MAUSAM, **67**, 4 (October 2016), 939-954

LETTERS

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SPLITTING OF OZONE HOLE OVER ANTARCTICA ~ ITS EFFECT ON TOTAL COLUMN OZONE AND ITS POSSIBLE CAUSES

1. Ozone is a minor constituent of the atmosphere. About 90% of the total ozone is found in the stratosphere from approximately 10 km to 50 km above the surface of the Earth (Kowalok, 1993), with a maximum concentration around 25 km altitude (Ghosh and Midya, 1994). The rest 10% of the total ozone is distributed in the troposphere and upper atmosphere. The total column ozone indicates both the tropospheric as well as stratospheric ozone over a specified region. Ozone plays an important role in the chemical kinetics of different ionospheric radiations (kvifte, 1973; Midya *et al.*, 2001). Stratospheric ozone plays an important role in protecting the Earth's surface against the harmful solar ultraviolet radiation (mainly UV-B) and controlling the temperature structure of the stratosphere (Ghude *et al.*, 2005). Ozone also influences cyclonic disturbances and other tropospheric phenomenon also (Mitra, 1992; Midya *et al.*, 2012).

It has been reported that ozone in the stratosphere is declining everywhere by smaller amount (Bojkov, 1992). The term ozone hole is applied to the regions where ozone depletion is severe and the level fall below 200 DU. In normal, ozone concentrations is about 300 to 350 DU. The annual thinning of ozone layer over Antarctica, during the polar spring time, was first reported by Farman *et al.*, 1985. Evidence of dramatic year to year decline in total ozone over Antarctic spring has also been reported (Schoeberl and Krueger, 1986). The total ozone over Antarctica has declined by 35%, integrated ozone between 14 km and 18 km by more than 70% while within the polar vortex ozone suffer depletion by more than 90% (Hofmann *et al.*, 1987). It has been confirmed that depletion of ozone over Antarctica starts from late August and reaches its minimum in mid October (Gardiner, 1988). Afterwards, verified by different investigators throughout the world (Jones and Shanklin, 1995; Midya and Jana, 2002; Sivasakthivel and Reddy, 2011).

Different theories are proposed for the dramatic decrease of ozone concentration over Antarctica during spring time.

(*i*) *Chemical theory* : There are different chemicals such as O_x (Chapman, 1930), HO_x (Thompson,1992), Cl_x and ClO_x (Molina and Rowland, 1974; Molina and Molina, 1987), Br and BrO_x (Wofsy *et al.*, 1975; Fan and Daniel, 1992), ClO_x and BrO_x (McElroy *et al.*, 1986), NO_x (Crutzen and Arnold, 1986; Andreae and Crutzen, 1997) etc. which undergo different chemical reactions hence are responsible for depletion of ozone.

It is proposed that the formation of ozone hole is due to catalytic depletion of ozone caused mainly by Cl radical from photolysis of CFCs on the surface of polar stratospheric clouds (PSC) (Toon and Turco, 1991; Fahey *et al.*, 1989).

