Photochemical Air Pollution

Danish Aspects

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Abstract: The report consists of a series of chapters on different aspects of photochemical air pollution with special emphasis on the situation in Denmark: Atmospheric processes, sources and emissions, measurements, effects on vegetation, modelling of long range transport and abatement strategies, and modelling of urban air pollution. The individual chapters have their own list of references and can - although cross-referenced - be read separately.

Trophosperic ozone in Denmark is mainly due to long range transport, sometimes with episodes originating in Central Europe. In Danish urban areas the main reaction is a decomposition of ozone (O_3) by nitrous oxide (NO) emitted from traffic. Therefore the ozone levels in Denmark are normally lower in cities than in the countryside. Consequently the health impact is modest.

Keywords: Air pollution, photochemistry, ozone, emission inventories, monitoring, critical levels, episodes, vegetation, long range transport, dispersion modelling

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Contents

Preface

Photochemical air pollution has become one of the major environmental problems, but with different impacts - and possibilities of abatement - in different parts of the world.

The present report gives a review of this complex phenomenon as seen in a Danish perspective. It is based on individual contributions from the following members of the Department of Atmospheric Environment at the National Environmental Research Institute:

A. Bastrup-Birk, R. Berkowicz, A.H. Egeløv, T. Ellermann, J. Fenger, K. Granby, O. Hertel, M.F. Hovmand, K. Kemp, L. Mortensen (present affiliation Danish Research Councils), F. Palmgren, E. Runge, E. Vignati, Z. Zlatev.

Although the report does not cover all relevant activities in Denmark, a comprehensive presentation has been attempted. All basic data on emissions and pollution levels are continously being updated; for the newest data the reader is referred to forthcoming Technical reports from the National Environmental Research Institute.

A short popular version - in Danish and based on preliminary material - was published in December 1995: Ozon som luftforurening (Ozone as air pollutant). Temarapport fra DMU 1995/3.

1 Statement of the problem and summary of results

Jes Fenger

Ozone - friend or foe?

In the atmosphere ozone plays two quite different roles. In the stratosphere the "ozone layer" protects the Earth from too much UV-radiation. In the troposphere, on the other hand, photochemical air pollution - or ozone pollution after its main component - has become a major environmental problem.

Tropospheric ozone is a secondary pollutant, which - together with other photochemical oxidants - is formed in a complex set of reactions between nitrogen oxides and volatile hydrocarbons under the influence of sunlight. Both primary and secondary pollutants can be transported over long distances, and photochemical episodes can be of European scale. Consequently there are no simple relations between local emissions and pollution levels. Chemical reactions in the troposphere are described in Chapter 2.

Emissions of primary pollutants

European emissions of nitrogen oxides and hydrocarbons have increased with the general increase in human activities since the industrialization in the last century. Now, however at least the emissions of nitrogen oxides appear to level off.

Danish emissions of nitrogen oxides from the energy sector have until recent years been increasing, mainly because of increased activity in the transport sector. Emissions of VOCs have likewise increased, but with a comparatively large contribution from domestic heating. The introduction of catalytic converters on petrol driven cars registered after 1 October 1990 will presumably reverse the trend.

Sources and emissions of precursors for photochemical pollution in Europe with special emphasis on Denmark are treated in Chapter 3.

Ozone levels

In Europe the rural levels of tropospheric ozone have roughly dobled within the last hundred years, but now appear to level off. In Denmark the ozone concentrations are measured routinely in three cities and at four rural locations. So far, however the time series have not been sufficiently long to demonstrate significant trends. Typical levels at rural sites are 25 ppb (50 $\mu g/m^3$) as annual mean values and with 98-percentiles of 1 h averages about the double. Similar levels are measured at roof tops in cities. At ground level in cities - and especially in street canyons with heavy traffic - the levels are much lower.

The origin of ozone in Denmark

Tropospheric ozone in Denmark is mainly due to long range transport, sometimes with episodes originating in central Europe. In cities the dominant reaction of O_3 is an oxidation of NO from car exhaust to NO_2. Therefore the levels of ozone and nitrogen dioxide vary oppositely and can in some respects behave like one specie. Furthermore, a reduction of urban emissions of nitrous oxide may lead to increased levels of ozone, as it is generally seen during weekends with less traffic.

Danish measurements of photochemical air pollution - especially ozone - are reviewed in Chapter 4.

Threshold values

A set of threshold values for ozone was implemented in Denmark in 1994. They are based on the directive 92/72/EEC, which aims at protecting both human health and vegetation. At present the thresholds for human health are only exceeded a few times per year, whereas the threshold for vegetation is frequently exceeded.

Impacts

Health aspects are not treated in this report, but are discussed in a recent report (in Danish) from the Danish National Environmental Protection Agency, Miljøprojekt nr. 352 1997: Evaluation of health impacts of air pollution from road traffic (P.B. Larsen, J.C. Larsen, J. Fenger, S.S. Jensen).

Ozone reacts with the surface in the respiratory system; the symptoms are coughing, dryness of the throat, and a general reduction in performance and wellbeing. According to WHO health effects can be attributed to ozone at 1 h. average levels above 100 $\mu g/m^3$.

Vegetation is most sensitive to ozone during the growing season and in the daytime. Ozone enters the leaves through the stomata and attacks the cell membranes. The result is i.a. a reduced photosynthesis. For Danish crops it may correspond to a 10% reduction in yield. Impacts on vegetation are reviewed in Chapter 5.

International and national reduction plans

The United Nations Economic Commission for Europe (UNECE) established around 1980 the socalled Geneva Convention on Long Range Transboundary Air Pollution. It comprises a series of protocols concerning the reductions of specific pollutants. The present nitrogen oxide protocol commits the undersigning countries to stabilize the emissions at the 1987-level. However, in a declaration Denmark and 11 other countries have undertaken a reduction of 30% (for Denmark compared with 1986) before 1999. A protocol on volatile organic compounds operates with a 30% reduction in emissions in the period 1985-1999.

Danish action plans comprise more long-term reductions. Thus "The Transport action plan" has as a goal 40% reductions in national emissions of nitrogen oxides and hydrocarbons in the period 1988-2000 and 60% reductions before year 2010.

Reduction scenarios

Long-range transport models of photochemical air pollution can be used to demonstrate the effects on ozone levels of changes in emissions. It appears that generally reductions in emissions of hydrocarbons are more effective than reductions in emissions of nitrogen oxides. However, even with simultaneous 95% reductions of both primary pollutants the ozone pollution may in some parts of Europe reach levels which are harmful to vegetation.

As discussed in Chapter 6 isolated Danish emission reductions will have a negligible effect in Europe as such, and they may even lead to a small increase in Danish ozone levels.

Photochemistry in urban areas

The photochemical reactions involving nitrogen oxides in urban Danish areas can simplified be accounted for by two reactions only: an oxidation of nitrous oxide to nitrogen dioxide by ozone, and the photodissociation of nitrogen dioxide. In chapter 7 it is shown how dispersion modelling including these reactions can adequately describe the pollution levels of nitrogen dioxide in urban streets.

As a preliminary to studies of urban air pollution with hydrocarbons modelling of these has been initiated.

Conclusion

For Denmark photochemical air pollution is a large scale phenomenon, which can only be marginally influenced by isolated national measures. Compared to Central- and Southern Europe the levels are modest, and there are only little direct impact on human health and wellbeing. The observed ozone levels are harmful to vegetation, and the planned reductions in emissions will not completely prevent damage.

2 Atmospheric Processes

Thomas Ellermann, Ole Hertel, Henrik Skov

2.1 Introduction

Importance of ozone

Ozone, O_3 is in many ways one of the most important compounds in the lower atmosphere. This despite the fact that ozone accounts for less than a millionth of the total mass of the atmosphere. The reasons for this are numerous:

- The majority of the atmospheric ozone, 90%, is confined to a layer in the lower stratosphere with a maximum concentration at an altitude of about 20 km - the so-called ozone layer (Figure 2.1). The ozone molecules in this layer absorb part of the ultraviolet radiation from the sun, which otherwise would have destroyed life on earth as we know it today.
- The photochemical reactions leading to the formation of the ozone layer itself create a temperature inversion, which stratifies the lower atmosphere into two layers - the troposphere and the stratosphere (Figure 2.1). The vertical mixing between these two layers is slow, and the physical and chemical processes differ significantly between the two layers. Moreover, the stratification is of great importance for the climatic system on Earth.
- Ozone is one of the few molecules which can be photolysed in the troposphere, e.i. cleaved by energy supplied by light penetrating the ozone layer ($\lambda>280$ nm). Photolysis of ozone leads to formation of highly reactive free oxygen atoms which initiate a cascade of radical reactions, thereby driving much of the chemistry in the troposphere.

- Ozone absorbs infrared radiation and it is therefore a greenhouse gas.
- Ozone itself is a poisonous and hazardous compound to most living organisms including human beings.

The importance of ozone and the changes observed in the recent decades in the atmospheric ozone concentrations - decrease in the stratosphere and increase in the troposphere - have lead to an enhanced study and understanding of the physical and chemical processes which control the atmospheric levels of ozone.

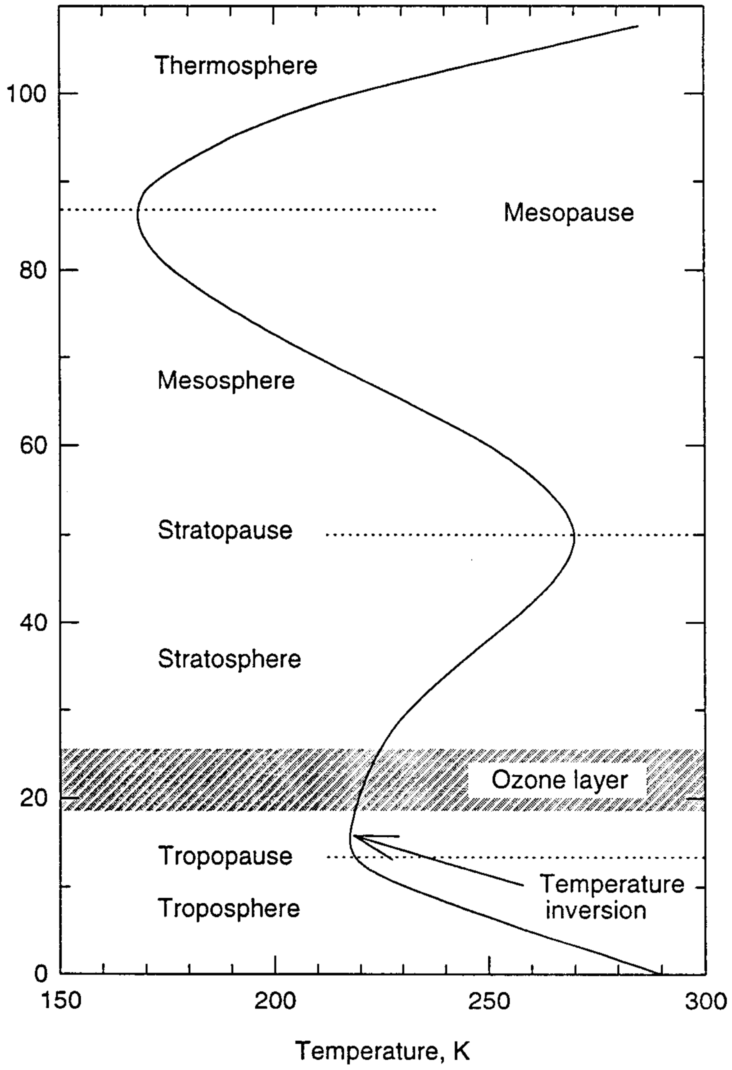


Figure 2.1. Stratification of the lower atmosphere. Note that the figure only indicates the band with the maximum mixing ratio of ozone layer.

Changes of ozone concentration

The concentration of an atmospheric compound in a given area is determined by: natural and man made emissions, chemical reactions leading to formation and degradation, atmospheric transport of the compound in and out of the area, and deposition to the surface. These processes appear as terms in the continuity equation, which is basis for models of atmospheric chemistry and which describes changes per time unit in the concentration of a compound, C, as the sum of the changes in the different processes:

$$\frac{d[C]}{dt} = \frac{d[C]_{\mathrm{emissions}}}{dt} + \frac{d[C]_{\mathrm{chemistry}}}{dt} + \frac{d[C]_{\mathrm{transport}}}{dt} + \frac{d[C]_{\mathrm{deposition}}}{dt} \qquad (2.1)$$

Emission

Only the three last terms are of direct importance for atmospheric ozone. The reason is that ozone is a secondary pollutant, i.e. it is not emitted to the atmosphere, but produced in the atmosphere by the chemical processes. Note, however that emissions of primary pollutants like the nitrogen oxides and the volatile organic compounds strongly influence the production of ozone. These emissions are described in Chapter 3.

Chemistry

Ozone is as mentioned a secondary pollutant and hence the chemical reactions leading to formation and degradation of ozone (the second term), is the key to an understanding of the levels and changes of the concentration of ozone. Sections 2.2 - 2.8 give an introduction to the gas phase chemistry relevant to ozone and describe the products formed along with ozone. Some of the products are likewise hazardous to the environment or unhealthy; - for example peroxy acetyl nitrate, PAN. Both the daytime hydroxyl radical chemistry and the nighttime nitrate radical chemistry is discussed. Processes in/on atmospheric aerosols are described briefly since the progressing understanding of these processes have shown that they play a crucial role for ozone formation and decay. They are illustrated in Section 2.10.

Transport

The transport processes play also a crucial role for the ozone concentration. These processes, described by the third term, include advection of the air mass by the wind, horizontal mixing of the different layers in the lower atmosphere, dispersion of the air mass due to small scale turbulence, and diffusion of the individual molecules. Measurements and model calculations have shown that episodes with high concentrations of ozone in Denmark are coupled to long-range transport of highly polluted air from central Europe. Section 2.11 gives a short introduction to the transport processes and describes some of the important meteorlogical parameters used to quantify the transport processes.

Deposition

The last important term in the equation describes the changes due to deposition, which removes the compound, i.e. ozone, from the atmosphere. Deposition occur either directly by deposition of gaseous ozone to the surface or by uptake of ozone in aqueous droplets which rain out. These processes, termed dry and wet deposition, are described in Section 2.12.

2.2 Structure of the atmosphere and types of chemistry

Stratification

An important feature of the atmosphere is that it consists of several layers characterized by different physical and chemical behaviour. The separations between the layers are created by temperature inversions which prevent fast mixing of the air masses between the different layers. The two lowest layers, the troposphere and the stratosphere, are the most important layers in relation to air pollution.

Troposphere

The troposphere comprises roughly the lowest 10 to 20 km of the atmosphere and quantitatively constitutes the main part of the atmosphere - about 90 % of the total mass of the atmosphere are found here. The troposphere is dominated by fast vertical mixing of the air masses. A molecule can travers the entire layer within a few days or down to few minutes in the updraft of large thunder storms (Wayne 1991).

3000 compounds

It is also here that the largest number of compounds are found. Nearly 3000 different compounds have been determined in the troposphere, though most of these are only found in trace concentrations. The high diversity of compounds comes from anthropogenic and biogenic emissions of compounds directly into the troposphere. Many of the compounds are processed and deposited again, and only the most stable compounds like nitrous oxide, N_2O, part of the methane, CH_4, many of the chlorinated compounds and the freons survive long time enough to be transported into the stratosphere. A process which typically takes decades.

Planetary boundary layer

The troposphere can be subdivided in the free troposphere and the planetary boundary layer, PBL. The planetary boundary layer is the lowest part of the troposphere, where most of the air pollution phenomena takes place. It is the region of the atmosphere, which is influenced by surface effects and ranges typically from ground level and up to 100 m to 2 km. One of the important features of the planetary boundary layer is the limited mixing of the air pollution between the planetary boundary layer and the free troposphere. The concentrations of air pollutants are therefore often much higher in the planetary boundary layer than in the free troposphere.

Stratosphere

The stratosphere is the second lowest of the main layers of the atmosphere ranging from 10-20 km and up to 50-60 km altitude. The vertical mixing in this layer is very slow due to the temperature inversion, which is created by the presence of the ozone layer. 90% of the atmospheric ozone reside in this layer, and it is therefore obvious that the processes taking place here are important for an overall understanding of ozone in the atmosphere. Moreover, it is in this layer that the dramatic decrease of the ozone concentration is observed due to man made air pollution. However, this report focuses on tropospheric ozone with special emphasis on the Danish situation and we refer to the numerous books and reviews on atmospheric chemistry for a detailed description of the stratospheric ozone chemistry and physics (e.g. Wayne 1991; Finlayson-Pitts, Pitts 1986; Fenger, Tjell 1994).

Radical chemistry

The main chemical reactions in the lower part of the atmosphere are driven by the formation of reactive free radicals, which are characterised by a single free electron. They are therefore highly reactive with half-lives often of the order of 10^{-3}-10^{-6} s. They react by transfer of the free electrons to other molecules thereby creating new radicals. In this way, once formed, radicals can initiate long chains of reactions, which only terminates for example by reaction of two radicals with each other.

Photolysis

The initial formation of the radicals occurs by photolysis of photochemically labile molecules; - e.g. certain molecules absorb sun light at specific wavelengths and the excess energy gained triggers a cleavage of the molecules. The sunlight available in the troposphere is restricted to wavelengths longer than about 280 nm. The more energetic UV-light, is as mentioned, absorbed in the higher layers of the atmosphere. Hence only molecules which absorbs at wavelengths above about 280 nm can be photolysed. Furthermore, the molecules must gain energy enough through the absorption of a light photon in order to be cleaved. Despite the numerous molecules present in the troposphere only a few molecules can be photolysed here. Of these are ozone, nitrogen dioxide, and formaldehyde the most important.

2.3 Photolysis of ozone in the troposphere

Photolysis of ozone

Initially, we forget about where the tropospheric ozone comes from and instead pay attention to the photolysis of tropospheric ozone, which leads to production of the most important radical for tropospheric chemistry - the hydroxyl radical, HO· (where the dot represents the free electron).

Formation of $O(^1D)$

Ozone photolysis leads to formation of highly reactive oxygen atoms in the excited singlet state, $O(^1D)$:

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \qquad (2.2)$$

where hv represents a photon with a wavelength in the range of about 280-310 nm. The majority of the excited oxygen atoms loose their excess energy through collisions with molecular nitrogen or oxygen resulting in the formation of ground state atomic oxygen, $O(^3P)$. Subsequently addition to molecular oxygen leads to reformation of ozone:

$$O(^1D) + N_2/O_2 \rightarrow O(^3P) + N_2/O_2 \qquad (2.3)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (2.4)$$

M represents any molecule present in the atmosphere. M is important, because it absorbs excess energy from the newly formed ozone molecule, which otherwise would have fallen apart immediately.

Hydroxyl radicals, HO·

A small fraction of the oxygen atoms reacts with water vapour, H_2O, present throughout the troposphere and form hydroxyl radicals:

$$O(^1D) + H_2O \rightarrow 2HO \qquad (2.5)$$

At 50 % humidity, 1 atm, and 25°C about 10% of O(^{1}D) react through this path. The formation of hydroxyl radicals requires the presence of the excited oxygen atoms O(^{1}D), which in the troposphere only can be formed through photolysis of ozone. The ground state oxygen atoms O(^{3}P) simply does not posses enough energy to react with water vapour.

Another pathway for production of HO· important for highly polluted areas, e.g. cities in central Germany, is photolysis of nitrous acid, HONO, which is producd heterogeneously through reaction of nitrogen oxides with aqueous droplets (see Reaction 2.32 and 2.34).

2.4 Methane oxidation

HO + hydrocarbons

HO· reacts with any compound containing hydrogen and carbon - i.e. most of the volatile organic compounds, VOC's, present as trace gasses in the atmosphere. The reaction with methane, CH_4, the globally most abundant organic compound in the troposphere (1.7 ppmv), will in the following be used to illustrate the type of reaction chains, which - once initiated - will result in the final oxidation of the organic compound to carbon dioxide, CO_2. The reaction chain for CH_4 oxidation begins with:

$$HO\cdot + CH_4 \rightarrow H_2O + CH_3\cdot \qquad (2.6)$$

$$CH_3\cdot + O_2 + M \rightarrow CH_3O_2\cdot + M \qquad (2.7)$$

$$CH_3O_2\cdot + NO \rightarrow CH_3O\cdot + NO_2 \qquad (2.8)$$

$$CH_3O\cdot + O_2 \rightarrow HCHO + HO_2\cdot \qquad (2.9)$$

The initial reaction is far the slowest of these. The atmospheric half-life of methane is about 4 years while the atmospheric half-lives for $CH_3\cdot$, $CH_3O_2\cdot$, and $CH_3O\cdot$ are less than 10 minutes.

Degradation of HCHO

Formaldehyde, HCHO, is one of the photochemically labile organic compounds in the troposphere. The consequtive degradation of HCHO can occur by photolysis or by reaction with HO· :

$$HCHO + h\nu \rightarrow H_2 + CO \qquad (2.10a)$$

$$HCHO + h\nu \rightarrow H + HCO\cdot \qquad (2.10b)$$

$$HCHO + HO\cdot \rightarrow H_2O + HCO\cdot \qquad (2.10c)$$

Subsequently, the hydrogen atom and the HCO· radical react with O_2:

$$HCO\cdot + O_2 \rightarrow CO + HO_2\cdot \qquad (2.11)$$

$$H\cdot + O_2 + M \rightarrow HO_2\cdot + M \qquad (2.12)$$

The fate of HCHO depends strongly on the local conditions; - e.g. the sunlight intensity and the concentraion of HO·. At noon on July 1 at 40°N latitude the atmospheric half-life of HCHO is about 3 h for sunny conditions. About 50%, 30%, and 20% of HCHO reacts by Reaction (2.10a), (2.10b), and (2.10c), respectively. At sunset the half-life increases to about 150-200 h and during the night virtually no degradation takes place (Finlayson-Pitts, Pitts 1986).

The carbon containing product of the degradation of HCHO is always CO, but the distribution of the hydrogen containing products depend on the local conditions. At the conditions described above 0.8 molecule of $HO_2\cdot$, 0.5 molecule of H_2, and 0.2 molecule of H_2O are produced for each molecule of HCHO degraded.

CO and H_2 oxidation

CO and H_2 are stable molecules, but they are oxidised in the troposphere through reactions with the hydroxyl radical:

$$CO + HO\cdot \rightarrow CO_2 + H \qquad (2.13)$$

$$H_2 + HO\cdot \rightarrow H_2O + H \qquad (2.14)$$

The chemical lifetimes due to reaction with HO· are about 1-2 months and 5 years for CO and H_2 respectively.

Hydroperoxyl radical, $HO_2\cdot$

The hydrogen atoms produced in Reactions 2.10b, 2.13 and 2.14 all react fast with O_2 thereby forming $HO_2\cdot$ (Reaction 2.12). For industrial areas, including Denmark, $HO_2\cdot$ will predominantly react with nitrogen monoxide, NO, which is emitted during combustion processes and typically appears at atmospheric concentrations on the ppbv level:

$$HO_2\cdot + NO \rightarrow HO\cdot + NO_2 \qquad (2.15)$$

Overall reaction, Reformation of HO·

The reaction mechanism for oxidation of methane at high NO concentration is illustrated in Figure 2.2. As shown the result is production of CO_2, H_2O, NO_2, and HO·. An important feature of the oxidation process is that the hydroxyl radicals are not only reformed during the process, but even extra hydroxyl radicals are formed. The hydroxyl radical acts therefore as a kind of catalyst, which initiates the oxidation.

2.5 Chemical formation of tropospheric ozone

Transport

So far, we have only discussed the importance of ozone photolysis without bothering about where the ozone comes from. A large part of the tropospheric ozone is transported down from the stratosphere, where the majority of atmospheric ozone is produced. The transport occurs by the so-called tropopause foldings. However, the magnitude of the downward transport is still under discussion and far from fully enlighted.

The mechanism for production of ozone in the stratosphere requires solar radiation in the range 185-220 nm. This radiation cannot penetrate down into the troposphere, and the chemistry responsible for formation of stratospheric ozone can therefore not take place in the troposphere.

