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PHOTOCHEMICAL OXIDANT EPISODES,
ACID DEPOSITION
AND GLOBAL ATMOSPHERIC CHANGE.

THE RELATIONSHIPS WITH EMISSION CHANGES
OF NITROGEN OXIDES AND
VOLATILE ORGANIC COMPOUNDS

Øystein Hov

ABSTRACT

Ozone (O_3) episodes in the atmospheric boundary layer over Europe are superimposed on a background level which is slowly increasing. The change in the background concentration is probably controlled by changes in the emissions of nitrogen oxides (NOx).

It is likely that a further increase in the emissions of NOx in Europe and elsewhere in the northern hemisphere will contribute to a continued rise in free tropospheric ozone, while the occurrence of ozone episodes in the boundary layer may not change much.

Nitrate (NO_3^-) derived from the emissions of NOx contributes significantly to acid deposition in Europe and elsewhere.

Integrated over one year and over all of Europe, there is probably a nearly linear relationship between a change in NOx emissions and the corresponding change in nitrate deposition.

A reduction in the emissions of NOx in a photochemical episode in Europe could lead to only a slight decrease in the concentration of the hydroxyl radical (OH) and ozone, while there might be a marked increase in hydrogen peroxide (H_2O_2). Then the conversion of NOx to nitrate would become slightly slower, while the conversion of SO_2 to sulphate would remain rather unchanged. The atmospheric lifetime of NOx- and S-species could remain the same or increase slightly.

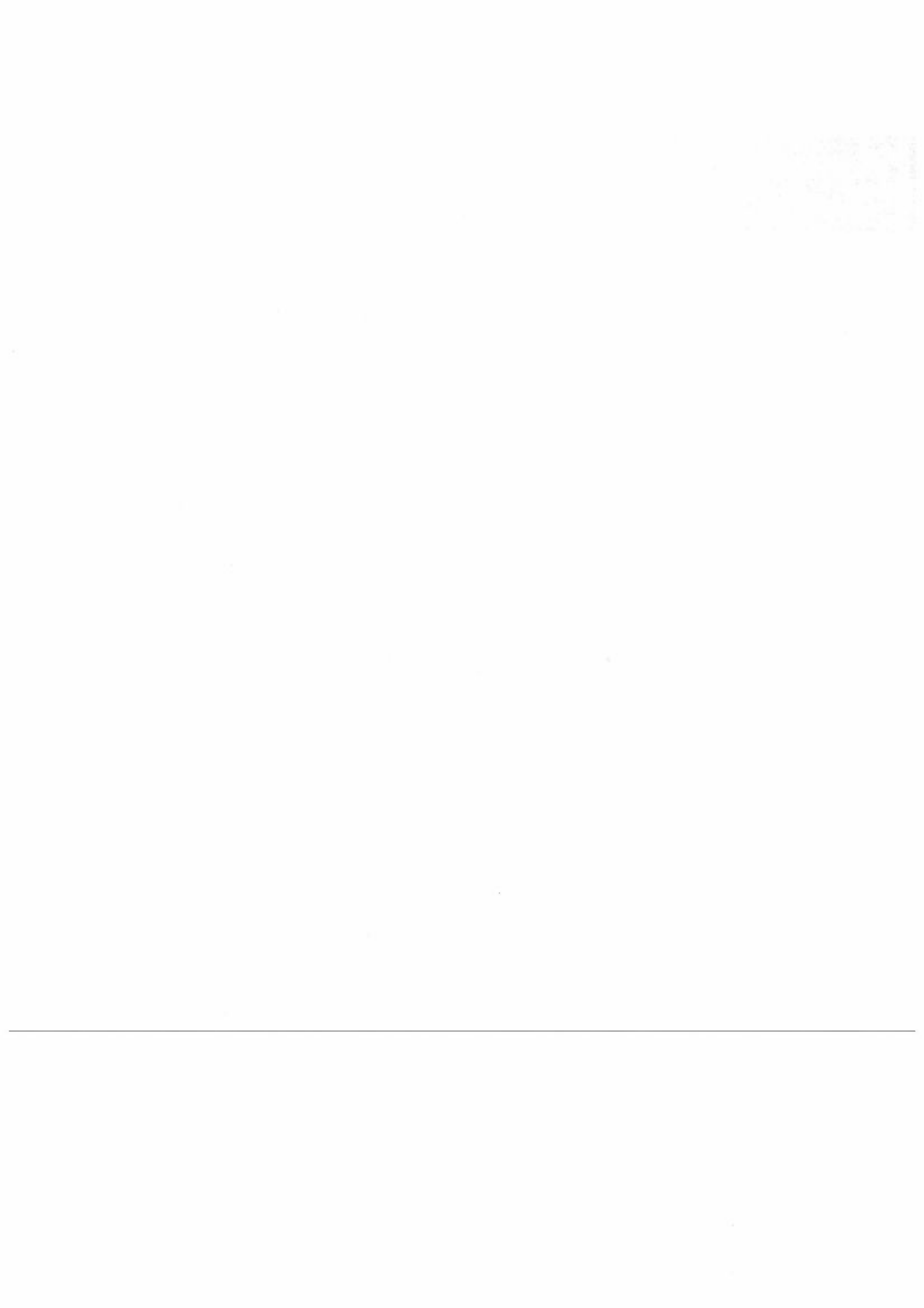
In clean air, a trend downwards in the emission of NOx (a few %/a) is shown in model calculations to cause a drop in the background concentration of O_3 and OH, while H_2O_2 increases. This means that the gas-phase conversion of SO_2 and NOx through the reaction with OH to sulphate and nitrate will become less efficient. Also the dark reaction converting NO_2 to the NO_3 radical and further to nitrate through the reaction with O_3 , would become slower, while the wet phase oxidation of SO_2 to sulphate would become more efficient. This means that reduced emissions of NOx would give rise to a more than proportional reduction in the nitrate formation, while the efficiency of sulphate

formation could increase. For the distribution of acid deposition this would imply an increase in the lifetime for S-compounds and a decrease in the lifetime for NO_x-compounds.

A decrease in global NO_x-emissions will cause a drop in the tropospheric O₃-increase and reduce the potential warming effect of tropospheric O₃. A decrease in global NO_x-emissions can come about by reducing the burning of fossil fuels, which would also reduce the emissions of N₂O. Reducing NO_x would also reduce tropospheric OH. With unchanged surface sources of CH₄, tropospheric CH₄ would increase in concentration more than today, contributing more to the surface warming than 0.14 K in fifty years. The combustion of fossil fuels is an important source of CO₂. Reducing the use of fossil fuels would contribute to a reduction both in NO_x- and CO₂-emissions.

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THE RELATIONSHIPS BETWEEN PHOTOCHEMICAL OXIDANT EPISODES, ACID DEPOSITION AND GLOBAL ATMOSPHERIC CHANGE, AND EMISSION CHANGES OF NITROGEN OXIDES AND VOLATILE ORGANIC COMPOUNDS

1 INTRODUCTION

Man-made emissions of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), sulphur dioxide (SO_2) and volatile organic compounds (VOC) contribute to the formation of secondary pollutants in the atmosphere. The following phenomena can be traced back in parts to anthropogenic pollution of NO_x , SO_2 and VOC: Elevated levels of photochemical oxidants during summer time high pressure situations over industrialized areas. Deposition of acid substances in and downwind of regions with high industrial activity or dense population. Gradual changes in the chemical composition of the atmosphere.

Key environmental issues deeply rooted in atmospheric pollution are: Damage to fresh water ecosystems, deterioration of building materials, increasing levels of toxic metals in surface and ground water, reduced crops, forest damage in Central Europe, expectation of a rise in the global mean surface temperature over the next decades.

The future evolution of these issues will be decisive for economic and social stability both regionally and globally.

Due to the significant and increasing political impact of these issues, they are dealt with in earnest by a series of international organizations and bodies. Due to their complexity and different range in space, rate of development and state of investigation there is a tendency to separate the investigation of the very interlinked fate of atmospheric pollutants, into different disciplines: "photochemical oxidants", "acid rain", "climatic change", etc. Different organizations both nationally and on an international level, are given the responsibility to investigate various parts of the problem. In this way the acid deposition problem is dealt with within EMEP (European Monitoring and Evaluation Programme) under ECE within the United Nations, climatic change is an issue mainly within WMO and lately OECD

has focused on photochemical ozone in its MAP-project (Major Air Pollutants). The Commission of the European Communities (CEC) supports research in all disciplines, but under different directorates. Issues which are strongly interlinked, are being dealt with as individual fragments.

This is perhaps unavoidable. On the other hand, when the results of research have become sufficiently reliable so that recommendations can be made and policies implemented to reduce the size and frequency e.g. of episodic occurrences of elevated ozone in Central Europe, great care should be taken to ensure that the policies devised are not counterproductive in the abatement of other air pollution problems.

In this paper the results of research into how to reduce photochemical oxidants and acid deposition over Europe will be presented. The main mechanisms behind the global atmospheric change will also be discussed, and these three issues will be held together. A review of the photooxidants-precursor relationship in Europe is given by Hov et al. (1986), of acid deposition by Hov et al. (1988) while global atmospheric change is reviewed in the report Atmospheric Ozone (1985).

2 PHOTOCHEMICAL OXIDANTS - MORE THAN EPISODES

Many countries have established ambient air quality standards or guidelines for ozone, e.g. the maximum hourly concentration is recommended not to exceed 50-100 ppb more than once per month. In the United States there is a legal standard for ozone: 120 ppb as an hourly average should not be exceeded more than once per year.

There are comprehensive networks of rural ozone measuring instruments in many European countries and in North America. Many stations have been in operation for nearly 15 years. The summertime episodic increase in the concentration of ozone is well established over large parts of Europe, North America and Japan.

In Figure 1 is shown the monthly mean ozone concentration at Rørvik, a rural site south of Gothenburg on the Swedish west coast, as an average for the three year period 1980-83. The monthly mean concentrations are calculated from hourly values (Grennfelt and Schjoldager, 1984). Also shown are the corresponding monthly averages for low and high pollution days, as characterized by the submicron particle count (less than 10 000 and more than 30 000 particles per litre of air, respectively). During the summer half year days with a high level of anthropogenic pollution (high particle count) are associated with elevated ozone, during the winter half year it is the other way around. This indicates that in the atmospheric boundary layer at high latitudes, ozone formation takes place only in the summer half year. The spring maximum in clean air is mainly due to a maximum influx from the upper troposphere during that part of the year, while it is seen that when all days are included (curve 1), anthropogenic pollution contributes to an increase in the spring maximum concentration and a shift towards mid summer in its occurrence.

