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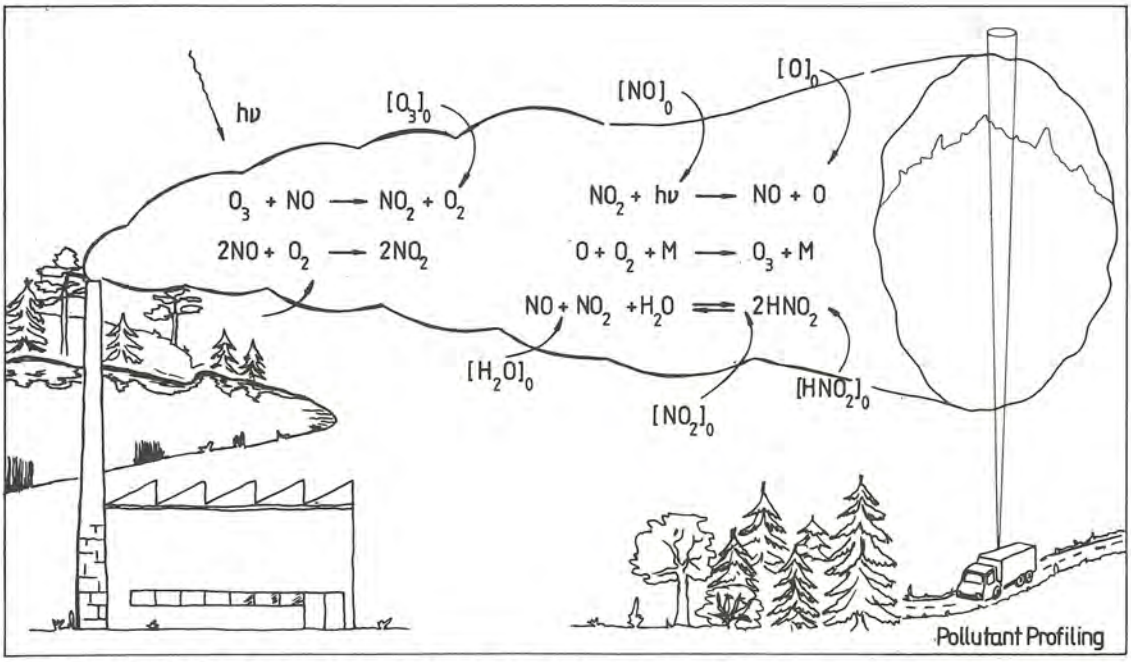

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Model verification

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Abstract

A plume dispersion model on local scale (0 - ~20 km) including atmospheric chemistry for nitrogen oxides was developed and presented in RMK 41 (1984). The model is designed for and used in practical environmental planning for e.g. coal-fired power plants. In this study a verification of the model by means of plume data from several European power plants has been performed. The verification shows that the model is capable of describing the NO_2-formation in power plant plumes in most weather situations in a fairly accurate way. No important systematic errors seem to be present and the correlation coefficient for NO_2-fractions of total NO_x is found to be about 0.7 out to at least 1 000 seconds after emission. The calculations are based only on routine meteorological data, emission data and ozone concentrations in the ambient air. Thus, the calculations have been performed in the same way as in the case of practical environmental planning, which gives a realistic picture of the potential of the model for practical applications. 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 controlled by the entrainment of ambient air.

Key words

Plume model, environmental planning, chemical transformation, nitrogen dioxide, air quality, verification

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LIST OF CONTENTS

1. INTRODUCTION

A plume model for calculation of different nitrogen oxides was developed at SMHI and first reported by Persson and Funkquist (1983). A more complete presentation of the model was given by Persson and Funkquist (1984). The model has been used for practical applications since 1983 but, so far, only some minor and fragmentary comparisons with measurements have been performed. Thus, there is a need for a presentation of a systematic test of the model, which is the purpose of this paper. Also, some minor developments of the model and a short sensitivity analysis will be shown. A verification of this kind should be a good basis for more extensive practical applications of the model in environmental planning and for further developments and wider applications.

2. SHORT PRESENTATION OF THE MODEL

The model is presented in detail in Persson and Funkquist (1984). Therefore only an outline will be given here, together with some improvements of the model formulations.

The in-plume oxidation of NO is a complicated process depending on a number of chemical and physical parameters. In the 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 while, simultaneously 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.
- The effect of very short time turbulent concentration fluctuations on the chemical transformations can be neglected.
- Wind speed is constant with height within each cross section of the instantaneous plume.

The first two assumptions can in certain situations be critical. They will be further discussed in the verification section.

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 varies. The area is a function of the distance from the source and depends on the inherent turbulence within the plume (especially at the initial stage) and the atmospheric turbulence (at larger distances).

The chemical reaction scheme first utilized in the model consisted of about 30 reactions with a few "summary" reactions, i.e. incomplete reactions since the intermediate stages are not specified. However, calculations 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 1 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. Chemical reactions considered in the model. 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 (°K).

	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 $2HNO_2 \rightarrow NO + NO_2 + H_2O$	$k_6 = 1.9\ 10^{-11}\ e^{-5000/T}$

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.

In Persson and Funkquist (1984) the dispersion of the instantaneous plume at distances larger than 5 km was given by means of σ-values based on ordinary Gaussian dispersion studies. This means that averaging times up to 1 hour were used instead of values for instantaneous plumes. Principally, the sampling time for the σ-values used should be as short as possible. Also, measured NO_2-data from power plant plumes, which are discussed in detail below, indicated that σ-values valid for shorter sampling times should be introduced. Therefore, Gifford's (1975) approach for obtaining 3-minutes σ-values from 1 hour σ-values is now used. The expression for σ (3 min) is $\sigma(3\ min) = \sigma(1\ h) \cdot (\frac{3}{60})^{0.2}$. The Gaussian σ-values for 1 hour sampling are obtained from an analysis by G Briggs, which is presented in (Gifford, 1975) and in Table 2. This gives a much better agreement between measured and calculated NO_2-fractions in plumes at larger distances than 5 km, which is discussed below.

TABLE 2. Briggs' dispersion parameters σ_y and σ_z as a function of downwind distance x(m).

Class	σ_y (m)	σ_z (m)
A	$0.22x\,(1 + 0.0001x)^{-1/2}$	$0.20x$
B	$0.16x\,(1 + 0.0001x)^{-1/2}$	$0.12x$
C	$0.11x\,(1 + 0.0001x)^{-1/2}$	$0.08x\,(1 + 0.0002x)^{-1/2}$
D	$0.08x\,(1 + 0.0001x)^{-1/2}$	$0.06x\,(1 + 0.0015x)^{-1/2}$
E	$0.06x\,(1 + 0.0001x)^{-1/2}$	$0.03x\,(1 + 0.0003x)^{-1}$
F	$0.04x\,(1 + 0.0001x)^{-1/2}$	$0.016x\,(1 + 0.0003x)^{-1}$

3. VERIFICATION

3.1 Selected cases of plume studies

The main difficulty with a verification of this kind is to obtain simultaneous data for all relevant parameters concerning power plant emissions, meteorological conditions, ambient ozone concentrations and different NO_x-compounds in the plume. The present verification will be based on studies from four different countries presented in the literature. These measurements were regarded as satisfactory for our purpose.

Data concerning plume measurements, emissions and meteorological conditions for the 34 studied cases are given in Table 3. Emission data and ozone concentrations were in most cases determined simultaneously with the plume studies, while meteorological data from the power plant site, with some exceptions, were not available.

3.2 Meteorological information

For most of the cases studied, data was obtained from a nearby routine meteorological observing station. Methods based on routine meteorological data were used to make a crude calculation of the sensible heat flux, H, the friction velocity, u_*, and the vertical wind profile. The net radiation at the ground, R_n, is calculated from solar elevation and cloudiness by a method developed by Nielsen et al (1981). The sensible heat flux can then be determined from the empirical relation $H = 0.4\,(R_n - 100)$, where H and R_n are given in Wm^{-2}. Using diagram 1, which is obtained from Omstedt (1983), the sensible heat flux and the wind speed at 10 m height can be used to determine the stability, the convective velocity scale, w_*, and a typical value for the mixing height. In the present model, we use five stability classes and denote them with block letters. The classification is done in agreement with Weil and Brower (1982). The classes are unstable - B, slightly unstable - C, neutral - D, slightly stable - E and stable - F. Diagram 1 shows classes A - D,

TABLE 3. Cases used in the comparison between model calculations and plume measurements. Name of power plant, time, available emission data, ozone concentration in the surrounding air and meteorological data are given. Wind speed at plume height (Uplume) and stability are calculated from routine meteorological data. For cases 1 - 12 also wind speed and stability given by KEMA are indicated (within parenthesis). Cases 1 - 11 refer to plants fired with oil or natural gas, where we assume an O_2-content of 2% in the exhaust gases. The other cases refer to coal fired power plants for which the O_2-content is assumed to be 4%. Emission velocity of the exhaust gases is put equal to 20 ms^{-1} for all cases and the ratio NO_2/NO_x in the emission is assumed to be 5% in all cases except nos 33 and 34, where we assume 2%. h_0 = stack height.

