STREET CANYON CONCENTRATIONS OF NITROGEN DIOXIDE IN OSLO.
MEASUREMENTS AND MODEL CALCULATIONS

BY

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ABSTRACT

Concentrations of NO_2 in excess of the frequently quoted exposure limit of 190-320 µg NO_2/m^3 as hourly mean, have repeatedly been recorded in a street in Oslo during the winter. In January 1981, the hourly mean concentrations exceeded 400 µg/m^3 on 7 days, the maximum was 540 µg/m^3. Summertime concentrations were much lower.

The spatial and temporal resolution of the NO_2 and NO_x concentration recordings strongly suggest that the high concentrations are associated with pockets of air of limited size. This points at a NO_2 production mechanism active before or just after the release of the exhaust gas. With a simple model of the combined effect of chemistry and dilution of the exhaust gas plume, it is shown that NO_2 generation through the reaction

$$NO + NO + O_2 \rightarrow NO_2 + NO_2$$
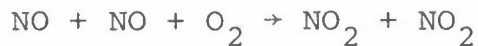
may explain some of the NO_2 formation. To account for the NO_2 measured, it is hypothesized that the NO_2 fraction of NO_x in car exhaust is much higher in the driving conditions found in Oslo during the winter, than what is recorded in the standard cycles for car exhaust emissions testing.

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1   INTRODUCTION

An international group of experts (1) has concluded that among the
oxides of nitrogen, only nitrogen dioxide have any significant
biological activity at ambient air concentration levels. Guide-
lines for the protection of public health has therefore been
developed only for nitrogen dioxide. A nitrogen dioxide concen-
tration of 940 μg/m^3 (0.5 ppm) has been selected as an estimate
of the lowest level at which adverse health effects due to short-
term exposure to nitrogen dioxide can be expected to occur. By
adopting a minimum safety factor of 3-5, the group of experts
agreed (1) that a maximum one hour exposure of 190-320 μg NO_2/m^3
(0.10-0.17 ppm) should be consistent with the protection of public
health and that this exposure should not be exceeded more than
once per month. A caution was added that it might be prudent to
lower the exposure limit in view of biological evidence of the
interaction of nitrogen dioxide with other air pollutants present,
and also in view of the fact that some populations are highly
sensitive to NO_2. No long term exposure limit has been suggested
due to lack of information on effects.

The exposure limit 190-320 μg NO_2/m^3 has been frequently exceeded
during the winter in street canyons in Oslo, as well as in other
cities in North Europe. As examples, an hourly mean concentration
of 540 μg/m^3 NO_2 was recorded in St. Olavs street in Oslo at
0900 h on 13 January 1981 (see Fig. 1), and 780 μg/m^3 of NO_2 was
measured in Gothenburg on 16 January 1980 on a downtown sampling
site, 20 m above the street level (2). At this site, more than
1000 μg NO_2/m^3 as hourly mean has been recorded on a number of
occasions during the last winters (Grennfelt, private communi-
cation). Kerbside air pollution measurements in London during the
years 1972-78 showed maximum hourly mean concentrations of NO_2 of
approx. 300 ppb (1 ppb of NO_2 is approx. 2 μg/m^3 of NO_2), with
the highest levels during the winter season (3). Measurements

in Frankfurt/M on a few winter days indicated average NO_2 concentrations as high as 240 ppb in the middle of the street for some categories of streets, with a substantial fall off towards the pavement (more than a factor 3) (4).

The monitoring of NO and NO_2 concentrations in a street canyon (St Olavs street) and a nearby rooftop in Oslo, has been carried out during selected winter and summer months for a few years. The highest NO_2 concentrations are found during the winter. In this study observations taken in January 1981 will be analysed, and a simple numerical model of the chemistry and turbulent mixing of the exhaust gases from vehicles will be presented.

2 NO_2 MEASUREMENTS

The concentrations of NO and NO_2 were monitored continuously during the time period December 1980-February 1981 on the pavement at a street level site in the center of Oslo, and at a nearby rooftop station assumed to be representative of the urban atmosphere away from the street canyons. The location of the sampling inlet is shown in Fig. 2. The measurements were made by cyclic chemiluminescence, where one detector operated in a cyclic mode in which the air alternatively passed through a NO_2 to NO converter or a bypass. The cycling time was 30 s, short enough to exclude the possibility of significant bias in measured NO_2 concentrations due to the separation in time between NO and NO_x measurement (5). The effect of the inlet residence time on the analysis as described in (6) was thought to be negligible, in particular during the winter when light intensities are low and the characteristic time for NO_2 dissociation rather long compared to the residence time of the air sample in the inlet of the instrument (5-10 s).

The instruments were calibrated in the laboratory and in the field by means of a NO_2 permeation tube system available commercially. The instrument output (NO_x and NO) was integrated to give hourly mean values by means of electronic integration, and the concentration of NO_2 was found by difference. Measurement errors in the

NO_2 concentration due to instrument drift and less than 100% efficiency of the converter, were thought to be less than 5%. The diurnal variation of the concentration of NO_2 (in $\mu g/m^3$) and the ratio NO_2/NO_x (volume) for all days in January 1981 when the NO_2 concentration exceeded 400 $\mu g/m^3$ as an average over one hour in St.Olavs street in Oslo, are shown in Fig. 1. This occurred on seven days, and the highest concentration was 540 $\mu g/m^3$ (13 January at 0900h).
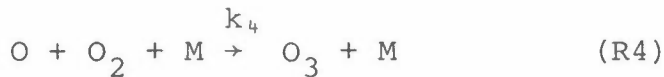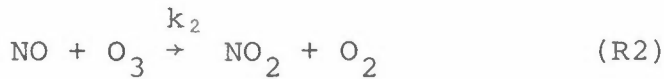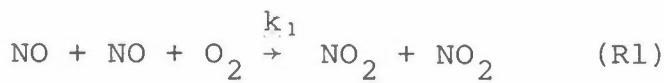
The daily maximum and minimum temperatures are also indicated at their times of occurrence, together with maximum and mean diurnal wind in ms^{-1} and degree of cloudiness expressed in fractions of 8, at 0700, 1300 and 1900 h. All the meteorological data were collected at The Norwegian Meteorological Institute approximately 2 km away from the site of measurement.

Several conclusions may be drawn from Fig. 1: The NO_2 concentration peaks were fairly well correlated with the peak in traffic density through the street. Temperature and cloudiness did not seem to influence the levels of NO_2 in a straightforward manner, because high NO_2 concentrations were found both on fairly warm (30 January) and cold days (26 January), in cloudy weather (21 January) and fairly clear weather (26 January). The winds were low on all the 7 days shown in Fig. 1, however, indicating that ventilation usually is poor on days with high NO_2 concentrations. The mean daily wind for the 7 days shown was less than 1 ms^{-1}, compared to 2.3 ms^{-1} for all of January. The ratio NO_2/NO_x stayed between .2 and .3 by volume when the NO_2 concentration was high on all the days shown in Fig. 1. This is a useful result, which is further illustrated in Fig. 3, where this ratio is plotted as a function of the NO_x concentration for January 1981 (upper curve). In the lower part of Fig. 3, the simultaneous NO_2 and NO_x concentrations obtained at rooftop are subtracted from street level NO_2 and NO_x, and the resulting NO_2/NO_x ratio plotted against NO_x. These concentrations are then believed to represent the immediate street contribution. It is fairly obvious that in this street approx. 25% is a fair estimate of the NO_2 fraction of NO_x by volume for medium to high NO_x concentrations during January 1981.

