Universal Journal of Environmental Research and Technology
 eISSN 2249 0256
Available Online at: www.environmentaljournal.org
Volume 2, Issue 6: 601-608

Open Access **Research Article**

Unusual Ozone Build-Up Due to Diwali at Dumdum (22.5°N, 88.5°E), India

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Abstract:

Analysis of total ozone column at Dumdum (22.5°N, 88.5°E), India during, before and after Diwali reveals an elevation in total ozone during Diwali and after few days for the period 2000-2010 due to spontaneous bursts in the absence of sunlight – namely, the exuberant mass of colour emitting sparklers which are lit during the Diwali night festivities that occurred every year during October and November. During burning, a significant portion of the emitted light by the sparklers which is composed of an oxidizer (potassium nitrate, potassium chlorate or potassium perchlorate), a fuel, regulators and binders constitutes a wavelength below 240 nm that is enough to dissociate atmospheric molecular oxygen into atomic oxygen enabling the formation reaction of ozone to takes place.

Keywords: Diwali festival, Ozone formation and depletion, Total ozone.

1.0 Introduction:

Ozone, though a minor constituent is one of the dominant components that controls atmospheric environmental quality, atmospheric chemical processes and chemical kinetics of the atmosphere. The concentration of ozone in the stratosphere is gradually declining, whereas the tropospheric counterpart displays the tendency to increase persistently due to human activities. Stratospheric ozone plays an important role in protecting mankind and the environment, but in the troposphere a too high amount of this species is harmful to human being and also to the environment. Tropospheric ozone, a key chemical constituent serves as a product and the participant of the photochemical reactions therein. The variation in concentration and distribution in ozone exerts an immediate effect on life time and distribution of other atmospheric chemical species such as SO_2, NO_2 and OH radicals, thereby influencing the composition and equilibrium of tropospheric chemistry. Concentration of ozone gradually increases from upper troposphere, attains maximum at an altitude of 25- 30 km and then gradually declined (Jana et al. 2010). From the annual cycle of ozone Jana et al. (2008) clearly show that total column ozone density gradually rose from January, attained the maximum value for the month of May and June, and then gradually decreased at Dumdum. Atmospheric ozone saves all forms of lives by absorbing harmful solar- UV radiation in the Earth. Solar-UV radiations are of three types-UV-A, UV-B and UV-C. Wavelength in the range of 100-280 nm is known as UV-C region which is completely absorbed by atmospheric O_3. UV-B rays of wavelength range 280 nm to 315 nm are partially absorbed by O_3, while UV-A rays of wavelength 315 nm-400 nm are weakly absorbed by O_3 and are therefore are more easily transmitted to the earth's surface (Jana and Nandi 2006).

The day-to-day fluctuations of total ozone in a column of air were found to be mainly caused by daily variations of the synoptic environment through either advection, convection or both [4]. In the horizontal plane, northerly advection causes an increase in total ozone, while advection from the south results in a decrease. Vertically downward motion associated with an upper troposphere trough results in a increase in total ozone, whereas, upward motion in association with upper level ridge results in a decrease (Reed 1950, Barsby and Diab 1995).

It is now well established that different environmental parameters may influence the variation of ozone concentration in different layers in the atmosphere. Ozone layer in the atmosphere also plays an important role in controlling different events occurring in troposphere, stratosphere and