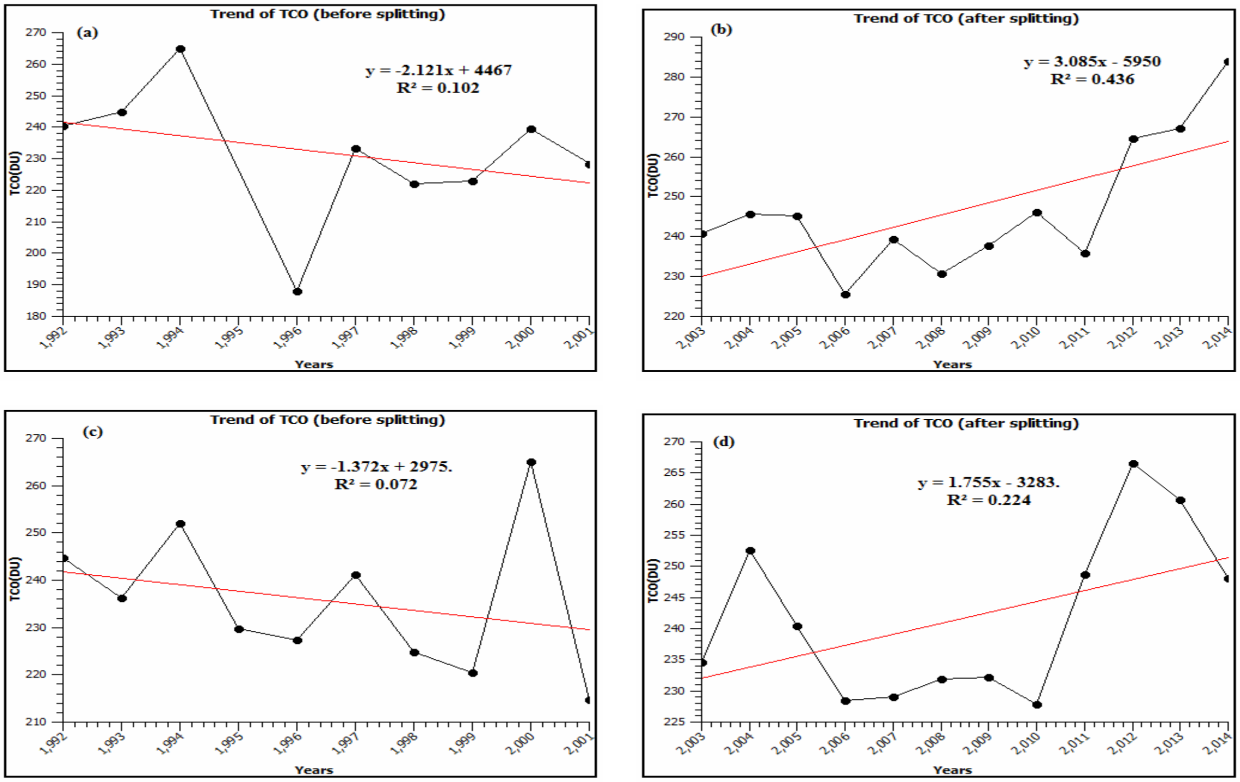
(*ii*) *Natural theory* : Natural phenomenon associated with solar cycle and radiations from sun are responsible for ozone depletion (Bekki *et al.*, 1991).

(*iii*) *Dynamical theory* : According to this theory, ozone is not depleted but distributed in the atmosphere; as a result, ozone hole is created (Jana and Nandi, 2005).

From research it has been found by several investigators that the Antarctica's ozone hole has shrunk into its smallest size (Newman, 2002) since 1988 and split into two pieces in 2002. Varotsos, 2003 explained that extremely large amplitude of planetary wave present breaks the Antarctic ozone hole in two small holes. The splitting of ozone hole attracts many scientists to work on this topic (Varotsos, 2002). It is also reported that the southern hemisphere polar stratosphere during September 2002 was characterized by the occurrence of an unprecedented major stratospheric warming (Varotsos, 2004; Savigny *et al.*, 2005).

Though several works on ozone depletion, ozone hole formation and ozone hole splitting, over Antarctica have been already done by several researchers, the long term effect of ozone hole splitting over Total Column Ozone (TCO) is still a topic of interest. The purpose of this paper is to check whether there is a change in long term TCO trend over Antarctica before and after the splitting of the ozone hole on 2002.

2. Satellite observational data of total column ozone for the Antarctic stations, Halley Bay and South Pole Observatory (SPO) is taken for the analysis. To check the effect of ozone hole splitting, the



Figs. 1(a-d). Trend of TCO over Antarctic station (a) Halley Bay before splitting of ozone hole from 1992-2001, (b) Halley Bay after splitting of ozone hole from 2003-2014, (c) SPO before splitting of ozone hole from 1992-2001 and (d) SPO before splitting of ozone hole from 2003-2014

