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A method for calculating the total ozone amount in the clear skies

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Abstract—— A new method for calculating the clear day total ozone amount was obtained by the regression analysis of the observation data of ozone, solar UV radiation, and meteorological parameters. With this method the monthly mean total ozone amounts for the year 1991 in Beijing were calculated. Generally, the calculated values agree well with the Dobson spectrophotometer measurements, the average relative deviation between them being less than 2.2%. According to the *F*-test, the photochemical reactions in the atmosphere, the solar UV radiation, and the aerosols are three most important factors to affect the column total ozone amount.

Keywords: total ozone amount; solar UV radiation; photochemical reaction.

1 Introduction

The atmospheric ozone layer which absorb almost totally the most harmful part of solar UV radiation is well known as a protection layer for the human being and biological environment. The discovery of ozone hole in the Antarctic region and the global trends of ozone concerns not only the scientists but also the publics and governments on the world scale (Wang, 1991)). It is of great importance to determine the atmospheric total ozone amount and to further study its variation characteristics.

2 Factors affecting the total ozone amount

To date the formation and maintenance of ozone hole are explained essentially by the processes of photochemical reactions, atmospheric dynamics, and solar activities. Hunt *et al.* (Wang, 1985) pointed out that the photochemical theory may be improved with inclusion of O_2-H_2O reaction and O_3-H_2O reaction. Their calculation results showed that it is necessary to consider the reactions of ozone with H_2O, radical HO_2, and radial OH in the ozone photochemical processes. The sensitivity study experiments by Liu *et al.* (Liu, 1990) with a 1-D atmospheric chemistry model indicated that the tropospheric ozone amount decrease with increasing H_2O quantity. That is because the increase in H_2O will result in an argumentation of the free radicals, such as OH and HO_2 and through the photochemical processes more ozone are transformed to O_2.

It is confirmed in a number of theoretical studies that H_2O in the stratosphere depletes ozone by the following processes(Wang, 1991; Hong, 1991; Mo, 1988):

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

the reaction product OH causes ozone reduction through the following catalytic reactions:

$$\begin{array}{l} OH + O_3 \longrightarrow HO_2 + O_2 \\ (1)\ HO_2 + O_3 \longrightarrow OH + 2O_2 \\ \hline 2O_3 \longrightarrow 3O_2\,(\text{net}) \end{array}$$

$$\begin{array}{l} OH + O_3 \longrightarrow HO_2 + O_2 \\ (2)\ HO_2 + O \longrightarrow HO + O_2 \\ \hline O + O_3 \longrightarrow 2O_2\,(\text{net}) \end{array}$$

$$\begin{array}{l} OH + O \longrightarrow H + O_2 \\ (3)\ H + O_3 \longrightarrow OH + O_2 \\ \hline O + O_3 \longrightarrow 2O_2\,(\text{net}) \end{array}$$

All these catalytic processes enhance the stratospheric ozone depletion.

The photochemical destruction of ozone in the troposphere takes place mainly by the processes as follows(Guo, 1991):

$$\begin{array}{l} O_3 + h\upsilon \longrightarrow O(^1D) + O_2\,(\lambda < 320\ \text{nm}) \\ O(^1D) + H_2O \longrightarrow 2OH \\ \hline O_3 + H_2O \longrightarrow O_2 + 2OH\ (\text{net}) \end{array}$$

$$\begin{array}{l} O_3 + 2OH \longrightarrow H_2O + 2O_2 \\ H_2O + O_3 \longrightarrow 2OH + O_2 \\ \hline 2O_3 \longrightarrow 3O_2\,(\text{net}) \end{array}$$

It is noted that the odd oxygen reduction is the main mechanism for ozone photochemical loss in the troposphere.

In the analysis of the variation of total ozone amount, the effect of atmospheric aerosols should also be included. It has been found that after the El Chichon volcanic eruption the total ozone amount in the north hemisphere has been reduced about 10% (equivalently about 30 DU; Li, 1989). In general, the violent volcano eject a huge amount of SO_2, H_2O and dusts into the stratosphere where the sulfate aerosols are formed and dispersed. Because of the heterogeneous reaction on the aerosol surface, the active chlorine are released which accelerate the ozone decomposition. On the other hand, by scattering and absorption the aerosols attenuate the solar UV radiation and indirectly affect the total ozone amount.

In summary, three primary factors, i.e., solar UV radiation, photochemical processes related to H_2O, and aerosols, have to be considered in the analysis of total ozone variations.

3 Observation data

From the first of January 1991 we began the measurements of daytime solar UV radiation at Xianghe Observatory, 70km away from Beijing. Simultaneous observation data about cloudiness, cloud type, sunshine, and meteorological parameters were also recorded. The instrument has three sensors, respectively for measuring the solar radiation in three wavelength regions: 270—3200nm, 400—3200nm, and 700—3200 nm. Through simple calculations, the daily sums of the solar UV radiant exposure (Q_{uv}) in the region 270—400 nm can be obtained. The relative accuracy of measurements is ±5%, with an instantaneous resolution of 1 W/m^2 and an integrated value of 0.01 MJ/m^2. The measurements of solar radiation can be displayed, printed, and recorded. The data of the daily sums of solar scattered radiant exposure(S) and solar direct radiant exposure(D) on the horizontal plane, water vapor pressure (E) at the ground and other conventional data are provided by Beijing Observatory. The data of total ozone amount (q_{O_3}) are obtained by the Dobson spectrophotometer at Xianghe.

4 Expressions of the primary factors

4.1 Solar UV radiation

This quantity is expressed as Q_{uv}, whose unit is MJ/m^2.

