B-8.2 Studies on chemical reactions related to tropospheric ozone budget

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Total Budget for FY1996-1998 : 23,841,000 Yen (FY 1998 ; 7,920,000 Yen)

Abstract: (1) Two major marine-derived halocarbons (methyl iodide and bromoform) were measured in the samples collected over western Pacific, eastern Indian Ocean, and Southern Ocean. They showed completely different latitudinal variations; Methyl iodide was more abundant at lower latitudes supporting its photochemical production in the seawater, and bromoform was abundant at coastal areas and at higher latitudes, suggesting more importance of macroalgae for its emission. (2) Particulate and gaseous bromine were observed over the Pacific for 2 years. It was found that gaseous Br concentration was higher than particulate form and increased up to 50-100 ng/m^3 in winter, when a lot of sea salt particles exist in the marine atmosphere. In most case, the gaseous Br concentration was higher in daytime than in nighttime. (3) Laboratory experiments on the heterogeneous reactions of ozone with NaCl, NaBr, and NaI as well as synthetic and natural sea salts have been conducted for the purpose of elucidating the mechanism of halogen release from sea salt in the marine atmosphere. Reaction of ozone with the synthetic and natural sea salt has a large uptake coefficient of ca. 1 x 10^{-3} and gave Br_2 as a product. From this result, it was deduced that this reaction is important as a source of active bromine in the marine boundary layer and bromine atoms is thought to give an significant effect on the ozone budget at lease in the marine boundary layer. (4) The effect of introducing halogen molecules on photochemical ozone concentration in a propene/NO/air/photoirradiation system following the attainment of the maximum ozone concentration was investigated. Although the photochemical ozone was depleted by the presence of halogen molecules, the concentration of halogen molecules injected was too high to explain the ozone depletion in the marine boundary layer.

Key Words: Tropospheric Ozone, Organic Halogen, Inorganic Halogen, Sea Salt Aerosol, Heterogeneous Reactions

1. Introduction

Since the lifetime of tropospheric ozone is relatively short (0.1 – 0.3 year), its concentration is variable and strongly depends on region as well as season. It is known that the concentration of ozone in a marine boundary layer (MBL) is often extremely low (< 15 ppbv). The following reasons are proposed for such low concentration of ozone in MBL. (1) The production rate of ozone is extremely slow in MBL due to low concentrations of its precursors, NOx and VOC. (2) Ozone is efficiently destroyed by catalytic cycles including halogen atoms which are generated by the photolysis of halogen compounds, such as halocarbons ($CHBr_3$, CH_3I,...) and/or halogen molecules (Cl_2, Br_2, I_2).

In this projects, the following investigations have been conducted to make it clear if the catalytic ozone destruction by halogen compounds is effective: (1) measurements of the concentrations of organic and inorganic halogen compounds in the marine atmosphere, (2) examinations of heterogeneous production of halogen molecules from sea salts, and (3)

model experiments for the destruction of photochemical ozone by addition of halogen molecules.

2. Global distribution of atmospheric marine-derived reactive halocarbons (bromoform and methyl iodide)

2-1. Objective

Among marine-derived halocarbons in the atmosphere, short-lived ones have been considered to influence the tropospheric ozone budget. Methyl iodide is a major marine-derived iodocarbon, and bromoform is a major bromocarbon; both of them are photo-dissociated in near-UV and visible regions, and generate iodine and bromine atoms, respectively. In the present study, latitudinal variation of these two halocarbons was studied for better understanding of their emission mechanisms.

2-2. Method

The latitudinal distribution of the halocarbons (30.8°N - 69.1°S) was obtained from two cruises; Western Pacific and Indian Ocean cruise KH-96-5 (Research ship "Hakuho"; December 15, 1996 to February 17, 1997); and cruise of the 39th Japanese Antarctic Research Expedition (Research ship "Shirase"; November 14, 1997 to December 16, 1997, February 15 to March 21, 1998). · All samples were collected using evacuated stainless steel canisters with inert surfaces, and were analyzed using preconcentration/capillary GC/MS after being transported to the laboratory.

2-3. Results and Discussion

Methyl iodide : Methyl iodide measured during 'Hakuho' and 'Shirase' cruises varied greatly, ranging from 0.1 to 4.9 pptv. Figure 1 shows the latitudinal variation of methyl iodide obtained from these cruises and the monitoring works done at Hateruma Island (lat 24.1°N, long 123.8°E), at Alert (Canada), in the Arctic (lat 82.5°N, long 62.3°W), and over the NW Pacific Ocean where 7 samples were collected between 42°N and 54°S. The variation was almost equivalent in NH and SH, with maximum in the tropics, suggesting more significant emission from the oceans at lower latitudes, since the decay rate of methyl iodide due to photodissociation is much higher in the lower latitudes. As for the production mechanism in the seawater, two possible processes have been suggested for methyl iodide: (1) phytoplankton activity, and (2) photochemical production. Its higher emission from lower latitudes than from higher latitudes found in the present study supports the latter process.