TABLE 1

The details about stations taken for analysis over Antarctica

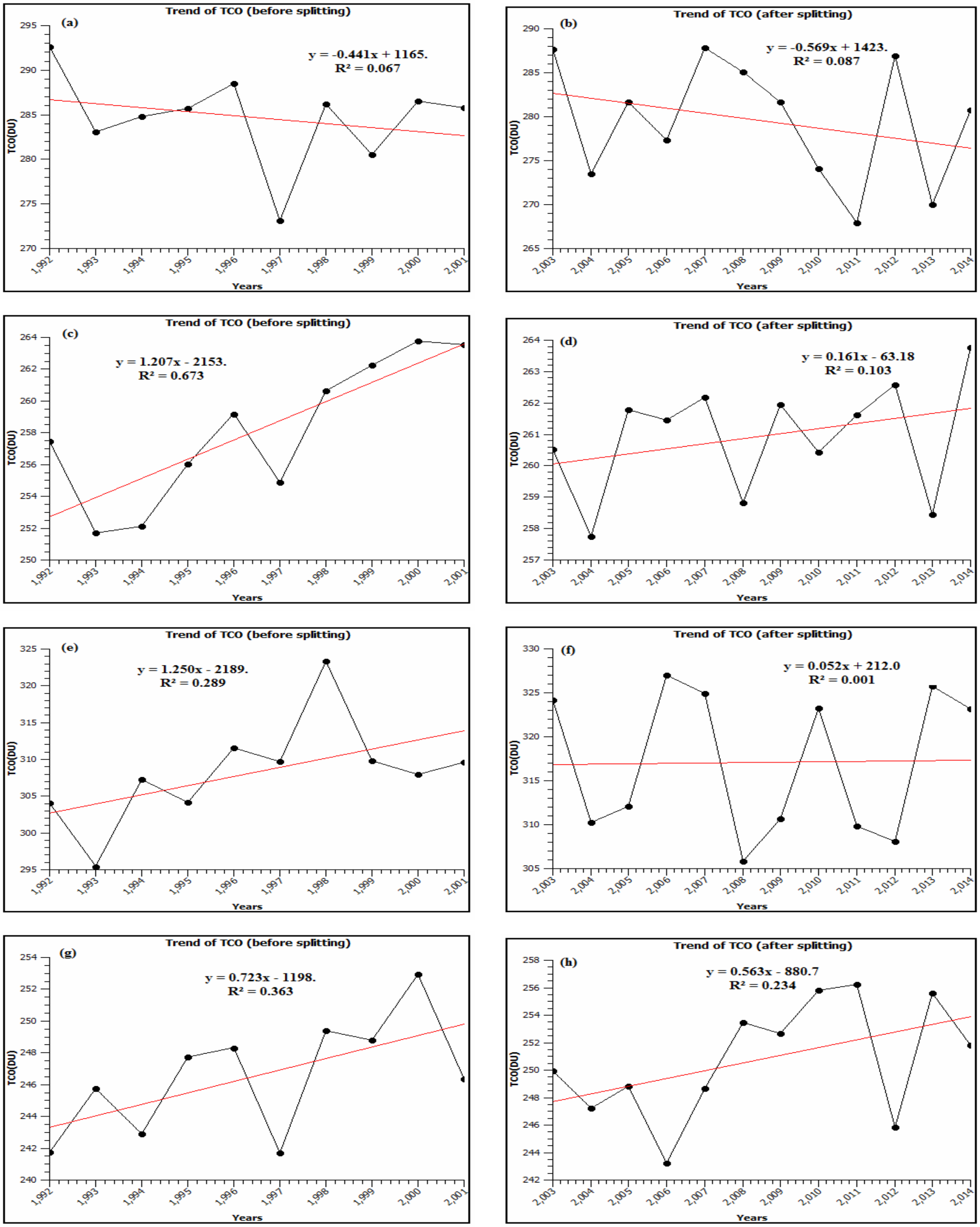
Station	Latitude	Longitude	Elevation	Time from UTC
Halley Bay	75° 60' S	26° 21' W	30 m	-2 hours
South Pole	89° 98' S	24° 80' W	2810 m	+12 hours
Perth	31° 91' S	115° 96' E	5 m	-8 hours
Mauna Loa	19° 53' N	155° 57' W	3397 m	-10 hours
Wallops Island, Virginia	37° 86' N	76° 51' W	13 m	-5 hours
Tutuila	14° 24' S	170° 56' W	42 m	-11 hours

