

**High-precision monitoring of variations of atmospheric compositions in background air at Minamitorishima using continuous measurements
(Abstract of the Final Report)**

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1. Introduction

The station of Minamitorishima (MNM; 24°17'N, 153°59'E, 9 m above sea level) is a unique monitoring site of background air at northern mid latitudes, which is situated on a remote coral island in the western North Pacific, about 1,900 km southeast of Tokyo. The station has been operated by the Japan Meteorological Agency (JMA) for the long-term operational observations of major trace gases such as carbon dioxide (CO₂), methane (CH₄), monoxide (CO) and ozone (O₃). For a better understanding of mechanism governing observed variations in the atmospheric greenhouse gases, various kinds of research observations with high-precision measuring techniques for a long term are needed to be integrated at MNM. High-precision measurements of the atmospheric oxygen/nitrogen ratio (O₂/N₂) and the stable carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotopic ratios in CO₂ are very useful to examine the factors governing variations in the atmospheric CO₂, while atmospheric hydrogen (H₂) and radon (Rn) indicate characteristic of continental air transport. Furthermore, continuous measurements of these components enable us to distinguish between the data influenced by transport of background air and short-term pollutant air. Developing precise O₂ standard gases for atmospheric observation traceable to SI (International System of Units) is also necessary for precisely detecting the long-term variation in atmospheric O₂/N₂ and inter-comparison of the O₂/N₂ data obtained from different laboratories; such precise O₂ standard gases have not been available yet.

2. Research Objectives

The purpose of this study is to continue and reinforce high-precise observations of the atmospheric O₂/N₂ ratio, H₂ and Rn concentrations and stable isotopic ratios in CO₂ at MNM in addition to the long-term operational observations of major greenhouse gases made by JMA. Continuous measurement systems of atmospheric O₂/N₂ and stable isotopic ratios in CO₂ will newly be installed at MNM to obtain the data with high time resolution, while the measurements of these components with flask sampling methods will also be continued to verify the precision of the continuous measurements. We will also develop precise O₂ standard gases for atmospheric observation traceable to SI. From analyses of the data at MNM thus obtained, we will construct the high-quality dataset of these components in the background air representative to northern mid latitudes and examine factors causing their variations.

3. Research Methods

3.1. Minamitorishima station

MNM (Marcus Island) has an area of 1.5 km² 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. In this study, sample air is collected using the atmospheric environmental monitoring system and the air intake mounted on the top of a 20 m high observational tower used for the JMA operational monitoring.

3.2. Measurement of the atmospheric O₂/N₂ ratio

In order to capture variations of O₂/N₂ ratio in the background air, continuous measurements of the atmospheric O₂/N₂ ratio have been carried out at MNM by employing a paramagnetic oxygen analyzer. The discrete flask air samples collected every two weeks have also been analyzed for O₂/N₂ ratio by using a mass spectrometer.

3.3. Measurement of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in atmospheric CO₂

Systematic observations of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the atmospheric CO₂ have been carried out at MNM by analyzing discrete flask air samples. Air samples have been collected once per week, and the measurements of their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in CO₂ have been made using a mass spectrometer at our laboratory. We have also made continuous measurement of CO₂ isotopes using a Cavity Enhanced Absorption Spectroscopy (CEAS) method at MNM since March 2018.

3.4. Continuous measurement of the atmospheric H₂ and Rn concentrations

For H₂ measurement, we use a gas chromatograph (GC) equipped with a reduction gas detector (RGD) in the JMA's measurement system. In this study, high-precision H₂ standard gases are prepared to determine the atmospheric concentrations from the output signal of the GC/RGD. 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.

