B-3.3 Studies on the Increase of Ozone in the Troposphere

Contact Person   Gen Inoue
Principal Research Scientist
Atmospheric Division and Global Environment Division,
National Institute for Environmental Studies,
Environment Agency Japan
16-2 Onogawa, Tsukuba, Ibaraki 305, JAPAN
Phone +81-298-50-2402, Fax +81-298-50-2468
e-mail inouegen@nies.go.jp

1. Introduction

The intrusion of stratospheric ozone to the troposphere was observed in summer over Siberia at the latitude of 67N. The increase of ozone up to 200ppb was accompanied by the remarkable decrease of CO, from 80 to 45ppb and CH_4 from 1.79 to 1.72ppb. The model calculation based on the real wind field combined with emission and chemical reaction sub models agreed well with the observation qualitatively. The change of the concentration of trace gases and the humidity have been evaluated to be reasonable.

The concentration of mono-halocarbons and inorganic halogenates in the oceanic air have been measured over West Pacific and Indian Sea. The concentration range of mono-halocarbons observed are as follows; CH_3I: 0.5-1ppt, C_2H_5I:0-0.2ppt, CH_3Br:0.5-2ppt. Inorganic bromine (presumably HBr, Br_2 and $BrNO_2$) was 20-160mg/m^3. These halogen containing compounds are one of the possible sink source of tropospheric ozone in the oceanic air.

The tropospheric ozone data have been analyzed to obtain a trend of increase by 2, 1 and 0.5% in the 0-2km, 2-5km and 5-10km altitude range, respectively, from the periods of 1968-79 to 1980-90. The larger increase of tropospheric ozone in low altitude can be ascribed to the increase of anthropogenic NOx emission increase, 4%/yr, in past twelve years.

2. Research Objective

The tropospheric ozone has come to be widely recognized to play an important role as a greenhouse gas. The IPCC report in 1995 evaluates the globally averaged radiative forcing increased from 1950 to the present day due to the increase of tropospheric ozone to be one forth of that by carbon dioxide. The first objective is to evaluate the increase of tropospheric ozone from the past data.

The sources of tropospheric ozone are the stratospheric ozone intruded into the troposphere and the photochemical ozone formed from NOx and hydrocarbon reaction system. The intrusion of stratospheric has been thought to be the main source of tropospheric ozone and there are a lot of reports about it. But the estimation in global scale is not so easy as the dynamics of strato-tropo exchange process is not well understood to evaluate quantitatively. The observation of this process is mainly in spring when it is very frequent and large in scale. The field study in summer season when

it is seldom and small in size also should be made to estimate the full season amount.

The loss process of tropospheric ozone is less understood. The photolysis, the chemical reactions and the destruction on surface are the main process. The ozone concentration in the oceanic air is lower than the continental one, and it has been ascribed to the less photochemical production over ocean. However, the concentration in the marine boundary layer less than the half of free troposphere is observed frequently, and some missing sink process may exists over the ocean. One of the candidates is the reaction of halogenated hydrocarbons emitted from the ocean.

In order to reveal these points, the following three research have been done.

1.Trend analysis of tropospheric ozone over Japan.

2.Intrusion of the stratospheric ozone to the troposphere in summer over Siberia.

3.Analysis of halogenated hydrocarbons emitted from the ocean.

3.Trend analysis of tropospheric ozone over Japan

  by H.Akimoto, Tokyo University

The trend of the increasing tropospheric ozone should be originated from the increase of nitrogen oxides, carbon mono-oxide and hydrocarbons by the increase of anthropogenic activities, especially the consumption of fossil fuel in global scale. In this context, the evaluation of this increment based on the emission inventory and the reaction model should be compared with the observation.