mesosphere. Dobson *et al*. (1946) observed that the average temperature of the earth is directly related to ozone concentration of stratosphere and fall in ozone concentration in the stratosphere takes place over England before the arrival of warm front at the ground surface. The rise in ozone content in the stratosphere occurs when cold front reaches near the ground level. Mitra (1992) reported the close relation between barometric height, tropospheric weather and ionospheric parameters of the upper atmosphere. It was observed that the minimum height of F region and average E ionization tend to follow the variation of barometric height. Correlation was observed between the lowest virtual height of E region and ground temperature at Standford, California, USA. Bates (1981) and Mackay *et al.* (1997) reported that the variation of solar UV radiation due to fall of stratospheric ozone concentration can influence tropospheric climate in several ways. Midya and Sarkar (2007) observed the correlation of the variation of stratospheric ozone with relative humidity and sharp depletion of absolute humidity related with Nor'wester over Kolkata. Mooley and Parthasarathi (1984) analyzed all-India summer monsoon (June to September) rainfall for the period 1871 to 1978. They reported that the highest and lowest rainfall country level was observed in the years 1961 and 1877, respectively. There was a continuous rise in 10-yr mean rainfall from 1899 to 1953. Rakecha and Soman (1994) observed that the annual extreme rainfall records of most of the stations over India were free from trend and persistence. The extreme rainfall series at stations over the west coast, north of 12^0 N and some stations to the east of the Western Ghats over the central parts of the Peninsula showed a significant increasing trend at 95% level of confidence. Stations over Southern Peninsula and over the lower Ganga valley had been found to exhibit at decreasing trend at same level of significance. Jana et al. (2010) reported the increase in concentration of total ozone over Kolkata (22.5^{o}N, 88.5^{o}E), India with the increase of cloud occurrences during the period from 1990 to 1995. This is due to the fact that low level large and more cloud occurrences reflect more solar radiations which enhance the photochemical reactions of ozone formations, as well as supply more amount of water vapour leading to the formation of upper tropospheric and lower stratospheric ozone. Jana et al. (2011) observed that the backscattered solar radiations by clouds enhance the photolysis rates of ozone precursors leading to formation of ozone above and below the clouds. Increased backscattered radiations raise the concentration of OH radicals that leads the ozone building processes. More lightening in clouds produces more amount of NOx which catalyzes higher formation processes of ozone. As a result, the concentration of ozone increases with the increase of cloud occurrences over Hyderabad (17.27^{o}N, 78.28^{o}E), India. Jana et al. (2012a) have reported that the stratospheric ozone concentration attained comparatively higher value in the months from July to September while lower tropospheric ozone concentration at the same time over Thumba (8.5^{o}N, 77^{o}E) and Bangalore (13^{o}N, 77.5^{o}E), India during the period 1979-2005. Yearly variation shows the increasing trend in tropospheric ozone but the decreasing trend in stratospheric ozone over the above stations from 1979 to 2005. Jana et al. (2012b) observed that monthly variation of ozone depicts that at all stations, the nature of monthly mean tropospheric ozone column was oscillatory and had increasing trends from October, 2004 to June, 2009. At most of the places over India it is observed that tropospheric ozone densities had increased sharply from the month of January, attained the maximum value in the month of May, then decreased steeply achieving the lowest value in the month of August and finally had increased gradually from August to December during this period. Seasonal variations clearly reveal that tropospheric ozone value attained maximum during pre-monsoon time and mimimum during monsoon time at all the stations except Simla and Srinagar. Winter, pre-monsoon and post-monsoon tropospheric ozone build up had been observed from 2004 to 2009, whereas monsoon ozone decline have been exhibited for the above period over most of the places in India. Tropospheric monthly mean, pre-monsoon, monsoon and post-monsoon ozone had enhanced with rise in latitude in Indian region. Attri et al. (2001) observed a significant build-up of O_3 by 9 ± 1 ppbv (parts per billion volumes) between 20:40 and 02:30 hours on Diwali night (7 November, 1999) at Delhi, India. No correlation was found between NOx concentration and O_3 production, indicating that the ozone was unlikely to have been generated in reactions involving NOx. A linear correlation between the total amount of inflammable material present in the sparklers and the cumulative ozone formed was obtained. There was no change in ambient NOx concentration before, during or after the festivals. In this paper, the effect of burning of sparklers on the diurnal fluctuation of total ozone column over Dumdum

(22.5°N, 88.5°E), India for the period 2000 to 2010 during and just after the Diwali festival has been discussed. A possible chemical explanation has been offered for this purpose.

