Tokai J Exp Clin Med., Vol. 27, No. 2, pp.35-42, 2002

Measurement of Atmospheric NO_2 Concentrations in Antarctica with NO_2 Filter Badge and Tube

Hideaki MATSUKI, Kenji YOSHIKAWA *,
Yukio YANAGISAWA ** and Hitoshi KASUGA ***

Tokai University School of Health Sciences
**Hokkaido University Institute of Environmental Science*
***The University of Tokyo School of Frontier Sciences*
****Professor Emeritus, Tokai University*

(Received February 18, 2002; Accepted May 14, 2002)

Nitrogen dioxide (NO_2) levels in Antarctica were monitored to determine background levels and distribution profile. The NO_2 levels were higher than those reported from tropical remote areas. The NO_2 concentrations gradually increased proceeding from the edge of the continent to the polar region, suggesting global pollutant transportation. To avoid artificial contamination of the data, a sled was used because motor vehicles discharge high levels of NO_2.
NO_2 tubes and filter badges were selected as monitoring devices because of their convenience of transportation in Antarctica. They are small in size, light and easy-to-handle, and usually employed in personal NO_2 exposure measurements. Because of severe Antarctica climate, the devices needed to be protected from the bitter cold. For that purpose, we designed an insulation container to shield the devices.
The fixed NO_2 monitoring site was Patriot Hill, located on the coast of the Weddell Sea. We also measured NO_2 concentration along the expedition route from the fixed site to the South Pole, along with the 80 degrees west longitude. The survey periods were during November 1992 and January 1993. NO_2 concentrations in Antarctica ranged from 1.0 to 2.8 ppb, which were relatively higher than previously reported background concentrations. The NO_2 concentrations increased when nearing to the South Pole, supporting the theory that atmospheric circulation converges in the polar regions. This indicated that air pollutants discharged in populated regions were widely spread to isolated areas, like the South Pole.

Key words : Antarctica, Ambient nitrogen dioxide, NO_2 filter badge, Wind tunnel, Low temperature

INTRODUCTION

Nitrogen (NO_2) levels in Antarctica were monitored reveal background levels and distribution profile. Since there are no significant emission sources in Antarctica, all pollutants must be discharged and transported from populated continents. In Japan, air pollution by sulfur oxides has caused chronic obstructive lung diseases since the early 1960's. The annual average concentrations of sulfur dioxide have gradually declined from a peak of 0.059 ppm in 1967 to 0.011 ppm in 1991 by adapting various mitigation measures. On the other hand, the concentrations of nitrogen dioxide (NO_2) have been unchanged or even slightly increased [4]. NO_2 is well known because of its adverse effects on pulmonary function. Chronic exposure to NO_2, even at low levels, may threaten public health as shown in many epidemiological studies [17]. We have reported the relationship between the levels of personal exposure to NO_2 and respiratory illness in Japan [3, 11, 12, 19], Hong Kong [8], and Brazil [5].

Atmospheric nitrogen oxides are discharged during combustion processes. The major sources of NO_2 are industrial and motor vehicles. In Antarctica, however, such

Hideaki MATSUKI, Department of Nursing, Tokai University School of Health Sciences, Bohseidai, Isehara, Kanagawa 259-1193, Japan E-mail: hmatsuki@is.icc.u-tokai.ac.jp Tel: 0463-90-2058 Fax: 0463-90-2074

sources do not exist. Information concerning NO_2 concentrations in Antarctica would be important and useful in helping to evaluate air pollution problems in Japan.

Our group, the Private Japanese Antarctic Expedition (PJAE), carried out an environmental survey proceeding from the shore of the Weddell Sea to the South Pole (80 degrees west longitude) and in Patriot Hill during the period from November 1992 to January 1993. This paper describes distribution profile of NO_2 concentrations in Antarctica and evaluates the performance of specially treated NO_2 tubes and filter badges under extraordinary climatic conditions.

