

C-1.2.1 International Cooperative Observations Based on IGAC Program Using an Aircraft

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Abstract In order to analyze the present status of the atmospheric environment of the Western Pacific region, aircraft observation of atmospheric pollutants over the East China Sea, the Yellow Sea, and the Sea of Japan were made. These missions were performed under collaboration with Korea and China since 1991 as a part of IGAC/APARE activity. Ozone, SO₂, NO_x, PAN, aerosols, and acidic gases were measured. Spatial distribution of those pollutants were obtained. Back trajectory analyses clearly showed the impact of emission in the Asian continent including the Korean Peninsula.

Key Words IGAC, Aircraft Observation, SO₂, NO_x, Ozone, Aerosols, Acidic gases

1. Introduction

The East Asian area is one of the largest regions for the anthropogenic emission of NO_x and SO₂.¹⁾ In fact, because of population growth and the rapid development of industrial activity, it has been projected that this area will become the largest source of NO_x and SO₂ in the world in the 21st century.²⁾ It is important to analyze the present status of air pollution over the East Asian region, to evaluate the amount of the anthropogenic emission, to accurately predict the future situation by the use of computer models and to apply these results to work out countermeasures. However, there is no intensive measurement of atmospheric pollutants such as SO₂, NO_x, and O₃ in this area. For the purpose of clarifying the present status of atmospheric pollution in the Pacific rim region of East Asia as well as of predicting the future situation in this area, the authors have been conducting an intensive field study named the IGAC/APARE/PEACAMPOT Survey since 1991.³⁾

2. Research Objectives and Flight Courses

(1) March, 1994: (Fig. 1) Between Oki Islands and Tsushima Islands over the Sea of Japan at each altitude of 8,500, 3,000, and 1,500 feet. West of Kyushu over the East China Sea at each altitude of about 8,500, 5,500, 3,000, and 1,500 feet. South of Cheju Island over the East China Sea at 8,500, 3,000, and 1,500 feet. And west of Korean Peninsula over the Yellow Sea at 8,500, 5,500, 3,000, and 1,500 feet. In the mission of our previous project in Nov. 1992, very high concentration of SO₂ was observed⁴⁾ over the Sea of Japan between Korea and Oki Island. Therefore, the objective of this year was to clarify more in detail the impact of the atmospheric pollutants from Korea and China around Korean Peninsula.

(2) Dec., 1994: (Fig. 2) West of Yaku Island over the East China Sea and between Yaku Island and Kyushu over the Osumi Strait at 8,500, 5,500, 3,000, and 1,500 feet. A valuable nature is conserved in Yaku Island, but acid deposition transported from the Asian continent is anticipated deteriorating the environment of the island. The objective of this year was to

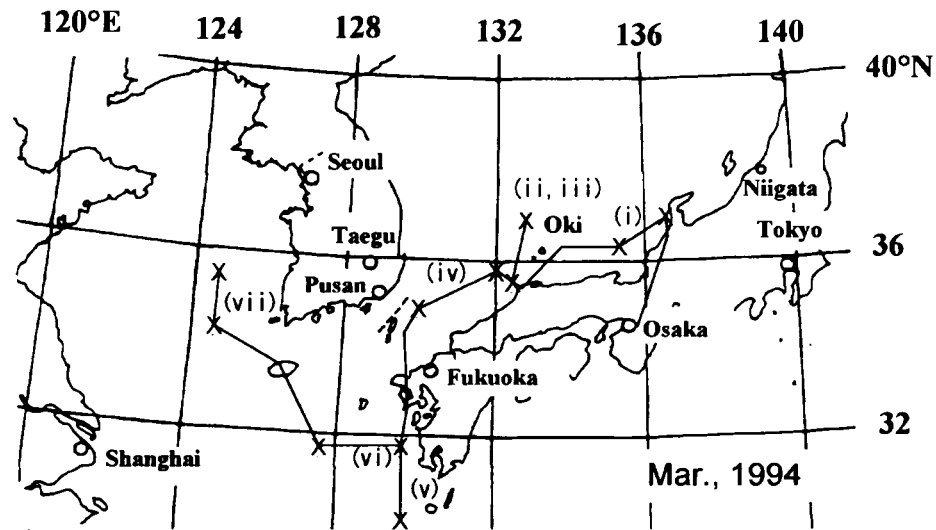


Fig. 1: Flight plans of the experiments in March, 1994.

