Triple oxygen isotopic compositions of atmospheric HONO: Evidence for the importance of primary sources

F. NAKAGAWA[1]*, R. NAKANE[1], U. TSUNOGAI[1], K. SUDO[1], I. NOGUCHI[2] AND T. YAMAGUCHI[2]

[1] Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, JAPAN (*correspondence: f.nakagawa@nagoya-u.jp)

[2] Hokkaido Institute of Environmental Sciences, N19 W12 Kita-ku, Sapporo 060-0819, JAPAN

The photolysis of tropospheric nitrous acid (HONO) has been recognized as a potentially important source of OH radicals, known as a representative oxidant in the atmosphere removing reductive trace gases such as methane and NMHCs. Atmospheric HONO could originate from both primary sources (direct emissions) and secondary sources (photochemical formation in the atmosphere). Their relative importances on the production of atmospheric HONO, however, have not been well understood. Here, we determined the triple oxygen isotopes of HONO because the $\Delta^{17}O$ values of HONO produced via "secondary formation" can be expected to have positive values as high as those of O_3 ($\Delta^{17}O$ = +30 ±10‰), while little anomaly ($\Delta^{17}O$ = 0‰) should be expected for HONO emitted directly from various sources on the earth surface, which enable us to quantify their relative importances on the atmospheric HONO.

Periodical sampling of atmospheric HONO was carried out once a month since December, 2014, at Hokkaido Institute of Environmental Sciences, Sapporo, Japan. The sample collection period was fixed to one week with a flow rate of 10 L/min. The $\Delta^{17}O$ value of HONO was determined by combining sensitive determination method on isotope compositions of NO_2^- [1, 2] with filter-pack method [3] in which HONO was collected as NO_2^- on alkaline impregnated filters. The daily mean $\Delta^{17}O$ values of HONO ranged from +6.9‰ to +10.7‰ through the observation periods, while the $\Delta^{17}O$ values of HONO showed higher value on the day time than the night time. The estimated mixing ratios of HONO derived from secondary formation in Sapporo was almost constant throughout the year of around 34% leading us to conclude that the direct emissions are the dominant HONO sources in Sapporo.

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[2] Tsunogai et al. (2010) *Atmos. Chem. Phys.* **10**, 1809-1820.
[3] Noguchi et al. (2007) *J. Jpn. Soc. Atmos. Environ.* **42**, 162-173