The episodic behaviour of elevated ozone concentrations in the atmospheric boundary layer is not readily seen in Figure 1 since monthly means are plotted. One can get an impression of the episodicity from Table 1, where a statistical summary of the hourly ozone concentrations from 24 European rural sites for April-September 1985 is presented (Grennfelt et al., 1987). It can be seen from Table 1 that the highest ozone concentrations at the various sites, fall on one or just a few days.

It is tempting to think of curve 2 in Figure 1 as unpolluted "background" ozone, not significantly affected by anthropogenic pollution. Measurements of ozone were numerous in the last century using Schönbein's test-paper. In 1876 a series of measurements was started at the Paris Municipal Observatory at Montsouris and continued for 31 years. ~~Other measurements were made around the Great Lakes in North~~ America in the last part of the nineteenth century. All of these values are only about half of the mean of surface ozone measurements taken in the same geographical regions during the last 10-15 years (Bojkov, 1986; Volz et al., 1986).

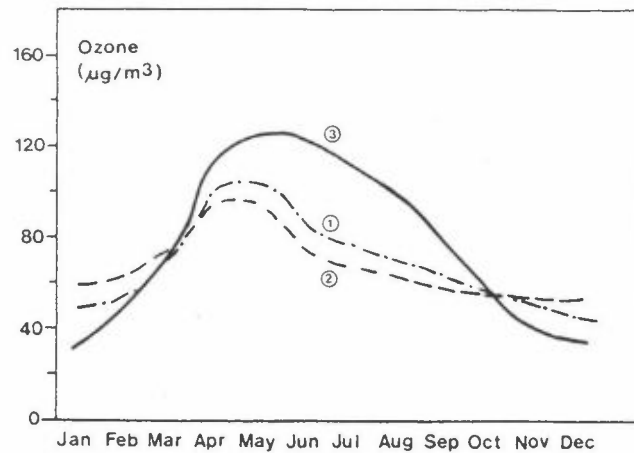


Figure 1: The yearly variation of ozone on Sweden's west coast during the three year period 1980-83 (line 1). The figure also shows the yearly variation of ozone, calculated for days when the number of submicrometer particles ($0.3-0.6 \mu\text{m}$) per liter of air is less than 10 000 (line 2) and for days when the corresponding number of particles is more than 30 000 (line 3). The concentration of submicrometer particles is an indicator of large-scale anthropogenic pollution. Hence line 2 represents clean air situations, while line 3 represents situations influenced by large-scale pollution (Grennfelt and Schjoldager, 1984).

Another comparison of present day's "background" ozone as compared to one century ago, is shown in Figure 2 (Volz et al., 1986). The average monthly ozone concentration for the rural station Westerland in the Federal Republic of Germany operated by Umweltbundesamt (UBA) for the time period 1980-85, is compared with ozone measurements between 1857 and 1871 at Emden, which is nearby. A typical ozone episode lasting a few days is also indicated. The Emden data show that the ozone levels were 11-15 ppb a century ago, comparable to the Montsouris-data (Figure 3).

Therefore, compared to the levels a century ago, ozone today is nearly doubled. The peak values in an episode do not add much to the average ~~over the year or over a growing season, which may be as important~~ numbers with respect to environmental damage as the hourly peak concentration over the year. Net primary production in photosynthesis and ozone are anticorrelated (Reich and Amundson, 1985).

Table 1: Number of hours (h) and days (d) with hourly ozone concentrations exceeding 120, 160, 200, 240 and 280 $\mu\text{g}/\text{m}^3$, and maximum hourly and daily ozone concentration ($\mu\text{g}/\text{m}^3$), April-September 1985. Concentrations in ppb are obtained by division with 2 (Grennfelt et al., 1987).

| STATION | Numbers of hours and days | | | | | | | | | | | | Maximum ozone concentrations | |
|----------------------|---------------------------|-----|------|-----|------|-----|------|----|------|----|------|----|------------------------------|-----|
| | Total | | >120 | | >160 | | >200 | | >240 | | >280 | | $(\mu\text{g}/\text{m}^3)$ | |
| | h | d | h | d | h | d | h | d | h | d | h | d | h | d |
| Illmitz | 4044 | 172 | 2226 | 168 | 994 | 123 | 405 | 65 | 152 | 32 | 46 | 13 | 446 | 197 |
| Gent St. Kruiswinkel | 3695 | 161 | 77 | 15 | 38 | 7 | 17 | 4 | 1 | 1 | | | 253 | 120 |
| Risø | 2875 | 122 | 107 | 22 | 19 | 4 | 3 | 1 | | | | | 210 | 146 |
| Brotjacklriegel | 3609 | 152 | 314 | 41 | 8 | 3 | | | | | | | 174 | 109 |
| Deuselbach | 4003 | 170 | 264 | 38 | 31 | 6 | | | | | | | 196 | 109 |
| Langenbrügge-Waldhof | 4198 | 183 | 473 | 67 | 149 | 23 | 76 | 15 | 15 | 7 | 1 | 1 | 286 | 138 |
| Schauinsland | 4281 | 183 | 1170 | 91 | 99 | 20 | 4 | 2 | | | | | 202 | 127 |
| Westerland | 4329 | 183 | 101 | 19 | 4 | 2 | | | | | | | 166 | 105 |
| Utö | 1415 | 58 | 26 | 7 | 1 | 1 | | | | | | | 198 | 120 |
| Eibergen | 3841 | 165 | 81 | 17 | 18 | 7 | | | | | | | 181 | 99 |
| Witteveen | 2582 | 87 | 88 | 16 | 17 | 6 | 3 | 1 | | | | | 217 | 112 |
| Birkenes | 1401 | 61 | | | | | | | | | | | 115 | 70 |
| Jeløya | 4306 | 181 | 53 | 12 | 22 | 5 | 14 | 5 | 1 | 1 | | | 266 | 118 |
| Langesund | 2648 | 110 | 29 | 5 | | | | | | | | | 133 | 113 |
| Aspvreten | 2928 | 121 | 272 | 30 | 62 | 6 | | | | | | | 198 | 173 |
| Norra Kvill | 1830 | 77 | 13 | 2 | 3 | 1 | | | | | | | 194 | 100 |
| Ringmäla | 3300 | 138 | 207 | 28 | 17 | 5 | 1 | 1 | | | | | 202 | 130 |
| Rörvik | 3954 | 172 | 233 | 39 | 35 | 8 | 5 | 1 | | | | | 214 | 127 |
| Vavihill | 3447 | 144 | 255 | 32 | 44 | 7 | 2 | 1 | | | | | 212 | 141 |
| Vindeln | 1808 | 78 | | | | | | | | | | | 120 | 65 |
| Bottesford | 4375 | 183 | 84 | 12 | 22 | 2 | 9 | 1 | | | | | 220 | 133 |
| Harwell | 3805 | 160 | 121 | 23 | 16 | 4 | 1 | 1 | | | | | 206 | 136 |
| Wray | 4223 | 181 | 51 | 11 | 4 | 1 | | | | | | | 176 | 113 |
| Sibton | 2228 | 99 | 50 | 11 | 5 | 1 | | | | | | | 192 | 125 |

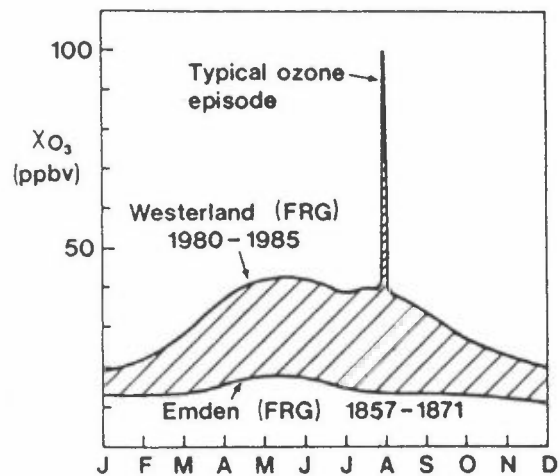


Figure 2: Illustration (cartoon) of comparison of background ozone at Emden (FRG, North sea coast) from historic records (Volz et al., 1986) with modern day ozone at the UBA Westerland (FRG, North sea coast) background station. Also shown is the enhancement of ozone during a typical episode (Hov et al., 1986).

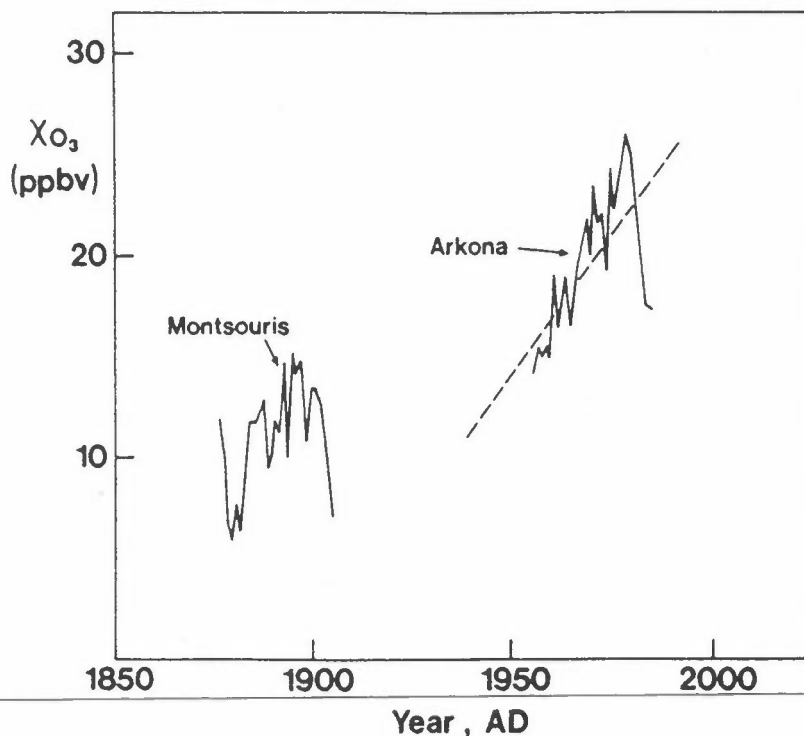


Figure 3: Surface near ozone at Monsouris 1876-1905 (Volz et al., 1986) compared to the Arkona series (Feister and Warmbt, 1987).

