

Determination on the triple oxygen isotopic composition of atmospheric nitrous acid (HONO)

NAKANE, Ray^{1*}; OHYAMA, Takuya¹; NAKAGAWA, Fumiko¹; TSUNOGAI, Urumu¹; NOGUCHI, Izumi²; YAMAGUCHI, Takashi²

¹Graduate School of Environmental Studies, Nagoya University, ²Hokkaido Institute of Environmental Sciences

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. There are two major formation pathways to produce atmospheric HONO, one is a process so-called “direct emission” in which HONO emits directly from various sources on the ground and the other “secondary formation” in which HONO is produced by chemical reaction of nitrogen compounds in the atmosphere. Their contributions to the production of atmospheric HONO, however, have not been well understood.

In order to quantify the contribution of HONO derived from secondary formation, we determined a triple oxygen isotope, $\Delta^{17}\text{O}$ value of atmospheric nitrous acid (HONO). $\Delta^{17}\text{O}$ value of HONO produced via secondary formation is expected to have highly positive values as those of O_3 ($\Delta^{17}\text{O} = +30 \pm 10 \text{‰}$), while no $\Delta^{17}\text{O}$ anomaly ($\Delta^{17}\text{O} = 0 \text{‰}$) should be observed for HONO which is emitted directly from various sources on the ground.

Atmospheric HONO was collected using filter-pack method (Noguchi et al., 2007) in which HONO accumulates on the K_2CO_3 impregnated filter as NO_2^- . Since HONO is collected as NO_2^- , we must be careful about oxygen exchange between NO_2^- and H_2O on the filter. If the sampling period becomes longer, $\Delta^{17}\text{O}$ of HONO could become smaller than the original value due to rapid oxygen exchange between NO_2^- and H_2O on the filter. Therefore, in order to decide appropriate sampling periods for $\Delta^{17}\text{O}$ measurement of HONO, we conducted a field sampling of atmospheric HONO during December 15-26, 2014, at Hokkaido Institute of Environmental Sciences, Sapporo, Japan. We arranged seven different periods (half a day, one day, two days, three days, four days, one week and two weeks) for atmospheric HONO collection. We also set two kinds of sampling flow rate for HONO sampling; faster flow rate (10 L/min) for shorter sampling periods (from half a day to three days) and slower flow rate (4 L/min) for longer sampling periods (from four days to two weeks). HONO-derived NO_2^- on the filter was extracted to pure water. After that, it was reduced to N_2O using HN_3 and then converted to O_2 via thermal decomposition and then introduced to IRMS for $\Delta^{17}\text{O}$ measurement. The concentration of NO_2^- and NO_3^- in the extracted water were measured by traditional ion chromatography to calculate NO_2^- yield (ratio of NO_2^- among the sum of NO_2^- and NO_3^-) on the filter.

We found clear difference on NO_2^- yield absorbed on the filter between the two sample flow rates. Low flow rate (4 L/min) result in lower NO_2^- yield of around 79% on average which coincide well with those reported previously (76%, Ohyama et al., 2012). Very high NO_2^- yield of more than 98% were observed in the filter collected at high rates (10 L/min). We concluded that we could prevent NO_3^- formation via reaction of NO_2^- with O_3 by collecting HONO in the condition of higher sample flow rate.

The result of $\Delta^{17}\text{O}$ value of HONO ranged from +6 ‰ to +9 ‰ through the observation periods. We could not find any $\Delta^{17}\text{O}$ depletion due to oxygen exchange between NO_2^- and H_2O on the filter during the collection periods. Assuming that $\Delta^{17}\text{O}$ value of HONO derived from secondary formation is +35 ‰, the contribution of HONO produced via secondary formation to atmospheric HONO was estimated to be about more than 20% demonstrating its significance on the formation pathway of atmospheric HONO in the winter of urban area.

Keywords: HONO, nitrous acid, triple oxygen isotope, source, winter, Sapporo