

B-1 (2) Studies on Temporal and Spatial Variability of Reactive Greenhouse Gases and Their Related Compounds in the Atmosphere

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1. INTRODUCTION

Methane is one of the important greenhouse gases (GHGs), but also methane and non-methane hydrocarbons (NMHC) are the key species which control the chemical reactions in the troposphere. This implies that they have indirect greenhouse effects through affecting the OH radical concentration and producing tropospheric ozone or stratospheric water. Monoterpenes and isoprene are also important chemical species which react with ozone, OH and NO₃ radicals rapidly. Therefore, it is important to not only identify the sources of the GHGs but also quantify the dynamics of GHGs and other atmospheric trace species which affect life-times and distributions of GHGs through chemical reactions in order to understand the underlying mechanisms of the increase of some GHGs.

Reduced sulfur compounds in the atmosphere belong to another category of important chemical species related to global warming. They are produced by bacterial activities in the ocean and soil, oxidized in the atmosphere, and then transformed into fine sulfate aerosols. The aerosols thus formed are the major source of cloud-condensation nuclei over the ocean, and the nuclei become cloud droplets which affect the global radiation budget and therefore global climate. Although a number of studies on reduced sulfur compounds have been made, their environmental dynamics and roles in the atmosphere have been remained uncertain.

In this research project temporal and spatial variabilities of GHGs and other important chemical species in the atmosphere related to global warming are investigated by several kinds of field measurement. This project has started with the following subjects: (1) Quantifying temporal and spatial variability of methane and NMHC in the troposphere: (2) Identifying the role

of monoterpenes and isoprene in the atmospheric chemistry: (3) Clarifying the atmospheric concentration and distribution of sulfur-containing organic compounds from the ocean.

The following has been made in each subject in the first fiscal year. **Subject(1):** Analytical method of measuring methane and NMHC in the background concentration levels has been established. Preparative survey for PEM-west campaign(international cooperative program for airborne measurement of atmospheric trace species in September-October, 1992, sponsored by NASA) was made. Also preliminary observation of methane and NMHC at Iriomote Island, Okinawa was carried out. **Subject(2):** Atmospheric concentration of isoprene and its diurnal variation in a subtropical forest were studied at Iriomote Island. **Subject(3):** Analytical methods of measuring dimethylsulfide(DMS) and methanesulfonic acid(MSA) have been developed. By use of these methods, seasonal variation of MSA were measured at Oki Island in Japan Sea, and also diurnal variation and latitudinal distribution of atmospheric DMS in the Pacific Ocean were observed.

2.METHOD

Subject(1): FID-gaschromatographic(GC) method was employed for the measurement of methane and NMHC. For methane analysis, about 2 ml of air sample was directly injected into a Molecular-Sieve 13X column(3 m). The precision was within 1 %. For NMHC analysis, NMHC in 500-1000 ml of air sample was trapped in a preconcentration column and then injected into a fused silica capillary column(50 m). The precision was within 10 % and the detection limit was about 20 pptC. Air samples were collected in evacuated stainless steel canisters.

Subject(2): One liter of air was collected with a sampling tube containing 0.7 g of Tenax GC. Analyses were made by the automatic preconcentration / capillary GC/Mass Spectrometry(MS) method. Organics collected in the sampling tube were thermally (230 C) desorbed and were introduced into the capillary GC column. Two ions ($m/z=67$ and 68) were monitored for isoprene. Detection limit of isoprene with this method is 10pg which corresponds to 4 ppt for one liter air sample.

Subject(3): The method used for the atmospheric DMS measurement was the same as that for isoprene described above except the ions monitored by $m/z=47$ and 62 . Detection limit by this method is also 10pg for DMS. For MSA analysis, aerosols were collected on a quartz fiber filter attached to a low volume sampler every month. MSA on the filter was ultrasonically extracted with water, and was analyzed by a gradient ion-chromatograph.