MATERIALS AND METHODS

(1) NO_2 measuring devices

Since the NO_2 measuring devices were to be transported by sleds, the devices had to be small in size, light weight and easy-to-handle. These criteria were met by the NO_2 filter badges (5 × 4 × 1 cm, 15 g) [18] and cylindrical NO_2 tubes (1 cm in diameter and 10 cm long, weighing 30 g) [13]. To collect NO_2, the filter badges contained absorbent paper and the NO_2 tube used silica gel. These media were soaked with triethanolamine (TEA), which reacts with NO_2 as follows [9],

$$2NO_2 + 2N(CH_2CH_2OH)_3 \rightarrow N(CH_2CH_2OH)_2(CH_2CH_2ONO) + N(CH_2CH_2CH_2)_2(CH_2CH_2ONO_2) + H_2O$$

The amounts of NO_2 collected were quantified by measuring absorbance after developing color with the Saltzman reagent.

(2) Protecting devices from very low temperatures

Even during the summer season (November to January) when our survey was conducted, the temperature in Antarctica has been known to −20 ℃ with a wind velocity of 10 m/sec [15]. These conditions adversely affect the operation of the monitoring devices. TEA loses considerable sensitivity in such subfreezing temperatures. To protect the NO_2 filter badges and NO_2 tubes from the harsh conditions, a container to provide insulation was developed (Fig. 1). The plastic container of 20 cm in length, width and depth, had an opening at one end to permit air to enter, and was installed with heating elements (Murata Mfg. Co. Hojistar) and a thermostat switch (Uchida UG5). The outside of the container was covered with polyethylene to provide insulation. These features made it possible to maintain the temperature in the container at 5 ℃ even when it was placed in a refrigerator set at −20 ℃. In Antarctica, photovoltaic cells, which our base camp and sleds were equipped with, were used as the power source.

(3) Wind tunnel test

We examined the container in a wind tunnel to confirm the insulation. A refrigerator (CE-2, size: 3.2 × 1.2 × 1.2 m, Wahple Co. Ltd.) was used to control temperature, into which the canister was placed (Fig. 2). NO_2 levels in the wind tunnel were monitored with a chemiluminescence meter (GLN-31, Denki Kagaku Co. Ltd.) located at point C (Fig. 2). The inside of the wind tunnel chamber was fitted with a shutter and a small fan

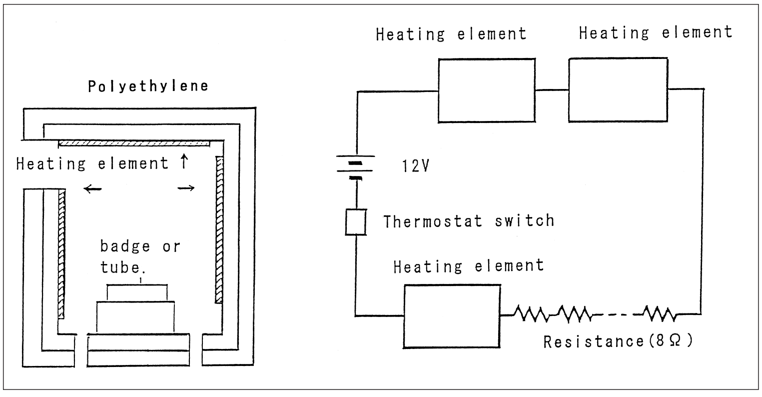

Fig. 1 Container for insulting NO_2 filter badges and NO_2 tubes against the cold.