V_0 = exhaust gas volume
T_0 = exhaust gas temperature
Mv = Maasvlakte on the North Sea 30 km W Rotterdam, with a total capacity of 1 050 MW h_0 = 175 m
Fl = Flevo on the IJsselmeer 45 km NE Amsterdam, total capacity 835 MW, h_0 = 150 m
Waalh and Gld = other powerstations in the Netherlands
Wilh = Wilhelmshaven on the North Sea, total capacity 700 MW h_0 = 280 m
Stau = Staudinger on the Main 20 km E Frankfurt, total capacity 1 500 MW operating at $\leq$ 900 MW, h_0 = 195, 250 m
Fin = Finnå 20 km W Helsinki on the south coast of Finland h_0 = 152 m
Asn = Asnäs 3 km S Kalundborg on the west coast of Sjælland h_0 = 120 m, (220 m)

Case no	Power plant	Day	Time	Emission data			O_3 (ppb)	Meteorological data		
				NO_x (gs^{-1}) as NO_2	V_0 (m^3s^{-1} at 0°C)	T_0 (°C)		Uplume (ms^{-1})	Temperature (°C)	Stability (Pasquill class)
Data from the Netherlands										
1	Mv	760608	11 - 14	111	193	130	125	6.0 (8.5)	28	B (C)
2	Fl	800423	12 - 15	445	301	130	55	6.1 (7.5)	8	C (C)
3	Mv	780815	9 - 12	197	360	130	40	14.0 (15)	21	C (C)
4	Mv	781129	13 - 16	217	377	130	20	5.4 (8)	2	D (C)
5	Waalh	810319	11 - 15	136	211	130	50	19.2 (15)	8	D (D)
6	Mv	780830	16 - 19	282	377	130	30	11.7 (10)	15	D (D)
7	Mv	751104	16 - 17	69.4	184	130	35	3.9 (5)	12	D (D)
8	Fl	811124	12 - 16	299	301	130	26	20.0 (17.5)	7	D (D)
9	Fl	800409	11 - 17	181	139	130	45	14.6 (15)	6	C (D)
10	Gld	800130	10 - 16	172	114	130	(5-) 25*	19.5 (15)	8	D (D)
11	Fl	810422	10 - 17	350	237	130	45	10.0 (8)	7	C (D)
Data from West Germany										
12	Wilh	820513	daytime	197[x]	360[x]	180[x]	55	7.0 (7)	10	E[xx] (D)
13	Stau	810730	"	"	"	"	35	6.4	21	C
14	Stau	810624	"	"	"	"	55	6.4	21	C
15	Stau	810728	"	"	"	"	25	2.0	20	C
16	Stau	800829	"	"	"	"	55	6.5	23	C
17	Stau	800821	"	"	"	"	45**	20.1	23	D

Case no	Power plant	Day	Time	Emission data			O_3 (ppb)	Meteorological data		
				NO_x (gs^{-1}) as NO_2	V_0 (m^3s^{-1} at 0°C)	T_0 (°C)		U_{plume} (ms^{-1})	Temperature (°C)	Stability (Pasquill class)
18	Stau	800820	daytime	197[x]	360[x]	180[x]	35	11.4	19	D
19	Stau	810721	"	"	"	"	5	3.1	17	D
20	Stau	810529	"	"	"	"	55	11.2	18	D
21	Stau	810722	"	"	"	"	10	6.5	19	C
22	Stau	810430	"	"	"	"	5	11.8	12	D
23	Stau	810804	"	"	"	"	70	3.0	28	B
Data from Finland										
24	Fin	811026	18 - 21	19.3	28	137	20***	4.5	1	E
25	Fin	811204	6 - 7	61.1	73	113	28***	10.8	2	E
26	Fin	811214	9 - 10	32.2	45	128	28***	8.5	-11	F
27	Fin	811214	10 - 12	32.2	45	128	20***	8.5	-9	F
28	Fin	820113	15 - 16	59.4	92	106	28***	3.3	-7	E
29	Fin	820113	17 - 18	59.4	92	106	28***	3.0	-6	E
30	Fin	820113	19 - 20	59.4	92	106	28***	5.8	-5	E
31	Fin	820128	20 - 21	78.7	95	105	32***	4.4	-13	F
32	Fin	820128	21 - 22	78.7	95	105	32***	6.0	-13	F
Data from Denmark										
33	Asn	840815	11 - 12	739	897	132	37	6.7	19	C
34	Asn	840815	12 - 14	591	717	126	37	5.9	20	C

* Probably 25 ppb is correct. The lower value seems to be influenced by a local NO-source.

** Ozone value obtained from a background station in Southern West Germany.

*** Estimated ozone values (see text).

x Estimated emission data based on information from similar plants.

xx The first few km slightly stable at plume level due to sea breeze. Further away slightly unstable.

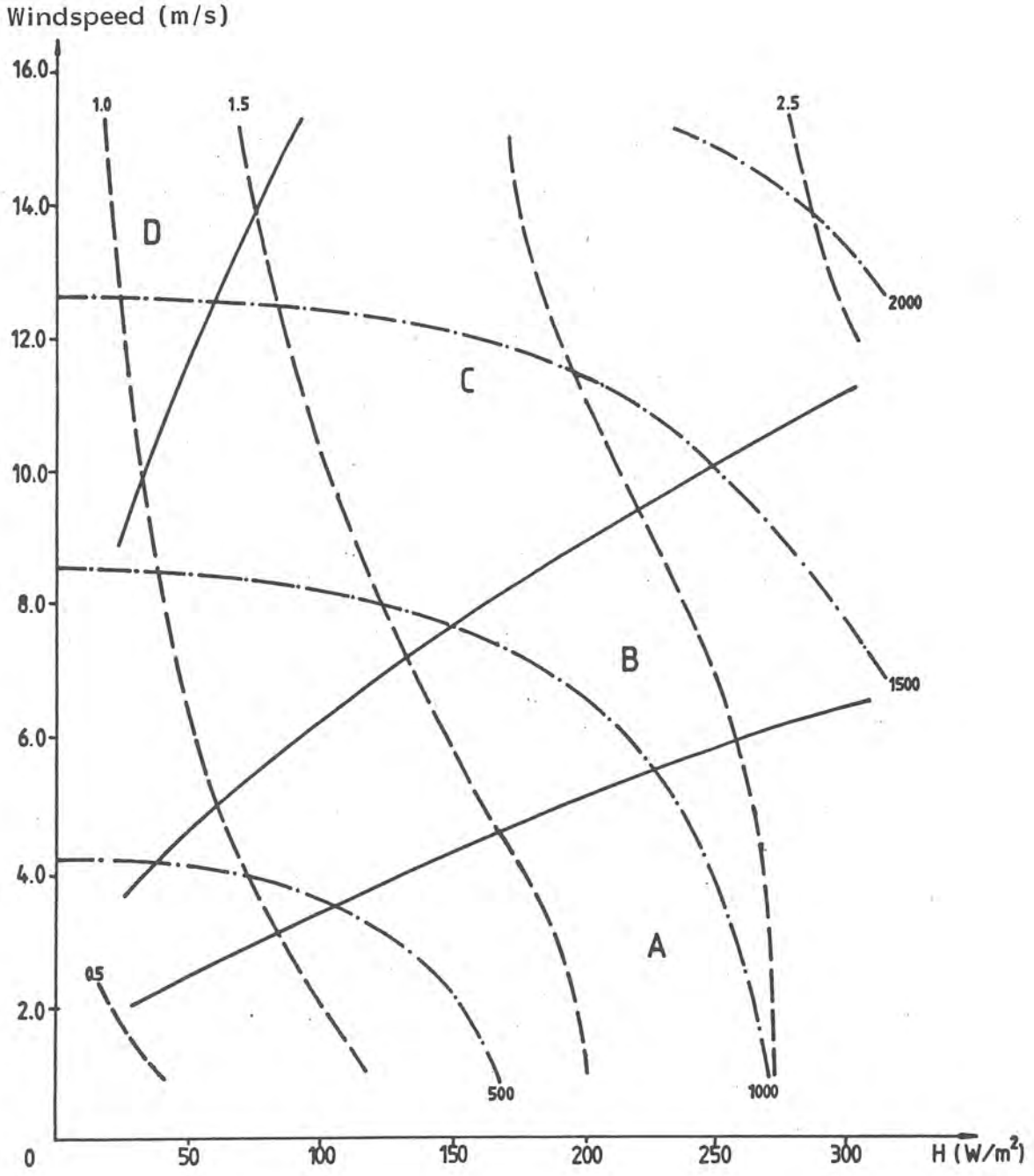


DIAGRAM 1. The stability classes (A - D) as a function of sensible heat flux, H, and wind speed at 10 m height. —·—· indicates the mixing height calculated according to F B Smith (1979), --- gives the convective velocity scale, w_*, and —— separates the stability classes. (After Omstedt 1983.)

though in our model application class A is put together with class B. A negative heat flux indicates stable stratification (classes E and F), where the well known Pasquill-Gifford-Turner classification scheme is used. The vertical wind profile is calculated in the way suggested by Businger et al (1971).

Using meteorological data determined in this way from routine meteorological observations always creates uncertainty in the results. However, this method is relevant for the verification, since that is the only way of getting meteorological data in many practical applications. Also, a more sophisticated method of using routine meteorological data, where vertical temperature soundings of the atmosphere are included, has been given by Omstedt (1984). That method can in practice easily be used for Swedish sites and in those cases improve the meteorological data used for the calculations.

In two cases nos 3 and 8, the wind conditions were very variable, making it especially difficult to correctly estimate the needed meteorological data.

Non-routine meteorological data were used for cases 24 - 32, involving measurements around Finnå power plant outside Helsinki, These data were obtained from a 300 m high mast west of Helsinki (Tammelin, 1984).