3. RESULTS AND DISCUSSION

Subject(1): Observation of the variation of methane and NMHC at Iriomote Island, Okinawa(24°22'N, 123°50'E), was performed on March 1991. Sampling was made at 2 sites on sea (which were located almost at both SE and NW ends of the island) and over the island at altitudes of 200 - 400 m by an airplane. The result of methane is depicted in Fig. 1. Abrupt increase of methane concentration in the night of 22th is clear. In that evening a front passed over the island and the wind direction changed from south to north. The increase of methane is reasonably explained by the change of air mass over the island from the south (air mass over the Pacific ocean with low methane concentration) to the north (that from the Asian continent with higher methane concentration). Simultaneous observation of other gases from anthropogenic origins will be helpful to elucidate the change. Analyses of NMHC are now under way.

Subject(2): Tropical and subtropical forests have been considered to be significant sources for biogenic volatile organics, but very few measurements for the compounds in tropical and subtropical forests have been reported before. Atmospheric concentration of isoprene in a subtropical forest at Iriomote Island was measured. Figure 2 shows the diurnal variation of isoprene during March 20 - 23, 1991. Twenty-one measurements of isoprene give an average concentration of 226 ppt, with 582 ppt at maximum and 15 ppt at minimum. On fine days, the concentration was much higher in the daytime than in the nighttime, which reflects its higher emission in the daytime. The concentration was about 500-600 ppt around the middle of the day and was less than 100 ppt in the evening and early in the morning. On cloudy days, however, isoprene concentration in the daytime was reduced to the same level as that at nighttime. This suggests that isoprene emission is stimulated when the solar radiation exceeds certain threshold value. The variation of isoprene concentration is now under precise analysis with other factors such as meteorological conditions.

Subject(3): Seasonal variation of MSA was measured at Oki Island (36°15'N, 133°20'E). The result is shown in Fig.3. It shows a significant seasonal variation with a maximum in June and very low concentration in wintertime. The variation could not be explained only with ambient temperature, seawater temperature, and/or solar radiation. The variation of chlorophyll in this area must be known.

Diurnal variation and latitudinal distribution of atmospheric DMS over the Pacific ocean were measured in February 1991. Diurnal measurements were performed in the region of 14°29'-16°31'S and 172°3'-173°37'E during Jan.31-Feb.2. Latitudinal distribution was measured during the cruise from 21°38'S (Feb.8) to 35°17'N (Feb.20), where air samples were collected at 10 a.m. and 10

p.m. every day. The results are shown in Fig.4 and in Fig.5, respectively.

It was found that atmospheric DMS was more abundant in the nighttime than in the daytime. As for the latitudinal distribution, higher concentration was observed around equator. The relationship between DMS and MSA or bromocarbons which were sampled in the same cruise, will give useful information on the cause of the observed distribution of DMS.

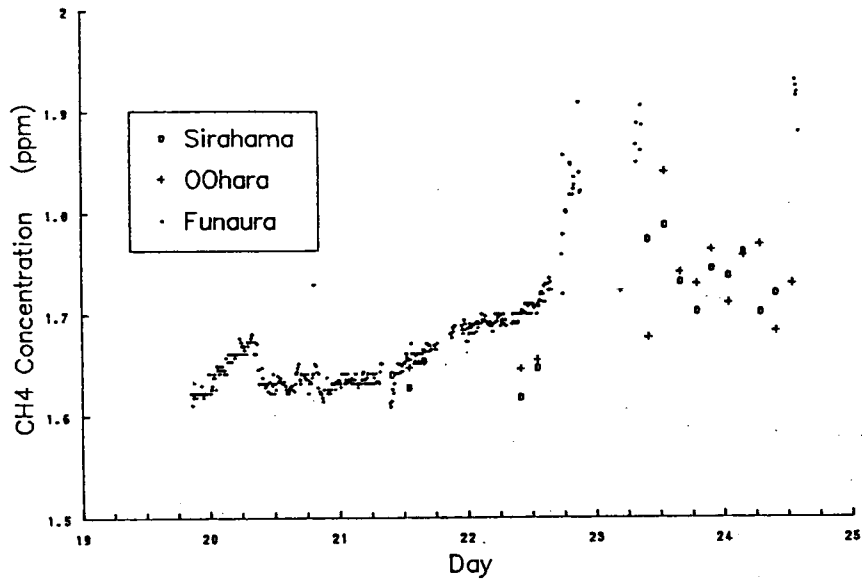


Fig.1 Diurnal variation of atmospheric methane at Iriomote Island (Mar.20-24, 1991).

