## A.2.1.1 Studies on source, distribution, and reactions of methyl bromide and its alternatives in the atmosphere

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**Abstract**        (1) Global distribution of methyl bromide obtained from cruise- and monitoring-studies showed a small decrease of atmospheric methyl bromide ($CH_3Br$) from mid- to high- latitude as well as a gradient between NH and SH with the ratio of 1.2-1.3 and occasional high concentration in the tropics.   These data as well as modeled distribution of man-made $CH_3Br$, were used to determine the distribution of natural $CH_3Br$. The modeled distribution was highly dependent on the assumed lifetime of atmospheric $CH_3Br$.   An almost equivalent distribution of natural $CH_3Br$ in both hemispheres with tropical maximum around 6pptv was obtained for the $CH_3Br$ lifetime of 1.3yr which gave man-made contribution of 4 pptv in NH and 2 pptv in SH, consistent with the previous trend study from Antarctic firn.   (2) Photooxidation processes of chloropicrin, which is one of substitutes for methyl bromide, and their impact on photochemical ozone were investigated by using a 6-$m^3$ photochemical chamber.   Phosgene was obtained as one of the main products in the photolysis of chloropicrin with a yield of unity.   Photochemical ozone formation was enhanced when chloropicrin was added to the propene/NO/air/photoirradiation system after the ozone concentration maximum had been reached. This implies that the ozone concentration in suburban and/or rural areas can increase if the amount of chloropicrin as a soil fumigant increases.   Atmospheric loss processes of   methyl isothiocyanate and propargyl bromide were also investigated.

Key Words        methyl bromide, distribution, sources, chloropicrin, photochemical ozone

## 1. Introduction

studies have shown average global mixing ratios of 9 to 10 pptv, with an average northern to southern inter-hemispheric ratio (IHR) of about 1.2 to 1.4 [3-5].

Known sources of $CH_3Br$ include anthropogenic uses as a fumigant, oceanic emissions, and emissions from biomass burning. Significant sinks are reactions with OH radicals, followed by oceanic uptake and loss to soils. Current assessments of the global budget [6] suggest that there is a substantial imbalance between total known sources, 122 Gg/y (range;) and total known sinks, 205 Gg/y (range;). However, there are great uncertainties in each flux estimation, especially for oceanic emissions, oceanic uptake and soil uptake, and the magnitudes for total sources and total sinks have large estimated range of 43 to 244 Gg/y and 36 to 315 Gg/y, respectively. As well, total lifetime of $CH_3Br$ ranges from 0.32 to 1.3 years with best estimate of 0.7 years, and the total industrial sources range from 10% to 40% of the magnitude of the total estimated sinks, with best estimate of 20%. Due to these uncertainties, it is difficult to evaluate how much reduction of bromine loading can be expected from the phaseout and termination of production of $CH_3Br$ or to assess the distribution of $CH_3Br$ expected in the future, after the total ban on man-made use in 2005.

More observational data (global and seasonal) are now required to constrain the distribution and magnitude of the sources and sinks.

In agricultural communities, some chemical alternatives to methyl bromide such as chloropicrin are being in place before the phase out. In order to understand their impact on local air quality, intensive research on their atmospheric chemistry are necessary.


2. Methyl bromide: observation and estimation for natural contribution
2.1 Objective

The purpose of this project is better understanding of the distribution of non-industrial (natural) emission of $CH_3Br$ in order to identify its sources and to assess its future distribution expected after the total ban of man-made use in 2005.


2.2 Method

The latitudinal distribution of $CH_3Br$ (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). In order to study the seasonal variation, periodical monitoring was also done at Hateruma Island, Japan, a small island (12.5 km²) situated 250 km east of Taiwan in the subtropics (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°N on board the cargo ship 'Skaugran', which sails regularly between Japan and Canada.