3 THE FORMATION OF NO$_2$ IN VEHICLE EXHAUST

A fairly simple model of the simultaneous effect of chemical
conversion of NO to NO$_2$ and turbulent dilution of the vehicle
exhaust plume was developed. It is rather similar to the power
plant plume model published by Schurath and Ruffing (7).

The formation of NO$_2$ in the exhaust gas was assumed to be
controlled by the reactions

$$NO + NO + O_2 \xrightarrow{k_1} NO_2 + NO_2 \qquad (R1)$$

$$NO + O_3 \xrightarrow{k_2} NO_2 + O_2 \qquad (R2)$$

$$NO_2 + h\nu \xrightarrow{J} NO + O \qquad (R3)$$

$$O + O_2 + M \xrightarrow{k_4} O_3 + M \qquad (R4)$$

The rate coefficients k_1, k_2 and k_4 as recommended by National
Bureau of Standards (9) are $6.6 \times 10^{-39} \exp(530/T)$ cm^6 molecules^{-2}
s^{-1}, $2.1 \times 10^{-12} \exp(-1480/T)$ cm^3 (molecule s)$^{-1}$ and $1.1 \times 10^{-34} \exp(510/T)$
$(510/T)$ cm^6 molecules^{-2}s^{-1}, respectively, where T is the tempera-
ture in K. Swedish studies (10) of the reaction R1 in polluted air,
summarized in (11), indicate that there is a significant contri-
bution to the oxidation of NO to NO$_2$ of reactions catalyzed on
street surface material, which gives an overall expression
$k_1 = 1.50 \times 10^{-40} \exp(1780/T)$ cm^{6}molecules^{-2}s^{-1} (11). k_1 at various
temperatures for the NBS-value and the catalyzed value are given
in Table 1.

Table 1: Values of k_1 at various temperatures.
Unit: cm^6 $molecule^{-2}s^{-1}$.

Temperature °C	k_1, NBS (9)	k_1, catalyzed (11)
12	4.2×10^{-38}	7.7×10^{-38}
0	4.6×10^{-38}	1.1×10^{-37}
-13	5.1×10^{-38}	1.4×10^{-37}

There is a factor 2 increase in k_1 in the catalyzed case when the temperature is lowered from $12^{O}C$ to $-13^{O}C$, while the difference is only about 20% for the values recommended by NBS.

The following system of equations is set up to describe the combined effect of chemistry and dilution with time in the exhaust gas plume:

$$\frac{D[NO]}{dt} = -k_1 [NO] [NO] [O_2] - k_2[NO] [O_3] - \frac{1}{V}\frac{DV}{dt}([NO]-[NO]_b) + J \cdot [NO_2] \tag{1}$$

$$\frac{D[NO_2]}{dt} = k_1 [NO] [NO] [O_2] + k_2[NO] [O_3] - J[NO_2] - \frac{1}{V}\frac{DV}{dt}([NO_2]-[NO_2]_b) \tag{2}$$

$$\frac{D[O_3]}{dt} = J[NO_2] - k_2[NO] [O_3] - \frac{1}{V}\frac{DV}{dt} ([O_3]-[O_3]_b) \tag{3}$$

$$\frac{D[O_2]}{dt} = -\frac{1}{V}\frac{DV}{dt} ([O_2]-[O_2]_b) \tag{4}$$

where brackets denote concentration.

D denotes the Lagrangian derivative along the trajectory of the exhaust gas puff. DV/dt is the Lagrangian derivative of the puff volume along its trajectory.

The initial conditions are

$[NO]_o$ = 1500 ppm, $[NO_2]_o$ = 0, $[O_3]_o$ = 35 ppb, $[O_2]_o$ = 5%.
Seinfeld (8, p.359) quoted 1500 ppm as a typical level of NO_x in
car exhaust. Swedish investigations (12) indicated that car
exhaust generally contained more than 2000 ppm of NO_x when driving
at speeds around 80 kmh^{-1}, 1200 ppm at 50 kmh^{-1}, and 500 ppm at
25 kmh^{-1}. The choice of 1500 ppm as initial NO_2 concentration
may therefore be an overestimate for the street canyon studied.

The background concentrations are

$[NO]_b$ = 225 ppb, $[NO_2]_b$ = 75 ppb, $[O_3]_b$ = 35 ppb, $[O_2]_b$ = 21%.
The values for $[NO]_b$ and $[NO_2]_b$ represented the average concen-
trations for 32 hours at a nearby rooftop measuring site in Oslo
from St.Olavs street, during the 7 days in January 1981 when the
NO_2 concentration in the street was highest.

In the model, the concentration of NO_x in the vehicle exhaust
was diluted to a level typical of a polluted situation in the
street canyon, after 100 s, by assuming that the amount of
initial NO_x was diluted 2500 times.

The amount of NO_2 formed through the reaction sequence R1-R4,
was critically dependent on how the mixing affected the NO
concentration during the initial few seconds after the release
from the exhaust pipe, and to what extent and for how long there
was an initial oxygen deficit. It is evident that the length
of the time period before the NO concentration drops significantly
is very important, since the square of the NO concentration
enters the rate equation for NO_2. To investigate how the NO_2
generation depends on the change of dilution with time, a number
of dilution functions were introduced. These are shown in Fig. 4.
For function 1, the dilution is very efficient initially,
resulting in a rapid decline in the NO concentration. For higher
function numbers, the length of time with a substantial NO
concentration in the exhaust gas plume increases.

In the ideal case with a stoichiometric air-fuel mixture, the combustion is complete with no oxygen or unburnt hydrocarbons in the exhaust. A more realistic measure for the oxygen content of exhaust is probably in the range 3-5% (8, p.360). The unburnt hydrocarbons were assumed not to play any role in the NO to NO_2 conversion in the street canyon. On a timescale of an hour or more in the sunlit atmosphere, conversion of NO to NO_2 through photochemical smog reactions is important. On the temporal scale of interest here, a few minutes only, the photochemical smog reactions were unimportant for the formation of NO_2 within the street canyon, but might indirectly influence the street canyon processes through the establishment of the roof top level of NO_2 (in this paper termed the background level of NO_2). To summarize, the following factors were thought to influence the NO_2 formation in vehicle exhaust in a street canyon, and were investigated further:

a) Choice of k_1 (NBS recommendations or catalyzed value)
b) Oxygen deficit initially in the exhaust gas
c) The degree of dilution and the intensity of mixing with time
d) Background concentrations of NO, NO_2 and O_3
e) The ratio of NO_2/NO_x in the exhaust emissions
f) Initial concentration of NO
g) Characteristic reaction time of the exhaust gases
h) Air temperature

With respect to point e), the NO_2/NO_x ratio in vehicle exhaust emissions seems to be quite variable, between 0 and 0.54 by volume from various mobile sources according to refs. 13-16. The ratio seems to be very close to zero in exhaust from vehicles equipped with internal gasoline combustion engines, and variable with respect to driving mode and make of car for diesel engines, with values up to 0.50 or more. NO_2/NO_x in diesel exhaust is low for full load driving conditions, higher at low load and reaching 0.56 for one make of cars during idle (14). This is an extreme value, however, with NO_2/NO_x ratios up to 0.05 or 0.10 by volume most commonly occurring in diesel exhaust.