Recently, the increase of tropospheric ozone in northern hemisphere has been report [1,2] and its effect on the global climate and the toxicity to the terrestrial ecosystem are discussed. These discussion is mainly based on the observation data in Europe, but nothing has been reported in Asia. The ozone sonde data of Kagoshima, Tukuba (Tateno) and Tsukuba obtained from World Sonde Data
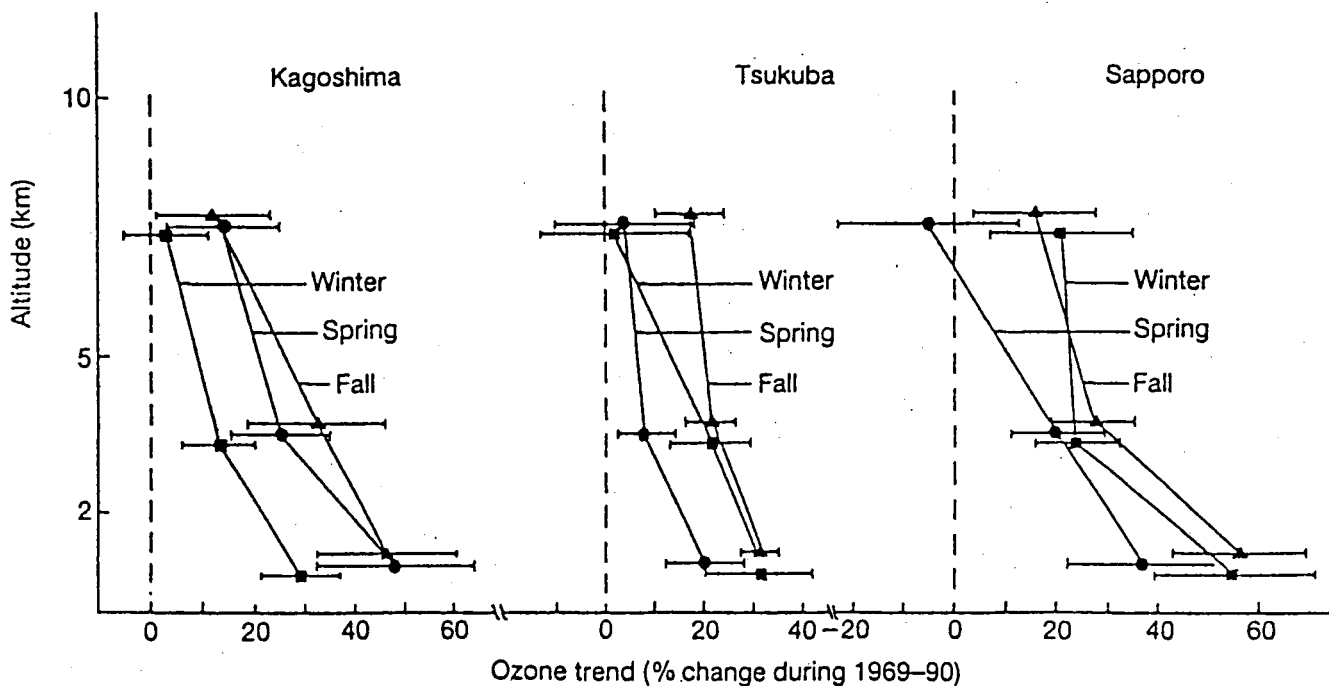

Fig.1   The trend of the tropospheric ozone mixing ratio at the altitudes of 0-2, 2-5 and 5-10km over Kagoshima, Tsukuba and Sapporo in 22 years (1969-1990)

Center has been analyzed. The data in the period from 1968 to 90, for 22 years, have been analyzed in the following manner. The ozone density data observed were interpolated at the interval of 100m, and then the average densities in the zone of 0-2, 2-5, 5-10,10-15km were obtained. The seasonal average values, winter (December - February), spring (March - May) and autumn (September - November), were obtained. This results were divided into two 11 years periods, Period I (1968-79) and Period II (1980-90), and averaged to compare with the model calculations.

The ozone increase trends for four seasons are shown in Fig.1 for three observatories, Kagoshima (130 ° 36 ′ E, 31 ° 35 ′), Tsukuba (140 ° 04 ′ E, 36 ° 01 ′) and Sapporo (141 ° 20 ′ E, 43 ° 04 ′). The significant increasing trend was detected for the low altitude data in three seasons. The data in summer is widely scattered because of frequent exchange of arimass. The increase rates at 0-2, 2-5 and 5-10km are 2, 1 and 0.5%/yr, respectively. The rate at lower altitude is larger suggesting the effect of photochemical ozone which is formed from nitrogen oxides, carbon mono-oxide and volatile organic carbons emitted by the anthropogenic activities on surface. In practice, the increase rate of anthropogenic nitrogen oxides emission in Asia is reported to be about 4% per year in past 12 years [4].
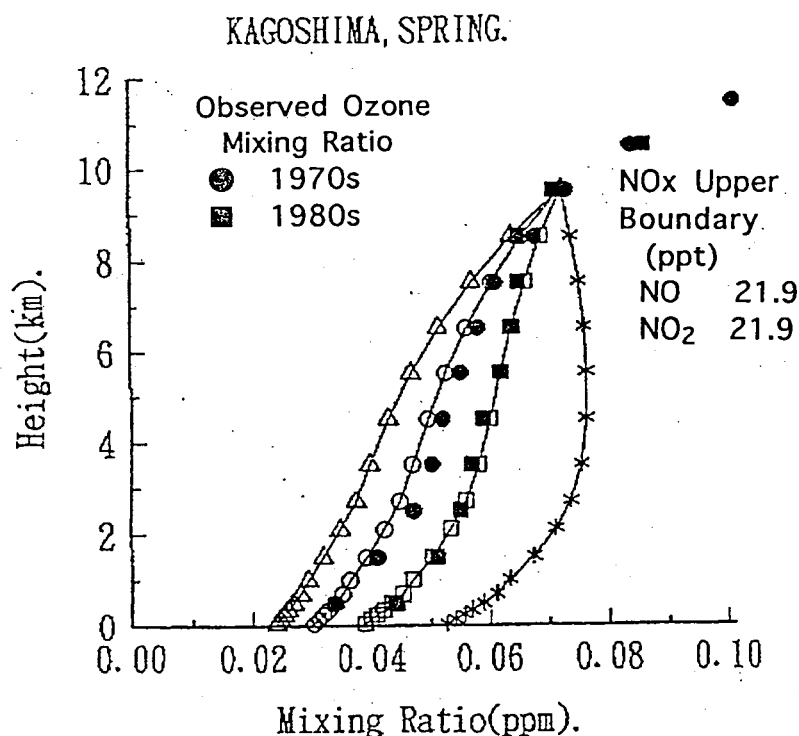

Fig.2 One dimensional chemical and transportation model calculation.

