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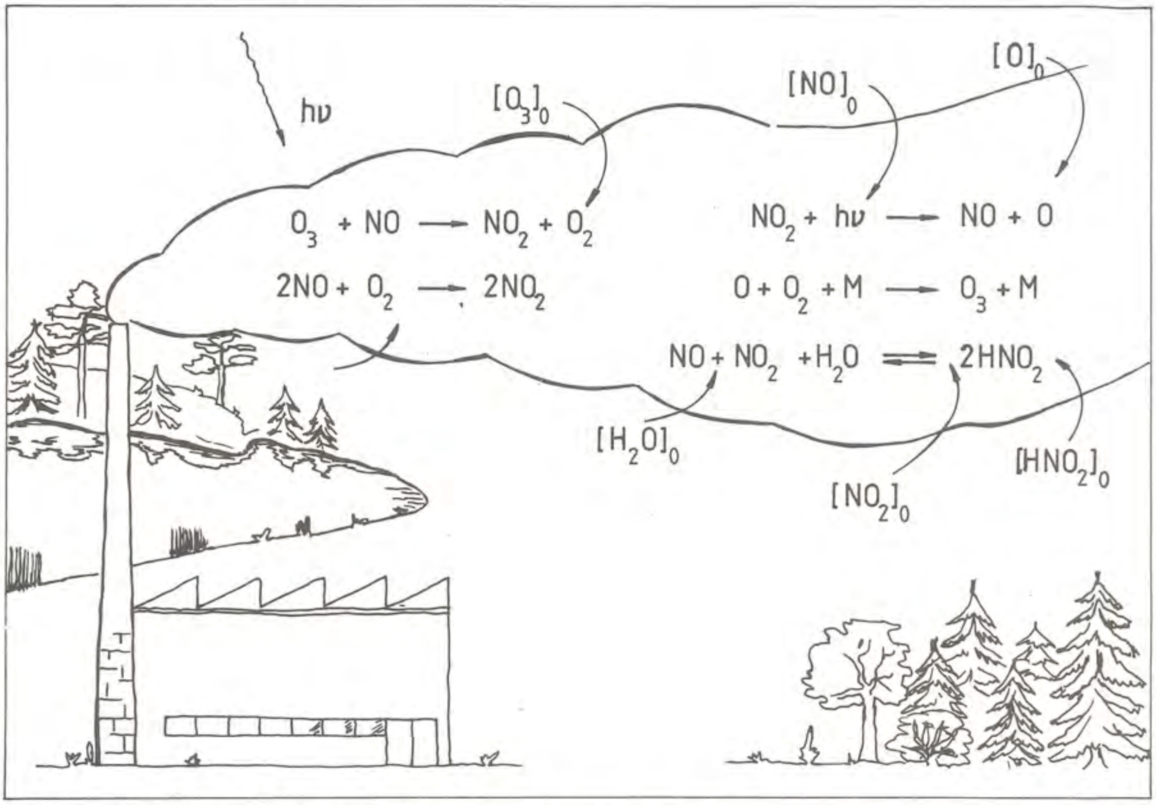

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Model description

by Christer Persson and Lennart Funkquist

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Abstract

A plume dispersion model on local scale (0 - $\sim$20 km) including atmospheric chemistry for nitrogen oxides is developed. The purpose of the study is to obtain a practical air quality model which can be used in environmental planning for e.g. coal-fired power plants. Problems concerning both high concentrations of NO_2 in the air and deposition of different nitrogen compounds to the ground are considered. The instantaneous plume dilution is described - assuming total mixing within the plume - as a function of emission parameters and meteorological conditions. The interplay of emissions, instantaneous plume dilution, entrainment of polluted ambient air, meteorological conditions and atmospheric chemistry processes determines the production or loss of the different compounds. On a local scale only six chemical reactions need to be included. On a somewhat larger scale the number of reactions needed increases substantially. For the numerical solution we have used the method by Gear. In order to obtain hourly mean values of different nitrogen oxides and long-term deposition values, conventional Gaussian respectively K-formulation procedures are used. Meteorological input data are obtained from climatological observations and also generated by a boundary layer model. From the results it is obvious that the meteorological conditions and the ambient ozone concentration are of great importance for the relative amount of NO_2 in the plume. On a local geographical scale the plume chemistry is diffusion controlled.

Key words

Plume model instantaneous dilution, chemical transformation, nitrogen oxides, nitrogen dioxide, air quality, deposition.

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1. INTRODUCTION

The local environmental impact of emission of nitrogen oxides (NO_x) from a power plant depends both on the concentration and the chemical nature of the species produced by the emitted material. The NO_x-emission consists to about 90-95% of nitric oxide (NO) but it will more or less rapidly be oxidized in the atmosphere. In the first step it is oxidized mainly to nitrogen dioxide (NO_2). As the negative effects on health by NO_2 are much more serious than those of NO, the NO_2-formation has to be considered. NO_2 is also more directly related to the acidification of the ground since it is deposited - mainly through dry deposition to vegetation - much more efficiently than NO. NO_2 also plays an essential part in many chemical processes in the atmosphere. The formation of secondary air pollutants such as nitric acid (HNO_3), ozon (O_3) and peroxyacetylnitrate (PAN) are some examples. When HNO_2 and HNO_3 are produced the wet deposition becomes important for the acidification. In studying these problems theoretical models including both atmospheric transport and dispersion and the necessary chemical reactions are of interest.