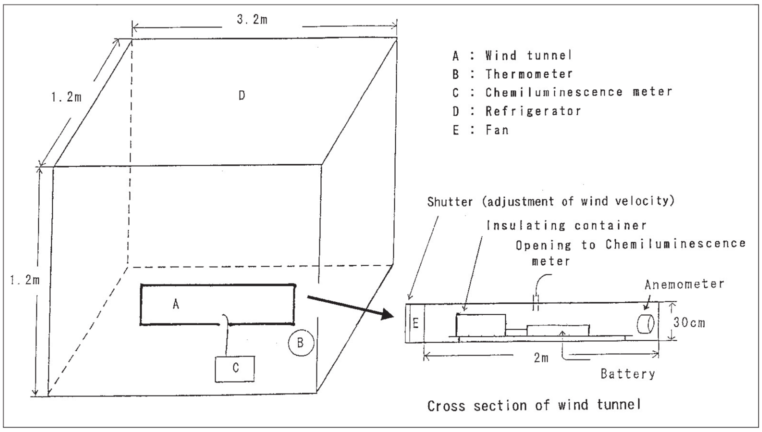

Fig. 2 Wind Tunnel Chamber

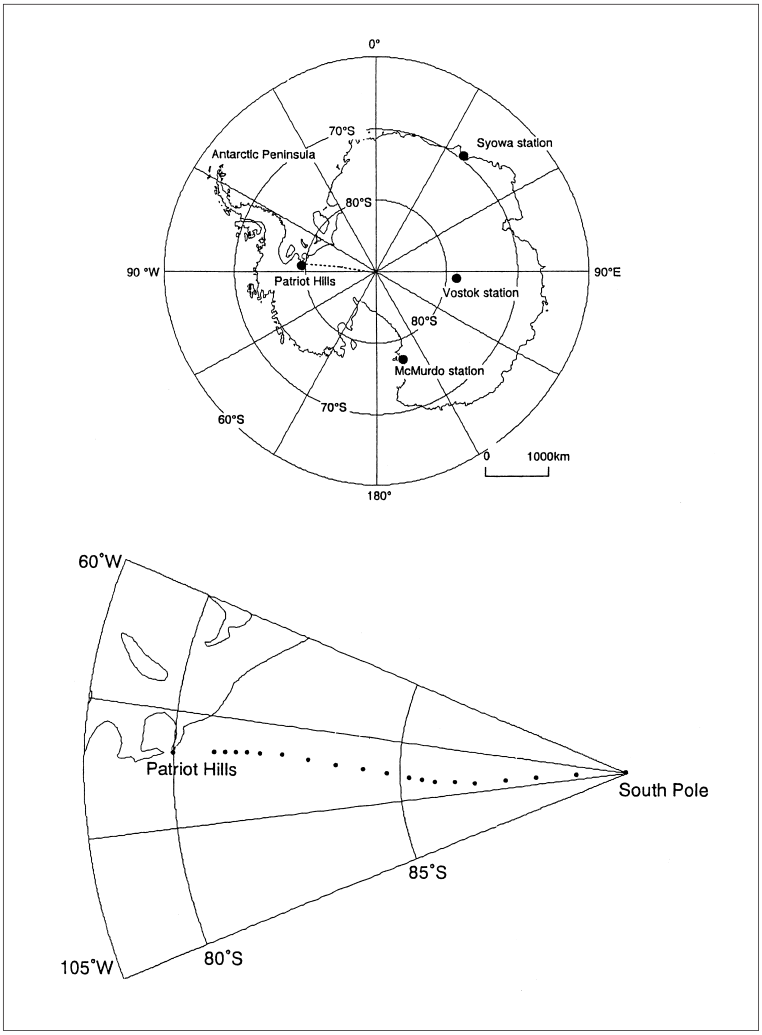

Fig. 3 Route of the Private Japanese Antarctic Expedition from the coast of the Weddell Sea to the South Pole.

(Section E) to manipulate wind velocities of 1, 5, and 10 m/sec. An anemometer (Isuzu) was used to monitor wind velocity. A gas cylinder containing 12 ppb of NO_2 (Nippon Sanso Co. Ltd.) was used to introduce known concentrations of NO_2 gas. Tests were conducted at − 10 and − 20 ℃ .

