

# Contribution of some ozone depleting substances (ODS) and greenhouse gases (GHGs) on total column ozone growth at Srinagar (34°N, 74.8°E), India

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A critical analysis has been made on the contribution of CFC-11, CFC-12, CFC-113, CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CCl<sub>4</sub>, CH<sub>3</sub>CCl<sub>3</sub>, HCFCs, halons, WMO (World Meteorological Organization) minor constituents, CH<sub>4</sub>, N<sub>2</sub>O and water vapour to the variation of total column ozone (TCO) concentration at the station in Srinagar (34°N, 74.8°E), India from 1992 to 2003. With the implementation of Montreal Protocol, though the concentrations of CFC-11, CFC-113, CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CCl<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub> had decreased, the concentrations of CFC-12, HCFCs, halons, WMO minor constituents, CH<sub>4</sub>, N<sub>2</sub>O and water vapour had increased, as a result of which TCO had risen from 1992 to 2003 at the above station. The nature of yearly variations of concentrations of the above ozone depleting substances and greenhouse gases as well as ozone has been presented. Possible explanations for build-up of TCO have also been offered.

## 1. Introduction

Though ozone is a minor constituent in the atmosphere, it plays an important role in chemical kinetics of the atmosphere and saves all biological lives by absorbing harmful UV rays from the sun. UV rays are of three types: UV-A, UV-B and UV-C. UV-C has wavelength ranging from 100 to 280 nm. It is completely absorbed by ozone (O<sub>3</sub>). UV-B rays of wavelength range of 280–315 nm are partially absorbed by O<sub>3</sub>, whereas UV-A rays of wavelength 315–400 nm are weakly absorbed by O<sub>3</sub> and are therefore more easily transmitted to the Earth's surface (Jana and Nandi 2006a). Ozone is not equally distributed in the atmosphere. Concentration of O<sub>3</sub> gradually increases from upper troposphere, attains maximum at an altitude of

25–30 km in the stratosphere and then gradually decreases (Jana *et al.* 2001). Recent ozone assessment confirms that ozone in the stratosphere is declining everywhere by a small amount (Bojkov 1992). But dramatic decrease of ozone concentration occurs at Antarctica during the spring time (Farman *et al.* 1985). It was also verified by different investigators throughout the world (Midya and Jana 2002). The ozone layer and its changes can alter the structure of atmospheric temperature as well as weather- and climate-related circulation pattern (Ravishankara *et al.* 2008). Several theories have been proposed for ozone depletion; natural, dynamical and chemical theories are mainly important (Ghosh and Midya 1994).

In natural theory, several natural processes such as volcanic eruption, solar cycle variations, etc. are

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responsible for the intense decrease in O<sub>3</sub> concentration at Antarctica (Bekki *et al.* 1997). According to dynamical theory, ozone is not depleted, it is redistributed in the stratosphere (Midya *et al.* 1999). Consequently, ozone hole is formed at Antarctica during spring time. Polar vortex is a small region of polar atmosphere isolated by the polar circulation during polar winter. In southern polar region, the polar vortex is usually centered over eastern Antarctica. Antarctic polar vortex is more intense than its arctic counterpart (Midya *et al.* 1999). In chemical theory, different chemicals such as Ox, Cl and ClOx, Br and BrOx, ClOx and BrOx, HOx, SOx, etc. are responsible for dramatic decrease of ozone concentration. Due to dramatic decrease of stratospheric ozone, more UV-B and UV-A solar radiation entering into the troposphere causes more surface warming, sea level rising, cataract and photokeratitis, sunburn and skin cancers, adverse affect on mechanical properties on synthetic (plastic) and naturally occurring polymers (woods) limiting their useful life, DNA change in marine microorganisms, balance of the ecosystem, environmental pollution and climate change.

The gases in an atmosphere that absorb and emit radiation within the thermal infrared range are known as greenhouse gases (GHGs) (Karl and Trenberth 2003). The main GHGs in the Earth are water vapour (H<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), ozone (O<sub>3</sub>) and chlorofluorocarbons (CFCs). Ozone-depleting substances (ODS) and their alternatives are potent GHGs that influence the climate of the earth by trapping terrestrial infrared radiation. Ozone itself is a GHG. The stratospheric ozone layer heats the stratosphere and indirectly the lower atmosphere troposphere. Thus, stratospheric ozone is a key component that affects climate. GHGs greatly affect the temperature of the Earth; without them, Earth's surface would be on average about 33°C (59°F) colder than at present (Treut *et al.* 2007).

Many GHGs such as carbon dioxide, methane, water vapour, and nitrous oxide occur naturally in the atmosphere, while others are synthetic. Those that are man-made include CFCs, hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) as well as sulphur hexafluoride (SF<sub>6</sub>). Atmospheric concentrations of both natural and man-made gases have been rising over the last few centuries due to the industrial revolution. According to Arrhenius's theory of global warming, increasing concentrations of GHGs in the atmosphere are causing an unprecedented rise in global temperatures, with potentially harmful consequences for the environment and human health (Treut *et al.* 2007). It was recognized in the early 20th century that GHGs

in the atmosphere caused the Earth's overall temperature to be higher than it would be without them. Global warming is the increase in the average temperature of Earth's near-surface air and oceans since the mid-20th century and its projected continuation. Global surface temperature is defined in the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report as the average of near-surface air temperature over land and sea surface temperatures. The most common measure of global warming is the trend in globally averaged temperature near the Earth's surface. Based on the Fourth Assessment Report (2007) by the IPCC, global surface temperature had increased by  $0.74 \pm 0.18^\circ\text{C}$  ( $1.33 \pm 0.32^\circ\text{F}$ ) over the period 1906–2005 during the 20th century (Treut *et al.* 2007). The rate of warming over the last half of that period was almost double that for the period as a whole ( $0.13 \pm 0.03^\circ\text{C}$  per decade vs.  $0.07^\circ\text{C} \pm 0.02^\circ\text{C}$  per decade). The urban heat island effect is estimated to account for about  $0.002^\circ\text{C}$  of warming per decade since 1900 (Trenberth *et al.* 2007). Temperatures in the lower troposphere had increased between  $0.13^\circ$  and  $0.22^\circ\text{C}$  ( $0.22$  and  $0.4^\circ\text{F}$ ) per decade since 1979, according to satellite temperature measurements. Temperature is believed to have been relatively stable over one or two thousand years before 1850, with regionally varying fluctuations such as the Medieval Warm Period and the Little Ice Age (Jansen *et al.* 2007). Philipona *et al.* (2009) observed the Mainland Europe's temperature rise of about  $1^\circ\text{C}$  since 1980. They reported that shortwave climate forcing from direct aerosol effects was lower than indirect aerosol cloud forcing, and the total shortwave forcing was two to three times larger than the long-wave forcing from rising anthropogenic GHGs. Almost three-quarters of all the shortwave and long-wave forcing energy had caused the turbulent fluxes, which increased atmospheric humidity and therefore the long-wave forcing by water vapour feedback. They also predicted that with present low anthropogenic aerosol and stable values in Europe, solar forcing would subside and future temperature would mainly rise due to anthropogenic GHG warming. Satheesh *et al.* (2007) reported a large reduction in surface-reaching solar radiation of as much as 10 to 15 W m<sup>-2</sup> or 1.7 K due to dust with a lower atmospheric warming of 0.3 to 0.5 K/day over the Afro-Asian region. During local noon, warming was as much as 3 K and corresponding surface cooling was 5.2 K. Large cooling of the Earth's surface simultaneous with warming of lower atmosphere might enhance the process of fog formation, especially in the morning hours. Portmann and Solomon (2007) observed the radiative forcing of stratospheric ozone during 1980–2000 to be

