Surface emission and atmospheric trend of N_2O isotopocules in the chemical transport model

Global mean atmospheric N_2O isotopic values and estimated global total emissions in model are shown in Figure S1. The emissions of four N_2O isotopocules ($^{14}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, and $^{14}N^{14}N^{18}O$) were estimated by a method used in Ishijima et al. (2015), but the photolytic fractionation was not tuned in this study. Thus estimated surface emissions were used to simulate atmospheric N_2O isotopocules, which were used for stratospheric analysis of this study. The isotopocule ratios of N_2O emitted from surface sources in model were temporally constant ($\delta^{15}N^{bulk}$ = -8.4 ‰, $\delta^{18}O$ = 32.4 ‰, SP = 14.0 ‰). Although the model was optimized against relatively old measurement data mainly for 1990s, simulated atmospheric values in recent years at the surface were very reasonable (Table S1), considering necessary order of precision for analysis of the large vertical profiles in the stratosphere in this study.

Supplementary Tables and Figures

Table S1. Annual mean mixing ratio, $\delta^{15}N^{bulk}$, $\delta^{18}O$, and SP of atmospheric N_2O for 2010 observed and simulated at Hateruma station.

Method	N_2O mixing ratio (nmol mol^{-1})	$\delta^{15}N^{bulk}$ (‰)	$\delta^{18}O$ (‰)	SP (‰)	Reference
Observation	323.3	6.6	44.2	18.3	This study (top-down by the ACTM)
Model	324.0	6.3	44.5	18.7	Toyoda et al. (2013)

Table S2: Sampling location, date, altitude range, and tropopause height of previous observations and this study plotted in Figs. 2, 3, and 5.

Location	Latitude/ Longitude	Sampling Date	Altitude (km)	Number of samples	Tropopause height (km)	Reference
Sanriku Balloon Certer, Japan (SBC)	39 °N/142 °E	4 June 1990	16.1–34.7	9	13.6	Toyoda et al. (2004)
		3 September 1998	14.9–29.5	11	15.8	Yoshida and Toyoda (2000); Toyoda et al. (2004)
		31 May 1999	14.7–34.5	11	12.1	Toyoda et al. (2001)
		28 August 2000	15.0–31.3	10	15.0	Toyoda et al. (2004)
		30 May 2001	14.9–33.8	11	13.8	Toyoda et al. (2004)
Kiruna, Sweden (ESR)	68 °N/20 °E	22 February 1997	10.2–25.6	10	10.2	Toyoda et al. (2004)
Syowa station, Antarctica (SYO)	69 °S/40 °E	3 January 1998	10.4–29.8	9	9.0	Toyoda et al. (2004)
Hyderabad, India (HDB)	18 °N/79 °E	26 March 1987	17–26	5	NA	Kaiser et al. (2006)
		29 Apr 1999	10–28	10	NA	Röckmann et al. (2001)
Eastern equatorial Pacific (EQP)	0 °N/105–115 °W	4–8 February 2012	20–29	4	17.0–18.2[a]	This work
Biak, Indonesia (BIK)	1 °S/136 °E	22–28 February 2015	17.2–27.4	6	17.4–19.3[a]	This work