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

Global distribution of $CH_3Br$ covering 82.5°N – 69.1°S was obtained from the two cruises ('Shirase' and 'Hakuho'), as well as from the monitoring at Alert, NW-Pacific and Hateruma (Fig. 1(a)). There were three features in the atmospheric $CH_3Br$ distributions. The first is a significant gradient between NH and SH as was found in the previous studies. IHR ratio, however, showed some difference depending on latitudes, and generally higher IHR was obtained from the data at higher

(a) $CH_3Br$ in the air (observed), $C_{obs}$

(b) Anthropogenic $CH_3Br$ in the air (estimated), $C_a$

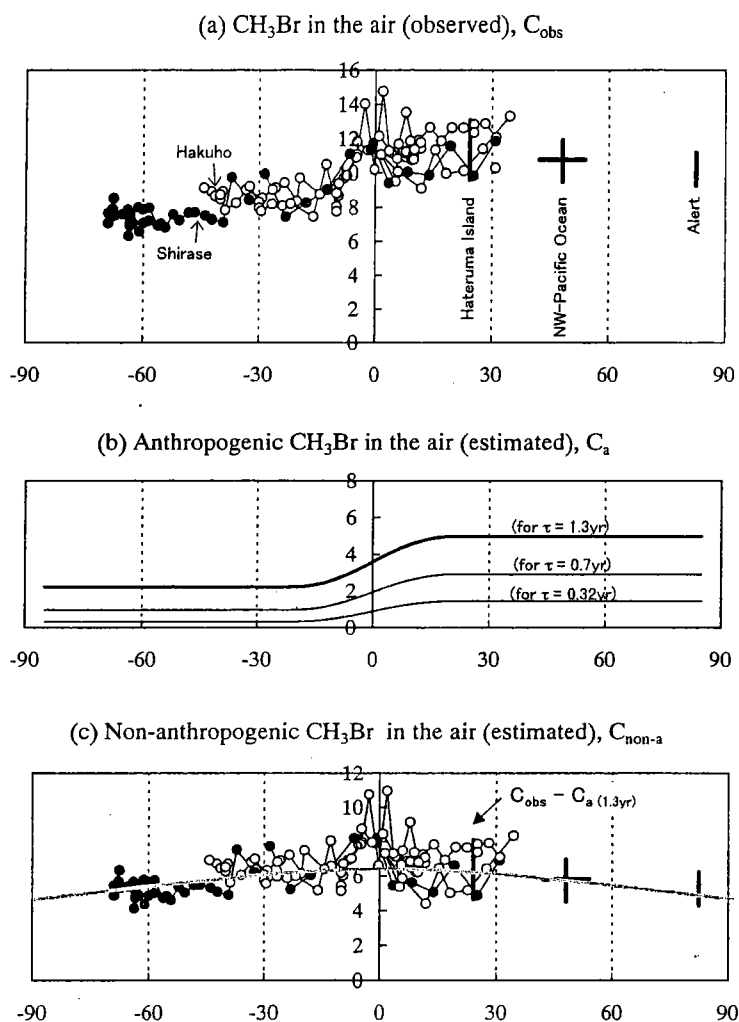(c) Non-anthropogenic $CH_3Br$ in the air (estimated), $C_{non-a}$

Fig. 1 (a) Latitudinal distribution of atmospheric methyl bromide ($C_{obs}$) from the 'Shirase' cruise (solid circles), from the 'Hakuho' cruise (open circles), and from monitoring stations at Alert, in the NW Pacific Ocean, and on Hateruma Island (mean ± 1σ). (b) Latitudinal distributions of anthropogenic methyl bromide ($C_a$) estimated from a 2-box model. (c) Latitudinal distribution of natural (non-anthropogenic) methyl bromide ($C_{non-a}$) estimated from observed distributions and the predicted anthropogenic contributions. Thick line represents the most probable background distribution of methyl bromide.

latitutude: IHR from the data of NH (0°N to 32°N) and SH (0°S to 32°S ) was 1.22, while that of NH (40°N to 54°N) and SH(40°S to 54°S) was 1.32. The second is an increases of $CH_3Br$ up to 15 pptv detected in some of the samples collected near the equator. The enhancement of $CH_3Br$ concentration in tropics should be attributed to the influence from tropical lands or coastal waters, since both of the two cruises in this study passed near the tropical islands. The third is a small decrease of atmospheric $CH_3Br$ from mid- to high latitude. Such a decrease of $CH_3Br$ toward higher latitude can also been seen in the SH data from eastern Pacific and Atlantic Ocean measured by Lobert et al.(1995), although

the authors have not mentioned about that. This trend would be related to either higher emissions at low latitudes or higher sinks at high latitudes.