The growing concentration of ozone in the remote troposphere is further documented in Figure 3 where the measurements at Cape Arkona at the coast of the Baltic Sea in the German Democratic Republic are shown for more than 30 years (Feister and Warmbt, 1987). These data support a linear increase in ozone by 1-3%/a.

A similar increase is found in the free tropospheric content of ozone in the northern hemisphere at the Hohenpeissenberg Observatory in Munich (Attmannspacher et al., 1984) and for north temperate latitudes based on Umkehr and ozone sonde measurements (Angell and Korshover, 1983).

It can be concluded that at least over north temperate latitudes, ozone episodes in the atmospheric boundary layer are superimposed on a background level which is slowly increasing at a rate of 1-3%/a.

2.1 CONTROLLING FACTORS OF EPISODIC AND LONG-TERM OZONE CHANGES

Anthropogenic emissions of VOC and NO_x are important both for the episodic occurrence of peak ozone (Hov et al., 1978) and for the long-term increase (Isaksen and Hov, 1987; Dignon and Hameed, 1985). As will be seen below the relative influence of VOC and NO_x-emissions on the building up of ozone is different in the two cases.

Several models have been developed to simulate the formation and transport of photochemical oxidants in the atmospheric boundary layer over Europe. One of them is the Norwegian trajectory model, first described and applied by Eliassen et al. (1982). This model has been used to calculate the concentration of ozone at 14 receptor points where ozone is being measured on an hourly basis for the time period 1-7 June 1982. Calculations were carried out every 6 h GMT. The EMEP grid area is shown in Figure 4, the 14 receptor points in Figure 5.

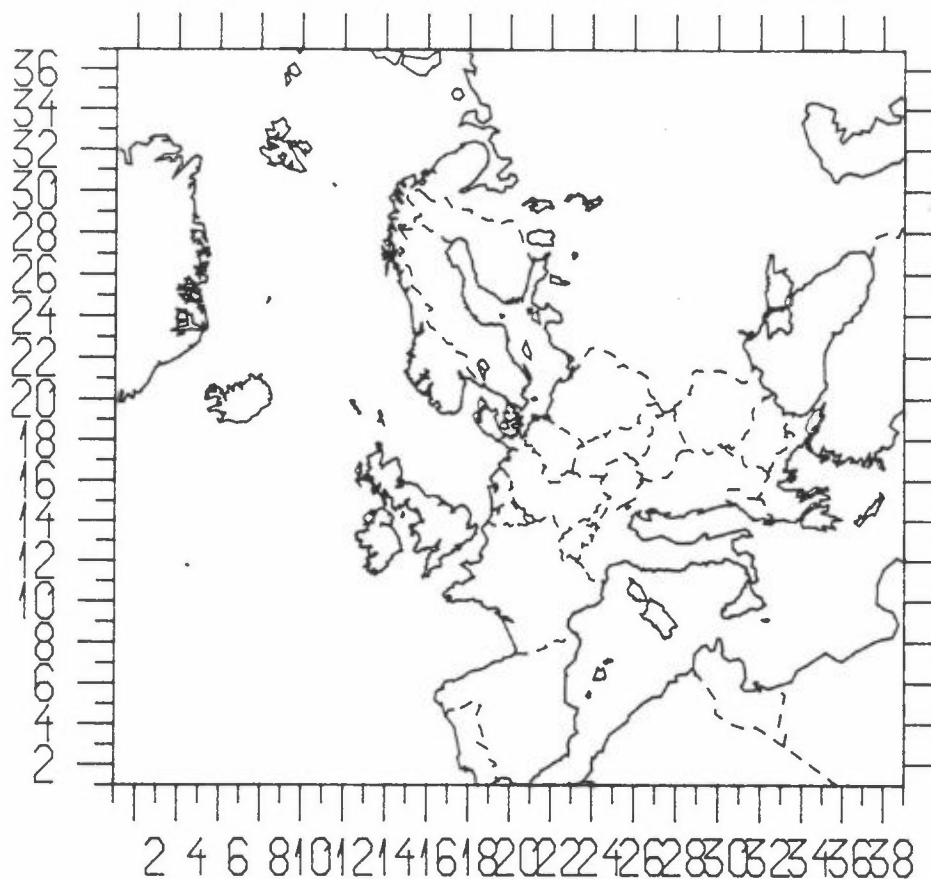


Figure 4: Map of Europe with the grid system used in the EMEP model.

The pollutants are assumed to be completely mixed vertically throughout the boundary layer which has a variable depth along the 96 h, 850 mb trajectories. The mixing height is determined by an objective analysis of the radiosonde data available inside the EMEP grid. During transport, emissions of VOC and NO_x are mixed into the air parcel according to the emission inventories for VOC and NO_x. Data for temperature, relative and absolute humidity and precipitation are also available in the EMEP grid on a 6-hourly basis. These data are used to calculate reaction rate coefficients and cloud cover. Dry deposition velocities for species like O₃, NO₂, PAN and HNO₃ are applied as recommended in the literature, and modified to be applicable to boundary layer average concentration rather than the concentration at 1 m, which is not explicitly calculated. Further details are given by Eliassen et al. (1982) and Hov (1987). The carbon bond mechanism CBM-X is used in this calculation (Whitten et al., 1984).

The emissions of VOC and NO_x in the EMEP grid for the period of calculation were based on estimates obtained within the PHOXA-project where model calculations are carried out on a subgrid of the EMEP grid (Bultjes, 1985).

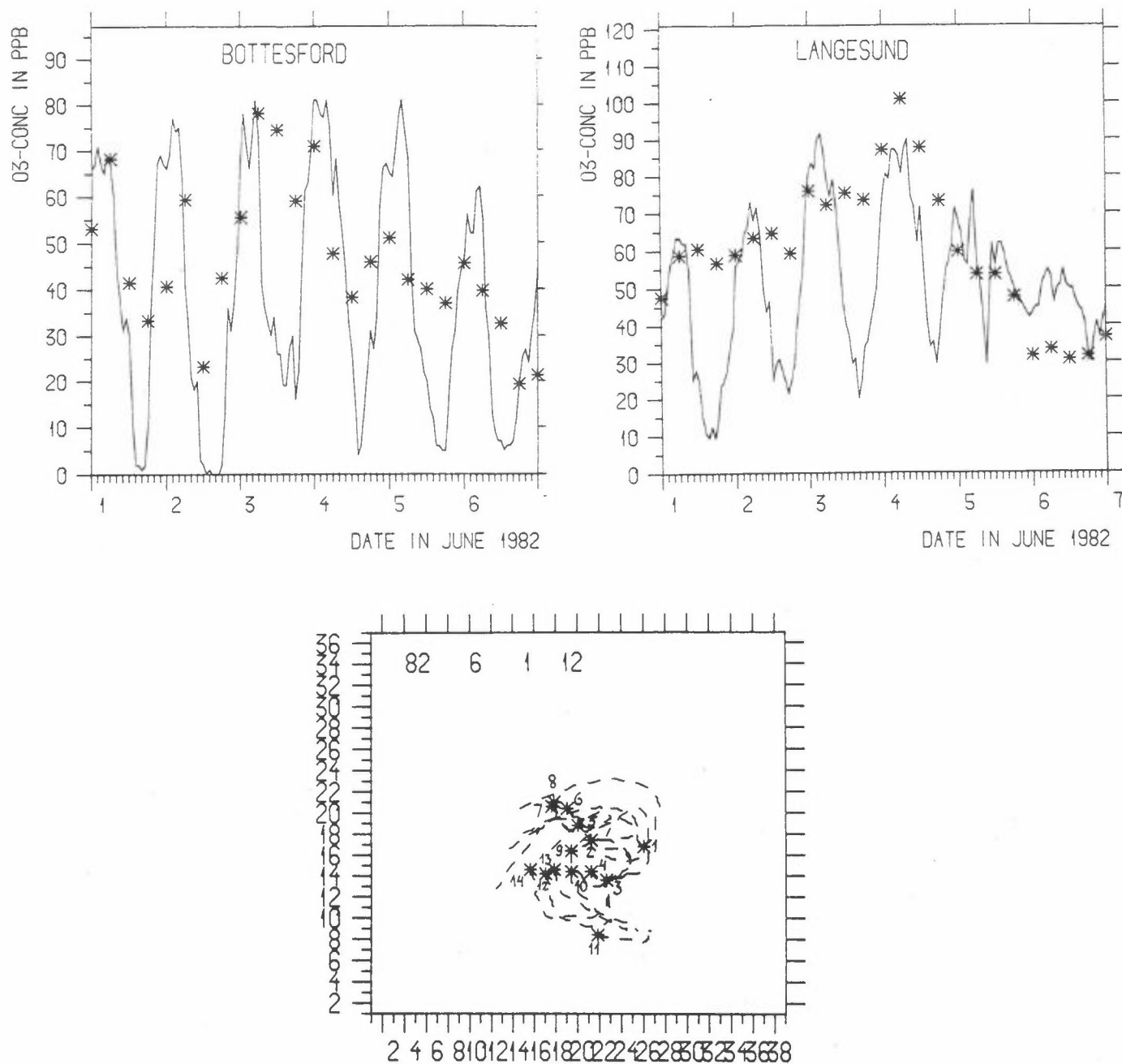


Figure 5: 96 h, 850 mb back trajectories to 14 rural measuring sites for O_3 in Europe, for arrival time 12 GMT, 1 June 1982. Also shown is measured hourly O_3 concentrations (full line) and calculated O_3 concentrations every 6h at Bottesford (site 12) in the UK and Langesund (site 7) in Norway for the time period 1-7 June 1982. (Station 1: Illmitz, Austria; 2: Langenbrügge, FRG; 3: Schauinsland, FRG; 4: Deuselbach, FRG; 5: Risø, Denmark; 6: Rörvik, Sweden; 7: Langesund, Norway; 8: Jeløy, Norway; 9: Sappermeer, NL; 10: Waarde, NL; 11: Colomiers, France; 12: Bottesford, UK; 13: Sibton, UK; 14: Stodday, UK).

