

## 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 ( $\Delta Ox$ ) 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  $\Delta Ox$  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