2.0 Materials and Methods:

Total daily column ozone densities in Dobson unit (DU) (1DU = 0.001 atm cm) over the station Dumdum have been obtained from internet website http//jwocky.gsfc.nasa.gov published from NASA, USA for the months of October and November from 2000 to 2010. Total ozone data has been measured by the satellites Nimbus-7 Total Ozone Mapping Spectrometer (TOMS), Earth probe TOMS and Ozone Monitoring Instrument (OMI). TOMS and OMI provide high resolution daily global information about the total ozone content of the atmosphere by measuring ultraviolet sunlight backscattered from the ground. OMI and the other instruments are working together effectively on the Aura platform. The OMI instrument employs hyper-spectral imaging in a push-broom mode to observe solar backscatter radiation in the visible and ultraviolet that improves the accuracy and precision of the total ozone amounts and also allows for accurate radiometric and wavelength self calibration over the long term. The instrument measures Earth's backscattered radiation with a wide-field telescope feeding two imaging grating spectrometers each of which uses a convective cloud differential (CCD) detector. Onboard calibration comprises a white light source, light emitting diodes (LEDs), and a multi-surface solar-calibration diffuser. A depolarizer removes the polarization from the backscattered radiation. It can measure many more atmospheric constituents than TOMS and provides much better ground resolution than GOME (Global Monitoring Experiment) (13 km x 25 km for OMI vs. 40 km x 320 km for GOME). The instrument is a contribution of the Netherlands's Agency for Aerospace Programs (NIVR) in collaboration with the Finnish Meteorological Institute (FMI) to the Aura mission. For this work, total ozone column (TOC) data were collected from OMI instrument which provides total ozone data from July 2004 to present. OMI data are gridded into one degree latitude and 1.25 degree longitude, latitude ranging from + 90° (North Pole) to -90° (South Pole). Rates of ozone fluctuation are obtained from linear trend analysis of variation of daily average total ozone for each year.

3.0 Results and Discussion:

A sparkler is a type of hand held firework that burns slowly over a long period of time that emits colored flames, a brilliant shower of sparks and other effects. Sometimes sparklers are called snowballs in reference to the ball of sparks which surrounds the burning part of the sparkler. A sparkler comprises of an oxidizer, a fuel, regulators and binders. Oxidizers produce oxygen to burn the mixture. These are usually potassium nitrate (KNO_3), potassium chlorate ($KClO_3$) or potassium perchlorate ($KClO_4$). They liberate oxygen on burning as follows:

$$2KNO_3\,(Solid) = 2KNO_2\,(Solid) + O_2\,(Gas).$$

Chlorates give up all of their oxygen, bringing about a more spectacular reaction. These can act also as explosives.

$$2KClO_3\,(Solid) = 2KCl\,(Solid) + 3O_2\,(Gas).$$

Perchlorates have more oxygen in them. They are more powerful, but potentially explosive.

$$KClO_4\,(Solid) = KCl\,(Solid) + 2O_2\,(Gas).$$

Beside these, barium nitrate or strontium nitrate may be used as an oxidizer.

The reducing agents such as sulphur and charcoal act as the fuel used to burn the oxygen that produces hot gas such as sulphur dioxide (SO_2) and carbon dioxide (CO_2), respectively. Metallic fuels, aluminium or magnesium or magnelium can produce white sparks, iron an orange branching sparks, titanium a rich white sparks and ferrotitanium a yellow gold sparks. Two reducing agents may be combined to accelerate or slow the speed of the reaction. Metals can also affect the speed of the reaction. Finer metal powders react more rapidly than coarse powder or flocks. Other substances such as cornmeal may also be added to regulate the reaction. Dextrine and nitrocellulose are commonly used as binders to hold the mixture together in the sparklers dampened by water or a shellac compound dampened by alcohol. The binder can serve as a reducing agent and as a reaction moderator. When burnt, a significant portion of the light emitted by the constituents of the sparklers has a wavelength below 240 nm. This emitted radiative energy is sufficient to dissociate atmospheric molecular oxygen into atomic oxygen that enables the reaction $O_2 + O \rightarrow O_3$ to take place (Reader and corliss 1982-83).

