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Ozone concentration studies near the ground at Poona-Part I : Diurnal, seasonal and other time variations and ozone flux measurements

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ABSTRACT. Using a Brewer bubbler ozone sensor, designed and developed in the Instruments Research Laboratories of the India Met. Dep. continuous measurements of ozone concentration near the ground were made at Poona (18°N, 73°E) for one year 1969-70. There is a marked diurnal variation in surface ozone concentration which clearly follows the diurnal variation of temperature and is again a maximum during the pre-monsoon hot season months and a minimum during the monsoon. The surface ozone concentration also shows a pronounced seasonal variation, with a minimum during the monsoon months and a maximum during the pre-monsoon hot weather months. A secondary maximum in ozone concentration occurs in the forenoon during the winter months, associated with the breakdown of temperature inversion that occurs near the ground.

From continuous measurements of surface ozone made with three electrochemical sensors exposed at three levels, 0, 15 and 35 m above the ground, the ozone flux was calculated using the rate of decay method used by Kroening and Ney, and Regener's profile method. The profile method gives values of $1 \cdot 71$ to $7 \cdot 04 \times 10^{11}$ mol/cm²/sec and the rate of decay method gives $4 \cdot 2$ to $5 \cdot 6 \times 10^{11}$ mol/cm²/sec which are in good agreement with the flux values reported by other investigators.

1. Introduction

The results of measurements of surface ozone concentration and ozone flux made at Poona from September 1969 to August 1970, with an electrochemical surface ozone recorder developed in the Instruments Research Laboratories of the Meteorological Office at Poona (Sreedharan and Tiwari 1971) are presented in the paper. The recorder consists of (*a*) a bubbler ozone sensor with reservoir, (*b*) a pump unit to bubble air through the sensor, (*c*) an electrical network for supplying a polarising potential to the bubbler and (*d*) a continuous chart recorder capable of full scale deflection for 2 microampere output. The ozone current is read directly from the record and ozone partial pressure p is calculated using the formula,

$$p = 4.31 \times 10^{-3} \times i\, T\, t$$

where, p=partial pressure of ozone in micromillibars,

i=sensor current in microamperes,

T=temperature of air in degree Kelvin and

t=time in seconds for pumping 100 ml of air.

Poona (18°30′N, 73°33′E) is situated on the Deccan Plateau, on the eastern side of the Western Ghats at a height of 600 m above mean sea level. The Meteorological Office is located in a thickly populated area, more or less in the centre of the greater Poona complex, with a population of over one million. The observatory, with its trees and lawns, forms a small green oasis in a mass of residential and office buildings and factories. Industrial belts extend about 5-km to the north and northeast of the observatory, and heavy traffic moves all day along the roads around the observatory. The city itself is ringed by low hills on all sides, except the NE-SE sector, at distances of about 15-20 km from the observatory.

The surface ozone sensors were exposed on the roof of the main observatory building at heights of 15 and 35 m above the ground, the lower sensor being located on the roof above the second floor and the higher on the top of the clock tower. The top sensor had an exposure free from obstructions, as there are no buildings taller than 20 m within a radius of 2 km of the observatory. The lower sensor cleared the tree tops by about 2 metres. For ozone flux measurements a third sensor was exposed near the ground, with the mouth of the ozone intake tube flush with the ground, the tube being then taken underground and brought up to the bubbler. The location was about 10 m from the main building within a rose garden, surrounded on three sides by buildings about 10 to 20 metres high.