$-0.15 \pm 0.1 \text{ W m}^{-2}$ . They predicted the future indirect radiative forcing from ozone over the 2000–2100 time horizon to be  $-0.1$  to  $0.1 \text{ W m}^{-2}$ , which would be small compared with corresponding range of total direct radiative forcing of 2.2 to  $6.2 \text{ W m}^{-2}$  for GHGs over this time horizon.

Naturally occurring GHGs contribute a mean warming effect of about  $33^\circ\text{C}$  ( $59^\circ\text{F}$ ). The major GHGs are water vapour, which causes about 36–70% of the greenhouse effect; carbon dioxide ( $\text{CO}_2$ ): 9–26%; methane ( $\text{CH}_4$ ): 4–9%; and ozone ( $\text{O}_3$ ): 3–7% (Kiehl and Trenberth 1997; Schmidt 2005; Russell 2007). Clouds also affect the radiation balance, but they are composed of liquid water or ice and so have different effects on radiation from water vapour.

Human activity since the Industrial Revolution has increased the amount of GHGs in the atmosphere, leading to increased radiative forcing from  $\text{CO}_2$ , methane, tropospheric ozone, CFCs and nitrous oxide. Concentrations of  $\text{CO}_2$  and methane had risen by 36% and 148%, respectively since 1750 (EPA 2007). These levels are much higher than at any time during the last 650,000 years, the period for which reliable data has been extracted from ice cores (Petit *et al.* 1999; Siegenthaler *et al.* 2005; Spahni *et al.* 2005). Less direct geological evidence indicates that  $\text{CO}_2$  values higher than this were last seen about 20 million years ago (Pearson and Palmer 2000). Fossil fuel burning had produced about three-quarters of the increase in  $\text{CO}_2$  from human activity over the last 20 years. The rest is mostly due to land-use change, particularly deforestation (IPCC 2001). Most of the observed temperature increase since the middle of the 20th century was caused by increasing concentration of GHGs, which results from human activity such as fossil fuel burning and deforestation (Angell 2000). Global dimming, a result of increasing concentrations of atmospheric aerosols that block sunlight from reaching the surface has partially countered the effects of GHG-induced warming.

In spite of releasing the by-products and waste from industrial processes into the atmosphere since two hundred years, efforts have been made only in the last century to understand their impact. A major effect of human input into the atmosphere is the thinning of ozone layer that could threaten all types of lives existing on earth and climate change induced by the emission of GHGs. Realizing this global as well as regional environmental problem, India agreed to sign the Montreal Protocol (1987) and the Kyoto Protocol (1997) for recovery of the ozone layer and to control the emission of GHGs. There has been a concerted effort to cut down the production and to phase out ODS, viz., CFC-11, CFC-12, CFC-113,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{CCl}_3$ , hydrochlorofluoro-

carbons (HCFCs), halons, WMO (World Meteorological Organization) minor constituents, etc. and to evolve the path of conversion from ODS to non-ODS.

The Kyoto Protocol determines the international limits on the emission of GHGs such as  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , etc. (Sihra *et al.* 2001) that also influence the variation of total atmospheric ozone column. The direct contribution of ODS to global climate change between 1750 (pre-industrial times) and 2005 in terms of radiative forcing was approximately 20% of that from  $\text{CO}_2$ . The combined radiative forcing from ODS and substitutes including HFCs is still increasing, but at much slower rate than in the 1980s. The total contribution of ODS and alternatives in 2005 was 15% of the contribution of major GHGs ( $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$ ). The contribution of ODS is expected to decline, whereas, that from GHGs is expected to continue to rise (Ravishankara *et al.* 2008).

In this paper, the lowering of concentrations of some ODS has been shown, increasing concentration of other ODS and some GHGs (methane, water vapour and nitrous oxide) has also been represented with lower rate over Srinagar ( $34^\circ\text{N}$ ,  $74.8^\circ\text{E}$ ), India which belongs to mountain, high altitude, colder and subtropical region having somewhat different features topographically and ecologically from 1992 to 2003. Although, a network of stations using Dobson spectrophotometer to measure total ozone covers Srinagar ( $34^\circ\text{N}$ ,  $74.8^\circ\text{E}$ ), New Delhi ( $29^\circ\text{N}$ ,  $77^\circ\text{E}$ ), Varanasi ( $25.5^\circ\text{N}$ ,  $83^\circ\text{E}$ ), Ahmedabad ( $23^\circ\text{N}$ ,  $72.6^\circ\text{E}$ ), Pune ( $18^\circ\text{N}$ ,  $73.6^\circ\text{E}$ ) and Kodaikanal ( $10^\circ\text{N}$ ,  $77^\circ\text{E}$ ), Jana *et al.* (2001) had also observed that the yearly, monthly, seasonal variation and annual cycle of total column ozone over Srinagar was somewhat different from that over other stations in India. As a result of continuous compliance of rules, regulation and amendments of Montreal and Kyoto protocols, the recovery of total column ozone over Srinagar has also been depicted which is not observed at other stations in India. The relative contributions to various ODS and different GHGs on this ozone recovery have also been critically analysed without considering seasonal effect, solar effect and the QBO (quasi-biennial oscillation) signal which is a quasi-periodic oscillation of the equatorial zonal wind between easterlies and westerlies in the tropical stratosphere with a mean period of 28 to 29 months. Although QBO is a tropical phenomenon, it affects the stratospheric flow from pole to pole by modulating the effects of extratropical waves. The effects of the QBO are not only confined to atmospheric dynamics, but also chemical constituents such as ozone, water vapour and methane are affected by circulation changes induced by the QBO. Through modulation

of extratropical wave propagation, the QBO has an influence on the breakdown of the wintertime stratospheric vortices and the severity of high latitude ozone depletion (Baldwin *et al.* 2001). Possible physical and chemical explanations have been offered for such variations.