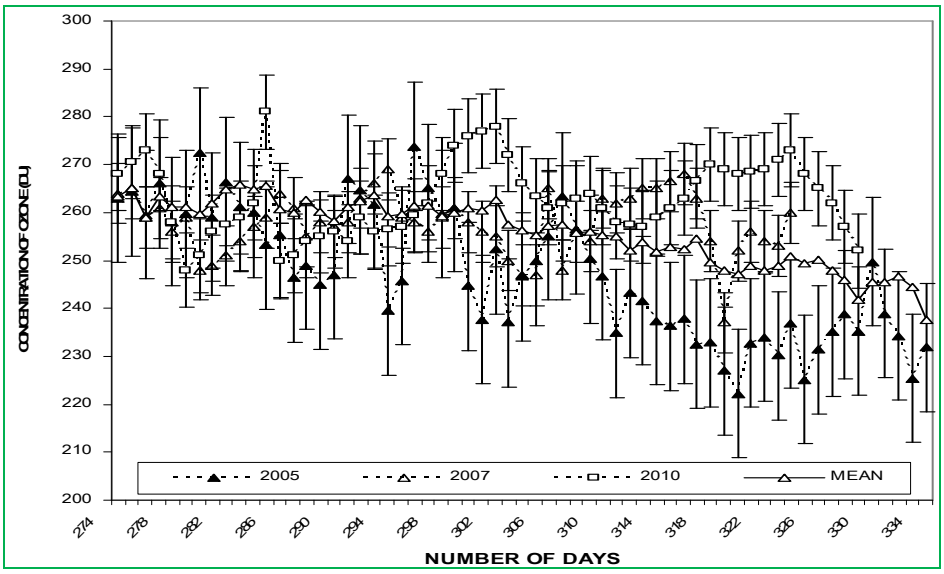

Figure 1. Variation of daily total ozone column from October to November over Dumdum (22.5°N, 88.5°E), India.

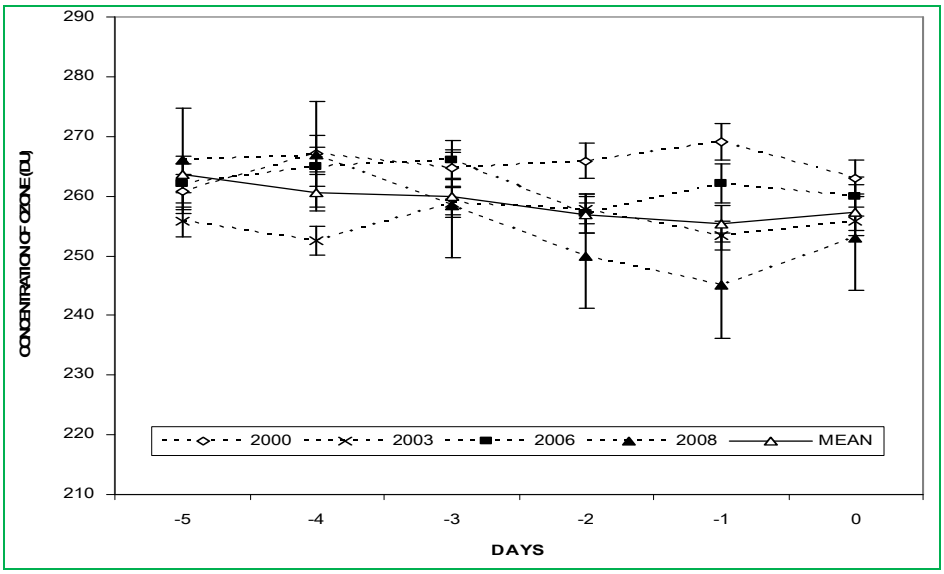

Figure 2. Variation of daily total ozone column from seven days before to Diwali over Dumdum (22.5°N, 88.5°E), India.

