Dr H Nieboer

IMG-TNO
INSTITUUT VOOR MILIEUHYGIENE
EN GEZONDHEIDSTECHNIEK TNO
Publikatie no. 747
Postbus 214 2600 AE DELFT

CONVERSION RATE OF NITROGEN OXIDES IN A POLLUTED ATMOSPHERE

R. Guicherit, K.D. van den Hout, C. Huygen
TNO Research Institute for Environmental Hygiene,
Delft, The Netherlands

H. van Duuren, F.G. Römer, J.W. Viljeer
N.V. KEMA, Environmental Research Department,
Arnhem, The Netherlands

Appears in the Proceedings of the 11th NATO-CCMS International Technical Meeting on Air Pollution Modelling and its Applications, Amsterdam, 24-27 November 1980

CONVERSION RATE OF NITROGEN OXIDES IN A POLLUTED ATMOSPHERE

R. Guicherit, K.D. van den Hout, C. Huygen

TNO Research Institute for Environmental Hygiene,
Delft, The Netherlands

H. van Duuren, F.G. Römer, J.W. Viljeer

N.V. KEMA, Environmental Research Department,
Arnhem, The Netherlands

INTRODUCTION

The major part of emitted NO_x is NO. The first step in the removal of NO_x from the atmosphere is the oxidation of NO into NO_2. Then, NO_2 in a range of reactions is converted into oxidation products such as nitrates, nitric acid and PAN. Besides, because of photolysis in the daytime, NO_2 will contribute to the formation of ozone.

Knowledge of the NO_x removal rate from the atmosphere is of importance for a number of reasons:
- for long range transport problems of NO_x in general and for estimation of the impact of urban NO_x on downwind areas in particular;
- for an understanding of tropospheric chemistry;
- for modelling exercises. Especially in models of the Gaussian plume type, conversion and annihilation of pollutants are treated by the introduction of some exponential loss term which is directly related to the removal rate of the pollutant under discussion.

NO_x may be emitted at ground level or by elevated sources (plume NO_x). Because the removal rate of NO_x emitted by elevated sources needs not per se be the same as that of NO_x emitted at ground level, the two cases will be treated separately.

The residence time (τ) for NO_x in an air mass near the ground in a well-mixed layer under average meteorological conditions is given by:

$$\tau^{-1} = \tau_d^{-1} + \tau_w^{-1} + \tau_c^{-1} \tag{1}$$

τ_d is the residence time by dry deposition removal
τ_w is the residence time by wet deposition removal
τ_c is the residence time by chemical conversion

The residence time of NO_x by dry deposition is given by:

$$\tau_d = H.\nu_d^{-1} \tag{2}$$

τ_d is the residence time (s)
H is the mixing depth (m)
ν_d is the deposition velocity ($m.s^{-1}$)

The loss rate of NO_x by dry deposition on an hourly basis amounts to:

$$\Delta NO_x = 1 - \exp(-3600.\tau_d^{-1}) \tag{3}$$

or:

$$\Delta NO_x = 1 - \exp(-3600.H^{-1}.\nu_d) \tag{4}$$

If H is assumed to be 1000 m and the dry deposition velocity ν_d for NO_x is assumed to be ½ of the dry deposition velocity for SO_2 i.e. 0.2 $cm.s^{-1}$, ΔNO_x is << 0.01 h^{-1} (TNO, 1980).

Loss of NO_x by wet deposition is given by:

$$c_t = c_o \exp(-\lambda t) \tag{5}$$

c_t is the pollutant concentration at time t
c_o is the original pollutant concentration
λ is the "wash out" coefficient (s^{-1}), estimated to be $\leq 10^{-5}$ s^{-1} (TNO, 1980)

Since $\tau_w = \lambda^{-1}$, this amounts to a residence time of NO_x by wet deposition of about 28 h. This calculation holds for a precipitation intensity of about 1 $mm.h^{-1}$. From this figure a yearly average removal rate of 0.001-0.002 h^{-1} and a residence time of 3 to 6 weeks may be calculated for precipitation duration and intensity valid for Western Europe.

The chemical conversion of NO_x is dependent on many factors. Smog chamber studies, modelling experiments and field monitoring reveal that the NO_x removal rate depends to a considerable extent on the degree of photochemical activity. From what has been discussed before, it seems that in many circumstances loss of NO_x by wet and dry deposition is small compared with chemical conversion. In the following paragraphs an estimate of the oxidation of NO and the removal rate of NO_x, mainly by chemical conversion reactions, will be given.

NO OXIDATION IN PLUMES

Unlike the oxidation of NO in the free atmosphere, the oxidation with oxygen also plays a role in the oxidation of NO in plumes. The major dark reactions in plumes are (Elshout et al., 1978; Van Duuren et al., 1979):

$$2NO + O_2 \xrightarrow{k_1} 2NO_2 \tag{6}$$

$$NO + O_3 \xrightarrow{k_2} NO_2 + O_2 \tag{7}$$

$$NO + RO_2^{\bullet} \xrightarrow{k_3} NO_2 + RO^{\bullet} \tag{8}$$

Because of absorption of UV irradiation the following reactions occur during daylight hours:

$$NO_2 + h\nu \xrightarrow{k_4} NO + O \quad (\lambda < 400 \text{ nm}) \tag{9}$$

$$O + O_2 + M \longrightarrow O_3 + M \tag{10}$$

$$O_3 + h\nu \longrightarrow O_2 + O_1^D \quad (\lambda < 320 \text{ nm}) \tag{11}$$

$$H_2O + O_1^D \longrightarrow 2OH^{\bullet} \tag{12}$$

In the daytime the so-called photo-stationary state can be reached in very well-mixed parts of the atmosphere:

$$[O_3]\,[NO] = \frac{k_4}{k_2}\,[NO_2] \tag{13}$$

In an atmosphere heavily polluted with hydrocarbons radicals will be generated. For this reason with reaction (7) competitive reactions will proceed. This results in a higher NO_2 level and consequently in the formation of ozone. This situation is especially of importance for plumes from industrial areas, such as the Rijnmond area, near Rotterdam (Van Duuren et al., 1979).