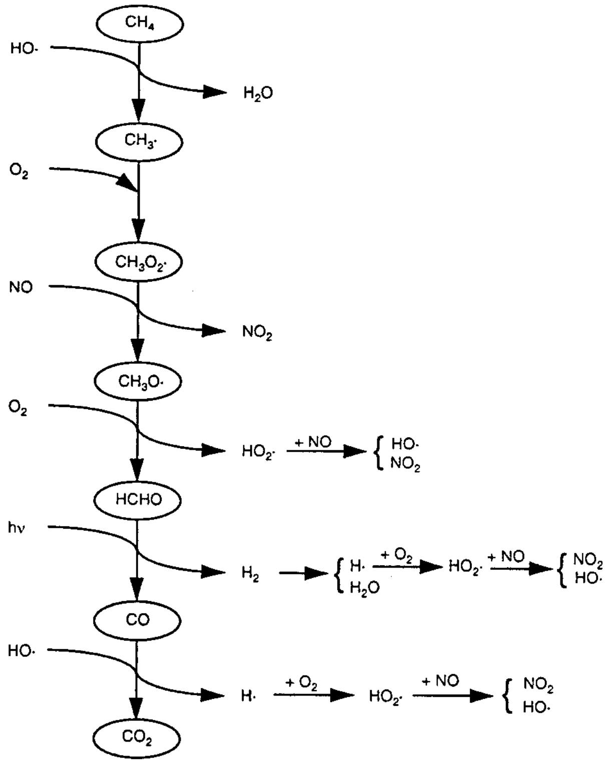


Figure 2.2. Oxidation of methane in the troposphere at high NO concentration - i.e. ppm level. Note that the conversion of HCHO to CO takes place via three channels and that only the most important channel has been shown.

NO and NO_2

Another chemical mechanism involving nitrogen dioxide is active in the troposphere. NO_2 absorbs light and photolysis (in the range from 280-400 nm) leads to production of free oxygen atoms in the ground state, $O(^3P)$:

$$NO_2 + h\nu \rightarrow NO + O(^3P) \tag{2.16}$$

As already stated these oxygen atoms cannot react with water vapour. Instead the main path is the reaction with molecular oxygen thereby leading to chemical formation of ozone in the troposphere:

$$O(^3P) + O_2 + M \rightarrow O_3 + M \tag{2.4}$$

Steady state $[O_3]$

The nitrogen oxide formed by photolysis of NO_2 (Reaction 2.16), reacts on the other hand fast with ozone:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{2.17}$$

A steady state situation will therefore often be established:

$$NO_2 \underset{k_{2.16}}{\overset{J_{2.1\rightarrow 6}}{\rightleftharpoons}} NO + O_3 \tag{2.18}$$

$J_{2.16}$ is the photolyses rate coefficient for NO_2 (Reaction 2.16) which is mainly a function of solar radiation. $k_{2.17}$ is the rate constant for Reaction 2.17 which depends on the temperature and which together with the reactant concentrations describes the rate of the reaction. Reaction 2.4 is commonly neglected due to the very high reaction rate.

The tropospheric ozone concentration is determined by the balance between formation by photolysis of NO_2 and decay through reaction with NO. This can be expressed by:

$$[O_3] = (J_{2.16} \cdot [NO_2])/(k_{2.17} \cdot [NO]) \qquad (2.19)$$

Ambient conditions

Establishment of the steady state occurs quite fast under typical tropospheric conditions. The annual mean concentration of ozone in Denmark is about 30 ppbv giving a mean half-life of NO due to Reaction 2.17 of roughly one minute. During daytime the steady state is therefore also established with a half-life on a minute scale. In general, except very close to sources of NO and NO_2 e.g. a street, it is assumed that the ratio between NO and NO_2 is in balance with the local ambient ozone concentration during daytime. Note, that changes of the ozone concentrations normally occur on longer time scales; i.e. typically of hours.

Constraints in the case of no VOC

The steady state forces important constraints on the amount of ozone which can be chemically produced by emissions of only NO and NO_2. First of all only the directly emitted NO_2 can lead to net formation of ozone in the steady state. Hence the chemical production of ozone cannot exceed the emissions of NO_2. Secondly, the maximum chemically produced ozone will be determined by the ratio between the emissions of NO and NO_2, which is typically 9 to 1. An estimate of the maximum ozone concentration due to solely NO/NO_2 can be calculated by use of data for $J_{2.16}$ and $k_{2.17}$. $J_{2.16}$, the photolytical rate constant have in ambient air typical been measured to about $9 \cdot 10^{-3}$ s^{-1} (Finlayson-Pitts, Pitts 1986, and references in there), but depends on latitude, season, time of day, and the amount of clouds. $k_{2.17}$ is $1.7 \cdot 10^{-14}$ $cm^{-3} molecule^{-1} s^{-1}$ at 20°C (DeMore et al. 1987). From Equation 2.19 we estimate the maximum ozone concentration to be only a few ppbv - a factor of ten lower than generally observed in ambient air.

High NO concentration

In the ambient troposphere the steady state will be affected by compounds which react with NO and NO_2. The presence of VOC's play the most important role in context of ozone formation. As illustrated with CH_4 some of the reactions involved in the oxidation of methane convert NO to NO_2 without consumption of ozone:

$$CH_3O_2\cdot + NO \rightarrow CH_3O\cdot + NO_2 \qquad (2.20)$$

$$HO_2\cdot + NO \rightarrow HO\cdot + NO_2 \qquad (2.21)$$

These reactions push the steady state balance towards higher ozone concentrations; i.e. the ratio between NO_2/NO is increased and hence the ozone concentration is also increased (see Equation 2.19).

One methane produce 4-5 ozone molecules

A simple estimate of the effect of methane oxidation can be obtained by use of stoichiometry - e.g. by counting the number of NO_2 molecules produced per molecule of methane oxidised. At high NO concentrations (ppbv level) oxidation of one molecule of methane leads to production of 4-5 NO_2 and 0-1 $HO\cdot$. Consecutively photolyses of NO_2 leads to production of 4-5 molecules of O_3.

Low NO concentration

This accounts only for the situations with high NO concentrations. NO concentrations of only a few pptv can be reached at remote areas; like the oceans or the free troposphere. Reactions (2.20) and (2.21) are very slow at these conditions and $CH_3O_2\cdot$ and $HO_2\cdot$ will also react with other trace components in the troposphere. The most important reactions are:

$$HO_2\cdot + O_3 \rightarrow HO\cdot + 2O_2 \tag{2.22}$$

$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2 \tag{2.23}$$

$$CH_3O_2\cdot + HO_2\cdot \rightarrow CH_3OOH + O_2 \tag{2.24}$$

No NO_2 is formed and hence no ozone can be produced. Moreover, Reaction (2.22) leads to a net loss of ozone.

Coupling to local conditions and transport

The assesment of the chemical formation of ozone due to methane oxidation becomes therefore highly linked to the ambient conditions. At high NO concentrations 4-5 molecules of ozone may be formed for each methane oxidised. At very low NO concentrations ozone destruction will occur and in the transition the ozone production and consumption may level out. The picture is actually more complex, because the methane oxidation may be initiated at one set of conditions, while the oxidation of HCHO, H_2, and CO may occur at totally different conditions. With half-lives ranging from 1-2 months up to years these molecules can be transported over long distances before they are degraded.

Methane, an example

The oxidation of methane is only important for the chemical formation of ozone on a global scale. However, methane oxidation was taken as an example because it illustrates, in a simple way, how the coupling of emissions of organic compounds and nitrogen oxides leads to production of ozone in the tropopshere. Moreover, it illustrates that the amount and distribution of sunlight, the concentration of $HO\cdot$, the concentration of nitrogen oxides, and the concentration of volatile organic compounds are important factors governing the chemical formation of ozone.

Chemical formation of tropospheric ozone

Other compounds like carbon monoxide (Reactions 2.13 - 2.16) and the Non Methane Volatile Organic Compounds, NMVOC, are also very important for the chemical formation of tropospheric ozone. Carbon monoxide is both emitted to, and produced in, the atmosphere and carbon monoxide is as important as methane for the tropopsheric ozone formation on a global scale. On a regional scale, i.e. Europe, the emissions of NMVOC are high and they play the main role for the chemical formation of ozone.

2.6 The hydroxyl radical

Importance of HO·

The hydroxyl radical plays a key role for the tropospheric chemistry of ozone. The primary formation of HO· occurs via ozone photolysis and the reaction between CH_4 and HO· is the rate determining step for the methane mediated production of tropospheric ozone. For other volatile organic compounds the reactions with HO· are often likewise the rate determining step for their transformation in the troposphere. Moreover, the hydroxyl radical reacts with many inorganic compounds and it is the most important radical for the daytime chemistry in the troposphere. The limitation to the daytime arise from the need of sunlight to prime the formation of HO·.

HO· degradation

The concentration of the HO· radical in the troposphere is determined by the balance between the formation via the photolysis of ozone (Reactions 2.2 and 2.5) and the chemical degradation. On the global scale the reactions with CO and CH_4 accounts for practically all of the consumption of HO· :

$$HO\cdot + CO \rightarrow CO_2 + H \qquad (2.25)$$

$$HO\cdot + CH_4 \rightarrow CH_3\cdot + H_2O \qquad (2.26)$$

Both of these reactions are slow, but globally they dominate since the concentrations of CO and CH_4 are significantly higher than the concentrations of the other reactants. From typically tropospheric concentrations of CO and CH_4 and the rate constants of Reactions 2.25 and 2.26 at 20°C the overall half-life of HO· in the troposphere can be determined to be less than a second:

$[CO] = 0.15$ ppmv; $\quad k_{2.25} = 2.4\cdot10^{-13}$ cm^3 molecule^{-1} s^{-1}

$[CH_4] = 1.7$ ppmv; $\quad k_{2.26} = 8.5\cdot10^{-15}$ cm^3 molecule^{-1} s^{-1}

$$t_{1/2} = \ln2/(k_{2.25}[CO] + k_{2.26}[CH_4]) = 0.6 \text{ s at } 20°C$$

These figures show also that on a global scale about 70% of HO· react with CO and 30% with CH_4.

On a local scale, e.g. in Denmark, the reactions of HO· with NO_2 and NMVOC's, often replace Reactions 2.25 and 2.26. This is due to the high concentrations of NMVOC's observed close to the high density emission areas and to the fact that the rate constants for the reactions of HO· with NMVOC's often are factors of thousands higher than the rate constant for Reaction 2.26.

HO· varaitions

Due to the fast turnover of HO· a steady state concentration of HO· will be established on a time scale of seconds. The concentration depends on the local rate of formation of HO· via photolysis of O_3 and on the local rate of degradation of HO·. Since the photolysis depends on the amount of light and since the steady state concentration is established on a second scale, there will be large changes in the HO· concentration with both diurnal, seasonal and geographical variations. For example there is a factor of 50 or more between the concentrations of HO· at equator and at the poles.

Typical concentrations

Daytime concentrations typical for Denmark fall in the range $0.5\text{-}5\cdot10^6$ radicals cm^{-3} - an extremely low concentration, about 10^4 times less than a ppbv. During the night the concentration is practically zero, because the source reactions disappear.

2.7 Nitrogen oxides

NO, NO_2

Nitrogen monoxide and nitrogen dioxide are, as described above, important for the ozone related chemistry in the troposphere. Practically all of the atmospheric NO and NO_2 arise from anthropogenic emissions to the atmosphere with NO concentrations being about 8-9 times higher than for NO_2. In the atmosphere these compounds are convertible through the steady state reactions and reactions with peroxy radicals:

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad (2.16)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (2.17)$$

$$NO + HO_2\cdot \rightarrow NO_2 + O(^3P) \qquad (2.27)$$

$$NO + RO_2\cdot \rightarrow NO_2 + RO\cdot \qquad (2.28)$$

where R symbolises an organic radical, e.g. $CH_3\cdot$.

NO_x

Reactions 2.16 and 2.17 are fast with half-lives of NO and NO_2 on the minute scale during daytime. Since the concentrations depend on each other, and since the reactions lead to no net loss of nitrogen oxides. These nitrogen oxides are typically refered to as NO_x. The concentration of NO_x is simply defined as the sum of the two compounds:

$$[NO_x] = [NO] + [NO_2] \qquad (2.29)$$

NO_x removal, formation of HNO_3

The main pathway for removal of NO_x in the troposphere is through reaction with the hydroxyl radical thereby leading to formation of nitric acid, HNO_3:

$$NO_2 + HO\cdot + M - HNO_3 + M \qquad (2.30)$$

Nitric acid is highly soluble in water. It is therefore, dissolved in rain drops and removed from the troposphere by wet deposition and makes up an important component of the acidic deposition. Another important sink of NO_x is the reaction of NO_2 with the peroxyacetyl radical, which leads to the formation of peroxyacetyl nitrate (see Section 2.8).

Formation of HONO

A similar, but less important, reaction is the reaction between NO and HO· forming nitrous acid, HONO:

$$NO + HO\cdot + M \rightarrow HONO + M \qquad (2.31)$$

Nitrous acid photolyse rapidly in daylight back to the reactants:

$$HONO + h\upsilon \rightarrow HO\cdot + NO \qquad \lambda < 400\ nm \qquad (2.32)$$

Therefore, HONO formed in the late evening can serve as a nighttime reservoir of HO·, which subsequently is liberated again the following morning, when sunlight starts up Reaction 2.32 again.

Aqueous phase

Aqueous phase chemistry, rain droplets etc., play also an important role for the removal of NO_x. In polluted areas with high NO_x concentrations and with low solar light intensity, as in the northern Europe, the reaction of N_2O_5 (see Section 2.7) with liquid water can be equal important as Reaction 2.30 or even be the dominant sink for NO_x:

$$N_2O_5 + H_2O_{aq} \rightarrow 2HNO_3 \qquad (2.33)$$

Moreover, from comparison of modelling and field studies, it appears that there must be another source of HONO which has a heterogeneous character.

$$2NO_2 + H_2O_{aq} \rightarrow HONO + HNO_3 \qquad (2.34)$$

Through Reactions 2.32 and 2.34 this will lead to the formation of HO· and thereby accelerate the chemical processes in the troposphere.

Other NO_x reactions

The reactions of NO_x with the hydroxyl radical are, as stated above, quantitatively the most important reactions. However, NO_x can also react with many of the intermediate oxygenated radicals formed during the oxidation of organic compounds and thereby produce various forms of nitrates and nitrites of which some are toxic and some act as sinks for tropospheric NO_x (see Section 2.8).

Half-life

The atmospheric half-life for removal of NO_x from the troposphere due to Reaction 2.30 is typically on the order of a few days. This is important because the majority of the NO_x emissions come from combustion processes and high NO_x concentrations are therefore located to industrial areas. The fast removal of NO_x from the troposphere will therefore lead to rapid decline of the NO_x concentration with the distance to industrial areas. A decrease of the concentration with a factor of 10 for each 1000 km distance to the sources is not unusual (Graedel, Crutzen 1993).

Typical concentrations

Typical NO_x concentrations in Denmark range from 5-20 ppbv in rural areas to 1000 ppbv in a street canyon in the centre of Copenhagen. Over the oceans the NO_x concentration can be roughly 10,000 times smaller - only a few pptv.

2.8 The nitrate radical

Formation

Another important link between the chemistry of the nitrogen oxides and ozone is the formation of the nitrate radical, $NO_3\cdot$

$$NO_2 + O_3 \rightarrow NO_3\cdot + O_2 \qquad (2.35)$$

Removal processes, photolysis

The $NO_3\cdot$ radical absorbs strongly in the visible wavelength range, 510-670 nm, and during daytime $NO_3\cdot$ is quickly photolyzed with lifetimes of about 5 s (Wayne et al. 1990). The main photolysis pathway is decomposition:

$$NO_3\cdot + h\nu \rightarrow NO_2 + O(^3P) \qquad (2.36)$$

Another important removal reaction during daytime is the reaction of NO with $NO_3\cdot$

$$NO + NO_3\cdot \rightarrow 2NO_2 \qquad (2.37)$$

Typical concentrations

Hence, as a result of Reactions (2.36) and (2.37) no $NO_3\cdot$ is present in the troposphere during daytime. However, at nighttime considerably $NO_3\cdot$ can be build up, because the main degrading reactions cannot take place. In Denmark typical nighttime concentrations have been estimated to 10-20 pptv (Nielsen et al. 1995).

N_2O_5

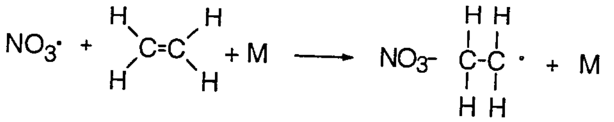
When present, the nitrate radical establishes an equilibrium with the nitric acid anhydride, N_2O_5:

$$NO_3\cdot + NO_2 + M \rightleftharpoons N_2O_5 + M \qquad (2.38)$$

Both the forward and the reverse reaction are fast and equilibrium is reached within minutes. N_2O_5 reacts only slowly with most compounds in the gas phase and therefore N_2O_5 serves as a reservoir for $NO_3\cdot$.

Reactions with VOC's

The nitrate radical reacts with many of the organic constituents in the troposphere. Especially important are the reactions of $NO_3\cdot$ with VOC's - here illustrated with ethene, CH_2CH_2:



$$NO_3\cdot + H_2C{=}CH_2 + M \longrightarrow NO_3\text{-}CH_2\text{-}CH_2\cdot + M \qquad (2.39)$$

Reaction (2.39) initiates a chain of radical reactions, which leads to the complete oxidation of ethene. The chemistry between $NO_3\cdot$ and VOC's are briefly discussed in Section 2.8 (For further details see Wayne et al. 1990; Fenger, Tjell 1994).

Nighttime initiator

The $NO_3\cdot$ radical acts - through the reactions with VOC's - as an initiator of the tropospheric chemistry in a similar way as the hydroxyl radical. However, while the HO· radical is active during daytime the nitrate radical is active during nighttime - the only period where a considerably $NO_3\cdot$ concentration can build up. Another difference is that the nitrate radical mainly reacts with unsaturated organic compounds.

Aqueous phase

Another important role is explicit through the equilibrium with N_2O_5. As discussed in Section 2.6 the aqueous phase chemistry of N_2O_5 is important for the formation of nitric acid and the removal of NO_x from the atmosphere.

2.9 Volatile organic compounds, VOC's

Hundreds of VOC's

The troposphere contains hundreds of volatile organic compounds emitted either due to natural or man made activities and as illustrated above these emissions have impact on the formation of tropospheric ozone. The tropospheric fate of volatile organic compounds differ from one compound to another and both the reaction pathways and the composition of the products depend on the chemical structure of the volatile organic compounds. Only a brief introduction to the chemistry of these compounds will be given here via some examples. For a detailed description of the reaction pathways governing the many different organic compounds we will refer to the literature (Finlayson-Pitts, Pitts 1986; Seinfeld 1986).

Initiaton pathways

Different mechanisms initiate the oxidation of volatile organic compounds. Some of these has already been mentioned:

- photolysis,
- reaction with the hydroxyl radical,
- reaction with the nitrate radical,
- reaction with ozone.

The importance of the different initiation pathways for the degradation of a specific VOC depends on the chemical structure of the compound. Only the most important initiation pathways will be mentioned in the following examples.

Alkanes

Butane

The chemistry of simple alkanes, C_xH_{2x-2}, has already been illustrated with methane. Even when the carbon chains become longer it is in principle the same kind of reactions which occur, but isomerisation reactions and C-C bond clevage can also occur. Figure 2.3 illustrates the oxidation of butane to various aldehydes, ketones, alcohols and organic nitrates. These compounds are subsequently deposited or further degraded.

Carbonyl compounds

Acetaldehyde

Photolysis and oxidation of formaldehyde, the most simple carbonyl compound, were discussed as a part of the methane oxidation. The second most important carbonyl compound is acetaldehyde, CH_3CHO. The degradation is initiated partly by photolysis and partly by reaction with the hydroxyl radical:

$$CH_3CHO + h\nu \rightarrow CH_3\cdot + HCO\cdot \rightarrow \cdots \rightarrow HCHO + CO \qquad (2.40)$$

$$CH_3CHO + HO\cdot \rightarrow CH_3C(O)\cdot + H_2O \qquad (2.41)$$

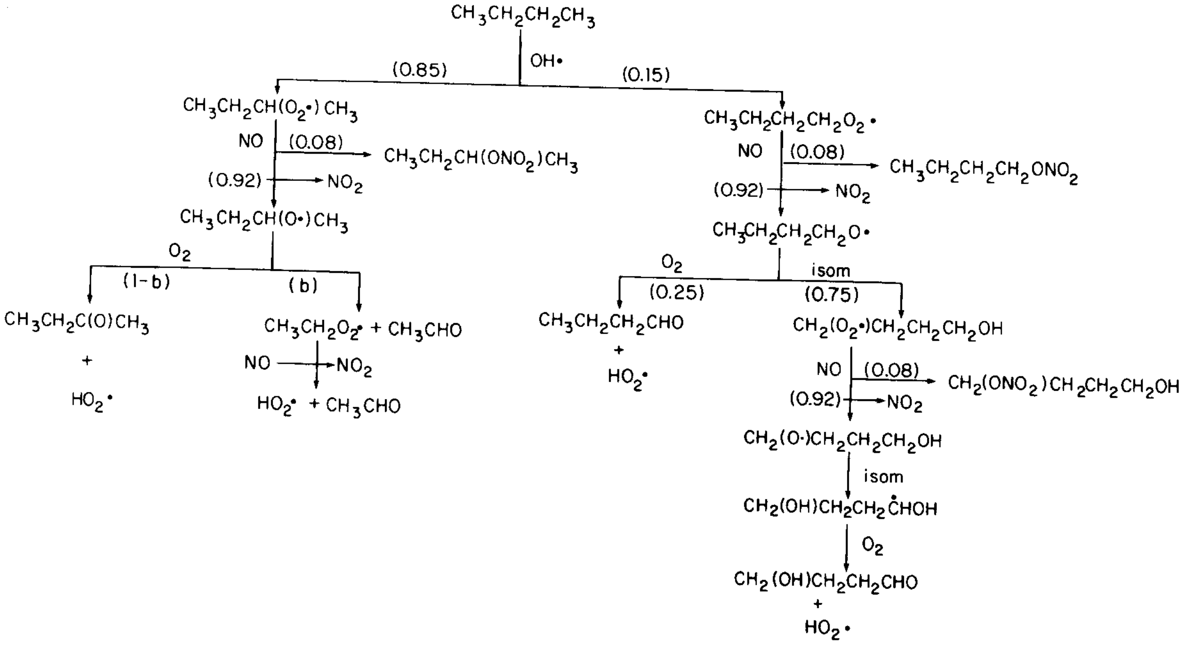


Figure 2.3. Degradation of butane in the troposphere. Initiation of the oxidation of butane in the troposphere occurs always by reaction with HO• . The figures in parenthesis gives estimated branching ratios. Note that the scheme lumpes reactions together; - e.g. the first step involves both abstraction of hydrogen atom (15% externally and 85% internally) by HO• and addition of oxygen. Both isomerisation and chain clevage is observed. (Reproduced after Seinfeld, 1986).

Photolysis branch

The photolysis branch (2.40) leads initially to cleavage of acetaldehyde to $CH_3\cdot$ and $HCO\cdot$; radicals which are also produced during the methane oxidation. Formaldehyde and carbon monoxide are formed subsequently during Reactions 2.6 - 2.9 and 2.11. For simplicity only the carbon containing compounds are shown in Reaction 2.40.