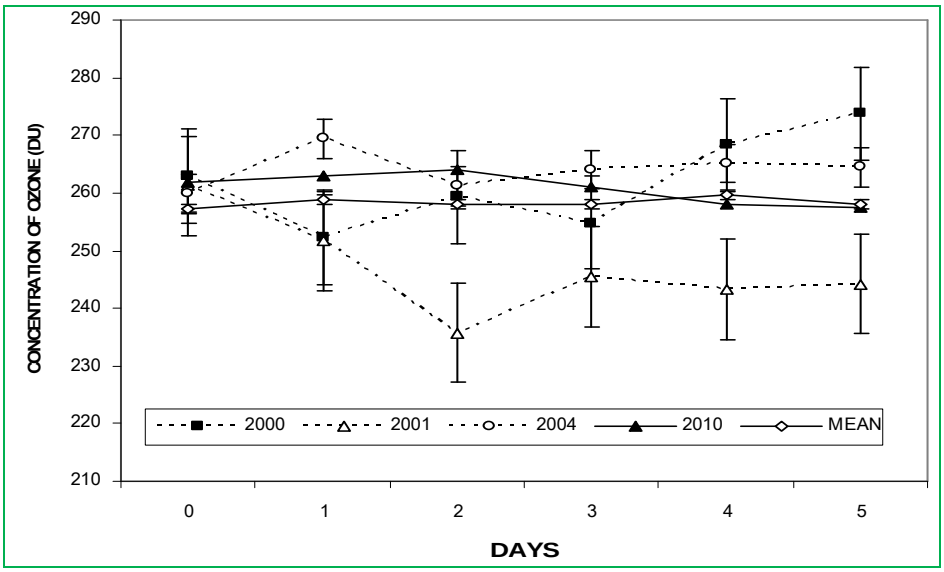

Figure 3. Variation of daily total ozone column during and few days after Diwali over Dumdum (22.5°N, 88.5°E), India.

Table 1. Rate of variation of ozone concentration.

Year	Rate of ozone fluctuation from October to November in DU per day	Rate of ozone fluctuation from seven days before Diwali in DU per day	Rate of ozone fluctuation during and just after Diwali in DU per day
2000	-0.508	0.5343	2.788
2001	-0.3347	-0.92	-2.874
2002	-0.427	-3.6857	1.72
2003	-0.4853	0.06	1.2886
2004	-0.3454	0.2777	0.3657
2005	-0.5917	-2.2914	1.3371
2006	-0.2792	-0.8	0.6571
2007	-0.034	0.5143	-1.9714
2008	-0.3692	-3.9857	1.8286
2009	-0.1785	-2.4286	-2.1714
2010	-0.0945	-3.3	-1.1571
Mean	-0.3517	-1.457	0.1637

The formation and destruction of ozone in the troposphere comprises a series of complex cycles in which atomic oxygen, molecular oxygen, carbon monoxide, oxides of nitrogen, water vapour, volatile organic compounds etc. are involved (Ramanathan et al. 1985, Lasis et al. 1990, Wang and Sze 1980, Crutzen and Zimmermann 1991, Walcek and Yuan 1995, Johnson et al. 1991). Ozone in the troposphere is produced by the addition of ground state oxygen atoms O (^{3}p) to molecular oxygen assisted by any third body M to ensure simultaneous momentum and energy conservation (Madronich 1993).

$$O(^3p) + O_2 + M \rightarrow O_3 + M.$$

The source of oxygen atom in the troposphere is not same as in the stratosphere where oxygen atoms are made by the photo dissociation of O_2 at UV wavelengths less than 240 nm. In the troposphere, only UV radiation with greater than 290 nm is available, because of essentially complete

absorption of shorter wavelengths by O_2 and O_3 above the tropopause. Atomic oxygen in the troposphere is produced by photo dissociation of NO_2 and tropospheric O_3 as follows:

i) $NO_2 + h\nu\ (\lambda = 424\ nm) \rightarrow NO + O$

ii) $O_3 + h\nu\ (\lambda = 300\text{-}320\ nm) \rightarrow O + O_2$

Tropospheric ozone is mainly formed by photochemical oxidation of carbon monoxide, methane and non-methane volatile organic compounds (NMVOCs) in the presence of nitrogen oxide radicals ($NOx \equiv NO + NO_2$). Oxidation begins with the reaction of CO with OH radical. The hydrogen atom thus produced rapidly reacts with oxygen molecule to give peroxy radicals. Peroxy radicals then continue to react with NO to NO_2 that is photolysed to atomic oxygen which reacts with O_2 to make a molecule of O_3.