Anthropogenic contribution to the global distribution of $CH_3Br$ ($C_a$) was calculated using a simple two-box model. The model assumes 90% of anthropogenic $CH_3Br$ (46Gg/yr, WMO(1998)) emitted in NH, and interhemispheric exchange rate of 1.2 yr Calculations was done for the possible total lifetime of atmospheric $CH_3Br$, 0.32-1.3 yr (WMO, 1998), and the results are shown in Fig.1(b). Calculated contribution of anthropogenic $CH_3Br$ ranged from 1.44 pptv in NH and 0.32 pptv in SH (for 0.32 y) to 4.97 pptv in NH and 2.2 pptv in SH (for 1.3y). Magnitude of anthropogenic releases could also be assessed if time series measurements before human agricultural use is available. South Pole firn air analyses dating back to 1880 (Elkins et al., 1996) showed 2-3 pptv increase of $CH_3Br$ after anthropogenic release of $CH_3Br$. The total lifetime of 1.3 yr gave best fit for this giving 2.2 pptv of anthropogenic $CH_3Br$ in SH. Knowing man-made contribution, we could calculate natural or non-anthropogenic $CH_3Br$ ($C_{non-a}$) by subtracting anthropogenic contribution, $C_a$ (Fig.1 (b)) from the observed $CH_3Br$, $C_{obs}$ as shown in Fig. 1(c). We got almost equivalent pattern of $CH_3Br$ in both hemisphere with a slight enhancement in the tropics. Higher level of $CH_3Br$ near tropical islands and its decreasing gradient from mid- to high latitudes suggest significant emission of this compound from tropical coastal lands, or from tropical forest fire, or from tropical coastal waters. Background $CH_3Br$ concentration derived from non-anthropogenic sources was around 6-7 pptv at lower latitudes and 4-5 pptv at higher latitudes. Such a distribution of atmospheric $CH_3Br$ would be the one which will be observed after the total ban of its anthropogenic use. Compared with the present concentration (NH;10-12pptv, SH;7-9pptv), we could expect the reduction of approximately 40% and 25% of $CH_3Br$ in NH and SH, respectively, for the future only having natural sources for $CH_3Br$.

Identification of tropical sources of $CH_3Br$ and re-evaluation of its total atmospheric lifetime are necessary for better understanding of $CH_3Br$ budget in the atmosphere.


3.Photooxidation Processes of Substitutes Methyl Bromide and Their Impacts on Air Quality
3.1 Introduction

Chloropicrin ($CCl_3NO_2$), MITC ($CH_3NCS$), D-D (1,3-dichloro-propene), and phosphine ($PH_3$) are proposed as its substitute for methyl bromide, which is phased out for the protection of the stratospheric ozone, and their use in agriculture is expected to increase. Hence, the impact of these substitutes and other potential alternatives, for instance propargyl bromide, on air quality should be assessed. In this project, the effect of chloropicrin in photochemical ozone formation was investigated. The atmospheric

loss processes of MITC and propargyl bromide were also studied.

## 3.2 Photooxidation of Chloropicrin($CCl_3NO_2$) and Its Impact on Photochemical Ozone

### 3.2.1 Objective

Chloropicrin (hereafter abbreviated as CP) is a pesticide widely used in agriculture for soil fumigation, and also used as one of the substitutes for methyl bromide. In Japan, the production of CP has increased, i.e., 5.7 kilotons in 1992 and 9.4 kilotons in 1997. Due to its volatility, it is expected that some proportion of CP injected into soil is emitted into the atmosphere.

CP has a broad absorption band with a peak at 280nm and the tail is extending up to 380nm. The photodecomposition is believed to be a dominant loss for CP. Since the estimated lifetime of CP in the atmosphere is one or a few days, CP may impact on the local air quality.

In this project, we studied the photolysis of CP in air and the effect of introducing CP on photochemical ozone formation in a propene/NO/air/photoirradiation system following the attainment of the maximum ozone concentration. It was examined whether CP contributes to the enhancement of ozone.

### 3.2.2 Experimental

A large-volume (6 m³) evacuable and bakable photochemical reaction chamber was used for all of the experiments. Nineteen 1-kW Xe-arc lamps were used for photoirradiation. The light intensity, determined by the $NO_2$ photolysis rate ($k_1$), was 0.20 min⁻¹. The concentrations of the reactants and products were monitored by means of an FT-IR with a White cell system (optical path length = 221.5 m). Ozone and NO/NOx were continuously monitored with a chemiluminescent ozone analyzer and a chemiluminescent NOx analyzer.

