Atmospheric monitoring for trace greenhouse gases at Minamitorishima
(Abstract of Final Report)

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1. Introduction

The station of Minamitorishima (24°18'N, 153°58'E, 9 m above sea level) is a unique atmospheric monitoring site in a clean air, where is situated on a remote coral island in the western North Pacific, about 2,000 km southeast of Tokyo. In order to advance the environmental monitoring activities for the background atmosphere, various kinds of research observations with high-precision measuring techniques are needed to be integrated at the Minamitorishima station. The station has been operated by the Japan Meteorological Agency (JMA) for long-term operational observations of major greenhouse gases. However, other related trace gases observations are limited at this station. In addition, Minamitorishima station is isolated from the human activities to accurately determine the background trends of anthropogenic halocarbons such as hydrofluorocarbons (HFCs) and perfluorocarbons (PFC), which are legally binding targets of the Kyoto Protocol. Thus, research observations should be newly introduced at this station to make better use of this station in Japan.

2. Research Objective

In this study, four kinds of research observations are main objectives to be newly integrated at Minamitorishima station. First, continuous measuring systems for atmospheric molecular hydrogen (H_2) and radon-222 (^{222}Rn) are tested and operated to collect their data as a chemical tracer for identifying air mass origin. Second, high-precision observation of atmospheric oxygen (O_2) using flask air sampling is introduced to obtain key information for the portioning of fossil-fuel emissions between terrestrial biosphere and ocean. Third, high-sensitivity measurements of anthropogenic halocarbons such as HFCs and PFCs start to capture their long-term trends as well as small seasonal variations. Fourth, high-precision technique for measuring stable isotopic ratios of carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) in CO_2 are used to examine the sources and sinks of CO_2 and their seasonal and

interannual variations. In addition, continuous isotope measuring system is improved. These data are analyzed to evaluate the usefulness of the integrated observation system established in this study.

3. Research Method

3.1. Minamitorishima station

The Minamitorishima (Marcus Island) has an area of 1.4 km^2 and is covered with sparse evergreen shrub and grass. Maritime air from easterly winds prevails throughout the year. Continental air masses from East Asia are sometimes transported by the synoptic-scale weather perturbations, but the influences of local sources and sinks within this small island are negligible for trace gas observations[1)]. Not only CO_2, but also carbon monoxide (CO), methane (CH_4), and ozone (O_3) have been measured by JMA operational monitoring since March 1993. Recently, new JMA atmospheric environmental monitoring system (JMA/AEM system) is replacing the old system. Sample air is collected from the top of a 20 m observational tower. A new observational tower was constructed in 2012.

3.2. Analytical method

For H_2 measurement, we use a gas chromatograph (GC) equipped with a reduction gas detector (RGD) in the JMA/AEM system. In this study, high-precision H_2 standard gases are prepared to determine the atmospheric concentration from the output signal of the GC/RGD. Atmospheric O_2/N_2 ratio is measured based on a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). Details are reported by Tohjima (2000)[2)]. Anthropogenic halocarbons such as HFCs and PFCs are measured by preconcentration/capillary gas chromatograph/mass spectrometry (GC/MS) according to the method by Yokouchi et al. (2005)[3)]. For the CO_2 isotopes measurement, pure CO_2 is extracted cryogenically from the air in the flask sample. The pure CO_2 is analyzed for the carbon and oxygen isotopic ratios using Nier-McKinney mass spectrometer (MS). Details are reported by Murayama et al. (2010)[4)]. For Rn measurement, we use a compact and sensitive Radon-222 measuring system by employing the electrostatic collection and by using the PIN photodiode detector. Details are reported by Wada et al. (2010)[5)].

