Distribution and isotopic composition of N_2O in the eastern Indian Ocean

*Sakae Toyoda[1], Kotaro Terajima[1], Naohiro Yoshida[2], Chisato Yoshikawa[3], Akiko Makabe[4], Fuminori Hashihama[5], Hiroshi Ogawa[6]

1. School of Materials and Chemical Technology, Tokyo Institute of Technology, 2. Earth-Life Science Institute, Tokyo Institute of Technology, 3. Research Institute for Marine Resources Utilization, Japan Agency for Marine-Earth Science and Technology, 4. Institute for Extra-cutting-edge Science and Technology Avant-garde Research (X-star), Japan Agency for Marine-Earth Science and Technology, 5. Department of Ocean Sciences, Tokyo University of Marine Science and Technology, 6. Atmosphere and Ocean Research Institute, The University of Tokyo

Nitrous oxide (N_2O) is a trace gas that contributes to both global warming and stratospheric ozone depletion. Its major sources are nitrification and denitrification by microorganisms in soils and waters. Emission of N_2O from the ocean to the atmosphere is estimated to take account for 20% of global N_2O sources. It has been known that production of N_2O is enhanced in the oxygen minimum zone (OMZ) and regions such as Arabian Sea and Eastern tropical Pacific act as strong N_2O source to the atmosphere because of turbulent fluxes from the thermocline. Although OMZ is also found in the northern part of eastern Indian Ocean, Bay of Bengal, N_2O saturation in the surface water and calculated flux to the atmosphere have been reported to be substantially lower than those in the western counterpart, Arabian Sea. Moreover, vertical N_2O profiles obtained in the western and central Bay of Bengal by the previous studies were significantly different, the latter showing only a small increase of N_2O in OMZ. In this study, we aimed at revealing vertical and meridional profile of N_2O and its production/consumption processes in the eastern Indian Ocean by concentration and isotopic analyses of N_2O and related species.

Seawater samples were collected at 9 stations along 88˚E meridian (16˚N–20˚S) from 8 to 27 November, 2018 during the KH18-6 cruise of R/V *Hakuho-maru*. At each station, samples taken at 14–15 depths in the range of 0–5000 m were subsampled into 230 mL glass vials followed by addition by 1 mL saturated $HgCl_2$ solution for sterilization and by sealing with butyl rubber stoppers. Each was then preserved at 4–6˚C in the dark. Concentration and isotope ratios of N_2O ($\delta^{15}N$, $\delta^{18}O$, and SP, ^{15}N-site preference in NNO molecule) were measured using a gas chromatograph-isotope ratio mass spectrometer (GC-IRMS) equipped with a gas extraction and cryogenic concentration unit.

Concentrations of N_2O in the surface water were 6–7 nmol kg^{-1} which corresponds to saturation of 99–115% with respect to the atmosphere. The values obtained at four stations in the Bay of Bengal (5–16˚N, 88˚E) were lower than those observed in the western Bay of Bengal (10–20˚N, 80–88˚E) in March–April 1991 and were similar to those obtained in the central Bay of Bengal (7–15˚N, 85–89˚E) in February 1995 and 1996. At each station, the concentration increased with depth and showed a maximum around the bottom of thermocline (150–300 m in the Bay of Bengal and 300–1000 m at southern stations). The subsurface N_2O maxima in the Bay of Bengal were coincided with the core of OMZ, and the highest concentration of 136 nmol kg^{-1} was observed at the northern most station. The highest value observed in this study is larger than that reported in the west and central Bay by a factor of two and ten, respectively. Isotope ratios of N_2O showed a linear relation with inverse concentration, but the relationship was different between surface layer (0–40 m), thermocline or upper OMZ (100–250 m), lower OMZ (250–1000 m), and deep layer (> 2000m).
The enhanced accumulation of N_2O in OMZ in the Bay of Bengal compared to past studies suggests two possibilities: (1) there is a large seasonal variability in the vertical diffusion of N_2O in this region because

mixed layer depth is largely affected by wind and rainfall driven by monsoon, flow rate of fresh water from the rivers, and so on, (2) N_2O production rate has been increased during the past 20 years due to change in local oxygen or nutrient concentrations. If (1) is the case, the accumulated N_2O might be emitted to the atmosphere in a month scale and the Bay of Bengal would act as a significant source. Isotopic signatures of N_2O source (end member value) were estimated using the relationship between isotope ratios and concentration for each layer in the Bay of Bengal for the first time. By comparing the end member values with the isotopic ranges of known N_2O production and consumption processes, which was deduced from isotope fractionation factors in the literature and isotopic signature of N_2O precursors obtained by this study or deduced from the literature, we estimate that N_2O is produced by both archaeal nitrification and denitrification in the upper OMZ whereas it is produced mainly by denitrification in the lower OMZ.

Keywords: greenhouse gas, ozone depleting gas, stable isotopes, Bay of Bengal, nitrification, denitrification