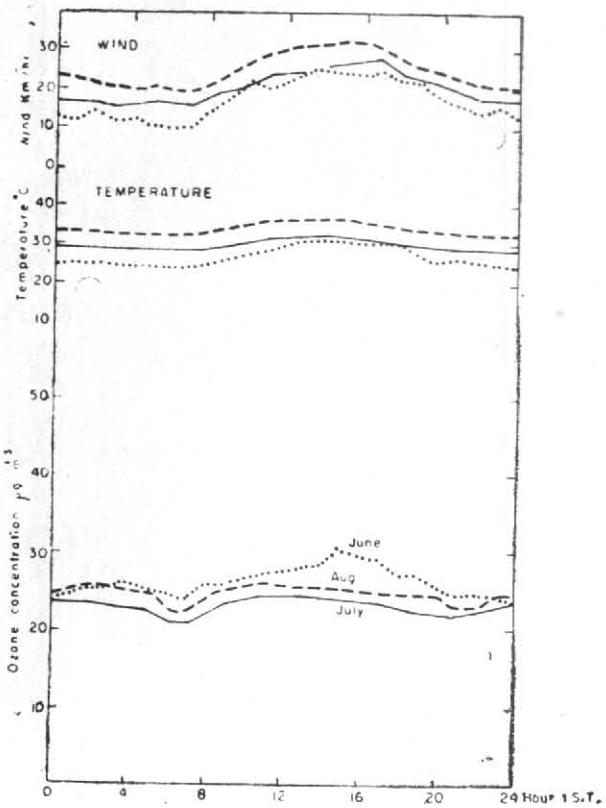

Fig. 1. Monsoon season

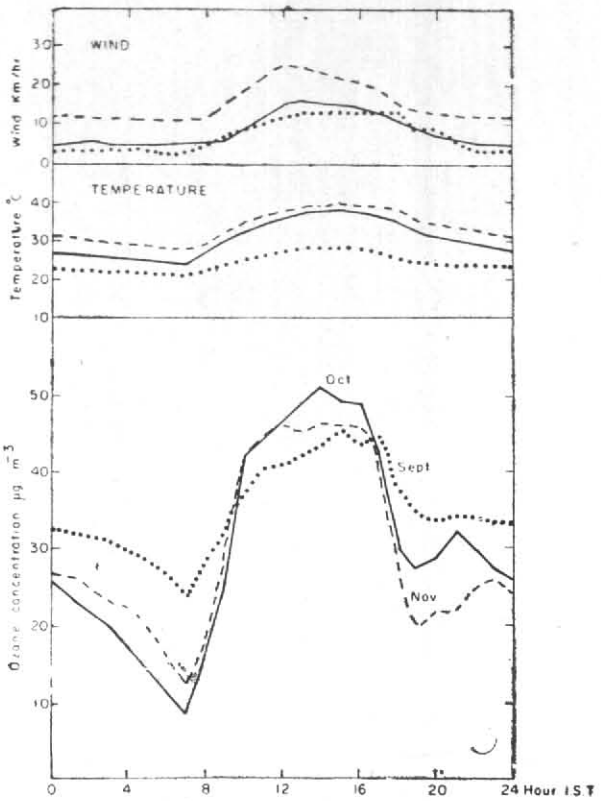

Fig. 2. Post-monsoon season

Mean hourly surface ozone concentration at Poona. Temperature and wind are presented by shifting the grid by 5 units.

To check the performance of the bubbler ozone sensor, independent measurements of the surface ozone were made by Ehmert's method. This was generally done between 1300-1500 hours local time when the ozone concentration is a maximum and fairly steady. The values obtained by both methods were found to agree within ± 5 per cent.

2. Diurnal variation of surface ozone

The ozone concentration near the ground is governed by factors which transfer the gas from the atmosphere to the ground. The continuous records of surface ozone obtained at Poona emphasize the predominant role of mixing processes in the transport of ozone in the lower troposphere. The problem is complicated since the orography of the observing site and temperature and wind profiles at different times of the day and associated mixing processes in the lower atmosphere affect he distribution of ozone.

The diurnal variation of surface ozone closely follows the diurnal variation of surface temperature. In fact, almost every individual fluctuation of ozone concentration is accompanied by a corresponding temperature change. A close correlation is also observed between wind and ozone concentration, particularly at night. The minimum surface ozone concentration occurs at the time of minimum temperature at about 0700 hours and the maximum in the afternoon between 1400-1600 hours local time coinciding with the maximum temperature epoch of the day (Figs. 1-4). With the advance of the day and the rise in air temperature, turbulence and mixing in the lower layers increase, with a resultant increase in the rate of replenishment of ozone from above and hence an increased concentration near the ground. During the night, replenishment of ozone is weak or very small, and there is also some destruction of ozone, resulting in low ozone concentration. With the onset of thermal turbulence after sunrise, there is a steep rise of ozone concentration during the forenoon and this is found to occur in most of the months and is prominent during December to March (Fig. 3).

3. Seasonal variations of surface ozone

Figs. 1-4 show the mean hourly values of surface ozone for the four seasons, monsoon (June to August), post monsoon (September to November), winter (December to February) and