In order to confirm the above inspection, one dimensional chemical reaction - diffusion model calculation has been made. Fig.2 shows the comparison between the vertical profile of ozone observed and the calculation when only the NO_x flux was changed fixing the other fluxes. The agreement is excellent when the NO_x flux was assigned to be 1×10^{10} molecule $cm^{-2}s^{-1}$ for the period I (1969-1979), and 2×10^{10} molecule $cm^{-2}s^{-1}$ for the period II (1980-1990), respectively. The profiles with the NOx flux of 0.5 and 4×10^{10} molecule $cm^{-2}s^{-1}$ are shown as well in Fig.2, and the deviation from the observation is significant. It also should be noted that the influence of

anthropogenic photochemical ozone up to free troposphere is evident although it is much smaller than near the surface. The greenhouse effect of ozone is maximum at the altitude of about 10km, and the effect of anthropogenic photochemical ozone caused by NOx emission increase is very effective.

4.Intrusion of the stratospheric ozone to the troposphere in summer over Siberia.

by G. Inoue and S.Maksyutov

In the middle and high latitudes, the intrusion of the stratospheric ozone to the troposphere is the main source of tropospheric ozone. It has been studied intensively by a research aircraft in U.S.A. and Europe in spring, but little is known how frequent and what is the size in summer season. High ozone concentration, about 80-100 ppb, is frequently observed over Siberia in summer season, and it has been ascribed to the tropospheric ozone intrusion. In order to confirm the occurrence of ozone folding in summer, the ozone concentration and other atmospheric constituents were measured during the transit flight of STEACE (Siberian Terrestrial Ecosystem, Atmosphere and Cryosphere Experiment) flight experiment.

The research aircraft, Illusin-18, from Central Aerological Observatory, has been used for this research flight. This aircraft is a turboprop engined passengers aircraft (about 100 passengers size) modified for the meteorological observation. The instruments installed are as follows: Navigation; INS, GPS, Loran, a radar altimeter. Meteorological; stagnation temperature, Lyman α hygrometer, due point hygrometer, semiconductor hygrometer, wind speed sensor system, solar radiation, surface temperature sensor, laser aerosol sensor.
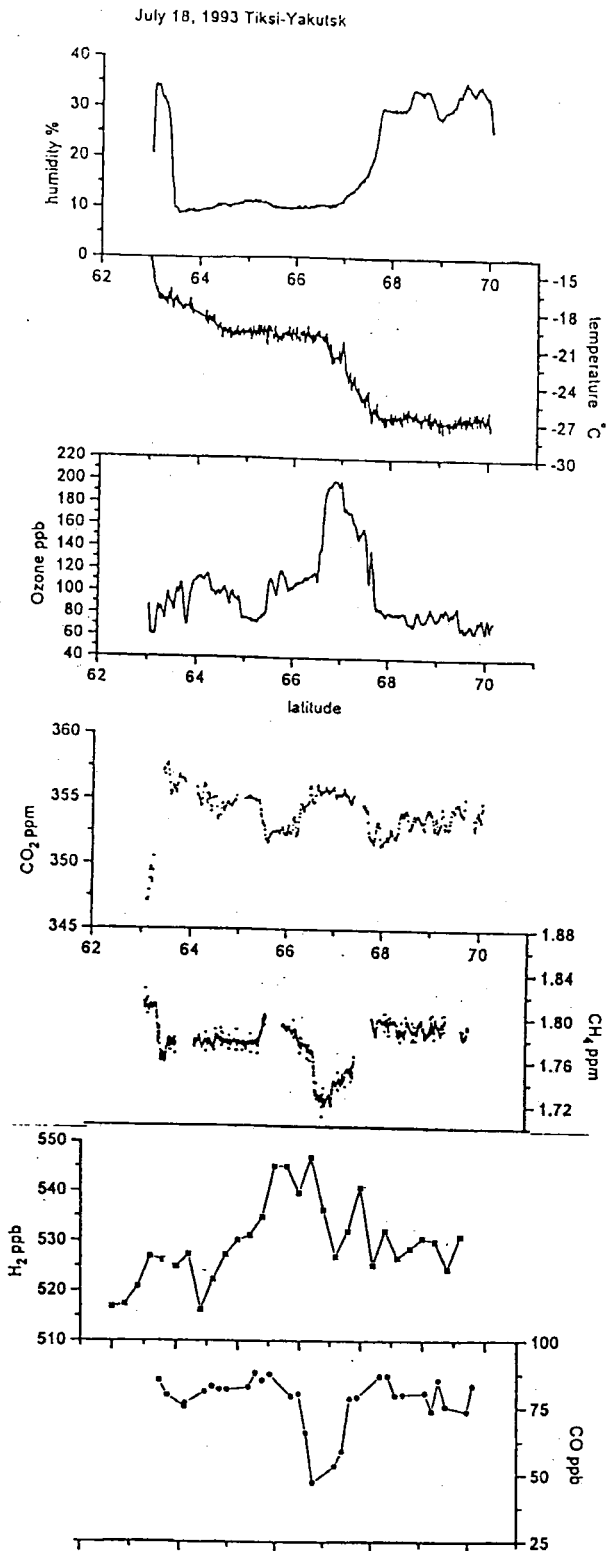