HO branch

The $HO\cdot$ branch (2.41) leads to formation of the acetyl radical, $CH_3C(O)\cdot$, which reacts further with O_2 :

$$CH_3C(O)\cdot + O_2 + M \rightarrow CH_3C(O)O_2\cdot + M \qquad (2.42)$$

The acetylperoxy radical may react with NO:

$$CH_3C(O)O_2\cdot + NO \rightarrow CH_3C(O)O\cdot + NO_2 \qquad (2.43)$$

$$CH_3C(O)O\cdot + O_2 \rightarrow CH_3O_2\cdot + CO_2 \qquad (2.44)$$

The methyl peroxy radical, $CH_3O_2\cdot$, is familiar from the methane oxidation and form formaldehyde through a series of reactions. The acetyl peroxy radical may also react with NO_2 to produce peroxy acetyl nitrate, PAN:

$$CH_3C(O)O_2\cdot + NO_2 + M \rightleftharpoons CH_3C(O)O_2NO_2 + M \qquad (2.45)$$

PAN

PAN is thermally unstable and an equilibrium between the acetyl peroxy radical and NO_2 on one side and PAN on the other side is established. The thermal lifetime of PAN depends strongly on the temperature - at 25°C it is 30 minutes, but already at 17°C it becomes three days and at -15°C it is several years. PAN is often produced along with ozone during smog episodes and in that respect it is important because it is an irritant to human beings. Moreover, PAN and similar other peroxy alkyl nitrates act as a tempory reservoir for NO_x; e.g they temporarily reduce the amount of free NO_x by tying up NO_x in less reactive compounds.

$NO_3\cdot$ reaction

It has been suggested that the reactions of $NO_3\cdot$ with aldehydes are important, however, from Table 2.1 it can be seen that the half-life for the reaction of $NO_3\cdot$ with for example acetaldehyde is about 15 days at 10 pptv $NO_3\cdot$ and 20°C. This reaction has therefore only importance at very high pollution levels where it is be an alternative source for PAN - Reaction 2.46 followed by Reactions 2.42 and 2.45:

$$NO_3\cdot + CH_3CHO \rightarrow HNO_3 + CH_3C(O)\cdot \qquad (2.46)$$

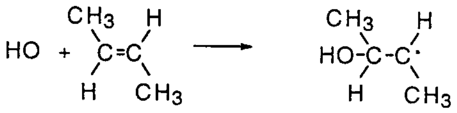
Alkenes

HO· addition

The chemistry of alkenes is quite complex since alkene breakdown can be initiated not only by reaction with HO·, but also by reaction with ozone and the nitrate radical. Furthermore, the HO· chemistry of alkenes differs also in the way that HO· reacts with them. So far, abstraction reactions have been shown, where the HO· radical abstracts a hydrogen atom and produce H_2O and an organic radical - e.g. Reaction 2.6. In the case of alkenes HO· adds to the double bound.

Trans-2-butene

For trans-2-butene the initiation reaction becomes:



(2.47)

The 2-hydroxy-3-butyl radical formed reacts then quickly with O_2 to form a peroxy radical, which in a series of steps involving NO and more O_2 leads to production of acetaldehyde or small amounts of organic nitrates (Figure 2.4).

Table 2.1. Half lifes ($t_{1/2}$) in hours for a number of selected hydrocarbons given with respect to reaction with O_3, HO·, and NO_3·. The halflifes at 295 K and 1 atm are calculated by use of the relevant rate constants and by assumption of the following concentrations: $[O_3]$ = 30 ppbv, corresponds to roughly the annual mean concentration for Denmark; [HO·] = $1 \cdot 10^6$ molecules cm^{-3}, approximately twice the estimated global day and night concentration estimated by Volz et al. (1981); $[NO_3 \cdot]$ = 15 pptv, typical night time concentration for Denmark, estimated by Nielsen et al. (1993). n.d. = not determined- typically because the rate constants are too low to be determined. The symbol ">" indicates for the alkanes that the halflifes all are higher than 150 years. For the other compounds the symbol indicates that only an upper limit has been determined for the rate constants. References to rate constants are: Mallard et al., 1993; Finlayson-Pitts and Pitts, 1986; Langer and Ljunström, 1994; Wayne et al., 1990, and references in there; Wallington et al., 1989.

	$t_{1/2}$ (O_3)	$t_{1/2}$ (HO·)	$t_{1/2}$ (NO_3·)
Alkanes			
Methane	>1,300,000	23,000	13,000,000
Ethane	>1,300,000	713	67,000
Propane	>1,300,000	160	24,000
Butane	>1,300,000	77	15,000
n-Heptane	>1,300,000	26	5,300
n-Octane	>1,300,000	21	3,800
2,2-dimethyl-propane	>1,300,000	229	n.d.
Cyclohexane	>1,300,000	26	7,400
Alkenes			
Ethene	89	23	2,700
Propene	15	7	56
Trans-2-butene	0.8	3	1
Isoprene	13	2	0.5
α-Pinene	2	0.4	0.9
β-Pinene	0.8	2	0.2
Alkynes			
Ethyne	>1,600	250	>27,000
Oxygen containing compounds			
Dimethyl ether	n.d.	84	180
Methyl *tert*-butyl ether	n.d.	58	840
Formaldehyde	>7,600	20	790
Acetaldehyde	>27,000	13	190
Acetone	n.d.	840	63,000
Methacrolin	150	6	n.d.
Aromatics			
Benzene	8,000,000	160	17,000
Toluene	13,000	32	7,700
o-Xylene	16,000	13	2,700
Phenol	n.d.	7	0,1
o-Cresol	620	5	0,2

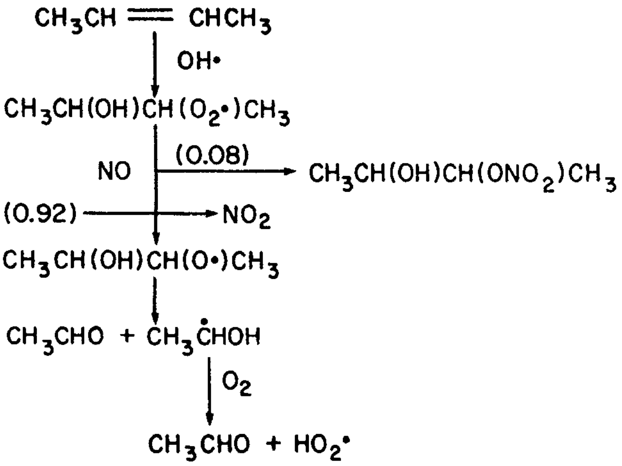
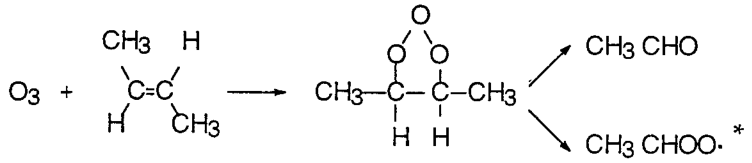


Figure 2.4. HO• addition to the doubble bond of trans-2-butene. The main products are estimated to 92% acetaldehyde and $HO_2\cdot$ and 8% 3-nitroxy-2-butanol. (Reproduced after Seinfeld, 1986).

Ozone reaction

The direct reactions of ozone with the alkenes are also quite different from the reaction previously described. The ozone molecule adds across the double bond to form a primary ozonide, an unstable ring structure, which rapidly decomposes into a carbonyl compound, here acetaldehyde, and an excited biradical - a Criegee intermediate:



(2.48)

The acetaldehyde reacts as described in Section 2.8.2. The reaction of the excited biradical (the * indicates that the radical is excited) is much more complex and the details have not been fully elucidated yet. Based on the present knowledge it is known that the excited Criegee radical may either be stabilised by transfer of excess energy to other molecules, M:

$$CH_3CHOO\cdot^* + M \rightarrow CH_3CHOO\cdot + M \tag{2.49}$$

or be further fractionated. There are several pathways, but they all lead to formation of CH_4, $CH_3O_2\cdot$ or $CH_3O\cdot$ and CO or CO_2. These products are accompanied by formation of $HO\cdot$ or $HO_2\cdot$ and consumption of molecular oxygen. The stabilised Criegee intermediate reacts with other constituents in the troposphere like NO, NO_2, SO_2 or H_2O. The carbon containing products are acetaldehyde or acetic acid, CH_3COOH, for example:

$$CH_3CHOO\cdot + NO \rightarrow CH_3CHO + NO_2 \tag{2.50}$$

$$CH_3CHOO\cdot + H_2O \rightarrow CH_3COOH + H_2O \tag{2.51}$$

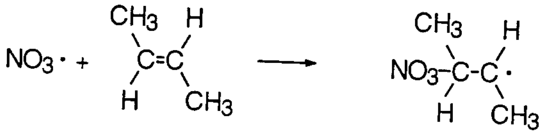
The reactions with NO and NO_2 have so far not been studied in details because it is difficult to carry out experiments with NO_x and O_3 present simultaneously due to their mutual Reactions 2.17 and 2.35.

$NO_3\cdot$ reactions

$NO_3\cdot$ reacts fast with alkenes. The half-lives for the reactions between $NO_3\cdot$ and for example the biogenic emitted isoprene and some terpenes are comparable or even shorter than the similar reactions with HO· (see Tabel 2.1).

Trans-2-butene

$NO_3\cdot$ reacts with alkenes by addition to the double bond which leads to the formation of an alkyl radikal e.g for trans-2-butene:



$$NO_3\cdot + \overset{CH_3}{\underset{H}{C}}{=}\overset{H}{\underset{CH_3}{C}} \longrightarrow NO_3{-}\overset{CH_3}{\underset{H}{C}}{-}\overset{H}{\underset{CH_3}{C}}\cdot \qquad (2.52)$$

This radical reacts further with oxygen similarly to the reactions of the alkyl radical (see previous Section).

Products

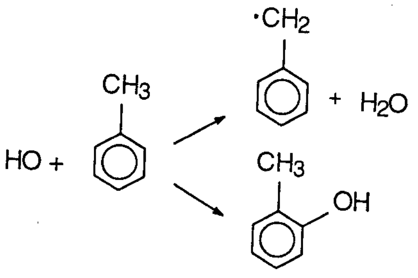
The main products formed in these reactions are simple aldehydes, ketones, NO_2 and, contrary to the similar HO· reactions, organic nitrates with at least one additional functional group. In the case of trans-2-butene the dominant nitrate produced is 3-nitroxy-2-butanone.

The organic nitrates have longer atmospheric half-lives than NO_2 and acts in the troposphere as temporate reservoirs of NO_x; - a role similar to PAN. NO_x is liberated again by photolytical or thermal degradation of the organic nitrate. Finally, the reactions of the more substituted alkenes as 2,3-dimethyl-2-butene with $NO_3\cdot$ can lead to small quantities of epoxides.

Aromatic compounds

Toluene

A large fraction of the VOC's in the troposphere consist of aromatic compounds such as benzene, toluene and xylene, which for example may account for up to 10% of unleaded gasoline. The only significant initiation pathway is by reaction with the hydroxyl radical. The HO· radical may add to the double bonds of the aromatic ring and in cases like toluene abstract a hydrogen atom from the methyl group:



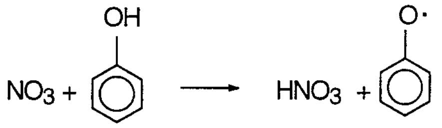
(2.53)

(2.54)

The drawing of the adduct symbolises that the free electron is shared by five of the carbon atoms in the ring. HO· may actually add to any of the four different carbon positions of the ring, but the drawn structure is the most important. The further reactions of these radicals involves reactions with O_2, NO, NO_2, and fragmentaion of the cyclic structure. The products are a variety of aromatic compounds like nitrotoluene, benzaldehyde, benzylnitrate, and smaller organic compounds like glyoxylic acid, methyl glyoxal, and pyruvic acid. All these compounds will subsequently be degraded in the troposphere by their own reaction pathways and/or, as for most of the acids, be removed from the troposphere by wet deposition.

NO_3· reaction

In general the reactions of aromatic hydrocarbons with NO_3· are too slow to be of importance in the troposphere. However, phenols react fast with NO_3· and the half-life is shorter with respect to reaction with NO_3· than with HO·. The reaction proceed mostly via hydrogen abstraction of the phenolic hydrogen atom e.g. for phenol.



(2.55)

Only little is known about the further fate of this intermediate but nitrophenols appear as some of the products.

Summary of the reactions of VOC´s

The examples above have shown the diversity of the atmospheric reactions. However there are some general features of which some are summarised below:

- The organic compounds emitted to the troposphere are reduced compounds. Due to the high oxygen content in the atmosphere the chemical reactions always lead to formation of oxidised products of which the most simple is carbon dioxide.
- Initiation of most of the reaction mechanisms for processing of the organic compounds occurs by reaction with the hydroxyl radical; this account for compounds containing C-H bonds. For compounds containing double bonds, C=C, the reaction mechanisms can also be initiated by reaction with ozone or with the nitrate radical. The last possible initiation mechanism is photolysis. However, only few organic compounds (i.e. formaldehyde) can be photolysed in the troposphere.
- Despite the difference in initiation pathway it is in general the initiation reaction which is the slowest and the rate determining step. The lifetime for the different organic compounds can therefore be determined solely by the rate of the initiation step. Table 2.1 lists rate constants for the initiation process and the atmospheric lifetimes for a series of typical organic compounds.
- Oxidation of the organic compounds often leads to formation of ozone; - e.g. as illustrated for methane. How much ozone is formed depends on the chemical structure of the organic compounds and on the physical and chemical surroundings; clouds, rain drops, NO_x concentrations etc.

2.10 Ozone chemistry in aqueous droplets and on particles

The concentration of tropospheric ozone is not only determined by the processes taking place in the gas phase. It is also stongly modified by processes involving the numereous atmospheric particles and droplets existing in the troposphere. Although generally viewed as very important, research and understanding of these processes still lack behind the study of the pure gas phase atmospheric chemistry, which is resonable well known at present. The reason is the complexity of the processes, and the technical difficulties involved. Many types and sizes of particles and droplets exist and in principle all particles or droplets are different from each other - each reflecting their own specific history and each making up their own little chemical system in contact with the surrounding air. Furthermore, the droplets have only a limited lifetime in the troposphere and often cloud droplets evaporate again as the environment of the clouds changes. Only in about 10% of the cases will the cloud droplets reach the surface in the form of rain.

Aqueous phase examples

Despite the difficulties, much information on the influence of particles and droplets has been achieved in recent years and a few examples will be given in the following to illustrate the impact of the processes in droplets and on particles on the concentration of ozone in the troposphere. The examples have been taken from the aqueous phase chemistry, which is the most important part of the non gas phase chemistry.

Alterations of gas phase concentrations

One of the most important ways that droplets and particles with a shell of water influence the ozone level is by altering of the concentration of the chemical compounds in the gas phase. Chemical compounds have very different solubility in water and hence important reactants may simply be removed from the gas phase by the droplets. This will slow down or alter the gas phase chemistry. The hydroxyl radical is an example of a radical which is stongly water soluble. In the presence of water droplets in a cloud the air will be scrubbed for HO· leading to a general decrease of the HO· mediated chemistry in the troposphere. The $HO_2\cdot$ radical, hydrogen peroxide, nitric acid, sulphuric acid and the organic acids are also highly water soluble and the respective gas phase concentrations will decrease in a cloud. Left behind in the gas phase are compounds like NO, CO and the non polar volatile organic compounds like methane.

Decreased ozone formation

The level of ozone in the troposphere depend, as discussed under the gas phase chemistry, on the gas phase oxidation of the volatile organic compounds. In general (but not always) an increase in the oxidation of the volatile organic compounds leads to an increase in the ozone concentration. The rate of the oxidation proces increases with increasing concentrations of free radicals (HO· and $HO_2\cdot$) and radical forming molecules, like formaldehyde. The presence of cloud droplets reduce the concentration of these compounds and hence slow down the formation of ozone.

Aqueous ozone chemistry

Another important factor is that ozone is weakly soluble in water, and that chemical transformations of tropospheric ozone may occur in the aqueous droplets. An example is the ozone destruction cycle involving HO·, HO_2· and formaldehyde, which are all strongly soluble. In water HO_2· is in equilibrium with H^+ and O_2^-:

$$HO_2\cdot \rightleftharpoons H^+ + O_2^- \tag{2.56}$$

The ions react with ozone thereby forming HO· which consecutively reacts with formaldehyde to reproduce HO_2· :

$$O_2^- + O_3 + H^+ \rightarrow HO\cdot + 2O_2 \tag{2.57}$$

$$HCHO + HO\cdot + O_2 \rightarrow HCOOH + HO_2\cdot \tag{2.58}$$

The reaction between HO· and formaldehyde giving formic acid, HCOOH, is the most common reaction for HO· in aqueous phase tropospheric chemistry. Formic acid may be further decomposed through the reaction:

$$HCOOH + HO\cdot + O_2 \rightarrow CO_2 + HO_2\cdot + H_2O \tag{2.59}$$

which followed by Reactions (2.56) and (2.57) leads to destruction of yet a molecule of ozone. Overall the reactions can be written as:

$$HCHO + 2O_3 \rightarrow CO_2 + 2O_2 + H_2O \tag{2.60}$$

Sulphur oxidation

Another example of importance for the Danish conditions is the oxidation of sulphur dioxide, SO_2, in droplets. SO_2 is soluble in water where two equilibria are established:

$$SO_2\,aq \rightleftharpoons H^+ + HSO_3^- \tag{2.61}$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-} \tag{2.62}$$

These equilibria depend on salinity and pH. All three sulphur species are oxidised by ozone disolved in the droplets:

$$SO_2\,aq + O_3 \rightleftharpoons SO_4^{2-} + 2H^+ + O_2 \tag{2.63}$$

$$HSO_3^- + O_3 \rightleftharpoons SO_4^{2-} + H^+ + O_2 \tag{2.64}$$

$$SO_3^{2-} + O_3 \rightleftharpoons SO_4^{2-} + O_2 \tag{2.65}$$

The oxidation with ozone is mainly important at low acidity in the droplets ($pH > 5$); a condition which often is seen during the summer in Denmark. Oxidation with hydrogen peroxide, H_2O_2, dominates at higher acidity.

Oxidation, ionic species

The reaction mechanism illustrates that the atmospheric fates of the organic compounds in aqueous droplets are oxidation, and that the chemistry in addition to the free radicals involves the reactions of ionic species.

Driving force

The driving force for the chemistry inside the droplets can either come from uptake of reactive species produced in the gas phase or the reactive compounds can be directly formed in the aqueous phase. For example, the source of HO· in the droplets is either photolysis of iron complexes in the aqueous phase, direct uptake of HO· from the gas phase, or uptake of H_2O_2 which is subsequently photolysed.

Evaluation of importance

The importance of the aqueous phase chemistry for the tropospheric ozone has been evaluated by Lelieved and Crutzen (1992). They have estimated that an air parcel typically spends 13-20 hours in a cloud free environment followed by 3-4 hours inside clouds. Based on model calculations they further estimate that the inclusion of aqueous phase processes, as illustrated above, can lead to a 40% reduction of the tropospheric ozone levels compared to simulation of pure gas phase chemistry. This reduction is observed for the NO_x rich conditions which is typical throughout Europe, including Denmark.

Depostion

These examples illustrate the direct effect that aqueous droplets have on atmospheric chemistry. A more simple effect is that the droplets, when they are deposited as rain, completely remove soluble compounds from the troposphere. This process is described further in Section 2.11.

2.11 Transport and dispersion

Atmospheric layers

In the introduction to this chapter the atmosphere was described as consisting of a number of different layers of which only the two lowest - the troposphere and the stratosphere - are of importance in connection with air pollution. Due to the difference in physical behavior, the troposphere can be further subdivided into different layers. In order to understand the mechansims behind these layers, it is necessary to have a brief introduction to turbulence.

Meteorological scales

The complex weather systems of the planet Earth are driven in most part by the inhomogeneties in radiation and pressure gradients. Dynamical processes act to redistribute circulation systems, patterns of rainfall and winds. Meteorological scales for motion can be categorised as (Seinfeld 1986):

- *Macroscale;* phenomena occurring on scales of thousands of kilometres, such as semipermanent high and low pressure areas residing over oceans and continents (synoptic scale is a common term for macro scale phenomena).
- *Mesoscale;* phenomena occurring on scales of hundreds of kilometres, such as land-sea breezes, mountain-valley winds, and migratory high and low pressures.
- *Microscale;* phenomena occurring on scales of the order of 1 m to 1 km, such as the meandering and dispersion of a chimney plume and the complicated flow around a building.

Each of these scales of motion plays a role in air pollution, however, on different time scales. Generally air pollution is transported by the wind a process normally termed advection.

Episodes

Periods of high levels of photochemical pollution i.a. ozone in Denmark appear during long range transport episodes (see Chapter 4). These episodes appear typically during high pressure situations over central Europe, which presses air masses towards north. During these episodes the pollution levels have a clear gradient from the high density emission areas in south towards north. When we experience high levels of photochemical pollution in Denmark, one must expect even higher levels in e.g. Germany.

Air pollution is, however, not only advected with the wind but also diluted by mixing with ambient air masses during the transport. This mixing is created by atmospheric turbulence, which we will return to in the following section.

Atmospheric turbulence

Importance of turbulence

The atmospheric flows are mainly turbulent. Parameters like wind speed, wind direction, temperature and pressure vary in time and space. When a flow is turbulent its variation is chaotic i.e. one cannot predict the deviation from the mean value to a given time. A turbulent flow consists of eddies which sizes, intensities and lifetimes are governing the turbulent mixing. Atmospheric turbulence is created in two different ways by either mechanical or thermal processes.

Mechanical turbulence

The mechanical turbulence is created by the wind shear created by stresses at the earth surface and is dominated by small eddies especially close to the surface. Above a smooth surface e.g. a grass field or a calm water surface, the turbulence is weak, whereas a rough surface e.g. high vegetation or buildings leads to strong turbulence.

Thermal turbulence

The thermal turbulence is formed by the heating of the air masses close to the surface. The heated air rises and is replaced by colder air moving downwards. The vertical movements of the air masses lead to the formation of large socalled convective eddies. These eddies have long lifetimes (in contrast to the mechanical eddies) which lead to periodic up and down drafts of up to 10 to 20 min duration.

Planetary boundary layer

Most air pollution phenomena take place in the lowest part of the troposphere; the socalled planetary boundary layer (PBL). This layer is defined as the region in which the atmosphere is influenced by surface effects through the vertical exchange of momentum, heat and water vapour. It is common to divide the PBL into three sublayers:

- From the surface and up to the roughness height, z_o. The order of magnitude of the roughness height is from mm to cm.
- From the roughness length, z_o, to the top of the surface layer, hs. In this layer the vertical fluxes of momentum, heat and water vapour is independent of height and the coriolis effect (the effect of the rotation of the earth). The surface layer is typically about 1/10th of the height to the top of the PBL.
- From the surface layer, hs, to the top of the PBL, z_i. The top of the PBL varies from about 100 m to about 2 km. z_i terms the lowest level of the atmosphere, where the surface no longer has an influence on turbulent transport.

Radio soundings

The height of the boundary layer can be determined from the vertical temperature profiles obtained by radio soundings. In Denmark radio soundings are performed on a routine basis two times a day in Jægersborg Statsskovdistrikt by the Danish Meteorological Institute. Radio soundings are, however, also performed by Risø National Laboratory in connection with various field campaigns.

The typical diurnal profile of the PBL height is shown in Figure 2.5. During night the wind stress of the surface is the only process creating turbulence. The height of the boundary layer will often be of the order of 50 m. At sunrise the incomming radiation starts to warm the surface and thermal turbulence is created. Thereby the height of the PBL starts to grow (at summer to the order of 1000 m - 1500 m) and the maximum height is reached in the afternoon. After sunset the surface starts to cool and a new lower boundary layer is formed. This may take place before the old boundary layer is broken down.