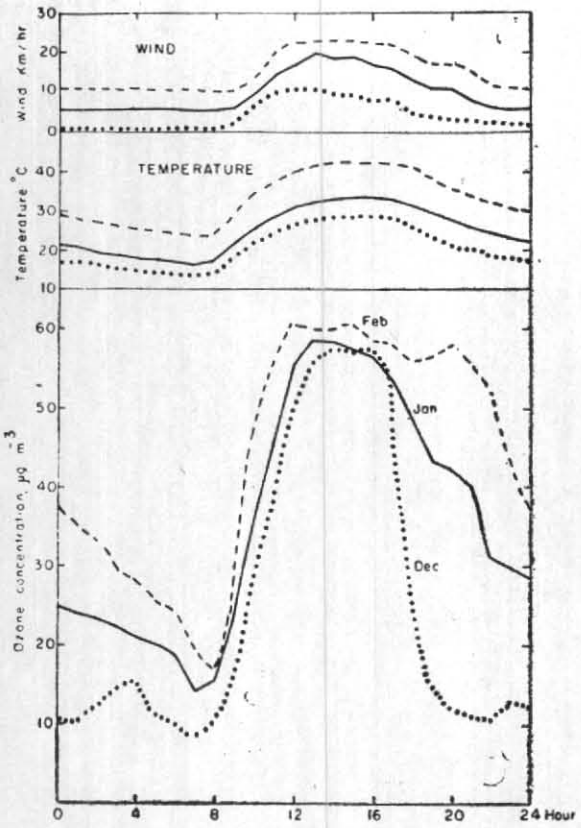

Fig. 3. Winter season

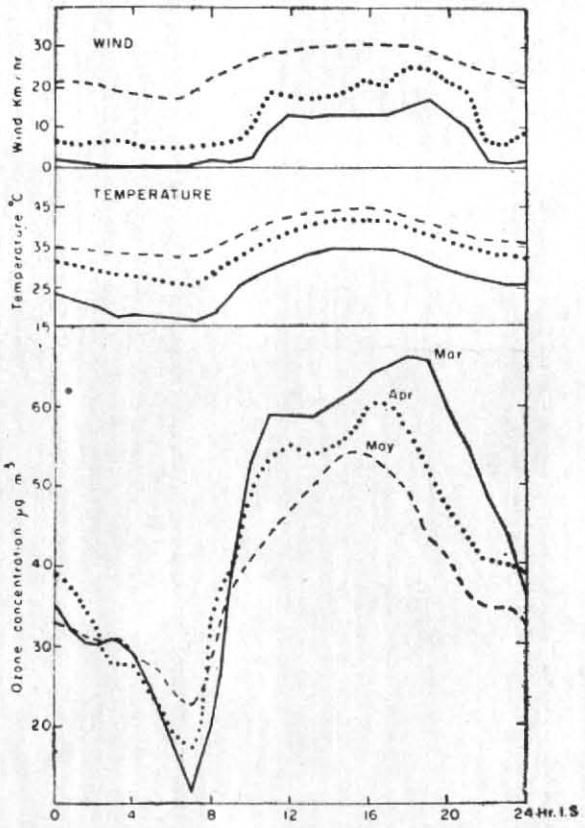

Fig. 4. Pre-monsoon hot season

Mean hourly surface ozone concentration at Poona. Temperature and wind are presented by shifting the grid by 5 units

the pre-monsoon hot season (March to May). Ozone, wind and temperature data for each month are also plotted in the diagrams. The mean maximum surface ozone concentration shows a pronounced seasonal variation with a minimum during the monsoon months and a maximum during the months December to May (Figs. 4 and 5).

The diurnal variation of ozone is also least during the monsoon season (Fig. 1) due to uniform turbulent mixing during both day and night, as evidenced by the high surface winds of about 15 to 20 km per hour throughout. The low value of ozone (about 24 μ gm $^{-3}$) during monsoon may also be due to the low rate of transfer across the tropopause in this season and the destruction within the highly humid troposphere.

The winter season is characterised by low ozone concentration during the night, followed by a steep increase after sunrise (Fig. 3). The duration of maximum ozone is also very short from 1300-1600 hours which also accounts for the low mean monthly value for December. With the increase in the duration of sunlit hours and of surface temperature, the duration of maximum ozone density increases resulting in an increase in the daily average values. January and February show a secondary increase at about 2000 hours corresponding to a secondary maximum in wind speed.

Due to low temperatures and clear skies during winter nights a stable layer (generally with a temperature inversion) is formed above the ground on most nights. This stable layer obstructs the free mixing in the layer near the ground resulting in very low ozone concentration, except on occasions when surface wind picks up and brings down fresh ozone from above the ground. In the morning after daybreak when this stable layer is removed, a surge of fresh air rich in ozone comes down and steep rise in ozone is registered. The forenoon surge often exceeds the main ozone maxima in the afternoon if there is a temperature inversion during the night. Measurements of ozone concentration across the inversion layer by Galbally (1968) agree well with the observations made at Poona.