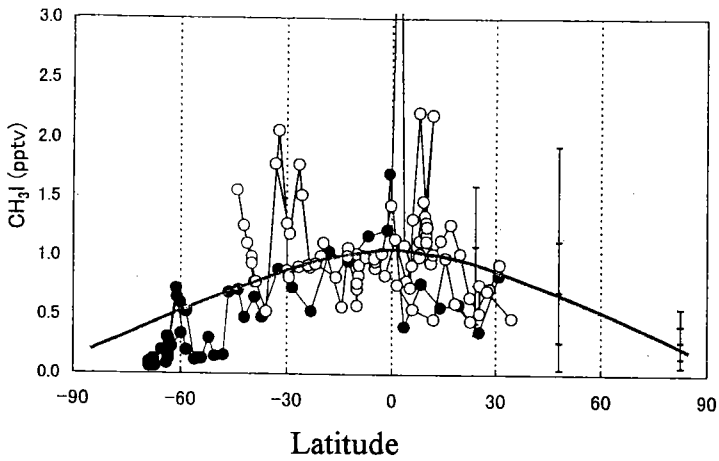

Fig. 1. Latitudinal variation of atmospheric methyl iodide

Bromoform : It is known that bromoform is released by temperate macroalgae, ice macroalgae and an additional planktonic source. Dataset from 'Hakuho' showed higher levels (>1 pptv) of bromoform near tropical islands, over the Strait of Malacca and over the western coast of Australia, while its concentration was generally low (around 0.4 pptv) over the open Indian Ocean, with an exception of higher values near 40° S where significant elevation of DMS was observed. In the dataset of 'Shirase', an increase in bromoform

levels at the west coast of Australia was found as in 'Hakuho' samples, and generally high concentrations (averaging ~1.5 pptv) were also observed over the Southern Ocean. Since the measurements at Alert in the Arctic showed 1 – 5 pptv of bromoform throughout the year[1], we could conclude that atmospheric concentration of bromoform was more abundant at higher latitudes as well as at productive coastal regions. These findings suggest the importance of macroalgae at coastal regions and ice-algae in polar regions for bromoform emission.

3. Measurements of inorganic bromine in the marine atmosphere

3-1. Objective

It was reported that inorganic halogen (Br and I) had a correlation with the low concentration of ozone in the Arctic atmosphere, suggesting the role of halogen in the ozone destruction in the polar region. In this work, the concentrations of particulate and gaseous bromine were observed periodically over the North Pacific for 2 years by using a ship to know the inorganic bromine concentration in the Pacific and its diurnal and seasonal variations.

3-2. Sampling Method

Automatic air sampler with 30 filter packs was made to take samples every half a day on a ship (Skaugran, Seaboard International Shipping), which is operated between Japan and Canada periodically. Filter pack was composed by Teflon filter for aerosol trap and alkali impregnated quartz filter for gaseous Br (like Br_2 and HBr). Sampling began in March 1997. Collected samples were extracted with 5ml of deionized water and ions were analyzed by ion chromatography.

3-3. Results

3-3-1. Diurnal variation

The clear diurnal variation of gaseous Br was observed in April 1997; gaseous Br concentration in the daytime was usually 2-6 times higher than that in nighttime. This suggests that the production of bromine compounds is promoted by sunlight and that the bromine compounds produced are rapidly consumed. The observed concentration level of gaseous Br was fairy high and comparable to the observed value in the spring Arctic.

3-3-2. Seasonal variation

Particulate and gaseous Br concentrations for 2 years over the Pacific are illustrated in Fig. 2. It was found that gaseous Br was several times higher than particulate form. Gaseous Br increased in winter and decreased in summer. Since the sea is rough in winter, a lot of sea salt particles are produced. Such increasing of sea salt particles must be related with increasing of gaseous Br concentration.