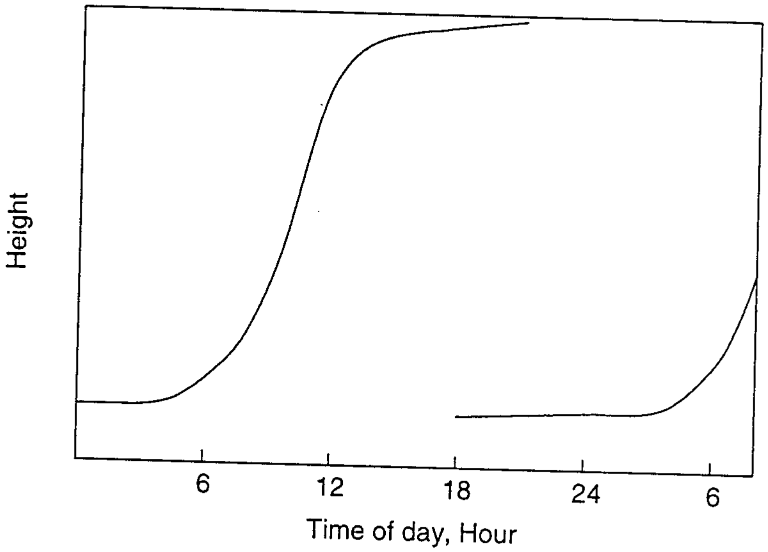


Figure 2.5. Typical diurnal profile of the boundary layer height; at night when the turbulence typically is low, the PBL height is also low. At sunset the surface is heated by solar radiation and the resulting thermal turbulence makes the PBL height grow. At sunset a new lower boundary layer is formed, which may be present before old PBL is broken down.

Stability

Stability classes

The vertical movements of the air masses in the boundary layer are strongly influenced by the stability conditions. Three different groups of stability conditions are typically defined: stable (where vertical movements are suppressed), neutral and unstable (where vertical movements are increased) (Figure 2.6).

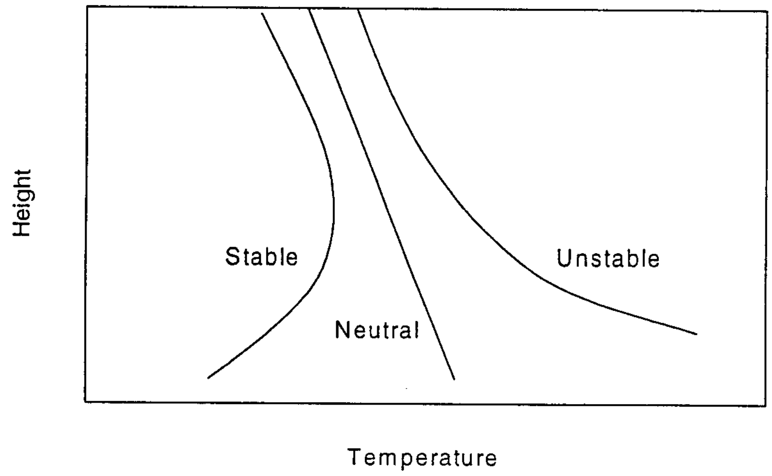


Figure 2.6. Temperature profiles of the lowest part of the atmosphere at stable, neutral and unstable conditions. At neutral conditions the temperature decreases by approximately one degree per 100 m (lapse rate ≈ -1°/100 m) and an air parcel moving vertically with heither by accellerated or subpressed in the movement. At stable conditions the lapse rate is less than -1°/100 m, an air parcel moving in the vertical is subpressed. At unstable conditons the lapse rate is higher than -1°/100 m and an air parcel moving in the vestical direct will be accellerated in the movement.

Neutral

For an air parcel, which is moving upwards, the ambient pressure is decreasing, and thereby the volume of the air parcel is expanded, and its temperature decreases. During neutral conditions for dry air the temperature in the PBL is decreasing by approximately one degree per 100 m. Based on the temperature gradient the lapse rate can be determined, which is a measure for the stability of the atmosphere.

Unstable

During daytime with sunshine the earth surface is heated. The air masses closest to the ground are heated by the warm surface and thereby thermal turbulence is created. In this case a lapse rate of more that one degree per 100 m is established. An air parcel with an initial upward movement will be accelerated. The warm air of the parcel is lighter than the ambient air, and this gives the air parcel a lift upwards which is termed buoyancy. The described situation is for unstable conditions.

Ozone gradient

Since ozone close to the surface is depleted over land by NO from mainly low sources (traffic) and by dry deposition (see Section 2.11), ozone concentrations are typically increasing with height towards the free troposphere (above the PBL). This also means that ozone concentrations generally will be highest during periods with high PBL and unstable conditions, since masses with high concentrations of ozone are brought down to the surface.

Stable

During night the surface is cooled due to radiation of heat. Thereby a condition where the temperature is decreasing less than 1 degree per 100 m is often established. During these stable conditions, an air parcel with an initial upward movement will meet ambient air which is warmer and thereby lighter than the air parcel. In this case the air parcel will be slowed down in the movement.

Stratification

When the lapse rate is different from -1°/100 m the atmosphere is called stratified, which means that the density of the air masses is changing with height. When the mechanical turbulence is large, the thermal stratification plays a minor role. In this case the atmosphere is termed neutral. It should be noted, however, that perfectly neutral conditions never appear in reality.

Meteorological parameters

In the following a number of basic meteorological parameters will be presented, in order to provide a quantitative description of stability and for an understanding of atmospheric fluxes. These parameters are: friction velocity, u, heat flux, H, the Monin-Obukhov length, L, and the convective velocity scale, w_*:

Friction velocity

The friction velocity, u_*, is a measure for the mechanical turbulence. During neutral conditions the value of u_* is related to the wind speed by:

$$u(z) = \frac{u_*}{\kappa}\ln(z / z_0) \tag{2.66}$$

where κ is von Karmans constant, (~0.35, in some cases a value of 0.4 is applied), z is the reference height, and z_0 the earlier introduced roughness length.

A typical order of magnitude for u_* is 10% of the wind speed in 10 m's height, but as is appears from (2.66) this depends on surface and stability conditions. Formula 2.66 is theoretically valid only for the surface layer (typically the lowest 10% of the PBL), but it is generally a good approximation for the lowest 100 to 200 m of the atmosphere.

Heat flux

The heat flux, H, is the amount of heat supplied from the atmosphere to the surface. The heat flux is negative during the night, when the heat is transported from the surface to the atmosphere. It should be noted that the direct radiation of heat is very small and the transfer of heat is mainly taking place by means of turbulent motions. A typical heat flux for Danish summer conditions is 300 W/m². The heat flux depends generally on the solar radiation, but also the surface conditions play an important role. A wet surface results in a smaller heat flux than a dry surface at the same solar radiation.

Monin-Obukhov

The Monin-Obukhov length, L, is numerically equal to the height over the surface in which the mechanical and the thermal production of turbulence is of equal size. L is expressed by:

$$L = \frac{-u_*^3 T \rho c_p}{\kappa g H} \tag{2.67}$$

where g is the gravitational acceleration (~9.8 m/s²), T is the absolut temperature of the air in Kelvin, ρ is the density of air, c_p is the heat capacity of air (at standard conditions $\rho c_p = 1300$ Ws K^{-1} m^{-3}), H is the heat flux and u_* the friction velocity. Note that H and L have opposite signs i.e. that L is negative in en unstable atmosphere (positive heat flux) and positive in a stable.

The Monin-Obukhov length is a measure for the stability of the atmosphere; in the unstable atmosphere L is negative and numerically small, in a very stable atmosphere L is positive and small, and in the near neutral atmosphere L is numerically large.

Mixing height

The PBL has earlier been described as the atmospheric layer, which is directly influenced by the surface conditions. Above the PBL the turbulence normally decreases rapidly, and it is therefore a good approximation that pollution is only dispersed within the PBL. Therefore the height of the PBL can be taken as the mixing height, zi, since the pollution is only mixed to this height.

The mixing height has a diurnal cycle. The stable atmosphere has a low zi, whereas the unstable atmosphere has a large mixing height. The stable mixing height is typically 100 to 200 m, where as the unstable mixing height can have values up to a couple of kilometers.

Convective velocity scale

During unstable conditions, where the temperature difference between air and ground is leading to convective eddies, the mixing height is determined by the size of these eddies. The speed by which these eddies move is termed the convective velocity scale, w_* and is expressed by:

$$w_* = \left(\frac{z_i g H}{T \rho c_p} \right)^{\frac{1}{3}} \tag{2.68}$$

where zi terms the height of the unstable (convective) mixing layer. The convective velocity scale is a measure for thermal turbulence and thereby for the dispersion during unstable conditions. A reasonable approximation is that the thermal turbulence dominates the mechanical, when w_* is larger than u_*. On a cloud-free summerday w_* can have values around 2 m/s. It should be noted, however, that w_* depends on the height above the surface, which can lead to different dispersion conditions for high and low emissions sources.

2.12 Deposition

Deposition types

Gases and aerosols are removed from the atmosphere to the ground by two processes: dry and wet deposition. Dry deposition is the removal directly to the surface, whereas wet deposition is the removal by cloud and rain droplets. For the ozone concentrations only dry deposition is important, since ozone is only weakly soluble in water. However, the small fraction of ozone, which is taken up by cloud droplets, can have an impact on the transformation of SO_2 to sulphate in the water phase for cloud droplets of high pH.

Dry deposition

Dry deposition is the removal by gravitation and turbulent transport of gases and aerosols to the surface. Dry deposition to land surfaces is determined by turbulent transport within the PBL and down to a thin laminar layer just above the surface, molecular diffusion through the laminar sublayer and finally transfer from the laminar sublayer and into the surface itself.

Resistance method

It is common to use the socalled resistance method to describe the dry deposition process. This name is caused by the analogy to the electricity theory, since the deposition velocity is expressed as the inverse value of the sum of a number of resistances:

$$v_d = (r_a + r_b + r_c)^{-1} \tag{2.69}$$

where r_a is the aerodynamical resistance, r_b is the laminar sublayer bulk resistance, and r_c is the surface resistance.

The turbulent transport in the atmosphere is expressed by the aerodynamic resistance. For neutral conditions the aerodynamic resistance can be expressed by:

$$r_a = \frac{1}{\kappa u_*} \ln\left(\frac{z_r}{z_0}\right) \tag{2.70}$$

where z_r is the reference height, and z_0 is the roughness height.

The aerodynamic resistance is larger over forrest than over a smooth surface, since the friction velocity depends on the surface conditions.

The laminar sublayer bulk resistance depends on the roughness height of the specie:

$$r_b = \frac{1}{\kappa u_*} \ln\left(\frac{z_{0c}}{z_0}\right) \tag{2.71}$$

where z_{0c} is the roughness length of the specie, for which Brusaert (1975) have developed some simple empirical expressions.

The surface resistance expresses the resistance for the uptake of the gases and aerosols on the surface itself. The surface resistance has been determined experimentally for many different species for different types of surfaces. For several species including ozone it can, however, be tricky to determine the surface resistance from experiments. The problem is that chemical reactions can perturb the results highly. Some trees and other plants emit species e.g. terpenes which react with ozone. There by protecting the plant from damage by the ozone. This removal of ozone can easily be taken as deposition in an investigation.

Dry deposition of ozone

Dry deposition of ozone to land surfaces is in general highly dependent on the vegetation. The dry deposition velocity is less during the nighttime than during daytime. This is because ozone is taken up through the stomata of the plants, and the deposition is therefore smaller when the plants stomata are closed. A typical dry deposition velocity of ozone is 0.2 cm/s during night and 0.6 cm/s during daytime.

Wet deposition

Wet deposition is the wash-out of gases and aerosols from the atmosphere. Wet deposition is in reality two different processes in-cloud and below-cloud scavenging. In-cloud scavenging is the removal of gases and aerosols to cloud droplets, and below-cloud scavenging the uptake of gases and aerosols by rain droplets during the fall through the atmosphere. In-cloud scavenging is in general by far the most efficient of these two processes, due to the much longer residence time in the atmosphere of cloud droplets compared to rain droplets.

Cloud condensation nuclei

Cloud droplets are formed by condensation of water vapour on cloud condensation nuclei (CCN), which can small particles of natural or anthropogenic origin. The cloud droplets take up gases and aerosols from the ambient air. Most clouds do not lead to rain, but evaporate and release the uptaken material as aerosols.

Scavenging coefficients

A common way to express wet deposition is by scavenging coefficients, which are based on the assumption of a fixed relation between the concentration in the gas phase and the concentration in the liquid phase of the cloud or rain droplet (scavenging ratio). The scavenging coefficient is expressed as:

$$\lambda = \frac{S_i I}{H_{sc}} \qquad (2.72)$$

where λ is the scavenging ratio, I is the rain intensity and H_{sc} is the height over which scavenging takes place.

In-cloud scavenging for gases can be expressed by the following expression:

$$S_i = \frac{1}{\frac{(1-cl)}{H_{eff} RT} + cl} \qquad (2.73)$$

where cl is the cloud water content, for which Asman and Jensen (1993) have developed an empirical expression,

$$cl = 2 \cdot 10^{-7} \cdot I^{0{,}36} \qquad (2.74)$$

where I is the rain intensity.

Similarly can in-cloud scavenging ratios for aerosols be calculated from,

$$S_i = \frac{f_{nuc}}{cl} \qquad (2.75)$$

where f_{nuc} is the activated part of the aerosols (according to Asman and Jensen (1993) f_{nuc} is 0.9).

Wet deposition of ozone

Wet deposition has little influence on ozone concentrations, since ozone is only weakly soluble in water. The uptake of ozone in cloud droplets has, however, an importance for the conversion of SO_2 to sulphate in the droplets.

2.13 Summery

The present chapter has given a general introduction to the governing atmospheric processes, which determine the tropsopheric ozone concentration. As apparent ozone is one of the most important compounds in the troposphere. One reason is that ozone is harmfull for the growth of vegetation and human wellbeing.Another reason is that ozone plays a key role for the chemistry of the troposphere having high impact on the chemical degradation of various hydrocarbons and taking part in chain reactions leading to formation of other photochemical compounds including several harmfull compounds, e.g. PAN.

The concentration of ozone in the tropopsphere depends on a number of factors. Ozone is a secondary pollutant and hence chemical reactions forming and consuming ozone are important. As important as the chemical reactions are the transport processes. The ozone concentration is influenced by downward transport of ozone from the stratosphere and mixing between the free troposphere and the planetary boundary layer. Only dry deposition of ozone to land surfaces plays a role whereas dry deposition to sea and wet deposition are marginal. Furthermore, ozone can be transported horisontally over wide ranges; this is important in a Danish perspective, where the ozone concentrations are highly influenced by long range transport from South and Central Europe.

Direct emission of ozone does not occur. However, anthropogenic emissions of nitrogen oxides and hydrocarbons have lead to a general increase in the tropospheric ozone concentrations (see Chapter 4) via the chemical chain reactions leading to formation of ozone. The central points in the chain reactions are the formation of organic peroxyradicals ($RO_2\cdot$), which react with NO to form NO_2. Subsequently NO_2 is photolysed and a net production of ozone appears when the oxygen atoms add to molecular oxygen:

$$RH + HO\cdot \rightarrow R\cdot + H_2O \qquad (2.76)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad (2.77)$$

$$RO_2\cdot + NO \rightarrow RO\cdot + NO_2 \qquad (2.78)$$

$$NO_2 + h\nu \rightarrow NO+O \qquad (2.79)$$

$$O + O_2 \rightarrow O_3 \qquad (2.80)$$

Both transport processes and chemical reactions are currently studied in Denmark. Results from these studies are among the presented work in the following chapters with emphasis on results obtained at the National Environmental Research Institute (NERI).

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3 Sources and emissions

Erik Runge

3.1 Overview of Sources

Anthropogenic sources

A substantial part of the chemical substances involved in photochemical air pollution are of anthropogenic origin. The activities resulting in emissions are among others combustion processes, where heat or energy are gained from combustion of fuels.

The emissions occurring from combustion depend on the fuel used, the quality of the fuel and the combustion process; examples of fuels can be, fossil gas, oil and coal or biogenic wood and straw. The quality of the fuel is important as the emission from the use of coal for some pollutants give higher emissions than the use of oil and visa versa. Finally the combustion process is important, and differences in the temperature in the process and the combustion technique can give rise to very different emissions. Thus, carbon monoxide emissions from combustion of wood in residential burners are 1000 times higher than from wood burned in large, central combustion plants.

Natural emissions

Also natural sources of photochemical active emissions exist. An example is emissions of volatile organic compounds (VOC) from trees, where conifers are emitters of terpenes and broad leafed trees emit other VOC's, mainly isoprene. This emission from trees is highly dependant on light intensity and temperature. In some countries, e.g. Sweden or Canada, the emission of VOC's from nature, can in the summer period be the main contribution of VOC's to the atmosphere.

In some cases it is not obvious whether the emissions should be considered anthropogenic or natural. This is e.g. the case with the just described VOC emissions from trees. As most of the forests in Denmark are cultivated and grown as a crop, with a 30 - 100 years rotation age, the VOC emissions from forests in Denmark could be seen as anthropogenic. Similarly the emission of methane from waste deposits is due to the natural process of degradation, but the deposits are of anthropogenic origin.

In the Corinair data base (European Environment Agency, 1995a) natural sources are:

- deciduous and coniferous forests,
- natural grass land,
- forests fires,
- humid zones,
- lakes, rivers, ground water, drainage, ditches, canals and open sea,
- termites, mammals and humans,
- volcanoes and
- near surface deposits.

This split between natural and anthropogenic emissions is likely to be changed for future inventories.

3.2 The Corinair database

Emission calculations

Emissions are either measured or calculated. In the Danish invento SO_2 and NO_x emissions from power plants are generally measur whereas other emissions are calculated. The calculations are based relevant statistics, e.g., energy statistics, and emission factors, emission factors are national or international agreed average e sions per unit of, e.g., fuel, product or other activity, which are in the emission compilation.

Corinair

The first Europe wide, common emission inventory was the Cor '85 inventory, comprising the pollutants SO_x, NO_x and VOC. The second was the Corinair '90 inventory, comprising the pollutants NO_x, NMVOC, CH_4, CO, CO_2, N_2O and NH_3 and covering 29 European countries. These two inventories were organised by DG Brussels.

EEA

In 1994 the European Environmental Agency (EEA), was found Copenhagen, Denmark, and took over the responsibility for the continuation of the Corinair programme.

Topic centre on air emissions

The EEA delegated the responsibility for the work with the fu development of the Corinair activity to the Topic Centre on Emissions, which is a consortium of European institutions, lea Umweltsbundesamt in Berlin. The Topic centre have arranged a network of national experts within each of the 29 participating European countries, who are responsible for compiling the national inventories.

Further the Topic Centre has suggested that the next Corinair inventory should be for the year 1994, with an update each year from th year on. In addition to the compounds included in the Corinair '90 inventory, as described above, the '94 inventory covers 8 heavy metals and 8 persistent pollutants.

Obligations

There are no legal obligations for the nations participating in the Corinair activity. But as this programme covers all of Europe, where all nations, in principle, are using the same guidelines and methods, and the aim of the Topic centre is that Corinair should be *the* European emissions system, Denmark has decided to participate in the programme.

Source sectors

The emissions presented here are for the year 1990, from the Corinair inventory (Corinair 1993), with the same sector/source split as used in that inventory. The sectors and sources which will also be used throughout this presentation are:

1. Public power, cogeneration and district heating plants.
2. Commercial, institutional and residential combustion plants.
3. Industrial combustion.
4. Production processes.
5. Extraction and distribution of fossil fuels.
6. Solvent use.
7. Road transport.
8. Other mobile sources and machinery.
9. Waste treatment and disposal.
10. Agriculture.
11. Nature.

These 11 main groups are compiled from a more detailed sector and source definition, in the Corinair inventory called the SNAP codes (Selected Nomenclature for Air Pollution). At the lowest level there are 277 SNAP codes in the 1990 inventory.

National inventories

Besides the international emission inventories, within Corinair, described above, time series of Danish emissions are compiled in the national emission inventory. In this inventory emissions, mainly from combustion processes for the years 1972-1994, are compiled. (Fenhann, Kilde 1994).

Compounds

In the present report yearly emissions of nitrogen oxides (NO_x = NO + NO_2), methane (CH_4), non-methane volatile organic compounds (NMVOC) and carbon monoxide (CO) are presented.

Uncertainty

The uncertainty of the emission inventories is difficult to estimate. Basis contributions are uncertainty arises from uncertainties in measurements of actual emission, in measurements used for emission factors and in activity statistics. Another source of uncertainty in emission inventories is the question of whether all sources contributing to emission of a specific pollutant are included in the inventory. This is often assumed to be the case for pollutants with combustion as the source. But for pollutants where other sources than combustion are important, e.g., emission of volatile organic compounds or methane it is not certain that all sources are included in the inventory, and hence the uncertainty on the total emission of these compounds is higher. The uncertainty on the inventories, of the different pollutants, is a more or less qualitative, subjective estimation.

Within the Corinair inventory system the uncertainty of the emission calculations of the pollutants have been rated as shown in Table 3.1. (McInnes 1996):

Table 3.1 Rating of accuracy in emission inventories

	NO_x	VOC	CO	CH_4
Public power, cogeneration and district heating plants	B	C	B	C
Commercial, institutional and residential combustion plants	C	C	C	C
Industrial combustion	B	C	B	C
Production processes	C	C	C	D
Extraction and distribution of fossil fuels	C	C	C	D
Solvent use		B		
Road transport	C	C	C	C
Other mobile sources and machinery	D	D	D	D
Waste treatment and disposal	B	B	B	
Agriculture	D	D	D	[illegible]
Nature	D	D	E	[illegible]

Pollutants rated:

A are based on a large number of measurements made at a large number of facilities that fully represent the sector,

B are based on a large number of measurements made at a large number of facilities that represent a large part of the sector,

C are based on a number of measurements made at a small number of representative facilities, or an engineering judgement based on a number of relevant facts,

D are based on a single measurements or an engineering calculation derived from a number of relevant facts and some assumptions, and

E are based on an engineering calculation derived from assumptions only.

This is an overall uncertainty estimation on the European 1990 inventory, and it is assumed to be by and large the same for the Danish inventory. As seen from the table there is no judgement of the uncertainty in percent, as this is difficult to assess. Nevertheless the inventories can be improved and the uncertainty reduced.

3.3 Nitrogen oxides

Anthropogenic sources

Nitrogen oxides ($NO_x = NO + NO_2$) are formed in combustion processes either from nitrogen containing impurities in the fuel or from N_2 in the combustion air. The main part of the NO_x emissions are in the form of NO, especially from gasoline cars, where more than 90% are emitted as NO. This is, however rapidly oxidized in the atmosphere to NO_2. (Cf. Chapter 2).

Natural sources

There are also natural processes in the soil contributing to emissions of NO_x. These emissions are, not included in the present inventory

Total emissions

The total European emissions were in 1990 18006 Gg as NO_2, and the Danish emissions were 273 Gg as NO_2.

Relative emissions

From Figure 3.1 it appears that emissions from 'Public power, cogeneration and district heating' and 'Road transport' are the most important sources of NO_x emissions both on a European and on a Danish level. These two sectors contribute 21% and 45% respectively to the total European NO_x emissions and 33% and 38% respectively to the total Danish NO_x emissions.

'Road transport' plus 'Other mobile sources' contribute with 58% of the total European NO_x emissions and 59% of the total Danish NO_x emissions.

From Figure 3.1 is also seen that the Danish NO_x emissions are relatively high, compared to the European, in the sector 'Public power, cogeneration and district heating'. This reflects that fossil fuels are dominant in the Danish energy system, whereas hydro- and nuclear power are more important in other European countries.

Uncertainty

The uncertainty on this inventory of nitrogen oxides, is assumed to be around 30%.

Emission per capita

From Figure 3.2 is seen that Denmark in 1990 had an emission of 53 kg NO_2 per capita. The European yearly average emission was 37 kg NO_2 per capita. The highest emission was in The Czech Republic, with 75 kg NO_2 per capita and the lowest European NO_x emission in Hungary, with 18 kg NO_2 per capita. It should be noted however, that even though the same system, Corinair '90 and the same instructions have been used by all the countries, it is national experts within each country, who have compiled the inventory. There may therefore be differences in the way in which the inventories have been carried out and how the sources and activities have been included in the inventory.

From Figure 3.3 is seen that there is no clear trend in the Danish NO_x emissions; the differences between the years are mainly due to yearly variation and to import/export of electricity.

