EVALUATION OF THE PRODUCTION AND THE DESTRUCTION OF OZONE IN THE LOWER ATMOSPHERE

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ABSTRACT

Observed surface ozone mixing ratio X_{ob} is partitioned into two parts ; X_{tr}, transported from the free troposphere and X_{ch}, chemically produced or destructed in the boundary layer. X_{tr} is estimated from the ozone concentration in the free troposphere and the wind speed. The ozone in the free troposphere estimated from surface ozone observations is consistent with that of ozonesonde data.

X_{ch} is obtained from the difference between X_{ob} and X_{tr}. X_{tr} increases with wind speed, while X_{ch} shows maximum at hourly wind speed of 1-2 m/s in the daytime. Contribution of X_{tr} to X_{ob} is larger than X_{ch} except for a short period in summer. X_{ch} is positive for April-October, but X_{ch} can be negative in winter, showing the net chemical destruction in the boundary layer. X_{ch} increases linearly with solar radiation, and is negative for daily global solar radiation below 8 MJ/m^2, which is about equal to the monthly mean in winter.

1. INTRODUCTION

Year-to-year variations of ozone at the surface and tropospheric levels are in general agreement with very few exceptions (Bojkov,1988). But the ozone at the surface and in the lower troposphere show complex seasonal trends and correlations with solar radiation. An increase in lower tropospheric ozone is obvious (Logan,1985; Bojkov, 1988; Wege et al., 1989). The summertime concentrations of ozone near the surface in rural areas of Europe and central and eastern United States may have increased by approximately 6-22 ppbv since 1940's (Logan, 1985). Bojkov (1988) showed that at rural stations the ozone increasing rate is greater in the lower troposphere than at the surface, and surface ozone during November-January is increasing at a greater rate than during May-October. Wege et al. (1989) have reported that the trends in ozone at Hohenpeissenberg show increases in winter and spring but trends are not significant in summer and autumn, and a trend is not present in data from recent years. At an urban station (Delft) ozone concentration shows no trend or at most a slight downward one (Guicherit,1988).

The relation between the surface ozone concentration and the solar radiation is expected since solar radiation determines the photochemical reactions. The positive correlations between peak hourly ozone and total insolation and hours of sunshine are obtained at rural sites (Colbeck and Harrison, 1985a). Monthly means of ozone show good correlation with monthly values of sunshine at Hohenpeissenberg (Volz et al.,1989). The correlations between ozone and solar radiation are different for each stations and depend on height and geographical conditions such as north/south and rural/industrial area (Schmidt,1989). Although no direct relationship between annual totals of solar radiation and surface ozone are shown, trend of both parameters are either positive (Dresden, Fichtelberg) or negative (Arkona) (Feister et al., 1989).

To apportion the relative contributions to ground level ozone concentrations from the stratosphere/troposphere and man-induced processes in polluted areas is a complex matter. It is essential to know the relationship between the ozone variation at the surface and in the lower troposphere. In this report, we estimate the ozone transported from the free troposphere. Then we obtain chemically produced or destructed portion of ozone in the boundary layer and show its correlation with wind speed and solar radiation.

2. VERTICAL TRANSPORT OF OZONE IN BOUNDARY LAYER

When the photochemical production and destruction are neglected, ozone concentration near the surface is determined by transport from the free troposphere and its destruction at the surface. For stationary and horizontally homogeneous conditions the vertical ozone flux F in the boundary layer is given by :

$$F = D\rho(dX/dz) = q\rho_0 X_0 \qquad (1)$$

where D is eddy diffusivity, ρ air number density, X ozone volume mixing ratio,q ozone destruction velocity at the surface, z height, ρ_0 and X_0 values at the surface. Vertical change of D is assumed :

$$D = u_* k(z + z_0)\beta / \{1 + u_* k(z + z_0)\beta / D_0\} \qquad (2)$$

where u_* is the friction velocity, z_0 the roughness length, k von Karman's constant and β parameter introduced to take account of stability. Above the surface layer we assume D approaches a constant value D_0 (Fabian and Junge, 1970). In the surface layer u_* can be obtained by logarithmic wind profile

$$u_* = ku/\ln\{(z_u + z_0)/z_0\} \quad (3)$$

where u is the wind speed at the level z_u which is the height of observation above the surface.

