An Experiment on the Atmospheric Diffusion of Chemical Reactive Material, NO, NO₂ in Short Distance

by

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Abstract

Short distance diffusion with chemical reaction experiment was investigated. NO, NO₂ and O₃ concentrations were measured within 120 m downwind from the source which emitted NO gas continuously into the atmosphere with background ozone. Very large fluctuation of NO_x concentration was observed, and average concentrations of instantaneous plumes were obtained. The results show that the sums [NO]+[NO₂] and [NO₂]+[O₃] are conserved under chemical reaction and that the photochemical decomposition rate of NO₂ is much smaller than its formation rate during the daytime when travelling time is less than 20 sec. And it is also shown the formation rate of NO₂ depends not only upon travelling time but on background ozone concentration, and also on the dilution rate due to turbulent diffusion.

A simple model of diffusion with reaction which is applicable within short distances from the source is presented. It gives fairly good agreement with observed concentrations in instantaneous plumes.

Introduction

Many measurements of pollutant plumes from a stationary elevated point source have recently been carried out by aircraft, and some diffusion models of reactive material in a large plume have been presented. Davis et al. (1974) showed that the following three reactions played a major role in the plume, but they at the same time suggested free-radical was also important over a few tens of kilometers downwind from the source.

On the other hand, White (1977) showed that free-radical reactions did not significantly affect the ozone concentration at distances less than 45 km, that the observed

plume profiles of O₃, NO₂ and NO were explained by the reactions (1)–(3) sufficiently, and that the concentrations would quickly approach a photo-stationary state in which NO₂ formation rate by reaction (3) should be equal to the decomposition rate by reaction (1).

Hegg et al. (1977) showed the absence of measurable ozone generation in fields near a power plant, but the system was not in a photo-stationary state as far as several tens of kilometers. It is a very important problem for the modeling of diffusion with reaction whether the system is in a photo-stationary state or not. Under a photo-stationary state, the following equation holds:

$$\frac{[\text{O}_3][\text{NO}]}{[\text{NO}_2]} = \frac{k_1}{k_3} \quad (4)$$

On the other hand, both sums, [NO_x] = [NO] + [NO₂] and [O₃] + [NO₂] + [O], are conserved during the chemical reactions (1)–(3). Then

the concentrations of NO, NO₂ and O₃ are given from the three equations: Eq. (4) and two equations just mentioned above (Kimura, 1978, White; 1977 and Bilger, 1978). However, if a photo-stationary state can not be assumed, detailed information on turbulent diffusion process will be necessary, and the modeling will be rather complicated. Lamb et al. (1978) and Shu et al. (1978) presented a model of second-order chemical reactions in a turbulent fluid using the numerical boundary layer model. Hegg et al. (1977) showed that departure of observed concentrations from a photo-stationary state is to be explained by a semi-theoretical equation. However, little detailed information on turbulent diffusion and reaction processes have been given by aircraft measurements so far.

The present experiment aims at obtaining basic data on reaction and diffusion in the simplest case in the atmosphere.

The field experiment

The experiment was performed during the period 29 August—2 September 1977 in a field under the observation tower of the Meteorological Research Institute, which is located about 60 km northeast of Tokyo. The field is circle-shaped having a 150 m radius and is flat and covered with lawn.

NO gas was emitted continuously from a point source for 10–20 minutes at a constant emission rate. A mixture of 5% NO and 95% N₂ was used for this purpose. Concentration of NO, NO₂ and O₃ were measured at two places 5–120 m downwind from the source. The emission point and the observation points were arrayed in the direction of surface wind at the same level of 1.5 m. Background concentrations were measured before and after each run. Fig. 1 presents the block-diagram of the experiment. The measuring instruments were Monitor Labs Model 8440 for NO and NO_x, and Model 8410 for O₃. All of them were chemi-luminescence detectors, which were adjusted to the response time of 5 sec. Wind speed and direction at the level of 1.5 m, insolation and net radiation

Fig. 1. Blok diagram of the experiment. X_1 and X_2 are downwind distances.

were observed at the same time. During the experiment, the sky was almost clear and the wind was moderate. The prevailing winds were easterly or southeasterly with 1–2.5 m/s in the daytime and were northeasterly with about 1 m/s or quite calm in the nighttime. The maximum concentration of background ozone in each day were 50–120 ppb, which appeared in the afternoon. The minimums were less than 10 ppb after midnight. The background concentration of NO_x ranged between about 3 ppb and 25 ppb. About 45 runs were carried out.