Model studies (Elshout and Steenkist, 1974; Varey et al., 1978; Cocks and Fletcher, 1979) have shown that the oxidation of NO with oxygen in plumes occurs close to the stack (transport times up to 200 s). For power station plumes with initial NO concentrations between 100 and 500 ppm, the degree of oxidation in the daytime is mostly less than 0.1 (Elshout and Steenkist, 1974; Varey et al., 1978).

NO oxidation with ozone is determined by the mixing velocity of the plume with ambient air, as was proved by Hegg et al. (1977). It was also confirmed experimentally that reaction (7) is diffusion controlled and that the NO_2/NO ratio is highest on the edges of the plume.

Varey et al. (1978) developed a numerical model for the calculation of NO oxidation in power station plumes. This model, based on reactions (6), (7), (9) and (10), also proved that the oxidation rate integrated over the plume cross-section is determined by the degree of mixing of the plume with ambient air, expressed in the eddy diffusivity D (Fig. 1.). Under stable atmospheric conditions (Pasquill stability class F, with $D \approx 0.1\ m^2.s^{-1}$ the oxidation of NO is mainly determined by the reaction with oxygen. Under good mixing conditions with D values of $> 10\ m^2.s^{-1}$, the reaction with ozone prevails. The model results of Varey et al. (1978) have been confirmed by measurements in plumes of the Maasvlakte power station (NO/NO_x emission ratio $\approx$ 0.98)(Elshout et al., 1978). In the period 1975-1980 measure-

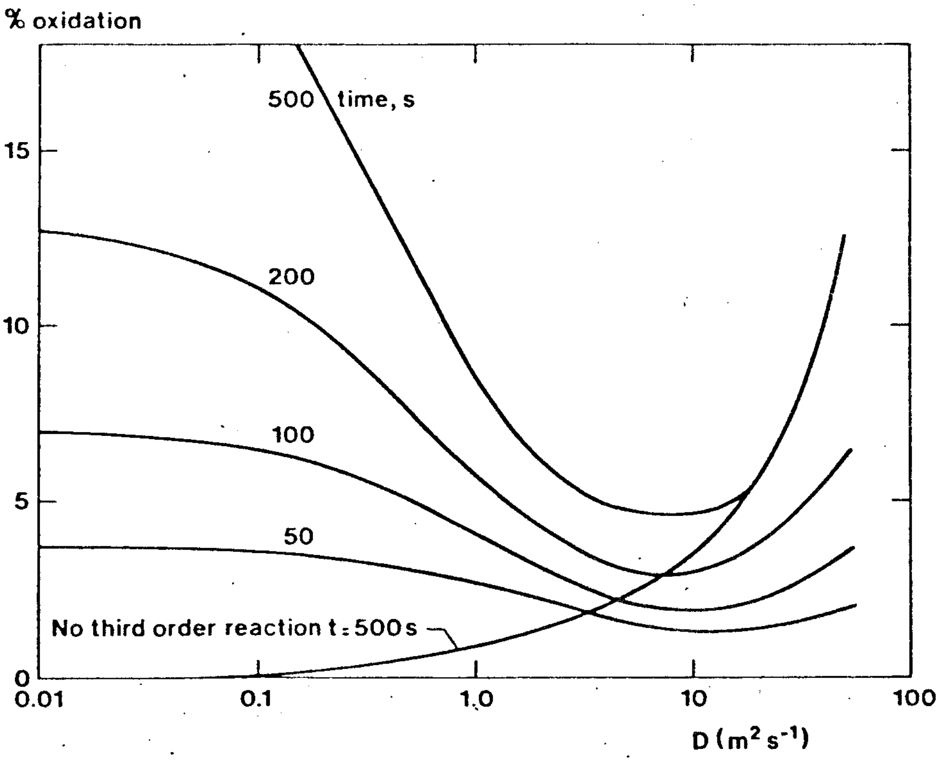


Fig. 1. Percentage oxidation, integrated over the plume cross-section as a function of D for various times. $[NO]_o$ = 450 ppm; $[O_3]_o$ = 0.03 ppm. Results of model calculations (Varey et al., 1978).

ments were carried out on 27 days at distances between 0.2 and 9 km from this power station (two 540 MW units). During these measurements with background concentrations of O_3 from 20 to 65 ppb, oxidation was found to be 50-60% (averaged over the plume cross-section). Fig. 2. shows the NO oxidation at the Maasvlakte power station as a function of the O_3 concentration. For Pasquill classes B and C (eddy diffusivity $D > 5\ m^2.s^{-1}$) oxidation increases with increasing O_3 concentration. However, under neutral conditions (eddy diffusivity $D \approx 1\ m^2.s^{-1}$) oxidation is independent of the O_3 concentration. In this case mixing of ozone into the plume is limited, so for the transport time of interest the oxidation rate is mainly controlled by the reaction with oxygen (Fig. 1.).

