

Estimating secondary formation of atmospheric HONO 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 atmospheric HONO production have not been well understood. Here, we determined a triple oxygen isotope of HONO because $\Delta^{17}\text{O}$ value of HONO produced via "secondary formation" is expected to have highly positive values as those of O_3 ($\Delta^{17}\text{O} = +30 \pm 10\%$), while no $\Delta^{17}\text{O}$ anomaly ($\Delta^{17}\text{O} = 0\%$) 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 $\Delta^{17}\text{O}$ measurement. Periodical sampling of atmospheric HONO was carried out once a month starting from 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. $\Delta^{17}\text{O}$ value of HONO was determined by combining sensitive determination method on isotope compositions of NO_2^- (Komatsu *et al.*, 2008; Tsunogai *et al.*, 2010) with filter-pack method (Noguchi *et al.*, 2007) in which to collect HONO as NO_2^- . The result of daily mean $\Delta^{17}\text{O}$ value of HONO ranged from +6.9% to +10.7% through the observation periods. $\Delta^{17}\text{O}$ value of HONO showed higher value on the day time than night time. The ratios of HONO derived from secondary formation in Sapporo was almost constant throughout the year (day and night : 34±2%, day : 66±8%, night : 21±2%) leading to conclusion that direct emissions are dominant HONO sources in Sapporo.

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