Plume models for nitrogen oxides have been presented by among others White (1977) and Peters and Richards (1977). These models include only three reactions and assume photostationary state. Carmichael and Peters (1981) apply chemical calculations on the NO-oxidation in an observed plume. Cocks and Fletcher (1982) present a model including a comprehensive chemical scheme coupled with a simple method for calculating the plume dispersion.

The present study is aiming at development of a practical air quality model for different nitrogen oxides, which can be used in environmental planning.

2. PLUME MODEL FOR NITROGEN OXIDES

2.1 Model assumptions

The oxidation of NO in plumes is a complicated process depending on a number of chemical and physical parameters. In this model the instantaneous plume dilution and the simultaneous chemical reactions in the plume are described in a Lagrangian coordinate system following the wind i.e. following a trajectory. We start with a segment of the plume, which is moved by the wind away from the source and at the same time the concentrations of different compounds are changed through dilution, entrainment of ambient polluted air, chemical reactions within the plume and deposition.

The following basic assumptions are made:

- The distribution of the pollutants is homogeneous ("top hat" concentration distribution) within each cross section of the instantaneous plume.
- Wind speed is constant with height within each cross section of the instantaneous plume.
- The effect of very short time turbulent concentration fluctuations on the chemical transformations can be neglected.

In order to describe the changes in concentrations in the instantaneous plume, we start with a simple expression for mass balance for each of the considered compounds. A balance in mass flux for a compound "i" through two cross sections of the plume, see Figure 1, separated in time with Δt can be expressed as:

$$\frac{\Delta C_i}{\Delta t} = P_i + C_{i0} \frac{2R\Delta R + \Delta R^2}{(R + \Delta R)^2} \frac{1}{\Delta t} - S_i - C_i \frac{2R\Delta R + \Delta R^2}{(R + \Delta R)^2} \frac{1}{\Delta t} \quad (1)$$

where

$C_i(t)$ = concentration of compound "i" in the instantaneous plume at time t downwind from the source

C_{i0} = concentration of compound "i" in the ambient air

$P_i(t)$ = production of compound "i" per unit volume through chemical reactions

$S_i(t)$ = sink of compound "i" per unit volume through chemical reactions

R = plume cross section radii

t = time

u = wind speed at plume level

The distance between the two cross sections is given by the expression $\Delta x = u\ \Delta t$.

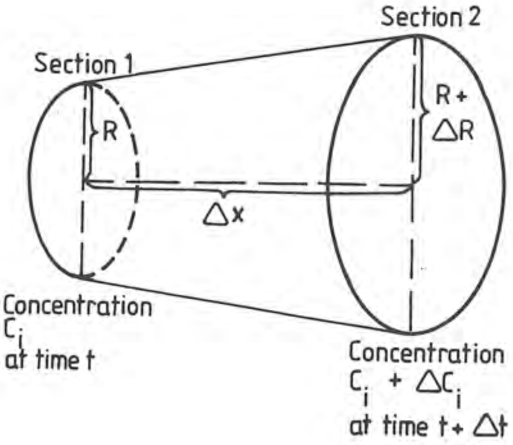

Figure 1.

If the instantaneous plume cross section area (A) is not circular, R in the expression above can be calculated through $R = \sqrt{A/\pi}$. Thus the concept "radii" still can be used.

2.2 Plume dispersion

With the assumption of a "top hat" concentration distribution the problem to describe the instantaneous plume dispersion can be reduced to a description of how the plume cross section area and thus R varies. R is a function of the distance from the source and depends on the inherent turbulence within the plume (especially at an initial stage) and the atmospheric turbulence (at larger distances). Different methods have been used to determine R according to Table 1. During the initial phase the rate of growth has been calculated from the simple relation $R = \beta \Delta h$, where Δh is the plume rise. The expressions for Δh, which are given in Table 1, have been derived mainly from Briggs (1975) and from Högström (1978). The constant β has been set equal to 0.65 for unstable conditions, 0.60 for neutral and 0.55 for stable conditions, cf. discussions by Briggs (1975) and Hanna (1982). The distance where the final plume rise occurs and the initial phase changes to the continued phase (cf. Table 1) is denoted by x_t, x_u or x_s in neutral, unstable or stable stratification respectively.

For the continued phase results from different plume measurements were used. Information about atmospheric dispersion of instantaneous plumes in stable or neutral conditions up to 7 km distance was obtained from Högström (1964). For unstable conditions the instantaneous plume dispersion at the initial stage was assumed to be the same as in neutral conditions. On larger distances no information could be found. Therefore σ-values based on ordinary Gaussian dispersion studies, i.e. an averaging time of 10 min or more, had to be used. However, at these rather large distances the length of sampling time is probably of somewhat minor importance.

According to the formula in Table 1 x_t goes to infinity when u goes towards 0. The same is true for x_u and x_s when the stratification becomes close to neutral. This is not realistic and has - for the time being - been handled through using a maximum of 5 km for the x-values. Since no general theory exists for the calculation of R, also another restriction has been introduced. The calculated R-value in stable or unstable stratification must satisfy the relation $R_{stable}(x) \leq R_{neutral}(x)$ respectively $R_{unstable}(x) \geq R_{neutral}(x)$. Otherwise the R_{stable} respectively $R_{unstable}$ is put equal to $R_{neutral}$. This restriction only is of importance occasionally at special combinations of emission patterns and meteorological conditions.