In CP photolysis experiments, 0.5-2.0 ppm of CP was introduced into the chamber, which contained air at 1 atm pressure. For photochemical ozone-formation experiments, the typical experimental procedure was as follows. After the chamber had been filled with purified air, propene (3.0 ppm) and NO (1.5 ppm), measured volumetrically using a capacitance manometer, were introduced into the chamber in a stream of pure nitrogen. Then, irradiation was initiated; photochemical ozone formed gradually and the maximum concentration was reached within 300 min. When the ozone concentration started to decrease, CP (0.2 to 6 ppm) was added to the reaction mixture.

### 3.2.3 Results and Discussion

#### 3.2.3.1 Photolysis rate and photooxidation products

The decay profile of CP (0.5 - 2 ppm) was observed with and without irradiation. When CP in air was irradiated, its concentration was decayed single exponentially and the decay rate was determined to be $1.1 \times 10^{-3}$ min$^{-1}$. The decay rate of CP without irradiation was $8.0 \times 10^{-5}$ min$^{-1}$. The photolysis rate of CP, JCP, was then determined to be $1.0 \times 10^{-3}$ min$^{-1}$. $J_{CP}/J_{NO2}$ was $5 \times 10^{-3}$, which is good agreement with the calculated value of $5.1 \times 10^{-3}$. This implies that the photodissociation yield of CP is almost unity.
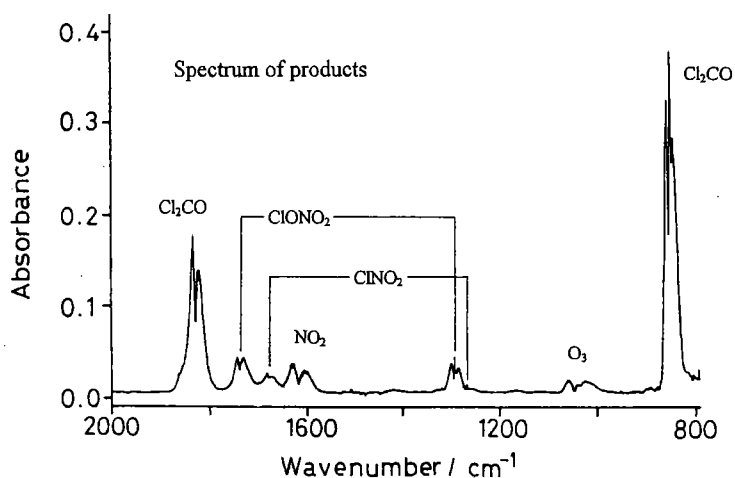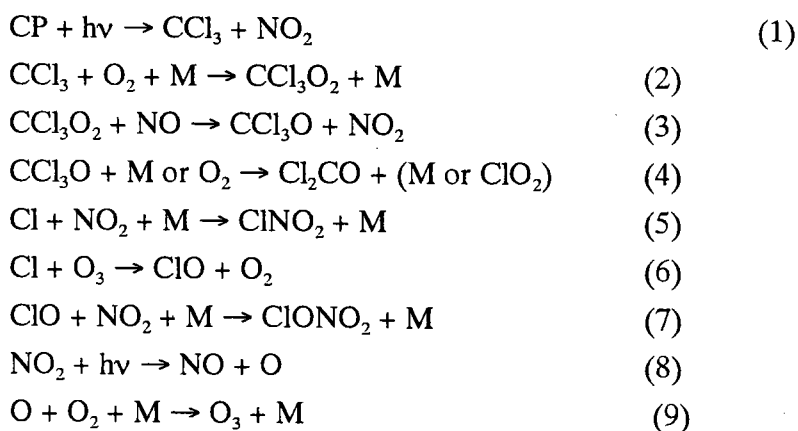


Fig. 2. FT-IR spectrum of products in CP/Air + hv system. The spectrum was synthesized by subtraction of the spectrum taken before irradiation from the spectrum taken after 6-hours irradiation.