The NO_x-emissions estimated by the PHOXA project for the pollution episode ending approx. 1 June 1982 was about twice the EMEP-estimate. The VOC-emission estimate for the PHOXA-area was approximately equal to the figure estimated by Eliassen et al. (1982), but in the PHOXA-estimate a considerable fraction was assumed to be of natural origin for this specific time period due to hot weather. The natural VOC-emissions were thought to play a negligible role by Eliassen et al. (1982). Calculations were made keeping the VOC-emissions as estimated in Eliassen et al. (1982) for the EMEP-grid, while the NO_x-emissions estimated in EMEP were doubled to match the PHOXA-estimates. These calculations were then repeated without changing the VOC-emissions, while the NO_x-emissions were cut by 50% to match the EMEP figures. Examples of the results for two of the most successful comparisons (Langesund on the south coast of Norway and Bottesford in the United Kingdom) are shown in Figure 5, where the PHOXA-emission estimates are used.

Calculations were then made where the emissions of VOC and NO_x were reduced throughout the EMEP grid by fixed percentages. This was done on the basis of two different reference calculations: With NO_x-emissions in line with the PHOXA-estimate and with these NO_x-emissions cut by 50% to fit the EMEP figures. In Table 2 is shown the results for ozone. The results are grouped into different regions.

In both cases a reduction in VOC-emissions alone efficiently reduce ozone. In case A, NO_x-emission reduction is calculated to increase ozone, while in case B ozone drops. A combined reduction of 25% in both NO_x and VOC is less efficient than reducing only VOC by 25% in case A, while in case B the reduction in ozone is then calculated to be larger than for separate reductions of 25% in VOC or NO_x.

Two conclusions can be drawn: VOC-emission reduction is calculated always to be more efficient in the abatement of episodic ozone than NO_x-emission reduction. In case A, the NO_x-emissions are so high that they actually suppress ozone formation, while in case B the NO_x-emissions are at a level where a decrease causes reduction of O₃.

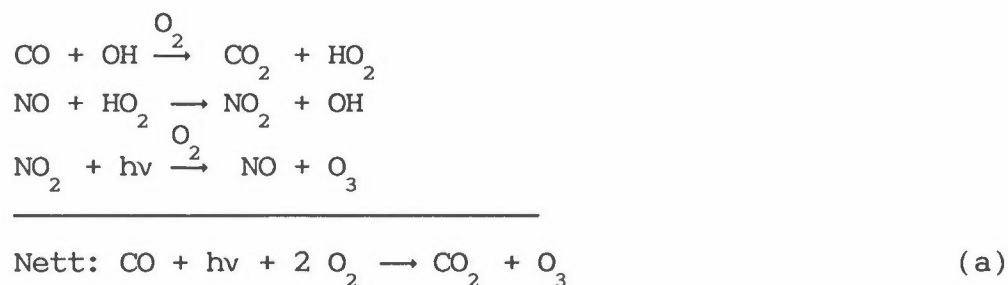
Table 2: Fraction of trajectories (in %) with more than 60 ppb O₃ at the arrival point in each of 4 geographical areas for the time period 1 June 12 GMT - 7 June 12 GMT 1982. The FRG sites are Schauinsland, Deuselbach and Langenbrügge, the Scandinavian sites are Langesund (N), Jeløya (N), Rørvik (S) and Risø (DK), the UK sites are Stodday, Bottesford and Sibton, and the Dutch sites are Sappermeer and Waarde.

| Case A PHOXA-estimates of VOC and NOx-emissions | | | | |
|---|-----------|--------------------|-------------|----------|
| Description | FRG sites | Scandinavian sites | Dutch sites | UK sites |
| Reference run | 54.7 | 45.0 | 38.0 | 13.3 |
| -25% in VOC | 20.0 | 23.0 | 4.0 | 6.7 |
| -50% in VOC | 0.0 | 5.8 | 0.0 | 0.0 |
| -25% in NOx | 64.0 | 58.0 | 62.0 | 22.7 |
| -50% in NOx | 54.7 | 55.0 | 62.0 | 26.7 |
| -25% in both NOx and VOC | 34.7 | 43.0 | 36.0 | 13.3 |
| +25% in both NOx and VOC | 64.0 | 44.0 | 38.0 | 13.3 |
| -75% in both NOx and VOC | 1.3 | 1.0 | 10.0 | 0.0 |

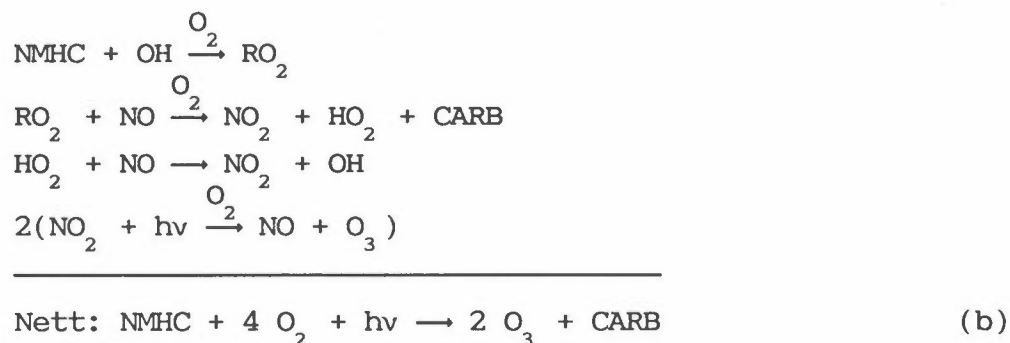
| Case B PHOXA-estimate of VOC, EMEP estimate for NOx-emissions | | | | |
|---|-----------|--------------------|-------------|----------|
| Description | FRG sites | Scandinavian sites | Dutch sites | UK sites |
| Reference run | 54.7 | 55.0 | 62.0 | 26.7 |
| -25% in VOC | 36.0 | 47.0 | 52.0 | 13.3 |
| -50% in VOC | 14.7 | 31.0 | 26.0 | 2.7 |
| -25% in NOx | 42.7 | 48.0 | 58.0 | 18.7 |
| -50% in NOx | 29.3 | 42.0 | 48.0 | 9.3 |
| -25% in both NOx and VOC | 32.0 | 44.0 | 50.0 | 10.7 |
| +25% in both NOx and VOC | 72.0 | 65.0 | 76.0 | 32.0 |
| -75% in both NOx and VOC | 1.4 | 0.0 | 8.0 | 0.0 |

On a global scale, the amount of NO_x present is assumed to be the controlling factor for ozone formation. Several studies support this conclusion.

The main sources for tropospheric ozone are transport from the stratosphere through the tropopause, and in situ photochemical formation. Ozone production takes place through the reactions.

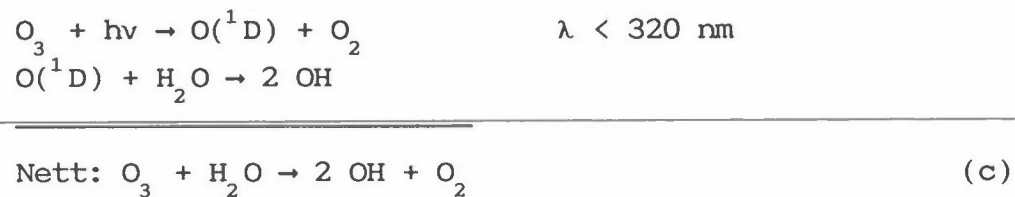


or through



where CARB denotes a carbonyl species (e.g. formaldehyde) and NMHC a nonmethane hydrocarbon molecule. Methane would undergo a similar decomposition.

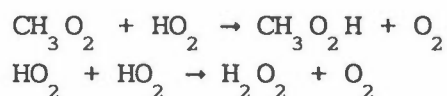
The main chemical loss of tropospheric ozone takes place through



and through



(c) is the most important chemical destruction process for tropospheric ozone. The presence of NOx is essential for the production reactions to occur. At very low NOx-levels (ppt), the HO_2 (RO_2) + NO \rightarrow OH (RO) + NO_2 reactions will not be the dominating conversion mechanisms for peroxy radicals, and reactions like



may convert the radicals into water soluble reservoir species like $\text{CH}_3\text{O}_2\text{H}$ and H_2O_2 .

It is only over the last few years that analytical techniques have been available allowing measurement of both ozone, NOx and individual hydrocarbons even at rural, clean sites where the concentration of NO and NO_2 may drop as low as 10 ppt, compared to the ppb-levels usually found in populated areas.

Extensive measurements have been carried out for several years at Niwot Ridge at 3050 m a.s.l. in the Rocky Mountains approximately 60 km northwest of metropolitan Denver in Colorado in the US. The prevailing winds are from the west, which bring in clean air. Sometimes easterlies transport pollution from Denver.

Liu et al. (1987) made a theoretical analysis of measurement data from ~~Niwot Ridge previously published by Fehsenfeld et al. (1983) and Parrish et al. (1986).~~ A photochemical model was applied to calculate the net chemical production of ozone as a function of the concentration of NOx. The measured concentrations of individual hydrocarbons (including CH_4), CO and NOx were fixed at sunrise, but allowed to vary over the day. The formation of ozone over a daily cycle of day-night shifts was calculated till steady-state was reached. The atmospheric

boundary layer was diluted through the pumping effect of the daily rise in the mixing height. Above the atmospheric boundary layer, fixed concentrations of O_3 , NOx, CO og CH_4 were assumed (40, 0.01, 200 and 1600 ppb, respectively), the rest of the model species (nonmethane hydrocarbons, carbonyls) were assumed to be negligible above the boundary layer. Ground removal was included using generally accepted values.

Liu et al. (1987) calculated the O_3 production per unit of NOx per day, and the result is shown in Figure 6 for summer and winter conditions. In the remote troposphere where NOx is extremely low, they found that the production of O_3 is limited by NOx. The O_3 -production per unit of NOx is independent of the level of NOx, and the formation of O_3 is a linear function of the NOx-mixing ratio. Parrish et al. (1986) found the same in their ozone measurements at Niwot Ridge for NOx-levels below 1 ppb during the summer. Liu et al. (1987) also found in their calculations (Figure 6) that the ozone production per unit of NOx is fairly independent of NOx when NOx exceeds 5 ppb, and that the O_3 -production at high NOx (more than 5 ppb) is approximately 1/4 of what it is at low NOx (less than 0.5 ppb).

The results obtained by Liu et al. are in line with what was found in the long-range transport calculation discussed in this section. At high NOx-concentrations, the O_3 -production per unit NOx is lower than with more moderate NOx-concentrations. Also, if the NOx-emissions are reduced in a situation where NOx is in the 0.5-5 ppb concentration range (see Figure 6), it is to be expected that the production of O_3 may increase even if NOx drops.