$$OH + CO \xrightarrow{[O_2]} H + CO_2$$

$$H + O_2 \rightarrow HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

$$NO_2 + h\nu\ (\lambda = 424\ nm) \rightarrow NO + O$$

$$O(^3p) + O_2 + M \rightarrow O_3 + M.$$

The net effect of these reactions is:

$$CO + 2\,O_2 \rightarrow CO_2 + O_3$$

The OH radical in the troposphere is produced by photo dissociation of nitrous, nitric acids, ozone (Tie et al. 2003) and hydrogen peroxide (Tie et al.2003) as follows:

$$HONO + h\nu\ (\lambda = 400\ nm) \rightarrow OH + NO$$

$$HNO_3 + h\nu\ (\lambda = 350\ nm) \rightarrow OH + NO_2$$

$$O_3 + h\nu\ (\lambda \leq 320\text{-}410\ nm) \rightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \rightarrow 2OH$$

$$H_2O_2 + h\nu \rightarrow 2OH$$

Peroxy radical is also made from the photolysis of formaldehyde (Tie et al.2003).

$$CH_2O + h\nu + 2O_2 \rightarrow CO + 2HO_2$$

The simplified form of troposoheric ozone formation from volatile organic compounds (VOCs) obeys the following steps:

$$VOC + OH + O_2 \rightarrow RO_2 + H_2O$$

$$RO_2 + NO + O_2 \rightarrow NO_2 + HO_2 + CARB\ (Secondary\ VOC)$$

$$HO_2 + NO \rightarrow NO_2 + OH$$

$$2(NO_2 + h\nu + O_2 \rightarrow NO + O_3)$$

$$Net: (NOx + OH) + VOC + 4\,O_2 \rightarrow 2O_3 + CARB + H_2O + (NOx + OH)$$

Where, R denotes organic radicals and CARB stands for carbonyl compounds.

The loss of tropospheric ozone is mainly due to the following reaction (Tie *et al*. 2003):

$$O_3 + h\nu\ (\lambda \leq 320\text{-}410\ nm) \rightarrow O(^1D) + O_2$$

OHx radicals are removed from the atmosphere by the formation of hydrogen peroxides, organic peroxides, nitric acids and other organic nitrates.

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2$$

$$OH + NO_2 \rightarrow HNO_3$$

Stevenson et al. (2006) proposed that the higher ozone production rates in the troposphere are due to higher NOx emission, higher isoprene emission, more detailed NMHC scheme and improved parameterization of process such as photolysis, convection and stratosphere-troposphere exchange. From the above mechanisms of tropospheric ozone production and loss, it is clear that solar radiation plays a key role.

Long and short-term annual cycle of total ozone column reveals that total ozone gradually rises from the month of January, attains the maximum value during the months of May and June, and then gradually decreases over Dumdum. Figure 1 depicts the diurnal variation of total ozone for the months of October and November over Dumdum for the period 2000 to 2010. Depletion of total ozone occurred in every year from October to November except the year 2010 with different rates. The rate of ozone decline varied from 0.5917 DU (2005) to 0.034 DU (2007) per Day shown in Table 1. The average rate of ozone decline was 0.3517 DU per Day for the above period.