Reductions

Within the Geneva Convention, under UNECE, a NO_x protocol has been agreed upon, stating that the national emissions in 1994 must not exceed the emissions in the year 1987. Further Denmark has signed an extra declaration stating a 30% reduction in the NO_x emissions as soon as possible and at the latest by 1998, using 1986 as a basis for the calculation of the reductions. A new protocol is under negotiation, covering not only NO_x but also NH_3.

Future

A decrease in the emissions over the coming years are expected, as the Danish government has taken measures to reduce the NO_x emissions. But especially for the transport sector it might be difficult to meet the agreed targets.

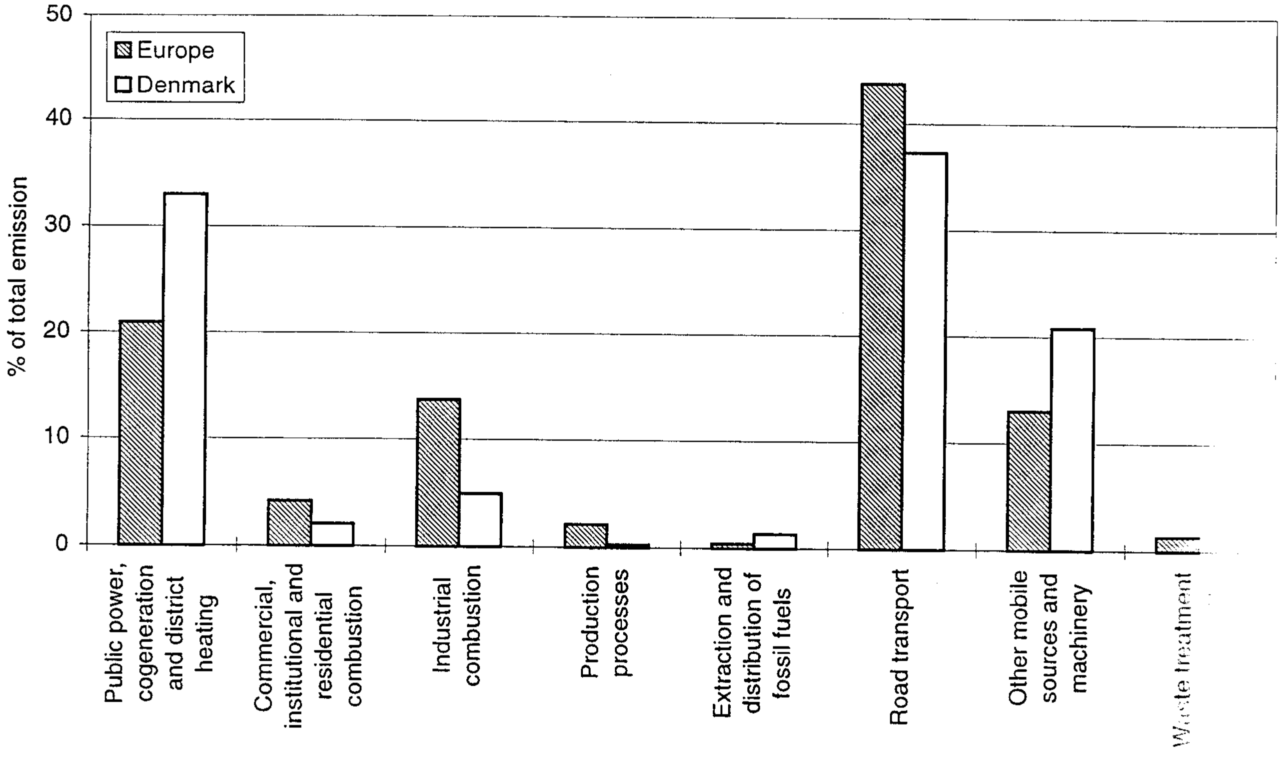


Figure 3.1. The relative contribution to the NO_x emissions to air for 1990 from the main source sector a European and a Danish level.

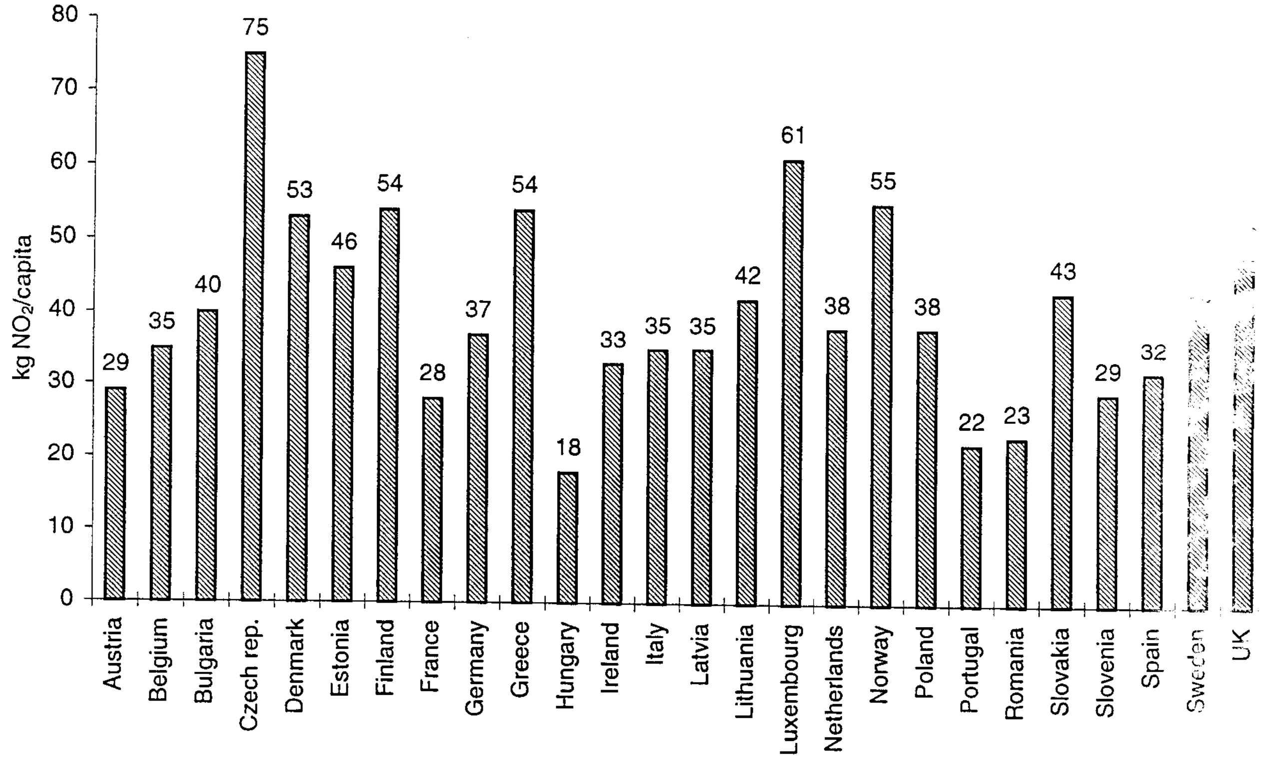


Figure 3.2. NO_x emissions to air per capita in 1990 for European countries (excluding emissions form nature). European mean 37 kg/NO_2/capita.

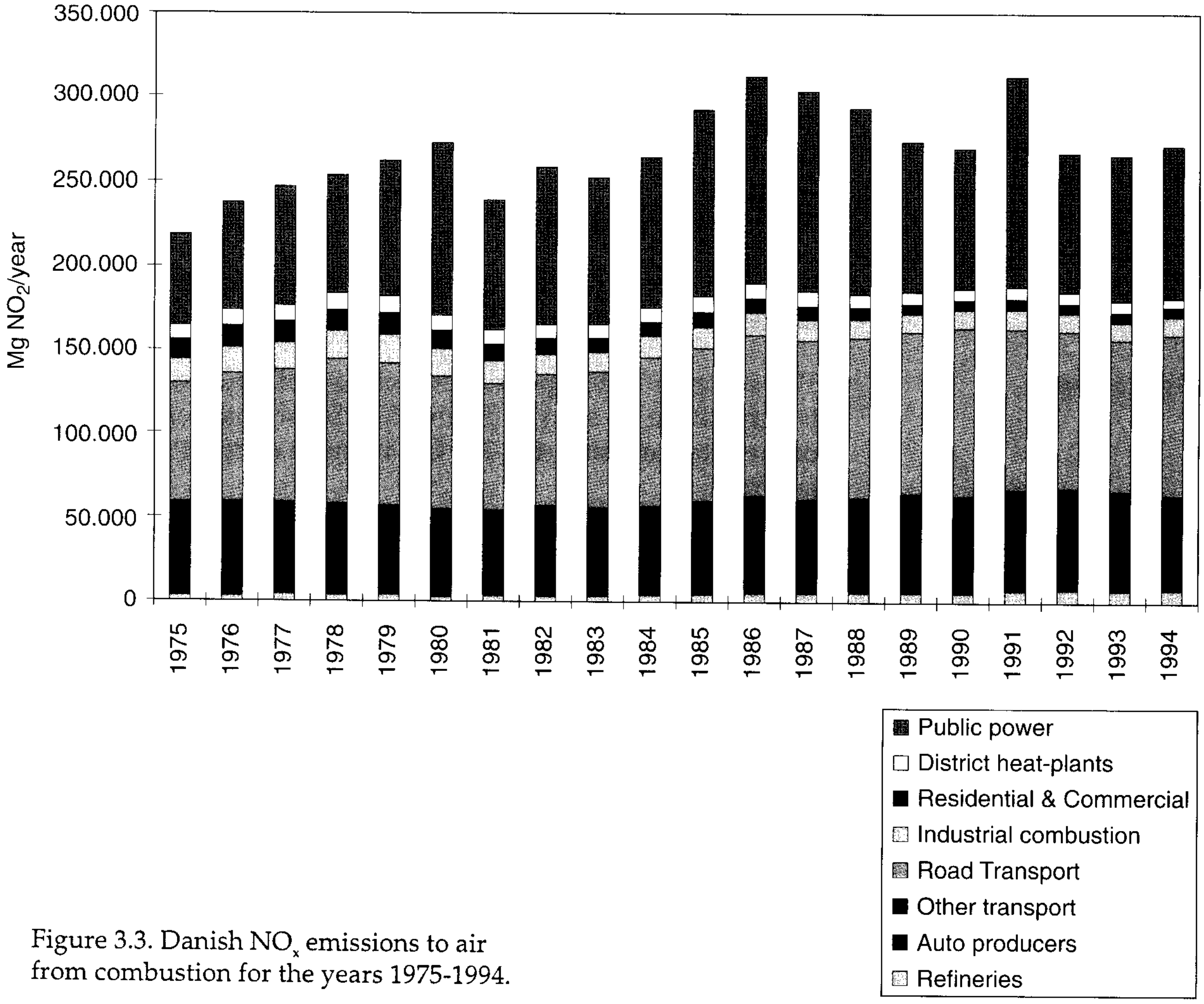


Figure 3.3. Danish NO_x emissions to air from combustion for the years 1975-1994.

3.4 Methane

The emission of methane is calculated separately, because the emission of methane is relative large and the chemical properties of methane are different from many of the other organic compounds.

The calculated emissions of 'Non Methane Volatile Organic Compounds' (NMVOC) are given in section 3.5.

Sources

Methane emissions are mainly due to ruminant digestion and other natural processes as degradation and fermentation.

Total emissions

The total European emissions were in 1990 45619 Gg CH_4 and the total Danish emission in 1990, has been compiled to 761 Gg CH_4.

Nature

From Figure 3.4 is seen that in Denmark, 'Nature' is the main source of methane, contributing with 47%.

The 354 Gg calculated under 'Nature' are compiled from:

Undrained and brackish marches	57%
Lakes	3%
Shallow saltwater	3%
Ground waters	1%
Open sea	1%
Near surface deposits	34%

It is seen that within the category 'Nature', marches and near surface deposits, are main contributors to Danish CH_4 emissions.

Agriculture

The second most important source of methane emission in Denmark is agriculture, as seen on Figure 3.4, this source contributes with 35%, of the total emission, the 263 Gg methane emitted from "Agriculture" are from:

Enteric fermentation in cattle	51%
Manure management	49%

Waste and disposal

The waste treatment and disposal category in Figure 3.4 contributes with 16% of the total yearly Danish methane emission.

Europe

On a European level, is the main source category 'Agriculture', has about the same relative level as in Denmark, followed by 'Nature' and 'Extraction and distribution of fossil fuels'(Figure 3.4). This last sector is a much more important source of methane emissions on a European level compared to the Danish level, because there is very little extraction in Denmark.

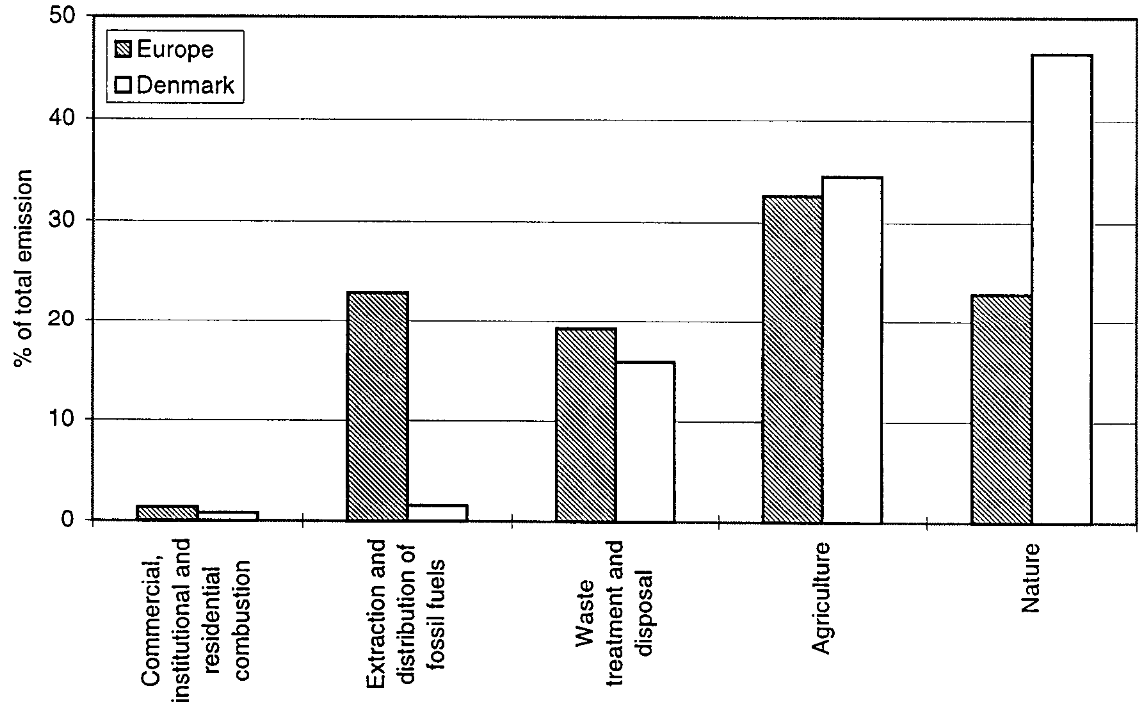


Figure 3.4. The relative contribution to the methane emissions to air for 1990, from the main source sectors on a European and a Danish level.

Uncertainty

It is also clear from the above that the main sources of methane emission are of a diffuse character. Emissions where the main contribution is from combustion processes, e.g., NO_x emissions, national statistics on fuel uses, are used as a basis for the emission calculation. Such statistics are reasonably reliable, as there is an economic interest in keeping use, and thus also the cost of energy low.

Especially for the methane emissions from nature, such reliable statis- tics do not exist, therefore the emission calculation is often based on more weak estimates. As a consequence the uncertainty on the methane emission inventory is greater than for the NO_x inventory. It is assumed that the uncertainty on the present methane inventory is not less than 50%.

Emission per capita

From Figure 3.5 is seen that the European average is 72 kg CH_4 /capita/year and the Danish average is 79 kg CH_4/capita/yr. Taking the above mentioned uncertainties and as mentioned under NO_x emissions, that the inventory has been compiled by individual national experts, the Danish methane emissions are on a European average.

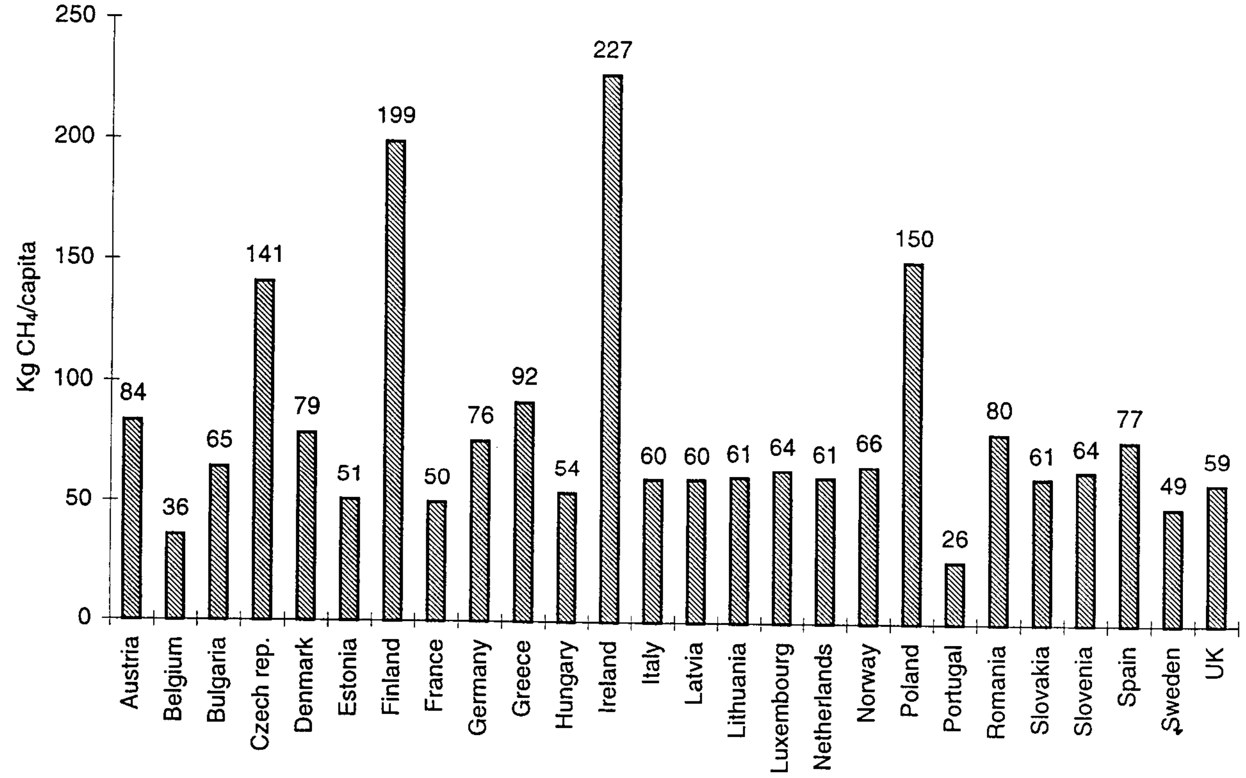


Figure 3.5. Methane emissions to air per capita in 1990 for European countries. (Excluding emissions from nature) . European mean 72 kg CH_4/capita.

From Figure 3.5 can also be seen that Ireland, Poland and the Czech republic are above the European average for methane emission. In Ireland a high methane emission have been calculated for agriculture, Poland has a very high emission calculated from 'Extraction and distribution of fossil fuels' and the Czech Republic has high emissions calculated from the sectors 'Extraction and distribution of fossil fuels' and 'Agriculture'.

Trend in emissions from combustion

Figure 3.6 shows that the emissions of methane from combustion processes increased by almost a factor two from about 1975 to about 1985. After 1987-88 there were a limited decrease in the emissions followed by an increase in 1991.

Trend in emissions

It should be noted that Figure 3.6 only shows methane emissions from combustion processes which only constitute about 2% of the total emissions. 'Waste treatment and disposal (16%), 'Agriculture' (35%) and 'Nature' (47%) are not included.

Trend in emissions from agriculture and nature

As the main agricultural source is cattle, the trend in the emissions follows the trend in number of cattle, which is expected to decrease slightly in the coming years. Emissions from nature are expected to be unchanged. Hence a small decrease in the methane emissions is expected.

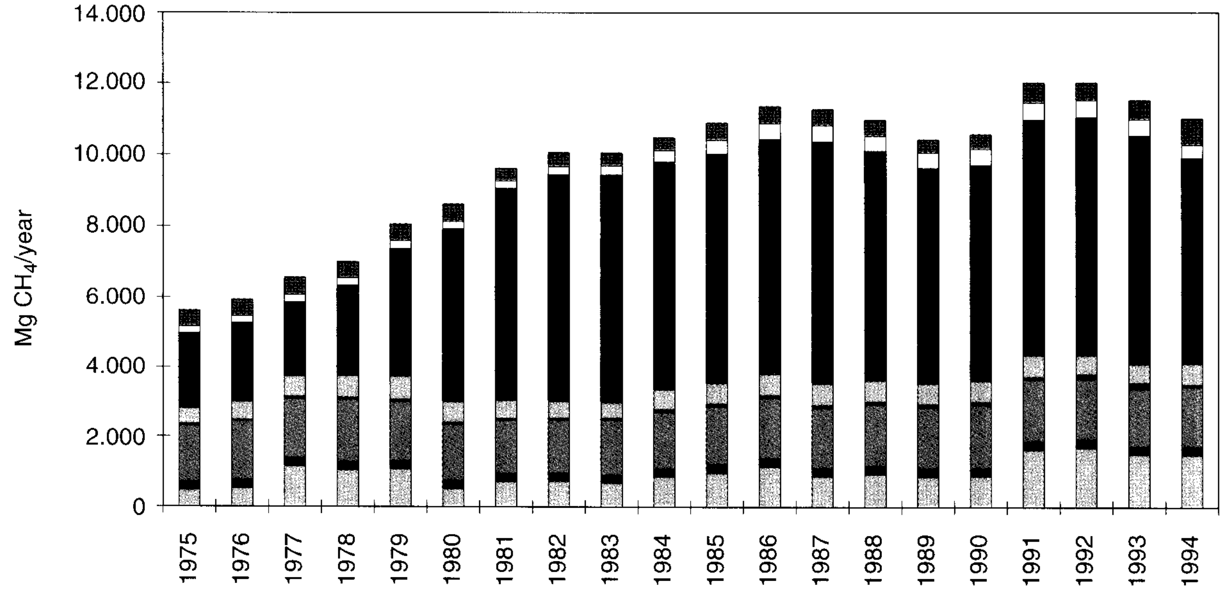


Figure 3.6. Danish methane emissions to air from combustion for the years 1975-1994.

3.5 Non Methane Volatile Organic Compounds

Chemistry

The volatile organic compounds is a large, often undefined, group of compounds. Some of them are pure hydrocarbons. Other contain one or more other atoms, as chlorine, iodine or bromide in the molecules. The compounds can contain both chain and ring structure.

The diversity in the compounds in the volatile organic group, is important, as the different compounds have very different reaction constants, and thus is of different importance in the potential formation of ozone.

It has on a European basis been attempted to find profiles of volatile compounds from different source categories, giving for example a long range of compounds from road traffic emissions. This speciation of the volatile organic compounds, has not yet been implemented in the Danish inventory.

Anthropogenic sources

There are two main anthropogenic sources of volatile organic compounds:

- evaporation of organic compounds, which can be from petrol, painting and degreasing
- incomplete combustion processes which give rise to a series of volatile organic compounds.

Natural sources

The main natural source of NMVOC in Europe is forests, emitting mainly terpenes and isoprenes, but also many other compounds. The emissions from forests depend i.a. on temperature and light intensity. In some countries, mainly in the southern Europe, the natural NMVOC emissions can in the summer months exceed the anthropogenic.

Total emissions

The total European NMVOC emissions in 1990 were 21972 Gg and the Danish emission were 178 Gg.