The winter pattern of diurnal variation continues up to March (Fig. 4). The secondary small increase in ozone amount around 1900-2000 hours in January develops through February and records a maximum value during March,

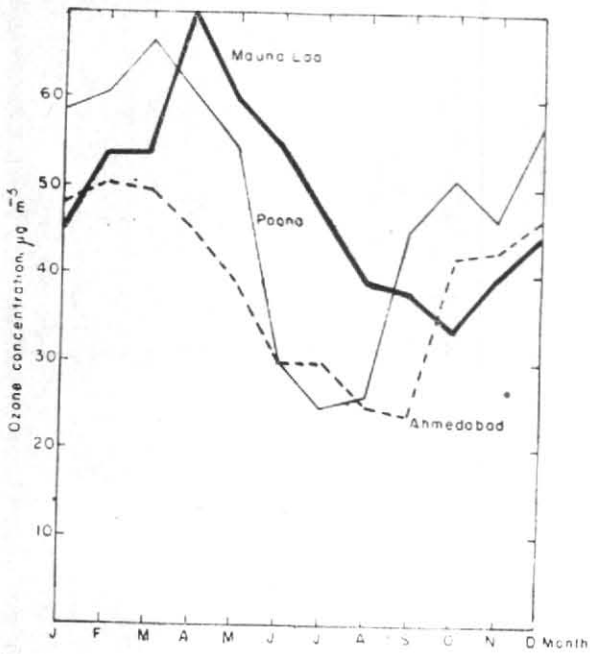

Fig. 5

Annual variation of surface ozone at Poona (18°N), Ahmadabad (23°N) & Mauna Loa (19°N)

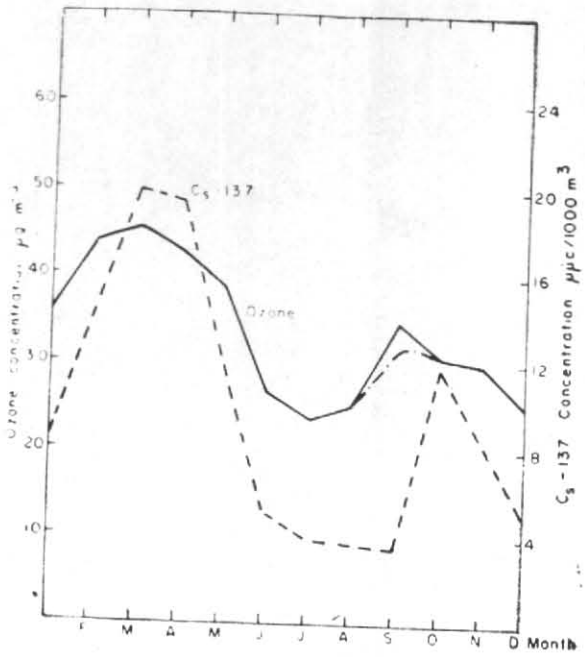

Fig. 6

Seasonal variation of surface ozone at Poona (1969-70) & Cs-137 at Bombay (1966)

thereafter slowly diminishing through April and disappears by May.

4. Annual variation of surface ozone

The annual variation of surface ozone at Poona is compared with those at Ahmadabad (23°N) and Mauna Loa (19°N) in Fig. 5. The Poona curve shows two maxima in contrast to the curves for Ahmadabad and Mauna Loa. The annual variation of surface ozone is explainable in terms of (*i*) the amount of ozone injected into the troposphere, (*ii*) the variation of the vertical exchange coefficient in the layer close to the ground and (*iii*) a constant ozone concentration above this layer. A close comparison of ozone variations with those of wind and temperature (Figs. 1 to 4) shows that most of the ozone changes are accompanied by either a wind change or a temperature change. The forenoon and afternoon maxima, in the months of January to April coincide with the corresponding wind maxima. In the month of March and April, a small increase in ozone concentration is observed between 0200-0500 hours in the early morning, but there is no evidence of a corresponding wind change. But the change in temperature profile for March suggests that the temperature and ozone changes might have resulted from advection or small scale vertical turbulence. This conclusion has to be accepted with a certain amount of reservation in view of the limited period of observation.

5. Comparison of surface ozone with radioactive tracers

Atmospheric ozone and artificial fission products, which serve as tracer elements in the study of the general circulation of the atmosphere, are different physically and chemically, but their modes of formation, distribution and destruction are similar. Fig. 6 shows the seasonal variation of surface ozone at Poona measured by the surface ozone recorder and of Cs-137 at Bombay reported by Rangarajan (1970). The data relate to different years. Both tracer elements showing a prominent maximum in March to May with a minimum from June to August, followed by a secondary maximum in September to October and minimum in December-January. Both the natural and artificial tracers would appear to be injected into the troposphere and transferred to the ground by similar mechanisms and to be affected by the southwest monsoon in an identical manner.

