

^{17}O -excess of nitrous acid (HONO) in urban atmosphere: quantification of its sources

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Nitrous acid (HONO) is an important trace gas in the atmosphere because it plays an important role in tropospheric cycling of hydrogen oxides (HO_x) and nitrogen oxides (NO_x) due to the photolysis reaction: $\text{HONO} + h\nu \rightarrow \text{OH} + \text{NO}$. The sources of atmospheric HONO, however, are not well understood, especially during the daytime, and need to elucidate the existing “unknown” sources, as well as precise estimation of formation rates of the “known” sources. The HONO sources can be divided into two categories: direct emissions and secondary formation. The former includes vehicle or industrial exhausts, biomass burning and soil microbial activities, while the latter indicates reactions of atmospheric NO, NO_2 or nitrate (NO_3^-) via homogeneous and/or heterogeneous, such as homogeneous gas phase formation reaction ($\text{NO} + \text{OH} \rightarrow \text{HONO}$), or the heterogeneous conversion of NO_2 on humid surface with a first-order for NO_2 ($2\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{ads}) \rightarrow \text{HONO}(\text{g}) + \text{HNO}_3(\text{ads})$). In order to estimate their relative importance, we used ^{17}O -excess of atmospheric HONO as tracer; $\Delta^{17}\text{O}$ values of HONO produced via secondary processes should have positive values owing to part/all of oxygen atoms originate from ozone ($\Delta^{17}\text{O} > +30\text{‰}$), while $\Delta^{17}\text{O}$ value in directly emitted HONO should be zero because its oxygen atoms derive from H_2O or O_2 .

In this study, the $\Delta^{17}\text{O}$ value of HONO was determined by combining sensitive determination method on isotopic compositions of NO_2^- [Komatsu et al. (2008), Tsunogai et al. (2010)] with filter-pack method [Noguchi et al. (2007)] in which HONO was collected as NO_2^- on alkaline (K_2CO_3) impregnated filters. In order to determine diurnal variation in $\Delta^{17}\text{O}$ value of HONO, an automated system for time-interval air sampling equipped with 6 four-stage-filter-packs were made and used it to collect atmospheric samples every 4 hours (16:00~20:00, 20:00~24:00, 0:00~4:00, 4:00~8:00, 8:00~12:00, 12:00~16:00, local time). The same K_2CO_3 impregnated filter, which is placed right after the first K_2CO_3 impregnated filter, was used to evaluate NO_2 -derived NO_2^- on the filter, and eliminate its influence on isotope measurements of atmospheric HONO.

Periodical sampling of atmospheric HONO was carried out at two sites; (1) at the roof of the Institute of Environmental Sciences in Sapporo, Japan (43° 04' 55" N, 141° 20' 00" E, 26m above ground) and (2) Graduate School of Environmental Studies, Nagoya University (35° 09' 07" N, 136° 58' 20" E). The sample collection period was fixed to 3 to 7 days and with a flow rate of 10L/min. The daily mean $\Delta^{17}\text{O}$ values of HONO ranged from +15‰ (December) to +17‰ (September) through the observation periods. The $\Delta^{17}\text{O}$ values of HONO showed large diurnal variation; maximum value was observed around noon, while minimum value was found at night. The increasing $\Delta^{17}\text{O}$ value after sunrise results from sunlight induced rapid production of HONO via secondary formation. There were no clear seasonal variation in $\Delta^{17}\text{O}$ (HONO) of urban atmosphere. The estimated contribution of HONO derived from secondary formation in Nagoya was almost constant throughout the year of around 60%, leading us to conclude that the secondary formation are the dominant HONO sources in Nagoya. The result is apparently higher than that at Sapporo (around 30%), which might be due to higher NO_2 concentration in Nagoya than that in Sapporo.

Keywords: HONO, triple oxygen isotopic composition

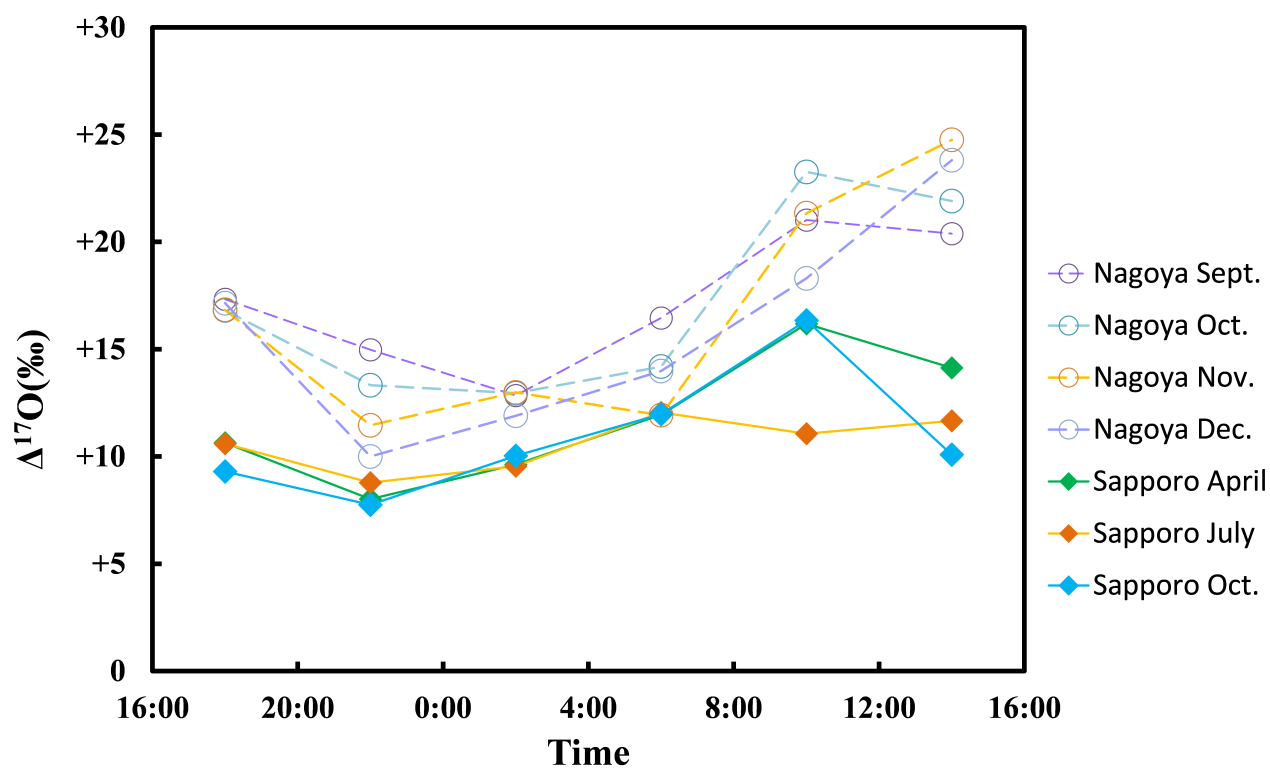


Figure 1. Temporal variation of HONO $\Delta^{17}\text{O}$ values at Nagoya and Sapporo.