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LONG-RANGE TRANSPORT OF
PEROXYACETYLNITRATE TO SCANDINAVIA

BY

ØYSTEIN HOV

COMMISSIONED BY THE
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NORWEGIAN INSTITUTE FOR AIR RESEARCH
P.O.BOX 130, N-2001 LILLESTRØM
NORWAY

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PREFACE

Norwegian Institute for Air Research was asked by The Norwegian State Pollution Control Authority in a letter of 26 March 1982 to investigate the question of formation and transport of peroxyacetylnitrate (PAN) in the lower atmosphere. The project was formulated to be an "investigation of episodes with relatively high PAN-concentrations in the Oslo-area (possibly also in Grenland) to determine the extent of long-range transport compared to local formation".

ABSTRACT

Model studies kept together with measurements, have shown that PAN may be transported in polluted air masses from continental Europe or the British Isles to Scandinavia. The persistence of PAN was comparable to that of ozone in an ageing air mass when the temperatures were fairly low (5-10^o). At higher temperatures the thermal decomposition of PAN made the compound less persistent than ozone. Over land, the situation may be different since the ground removal is typically 3 times more efficient for ozone than for PAN.

PAN seemed to be only slightly perturbed when an ageing air mass was exposed to emissions of HC, NO_x or both, from area sources of moderate strength. The persistence of PAN was greater or comparable to that of ozone when an ageing air mass was exposed to NO_x emissions of strength comparable to what is found in urban areas.

During time periods when air masses accumulate HC and NO_x pollution from sources in Europe and then move towards Scandinavia without any synoptic scale break up of the atmospheric boundary layer (e.g. frontal passages), elevated PAN concentrations in southern Norway or Sweden in the range 1-5 ppb (1 ppb of PAN is equivalent to 5 µg/m³) may to a large extent be caused by long-range transport.

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LONG-RANGE TRANSPORT OF PEROXYACETYLNITRATE
TO SCANDINAVIA

1 INTRODUCTION

Long-range transport of air pollutants has been an important issue, scientifically and politically, in Western Europe and in North America since the end of the 1960's. In the OECD programme on long-range transport of air pollutants (LRTAP), it was concluded that "sulphur compounds do travel long distances (several hundred kilometers or more) in the atmosphere", and "the air quality in any one European country is measurably affected by emissions from other European countries". It was furthermore said that "In general the concentrations and the resulting total deposition of sulphur compounds are at a maximum in the major emission areas and decline with increasing distance from them. However, certain localised areas (e.g. southern Scandinavia and Switzerland) have higher total deposition figures than would be expected by their distance from the major sources", (OECD, 1977,1979). The conclusions in the LRTAP project were based on both measurements and model calculations.

In the beginning of the 1970's, the monitoring of ozone in north-western Europe provided evidence that ozone and its precursors, could be transported over long distances from their place of origin. The development of a method of analysis for halogenated hydrocarbons (gas chromatography with electron capture detector) made it possible to measure an anthropogenic tracer like trichlorofluoromethane (CCl_3F) together with ozone. In this way it was shown that concurrent high concentrations of ozone and CCl_3F could be found on remote sites with one day or more in transport time from the pollutant sources. Cox et al. (1975) and Cox (1977) report on such measurements from Adrigole in Southern Ireland on the Atlantic Coast. Later it was shown theoretically that ozone

has a chemical lifetime of one week or more in ageing air masses previously polluted with hydrocarbons and nitrogen oxides and moving over rural areas (Hov et al., 1978). The decay time of ozone is then determined by ground removal, which is fairly efficient during daytime over land, but very slow over sea surfaces. It has later been demonstrated both from trajectory analysis and in theoretical calculations, that long-range transport of ozone to Scandinavia is commonly occurring in the summer months. Sometimes the source regions of hydrocarbons and nitrogen oxides may be located several days and a thousand or more kilometers away (Schjoldager et al., 1981, Eliassen et al., 1982).

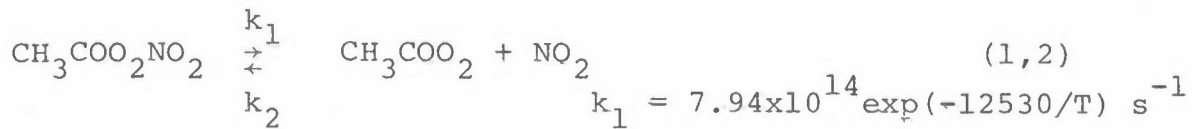
It has been demonstrated that also the precursors of ozone, hydrocarbons and nitrogen oxides, may be transported over long distances. Meridional crosssections taken along the Mid-Atlantic show that anthropogenic, low reactivity hydrocarbons like acetylene, ethane and propane accumulate in the lower troposphere at mid-latitudes in the Northern Hemisphere (Rudolph et al., 1982). The concentrations of more reactive hydrocarbons or the oxides of nitrogen do not show a similar behaviour. Their concentration distribution is rather a result of the balance between production and removal processes on a more limited spatial and temporal scale. The lifetime of the oxides of nitrogen is rather short (less than one or two days in the summer). Acidic nitrates, derived in the atmosphere from the oxides of nitrogen, may be transported over hundreds or perhaps thousands of kilometers, however. This is shown through the monitoring of the composition of precipitation over Europe and North America. Deposition rates of nitrate in precipitation over northeast Canada exceed local emission rates of NO_x from fossil fuels by factors as large as 10 (Logan, 1982). Another indication of the persistence of nitrate in the troposphere is given by measurements of gas phase and particulate nitrate in the atmospheric boundary layer and in the free troposphere over western North America and over the Pacific as far south as New Zealand. There is a pronounced maximum between 30° - 50° N latitude (Huebert and Lazrus, 1980).

The most abundant forms of odd nitrogen in the troposphere are probably NO, NO₂ (together denoted NO_x), NO₃, N₂O₅, HNO₂, HNO₃, HO₂NO₂ and peroxyacetylnitrate (PAN). The role of organic nitrate (PAN) in the lower troposphere outside industrial or urban areas has not been much investigated. PAN has been taken as an important indicator of photochemical smog formation, but its role in long-range transport of nitrogen species has not been much studied. The purpose of this paper is to examine the possibility of long-range transport of PAN, with transport from England or the European continent to southern Scandinavia as an example.

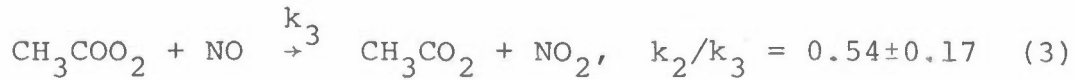
2 PREVIOUS STUDIES OF THE LONG-RANGE TRANSPORT OF PAN

It is only over the last 3-4 years that observations of the concentration of PAN have become available in Scandinavia. Nielsen et al. (1981) concluded from trajectory analysis and the measurement of ozone, PAN, visibility and particle count at several sites in Sweden and Denmark, that during so called "white episodes" (Brosset, 1976) with long-range transport of ozone and visibility-reducing aerosols (sulphates), high PAN concentration levels also occurred. The comparison of these PAN levels with those observed in optimal conditions for formation of PAN from local sources, indicated that long-range transport contributed substantially to the presence of PAN. A similar analysis of the PAN measurements done by NILU in Maridalen near Oslo, tend to support the conclusion that long-range transport of PAN to southern Scandinavia does occur (Schjoldager et al., 1983).

The kinetic studies by Cox and Roffey (1977) of the behaviour of PAN in a flow apparatus showed that the observed oxidation of NO to NO₂ in the presence of PAN and its dependence on the ratio [NO]/[NO₂], could be best explained if PAN exists in reversible equilibrium with its precursor species, i.e. the acetylperoxy radical and nitrogen dioxide:



Reaction 2 competes with reaction 3:



The acetoxy radical (CH_3CO_2) falls readily apart and forms CO_2 and a methyl radical (CH_3). When NO_2 is the dominant oxide of nitrogen present in the atmosphere, the decomposition of PAN is slower than the result of reaction 1 alone. If it is assumed that the acetylperoxy radical is in photochemical equilibrium, the rate at which PAN is destroyed because of reactions 1-3 is given by (Cox and Roffey, 1977):

$$\frac{d}{dt} \ln[\text{PAN}] = -k_1 \left\{ 1 - \frac{1}{1 + (k_3[\text{NO}]/k_2[\text{NO}_2])} \right\} \quad (i)$$

The chemical half-life of PAN for four typical atmospheric regimes, i.e. rural and urban air during daytime and nighttime, calculated from eq. (i) is given in Table 1 (reproduced from Cox and Roffey, 1977).

Table 1: Half-life (h) of PAN with respect to thermal decomposition for various atmospheric regimes. Figures in paranthesis indicate $[\text{NO}]/[\text{NO}_2]$ ratios applied (Cox and Roffey, 1977).

	Day 25°C	Night 15°C
Urban	2.7 (0.1)	2.8 (1.0)
Rural	0.7 (0.32)	∞ (0)

It is assumed that nitric oxide is completely removed by reaction with ozone in rural air at night. At night in urban air, the concentration of NO may exceed the amount of ozone necessary to oxidize all of NO to NO₂, and the ratio [NO]/[NO₂] may reach 1 or even higher. In this case reaction 1 is a measure of the actual loss of PAN. The daytime [NO]/[NO₂] ratios are estimated assuming the following photostationary state equation:

$$\frac{[\text{NO}][\text{O}_3]}{[\text{NO}_2]} = 16 \text{ ppb} \quad (\text{at } 298 \text{ K and } 45^\circ \text{ solar zenith angle}) \quad (\text{ii})$$

Using 160 and 50 ppb as urban and rural ozone concentrations, respectively, Cox and Roffey (1977) arrived at the [NO]/[NO₂] ratios given in Table 1. It is apparent that at nighttime in rural air, PAN is a stable compound in the atmosphere.

The strong temperature dependence of the thermal decomposition of PAN, led Crutzen (1979) to propose that the relatively long lifetime of organic nitrates in the middle and upper troposphere could lead to their transport to remote locations and influence the local NO_x chemistry. Model calculations have indicated that PAN may possibly be important in the chemistry of the remote troposphere (Isaksen, 1979; Singh and Hanst, 1981, Brewer et al., 1982). Particularly, as suggested by Singh and Hanst (1981), organic nitrogen oxides may be as much or more abundant as NO₂ or HNO₃. Organic nitrogen oxides are in chemical equilibrium with NO₂ (through reactions 1 and 2) and act as a reservoir of inorganic NO_x.