3.3 Measurements from the Netherlands and West Germany

Field studies on the oxidation rates of NO in power plant plumes were carried out by N.V. KEMA, Arnhem, the Netherlands, with direct measurements of the concentrations of the gaseous components in the plume using an aircraft or a van equipped with instruments, and by UBA, Frankfurt, West Germany, with Barringer remote sensing spectrometers (COSPEC). Results from the measurements are presented by Elshout and Beilke (1983) and (1984). More detailed information about the measurements in the Netherlands and for Wilhelmshaven have also been supplied by Dr Elshout through private communications. Those studies therefore provide the most complete set of plume data, necessary emission data, ozone concentrations and meteorological data available for this verification.

The Barringer spectrometer used in these plume studies can measure overhead burdens of SO_2 and NO_2 simultaneously. With the NO_x/SO_2 emission ratio of the power station as a reference value, the measurements of NO_2/SO_2 ratio in the plume allow the oxidation ratio of NO to NO_2 to be estimated. The measured and calculated results are all given as a oxidation ratio NO_2/NO_x integrated over the plume cross section, where $NO_x = NO + NO_2$.

The studied power stations in the Netherlands were oil- or gas-fired, while the power stations of Wilhelmshaven and Frankfurt in West Germany were coal-fired. Further details about the power plants are given in Table 3, together with emission data, ozone concentrations at the power plant and meteorological data (determined as in 3.2) for the studied cases.

For the power plants in West Germany no detailed emission data could be obtained but had to be estimated. Information from case no 3, which is a plant operating with roughly the same capacity, and similar plants was used.

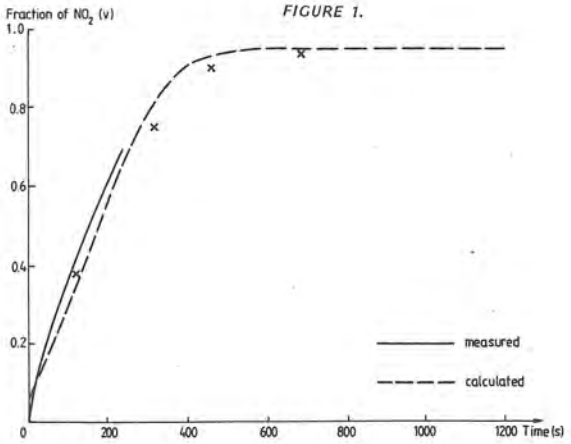
Comparisons between measured and model calculated values of NO_2/NO_x-ratios are presented in Figures 1 - 11 for the Dutch power plants and in Figures 12 - 23 for the plants in West Germany. In most cases the agreement between calculated and measured values is good. Case no 23 should, however, be treated separately since there is a very stable layer (strong inversion) aloft, which is of great importance for the results. The inversion could

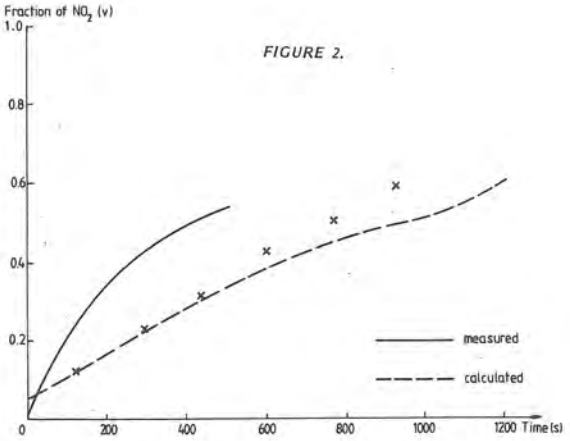
not be obtained from the ground based routine meteorological data but was indicated in UBA's plume data collection. The importance of how quickly the plume is caught in the inversion is illustrated in Figure 23. In the calculations we have assumed no entrainment after the plume was trapped in the inversion and, thus not used the ordinary expression for stable stratification.

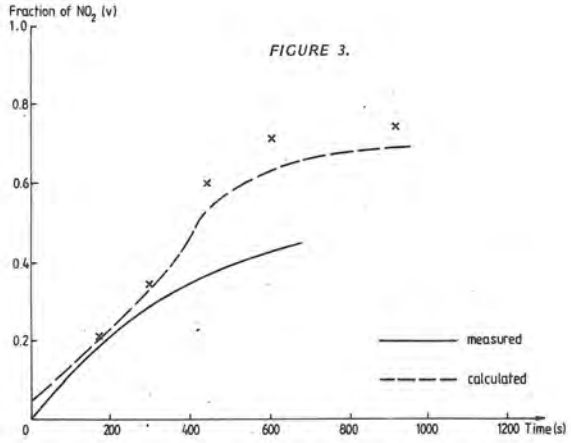
In two cases measured NO_2/NO_x-ratios disagree completely with the calculated values. In case no 7 the measured ratio is surprisingly low close to the source. The measurements indicate that all NO_x is emitted as NO and not oxidized at all before a travel time of 100 sec. This seems to be an unrealistic low NO_2-ratio and could possibly indicate uncertainties in the measurements. In case no 8 the meteorological situation was specifically difficult to describe and the meteorological information used for the calculations might be incorrect. A very deep low passed north of the Netherlands and caused hard westerly winds accompanied by heavy showers with hail at some places. The occurrence of very pronounced convective clouds indicates that a more effective dilution of the plume could have taken place, compared to what was calculated for neutral stability. Also, the wind speed at plume height is variable and difficult to determine in this case.

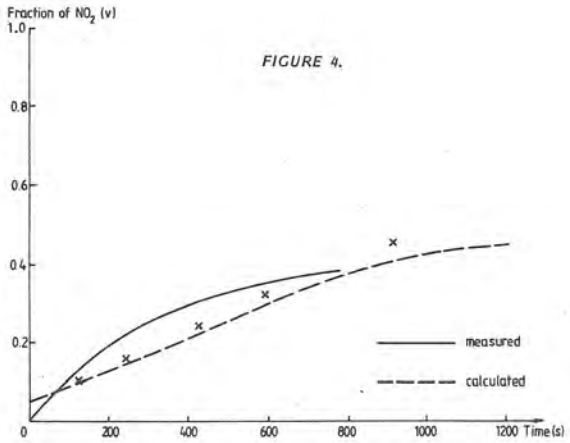
In Table 4 statistical information of measured and calculated NO_2-fractions in plumes is compared. All cases from the Netherlands and West Germany, except for the above discussed case no 23, are included (22 cases). Since it is possible that the measured values in case no 7 could be incorrect, comparisons where case no 7 is excluded are also shown in Table 4. The correlation coefficient between measured and calculated NO_2-fractions is around 0.75 for all plume travel times between 100 to 1 000 seconds, which must be regarded as a good correlation. Also, in the mean NO_2-fractions, there is a good agreement between measurements and model calculations, although the calculated NO_2-fractions are a little too low during the first 200 seconds. Also, the standard deviations are smaller for model calculated values than for measured during the first 200 seconds. The assumed constant value of 5% NO_2 in the emission can be one reason for that.

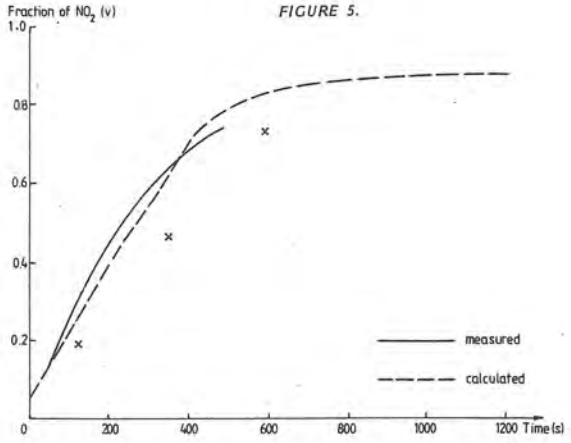
It should be pointed out that the calculated NO_2-fraction in the plume changes with transport time only due to three main processes: O_2-reaction, O_3-reaction and photo dissociation of NO_2. The other chemical reactions are of minor importance. Principally, also the entrainment of background NO and NO_2 can be important. However, when plume concentrations are much higher than ordinary background concentrations, like in the verification cases, this effect is of no importance. Therefore, in this study, the background air was assumed to be free of NO_x.

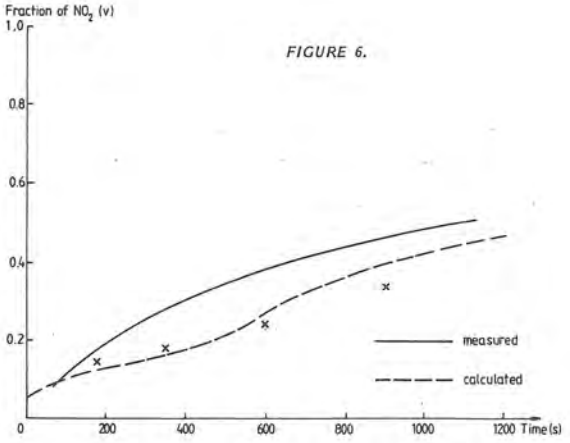




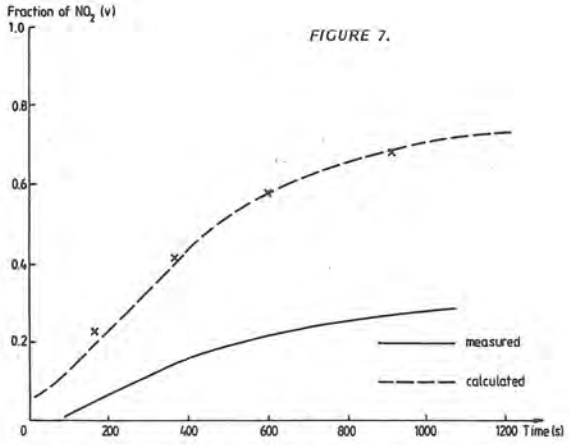








FIGURES 1 - 11. Comparisons between measured and calculated NO_2/NO_x-ratio, as a function of time after emission, in the power plant plumes of cases 1 - 11 respectively. The calculated values based on routine meteorological data are given by ---- and (x) indicate those based on meteorological data given by KEMA.