Figure 2 shows the IR spectrum of the products in CP/Air + hv system. The spectrum was obtained by the subtraction of the spectrum taken before irradiation from that taken after 6 hours irradiation. The figure indicates the presence of phosgene ($Cl_2CO$), ozone ($O_3$), nitrogen dioxide ($NO_2$), chlorine nitrate ($ClONO_2$), and nitryl chloride ($ClNO_2$). Among them, phosgene is a dominant products and its formation yield was almost unity. According to the C-N scission mechanism, the CP photolysis reaction pathway is as follows:

$$CP + hv \rightarrow CCl_3 + NO_2 \tag{1}$$
$$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M \tag{2}$$
$$CCl_3O_2 + NO \rightarrow CCl_3O + NO_2 \tag{3}$$
$$CCl_3O + M \text{ or } O_2 \rightarrow Cl_2CO + (M \text{ or } ClO_2) \tag{4}$$
$$Cl + NO_2 + M \rightarrow ClNO_2 + M \tag{5}$$
$$Cl + O_3 \rightarrow ClO + O_2 \tag{6}$$
$$ClO + NO_2 + M \rightarrow ClONO_2 + M \tag{7}$$
$$NO_2 + hv \rightarrow NO + O \tag{8}$$
$$O + O_2 + M \rightarrow O_3 + M \tag{9}$$

Reaction 6 contributes to ozone depletion, whereas reactions 8 and 9 contribute to ozone formation.
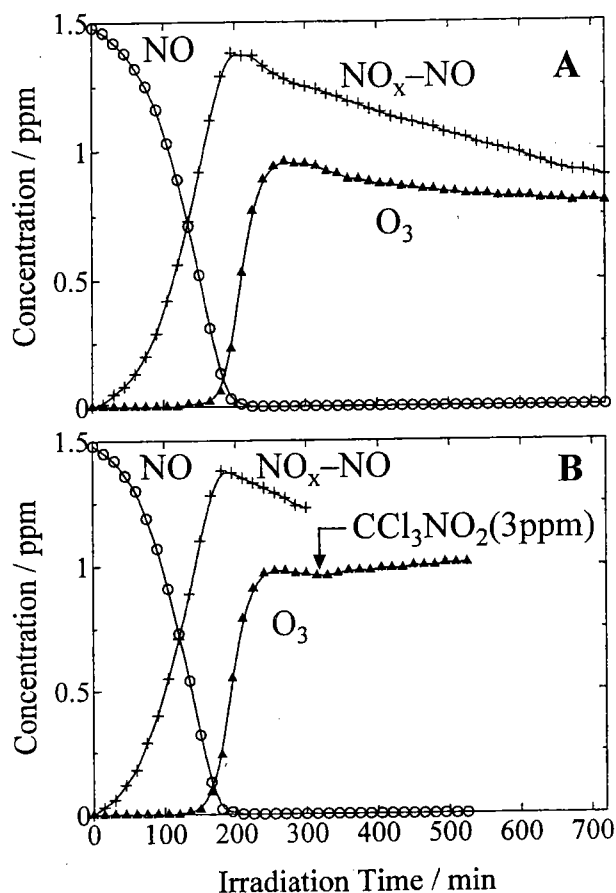
$C_3H_6$(3ppm)/NO(1.5ppm)/Air + hν (+CP)



Fig. 3. Time profiles are shown for ozone, NO, and NOx-NO in both the absence (A) and presence (B) of added CP. Since the NOx analyzer has sensitivity to CP, only NO was monitored by the analyzer after introducing CP.
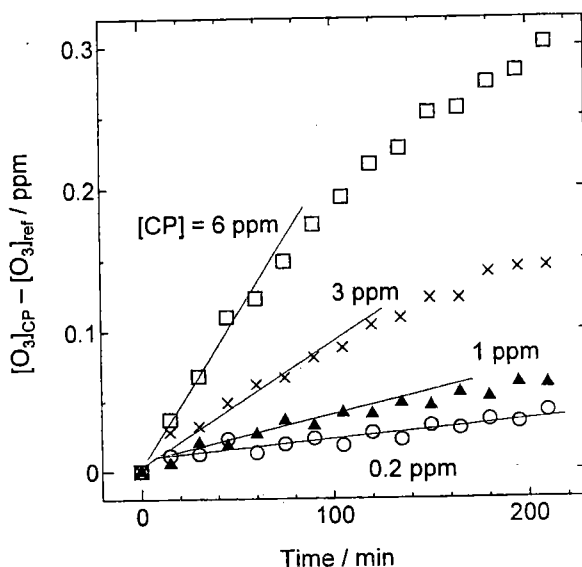