2.3 Chemical reactions

The reaction scheme first utilized in the model is presented in the Appendix. This scheme consists of about 30 reactions with a few "summary" reactions, i.e. incomplete reactions since the intermediate stages are not specified. Calculations however showed that on a local scale (0 - ~20 km) only six reactions were of importance for the NO_x-chemistry. These are given in Table 2 together with their rate constants. The photo dissociation rate has been determined for 60°N at different times of the day and year according to a method developed by Isaksen et al (1977). Other rate coefficients were obtained from Grennfelt and Sjödin (1982).

Table 1. Theoretical expressions used in order to describe the instantaneous plume dilution.

INITIAL PHASE (only inherent turbulence)	CONTINUED PHASE (inherent + atmospheric turbulence)
UNSTABLE	
$0 < x \le x_{ins}$ (x_u maximum 5 km)	$x > x_u$
x_u = maximum of $\left(4.44\,\frac{F^{2/3}\,u^{3/5}}{q^{3/5}}, \frac{20\,F_m^{1/2}}{u}\right)$ $q = \frac{w_*^3}{z_i}$ $R = \beta\Delta h = \beta\left[\frac{8.33\,F_m\,x}{u^2} + \frac{4.17\,F\,x^2}{u^3}\right]^{1/3}$	$R^2 = R^2(x_{ins}) + 2\sigma_{zr}\sigma_{yr}$ or $R = \sqrt{\frac{z_i\,B}{\pi}}$ where $B = \sqrt{2\pi}\;\sigma_{yr}$
NEUTRAL	
$0 < x \le x_t$ (x_t maximum 5 km)	$x > x_t$
x_t = maximum of $\left(\frac{3000\,F}{u^3}, \frac{20\,F_m^{1/2}}{u}\right)$ $R = \beta\Delta h = \beta\left[\frac{8.33\,F_m\,x}{u^2} + \frac{4.17\,F\,x^2}{u^3}\right]^{1/3}$	$R^2 = R^2(x_t) + 2\sigma_{zr}\sigma_{yr}$ or $R = \sqrt{\frac{z_i\,B}{\pi}}$ where $B = \sqrt{2\pi}\;\sigma_{yr}$
STABLE	
$0 < x \le x_s$ (x_s maximum 5 km)	$x > x_s$
$x_s = \frac{4.5\,u}{\omega}$ $\omega = \left(\frac{g}{\theta_a}\,\frac{d\theta_a}{dz}\right)^{1/2}$ $R = \beta\Delta h = \beta\;2.0\left(\frac{F}{u\omega^2}\right)^{1/3}\left(1 + \left(1 + \left(\frac{\omega F_m}{F}\right)^2\right)^{1/2}\right)^{1/3}\left(\frac{x}{x_s}\right)^{1/3}$	$R^2 = R^2(x_s) + 2\sigma_{zr}\sigma_{yr}$

Nomenclature to Table 1:

x = horizontal coordinate along the plume

F = buoyancy flux of the source = $\frac{V_0 g}{\pi} \times \frac{T_0 - T_a}{T_0}$

V_0 = source volume flux

T_0 = absolute temperature of gases emitted from stack

T_a = absolute temperature of ambient air

w_* = scaling velocity for a convective mixing layer

w_* = $\left(\frac{g}{T_a}\,\overline{w'\theta'}\,z_i\right)^{1/3}$

$\overline{w'\theta'}\rho c_p$ = sensible heat flux at the ground
ρ = air density
c_p = spec. heat of the air

w = vertical speed of the air

θ = potential temperature

prime indicates fluctuations

z_i = mixing height

F_m = momentum flux of source = $\frac{\rho_0}{\rho_a} \times \frac{w_0 V_0}{\pi}$

ρ_0 = density of effluent

ρ_a = density of ambient air

w_0 = efflux velocity of effluent

u = air speed along the x-axis

Δh = plume rise

ω = Brunt-Väisälä frequency

g = gravitational acceleration

θ_a = potential temperature of ambient air

β = entrainment constant

σ_{zr} = Gaussian vertical dispersion parameter for instantaneous plumes

σ_{yr} = Gaussian horizontal dispersion parameter for instantaneous plumes

Table 2. Chemical reactions considered in the model (see also the Appendix). Reaction rates for three component reactions are given in cm^6 $molecules^{-2}s^{-1}$, for two component reactions in cm^3 $molecules^{-1}$ s^{-1} and dissociation rates in s^{-1}. T = temperature of the plume (^oK).

		Reaction rates
R1	$NO_2 + h\nu \rightarrow NO + O(^3P)$	$j_1 = 0 - 6.2\ 10^{-3}$
R2	$O(^3P) + O_2 + M \rightarrow O_3 + M$	$k_2 = 1.1\ 10^{-34}\ e^{510/T}$
R3	$O_3 + NO \rightarrow NO_2 + O_2$	$k_3 = 2.1\ 10^{-12}\ e^{-1450/T}$
R4	$2NO + O_2 \rightarrow 2NO_2$	$k_4 = 1.5\ 10^{-40}\ e^{1780/T}$
R5	$NO + NO_2 + H_2O \rightarrow 2HNO_2$	$k_5 = 6.0\ 10^{-38}$
R6	$2HNO_2 \rightarrow NO + NO_2 + H_2O$	$k_6 = 1.9\ 10^{-11}\ e^{-5000/T}$

The reactions R1-R4 are by far the most important on this scale, which was shown in our first calculations and also has been shown in a study by Cocks and Fletcher (1982), where a very large number of reactions were included.