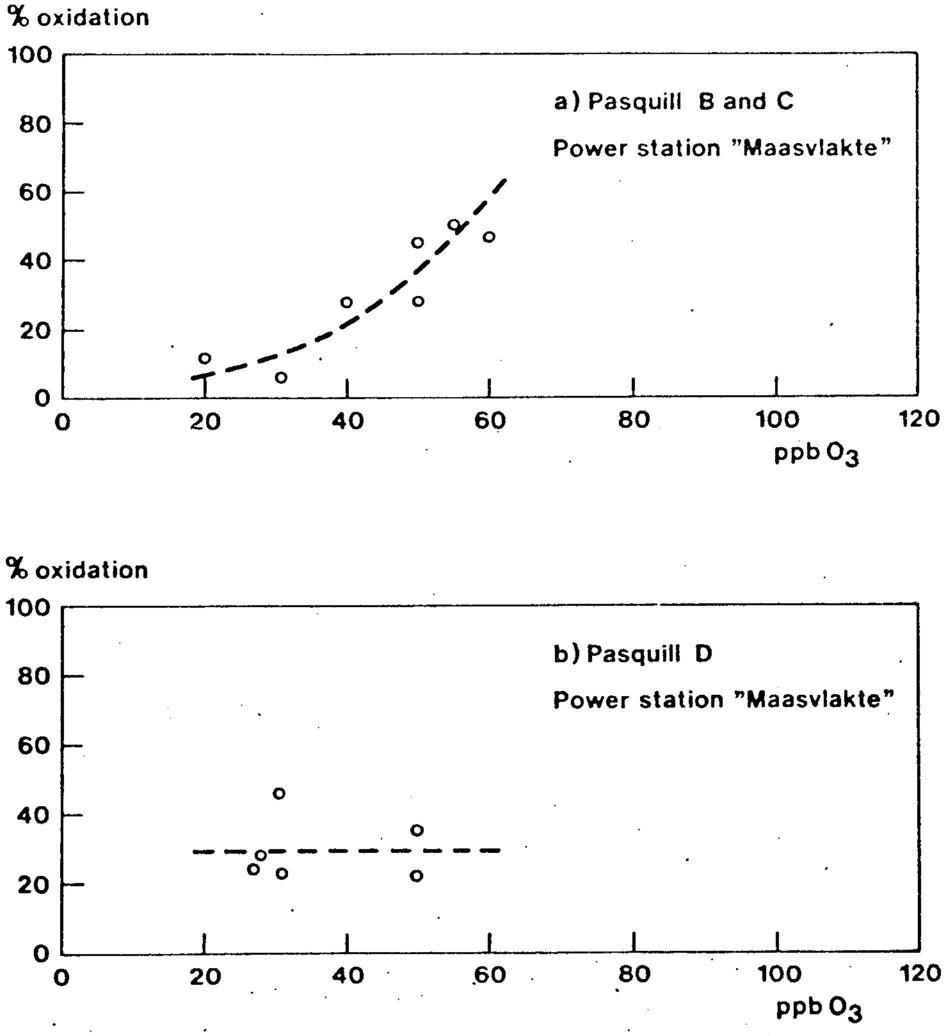


Fig. 2. Oxidation of nitric oxide in power station plumes. Percentage oxidation, integrated over the plume cross-section, as a function of the ambient ozone concentration for various Pasquill stability classes. Travelling time 500 s.

Measurements by Melo et al. (1978), carried out under more stable conditions than those in Fig. 1., show that even at high O_3 concentrations up to 110 ppb the oxidation is independent of the O_3 concentration (approximately 0.1 for a travelling time of 500 s). This implies that under these conditions the reaction with oxygen is the main contribution to the formation of NO_2.

Cocks and Fletcher (1979) developed a reactive plume model to study the gas phase reactions in power station plumes. This model enables the oxidation of NO to be calculated. The model has been applied for five well-defined measurements of those carried out at the Maasvlakte power station: distance 2-9 km, travelling time 150-900 s, O_3 concentration 20-55 ppb, unstable to neutral atmosphere. The results of the calculated values of the NO/NO_x ratio (average value for the plume cross-section) agree with the values found. The calculated values vary between 0.41 and 0.86 and those measured between 0.60 and 0.81. The mean value of the difference between measured and calculated ratio was found to be 0.09; the largest difference amounts to 0.20 (absolute value).

NO_x REMOVAL RATE IN A POLLUTED ATMOSPHERE

The concentration of a reactive pollutant in an urban atmosphere changes with time as a result of chemical conversion reactions, changes in emissions, and by dispersion and/or dilution. On the other hand the concentration of an "inert" pollutant in an urban atmosphere will only change with time as a result of changes in emissions, and by dispersion and/or dilution. If a reactive species and an "inert" species have a common source it can be shown (Chang et al., 1979) that

$$k_r = - \frac{\Delta(\ln R.I^{-1})}{\Delta t} \qquad (14)$$

k_r is the lower bound of the pseudo first-order reaction rate coefficient for the reactive species

R and I are the concentrations of the reactive and "inert" species respectively.

From equation (14) it follows that from the daily trend of the NO_x/CO ratio (CO is treated here as an inert species), obtained by long-term average aerometric data measured at a fixed ground station, the removal rate of NO_x can be estimated; on condition, however, that NO_x and CO have a common source.

The main source of CO in The Netherlands is automobile exhaust gas. Automobile exhaust gas is also a major NO_x source. Guicherit and Hoogeveen (1978) have shown that the amount of NO_x in air parcels, reaching a sampling site, which is attributable to mobile (automotive) sources can be estimated by comparing the NO_x to acetylene ratio typical of mobile source emissions for various driving conditions. Acetylene is regarded as a traffic tracer. The ratio of NO_x/C_2H_2

Table 1. NO_x removal rate, k_r (h^{-1}), from sunrise to sunset (lower bound)

winter (1975)	0.01
summer (1975)	0.05
photochemical episodes (1975) O_3 (max.) > 200 $\mu g.m^{-3}$	0.14
September (1973) average maximum O_3 concentration 150 $\mu g.m^{-3}$	0.12

Table 2. Summary of the most important removal reactions of NO_2 in ambient air

$NO_2 + OH \rightarrow HNO_3$	$k_5 = 1.1 \times 10^{-11}\ cm^3.mol^{-1}.s^{-1}$ Hamson and Garvin (1978)
$NO_2 + O_3 \xrightarrow[\text{steps}]{\text{intermediate}} HNO_3$	k_6 net.
$NO_2 + RCO_3 \xrightarrow[\text{steps}]{\text{intermediate}} PAN$	k_7 net

depending on driving conditions varied from 3 to 8 in 1975. For higher ratios it is concluded that other major emission sources are involved. In the analysis of the daily trend of the NO_x/CO ratio, only those wind directions were considered for which the major emission source was established to be automobile traffic.

