Vertical Profiles and Temporal Variations of Greenhouse Gases in the Stratosphere over Syowa Station, Antarctica

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Abstract

Stratospheric air sampling using balloon-borne cryogenic air samplers was conducted over Syowa Station, Antarctica in four austral summers between 1998 and 2013. The CH4 and N2O mole fractions decreased with increasing altitude due to chemical reactions and photodissociation in the stratosphere, and a compact positive correlation between CH4 and N2O was found in their vertical profiles. The vertical profiles of CO2 and SF6 mole fractions showed high values in the lower stratosphere, decreasing gradually with altitude, and then becoming almost constant at altitudes above 18 km. Stratospheric CO2 and SF6 above 18 km over Antarctica increased secularly at the respective average rates of 1.82 ± 0.31 ppm year−1 and 0.26 ± 0.01 ppt year−1 during the study period. The CO2 and SF6 mole fractions increased in the Antarctic stratosphere, but were delayed 4.5 ± 0.5 and 5.6 ± 0.2 years, respectively, compared to the tropical troposphere. The secular increase in stratospheric CH4 was also detected by classifying the measured mole fractions in terms of the N2O depletion in the stratosphere.

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1. Introduction

Atmospheric greenhouse gases, such as CO2, CH4, and N2O, have significantly increased since the late 18th century. To address global climate change due to human activities, it is crucial to identify spatio-temporal variations in greenhouse gases in the atmosphere. For that purpose, a number of observations have been conducted. However, only a few research groups have been devoted to observations in the stratosphere using scientific balloons, aircraft, and satellites (e.g., Bischof et al. 1985; Schmidt and Khedim 1991; Nakazawa et al. 1995; Engel et al. 2017; Rosenlof et al. 2011). Therefore, our knowledge of variations in stratospheric greenhouse gases remains insufficient. In particular, their behavior in the Antarctic stratosphere is not yet well understood, because long-term observations of related gases have been primarily conducted at northern middle latitudes (e.g., Schmidt and Khedim 1991; Nakazawa et al. 2002; Aoki et al. 2003; Engel et al. 2009).

To elucidate vertical distributions and temporal variations in greenhouse gases in the Antarctic stratosphere, we collected air samples using large balloon-borne cryogenic air samplers over the Japanese Antarctic station, Syowa (69.00°S, 39.58°E), in the austral summers in 1997/98 and 2003/04. Subsequently, we also collected stratospheric air using newly developed compact cryogenic air samplers over Syowa in the austral summers in 2007/08 and 2012/13.

In this study, we present all measured values of CO2, SF6, CH4, and N2O mole fractions obtained from these observations as their first-long-term records in the Antarctic stratosphere and discuss their stratospheric vertical profiles over Antarctica. The secular trends in stratospheric CO2, SF6, and CH4 mole fractions are also discussed.

2. Method

Air samples were collected from the stratosphere over Syowa using two types of samplers; the first was a cryogenic air sampler with liquid helium as a coolant (Honda et al. 1996), hereafter referred to as the cryo-sampler; the other was a compact cryogenic air sampler equipped with a Joule-Thomson mini cooler (Morimoto et al. 2009), hereafter referred to as the JT-sampler. Stratospheric air was collected using the cryo-sampler on 3 January 1998, 26 December 2003, and 5 January 2004 (Sugawara et al. 2010). The JT-sampler was used to collect stratospheric air on 4 January 2008, 31 December 2012, and 10 January 2013. The air sampling procedures using the two samplers are described in detail in Nakazawa et al. (1995) and Morimoto et al. (2009). By performing the air storage tests over 1−3 months for each sampler, the measured CO2 mole fraction values of the air collected in the JT-sampler were corrected by 0.0–1.0 ppm, while no correction was applied to those in the cryo-sampler. Each air sampler was launched using a scientific plastic balloon, and landed on the sea ice using a parachute after collecting the stratospheric air at assigned altitudes between 10 and 30 km. The dates and altitudes of air sampling are summarized in Table 1. The samples obtained in 2003 showed anomalous mole fraction values of CO2 for an unknown reason, and we failed to collect high quality samples at 22.3, 24.7, 27.3 km on 31 December 2012 and 19.6 km on 10 January 2013 due to technical issues. Therefore, data from these altitudes and dates were not used for this study.