Relative emissions

From Figure 3.7 is seen that 'Road transport' is the most important source of NMVOC in Denmark contributing with 56%. The second most important source is 'Solvent use' contributing with 19% of the total Danish NMVOC emission.

The same pattern is seen on a European level, where 'Road transport' is the main source sector, but here only contributing with 31%. On a European level 'Solvent use' is also the second most important source sector with app. 22%. The third most important for Europe is the group 'Nature' with 20% of the total emissions.

Road transport

For the most important Danish source group 'Road transport' the 98 Gg emitted have for 1990 been calculated from:

Passenger cars	49%
Light duty vehicles	4%
Heavy duty vehicles and busses	7%
Mopeds and motorcycles	4%
Gasoline evaporation	36%

It is seen that the major part of the VOC emission is due to passenger cars and gasoline evaporation.

Solvent evaporation

Within this source group, the main contribution comes from 'Paint application', with 74% of the 34 Gg emitted in this group.

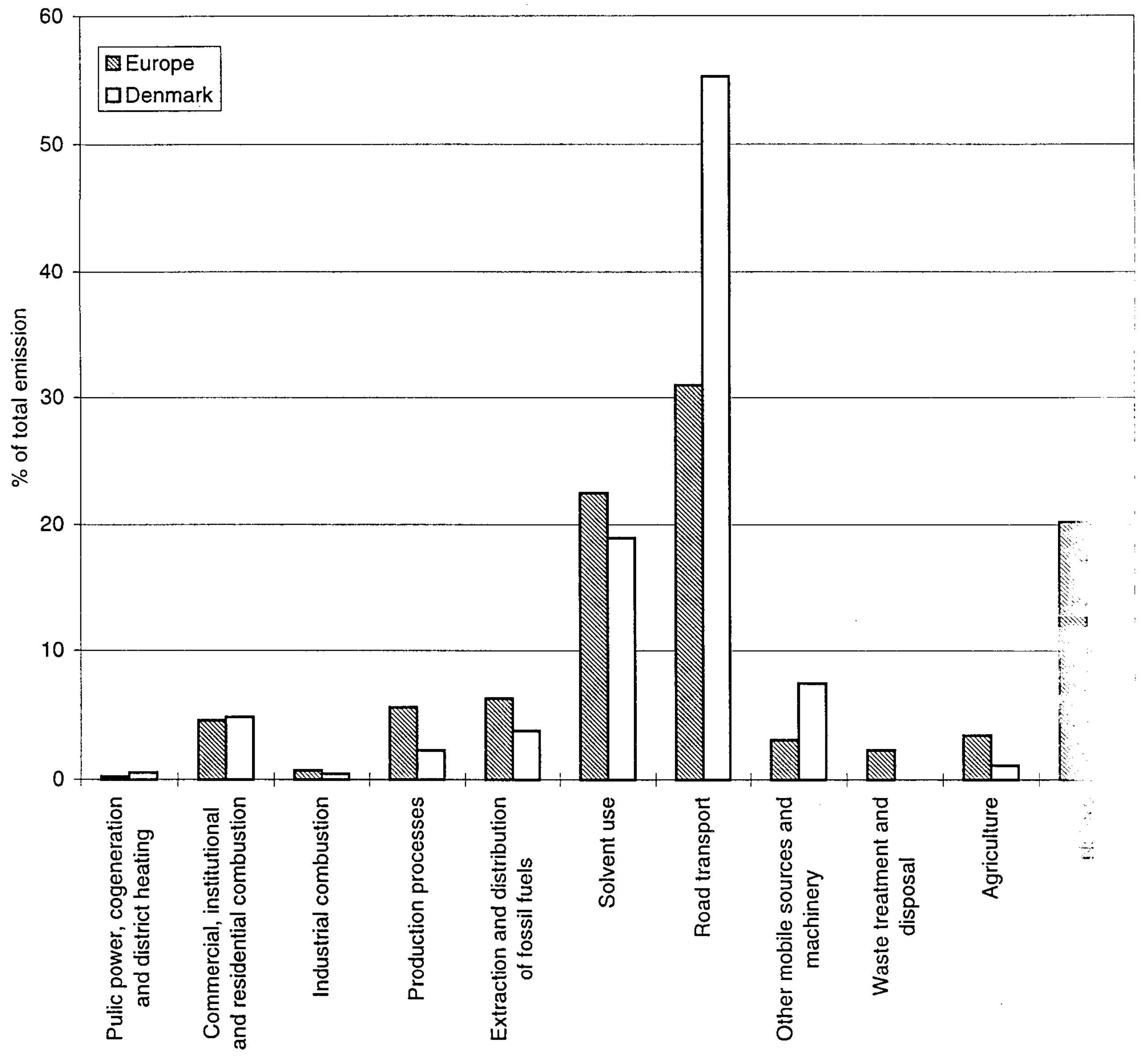


Figure 3.7 The relative contribution to the NMVOC emissions for 1990, from the main source sectors on a European and a Danish level.

Uncertainty

It should be noted, however that the NMVOC inventory is the most uncertain of the inventories presented here. It is not even agreed how high the uncertainty on the compilation is, but a factor of two or three has been proposed. The inventory presented here gives the best estimate of the NMVOC emission in Denmark. Future work and inventories will give a more reliable estimate.

This high uncertainty on the NMVOC emission inventory of course also influences the uncertainty of the model calculations, where the inventory is used as model input.

Emission per capita

From Figure 3.8 is seen that Denmark is not among the highest contributors to NMVOC emission in Europe. The European average is 36 kg/capita/year and the Danish emission is 33 kg/capita/year. It is not a validation nor an estimation of the uncertainty in the Danish NMVOC emission inventory, but at least the Danish emission per capita is on the average of what is estimated in Europe as a whole.

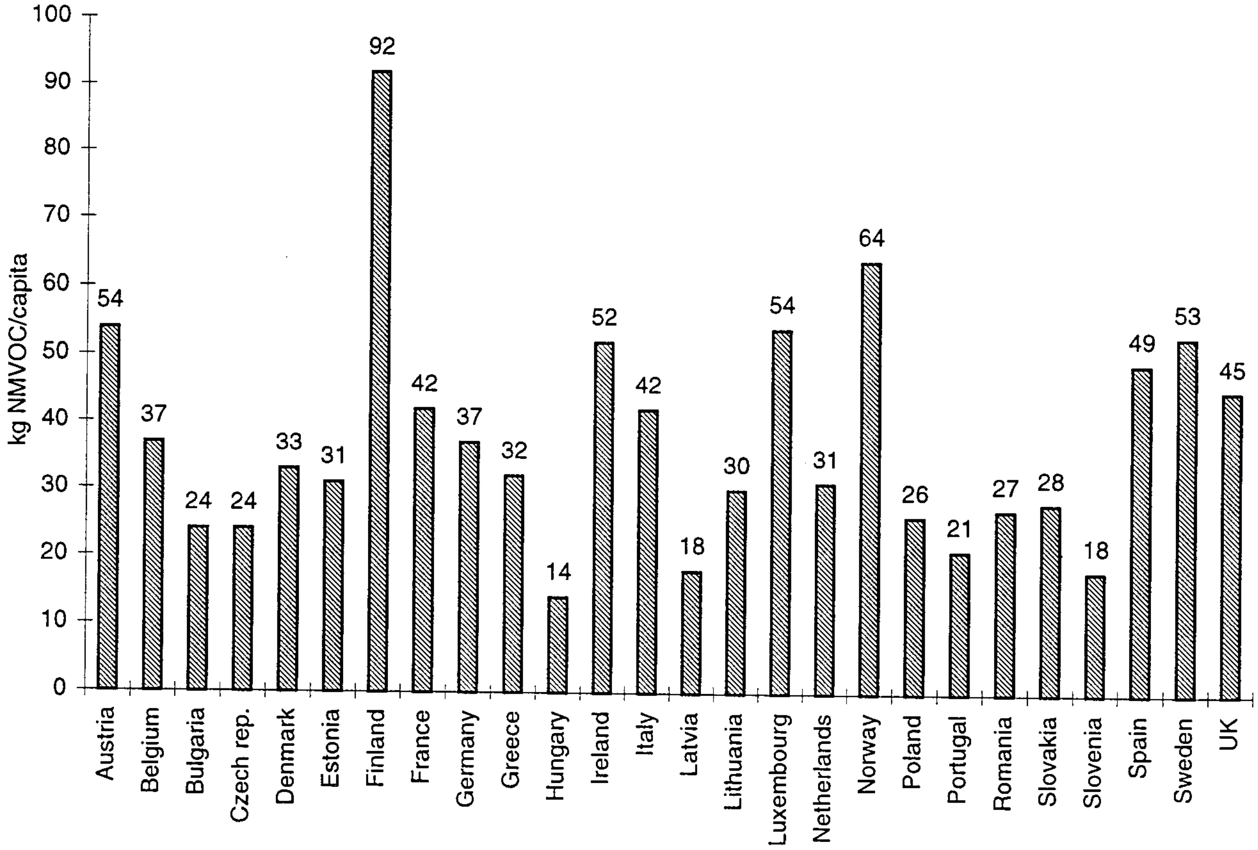


Figure 3.8. NMVOC emissions to air per capita in 1990, for European countries. (Excluding emission from nature). European mean 36 kg NMVOC/capita.

Trends in emissions

It is seen from Figure 3.9 that there is no clear trend in the Danish emissions of NMVOC from combustion. A slight decrease was seen in the beginning of the 1980ties, followed by an increase in the late 1980ties. The decrease seen from 1990 to 1994 is thought to be a 'real' decrease, and not only temporal variations over the years.

Reductions

Within the Geneva Convention under UNECE a NMVOC protocol has been ratified by the member countries. In this protocol the signing countries commit themselves to a 30% reduction in the NMVOC emissions based on the 1985 emission before 1999.

Denmark is expected to sign the protocol

The main reductions are expected to be from increasing use of catalysts on passenger cars, but also from an agreement between the Danish Industry and the Ministry of Environment, on reductions of MNVOC emissions from industry over the years.

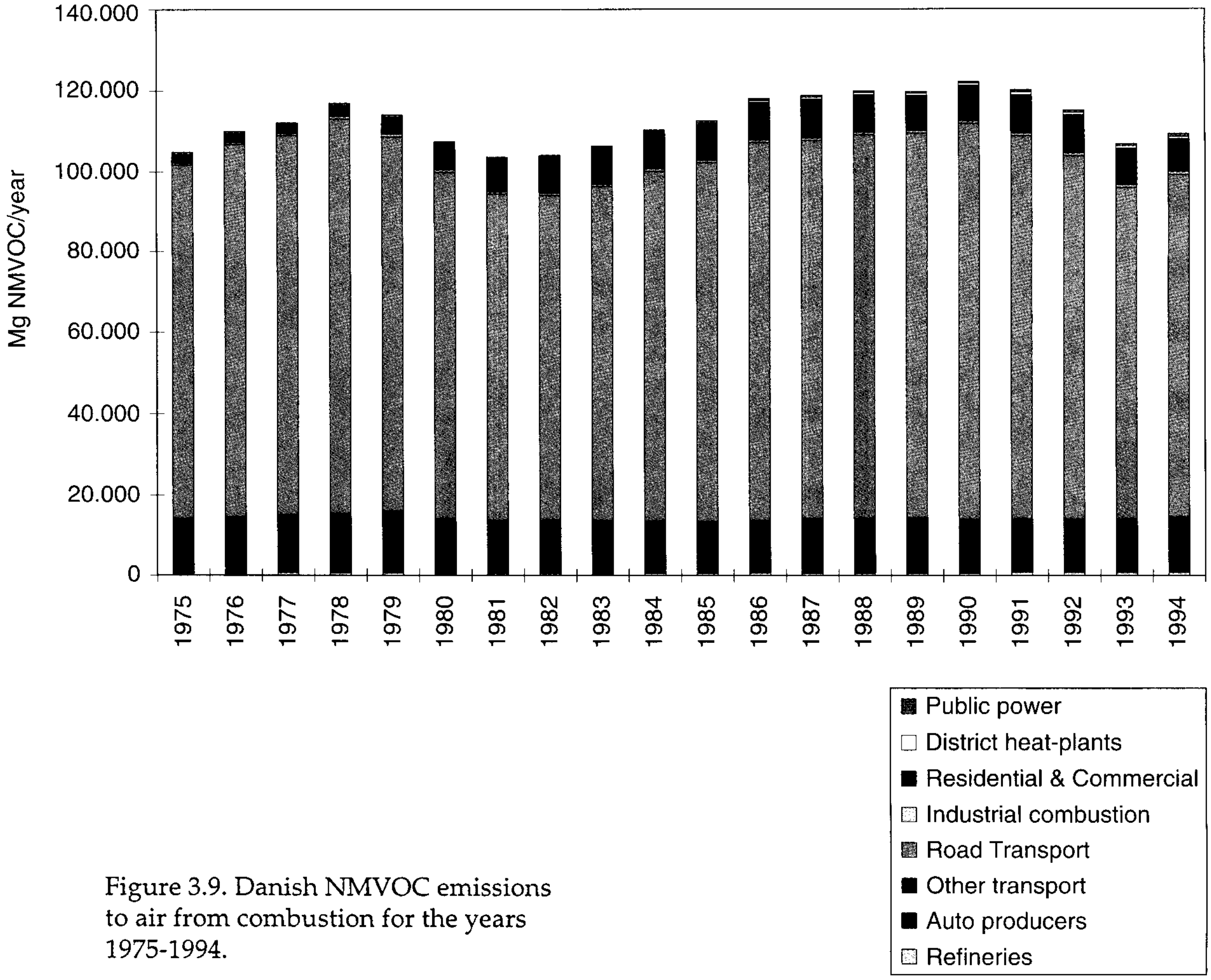


Figure 3.9. Danish NMVOC emissions to air from combustion for the years 1975-1994.

3.6 Carbon monoxide

Sources

CO is formed by incomplete combustion. The more complete a combustion is, the more energy is gained from the process, therefore combustion processes are normally optimised to get the most perfect and complete combustion of the fuel as possible.

Total emissions

The total European CO emissions were in 1990 70364 Gg as CO. The Danish emissions were 789 Gg.

Relative emissions

Road transport is the main source of CO emission in Denmark, with 546 Gg or 69% of the total emission. Within this group, the emissions are calculated as follows:

Passenger cars	85%
Light duty vehicles	7%
Heavy duty vehicles and busses	6%
Mopeds and motorcycles	2%

It is from this seen that within the source 'Road transport', passenger cars are the main contributor to CO emissions in Denmark.

From Figure 3.10 is seen that apart from 'Road transport', the source group 'Commercial, institutional and residential combustion' is contributing with 18% or 140 Gg CO/year of the total Danish CO emission in 1990. Within this group 138 Gg CO or 98% of the emissions are due to burning of wood and wood waste in residential stoves, where the emissions are relative large because the combustion process is inefficient.

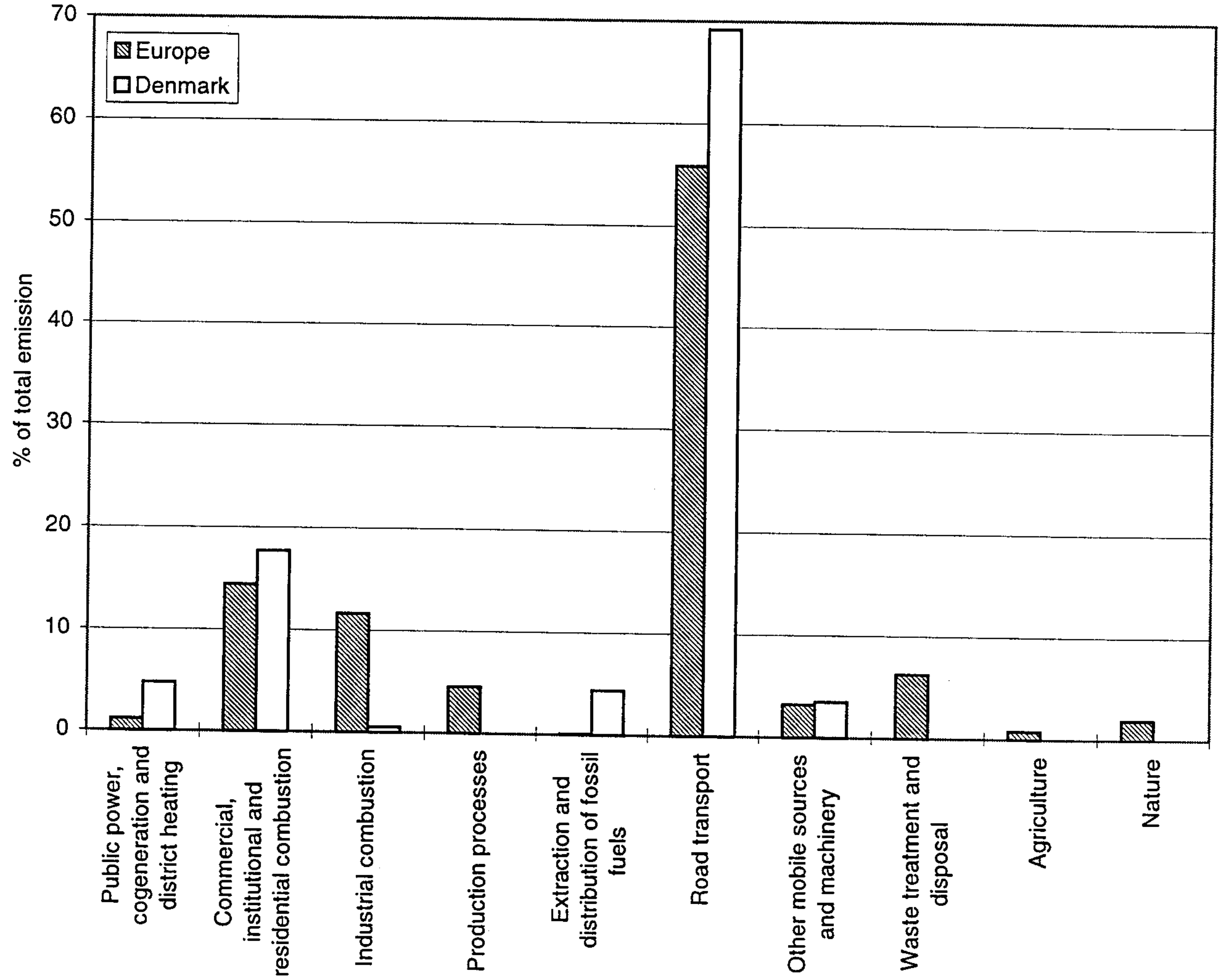


Figure 3.10. The relative contribution to the CO emissions to air for 1990 from the main source sectors on a European and a Danish level.

On a European level the pattern is the same as for the Danish emissions, with 'Road transport' as the most important source group followed by 'Commercial, institutional and residential combustion'.

Uncertainty

The uncertainty on the Danish CO emission inventory is assumed to be 30-40%. For emissions from 'Road traffic' the uncertainty is less, for emissions from 'Residential combustion' the uncertainty is much greater. This is due to the uncertainty in the statistics on how much wood is burned in private homes and also in the emission factor, which is highly dependent on the combustion efficiency, and therefore depend on individual regulation of the stove. An average emission factor have been used in estimating CO emission from residential combustion of wood.

Emission per capita

In Figure 3.11 is shown the calculated yearly emissions of CO for European countries in kg CO/capita/year. It is seen that the Danish emission is not very different from the emissions reported for other countries. The European average is 142 kg CO/capita/year and the Danish emission is 154 kg/capita/year.

Why Luxembourg have calculated such a relatively large CO emission/capita, is not known, but Luxembourg have reported a fairly large emission from the source sector 'Industrial combustion'; 57% of the total CO emission in Luxembourg is calculated from this source sector, while only about 1% of the Danish CO emission is calculated for this source category.

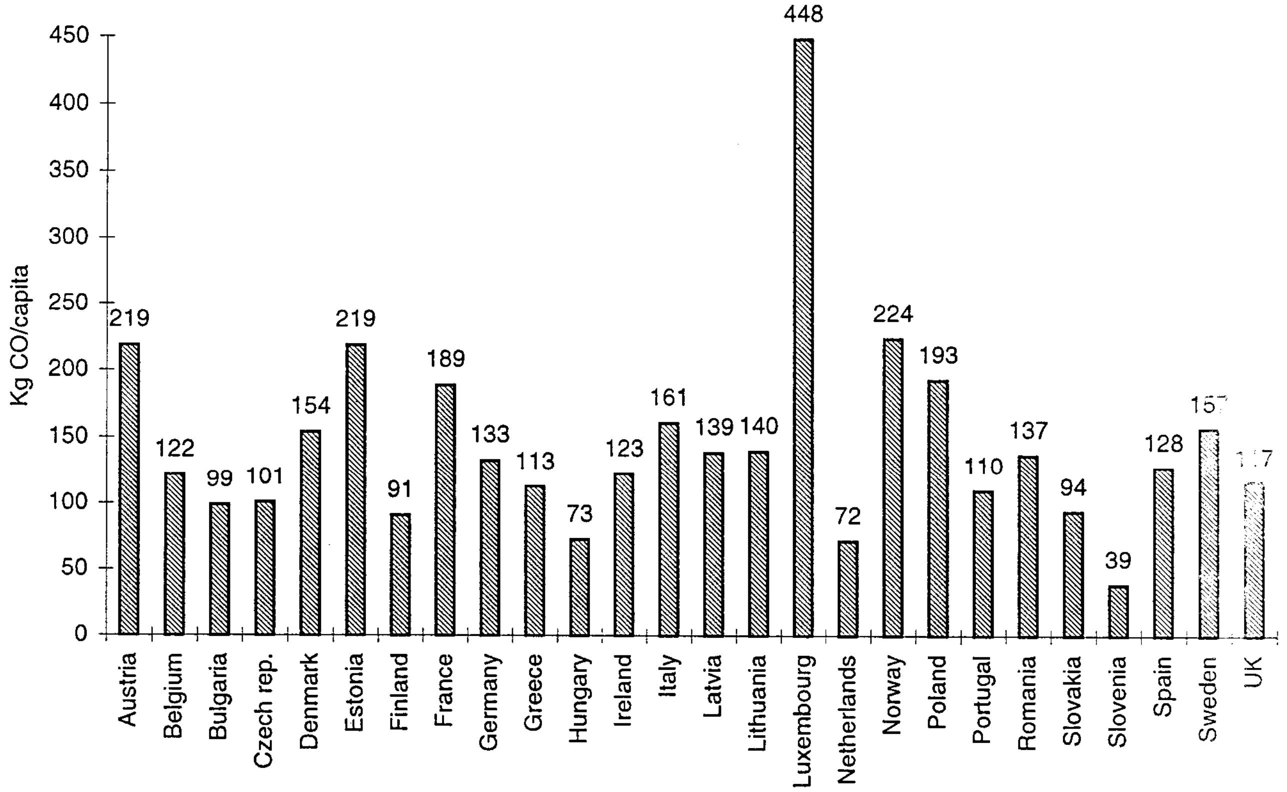


Figure 3.11. CO emissions to air per capita in 1990, for European countries. (Excluding emission from nature). European mean 141 kg CO/capita.

