Preparation of O_2/N_2 dataset from the surface to the middle stratosphere around Japan traceable to NMIJ gravimetric scale

*Shigeyuki Ishidoya[1], Shinji Morimoto[2], Kazuhiro Tsuboi[3], Satoshi Sugawara[4], Daisuke Goto[5], Nobuyuki Aoki[1], Shohei Murayama[1], Yosuke Niwa[6], Shuji Aoki[2], Hidekazu Matsueda[3], Kentaro Ishijima[3]

1. Advanced Industrial Science and Technology, 2. Tohoku University, 3. Meteorological Research Institute, 4. Miyagi University of Education, 5. National Institute of Polar Research, 6. National Institute for Environmental Studies

Atmospheric delta(O_2/N_2), defined by $[(O_2/N_2)_{sample}/(O_2/N_2)_{ref} -1]x10^6$, has been widely used to evaluate the global CO_2 budget and air-sea O_2 flux (e.g. Manning and Keeling, 2006; Tohjima et al., 2015). However, an absolute value of $(O_2/N_2)_{ref}$ has not been determined by each laboratory with required high-precision, which prevent a direct comparison of the observed delta(O_2/N_2) among the laboratories. To resolve the problem, Aoki et al. (2019) developed O_2, N_2, Ar and CO_2 standard mixtures with sufficient precision (less than 5 per meg in delta(O_2/N_2)) to determine the absolute value of $(O_2/N_2)_{ref}$ traceable to gravimetric scale of National Metrology Institute of Japan (NMIJ/AIST scale). For the direct comparison of delta(O_2/N_2), it is also known that natural and artificial molecular-diffusive fractionations must be considered especially for the aircraft and scientific balloon observations (e.g. Ishidoya et al., 2013, 2014; Stephens et al., 2021). In the present study, we prepare the tropospheric and stratospheric O_2/N_2 dataset around Japan traceable to NMIJ/AIST scale. For this purpose, we corrected an effect of the diffusive fractionations on delta(O_2/N_2) by using the simultaneously measured delta(Ar/N_2) and stable isotopic ratios of N_2, O_2 and Ar. The correction is applied to the air samples collected onboard MD90, B737, CRJ, ERJ and C130 aircrafts (updated from Ishidoya et al., 2012, 2014) and a stratospheric scientific balloon (updated from Ishidoya et al., 2013) over Japan; some air samples were measured by Environmental Management Research Institute of AIST (EMRI/AIST) and the others were by Tohoku University (TU) on their own scales. Then, we converted the corrected delta(O_2/N_2) to the NMIJ/AIST scale based on the inter-comparison experiments using our gravimetric standard mixtures (Aoki et al., 2021). We also applied the scale conversion to the delta(O_2/N_2) observed at some surface stations; Takayama, Minamitorishima and Ryori, Japan (updated from Ishidoya et al., 2017 and our unpublished data). From the prepared delta(O_2/N_2) dataset, we found secular decreasing trends of delta(O_2/N_2) for the period 1999-2020 both for the tropospheric and the stratospheric data, of which change rates were consistent with those reported by Scripps O_2 program (Keeling and Manning, 2014). We also confirmed that the spatial variations in the tropospheric and the stratospheric delta(O_2/N_2) were generally consistent with those expected from the surface O_2 flux and the atmospheric transport. These results suggest that we can compare each laboratory’ s delta(O_2/N_2) values, obtained by analyzing the air samples collected at various observational platforms, with a traceability to NMIJ/AIST.

Acknowledgements

We thank crews and staffs of Japan Airlines and J-Air for their kind cooperation to the air sampling on board MD90, CRJ, B737 and ERJ and staffs of Tohoku University for their works to analyze the air samples. We also thank staffs of Japan Meteorological Agency for their works to collect the air samples on board C130 and maintain the continuous measurements at Minamitorishima and Ryori. We would like to acknowledge many staffs of Japan Ministry of Defense for supporting the C-130H aircraft observation.

This study was partly supported by the JSPS KAKENHI Grant Number 15H02814, 18H03365, 19H01975, 19K03963 and 19K05554, and the Global Environment Research Coordination System from the Ministry of the Environment, Japan (grant nos. METI1454 and METI1953).

Keywords: atmospheric O2/N2 ratio, aircraft observation, scientific balloon, diffusive fractionation of O2 and N2, gravimetric standard gas

