

## Measurement on the $^{17}\text{O}$ -excess of tropospheric nitrogen oxides

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Nitrogen oxides are important trace gases that influence the concentrations of atmospheric oxidants that drive tropospheric and stratospheric chemistry. Triple oxygen isotopes ( $\Delta^{17}\text{O}$  values; deviation of  $^{17}\text{O}$  from the mass dependent fractionation line) have been used to understand complex chemical systems such as the cycling and oxidation of NOx. For example,  $\Delta^{17}\text{O}$  values of atmospheric nitrate ( $\text{HNO}_3$ ,  $\text{NO}_3^-$ , and p- $\text{NO}_3^-$ ), indicates the proportion of NOx that reacts with ozone ( $\text{O}_3$ ) during its oxidation (Michalski *et al.*, 2003; Tsunogai *et al.*, 2010; Nelson *et al.*, 2018).  $\Delta^{17}\text{O}$  values of atmospheric nitrous acid (HONO; recognized as a potentially important source of OH radicals) have also been used recently to decipher their production pathways. In these studies, however, predicted  $\Delta^{17}\text{O}$  values were used for  $\text{NO}_2$ . Here, we tried to establish a method to determine  $\Delta^{17}\text{O}$  values of atmospheric  $\text{NO}_2$ .

$\Delta^{17}\text{O}$  value of  $\text{NO}_2$  was determined, together with  $\Delta^{17}\text{O}$  value of HONO, by combining sensitive determination method on isotope compositions of  $\text{NO}_2^-$  (Komatsu *et al.*, 2008; Tsunogai *et al.*, 2010) with a slightly modified filter-pack method (Noguchi *et al.*, 2007), in which both  $\text{NO}_2$  and HONO were collected simultaneously as  $\text{NO}_2^-$  on triethanolamine (TEA)-coated filter and alkaline ( $\text{K}_2\text{CO}_3$ ) impregnated filter, respectively. Periodical sampling of atmospheric  $\text{NO}_2$  and HONO was carried out at Hokkaido Institute of Environmental Sciences, Sapporo and at Nagoya University, which is located in a suburban area of Nagoya City. The sample collection period was fixed to one week with a flow rate of 10 L/min. In order to determine diurnal variation in  $\Delta^{17}\text{O}$  value of  $\text{NO}_2$  and 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. The  $\Delta^{17}\text{O}$  values of  $\text{NO}_2$  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 chemical reaction of NOx in the urban atmosphere.

Keywords: nitrogen oxides, troposphere, triple oxygen isotope