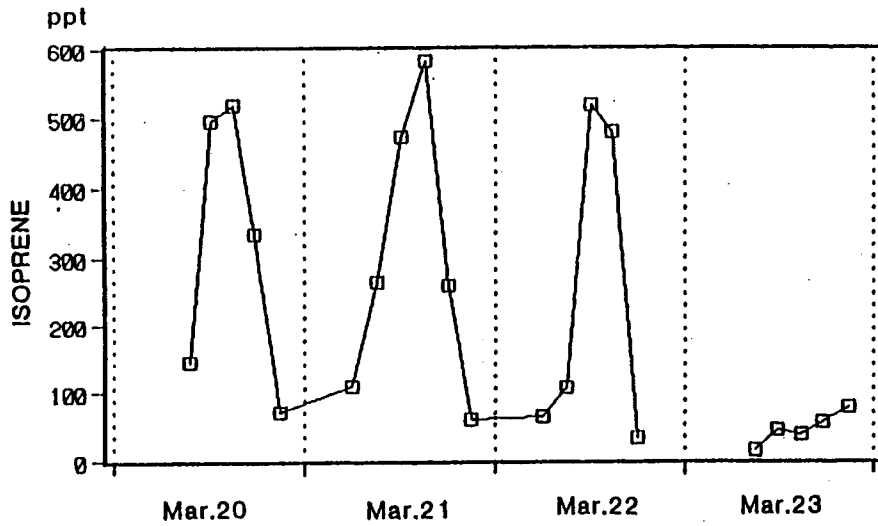


Fig.2 Diurnal variation of isoprene in the atmosphere of a subtropical forest (Iriomote Island, Mar.20-23, 1991).

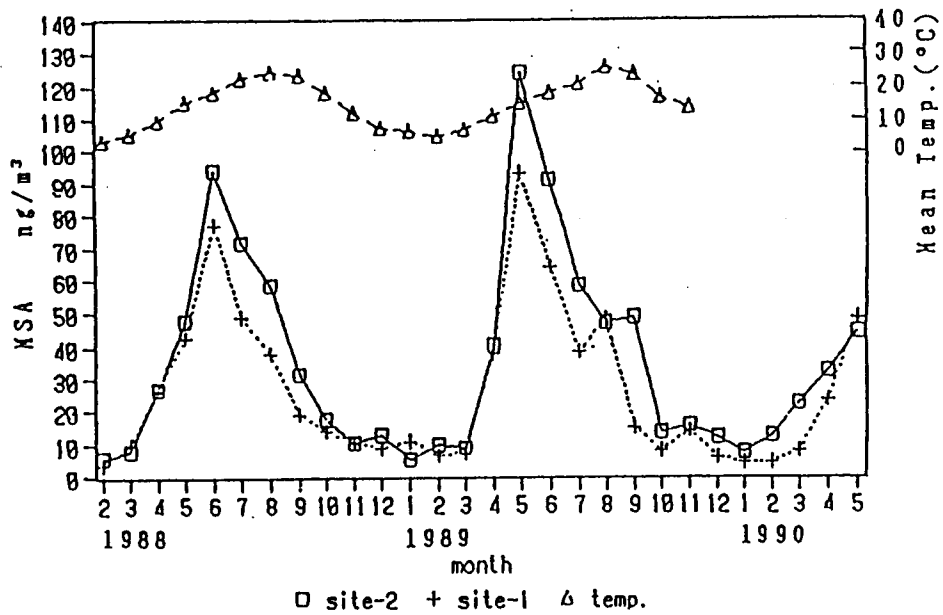


Fig.3 Seasonal variation of methanesulfonic acid in the atmosphere (Oki Island, 1988 - 1990).