During the day absorption of ultraviolet radiation by NO_2 leads to destruction of NO_2 and formation of O_3, through R1 and R2. In reaction R3 the rate of NO-oxidation depends on complex interactions between the turbulent mixing of the plume (NO) with the surrounding air (O_3) and chemical kinetics. At daytime in the absence of other reactions an equilibrium between the reactions R1, R2 and R3 is achieved. The expression $[NO][O_3]/[NO_2] = j_1/k_3$ can be derived for that situation. The reaction R4, where the production of NO_2 is proportional to the square of the NO-concentration, has been studied in some detail by Lindqvist et al (1982) and their expression for the reaction rate is used.

2.4 Numerical method for calculating the instantaneous concentration

Explicit expressions for $(\frac{dC_i}{dt})_{chem} = P_i - S_i$ with notations according to equation 1, were obtained from the reaction scheme in Table 2. According to the assumptions made in section 2.1, to neglect short turbulent concentration fluctuations, the chemical part of equation 1 can be solved separately. This part forms a system of coupled, non-linear ordinary differential equations. Because of widely differing time constants in the system difficulties arise when a conventional ordinary differential equation solver is applied. This kind of systems are called stiff and their solution requires that the stepsize is smaller than the smallest time constant in the system. In this study the system contains a very fast transient originating from reaction R4. Thus the solution procedure has to take this into account until this transient smooths down and a larger stepsize can be used. This implies that the system does not have to be stiff all the time. For example rapid changes may take place after a certain amount of time which again make the system stiff. This is the case when solving the system arising from the reactions in the Appendix.

It is obvious that a satisfactory solver for this kind of system has to use a variable stepsize. One such method is Gear's method, which, in a modified version by Hindmarsh (1974), has been used in this application. The method uses both a variable stepsize and a variable order to the difference approximation.

2.5 Calculations of one hour mean concentration values

Normally in practical applications, one hour mean values of concentration at fixed geographical locations around a power plant are of prime interest. Those values can be obtained through a combination of:

- information concerning the instantaneous plume, given by equation 1
- information of the concentration in the ambient air
- calculation routines from a conventional Gaussian model for one hour sampling time.

The probability, k, for the point (x, y, z) to be localized within the instantaneous plume is

$$k = \frac{\Pi R^2}{2\Pi\sigma_y\sigma_z} \left[e - \frac{(z-h_{eff})^2}{2\sigma_z{}^2} + e - \frac{(z+h_{eff})^2}{2\sigma_z{}^2} \right] e - \frac{y^2}{2\sigma_y{}^2}$$

where h_{eff} is the effective chimney height and $\sigma_y(x)$ and $\sigma_z(x)$ are Gaussian dispersion parameters for one hour sampling time. The one hour mean concentration $\bar{c}_i$ is obtained from

$$\bar{c}_i(x, y, z) = k \cdot c_i(\text{instantaneous plume}) + (1-k)c_{i0}\ (\text{ambient air})$$

2.6 Calculation of deposition

It is possible to estimate deposition values for different nitrogen oxides rather easily by combining the solution of equation 1 with a conventional K-model. K here stands for the eddy diffusivity.

From the calculated concentrations, $c_i(x)$, we can obtain $Q_i(x) = u\iint c_i(x)dydz$, which indicates the "effective source strength" for the compound "i" at the distance x. Subsequently the K-model gives the deposition. When dealing with cases, where the deposition is important, equation 1 can be complemented with a term that substracts the deposited part given by the K-model. I our practical applications we have used the model given by Persson and Omstedt (1980).

3. RESULTS FROM APPLICATIONS TO POWER PLANTS

Below are given some examples of results obtained in practical applications. The meteorological information used for the studied situations is given in Table 3. Assumed ambient concentrations, which are typical for rural parts of southern and middle Sweden, are presented in Table 4.

Table 3. Meteorological information used for the studied situations. Data is obtained from Västerås (1949-69) and aerological soundings from Stockholm/Bromma (1970-74).

	Normal winter	Cold winter	Normal spring	Normal summer	Warm summer
Mean temp. (°C)	-2.4	-14.5	+4.0	+16.3	+22.0
Temp. amplitude (°C)	5.2	8.0	7.0	9.8	12.6
Temperature at meteorological station:					
Mean minimum (°C)	-5.0	-18.5	+0.5	+11.4	+15.7
Mean maximum (°C)	+0.2	-10.5	+7.5	+21.2	+28.3
Forest ground temp.:					
Mean minimum (°C)	-5.0	-18.5	+0.5	+11.4	+13.7
Mean maximum (°C)	+0.2	-10.5	+7.5	+21.2	+29.3
City ground temp.:					
Mean minimum (°C)	-2.0	-13.5	+2.0	+14.4	+19.7
Mean maximum (°C)	+1.7	- 8.0	+8.5	+22.2	+31.3
Field ground temp.:					
Mean minimum (°C)	-8.0	-24.5	-2.5	+ 9.0	+12.5
Mean maximum (°C)	+0.2	-10.5	+8.5	+22.2	+30.5
Geostrophic mean wind (m/s)	7.5	4.0	7.1	6.9	4.3
Approximate wind at plume level (m/s)	6.7	4.0	6.3	6.0	4.0
z_0 field (m)	0.002	0.002	0.008	0.02	0.02
z_0 forest (m)	0.6	0.6	0.6	0.6	0.6
z_0 city (m)	1.0	1.0	1.0	1.0	1.0
Aerological sounding data:					
Temperature stratification $\frac{dT}{dz}$ 00GMT (°C/km) close to ground	-5.0	+11.6	-2.1	-2.5	+13.1
Mixing height, z_i, 12GMT (m)	600	100	1600	1500	1900

Table 4. Assumed ambient concentrations. The values are obtained from Swedish Environmental Research Insitute (IVL).