From Eqs.(1)-(3), we can obtain ozone mixing ratios, X_{tr}, at the level z_u and $X(z_h)$ at the top of the boundary layer z_h. The ratio $X_{tr}/X(z_h)$ is given by :

$$X_{tr}/X(z_h) = (1/C_2)(qC_0 + u)/(qC_1/C_2 + u) \quad (4)$$

where $C_0 = (1/\beta k^2)[\ln\{(z_u + z_0)/z_0\}]^2$, $C_1 = 1/(\beta k^2)\ln\{(z_u + z_0)/z_0\}[\ln\{(z_h + z_0)/z_0\} + z_h/H]$, $C_2 = 1 + (qz_h/D_0)\{1 + z_h/(2H)\}$, and H is the scale height of the lower atmosphere. Eq.(4) shows that $X_{tr}/X(z_h)$ is determined by the wind speed and supplemental parameters of z_h, q, D_0 and β.

3. OZONE IN THE FREE TROPOSPHERE AND TRANSPORT TO THE SURFACE

Surface ozone has been monitored at Uji (34.9°N, 135.8°E), a suburb of Kyoto, by u.v. absorption type instrument (Dasibi, Model 1006-AHJ) since May 1990 at the height of about 10 m above the surface together with meteorological parameters. On days when the maximum hourly wind speed exceeds 3.5.m/s and the daily global solar radiation is below 13 MJ/m^2, hourly ozone mixing ratio X_{tr} determined by vertical transport is given by the experimental equation :

$$X_{tr} = A(u - 0.30)/(u + 0.34) \quad (5)$$

where u is wind speed (m/s), and A corresponds to $X(z_h)/C_2$ defined in Eq.(4). Observed surface ozone tends to zero at $u = 0.3$ m/s, and it is very rare when $u < 0.3$ m/s. An example is given in Fig.1, showing the relation between the wind speed and the ozone concentration observed or estimated by Eq.(5). When hourly wind speed is 5 m/s observed ozone concentration is 85% of the upper limit A. Guicherit (1988) has shown that the monthly ozone concentration increases with wind speed and saturates at 12 m/s.

The combination of parameters z_h, D_0, q and β is determined so that Eq.(4) agrees with experimental Eq.(5), with replacement of u in Eq.(4) by $u - u_0$, where u_0 is the correction term. For $z_h = 1000$ m, 1500 m and 2000 m the degree of coincidence was tested for ranges $D_0 = 1 - 20$ m^2/s, $q = 0.001 - 0.01$ m/s, and $\beta = 0.1 - 1.0$. Satisfactory agreement was obtained for the combinations; for $z_h = 1000, D_0 = 20, q = 0.004, \beta = 1.0$ and for $z_h = 2000, D_0 = 20, q = 0.0025 - 0.0010, \beta = 0.3 - 0.6$, with $C_2 = 1.11 - 1.28$. The best fit is for $z_h = 2000$ m, $D_0 = 20$ m^2/s, $q = 0.0025$ m/s and $\beta = 0.6$ with $C_2 = 1.28$. In the following analysis we adopt this combination of parameters.

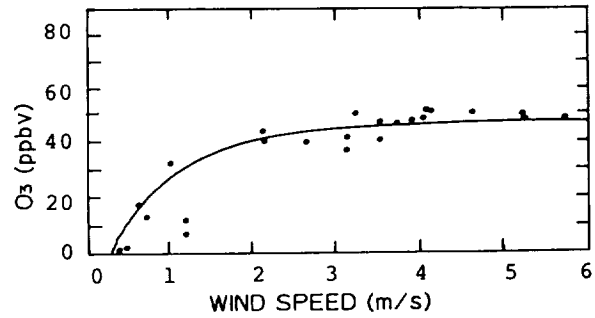

Fig. 1 Surface ozone and wind speed. Dots show the observed value and solid curve is estimation by Eq.(5) with $A = 55$ ppbv, on 8 May 1991. Total global solar radiation is 5.5 MJ/m^2.

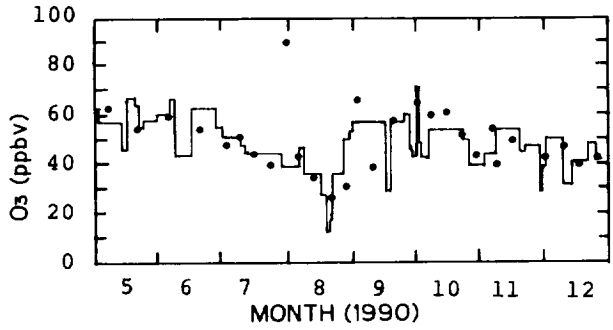

Fig. 2 Ozone in the free Troposphere. Solid line shows the estimated daily $X(z_h)$ values and dots represent ozonesonde data at 700 hPa at Tsukuba for May - December 1990.