The daily trend of the NO_x/CO ratio measured at a ground station near Delft (1973 and 1975 data) is given in Figs. 3. and 4. From the graphs the removal rate of NO_x has been calculated. The results are shown in Table 1.

The most important reactions of NO_2 in ambient air are given in Table 2.

From the September removal rate of NO_x based on reaction with OH radicals only, an OH radical concentration of 3×10^6 molec.cm^{-3} can be deduced. From measurements in this part of The Netherlands it follows, however, that the PAN/HNO_3 ratio is about 1. Further, it is assumed that 75% of the HNO_3 formation is due to reaction of NO_2 with OH and 25% by reaction of NO_2 via O_3. So a more realistic OH

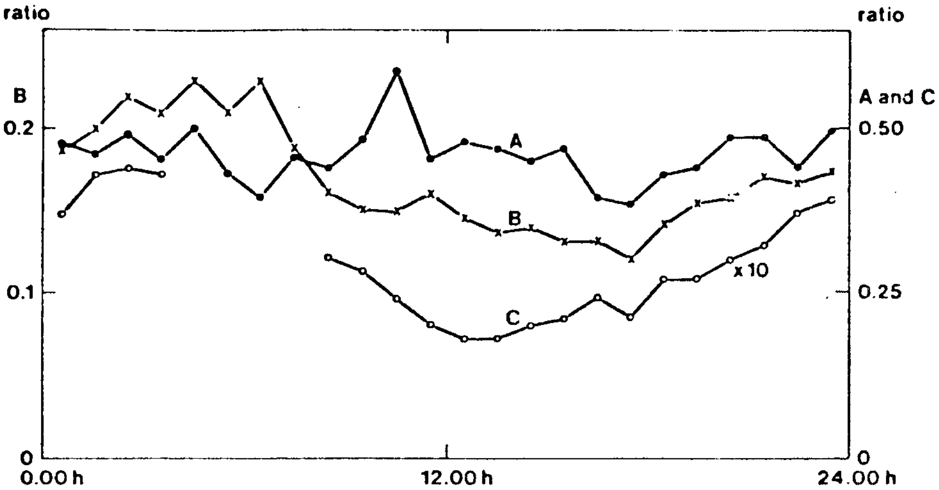


Fig. 3. Daily trend of pollutant ratios (September 1973 data)
A: i-pentane/acetylene ratio
B: propylene/acetylene ratio
C: NO_x/CO ratio

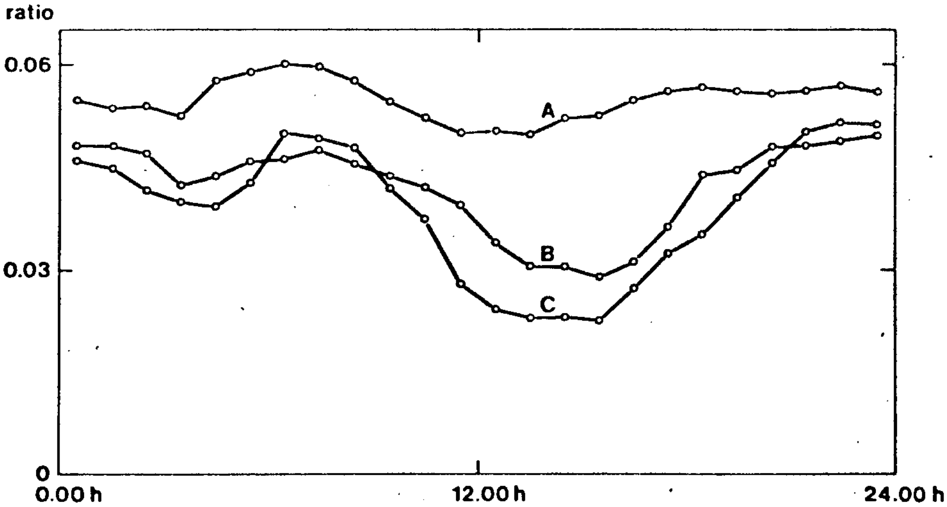


Fig. 4. Daily trend of the NO_x/CO ratio (1975 data)
A: winter data January, February, March, October, November, December
B: summer data April through September
C: days with photochemical smog formation (O_3 concentrations > 200 μg.m^{-3})

Table 3. Calculated average OH radical concentration (from sunrise to sunset)

period	NO_x removal rate from Table 1. (h^{-1})	OH concentration ($molec.cm^{-3}$)	literature quotations
winter average (1975)	0.01	$< 2.5 \times 10^5$	$\approx 1 \times 10^5$ Fishman and Crutzen (1978)
summer average (1975) O_3 (max.) = 90 $\mu g.m^{-3}$	0.05	5×10^5	$\leqq 1 \times 10^6$ Ehhalt et al. (1980) $(3.5\text{-}5) \times 10^5$ Fishman and Crutzen (1978)
September (1973) O_3 (max.) = 150 $\mu g.m^{-3}$	0.12	$(5\text{-}10) \times 10^5$	5×10^5 Fishman and Crutzen (1978)
smog formation (1975) $O_3 > 200\ \mu g.m^{-3}$	0.14	1.5×10^6	2×10^6 Derwent and Hov (1979) 1.2×10^6 Guicherit et al. (1978)

radical concentration of about 10^6 $molec.cm^{-3}$ is obtained. Table 3. summarizes the OH radical concentrations following this procedure. These OH radical concentrations are in accordance with those determined from the removal rate of i-pentane (0.01 h^{-1}) and propylene (0.07 h^{-1}). This removal rate is derived from the daily rate of the i-pentane/acetylene and propylene/acetylene ratio for September 1973 (Fig. 3.). From the equations

$$k_{r_{iC_5H_{12}}} = k_a . [OH] \qquad (15)$$

and

$$k_{r_{C_3H_6}} = k_b . [OH] + k_c . [O_3] \qquad (16)$$

the OH radical concentrations of 9×10^5 $molec.cm^{-3}$ and 5×10^5 $molec.cm^{-3}$ can be calculated for September using $k_{(a,b,c)}$ values from Greiner (1970), Atkinson and Pitts (1975) and Hamson and Garvin (1975).