Fig.3 The distribution of a) relative humidity, b) temperature, c) ozone, d) carbon dioxide e) methane, f) hydrogen and g) carbon monoxide observed in 18, July, 1998 along 130E from Tiksi to Yakutsk at the altitude of 7000m.

Chemical; UV ozone sensor, electrochemical ozone sensor, GC and continuous methane senor, non-dispersive CO_2 sensor, GC H_2 and CO sensor,and fluorescence SO2 sensor. The canister sampling, 200 samples during 80 hours flight, has been performed as well to measure CO_2, CH_4, N_2O, $^{13}CO_2$ concentrations.

The result obtained during the transit flight between Yakutsk (60° N) and Tiksi (70° N) along 130° E is shown in Fig.3. The ozone observed during the flight at the altitude of 6,800m from Yakutsk (10:50 in local time) to Tiksi (13:30) was between 50 to 100ppb, and 75ppb on average. On the return flight from 15:00 to 17:30, very high ozone concentration of 200ppb was recorded for 15 minutes at the latitude of 67° N and the altitude of 7,000m. At the same time, the decrease of CO from 77ppb to 40ppb, and CH_4 by 0.08ppm was observed with a similar pattern. The air temperature and the humidity jumped up from -27 to -19°C and down from 30 to 10%, which correspond the decrease of absolute humidity by 30%, respectively. The changes of H_2 and CO_2 concentration were not clear. The wind velocity (about 31-35m/s) and the direction (210°) did not change almost at all.
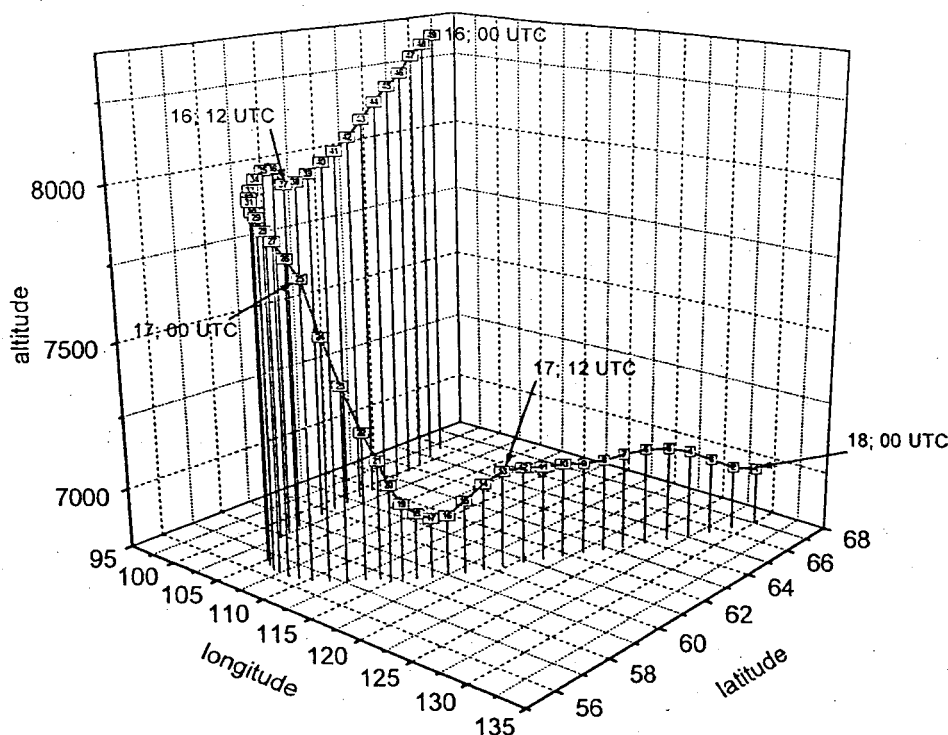
July 18, 1993

Fig.4   Back trajectory calculation suggests that the stratospheric ozone penetrated to the stratosphere about 28 hours over Baikal lake.