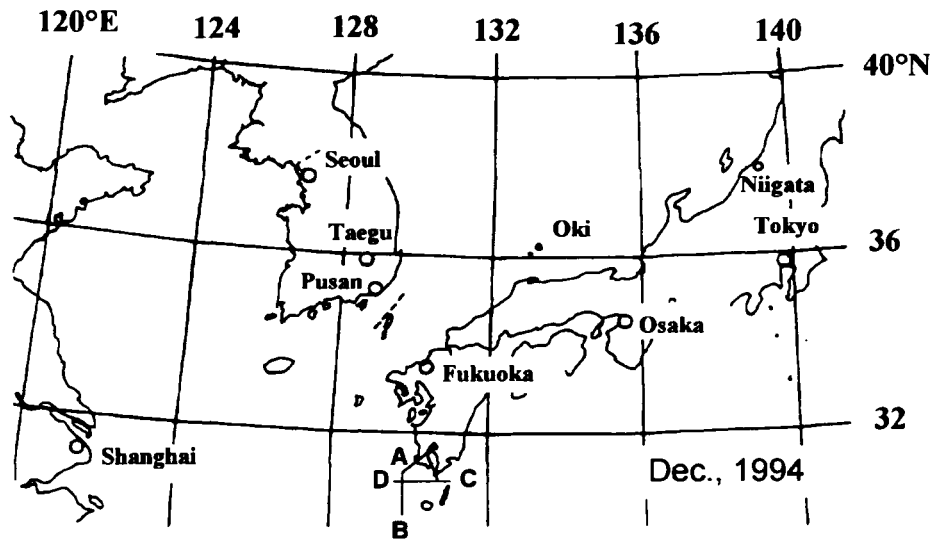


Fig. 2: Flight plans of the experiments in December, 1994

clarify the impact of the acidic substances from China.

(3) Nov. , 1995: (Fig. 3) Northern part of the Sea of Japan starting from Niigata. The westbound flights were Niigata → off the north-east coast of Sado → Noto and back. The northbound flights were Niigata → off the north-east coast of Sado → off the west coast of Akita and back. Two flights were made to both the directions at the altitude of 9,000, 5,500, 3,000, and 1,500 feet. The objective of this year was to see the impact of the northern part of the Asian continent.