2.1 Precipitation scavenging of PAN

The stability of PAN in the atmosphere is determined by the combined efficiency of the removal mechanisms: gaseous processes, aerosol scavenging or dry deposition. With respect to the role of PAN in precipitation, the views have been rather diverse. Holdren et al., 1982, concluded from laboratory and field studies

that organic nitrogen compounds may significantly influence the chemistry of precipitation. Field studies carried out at a rural site in northeast Indiana during April 1981, showed that measurable levels of PAN were always present during the entire month. The average hourly PAN concentration was 0.46 ppb, and the levels only rarely dropped below 0.2 ppb. It was concluded that PAN is ubiquitous in the atmosphere, and at concentrations comparable to those for nitric acid (Holdren et al., 1982; Spicer et al., 1982; News Focus, 1982). It was further concluded that laboratory studies had demonstrated the solubility of PAN in rainwater where it gradually decays in solution to nitric acid and one or more organic products. The lifetime of PAN in water was 132 min at 5°C, 71 min at 15°C and 23 min at 25°C. Holdren et al. also concluded that it is likely that PAN can affect rainfall acidity by serving as an oxidizing agent where soluble gases such as SO₂ and NO₂ are oxidized to their strong acids in water droplets. The solubility of PAN in laboratory water led Logan (1982) to conclude that PAN would be removed from the atmosphere by aerosol processes so rapidly that it is unlikely that PAN from urban areas should persist long enough to contribute significantly to acidic nitrates in remote regions.

A different view is held by Cox and Penkett (1982). They state that it is most unlikely that PAN could be an important oxidant in atmospheric droplets. PAN is not readily taken up by water surfaces. Its measured deposition velocity to water surfaces is less than 0.05 cm/s (Garland and Penkett, 1976). Observations of PAN in the atmosphere at Harwell, UK, suggest that its concentration in the atmosphere remains stable in the presence of falling rain (D.H.F. Atkins, unpublished observations). In fact, the Battelle Columbus workers found the same in their records of PAN concentrations in rural air (Spicer 1982, private communication). The remarkable stability of the PAN concentrations found during the Battelle field study at the remote site in Illinois, indirectly support the view held by Cox and Penkett.

2.2 Dry deposition of PAN

Two extensive reviews of gaseous dry deposition have been published over the last 3-4 years (Garland, 1979, Sehmel, 1980). There is only one experimental determination of the dry deposition velocity of PAN (Garland and Penkett, 1976). Sehmel (1980) quotes only a calculated value of 0.8 cm/s for PAN deposition on an alfalfa surface, based on the work of Hill (1971). Garland and Penkett studied the dry deposition of PAN to grass, soil and water surfaces in a wind tunnel. Grass and soil were found to remove PAN with deposition velocity around 0.25 cm/s, but seawater and deionised water surfaces did not remove PAN at appreciable rates (< 0.02 cm/s).

It seems that the removal of PAN over water surfaces is negligible. Over land during night with low nocturnal inversion, a decline in the PAN concentration may be explained by the effect of ground removal.

Several authors have stated that PAN and PAN homologues are so stable under atmospheric conditions that e.g. PAN is considered a better indicator of photochemical air pollution than ozone, which is only partially a product of photochemical reactions in the troposphere (Nieboer and van Ham, 1976; Schurath and Wipprecht, 1979; Cox and Penkett, 1982).

3 MODELLING OF LONG-RANGE TRANSPORT OF PAN

Arguments based on trajectory analysis and measurements of PAN, O₃ and visibility, have been presented in support of long-range transport of PAN to several sites in Scandinavia (Nielsen et al., 1981, Schjoldager et al., 1983). From the discussion of the gas-phase stability of PAN (Cox and Roffey, 1977) the precipitation scavenging of PAN (Cox and Penkett, 1982) and the ground removal of PAN (Garland and Penkett, 1976) it can be concluded that PAN and its homologue species are rather stable in the atmosphere, with potential of being transported over long distances.

In the following, a model analysis will be presented of the persistence of peroxyacetyl nitrate in ageing air masses. A hypothetical case was considered. Emissions of hydrocarbons, nitrogen oxides and sulphur dioxide took place at a rate corresponding to estimated average UK emissions in 1975. The affected air mass was represented by a box thought to move slowly over the British Isles for approx. $2\frac{1}{2}$ days, and then it subsequently moved with the mean wind towards Scandinavia. In a fair weather situation with low winds, it may typically take two days before such an air mass reaches Scandinavia.

In the model calculation was used the available data on gas chemistry, persistence to wet removal and ground deposition efficiency, to describe the fate of PAN in an air mass which was moving across the British Isles towards Scandinavia.

3.1 Model description

The model applied was developed by Derwent and Hov (1979, 1980a, 1982). An illustration of the model is given in Fig. 1. It was a box type model in which instantaneous mixing of pollutants was assumed. The mixing height was taken as 1300 m, which was found to be the mean inversion height at midday during the three summer months based on balloon ascents at Cardington, Bedfordshire in England (Derwent and Hov, 1982).

The approach used to represent this situation in the model was the following. The mixing height was kept constant at 1300 m day and night. During the day, both primary and secondary species were deposited corresponding to their deposition velocities. During the night over land when a shallow, stable boundary layer was established, only primary species (i.e. those emitted) were assumed to be deposited. Secondary pollutants, like ozone and PAN, generated during the previous day(s), were assumed to have zero deposition rate at night. Only a small fraction of the total boundary layer column of secondary species is trapped underneath the nocturnal inversion over land, and even though these compounds may be completely depleted in the shallow layer

next to the ground during the night (Garland and Derwent, 1978), the influence on the total budget in the boundary layer is minimal (with a 40 m deep nocturnal boundary layer, only 40/1300 - 3% is depleted through deposition), and was disregarded in the present model approach. Over sea, the heat capacity of the ocean prevents a shallow nocturnal boundary layer to be established, and the deposition velocities were kept the same both day and night.

The assumption of horizontal homogeneity is only justified when the precursor sources are evenly distributed in space. Traffic and domestic emissions may satisfy this assumption rather well. In cases with large single sources, such as power plants and oil refineries, a realistic model picture should look more like an assembly of plumes which eventually may interact with each other, rather than a volume where all emissions interact all the time.

The assumption of complete mixing may therefore seem unrealistic. However, it is sufficient that the time scale of the various physical and chemical processes are represented correctly relative to each other. In the present model formulation this means that vertical and horizontal mixing must be faster than chemical development. It is well established that the time scale of oxidant generation is several hours or more. The assumption of instantaneous mixing therefore is reduced to the assumption that complete mixing takes less than a few hours to achieve. That assumption may be partially satisfied in photochemical episodes.

3.2 Mathematical formulation

Each model species should satisfy the continuity equation, written as

$$\frac{dC}{dt} = P_e + P_{ch} - (L_{ch} + L_d)C \quad (iii)$$

where C was the concentration of the compound in question, P_e emission term, P_{ch} and L_{ch} C chemical production and loss, and L_d C was the loss rate due to ground removal. The emission term

was defined as

$$P_e = \frac{\psi}{H} \quad (\text{iv})$$

where ψ was the emission flux of the species in question, and H was the mixing height. The deposition was defined as

$$L_d C = \frac{v_d}{H} C \quad (\text{v})$$

where v_d was the deposition velocity (see Table 2). The pollutants which were emitted, were assumed to be removed by dry deposition at night, while the secondary pollutants were assumed to be unaffected.

Table 2: Deposition velocities, cm/s.

Species	Over land		Over sea		References
	day	night	day	night	
O ₃	0.6	0	0	0	Garland and Derwent (1978).
SO ₂	0.8	0.8	0.8	0.8	Garland (1977)
HNO ₃	0.8	0.0	0.8	0.8	Same as for SO ₂
NO ₂	0.5	0	0	0	Grennfelt, private communication
PAN and homologues	0.2	0	0	0	Garland and Penkett (1976)
H ₂ SO ₄	0.1	0	0.1	0.1	Value appropriate for submicron particles

3.3 Numerical procedure

The chemical equations were solved by using a quasi-steady state approximation (QSSA) method (Hesstvedt et al., 1978). The accuracy of the results has been assessed by comparison runs with FACSIMILE, a variable order Gear's method with an error limit of 0.1% (Chance et al., 1977). The agreement between the QSSA-method and FACSIMILE, was better than 1% for most species, at a cost of CPU time about 1/3 of the requirements of FACSIMILE, and with very modest storage requirements (no Jacobians involved) (Derwent and Hov, 1979). The error limit on the results presented here is therefore approx. 1%.

The diurnal variation of solar fluxes was modelled, corresponding to summer at 50°N. The dissociation rates were calculated using the scheme developed by Isaksen et al. (1977). A diurnal variation in temperature (daily max 25°C, daily mean 16.8°C) and relative humidity was also included. Relative humidity was given a maximum value close to 85% around dawn and a minimum of 45% around noon.

3.4 Emissions

NO, SO₂, CO and various hydrocarbons were emitted into the model volume (see Table 3). The emissions of the various species were split into 8 source categories: (1) petrol-engined motor vehicle exhaust emissions, (2) diesel-engine emissions, (3) petrol-engine evaporative emissions, (4) stationary fuel combustion, (5) solvent usage, (6) industrial processes (except petrochemical industry), (7) petrochemical industry and (8) natural gas leakage. The emissions were calculated on an annual basis for 1975, generally using a combination of emission factors and statistics of total fuel consumption, or other relevant data. The detailed procedure and results are outlined elsewhere (Derwent and Hov, 1979), and the total emissions of each species are given in Table 3. The emissions were not given any diurnal variation in the model. This may be justified because the main interest was the development over several days, and not primarily the effects which occur on the time scale of few hours.

Table 3: Average U.K. emissions* in molecules $\text{cm}^{-2}\text{s}^{-1}$ (Derwent and Hov, 1979).