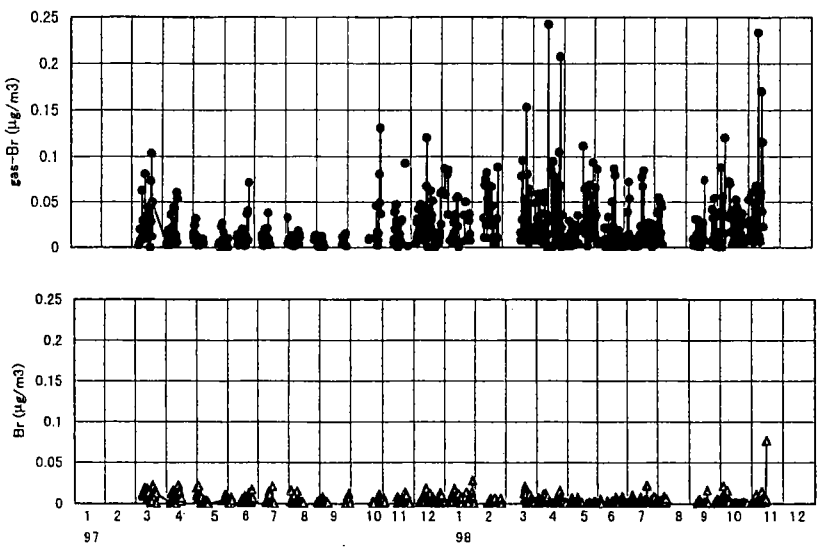

Fig. 2. Concentrations of gaseous and particulate Br observed for 2 years (Mar. 1997 – Nov. 1998)

It is necessary to study vertical distribution of gaseous Br concentration over the ocean to assess the

influence of Br to ozone budget in the troposphere.

4. Heterogeneous reactions of ozone with sea salts

4-1. Introduction

Although the role of halogens on ozone budget in the troposphere has been a keen interest in recent years, the initial process of active halogen release into the atmosphere has been left as a puzzle. One of the possibility is the reaction of sea salt with nitrogenous species such as N_2O_5, which has been studied by laboratory experiments. However, recent observations have suggested Cl_2 is present at a level of as high as a few tens of pptv in a clean marine boundary layer where the concentration of nitrogenous species is very low. In order to elucidate a possible mechanism of halogen release in the remote marine atmosphere in the absence of nitrogenous species, reactions of ozone with model compounds of sea salt have been studied in a laboratory in the present investigation.

4-2 Objectives

Heterogeneous reactions of ozone with model sea salt compound i.e. NaCl, NaBr and NaI as well as synthetic and natural sea salt are studied by laboratory experiments in order to obtain uptake coefficient of those reactions quantitatively.

4-3 Experimental method

Experimental set-up composed with a Knudsen cell reactor coupled with mass spectrometer has been used to study uptake coefficients, products and the their yields of the heterogeneous reactions of ozone with alkaline halides, and synthetic and natural sea salts.

4-5 Results and discussion

Uptake reactions of O_3 with NaBr and synthetic sea salt (Aqua Ocean) were studied by using the Knudsen cell reactor. In the case of NaBr no uptake of O_3 nor any product signal was observed when the plunger was lifted up and O_3 was contacted with the reactant, which means the uptake coefficient is smaller than 1×10^{-5}. On the contrary, O_3 signal decreased significantly and the product signal at m/e=160 for Br_2 appeared when the plunger was lifted up. The yield of Br_2 against the uptake of O_3 was 50-100%. Similar amount of release of Br_2 was observed for another synthetic sea salt (Instant Ocean) and natural sea salt.

The uptake coefficients of ozone with Instant Ocean and natural sea salt was obtained as $(1.4\pm1.1)\times10^{-3}$ and $(9.7\pm4.6)\times10^{-4}$, respectively. Thus, the typical uptake coefficient was deduced to be ca. 1×10^{-3}, which is unexpectedly large compared to theoretical prediction. This may be ascribed to trace species contained in the sea salt, which is responsible to enhance the bromine release reaction. In order to confirm such possibility, experiments with $MgBr_2$ and $CaBr_2$ has been conducted. Large uptake coefficients of 1×10^{-3} and $(6.3\pm3.0)\times10^{-4}$, respectively, which is comparable to the above reaction with synthetic and natural sea salts, indicating the possible effect of trace species in the sea salt. The uptake coefficients of the reaction of ozone with NaCl was $<1\times10^{-5}$ as expected, whereas that for NaI was as large as $(1.8\pm0.5)\times10^{-2}$ giving I_2 as a product.

By using the obtained uptake coefficients and Br_2 formation yield, it can be estimated that Br_2 release in the heterogeneous reaction of ozone with sea salt is an important source of bromine in the clean marine atmosphere, which could affect significantly the tropospheric ozone budget.

5. Depletion of photochemical ozone by addition of halogen molecules (Cl_2, Br_2, and I_2)

5-1. Introduction

It has been proposed that the photochemical ozone in a marine boundary layer (MBL) is destroyed by catalytic cycles including halogen atoms. The proposed mechanisms appear to be similar to that for the stratospheric ozone depletion by halogens. However in the

troposphere, the varieties of trace gases are far more abundant and their distribution is much more complex than in the stratosphere. This makes it difficult to assess the impact of halogen compounds on photochemical ozone in the troposphere. In this study, the effect of introducing halogen molecules such as Cl_2, Br_2, and I_2 on photochemical ozone concentration in a propene/NO/air/ photoirradiation system following the attainment of the maximum ozone concentration to demonstrate how efficiently halogen atoms destroy the photochemical ozone.