(4) Measurement of Atmospheric NO_2 Concentrations in the Antarctica

A base camp was up at Patriot Hill, located on the coast of the Weddell Sea, in the southern part of the Ellesworth Mountains on November 8. Three of the five PJAE members set out for the South Pole on November 19, 1992, pulling their sleds at 80 degrees west longitude. They reached the South Pole on January 16, 1993. The route they followed is shown in Fig. 3. During the transit, they monitored 24-hour average NO_2 concentrations with the NO_2 tube every 2 days. NO_2 levels at the base camp were surveyed using the NO_2 filter badges every 2 to 6 days, from November 15, 1992 to January 12, 1993.

RESULTS

(1) Wind tunnel tests

Five insulating containers were examined for their ability to protect the NO_2 filter badges and NO_2 tubes from the cold. The temperature inside the insulating container ranged from 3 to 10℃ and the results indicated (Table 1), that TEA would not freeze even under the most unfavorable conditions.

Five NO_2 filter badges and five NO_2 tubes were tested for NO_2 sampling ability NO_2 concentrations measured with the samplers slightly decreased with decline in temperature and acceleration of wind velocity (Table 2). Table 3 shows mean percent differences between NO_2 measured with the samplers to NO_2 concentrations in the wind tunnel, indicated with a chemiluminescent monitor. The NO_2 tube showed slightly lower readings than the filter badges in all cases. Although the differences were slight, the measured NO_2 concentrations were corrected using the mean percent differences. For example, when NO_2 tubes were used at temperatures higher than − 10 ℃ and wind velocity less than 1 m/s, NO_2 concentrations were corrected using the following equation:

corrected NO_2 value = (100/93.2) × NO_2 concentration by NO_2 tube.

(2) Climatic data and atmospheric NO_2 in the Antarctic

On route from the coast of the Weddell Sea to the South Pole, the temperature ranged between − 10 and − 20 ℃ with a maximum wind velocity of 10 m/s (Table 4). The NO_2 levels measured by the PJAE members, using NO_2 tubes ranged from 1.0 to 2.8 ppb. The concentrations increased on approaching the South Pole. NO_2 concentrations at the edge of the Antarctic, from Nov. 19 to Dec. 4, was 1.25 ppb, and was 2.10 ppb at the polar region, from Dec. 27 to Jan. 16. This difference was statistically significant ($p < 0.01$). Correlation coefficient between temperature and NO_2 levels was − 0.578, which is statistically significant ($p < 0.001$).

At Patriot Hill, the temperature between −2 and −18 ℃ , with maximum wind velocity of 10 m/s. The NO_2 concentrations measured with the NO_2 filter badge were between 1.1 and 1.8 ppb with no major fluctuations (Table 5).

DISCUSSION

A chemiluminescence method was used as the gold standard for NO_2 measurement. This method is recommended for its stability and high sensitivity [4]. According to the wind tunnel experiments, the NO_2 intake level if the tubes was slightly lower than that of the NO_2 badges. The tubes and badges showed very good agreement with the gold standard. This indicated that the insulation containers could protect the NO_2 samplers from the severe weather conditions. The NO_2 tubes are less sensitive than the NO_2 filter badges because of differences in NO_2 uptake areas. Nevertheless, we used the NO_2 tubes for our survey because they are better under wet conditions compared with the NO_2 filter badges. When comparing NO_2 concentrations measured near the base camp with both tubes and filter badges, the concentrations were almost identical. This demonstrate that the insulation containers were effective and that both measuring devices were fairly accurate.

Few report exist on atmospheric NO_2 concentrations in the Antarctic. The Japanese Antarctic Expedition Survey Team has been monitoring NO_2 concentrations in the atmosphere, the ice fields, and interstitial air in snow since 1967. According to their results, the NO_2 concentrations in the snow gradually increased as they neared the South Pole from the coast, at the southern part of the Syowa Base [15, 16].