4. Results and Discussion

4.1. Flask samples

By using the sampling methods that were established in the first year, we have continued the flask sampling. For the O_2 measurement, the air samples were collected in duplicate twice a month. The total of 120 flask air samples was collected from September in 2011 to February in 2014. For the halocarbon measurement, the air samples were collected in triplicate twice a month. The total of 209 flask air samples was collected from June in 2011 to March in 2014. For the CO_2 isotope measurement, frequent air sampling was made once a week. The total of 149 flask air samples was collected from June in 2011 to February in 2014. We performed the comparison tests between old and new observational tower, and confirmed that there is no difference between the two sampling lines. We have collected the sample air from the new one since January 2013.

4.2. H_2 variation

Figure 1 shows observed H_2 variations from November in 2011 to December in 2013 at Minamitorishima. The H_2 concentrations varied from 490 ppb to 560 ppb with a mean of about 520 ppb. The H_2 concentrations clearly show several episodic events with enhanced peaks on a synoptic scale in winter. This result indicates that H_2 increases are caused by the long-range transport of Asian polluted air masses to the station. Thus, it is confirmed that H_2 is a good tracer for identifying air mass origin in winter season. On the other hand, the H_2 concentrations are high and stable in summer season. This result indicates that we observed the air mass of marine, and the influence of soil absorption was small.

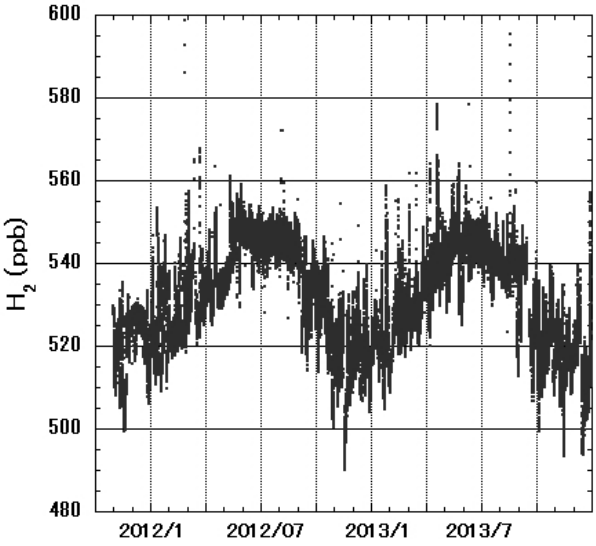

Figure 1. H_2 variations at Minamitorishima from November 2011 to December 2013.

4.2. O_2/N_2 variation

Time series of atmospheric CO_2 concentration, O_2/N_2 ratio and APO (Atmospheric Potential Oxygen; $APO=O_2+1.1 \times CO_2$) are shown in Figure 2. The seasonal variation of the atmospheric CO_2 shows the maximum value in May and minimum value in September, while that of O_2 concentration shows the minimum value in March and maximum value in September. We found that APO has same seasonality as O_2/N_2 ratio. For comparison, we also plot the best fit curves of the data observed at Hateruma station (HAT; 24°3'N, 123°49'E), which is located on the same latitude as MNM in the Pacific region, as broken lines in Fig. 2. It is clearly shown that the O_2/N_2 ratio and CO_2 concentration at MNM are higher and lower than those at HAT, respectively. These differences indicate that the influence of Asian continental air masses is relatively less at Minamitorishima during winter, suggesting that Minamitorishima is suitable for observing the background O_2/N_2 variation. As for the seasonal