THE NO_x REMOVAL RATE IN PLUMES

The removal of NO_x from the atmosphere is to a considerable extent effected by the oxidation of NO_2 to secundary products such as nitric acid (nitrates) and PAN. Hydrocarbons as a source of reactive radicals and ozone both natural and as a product of photochemical air pollution play a role in this oxidation process.

As to the NO_2 conversion in power station plumes, it was explained before that the oxidation process in plumes highly depends on mixing with ambient air. Because of the relatively low ozone and hydrocarbon concentrations compared with those of NO_x in the plume, no oxidation products will be formed. If, however, under suitable meteorological conditions such a plume mixes with an urban-industrial plume, this will be possible. According to Cocks and Fletcher (1979) very little nitric acid was produced from NO_x in the plume after a 100 min travelling time. High concentrations of hydrocarbons, however, attribute considerably to the formation of N-containing acids (Cocks and Fletcher, 1979).

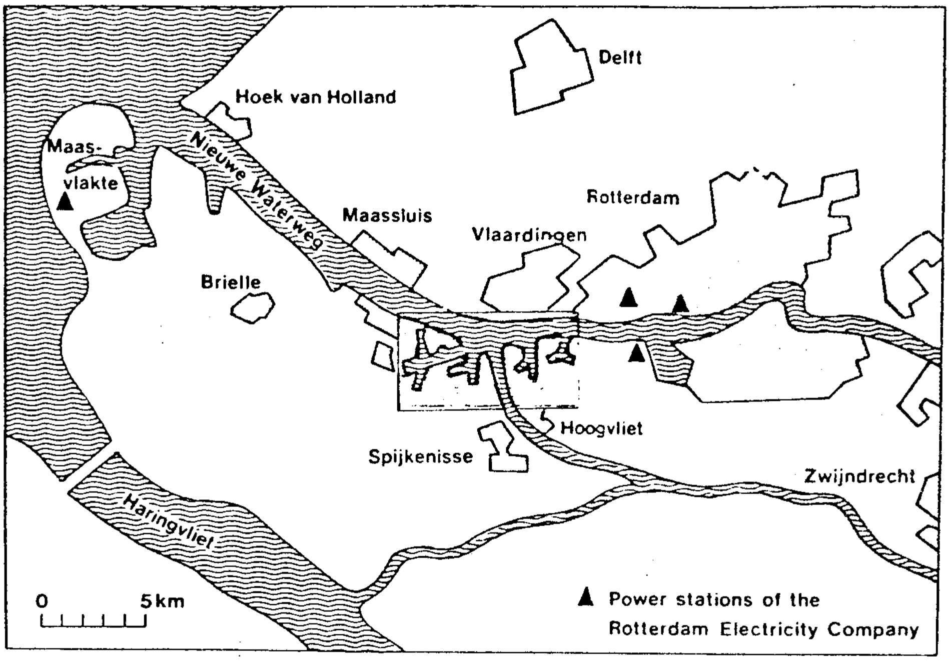
According to (provisional) measuring results by Hegg and Hobbs (1979) NO_x conversion to nitrate in the plumes of three coal-fired power stations is limited. The conversion of NO_2 to nitrate was calculated and for one of the measurements values between 0.003 h^{-1} and 0.005 h^{-1} were found for distances of 5 and 27 to 43 km respectively. Forrest et al. (1979) carried out measurements in the plume of an oil-fired power station in which they also found low values which hardly differed from the background values. During two measurements some formation of nitrate from NO_x was detected at distances of 5 and 16 km. As was the case for the measurements by Hegg and Hobbs (1979), nitric acid was not determined so that for this reason the calculated conversion rate may have been too low. In refinery plumes at Los Angeles Parungo et al. (1980) measured relatively large nitrate particulates that had not been emitted as primary components. It was assumed that heterogeneously produced nitric acid ($3NO_2 + H_2O \rightarrow 2HNO_3 + NO$) reacted with NaCl to form nitrate particulates. These nitrate particulates melt at a relative humidity as low as 60% and can grow to large particulates (1-10 μm) before equilibrium is reached. According to the authors inorganic nitrate can be produced on cloudy days and at night. One of their conclusions is that under these conditions the reaction $M + OH + NO_2 \rightarrow HNO_3 + M$ is not the most important one for the formation of nitrate, for on sunny days with expected high OH radical concentrations no increase in the amount of inorganic nitrate is found.

For the determination of the NO_x removal rate in urban areas Spicer (1980) has carried our measurements in isolated plumes of Phoenix (Arizona) and Boston (Massachusetts). The flights were arranged in such a way that the measuring data refer to the same air parcel. During these measurements, besides NO_x, oxidation products, tra- tracer concentrations, and also various other parameters were determined. The measurements at Phoenix showed a NO_x removal rate of $< 0.05\ h^{-1}$. This result has to be considered as provisional. From the experiments at Boston the expected NO_x concentration was calculated from the initial urban tracer/NO_x ratio and the downwind tracer concentration. Based on these experiments, the rate of the NO_x removal from the Boston air varied from 0.14 to 0.24 h^{-1}, with an average rate and life time of 0.18 h^{-1} and 5.8 h respectively. The reported values are applicable only to daylight hours under photochemical conditions (maximum O_3 concentrations in the plume 90 to 140 ppb).