The numerical solution of eq. (1)-(4) was not straightforward due to the highly variable time constants involved and the strong coupling in particular between eq. (1) and (2). To simplify the numerical integration, the following differential equations replaced eqs. 1 and 2 (17).

$$\frac{D[NO_x]}{dt} = -\frac{1}{V}\frac{DV}{dt}([NO_x] - [NO_x]_b) \tag{5}$$

where NO_x is the sum of NO and NO_2, and

$$\frac{D([O_3] - [NO])}{dt} = k_1 [NO][NO][O_2] - \frac{1}{V}\frac{DV}{dt}([O_3]-[NO]$$
$$- ([O_3]_b - [NO]_b)) \tag{6}$$

$[O_3]$ was calculated from eq. 3, [NO] from eq. 6, and $[NO_2]$ from eq. 5. Eqs. 3,4,5 and 6 were solved by a QSSA (Quasi-Steady State Approximation) technique described in ref. 17 and independently using a Gear-routine (18,19). The numerical error associated with the computations, was negligible.

4   RESULTS AND DISCUSSION

In Fig. 5 is shown the development with time of the concentrations of NO and NO_2 in the exhaust gas, for various dilution functions, in the case with temperature $0^{\circ}C$, and using the catalyzed value for k_1. In all cases the NO_x concentration after 100 s of integration, was the same (0.90 ppm). The NO_2 fraction varied with the development with time of the dilution, however, as shown in Fig. 6. Three processes contributed to the NO_2 concentration in the exhaust gas: I. Mixing with ambient air where the NO_2 concentration was 75 ppb. II. Reaction between NO and O_3 where, in a small fraction of a second, ozone (the ambient ozone level was here taken to be 35 ppb) was depleted and an equivalent amount of NO_2 was generated. Dilution and reaction between NO and O_3 consequently contributed approx 110 ppb of NO_2 in the runs shown in Figs. 5 and 6. III. The amount of NO_2 generated after 100 s through the

reaction between NO, NO and O_2 for a case where the reactions
R2-R4 were put to zero, is shown in Table 2.

Table 2: Amount of NO_2 generated through reaction R1 after
100 s. T = 273K, catalyzed value of k_1, $J = k_2 = 0$
(cpr. reactions R2, R3).

Dilution function	Amount of NO_2 formed (ppb)
1	3.5
2	4.4
3	26
4	33
5	40
6	53
7	56
8	94

It can be seen from Figs. 5 and 6 and Table 2 that the choice of
dilution function was critical for the formation of NO_2. Signi-
ficant quantities were formed only when the initial dilution is
slow enough to leave some time for reaction R1 to act efficiently.

In Fig. 6 it is shown how a fairly constant level of NO_2/NO_x is
reached quite rapidly. The ratio was typically 0.10-0.20, and
the NO_2 concentration after 100 s 110-200 ppb (Fig. 5). These
numbers are comparable to, or lower than, the measured NO_2-
concentrations and NO_2/NO_x ratios shown in Fig. 1 indicating that
the processes modelled contributed to the NO_2 generation in
St.Olavs street in Oslo.

The production of NO_2 in ppm/s through reaction R1 for various
dilution functions is shown in Fig. 7. A marked change occurred
when moving from function 2 to 3. For function 2 and lower, there
was a slight NO_2 formation initially, declining rapidly. For
functions 3 and higher, the high initial NO concentration was
maintained for a few seconds, leading to NO_2 formation. As the

mixing was intensified, the oxygen deficit was removed, leading
to a brief peak in the NO_2 production rate.

4.1 Factors influencing the NO_2 formation

The influence of the factors a)-h), discussed in section 3,
on the NO_2 formation in the vehicle exhaust, will now be addressed.

a. The NO_2 formation was much larger when the catalyzed value for
k_1 was applied. There was typically a threefold increase in
net NO_2 formation at 260K for the catalyzed case, compared to the
case where the NBS value for k_1 was used (Table 3). The NO_2/NO_x
went up as well, but it should be remembered that the total
NO_2 concentration was determined by the ambient level of NO_2,
the amount of NO oxidized through reaction with O_3, and the
contribution from reaction R1. As long as the two former
processes dominate, a sizeable increase in net NO_2 formation
through R1 does not give rise to much higher NO_2/NO_x ratios.

*Table 3: Net formation of NO_2 (in ppb) through reaction $NO+NO+O_2$
$\rightarrow NO_2 + NO_2$ (R1), after 100s of integration and 2500 times
dilution of the initial mixture (1500 ppm of NO, zero of
NO_2, 5% of O_2) of vehicle exhaust for two temperatures and
two choices of k_1. Ambient air concentrations are 225 ppb of
NO, 75 ppb of NO_2, 35 ppb of O_3. Also shown is the NO_2/NO_x
ratio (volume) in the exhaust after 100s.*

Dilution function no.	Net NO_2 formed (in ppb) NO_2/NO_x (volume), in paranthesis			
	273 K		260 K	
	k_1 (NBS)	k_1 (catalyzed)	k_1 (NBS)	k_1 (catalyzed)
1	0 (.12)	1.7 (.12)	0 (.12)	2.5 (.13)
2	0 (.12)	1.9 (.12)	0 (.12)	2.8 (.13)
3	8.1(.13)	22 (.15)	8.2 (.13)	30 (.16)
4	11(.13)	29 (.15)	12 (.14)	39 (.17)
5	14(.14)	35 (.16)	15 (.14)	48 (.18)
6	21(.15)	48 (.18)	22 (.15)	64 (.19)
7	21(.15)	50 (.18)	23 (.15)	67 (.20)
8	37(.16)	83 (.21)	39 (.17)	1.1×10^2(.24)

b. The initial molecular oxygen deficit in the vehicle exhaust exerted a controlling power on the intensity of NO_2 formation. In Table 4 is shown net NO_2 formation through reaction R1 in the case of zero oxygen initially, 5% which probably is fairly realistic, and ambient level.

Table 4: *Net NO_2 formation (in ppb) through reaction R1 for various levels of molecular oxygen initially: 0.5 and 21%, for T = 273K, catalyzed values of k_1, otherwise the same case as shown in Table 3.*

Dilution function	Initial oxygen (%)		
	0	5	21
1	1.6	1.7	2.0
2	1.7	1.9	2.3
3	17	22	37
4	17	29	64
5	16	35	89
6	15	48	1.3×10^2
7	34	50	97
8	68	83	1.3×10^2

c. The choice of dilution factor affects the NO_2 formation significantly, as is shown in Table 5.

Table 5: Influence of the dilution factor on the formation of NO_2, otherwise the same case as Table 4.