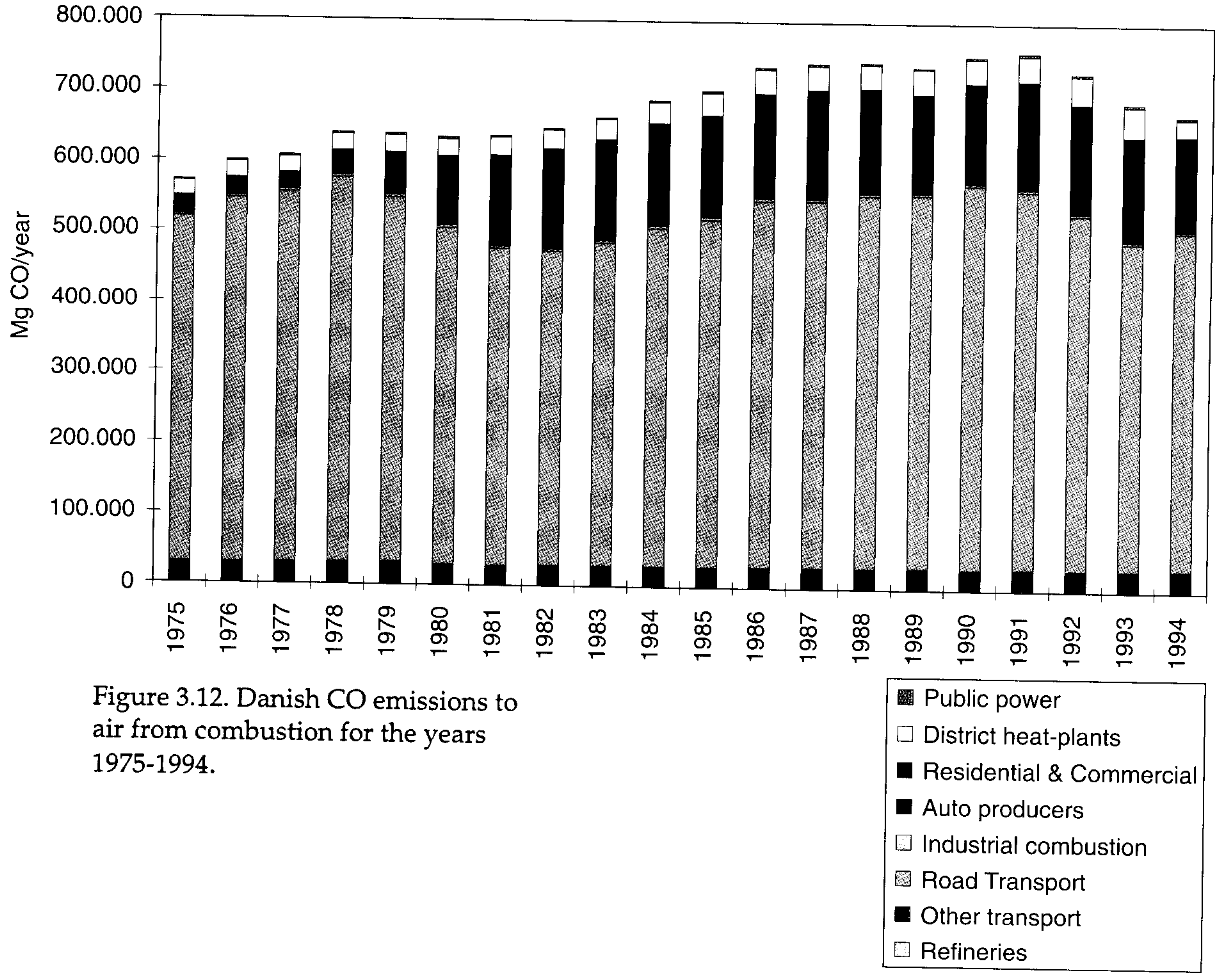


Figure 3.12. Danish CO emissions to air from combustion for the years 1975-1994.

3.7 Summary

It is shown that for NO_x, NMVOC and CO a main source of emission is transportation, compiled in the two groups 'Road transport' and 'Other mobile sources and machinery'.

The legislation and introduction of catalyst converters on cars registered since 1990 will reduce the emissions from individual cars.

For CH_4 the main source groups are 'Agriculture' and 'Nature', where it can be difficult to distinguish the two groups. It is not expected that the emissions from these source groups will change very much over the coming years.

3.8 References

The tables and figures in this chapter are based on the following reports:

Corinair 1993. The atmospheric emissions inventory for Europe. Leaflet XI/74/93-EN.

European Environment Agency 1995a. Corinair 1990 summary tables, Fifth Set, august 1995. EEA, Copenhagen, Denmark

European Environment Agency 1995b. Corinair 90 Summary. Corinair 90: Summary Report nr. 1. EEA, Copenhagen, Denmark.

European Environment Agency 1995c. Corinair 90 Summary. Corinair 90: Summary Report nr. 2. EEA, Copenhagen, Denmark.

European Environment Agency 1995d. Corinair 90 Summary. Corinair 90: Summary Report nr. 3. EEA, Copenhagen, Denmark.

Fenhann, J., Kilde, N.A. 1994. Inventory of Emissions to the Air from Danish Sources 1972-1992. Risø National Laboratory, Roskilde, Denmark. 111 pp.

McInnes, Gordon (ed.) 1996. Atmospheric emission inventory guidebook, 1st edition A joint EMEP/Corinair production, prepared by the EMEP Task Force on Emission Inventories - European Environment Agency, Copenhagen, Denmark.

4 Measurements of photochemical pollutants

Kit Granby, Kåre Kemp, Finn Palmgren,
Mads Hovmand, Axel Egeløv

4.1 Introduction

The precursors of ozone are regulated by national legislation and international conventions, and ozone is monitored and exceedances of threshold values are reported. Results of monitoring of ozone and other photochemical products are presented in the following. As ozone like many other air pollutants is dispersed over larger areas, the first section is devoted to ozone monitoring on a European scale. Subsequently ozone monitoring on a national scale is presented with emphasis on geographical variation, trends, diurnal and seasonal fluctuations, meteorological parameters, deposition and depletion in urban areas. Furthermore, the legislation and exceedances of threshold values are discussed, and an example of a long range transport episode of ozone is presented. Finally, some additional observations of photochemical products from selected field campaigns are presented.

4.2 Pollution on a European scale

EMEP

In clean air, ozone has a lifetime of several weeks and can therefore be transported throughout large parts of the Northern Hemisphere before being destroyed chemically or depleted physically (Liu 1987). Thus, ozone episodes are mostly large scale phenomena rather than local events. It is therefore necessary to investigate ozone pollution on a European scale. EMEP (European Monitoring and Evaluation Programme) is a cooperative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe. As part of the EMEP programme ozone has been monitored since 1988.

TOR (Tropospheric Ozone Research)

The international EUREKA (European Research Coordination Agency) research project EUROTRAC (European Experiment on the Transport and Transformation of Environmentally Relevant Trace constituents in the Troposphere over Europe) also focus on photochemical oxidants. In the subproject TOR (Tropospheric Ozone Research) ozone and photooxidant occurrence in rural areas of Europe have been investigated since 1989.

Geographical variation

Ozone map of Europe

Figure 4.1 which is based on ground level measurements from the EMEP and TOR networks (Beck, Grennfelt 1994) shows the average diurnal maximum ozone concentrations (ppb) measured over the period April-September 1989. One hour mean diurnal maxima are used, because these values are reached in the afternoons when horizontal and vertical inhomogeneities between the locations are smallest. In general, the ozone concentrations increase from Northwest towards Southeast. The average ranges are typically 30-40 ppb in Norway, Sweden, Ireland and Scotland, 40-50 ppb at the west coast of the continent and 50-70 ppb in the south-eastern part of the network area. Diurnal maxima above 70 ppb occur in South Germany. Due to lack of connected monitoring sites, the extension of the increase to the south and east of Europe is not quantified.

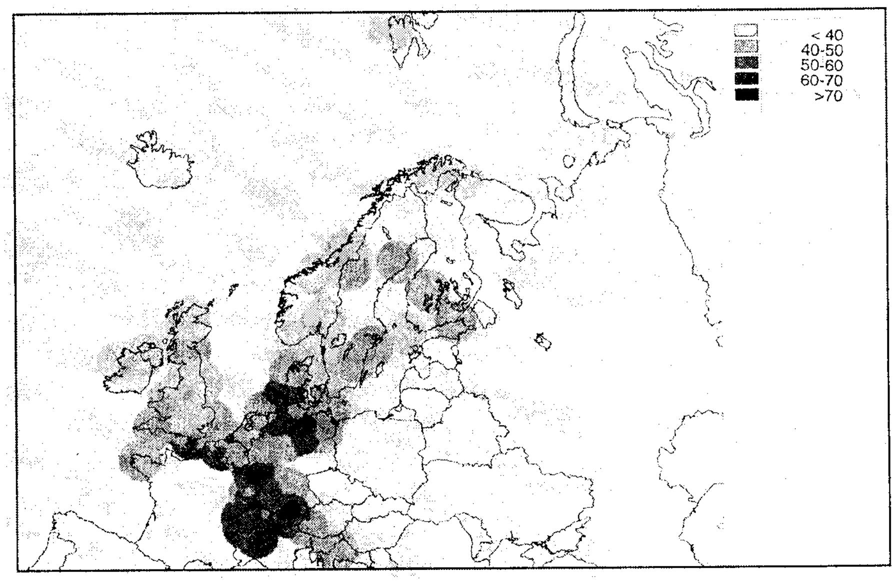


Figure 4.1. The average diurnal maximum ozone concentrations (ppb) measured over the period April-September 1989 (updated from Beck, Grennfelt 1994).

Longitudinal and latitudinal variations

Measurements for the period 1989-1993 from parts of the TOR network including Danish observations from Lille Valby have recently been analyzed (Scheel 1994). The monitoring locations are shown on the map at Figure 4.2. Seasonal averages of ozone in the boundary layer as function of longitude and latitude and for altitudes <200 m are presented in Figure 4.3. The ozone data are grouped after season, *i.e.* summer (May-August), winter (November-February) and transition periods (March-April and September-October).

Figure 4.2. The location of the TOR stations, where the results presented in Figure 4.3 have been obtained.

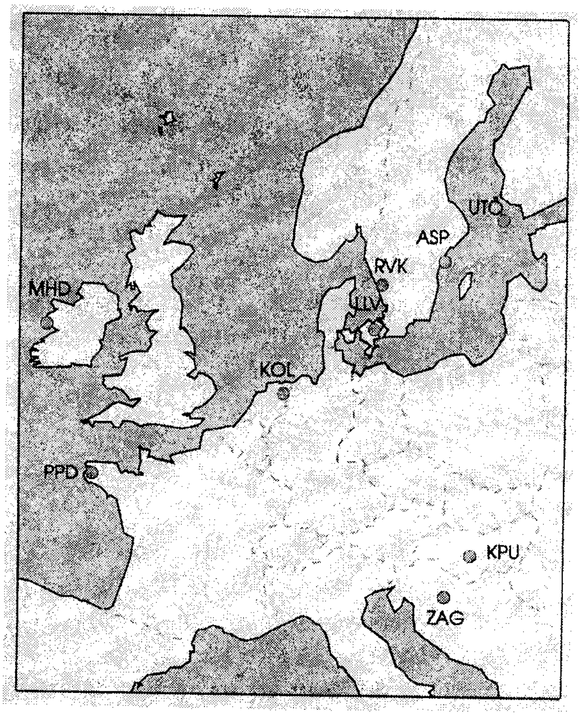
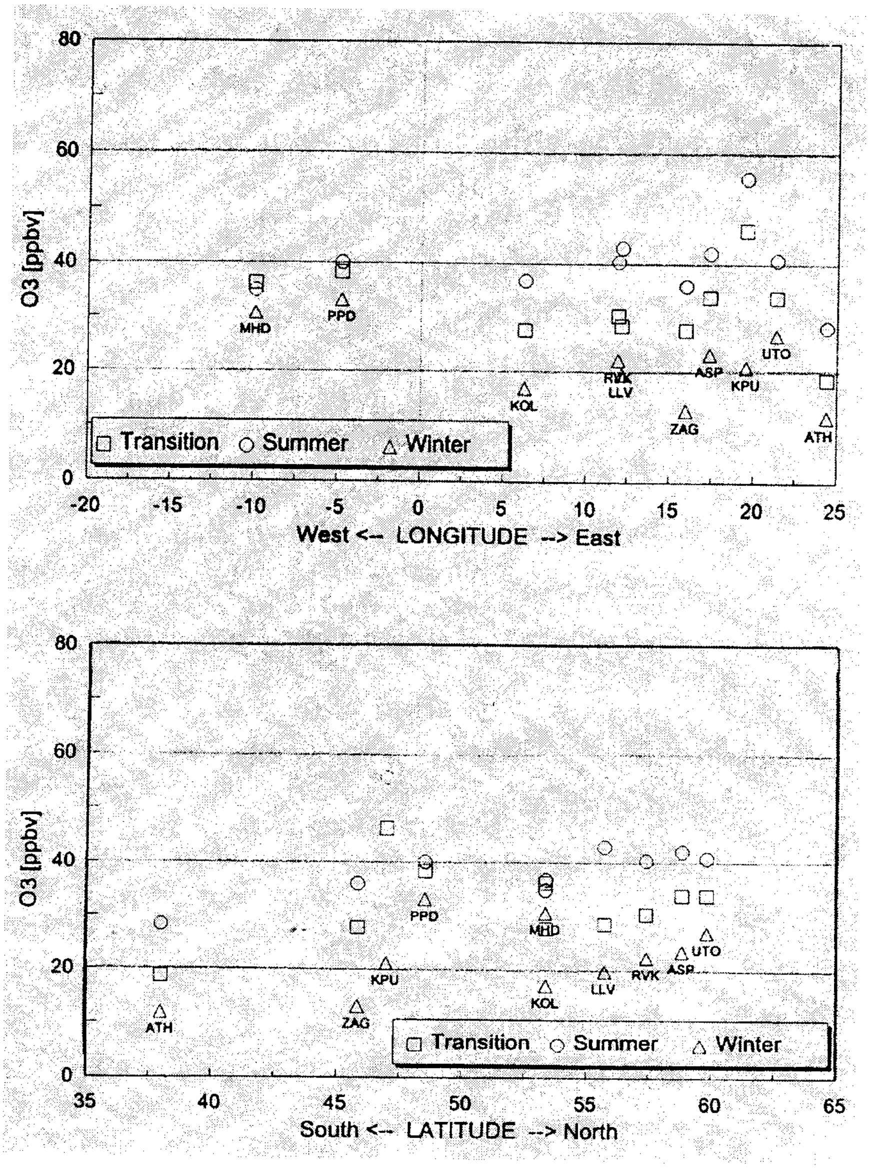


Figure 4.3. Seasonal averages of O_3 (1989-1992/93) as a function of longitude and latitude for TOR stations below 200 m´s altitude (from Scheel 1994). The data are grouped in summer (May-August, winter (November-February) and transition periods (March-April and September-October).



Winter and transition periods

During the winter and transition periods the ozone concentrations over Central Europe were lower than at the west coast of Europe, because NO titration (the reaction O_3+ NO → O_2+ NO_2) caused a higher ozone deficit over the continent (Scheel 1994).

Summer

In contrast, the summer concentrations over Central Europe were higher than at the westerly stations Porspoder (PPD) in Brittany and Mace Head (MHD) on the west coast of Ireland. The Mace Head station is supposed to measure the European boundary layer background of ozone (Beck, Grennfelt 1993). Higher NO_x concentrations and higher temperatures in summer may explain the higher ozone concentrations on the continent.

Highest concentrations in Hungary

A comparison of results from the Scandinavian stations (LLV, RVK, UTÖ) with the Netherlands (KOL) shows an increase from Southwest to Northeast in winter and transition periods (Figure 4.3) due to reduced ozone removal at longer distances from the major NO_x sources. The investigation by Scheel (1994) shows the highest ozone concentration in summer at the station K-Puszta (KPU), Hungary. This is in accordance with the above mentioned positive gradient from Northeast to Southwest of Europe (Beck, Grennfelt 1993). The stations Athens (ATH) and Zagreb (ZAG) are excluded because they are urban stations and hence not representative for their regions.

$O_x = O_3 + NO_2$

More than 90% of NO_x is emitted as NO which within minutes reacts with O_3 forming NO_2 (O_3+ NO → O_2+ NO_2). This can be expressed by the quantity oxidant ($O_x = O_3 + NO_2$) noting that O_x is a conservative quantity over a short time scale (Kley 1995).

Diurnal variation in Denmark compared to Finland

The diurnal variation in cumulative frequency distributions of ozone and O_x (O_3 + NO_2) for Lille Valby (LLV) Denmark and Utö Island (UTÖ) Finland are shown in Figure 4.4. Lille Valby shows larger ratios in concentrations between daytime and night-time than Utö. This is caused by larger ozone depletion due to relatively large NO_x concentrations at Lille Valby. The relatively low NO_x concentrations at Utö, the weaker night-time inversion over the sea caused by the large heat capacity of the water and the lower deposition velocity for ozone to the sea surface explain the smaller diurnal variation. The highest concentrations have similar frequency at the two stations.

Trends

Changes within the last century

One of the longest ozone records in Europe is from Arkona at the German island Rügen in the Baltic Sea (Figure 4.5). The annual mean ozone concentration has increased from 15 ppb in 1956 to 24 ppb in 1983 at an average rate of 0.35 ppb per year. These records have been compared to measurements from the period 1876-1910 made at the Montsouris Observatory in the outskirts of Paris (Volz, Kley 1988). The measuring technique used at Montsouris (iodine catalysed oxidation of arsenite in neutral aqueous solution) has been evaluated and the data corrected for interference. The average ozone concentration for the 1876-1910 period was 11 ppb. Apparently, the background ozone level has more than doubled since the beginning of this century. However, the measurements at Monsouris may have been relatively low due to nocturnal inversions. Recently Staehelin *et al.* (1994) concluded that most of the increase of tropospheric ozone has occurred after the 1950's.

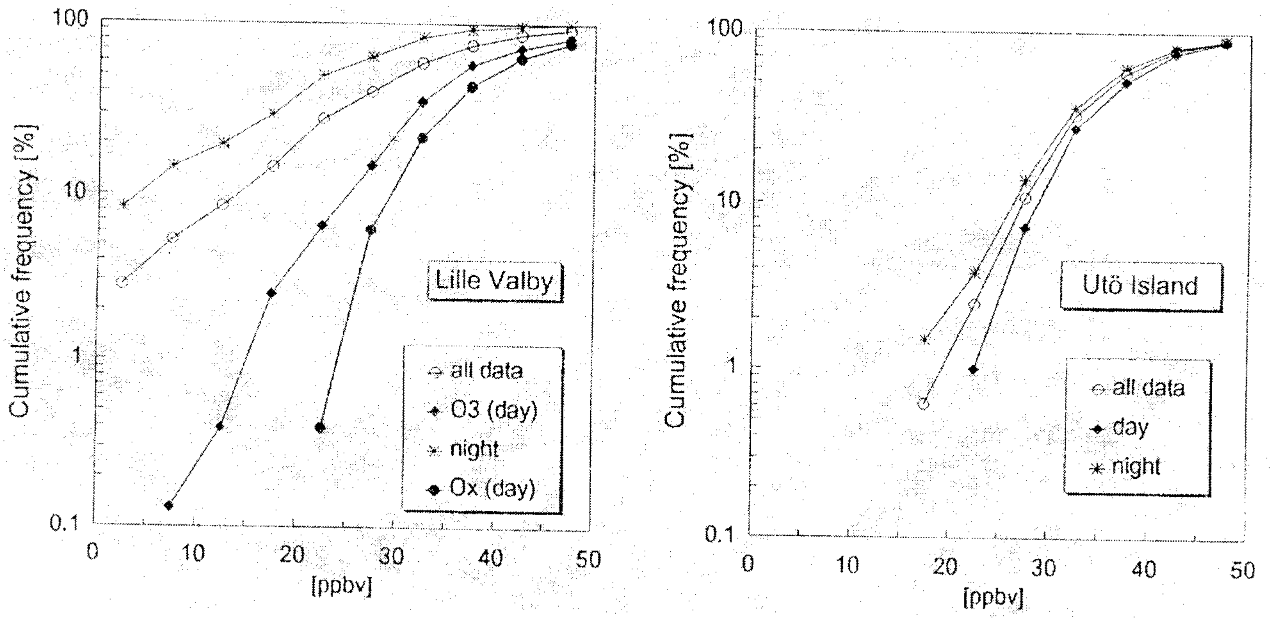


Figure 4.4. Cumulative frequency distributions for O_3 in the summer 1991, at different times of the day measured at Lille Valby, Denmark located 30 km West of Copenhagen and at Utö Island, Finland located in the Baltic Sea 80 km Southwest of the mainland (from Scheel 1994).

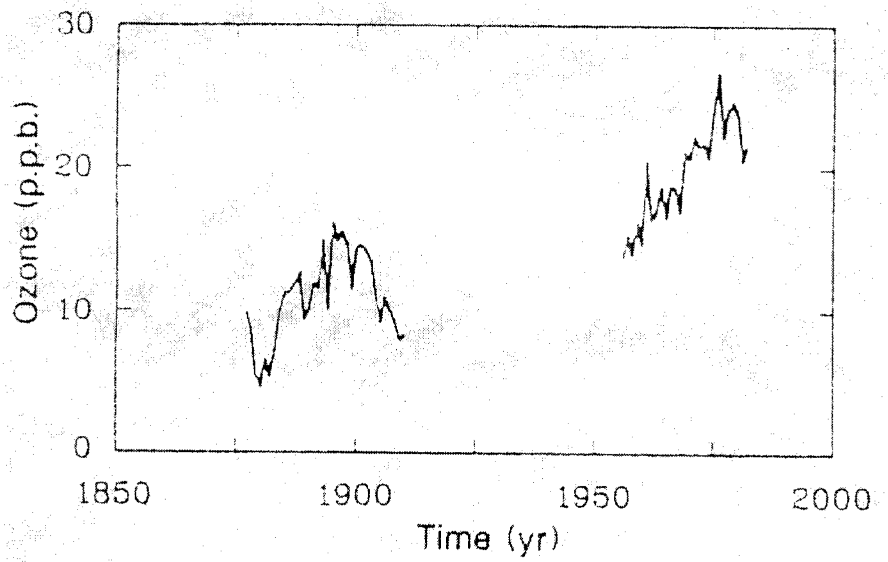


Figure 4.5. Annual mean O_3 concentrations at Montsouris (1876-1910) and at Arkona (1956-83) (from Volz, Kley 1988).

Recent changes

Other investigations show a continuation of the ozone increase up to recent years. At the mountain site Zugspitze (2,962 m) in South Germany, observed monthly averages from 1978-1993 show a significant increase of 0.8 ppb yr^{-1} (Figure 4.6) (Sladkovic *et al.* 1994). The positive trend has slowed down during the recent years and in 1994 the annual growth rate was close to zero. At the "close to background" station Mace Head in Ireland, a small positive trend of 0.18 ppb yr^{-1} was observed (1987-1993) (Simmonds 1994) which are lower than previous similar trend estimates.

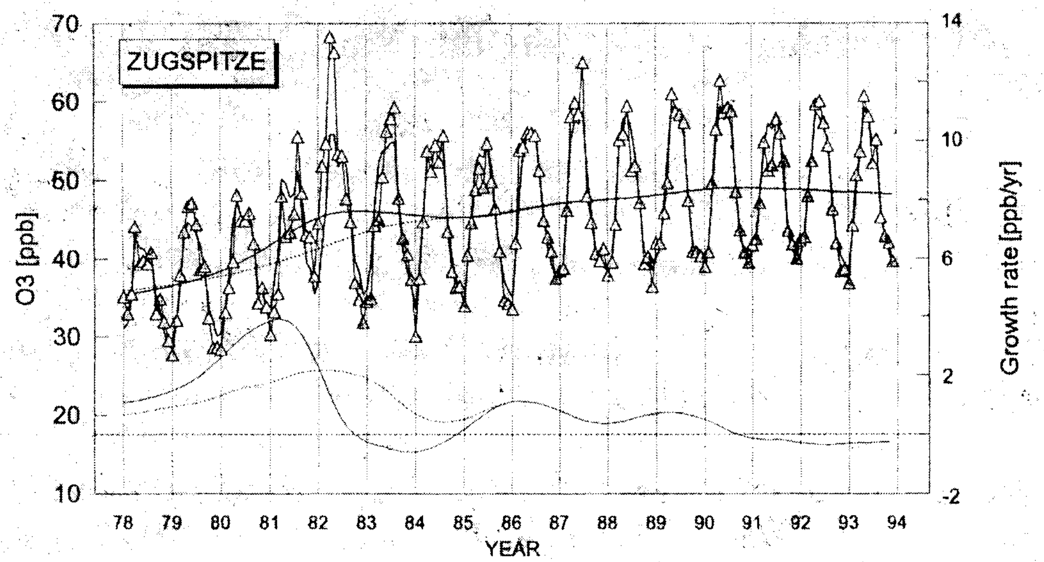


Figure 4.6. Monthly mean O_3 concentrations at Zugspitze together with the harmonic regression curve and its trend components (smoothed thick curve). In addition the variations of the growth rate (derivative of the trend curve [ppb yr^{-1}] are shown at the bottom. Since the O_3 concentrations in 1981-82 were unusually high (witout indication of analytical errors) separate trend estimates ignoring the data from Aug. 81- May 82 are shown for comparison (dotted lines). For the 16 years of observations the average growth rate amounts 0.81 ppb yr^{-1} (from Sladkovic et al. 1994).