Species	Emission	Species	Emission
NO	2.81×10^{11}	CH ₃ CHO	4.94×10^8
SO ₂	4.23×10^{11}	C ₂ H ₅ CHO	3.70×10^8
CO	2.94×10^{12}	C ₃ H ₇ CHO	1.51×10^8
CH ₄	1.22×10^{12}	iC ₃ H ₇ CHO	6.79×10^7
C ₂ H ₆	4.07×10^{10}	C ₄ H ₉ CHO	3.46×10^7
C ₃ H ₈	8.64×10^9	CH ₃ COCH ₃	3.48×10^9
nC ₄ H ₁₀	2.19×10^9	CH ₃ COC ₂ H ₅	2.43×10^9
iC ₄ H ₁₀	9.88×10^9	methylpropylketone	1.24×10^7
nC ₅ H ₁₂	1.80×10^{10}	methyl-i-propylketone	1.24×10^7
iC ₅ H ₁₂	3.20×10^{10}	CH ₃ OH	1.24×10^7
C ₂ H ₄	2.56×10^{10}	C ₂ H ₅ OH	1.75×10^{10}
C ₃ H ₆	9.58×10^9	1-butene	3.30×10^9
C ₂ H ₂	2.41×10^{10}	2-butene	4.43×10^9
toluene	1.81×10^{10}	2-pentene	2.02×10^9
o-xylene	7.04×10^9	1-pentene	3.62×10^9
m-xylene	7.04×10^9	2-methyl-1-butene	3.12×10^9
p-xylene	7.04×10^9	3-methyl-1-butene	2.19×10^9
ethylbenzene	7.04×10^9	2-methyl-2-butene	5.04×10^9
HCHO	2.84×10^9	butylene	1.24×10^8
		benzaldehyde	3.87×10^8

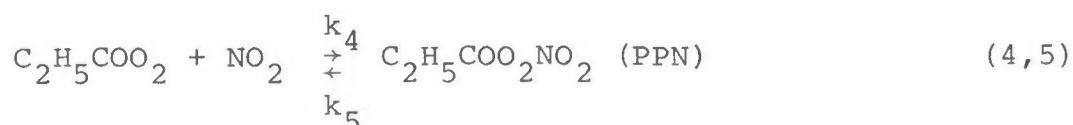
* Base year 1975.

3.5 Chemistry

The chemical formulation of the model included approx. 145 intermediate and end products, in addition to the 40 emitted species. About 300 reactions were required to describe the degradation pathways. A detailed discussion of the scheme was given by Derwent and Hov (1980a). Later revisions were based on the work by Atkinson et al. (1979,1982), Hampson and Garvin (1978), NASA (1981,1982) and McRae et al. (1982).

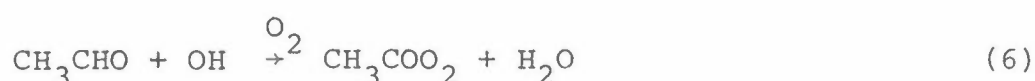
In the present work, the emphasis was put on the reaction pathways which led to the formation of peroxyacetylnitrate or its homologues.

The only known pathway to form PAN is through the reaction of acetylperoxy radicals with NO_2 (R2). Peroxypropionynitrate (PPN) is the most important homologue of PAN in the atmosphere, and is formed through the reaction

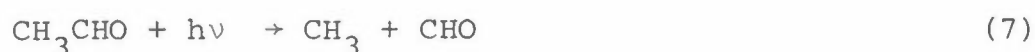


where k_4 and k_5 are assumed to be the same as k_1 and k_2 , respectively. Measurements at Harwell have regularly shown that the ratio between peaks of PAN and PPN is fairly constant, and is usually around 6-8 (Penkett et al., 1975). A number of homologues of PAN is probably formed in polluted air. The relative concentrations of a range of PAN homologues in a calculation of the chemistry in the London urban plume 4 h downwind of the city, are shown in Fig. 2 (Derwent and Hov, 1979).

Acetylperoxy radicals are mainly formed through the reaction between acetaldehyde and the hydroxyl radical:

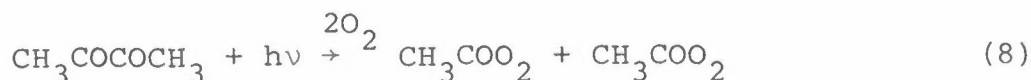


Acetaldehyde is a common aldehyde in the atmosphere, usually second in concentration only to formaldehyde. It is an important intermediate species in the decomposition chains of most of the hydrocarbons in the atmosphere, and it has a halflife of typically 6-10 h in sunlight. An equally important decomposition pathway is through photodissociation:



The two radicals formed, do not affect the formation of PAN directly. In polluted air typically one half of the acetaldehyde molecules lead to the formation of acetylperoxy radicals.

Biacetyl is an important intermediate species during the decomposition of o-xylene in the atmosphere. Biacetyl is readily photolysed (half-life less than 1 h in sunshine) forming two acetylperoxy radicals:



Widely differing degradation pathways are available to the different hydrocarbons included in the chemical model (Table 3). Ozone production requires the production of peroxy radicals in the hydrocarbon degradation, a condition which is generally satisfied. PAN can only be formed from a particular hydrocarbon if it produces an acetylperoxy radical in its degradation. Methane and acetylene do not have the required structure, for example. The 36 nonmethane hydrocarbons in the model have a fairly even distribution with respect to ozone production, while a much more uneven distribution is observed for PAN (Derwent and Hov, 1980b). This means that a correct composition of the hydrocarbon emissions in the model is very important for a satisfactory calculation of the absolute concentration of PAN, while it is less critical for ozone. The significance of the choice of the nonmethane hydrocarbon emissions is treated in the following section (Hov, 1982).

3.6 Composition of nonmethane hydrocarbon emissions

The composition of the hydrocarbon emissions from important source categories, like motor vehicles, is very complex, and may vary with mode of driving, composition of gasoline, condition of the engine etc. The most reasonable approach in model work may be to represent the hydrocarbon precursor mixture by just a few of the most abundant species. The way in which the selection of such a representative hydrocarbon mixture is made, however, has a significant influence on the overall model results. This will be discussed in this section.

Six simplified compositions were selected, two of them taken from EPA publications (mixtures No. 4 and 6, see legend of Table 4). Four others were constructed, usually with five hydrocarbons. For some mixtures, the dividing lines between the amounts attributed to each species were drawn on the basis of the reactivity distribution of the original UK inventory. Reactivity of a hydrocarbon is only one aspect of the secondary pollutant generation, however. Other important factors describe the stoichiometry, that is how much of a given pollutant is generated per hydrocarbon degraded, and inventory, that is how much is emitted of a given hydrocarbon species.

Comparison of the performance of the various mixtures was done for a situation where the development of each mixture was followed for 7½ days. The total hydrocarbon emissions were identical for all mixtures on a mass basis, equal to the average UK-1975 release.

In Table 4 is given the peak or near-peak concentration of ozone, PAN and hydroxyl for every day for the UK mixture (No. 1), and for all the other 6 mixtures relative to the UK case. In Table 4 is also given the geometric mean of the ratios for the whole period.

The performance relative to the UK mixture is seen to be quite dependent on time, with the largest discrepancies on days 2 and 3.

Table 4: Model calculations for 8 days of ozone, PAN and hydroxyl. All calculations were done with identical emissions on a mass basis, equal to the UK release for 1975 (Derwent and Hov, 1979). The calculations were done with 7 different compositions of the hydrocarbon emissions, and started at tropospheric background concentrations at 12 am on day No. 1.

Mixture No.	Composition
1	UK emissions for 1975, the hydrocarbons distributed among 35 species.
2	20% of total hydrocarbon on each of C_3H_8 , nC_4H_{10} , C_2H_4 , C_3H_6 and <i>m</i> -xylene.
3	C_3H_8 , nC_4H_{10} , C_2H_4 , C_3H_6 and <i>m</i> -xylene distributed according to reactivity to represent the total NMHC spectrum as estimated for mixture 1 (Hov and Derwent, 1981).
4	25% as C_3H_8 , 75% as nC_4H_{10} , 2% as CH_3CHO and 1% as $HCHO$ on a C basis (Dodge, 1977).
5	UK mixture distributed among C_3H_6 , nC_4H_{10} , $HCHO$ and CH_3CHO according to reactivity.
6	"Urban mix" as recommended by Glasson and Wendschuh, 1977 (9.2% as C_2H_6 , 18.3% as C_3H_8 , 23% as nC_4H_{10} , 10.3% as iC_5H_{12} , 11.6% as C_2H_4 , 8.2% as C_3H_6 , 13.6% as toluene, 5.3% as <i>m</i> -xylene).
7	30% as C_2H_6 , 10% as nC_4H_{10} , 20% as C_2H_4 , 10% as C_3H_6 , 30% as <i>m</i> -xylene.

Ozone at 6 pm

Hydrocarbon mixture No.	1	2	3	4	5	6	7
Day No.	ppb	Concentration ratio relative to mixture 1					
1	8.2	1.13	1.05	1.16	1.33	0.91	1.07
2	35.7	1.56	1.33	1.37	1.80	.85	1.46
3	74.5	1.28	1.21	1.25	1.39	.89	1.23
4	108.6	1.12	1.10	1.14	1.19	.99	1.09
5	129.8	1.08	1.08	1.12	1.13	1.03	1.05
6	144.3	1.05	1.07	1.10	1.10	1.04	1.03
7	154.1	1.04	1.06	1.10	1.09	1.05	1.02
8	161.1	1.04	1.06	1.09	1.08	1.05	1.02
Geometric mean of ratios		1.15	1.12	1.16	1.25	.97	1.11

Table 4 cont.

PAN at 6 pm

Hydrocarbon mixture No.	1	2	3	4	5	6	7
Day No.	ppb	Concentration ratio relative to mixture 1					
1	.02	1.69	1.37	1.74	2.85	.73	1.46
2	.18	2.62	2.23	2.49	3.86	.75	2.41
3	.68	1.52	1.69	2.15	2.24	.84	1.36
4	1.20	1.22	1.44	1.90	1.82	1.12	1.06
5	1.52	1.17	1.41	1.87	1.74	1.17	1.01
6	1.76	1.14	1.39	1.85	1.69	1.18	.99
7	1.93	1.13	1.38	1.83	1.66	1.18	.98
8	2.05	1.11	1.37	1.81	1.63	1.17	.98
Geometric mean of ratios		1.39	1.51	1.94	2.08	1.00	1.22

Hydroxyl at noon

Hydrocarbon mixture No.	1	2	3	4	5	6	7
Day No.	*	Concentration ratio relative to mixture 1					
1							
2	5.91	1.51	1.26	1.37	1.95	.84	1.36
3	7.15	1.47	1.38	1.52	1.43	.81	1.37
4	9.49	.95	.96	.94	.93	.97	.96
5	8.28	1.00	.99	.99	1.00	.96	1.00
6	7.67	1.01	1.01	1.01	1.02	.99	1.01
7	7.24	1.02	1.02	.99	1.04	1.00	1.02
8	6.91	1.03	1.02	1.04	1.05	1.00	1.02
Geometric mean of ratios		1.11	1.07	1.09	1.14	.94	1.08

* Concentration in 10^6 molecules cm^{-3}

For ozone and hydroxyl, the results fell quite well in line for all mixtures on days 5-8. The prediction of PAN showed more spread. These results were expected when it is kept in mind that the ozone and hydroxyl production is comparable for most hydrocarbons. PAN is more sensitive to the structure of the hydrocarbon precursor. Mixtures 4 and 5 gave the poorest result compared to the UK case, while 2,3 and 7 were quite similar. All mixtures except no. 6 overestimated secondary pollutant yield compared to the UK case. Mixture no. 6 comprised as many as eight different hydrocarbons.