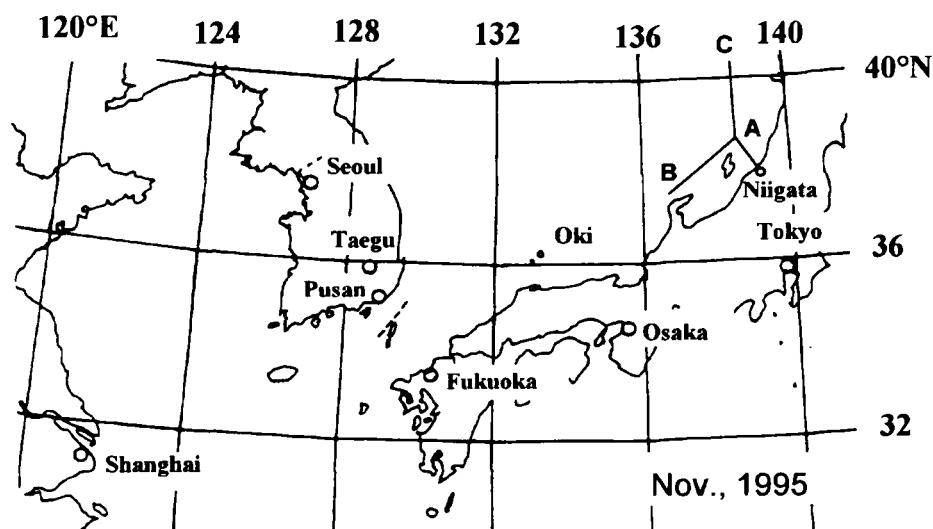


Fig. 3: Flight plans of the experiments in November, 1995

3. Research Methods

Pollutants measured on board were listed in Table 1.

Table 1: Pollutants measured on board and experimental techniques

pollutant	experimental technique
SO ₂	pulse fluorescence
Ozone	UV absorption
NO _x	Ozone chemiluminescence
PAN	Collection on a low temperature column
HC	Grab sampling
Aerosols	High volume sampler
Acidic gases	Diffusion scrubber

The aircraft employed was either a reciprocal twin-engined airplane, Cessna 404, or a turboprop twin-engined one, Fairchild Swearingen SA226-AT (Merlin IV); both are chartered from Showa Aviation Co., Ltd., Japan.

For Cessna 404 outside air was introduced into the airplane through a 3/8" Teflon tube running from the nose of the airplane to a glass manifold located in the middle of the cabin. For Merlin IV a 3/8" Teflon tube was connected to the air inlet settled on a window ahead of the air intake of the engine. In both the case the other end of the tube was connected to a glass manifold through which each instrument sampled air. For the high volume sampler, a 1" stainless steel tube was also set on the co-pilot's window for Cessna 404 or the same window as above for Merlin IV.

Ozone was monitored with TECO Model 49 UV absorption ozone analyzer with 4 sec switching of the light pass for its dual cell system. Pressure and temperature were automatically corrected.

SO₂ was measured with TECO Model 43S pulse fluorescence SO₂ monitor. Outer temperature and humidity were measured by use of a Vaisala HMP133Y thermometer-hygrometer.

Measurement techniques of NO_x and acidic gases are described later.

Isobaric back-trajectories were calculated for the 800, 850, 900, 950, and 1000 hPa pressure levels, based on the program by Hayashida-Amano et al.⁵⁾. The global wind field data compiled and analyzed by Japan Meteorological Agency were used as input data. Those data were available for 0000 and 1200 UT over a 1.825° mesh at each level.

4. Results and Discussion

[1] SO₂ and nss-Sulfate

(1) March, 1994 Flights

On March 10, the flight course was similar to that of Nov. 12, 1992; very high concentration of SO₂ was observed in that experiment. However, the concentration of SO₂ on March 10 was quite low. Back trajectory analysis suggested that the air mass caught passed over the north of Korea and not affected by the large emission sources in Korea.