Dilution function	Dilution factor		
	1000	2500	5000
1	11 (.08)	1.7 (.12)	0 (.18)
2	13 (.08)	1.9 (.12)	0 (.18)
3	69 (.12)	22 (.15)	3.4 (.19)
4	81 (.13)	29 (.15)	6.9 (.19)
5	94 (.14)	35 (.16)	10 (.20)
6	1.2×10^2 (.15)	48 (.18)	17 (.21)
7	1.3×10^2 (.16)	50 (.18)	15 (.21)
8	2.0×10^2 (.20)	83 (.21)	30 (.23)
$k_1 = 0$	0 (.07)	0 (.12)	0 (.18)

The NO_2/NO_x ratios tended to rise as the dilution factor increased, but it should be kept in mind that a sizeable part of NO_2 was made up by the ambient air level (75 ppb) and NO_2 formed through reaction R2. The ratio between NO_2 generated through reaction R1 and total NO_x at the end of the integration decreased as the dilution factor increased.

d. The amount of NO_2 formed through reaction R1 was not significantly affected by the choice of ambient air concentration of NO, NO_2 or O_3. As long as the initial NO concentration in the exhaust was much larger than the ambient level (e.g., a factor 100), ambient air NO would not influence the NO_2 formation through R1 in the exhaust.

e. It was mentioned in section 3 that the initial NO_2/NO_x ratio in diesel exhaust depends on the make and condition of the car as well as the driving mode, with values as high as 0.50. Ratios in the range 0.05-0.10 seem to be typical for diesel engines, however.

Table 6: Influence of the choice of initial ratio NO_2/NO_x in the vehicle exhaust on the net NO_2 formation through reaction R1 (in ppb), otherwise as the case shown in Table 3 (T = 273K, catalyzed value for k_1).

Dilution function	Initial NO_2/NO_x (volume)		
	0	0.15	0.30
1	1.7	0	0
2	1.9	0	0
3	22	14	6.3
4	29	19	9.7
5	35	23	13
6	48	33	19
7	50	34	20
8	83	58	35

In table 6 is shown some results for the net NO_2 formation through reaction R1 when the initial NO_2 fraction of vehicle exhaust NO_x (1500 ppm) was varied. In the case with initial NO_2/NO_x equal to 0.30, only 1050 ppm of NO was available initially, and it can be seen that this causes a significant reduction in NO_2 formation through R1 where the NO concentration enters the rate expression in the square power. The total NO_2 concentration at the end of the integration increased with increasing initial NO_2/NO_x, however, from approximately the sum of 75 ppb (ambient NO_2) + 35 ppb (NO_2 formed through R2) + net generated through R1 in the case with zero NO_2 initially, to approximately 75 ppb + 35 ppb + 90 ppb (initial NO_2) + R1 in the case with 15% NO_2 initially, to approximately 75 pp + 35 ppb + 180 ppb + R1 in the case with 30% NO_2 of the total initial NO_x concentration in the car exhaust.

f. The results from Table 6 also give an indication about the significance of choice of initial NO concentration on the NO_2 formation through reaction R1. As the initial mixing became

very slow, the ratio between the amounts of NO_2 formed through R1 for various choices of initial NO_2/NO_x, approached the ratio between the square of the inital NO concentrations.

g. If the time required to dilute the vehicle exhaust to the street canyon concentration level was reduced, the NO_2 generation through R1 was reduced since the time period during which the NO concentration remained high, became shorter. Some numbers are given in Table 7, where the time required to dilute the exhaust 2500 times was reduced to 50s and increased to 200s.

Table 7: Net NO_2 formation (in ppb) through R1 after integrations of 50, 100s and 200s length, respectively, otherwise the same case as shown in Table 3 (273K, catalyzed value for k_1).

Dilution function	Time required to dilute 2500 times		
	50s	100s	200s
1	0	1.7	5.4
2	0	1.9	6.9
3	6.9	22	47
4	14	29	53
5	21	35	59
6	33	48	71
7	21	50	98
8	37	83	1.5×10^2

h. A lowering of the air temperature increased the value of k_1, and the formation of NO_2 through reaction R1 was consequently speeded up. This effect was discussed in point a) above.

5   CONCLUSIONS

This model study has shown that it is possible to identify gas
phase atmospheric processes (reactions R1 and R2) active also in
the dark, which may contribute significantly to the concentrations
of NO_2 found in street canyons. The intensity and time dependence
of the mixing of the vehicle exhaust has a critical influence
on the NO_2 formation through reaction R1, however, and only when
the mixing during the initial few seconds is extremely slow, does
reaction R1 contribute significantly to the NO_2 formation. The
effect of a decrease in temperature and the catalytic effect of
street surface material may increase the net NO_2 formation through
reaction R1 approx. 3 times at $-13^{O}C$ compared to the situation
in clean air at $0^{O}C$. This effect is even more pronounced if the
temperature is lowered further. The initial concentration of NO
is important for the NO_2 formation through R1 due to the quadratic
dependency on the NO concentration in the formation rate expression
for NO_2. It has a less than additive effect on the NO_2 concentration
if a fraction of NO_x initially is made up of NO_2. On the other
hand, changes in the ambient levels of NO, NO_2 or O_3 have only a
additive effect on the NO_2 concentration. The magnitude of the mole-
cular oxygen deficit initially in the vehicle exhaust has a
controlling effect on the NO_2 formation through reaction R1.
A lower limit of the amount of NO_2 that may be found in a street
canyon, can be found by just adding up the rooftop levels of NO_2
and O_3. To improve this estimate, a small fraction of the NO_x
found in the street canyon can be added, thought to represent
the contribution from reaction R1. Depending on the geometry and
the mixing conditions in the street canyon, this study indicates
that typically 5-10% of street level NO_x can be taken as NO_2 formed
through R1.