In the experiment, a very large fluctuation of NO_x concentration was observed. Fig. 2 shows an example of time variation of the concentration at 53 m downwind from the source. Peaks of both NO and NO₂ usually appear at the same time, which indicates that a meandering instantaneous plume crosses this observation point. And the reduc-

Fig. 2. An example of time variation of concentrations observed at 53 m downwind from the source.

tion of O_3 , which is at the time of the peaks, can be explained by reaction (3).

Chemical conservation

As mentioned above, if only reactions (1)–(3) control the system, the sums $[NO] + [NO_2]$ and $[O_3] + [NO_2] + [O]$ will be conserved. In the second sum, $[O]$ can be neglected because it is very little. In this case, R_Q defined by the following equation should be constant at any point in the plumes, and be equal to the ratio of $[NO_2]$ to $[NO_x]$ in the emission gas:

$$R_Q = \frac{[NO_2] + [O_3] - [NO_2]_{BG} - [O_3]_{BG}}{[NO] + [NO_2] - [NO]_{BG} - [NO_2]_{BG}} \quad (5)$$

where $[NO]_{BG}$, $[NO_2]_{BG}$ and $[O_3]_{BG}$ are the background concentrations. If free-radical reactions or other reactions to be described later affect the concentrations, R_Q will not be constant.

As the travelling time was less than a few minutes in this experiment, it was presumable that free-radical reactions were not important. However, NO_2 might also be formed by the following reaction when the NO concentration is very high (Seinfeld, 1975):

Since reaction (6) is a third order reaction, it will be unimportant in the case of low NO concentration. For example, if the background ozone is 30 ppb, the NO_2 formation caused by reaction (6) will be much less than one by reaction (1) except when the NO concentration is higher than 10^4 ppm (1%). Therefore, reaction (6) need not be considered in the ordinary polluted atmosphere. But we have to pay some attention to this reaction, because 5% NO gas was used for emission gas in this experiment.

Figs. 3 and 4 show R_Q given by the experiment in the daytime and the nighttime respectively. R_Q was calculated from average concentration of each instantaneous plume, and the mean value and standard deviation of R_Q were calculated in each run and each

Fig. 3. R_Q and standard deviation in the daytime. Emission rate of NO : 1, 3 and 10 cc/sec.

Fig. 4. The same as Fig. 3, but in the nighttime.

downwind distance. The figures show them in case that instantaneous plumes were observed over ten times in a run. Significant difference of R_Q from the expected value, which must be 0 in this case, is not recognized at any travelling time, but the standard deviation is rather large in the daytime. This large standard deviation will be explained by the fact that the fluctuation of background concentration was relatively large and that the accuracy of measurement became rather low because the concentration decreased very fast under the thermally unstable condition. In the nighttime, however high concentration was kept up for a long time and it was much clearer that R_Q does not depend on travelling time.

Formation and decomposition rate of NO_2

NO_2 formation rate $k_3[NO][O_3]$ and decomposition rate $k_1[NO_2]$ can be estimated from the observed concentrations. But the

rate constant k_1 depends on the light intensity. It is assumed that k_1 is proportional to the insolation and is 0.48 min^{-1} at $50 \text{ cal/cm}^2\text{h}$.

Fig. 5 shows the comparison of $k_3[\text{NO}][\text{O}_3]$ and $k_1[\text{NO}_2]$ which are estimated from averaged concentration in some typical daytime runs. The solid line indicates the photo-stationary state in which the formation rate is equal to the decomposition rate. Each of the data indicates that the NO_2 formation rate is much larger than the decomposition rate. The ratio of the decomposition rate to the formation rate depends on travelling time, and it seems to increase with travelling time. The decomposition rate is generally less than 10^{-1} times of the formation rate when the travelling time is less than 20 sec. This result suggests that the NO_2 concentration is controlled only by diffusion and reaction (3) even in the daytime at such short distances from the source. Consequently, it becomes easy to model the formation rate of NO_2 at short distances.

Fig. 5. Scatter plot of photochemical decomposition rate of NO_2 vs. formation rate in the daytime at various downwind distances X . T is travelling time corresponding to X .