Table 1 Mean Temperatures inside the insulating containers* test in refrigerator.

Temp. in Refrigerator	Wind Velocity (m/s)	Temp. in Refrigerator (℃)
−10℃	1	10
	5	8
	10	7
−20℃	1	7
	5	5
	10	3

* Number of insulting container tested = 5

Table 2 NO_2 intake by NO_2 filter badges and NO_2 tubes in the wind tunnel test.

	Testing Device	− 10℃	− 20℃
Wind velocity 1 m/s	Chemil. method	11.7 (11.4 ～ 11.9)	11.0 (10.6 ～ 11.3)
	NO_2 tube	10.9 (9.1 ～ 11.2)	10.1 (8.6 ～ 10.9)
	NO_2 badge	11.3 (9.5 ～ 12.5)	10.8 (8.6 ～ 12.2)
Wind velocity 5 m/s	Chemil. method	11.3 (11.0 ～ 11.6)	10.7 (10.5 ～ 10.9)
	NO_2 tube	9.9 (8.8 ～ 10.8)	9.6 (8.4 ～ 10.9)
	NO_2 badge	10.4 (8.5 ～ 11.3)	10.2 (9.1 ～ 11.1)
Wind velocity 10 m/s	Chemil. method	10.7 (10.5 ～ 10.9)	10.2 (10.0 ～ 10.4)
	NO_2 tube	9.2 (8.4 ～ 10.7)	9.1 (8.6 ～ 9.7)
	NO_2 badge	9.7 (8.7 ～ 10.8)	9.9 (9.0 ～ 10.8)

(   ): Range
Chemil. method: Chemiluminescence method

Table 3 % NO_2 intake by NO_2 tubes and NO_2 filter badges in wind tunnnel test. (NO_2 level monitored by chemiluminescence was regarded as 100)

Temp. in refrigerator	Wind Velocity (m/s)	Monitoring Device	NO_2 intake (%)
− 10℃	1	Tube	93.2
		Filter badge	96.6
− 20℃		Tube	91.8
		Filter badge	98.2
− 10℃	5	Tube	87.6
		Filter badge	92.1
− 20℃		Tube	89.7
		Filter badge	95.3
− 10℃	10	Tube	86.0
		Filter badge	90.6
− 20℃		Tube	89.2
		Filter badge	97.1

Table 4 Climate data obtained going from the coast of the Weddell Sea to the South Pole.

Date	Location South latitude		Location West longitude		Climate condition	Temp. (℃)	Wind Velocity (m/sec)	NO_2 concentration after correction (ppb)
1992 Nov. 19	80°	59′	81°	16′	Fine	− 17	6	1.3
22	81	22	81	22	Fair	− 17	1	1.2
25	81	38	81	21	Fine	− 13	10	1.1
27	81	57	81	24	Cloudy	− 15	< 1	1.0
30	82	23	81	26	Fine	− 12	9	1.4
Dec. 4	82	54	81	45	Fair	− 10	3	1.5
6	83	13	82	00	Fine	− 12	1	1.3
9	83	45	82	25	Fair	− 12	8	1.2
13	84	17	83	26	Fine	− 14	3	1.4
15	84	40	84	19	Fine	− 12	< 1	1.5
18	85	13	85	58	Fine	− 14	7	1.3
22	85	39	86	50	Snowy	− 11	3	1.5
24	86	00	85	58	Cloudy	− 15	6	1.6
27	86	33	86	48	Snowy	− 12	< 1	1.9
31	87	08	86	59	Cloudy	− 16	< 1	1.6
1993 Jan. 4	87	81	87	10	Fine	− 21	5	1.8
7	88	26	86	48	Fair	− 18	3	2.0
11	89	03	86	41	Fine	− 18	2	2.8
16	90	00	−		Fine	− 24	< 1	2.5

Table 5 Climate data and NO_2 concentrations in the ambient air measured at Patriot Hill base camp using NO_2 filter badges.