The NO_x conversion rate with regard to that of SO_2 was calculated from the measuring results of the plume of the Rijnmond industrial area (Van Duuren et al., 1979). The measurements were carried out by day and focussed on that part of the industrial area occupied with the major oil refineries and chemical industries (Fig. 5.). Each flight consisted of three tracks flown at four different altitudes (150, 300, 450 and 600 m). Track 1 was located at 2-14 km upwind the industrial area. Track 2 was located immediately behind the area, and track 3 was at 15-20 km downwind. Track lengths were 12-18 km. The flight scheme was: measurements at 150 m on tracks 1, 2 and 3 respectively, then at 300 m in the same sequence and so on for the other altitudes. This implies that the measurements were done in three different air parcels. It is assumed, however, that the air pollution pattern is uniform within the approximate 2 h duration of the measurements.

The flights were carried out on days when the area between tracks 2 and 3 was a rural area. It was assumed that no major NO_x and SO_2 was emitted anymore in this area. As to SO_2 the measuring results confirmed this assumption. Because the SO_2 removal rate is relatively low with regard to that of NO_x this component can be used as a tracer for the determination of the NO_x removal rate. From differences in average NO_x and SO_2 concentrations between tracks 2 and 3 (averaged for the altitude of 150-600 m) for three measuring days 18-23% of NO_x available on track 2 was calculated to have disappeared between the two tracks.

The transport times were calculated from wind velocity averaged for the altitude interval, and wind velocity was estimated from the surface wind velocity. The NO_x conversion rate calculated in that way amounts to 0.25-0.40 h^{-1}. Considering any errors in wind velocity estimated and in relatively low NO_x and SO_2 concentrations, the NO_x conversion rate will have been at least 0.15 h^{-1}. The O_3 concentration at the time of measurements was 25-30 ppb. Under photochemical conditions (temperature 24°C, O_3 concentration 80-100 ppb), a conversion rate of 0.19 h^{-1} was measured. During that flight, tracks 2 and 3 were located at distances of 10 and 40 km from the industrial area. The altitude was between 250 and 900 m. The average wind velocity in the mixing layer, mixing height 1000 m, was determined with a weather balloon.



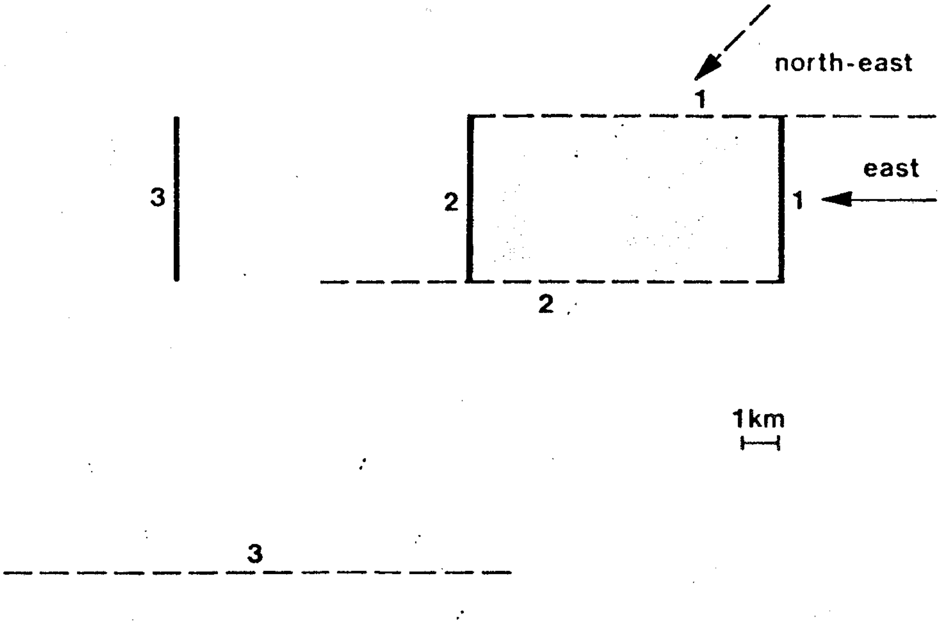


Fig. 5. The Rijnmond measuring area; locations of flight track patterns at winds from east and north-east.

NO OXIDATION IN A POLLUTED ATMOSPHERE

Fig. 6. shows the daylight hourly curves for the $NO_2/(NO+NO_2)$ ratio for an urban area for the winter months (January, February, November and December 1975) and for the summer months (May through August 1975). In winter, the NO_2 concentration proves to be approximately 50% of the NO_x concentration with only slight variations during the day. In summer, on the other hand, the NO_2 concentration early in the morning at the beginning of the rush-hour makes up 30% of the NO_x concentration, increasing up to nearly 80% within a few hours. Then there is a gradual increase up to 85% till 15.00h, decreasing to approximately 50% after sunset.

According to Chang et al. (1979), the conversion rate is:

$$k_{r(NO \rightarrow NO_2)} = \frac{1}{1 - NO_2/(NO + NO_2)} \left[\frac{\Delta NO_2/(NO + NO_2)}{\Delta t} \right] \tag{17}$$

This is based on the assumption that NO_2 is converted so much more slowly, that the NO_2/NO_x ratio is hardly affected by it. So in fact, $k_{r(NO \rightarrow NO_2)}$ is larger. From Fig. 6. conversion rates of > 0.35 h^{-1} are calculated.