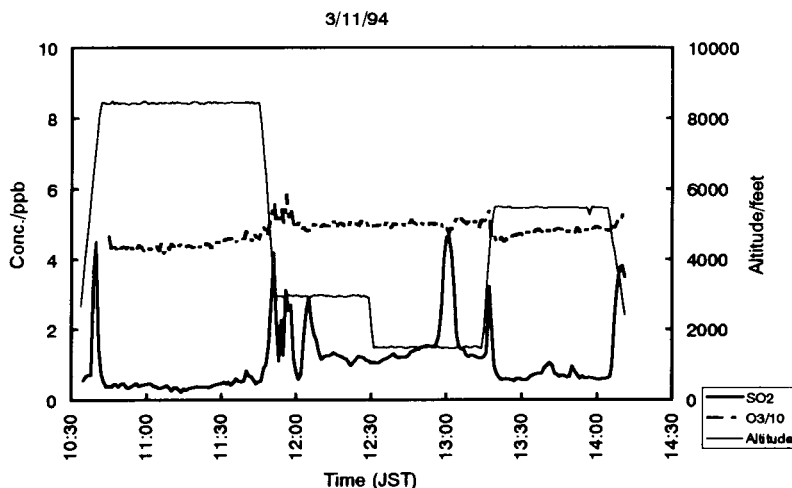


Fig. 4: Ozone, and SO₂ over the Sea of Japan on 3/11/1994

On March 11, several high concentration peaks of SO₂ were observed between Oki and Tsushima over the Sea of Japan (Fig. 4). Wind blew from north-west. It indicates that we came across several plumes containing much SO₂ emitted in Korea. Back trajectory analyses also support this contention.

(2) December, 1994 Flights

The concentration of SO₂ over the East China Sea was very low. On Dec. 14 the concentration of SO₂ in the west of Yaku Island over the East China Sea was as low as 0.2 ppb (Fig. 5), although wind blew from west or north-west. In contrast the concentration of nss-sulfate was generally higher over the East China Sea than over the Sea of Japan.

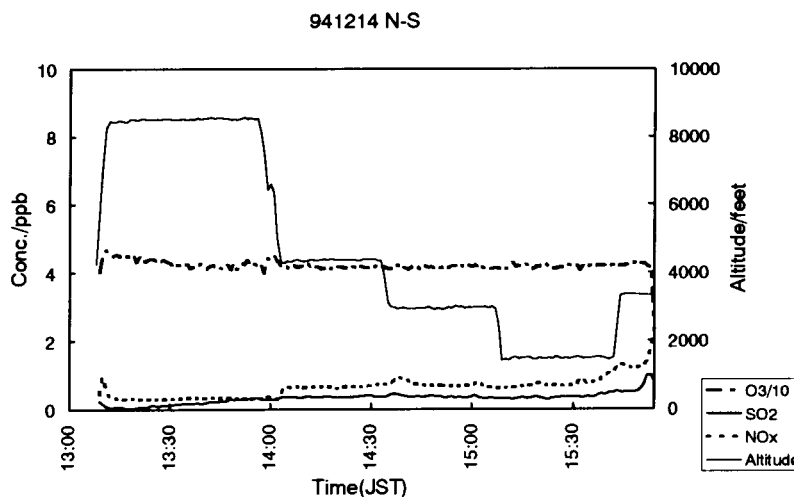


Fig. 5: Ozone, NO_x, and SO₂ over the East China Sea on 12/14/1994

(3) November, 1995 Flights

The concentrations of NO_x and SO₂ was very low (Fig. 6) when north-west monsoon brew. The upstream of the monsoon is the northern part of Asia, where no large emission

source of atmospheric pollutants exists.

(4) The ratio of nss-SO_4^{2-} to SO_2

The lifetime of SO_2 above seas is very short and no long range transport is expected. But its oxidation product, sulfate aerosols, is very long-lived and can be transported very far. Thus, the ratio of nss-sulfate to SO_2 can be a good indicator of the distance of transport. In this study we found that the ratio was high, around 1.5, below the marine boundary layer over the East China Sea. In contrast, the ratio was generally low, less than 0.5, over the western part of the Sea of Japan.