	Warm summer	Other periods
O_3	90 ppb	30 ppb
NO	0.5 ppb	0.5 ppb
NO_2	2.0 ppb	2.0 ppb
HNO_2	0.1 ppb	0.1 ppb

In Figures 2, 3 and 4 some results are summarized from calculations for a 270 MW coal-fired power plant. The rather small emission from this power plant was assumed to be as given in Table 5.

Table 5. Emission data for a 270 MW power plant.

	Winter	Spring	Summer
NO	26 g/s	16 g/s	7 g/s
NO_2	1.9 "	1.5 "	0.6 "

This corresponds to a NO_x-concentration of about 170 ppm in the stack (denoted 1Q). Some examples in the figures also refer to a concentration of about 500 ppm (denoted 3Q).

During daytime the well known steady state from reactions R1, R2 and R3 is successively achieved. From Figure 2 we see that in this case it is reached after about 4 km during a normal summer day. At night time on the other hand, we get a total oxidation of NO. In this example it occurs after about 10 km transport in summer, see Figure 2, and at a very much greater distance in winter. The slow oxidation in winter is due to the stable stratification and also to some degree to a lower O_3 concentration in the ambient air. When high NO-concentrations (> 1 ppm) occur, the reaction R4 is of importance for the formation of NO_2. That can happen very close to the stack and also a bit further away when the plume mixing is poor.

The calculated one hour mean concentrations in Figure 3 show that the largest NO_2-concentrations are obtained at night and at a distance of 10-15 km from the source, not close to the source during unstable conditions at daytime, which is typical for an inert compound.

Figure 4 illustrates a possible urban fumigation situation during a warm summer night. Outside the city the stratification is very stable while over the urban area, due to the heat island effect, the stratification is slightly unstable. Information about mixing height and atmospheric turbulence was obtained from a two-dimensional boundary layer model, which has been developed by Bodin (1979).To parameterize the turbulence in the boundary layer the turbulent energy equation is used in this model.

In Figures 5 and 6 some examples of results are given from calculations, where the effect of different fuels and sizes of power plants were studied. The presented results were obtained with the assumption of normal meteorological conditions in springtime for southern Sweden and with the emission data given in Table 6.

The results in Figures 5 and 6 refer to daytime conditions only, when the photochemical equilibrium eventually is reached. We can see that this happens at a distance of less than or about 1 km for the very small plants of 0.1 or 1.0 MW. For the 100 MW power plant the calculations indicate that photochemical equilibrium is reached at a distance of 7 km or more. That is quite far beyond the distance where the maximum concentration at ground level is reached for inert compounds.

