

An estimate of the conversion rates of SO_2 to SO_4^{2-} and NO_2 to $\text{HNO}_3 + \text{NO}_3^-$ for the evaluation air pollution in Beijing

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Abstract—The conversion rates of SO_2 to SO_4^{2-} and NO_2 to $\text{HNO}_3 + \text{NO}_3^-$ are estimated from the field data obtained in Beijing in summer, 1988. The results show that the conversion rate of NO_2 is about four times as much as that of SO_2 ; The conversion rates have a diurnal variation in a day. On the average, the rate of SO_2 is estimated to be $4.7\% \text{ h}^{-1}$ during the daytime and $3.4\% \text{ h}^{-1}$ during the nighttime. Similarly, the rate of NO_2 is estimated to be $17.2\% \text{ h}^{-1}$ and $12\% \text{ h}^{-1}$ respectively.

Keywords: sulphur dioxide; nitrogen oxide; computer modeling; conversion rate; oxidation.

INTRODUCTION

The transformation of NO_x to NO_3^- is a complex process in which photochemical oxidants are formed in the lower troposphere by reaction of hydrocarbons with nitrogen oxides under the effect of solar irradiation and their subsequent reactions with the short-lived radical species produced. It also depends on the dry deposition of pollutant particles, gas composition of the atmosphere (Venkatram, 1982), and a number of physical variables such as geographical latitude, season, solar intensity and ambient ozone concentration (Wilson, 1979). The ultimate oxidants are PAN, HNO_3 , and NO_3^- . Besides complication in the gas phase reactions, the oxidation of SO_2 also includes the air oxidation, catalytic oxidation in liquid droplets, and

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catalytic oxidation on dry surfaces of aerosol particles. The ultimate oxidant is H_2SO_4 . The conversion rate is an important parameter for quantitative description of the processes. A great number of field and chamber experiments have been performed by many researchers, and various mechanisms have been proposed and computer models developed for calculating the parameters, with a series of rational hypotheses. Table 1 and 2 show the results achieved for recent years.

In the research into air pollution of Beijing area for estimating the extent of pollution and for explaining the mechanisms of oxidation, transformation and deposition of pollutants, we conducted a series of field experiments in June, 1988, and the conversion rates of SO_2 and NO_2 were obtained through the model calculation.

Table 1 Conversion rate ($\% \text{h}^{-1}$) of SO_2 to SO_4^{2-}

Author (Time)	Field or chamber	Conversion rate, $\% \text{h}^{-1}$
Calvert <i>et al.</i> (1978)	Urban atmosphere (In the troposphere)	4.0
Chang (1979)	Power plant plume	0.5-4
Mcnaughton <i>et al.</i> (1980)	Urban atmosphere Urban plume (Includ conversion)	< 3.6 > 10
Endlish <i>et al.</i> (1984)	Urban plume	0.36-2.65

Table 2 Conversion rate ($\% \text{h}^{-1}$) of NO_2 to $\text{HNO}_3 + \text{NO}_3^-$

Author (Time)	Field or chamber	Conversion rate, $\% \text{h}^{-1}$
T. Okita (1979)	Urban plume	1.2-8.2 ($\text{HNO}_3, \text{NO}_3^-$)
Forrest <i>et al.</i> (1981)	Coal power plant (Summer)	3-12 (NO_3^-)
Spicer (1982)	Urban plume	23 (PAN, $\text{HNO}_3, \text{NO}_3^-$)
Spicer <i>et al.</i> (1983)	Chamber	14-32 (PAN, HNO_3)
Sakamoto <i>et al.</i> (1984)	Urban plume (Summer)	1-10 ($\text{HNO}_3, \text{NO}_3^-$)

DESCRIPTION OF THE MODEL

Most of the sulphur from industrial and urban sources are emitted as sulphur dioxide, SO_2 , accompanied by a small proportion of primary sulfates, SO_4^{2-} . For a well-mixed, Lagrangian air mass, the changes in SO_2 reactant concentration, R , and SO_4^{2-} product concentration, P , may be expressed as (Chang, 1979):

$$\frac{dR}{dt} = Sr - kR - kgR - kdR \quad (1)$$

$$\frac{dP}{dt} = Sp + kR - kpP - kdP \quad (2)$$

where Sr and Sp are source strengths of SO₂ and SO₄²⁻; k is the pseudo-first-order conversion rate coefficient of SO₂ to SO₄²⁻; kg and kp are dry deposition rate coefficients of SO₂ and SO₄²⁻ respectively; kd is the dispersion/dilution rate coefficient. In Equations (1) and (2), the concentration changes due to subsequent reactions, dry deposition, dispersion and dilution are considered. By defining the ratio, $G = R/(R + P)$, G satisfies the rate equation:

$$\frac{dG}{dt} = \frac{Sr(1-G)^2}{P} - \frac{SpG(1-G)}{P} - kG - kgG(1-G) + kpG(1-G) \quad (3)$$