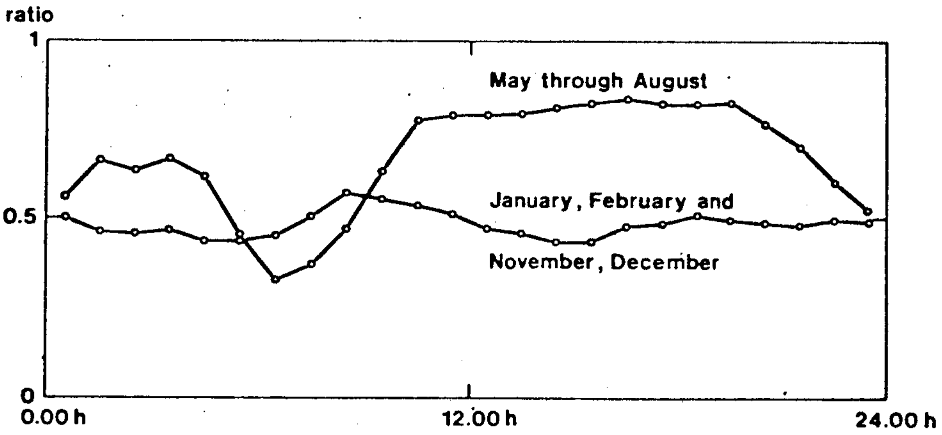


Fig. 6. Daily trend of the $NO_2/(NO+NO_2)$ ratio at Delft in 1975.

DISCUSSION

The oxidation of the primary emittent NO into NO_2 is the essential first step in the removal of NO_x from the atmosphere. It has been proved that the atmospheric conditions (time of the day, season, turbulence) strongly determine the oxidation rate of NO both in individual plumes and at ground level. The measured data are summarized in Table 4.

Though NO_x removal is mainly governed by chemistry, it is for reasons of not fully understood measuring techniques that we are faced with difficulties and sometimes the impossibility to determine the NO_x removal rate from the measured data of secondary products as well as gaseous components. For instance, when studying the results of chemiluminescent measurements of NO_2, concentrations too high a value (and consequently too low a removal rate) shall have to be reckoned with, depending on the converter type used.

An accurate determination of the travelling time of air parcels in plume measurements is essential for the calculation of the removal rate and the residence time. Besides, in case of k_r determination in plumes, corrections have to be made for SO_2 losses due to dry deposition.

Table 4. Conversion of NO into NO_2 under different atmospheric conditions

measurement	degree of oxidation (%) (NO_2/NO_x)	conditions
power plant plume*	5	stability class B, C; travelling time 500 s; O_3 concentration 20 ppb; 7 flights
	60	idem; O_3 concentration 60 ppb
	30	stability class D; travelling time 500 s; O_3 concentration 25-50 ppb; 6 flights
urban atmosphere**	45-55	winter, maximum increase between 6.30h-8.30h MET
	30-80	summer, maximum increase between 6.30h-10.30h MET

* - averaged over the plume cross-section
- initial NO_2/NO_x ratio about 2%

** maximum differences for averaged values

Because of limitations in the measuring equipment, the results have to be regarded as not conclusive. Nevertheless, the results generally agree fairly well with values mentioned in the literature for $k_r < 0.15\ h^{-1}$ on ground level (polluted atmosphere) and $k_r > 0.15\ h^{-1}$ in plumes. The results have been listed in Table 5.

Table 5. Survey of data for the NO_x removal rate in urban atmospheres and urban plumes

method	removal rate (h^{-1})	remarks	reference
		urban atmosphere	
NO_x/CO	0.01	Delft 1975, lowest value, winter daytime	this article
	0.05	Delft 1975, summer average	this article
	0.14	Delft 1975, highest value, photochemical episodes, $O_3 > 200\ \mu g.m^{-3}$	this article
	0.04	Los Angeles 1970-1975, lower bound, all seasons 8.00h-16.00h value	Chang et al.(1979)
	0.11	Los Angeles 1970-1975, average 9.00h-13.00h value for May-October	Chang et al.(1979)
$\frac{PAN+HNO_3}{NO_x+PAN+HNO_3}$	0.05	Los Angeles basin 1973, 5 weeks summer period, 10.00h-14.00h	Spicer *in*: Chang et al. (1979)
	0.04	St. Louis 1973, 5 weeks summer period 8.00h-13.00h	Spicer *in*: Chang et al. (1979)
		urban plume	
NO_x/C_2H_5 & NO_x/CH_4	0.09	LARPP study 5 November 1973, 8.00h-13.00h, O_3 100 ppb	Calvert *in*: Chang et al. (1979)
tracer/NO_x	0.18	Boston 1978, 4 experiments (0.14-0.24 h^{-1}), photochemical conditions, O_3 90-140 ppb (tracers CO, F-11, C_2H_2)	Spicer (1980)
SO_2/NO_x	≧0.15	Rijnmond (Rotterdam) April 1977-August 1978, 2 experiments, O_3 25-30 ppb	this article
	0.19	idem, August 1979, 1 experiment, O_3 80-100 ppb	this article

An important assumption adapted in this study, is the neglect of the mixing of relatively old pollutants into the air considered in equation (14). More specifically, for the aeroplane measurements the air outside individual stack plumes as well as urban-industrial plumes, containing pollutants of a generally different composition, is gradually mixed into the plume. In the case of the ground monitoring measurements, the aged smog layer, transported at night above the nocturnal inversion layer and mixed downward in the morning, may be of importance. When this air mass contains relatively clean air, or air with a concentration ratio of reactive and inert pollutants comparable with that of the air considered in equation (14), the influence on the results is rather small. At present, however, this effect has not yet been fully evaluated. One of the difficulties is that the nocturnal chemistry of aged smog is not well established, and consequently the early morning concentrations of NO_x aloft are unknown. Insight into this might probably be gained from aeroplane measurements performed in the early morning.

Another point that requires further evaluation, is the assumption, used in the derivation of equation (14), that the sources are horizontally homogeneously distributed. Although this is clearly not the case, it is not evident how strictly this condition should be met. The averaging over many days, that has been performed, implies averaging over many wind directions and wind speeds. This tends to smooth the distribution of times of travel, which determines the time available for reaction. To clarify this it might be interesting to use results obtained from monitoring stations at various distances from important source areas.