More than four samples of $X(z_h)$ per month are obtained, with the condition of maximum wind speed and global solar radiation as stated before. Fig. 2 shows the daily $X(z_h)$ estimated from surface ozone and the ozone mixing ratio at 700 hPa level by ozonesonde data at Tsukuba/Tateno (36.0°N,140.1°E) about 400 km east of Uji. The same daily value of $X(z_h)$ is adopted until a new sample is obtained. Apart from a few exceptions, the agreement is reasonable. Monthly mean values show better agreement, and it is recognized that the ozone in the free troposphere $X(z_h)$ has two maxima in spring and autumn, and minima in winter and summer. This seasonal variation in the lower troposphere is due to the transport from the stratosphere.

The ozone mixing ratio determined by vertical transport X_{tr} is estimated from wind speed by Eq.(5) applying the $X(z_h)$ obtained above. Denoting the observed ozone at the

surface as X_{ob}, the difference between X_{ob} and X_{tr}, i.e., $X_{ch} = X_{ob} - X_{tr}$, is interpreted as the part produced from chemical reactions in the boundary layer apart from the destruction at the surface.

Monthly means of X_{ob} and X_{tr} in the daytime are shown as a function of wind speed in Figs. 3(a) and 3(b) for summer and winter, respectively. In summer the difference between observed and transported ozone i.e., the photochemical effect is positive and maximum at wind speed 1-2 m/s, and vanishes above 5 m/s (Fig.3(a)). In winter, the net photochemical effect is very small with negative effect for wind speed below 0.5 m/s.

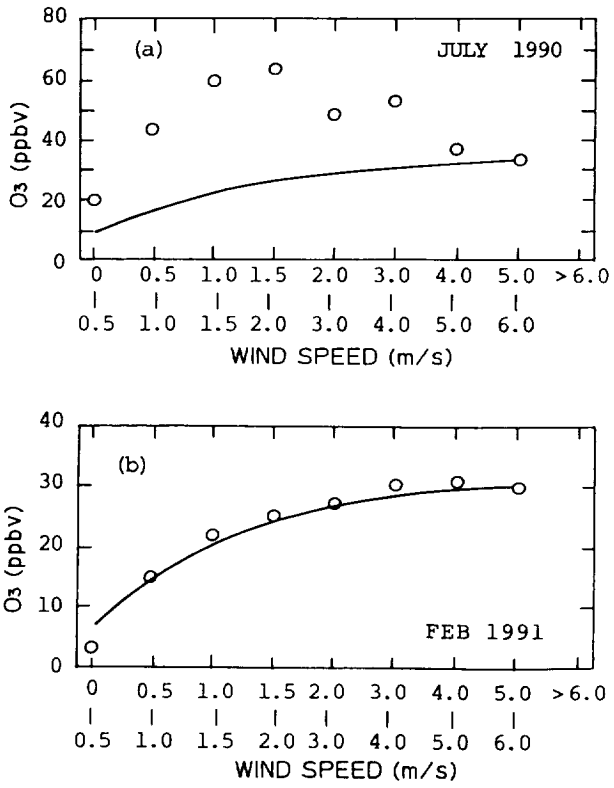

Fig. 3 Monthly means of observed and transported ozone as a function of wind speed in the daytime. Circles show observed ozone X_{ob} averaged over hourly wind speed intervals 0.5 m/s or 1.0 m/s, and solid curve shows the transported ozone X_{tr}. Summer case (a) for July 1990 and winter case (b) for February 1991 are shown.

4. SEASONAL VARIATIONS OF TRANSPORTED OZONE AND CHEMICAL EFFECTS

Fig. 4 shows the seasonal variations of $X(z_h)$, X_{ob}, X_{tr} and X_{ch} in the daytime. X_{tr} has the maximum in spring corresponding to the $X(z_h)$, with higher value in 1991 than 1990. Small humps (secondary maxima) are seen for both $X(z_h)$ and X_{tr}. X_{ch} has the maximum in summer, and the minimum in winter. In winter X_{ch} is nearly zero or negative, which shows net chemical destruction.