The concentration of CO starts to decreases from the altitude of 13km, and drastically at around 20km in general. It is due to the high concentration of OH driven from the reaction of $O(^1D)$ from the photolysis of O_3 and gaseous H_2O. The reaction rate constants of OH with CH4 and CO at -23°C are 2.6×10^{-15} and 2.4×10^{-13} cm^3 $molec^{-1}s^{-1}$, respectively. So, the ratio of the reaction rates of OH with CH_4 at 1.78 ppm and CO at 77 ppb are 1:4, and this ratio will be 1:2 when the CO concentration decrease to 40ppb. As the reaction of CH_4 with OH is accompanied by the formation of one CO molecule, the net loss rates of CO and CH_4 are almost the same. In this simplified

estimation, some important process are neglected but the CH_4 decrease observed is quite reasonable in amount. In the case of hydrogen, the reaction rate with OH radical is $1.8 \times 10^{-15} \, cm^3 \, molec^{-1}s^{-1}$, and only 4% of OH reacts with H_2. The reaction of OH with CH_4 is followed by the formation of H_2CO, and bout 0.3 molecule of hydrogen is formed from the photolysis of H_2O; $0.3 \times H_2$ is formed from on H_2 molecule. So, there is no loss or rather small gain of H_2 is expected.

The low humidity in the air is generally accepted as an evidence of stratospheric air intrusion, but no decrease was observed in this case. If the background tropospheric ozone and water mixing ratio is 80 ppb and 225 ppm (relative humidity is 30% at $-23°C$), respectively, and the stratospheric ozone concentration is 1,300 ppm, which is a typical concentration in the tropopose, the percentage of stratospheric air in the observed area where the ozone mixing ratio was 119 ppb is 9%. As the water vapor mixing ratio is about 5 ppm in the stratosphere, the decrease of water vapor is expected to be only 9%. This amount is quite small in comparison with the difference of water vapor content between the two air masses between which our airplane passed through.

Some model calculations have been performed to compare with the observation. The simulation calculation of concentration has been done by use of the wind filed from the ECMWF data base combined the emission and the chemical reaction models. It is well established that the high potential vorticity in the troposphere is a good evidence of the stratospheric air intrusion. A narrow belt of potential vortesity at the altitude of 7000m was observed from (120°E, 60°N) to the north-east direction at that time. The high ozone concentration by 130ppb, the low CH_4 and CO by concentration by 0.01-0.02ppm and 20ppb, respectively, along this belt are well simulated. The amount of change is quite similar to the observation in spite of poor resolution of ECMWF data base.

The back trajectory of the air from the time of location of high ozone observation for 2 days is shown in Fig. 4. The penetration of tropopose air penetrated about 28 hours along the seam of the jet stream over Baikal lake down to 7000m, and transported to the north-east direction.

5.Measurements of methyl iodide, ethyl iodide, bromoform and dibromomethane over the ocean (East and Southeast Asian seas and the Western Pacific)
by Y. Yokouchi and H. Mukai
5-1.Experimental

Air samples were collected during three cruises: (1)Western Pacific Cruise 1 (January 31 - February 20, 1991), (2) Western Pacific Cruise 2 (September 16 - October 25, 1992) and (3) East and Southeast Asian Cruise (East China Sea-South China Sea-Bay of Bengal; January 25 - March 9, 1994). During most of these cruises, samples were collected once during the daytime and once at night. The numbers of samples obtained during Western Pacific cruise (1), Western Pacific cruise (2) and East and Southeast Asian cruise were 23, 48 and 73, respectively.

The samples were taken on board at the front of the uppermost deck, forward of any potential contamination from the stack. With only a few exceptions during the Asian coastal cruise, the samples were collected while the ship was underway. Sampling of defined air volumes (1 or 2 liters) was done by adsorption on Tenax TA in stainless steel tubes of 1/4" o.d.. The air flow through the trap was controlled and measured with a mass flow controller. The sampled tubes were stored in a clean box and were analyzed within a month after the cruises. Volatile halocarbons in the air samples were analyzed with a technique for which the details were published earlier (Yokouchi et al., 1996).

Briefly, organics collected in the adsorption tube were thermally desorbed into a small trap cooled to 0 C. The subsequent procedure involved thermal desorption of the components from the small trap, their transfer with a helium gas stream into a capillary GC column (Poraplot Q, 0.32 mm ID x 10m) and then MS detection in selective ion monitoring mode. The target compounds and the monitored ions for their quantification are bromoform ($CHBr_3$; m/z 173), dibromomethane (CH_2Br_2; m/z 174), methyl iodide (CH_3I; m/z 142), ethyl iodide (C_2H_5I; m/z 156), chloroiodomethane (CH_2ClI; m/z 176), diiodomethane (CH_2I_2; m/z), tetrachloroethylene (C_2Cl_4; m/z 166) and trichloroethylene (C_2HCl_3; m/z 130). Some of these compounds were analyzed only during specific cruises.