From Figure 6 it is seen that for NOx-concentrations below 0.5-1 ppb, the chemical production of ozone in the troposphere is nearly proportional to the concentration of NOx. Measurements of NO and NO_2 in the ~~atmospheric boundary layer over rural areas in industrialized countries,~~ over the oceans and in the free troposphere, indicate that the concentration of NOx is below 0.5 ppb as a rule rather than as an exception. The near proportionality between the chemical production of O_3 and NOx, is probably a reality in a very substantial part of the troposphere. Measurements of NOx in the non-urban troposphere are reviewed by Fehsenfeld et al. (1988).

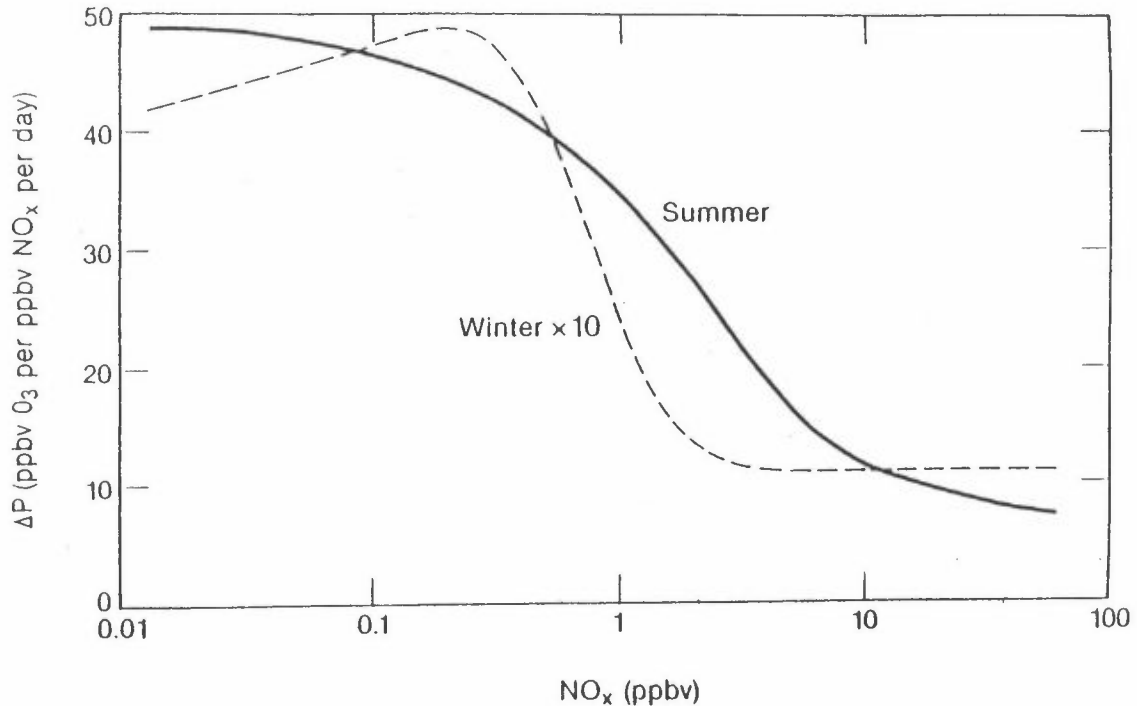


Figure 6: Photochemical production rate ΔP calculated as a function of NO_x mixing ratios for summer and winter conditions (Figure from Liu et al. (1987) where also more details can be found).

Dignon and Hameed (1985) used a one-dimensional latitudinal model of the troposphere to analyse why tropospheric ozone in the northern hemisphere is increasing. They found that a significant portion of its increase may be attributed to the increase in global anthropogenic NO_x -emissions during the last decades, while the contribution of CH_4 to the increase is quite small.

Isaksen and Hov (1987) applied a global meridional model of the troposphere to derive a relationship between long-term changes in the emissions of NO_x and CH_4 , and the changes in species like O_3 and hydroxyl.

In Figure 7 is shown the results at 50°N latitude of two different model calculations. In the first case, the emissions of NO_x were increased by 3%/a for 30 years, in the other case the tropospheric concentration of CH_4 was increased by 1.5%/a for 60 years. It is seen that the annual growth in O_3 is much more pronounced in the NO_x increase case than in the CH_4 case, in particular in the lower troposphere.

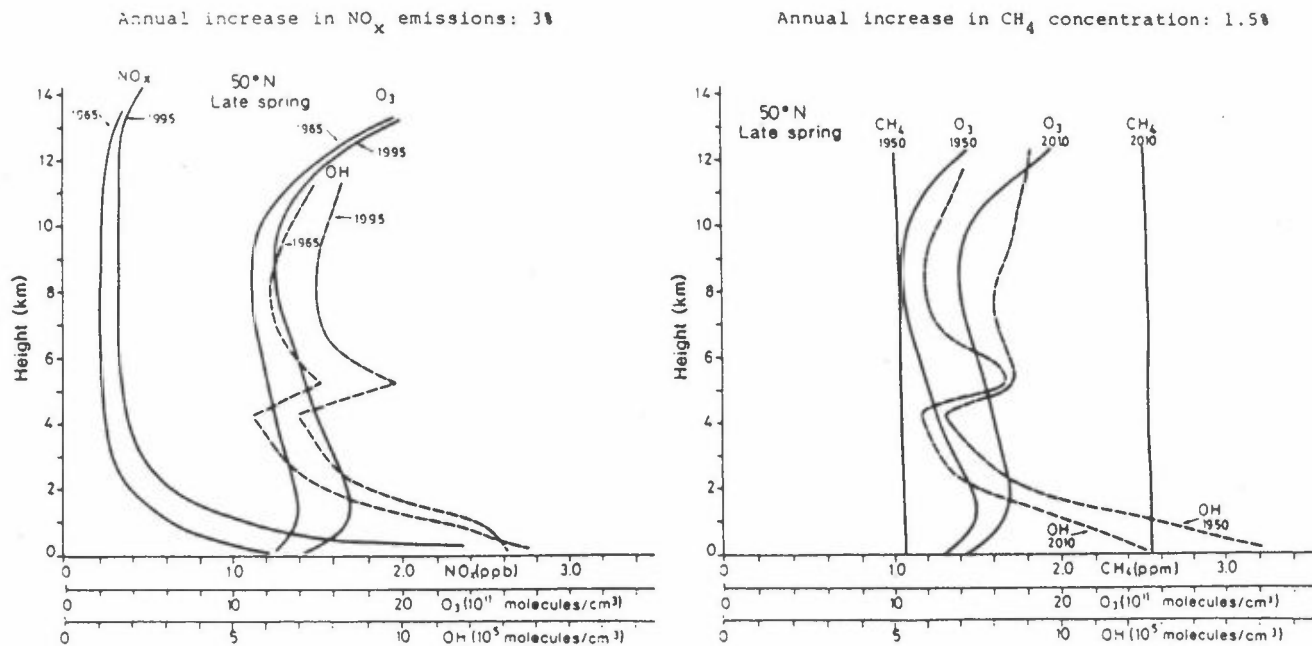


Figure 7: The distribution of the concentration of O_3 , NO_x and OH with height at 50°N , late spring (end of May) for 1965 and 1995 in a model calculation with an annual increase in NO_x -emissions of 3%, and the distribution of O_3 , CH_4 and OH for 1950 and 2010 in a calculation where the concentration of CH_4 increased by 1.5%/a (Isaksen and Hov, 1987).

2.2 CONCLUSIONS. EFFECT OF CHANGING NO_x -EMISSIONS ON EPISODIC AND LONG-TERM OZONE CHANGE.

Ozone episodes in the atmospheric boundary layer over Europe are superimposed on a background concentration which is slowly increasing. The increase in the background concentration is probably controlled by increasing NO_x -emissions. The episodic peaks in atmospheric boundary layer ozone are more efficiently reduced by reducing the VOC-emissions than the NO_x -emissions.

A further increase in European NO_x -emissions may not change much the occurrence of boundary layer ozone episodes. Such episodes take place only in the summer half year and only a few weeks per year (cpr. Table 1). The emissions of NO_x are highest during the winter half year, when the photochemical activity at mid and high latitudes is small. This means that the chemical half life of both the NO_x and VOC is so long that atmospheric transport and physical removal processes become very important.

NO_x in the atmospheric boundary layer is partly converted into nitric acid or nitrate, species which contribute directly to acid deposition either through dry deposition or precipitation, and partly NO_x is converted into reservoir species like peroxyacetyl nitrate (PAN) which has a chemical lifetime of many days and even weeks at the low temperatures found in the winter and in the free troposphere. NO_x can also be transported out of the boundary layer and into the free troposphere through the diurnal pumping of the boundary layer, through convective motion and thunderstorms (Dickerson et al., 1987) and when the boundary layer is breaking up due to frontal passage or mountainous terrain.

This means that in situations with atmospheric boundary layer breakup, or when the chemical conversion is slow, the precursors may be transported into the free troposphere where the physical removal processes (precipitation and ground removal) are slow or nonexistent. Consequently the lifetime is longer than in the boundary layer, giving room for mixing and dilution to occur to concentration levels (NO_x in the sub ppb range) where the ozone production is very efficient.

It is likely that a further increase in the NO_x-emissions in Europe and elsewhere in the northern hemisphere, will contribute to a continued rise in free tropospheric ozone, while the occurrence of ozone episodes in the boundary layer may not change much. The deposition of acid compounds will increase as a consequence of rising NO_x-emissions. This topic is dealt with in the following.

3 NO_x-EMISSIONS AND ACID DEPOSITION

NO and NO₂ are together with SO₂, the most important precursors of components which contribute to acid deposition. In this section a ~~review will be given of information about trends in acid deposition,~~ and it will be discussed how a slow global increase in species like O₃ and CH₄ may change the oxidation mechanism of NO_x.

Ice cores from south Greenland have been analysed with respect to trace impurities such as chloride, nitrate and sulphate. Mayewski et al. (1986) analysed an ice core drilled about 40 km away from a previous core site (Dye 3) in south Greenland. The core covered the period 1869 to 1984. The data showed that excess (nonseasalt) sulphate had increased threefold since approximately 1900, and the nitrate concentration had doubled since 1955. They attributed the increases to the deposition of those species from air masses carrying North American and European anthropogenic emissions. Neftel et al. (1985) reported similar findings.