Date	Climate condition	Temp. (℃)	Wind Velocity (m/sec)	NO_2 concentration after correction (ppb)
1992 Nov. 15	Cloudy	− 18	3	−
19	Fine	− 14	1	−
21	Snowing	− 13	< 1	−
24	Fair	− 12	10	−
27	Cloudy	− 18	7	1.2
30	Fine	− 12	8	1.3
Dec. 3	Cloudy	− 11	9	1.2
6	Snowing	− 12	5	1.8
9	Cloudy	− 9	8	1.6
12	Fine	− 10	10	1.1
18	Fine	− 12	2	1.5
21	Fair	− 10	4	1.3
23	Fine	− 12	1	1.8
27	Fine	− 12	1	1.6
30	Fair	− 10	4	1.6
1993 Jan. 3	Cloudy	− 11	3	1.5
6	Cloudy	− 6	1	1.6
9	Cloudy	− 7	< 1	1.6
12	Cloudy	− 2	5	1.5

Since Antarctica is a deserted continent, there are no major stationary and mobile sources of NO_2 as in other continents. However, the observed NO_2 levels in Antarctica exceeded previously reported background levels [6]. Our results showed NO_2 concentrations ranging from 1.0 to 2.8 ppb. The average in to polar region was higher than at the edge of Antarctic. The NO_2 molecules found in Antarctic must be transported from populated area where people use energy and discharge nitrogen oxides into the atmosphere, For example, the annual mean NO_2 concentration in Japan was 29 ppb in 1992 [4].

The polar regions play an important role in the circulation of heat and water around the globe. By virtue of their cooling mechanism, they help circulate the atmosphere and sea water. It is presumed that substances released into the atmosphere naturally or as a result of human activity will follow the heat and atmospheric currents that move from low to high latitudes and will be transported to the polar regions. In this way, the particulate matter released by volcanic explosions is said to be sent into the stratosphere and transported from the equatorial regions to the polar caps [7].

Caricchia *et al.* [2] measured polycyclic aromatic hydrocarbons (PAH) in atmospheric particulates at the Italian base in Antarctic from 1991 to 1997 and found that levels of PAH has been increasing. They assumed the cause was due to increasing combustion combined with human activity in other continents and PAH was carried with the particulate matter by atmospheric transport. In addition, Ayotte *et al.* [1] reported that persistent contaminants such as heavy metals and organic compounds are transported from distant sources to the Arctic by oceanic and atmospheric currents.

The existence rate of NO (NO/(NO + NO_2)) in the antarctic atmosphere was not clear, because the analytical principle of the NO_2 filter badge and tube adoppted Salzman method, that is, NO was oxidized to NO_2 by N-(1-Naphthyl)ethylenediamide dihydrochloride [9]. Luis *et al.* [10] studied air pollution in Argentina, the country nearest to Antarctica. They reported a range of NO from 48-62%.

Although our survey measured atmospheric NO_2 concentrations in Antarctica only once, we found that the polar region was more polluted than the edge of the Antarctic, suggesting the transportation of air pollutants by atmospheric circulation. We urge the international study consortium, the International Trans-Antarctic Scientific Expedition (currently under preparation), to provide more information regarding other noxious agents to reveal the global scale dispersion of air-borne pollutants. Since nitrogen oxides are one of the chemicals responsible for the stratosphere ozone depletion, the vertical distribution and chronological changes in the nitrogen dioxide concentrations are of great importance.

ACKNOWLEDGEMENTS

The authors wish to thank Mr. Naoyuki Matsubara, Mr. Tetsuya Sano, Mr. Satoshi Ishimaru, and Mr. Kouichi Harada for their excellent work in Antarctica. We also take this opportunity to thank ADVANTIC, Toyo Roshi Co. Ltd. and Shibata Scientific Technology Co. Ltd. for their generous cooperation.