It can be seen that mixture 7 predicted approximately 40% more ozone and hydroxyl, and a factor two higher PAN, than the UK mixture on day no. 2, while the results fell in line on days 5-8. It cannot be claimed that these numbers represent the uncertainty of model predictions with respect to choice of composition of the hydrocarbon emissions. A substantial error is linked to this choice, however.

As the number of days increased, the daily increase in ozone approached zero. This means that the production of ozone balanced the loss due to ground deposition and chemistry. The time scale for reaching a near steady state level could be measured by the reactivity of the slowest-reacting nonmethane hydrocarbons. It turned out that after 7-10 days, all hydrocarbons which were attacked by hydroxyl only, reached a fairly steady level on a diurnal average basis. Olefins also react with ozone, and were suppressed due to the increasing ozone levels. The assumption of identical mass of HC emissions was in the end sufficient to reach almost the same ozone level in all cases regardless of the composition of the hydrocarbon emissions.

The calculated concentration of PAN was strongly dependent on the choice of composition of the hydrocarbon emissions. A difference of more than a factor of 4 was found in the concentrations of PAN

for equal emissions. This difference was much less pronounced for ozone or hydroxyl.

4 RESULTS OF MODEL CALCULATIONS

The chemical lifetime of PAN in the atmosphere is dependent on the temperature, and the $[\text{NO}]/[\text{NO}_2]$ ratio. The diurnal temperature profile chosen for the calculations over land corresponded to the conditions observed during a nice, sunny day at Harwell, Oxfordshire, on June 16, 1973. It is shown in Fig. 3. Over sea the corresponding diurnal average temperature (15.7°C) was used. Temperatures 5°C and 10°C lower and 5°C higher than this were also used. The relative humidity is also shown in Fig. 3. It was used together with temperature data to calculate the water vapor concentration.

The most important questions to be answered in this model study, were the following:

- What is the persistence of peroxyacetylnitrate in an ageing air mass being transported over sea, for different temperatures?
- How is the persistence of PAN compared with ozone?
- How is PAN affected by new emissions of NO_x , HC or both? How is the behaviour of PAN compared with ozone?

Various emission scenarios were established to shed some light on these questions, see Table 5.

Table 5: Emission scenarios on days 5,6 and 7, cpr. Figure 1.

a) Zero emissions
b) UK emissions
c) Nitric oxide emissions as in the UK, zero of other species
d) Nitric oxide emissions 10 times average UK release, zero of other species.

4.1 Persistence of PAN in an ageing air mass

The development with time of the concentrations of O₃ and PAN, together with the ratio [NO₂]/([NO]+[NO₂]), is shown in Fig. 4 in the case of no emissions after 6 a.m. on day 4.

When O₃ and PAN were compared, it was seen that ozone was more persistent than PAN in an ageing air mass over a sea surface, regardless of temperature. When the air mass left the UK, the ozone concentration was approx. 70 ppb. It rose to about 100 ppb during the first day over sea, and increased slowly to 105-125 ppb, depending on temperature. It can be concluded that in the absence of ground removal, the gas chemical sink for ozone, notably



was not sufficient to outweigh the chemical generation of ozone from long-lived hydrocarbons emitted in the UK. In Fig. 5 is shown the development with time of the sum of the concentration of the hydrocarbons. The change in composition with time of the sum of the hydrocarbons and of the paraffins, is also shown. After approx. 2 days over sea, the concentration of the sum of nonmethane hydrocarbons was reduced by 50% compared to the situation at 6 am on day 4. The composition, however, was very different. Reactive species like olefins and aromatic compounds were nearly depleted. Less reactive species like acetone,

acetylene and paraffins made a much larger contribution to the total hydrocarbon concentration in the air than what was originally present in the UK emissions. Of the paraffins, the least reactive species (ethane) dominated in abundance (Fig. 5).

The behaviour of the concentration of PAN in air transported from the UK, was quite dependent on temperature. This can be seen from Fig. 4. In the case with highest temperature, the PAN concentration dropped from a maximum of 1.7 ppb at 16h on day 4, to .4 ppb at midnight on day 8. In the case with the lowest temperature, the concentration barely dropped at all. Also, the diurnal variation was very slight. The concentration did not change at night when the deposition did not act, because all of NO_x was present as NO_2 . The $[\text{NO}_2]/([\text{NO}]+[\text{NO}_2])$ is shown at the bottom of Fig. 4. The behaviour of PAN over sea from England for various temperatures is summarized in Table 6. A chemical lifetime was calculated from the decline in the PAN concentration, i.e. determined from the net chemical loss.

Table 6: Maximum PAN concentration (C_{max}) on day 4 and minimum concentration (C_{min}) on day 8. Characteristic decay time (τ) for PAN was calculated from the expression

$$C_{min} = C_{max} \exp \left(- \frac{\Delta t}{\tau} \right) \text{ where } \Delta t \text{ was the span between the times of occurrence of } C_{max} \text{ and } C_{min}.$$

Diurnal mean temp. ($^{\circ}\text{C}$)	C_{max} (ppb)	C_{min} (ppb)	Δt (h)	τ (h)	$1/k_1$ (h)
20.8	1.7	.4	106	66	1.2
15.8	2.2	.9	104	122	2.4
10.8	2.5	1.9	82	270	5.2
5.8	2.9	2.7	58	836	11.5

The chemical lifetime of PAN was calculated to be significantly longer than the value determined from the thermal decomposition rate coefficient, even when the $[\text{NO}]/[\text{NO}_2]$ ratio was taken into account.

Eq. (i) given by Cox and Roffey (1977) apparently underestimated the chemical lifetime of PAN. The explanation is that the concentration of acetylperoxy radicals during daytime is not determined by the equilibrium reactions (1), (2) and (3). At night the equilibrium is a fairly good approximation, predicting no net loss of PAN when $[NO] \ll [NO_2]$. During daytime, however, there is a steady production of acetylperoxy radicals in particular through reaction 6, and to a less extent through reaction 8. Eq. (i) therefore has to be modified during daytime:

$$-\frac{d}{dt} \ln [PAN] = k_1 \left(1 - \frac{1 + P/k_1 [PAN]}{1 + \frac{k_3}{k_2} \frac{[NO]}{[NO_2]}} \right) \quad (vi)$$

where

$$P = k_6 [OH][CH_3CHO] + 2 k_8 [CH_3COCOCH_3] \quad (vii)$$

The effect of this modification can be read out of Table 6. The second term in the paranthesis on the right hand side of eq. (vi) is closer to 1 than the similar term in eq. (i). This causes an increase in the chemical lifetime of PAN. At the lowest temperature (5.8°C diurnal mean), the concentration of PAN hardly changed at all during days 4-8, which was analogous to the behaviour of ozone for this temperature. In order to compare the atmospheric persistence of ozone and PAN any further, it should be remembered that the ground removal rate of O_3 is typically three times that of PAN over land.

The concentrations of NO_2 , HNO_3 and OH for the first emission scenario are shown in Fig. 6. The concentration of NO_2 dropped quickly after passage of the source areas of pollutants. The decline of HNO_3 was mainly determined by the deposition. The concentrations of NO_2 and HNO_3 appeared to be only slightly dependent on temperature. Hydroxyl was calculated to have a fairly uniform **maximum concentration in the case with the highest temperature.** The maximum concentrations on days 6, 7 and 8 were much lower when the temperature was lowered. In Fig. 7 is shown the budget of

nitrogen species; what was emitted, deposited and what remained in the air. This was done for 4 different temperatures. At the lower temperatures, PAN and PAN homologues were the dominant gaseous nitrogen species according to these calculations.

4.2 Persistence of PAN to fresh emissions of precursors

It has been suggested that PAN is a better indicator than ozone of photochemical activity in polluted air. The concentration of PAN in the unpolluted troposphere is a few hundred ppt (Singh and Hanst, 1981). In polluted air, concentrations 10-100 times higher may be found. The surplus of ozone in polluted air is typically a factor of 2-5 above the tropospheric background level.

The increase in concentration in polluted air compared to clean air, is of importance when PAN as an indicator of photochemical pollution is judged. The effect of local pollution sources of HC, NO_x or both is also of importance. It is well known that representative measurements of ozone on a regional scale requires that the monitoring takes place away from local pollution of NO_x. Also, the efficient ground removal of ozone makes it difficult to arrive at a reasonable boundary layer mean concentration based on ground measurements, except during strong convective mixing or at coastal sites during periods with wind from the sea. The persistence of ozone in an ageing air mass exposed to fresh emissions of NO_x, HC or both, is illustrated in the left part of Fig. 8. UK emissions on days 6-8 are seen to cause a slight increase in the concentration of ozone. Ground removal over land caused ozone to drop at night.

Nitric oxide emissions only caused the concentration of ozone to decline. Nitric oxide emissions at a rate typical of an urban area (lower figure), caused ozone to drop significantly within a few hours. The effect of changes in temperature was very slight for ozone.

The time development of the concentration of PAN for the same emission scenarios, is shown to the right in Fig. 8. To evaluate

the impact of the emissions on days 6-8, the PAN concentration curves for the lowest temperature may be considered. It has been shown previously that the decay time of PAN was then very long and departures in the concentration from a slow decline were therefore a direct measure of how PAN reacted to fresh emissions of HC, NO_x or both. In the case of UK emissions of both HC and NO_x, the effect on the concentration of PAN was significant (upper Figure). In the case of exposure of aged air to fairly low NO_x emissions (average UK, middle graph), ozone was more persistent than PAN at all temperatures. When the ageing air was exposed to urban NO_x emissions, however, the concentration of ozone dropped more quickly than that of PAN, in particular for the lower temperatures (cpr. Fig. 8, lower graphs, and Table 7).