The air samples collected were analyzed at Tohoku University for the mole fractions of CO2, CH4, N2O, and SF6 in 3−5 months after air sampling. The analyzers, analytical precision, and calibration scales for measurements of the respective components are summarized in Table 2.
3. Results and discussion

Figures 1a and 1b show vertical profiles of CH$_4$ and N$_2$O mole fractions in the stratosphere over Syowa obtained in 1998 and 2004 using the cryo-sampler and in 2008 and 2012/13 using the JT-sampler. Daily mean CH$_4$ mole fraction observed at Syowa (Aoki et al. 1992) on the day each profile was obtained, as well as the N$_2$O and SF$_6$ mole fractions measured using a grab sampling method at the station on the date close to the day of stratospheric air sampling, are plotted in the figure with reference to the surface values. CH$_4$ is destroyed by chemical reactions with OH, O(1D) and Cl, and N$_2$O by photodissociation and reactions with O(1D) in the stratosphere (e.g., Nakazawa et al. 2002). As shown in Figs. 1a and 1b, both CH$_4$ and N$_2$O mole fractions decrease with increasing altitude, as expected. The mean rates of decrease in the CH$_4$ profiles for 1998 (10.4−29.8 km), 2004 (10.2−29.4 km), and 2012/13 (14.6−28.5 km), defined as a slope of linear lines fitted to each profile, were calculated as 38.6 ± 4.0, 38.0 ± 2.7, and 36.8 ± 11.3 ppb km$^{-1}$, respectively. These rates are in good agreement with each other within the estimated uncertainties. The corresponding rates of decrease in the N$_2$O profiles were calculated as 11.4 ± 0.8, 10.4 ± 0.6, and 9.8 ± 3.1 ppb km$^{-1}$, which are also close to each other. The slopes for the 2008 profiles were not calculated because there were only two data points.

Sugawara et al. (1997) also observed a similar CH$_4$ profile in the stratosphere over the northern part of Japan using the cryo-sampler. Their measured CH$_4$ mole fraction values decreased rapidly from 14 to 34.7 km with a rate of about 38 ppb km$^{-1}$. Vertical N$_2$O profiles similar to our result were obtained in the stratosphere over India, France, Sweden (Harnisch et al. 1998) and Japan (Toyoda et al. 2004), but their rates of decrease are about 12−20 ppb km$^{-1}$, which are slightly larger than the values over Syowa.
It is seen from Fig. 2 that the CH₄ and N₂O mole fractions observed over Syowa are positively correlated well with each other. Such a compact correlation was also reported by Michelsen et al. (1998) by examining the mole fractions of CH₄ and N₂O over a wide range of altitudes and latitudes, as well as by Nakazawa et al. (2002) from their measurements of the two variables over Japan, Scandinavia and Antarctica.

Figures 1c and 1d show vertical profiles of CO₂ and SF₆ mole fractions observed in the stratosphere over Syowa in 1998, 2004, 2008, and 2012/13. As shown in the figure, the CO₂ and SF₆ mole fractions decrease rapidly with altitude from 10 to 18 km and then show almost constant values. The rates of decrease in CO₂ (SF₆) above 18 km are calculated to be 0.05 ± 0.04 and −0.02 ± 0.03 ppm km⁻¹ (0.01 ± 0.01 and 0.03 ± 0.01 ppm km⁻¹) for 1998 and 2004, respectively, and the corresponding rates below 18 km are 0.43 ± 0.14 and 0.35 ± 0.20 ppm km⁻¹ (0.12 ± 0.04 and 0.10 ± 0.04 ppm km⁻¹). In the stratosphere, there are no SF₆ sources and sinks. Although oxidizing CH₄ in the stratosphere produces CO₂, its contribution to stratospheric CO₂ mole fraction is 0.8 ppm at most, even if the observed vertical CH₄ profiles, decreased from about 1700 ppb at 10 km to about 900 ppb at 30 km, were formed only by the oxidation of stratospheric CH₄. Therefore, the steep gradients of CO₂ and SF₆ profiles below 18 km would be primarily influenced by transportation of tropospheric air with high mole fractions.