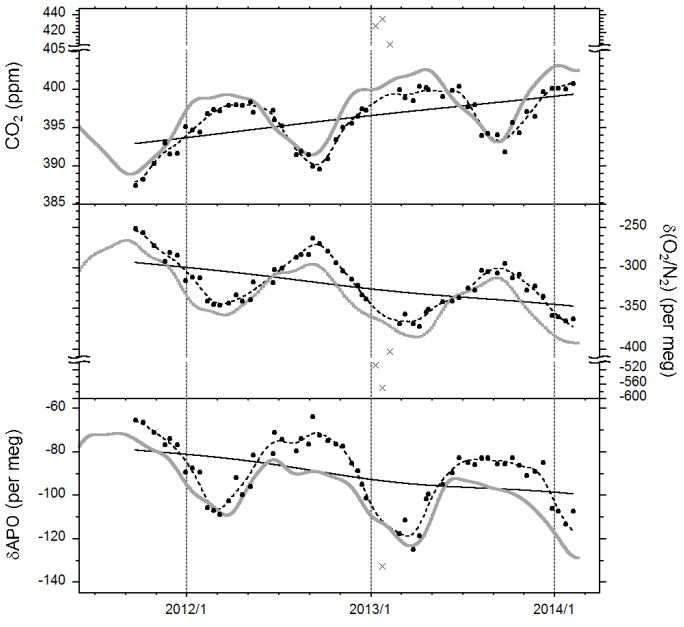

Figure 2. Time variation of (top) CO_2 concentration, (mid.) O_2/N_2 ratio, and (bottom) APO during the period from September 2011 to February 2014 (open circles). Black broken lines represent the best fit curves at Minamitorishima. Grey lines are the best fit curves at Hateruma Island.

variation of APO, although there is good agreement in the minimum values between MNM and HAT, the maximum value at MNM was found to be by 4 ppm higher than that at HAT. These results seem to suggest that the observation at MNM is more affected by O_2 release from the ocean than that at HAT.

4.3. Halocarbon variation

Sixty-eight datasets of halocarbons were obtained from Minamitorishima during this study period (June 2011~March 2014). Figure 3 shows the temporal variations of HFC-23, HFC-125, HFC-32, HFC-134a, HFC-227ea, PFC-116, PFC-218, SF_6 . The annual average mixing ratios for 2013 were 76.3ppt for HFC-134a, 27.1ppt for HFC-23, 15.4ppt for HFC-143a, 14.5ppt for HFC-125, 8.3ppt for HFC-32, 8.2ppt for HFC-152a, 4.2ppt for PFC-116, 1.4ppt for PFC-318, 0.61ppt for PFC-218, and 8.3ppt for SF_6. HFCs, PFCs and SF_6 were found to have increased significantly for the last year. The annual changes in their mixing ratios were 7.4% for HFC-134a, 5.4% for HFC-23, 7.1% for HFC-143a, 14.1% for HFC-125, 16.6% for HFC-32, 2.5% for PFC-116, 3.2% for PFC-318, 2.3% for PFC-218, and 4.7% for SF_6. Rapid increase of HFC-32 and HFC-125 which are primary replacements of HCFC-22 in air-conditioning system applications was remarkable.

Most of the observed HFCs and SF_6 showed seasonal variations, higher in winter than in summer. Considering the site is typically affected by oceanic air masses from the south in summer and by continental air masses from the north-west in winter, the seasonal trends are likely to be reflecting their latitudinal variations.

