The Concentrations of Nitrogen Dioxide and Ozone in the Air at Inland and Seashore in Japan

by

Kiyoshi Kawamura and Sumiko Sakurai

Meteorological Research Institute, Tokyo

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Abstract

Four separate series of observations of surface NO_2 and ozone were made at inland (Sudagai) and seashore (Tomisaki) stations in the central part of Honshu, Japan.

The results of NO_2 determination showed a diurnal variation with two maxima respectively at about one hour after sunrise and one to two hours after sunset. The NO_2 concentrations on the evenings of fine days were extraordinarily high when the snow around the inland station was gradually melting. On the other hand, the concentrations in maritime air in winter were very low, being $1.5 \mu\text{gNO}_2/\text{m}^3$ on the average when there was a strong wind with a prevailing SW or SSW-component. At the inland station, the winter and the summer average values were the same, being $3.6 \mu\text{gNO}_2/\text{m}^3$, and the average values in early autumn and winter at the seashore station were respectively 3.7 and $7.3 \mu\text{gNO}_2/\text{m}^3$.

At the inland station the average concentrations of ozone during the daytime in winter and summer were respectively 23 and $26 \mu\text{gNO}_2/\text{m}^3$. These values are lower than those in early autumn and winter at the seashore station, though the altitude of the former station is 701 meters above the sea level. This is explained by taking the topographic situation of the inland station into consideration.

1. Introduction

The observation of NO_2 in unpolluted air has recently been made by several authors at a number of places. According to the observation made on land, the concentration ranges from 2 to $4 \mu\text{gNO}_2/\text{m}^3$ of the air at NTP. On the other hand, much lower values than $2 \mu\text{gNO}_2/\text{m}^3$ were obtained by LODGE, MACDONALD and VIHMAN (1960) in the mid-Pacific during two summers. These results suggest that the main source of NO_2 in the clean air lies on land. Up to now, there have been two different views on the source of NO_2 on a global basis: one is the soil origin hypothesis (MIYAKE, KAWAMURA and SAKURAI, 1961b and JUNGE, 1963) and the other considers the main source to be the oxidation of atmospheric NH_3 (GEORGI 1963). As to the rate of emission of NO_2 from the soil, one of the present authors, KAWAMURA (1964), carried out observations at Tokyo and showed that the observed rate during the daytime ranged from 1 to $4 \times 10^{-3} \mu\text{gNO}_2 \text{ cm}^{-2} \text{ hr}^{-1}$. By these observations, he reconfirmed that a considerable part of NO_2 in the clean air originates from the soil.

The rate of NO_2 emission from the soil, as well as the concentration of NO_2 in the surface air, may change when the ground is covered with snow. At a seashore station, the NO_2 concentration may be influenced by the surface meteorological conditions, especially by the direction of the prevailing wind. To examine these changes in NO_2 concentration, the Sudagai Weather Reporting Station ($36^\circ 52' \text{N}$, $139^\circ 04' \text{E}$), Gunma Pref., and the Tomisaki Weather Station ($34^\circ 55' \text{N}$, $139^\circ 50' \text{E}$), Chiba Pref., were chosen as the observation sites. The former station (an inland one) is in the Mikuni mountain range with an altitude of 701 meters above sea level and is located about 75 km east of the Japan Sea. The surrounding country is famous as a snowy area. The latter (a seashore station) is, on the other hand, situated on the Pacific shore only about 50 meters off the shore-line. Two separate series of observations on the surface NO_2 and ozone were made at the two stations; in winter, 1961 and summer, 1962 at the inland station, and in early autumn, 1963 and winter, 1965 at the seashore. The results of these observations will be described and discussed in this paper.

2. Methods of observation

An electro-chemical method (EHMERT, 1952) was used for ozone measurement. The solution for absorbing ozone contains potassium iodide, potassium dihydrogen phosphate, disodium hydrogen phosphate and a small amount of sodium thiosulfate. Two reaction chambers are connected in series and 10 liters of air was passed at a flow rate of 1.2 l/min. The first chamber was used for a sample and the second for a blank.

Nitrogen dioxide in the air is collected by sucking the air (1.2 l/min.) through a fritted glass bubbler (MIYAKE *et al.*, 1961b) containing Griess-Saltzman's solution (SALTZMAN, 1954) for 1 to 4 hours. The degree of pink coloration is visually compared with standards. It must be noted that in winter, 1961 and summer, 1962 at the inland station collections were done respectively by using two sets of apparatus and an automatic gas sampler manufactured by Kimoto Engineering Company, Ltd., Osaka, Japan. The volume of the air sample was 105 liters on the average, for which the limit of detection was about $0.3 \mu\text{gNO}_2/\text{m}^3$. Since the determination of NO_2 is disturbed by ozone, it is necessary to remove ozone from the air. To do so, a plug (diameter: 0.8 cm and length: 15 cm) of glass wool with a manganese dioxide coating was prepared following Saltzman's procedure, which decomposed about 85 percent of ozone in the air at the flow rate given above.