## 2. Data and analysis

The concentrations of ODS are obtained from the website <http://www.esrl.noaa.gov/gmd/odgi>. The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) can measure the concentration of gases that contribute to the depletion of ozone layer. Among several satellite missions, the MIPAS, on-board ENVISAT limb sounds the upper troposphere and stratosphere. Measurements from MIPAS, both in their original configuration and new configuration have been analysed with two-dimensional tomographic geo-fit-multi-target retrieval (GMTR) system. The retrieved fields of pressure, temperature and volume mixing ratio (VMR) of key atmospheric gases ( $\text{H}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{HNO}_3$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{NO}_2$ ) and additional minor species (CFC-11, CFC-12,  $\text{N}_2\text{O}_5$ ,  $\text{COF}_2$ , etc.) are stored in the MIPAS2D database. NDACC (Network for the Detection of Atmospheric Composition Changes) provides data with confidence and stability of different time series. At present, the NDACC includes more than 70 research stations throughout the world, equipped with active and passive remote sensing instruments to monitor the atmospheric composition and its link to climate change. The recent validation exercises have concerned the Global Ozone Monitoring by Occultation of Stars (GOMOS), the MIPAS and the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) instruments dedicated to atmospheric chemistry on-board the ENVISAT European platform launched in March 2002 (Zerefos *et al.* 2009). The concentrations of ozone at Srinagar ( $34^\circ\text{N}$ ,  $74.8^\circ\text{E}$ ), are also collected from the website <http://jwocky.gsfc.nasa.gov> published by NASA, USA for the period 1992–2003. Monthly mean ozone concentrations have been calculated from daily mean ozone values. Yearly mean concentrations of ozone have then been computed from monthly mean ozone values. Total column ozone in this study includes retrievals from Nimbus 7 (November 1978 to May 1993) and Earth Probe (EP) (July 1996 to December 2005) total ozone mapping spectrometer (TOMS). The TOMS programme began with the launch of TOMS Flight Model #1 on the Nimbus-7 spacecraft on 27 October 1978. The version 7 processed data from the solar backscattered ultraviolet instrument (SBUV) include a revised calibration

and an improved algorithm. Meteor-3 TOMs, the first American instrument aboard a Russian spacecraft launched from the Plesetsk facility near the White Sea on cyclone booster was used to measure the total ozone from August 1991 to November 1994. Data obtained from the EP–TOMS were intended to complement data obtained from ADEOS (Advanced Earth Observing Satellite) TOMS, which provided complete equatorial coverage due to its higher orbit. Ozone Monitoring Instrument (July 2004 to present), a contribution of the Netherlands's Agency for Aerospace programme in collaboration with the Finnish Meteorological Institute to the EOS Aura Mission also measures total column ozone as well as  $\text{NO}_2$ ,  $\text{SO}_2$ , BrO, OClO and aerosol. The equations of variations of ODS, GHGs and total column ozone density over Srinagar from 1992 to 2003 are obtained from simple linear regression technique which is based on the least square principle. Correlation coefficients are computed from Pearson's formulae of coefficient of correlation.

## 3. Results and discussion

The nature of yearly variation of CFC-11, CFC-12 and CFC-113 from 1992 to 2003 depicted in figure 1 clearly reveals that CFC-11 and CFC-113 had gradually decreased, while CFC-12 had gradually increased in the mid-latitude region for the aforesaid period with different rates shown in table 1. However, Jana and Saha (2011) observed sharp global increase both in CFC-11 and CFC-12 concentrations from 1979 to 1996. Natural sources of chlorine include volcanoes and ocean spray having no impact on stratospheric ozone as chlorine being soluble is washed out of the atmosphere before reaching the stratosphere. The main source of chlorine in the stratosphere is anthropogenic, arising from CFCs. CFCs are a class of volatile organic compounds that have been used as refrigerants, aerosol propellants, foam blowing agents and as solvents in the electronic industry. They are chemically so inert that the natural reagents which remove most atmospheric pollutants do not react with them, so after many years they drift up to the stratosphere where short wave UV rays dissociate them. CFCs were invented (Solomon 1990) in 1928, but came into large-scale production only after 1950. The most important CFCs responsible for ozone depletion are trichlorofluoromethane,  $\text{CFCl}_3$  (usually called CFC-11 or R-11), dichlorodifluoromethane,  $\text{CF}_2\text{Cl}_2$  (CFC-12 or R-12) and 1,1,2 trichlorotrifluoroethane,  $\text{CF}_2\text{ClCFCl}_2$  (CFC-113 or R-113). 'R' stands for 'refrigerant'. Occasionally, CFC-12 is referred to as 'F-12' where 'F' stands for 'freon', DuPont's trade name for these compounds.

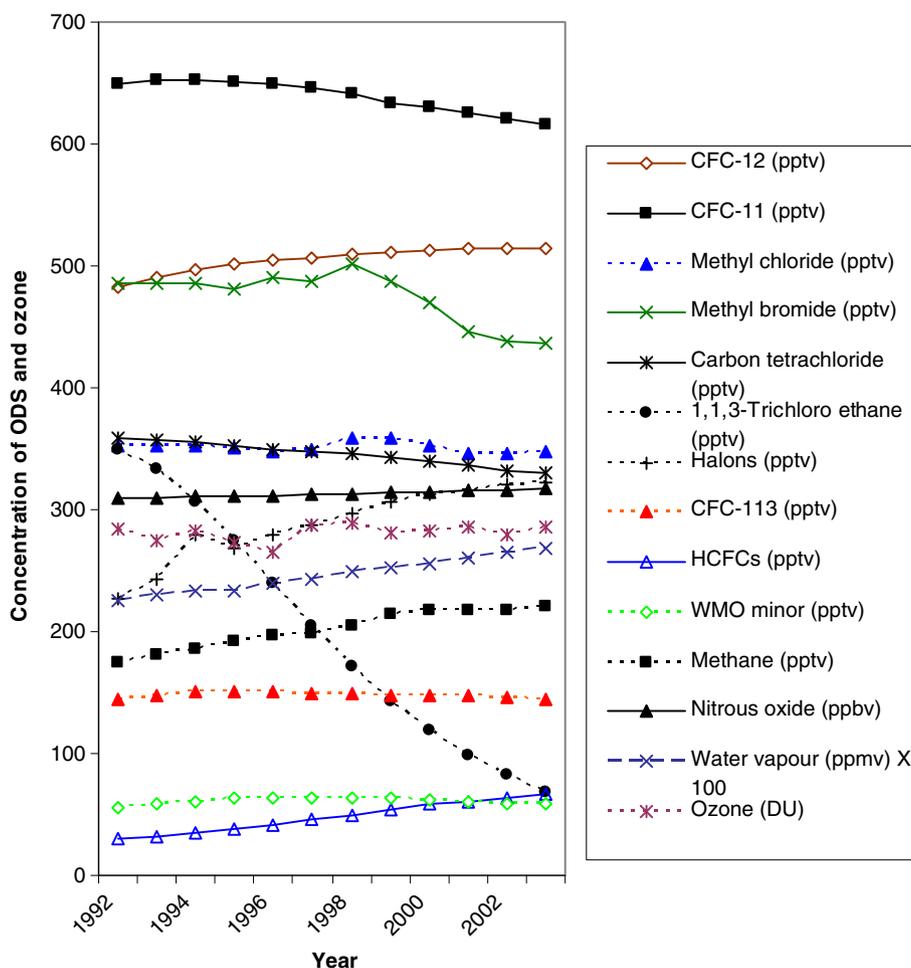


Figure 1. Variations of concentrations of CFC-11, CFC-12, CFC-113, CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CCl<sub>4</sub>, CH<sub>3</sub>CCl<sub>3</sub>, HCFCs, halons, WMO minor constituents, CH<sub>4</sub>, N<sub>2</sub>O, water vapour and total column ozone over Srinagar (34°N, 74.8°E), India from 1992 to 2003.