TABLE 2

The analysis of Ozone Depleting Potential (ODP) over Antarctica

Chemical name	Lifetime (yrs)	ODP (WMO 2011)
CFC-11 (CCl_3F) Trichlorofluoromethane	45	1
CFC-12 (CCl_2F_2) Dichlorodifluoromethane	100	0.82
CFC-113 ($C_2F_3Cl_3$) 1, 1, 2 Trichlorotrifluoroethane	85	0.85
Methyl Chloroform ($C_2H_3Cl_3$) 1, 1, 1 trichloroethane	5	0.16
CCl_4 Carbon tetrachloride	26	0.82
Halon 1211 (CF_2ClBr) Bromochlorodifluoromethane	16	7.9

years 1992-2001 are chosen as the period before splitting of the ozone hole and the years 2003-2014 are considered as the period after splitting of the ozone hole. To support the observations, the Ozone Depleting Substances (ODS), O^{18}/O^{16} ratio in CO_2 data are analyzed. Satellite data of TCO over few stations near Antarctica are also taken for analysis. The data of total column ozone, ODS, and O^{18}/O^{16}ratio in CO_2 are taken from http://www.esrl.noaa. gov/gmd/dv/data/. The stations taken for analysis are Perth, Mauna Loa, Wallops Island and Tutuila. Details about these stations are presented in Table 1.



Figs. 2(a-h). Trend of TCO over nearby station (a) Perth before splitting of ozone hole from 1992-2001, (b) Perth after splitting of ozone hole from 2003-2014, (c) Mauna Loa before splitting of ozone hole from 1992-2001, (d) Mauna Loa after splitting of ozone hole from 2003-2014, (e) Wallops Island before splitting of ozone hole from 1992-2001, (f) Wallops Island after splitting of ozone hole from 2003-2014, (g) Tutuila before splitting of ozone hole from 1992-2001 and (h) Tutuila after splitting of ozone hole from 2003-2014

To find the trend of total column ozone before and after the splitting of ozone hole over Antarctica, the yearly averaged value of TCO for both Halley bay and SPO are plotted against years within our period of study. The trend of TCO is assessed through simple linear regression between TCO and years. To validate the results obtained, same trend analysis is done over the stations near Antarctica.

To analyze the result obtained from the trend analysis of TCO, the value of few ozone depleting substances (ODS) over Antarctica: CFC-11, CFC-12, CFC-113, Methyl chloroform, Carbon tetrachloride, Halon-1211 are considered. The ozone depleting potential (ODP) of each of these ODS are mentioned in Table 2. These ODS data are averaged for each year and are also plotted against years. The result is also verified with O^{18}/O^{16} ratio in CO_2 over Antarctica. These data are also averaged for each year and plotted against years before and after splitting of ozone hole over Antarctica.

3. The total column ozone trend over two Antarctic stations Halley Bay and SPO is showing a decreasing trend during the period taken for study before splitting of ozone hole on 2002 [Figs. 1(a&c) respectively] and an increasing trend after splitting of ozone hole [Figs. 1(b&d) respectively]. To describe the observation TCO value of the nearby stations during the same period of study are analyzed. One of the nearby stations Perth depicts a decreasing trend both before and after splitting of the ozone hole while three other nearby stations Tutuila, Mauna Loa and Wallops Island are showing an increasing trend for both time periods. In the case of Perth the rate of decrease of TCO trend is much more pronounced after the splitting of ozone hole [Figs. 2(a&b)] while in the case of Tutuila [Figs. 2(g&h)], Wallops Island [Figs. 2(e&f)] and Mauna Loa [Figs. 2(c&d)], the rate of increase of TCO trend has been much suppressed after the splitting of ozone hole.

TCO trend analysis over the nearby stations (Perth, Mauna Loa, Wallops Island, Tutuila) indicates that there may be an enhanced transport of ozone from these stations towards Antarctica after the splitting of ozone hole which may cause the increasing trend over the Antarctic stations (Halley Bay & SPO). The enhancement of ozone transport from the nearby stations may be due to higher rate of diffusion of ozone from these stations to the Antarctic stations. Again the sudden stratospheric warming (SSW) phenomenon after the splitting of ozone hole in 2002 reduces the polar vortex activity (Varotsos, 2004) and may enhances the drag of ozone from the nearby stations.