5-2. Results and Discussion

Substantial variations in the ambient concentrations of halocarbons along the cruise tracks were observed. Maximum, minimum, and mean values for each compound are summarized in Table 1.

1) Bromocarbons

Ambient concentrations of $CHBr_3$ and CH_2Br_2 over the Western Pacific were in the range of 0.13 - 2.9 pptv and 0.14 -1.58 pptv, respectively (Table 1), with mean values in reasonable agreement with previously reported concentrations over the North Atlantic and in the Arctic (Class &
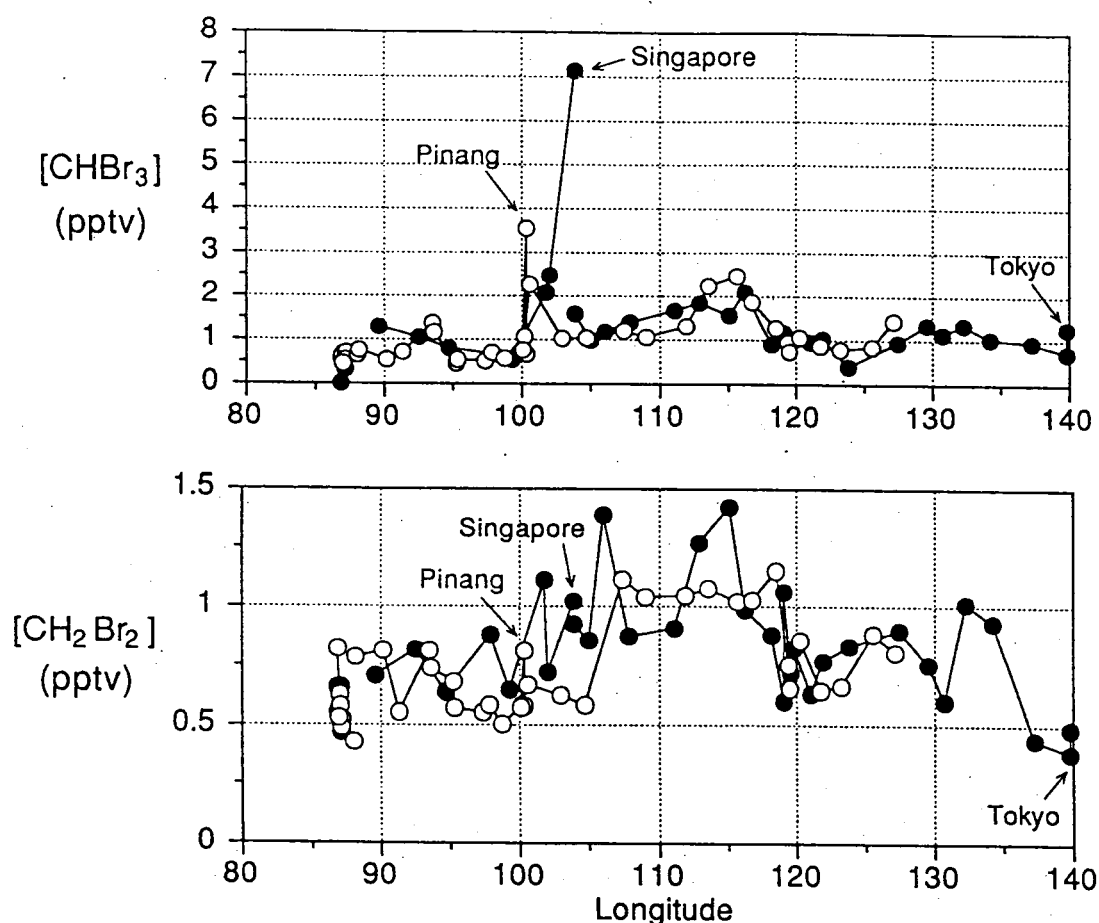

Fig. 5 Longitudinal variation of bromoform and dibromomethane measured over East and Southeast Asian seas during Jan-Mar, 1994. ●: east-to-west transect,○: west-to-east transect.

Ballschmiter,1988; Bottenheim et al+,1990; Yokouchi et al., 1996). The latitudinal variations of $CHBr_3$ and CH_2Br_2 were similar except for the samples from the east of Austraria around 20-22S during cruise (1), where the highest concentration of bromoform was observed.