3.5. Development of precise O₂ standard gases for atmospheric observation

A goal of this study is to produce O₂ standard gases traceable to SI with expanded uncertainties of 1 ppm or less using a gravimetric method in which pure O₂ and N₂ gases are filled into a cylinder. To achieve 1 ppm uncertainty, pure O₂ gas filled in a small vessel was weighed with a mass comparator of which capacity fits to the vessel's weight. We verified reproducibility of the O₂ standard gases by comparing O₂ mole fractions using O₂ analyzers. We did intercomparison of the O₂ standard gases and analyzed the results until the end of March 2019. Stability and drift of a paramagnetic O₂ analyzer was studied. The pressures at the inlet and outlet of the analyzer and temperature of the detection unit were stabilized to reduce drift of the analyzer's signal output.

4. Results and Discussions

4.1. Measurement of the atmospheric O₂/N₂ ratio

Figure 1 shows the O₂/N₂ ratio, CO₂ concentration, and APO observed at MNM. As seen from Fig. 1, not only the seasonal variations but also the 24-hour mean values of O₂/N₂ ratio varied in opposite phase with those of CO₂ concentration. Based on analyses of the relationship between the O₂/N₂ ratio and CO₂ concentration, it was suggested that the main contributors of seasonal variations in the O₂/N₂ ratio at MNM are the terrestrial biospheric activities in summer,

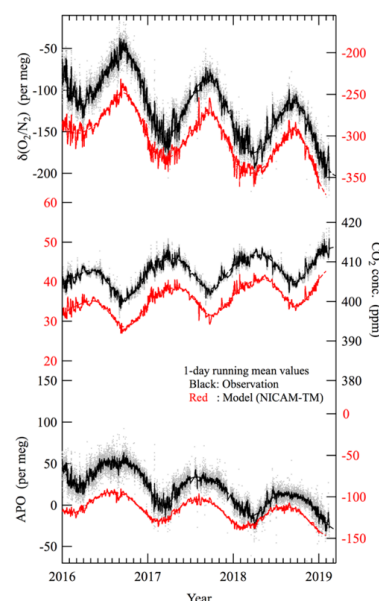


Fig. 1. Variations in O₂/N₂ ratio, CO₂ concentration and APO observed at MNM. Gray dots and black solid lines show 1- and 24-hour mean values, respectively. Red solid line shows the 24-hour mean values simulated by using NICAM-TM. Dashed lines show best-fit curves to the observed and simulated values.

both the terrestrial biospheric activities and air-sea O_2 flux in winter, and the air-sea O_2 flux in spring.

In Fig. 1, we also show the O_2/N_2 ratio, CO_2 concentration, and APO simulated by an atmospheric transport model (NICAM-TM). General features of the observed seasonal and short-term variations of O_2/N_2 ratio and CO_2 concentration were reproduced by the model. On the other hand, the short-term variations of the simulated APO underestimated the observed variations significantly. We decomposed the simulated values into the components of fossil fuel combustion, terrestrial biospheric activities, air-sea O_2 and N_2 fluxes and air-sea CO_2 flux, and found the main contributor of the short-term variations of O_2/N_2 ratio and CO_2 concentration was fossil fuel combustion especially in winter. It was also found that the short-term variations of APO were driven mainly by the air-sea O_2 and N_2 fluxes, which suggests that the monthly air-sea O_2 and N_2 flux climatology incorporated into the model was not appropriate to use to reproduce the short-term variations of the APO precisely.

4.2. Measurement of $\delta^{13}C$ and $\delta^{18}O$ in atmospheric CO_2

The CO_2 concentration showed a clear seasonal cycle in opposite phase with the $\delta^{13}C$ cycle. Comparative analyses between both of the seasonal components suggested that the cycles are due mainly to a seasonal-dependent CO_2 exchange with C_3 plants in land biosphere. $\delta^{18}O$ also showed a clear seasonal cycle, but the cycle was out of phase with those of CO_2 and $\delta^{13}C$. Secular increase of the CO_2 concentration and decrease of $\delta^{13}C$ due to anthropogenic CO_2 emission were seen in the time-series of the data obtained from flask sampling since 2011, accompanied by year-to-year variations in opposite phase with each other, while $\delta^{18}O$ showed a secular increase trend until 2016 and then a decrease trend. These secular trends may reflect variations in global carbon and hydrological cycles associated with the ENSO events.

