Constraining the origin of tropospheric nitrous acid using triple oxygen isotopes as tracers

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The photolysis of nitrous acid (HONO) has been recognized as a potentially important source of OH radicals, which is known as a major oxidant in the atmosphere removing reductive trace gases such as methane and NMHCs. Atmospheric HONO originates from both primary sources (direct emissions) and secondary sources (chemical formation in the atmosphere), however, their contributions to the atmospheric HONO production have not been well understood. Here, we determined a $\Delta^{17}O$ value of HONO together with $\Delta^{17}O$ value of $NO_2$and NO, because $\Delta^{17}O$ value of HONO produced via “secondary formation” is expected to have highly positive values as those of NO_2, while no $\Delta^{17}O$ anomaly should be observed for HONO which is emitted directly from various sources on the ground, making it possible to quantify their contribution to the atmospheric HONO production with $\Delta^{17}O$ measurement.

$\Delta^{17}O$ values of HONO, $NO_2$and NO was determined by combining sensitive determination method on isotope compositions of NO_2^-(Komatsu *et al.*, 2008; Tsunogai *et al.*, 2010) with a slightly modified filter-pack method (Noguchi *et al.*, 2007), in which HONO, $NO_2$and NOxwere collected as NO_2^-on alkaline (K_2CO_3) impregnated filter, triethanolamine (TEA)-coated filter, and mixture of 2-Phenyl-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (PTIO) and TEA-coated filter, respectively. Atmospheric HONO, $NO_2$and NO were collected at Nagoya University, which is located in a suburban area of Nagoya City. The sample collection period was fixed to three days with a flow rate of 10 L/min for HONO or $NO_2$and 1 L/min for NO, respectively.The $\Delta^{17}O$ values of $NO_2$and HONO showed similar diurnal variations; higher value on the day time than the night time. The result suggests that the atmospheric HONO is formed mainly by both direct emission and chemical reaction of NO_2 in the urban atmosphere.

Keywords: nitrous acid, triple oxygen isotopes, urban air, nitrogen dioxide, nitrogen monoxide