CFCs are named according to the quantity of each atom in the molecule. The first digit is the number of carbon atoms minus one, the second is the number of hydrogen atom plus one and the third is the number of fluorine atoms and the letter identifies the isomer of the chemical.

Table 1. Trends of ozone depleting substances (ODS), greenhouse gases (GHGs) and ozone over Srinagar (34°N, 74.8°E), India.

Atmospheric constituents	Rate of variation per year	Significance of variation trend	Standard deviation (SD)	Correlation coefficient with ozone
CFC-11 (pptv)	-3.5175	Insignificant	13.28	-0.35
CFC-12 (pptv)	2.6259	Insignificant	10.2	0.19
CFC-113 (pptv)	-0.2343	Insignificant	2.53	-0.37
CH <sub>3</sub> Cl (pptv)	-0.3636	Insignificant	4.34	0.25
CH <sub>3</sub> Br (pptv)	-4.5	Insignificant	22.07	-0.14
CCl <sub>4</sub> (pptv)	-2.6713	Significant	9.69	-0.29
CH <sub>3</sub> CCl <sub>3</sub> (pptv)	-27.667	Significant	100.42	-0.33
HCFCs (pptv)	3.559	Significant	12.84	0.33
Halons (pptv)	8.0804	Insignificant	30.6	0.3
WMO minor (pptv)	0.1189	Insignificant	2.92	-0.11
CH <sub>4</sub> (pptv)	4.3405	Significant	15.97	0.26
N <sub>2</sub> O (ppbv)	0.7609	Significant	2.74	0.31
Water vapour (ppmv)	0.0396	Significant	14.33	0.33
Ozone (DU)	6.8	Insignificant	6.98	

The yearly variations of HCFC,  $\text{CH}_3\text{CCl}_3$ ,  $\text{CH}_3\text{Cl}$  and  $\text{CCl}_4$  have also been represented in figure 1. The yearly concentrations of  $\text{CH}_3\text{CCl}_3$ ,  $\text{CH}_3\text{Cl}$  and  $\text{CCl}_4$  had fallen smoothly, whereas the amount of HCFC had risen gradually for the above period by different rates depicted in table 1. Other ozone-depleting CFC-related compounds are HCFCs such as  $\text{CHClF}_2$  (HCFC-22, R-22), carbon tetrachloride (tetrachloromethane),  $\text{CCl}_4$ , methyl chloroform (1,1,1 trichloroethane),  $\text{CH}_3\text{CCl}_3$  (R-140a) and methyl chloride (chloromethane),  $\text{CH}_3\text{Cl}$ . Only methyl chloride has a large natural source. It is formed biologically in the oceans and chemically from biomass burning. CFCs and  $\text{CCl}_4$  are nearly inert in the troposphere and have lifetimes of about 50–200 years. Their major sink is photolysis by UV radiation (Rowland 1989, 1991). Hydrogen-containing halocarbons are relatively more reactive and are removed in the troposphere by reactions with OH radicals. This process is however slow and they live long enough for about 1–20 years for a substantial fraction to reach the stratosphere.

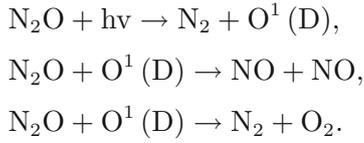
The yearly variations of methyl bromide ( $\text{CH}_3\text{Br}$ ), halons and WMO minor have been represented in figure 1. The yearly amount of  $\text{CH}_3\text{Br}$  had declined gradually, but the concentration of halons and WMO minor had increased slowly for the said period. The largest source of stratospheric bromine is  $\text{CH}_3\text{Br}$ . Much of it is naturally produced in the oceans, but a significant portion is manmade (Khalil et al. 1993). It is mostly used as a fumigant.  $\text{CH}_3\text{Br}$  is produced during biomass burning which can be either natural or anthropogenic (Mano and Andreae 1994; Shorter et al. 1995). Methyl bromide is also produced in the combustion of leaded gasoline which uses ethylene di-bromide as a scavenger (WMO 1994). Another important source of bromine is the family of halons, widely used in fire extinguishers. Similar to CFCs, these compounds have long atmospheric lifetimes; e.g.,  $\text{CF}_3\text{Br}$  has lifetime of about 65 years. Very little of these compounds is lost in the troposphere (WMO 1994). WMO minor (Daniel et al. 2007) is represented by a mixture of CFC-114, CFC-115, H-2402 and H-1201.

Variation of methane concentration depicted in figure 1 in mid-latitude region for the same period showed a continuous rise in methane from 1992 to 2003 by 4.3405 ppbv per year as shown in table 1. Jana and Saha (2011) had also observed the sharp global increase in  $\text{CH}_4$  concentration from 1979 to 1996. The mixing ratio of atmospheric  $\text{CH}_4$  varied between 350 and 750 ppbv from 110,000 to 300 years ago (Brook et al. 1996). Ice core samples have revealed that the  $\text{CH}_4$  growth rate increased with the industrial revolution, to a level of 14 ppbv per year by the 1970s (Etheridge et al. 1992). The first extensive measurements of the global distribution

of atmospheric methane were conducted in 1978 (Blake et al. 1982) and additional global monitoring networks were established in the early 1980s (Prinn et al. 2000). Between 1978 and 1987, Blake and Rowland (1988) reported an 11% increase in the global tropospheric  $\text{CH}_4$ -mixing ratio, at an average annual increase of  $16 \pm 1$  ppbv per year. The amount of methane continued to increase with significant inter-annual variability, but the growth rate slowed down in the 1980s (Khalil and Rasmussen 1993) and continued to decline in the 1990s (Dlugokencky et al. 1998). Simpson et al. (2002) observed an increase of tropospheric methane by 1.1% ( $19.5 \pm 1.7$  ppbv) over the five-year period 1996–2000, with striking fluctuations in its annual growth rate, whereas the global  $\text{CH}_4$  growth rate reached  $15.9 \pm 0.7$  ppbv per year in 1988, the growth rate was  $-2.1 \pm 0.8$  ppbv per year in 2000. It has been reported that the concentration of  $\text{CH}_4$  had been increasing at the rate of 1% per year, but recently had slowed down approximately by 0.5% per year (Karlsdottir and Isaksen 2000).

