Response of total ozone reactivity analyzer to mixture of gaseous isoprene and NO

*Jun Matsumoto[1], Roberto Sommariva[2]

1. Faculty of Human Sciences, Waseda University, 2. School of Geography, Earth and Environmental Sciences, University of Birmingham

Biogenic volatile organic compounds (BVOCs) have been focused on as precursors of tropospheric ozone (O_3) and secondary organic aerosols. Various species of BVOCs have C=C double bonds and can react with O_3. To capture BVOCs comprehensively, a total ozone reactivity (R_{O3}, the sum of k_i[VOC_i]) analyzer has been developed [1-4]. R_{O3} of sample BVOCs can be determined when decrease of O_3 due to BVOCs+O_3 is precisely monitored. In our previous studies, the detection limit of the analyzer reached 6.3×10^{-5} s^{-1} (*S/N*=3, 60-s average, 50-s reaction) [4]. To apply the analyzer to field observations where the samples consist of multiple compounds, characteristics of the analyzer should be explored further. For example, nitric oxide, NO, which exists significantly everywhere in the troposphere, can react with ozone rapidly. When BVOCs are captured as R_{O3}, NO can be detected simultaneously. A model study reported that, even when R_{O3} in the forest atmosphere is focused, contribution of NO to R_{O3} can be critical [5]. Generally, NO concentration can be captured easily utilizing an NO analyzer. Thus, if dependence of the output of R_{O3} analyzer on NO concentration is understood, contribution of NO to observed R_{O3} can be separated and R_{O3} due to BVOCs can be accurately quantified. In this study, mixtures of isoprene and NO standard gases were prepared and response of R_{O3} analyzer to the mixtures was experimentally captured in order to explore the possibilities of the standard addition method of NO to BVOCs samples. As a result, among the isoprene standard sample (A) and NO-added isoprene samples (B, C, D), a strong correlation was observed between the concentration of NO and the measured R_{O3} as shown in Fig.1. The intercept of the regression line agreed well with the observed R_{O3} of isoprene standard sample (A). It was experimentally confirmed that, when NO addition was conducted, the contribution of BVOCs (isoprene in the figure) to R_{O3} could be determined as the intercept of the regression line between NO concentration and measured R_{O3}. Consequently, the method of standard addition to separate the contribution of NO from observed R_{O3} was established. Evaluation of BVOCs as R_{O3} is possible even when NO coexists in the sample. As a next step, application of this method to R_{O3} observations for studying BVOCs emission from real plants and/or ambient samples is promising.

[1] Matsumoto, J., AGU Fall Meeting 2011, USA, A51A-0232 (2011).
[2] Matsumoto, J., Aerosol Air Qual. Res., 14, 197-206 (2014).
[3] Matsumoto, J., 1st OH Reactivity Specialists Uniting Meeting, Germany (2014).
[4] Matsumoto, J., Chem. Lett., 45, 1102-1104 (2016).
[5] Mogensen et al., Atmos. Chem. Phys., 15, 3909-3932 (2015).

Keywords: biogenic VOCs, nitrogen oxides, standard addition method

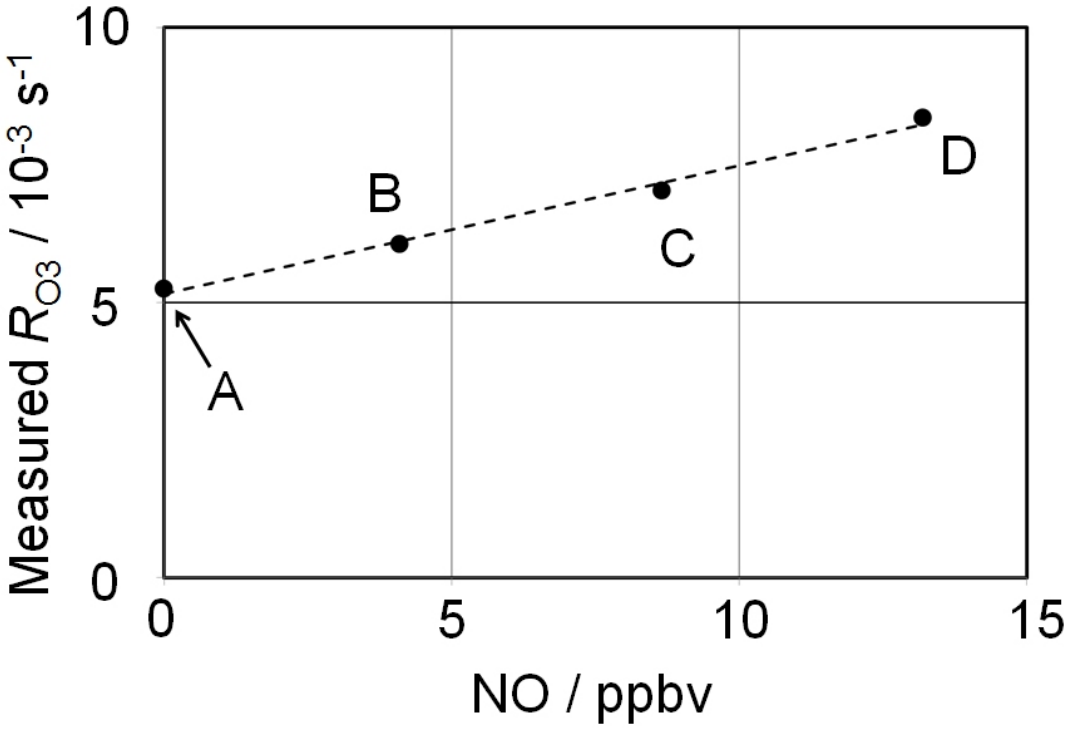

Fig.1 Observed relationship between NO mixing ratio and measured ozone reactivity. A: isoprene standard sample. B, C, D: NO-added isoprene samples. Regression line (dashed line): slope 2.3×10^{-4} s^{-1} $ppbv^{-1}$, intercept 5.2×10^{-3} s^{-1}.