The calculations therefore indicated that on days with maximum temperatures less than around 20°C (diurnal mean temperatures below approx. 11°C with the diurnal variation adopted here), PAN in an ageing air mass was less sensitive than ozone to high emissions of NO_x. The choice of a site for measuring regional concentration levels is therefore less sensitive to the influence of local sources of NO_x in the case of PAN than in the case of ozone.

Table 7: Lifetimes of O₃ and PAN (in h) in the case with low temperature (5.7°C diurnal mean) for different emission scenarios.

Emission scenario	PAN	O ₃
Nitric oxide emissions as in the UK (1975) on days 5,6 and 7, zero of other species	74	182
Nitric oxide emissions 10 times average UK release on days 5,6 and 7, zero of other species	43	15

5 MEASURED VS. CALCULATED CONCENTRATIONS OF OXIDANTS IN
AGEING AIR

Model calculations have been presented where an air mass accumulated UK emissions of HC, NO_x and SO₂ for 2-3 days, whereafter it was transported over sea towards Scandinavia. It was a hypothetical case. Analogous situations have been analysed and the findings with respect to trajectories, ozone and PAN concentrations published (Nielsen et al., 1981, Grennfelt et al., 1982a, Schjoldager et al., 1983). The period most extensively studied covers Sept. 2-9, 1980, with measurements of ozone and PAN on the southwest coast of Sweden (Göteborg, Rørvik), Risø in Denmark and Maridalen near Oslo. 96 h trajectories to Rørvik for September 3 and 4, 1980 are shown in Fig. 9, as well as trajectories (noon arrival) to Maridalen for Sept. 7-9. In Fig. 10 are shown measurements for these periods (Grennfelt et al., 1982a; Schjoldager et al., 1983). The air masses traced in Fig. 9 seemed to be exposed to UK and continental emissions for a time period of length one day or more, whereafter the North Sea was crossed. Although no direct comparison with e.g. Fig. 4 was possible, the general features could be compared. The computed ozone concentrations were in the range 100-125 ppb (200-250 µg/m³) regardless of temperature, upon arrival in southern Scandinavia. This was in fair agreement with recorded ozone (cpr. Fig. 10). PAN concentrations in Maridalen during the night between Sept. 8 and 9 peaked around 25 µg/m³ (approx. 5 ppb). The peak PAN concentration was 3.5 ppb in Göteborg and 4.2 ppb at Risø in situations where long-range transport was likely during the first days of Sept. 1980. The temperature in Maridalen was on the average approx. 15°C on Sept. 7-9, and probably somewhat lower during the passage of the North Sea. According to Fig. 4, a likely concentration range of PAN should be 1-3 ppb after 1-2 days over sea, with only slight variation in the diurnal concentration. It is therefore concluded that a major part of the recorded PAN concentrations in southern Scandinavia during the period Sept. 2-9, 1980, was made up of PAN transported across the North Sea.

More information on the nitrogen budget in air arriving at Rørvik and unaffected by local sources, was given by Grennfelt (1978, 1979) and Grennfelt et al., 1982b. Some of the conclusions from the measurements at Rørvik may be kept together with the calculations. First of all, virtually no nitric oxide remained in long-range transported air. This is in good agreement with the calculations (Fig. 4, lower part). The dominant oxidized nitrogen compound in a long-range transported air mass is usually NO_2 , which is not consistent with the calculations (Fig. 6). The concentration of NO_2 was calculated to drop significantly in a matter of a few hours after leaving the source areas of NO_x . HNO_3 declined more slowly. Most of the nitrates seem to be present in the air as gaseous material in long-range transport episodes during the summer. The distribution of nitrates between gaseous and particulate nitrates is very dependent on the relative humidity. There is probably a significant transfer between gas and particle phase during the day due to the diurnal variation in relative humidity. The formation of HNO_3 seemed to be overestimated in the model. The main process whereby HNO_3 was formed, was through the reaction



The efficiency of this reaction path may be overestimated, or there is a faster feedback mechanism from HNO_3 to NO_2 than what current data for HNO_3 photolysis or reaction with OH seems to indicate.

6 CONCLUSIONS

PAN may be transported in polluted air masses from continental Europa or the British Isles to Scandinavia. The persistence of PAN was comparable to that of ozone in an ageing air mass when the temperatures were fairly low ($5-10^\circ\text{C}$). At higher temperatures the thermal decomposition of PAN made the molecule less persistent than ozone. Over land, the situation may be different since the

ground removal is typically 3 times more efficient for ozone than for PAN.

PAN seemed to be only slightly perturbed when an ageing air mass was exposed to emissions of HC, NO_x or both from area sources of moderate strength. The persistence of PAN was better or comparable to that of ozone when an ageing air mass was exposed to NO_x emissions of strength comparable to what is found in urban areas.

During time periods when air masses accumulate HC and NO_x pollution from sources in Europe and then move towards Scandinavia without any synoptic scale break up of the atmospheric boundary layer (e.g. frontal passages), elevated PAN concentrations in southern Norway or Sweden in the range 1-5 ppb may to a large extent be caused by long-range transport.

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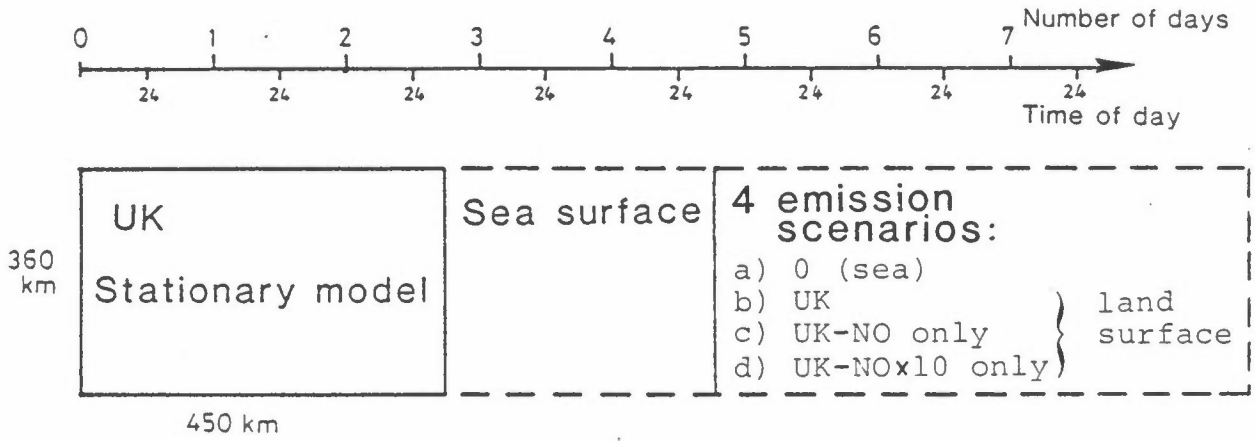


Figure 1: Illustration of the model. An air mass was followed in a Lagrangian way, assuming average UK emissions for approx. 2½ days. Transport over a sea surface was then modelled for 2 days. Thereafter 4 emission scenarios were modelled:

- a) continued transport over a sea surface
- b) transport over land with average UK emissions of NO_x, SO₂ and HC,
- c) transport over land with NO_x emissions only, equal to the UK average NO_x emission, and
- d) same as c) but with the NO_x emissions increased by a factor 10.

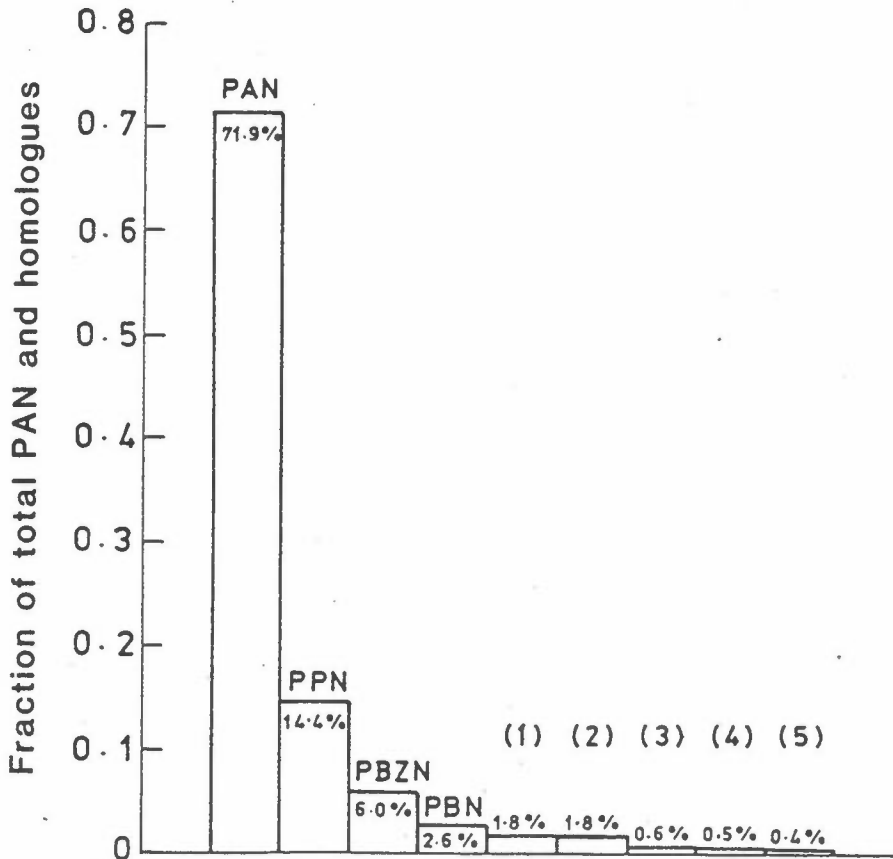


Figure 2: Relative concentrations of the peroxyacylnitrates 4 hours downwind of London in a London urban plume model. (Derwent and Hov, 1979). (1) peroxy-*i*-propionyl nitrate, (2) peroxy methylbenzoyl nitrate, (3), (4) and (5) peroxyvaleryl nitrates.