To verify the observations over Antarctic stations, ODS trends are also analyzed which showing that there is a sharp decrease of ODS's after the splitting of ozone hole.

CFC's are made up of chlorine, fluorine and carbon atoms. They may decompose as they move from troposphere to stratosphere releasing Cl radical that acts as a catalyst for ozone depletion. The mechanism (Molina and Rowland, 1974) is as follows:

$$CFCl_3 \rightarrow CFCl_2 + Cl \quad (1)$$

$$\text{Or, } CF_2Cl_2 \rightarrow CF_2Cl + Cl \quad (2)$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad (3)$$

$$ClO + O \rightarrow Cl + O_2 \quad (4)$$

$$\text{Net : } O_3 + O \rightarrow 2O_2 \quad (5)$$

Again, ClO dimer is also involved in ozone depletion (Molina and Molina, 1987)

$$ClO + ClO + M \xrightarrow{K} (ClO)_2 + M \quad (6)$$

$$(ClO)_2 + h\nu \rightarrow Cl + ClOO \quad (7)$$

$$ClOO + M \rightarrow Cl + O_2 + M \quad (8)$$

$$2(Cl + O_3 \rightarrow ClO + O_2) \quad (9)$$

$$\text{Net : } 2O_3 \rightarrow 3O_2 \quad (10)$$

where, $h\nu$ denotes UV-photon and M signifies collisional Chaperone, either N_2 or O_2 and K is the pressure-temperature dependent rate constant of the rate limiting step.

Halons also release Br radical along with Cl radical which also depletes ozone (McElroy *et al*., 1986)

$$ClO + BrO \rightarrow Cl + Br + O_2 \quad (11)$$

$$ClO + BrO \rightarrow Br + OClO \quad (12)$$

$$ClO + BrO \rightarrow BrCl + O_2 \quad (13)$$

$$BrCl + h\nu \rightarrow Br + Cl \quad (14)$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad (15)$$