During the East and Southeast Asian Coastal cruise, concentrations of $CHBr_3$ as high as 7 and 3.5 pptv were observed in the samples collected in the harbors of Singapore and Pinang where concentrations of chlorophyll-a were higher than those observed in other areas. The similarity of the east-to-west and west-to-east transects of both $CHBr_3$ and CH_2Br_2 (Fig. 5) suggests that the emission of bromocarbons is greatly influenced by the distribution of source algae. Rather high concentrations of $CHBr_3$ and CH_2Br_2 were observed north of Borneo and the lowest concentrations were observed over the Bay of Bengal. Excluding data from harbor samples, the correlation coefficient for these two compounds was 0.6. The greater variability of $CHBr_3$ compared to CH_2Br_2 might be explained by its higher reactivity in the atmosphere.
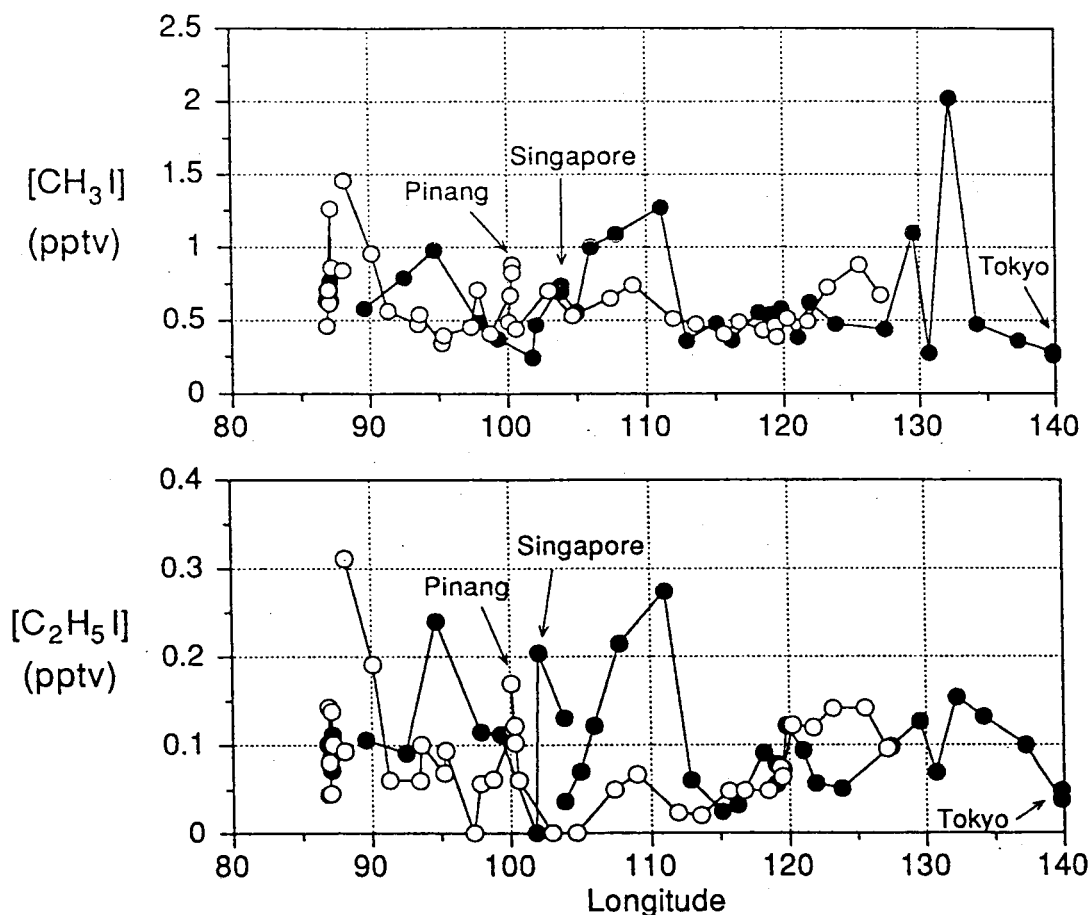

Fig. 6 Longitudinal variation of methyl iodide and ethyl iodide measured over East and Southeast Asian seas during Jan-Mar, 1994. ●: east-to-west transect, ○: west-to-east transect.

2) Iodocarbons

CH_3I in the samples from Western Pacific cruise (2) and from the East and Southeast Asian Cruise was measured. During the Asian cruise, three other iodocarbons, C_2H_5I, CH_2I_2 and CH_2ClI, were also measured. C_2H_5I, which had not previously been found in the atmosphere, was observed, but the latter two compounds could not be detected.

The mean and maximum concentrations of CH_3I over the Western Pacific were 0.9 pptv and 5.0 pptv, respectively, in reasonable agreement with previous results [Rasmussen et al., 1982(a)]. The highest concentration of CH_3I was observed in the sample collected at windless night around 29N.

CH3I observed during the Asian coastal cruise ranged from 0.24 to 2.0 pptv (Fig. 6). Unlike the bromocarbons discussed above, the longitudinal variations in CH_3I concentrations showed considerable differences between the east-to-west and west-to-east transects, despite very similar cruise tracks. For example, CH_3I concentrations between 105 and 112E along the east-to-west transect were much higher than those measured along the west-to-east transect. Similar variations were found for the other iodocarbon, C_2H_5I (Fig. 6), and their correlation coefficient was 0.61, suggesting that the emission and/or decomposition of these iodocarbons is controlled by some common processes. Rapid destruction of iodocarbons due to photodissociation of very weak C-I bonds might be important. Neither CH_2I_2 nor CH_2ClI, both of which had been detected in the Arctic in autumn and winter (Class and Ballschmiter, 1988; Yokouchi et al., 1996), were detected in the present study. It is very probable that these compounds are photodecomposed very rapidly in low latitude areas even if they are emitted from the ocean.