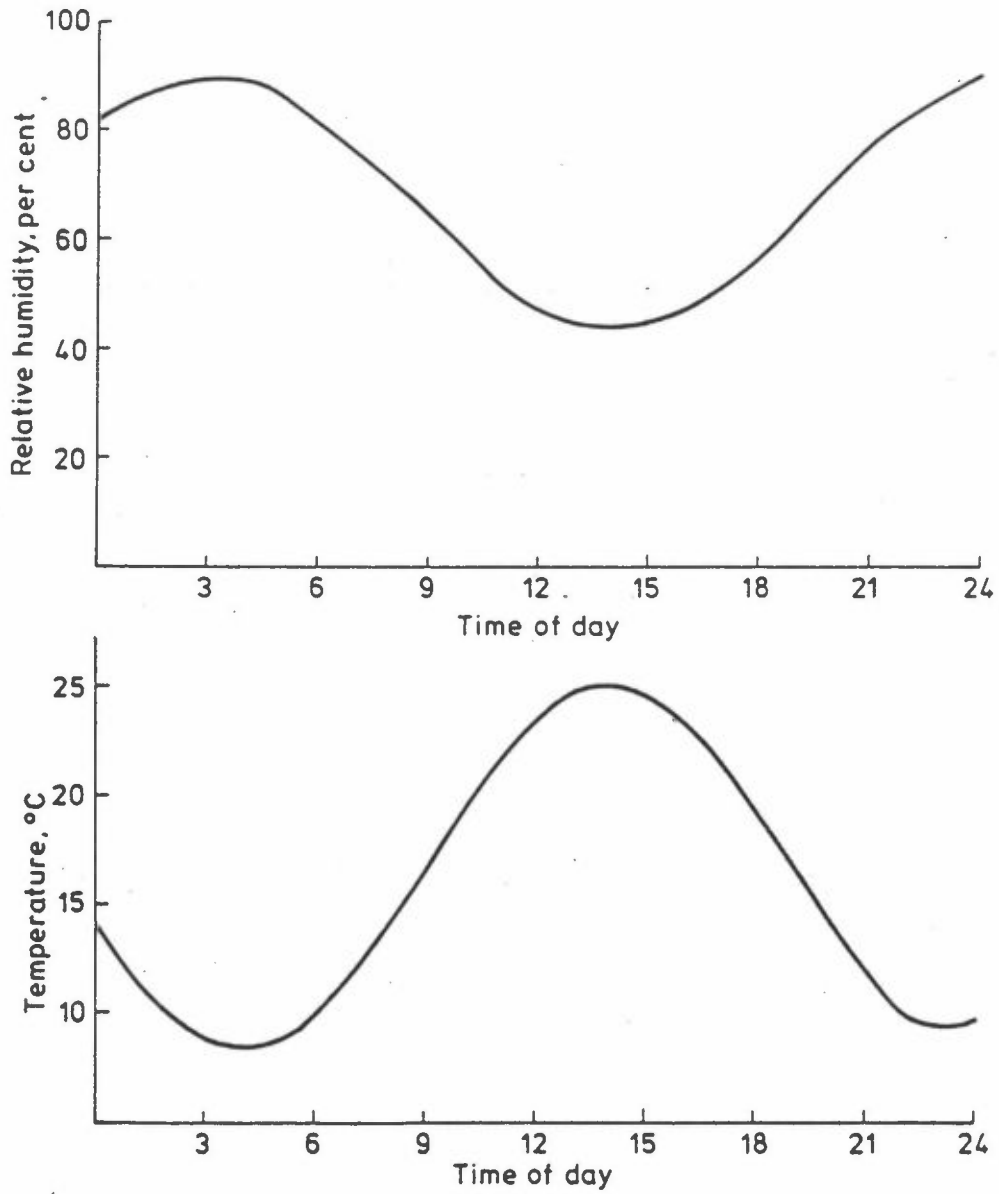


Figure 3: Diurnal variation of temperature and relative humidity as applied over land surfaces in the model (corresponded to the conditions on 16 June 1973 at AERE Harwell, Oxfordshire, Derwent and Hov (1979)).

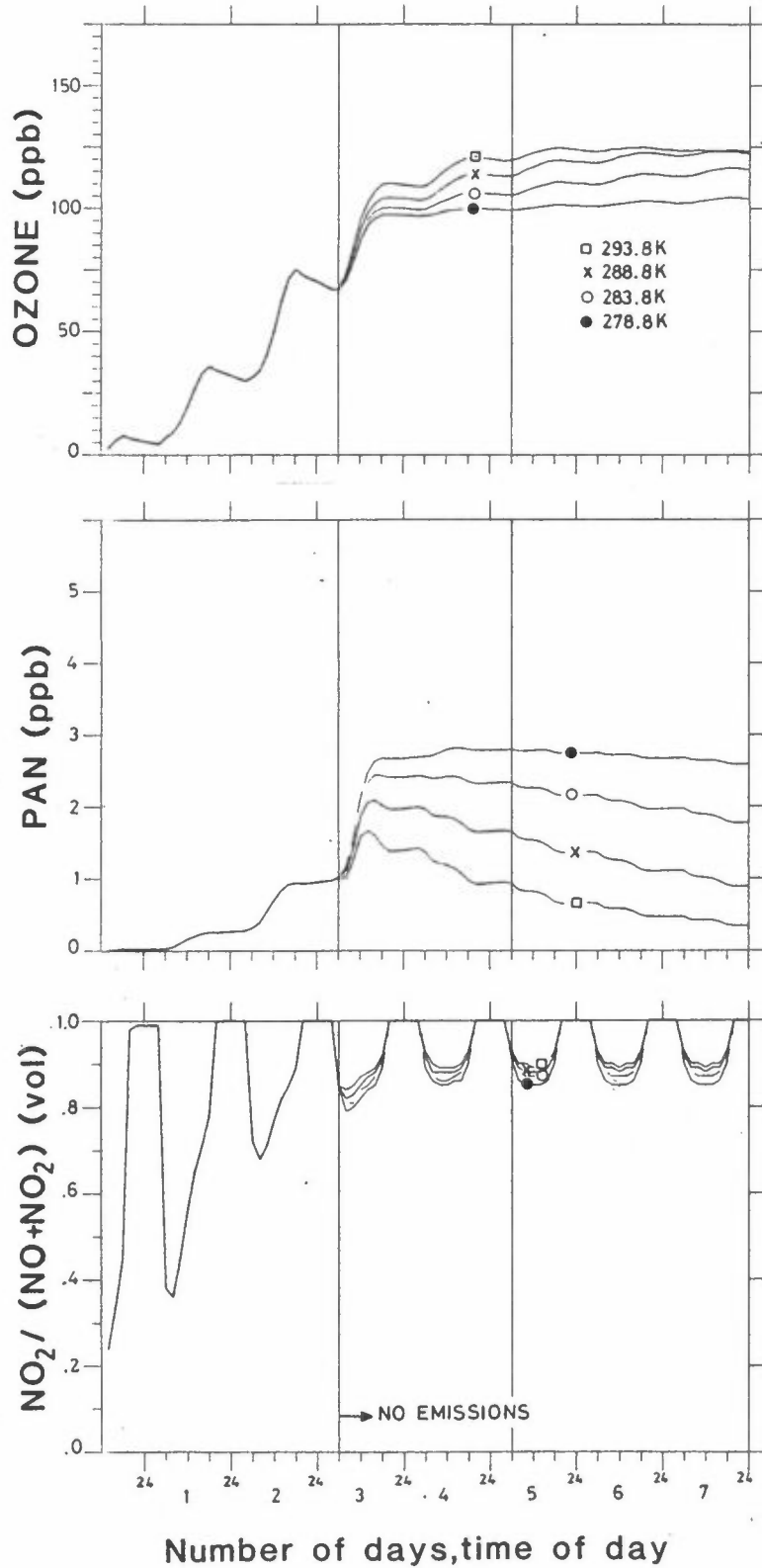


Figure 4: Development with time of the concentrations of O₃ and PAN and the ratio (volume) NO₂/(NO+NO₂) for 4 temperatures (diurnal means of 278.8K, 283.8K, 288.8K and 293.8K) and for emission scenario denoted by a) (see Fig. 1).

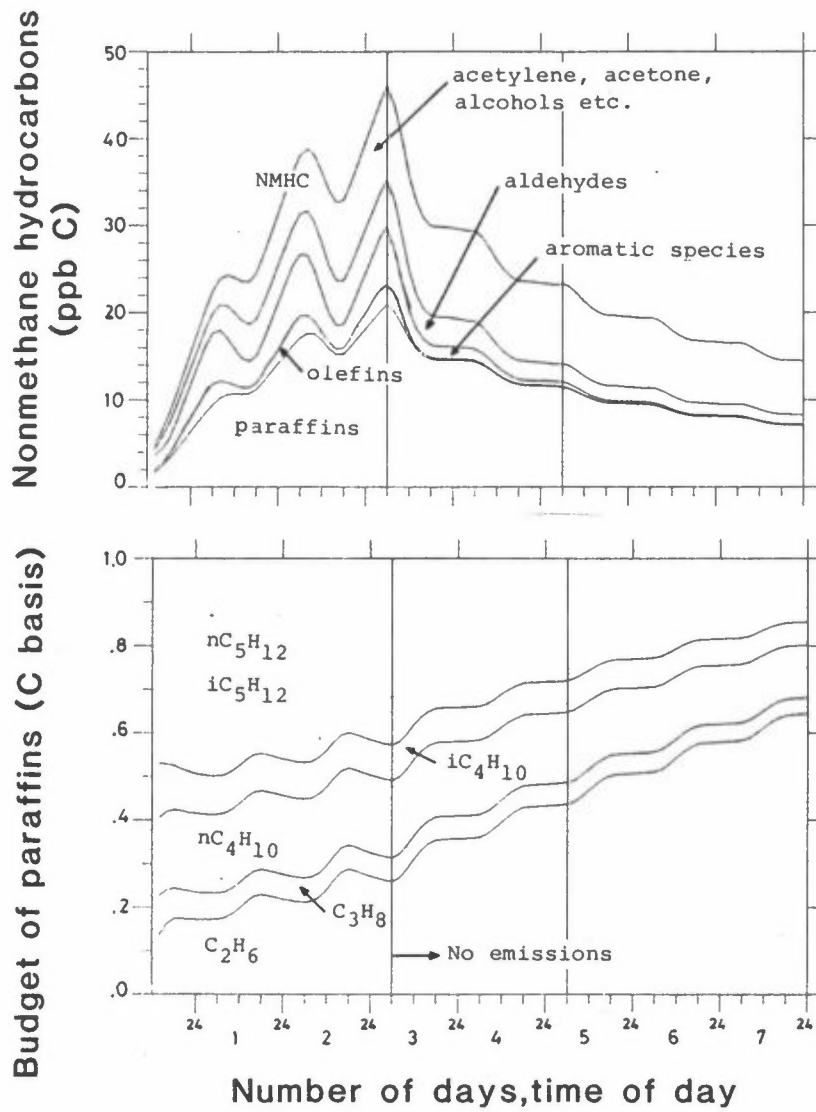


Figure 5: Development with time of the nonmethane hydrocarbons (NMHC) and their composition (upper diagram), and of the relative composition of the paraffins (on a C-atom basis), lower diagram. Emission scenario a) and temperature 288.8K as a diurnal mean, were chosen.