3. Results of observation

The observation of NO_2 and ozone in the air at the inland station was made twice: during the periods from 1st to 12th December, 1961 and from 30th July to 10th August, 1962. The results are shown respectively in Figs. 1 and 2, with the atmospheric pressure and the weather conditions. Two separate series of observation were also made at the seashore station: during the periods from 30th August to 9th September, 1963 and from 2nd to 16th February, 1965. The results of observation at the seashore station are given respectively in Figs. 3 and 4, with the surface wind data etc. In these figures, it is noticed that during the daytime there is a

Fig. 1. Concentrations of NO_2 and ozone in the air observed at the inland station in winter of 1961.

Fig. 2. Concentrations of NO_2 and ozone in the air observed at the inland station in summer of 1962.

Fig. 3. Concentrations of NO_2 and ozone in the air observed at the coastal station in early autumn of 1963.

Fig. 4. Concentrations of NO_2 and ozone in the air observed at the coastal station in winter of 1965.

positive relationship between the ozone concentration and the atmospheric pressure, as pointed out by AUER (1939) and others. The ozone concentration at the inland station in summer generally shows a remarkable diurnal variation with the maximum near the noon as pointed out by many authors, while no similar variation was observed from 7th to 12th December, 1961, when the ground was covered with snow (see Fig. 1). This suggests that the snow cover protects ozone from destruction through chemical reactions with the soil, plants, etc. At the seashore station, on the other hand, the ozone concentration did not show a remarkable nocturnal decrease as was seen at the inland station during the summer. This indicates that under weather conditions at the seashore station the ground air at night is well mixed by turbulence.

The average concentration of ozone during the daytime at the two stations are given in Tab. 1, with those obtained at the western suburb of Tokyo and at the top and the side of Mt. Norikura (MIYAKE, KAWAMURA and SAKURAI, 1961a and 1961b).

Table 1. Average concentrations of ozone during the day observed at different locations in Japan

Location	Altitude (m)	Time	O ₃ ($\mu\text{g}/\text{m}^3$)
Top of Mt. Norikura	2770	Sept. 1959	58
"	"	Aug.-Sept. 1960	30
Side of Mt. Norikura	1450	Sept. 1959	35
"	"	Aug.-Sept. 1960	28
Sudagai	701	Dec. 1961	23
"	"	July-Aug. 1962	26
Tomisaki	12	Aug.-Sept. 1963	30
"	"	Feb. 1965	46
Tokyo	—	Aug.-Sept. 1958	16
"	—	Feb. 1958 and 1959	20

The ozone values at Tokyo are only about half of those at Tomisaki. Since the surface air at Tokyo is polluted by various man-made sources, this comparison seems to show that at Tokyo a considerable part of ozone was destroyed through the chemical reactions with contaminants. Although the altitude of the station at Sudagai is 701 meters above the sea, the ozone concentration is lower than that at Tomisaki. The former station is located in the middle of a small basin surrounded by mountains. The average height difference between the station and the tops of the surrounding mountains is about 100 meters and the horizontal distances between them are 600 meters on the average. Because of the topographic situation near the station, the wind speeds during the periods of observation were very low, being mostly below 4 knots. In such calm weather, a thermal stratification of the surface air is liable to occur, which will hinder the downward stream of ozone. The ozone value obtained in early autumn at Tomisaki agrees well with those obtained in summer and early autumn by TEICHERT (1955) in Germany.

The inland station is a suitable location to observe the surface NO₂ which is originated from the soil, because the station is far from towns and is located at