A simple model of diffusion with reaction

Since only the reaction (3) plays an essential role as described above, $[\text{NO}_2] + [\text{O}_3]$ and $[\text{NO}] + [\text{NO}_2]$ are stoichiometrically invariant even though diffusion process takes place as well as reaction process. They are given by the following equations:

$$[\text{NO}] + [\text{NO}_2] = \chi + [\text{NO}]_{BG} + [\text{NO}_2]_{BG} \quad (7)$$

$$[\text{NO}_2] + [\text{O}_3] = (1-r)\chi + [\text{NO}_2]_{BG} + [\text{O}_3]_{BG}. \quad (8)$$

Here, χ is the component of $[\text{NO}_x]$ which comes from the source, and r is the ratio of $[\text{NO}]$ to $[\text{NO}_x]$ in the emitted gas. As photochemical decomposition is not being considered, $[\text{NO}]_{BG}$ should be neglected. The actual $[\text{NO}]_{BG}$ has to be considered as a non-reactive gas in this model. If it is assumed that χ is uniform in the instantaneous plume, and that the diffusion process is quasi-stationary, χ is written as

$$\chi = \frac{Q}{\pi \sigma_z \sigma_y U}. \quad (9)$$

Here, Q is the emission rate, U is the mean velocity, and σ_z and σ_y are the vertical and lateral width of the plume respectively. The diffusion process is expressed in Lagrangian form as follows:

$$\begin{aligned} \frac{d\chi}{dt} &= \frac{Q}{\pi U} \frac{d}{dt} \left(\frac{1}{\sigma'_z \sigma'_y} \right) \\ &= \sigma'_z \sigma'_y \chi \frac{d}{dt} \left(\frac{1}{\sigma'_z \sigma'_y} \right) \end{aligned} \quad (10)$$

where $x = Ut$ and $\sigma'_z(t) = \sigma_z(Ut) = \sigma_z(x)$.

$[\text{NO}]$ should follow the same diffusion process, but the reaction process should be considered at the same time.

$$\begin{aligned} \frac{d[\text{NO}]}{dt} &= \left(\frac{d[\text{NO}]}{dt} \right)_{DIFF} + \left(\frac{d[\text{NO}]}{dt} \right)_{CHEM} \\ &= \sigma'_z \sigma'_y [\text{NO}] \frac{d}{dt} \left(\frac{1}{\sigma'_z \sigma'_y} \right) \\ &\quad - k_3 [\text{NO}][\text{O}_3] \end{aligned} \quad (11)$$

$[\text{O}_3]$ can be eliminated by the use of Eqs. (7) and (8).

$$\begin{aligned} \frac{d[\text{NO}]}{dt} &= \sigma'_z \sigma'_y [\text{NO}] \frac{d}{dt} \left(\frac{1}{\sigma'_z \sigma'_y} \right) \\ &\quad - k_1 [\text{NO}] \{ [\text{O}_3]_{BG} + [\text{NO}] - r\chi \}. \end{aligned} \quad (12)$$

If the relative NO concentration is defined as

$$\varphi \equiv \frac{1}{r\chi} [\text{NO}], \quad (13)$$

$d\varphi/dt$ is then given by Eqs. (10) and (12).

$$\begin{aligned}\frac{d\varphi}{dt} &= \frac{1}{r\chi^2} \left\{ \chi \frac{d}{dt} [\text{NO}] - [\text{NO}] \frac{d}{dt} \chi \right\} \\ &= -\frac{k_3[\text{NO}]}{r\chi} \{ [\text{O}_3]_{BG} + [\text{NO}] - r\chi \}. \quad (14)\end{aligned}$$

Now, non-dimensional travelling time τ , and the non-dimensional NO_x component from source ν are defined as follows:

$$\begin{aligned}\tau &= k_3[\text{O}_3]_{BG} t \\ \nu &= \frac{r\chi}{[\text{O}_3]_{BG}} = \frac{rQ}{\pi U \sigma'_z \sigma'_y [\text{O}_3]_{BG}}.\end{aligned}$$

Then Eq. (14) is written as

$$\frac{d\varphi}{d\tau} = -\varphi \{1 + \nu(\varphi - 1)\}. \quad (15)$$

Eq. (15) cannot be integrated directly, because ν depends on τ . But it can be assumed as

$$\nu \propto (\sigma'_z \sigma'_y)^{-1} \propto \tau^{-p}.$$

ν is interpreted as a past concentration of the air mass, of which the concentration is ν_0 at present time $\tau = \tau_0$.