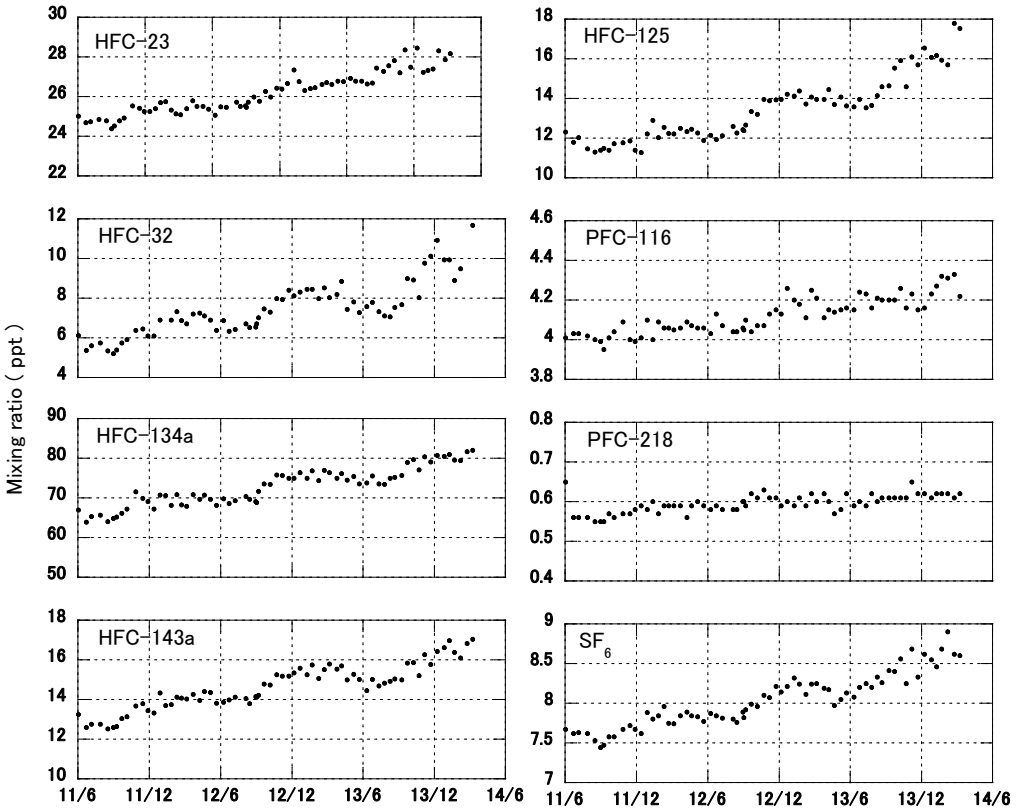

Figure 3. Atmospheric mixing ratios of eight halocarbons at Minamitorishima (June 2011~March 2014)

4.4. CO_2 isotopic ratio variation

Figure 4 shows time variations of CO_2 concentration, $\delta^{13}C$, and $\delta^{18}O$ from June 2011 to February 2014 at Minamitorishima, together with continuous CO_2 measurements from JMA/AEM system. It is clearly found that the CO_2 data from the flask samplings well agree with the continuous measurements, indicating suitable flask sampling as well as no drift of CO_2 content in the flask until analysis. The CO_2 concentrations show a clear seasonal variation with a decrease from summer to early autumn and an increase from late autumn to early spring. In contrast, the $\delta^{13}C$ data are anticorrelated with the concentrations, due mainly to a seasonal-dependent CO_2 exchange with C_3 plants on land biosphere. The $\delta^{18}O$ data are not correlated with $\delta^{13}C$ and CO_2 concentration due probably to influences by complicated processes, showing a seasonal variation with a decrease of summer - late autumn and increase thereafter until early summer. In addition, secular increase of CO_2 concentration and decrease of $\delta^{13}C$ due to anthropogenic CO_2 emission were also observed. Thus, we confirmed that the CO_2 isotope data could provide us useful information to elucidate the factors governing the concentration variations observed at Minamitorishima.