By introducing the ratio, $F = 1 - G = P/(R + P)$ into Equation (3) results in:

$$\frac{dF}{dt} = -\frac{SrF^2}{P} + \frac{SpF(1-F)}{P} + k(1-F) + kgF(1-F) - kpF(1-F) \quad (4)$$

The advantage of Equations (3) or (4), compared to Equations (1) and (2), is that kd is eliminated. Equation (4), neglecting dry deposition, was used to estimate the NO_x conversion rate in urban atmospheres (Chang, 1979). In former experiments, one interesting feature was that the ratio F remained relatively constant during an 8-h (1200–2000 CDT) period (Forrest, 1979). We also found the feature during the surveying period in our field experiments. Since F remained approx constant for each period, i.e., $dF/dt \approx 0$, it is convenient to use Equation (4). By introducing $dF/dt = 0$ into Equation (4) and neglecting the second term ($Sp/Sr = 0.02$, Forrest, 1979), equation (5) obtained:

$$K = \frac{Sr * F}{P(1-F)} - kg * F + kp * F \quad (5)$$

The same simplification was used in calculation of conversion rates of NO₂.

In Equation (5), the deposition coefficients, kg and kp per h are estimated by use of a box model (Chang, 1979):

$$kg = 36vg/H; \quad kp = 36vp/H \quad (6)$$

where vg and vp are deposition velocities (cms⁻¹) and H is mixing depth (m).

The field experiments were performed at four sites in Beijing in consideration of prevailing wind direction: Dongdan, Xiaozhuang, langfang and Shisanling from 17 to 21 June, 1988. The distribution of these sites are shown in Figure 1. The site Dongdan represents heavily polluted urban atmosphere; Xiaozhuang represents the suburb with clean air; langfang and Shisanling are typical country towns near the suburb.

Samplers for gaseous and particulate pollutants, their sampling methods and analytical methods for determination of chemical components used in this study are summarized in Table 3.

Table 3 Sampling and analysis methods

Species	Sampling		Analytical method
	Method or sampler	Filter	
SO_4^{2-}	High-volume air sampler	Pallflex tissue quartz	I. C.
NO_3^-	High-volume air sampler	Pallflex tissue quartz	I. C.
HNO_3	Tandem two filters	PTFE/Polyamide	I. C.
SO_2	Tandem two filters	PTFE/ K_2CO_3 (Impregnated quartz)	I. C. (After H_2O_2 oxid)
NO_x	Passive sampler (Filter badge)	TEA impregnated filter (Cr_2O_3 filter)	NEDA
NO_2	Passive sampler (Filter badge)	TEA impregnated filter	NEDA

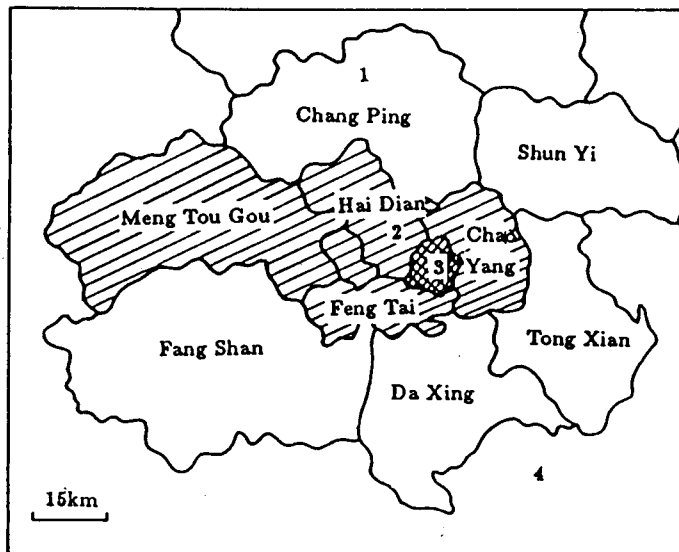


Fig.1 The distribution of surveying sites in Beijing area

Urban District	1. Shi San Ling	Suburb District	2. Xiao Zhuang
Country Town	3. Dong Dan	Surveying Site	4. Lang Fang

The results provided SO₂, SO₄²⁻, NO₂, NO₃⁻, HNO₃ concentration data appropriate for the estimation of the SO₂ and NO₃⁻ conversion rates in the urban atmosphere.