Yearly variation of  $\text{N}_2\text{O}$  represented in figure 1 in mid-latitude region during the above period shows a slow increasing trend. Jana and Saha (2011) had also observed a global positive trend in the concentration of  $\text{N}_2\text{O}$  by 0.7301 ppbv per year for the period 1979 to 1996. Oxides of nitrogen ( $\text{NO}_x$ ), another component of atmospheric ozone formation and depletion is mainly emitted from fossil fuel burning in the automobiles, decomposition of various nitrate and nitrite salts and by the reaction between atmospheric nitrogen and oxygen during lightning. Akimoto (2003) has observed that the  $\text{NO}_x$  emission in Asia is increasing at a faster rate. On the basis of a detailed study on  $\text{NO}_x$  emission in the Asian region, Kunhikrishnan et al. (2006) concluded that photochemical transformation and losses of  $\text{NO}_x$  are uncertain due to lack of sufficient observations. Nitrous oxide is one of the most important oxides of nitrogen for heat budget of the terrestrial atmosphere and its radiative effect on climate change is thought to be 200 times stronger than  $\text{CO}_2$  on a per molecule basis (Ramanathan et al. 1985; Rodhe 1990). Besides,  $\text{N}_2\text{O}$  plays an important role in the depletion of atmospheric ozone (Nevisen and Holland 1997). Such a concentration is generally ascribed to direct emission of  $\text{N}_2\text{O}$  into atmosphere through fertilizer production, crop production, fossil fuel combustion, biomass burning, adipic acid production, nitric acid production and sewage, as well as enhancement of biogenic  $\text{N}_2\text{O}$  emission by additional fixation of nitrogen by cultivation of leguminous plants and deposition of anthropogenic nitrogen compounds through the atmosphere (Kroeze et al. 1999).  $\text{N}_2\text{O}$  is chemically inert in the troposphere and is destroyed by photolysis

and reaction with excited atomic oxygen in the stratosphere as follows:



The ratio of  $\text{N}_2\text{O}$  destruction by first reaction to that by last two reactions was estimated to be 92.8 and the corresponding ratio of second to third reaction was found to be 42.58 (Solomon *et al.* 1996). Total loss rate of  $\text{N}_2\text{O}$  by these reactions was estimated to be 9–16 TgN/yr (Nevisen and Holland 1997) and  $\text{N}_2\text{O}$  had been

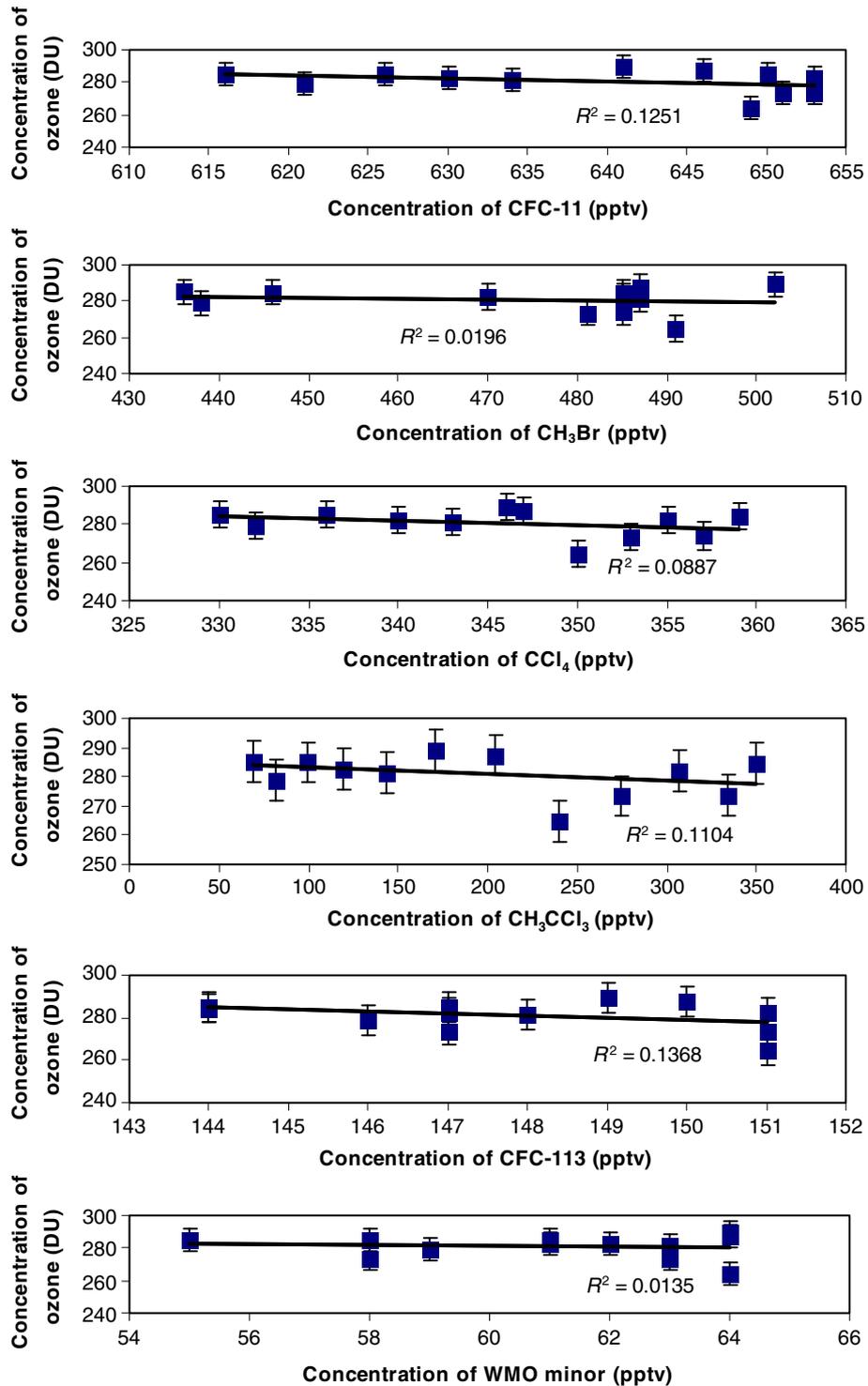


Figure 2. Scattered variation of total column ozone with the concentrations of CFC-11,  $\text{CH}_3\text{Br}$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{CCl}_3$ , CFC-113 and WMO minor.

accumulated in the atmosphere at a rate of about 3–5 TgN/yr (Nevisen and Holland 1997). The atmospheric concentration of N<sub>2</sub>O has been increasing due to human activities by 0.5–1.2 ppbv per year for the last few decades (Machida *et al.* 1995). Current estimates of the global production of N<sub>2</sub>O range widely from 10 to 17 Tg N/yr (IPCC 1995). On the basis of aircraft measurements of the tropospheric N<sub>2</sub>O concentration over Japan during the period from October 1991 to June 1999, Ishijima *et al.* (2001) showed the secular increase with mean rates of 0.50 to 0.64 ppbv/yr for selected height intervals of 0.2, 2–4, 4–6, 6–8 and 8–10 km tropopause.