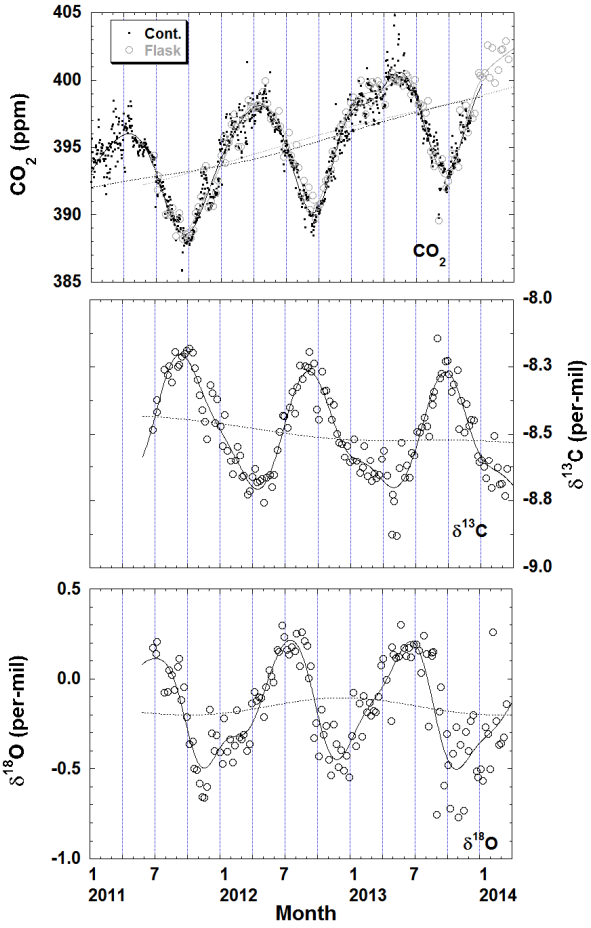

Figure 4. Time variations of atmospheric CO_2 concentration and its $\delta^{13}C$, and $\delta^{18}O$ at Minamitorishima

4.5 Radon variation

Figure 5 shows hourly mean concentrations of atmospheric Rn observed at MNM. The observed temporal variations of the Rn concentration clearly show a distinct seasonal cycle, as well as high-frequency synoptic variations. A seasonal cycle was observed with a maximum in the winter season around December - January and a minimum in the summer season around July - September. It is noted that the summer minimum at MNM with a very low value of less than 0.2 Bq $m^{-3,}$ indicating the value to be a baseline concentration over the western North Pacific. These results suggest that the observed Rn seasonal cycles at various locations are influenced primarily by the seasonal exchange of continental and maritime air masses over the western North Pacific.

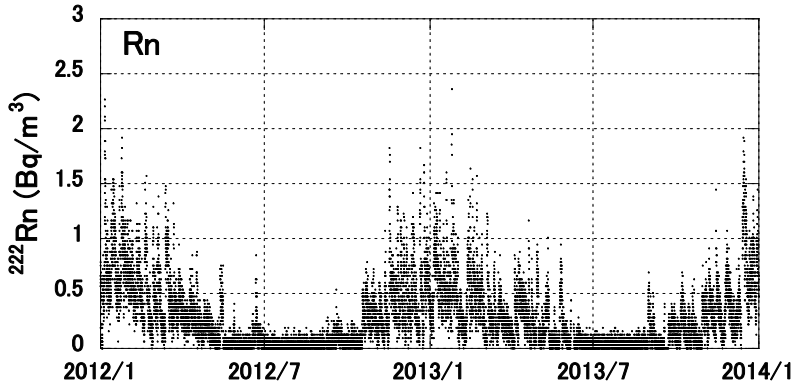

Figure5. Time series of hourly atmospheric Rn concentration observed at Minamitorishima in 2012-2013

References

1) Wada, A., and Coauthors, 2007: Influence of continental air mass transport on atmospheric CO_2 in the western North Pacific. J. Geophys. Res., 112, D07311, doi:10.1029/2006JD007552.

2) Tohjima, Y., 2000: Method for measuring changes in the atmospheric O_2/N_2 ratio by a gas chromatograph equipped with a thermal conductivity detector, J. Geophys. Res., 105, 14575-14584.

3) Yokouchi, Y., and Coauthors, 2005: Estimates of ratios of anthropogenic halocarbon emissions from Japan based on aircraft monitoring over Sagami Bay, Japan. J. Geophys. Res., 110, D06301, doi:10.1029/2004JD005320.

4) Murayama, S., and Coauthors, 2010: Seasonal variations of atmospheric CO_2, $\delta^{13}C$, and $\delta^{18}O$ at a cool temperate deciduous forest in Japan: Influence of Asian monsoon. J. Geophys. Res., 115, D17304, doi:10.1029/2009JD013626.

5) Wada, A., and Coauthors, 2010:Development of a Compact and Sensitive Electrostatic Radon-222 Measuring System for Use in Atmospheric Observation, Journal of the Meteorological Society of Japan, Vol.88,No.2,pp.123-134,2010.