4.2 Water vapor

The free radicals such as OH, HO_2, and H coming mainly from H_2O decomposition play important catalytic roles in nearly all kinds of photochemical reactions to affect total ozone amount(Su, 1989). Moreover, all kinds of photochemical reactions in the atmosphere are directly or indirectly related to the solar UV radiation. So, the influence of H_2O through the photochemical reactions on ozone can be expressed by the absorption of solar UV radiation. For each photochemical reaction process, the absorption of UV radiation depends mainly on the reactive component density which varies with altitude, time, and geographical location. It is not practical to determine how UV energy is absorbed by these very complex photochemical reaction processes and it is a big problem to express the quantity of UV radiation consumed by photochemical reactions.

Considering the relationship between total solar radiation and solar UV radiation, the total absorption of solar UV radiation by all photochemical reactions may be related indirectly to that of total solar radiation by H_2O. Based on the radiative transfer theory, this term is expressed in the form $A * \exp(-kwm)$, where k being the mean absorption coefficient of water vapor for solar radiation (0.7—2.845μm), w water vapor content in the whole atmospheric column derived from empirical relation between w and the water vapor pressure(E) at the ground, and m the air mass at noon. A is an empirical constant representing the ratio of the UV energy consumed by photochemical reactions over the total solar radiation absorbed by H_2O, i.e., $Q'_{uv}/Q' = A$, which is determined by the regression analysis. This phytothesis is based on that the ratio of solar UV radiation to total solar radiation at the ground is constant, and is not influenced by contribution of each factor. In fact, the hypothesis had been verified by many results((Zhou, 1986; Ji, 1989). On the basis of 1990—1991 two-year data for the clear atmospheres, A has been proved as a constant(Bai, 1992).

4.3 Atmospheric aerosols

The contribution of atmospheric aerosols (especially volcanic aerosols) to the depletion of total ozone amount through the absorption and scattering of UV radiation can be expressed basically by $\exp(-S/D)$, it has been demonstrated (Marvin, 1976; Shao, 1982) that the atmospheric turbity is better represented by the factor S/D than by Link's turbidity factor and S/D is more sensitive to the aerosol variation than Link's factor.

5 Method for total ozone amount calculation

In order to clearly see the variation characteristics of total ozone amount, only the data in clear days (i.e., cloudiness $N<2$) are taken in the study. In the calculations, the quantities Q_{uv}, S, D, q_{o_3}, $W(E)$ are monthly averaged values for all clear days.

By the correlation analysis of the data in 1991 and the F-test, it is found that in the clear skies, water vapour is the most important factor affecting total ozone amount with a F-test value of 22.06, the second important factor is the solar UV radiation with a F-test value of 18.25; and the third one is aerosols having a F-test value of 2.05. From these correlation analysis, a non-linear regression equation is obtained for calculating the total ozone amount in clear skies:

$$q_{O_3} = A_1\exp(-kwm) + A_2 Q_{uv} + A_3\exp(-S/D) + A_0, \quad (1)$$

where Ai $(i=0,1,2,3)$ are constants determined by the regression analysis.

In order to evaluate the contribution of each factor, besides Eq. (1), two equations are used to calculate the monthly mean total ozone amounts as well as their relative deviations (δ), correlation coefficients (R), and standard deviations (σ) relative to the observed values q_{O_3}(obs.):

$$q'_{O_3} = A'_1\exp(-kwm) + A'_0, \quad (2)$$

$$q''_{O_3} = A''_1\exp(-kwm) + A''_2 Q_{uv} + A''_0, \quad (3)$$

$$q_{O_3} = A_1\exp(-kwm) + A_2 Q_{uv} + A_3\exp(-S/D) + A_0. \quad (4)$$

The calculation and observation results are given in Table 1. It is seen that in all cases, calculation results agree quite well with observations, particularly, the Eq. (1) giving the best agreement. That means that the more factors are considered, the more precise the calculation are.

Table 1 The observation and calculation values and their biases(%) of the monthly mean values (q_{O_3}) of the total ozone amount in clear skies

r, month	q_{O_3}(Obs.)	Eq. (2)		Eq. (3)		Eq. (4)	
		q_{O_3}(Cal.)	δ,%	q_{O_3}(Cal.)	δ,%	q_{O_3}(Cal.)	δ,%
1	378.5	348.7	−7.87	368.0	−2.78	375.2	−0.87
2	406.3	399.3	−1.73	419.7	3.30	422.2	4.03
3	404.2	395.8	−2.09	411.9	1.90	407.0	0.69
4	412.3	406.9	−1.31	407.2	−1.23	408.1	−1.03

Table 1 (continued)

5	401.0	395.8	−1.30	388.3	−3.17	382.9	−4.51
6	366.6	382.6	4.36	364.3	−0.63	366.1	0.03
7	353.3	369.0	4.44	343.9	−2.66	348.9	−1.24
8	305.3	344.3	12.77	324.9	6.44	317.1	3.86
9	322.8	348.5	7.11	340.5	5.48	338.7	4.93
10	341.0	338.2	−0.81	330.8	−2.97	339.3	−0.51
11	327.3	321.6	−1.74	326.5	−0.25	323.0	−1.30
12	360.6	331.3	−8.12	353.1	−2.09	349.6	−3.04
$\bar{\delta}$,%		4.47		2.74		2.17	
R		0.829		0.947		0.958	
σ		0.0069		0.0042		0.0040	

6 Conclusions

It is demonstrated by correlation analysis that water vapor is the most important factor to affect the total ozone amount, i.e., all photochemical reaction processes related to H_2O are most of importance; the next important factor is the solar UV radiation, and third one is the atmospheric aerosols. The method proposed in this paper for calculating total ozone amount gives satisfactory results for the 1990—1991 two-year data. In comparison with the observations, maximum relative deviation of calculations is 4.93% and the mean deviation for 12 months is less than 2.2%.

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