the bottom of a small basin. On the 4th, 7th, 8th and 9th December, 1961, it was snowy. The NO_2 concentrations on the days from the 1st to about noon of the 9th were low, ranging mostly from 1 to $3\mu\text{g}/\text{m}^3$. On clear days, namely on the 3rd, 5th and 8th, the NO_2 concentration showed a marked diurnal variation with at least one maximum in the evening. On the 8th December when the observation was done for 24 hours, a morning maximum of NO_2 was observed besides the evening maximum. The times of sunrise and sunset at Sudagai during the period of observation were respectively about 06:40h and 16:30h, but the actual sunrise and sunset were respectively 08:10h and 14:40h owing to the shadows of the surrounding mountains. Fig. 1 therefore shows that the two maxima occurred respectively a little after sunrise and a few hours after sunset, in agreement with the results obtained at the side of Mt. Norikura by MIYAKE, KAWAMURA and SAKURAI (1961b) and at Tokyo by KAWAMURA and SAKURAI (1963). The ground was at one time covered by 28 cm depth of snow on the 9th, then it gradually melted down to 11 cm on the 12th. The weather was fine and calm throughout the days and the concentration of NO_2 showed a striking maximum in the evening. Especially, at 16:24h on the 10th the highest value of $21\mu\text{gNO}_2/\text{m}^3$ was observed. On the 10th when the snow began to melt, about 10 percent of the soil surface around the station was exposed to the atmosphere, and on the 12th about 30 percent. If NO_2 is released from the soil as a result of microbiological reactions as in the case of N_2O (ADEL, 1951 and ARNOLD, 1954), the soil condition as well as the fine and calm weather may be the optimum condition for their activities, which may lead to a high concentration of surface NO_2 . The occurrences of the morning and evening peaks in NO_2 concentration in polluted air were explained by taking account of meteorological conditions, such as the formation of surface temperature inversion at night and the emission of NO_2 from the man-made sources (HAMMING, MACPHEE and TAYLOR, 1959 and KAWAMURA and SAKURAI, 1963). According to KAWAMURA (1964), the emission of NO_2 from the soil begins with sunrise continuing till late at night, and on a fine day the rate of emission shows its maximum within several hours after sunrise. The diurnal variation of NO_2 in the clean air can therefore be explained by replacing the NO_2 -emission from the man-made sources in urban conditions with that from the soil. In the first half of the period of observation made at the inland station in summer, the weather was relatively fine as is seen in Fig. 2 and the NO_2 generally showed a diurnal variation which, however, is smaller than that in winter, while no similar variation was observed in the second half.

In the two separate series of observations at the inland station, we have made the NO_2 determination for 24 hours for four consecutive days in winter and for nine days in summer. The average concentrations of NO_2 observed during the two periods are given in Tab. 2, in which the results of observation are classified into the day and the night values. The table shows that the night value in winter agrees well with that in summer within the error of observation, while the concentration during the day is higher in summer than in winter.

In contrast to the inland station, there were occasionally windy days at the sea-shore station. As is seen in Figs. 3 and 4, there was a close relation between the NO_2 concentration and the direction of the wind. On days when a strong wind with SW or SSW-component (onshore wind) blew, both ozone and NO_2 concentrations were

Table 2. The average day and night values of NO_2 observed on the days when the measurement has been done on a 24-hour basis

Time	$\text{NO}_2 (\mu\text{g}/\text{m}^3)$	
	day	night
Winter (1961)	2.0	2.7
Summer (1962)	3.7	2.9

low and showed a smaller diurnal variation. This is seen in the data on 31st August, 2nd and 3rd September, 1963 shown in Fig. 3 and on 3rd, 5th and 14th February, 1965 shown in Fig. 4. The average values of the wind speeds and the NO_2 concentrations when a strong wind prevailed were respectively 22 knots and $1.5 \mu\text{gNO}_2/\text{m}^3$ in February and 19 knots and $2.3 \mu\text{gNO}_2/\text{m}^3$ in August and September. LODGE, MACDONALD and VIHMAN (1960) observed the trace substances in the air at the mid-Pacific during two summers and reported that NO_2 levels were below the limit of detection (about $2 \mu\text{gNO}_2/\text{m}^3$) in the method used during 94 percent of the time. Our NO_2 values obtained on windy days in winter is in accordance with those given by LODGE and others. On days when the weather is fine and the wind with *N*-component (offshore wind) blows, the NO_2 concentrations were generally high and showed a diurnal variation as is seen in Fig. 1. The times of sunrise and sunset at Tomisaki during the periods of observation were respectively about 05:15h and 18:07h in early autumn and 06:33h and 17:15h in winter. The data in Figs. 3 and 4 therefore show that most of the evening maximum in NO_2 appeared about one hour after sunset and the morning maximum one hour and a half after sunrise. Therefore, the times of occurrences of these NO_2 peaks completely agree with those obtained at the inland station. There are some fishermen's cottages near the observation station and the center of Tateyama city lies beyond the small hills about 10km north of the station. In addition, commercial and industrial areas, such as Tokyo and Kawasaki, are located to the north of the station. The concentrations of NO_2 on the 8th, 9th, 10th and 12th February shown in Fig. 4 were very high and the average value on these days was $13.3 \mu\text{gNO}_2/\text{m}^3$, which was even comparable to the concentrations frequently observed at dawn in the western suburb of Tokyo (KAWAMURA and SAKURAI, 1963). Judging from the daily surface weather maps and the local wind at the observation station, it seems that the higher NO_2 values on these days are due to the inflow of the urban air. As was mentioned above, the summer NO_2 data at the inland station frequently exhibited no diurnal variation. But, at the seashore station where the air is thermally more unstable than at the inland station, a diurnal variation was generally observed not only in winter but also in early autumn, and the reason for this inconsistent result is unknown.

