

Direct measurements of photochemical ozone production rate at a forest area in Japan during summer of 2014

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We developed a direct measurement system of photochemical ozone production rate in order to evaluate ozone concentration variations quantitatively. In fact, this system measures oxidant ($Ox = O_3 + NO_2$) production rate. The use of Ox can ignore the concentration variations of O_3 due to titration of O_3 by NO. The field campaign was performed at Wakayama, a remote site, in Japan during summer of 2014. Measurement parameters were photochemical net Ox production rate ($P-L(Ox)$), $[O_3]$, $[NO]$, $[NO_2]$, $[RO_2]$, $[VOCs]$, OH reactivity, photolysis frequencies of various trace species and so on.

The $P-L(Ox)$ measurement system has "reaction" and "reference" chambers. The reaction and reference chambers (17.1-cm inner diameter and 50-cm length) are made of quartz and Pyrex, respectively. Inner walls of both the chambers are coated with clear Teflon films to avoid wall loss of O_3 . An outer wall of the reference chamber is coated with a UV-cut film (50% cutoff wave length of 405 nm). Both the chambers were put in an outdoor location to be exposed directly to sunlight. Ambient air is introduced into both the chambers. In the reaction chamber, photochemical reactions proceed to generate Ox. On the other hand, Ox is not generated in the reference chamber. The difference of Ox concentrations (ΔOx) in air from the two chambers is the Ox produced by photochemical reactions in the reaction chamber. The $P-L(Ox)$ is obtained by dividing ΔOx by a mean residence time of air in the reaction chamber. Ox concentrations were obtained as follows. O_3 in Ox is converted into NO_2 by the reaction of O_3 with large excess of NO, and then the NO_2 concentration is measured by a laser-induced fluorescence technique.

The field campaign was conducted at Field Science Education and Research Center, Kyoto University, Wakayama Forest Research Station, in Wakayama Prefecture, Japan. Observation site is in forest area and anthropogenic sources of air pollutants are very low. Observations were conducted from 28 July to 8 August. Most periods of the campaign, O_3 concentrations were approximately 10 ppbv in the daytime. $NO_x (= NO + NO_2)$ concentrations were less than about 1 ppbv throughout the campaign. BVOCs (Biogenic Volatile Organic Compounds) concentrations were high. Results of $P-L(Ox)$ and Ox concentration on 6 August were reported in this abstract. A diurnal variations were observed for $P-L(Ox)$ and Ox concentration, and the maximum rate and concentration were observed around noon. Ox concentration increased in the early morning, while $P-L(Ox)$ was still 0 ppbv h^{-1} and then increased after a few hours. This result shows that O_3 concentration is increased by non-photochemical factors in the early morning. Vertical mixing of air is weak at night and O_3 concentration near the surface of the ground decreases by deposition, reactions with olefin and so on. Surface of the ground is gradually warmed by sunlight in the morning and vertical mixing of air is activated. O_3 concentration would increase because of O_3 influx from above. $P-L(Ox)$ achieved a peak value around noon and photochemical O_3 production was active in the daytime. Ox concentration did not increase around noon, however. This suggests that O_3 increase by photochemical production competes against O_3 decrease by non-photochemical factors such as deposition, advection, and reactions of O_3 with olefin.

Keywords: photochemical ozone production rate, oxidant, forest area