$$\nu = \nu_0 \zeta^{-p}$$

where,

$$\zeta = \tau / \tau_0.$$

The value of p can be estimated from the separation of a pair of particles which has been discussed in detail by Pasquill (1974). Namely, at a small travelling time, σ'_z and σ'_y are approximately proportional to travelling time τ . Therefore, the value of p should be about 2 for the plume from the point source, and about 1 for the plume from the line source. Now, Eq. (15) will be written as

$$\frac{d\varphi}{d\zeta} = -\tau_0 \varphi \{1 + \nu_0 \zeta^{-p} (\varphi - 1)\}. \quad (16)$$

The relative concentration of NO is given as a function $\varphi(\nu_0, \tau_0)$ which depends only on ν_0 and τ_0 , and it is the solution of Eq. (16) at $\zeta=1$, with the initial condition $\varphi=1$ at $\zeta \rightarrow 0$. Unfortunately, the solution can not be written as an analytical function except when p is equal to 1. The solution at $p=1$ is

$$\varphi(\nu, \tau) = \nu^{-1} \tau^{-\tau\nu-1} e^{-\tau} \{ \gamma(\tau\nu, 1) - 1 \}^{-1} \quad (17)$$

where $\gamma(z, p)$ is an incomplete Gamma function. But anyway, it is more convenient to use a numerical table which is given by the numerical integration of Eq. (16). Fig. 6

Fig. 6. Theoretical non-dimensional NO concentration φ_2 which is the solution of eq. (16) in case of $p=2$.

shows the function $\varphi(\nu, \tau)$ at $p=2$. The function φ has the following asymptotic characteristics:

$$\varphi \rightarrow e^{-\tau}, \quad \text{when } \nu \rightarrow 0 \quad (18)$$

$$\left. \begin{aligned} \varphi &\rightarrow 0 \quad (\nu \leq 1) \\ \varphi &\rightarrow 1 - \frac{1}{\nu} \quad (\nu > 1) \end{aligned} \right\}, \quad \text{when } \tau \rightarrow \infty \quad (19)$$

Eq. (18) means that it will be good approximation to be treated as first-order reaction when the concentration of NO_x from the source is low enough compared with background ozone. And the meaning of Eq. (19) is as follows: If $[\text{NO}_x]$ from the source is larger than background ozone, $[\text{NO}]$ must be 0, and if it is not, $[\text{O}_3]$ must be 0. Namely O_3 and NO can not be coexistent when the travelling time is large enough.

Comparison with the experiment

Fig. 7 shows some examples of experimental results of the relative NO concentration which are the average of the data classified into 8×8 divisions according to the values of τ and ν . The cases of $0.3 < \nu \leq 0.5$

Fig. 7. Theoretical non-dimensional NO concentration ϕ_2 (solid line) and observed one with standard deviation.

and $4.0 < \nu \leq 8.0$ are shown in the figure. The vertical bars mean the standard deviation for each value. The result shows that the relative NO concentration depends not only on non-dimensional travelling time τ but also on non-dimensional NO_x concentration ν , and it depends more largely on τ in the case of smaller ν . The solid lines show the theoretical function ϕ at $\nu=0.5$ and $\nu=5.0$ which can mostly explain the experimental results. But the theoretical values are slightly underestimated.

The comparison of experimental and theoretical relative NO_2 concentrations (NO_2/NO_x) is plotted in Fig. 8. The observed values are the average of the data classified according to ν in each run. These are somewhat scattered and the theoretical values are somewhat larger. This overestimation corresponds to the underestimation in Fig. 7. The reason for the overestimation is not clear, but it may be related to the assumption of uniform concentration in the instantaneous plume. It may be because the fluctuation of NO concentration will decrease the formation rate of NO_2 . This error would be more serious if the model were applied to the averaged concentration of a long period, instead of being an instantaneous plume. One of the reasons for the scattering would

Fig. 8. Scatter plot of estimated relative NO_2 concentration vs. observed one. t is travelling time.

be that the observed concentration is often low in the case of a high relative NO_2 concentration, enhancing measuring errors and the effect of the fluctuation of the background concentration. So the observed absolute NO_2 concentration and the theoretical one give rather good agreement, as is shown in Fig. 9, which is equivalent to Fig. 8 weighted with concentration.