Fig. 5 shows the results of observation of the tropospheric NO_2 made at different continental and maritime locations by the present authors and other investigators. In the figure the graph on the left is arranged in the order of the height of observation stations and that on the right is in the order of the degree of pollution. Both the summer and winter average values at Sudagai were $3.6 \mu\text{gNO}_2/\text{m}^3$, while at Tomisaki where the air seems to be frequently contaminated by the inflow of the urban air, the concentration in winter was considerably higher than that in early autumn. Although the winter observation at Sudagai showed an extraordinary high concentration of NO_2 in the latter half of the observational period, the concentrations on

Fig. 5. Average concentrations of tropospheric NO_2 observed at various continental and maritime locations

the first half (from 1st to 6th December) when the ground was not covered with snow were generally low, and its average was $2.4 \mu\text{g NO}_2/\text{m}^3$. This is two-thirds of the summer average value at the same station. If we compare NO_2 in the clean air in different seasons when the soil is not covered with snow, the above result seems to suggest that the concentration is higher in summer than in winter. Fig. 5 does not necessarily show that except for the data at Tokyo, the NO_2 concentration decreases with the increasing height of the observation station. Particularly, the values at the last three continental stations show a trend of variation which is contrary to expectation, though all of these observations were made in the same season of year. Since there is an ascending air current along the mountain slope caused by the solar radiation, the observed data at a mountain station generally show the concentration of NO_2 in the lower air rather than in the air at the level of the station. The values shown in Fig. 5 therefore do not necessarily represent a true vertical profile. The NO_2 values at Florida

and Hawaii are nearly equal to those at St. Moritz, the top of Mt. Norikura and the Zugspitze, and are a little higher than the values obtained in the mid-Pacific by LODGE *et al.* (1960) as well as at Tomisaki in winter when the maritime air flows into the observation site. This suggests that the air at Florida and Hawaii is subject to the influence of NO_2 which originates in the soil.

4. Concluding remarks

1. It is reconfirmed that the NO_2 concentration in the unpolluted air exhibits a diurnal variation which is similar to that obtained for the polluted air at Tokyo. This supports our previous view that the main source of the surface NO_2 is the soil.

2. From the NO_2 data obtained by the present authors and other investigators, it is estimated that the concentration in the maritime air is about $2 \mu\text{g NO}_2/\text{m}^3$ at the highest.

3. The concentration of NO_2 in the clean air is a little higher in summer than in winter.

4. From a series of ozone observations by Miyake and the present authors carried out up to now at various locations in Japan, it is concluded that the concentration is strongly affected by the local conditions.

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須田貝および富崎で観測した大気二酸化窒素およびオゾンの濃度

川 村 清・桜 井 澄 子

1961年の冬と1962年の夏に群馬県須田貝で、また1963年の初秋と1965年の冬に千葉県富崎で大気二酸化窒素 (NO_2) およびオゾン濃度を観測した。その結果、 NO_2 濃度は日出後約1時間および日入後1～2時間においてそれぞれ極大値をとるような規則正しい日変化を示した。この変化の傾向はわれわれがさきに乗鞍岳の山腹および東京でえたものと完全に一致する。汚染大気中におけるこの日変化は気象条件、特に逆転層の形成および汚染源からの NO_2 放出における日変化を考えることによって説明されている。清浄な大気中での場合は人工的発生源のかわりにわれわれが提出した土じょうからの NO_2 放出説をとり入れることによって説明できるだろう。

須田貝の観測点近くの積雪が溶けている日の夕方に高濃度の NO_2 が観測された。大気に露出した地面からの NO_2 放出速度がこれらの日において異常に大きかったのかも知れない。太平洋の沿岸にある富崎では強い海風するとき NO_2 濃度が低く、特に冬のときは平均して $1.5\mu\text{g}/\text{m}^3$ であった。須田貝における NO_2 濃度の平均値は夏、冬共に $3.6\mu\text{g}/\text{m}^3$ であったが、富崎での初秋および冬の値はそれぞれ 3.7 および $7.3\mu\text{g}/\text{m}^3$ であった。富崎の冬における値は大きい、これは観測点北方にある諸都市の汚染された空気が流入したためと考えられる。

須田貝の観測点は海拔 701m にありながら富崎におけるよりもオゾン濃度は低かった。これは前者が小さな盆地に位置しているため、風が弱く、従ってじょう乱等による大気の上下混合が不活発なために生じたと考えられる。