6. Variation of surface ozone with height

In order to study the variation of surface ozone concentration with height in the boundary layer, three ozone sensors were installed at 0, 15 and 35 metres above the ground. The output from all three sensors were fed to the same recorder. A sample record is shown in Fig. 7. The uppermost sensor almost invariably records more ozone than the lower sensors and there always exists a positive gradient of ozone with height above the ground. But on a few occasions in

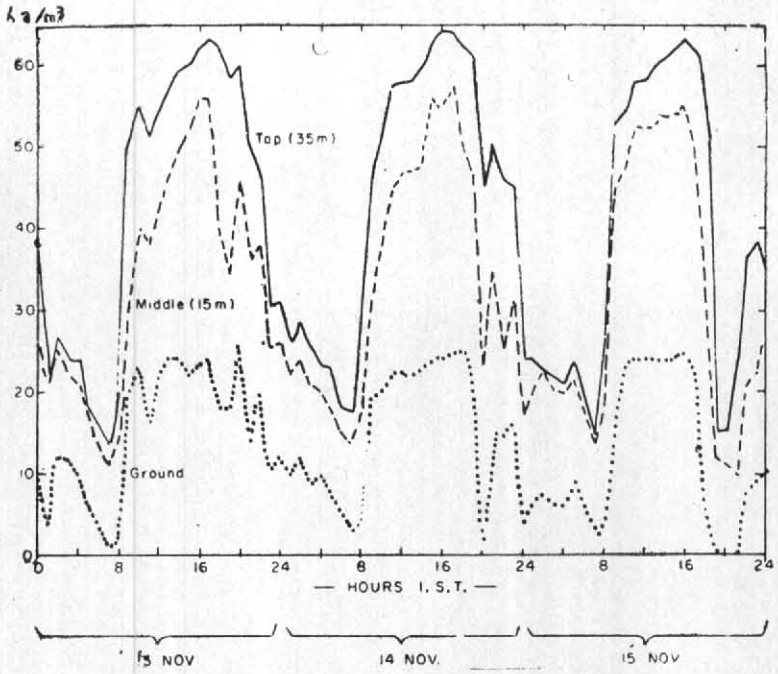

Fig. 7

Ozone concentration at 3 levels

the morning (about 0500-0800 hours) the higher sensor reported lower ozone values, presumably as a result of pollution. Smoke particles from neighbouring chimneys rise and form a layer of suspended particles about 30-40 metres above the ground particularly on calm mornings and this layer of ozone-destroying pollutants affect the higher sensor more than the lower one. The magnitude of the fluctuations at these levels changes with mixing conditions. Under well mixed conditions all levels record almost equal ozone concentration.

It was also noticed that even when the intake tube was 5 cm above the ground, most of the fluctuations shown by higher sensor were reproduced by the ground sensor too. When the intake tube of the ground sensor was put flush with the ground the small fluctuations are damped out. It is evident from this that the major destruction of ozone takes place right at the ground.

7. Ozone flux measurement

7.1. Theoretical estimates of ozone flux at the sink have been made by Dutsch (1946), Lettau (1951) and Regener (1954). Paetzold (1955) gave the flux value at the source as equal to 5×10^{10} to $2\cdot5\times10^{10}$ molecules/cm^2/sec from considerations of the vertical distribution of ozone in the stratosphere. During the Great Plains Turbulence Field Program in 1953 an experimental determination of ozone flux at the sink was made by Regener (1957). He measured the ozone density simultaneously at four levels (0·4, 1·6, 6·25 and 12·5 metres) above the ground at O'Neill, Nebraska. Assuming that the eddy diffusivity for ozone is equal to the eddy diffusivity for momentum, he obtained a value for ozone flux from $0\cdot87$ to $2\cdot50\times10^{11}$ mol/cm^2/sec. Kroening and Ney (1962) determined the ozone flux at Minneapolis, Minnesota to be 6×10^{10} mol/cm^2/sec. Following Regener's method, Kelley and Mc Taggart-Cowan (1968) in Alaska and Galbally (1968) in Australia have reported ozone flux ranging from 1 to 5×10^{11} mol/cm^2/sec.

Recently, Regener and Aldaz (1969) measured the ozone flux for different surfaces by the 'box method' and estimated the global strength to lie between 5·4 and $8\cdot6\times10^{29}$ molecules/sec. The flux of ozone into the earth's surface is given by

$$F=Kn \qquad (1)$$

where K is the reaction constant and n is the number of ozone mol/cm^3. On substituting for n in the usual unit of surface ozone concentration ($\mu g/m^3$), F is given by