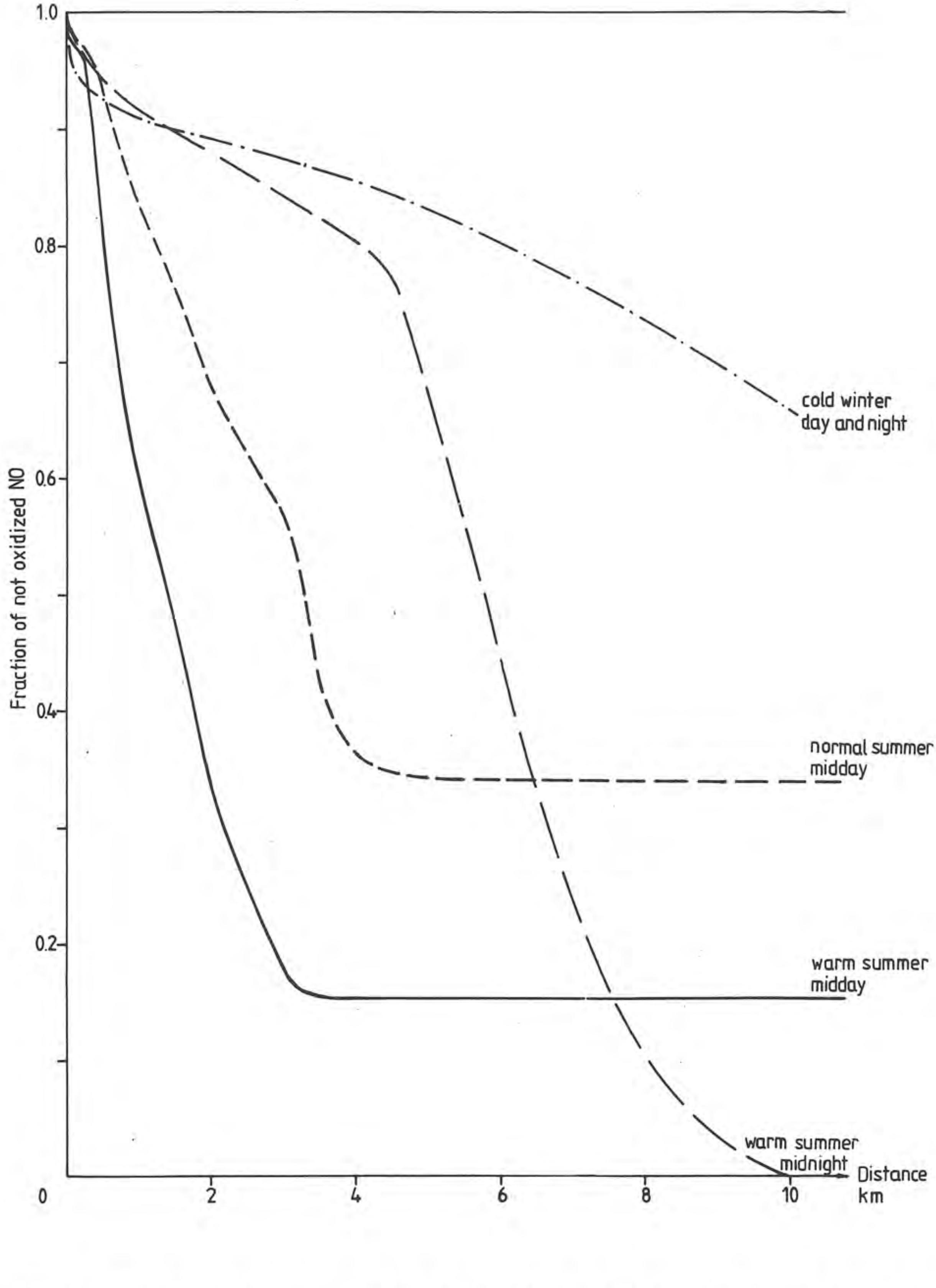

Figure 2. Calculated fraction of not oxidized NO in the emitted plume given as a function of distance from the source. The curves refer to a 270 MW coal-fired power plant for some different meteorological situations.

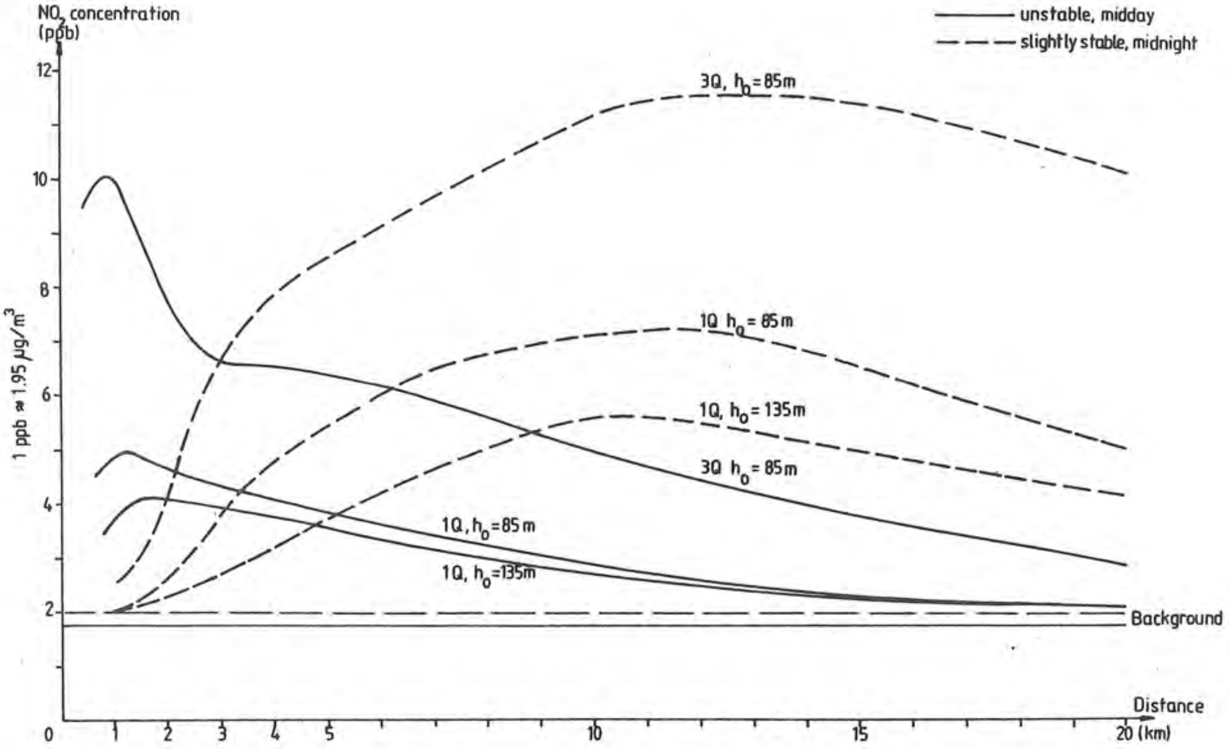

Figure 3. Calculated 1-hour mean concentrations at ground level just below the plume given as a function of distance from the source. The results refer to a 270 MW power plant for normal meteorological conditions at springtime in southern Sweden. 1Q refer to 170 ppm NO_x-concentration in emission and 3Q refer to 500 ppm.

