

Development of a direct measurement system of photochemical ozone production rate in the troposphere

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Recently, ozone concentrations in the troposphere have been rising in spite of a steady decrease in concentrations of ozone precursors such as NO_x and volatile organic compounds. Photochemical production processes of ozone are non-linear to concentrations of ozone precursors. In addition, ozone concentration variations are influenced by meteorological factors such as transport and deposition processes as well as photochemistry. It is useful that the meteorological and photochemical factors could be divided to discuss ozone concentration variations. In order to discuss only "photochemical" factors for ozone production, a direct measurement system of photochemical ozone production rate has been developed.

Ambient air is introduced into "reaction" and "reference" chambers. The reaction and reference chambers (171-mm inner diameter and 500-mm length) are made of quartz and Pyrex, respectively. Inner walls of both the chambers are coated with Teflon to avoid wall loss of ozone. An outer wall of the reference chamber is coated with a UV-cut film (50%-cutoff wavelength of 405 nm). In the reaction chamber, photochemical reactions proceed to generate ozone. On the other hand, ozone is not produced photochemically in the reference chamber. Air passed from the reaction and reference chambers is introduced into "NO-reaction" tubes to convert O_3 to NO_2 in the presence of a high concentration of NO, and then the air is introduced into an NO_2 measurement system by a laser-induced fluorescence technique. Increment of ozone (ΔO_3) is defined by the difference of NO_2 concentrations derived from the reaction chamber and those from reference chamber. The ozone production rate is obtained by dividing ΔO_3 by a mean residence time of air in the reaction chamber (τ). In this system, O_3 concentrations are not directly measured but NO_2 concentrations converted by the reaction of O_3 with excess NO are observed. This is because the photostationary states between NO_x and O_3 are different between in the reaction and reference chambers, and ozone concentrations vary apparently. The sum of ozone and NO_2 concentrations (abbreviated as PO) are kept in the different photostationary states, so that this instrument measures production rates of PO instead of those of ozone practically.

Important parameters in this system are (1) ultraviolet transmittance of the reaction and reference chambers, (2) τ , and (3) conversion efficiency of O_3 to NO_2 in the NO-reaction tube. For (1), we measured solar spectra at inside and outside of the chambers using a spectroradiometer. Almost a hundred % of solar UV was transmitted into the reaction chamber. A wall of the reference chamber cut off solar UV adequately. For (2), about 10 ppmv of pulsed NO_2 was added into the reaction chamber and temporal variations of LIF signals were measured. τ was calculated to be 22.1 ± 0.5 min using the temporal variation the signals. For (3), quantitative conversions of O_3 up to 160 ppbv by NO in the NO-reaction tube were confirmed under the excess NO condition 0.97 ppmv.

Keywords: photochemical ozone, direct measurement of ozone production rate, laser-induced fluorescence