$$Br + O_3 \rightarrow BrO + O_2 \quad (16)$$

$$\text{Net : } 2O_3 \rightarrow 3O_2 \quad (17)$$

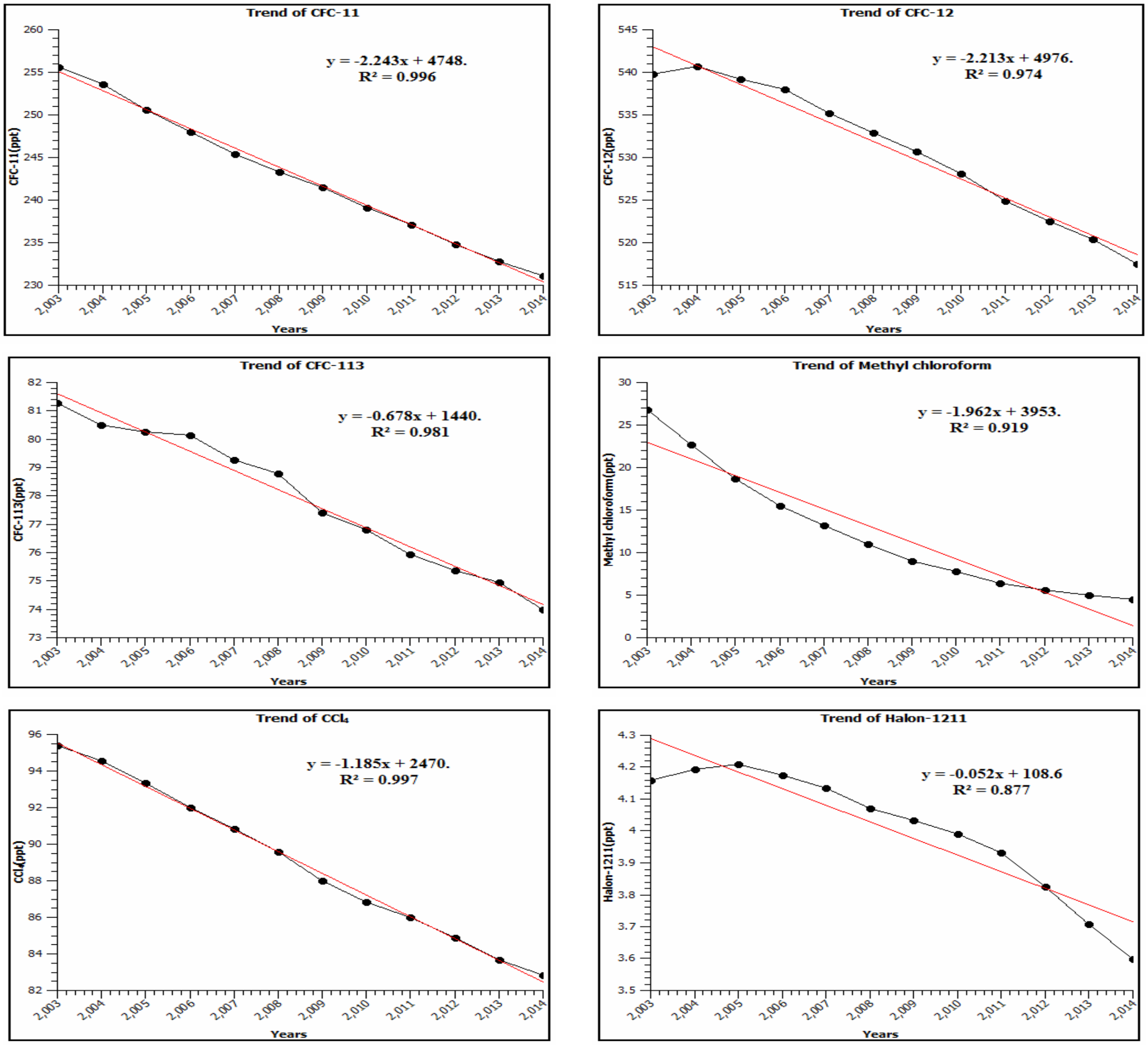
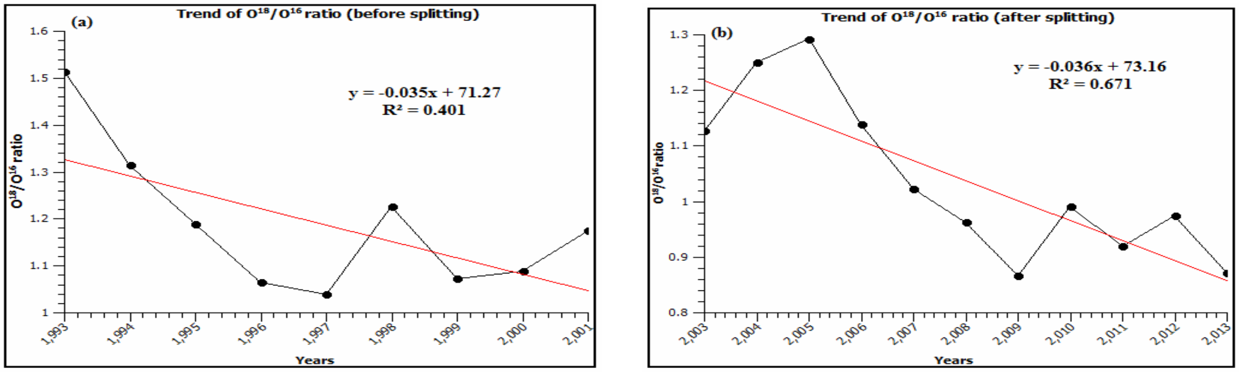


Fig. 3. Trends of ozone depleting substances (ODS) over Antarctica after splitting of ozone hole



Figs. 4(a&b). Trends of O^{18}/O^{16} ratio in CO_2 over Antarctica (a) before splitting of ozone hole and (b) after splitting of ozone hole

All the ozone depleting substances (CFC-11, CFC-12, CFC-113, Methyl chloroform, Carbon tetrachloride, Halon-1211) (Fig. 3) are showing a decreasing trend after splitting. The decrease of ODS over Antarctica supports the observation as the decrease of ODS causes less destruction of ozone over that region. So net amount of ozone over that region increases which causes the increasing trend of TCO over Antarctica after splitting.