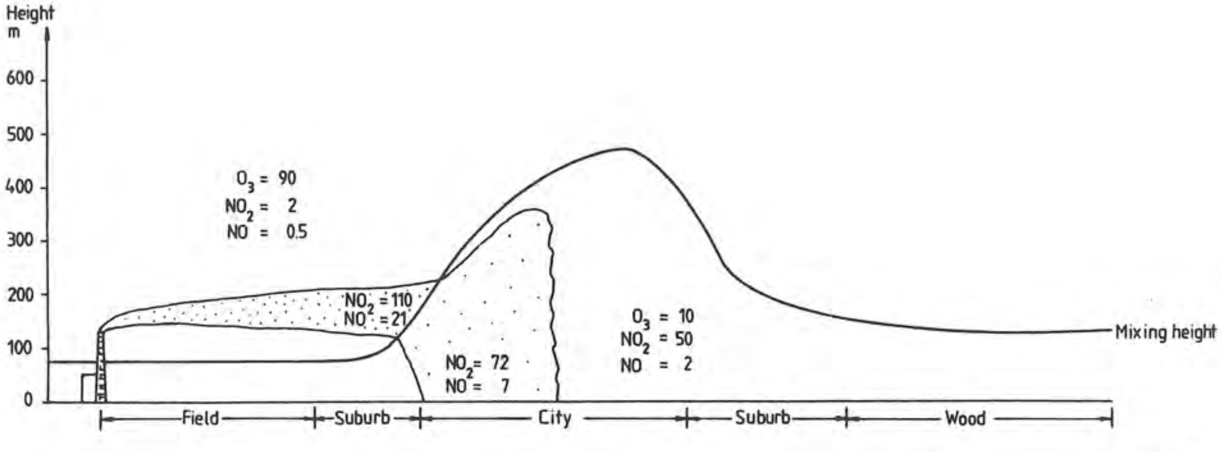

Figure 4. An attempt to simulate urban fumigation of a power plant plume during a summer morning. Information of the mixing height and atmospheric turbulence was obtained from a boundary layer model. Concentrations in the surrounding air were obtained from Swedish Environmental Research Insitute.

Table 6. Emission data used in the study of different fuels.

	Emission			
	NO	NO_2	O_2	H_2O(v)
100 MW				
Coal	14.5 g/s	2.48 g/s	4 %	7 %
Peat	10.4 "	1.76 "	4 "	22 "
Wood	7.75 "	1.32 "	4 "	25 "
Oil	7.75 "	0.626 "	1 "	10 "
Gas	5.22 "	0.420 "	1 "	17 "
10 MW				
Coal	0.985 "	0.263 "	5 "	6 "
1.0 MW				
Coal	0.111 "	0.030 "	8 "	5 "
0.1 MW				
Coal	0.124 "	0.0034 "	10 "	4 "

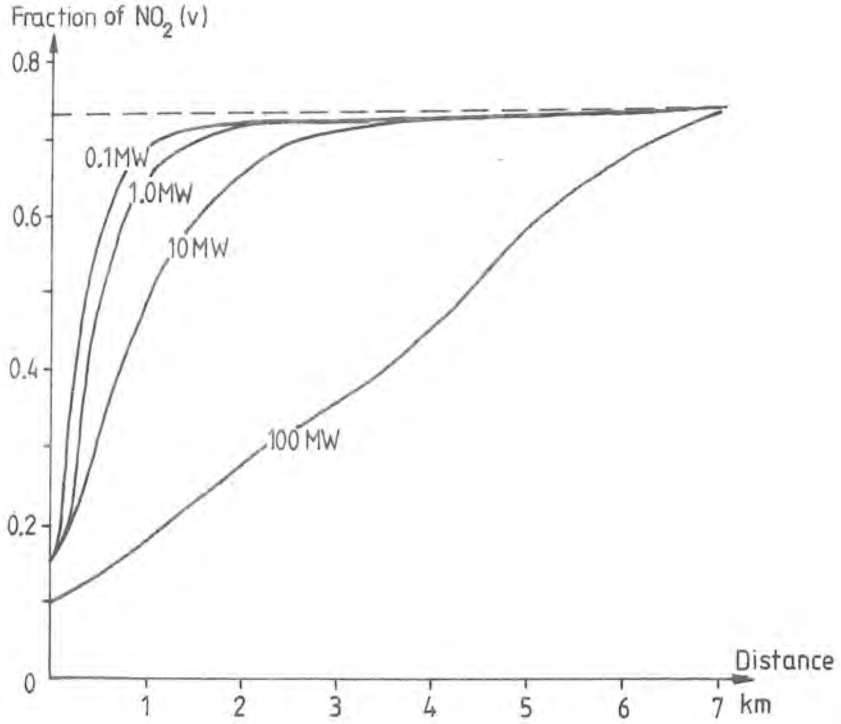

Figure 5. Calculated NO_2-fraction of the total emitted NO_x in the plume as a function of distance from the source. The curves refer to coal-fired plants of 0.1, 1.0, 10 and 100 MW respectively. The calculations were performed with the assumptions of normal meteorological conditions for southern Sweden at midday in springtime.

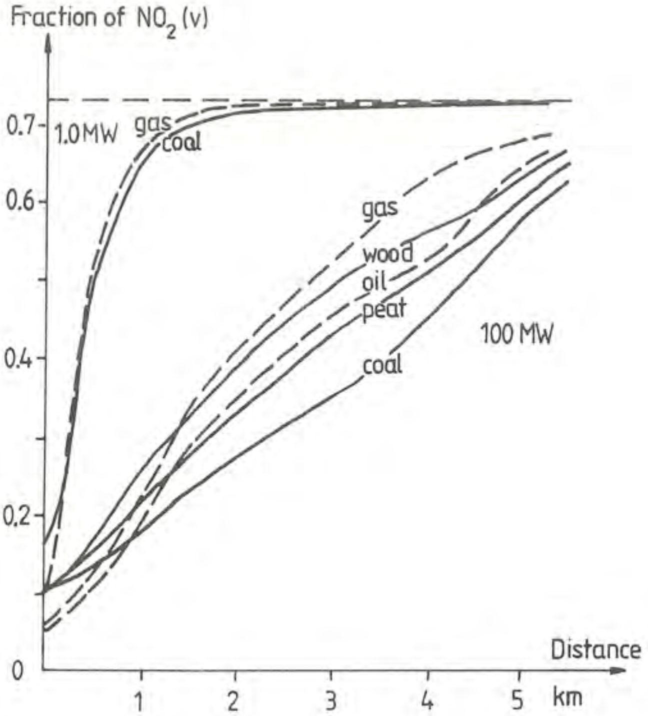

Figure 6. Calculated NO_2-fraction of the total emitted NO_x in the plume as a function of distance from the source. The curves refer to power plants of 100 MW and in two cases of 1.0 MW. The calculations were performed for the following five different fuels: coal, peat, wood, oil and gas.