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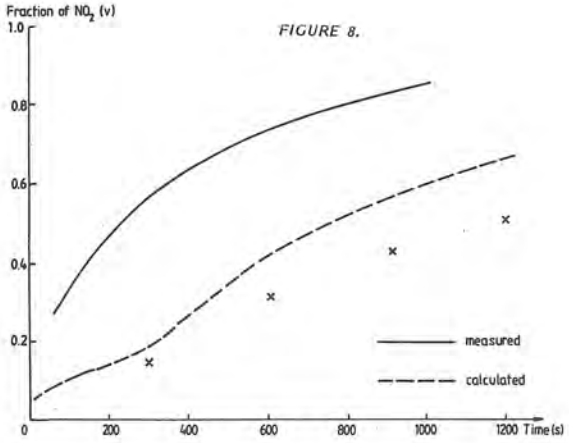
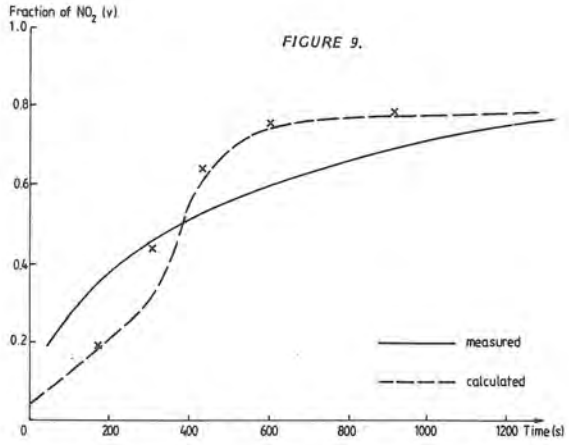


FIGURE 8.



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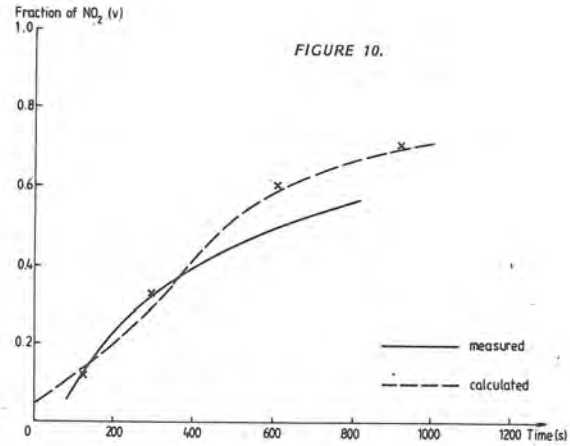

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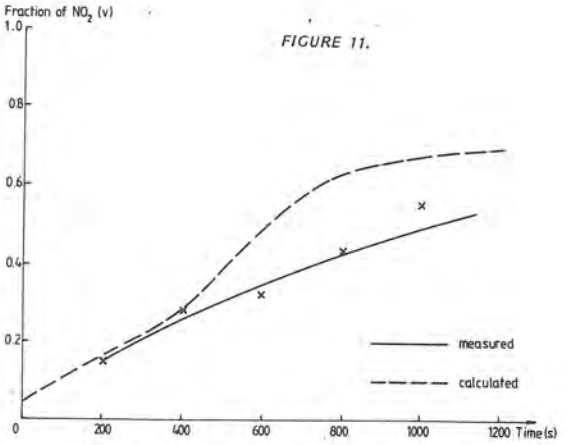


FIGURE 11.

FIGURES 7 - 11. See text on previous page.

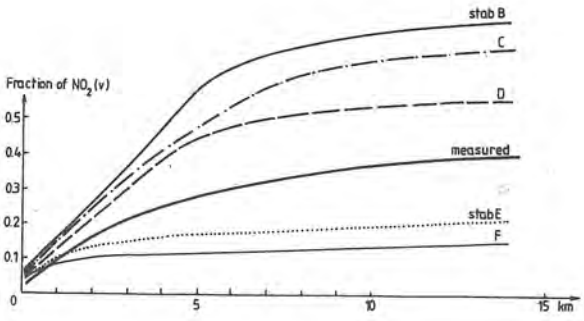


FIGURE 12. Same as figure 1 - 11 for case no 12. Calculations have been performed for all stability classes as an illustration of the sensitivity of this parameter (cf section 4.1).

FIGURE 13.

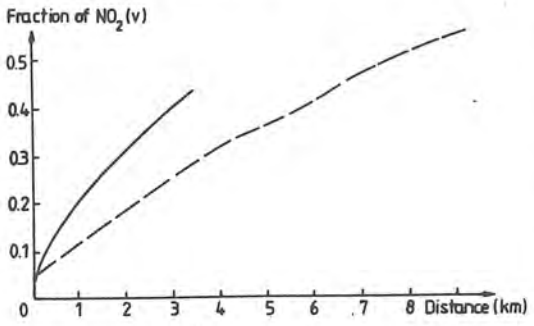


FIGURE 14.

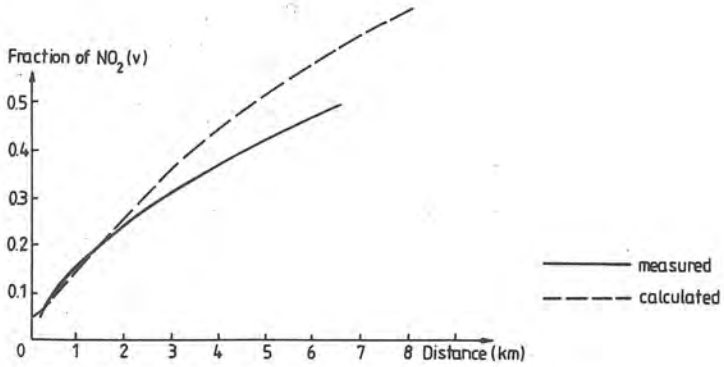
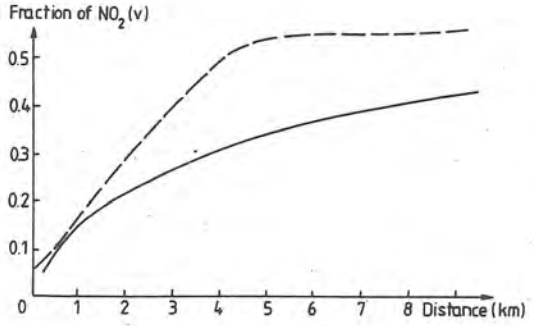


FIGURE 15.



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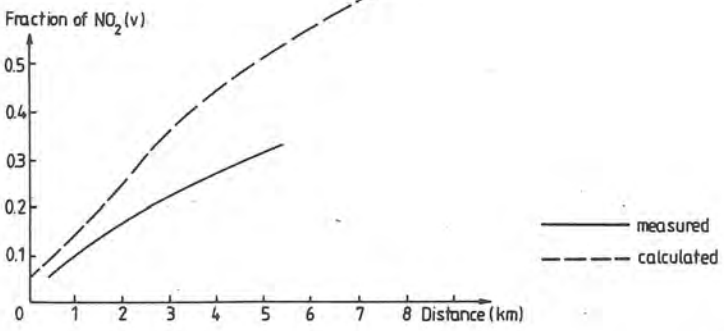
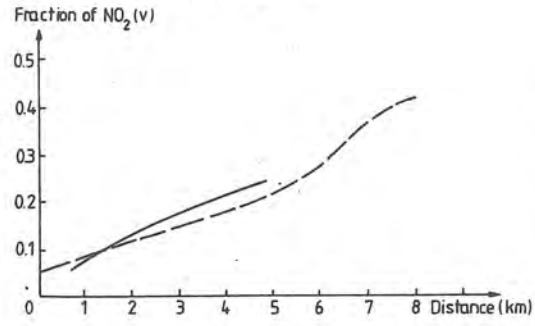


FIGURE 17.



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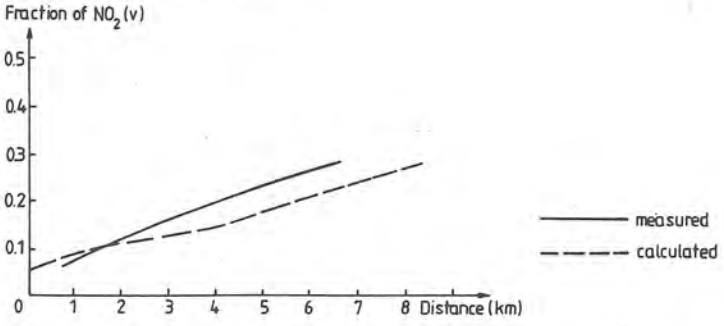


FIGURES 13 - 22. Comparisons between measured and calculated NO_2/NO_x-ratio, as a function of distance from the source, in the power plant plumes of cases 13 - 22 respectively.