The time resolution of the recorded NO_2 concentrations indicated that the hourly mean values were made up of a number of peak values, representing exhaust puffs of various age and degree of dilution. The large spatial and temporal variability in the NO_2 concentrations point at a NO_2 production mechanism active before, or in the first seconds after, the release of the exhaust gas. It was concluded above that NO_2 formation through reaction R1 may contribute significantly to the NO_2 levels found in the street canyon, but only under extreme conditions with respect to initial mixing of the exhaust gas plume, would this contribution be substantial. The hypothesis is therefore put forward, that the NO_2 fraction of NO_x in car exhaust is much higher in the driving conditions found in Oslo during the winter, than what is recorded in the standard cycles for car exhaust emissions testing.
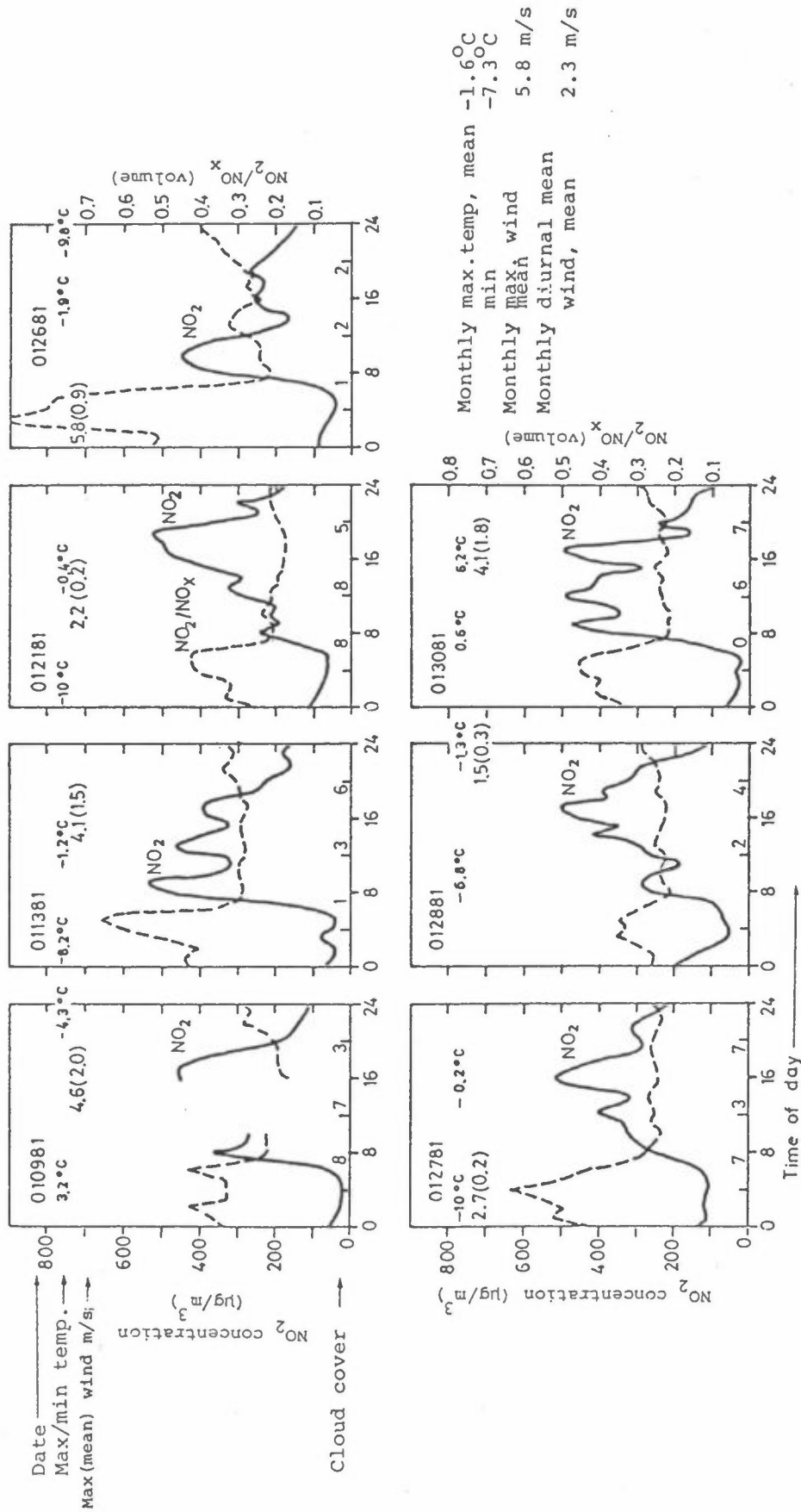