The primitive terrestrial atmosphere was oxygenic in nature and ozone was produced by photodissociation of water vapour. The variation of

water vapour shown in figure 1 indicates a positive trend. The main source of water vapour in the atmosphere over Srinagar is the monsoon wind that carries huge amount of water vapour from the Indian Ocean, the Arabian Ocean and the Bay of Bengal. Jana and Saha (2011) had also reported that water vapour had increased globally by 0.0376 ppmv per year from 1979 to 1996.

The variation of ozone concentration represented by figure 1 clearly depicts an increasing trend in total ozone column over Srinagar by 6.98 DU per year for the above period, whereas, Jana and Nandi (2005, 2006b and 2006c), Jana *et al.* (2008, 2010 and 2011) had reported clear fall in total column ozone (TCO) over several stations in India, namely, New Delhi (29°N, 77°E), Trivandrum (8.25°N, 76.9°E), Dumdum (22.5°N, 88.5°E), Ahmedabad

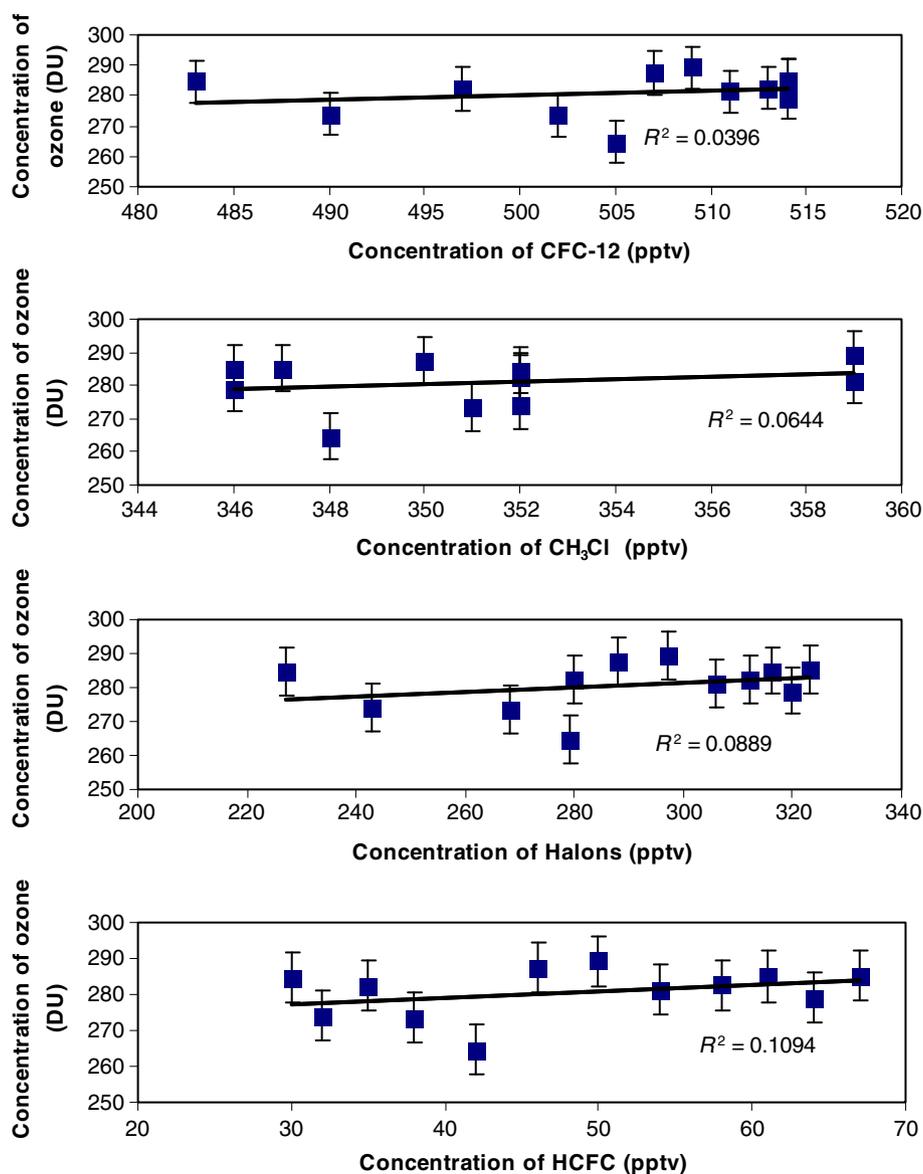
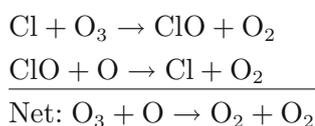


Figure 3. Scattered variation of total column ozone with the concentrations of CFC-12, CH<sub>3</sub>Cl, halons and HCFCs.

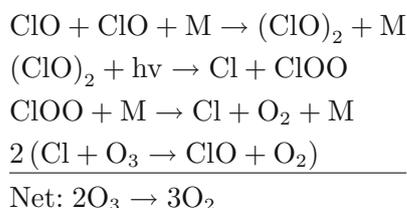
(23°N, 72.5°E), Varanasi (25°N, 83°E) and sharp decline in TCO over Halley Bay (76°S, 27°W) at Antarctica.

Randeniya *et al.* (2002) also reported that halogen loading of the atmosphere has peaked and stratospheric ozone levels are expected to recover to pre-1980 levels in this century. Figure 2 represents the little scattered decline of total mid-latitude ozone with increase in concentrations of CFC-11, CH<sub>3</sub>Br, CCl<sub>4</sub>, CH<sub>3</sub>CCl<sub>3</sub>, CFC-113 and WMO minor and *vice versa* with different rates. The rates of ozone fluctuations were 0.1881, 0.0443, 0.2146, 0.0231, 1.017 and 0.2779 DU per pptv, respectively. As the amounts of CFC-11, CH<sub>3</sub>Br, CCl<sub>4</sub>, CH<sub>3</sub>CCl<sub>3</sub>, CFC-113 except WMO Minor had declined from 1992 to 2003, the rates of ozone depletion would decrease by the above rates, respectively, that would cause the build-up of mid-latitude ozone. The anti-correlation nature between ozone and the above ODS has been supported by their poor negative correlation. The coefficient of correlation varies from -0.37 (CFC-113) to -0.11 (WMO minor). Though the gradual increase of WMO minor constituents from 1992 to 2003 would enhance the decrease of ozone concentration, the net build-up of mid-latitude ozone took place due to greater effect caused by the gradual decrease of other ODS as well as the growth of ozone precursors viz. methane, nitrous oxide and water vapour.

