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Concentrations and behaviour of surface O_3, NO and NO_2 at Delhi

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Ambient concentrations of O_3, NO and NO_2 at Delhi were studied at National Physical Laboratory, New Delhi. Analysis of the data revealed the highest concentrations of O_3 during winter which may be due to lowering of inversion layer. During monsoon, O_3 concentrations were minimum which may be due to the wash out effect by unpolluted monsoonal air masses. Durng day, O_3 concentrations were maximum in afternoon when the concentrations of NO were minimum and those of NO_2 were also low. The concentrations of O_3 were observed to be higher at 30 m than at 13 m above the ground.

1 Introduction

The increasing concentrations of tropospheric ozone have become a matter of crucial importance during past few years. The enhanced concentrations of ozone in the troposphere have adverse effects on human health and vegetation[1]. The concentrations of ozone in troposphere are mainly contributed by two processes, viz. downward distribution of stratospheric ozone[2,3] and photochemical production of ozone[4-6]. The latter depends on its precursors NO, NO_2 and hydrocarbons in the atmosphere. These precursors have been extensively studied for their role in the formation of tropospheric ozone[7-11]. In urban areas, these precursors are emitted by various anthropogenic sources such as industries, biomass burning and oil burning[12-14], while in rural areas the precursors are due to biomass burning or natural biological processes[15-17].

A number of studies have been reported on tropospheric ozone behaviour and concentration from different parts of the world[18-25] except from South Asian regions where studies have been rather limited[26-29]. Since, in this region, the industrialization and urbanization are increasing rapidly, it is important to study the ozone behaviour and concentration along with its precursors.

The present study was carried out at Delhi which is one of the highly polluted cities in the world. In this study, concentrations and behaviour of O_3, NO and NO_2 have been determined during 1995 and 1996 and an effort has also been made to compare the concentrations of O_3 at two different heights of 13 m and 30 m above the ground at National Physical Laboratory, New Delhi.

2 Sampling and analysis

Sampling for ozone, NO_2 and NO_x was carried out at National Physical Laboratory, New Delhi, using impinger method. Samples were collected at 1000, 1400 and 1700 hrs IST during the day.

Ozone samples were collected at two different heights, 13 m and 30 m, above the ground. Samples were collected by passing air through impinger for 30 min at a flow rate of 0.5 LPM using neutral KI method. This method is used for the determination of total oxidants, but for oxidants other than ozone it has very slow response. In this method, NO_2 has positive interference, i.e. 10% stoichiometrically. This has been corrected by subtracting 10% of NO_2 values from O_3 concentrations. Negative interference of SO_2 was eliminated by putting SO_2 scrubber[30] before impinger.

NO_2 samples were collected at 13 m height using sodium arsenite method. Similar to NO_2, samples of NO_x were also collected using sodium arsenite method. For NO_2 and NO_x, the sampling time was 1 h and flow rate 1 LPM. The collection of NO_x was performed by putting a small U-tube of chromic oxide before the impinger to oxidize NO to NO_2 and finally the total NO_2 (NO_2 + oxidized NO) was collected in impinger. The concentrations of NO were calculated by subtracting NO_2 values from NO_x.

The analysis of ozone, NO_2 and NO_x was performed by using UV-vis spectrophotometer (Perkin Elmer Lamda 3) at 352, 540 and 540 nm respectively.

Table 1—Mean concentrations of O_3, NO and NO_2 at Delhi

Season	O_3 ppb	NO_2 ppb	NO ppb
Pre-monsoon	24.9	16.4	25.2
Monsoon	21.8	—	—
Post-monsoon	37.6	—	—
Winter	49.6	—	—

— Not available

3 Results and discussion

3.1 Seasonal behaviour

Table 1 gives the mean concentrations of ozone during pre-monsoon, monsoon, post-monsoon and winter seasons. The concentrations of NO and NO_2 are available only for pre-monsoon period. The concentrations of ozone are highest during winter, followed by post-monsoon, pre-monsoon and monsoon. Ozone concentrations are more than twice in winter than in monsoon season.