Chemical analysis of ice core samples from Dye 3, Greenland showed that nitrate fluxes had risen to about 30% above natural levels by the 1950s, while sulphate fluxes had risen to about 3 times natural levels by the 1950s and were approximately proportional to anthropogenic input. There was a peak in the deposition of nitrate and sulphate in the late winter and early spring, coinciding with the Arctic haze maximum (Finkel et al., 1986).

The composition of precipitation (sulphate, nitrate, pH, other ions) and of air (SO_2 , sulphate) has been measured in the EMEP network throughout Europe since 1978. Clear trends are difficult to derive yet, but for most stations there is evidence for a decreasing concentration of SO_2 in air with time. There is also a downward trend in sulphate in precipitation at Eskdalemuir in Scotland, and also at Tange in Denmark and Ahtäri in Finland, while no trend was observed at Birkenes in south Norway for the time period 1979-1984 (Semb and Dovland, 1986).

Precipitation data for EMEP for the period 1980-84 indicate that there is an increase in the annual mean nitrate to non-marine sulphate equivalent ratio (Nodop, 1986). An analysis of the nitrate content of ~~monthly precipitation samples collected in the European Air Chemistry~~ Network (EACN) during the period 1955 to 1979 showed that all stations but one had an increase in concentration during the 25 year period. The annual increase in nitrate concentration between the late 1950s and early 1970s was in the range 3-6% at 75% of the stations (Søderlund et al., 1985).

Aerosol measurements at a rural site in the UK (Harwell) from 1957 to 1974 showed a more than doubling of the nitrate concentration and only a 20% increase in sulphate (Salmon et al., 1978), see Figure 8.

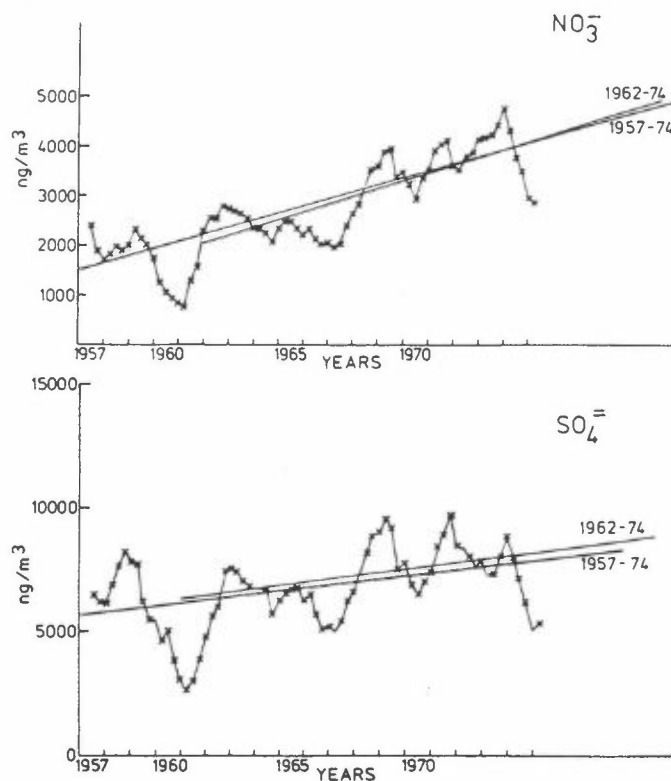


Figure 8: Increase in nitrate and sulphate concentration in the aerosol measured at Harwell, U.K., over the years 1957 to 1974 (Salmon et al., 1978).

During the last decade decreasing SO_2 -emissions in many countries in Europe have caused the concentration of SO_2 in air and sulphate in air and precipitation, to decline at many rural measuring sites. The same decline is not found for nitrate in rain, while the data for nitrate in air are too scarce to draw any conclusion. For ammonium in rain long data series are scarce, but there are indications of an upward trend (SFT, 1986).

On a long-term basis and averaged over a large area, e.g. for the annual mean over Europe, there is a linear relationship between the change in emissions of SO_2 and the deposition of S-compounds. This is probably nearly the case also for the relationship between a change in NO_x emissions and the deposition of compounds derived from NO_x .

The conversion of SO_2 to sulphate mainly takes place through



where SO_3 reacts rapidly with water vapour



When species like H_2O_2 and O_3 are dissolved in cloud water, they readily oxidize dissolved SO_2 . The H_2O_2 -mechanism is rather insensitive to the acidity of the water, while the ozone-mechanism is very slow at low pH. Gaseous hydrogen peroxide is a major oxidant leading to sulphuric acid generation in cloud water (for a review, see Hov et al., 1988).

Emissions of NO are converted to NO_2 through the very fast reaction



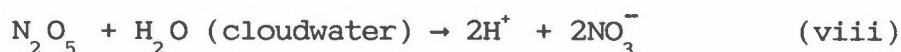
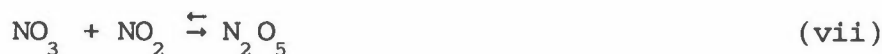
Conversion to nitric acid HNO_3 takes place through



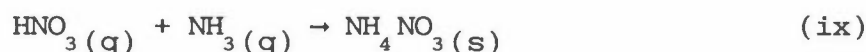
which is about 10 times faster than the rate constant for the SO_2 -reaction.

The OH-radical vanishes at night. Measurements both in the U.S. (Calvert et al., 1985) and in Europe (Schaug et al., 1987) show that there is a strong seasonal dependence in the sulphate deposition suggesting a dominating photochemical influence on the gas and liquid phase chemistry. For the deposition of nitrate, there is no strong variation with season. Both OH and H_2O_2 vary strongly with season, supporting that a major part of the oxidation of SO_2 takes place through reaction with OH in the gas phase and H_2O_2 in the liquid phase.

The formation of nitrate in the winter and in the dark mainly takes place through



Nitrate dissolved in water droplets is in equilibrium with nitric acid (HNO_3). Nitric acid is also in equilibrium with ammonium nitrate through



where g denotes gas and s solid. Ammonium nitrate dissolves into ammonium and nitrate in water. The equilibrium constant is dependent on temperature and relative humidity (Stelson and Seinfeld, 1982).

NO_2 is also converted into peroxyacetylnitrate through



where Δ is strongly temperature-dependent (slow at low temperatures).

In photochemical episodes, both OH, CH_3COO_2 , H_2O_2 and O_3 increase in concentration, which means that the conversion of NOx and SO_2 to nitrate, PAN and sulphate is faster than usual. The dry deposition velocity of nitrate and sulphate aerosols is smaller than for SO_2 or NO_2 . There is usually very little precipitation in photochemical episodes, favouring a long atmospheric lifetime of S- and NOx-species. On the other hand winds are usually low and vertical mixing poor in stagnant, anticyclonic weather conditions, which means that the extent of long-range transport or mixing with free tropospheric air do not increase as much as the lifetime increases.

A reduction in the NO_x-emissions could have the following impact on acid deposition in photochemical episodes: O₃ and OH could decrease only slightly, while H₂O₂ would increase. This means that the formation of nitrate would slow down slightly, while the conversion of SO₂ to sulphate would remain rather unchanged.

Acid deposition is of concern in episodes, but environmental damage is mainly linked to the integrated acid deposition over a long time period. This has become very evident in South Norway, where a doubling of the nitrate content of freshwater lakes has taken place between 1974-75 and 1986, without any significant change in the nitrate deposition, indicating a saturation effect (SFT, 1987).

An attempt was made by Hov and Isaksen (1986) to show how slow changes in the emission of NO_x and CH₄ would influence the formation of sulphate and nitrate in the global atmosphere. A global, 2-dimensional meridional model which is described elsewhere (Isaksen et al., 1985; Isaksen and Hov, 1987), was applied to calculate the change in the global distribution of OH, H₂O₂, O₃ and NO₂ as the emissions of NO_x and CH₄ were changed separately.

Long-term calculations were carried out with 1980 as the base year for two different cases: An increase in the anthropogenic NO_x-emissions by 3%/a, that is 2.1%/a in the total NO_x-emissions, and 1.5%/a increase in the methane concentrations. The calculations were speeded up by computing explicitly only the first year, the base year (1980) and the last year.

For methane, a 60 yr period was covered with 1950 as the first and 2010 as the last year. The response time to changes in the emissions was so fast that sufficient convergence was achieved already after one year of model simulation.

For methane it was chosen to change the concentration by approximately the amount observed to be the annual increase globally, rather than to increase the emission rate since it would require a calculation covering several decades for methane to reach steady state.

In Figure 9 is shown the meridional distribution at the end of May of NO_x ($= \text{NO} + \text{NO}_2$), O_3 , OH and H_2O_2 with height in 1965 and 1995 in a 30 years' calculation with an annual increase in the anthropogenic NO_x -emissions of 3%. In the southern hemisphere there was not much change in the concentrations, while in the lower part of the northern hemisphere up to 0.9%/a increase in ozone was calculated, 1.4%/a in OH , 2.1%/a in NO_x while there was a drop in H_2O_2 of 0.5%/a or less.