Fig. 4. The difference between the ozone concentration with CP ($[O_3]_{CP}$) and without CP ($[O_3]_{ref}$) is plotted versus the time following the introduction of CP.
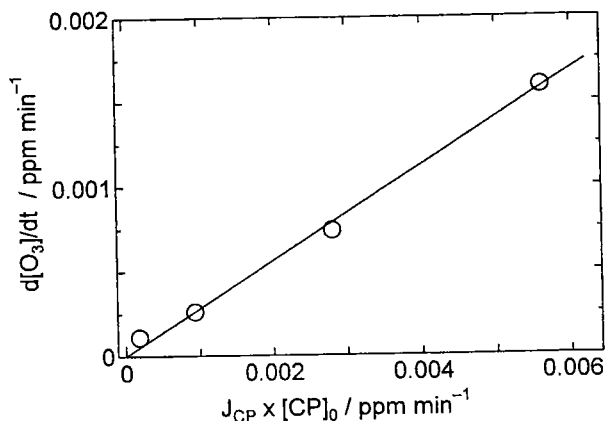


Fig. 5. The ozone increment rate is plotted versus the CP decrement rate.introduction

### 3.2.3.2 Impact of Photooxidation of CP on Photochemical ozone concentration

CP was added to the propene/NO/air photoirradiation system after the maximum ozone concentration have been reached following 300 min of irradiation. An ozone increase was observed when more than 3 ppm of CP was introduced. The addition of CP of less than 1 ppm did not show a clear increase, although a delay in the depletion rate of ozone was observed. Figure 3 shows the time profiles of ozone, NO, and NOx-NO in both the absence and presence of CP. An increase in the ozone concentration can be seen in Fig. 3(B), following the introduction of CP.

Figure 4 shows the difference between the ozone concentration with CP ($[O_3]_{CP}$) and without CP ($[O_3]_{ref}$) as a function of time, following the introduction of CP. As the concentration of added CP increased, the formation of ozone increased. The ozone

concentration increased linearly, particularly at the early stage. From the slopes of the plots in Fig. 4, the increase in the ozone concentration per unit time could be calculated (ozone increment rate). The ozone increment rate was plotted against the CP decrement rate; the resulting straight line is shown in Fig. 5. The slope is 0.25, which means that one molecule of ozone is formed for every four molecules of CP which react.

Recently, the rural areas, such as Gunma, Saitama, and Tochigi Prefectures in Kanto region, the higher concentrations of photochemical ozone are observed. CP is used in these rural areas, especially Gunma Prefecture. Our experimental results suggest that if the amount of CP emanating from cultivated soil becomes larger, the degree of photochemical smog pollution can be increased.

### 3.3 Atmospheric loss of MITC and propargyl bromide

The loss processes of MITC and propargyl bromide in the atmosphere were also investigated by using the photochemical reaction chamber. In the case of MITC, photodissociation was found to be important. The atmospheric lifetime of MITC by photolysis could be estimated to be less than a week. In the case of propargyl bromide, photolysis and OH reaction were found to be important and the atmospheric lifetime could be estimated to be about a few days.

References

1) UNEP (United Nations Environment Programme), Production and Consumption of Oozne Depleting Substances 1986-1995, Ozone Secretariat, Nairobi, Kenya (1997).

2) S. A. Penkett et al., An interhemispheric comparison of the concentrations of the cocentrations of bromine compounds in the atmosphere, Nature, 318, 550-553 (1985).

3) J. M. Lobert and J. H. Butler, "Blast94: Bromine latitudinal air/sea transect 1994," NOAA Technical Memorandum ERL CMDL-10 (1995).

4) O. W. Wingenter et al., Seasonal variation of tropospheric methyl bromide concentrations; Constraints on anthropogenic input, Geophy. Res. Lett., 25, 2797-2800 (1998).

5) "Assessment of Ozone Depletion: 1998", WMO Global Ozone esearch and Monitoring Project, Report No. 44, (1998).