The higher concentrations of ozone during winter season are characteristics of polluted region as well as of higher degree of dynamic activities. These higher ozone concentrations may also be attributed to the most effective stratosphere-troposphere exchange during the winter season[2,31]. This was found in agreement of daily average meteorological data for temperature and relative humidity (RH) available from Indian Agricultural Research Institute (IARI), New Delhi. The correlation coefficient (0.50) significant at 0.01 level was observed for ozone concentration and temperature. However, with RH this correlation was found to be insignificant.

The lowest concentrations of ozone during monsoon may be due to wash out of ozone and its precursors by unpolluted monsoonal air masses.

3.2 Diurnal behaviour

Figure 1 shows the variation of concentrations of O_3, NO and NO_2 during daytime. It shows that maximum of ozone concentration is at around 1400 hrs IST and is very close to the variation of the surface temperature. NO concentration is minimum at 1400 hrs IST and that of NO_2 is maximum at 1000 and minimum at 1700 hrs IST. The figure also shows that NO concentrations are always higher than those of NO_2.

The afternoon peak of ozone indicates that increased photochemistry within the pollution

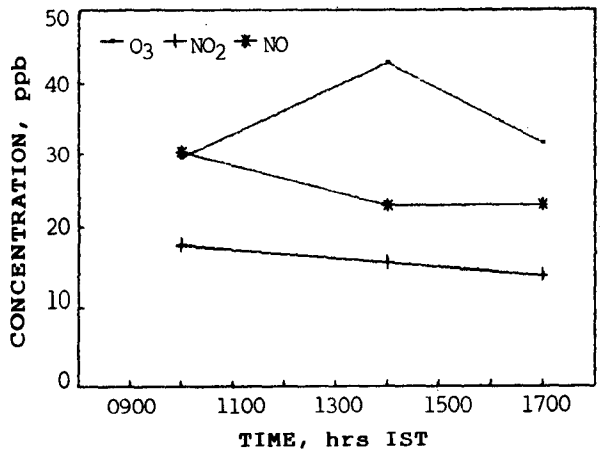

Fig. 1—Variation of concentrations of O_3, NO_2 and NO during daytime.

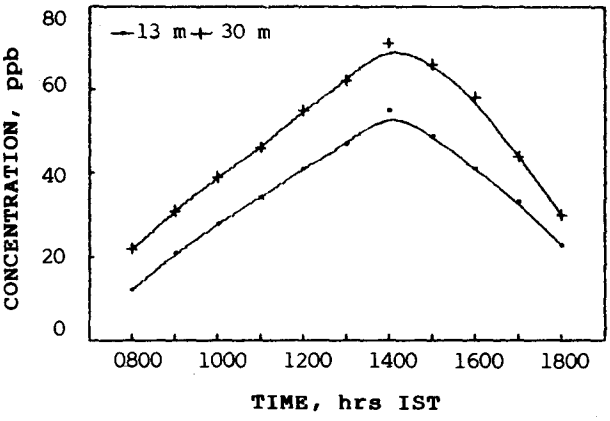

Fig. 2—Variation of ozone concentration at two different heights at NPL, New Delhi.

boundary layer due to higher concentrations of NO_x and hydrocarbons. The higher O_3 concentrations during afternoon may also be attributed to downward diffusion of ozone. The relatively more stable surface layer formed during nighttime starts breaking up after sunrise and the formation of convective boundary layer reaches its maximum during afternoon, resulting in mixing of O_3 from upper level to mixing layer. After 1400 hrs IST, it again starts decreasing because of decrease in mixing of ozone-rich air.

In all the measurements, NO values exceeded NO_2 which may be due to site characteristics. The sampling site is in close vicinity of heavy vehicular traffic and a large amount of NO may be contributed by various types of vehicles.

3.3 Ozone concentration at two different heights

The variation of ozone concentration at two different heights at NPL is shown in Fig. 2. Hourly data during daytime show that ozone concentration is higher at 30 m than at 13 m height, indicating its correlation with UV radiation. Due to

attenuation, the intensity of UV radiation is decreased with the decrease in height[32]. The destruction of ozone also occurs due to the presence of buildings and vegetation in close vicinity and also due to eddy mixing near the surface.

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