Figure 1: Street canyon measurements of NO_2 and NO_2/NO_x in St. Olavs street in Oslo, January 1981, for all days with hourly NO_2 maximum exceeding 400 $\mu g/m^3$. On the diagram is indicated date, max- and min temperature in °C together with time of occurrence, wind max and time of occurrence and diurnal mean wind in m/s, cloud cover in fractions of 8 at 7, 13 and 19 hrs. Also indicated is monthly mean max- and min temperature, max- and diurnal mean wind.
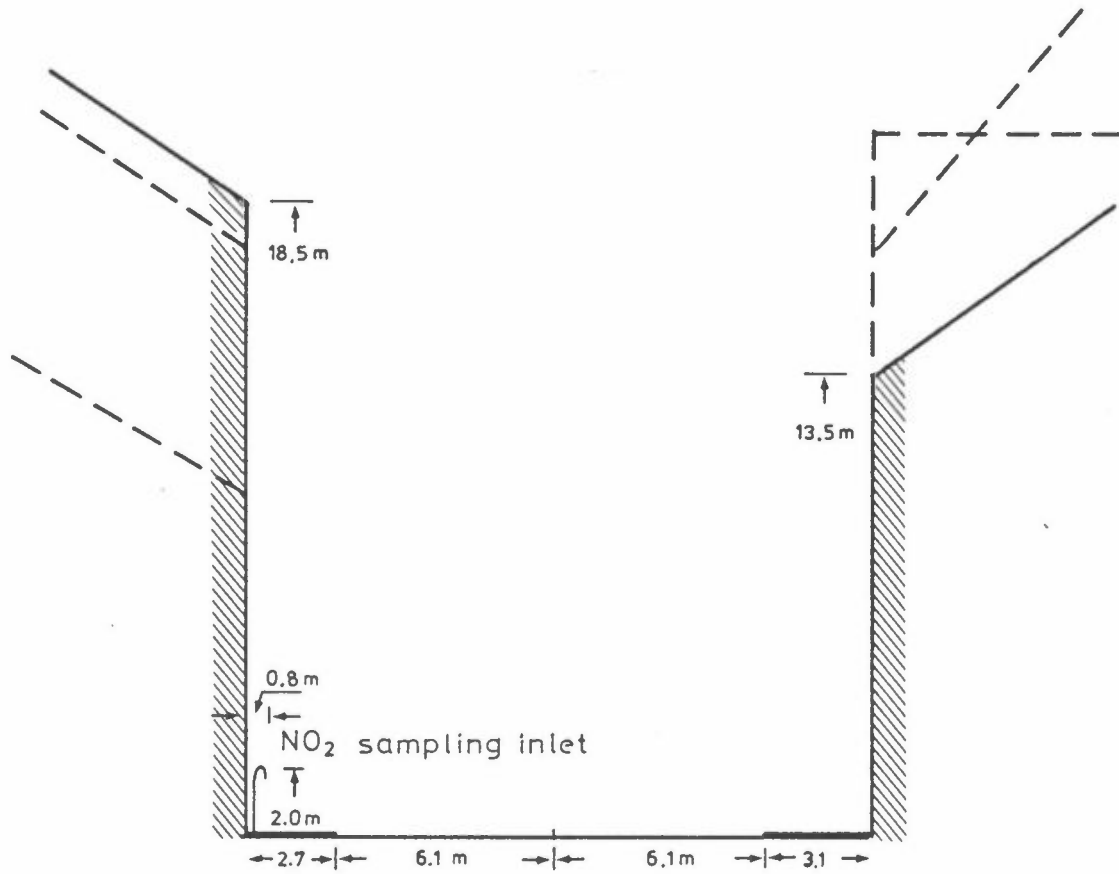
Figure 2: Location of the sampling site in the street canyon. Neighbouring rooftops are indicated.
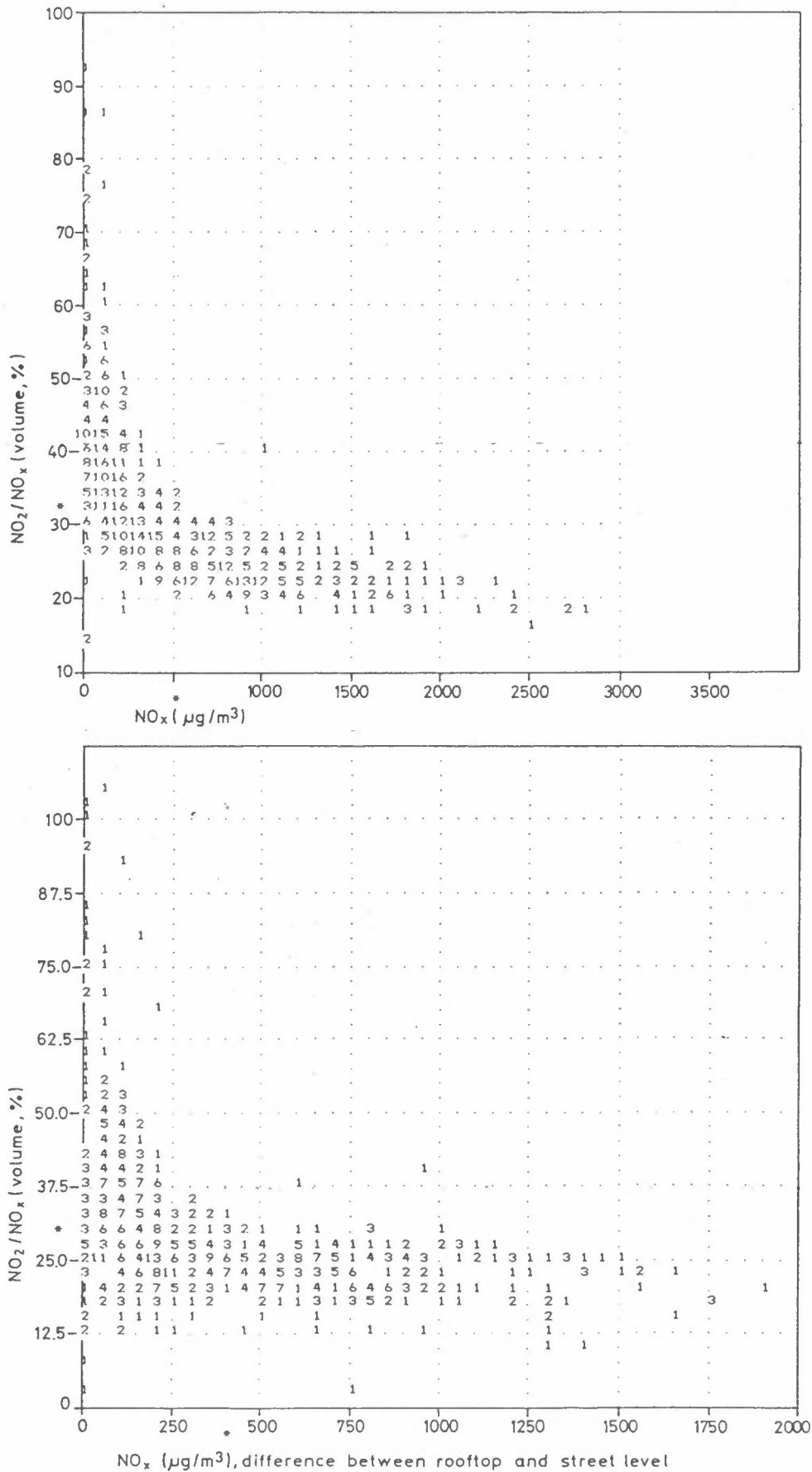
Figure 3: Street canyon measurements of the ratio NO_2/NO_x (by volume) as a function of the NO_x concentration for St. Olavs street in Oslo, January 1981. The numbers on the diagram indicate the number of observations with coordinates which coincide (upper part). In the lower part, NO_2/NO_x is shown as a function of NO_x where the measured roof top concentrations of NO_2 and NO_x are substracted to give what is thought to be the net contribution to the NO_2 and NO_x concentrations from vehicle exhaust in the street.