Table 4 presents the model parameters used in our calculations.

Table 4 Model parameters

Parameters	Reference
SO ₂ dry deposition velocity (<i>v_g</i>) = 1 × 10 ms ⁻¹	Garland, 1978
SO ₄ ²⁻ dry deposition velocity (<i>v_p</i>) = 0.1 × 10 ms ⁻¹	Garland, 1978
Average mixed layer height (<i>H</i>) = 500 m *	
Source strength for SO ₂ (<i>S_r</i>) = 4.76 μg m ⁻³ h ⁻¹ **	
Source strength for NO _x (<i>N_r</i>) = 2.72 μg m ⁻³ h ⁻¹ **	
Emission ratio at source	
$S_r/S_p = N_r/N_p$ *** = 0.98/0.02	Venkatram, 1982
	Chang, 1979

* offered by The Meteorological Bureau of Beijing.

** offered by The Environmental Protection Bureau of Beijing.

*** *N_r* and *N_p* are source strengths of NO_x and NO₃⁻.

RESULTS AND DISCUSSION

The conversion rates of SO₂ and NO₂ as a function of time of the day are shown in Figure 2, 3. Note that the maximum rates occur near the noontime when the solar irradiation is maximum, and the minimum rates occur in the morning when the atmosphere is rich in NO_x and the solar intensity is weak. We can also see that the conversion rates of SO₂ and NO₂ have relatively lower values in 24-h period at the heavily polluted district, the case at site Xiaozhuang is similar to Langfang. But at Shisanling, the case has some different. First, the values of conversion rates are obviously higher; the second, in 6–10h period the conversion rates have not tendency to drop in. The reasons may be that there is not any large pollutant emission source at Shisanling, and ambient air is very clean, the effects of diffusion and dilution are strong. At other sites, amounts of emissions and the weaker solar intensity give rise to the conversion rates slow down in 6–10h period.

Table 5, 6, 7 show the results calculated by the model. The variation range of the conversion rate for SO₂ is 0.2–11.4 % h⁻¹ and for NO₂ is 0.7–34.7 % h⁻¹. The values for NO₂ are

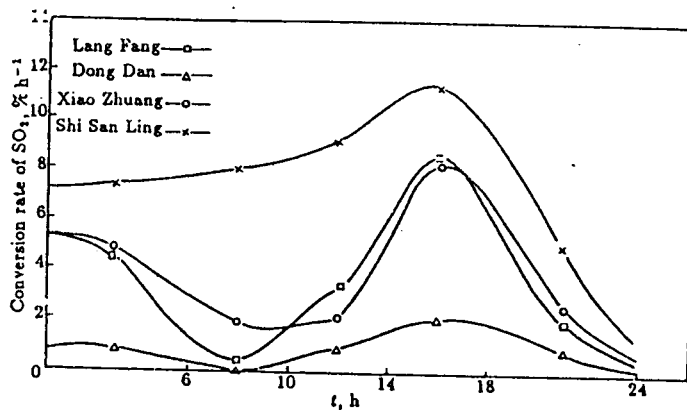


Fig. 2 The diurnal variation curve of the conversion rate of SO_2 to SO_4^{2-}

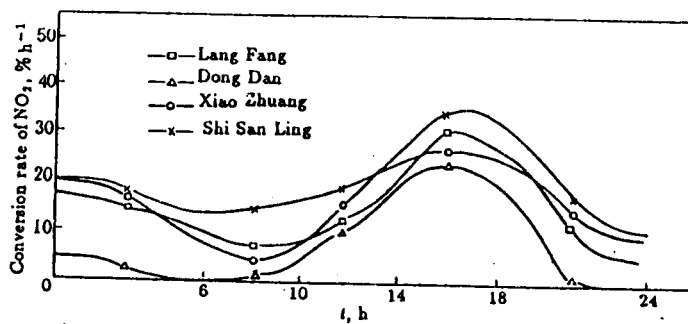


Fig. 3 The diurnal variation curve of the conversion rate of NO_2 to $\text{HNO}_3 + \text{NO}_3^-$

about four times as many as those of SO_2 . The main reason causing these differences is that the gas-phase oxidation rates of NO_2 are much greater than those of SO_2 in the troposphere (Calvert, 1983).