5-2. Experimental

A 6-m^3 evacuable and bakable photochemical reaction chamber was used for all of the experiments. Nineteen 1-kW Xe arc lamps were used for photodissociation. The concentrations of the reactants and products were monitored by means of a FT-IR coupled with a white cell with a 221.5-m path length. Ozone and NO/NO_x were continuously monitored with chemiluminescence ozone and NO_x analyzers, respectively. All experiments were carried out at 303 K.

5-3. Results and Discussion

Figure 3 shows the time profiles of ozone, NO, and NO_x–NO concentrations measured in the C_3H_6(3ppm)/NO(1.5 ppm)/Air + hν system as a function of irradiation time. The solid lines in the figure depict the profiles of [O_3], [NO], and [NO_2] calculated by a photochemical model of the system. As can be seen, the observed profile of [O_3] could be reasonably reproduced by the model calculation.

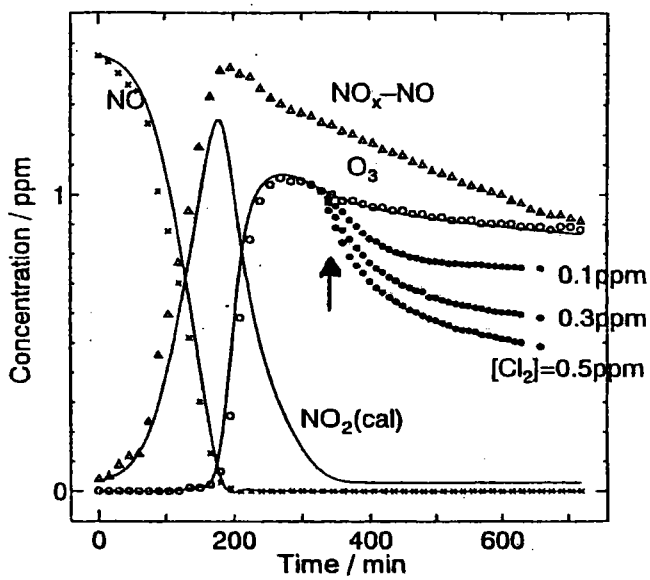

Fig. 3. Time profiles of O_3 (○), NO (×), and NO_x –NO (△) measured in the C_3H_6/NO/Air+hν system. Time profiles of O_3 measured after the injection of Cl_2 (0.1, 0.3, and 0.5 ppm) are shown by closed circles.

In order to examine the effect of the addition of Cl_2 on the ozone concentration, Cl_2 was introduced in the system after photochemical ozone concentration reached maximum (shown by arrow in Fig. 1). The observed profiles of [O_3] after the introduction of Cl_2 ([Cl_2] = 0.1, 0.3, and 0.5 ppm) were plotted in the same figure by closed circles. It was recognized that ozone concentration started decreasing as soon as Cl_2 was introduced and the ozone depleted more efficiently with increasing the concentration of Cl_2 added. A chemical model including known chlorine chemistry failed to reproduce the observed ozone depletion. The model rather suggested that ClOx cycles were not efficient under our experimental conditions because Cl atoms reacted with other trace gases, such as H_2CO and CH_3CHO, more dominantly than with ozone. It is, therefore, necessary to consider a new reaction scheme to explain the observed ozone depletion. Although the reaction mechanisms are not clear, the experimental results indicate that the relatively high concentration of Cl_2, such as sub-ppmv level, is necessary to reduce the ozone concentration.

Similar experiments were conducted by introducing Br_2 and I_2 into the system. Ozone depletion was also observed when about 10 ppbv of Br_2 or I_2 was introduced. The concentration of Br_2 and I_2 injected was about one order of magnitude lower than that of Cl_2. This means that the depletion of photochemical ozone by the addition of Br_2 or I_2 is more

effective than the case of Cl_2. Since the ozone depletion by Br_2 and I_2 could not be reproduced by a simple chemical model, a new chemical scheme should be considered to explain the observed ozone decays in the Br_2 and I_2 system. The concentration of Br_2 and I_2 introduced was the order of 10 ppbv, which was much higher than their expected concentration in the marine atmosphere (« 1ppbv).

The present work could demonstrate that the presence of halogen molecules makes the photochemical ozone concentration reduce. However, the concentration of halogen molecules used in this work was too high to explain the ozone depletion in MBL. Since our experiments were conducted under the high NO_x concentration conditions, additional experiments under the low NO_x concentration conditions would be desired to understand further the role of halogen molecules on the photochemical ozone.

References

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