SUMMARY

The removal of NO_x from the atmosphere is to a great extent determined by chemistry. As, in general, these chemical pathways proceed through NO_2, also a description and determination of the oxidation of NO into NO_2 in plumes and urban (polluted) atmospheres is given.

For power station plumes the degree of oxidation (NO_2/NO_x) strongly depends on the stability of the atmosphere. Model calculations for a travelling time of 500 s are qualitatively in accordance with measured values. These are 30% for stability class D and O_3 concentrations of 25-50 ppb and between 5 and 60% for classes B and C and O_3 concentrations between 20 and 60 ppb respectively. For the removal rate ($k_{r(NO \rightarrow NO_2)}$) in an urban atmosphere a value of $> 0.35\ h^{-1}$ can be calculated.

For the determination of the NO_x removal rate in an urban atmosphere the procedure followed by Chang et al. was used. Thus for the daily trend of the NO_x/CO ratio lower bounds for k_r of $0.01\ h^{-1}$

during the winter daytime and of 0.14 h^{-1} during photochemical episodes (maximum O_3 concentration > 200 $\mu g.m^{-3}$) were found. From k_r derived OH radical concentrations are in agreement with concentrations derived from the removal rate of i-pentane and propylene in the same air parcels.

The NO_x removal rate has also been determined in an industrial plume (Rotterdam area). The calculations are based on the assumption that SO_2 is far more slowly removed than NO_x. The removal rate amounts to at least 0.15 h^{-1} taking into account the deviation in the estimated wind speed.

Under photochemical conditions (O_3 concentrations 80-100 ppb) for longer distances and a well-known transport time, a removal rate of 0.19 h^{-1} was determined.

In a survey of the measured results and values from literature for k_r the comparability of the two different cases appeared to be satisfactory. Nevertheless the data must be interpreted with care, because several assumptions had to be made.

REFERENCES

Atkinson, R. and Pitts Jr., J.N., 1975, Rate constants for the reaction of OH-radicals with propylene and butenes over the temperature range 297-425°K, J. Chem. Phys. 63:3591

Chang, T.Y., Norbeck, J.M. and Weinstock, B., 1979, An estimate of the NO_x removal rate in urban atmosphere, Environ. Science Technol. 13:1534

Cocks, A.F. and Fletcher, I.S., 1979, A model of the gas-phase chemical reactions of power station plume constituents, CERL laboratory report no. RD/L/R 1999

Derwent, R.G. and Hov, O., 1979, Computer modelling studies of photochemical air pollution formation in North-West Europe, AERE report R, 9434, HMSO, London

Duuren, H. van, Elshout, A.J., Römer, F.G., Viljeer, J.W. and Noks, E., 1979, Luchtverontreiniging boven de Rijnmond, Elektrotechniek 57:267

Ehhalt, D., Perner, D. and Platt, U., 1980, Trace gas measurements by optical absorption, Communication by Platt at the COST 61A bis Workshop on transport and modelling (The Hague)

Elshout, A.J., Duuren, H. van, Viljeer, J.W. and Noks, E., 1978, De oxidatie van stikstofmonoxide in rookpluimen, Elektrotechniek 56:429

Elshout, A.J. and Steenkist, R., 1974, A numerical approach to the effect of the oxidation of NO in the dispersion of these pollutants from a point source, N.V. KEMA technical note

Fishman, J. and Crutzen, P.J., 1978, The distribution of the hydroxyl-radical in the troposphere, Atmospheric Science paper no. 284, Colorado State University

Forrest, J., Garter, R. and Newman, L., 1979, Formation of sulfate ammonium and nitrate in oil-fired power plant plume, Atm. Environment 13:1287

Greiner, N.R., 1970, Hydroxyl radical kinetics by kinetic spectroscopy VI. Reactions with alkanes in the range 300-560°K, J. Chem. Phys. 53:1070

Guicherit, R., Blokzijl, P.J. and Plasse, C.J., 1978, Some notes on the abatement of photochemical ozone production, IMG-TNO report

Guicherit, R. and Hoogeveen, A., 1978, in:"Photochemical smog formation in The Netherlands", TNO-report, R. Guicherit, ed., Delft

Hamson, R.F. and Garvin, D., 1975, Chemical kinetic and photochemical data for modelling atmospheric chemistry, National Bureau of Standards Technical Note 866, USGPO, Washington D.C.

Hamson, R.F. and Garvin, D., 1978, Reaction rate and photochemical data for atmospheric chemistry, National Bureau of Standards, Special Publ. 513, USGPO, Washington D.C.

Hegg, D., Hobbs, P.V., Radke, L.F. and Harison, H., 1977, Reactions of ozone and nitrogen oxides in power plant plumes, Atm. Environment 11:521

Hegg, D.A. and Hobbs, P.V., 1979, Some observations of particulate nitrate concentrations in coal-fired power plant plumes, Atm. Environment 13:1715

Melo, O.T., Lusis, M.A. and Stevens, R.D.S., 1978, Mathematical modelling of dispersion and chemical reactions in a plume - oxidation of NO to NO_2 in the plume of a power plant, Atm. Environment 12:1231

Parungo, F.P., Pueschel, R.F. and Wellman, D.L., 1980, Chemical characteristics of refinery plumes in Los Angeles, Atm. Environment 14:509

Spicer, C.W., 1980, The rate of NO_x reaction in transported urban air, Proc. of the 14th International Colloquium Paris, Studies in Environmental Science Vol. 8:181

TNO report 1980, Rekensysteem Luchtverontreiniging VII. Deelonderwerp: Verwijderingsprocessen SO_2, NO_x, CO en sulfaat, L.A.M. Janssen, ed., CMP-TNO, Delft

Varey, R.H., Sutton, S. and Marsh, A.R.W., 1978, The oxidation of nitric oxide in power station plumes. A numerical model, CERL laboratory note no. RD/L/N184/78