Abstract

[Research Title]

Diagnosis of dynamics and chemistry of reactive nitrogen oxides in the formation of photochemical oxidants

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[Abstract]

In Japan, the concentrations of precursors of photochemical oxidants, such as nitrogen oxides (NOx) and non-methane hydrocarbons (NMHCs), are decreasing annually, but improvements in the photochemical oxidant concentration level have recently stagnated. We conducted extensive seasonal observations in Tokyo to determine the cause of this, and we measured a wide range of non-methane volatile organic compounds and speciated reactive nitrogen NOy. In the intensive observation, NO, NO_2, ΣPANs (peroxy acyl nitrates), ΣONs (organic nitrates), HONO, HNO_3, H_2O_2, SO_2, O_3, 28 NMHCs, and 10 oxygenated volatile organic compounds (OVOCs) were measured simultaneously. The ΣPNs and ΣONs were measured by thermal dissociation-cavity attenuated phase shift (CAPS) spectroscopy, which was modified for use in urban and/or suburban atmosphere. The HONO, HNO_3, and H_2O_2 were measured by negative ion chemical ionization mass spectrometry using $I^-\cdot(H_2O)_n$ as the reagent ion. A selected-ion flow-tube mass spectrometer was used to measure the NMHCs and OVOCs. In 2022, observations were made at Tokyo Metropolitan University, a suburban location, and in 2023, at Tokyo Metropolitan Research Institute for Environmental Protection, an urban location. Since PANs were formed early in the day in the presence of relatively high concentrations of acetaldehyde, and an enhancement of PANs in the morning seems to bring a rapid rise in O_3, it is thought that small OVOCs, such as acetaldehyde, may play an important role in recent photochemistry related to ozone formation in urban areas of Japan. Indeed, we showed that the contribution of formaldehyde and acetaldehyde to the ozone formation potential among VOCs was substantial from 6 to 9 am.

In addition, continuous observations of PANs were conducted at urban (Koutou-ku and Sakai-shi) and suburban (Tokorozawa-shi, Hachioji-shi, and Tsukuba-shi) sites. In summer, potential ozone ($PO = O_3 + NO_2$) and PANs typically indicate diurnal variations, with peaks in the afternoon. PO is correlated with PANs on sunny days. High temperature and low NOx/NMHC ratios were frequently associated with high PO and PANs events. It was suggested that high PO and PANs concentrations could be observed when the photochemical activities were high and the regime of photochemical ozone formation was NOx-limited. Consequently, the

practical utility of the PANs monitor was confirmed during the long-term continuous observation of PANs. It was also confirmed that the correlation between total PANs and PO could be promising for evaluating and capturing photochemical ozone, including outstanding ozone events.

[References]

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