radiation is defined by the Commission Internationale d'Eclairage (CIE) as the waveband between 280 to 315 nm. Environmental UV-B radiation is highly variable. Some of these variations are easily quantified, such as due to changes in the solar elevation with latitude, time of day and season. Generally, the solar spectrum reaching the Earth's surface has been modified by the atmosphere through which the radiation passes. The wavelength dependence of the attenuation is determined by the atmospheric constituents and scattering process (Adam and Shazly, 2007). Three factors affect the transmission of solar radiation to the Earth's surface. These are absorption in the atmosphere (f_A) by O_3 and air pollutants; scattering back to space (f_S) by molecules, clouds and aerosols (haze), and absorption by the ground (f_G) (Fig. 1.3.).

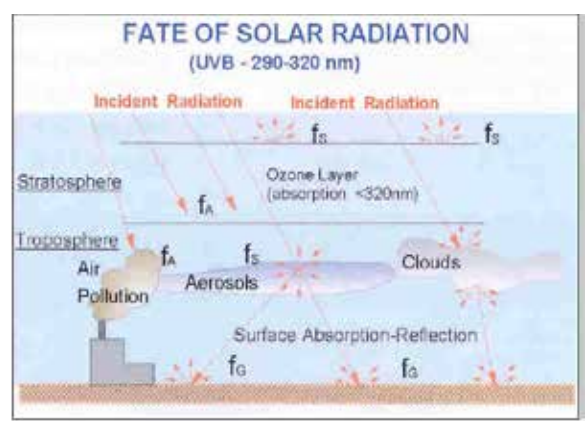

Fig. 1.3 The major factors affecting the transmission of solar radiation to the Earth's surface

If the ground is covered by snow or ice, absorption is low. The reflectivity of the ground is expressed as the "albedo". The albedo of clean snow is almost one (100% reflection) reflecting a large portion of the radiation. The sum of absorption and scattering ($f_A+f_S+f_G$) is equal to the total irradiance entering the atmosphere (Németh et al., 1996). The factors responsible for UV-B radiation reaching the Earth's surface are:

Solar zenith angle (SZA): The angle of the sun depends on three factors- the latitude, the time of year and the time of day. SZA is the angular differences in degrees between directly overhead and the sun actual position (Fig. 1.4). If the sun is directly overhead the SZA would be zero. This can occur only at latitudes between 23.5 ºN and 23.5 ºS.

Thus, in the northern and southern latitudes greater than 23.5°, the sun never reaches a SZA of zero degrees. At large SZAs, when the sun appears low in the sky, atmospheric gases and aerosols absorb more UV-B radiation owing to the longer path length that photons must travel. Variations in SZA cause clear diurnal and annual variations in surface UV-B radiation levels. The SZA is also responsible for most of the latitudinal variation in surface UV-B radiation levels (International Arctic Science Committee, 2007).

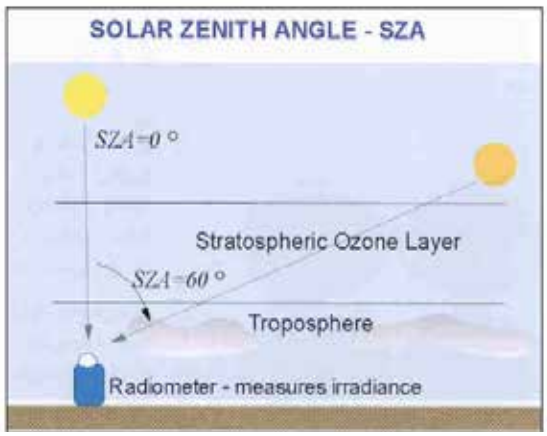

Fig. 1.4 Correlation between sun angle and the length of the path of UV-B radiation

Sun-earth distance: Sun can be regarded as the point source and thus the irradiance at a point in space varies with the inverse of the square of the distance from the sun. The earth circles the sun in an elliptical orbit and so the distance from the sun depends on the time of the year.

Aerosol: Aerosols consist of tiny solid particles or liquid drops suspended in the air. Aerosols are both natural and anthropogenic. Aerosols attenuate UV-B, as well as other wavelengths of solar radiation mainly by scattering.

Clouds: Clouds have a large effect on irradiance at the earth's surface (Bais et al., 1993). In most cases, clouds decrease ground level UV-B, but can also enhance it. Enhancement occurs when a small part of the Earth is cloud covered and the sun is not completely covered by clouds. Clouds can reduce UV-B radiation significantly but particularly if cloud cover is greater than 50% (Németh et al., 1996). When cloud cover is 25% the UV-B dose reaching the surface is 15% higher than in the case of a cloudless sky (Németh et al., 1996). Clouds and aerosols scatter radiation, while air pollutants such as SO_2 can absorb as well as scatter UV radiation. Absorption of UV by gases other than O_3 is generally a small factor except in highly polluted areas.

1.6. Effects of UV-B on the plants

The effects of UV-B wavelengths vary with the fluence rate of exposure. Damage may be caused by exposure to relatively high fluence rates of UV-B (Kim et al., 1998). The effect on the plant will be determined not only by the amount of UV-B but also by the wavelength (Ulm et al., 2004; Shinkle, 2004, 2005), the degree of prior acclimation, and to some extent by interaction with other environmental factors (Caldwell et al., 2007). Plants generally adapt to changes in UV-B radiation by activating an array of protective responses that include morphological changes (Ballare et al., 1996; Furness et al., 2005), increased DNA repair capacity (Britt and Fiscus, 2003), induction of protective compounds (Mazza et al., 2000) and increased levels of antioxidants (Jansen et al., 2008). The harmful effects of UV-B radiation, such as damage to DNA, proteins and membranes, leading to altered metabolism, are often ascribed as a consequence of reactive oxygen species (ROS) production (Strid et al., 1994). Smith et al. (2000) studied the responses of a number of vegetable crops to UV-B and reported that a rapid growth rendered this group of plants more sensitive to injurious effect of UV-B radiation. UV-B radiation affects plant growth and function mostly through its absorption by proteins, nucleic acids and lipids, and the subsequent deleterious effects on membrane integrity and function (Hollosy, 2002). DNA is particularly sensitive to UV-B radiation because absorption of UV-B causes phototransformation resulting in the production of cyclobutane pyrimidine dimmers (CPDs) and pyrimidine (6-4) pyrimidinone dimmers (6-4 PP's) causing DNA mediated damage (Britt et al., 1993). Proteins are also vulnerable to UV-B because aromatic amino acids particularly tryptophan, absorbs in 280-320 nm UV-B spectrum region.

Under field conditions, plants usually experience several stresses simultaneously. Sensitivity of plants to UV-B is influenced by the existing microclimatic conditions including the water regimes, ambient levels of visible radiation and nutrients (Murali and Teramura, 1985a,b). Co-occuring stresses can lead to increased sensitivity (Dube and Bornman, 1992) or decreased sensitivity (Murali and Teramura, 1985a) to enhanced level of UV-B. Sensitivity of the species was also correlated with N availability (Hunt and McNeil, 1998).

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