3) Tetrachloroethylene and trichloroethylene

C_2Cl_4 and C_2HCl_3 which are major short-lived halocarbons emitted anthropogenically, were measured for comparison to marine derived halocarbons.

Table 1. Concentrations of bromoform, dibromomethane, methyl iodide, ethyl iodide, tetrachloroethylene and trichloroethylene over the ocean.

Compound	Cruise	Mean (pptv)	Maximum (pptv)	Minimum (pptv)
CHBr3	Western Pacific (1)	1.01	2.9	0.28
	Western Pacific (2)	0.63	1.91	0.13
	East and Southeast Asian seas	1.2	7.1	0.32
CH2Br2	Western Pacific (1)	0.87	1.36	0.47
	Western Pacific (2)	0.59	1.58	0.14
	East and Southeast Asian seas	0.77	1.42	0.38
CH3I	Western Pacific (2)	0.87	5.0	0.05
	East and Southeast Asian seas	0.63	2.0	0.24
C2H5I	East and Southeast Asian seas	0.09	0.31	<0.03
C2Cl4	Western Pacific (1)	6.6	40.0	0.68
	Western Pacific (2)	1.90	27.9	0.36
	East and Southeast Asian seas	9.5	70.0	1.77
C2HCl3	Western Pacific (2)	0.48	13.5	<0.1
	East and Southeast Asian seas	14.7	261	<0.1

Ambient concentrations of C_2Cl_4 and $CHCl_3$ over western Pacific Ocean were in the range of

0.4 - 40.0 pptv and <0.1 - 13.5 pptv, respectively. As was found in a previous study (Rasmussen et al., 1982(b)), the latitudinal distribution of C2Cl4 in the northern hemisphere was significantly different from that in the southern hemispheres. The mean concentration of C_2Cl_4 in the southern hemisphere, 1.4 pptv, was lower than those previously reported for the eastern Pacific or Atlantic, 5-14 pptv. This decrease should be partly the result of declines in the global production of C_2Cl_4 over the years. C_2HCl_3 was detected at lower concentration than 1 pptv over the western Pacific except for the two samples collected at 9.4°N (2.9 pptv) and 34.3°N (13.5 pptv).

During the Asian cruise, these two chloroolefins declined gradually, from 140E to 120E, and the minimum was found north of Sumatra at around 97°E. The concentrations of these anthropogenic halocarbons in the harbors of Singapore and Pinang, were elevated, but the effects seem to be very local. The ratio of maximum to minimum concentration of C_2HCl_3 and C_2Cl_4 were 1000 and 30, respectively, suggesting very rapid disappearance of these anthropogenic halocarbons over the ocean. More significant declines in C_2HCl_3 concentrations compared to those of C_2Cl_4 by a factor of 30 is consistent with the former compound's much higher reactivity with OH radicals.

Bottenheim, J.W., L.A.Barrie, E.Atlas, L.E.Heidt, H.Niki, R. A.Rasmussen and P.B.Shepson, Depletion of lower tropospheric ozone during arctic spring: The polar sunrise experiment 1988 , J. geophys. Res., 95, 18555-18568, 1990.
Chameides, W.L. and D.D.Davis, Iodine: Its possible role in tropospheric photochemistry, J. geophys. Res., 85, 7383-7398, 1980Gschwend, P.M., J.K.MacFarlane, K.A.Newman, Volatile halogenated organic compounds released to seawater from temperate marine macroalgae, Science, 227, 1033-1035, 1985.
Class, Th., K.Ballschmiter, Chemistry of organic traces in air VIII: sources and distribution of bromo- and bromochloromethanes in marine air and surfacewater of the Atlantic Ocean, J.Atmos. Chem., 6, 35-46, 1988
Rasmussen, R.A., M.A.K.Khalil, R.Gunawaroena and S.D.Hoyt, Atmospheric methyl iodide (CH3I), J. geophys. Res., 87, 3086-3090, 1982
Rasmussen, R.A., M.A.K.Khalil, A.J.Crawford and P.J.Fraser, Natural and anthropogenic trace gases in the southern hemisphere, Geophys. Res. Lett., 9, 704-707, 1982.
Solomon, S., R.R.Garcia, and A.R.Ravishankara, On the role of iodine in ozone depletion, J. Geophys. Res., 99(D10), 20491-20499, 1994
Y.Yokouchi, L.A.Barrie, D.Toom, H.Akimoto, The seasonal variation of selected natural and anthropogenic halocarbons in the Arctic troposphere, Atmos. Environ 10/11, 1723-1727, 1996