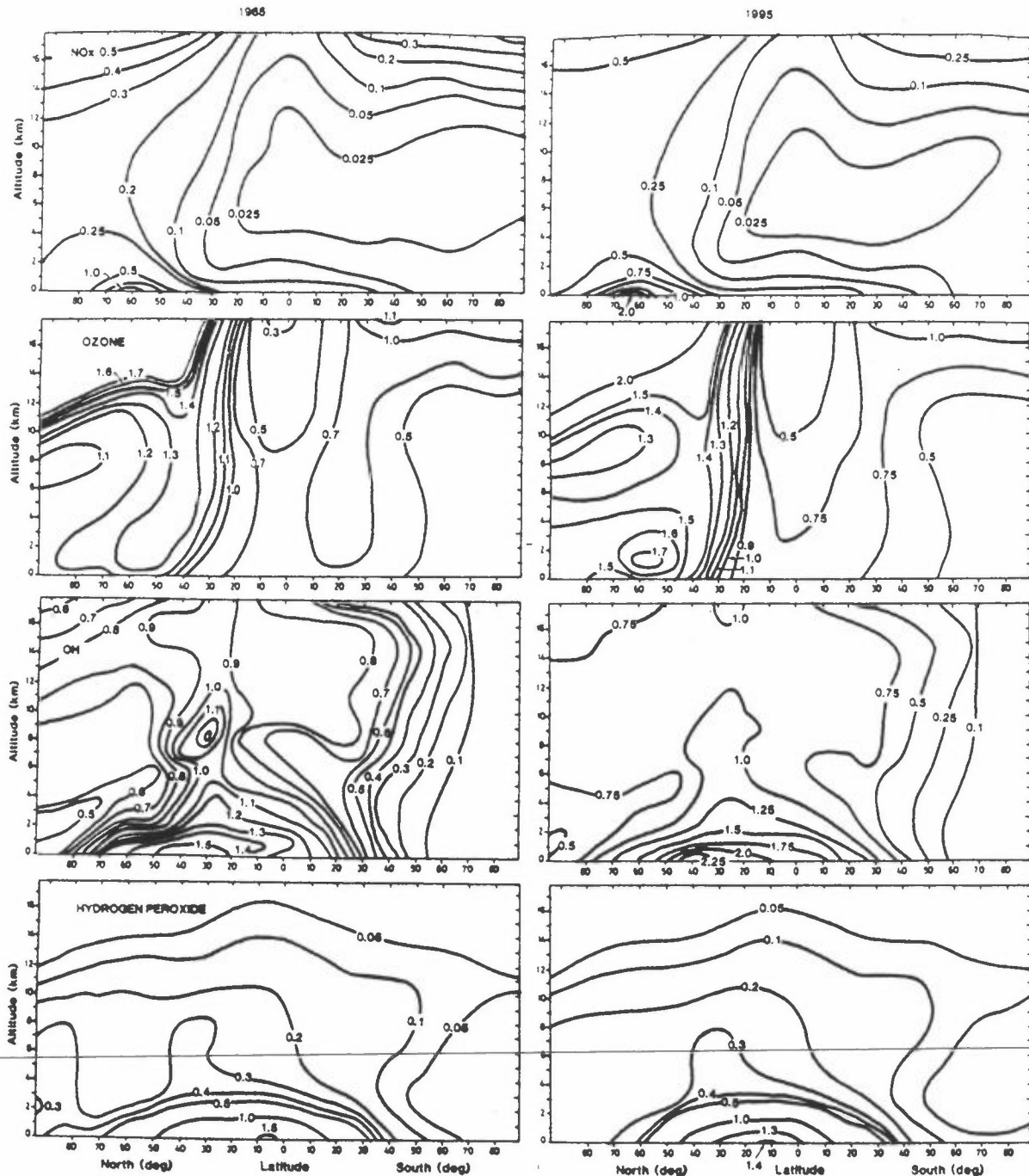


Figure 9: The meridional concentration with height at the end of May for NO_x (in ppb), O_3 (in 10^{12} molecules/cm³), OH (in 10^6 molecules/cm³) and H_2O_2 (in ppb) in 1965 (left column) and 1995 (right column) for a calculation where the global anthropogenic NO_x -emissions increased by 3%/a (Hov and Isaksen, 1986).

The increase in NOx was largely as NO₂. This means that the formation of nitric acid through reaction (v) increased more than the increase in total NOx-emission in the lower troposphere at mid northerly latitudes. The rate of formation of nitric acid increased by nearly (2.1 + 1.4)%/a or 3.5%/a there.

The increase in OH that was calculated for increasing NOx-emissions would also enhance gas-phase sulphate production through reactions (i) followed by (ii) and (iii). The wet-phase conversion of dissolved SO₂ to sulphate would proceed at a slower rate, however, since it is mainly controlled by H₂O₂ which was calculated to decline as NOx goes up. This is due to the suppression of HO₂-radicals with increasing NO. At high pH wet-phase sulphate formation could be enhanced since dissolved ozone than is active in the oxidation.

In Figure 10 is shown the meridional distribution at the end of May of O₃, OH and H₂O₂ with height in 1950 and 2010 in a calculation where the concentration of CH₄ increased by 1.5%/a over 60 years. Changes in O₃, OH and H₂O₂ were calculated to occur throughout the troposphere and in both hemispheres.

In the lower part of the troposphere in the northern hemisphere O₃ was calculated to increase by about 0.4%/a, OH to decrease by 0.5%/a and H₂O₂ to increase by about 0.5%/a.

The decrease in OH arose from the increase in its loss through reaction with CH₄. The concentration of hydroxyl decreased less than CH₄ went up, however, which means that the flux of material through the reaction



increased and led to the formation of more O₃ and HO₂-radicals in the decomposition reactions of CH₄, and consequently also H₂O₂ went up since the production is determined by



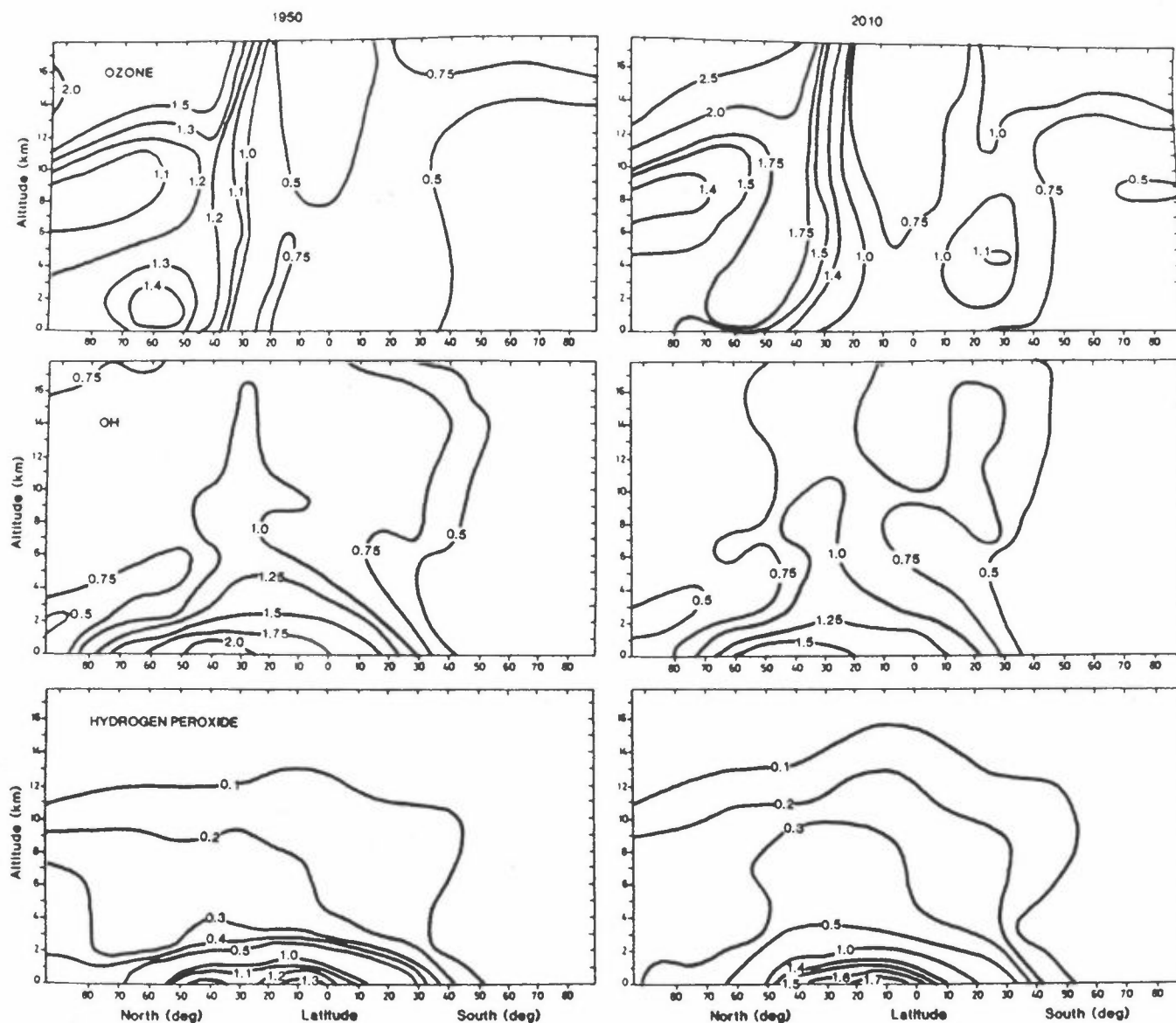


Figure 10: The meridional concentration with height at the end of May for O_3 (in 10^{12} molecules/cm³), OH (in 10^6 molecules/cm³) and H_2O_2 (in ppb) in 1950 (left column) and 2010 (right column) for a calculation where the tropospheric concentration of CH_4 was increased by 1.5%/a (Hov and Isaksen, 1986).

The calculations showed that to increase CH_4 only leads to a decrease in the conversion of NO_2 and SO_2 to nitrate and sulphate through the OH-reactions. The formation of nitrate in the dark would increase due to the O_3 increase, and the liquid phase conversion of SO_2 would likewise become more efficient.

Reaction (viii) was not included in the model calculations, but the results from the model runs with changes in NOx-emissions and CH_4 -concentrations can be used to get an indication about the change in the nitrate formation during the winter and during the night, provided that a process like reaction (viii) then is the main pathway for nitrate formation.

The rate of formation of the NO_3 -radical at night is controlled by reaction (vi). The formation rate of the NO_3 -radical increases as the sum of the increase in NO_2 and O_3 . The concentration of N_2O_5 is given by the equilibrium (vii) and is shifted to the right which means that $\text{N}_2\text{O}_5 \gg \text{NO}_3$ at night at atmospheric temperatures. This means that the formation rate of nitrate through reaction (viii) at night in the lower mid latitude northern troposphere increases as the sum of the increases in NO_2 and O_3 .

It can be concluded that to increase the global NOx-emission enhances both the photochemical conversion of NO_2 to HNO_3 through reaction with OH, and even more enhances the efficiency of the dark reaction where N_2O_5 reacts with water droplets. The sulphate formation is increased since OH goes up, while the liquid phase conversion becomes less efficient due to a suppression of H_2O_2 as NOx increases.

A picture of the combined effect of increasing the anthropogenic NOx-emissions by 3%/a and the CH_4 -concentrations by 1.5%/a can be gained by just adding the calculated annual changes in the concentrations together. At mid latitudes in the lower part of the troposphere in the northern hemisphere, O_3 would increase at a rate of 1.3%/a, OH increase by 0.9%/a, NOx would increase by 2.1%/a while H_2O_2 would remain virtually unchanged. Measurements of H_2O_2 in ice samples drilled on North Central Greenland seem to support that H_2O_2 in the air has not changed much in this century (Neftel et al., 1984).