[a] Cold point tropopause. NA: not available

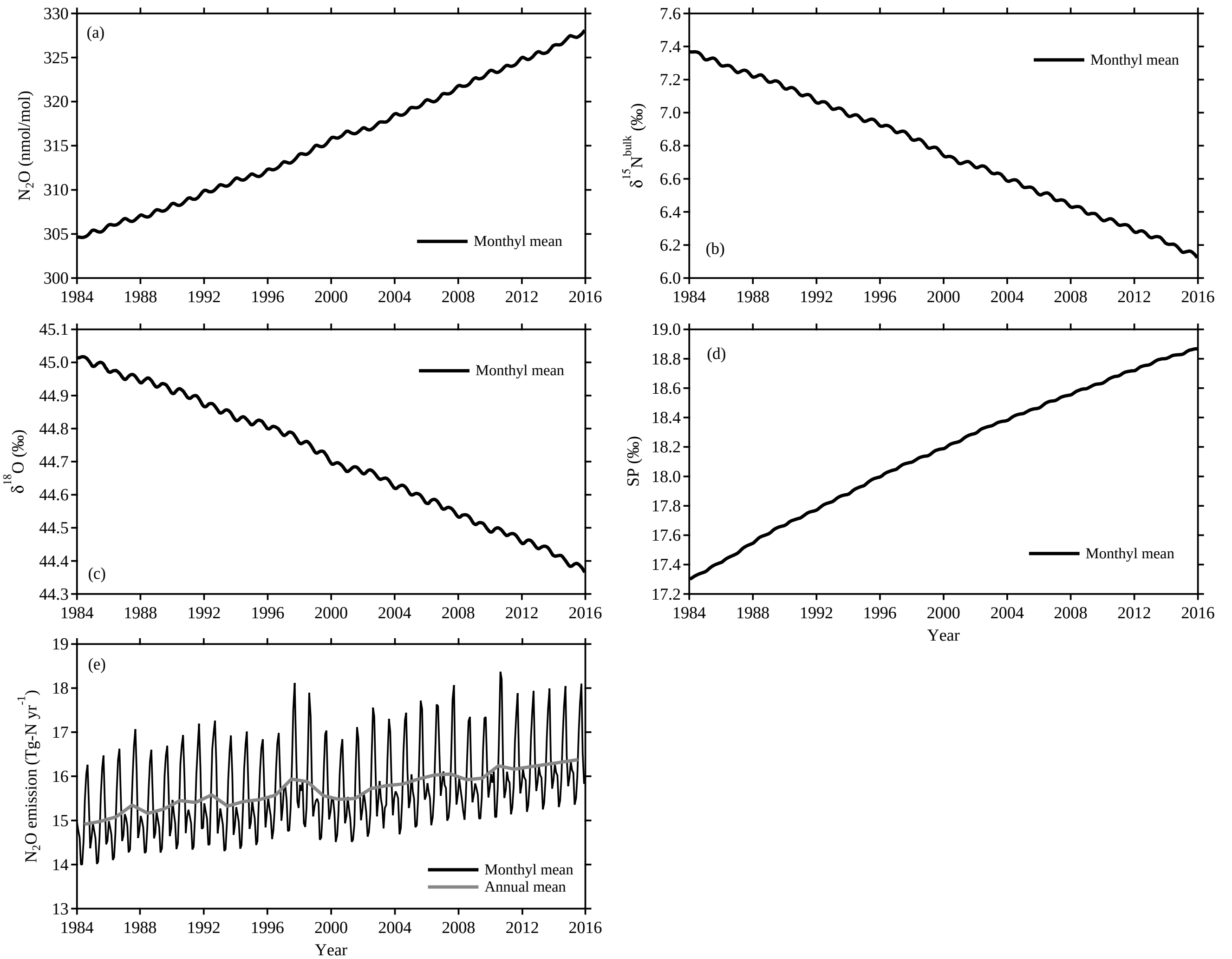

Figure S1: Global monthly mean mixing ratio (a), $\delta^{15}N^{bulk}$ (b), $\delta^{18}O$ (c), and SP (d) of atmospheric N_2O, and global total monthly and annual N_2O emissions (e) in model.