FIGURE 19.

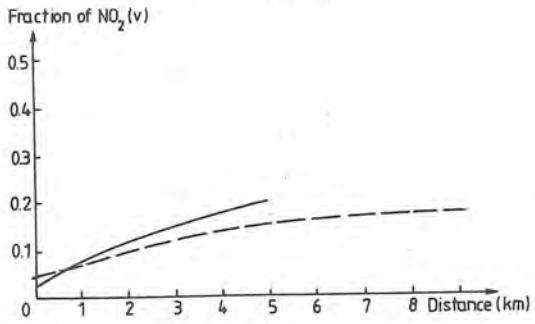
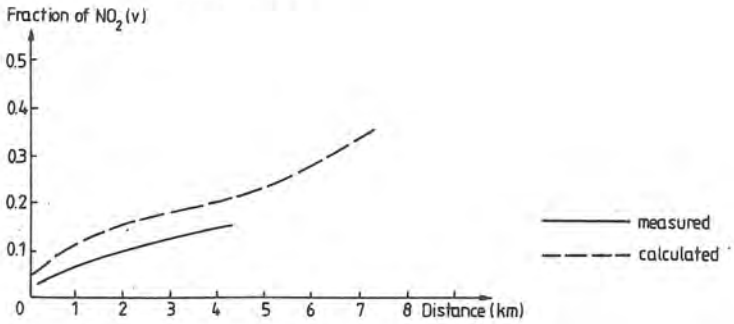


FIGURE 20.



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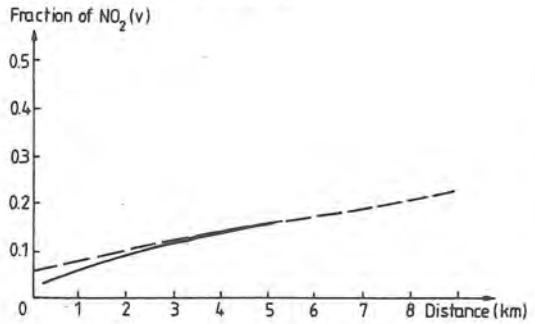
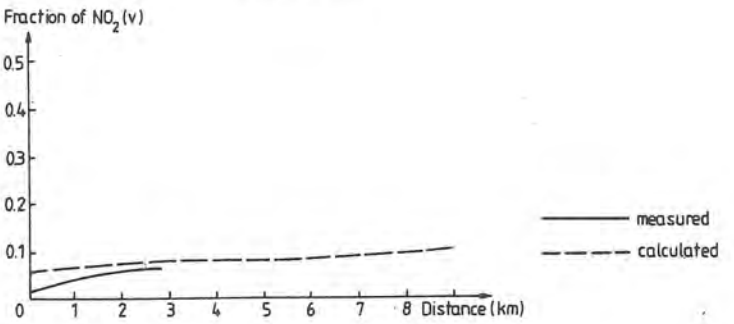


FIGURE 22.



FIGURES 19 - 22. See text on previous page.

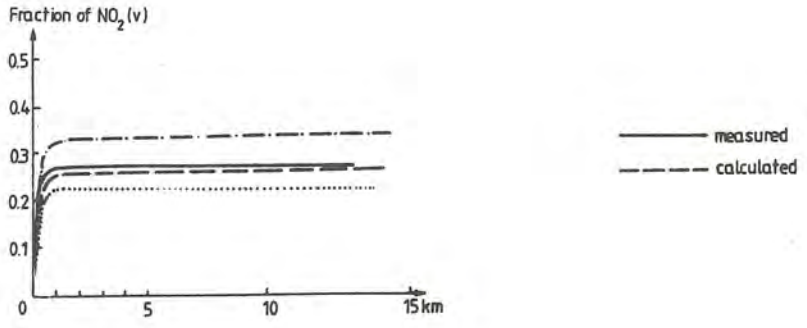


FIGURE 23. Comparison between calculated and measured NO_2-fractions in the plume for case no 23. Measured values indicated by ——. Calculated values assuming that the plume reached the inversion after 250 sec (780 m) indicated by · · · · ·, assuming 300 sec (930 m) indicated by - - - - - and assuming 400 sec (1 230 m) indicated by ooooo.

TABLE 4. Comparisons between measured and calculated NO_2-fractions (%-units of total NO_x) in plumes expressed in terms of mean values, standard deviations and correlation coefficients. Data from the Netherlands and West Germany have been used.

	Time after emission									
	100 s		200 s		400 s		600 s		1 000 s	
All cases	*Meas.*	*Calc.*	*Meas.*	*Calc.*	*Meas.*	*Calc.*	*Meas.*	*Calc.*	*Meas.*	*Calc.*
Mean NO_2-fraction (%)	13.5	11.8	21.5	18.5	30.6	29.5	37.2	39.7	48.4	53.8
Stand.dev.(%)	10.3	5.6	15.2	11.9	17.5	16.6	16.2	18.9	22.0	21.2
Corr.coef.	0.69		0.77		0.69		0.52		0.54	
All cases except case no 7	*Meas.*	*Calc.*	*Meas.*	*Calc.*	*Meas.*	*Calc.*	*Meas.*	*Calc.*	*Meas.*	*Calc.*
Mean NO_2-fraction (%)	14.1	11.7	22.1	18.2	31.4	28.7	38.3	38.4	51.3	51.1
Stand.dev.(%)	10.2	5.9	15.2	12.1	17.7	16.7	16.2	18.8	22.0	21.4
Corr.coef.	0.74		0.81		0.77		0.64		0.77	
No of cases	21		22		19		15		8	

3.4 Measurements from Finland

During the winter 1981 - 82 the Swedish Water and Air Pollution Research Laboratory (IVL) had two ground-based stations for continuous measurements of NO and NO_2 near Finnå power plant in a western suburb of Helsinki. During several short periods these stations were influenced by the plume of the Finnå power plant. These episodes, each with a length of 1/2 to 1 h, are presented in Table 3 together with detailed emission data, also obtained from IVL (Grennfelt, 1982), and meteorological data from a 300 m high mast in the area. The only ozone station available in the area was situated in central Helsinki and obviously often influenced by local NO-emission. Ozone-data from Helsinki (Landes, 1982) was therefore supplemented by ozone-data from Swedish background stations applied by means of a synoptic meteorological analysis. This may be regarded as a very uncertain method. However, the cases in Finland occurred during the winter when the ozone concentration was fairly constant, making it less critical for the calculations.

Table 5 shows that model calculations based on the observed stability in the rural environment always gave too high NO_x-concentrations in the plume compared to observed NO_x-concentrations. It is plausible that the stratification in the more urban areas around the measuring stations is more unstable than that near the meteorological mast, located in a rural area. Also, the fact

that the ground based stations were hit by the plume indicates that the stability was less stable than at the meteorological mast. In Table 5 the stability necessary to obtain a complete agreement between observed and calculated NO_X-concentrations in the plume is shown for each case.

Assuming complete agreement for NO_X-concentrations, we obtained the NO_2-fractions given in Figure 24. Calculations agree satisfactorily with observations, except for data from the day 1982-01-28. There is also a pronounced dependence on the NO_X-concentration in the plume. Low NO_X-concentration gives a high NO_2-fraction and vice versa. This clearly indicated that, in these cases, the entrainment of ambient ozone- and the O_3-reaction with NO controls the NO_2-production.