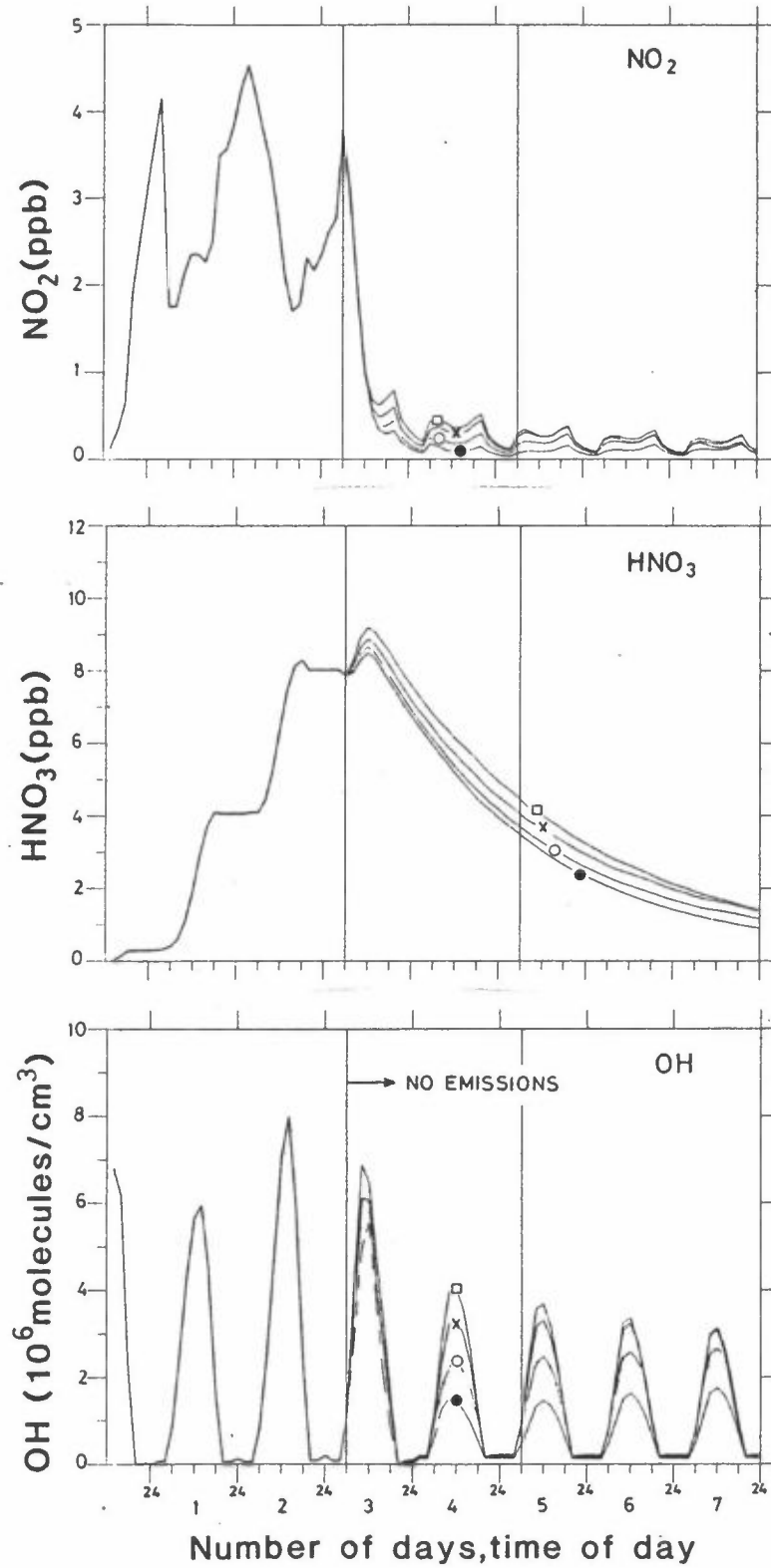


Figure 6: Development with time of the concentrations of NO₂, HNO₃ and OH in the case of emission scenario a), Fig. 1, and for 4 temperatures (□ : 293.8K, X: 288.8K, O: 283.8K and ● : 278.8K).

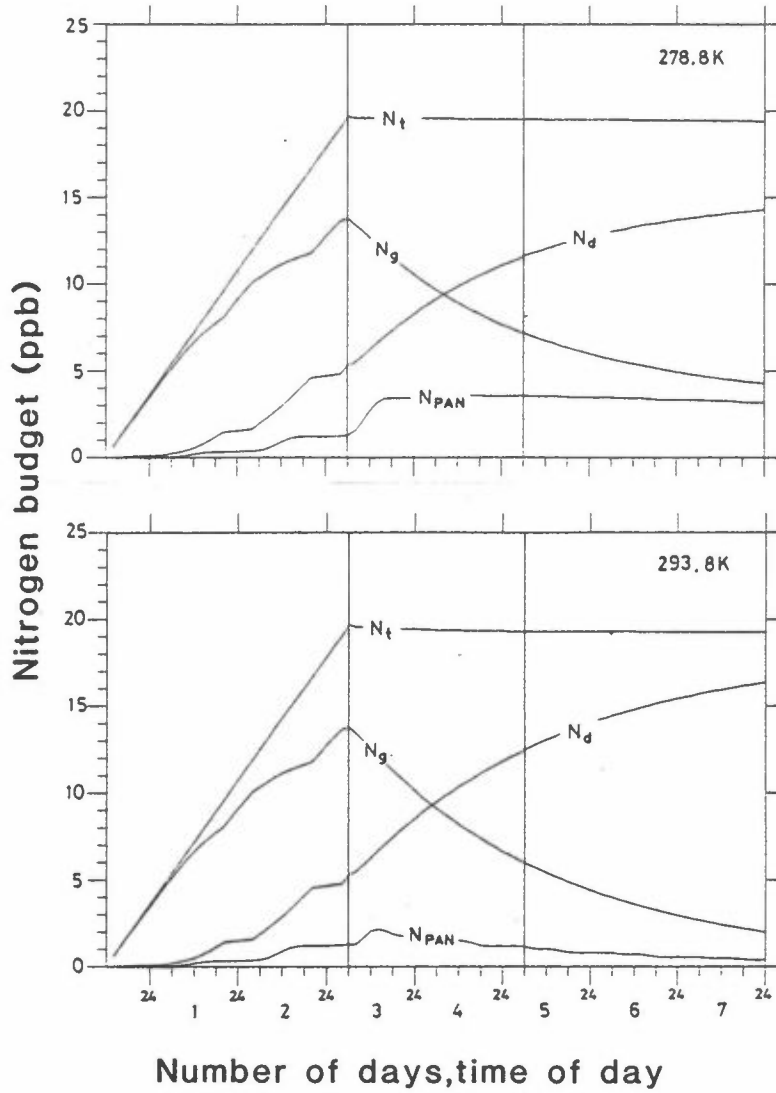


Figure 7: Development with time of the budget of nitrogen, in the case of emission scenario a) (cpr. Fig. 1), and for two diurnal mean temperatures. N_t : total emitted NO_x . N_g : total nitrogen in the gas phase (sum of the airborne concentrations of NO , NO_2 , HNO_3 , HO_2NO_2 , HNO_2 , NO_3 , N_2O_5 , PAN and homologues). N_d : total accumulated deposited nitrogen. N_{PAN} : sum of the concentrations of PAN and its homologues.

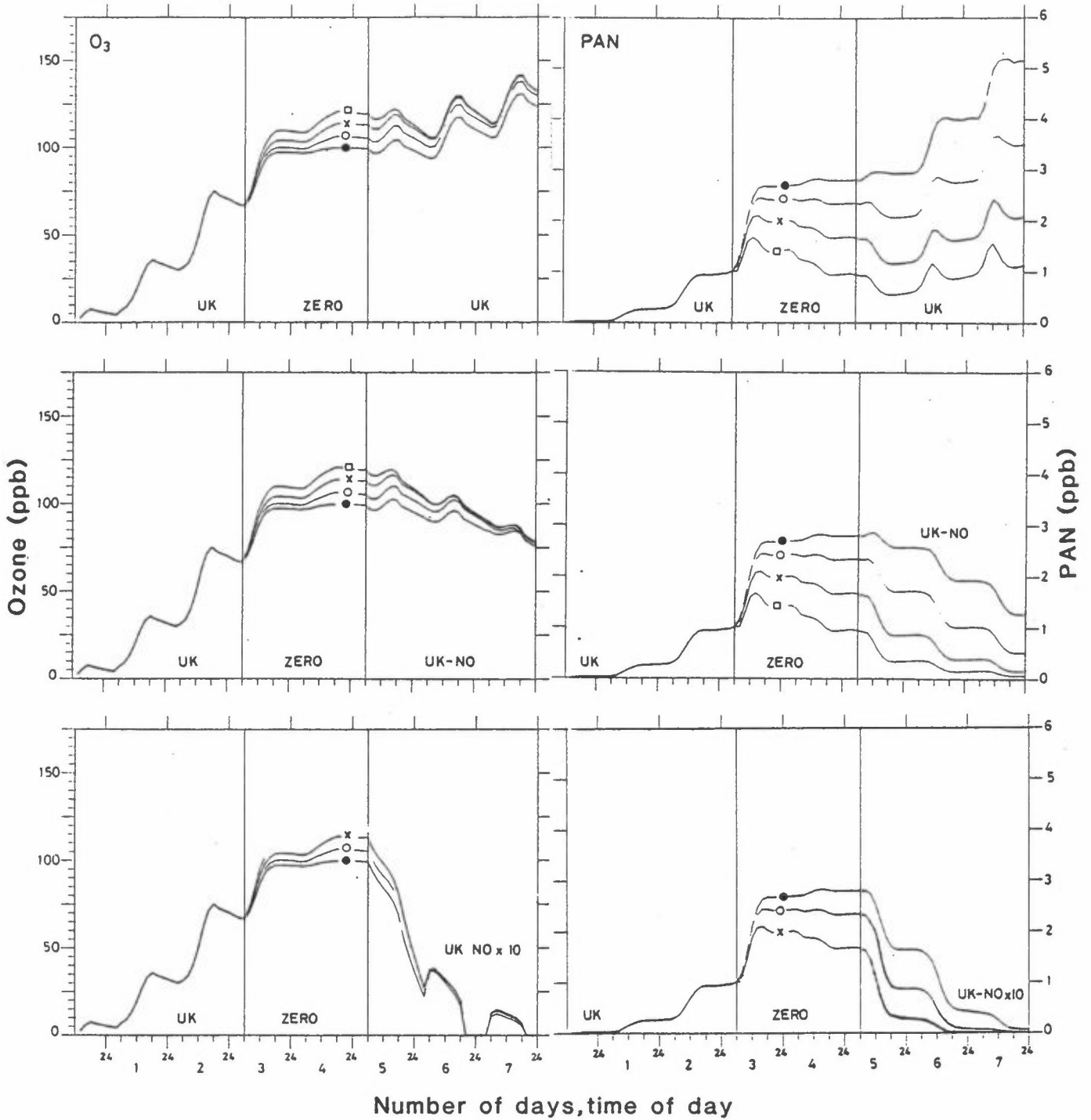


Figure 8: Development with time of the concentrations of O₃ and PAN for emission scenario b) (upper pair of graphs), c) (middle graphs), d) (lower pair of graphs), and for a range of diurnal mean temperatures (□ : 293.8K, X: 288.8K, O: 283.8K and ● : 278.8K).