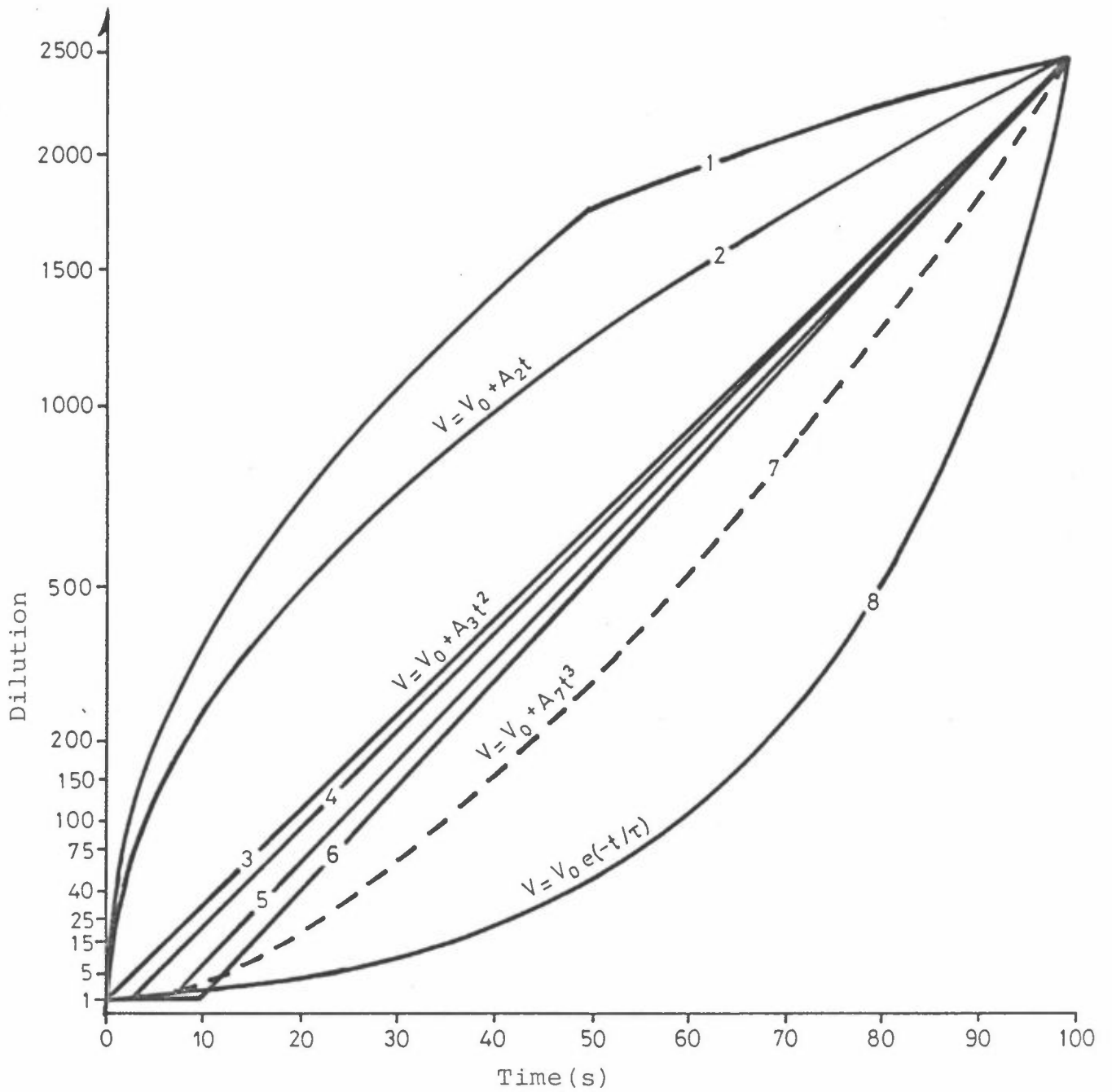
Figure 4: Dilution as a function of time, for 8 cases of exhaust puff volume development.
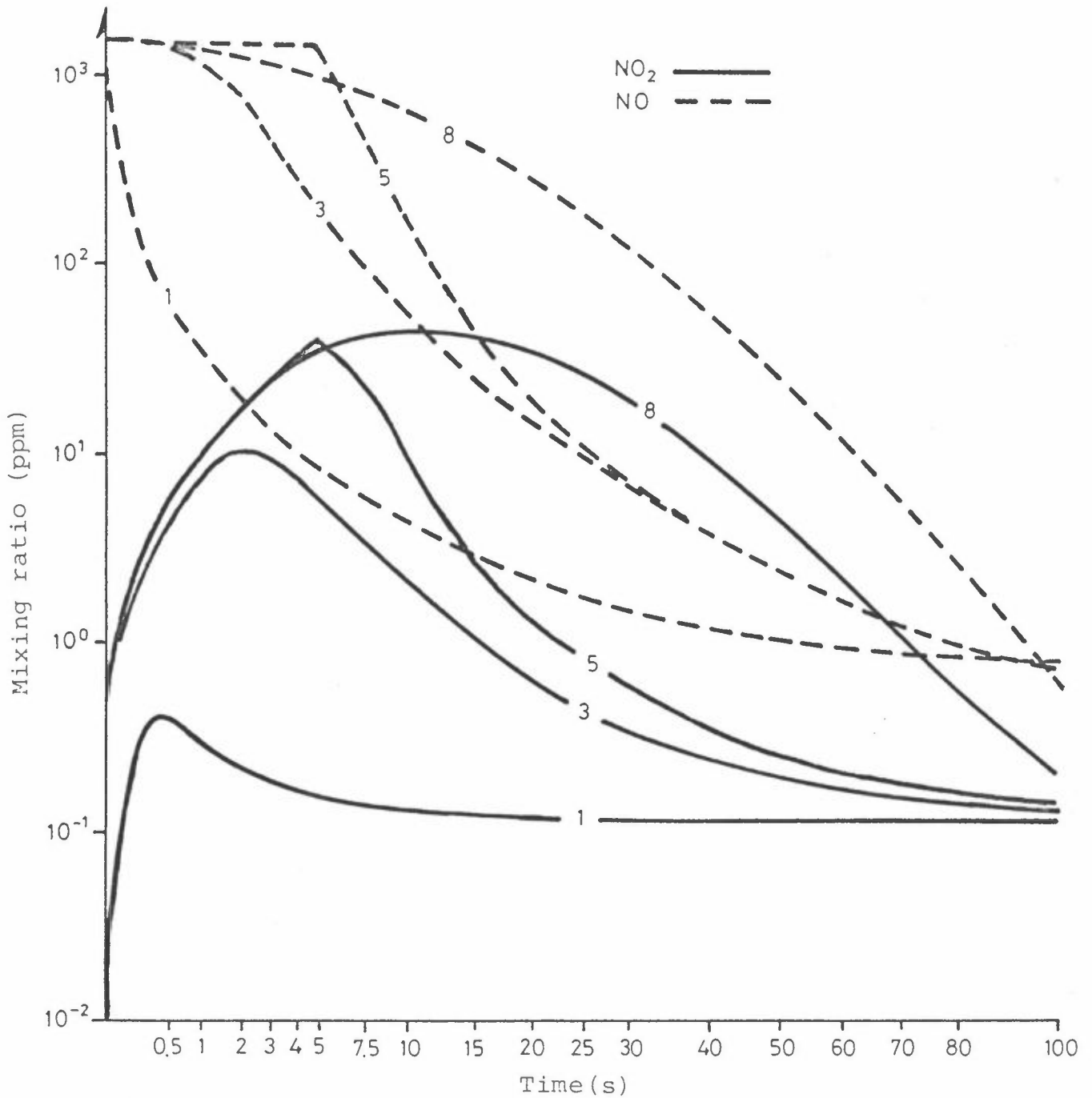
Figure 5: Calculated NO_2 and NO concentrations as a function of time for dilution functions 1,3,5 and 8 in a case with 1500 ppm of NO, zero NO_2 and 5% of O_2 present initially, the vehicle exhaust was diluted 2500 times in 100s. The ambient levels of NO, NO_2 and O_3 were 225, 75 and 35 ppb, respectively. The temperature was $0^\circ C$, and the catalyzed value for k_1 was applied.
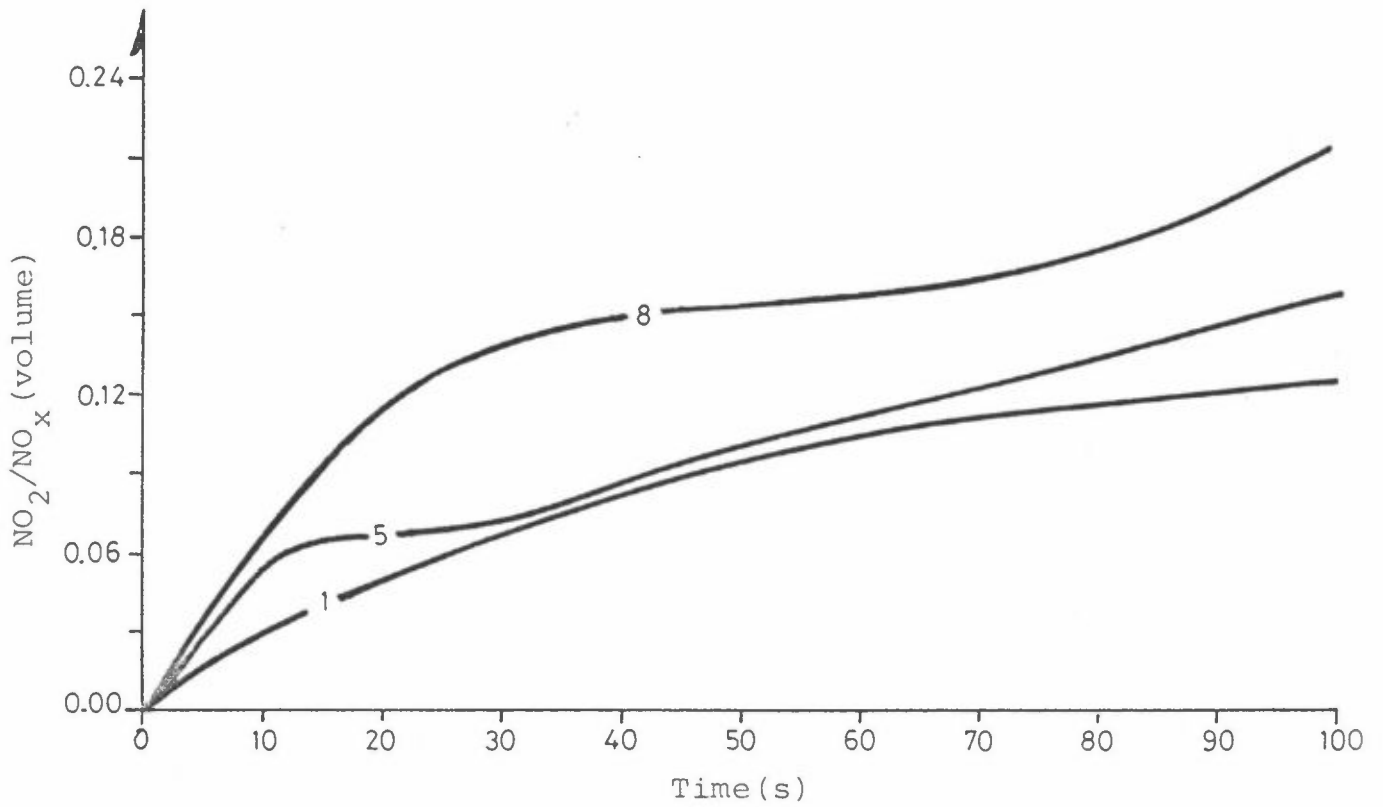
Figure 6: NO₂/NO_x (by volume) for dilution functions 1,5 and 8 for the same case as shown in Fig. 5.
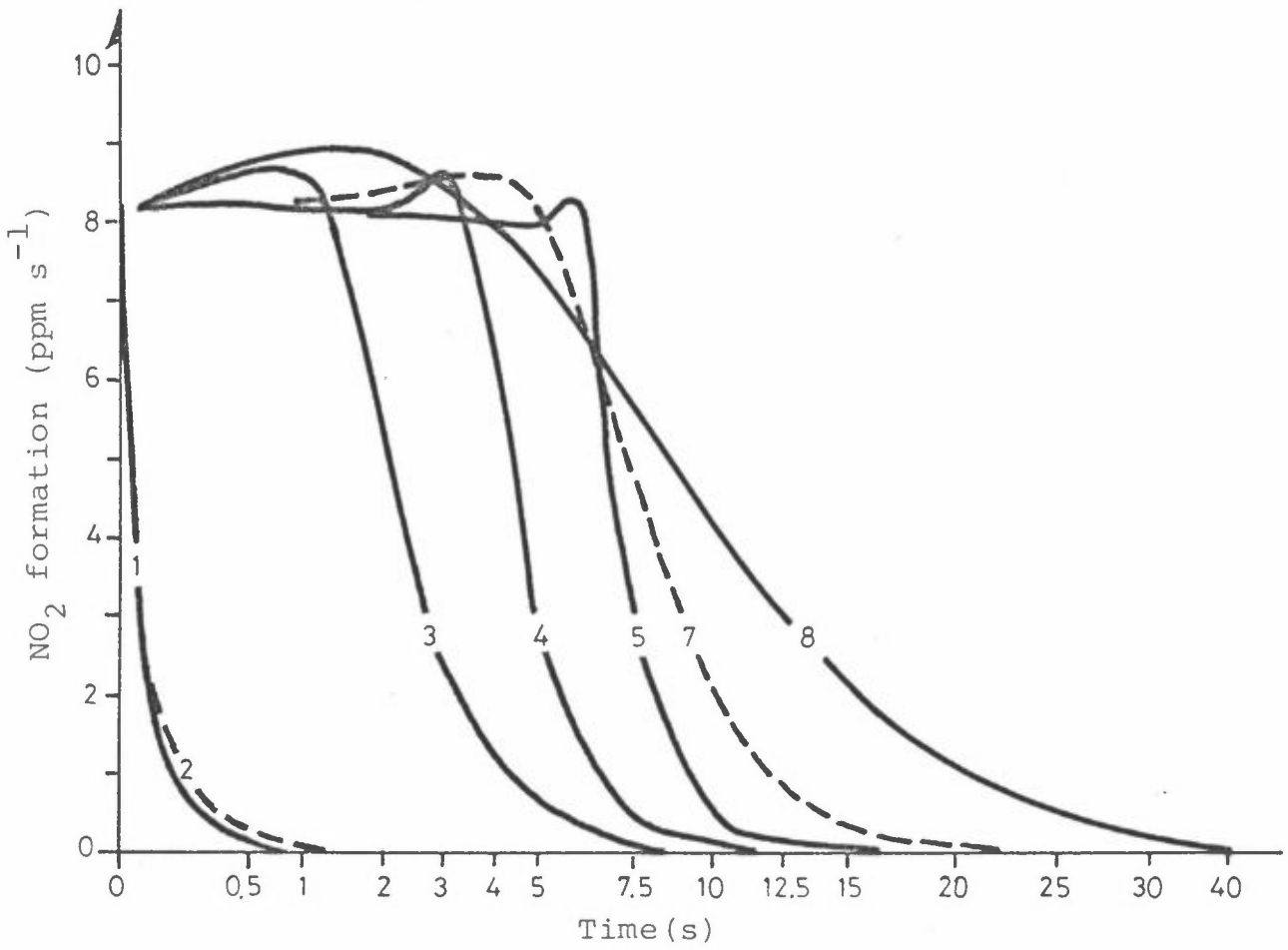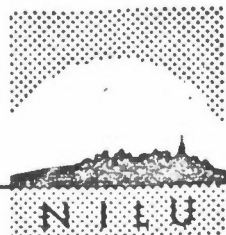
Figure 7: The rate of production of NO₂ through reaction R1 in ppm/s, as a function of time, for various dilution functions (indicated on the graphs), and for the same case as in Fig. 5.

