

Distribution and temporal variation of isotopomer ratios in tropospheric N₂O

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Nitrous oxide (N₂O) acts as a greenhouse gas in the troposphere and also participates in ozone chemistry in the stratosphere. Its global budget has not been closed because estimates of fluxes from natural and anthropogenic sources have large uncertainty. Nitrogen and oxygen stable isotope ratios in N₂O have been found to be useful parameters to estimate its origin and processes such as production, transportation, and decomposition. We developed an analytical method for isotopomer ratios which include intramolecular ¹⁵N distribution as well as conventional elemental isotope ratios, and have been making researches on the distribution of N₂O isotopomers in the atmosphere, ocean, and the gases from various sources, as well as their fractionation during the simulated production/decomposition reactions. Here we report monitoring results of N₂O isotopomer ratios in the troposphere observed in Hateruma island, Japan (24N, 124E) and Siberia near Novosibirsk, Russia (55N, 83E).

Air samples are collected monthly into 1~3-liter glass or stainless steel flasks at 1.5~3 kg/cm² using a pump. In Hateruma, air is taken from a tower (46.5 m above sea level) of NIES monitoring station. In Siberia, air is sampled at 500 m and 7000 m above surface using an air plane. After concentration of trace gases such as CO₂, CH₄, and N₂O are measured at NIES, isotopomer ratios $\delta^{15}\text{N}^{\text{bulk}}$, $\delta^{18}\text{O}$, and site preference (difference between isotope ratios at central and terminal N in the NNO molecule) are measured at Tokyo Tech. Analytical precision for about 300 ml STP air sample is 0.1 permil, 0.2 permil, and 0.5 permil, respectively.

In order to estimate non-contaminated, baseline concentration and isotopomer ratios in the subtropical latitudes, data obtained at Hateruma were sorted by origin of the observed air mass using backward trajectory analysis. From the data for maritime air mass, it is found that, for the period between 1999 and 2006, N₂O concentration increased at the rate of about 0.6 ppb/yr while $\delta^{15}\text{N}^{\text{bulk}}$ decreased by 0.3-0.4 permil. Linear regression analysis for $\delta^{18}\text{O}$ and site preference during the same period showed a slight decrease and increase, respectively, but uncertainty of their trends is large. The isotopomeric results are consistent with the rates for the past 100 years obtained from Antarctic firn air analysis [Sowers et al., 2002; Roeckmann et al., 2003] or those for recent 12 years obtained from archived Antarctic air samples [Roeckmann and Levin, 2005]. The decreasing trend of $\delta^{15}\text{N}^{\text{bulk}}$ suggests that isotopically depleted N₂O produced by microorganisms in natural or agricultural soils is responsible for the N₂O increase in the atmosphere.

The concentration and isotopomer ratios observed over Siberia between 2005 and 2006 almost coincide with those at Hateruma for the same period, and secular trend has not been recognized. However, data at 500 m and 7000 m are sometimes different, which may reflect the surface sources or intrusion of stratospheric air.