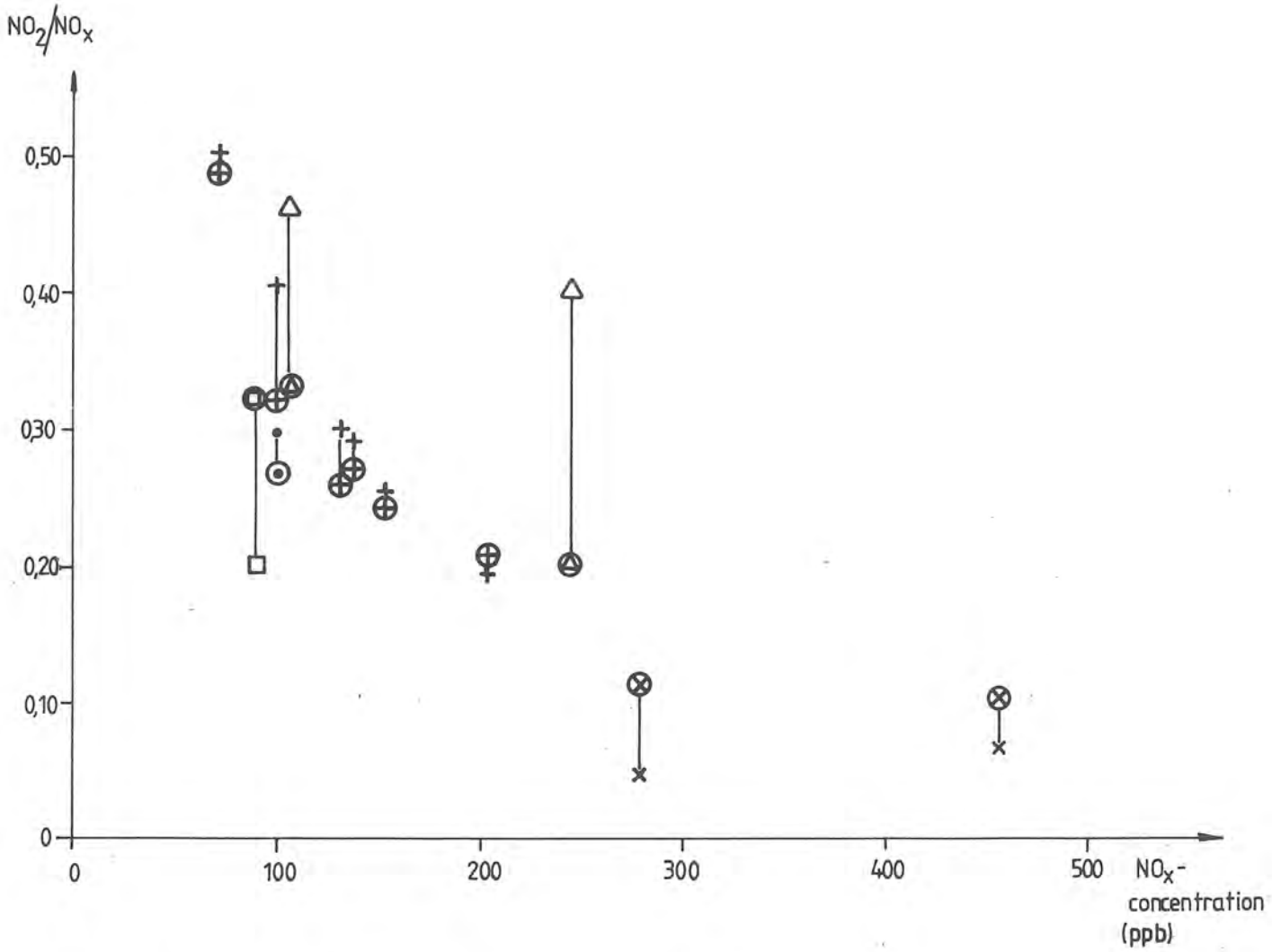


FIGURE 24. Observed and calculated NO_2/NO_X-ratio as a function of NO_X-concentration in the plume of Finnå. The stability in the calculation was adjusted to obtain complete agreement between observed and calculated NO_X-concentrations in the plume, cf Table 5. Measured values are circled while calculated values are not.

•	*1981-10-26*	+	*1982-01-13*
□	*1981-12-04*	Δ	*1982-01-28*
x	*1981-12-14*		

TABLE 5. Comparison between observed and calculated NO_x-concentrations during episodes when the Finnå power plant plume is affecting one of the measuring stations at a distance of 1 600 m or 2 000 m. Also the necessary stability assumption, which is needed in order to obtain agreement between observed and calculated NO_x-concentration in the plume, is given. Stability class DE indicates slightly stable (somewhere in between D and E, not exactly the same in each case).

Case no	Observed stability in rural environment	NO_x-concentration (ppb) in the instantaneous plume		Necessary stability for calculating same NO_x-conc. as observed
		Observed	Calculated	
24	E	101	155	DE
25	E	92	580	C
26	F	278	565	E
27	F	452	565	EF
28	E	71	342	D
28 a	E	139	342	DE
29	E	203	362	DE
29 a	E	152	362	DE
30	E	137	238	DE
30 a	E	101	238	DE
31	F	103	1 200	D
32	F	243	1 080	DE

3.5 Measurements from Denmark

Plume measurements of NO_2 around the Asnäs power plant outside Kalundborg were carried out by the Swedish Water and Air Pollution Research Laboratory (IVL) and are presented by Galle (1985). A remote sensing spectrometer, COSPEC, only operating on one compound at a time, was used. Two episodes during the day 1984-08-15 have been selected (cases 33 and 34 in Table 3). Stability and wind speed were determined according to the method presented in section 3.2.

In the present measurements only the total integrated NO_2 in a plume cross section could be determined, not the NO_2-fraction of total NO_x. In Figures 25 and 26 comparisons are made between calculated and measured NO_2-amounts in the plume. We can see that the values are of the same order of magnitude. However, for short distances, the measured amounts are smaller than those obtained from the model and vice versa for larger distances. In case no 33 the observed NO_2-amount at 10 km represents about 100% of the total NO_x-emission, assuming we have used the correct wind speed in the model. Similarly, the observed NO_2 amount represents about 90% of the total NO_x-emission at 14 km in case no 34.

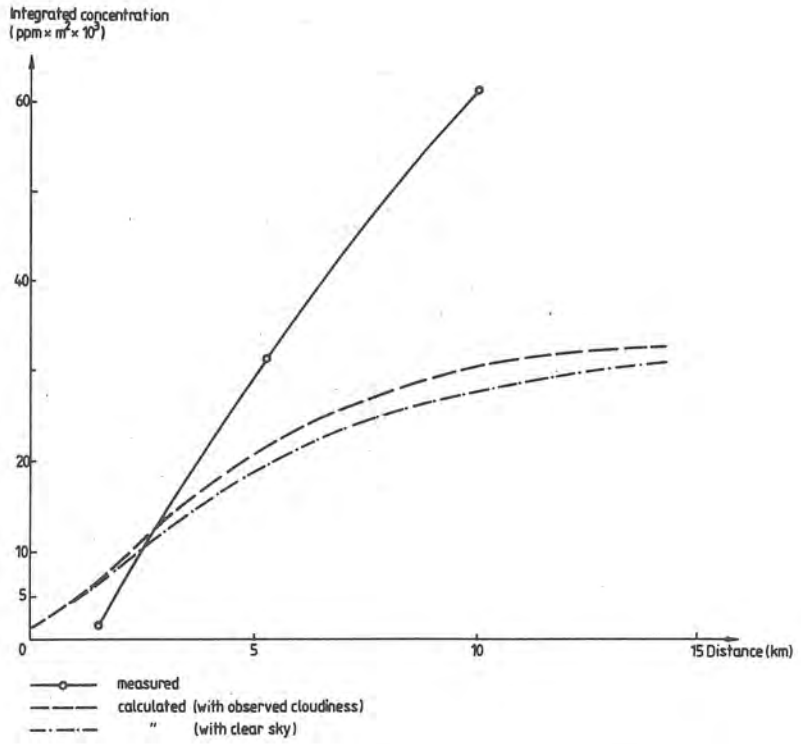


FIGURE 25. Comparison between measured and calculated integrated concentration of NO_2 as a function of distance from the source for case no 33.

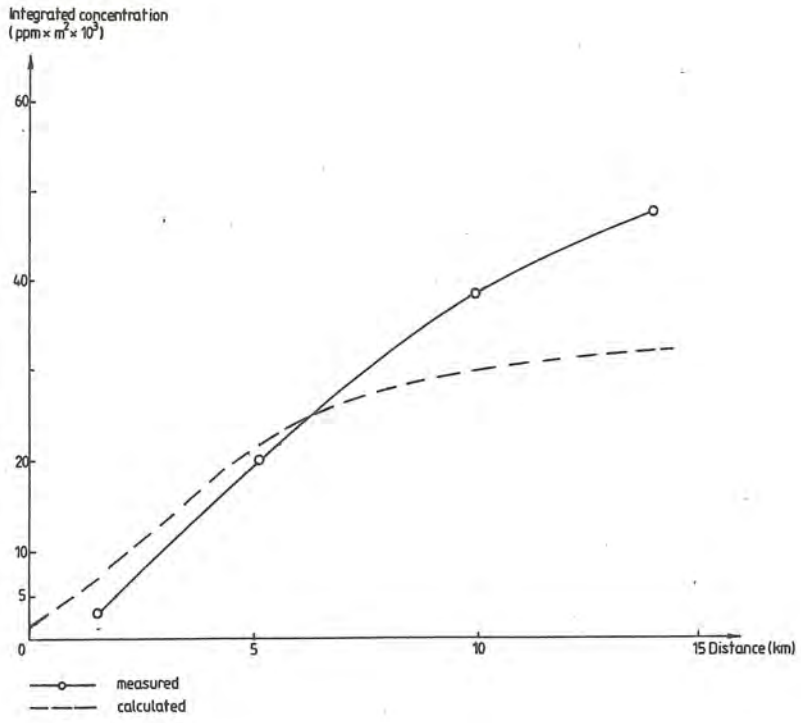


FIGURE 26. Comparison between measured and calculated integrated concentration of NO_2 as a function of distance from the source for case no 34.

Some possible explanations for the discrepancy are:

- The wind speed at plume level in the model is too strong at larger distances. It is possible that this can contribute somewhat, but it is unlikely to be the whole explanation. To get an agreement in case no 33, the wind speed has to be reduced by a factor of two at 10 km, which is very unlikely.

- Instrument defects.

- Deviations in the wind direction at plume level. The evaluation of data from the COSPEC requires a correction for the angle between the path used for traversing the plume and the travel direction of the plume.

- Interference from other NO_x-sources, which cannot be excluded in the present cases.

4. DISCUSSION OF THE MODEL

4.1 Limited sensitivity analysis

In the present study a few examples of sensitivity analysis in connection with the verification will be shown. The influence of stability in case no 12, Wilhelmshaven, is presented in Figure 12. Here the difference in NO_2-fraction is particularly large between stable and neutral stability. However, the features depend to a large degree on the combination of emission, ozone concentration and meteorology. Also, generally, the two meteorological factors stability and wind speed are of large importance.

In case no 23, where the plume is trapped in an inversion aloft, the time for the plume to reach the inversion is very important. In Figure 23 this effect is illustrated. No meteorological information is available to determine the exact position of the inversion, only a visual obervation that the plume was trapped in a very stable layer aloft.