Similar CO₂ and SF₆ profiles were obtained over the Arctic, France, and India using a balloon-borne cryogenic air sampler from 1987 to 1995 (Harnish et al. 1998; Strunk et al. 2000). Aoki et al. (2003) and Engel et al. (2009) also observed similar CO₂ profiles at northern mid-latitudes. However, their results showed that the difference in CO₂ mole fraction between the middle and lower stratosphere was about 7–8 ppm, which is twice as large as our finding obtained in the Antarctic stratosphere. Such a latitude-dependent vertical CO₂ difference could be mainly related with the effects (1) that the mole fraction of upper tropospheric CO₂ is higher in the northern hemisphere than in the southern hemisphere on average (Matsueda et al. 2015) and the tropospheric and stratospheric air exchange occurs through various processes, such as blockings, cut-off cyclones, and tropopause folds (e.g., Holton et al. 1995), and (2) that the tropospheric air with high CO₂ mole fractions, intruded into the stratosphere in the tropics, has a stronger influence on lower stratospheric CO₂ in northern mid-latitudes than in Antarctica, since its poleward transport through the lower stratosphere is faster in the northern hemisphere than in the southern hemisphere (Flury et al. 2013).

In addition, Figs. 1c and 1d also show that the stratospheric CO₂ and SF₆ mole fractions increase with time. To examine such increasing trends, the mole fractions of CO₂ and SF₆ measured above 18 km, where values become almost constant, were simply averaged and plotted in Fig. 3. The long-term trend derived by applying a digital filtering technique (Nakazawa et al. 1997) to the CO₂ record obtained from continuous measurements at Syowa (Morimoto et al. 2003) is also shown in Fig. 3a. We also measured the SF₆ mole fraction at the station based on weekly air sampling (our unpublished data); the long-term trend for the 2004–2013 period obtained using the digital filtering technique is shown in Fig. 3b. As shown in Figs. 3a and 3b, the stratospheric CO₂ and SF₆ increased secularly with a few years of delay, compared to their increasing trends at Syowa. The average rates of increase in stratospheric CO₂ and SF₆ for the 1998–2013 period were calculated from our observational results as 0.22 ± 0.02 ppm yr⁻¹ and 0.22 ± 0.01 ppt yr⁻¹, respectively. The rate of increase in stratospheric CO₂ is in good agreement with the result at Syowa (1.88 ppm yr⁻¹) for the same period. Aoki et al. (2003) reported from their balloon observations over Japan for the 1985–2000 period that stratospheric CO₂ increased at 1.4 ppm yr⁻¹, which is close to the value obtained from their aircraft observations in the upper troposphere over Japan for the same period. The discrepancy between the rates of increase in CO₂ reported by Aoki et al. (2003) and this study is probably ascribed to the different observation periods, since the CO₂ growth rate increased secularly for the period covered by the two observations (e.g., GLOBALVIEW-CO₂, 2013).