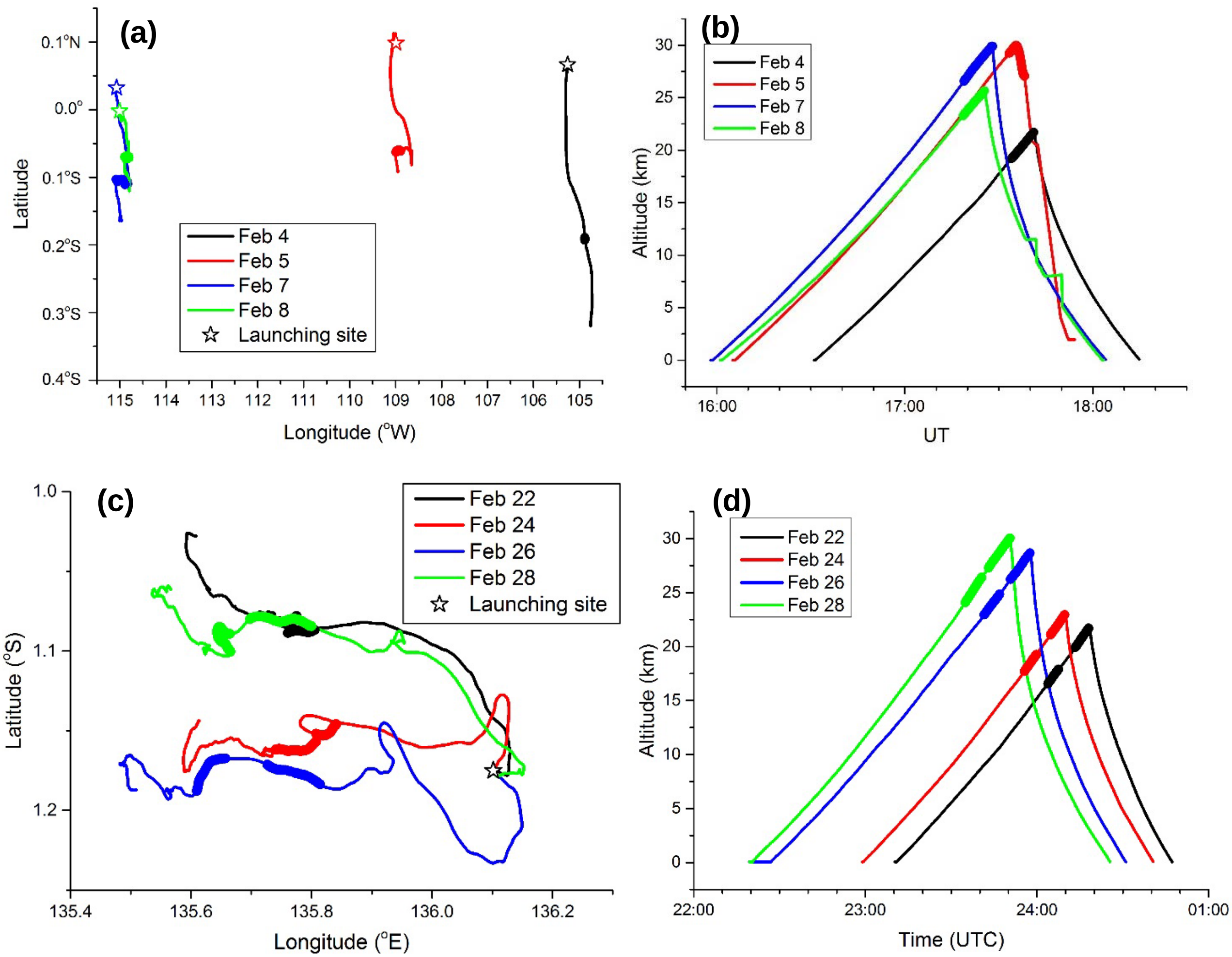

Figure S2: Trajectories of the balloons launched from Hakuho-maru in the eastern equatorial Pacific (a, b) and LAPAN observatory at Biak island, Indonesia (c, d). Panels (a) and (c) show horizontal trajectories; panels (b) and (d) show time-altitude trajectories. Sampling positions are shown by solid circles.

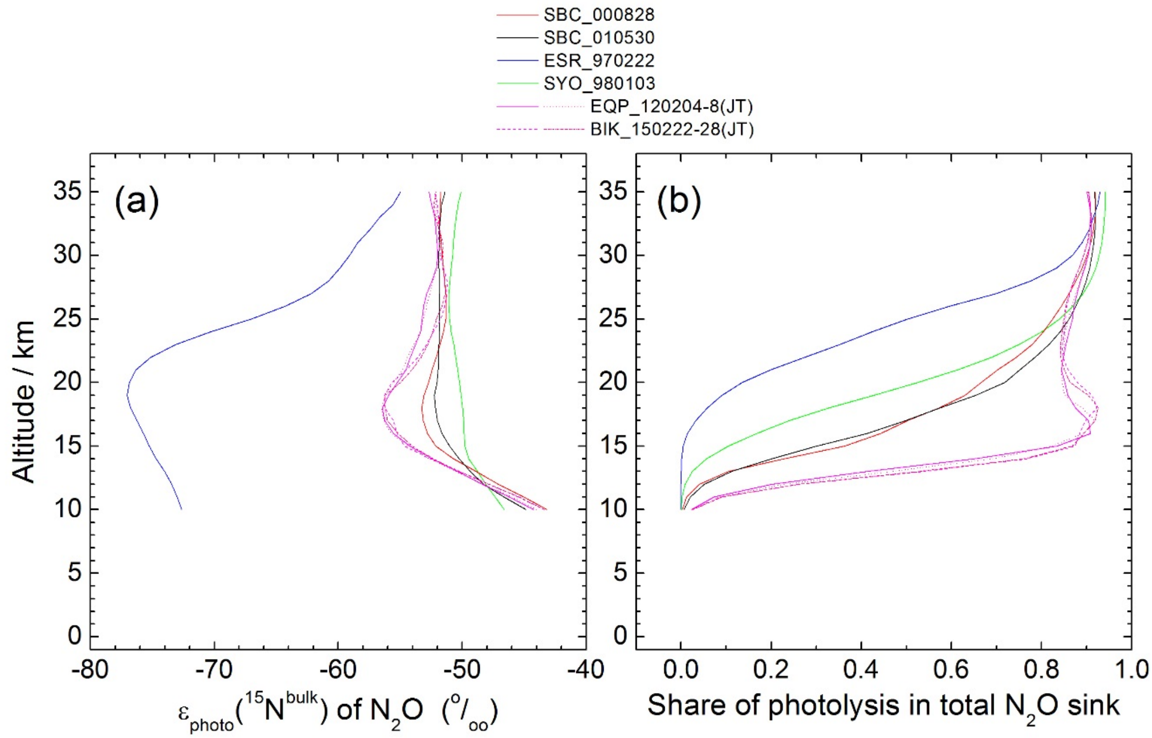

Figure S3: Vertical profiles of parameters derived from N_2O decomposition rates used in the ACTM. (a), $\varepsilon(^{15}N^{bulk})$ for photolysis; (b), share of photolysis in the total N_2O sink. Note that absolute value of photolysis rate constant is smaller in the lower stratosphere and polar stratosphere.