Table 5 The conversion rates of SO_2 to SO_4^{2-} ($\% \text{ h}^{-1}$)

Site	Langfang	Dongdan	Xiaozhuang	Shisanling
Hour periods				
0-6	4.5	0.7	4.6	7.3
6-10	0.3	0.2	2.0	8.1
10-14	3.5	0.9	2.2	9.2
14-18	8.6	2.0	8.4	11.4
18-24	2.0	0.8	2.7	4.9

Table 6 The conversion rates of NO_2 to $\text{HNO}_3 + \text{NO}_3^-$ ($\% \text{ h}^{-1}$)

Site	Langfang	Dongdan	Xiaozhuang	Shisanling
Hour periods				
0-6	10.9	2.8	16.0	16.3
6-10	8.0	0.7	4.4	15.0
10-14	12.7	11.2	16.9	19.6
14-18	31.6	24.0	27.2	34.7
18-24	14.4	1.2	15.1	19.1

The oxidation of SO_2 in gas-phase occurs primarily via its reaction with hydroxyl (OH) radicals (Atkinson, 1984). Major aqueous sulfate formation mechanisms include the reactions of dissolved SO_2 with H_2O_2 , O_3 and O_2 (catalyzed by Mn^{2+} and Fe^{3+}) (Jacob, 1983; Seigneur, 1984). These photochemical oxidants and active radicals play an important role in the acceleration of generation of HNO_3 . In suburb, where the air is relatively clean air, the concentration of these active oxidizing species are higher, and their disappearing from the troposphere is slower, but in urban, there are much more competitive reactions with these active oxidizing species because of the existence of various impurities. So the conversion rates of SO_2 and NO_2 in suburb are greater than those in urban (Table 7). All values during the daytime are greater

than the nighttime because of the effects of solar irradiation.

Table 7 The average conversion rates of SO₂, NO₂ (% h⁻¹)

	SO ₂		NO ₂	
	Suburb	Urban	Suburb	Urban
Day	6.0	1.0	18.9	11.9
Night	4.3	0.7	15.3	2.0

On the average, the conversion rates of SO₂ to SO₄²⁻ are 4.7% h⁻¹ in the daytime, and 3.4% h⁻¹ in the nighttime. The conversion rates of NO₂ to HNO₃+NO₃⁻ are 17.2 %h⁻¹ and 12%h⁻¹, respectively.

REFERENCES

- Atkinson, R. and Lloyd, A. C., *J. Phys. Chem. Ref.*, 1984, Data 13: 315
- Calvert, J. G., Su F., Bottenheim, J. W. and Strausz, O. P., *Atmos. Envir.*, 1978, 12:197
- Chang, T. Y., *Atmos. Envir.*, 1979, 13:1663
- Calvert, J. G., Stockwell, W. R., *Envir. Sci. Technol.*, 1983, 17(9): 428A
- Endlich, R. M., Nitz, K. C., Brodzinsky, R. and Bhumralkar, C. M., *Atoms. Envir.*, 1984, 18:2345
- Forrest, J., Schwartz, S. E. and Newman, L. *Atoms. Envir.*, 1979, 13:157
- Jacob, D. J. and Hoffmann, M. R., *J. geophys. Res.*, 1983, 88: 6611
- Mcnaughton, D. J. and Scott, B. C., *J. Air Pollut. Control Ass.* 1980, 30:272
- Spicer, C. W., *Science*, 1982, 215:1095
- Spicer, C. W., *Envir. Sci. Technol.*, 1983, 17:112
- Seigneur, C. and Saxena, P., *Atmos. Envir.*, 1984, 18:2109
- Venkatram, A., Ley, B. E. and Wong, S. Y., *Atoms. Envir.*, 1982, 16(2):249
- Wilson, W. E. and Gillani, N. V., *Exchange Processes, Sofia, Eulgaria*, 1979, 157