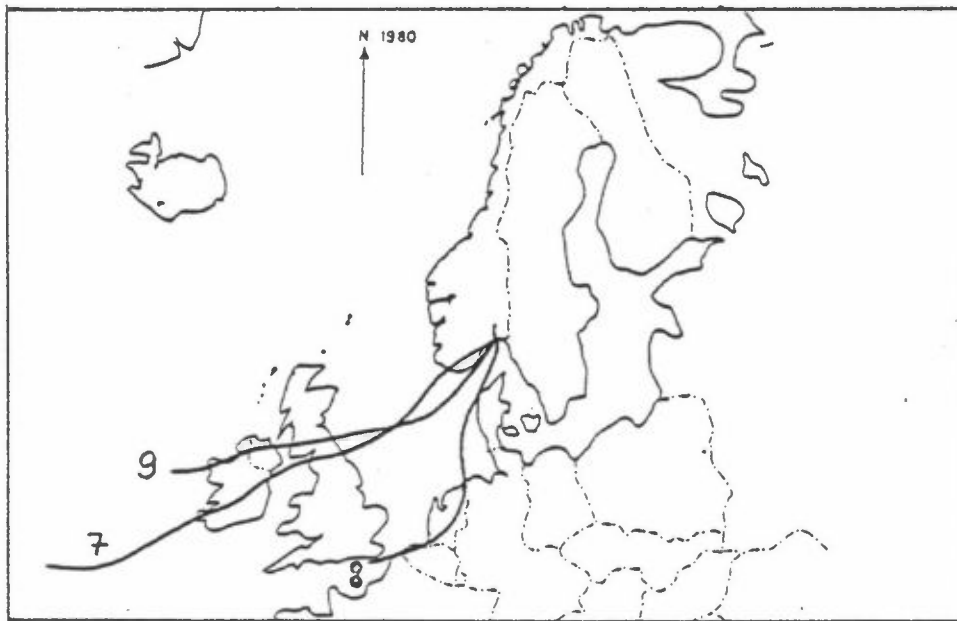
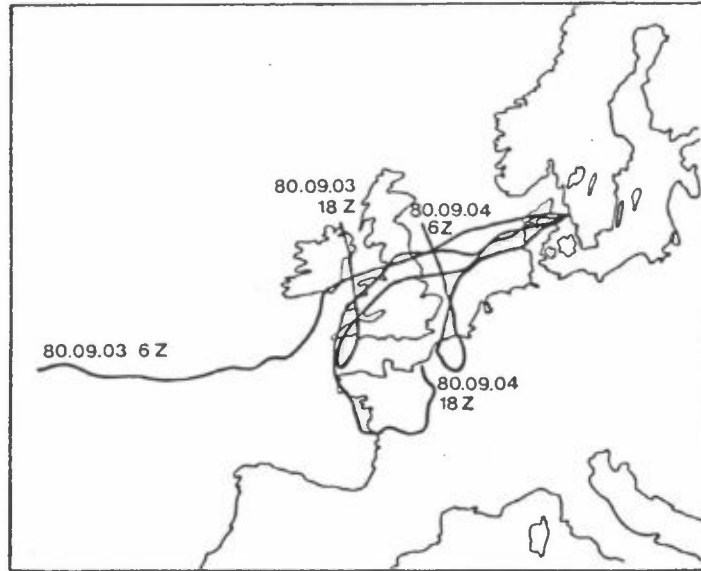


Figure 9: Trajectories (850 mb, 96-h) for Rørvik, September 3-4, 1980 (0700 and 1900 MEST)(Grennfelt et al., 1982a)(upper graph). Trajectories (850 mb, 96-h) for Oslo, 1200 GMT, September 7-9, 1980 (Schjoldager et al., 1983)(lower graph).

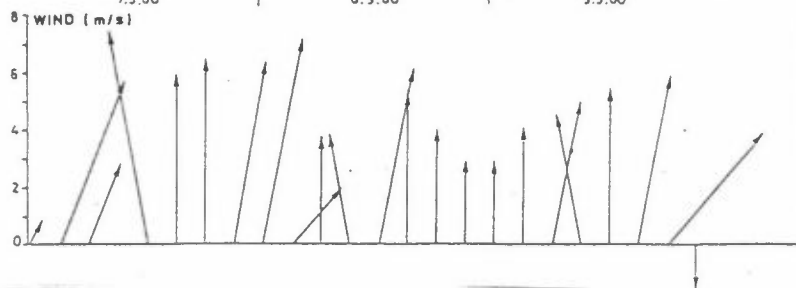
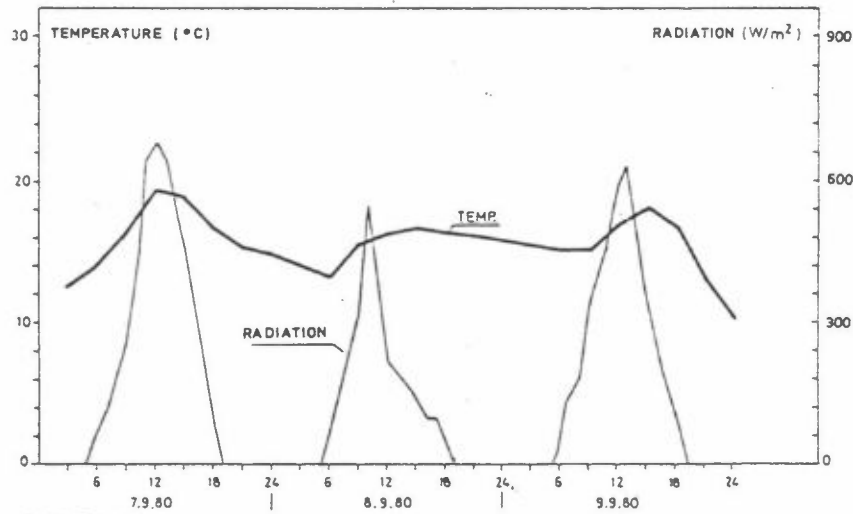
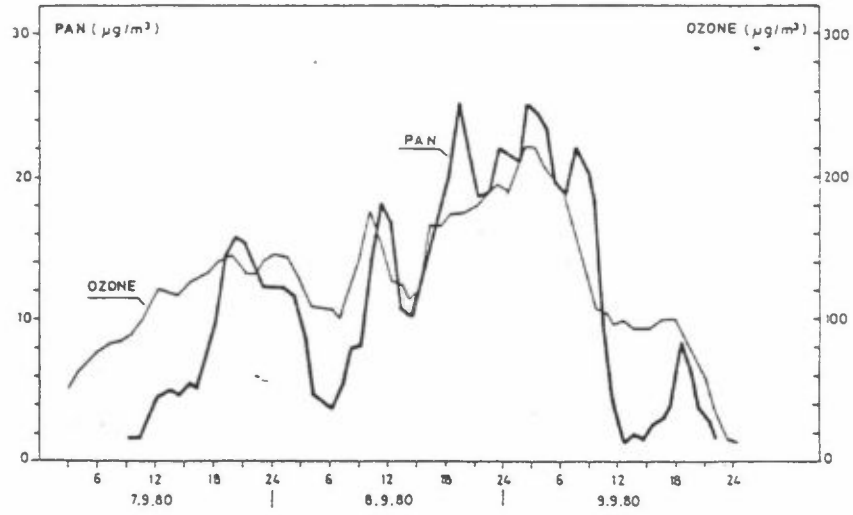
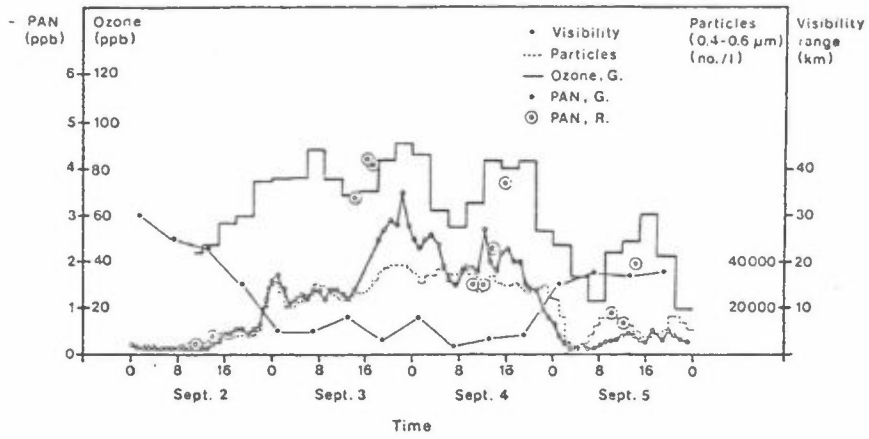


Figure 10: The variation of the concentration of PAN and other atmospheric constituents in Gøteborg (G) and at Risø (R) for the period September 2-5, 1980 (Grennfelt et al., 1982a)(upper graph). The variation of the concentration of PAN and O₃ in Maridalen September 7-9, 1980, together with temperature, radiation and wind-speed and direction at Blindern, Oslo, (lower graph)(Schjoldager et al., 1983).