Fig. 9. The same as Fig. 8, but absolute NO_2 concentration.

Fig. 8 and 9 show that the accuracy of the model does not decrease even if the travelling time is larger than 30 sec. Note that according to Fig. 5, the photochemical decomposition of NO_2 is not negligible any longer at such a long traveling time, but it is considered in the model. It seems that the present model is applicable a little longer than the expected range. This may be because estimation of the NO_2 concentration in the NO rich air mass is not so sensitive to photochemical decomposition.

Discussion

Summary of the results:

(1) Both sums of $[\text{NO}] + [\text{NO}_2]$ and $[\text{NO}_2] + [\text{O}_3]$ can be considered to be conserved when travelling time is less than about one minute though $[\text{NO}]$ and $[\text{NO}_2]$ are mixed with background pollutants by turbulent diffusion.

(2) Photochemical decomposition of NO_2 is negligible if travelling time is less than 20 sec. even in the daytime.

(3) NO_2 concentration calculated from the reactive-diffusion model, which is based upon two hypotheses mentioned above, gives fairly good agreement with the experimental results.

(4) Formation rate of NO_2 depends not only on travelling time and background concentration but also on the dilution rate due to turbulent diffusion.

The present model can be applied only in cases where travelling time is short and concentration is much different from the photo-stationary state. On the other hand, NO_2 concentration can be estimated from the algebraic equations in a photo-stationary state as mentioned in the first section. But it has not yet been made clear how we can estimate the applicable limit of the present model and make a simple model which is applicable in the intermediate region in which neither the present model nor the algebraic equations can be used.

The present model has to be applied only to mean concentration in the instantaneous

plume, but not to ones averaged over a long duration (say 10 min). To estimate the latter, we need not only the averaged NO_x concentration but also their probability density function. But the diffusion model which gives a probability density function has not yet been studied well enough. This depends upon future studies.

As NO emitted from an automobile is well mixed by the turbulence generated by the automobile itself, the diffusion process will be much different from the one in the simple case like the present experiment. Accordingly, the formation rate of NO_2 will be different from ours. Fig. 10 shows the relationship of NO_2 concentrations which were observed near the roadway and were estimated by the present model on the assumption that NO_x and background concentration are given and $p=1$ because the roadway is a line source. Here the concentrations were observed at some within about 100 m downwind from the source and at some altitudes not exceeding 15 m, in July, 1977, by Japan Environment Agency and the Osaka Prefectural Government.

Fig. 10. Scatter plot of estimated NO_2 concentration vs. observed near the roadway.

To make sure of the assumption of the model, the figure shows the data observed only at night when no decomposition of NO_2 takes place. Fig. 11 shows the same as Fig. 10 but the calculated NO_2 is the asymptotic

Fig. 11. The same as Fig. 10, but nondimensional travelling time $\tau \rightarrow \infty$ is assumed.

totic values when $\tau \rightarrow \infty$. Fig. 11 shows better agreement than Fig. 10. These results suggest that the formation rate of NO_2 near the roadway is much larger than the experimental result, and imply that a photo-stationary state can be assumed even at rather short downwind distances from roadway. The modeling of the photochemical reaction with the complex diffusion process still remain for future studies.

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NO , NO_2 の短距離反応拡散実験

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要 約

短い風下距離での反応拡散実験を行なった。オゾンバックグラウンド濃度として含む大気中に NO ガスを放出し、風下距離 120 m までのいくつかの地点において NO , NO_2 及び O_3 濃度の連続測定を行なった。 NO_x 濃度の非常に大きな変動が観測されたが、瞬間ブルーム中の各汚染質の平均濃度が得られた。この結果、反応があっても $[\text{NO}] + [\text{NO}_2]$ 及び $[\text{NO}_2] + [\text{O}_3]$ の各濃度和は保存していること、日中であっても移流時間が 20 秒以内では NO_2 の光分解速度はその生成速度とくらべてかなり小さいことがわかった。また NO_2 の生成速度は移流時間とオゾンのバックグラウンド濃度だけでなく乱流拡散による希釈率にも依存していることが明らかになった。

発生源からの風下距離が比較的小さい場合に適用できる保存則から導いた反応拡散モデルを提案し、瞬間ブルーム中の実測との比較でかなり良い結果を得た。