The influence of cloudiness on the NO_2-fractions is normally of minor importance. An example is shown in Figure 25, where results for observed cloudiness of 6/8 high and medium high clouds are compared with results for clear sky.

The size of the emission is of great importance for the NO_2-ratio in the plume. Figure 27 gives an illustration of this obtained from the model.

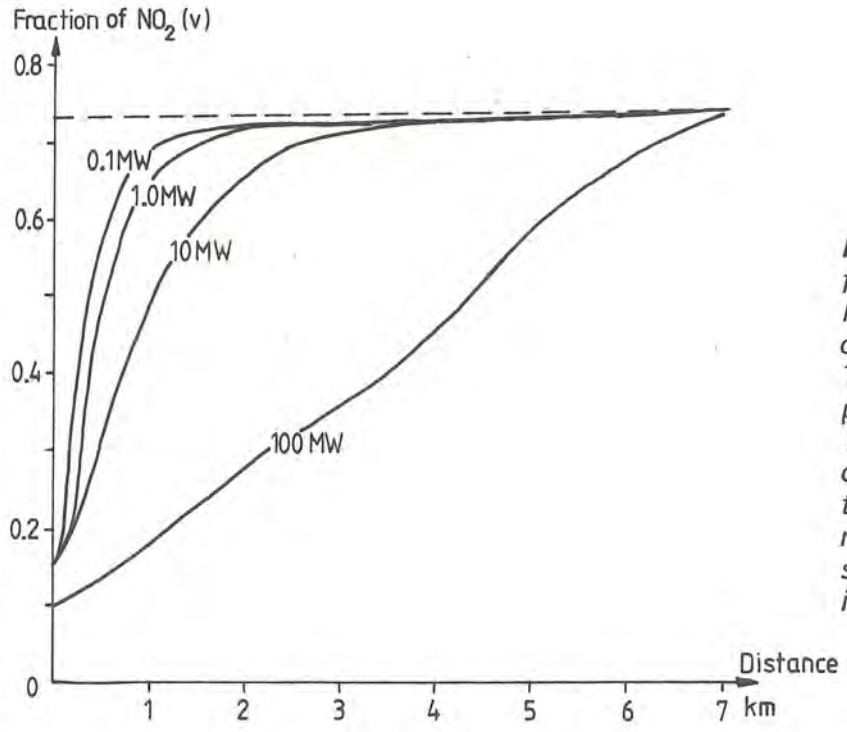


FIGURE 27. Calculated NO_2-fraction of the total emitted NO_X in the plume as a function of distance from the source. The curves refer to coal-fired plants of 0.1, 1.0, 10 and 100 MW respectively. The calculations were performed with the assumptions of normal meteorological conditions for southern Sweden at midday in springtime.

4.2 Deviations from photo-stationary equilibrium

The $NO_X - O_3$ system together with the incoming sunlight, described by reactions 1 - 3, create a photo-stationary equilibrium given by the equation

$$\psi = \frac{k_3[NO][O_3]}{j_1[NO_2]} = 1$$

when the mixing is complete and enough time has passed. Observed values of ψ are generally > 1 and it has been assumed to indicate inhomogeneous mixing of O_3-rich and NO-rich air. This problem is discussed and measured values are given by Elshout and Beilke (1984).

Some examples of ψ-values obtained from the present model calculations are presented in Figure 28. The ψ-values clearly deviate from 1 and decreases with larger distances. Calculations based on data from Finland show much larger ψ-values than those based on data from the Netherlands. Since the present model assumes homogeneous mixing within each cross-section of the plume, the calculated deviations from photo-stationary equilibrium are created only through different time rates for the entrainment and the chemical reactions. As long as the ψ-values are much larger than one, the chemical reactions in the plume must be slow compared to the entrainment. The higher values for the cases from Finland are probably caused by small dissociation rates due to low altitude of the sun.

Observed ψ-values by Elshout and Beilke are higher than those calculated by the model for the same cases from the Netherlands, as indicated in Figure 28. It is plausible to assume that the model assumption of instantaneous homogeneous mixing could create discrepancies. A real plume has a mixture of "plume-parcels" and "ambient air-parcels", which delays the mixing rate within the plume. This can lead to an increase in the ψ-values. However, our model calculations of NO- and NO_2-concentrations agree rather well with observed data from the Netherlands, as was shown in section 3. Therefore, the disagreement in the ψ-values could perhaps also be due to that the observed ψ-values from the Netherlands are based on smaller dissociation values or too high ozone values are measured in the plume.

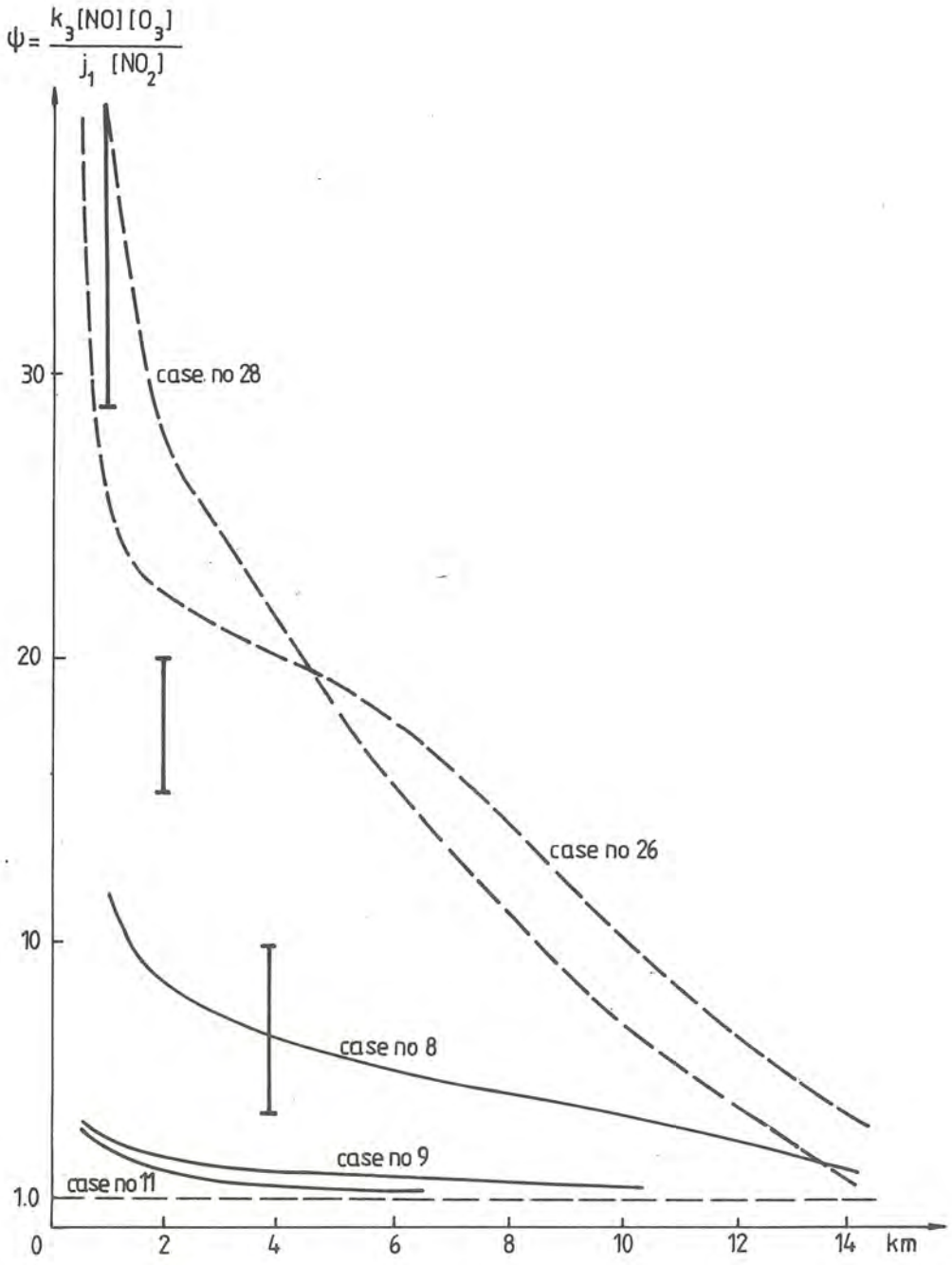


FIGURE 28. The photostationary state relationship in some plumes as a function of distance from the stack.

----- *calculated for two cases from Finland*

——— *calculated for three cases from the Netherlands*

I *observed interval for the same three cases from the Netherlands (Elshout and Beilke, 1984)*

4.3 Importance of the O_2-reaction

The importance of the O_2-reaction (reaction 4) has been discussed by several authors. Lindqvist et al (1982) have determined conversion rates for the reaction at different conditions, and results presented by Elshout and Bielke (1984) indicate that this reaction is of some importance for the power plant plumes studied in cases 1 - 12 in this verification. In Figure 29 a comparison between measured and calculated values of $[NO_2 - (O_3)]/NO_x$ is given. The excess of NO_2 with respect to the corresponding O_3 deficit can be assigned to the O_2-reaction. The other part of NO_2 is formed from the reactions of NO with O_3. The model calculation only gives a few extra %-units of NO_2 from the O_2-reaction, while measured values indicate more. The situations are similar for all cases 1 - 12. A reason for this discrepancy could be the model assumption of homogeneous mixing, which will be further discussed in the next section. However, an overestimate of measured O_3-concentration in the plume could also be of importance, which would be in agreement with the results for the photo-stationary ratio.