4. DISCUSSION AND CONCLUSIONS

Our calculations indicate that the mixing between the instantaneous plume and the ambient air is a very important factor for the NO_2 production in power plant plumes. The mixing depends on the spectrum of turbulent motions and in situations where the time scale for mixing is larger then the time scale for chemical reactions, the chemistry in the plume is controlled by the rate of mixing. For power plant plumes on a local geographical scale we have such a situation, thus oxidation of NO to NO_2 there is a diffusion controlled process. In unstable atmospheric conditions the production of NO_2 is large while in stable conditions the production is small. These problems have also been discussed by Elshout and Bielke (1983) in connection with results from measurements of NO and NO_2 in power plant plumes.

At daytime with slightly unstable conditions the results show that the reaction R3 is by far the most important for the formation of NO_2 in the plume. Eventually the photochemical equilibrium is reached, which however takes some time due to the successive entrainment of ozon. At nighttime with stable stratification the reaction R4 normally is important for the NO_2 formation, although the shortage of O_2 in the emission can reduce the importance of this reaction during the first seconds after emission. At larger distances, when some dilution and entrainment of O_3 has taken place, the R3 reaction dominates also in stable conditions.

From the study it is obvious that emission conditions, meteorological factors and ambient ozone concentration are of great importance for the relative amount of NO_2 in the plume.

It should, however, be kept in mind that our assumption of homogeneous mixing within the plume may be critical in some cases. In reality, in an instantaneous plume a more or less heterogeneous mixture of "plume-parcels" and "ambient air-parcels" will be formed by the turbulent eddies. It is molecular diffusion, which at the boundaries of the eddies leads to local mixing, that makes the reaction between NO and O_3 possible. If the local mixing by the eddies is slow, the oxidation to NO_2 according to reaction R3 is delayed. On the other hand the importance of reaction R4 close to the source may then be increased. A verification of the model can hopefully indicate somewhat of how important this assumption is. Sensitivity analysis and verification of the model is planned to be performed later in 1984.

Finally, it can be of interest to note that NO_2 is a yeallowish brown gas, which can be seen in certain plumes and over larger urban areas at days with higher concentrations.

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LARGER REACTION SCHEME

Below is given the reaction scheme first utilized in the model. The reactions R10-R15 are "summary" reactions, i.e. incomplete reactions since the intermediate stages are not specified (see Rodhe et al, 1981). Calculations showed, however, that on a local scale only reactions R1-R6 had to be included.

R 1 $NO_2 + h\nu \rightarrow NO + O(^3P)$
R 2 $O(^3p) + O_2 + M \rightarrow O_3 + M$
R 3 $O_3 + NO \rightarrow NO_2 + O_2$
R 4 $2NO + O_2 \rightarrow 2NO_2$
R 5 $NO + NO_2 + H_2O \rightarrow 2HNO_2$
R 6 $2HNO_2 \rightarrow NO + NO_2 + H_2O$

R 7 $O_3 + h\nu \rightarrow O_2 + O(^1D)$
R 8 $O(^1D) + M \rightarrow O(^3P) + M$
R 9 $O(^1D) + H_2O \rightarrow 2OH$
R10 $CO + OH \rightarrow - - - \rightarrow HO_2 + CO_2$
R11 $CH_4 + OH \rightarrow - - - \rightarrow CH_2O + HO_2$
R12 $C_2H_4 + OH \rightarrow - - - \rightarrow HO_2 + 2CH_2O$
R13 $CH_2O + OH \rightarrow - - - \rightarrow CO + HO_2$
R14 $CH_2O + h\nu \rightarrow - - - \rightarrow CO + 2HO_2$
R15 $CH_2O + h\nu \rightarrow - - - \rightarrow CO + H_2$
R16 $2HO_2 \rightarrow H_2O_2 + O_2$
R17 $HO_2 + OH \rightarrow H_2O + O_2$
R18 $H_2O_2 + OH \rightarrow HO_2 + H_2O$
R19 $H_2O_2 + h\nu \rightarrow 2OH$
R20 $NO + HO_2 \rightarrow OH + NO_2$
R21 $NO_2 + OH \rightarrow HNO_3$
R22 $O(^3P) + NO_2 \rightarrow O_2 + NO$
R23 $O_3 + h\nu \rightarrow O(^3P) + O_2$
R24 $O_3 + NO_2 \rightarrow O_2 + NO_3$
R25 $O_3 + OH \rightarrow O_2 + HO_2$
R26 $O_3 + HO_2 \rightarrow 2O_2 + OH$
R27 $NO + NO_3 \rightarrow 2NO_2$
R28 $NO + OH \rightarrow HNO_2$
R30 $OH + HNO_2 \rightarrow NO_2 + H_2O$
R31 $HNO_2 + h\nu \rightarrow NO + OH$

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