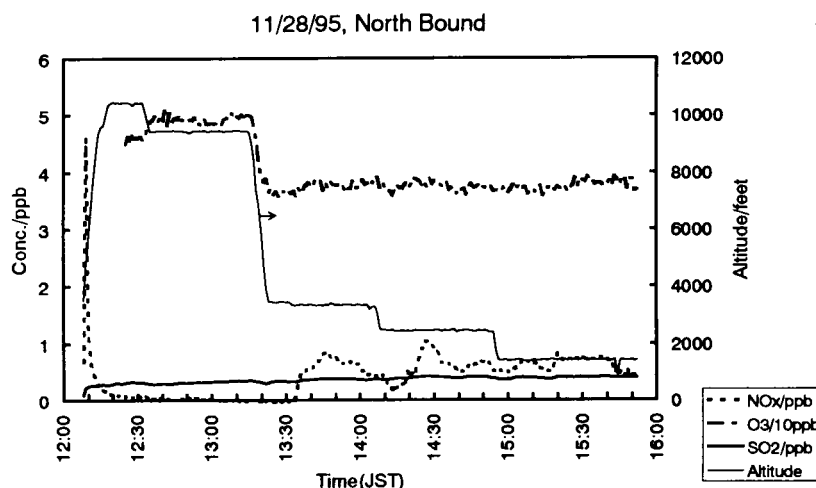


Fig. 6: Ozone, NO_x, and SO₂ over the Sea of Japan on 11/28/1995

[2] Spatial distribution of NO_x

(1) Measurement technique

Measurements of nitrogen oxides were made with an ozone-chemiluminescence NO-NO_x analyzer (TECO, Model 42S). A commercial analyzer was modified for the aircraft measurement and for improvement of its detection limit. Major modifications were 1) the use of flow-controlled air sampling with a thermal mass-flow-meter system, which improved a pumping ability to reduce pressure in its chemiluminescence chamber and 2) the use of pure oxygen to make ozone. In this analyzer a molybdenum converter operated at 320 °C was used to convert nitrogen oxides to NO. Conversion efficiency for nitric acid and some organic nitrates has not been established; maybe less than unity. Thus, the nitrogen species detected as NO_x with this analyzer include some part of NO_y.

NO and NO_x were measured by switching the sample air flow among three modes. One was NO mode that measured NO without making sample air pass through the converter. Another is NO_x mode that measured NO_x with making sample air pass through the converter. The other was pre-reactor mode. In this mode the chemiluminescence from NO + ozone reaction completed in an extra volume inserted before the chemiluminescence chamber. A sequence of the three modes made one set of NO and NO_x measurement and took 30 sec. In this measurement we got two minutes running mean (four intermittent measurements for one species) as an averaged value. That gave detection limit of 25 ppt with S/N ratio of one.

(2) Results and Discussion

All the data of NO_x concentrations measured in this project are shown in Fig. 7. Data obtained in the previous project are included. The concentration of NO_x decreases with altitude. The data shown in Fig. 7 indicate following characteristics.

- 1) NO_x distributes almost uniformly from 0.2 to 1 ppb in the free troposphere above 5,000 feet.
- 2) In the boundary layer the concentration of NO_x is 1-4 ppb. Variation of the concentration is very large depending on time and places.
- 3) All high concentration of NO_x in free troposphere (more than 1 ppb) was observed over the East China Sea.

4) High concentration of NO_x was observed over the East China Sea regardless of in boundary layer or in free troposphere.