In order to test the importance of the O_2-reaction for the simulated NO_2-values in other situations than those included in the verification, we have performed some calculations for a rather large emission source. We assume flue gas emission of 200 Nm^3/s with 200 or 400 ppm NO_x and an ozone concentration of 30 ppb. Three different weather situations are represented in Figure 30. It is shown that the O_2-reaction is of large importance for the calculated NO_2-production when the stratification is very stable. With an emitted NO_x-concentration of 400 ppm more than 70% of the produced NO_2 at 1 500 sec comes from the O_2-reaction. For netural and, especially, unstable stratification the O_2-reaction is of little importance.

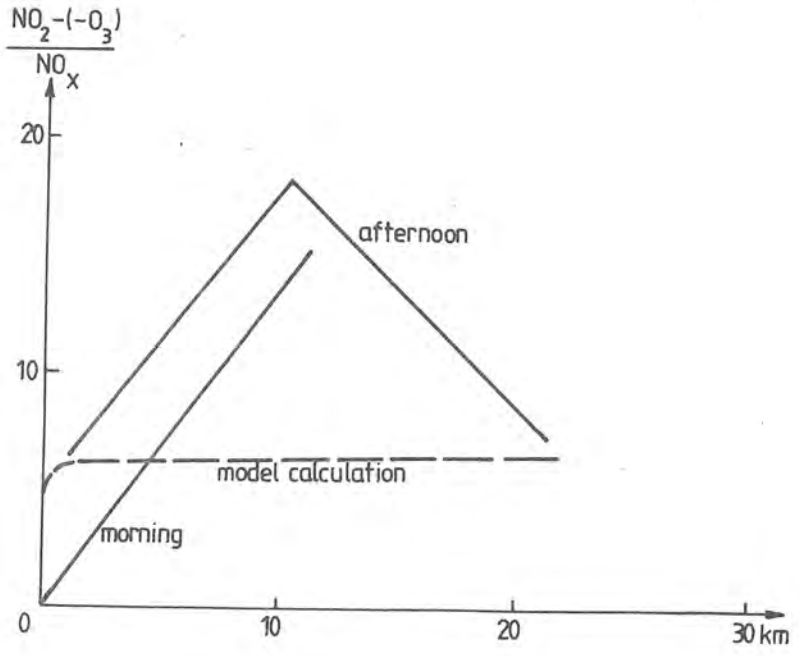


FIGURE 29. Comparison between measured and calculated amount of NO_2 produced by the O_2-reaction in case 12, Wilhelmshaven, cf text.

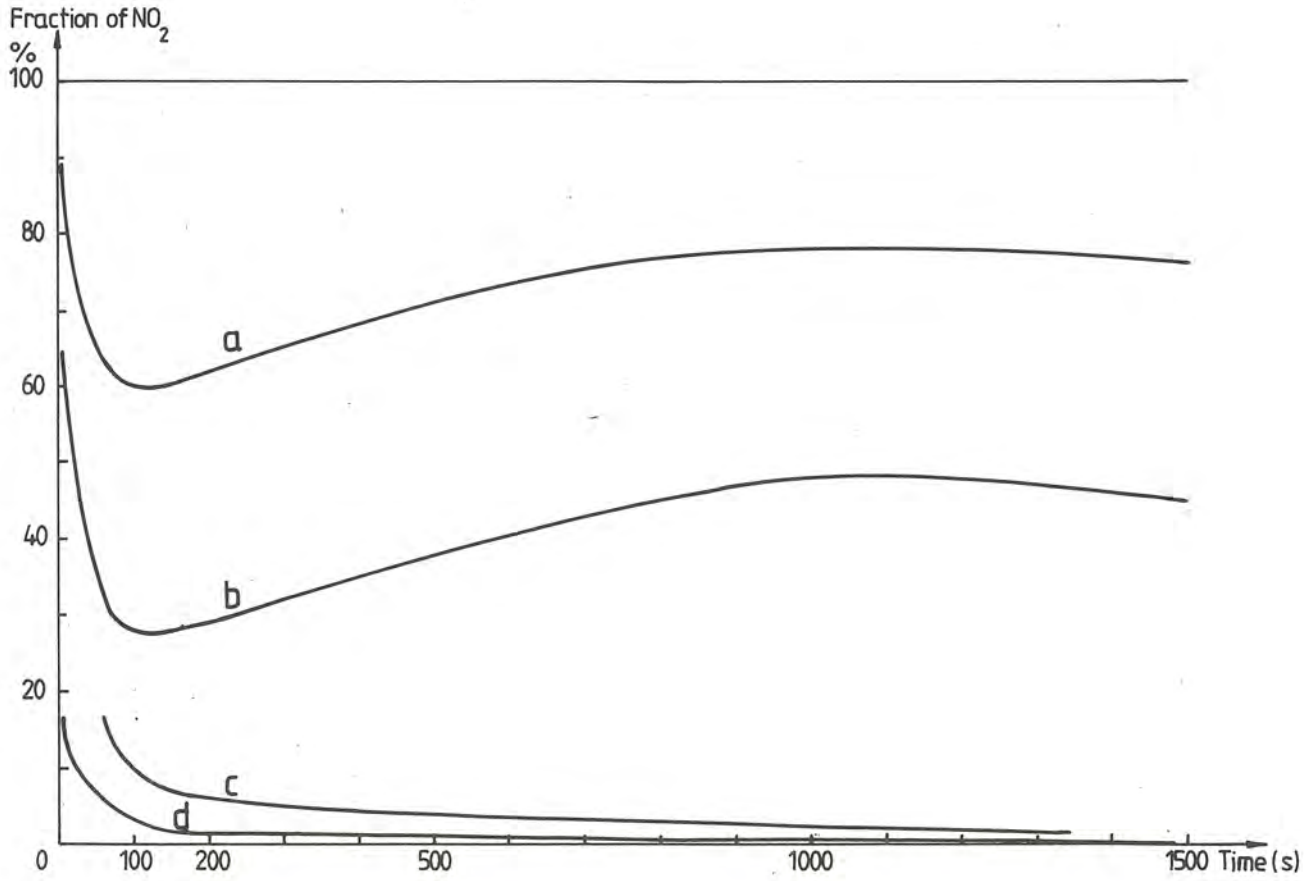


FIGURE 30. Calculated fraction (%) of NO_2 formed in the plume through the O_2-reaction, given as a function of time after emission. The curves represent the following four situations:

a) Night, wind speed at plume level = 4 m/s, very stable, NO_X = 400 ppm

b) Night, wind speed = 4 m/s, very stable, NO_X = 200 ppm

c) Day, wind speed = 10 m/s, neutral, NO_X = 200 ppm

d) Day, wind speed = 4 m/s, very unstable, NO_X = 200 ppm

4.4 Inhomogeneous mixing

The model assumption of homogeneous mixing within each cross-section of the plume may be critical in some cases, which has been pointed out in the discussions above. 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 e.g. NO and O_3 possible. It should be expected that the assumption of homogeneous mixing causes a somewhat faster (but not larger) formation of NO_2 through the O_3-reaction and a suppression of the formation through the O_2-reaction. The verification in this study of real power plant plumes shows, however, no pronounced systematic discrepancy, which can be attributed to the assumption of homogeneous mixing. The reason might be that in ordinary power plant plumes, under not too extreme weather conditions, these effects are too small to be revealed in a verification of this kind. It is possible that the effect on the O_3-reaction as a whole is small and the effect on the O_2-reaction is only of importance for high NO_x-concentrations in the emission and with very stable stratifications. In those situations the importance of inhomogeneous mixing can probably increase substantially.

A natural and convenient way of introducing inhomogeneous mixing in the model would be to deal with both "unmixed" and "mixed" flue gases and ambient air. The exchange between these boxes can, however, only be described from more extensive plume measurements.

In a paper by Georgopoulos and Seinfeld (1985) a mathematical model for calculating the instantaneous internal plume concentration variance is described. The method they suggest could be used to calculate concentration fluctuations in point-source plumes, which could be used for a more strict modelling of nonlinear chemical processes. But incorporating this method would involve an extensive mathematical solution.

5. CONCLUSIONS

The present verification shows that the model is capable of describing the NO_2-formation in power plant plumes in most weather situations in a fairly accurate way. No important systematic errors seem to be present and the correlation coefficient for NO_2-fractions of total NO_x in large power plant plumes is found to be about 0.7 out to at least 1 000 seconds after emission. It is important to note that the calculations are based only on routine meteorological data, emission data and ozone concentrations in the ambient air. Thus, the calculations have been performed in the same way as in the case of practical environmental planning, which gives a realistic picture of the potential of the model for practical applications.

It is not possible from the verification to find any systematic discrepancies in the results due to the assumption of homogeneous mixing within the plume. However, it is obvious that the inhomogeneity, which can be found in real plumes, should be very important in certain extreme weather situations. For more "normal" weather situations and ordinary power plant plumes, the inhomogeneity seems to be of minor importance for the NO_2-production.

A tentative modelling of the inhomogeneous mixing could easily be done through an introduction of two "boxes" in the plume: "unmixed flue gases" and "mixed plume". But this demands more measured data from plumes. Another interesting further development of the model would be to include the formation of other hazardeous compounds through the oxidation of ozone. For example the formation of water soluble mercury in plumes, where the emission mainly consists of the volatile mercury vapour (Hg^0).

6. ACKNOWLEDGEMENTS

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