Figure 2 shows variations in daily mean of atmospheric CO_2 concentration and its $\delta^{13}C$ and $\delta^{18}O$ obtained from continuous measurement. Not only seasonal cycles but also short-term variations can be seen; the latter variations are synchronized with one another. The continuous measurement has enabled us to capture such short-term variations, which should contribute to better understanding of the variations in CO_2 and its isotopes in background air.

4.3. Continuous measurement of the atmospheric H_2 and Rn concentrations

We started H_2 concentration measurements since November 2011. The H_2 concentration varies from 490 ppb to 590 ppb with a mean of about 530 ppb, clearly showing a seasonal cycle with a maximum in the summer and a minimum in the winter. The seasonal amplitude was about 25 ppb. We found several episodic events with enhanced peaks on a synoptic scale from winter to early spring and that the diurnal variation amplitude of H_2 is very small at about 0.7 ppb at MNM.

Figure 3 shows hourly mean concentrations of atmospheric Rn observed at MNM. Because MNM is a remote coral island away from continent, we observed 2.8 $Bq\ m^{-3}$ or less of low Rn concentrations. Seasonal variation was observed

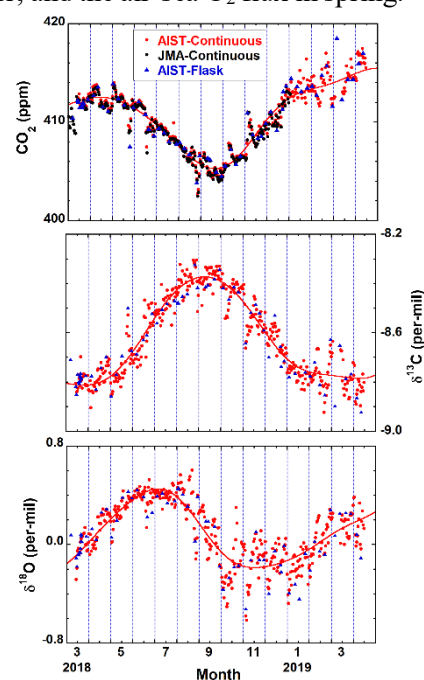


Fig. 2. Variations in daily mean of atmospheric CO_2 concentration (top), and its $\delta^{13}C$ (middle) and $\delta^{18}O$ (bottom) at MNM obtained from continuous measurement. The daily mean CO_2 obtained from JMA continuous measurement and CO_2 and its isotopes from flask sampling are also given.

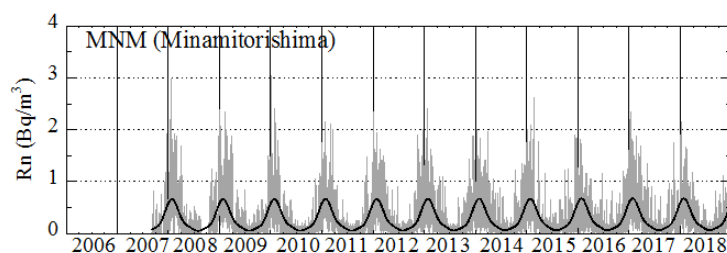


Fig. 3. Variation in atmospheric Rn concentration observed at MNM.

with a maximum in winter season around December-January and a minimum in summer season around July-September. The summer minimum Rn shows very low values of less than 0.2 Bq m^{-3} , indicating the values to be baseline concentrations of maritime air masses over the western North Pacific. On the other hand, the observed temporal variations of the Rn concentration clearly show high-frequency synoptic variations consisting of episodically enhanced Rn peaks on timescales less than one week during the winter through early spring. These peaks are caused by the influence of continental air masses. We established Rn data selection methods by eliminating the data influenced by continental air masses based on the enhanced Rn peaks. These methods indicated that more precise estimation of the variations in the trace gases such as CO_2 , CO, and CH_4 for the background air at MNM can be made from the remaining data (Fig. 4).