NO_x* vs. Altitude in PEACAMPOT-Aircraft Obsv.91-95

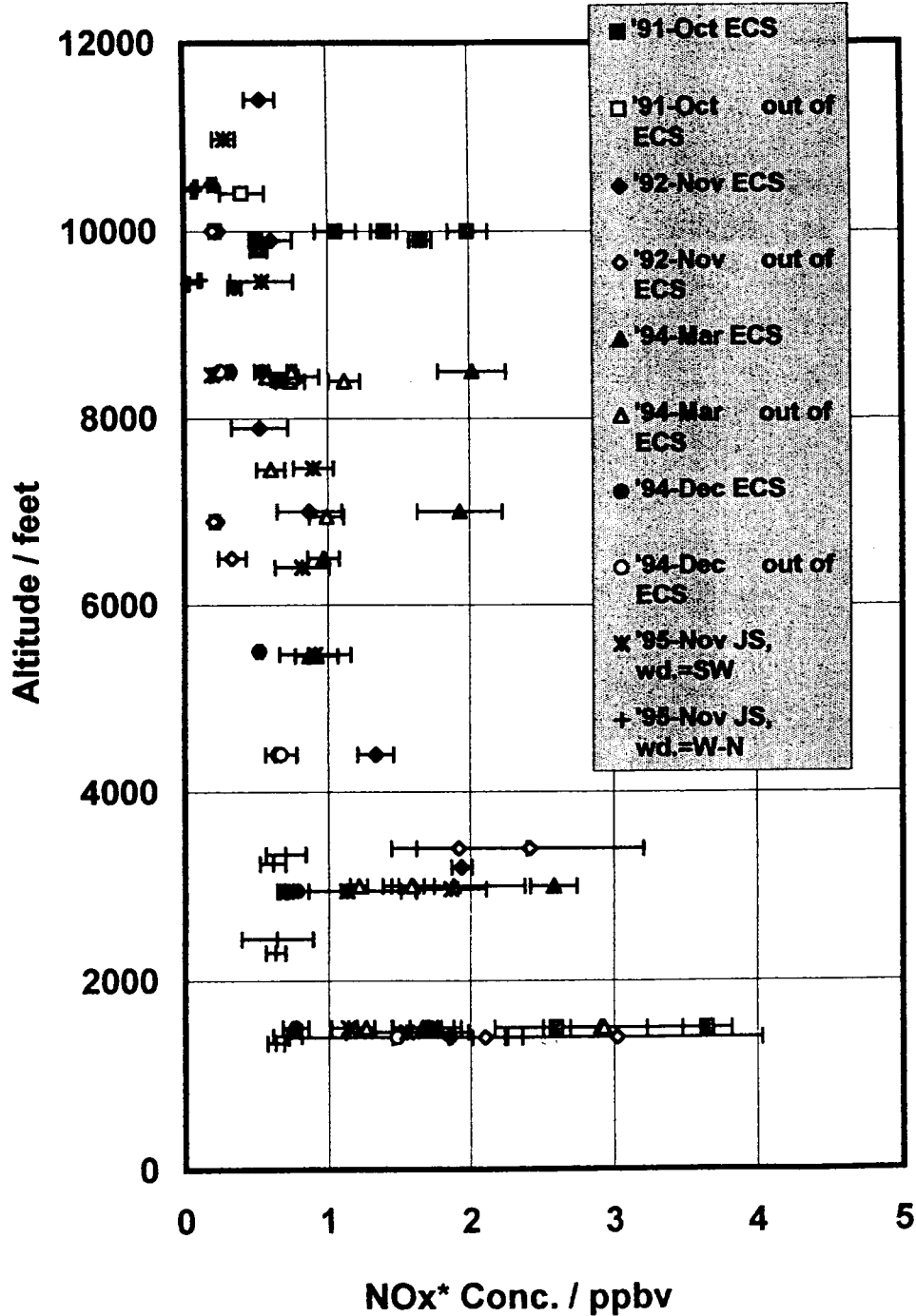


Fig. 7: Vertical distribution of NO_x

[3] Measurements of Atmospheric Trace Components (HCl, HNO₃, SO₂, HCHO, CH₃CHO, and H₂O₂) with Diffusion Scrubber

(1) Methods

1) Diffusion scrubber

Diffusion scrubber is an instrument to collect gases by use of the difference of diffusion coefficients of gases and aerosols.⁶⁾ It is composed of a dual tube. The inner tube is made of porous PTFE and the outer tube is made of Pyrex. Absorbent solution is filled between the two tubes. Gas molecules pass through the porous PTFE and collected in the solution, but aerosols not. Effective length of the diffusion scrubber used was 50 cm. Inner and outer diameter of the porous PTFE tube was 4 mm and 5 mm, respectively. Inner and outer diameter of the glass tube was 6.6 mm and 9 mm, respectively.