$$F=1\cdot25\times10^{10}\,Kq \text{ mol/cm}^2\text{/sec} \qquad (2)$$

The 'box method' is convenient for determining

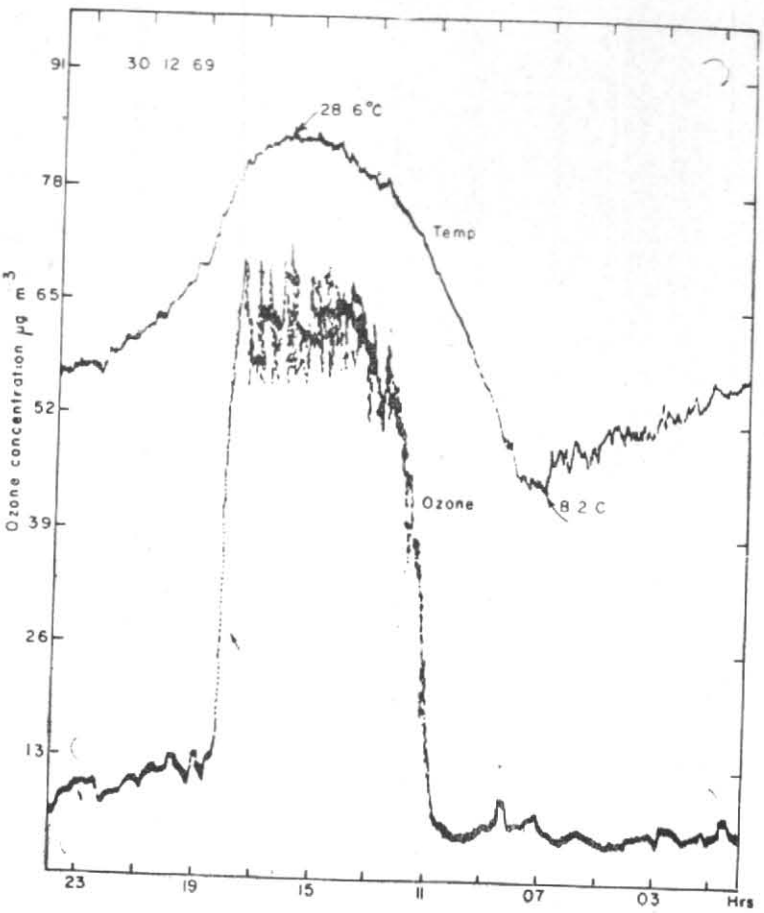

Fig. 8

Ozone record of 30 Dec 1969, used for flux measurement (Arrow indicates the sharp decrease of ozone density)

the values of the reaction constant K for different types of surfaces. The equipment consists of a box shaped frame, covered inside with Mylar film, whose bottom is open. The box is kept on the test surface and a small amount of ozone is injected into the box and the rate of decay of the partial density of ozone is measured. The rate of decrease is inversely proportional to K and the value of the reaction constant for particular surface is obtained by the relation : $T=h/K$ where h is the height of the box.

7·2. *Flux measurement at Poona by rate of decay method*

Kroening and Ney (1962) measured the sink strength by determining the rate of decay of ozone below the inversion level, immediately after the formation of a temperature inversion. During the study at Poona many instances have occurred when, with the formation of a stable layer near the ground and calm wind, ozone density has rapidly dropped to near zero values. Such conditions are found during winter when, with the change of the thermal regime, the day time concentration of ozone rapidly comes down to the lowest night value and remains so throughout the night. A few of such cases were used for determining the sink strength at Poona, one of which is illustrated in Fig. 8. The ozone sensor on this day was exposed on the roof of the meteorological office building at a height of 14·5 metres (the value of h in the equation) above ground level. The time required for destruction of the amount of ozone contained from the ground to the sensor level was calculated from the continuous record. Using Eq. (2), the flux value estimated on 5 such occasions is given in Table 1.

The average flux value at Poona is found to be $4{\cdot}83 \times 10^{11}$ mol/cm²/sec. The value is strictly applicable only to the particular local surface in the observatory compound, surrounded by green trees, grass and buildings but gives probably the first direct measurement of ozone flux in the tropics. It is assumed in the present computation that the sudden decrease of ozone to near zero

value is due to stoppage of transport from the troposphere, which holds good since there is no production in the unpolluted atmosphere near the ground.

7.3. *Flux measurement by the profile method*

With the extension of the ozone measurement from two to three levels (35 m, 15 m, 0 m) it became possible to compute the ozone flux by the widely used profile method. The hourly wind observations were taken at 0·5, 1·0, 2·0, 7·5 and 35 m above the ground. Temperature observations were also taken at the lowest three levels. The wind speeds at these levels were plotted against the logarithm of the height and only those observations which satisfied the neutral stability criteria (Swinbank 1964) were chosen for the flux computation. The friction velocity (u^*) was estimated by using a friction or drag coefficient which was evaluated from the formula (Swinbank 1964)

$$\sqrt{\overline{C_{0\cdot5}}} = \frac{k\,(u_{7\cdot5}-u_{0\cdot5})}{u_{0\cdot5}\ln 7.5/0.5} \qquad (3)$$

where k is Von Karman's constant, u is the horizontal wind speed and the subscripts refer to the levels of observation. An average value of 0·4 has been used for k. From a number of observations, the mean value of $C_{0\cdot5}$ was found to be 0·086 and the friction velocity computed from

$$u^* = 0\cdot086\ u_{0\cdot5} \qquad (4)$$

Now from the equality of transfer coefficients for ozone and momentum in neutral condition, the ozone flux (FO_3) is derived from:

$$FO_3 = u^{*2} \times \frac{(O_3)_2-(O_3)_1}{u_2-u_1} \qquad (5)$$

The value of ozone flux estimated along with the wind and ozone data used for the computation is given in Table 2.

