Secular trend of atmospheric N_2O isotopocule ratios observed at Syowa staion, Antarctica

*Sakae Toyoda[1], Tsutomu Mizuno[1], Daisuke Goto[2], Shinji Morimoto[3]

1. School of Materials and Chemical Technology, Tokyo Institute of Technology, 2. National Institute of Polar Research, 3. Center for Atmospheric and Oceanic Studies, Tohoku University

Nitrous oxide (N_2O) is one of the increasing greenhouse gases in the troposphere and is the most important stratospheric ozone-depleting gas in the 21st century. Sources of atmospheric N_2O include oceans, natural soils, and human activity such as agriculture, fossil fuel combustion, and chemical industry. In addition to conventional concentration or flux measurements of N_2O, isotopocule ratios of N_2O, which include not only elemental $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios but also site-specific $^{15}N/^{14}N$ ratio in asymmetric NNO molecule, have been used as parameters to infer the origin and production–consumption mechanisms of N_2O. Since secular trend of isotopocule ratios of atmospheric N_2O can be used to deduce relative contribution from each source, several efforts have been made by analyzing air trapped in the polar firn or air samples collected at monitoring stations. However, there have been only a few reports on long-term monitoring of atmospheric N_2O isotopocule ratios in the Southern Hemisphere. Moreover, the north-to-south gradient of isotopocule ratios remains uncertain because published data by different laboratories cannot be compared directly due to calibration problems.

In this study, we aimed at revealing isotopocule ratios of atmospheric N_2O and their trend in the Southern Hemisphere, and comparing with their counterparts in the Northern Hemisphere which were measured by the same laboratory. Surface air samples were collected into an aluminum cylinder at about 15MPa at Syowa station, Antarctica (69˚S, 40˚E) with 2–4 month interval in 1998–2020. They have been archived at NIPR, and were sub sampled to 1-L glass flasks for concentration and isotopic analyses of N_2O.
Isotopocule ratios of N_2O were measured using a GC-IRMS system which is also used to elucidate the secular trend of N_2O isotopes at three Northern Hemispheric sites, Hateruma Island, Japan (24˚N, 124˚E), Novosibirsk, Russia (55˚N, 83˚E), and Churchill, Canada (59˚N, 94˚W). Concentration was measured with GC-ECD.
Results showed that the bulk nitrogen isotope ratio ($\delta^{15}N^{bulk}$) in N_2O at Syowa station is decreasing at the similar rate (about -0.04‰ yr^{-1}) as observed in the Northern Hemispheric sites. When compared at the same year, the value of $\delta^{15}N^{bulk}$ is about 0.2‰ higher in the southern hemisphere. The oxygen isotope ratio ($\delta^{18}O$) also shows decreasing trend that is similar to the trend in the Northern Hemisphere, but north-to-south gradient is not detectable with the precision of the analysis. The ^{15}N-site preference in N_2O (SP) does not show secular increasing nor decreasing trend, and north-to-south gradient is not detectable.

These results suggest that contribution from southern hemispheric sources to atmospheric increase in N_2O is very small if we take into account the fact that concentration is higher in the Northern Hemisphere and that distributions of natural and anthropogenic sources are different between the two hemispheres. Further analysis of isotopic signature of N/S sources with simple model approaches will be discussed.

Keywords: Greenhouse gas, Stable isotope ratio, N2O, Southern Hemisphere