The isotopic oxygen (O^{18}/O^{16}) ratio in CO_2 acts as a precursor of temperature which has an adverse relationship with temperature. To validate our results over Antarctic stations the trend analysis of this ratio is performed. It is observed that the isotopic oxygen (O^{18}/O^{16}) ratio of CO_2 has a decreasing trend before and after splitting of ozone hole [Figs. 4(a&b)] though after the splitting of the ozone hole, the rate of decrease is much pronounced.

The higher decreasing trend of O^{18}/O^{16} ratio in CO_2 over Antarctica after the splitting of ozone hole indicates an increasing rate of temperature over that region. The formation of ozone is an endothermic process, so increase of temperature causes the higher production of ozone (Le-Chatelier's principle). The decreasing trend of the ratio or the increasing trend of temperature supports the observations of increasing TCO trend over Antarctica after splitting of ozone hole in accordance to the Le-Chatelier's principle.

4. The use of ODS over Antarctica have been reduced substantially after several treaty for protection of ozone layer like Vienna Convention, Montreal Protocol and being banned by WMO, thus lowering the chance of ozone depletion hence favouring ozone formation. The sudden stratospheric warming after the splitting of ozone hole as mentioned by Varotsos, 2004, reduces the polar vortex activity and drags ozone from the nearby stations like Perth, Mauna Loa, Wallops Island and Tutuila. As a result ozone concentration over Antarctic stations slightly increases after splitting. It agrees fairly well with our observed results and increased of temperature is also verified considering the variations of O^{18}/O^{16} ratio in CO_2 over Antarctica.

References

Andreae, M. O. and Crutzen, P. J., 1997, "Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry", *Science*, **276**, 1052-1058.

Bekki, S., Towmi, R., Pyle, J. A. and Jones, A. E., 1991, "Future aircraft and global ozone", *Nature (UK)*, **354**, 193-194.

Bojkov, R. D., 1992, "Changes in polar ozone-Scientific assessment of ozone depletion", *WMO Bulletin*, **41**, 171-180.

Chapman, S., 1930, "A theory of upper atmospheric ozone", *Mem. R. Met. Soc. (UK)*, **3**, 103-123.

Crutzen, P. J. and Arnold, F., 1986, "Nitric acid cloud formation in the cold Antarctic stratosphere : A major cause for the springtime ozone hole", *Nature*, **324**, 651-655.

Fahey, D. W., Kelly, K. K., Ferry, G. V., Poole, L. R., Wilson, J. C., Murphy, D. M., Loewenstein, M. and Chan, K. R., 1989, "In Situ Measurements of Total Reactive Nitrogen, Total Water Vapor, and Aerosols in Polar Stratospheric Clouds in the Antarctic Stratosphere", *J. Geophys Res.*, **94**, 11299-11315.

Fan, S. M. and Daniel, J. J., 1992, "Surface ozone depletion in Arctic spring sustained by bromine reactions on aerosols", *Nature (UK)*, **359**, 522-524.

Farman, J. C., Gardiner, B. G. and Shankline, J. D., 1985, "Large losses of total ozone in Antarctica reveal seasonal ClOx/NOx interaction", *Nature*, **315**, 207-210.

Gardiner, B. G., 1988, "Comparative morphology of the vertical ozone profile in the Antarctic spring", *Geophys. Res. Lett.*, **15**, 901-904.

Ghosh, S. N. and Midya, S. K., 1994, "Atmospheric ozone, its depletion and Antarctic ozone hole", *Ind. J. Phys.*, **68B**, 6, 473-493.

Ghude, S. D., Kumar, A., Jain, S. L., Arya, B. C. and Bajaj, M. M., 2005, "Comparative study of the total ozone column over Maitri, Antarctica during 1997, 2002 and 2003", *Int. J. Remote Sensing*, **26**, 16, 3413-3421.

Hofmann, D. J., Harder, J. W., Rolf, S. R. and Rosen, J. M., 1987, "Balloon-borne observations of the development and vertical structure of the Antarctic ozone hole in 1986", *Nature*, **326**, 59-62.

