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Atmospheric Environment 39 (2005) 4419–4423
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

An empirical correlation between surface O_3 and its factors

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Received 18 March 2004; received in revised form 16 September 2004; accepted 16 September 2004

Abstract

Observations were made of surface O_3, NO_x, UV radiation, and meteorological parameters at DBR, Guangdong province, and the statistical relationship of O_3 to its factors (NO_x, water, scattering, UV radiation) was studied. An empirical method was applied to estimate O_3. The calculated value agrees well with that observed under different sky conditions, and averaged relative biases of daily O_3 concentrations in clear and all sky conditions were $\leqslant 7\%$. A good correlation was found between O_3 and the ratio of NO_2/NO in clear and all sky conditions, and correlation coefficients between O_3 and NO_2/NO were more than 0.90. This empirical method can be used as a tool to analyze the relationship between O_3 and the factors affecting it. The analysis shows that O_3 is more sensitive to the change of NO and NO_2 than that of other factors.

Keywords: Surface O_3; NO_x; UV radiation; Aerosol; Water vapor

1. Introduction

O_3 is a key trace gas in the earth's troposphere. Photodissociation of O_3 near 300 nm wavelength in the presence of water vapor yields OH radicals, which controls the lifetime of many gases (Levy, 1971). During daytime, photochemical processes mainly control the O_3 production and destruction. As a result of anthropogenic emissions of NO_x, tropospheric O_3 has substantially increased over preindustrial values (Volz and Kley, 1988), most notably East Asia, due to the continued rapid increase of NO_x emissions from East Asia (Streets and Waldhoff, 2000). Increases in tropospheric O_3 contribute to radiative forcing of the atmosphere (IPCC, 1996). High concentrations of O_3 in the lower troposphere have a deleterious effect on human health and vegetation. In model calculations of tropospheric O_3, uncertainties in kinetics and other variables may be assessed, but the chemistry of organic compounds often cannot. On the other hand, it maybe another practical method to explore the complex chemical and photochemical processes of O_3 and relationships between O_3 and its major factors in the troposphere by an empirical analysis.

2. Instruments and observation

Field experiments were made at Dinghushan Biosphere Reserve (DBR) (23°10′N, 112°32′E), Guangdong

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doi:10.1016/j.atmosenv.2004.09.070

province. The continuous measurements of surface O_3, NO, NO_2, solar spectral radiation, meteorological parameters have been made at DBR between June 1998 and December 1998. DBR is a subtropical evergreen broad-leaf forest. The instruments were installed on a building surrounded by forest. O_3 and NO_x measurements were made using Thermo Environment Inc. Model 49 O_3 analyzer and model 42S NO–NO_2–NO_x analyzer; the analyzers were calibrated periodically. The observational instruments of solar radiation consist of two parts. (1) Four sensors, their wavelength ranges are 290–3200 nm, 400–3200 nm, 700–3200 nm, and 290–400 nm (TUVR, Eppley Laboratory Inc.). (2) Solar radiation recorder, model RYJ-2; its accuracy is $\pm 5\%$. The data collecting frequency for gases and solar radiation was 1 Hz, the air temperature (dry and wet bulb), cloudiness, and weather conditions were observed hourly.

3. The relationship between the surface ozone and the factors affecting it

3.1. The relationship between O_3 and NO_2/NO

Based on 6 months data from June to December 1998 in DBR, a good relationship between O_3 and NO_2/NO was found. In clear sky (cloudiness $<3/10$) and all sky (cloudiness $\leqslant 9/10$) conditions, the ratio of NO_2/NO and O_3 concentration increase or decrease basically in the same phase. In clear sky condition, the correlation coefficient (R) between O_3 and NO_2/NO was 0.91 for 113 hourly averaged values, and 0.93 for 20 daily values. In all sky condition, 0.91 for 317 hourly averaged values, and 0.79 for 46 daily values. Figs. 1a and b show the variation of O_3 and NO_2/NO, NO, NO_2 for 113 hourly averaged values in clear sky during June and December 1998 in DBR.

High or low O_3 concentrations are correlated by the ratio of NO_2/NO. The ratio NO_2/NO may be called O_3 indicator and may reflect the degree of atmospheric oxidation power. In this paper, we present an empirical method to study complicated relationship between O_3 and its factors.

3.2. A good empirical correlation between O_3 and the main factors affecting it

The O_3 photochemical processes are driven by solar UV (290–400 nm) radiation. When UV transfers through the atmosphere, 3 main aspects should be considered simply. (1) Direct UV absorption by some gases, including NO_2, O_3. The absorption of NO, NO_2, and O_3 to UV are empirically expressed by $e^{-k_i n_i m}$, respectively. k_i ($i = 1, 2, 3$) are the averaged absorption coefficients of NO, NO_2, and O_3 in the UV band (290–400 nm), and 1, 8.61×10^4 and 3.26×10^5 $(\text{Pa cm})^{-1}$, respectively (Schneider et al., 1987; Gushin, 1963). NO has no direct UV absorption, but it plays important role in O_3, NO_2 chemical and photochemical reactions. So, an expression similar to that for NO_2 was used. For NO, k_1 was set to $1\,\text{Pa cm}^{-1}$. n_i ($i = 1, 2, 3$) are

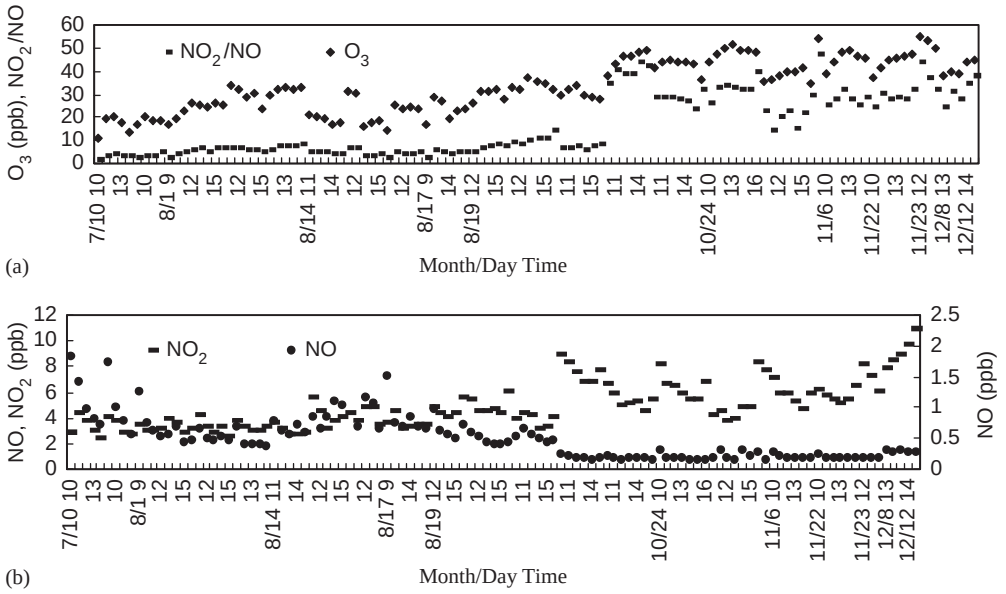

Fig. 1. (a) Variation of O_3 and NO_2/NO at DBR in clear sky from June to December in 1998. (b) Variation of NO, and NO_2 at DBR in clear sky from June to December in 1998.