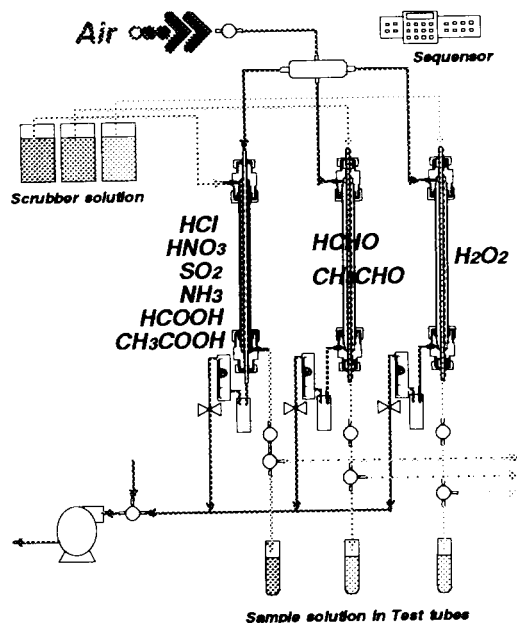


Fig. 8: Collection system using diffusion scrubbers

After flights each sample was cooled and transported to Keio University for analyses.

(2) Results and Discussion

Concentration levels of HCl, HNO₃, SO₂, HCHO, CH₃CHO, and H₂O₂ measured in the experiments of Mar. 1994, Dec. 1994, and Nov. 1995 are listed in Table 2. The vertical

Table 2: Concentrations of trace gases in the troposphere

Date	Location		HCl	HNO ₃	SO ₂	HCHO	CH ₃ CHO	H ₂ O ₂
'94 3/7-14	Sea of Japan East China Sea Yellow Sea	Av.	0.19	0.10	0.83	0.53	0.33	
		Std.	0.13	0.11	0.76	0.34	0.17	
		Max.	0.57	0.45	3.84	1.50	0.72	
		Min.	0.03	0.01	0.07	0.09	0.07	
		n	16	19	19	17	15	
'94 12/12-14	East China Sea Ohsumi Strait	Av.	0.26	0.10	0.51	0.33	0.15	0.20
		Std.	0.37	0.06	0.57	0.31	0.20	0.14
		Max.	1.68	0.28	2.77	0.94	0.94	0.44
		Min.	0.08	0.03	0.09	0.06	0.04	0.04
		n	21	24	24	22	21	15
'95 11/26-28	Sea of Japan	Av.	0.12	0.15	0.42	0.42	0.22	0.46
		Std.	0.06	0.12	0.20	0.20	0.18	0.35
		Max.	0.27	0.49	0.93	0.88	0.83	1.64
		Min.	0.01	0.01	0.11	0.07	0.03	0.03
		n	30	33	33	30	27	31

Table 2 (Continued)

Date	Location	HCl	HNO ₃	SO ₂	HCHO	CH ₃ CHO	H ₂ O ₂
Overall		Av. 0.17	0.13	0.59	0.47	0.25	0.46
		Std. 0.21	0.11	0.54	0.31	0.19	0.39
		Max. 1.68	0.52	3.84	1.50	0.94	1.64
		Min. 0.01	0.01	0.07	0.06	0.03	0.03
		n 81	83	95	91	84	57