In 1990, observed ozone X_{ob} shows the maximum in July due to the large chemical effect, while the maximum is in May in 1991 due to the strong transport from the free troposphere. During the night (not shown) X_{tr} is 12 - 27 ppbv with weak seasonal variation. X_{ob} is lower than X_{tr} by 10 ppbv at most,showing net chemical destruction in all months.

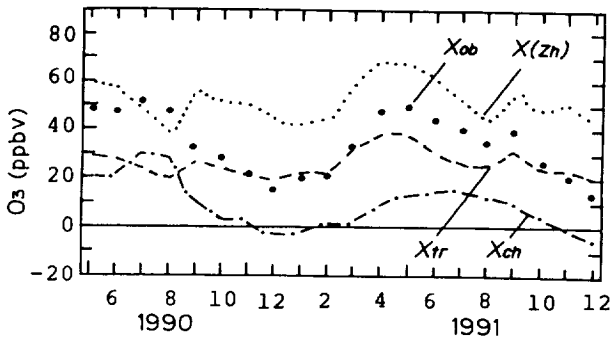

Fig. 4 Variation of monthly mean ozone in the daytime. Dotted line shows ozone mixing ratio in the free troposphere $X(z_h)$; Filled circles, observed surface ozone X_{ob} ; Broken line, transported X_{tr} ; Dash-dot line, chemically produced X_{ch}.

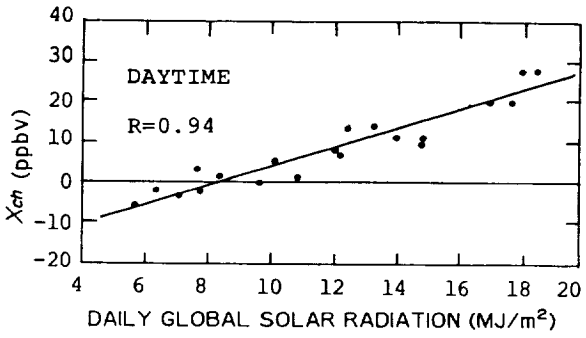

Fig. 5 Global solar radiation and X_{ch}. Monthly means of X_{ch} in the daytime are plotted against the the monthly means of daily global solar radiation. The regression line is shown with the correlation coefficient R=0.94.

5. SOLAR RADIATION AND X_{ch}

Monthly means of X_{ch} in the daytime are closely correlated with those of global solar radiation as shown in Fig. 5. The correlation coefficient is 0.94. It is seen that below about 8 MJ/m^2 per day X_{ch} is close to zero or negative, showing net chemical destruction. Above 8 MJ/m^2

per day (April-September), net chemical production is observed, amounting to 30 ppbv which is more than half of X_{ob} in summer months.

6. DISCUSSION

The parameters z_h, D_0, q and β in Eq.(4) determined to satisfy the experimental Eq.(5) are kept fixed throughout the period. It means to use the mean values for parameters and for C_2. This assumption is justified as the ozone in the free troposphere $X(z_h)$ shows good agreement with ozonesonde data as shown in Fig. 2. Estimated ozone destruction velocity, $q = 0.0025$ m/s, is within the range of $q = 0.001 - 0.008$ m/s over land with grass obtained directly (Aldaz, 1969; van Dop et al., 1977; Garland and Derwent, 1979; Galbally and Roy, 1980; Lenschow et al., 1981; Colbeck and Harrison, 1985b).

Photochemical effect on surface ozone would be highest in summer as shown by X_{ch} in Fig. 4. But it does not necessarily lead to the summer maximum in X_{ob}. Surface ozone X_{ob} shows the maximum in May in 1991 at Uji due to strong transport from the free troposphere. Singh et al. (1978) showed the model wherein photochemical effect at remote sites is recognized from June to October, but the net photochemical production is observed from April to October in the daytime at Uji, a suburb of Kyoto.

Monthly means of daily averaged X_{tr} show the seasonal variation ranging from 20 to 30 ppbv (not shown). Corresponding value of X_{ch} is positive in summer season and negative in winter season, deviations being less than ± 10 ppbv. So the effect of X_{ch} on X_{ob} is relatively small, which means surface ozone is close to that transported from the free troposphere in yearly mean as suggested by Galbally et al. (1986) for rural sites.

It is usual to study the correlation between global solar radiation or u.v. radiation and surface ozone X_{ob} (Colbeck and Harrison,1985a; Volz et al.,1989; Schmidt,1989). It is more reasonable to adopt X_{ch} instead of X_{ob}.

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