The observed SF₆ mole fraction data at Syowa yielded an increasing rate of 0.23 ± 0.00 ppt yr⁻¹ for the 2004–2013 period (our unpublished data), which is in agreement with the value derived for stratospheric SF₆. The SF₆ mole fractions over Antarctica were also observed using MIPAS (Michelson Interferometer for
Passive Atmospheric Sounding) aboard ENVISAT (Environmental Satellite) (Haenel et al. 2015). By analyzing the MIPAS monthly zonal mean data at 67.5°S in January of 2002–2012, we estimated the rate of increase in SF$_6$, at 25 km to be $0.19 \pm 0.04$ ppt yr$^{-1}$. The estimated rate is slightly lower than our tropospheric and stratospheric values on average, but both results are in agreement with each other in a margin of uncertainty. Our data obtained for the Antarctic stratosphere will be indispensable for validating satellite-based SF$_6$ observations.

Because there are no strong CO$_2$ and SF$_6$ sources in the stratosphere, increases in stratospheric CO$_2$ and SF$_6$ are mainly attributable to an intrusion of tropospheric air into the stratosphere. In general, tropospheric air enters the stratosphere in the tropics, and then moves toward middle and high latitudes over a few or several years. This circulation is well known as the Brewer-Dobson circulation. Due to this circulation, the tropospheric mole fraction levels of CO$_2$ and SF$_6$ are observed in the stratosphere with some years of delay (e.g., Waugh and Hall 2002). We calculated approximate lag times of CO$_2$ and SF$_6$ between the troposphere and stratosphere. In this calculation, the averages of CO$_2$ and SF$_6$ mole fractions above 18 km over Syowa were compared with the respective secular trends observed at Mauna Loa (19.54°N, 155.58°W, 3397 m above sea level), Hawaii by the NOAA/ESRL GMD (Dlugokencky et al. 2017) since 1969 and the NOAA/ESRL halocarbons in situ program (e.g., Rigby et al. 2010) since 2000. Prior to comparison, 0.2 ppm was added to the NOAA CO$_2$ data to adjust the NOAA scale (WMO-X2007) to our scale (TU-2010). Since we confirmed that our SF$_6$ scale (TU-2002) is consistent with the NOAA scale (WMO-2014) within ±0.07 ppt, no correction was applied to the SF$_6$ data. The resultant lag times of CO$_2$ and SF$_6$ mole fractions were 3.8, 5.1, 4.5, and 4.7 years for the 1998, 2004, 2008, and 2012/2013 observations, respectively, with a mean of 4.5 ± 0.5 years. The respective SF$_6$ lag times calculated for 2008 and 2012/2013 observations were 5.7 and 5.4 years, and their 5.6 ± 0.2 year average was about one year larger than that of CO$_2$. These results indicate that the stratospheric air over Syowa was older by about 4–6 years than the tropical tropospheric air. The difference in the estimated time lag between CO$_2$ and SF$_6$ was also reported by previous studies (e.g., Andrew et al. 2001; Sugawara et al. 2017), however, the cause is not yet understood well. The downward transport of the mesospheric air with low SF$_6$ mole fractions is suggested as one of possible candidates (e.g., reddmann et al. 2001; Linz et al. 2017).

An increase in tropospheric CH$_4$ has been observed at various places worldwide, but such a trend is not clearly observable in our stratospheric CH$_4$ mole fractions provided in Fig. 1. To examine the secular trend in CH$_4$ in the Antarctic stratosphere, we analyzed our CH$_4$ and N$_2$O mole fraction data using a method similar to Rohs et al. (2006). In this analysis, we first calculated the depletion in the N$_2$O mole fraction ($\Delta$N$_2$O) that occurred during its transportation from the troposphere to stratosphere over Syowa using the following equation:

$$\Delta$$N$_2$O = C$_{trp}$($t - T_a$) - C(t).