Figure 3 denotes the scattered growth of mid-latitude total ozone for the period 1992–2003 with the rise in concentrations of CFC-12, CH<sub>3</sub>Cl, halons and HCFCs. CFCs, HCFCs, halons, CH<sub>3</sub>Br and other CFC-related ozone-destroying molecules themselves do not deplete ozone. First of all, they are photolysed to produce atomic Cl and Br radicals which can catalyse the destruction of ozone by a number of mechanisms. In 1974, Molina and Rowland first suggested the following chlorine-catalysed ozone depletion:

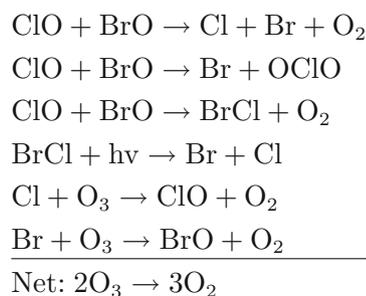


Molina and Molina (1987) suggested that a ClO dimer is formed in the following reactions:

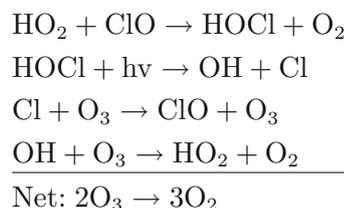


where hν denotes an UV-photon and M signifies a collisional chaperone, either N<sub>2</sub> or O<sub>2</sub>.

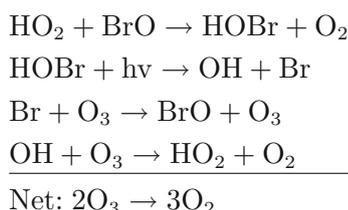
Bromine concentrations in the stratosphere are much smaller than chlorine concentrations. However, atom-for-atom Br is 10–100 times as effective as Cl in destroying ozone. The reason is that there is no stable reservoir for Br in the stratosphere – HBr and BrONO<sub>2</sub> are very easily photolysed so that nearly all of the Br is in a form that can react with ozone. McElroy *et al.* (1986) suggested chlorine–bromine coupled O<sub>3</sub> destruction mechanism as follows:



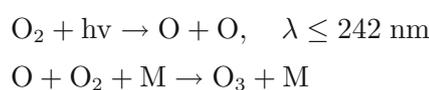
Solomon *et al.* (1986) suggested Cl and HOx coupled ozone-depletion mechanism as follows:



Wayne (1991) suggested Br and HOx catalysed ozone depletion mechanism as follows:



Scinocca *et al.* (2009) investigated the sensitivity of northern hemisphere polar ozone recovery to a scenario in which there is a rapid loss of Arctic summer sea ice in the first half of the 21st century. The near 10% reduction of sea ice extent realized in March (Meier and Stroeve 2008) would reduce the photolysis rates in the stratosphere by almost 10%. This reduction would only slow down gas phase photochemical ozone destruction. Harfoot *et al.* (2007) reported the all-integrative relationship between globally averaged O<sub>3</sub> and atmospheric O<sub>2</sub> abundances and observed a monotonic rise of global annual mean column O<sub>3</sub> with increasing atmospheric O<sub>2</sub>. The steps of O<sub>3</sub> formation from O<sub>2</sub> are as follows:



Methane that plays a critical role in the chemistry and radiative balance in the atmosphere (Seinfeld 1999) is also an important constituent of atmospheric ozone precursors and released from energy use, paddy fields, domestic ruminants, landfills, wetland, marshy land, termites, biomass burning, etc. (Rasmussen and Khalil 1984).

Figure 4 represents the scattered growth of total column ozone with the increase in concentrations of  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and water vapour and vice versa at different rates. The rates of ozone fluctuations were 0.1362, 0.4079, 0.068, 0.1798, 0.1131, 0.7921 DU (per ppbv for  $\text{N}_2\text{O}$ ) and 0.1654 DU per pptv, respectively.

The mid-latitude concentrations of CFC-12, halons, HCFCs,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and water vapour had gradually increased from 1992 to 2003, while the concentration of  $\text{CH}_3\text{Cl}$  had decreased. Due to increase in the amount of ODS such as CFC-12,

halons and HCFCs, the concentration of ozone should fall through the above depletion reactions catalysed by Cl, Br, ClO and BrO radicals produced from these ODS by photolysis. But, mid-latitude total ozone had increased slowly from 1992 to 2003, which clearly indicates that the rate of ozone formation due to loss of other ODS concentrations and growth of ozone precursors was predominant over the rate of ozone depletion caused by the enhancement in concentrations of ODS. As the amount of  $\text{CH}_3\text{Cl}$  had decreased from 1992 to 2003, the rate of depletion of ozone should decrease because of less amount of Cl radical produced by photolysis and consequently ozone concentration should increase from 1992 to 2003 as observed in variation of ozone from 1992 to 2003.

Dvortsov and Solomon (2001) proposed the following cycle of  $\text{O}_3$ -formation by  $\text{CH}_4$  and  $\text{NO}_x$

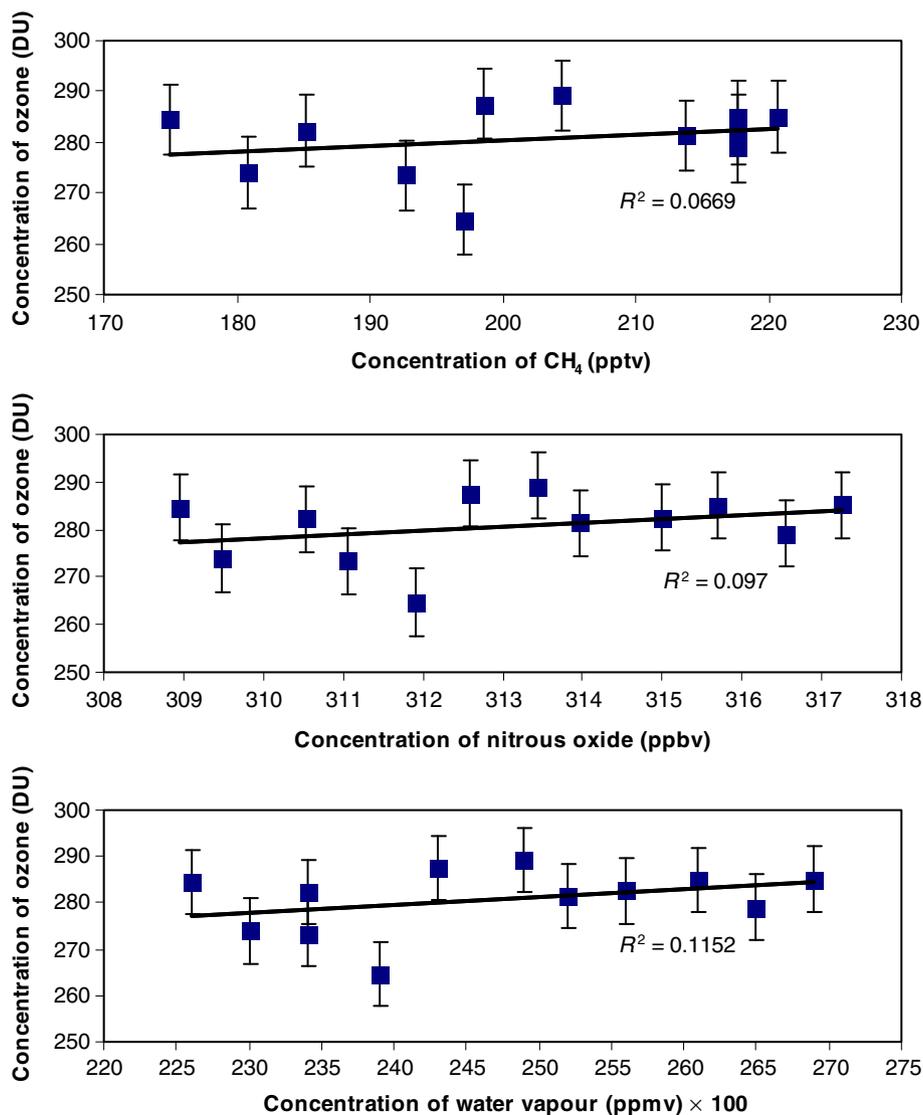
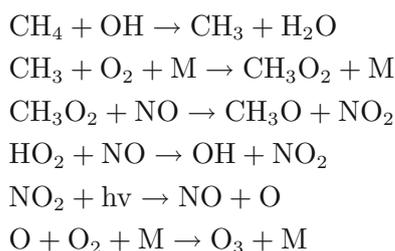
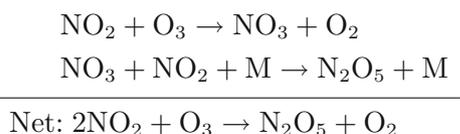