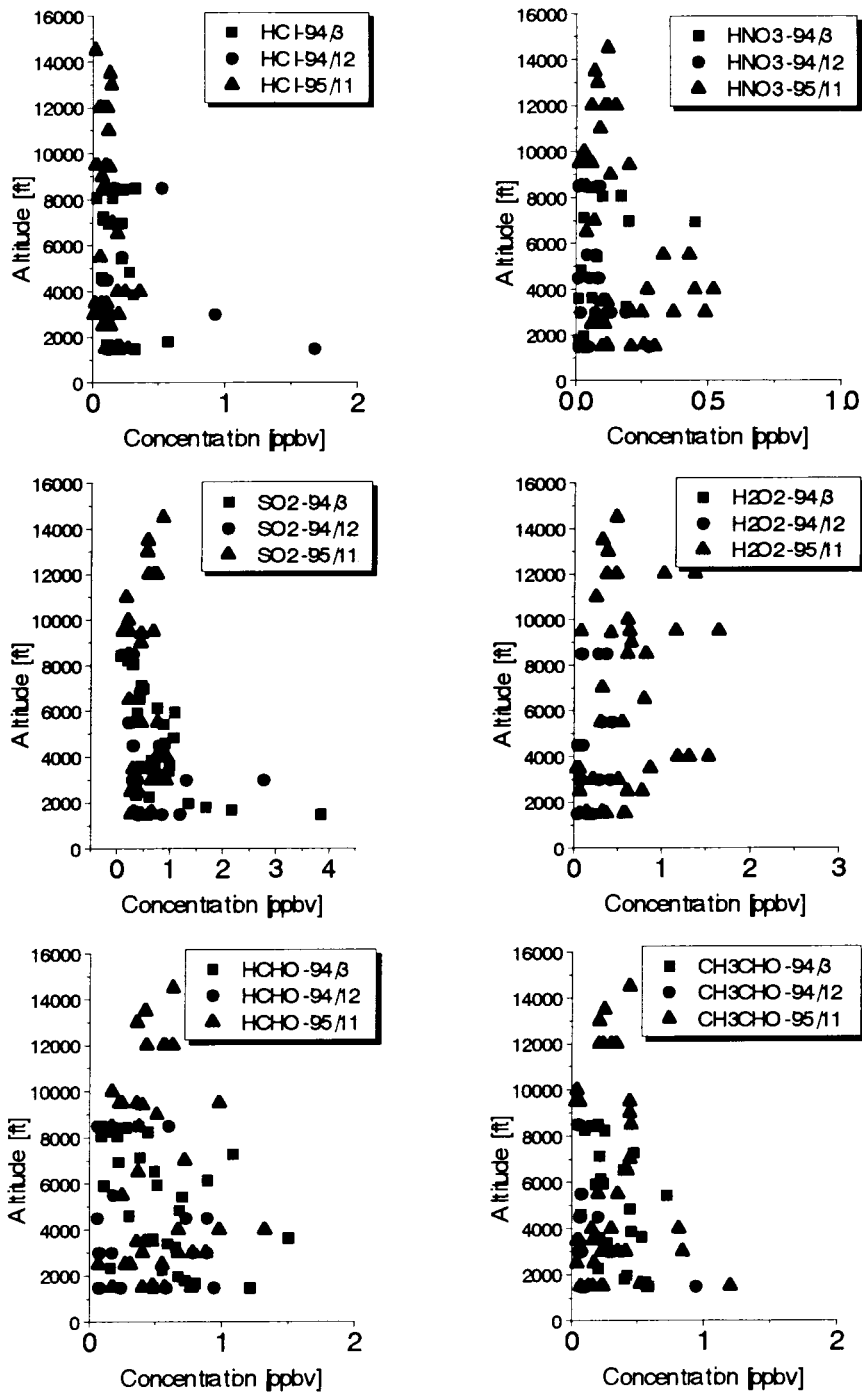


Fig. 9: Vertical distribution of trace gases over the East China Sea and the Sea of Japan

distribution of each gas is shown in Fig. 9. The concentration of HCl, HNO₃, HCHO, and CH₃CHO decreased with altitude. In contrast H₂O₂ increased with altitude. It is because formation of H₂O₂ by the self reaction of HO₂ radicals ($\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$) mainly takes place in free troposphere. Suppression of the formation of H₂O₂ by NO_x ($\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$) at lower altitudes may also contribute to the above distribution of H₂O₂.

The air masses observed in these missions are classified into 4 categories on the basis of back trajectories. Namely, 1) from Russia or North Korea, 2) from Korea, 3) from China, and 4) from Japan. It was found that the concentrations of SO₂, HCHO, and CH₃CHO were high in the air mass of the category 2. H₂O₂ was high in the air mass of the category 1.

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