The implication of these numbers is that at mid latitudes in the lower troposphere, the rate of formation of HNO_3 through the OH-route would increase somewhat more than the increase in NOx-emission.

The rate of formation of sulphate through the OH-route would increase by about 0.9%/a plus the rate of increase in the SO_2 concentration, while the liquid phase conversion would increase approximately at the same rate as the increase in the SO_2 concentration.

The mean winter concentration of the sum of nitrate and nitric acid in air and precipitation should have increased more than the summer values at mid latitudes in the northern hemisphere during years with increasing NOx-emissions. The findings also suggest that the fraction

that nitric acid + nitrate makes up of lower tropospheric NO_y (\approx NO_x + PAN + HNO₃ + nitrate), has increased more than the fraction that sulphate makes up of lower tropospheric SO_x (\approx SO₂ + sulphate) during times with increasing SO₂ and NO_x emissions.

3.1 CONCLUSIONS. CHANGES IN ACID DEPOSITION WHEN NO_x- AND VOC-EMISSIONS ARE CHANGED.

Nitrate derived from the emissions of NO_x, contributes in a significant way to acid deposition in Europe and elsewhere.

Integrated over one year and over all of Europe, there is probably a nearly linear relationship between a change in NO_x-emissions and the corresponding change in nitrate deposition.

A reduction of NO_x-emissions in a photochemical episode in Europe could decrease OH and O₃ only slightly, but with a marked increase in H₂O₂. This favours a somewhat slower conversion of NO_x to nitrate while the conversion of SO₂ to sulphate would remain rather unchanged.

In clean air, a trend downwards in the NO_x-emissions could cause a drop in the background concentration of O₃ and OH, while H₂O₂ increases. This means that the gas-phase conversion of SO₂ and NO_x through the reaction with OH to sulphate and nitrate will become less efficient. Also the dark reaction converting NO₂ to the NO₃-radical and further to nitrate through the reaction with O₃, would become slower, while the wet phase oxidation of SO₂ to sulphate would become more efficient. This means that reduced NO_x-emissions would give rise to a more than proportional reduction in the nitrate formation, while the efficiency of sulphate formation could increase. For the distribution of acid deposition this would imply an increase in the lifetime for S-compounds and perhaps also for NO_x-compounds.

4 GLOBAL ATMOSPHERIC CHANGE

The anthropogenic emissions of VOC and NO_x are also linked to another very important environmental issue: The increase in the atmospheric concentration of infrared absorbing species. This can give rise to climatic change since such gases modify the radiation energy balance of the earth-atmosphere system. The climatic effect of increasing CO₂ has been much studied, but the combined effect of other trace gases in warming the surface-troposphere system can in the future be as large as the warming due to CO₂ alone (Ramanathan et al., 1985; Hansen et al., 1982).

In Atmospheric Ozone (1985), the following overview of atmospheric trends was given: "The concentrations of halocarbons, methane, nitrous oxide (N₂O), odd nitrogen and carbon monoxide appear to be increasing at present on a global basis, by 5%/a for CFC-11 and CFC-12, 7%/a for CH₃CCl₃, 1%/a for CH₄, 0.2%/a for N₂O and 1-2%/a for CO. Available evidence indicates that increases in levels of CH₄, CO₂ and N₂O have been sustained for long periods and the increases derive from nondiscretionary, large scale human activities, mainly food and energy production. From this viewpoint, it would be expected that trends in CO and NO_x may also have been sustained for a long time. It seems improbable, therefore, that present trends toward increasing concentrations will be arrested or reversed in the near future. On the contrary, analysis of the historical records and the present imbalances between sources and sinks suggest that we might anticipate a gradual acceleration of present increases, and that substantial rates of accumulation in the atmosphere should be sustainable for long periods. This view is conditioned on the postulate that global population and associated economic activity will continue to increase at appreciable rates for some time. We reach similar conclusions in the case of halocarbons which are purely of industrial origin."

In section 2 in this paper, it was shown how measurements of ozone at clean air sites and in the free troposphere in the northern hemisphere, indicate a 1-2%/a increase in the ozone concentration there. Model calculations indicate that increasing anthropogenic NO_x-emissions have been the driving force behind the increase in tropospheric ozone.

The increase in CH_4 is probably due in parts to an increase in source strength and partly due to a suppression of tropospheric OH as CH_4 goes up, which increases the lifetime of CH_4 (Thompson and Cicerone, 1986; Isaksen and Hov, 1987). The sources for CH_4 are largely natural, but losses from natural gas production and distribution are important for the total source strength of CH_4 .

The increase in CH_4 in the troposphere is also controlled by the abundance of OH, which is controlled to a large extent by O_3 and NOx. A decrease in NOx-emissions on a global scale would tend to reduce O_3 and OH, increase the lifetime of CH_4 and allowing a more than proportional increase in atmospheric concentration.

N_2O is not decomposed in the troposphere, but an important source for N_2O is the combustion of coal and fossil fuels with a high content of nitrogen. When burning, organically bound nitrogen is released as N_2 , N_2O or NOx. A reduction in the consumption of fossil fuel would reduce both N_2O and NOx-emissions.

The halocarbons CFC-11 and CFC-12 are inert in the troposphere and are decomposed by short wavelength UV-light in the stratosphere. Methylchloroform reacts with OH in the troposphere, with a chemical lifetime of 5-7 years. Since the emissions of NOx are important for OH, there is a link between the growth in NOx-emissions and tropospheric CH_3CCl_3 .

The chemical lifetime of CO in the troposphere is a few months only, and it is controlled by OH. The sources of CO are approximately evenly split between direct emissions due to fossil fuel combustion, wood burning and burning in connection with agriculture in temperate and tropical regions, and atmospheric production from the oxidation of anthropogenic hydrocarbons, CH_4 and natural hydrocarbons (Logan et al., 1981; Atmospheric Ozone, 1985). The oxidation of CH_4 accounts for perhaps 25% of the total tropospheric source of CO. It is likely that tropospheric OH is declining at a slower rate than CH_4 increases (Isaksen and Hov, 1987), which indicates that the source of tropospheric CO is increasing and the sink process slowing down in efficiency, leaving room for CO to go up. The link with NOx-emissions is again the important control that NOx exerts on tropospheric O_3 and OH.

Ramanathan et al. (1985) made projections of the increase in atmospheric infrared absorbing gases that can be expected from 1980 to 2030, and calculated the equilibrium surface temperature in 2030 using a radiative-convective model. The cumulative equilibrium surface temperature warming is shown in Figure 11. The surface warming due to all the trace gases in Figure 11 is 1.54 K, more than twice the warming due to CO_2 alone. The largest warming effect besides CO_2 is due to the CFCs (CFC-11 and CFC-12). The warming due to stratospheric ozone depletion ($\text{O}_3(\text{ST})$) is also indirectly due to CFCs. There is also a nonnegligible surface warming due to increases in CH_4 (0.14 K), N_2O (0.1 K) and tropospheric O_3 (0.06 K), together 0.3 K or about 20% of the total warming (about 42% of the warming due to CO_2).

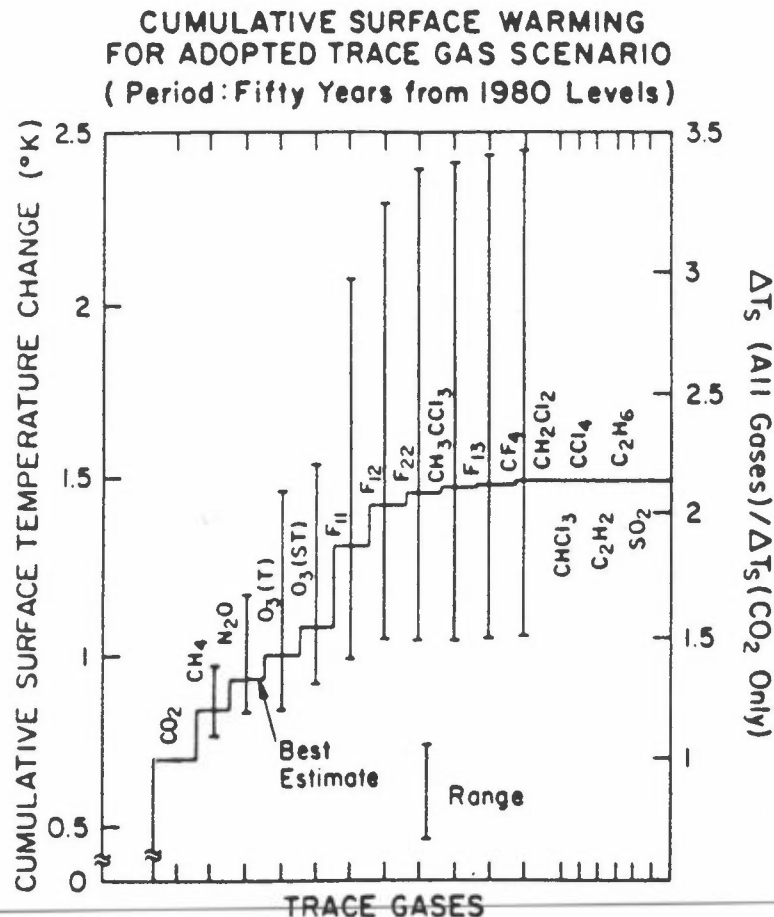


Figure 11: Cumulative equilibrium surface temperature warming due to increase in CO_2 and other trace gases. Increases in gas amounts from 1980 values to 2030 (Ramanathan et al., 1985).

4.1 CONCLUSIONS. THE LINK BETWEEN NO_x- AND VOC-EMISSIONS AND GLOBAL CLIMATIC CHANGE.

A decrease in global NO_x-emissions will cause a drop in tropospheric O₃, which will reduce the warming effect of tropospheric O₃. A decrease in global NO_x-emissions can come about by reducing the burning of fossil fuels rich on nitrogen, which would also reduce the emissions of N₂O. A reduction in NO_x would also reduce tropospheric OH. With unchanged surface sources of CH₄, tropospheric CH₄ would increase in concentration more than today, and contribute more to the surface warming than 0.14 K in fifty years. The combustion of fossil fuels is an important source of CO₂. A reduction in the use of fossil fuels would contribute to a reduction both in NO_x- and CO₂-emissions.

ACKNOWLEDGEMENT

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