Figure 4. Scattered variation of total column ozone with the concentrations of  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and water vapour.

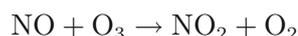
catalysts if oxides of nitrogen are present in the atmosphere in sufficient quantities:



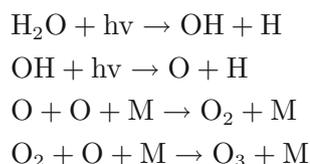
If oxides of nitrogen are not present in sufficient amount, they will deplete stratospheric ozone as follows:



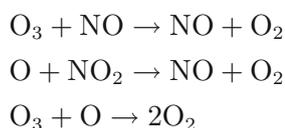
Again, NO can directly destruct the atmospheric ozone as follows:



The mechanism of ozone formation by photodissociation of water vapour is as follows:



Dvortsov and Solomon (2001) proposed the following cycle of ozone destruction by CH<sub>4</sub> and NO<sub>x</sub> catalysts:



Increased lower boundary N<sub>2</sub>O concentrations lead to more available stratospheric NO<sub>x</sub> to participate in O<sub>3</sub> destruction cycles and this reduces column O<sub>3</sub>. Conversely, lowering the N<sub>2</sub>O flux reduces available stratospheric NO<sub>x</sub> with a resultant increase in column O<sub>3</sub>. Increasing SST (sea surface temperature) causes an increase in stratospheric HO<sub>x</sub>, which in turn drives increases in column O<sub>3</sub> over the O<sub>2</sub> range of about 0.7–2 present atmospheric level (PAL). This occurs because of enhanced removal of catalytic NO<sub>x</sub> through a reaction that occurs in active reservoir species, for example, (HO + NO<sub>2</sub> + M → HNO<sub>3</sub> + M). West *et al.* (2007) reported that reduction in surface NO<sub>x</sub> emissions decrease O<sub>3</sub> and global concentration of the hydroxyl radical. Since reaction with OH is the major sink for CH<sub>4</sub>, NO<sub>x</sub> emission reductions increase the atmospheric lifetime and

concentration of CH<sub>4</sub> (lifetime: 9 years). In the case of NO<sub>x</sub> controls, the CH<sub>4</sub> increase induces a long-term O<sub>3</sub> increase which partially counteracts the short-term O<sub>3</sub> decrease.

#### 4. Conclusions

Concentrations of CFC-11, CFC-113, CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CCl<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub> had lowered gradually by 0.54%, 0.16%, 0.1%, 0.92%, 0.74% and 7.9% per year, respectively from 1992 to 2003 over Srinagar (34°N, 74.8°E), India, while that of CFC-12, HCFCs, halons, WMO minor constituents, CH<sub>4</sub>, N<sub>2</sub>O and water vapour had increased with different rates for the same period by 0.54%, 11.85%, 3.6%, 0.21%, 2.48%, 0.25% and 1.75% per year, respectively. The net result was that there was the slow growth in the TCO concentration by 0.17% per year over Srinagar (34°N, 74.8°E) from 1992 to 2003. As the concentrations of CFC-11, CFC-113, CH<sub>3</sub>Br, CCl<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub> had decreased gradually from 1992 to 2003, the amount of Cl and Br radicals produced by photodissociation of these molecules would be lower for the above period causing the lowering ozone declining reactions which lead to the gradual rise in TCO. Though the concentration of CFC-113 had decreased slowly, it had contributed to the maximum build-up of TCO (1.017 DU) per unit decrease in concentration. But, in case of CH<sub>3</sub>Cl, the TCO was decreasing, though very little with the minute lowering of CH<sub>3</sub>Cl, indicating that ozone-depletion processes catalysed by other ODS played a major role. Again, when the concentrations of CFC-12, HCFCs, halons and WMO minor constituents had increased slowly from 1992 to 2003, the amount of Cl and Br radicals formed from these ODS would be higher, which led to more ozone-depletion rates. The lowering in concentration of other ODS and enhancement of CH<sub>4</sub>, N<sub>2</sub>O and H<sub>2</sub>O vapour that led to the net growth in TCO became predominant over the growth of these ODS. Consequently, scattered diagram of increasing TCO with increasing concentrations of CFC-12, HCFCs and halons has been obtained. As concentration of WMO minor constituents increased, Cl and Br radicals would increase and consequently TCO would decrease. The rise in CH<sub>4</sub>, N<sub>2</sub>O concentrations and H<sub>2</sub>O vapour could influence the formation of tropospheric ozone, hence the rate of productions of TCO became more dominant over the rates of depletion which led to the overall growth of TCO with increase in these atmospheric constituents. The growth of TCO over Srinagar (34°N, 74.8°E) from 1992 to 2003 may be attributed to the gradual decline in concentrations of CFC-11, CFC-113, CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CCl<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub>

and predominant rates of ozone formation reactions over ozone destruction reactions and tropospheric ozone formation reactions catalysed by CH<sub>4</sub>, N<sub>2</sub>O and water vapour in the atmosphere. The weak dependence of variation of TCO over Srinagar with the above ODS and GHGs as revealed in their respective low positive or negative correlation coefficient values might be due to comparable rates of ozone formation and depletion processes governed by the large number of ozone-producing and ozone-depleting atmospheric gases. One or few atmospheric gases are not only responsible for such variation of ozone levels, although the results might improve with longer period of observation and more data.

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