The diurnal variation of total ozone column over Dumdum before seven days from Diwali is represented in Figure 2. It clearly shows that total ozone column decline occurred in the most of the years except the years 2000, 2003, 2004 and 2007. The rate of ozone fall altered from 3.9857 DU (2008) to 0.8 DU (2006) per day. The average rate of ozone depletion was 1.457 DU per day for the period 2000 to 2010 shown in Table 1. Figure 3 depicts the diurnal variation of total ozone column during Diwali and three days after it. Usually, sparklers are lit on the night of Kalipuja, Diwali and sometime one night before them. Kalipuja and Diwali festivals occur on two consecutive days or in few years they fall on the same day. For that reason, we consider the day that is two days before the day of Diwali as the 0 day. It is revealed that total ozone column rise was observed in the most of the years except the years 2001, 2007, 2009 and 2010 with different rates during and just after Diwali. The rate of ozone increase varied from 0.3657 DU (2004) to 2.788 (2000) DU per day. The average rate of ozone rise was 0.1637 DU per day for the period 2000 to 2010. The rate of ozone decline

was noticed for the years 2001, 2007, 2009 and 2010 by 2.8714 DU, 1.3714 DU, 2.1714 DU and 1.1571 DU per day, respectively shown in Table 1.

Analysis of results clearly depicts that the total column ozone had sharply declined from October to November for every year over the station Dumdum for the period 2000 to 2010 with average rate of ozone depletion by 0.3517 DU per day. From seven days before the Diwali festival, the decline in total ozone column was also observed in the most of the years with the average rate of 1.457 DU per day except the years 2000, 2003, 2004 and 2007 that indicated comparatively lower rate due to shorter period of observation while total ozone column build-up was noticed during and just after the Diwali festival in the most of the years with average rate of ozone rise by 0.1637 DU per day over Dumdum which indicated the signature of ozone sources due to burning of sparklers during Diwali. In the years of 2000, 2003 and 2004, the rates of ozone rise increased from 0.5343 DU, 0.06 DU and 0.2777 DU to 2.788DU, 1.2886 and 0.3657 DU per day, respectively, from before to during and after Diwali that supports more ozone formation processes because of Diwali. But in case of 2001, the rate of ozone depletion increased from 0.92 DU to 2.8714 DU per day, whereas in 2007 the rate of ozone fluctuation varied from 0.5143 DU to -1.3714 DU per day from before to during and just after Diwali which supported the ozone destruction processes because of burning of sparklers.

During burning of sparklers at nighttime, the concentration of oxides of nitrogen becomes lower than at day time, which will favour the destruction processes of ozone instead of formation processes. In addition, the amounts of oxides of nitrogen, carbon monoxide, methane and non-methane volatile organic compounds do not alter very much before, during and few days after Diwali, they have then very little effect on the fluctuation of total ozone content. So, it is the significant portion of light of wavelength less than 245 nm emitted from burning of sparklers that induces dissociation of molecular oxygen in absence of sunlight which enhances tropospheric ozone formation in one hand and the molecular oxygen produced from the combustion of constituents of sparklers such as potassium nitrate, potassium chlorate etc. forms tropospheric and stratospheric ozone catalyzed by oxides of nitrogen, carbon monoxide etc. and also by solar radiation at day time on the other hand. The produced ozone thus formed raises total ozone column by the process of advection and diffusion. These two mechanisms favor some total ozone column build up during and few days after for every year from 2000 to 2010 except the two years 2001 and 2007 at Dumdum. But in case of 2001 and 2007, horizontal and vertical advection of wind that causes destruction of total ozone column may play predominant role.

4.0 Conclusion:

It is concluded that firstly, the diurnal total ozone column over Dumdum gradually decreased from October to November by an average rate of 0.3517 DU per day for the period from 2000 to 2010.The sparklers are lit during the Diwali festival celebrated every year during October or November at Dumdum, India. Secondly, the rate of the diurnal total ozone column decline increased to1.457 DU per day from seven days before to Diwali. Thirdly, the diurnal total ozone column increased during and after few days by 0.1637 DU per day for the period 2000 to 2010 due to light of wavelength less than 240 nm emitted from burning sparklers that are sufficient to dissociate atmospheric molecular oxygen to atomic oxygen and enhanced molecular oxygen produced from burning sparklers enabling the reaction $O_2 + O \rightarrow O_3$ in absence of sunlight and other ozone formation processes catalyzed by oxides of nitrogen , carbon monoxide etc to take place in presence of sunlight. Fourthly, the ozone thus produced in turn contributed total ozone column build up through convection, diffusion and advection processes.

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