Here, C(t) is the N$_2$O mole fraction observed in the stratosphere over Syowa at time t, $T_a$ is the age of stratospheric air for the observed C(t), and C$_{trp}$($t - T_a$) is the tropospheric N$_2$O mole fraction at time t − $T_a$. In this calculation, the N$_2$O mole fraction data from Mauna Loa, from the NOAA/ESRL halocarbons in situ program, were used for C$_{trp}$, and the CO$_2$ lag times were used for $T_a$ to exclude possible influence by the mesospheric air. The measured values of CH$_4$ mole fraction are plotted in Fig. 4 against $\Delta$N$_2$O. As shown in the figure, the relationship between $\Delta$N$_2$O and CH$_4$ for each year is almost linear, and the line shifts upward year by year. This implies that the secular CH$_4$ increase can be detected by classifying the measured values of CH$_4$ mole fraction in terms of $\Delta$N$_2$O. Then, the average CH$_4$ mole fractions for four ranges of $\Delta$N$_2$O, i.e., 50–100, 100–150, 125–175, and 150–200 ppb, were calculated from a linear line fit to the $\Delta$N$_2$O-CH$_4$ correlation plots for each observation. The obtained average values are plotted in Fig. 5 against year, together with long-term trend and best-fit curve of the CH$_4$ mole fraction data at Syowa (Aoki et al. 1992). It should be noted that the stratospheric CH$_4$ mole fractions are shifted back by $T_a$ in Fig. 5 to directly compare their temporal changes with those at Syowa.

In Fig. 5, the stratospheric CH$_4$ mole fraction over Syowa clearly increases for the 1998–2013 period. The rates of increase in the CH$_4$ mole fraction were $4.2 \pm 0.1$, $4.8 \pm 0.1$, $4.5 \pm 0.4$, and

![Fig. 4. Correlation plots of CH$_4$ and $\Delta$N$_2$O observed in the stratosphere over Syowa Station (cf. text).](image)
3.6 ± 1.5 ppb yr⁻¹ for the respective ΔN₂O ranges of 50–100, 100–150, 125–175, and 150–200 ppb. On the other hand, the CH₄ data from Syowa yield 3.6 ± 0.1 ppb yr⁻¹ for the period of 1995.8–2010.8 and 3.9 ± 0.1 ppb yr⁻¹ for 1993.5–2008.5, which can be compared to the respective results for the ΔN₂O range of 50–100 ppb and the ΔN₂O ranges of 100–150, 125–175, and 150–200 ppb. Although the rates of increase in stratospheric CH₄ are slightly larger than the values at Syowa, the present analysis indicates that the secular increase in stratospheric CH₄ can also be detected over Antarctica from the measured values using the N₂O depletion during transport of air from the tropical troposphere to the Antarctic stratosphere. At Syowa, the CH₄ mole fraction increased steadily in the 1980s and 1990s, stagnated around 2000, and then increased again from 2006. Such an irregular change in the CH₄ mole fraction was observed globally (e.g., Dlugokencky et al. 2009). However, the CH₄ stagnation is not clearly detectable in the stratosphere over Syowa at this stage, because the stratospheric CH₄ data over Syowa is sparse.

4. Summary

To understand the vertical distributions and temporal variations in CO₂, CH₄, N₂O, and SF₆ in the Antarctic stratosphere, we collected air samples over Syowa station in the austral summers of 1997/98, 2003/04, 2007/08, and 2012/13 using balloon-borne cryogenic air samplers and JT-samplers. The samples were analyzed for mole fractions of the respective constituents at Tohoku University in 3–5 months after air sampling. The CO₂ and SF₆ mole fractions had high values in the lower stratosphere, decreased with altitude and became almost constant above 18 km. By comparing the average mole fractions of CO₂ and SF₆ above 18 km over Syowa with tropospheric data from Mauna Loa, the lag time in secular increase was estimated as 4.5 ± 0.5 years for CO₂ and 5.6 ± 0.2 years for SF₆. The CH₄ and N₂O mole fractions decreased with increasing altitude due to chemical reactions and photodissociation in the stratosphere. By taking into account the N₂O depletion during transport of air from the tropical troposphere to the Antarctic stratosphere, the secular increase in stratospheric CH₄ can be detected from measured values.

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