4.4. Development of precise O_2 standard gases for atmospheric observation

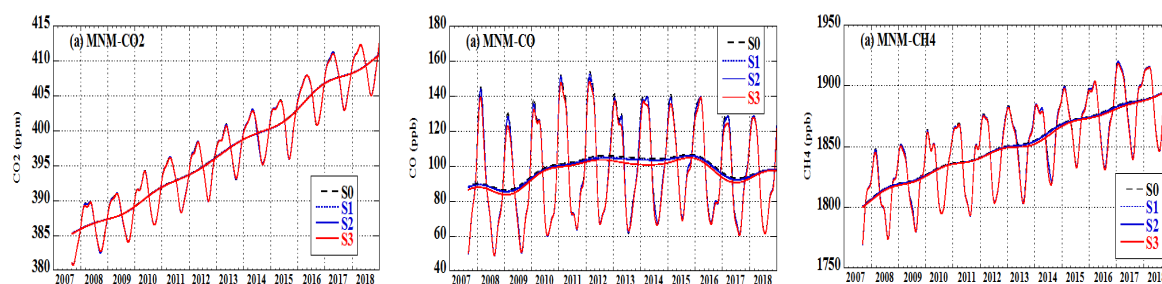


Fig.4. Comparisons of fitting curves of CO_2 , CO, and CH_4 at MNM between no data selection (S0) and Rn data selections (S1, S2, and S3).

We developed and studied a new weighing system of upper placing type to weighing a small vessel for O_2 filling. The system was designed to minimize the convention around a mass comparator, and the uncertainty for the weighing was 0.12 mg. We evaluated uncertainty for our weighing method with an updated mass comparator for 9.5-L cylinders, and the uncertainty was improved from 3 mg to 0.8 mg. The deviations of mass reading due to temperature, buoyancy, and adsorption effect were studied. We found that main factor for the deviation was temperature differences between sample and reference cylinders.

As uncertainties of atomic weights defined by the IUPAC are main factor for the O_2 standard gases, we determined molecular weights of N_2 and O_2 used in the source gases within the target uncertainty ($1/200,000$ in relative) using a mass spectrometry.

We investigated sensitivity of output of a paramagnetic O_2 analyzer to the temperature of the detection unit. The results show that the temperature coefficient is zero at the O_2 concentration of 20.7 % and the uncertainty of the measurement using the paramagnetic O_2 analyzer was 0.7 ppm which is enough small to verify precise O_2 standard gases.

We prepared five O_2 standard gases by the gravimetric method for an intercomparison experiment in 2017, and we verified the five O_2 standard gases with a high precision O_2 analyzer system which was developed in 2015. The O_2 concentrations in the standard gases were consistent within 1 ppm as shown in Fig. 5. This shows that the O_2 standard gases can be prepared with the target uncertainty. To determined span and scale differences of O_2/N_2 ratios among four institutes (EMRI/AIST, NIES, TU and SIO), we did an intercomparison using the five O_2 standard gases prepared by NMIJ/AIST. The preliminary results have been overall analyzed and discussed.

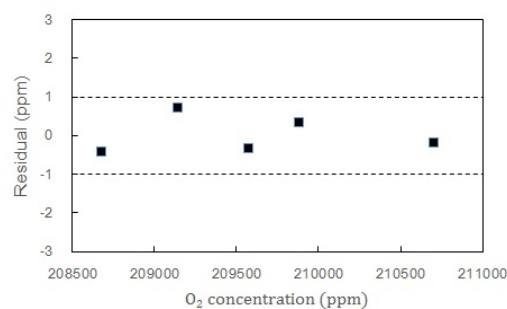


Fig. 5. Residuals from calibration line for O_2 concentration in standard gases.