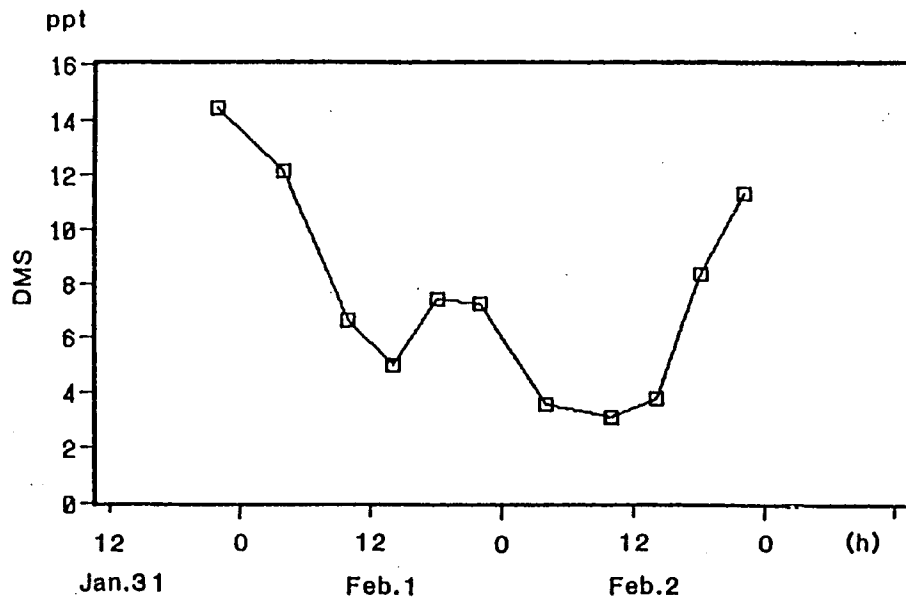


Fig.4 Diurnal variation of dimethylsulfide in the atmosphere over the Pacific Ocean (Jan.31-Feb.2, 1991).

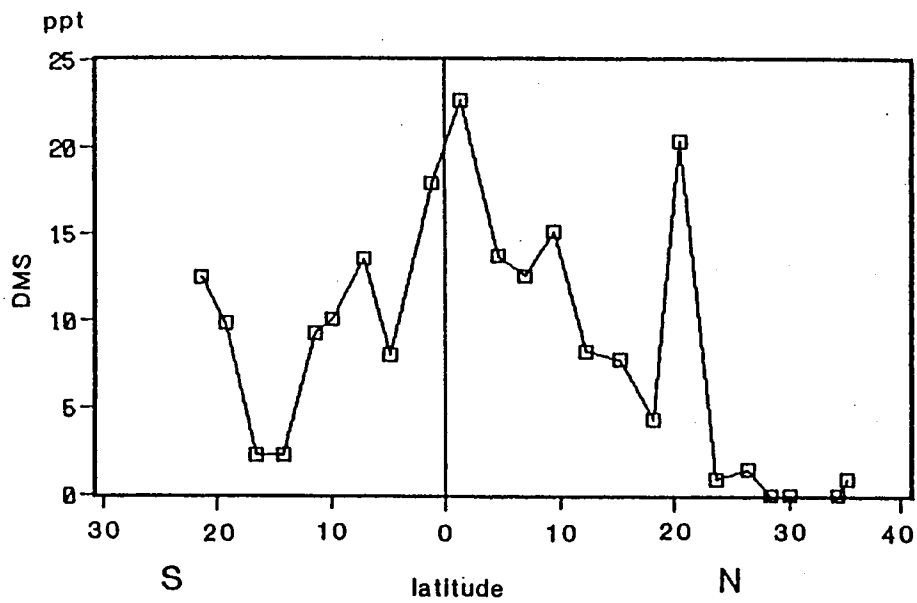


Fig.5 Latitudinal variation of dimethylsulfide in the atmosphere over the Pacific Ocean (February, 1991).