The values of ozone flux at Poona, computed from both the methods, are of the same order and are also in good agreement with the flux values reported by various investigators. Table 3 presents the ozone flux values at different places.

8. Variation of ozone density near the ground

Continuous measurement of ozone concentration at different levels on the Meteorological Tower at Poona indicated that a downward negative gradient of ozone is always maintained. In Fig. 9 the ozone density at two levels (35 and 15 m above ground) is shown for 2 May 1970, on this particular day concentration is higher than the normal but the values of both the sensors are in good agreement. Both sensors are exposed well above the local trees and buildings and all the ozone fluctuations are identically reproduced indicating that the effect of ground destruction is not very effective. However, the lower sensor always reads less than the upper one; the difference varies with the variation of mixing conditions near the ground. At times of strong mixing or when there is a sudden surge of ozone from above, both sensors register same value (at 0900 hours in Fig. 9). The downward flux of ozone is related to the ozone gradient dO_3/dz and the coefficient of vertical eddy diffusion A by the relation:

$$FO_3 = A.\frac{dO_3}{dz} \qquad (6)$$

The average flux for Poona has been calculated to be $4\cdot83\times10^{11}$ mol/cm²/sec; from the observed gradient between 35 and 15 at different times of the day, the coefficient of vertical eddy diffusion can be computed. Table 4 gives the coefficient of eddy diffusion on 2 May 1970. Thus, in the month of May, when mixing is quite high, the coefficient of eddy diffusion varies from 10^3 to 10^4 cm²/sec. During winter nights the value will be very much low. This range of the coefficient of vertical eddy diffusion is in good agreement with Kroening and Ney's value.

TABLE 1

Ozone flux at Poona

Date	Day time ozone concentration (μgm^{-3})	Time of ozone destruction upto sensor level (14·5 m) (min)	Ozone flux (10^{11}mol/cm²/sec)
30 Dec 1969	65	36·8	4·23
31 Dec 1969	55	33·0	5·03
1 Jan 1970	53	36·0	4·44
28 Jan 1970	65	35·0	5·61
8 Feb 1970	52	32·2	4·85