Jana, P. K. and Nandi, S. C., 2005, "Effect of solar parameters on Antarctic, arctic and tropical ozone during the last solar cycle", *Ind. J. radio and space Phys.*, **34**, 114-118.

Jones, A. E. and Shanklin, J. D., 1995, "Continued decline of total ozone over Halley, Antarctica, since 1985", *Nature*, **376**, 409-411.

Kowalok, M. E., 1993, "Common threads - Research lessons from acid rain, ozone depletion, and global warming", *Environment*, **35**, 6, 13-38.

Kvifte, G., 1973, "Alkali Chemistry Problems of the Upper Atmosphere", *Physics and Chemistry of Upper Atmosphere, Astrophysics and Space Science Library*, **35**, 158-168.

McElroy, M. B., Salawitch, R. J., Wofsy, S. C. and Logan, J. S., 1986, "Reduction of Antarctic ozone due to synergistic interactions of chlorine and bromine", *Nature(UK)*, **321**, 759-762.

Midya, S. K., Sarkar, H. and Manna, A., 2001, "Antarctic O_3 depletion-its effect on the variation of Li 6708Å emission line intensity at McMurdo and Halley Bay", *Czech. J. Phys.*, **51**, 609-614.

Midya, S. K. and Jana, P. K., 2002, "Atmospheric ozone depletion and its effect on environment", *Ind. J. Phys.*, **76B**, 107-138.

Midya, S. K., Dey, S. S. and Chakraborty, B., 2012, "Variation of the total ozone column during tropical cyclones over Bay of Bengal and the Arabian Sea", *Meteorology and Atmospheric Phys.*, **117**, 63-71.

Mitra, S. K., 1992, "The upper atmosphere", Asiatic Society, Calcutta, India.

Molina, M. J. and Rowland, F. S., 1974, "Stratospheric sink of chlorofluromethanes : Chlorine atom catalysed sink of ozone", *Nature (UK),* **249**, 5460, 810-812.

Molina, L. T. and Molina, M. J., 1987, "Production of Cl_2O_2 from the self reduction of the CLO radical", *J. Phys. Chem. (USA)*, **91**, 2, 433-436.

Newman, P., 2002, "Incredible shrinking ozone hole", *Science news*, NASA, (http://wwwsciencenasagov/).

Savingny, C. V., Rozanov, A., Bovensmann, H., Eichmann, K. U., Noël, S., Rozanov, V. V., Sinnhuber, B. M., Weber, M., Burrows, J. P. and Kaiser, J. W., 2005, "The Ozone Hole Breakup in September 2002 as Seen by SCIAMACHY on ENVISAT", *American Meteorological Society*, **62**, 721-734.

Schoeberl, M. R. and Krueger, A. J., 1986, "Overview of the Antarctic ozone depletion issue", *Geophys. Res. Lett.*, **13**, 1191-1192.

Sivasakthivel, T. and Reddy, K. K. S. K., 2011, "Ozone Layer Depletion and Its Effects: A Review", *International Journal of Environmental Science and Development*, **2,** 1, 30-36.

Thompson, A. M., 1992, "The oxidising capacity of the earth's atmosphere : probable past and future changes", *Science (USA),* **256**, 1157-1165.

Toon, O. B. and Turco, R. P., 1991, "Polar Stratospheric Clouds and Ozone Depletion", *Scientific American*, **264**, 6, 68-74.

Varotsos, C., 2002, "The southern hemisphere ozone hole split in 2002", *Environmental Science and pollution*, **9**, 6, 375-376.

Varotsos, C., 2003, "What is the lesson from the unprecedented event over Antarctica in 2002?", *Environ. Sci. Pollut. Res. (Germany),* **10**, 2, 80-81.

Varotsos, C., 2004, "The extraordinary events of the major, sudden stratospheric warming, the diminutive Antarctic ozone hole, and its split in 2002", *Environmental Science and pollution Research,* **11**, 405-411.

Wofsy, S. C., McElroy, M. B. and Yung, Y. L., 1975, "The chemistry of atmospheric bromine", *Geophys. Res. Lett (USA),* **2**, 215-218.

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