REFERENCES

1) Ayotte P, Dewailly E, Bruneau S, Cini S, Cremisrareau H, Vezina A: Arctic air pollution and human health: what effects should be expected? The Science of the Total Environment. 160, 529-537, 1995.
2) Caricchia AM, Chiararini S, Cremisini C, Morabito R, Perini A, *et al.*: Determination of PAH in atmospheric particles in the area of the Italian base in Antarctica: Report on monitoring activities during the last three scientific expeditions. Environmental Pollution. 87, 345-356, 1955.
3) Dassen WG, Matsuki H, Kasuga H, Misawa K, Yokoyama H, Shimizu Y: Determinants of indoor NO_2 concentration and the personal exposure of children and their mothers (in Japanese). Tokai J. Exp. Clin. Med. 12, 83-95, 1987.
4) Environment Agency Government of Japan: Quality of the Environment in Japan, Health Welfare and Environmental Problems Research Society, 3-8, 1993.
5) Hamada GS, Kowalski LD, Murata Y, Matsushita H, Matsuki H: Wood stove effects on indoor air quality in Brazilian home. Tokai J. Exp. Clin. Med. 17, 145-153, 1991.
6) Hori M, Suzuki S, Sawaragi Y, Higuti I: Surveillance of environmental air in Tokyo, University of Tokyo Press, 1984, 22 pp. (in Japanese).
7) Iwasaki Y: Ozone hole, Shokado Publishing Company, 1990, 51 (in Japanese).
8) Koo LC, Ho JHC, Ho CY, Matsuki H, Shimizu H, Mori T, Tominaga S: Personal exposure to nitrogen dioxide and its association with respiratory illness in Hong Kong. Am. Rev. Resp. Dis. 141, 1119-1126, 1990.
9) Levaggi DA, Siu W, Feldstein M.: Quantitative separation of nitric oxide from nitrogen dioxide at atmospheric concentration. Environ. Sci. Technol. 6, 250-252, 1972.
10) Luis E, Olcese BM: Some aspects of air pollution in Cordoba, Argentina. Atmospheric Environment, 36, 299-306, 2002.
11) Matsuki H, Kasuga H, Osaka F, Yanagisawa Y, Nishimura H: Epidemiological study in the assessment for cigarette smoking effects and personal exposure to nitrogen dioxide in winter season using urinary hydroxyproline to creatinine ratio. Japanese J. Public Health, 30, 166-176, 1983 (in Japanese).
12) Matsuki H, Kasuga H, Osaka F, Yanagisawa Y, Nishimura H: A comparative study on the health effects of indoor pollution with special reference to nitrogen dioxide in winter and summer. Japanese J. Public Health, 32, 549-559, 1985 (in Japanese).
13) Matsumura T, Kametani K, Takeda M, Nagasawa C, Takeda H, *et al.*: Development of simplified simultaneous determination method for nitrogen dioxide and formaldehyde in air. Japanese J. Public Health, 33, 754-760, 1986 (in Japanese).
14) Selinus O: Large-scale monitoring in environmental geochemistry. Applied Geochemistry, 11, 251-260, 1996.
15) Wada M, Aoki S, Seko K: Report of meteorological research observations by the 29th Japanese Antarctic Research Expeditions in 1988, Antarctic Record, Ministry of Education of Japan, 34, 46-75, 1990.
16) Watanabe O: "How are climatic and environmental signals preserved in an ice sheet? " J. Geog, 100, 988-1006, 1991
17) World Health Organization: Estimating human exposure to air pollutants. WHO publication, 1982. 1 pp.
18) Yanagisawa Y. and Nishimura H: A badge type personal sampler for measurement of personal exposure to NO_2 and NO in ambient air Environ International. 8, 235-242, 1982.
19) Yanagisawa Y, Nishimura H, Matsuki H, Osaka F, Kasuga H: Estimation of annual of NO_2 exposure from short period measurements. J. Japan. Soc. Air Pollution. 19, 292-299, 1984.