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TITTEL	PROSJEKTLEDER Steinar Larssen
Street canyon concentrations of nitrogen dioxide in Oslo. Measurements and model calculations.	NILU PROSJEKT NR 20281

FORFATTER(E) Øystein Hov Steinar Larssen	TILGJENGELIGHET ** A
	OPPDRAGSGIVERS REF.

OPPDRAGSGIVER Statens forurensningstilsyn

3 STIKKORD (á maks.20 anslag)		
Nitrogendioksyd	Biltrafikk	Modell

REFERAT (maks. 300 anslag, 5-10 linjer)

Nitrogendioksyd (NO_2) ble målt i konsentrasjoner opp til 300 ppb som timesmiddel i St.Olavs gate i Oslo i januar 1981. NO_2 i gatenivå stammer trolig dels fra blanding med NO_2-holdig luft over gaten, dels dannes NO_2 gjennom reaksjonene $NO+O_3 \rightarrow NO_2+O_2$ og $NO+NO+O_2 \rightarrow NO_2+NO_2$, og dels slippes trolig NO_2 direkte ut med exhaust fra biltrafikken. Målingene viser at forholdet NO_2/NO_x lå i området 0.10-0.30 (volum) når konsentrasjonen av NO_2 var høy.

TITLE

ABSTRACT (max. 300 characters, 5-10 lines.

Nitrogen dioxide in the concentration ranges measured in a street canyon in Oslo in January 1981 (up to 300 ppb) is explained by a combination of mixing with aloft air, the reactions $NO+O_3 \rightarrow NO_2+O_2$ and $NO+NO++O_2 \rightarrow NO_2+NO_2$, and the direct release of NO_2 in the car exhaust. The measurements showed that the ratio NO_2/NO_x fell between 0.10 and 0.30 (volume) when the NO_2 concentration was high.