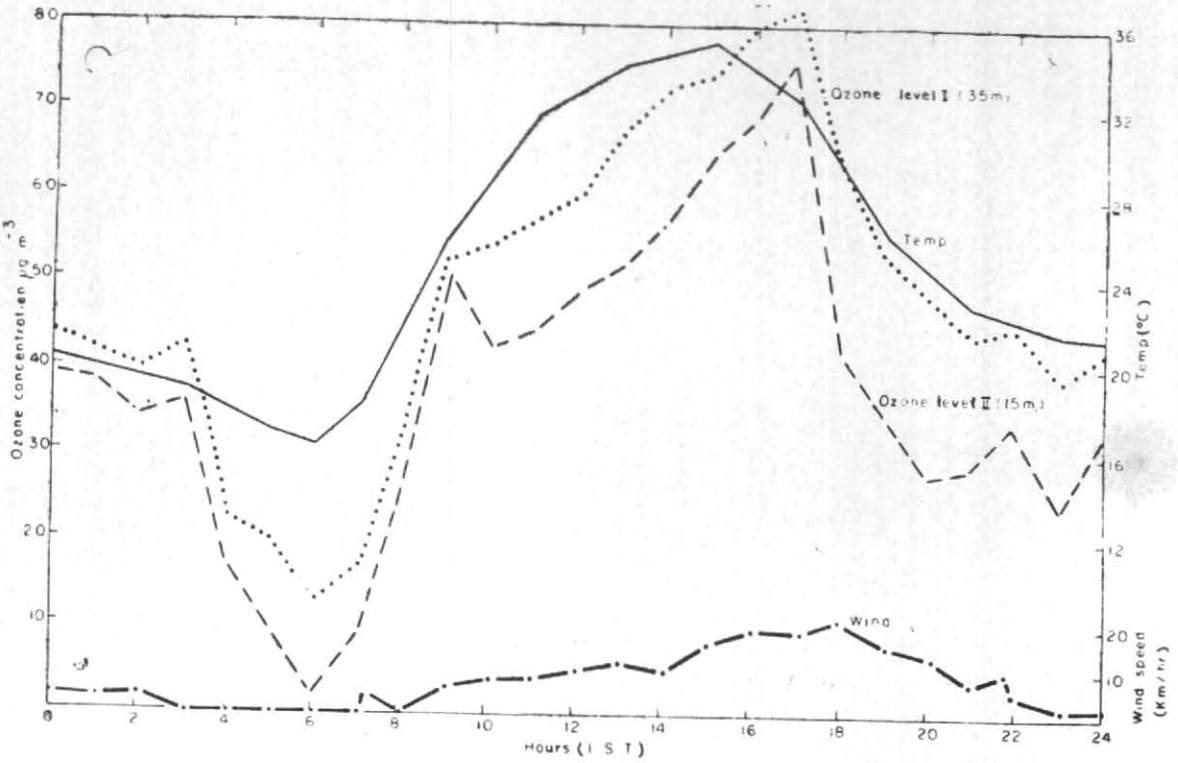

Fig. 9

Ozone and temperature variation on 2 May 1970

TABLE 2

Wind and ozone data used for flux measurement

Date 1971	Time (IST)	Wind speed at height (m) cm sec^{-1}					Ozone concentration at height (m) in (10^{11} mol cm^{-3})		Friction velocity u^* (cm sec^{-1})	Ozone flux (FO_3) (10^{11} mol cm^{-2}sec^{-1})
		0·5	1·0	2.0	7·5	35·0	35	15		
5 March	1300	123·2	137·2	150·4	224·0	322·0	7·62	6·49	10·6	3·02
5 March	1700	128·8	145·6	168·0	196·0	252·0	8·00	6·37	11·0	7·04
5 March	1800	200·6	184·8	254·8	280·0	336·0	7·87	6·12	17·3	9·33
6 March	0900	46·0	48·0	53·2	75·0	84·0	4·75	3·25	4·0	1·71
6 March	1000	199·0	218·4	240·8	308·0	370·0	6·88	4·62	17·1	1·94
6 March	1300	280·0	336·0	400·4	420·0	504·0	7·87	5·63	24·1	3·07
6 March	1500	190·0	243·6	266·0	336·0	392·0	8·44	6·25	16·3	2·05

TABLE 3

Values of ozone flux determined by different investigators from near neutral observations

Site	No. of obs.	Friction velocity (u^* cm sec^{-1})	Ozone flux FO_3 (10^{11} mol cm^{-2} sec^{-1})
(Regener 1957)			
O'Neill (41·5°N, (98·6°W)	1	19	1·8
(Kroening and Ney 1962)			
Minneapolis (45°N, 95°W)			0·6
(Kelley and Mc Taggart Cowan 1968)			
Pt. Barrow (71°N, 156°W),	4	23	6·3
(Galbally 1971)			
Edithvale, Victoria	13	64	3·67
Hay (34°·5°S, 144·9°E)	33	49	4·3
(Measurement of rate of decay)			
Poona (18·3°N, 73·5°E)	5		4·83
(Profile method)			
Poona (18·3°N, 73·5°E)	7	14·3	4·02

TABLE 4

The coefficient of eddy diffusion on 2 May 1970

Time	Ozone concetration (μgm^{-3}) at level (m a. g.l.)		Vertical gradient	coefficient of eddy diffusion
IST	35	15	(mol/cm^3/cm)	(cm^2/sec)
0600	13·0	2	$8·7\times10^{7}$	$4·4\times10^{3}$
1700	82·0	76·0	$3·77\times10^{7}$	$1·27\times10^{4}$
2000	48·0	28·0	$1·25\times10^{8}$	$3·86\times10^{3}$

9. Conclusion

Analysis of one year's data of surface ozone recorded at Poona by the electrochemical bubbler sensor and the ozone flux measurement reveal the following results:

(1) The ozone concentration near the surface undergoes a pronounced diurnal variation with a minimum occurring in the morning around 0700 hours and maximum in the afternoon between 1400 and 1600 hours, except during March when it occurs late in the evening at about 1800 hours. The diurnal variation is a minimum during July-August and a maximum during March-April, the range being 4-5 μgm^{-3} and 50-55 μgm^{-3} respectively;

(2) The annual variation of average daily ozone has a maximum value of about 46 μgm^{-3} occurring in March and minimum of about 24 μgm^{-3} in July, followed by a secondary maximum and minimum in September and December respectively;

(3) Both ozone measured at Poona (1969-70) and radioactive tracers measured at Bombay (1966) show similar pronounced decrease in concentration during the southwest monsoon period;

(4) The value of ozone flux at Poona, estimated from the rate of decay of ozone in a stable layer, is found to be $4·82\times10^{11}$ mol/cm^2/sec while the profile method gives a flux value $4·02\times10^{11}$ mol/cm^2/sec. These values are in good agreement with the ozone flux obtained by different investigators elsewhere at other latitudes;

(5) From the average ozone flux and ozone density at two levels, the coefficient of eddy diffusivity is calculated for the month of May and is found to be of the order of 10^3-10^4 cm^2 sec^{-1}.

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