Scandinavian trends

At Birkenes in Southern Norway a significant positive trend of 1 ppb yr^{-1} was found for the period 1988-93 (Solberg *et al.* 1994). In Sweden trend analyses based on monthly means of diurnal maxima for the growing season April-September 1985-1990 show a positive trend in the central part of Sweden (Jelöya: +0.7 ppb yr^{-1}) but a negative trend in South Sweden (Rörvik: -1.1 ppb yr^{-1}). The negative trend at e.g. Rörvik near Gothenbourg may be due to an increase in local NO emissions (Vilborg 1993).

In conclusion the European background ozone concentrations have increased significantly since the 1950's but in generel the increase has ceased within the recent years.

4.3 The Danish ozone measuring programme

Ozone is measured continuously at rural and urban sites within the framework of the Background Monitoring Programme (Skov *et al.* 1994), the Ion Balance Programme (Hovmand *et al.* 1994) and the Urban Air Quality Monitoring Programme (Kemp *et al.* 1996).

Analytical method

Most of the measurements have been carried out with monitors based on UV-absorption. The first few years of the programme at the station Ulborg a monitor based on chemiluminescence with ethylene was used. The results presented are calculated from hourly averages. The accuracy is estimated to be ± 1 ppb or ±1.5% of reading.

Monitoring stations

The monitoring stations are listed in Table 4.1. The stations at urban sites reported here are all located at roof tops near the centre of the cities. The rural stations are located at open plain sites without buildings or trees. The forest stations are located above the canopy. For the stations where meteorological measurements are not performed representative data is available from nearby locations. Some of these data have kindly been supplied by Risø National Laboratory. In 1995 ozone measurements were established at the station Keldsnor in order to fulfil the obligations of the EU directive on ozone. The station will be used for the evaluation of the transport of ozone and nitrogen oxides from our southerly neighbour countries.

Table 4.1. Monitoring stations in 1995. The meteorological measurements comprise wind direction, wind speed, ambient temperature, relative humidity and global radiation.

Station	Location	Start date	Parameters
Ulborg	forest	Sep. 1985	O_3, meteorology
Frederiksborg	forest	Sep. 1985	O_3
Lille Valby	rural	Jun. 1991	O_3, NO, NO_y, SO_2
Aalborg	urban background	Dec. 1992	O_3, meteorology
Odense	urban background	Aug. 1992	O_3, meteorology
Copenhagen	urban background	Apr. 1993	O_3, meteorology
Keldsnor	rural	Jan. 1995	O_3, NO, NO_y

4.4 Ozone measurements in Denmark

Geographical variation

The variation of ozone with the wind direction is shown in Figure 4.7. All Danish monitoring stations are included i.e. the rural or forest stations: Ulborg, Lille Valby, Frederiksborg and the urban background stations: Copenhagen, Odense and Aalborg. Summer period, May-August 1993-1994 and winter period, November-February 1993-1994, are presented.

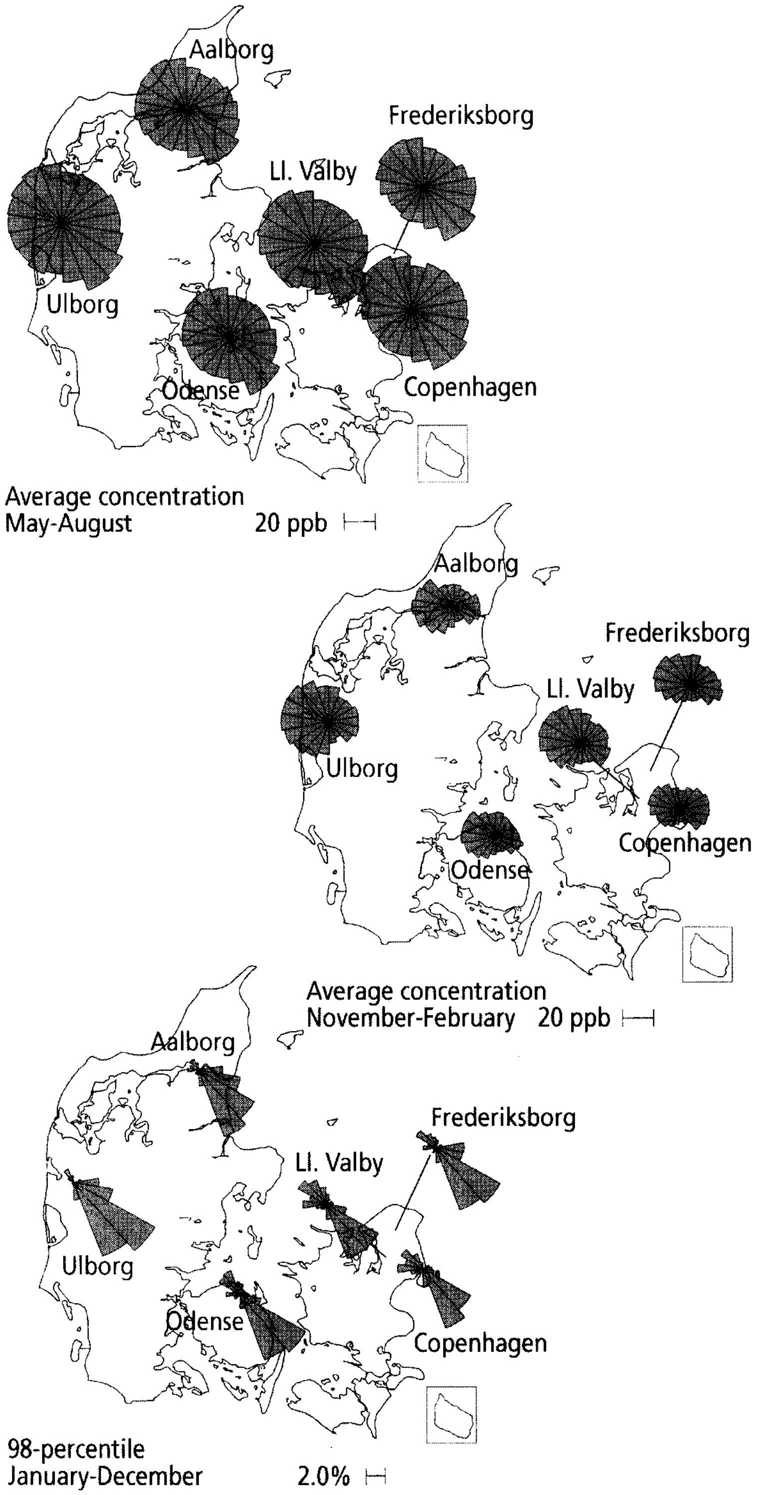


Figure 4.7. Wind roses for hourly ozone concentrations measured in 1993 and 1994. a-b) The radii of the circle sections are proportional to the average concentrations for wind directions corresponding to the section. c) The radii of the circle sections are proportional to the number of hourly measurements in 1993 and 1994 above the 98-percentile i.e. 56.8, 55.0, 57.1, 54.6, 52.4, 58.9 ppb for respectively Copenhagen, Frederiksborg, Lille Valby, Odense, Aalborg and Ulborg.

Winter

During the winter the lowest concentrations were found for southerly wind directions. The low ozone concentrations were due to titration by nitrogen monoxide forming nitrogen dioxide. This reaction has affected all Danish monitoring sites and they were all significantly influenced by NO_x emissions from Central Europe and to a less extent by NO_x emissions from Danish cities (it should be mentioned that the urban stations are urban background stations located at the roof tops and not in the street canyons). During the winter the highest ozone concentrations occurred for westerly winds.

Summer

During the summer the highest concentrations occurred for southeasterly wind directions. This can be seen more clearly from the frequency of concentrations above the 98 percentile (e.g. 57.6 ppb for Lille Valby) relative to the total number of events for each 20° wind sector. The uniform wind direction dependence at the six Danish stations indicates that only a minor part of ozone was produced locally. Usually it takes 24 hours or more to build up significant amounts of photochemical air pollution. This means that local sources have little influence on the ozone formation but they may affect ozone depletion. It is more likely that the photochemical pollution was built up during high pressure periods over Eastern and Central Europe and transported to Denmark.

'European background'

The concentrations were about 35 ppb when the wind arrived from west to north. This is the same level of the ozone concentrations as measured at Mace Head, Ireland, which is regarded as a European background station.

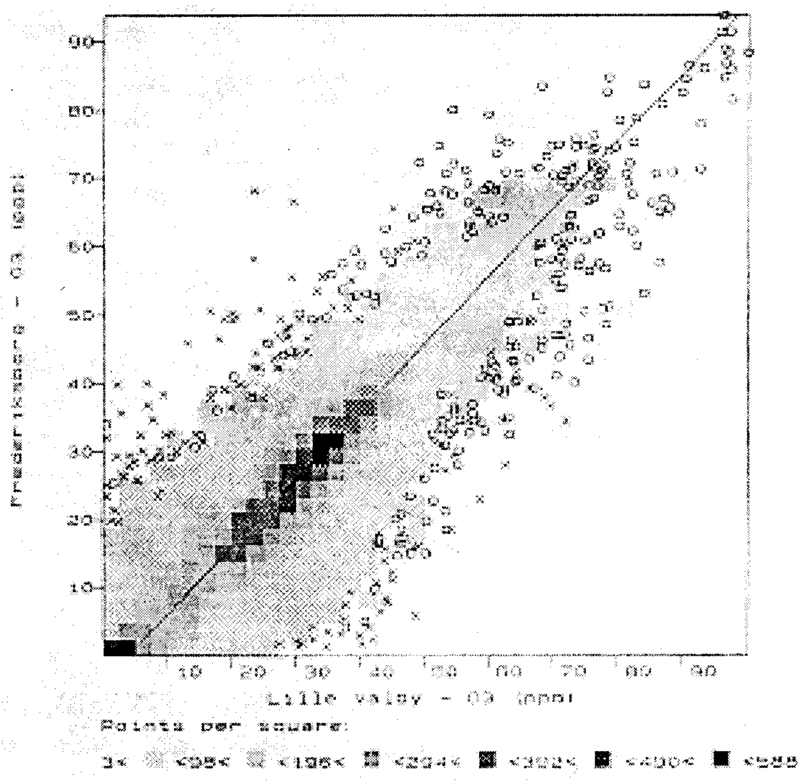
Correlation between stations

Results of hourly mean values from the rural and forest sites are compared i.e. a) Frederiksborg versus Lille Valby and b) Ulborg versus Lille Valby (Figure 4.8) The data from Frederiksborg and Lille Valby both located on Zealand and influenced by NO_x emissions from e.g. the Greater Copenhagen, show a strong correlation with an intercept close to zero. The more remote Ulborg station show weaker correlation with Lille Valby and a positive intercept. The positive intercept can be explained by lower frequency of low ozone concentrations at the Ulborg station due to lower NO emissions in the area and in the areas that the air mass has passed before arriving to the station.

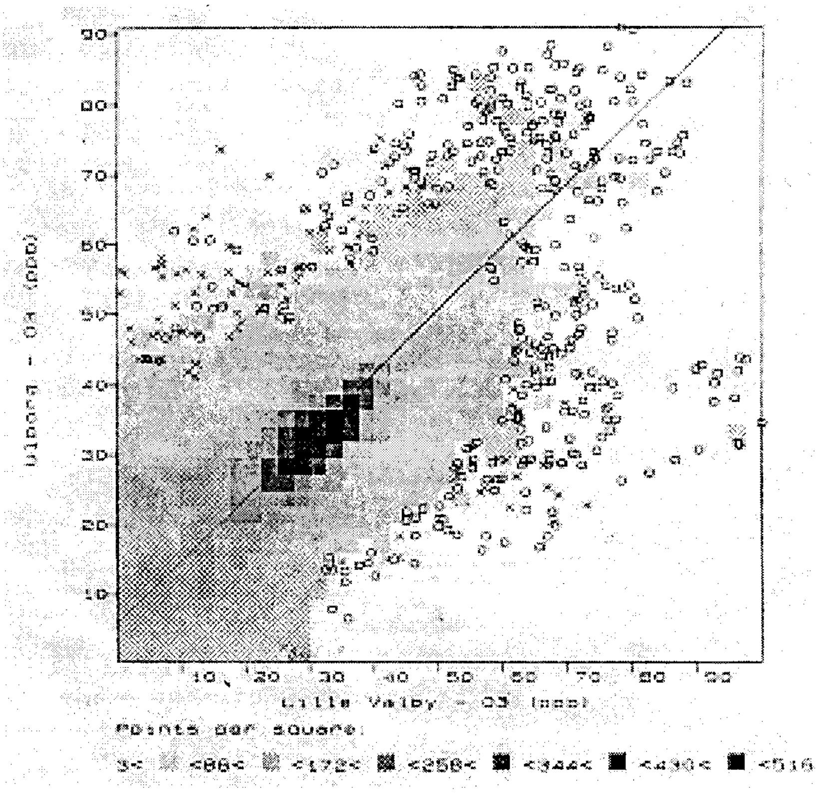
Trends of ozone concentrations in Denmark

Trends of monthly means

The longest ozone records in Denmark are from the Ulborg station in West Jutland where the monitoring site is located in a forest clearing. The sampling inlet has been elevated in steps to a level just above the top of the trees (the last elevation of the inlet was in May 1991). Deposition to the canopy is therefore not expected to affect the ozone concentrations significantly. Monthly average ozone concentrations from August 1985 - December 1994 do not show a significant trend (Figure 4.9).



a) C (Frederiksborg) = 0.99 C(Ll. Valby) - 3.9 (ppb), $R^2 = 0.89$



b) C(Ulborg) = 0.90 C (Ll. Valby) + 5.8 (ppb), $R^2 = 0.70$

Figure 4.8. Scatterplots for ½-hourly O_3 measurements in 1993 and 1994. the plot area is divided into 40 x 40 squares, which are shaded according to the scale below the figures. If the number of points in a square is ≤ 3 the single points are drawn as x for night and o for day measurements. The total number of points is above 30000 on each of the figures. The orthogonal regression lines are drawn.

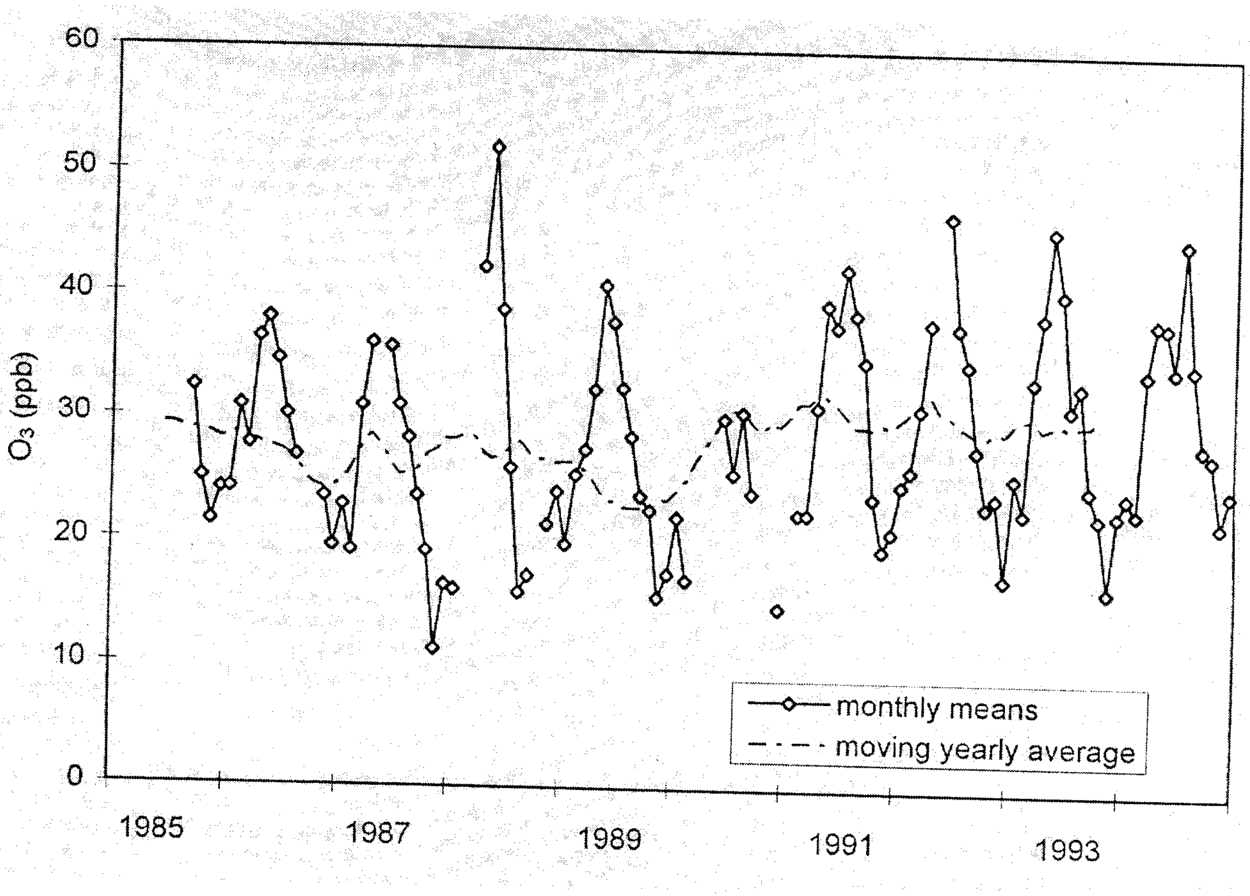


Figure 4.9. Monthly mean ozone concentration, measured at Ulborg, West Jutland Sep. 1985 - Dec. 1994.

Trend of growing seasons

Trend analyses from e.g. a Swedish investigation (Vilborg 1993) was based solely on results from the growing season defined as the period from April-September, when the ozone may cause injury on the vegetation. At Ulborg, the monthly averages from the growing seasons show a positive trend of 2.25 ppb yr^{-1} at the 90% level for the period August 1985 - December 1994.

Trend in relation to wind direction

In order to analyse whether the positive ozone trend is related to transport from specific directions, the annual summer and winter averages were calculated for each of the following wind sectors, 0-90° (NE), 90-180° (SE), 180-270° (SW) and 270-360° (NW) degrees (Figure 4.10). For the summer period (May-August) the SE sector at Ulborg shows a significant positive trend of 1.8 ppb yr^{-1} and the other sectors show no trend. The SE sector does also show a small but significant negative trend for the winters (November-February). The negative trend during the winters may be due to increasing NO_x emissions over Central Europe.

Diurnal variation

Afternoon maximum

The ozone concentration generally reach a maximum in the afternoon. One reason for that is a build up during the day from reactions including NO_x and hydrocarbons in the sunlight. Another reason for the afternoon maxima is the increase in the planetary boundary layer during the day which causes influx of higher ozone concentrations from aloft and dilutes the local NO_x concentrations.

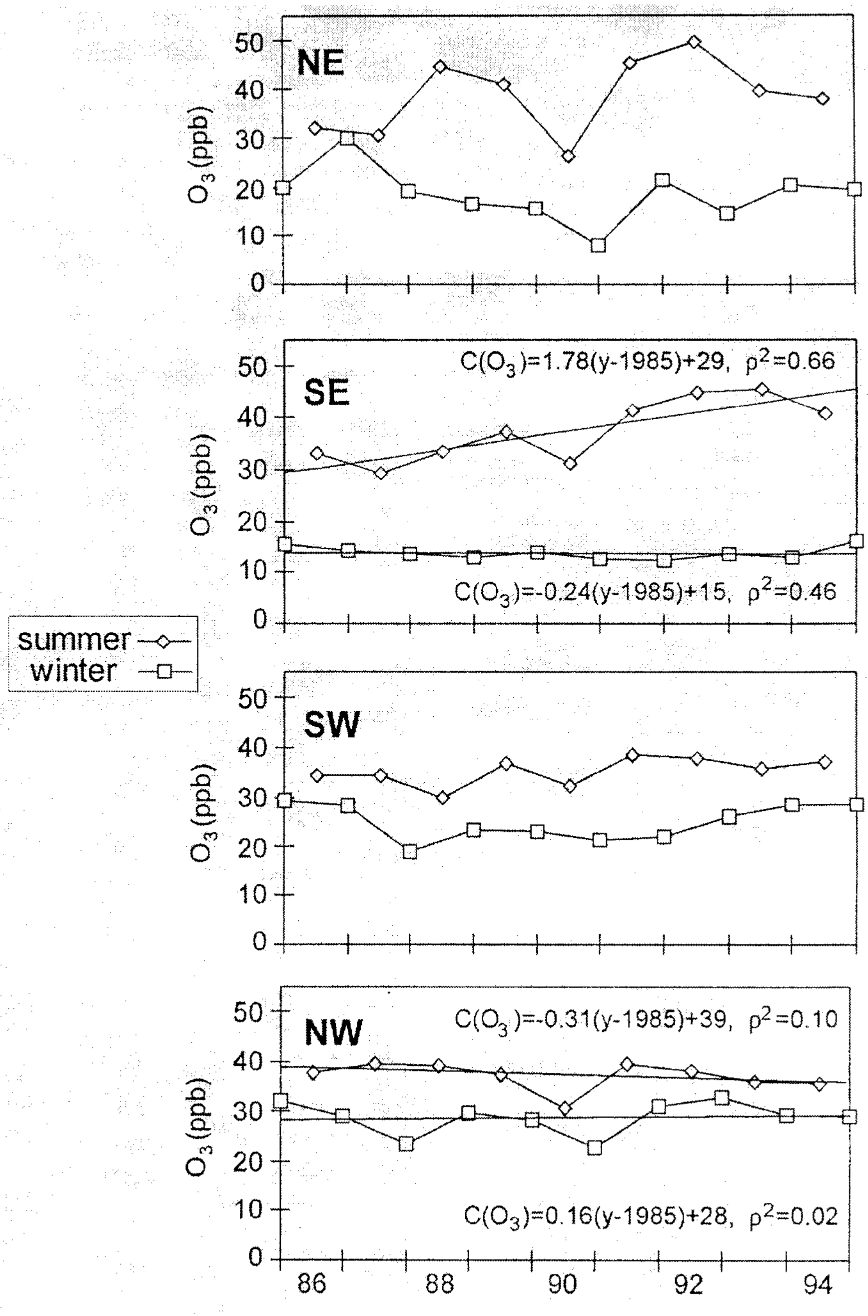


Figure 4.10. Trends 1985 - 1994 based on yearly mean values corresponding to four wind direction sectors. The classical regression lines are drawn for the north-west and south-east sector. Measurements as in Figure 4.9.

Night minimum

During the night the ozone concentration decreases due to reduction in the mixing from aloft and an enhanced depletion in the relatively shallow nocturnal mixing layer by deposition and by NO titration of ozone.

Summer, Ulborg and Lille Valby

The diurnal variation in ozone and O_x from Ulborg and Lille Valby are shown for summers (May-August 1991-94) and winters (November-February 1991-94) (Figure 4.11). The diurnal variations were most pronounced during the summer. The maximum levels occurred in the afternoon at about 15.00 h i.e. about 3 hours later than the diurnal peak of global radiation. The maximum ozone concentrations during the summer were approximately 45 ppb for the rural station Ulborg as for well as the semirural station Lille Valby. The minimum concentrations of 32 ppb at Ulborg and 25 ppb at Lille Valby occurred in the early morning between 4.00 h and 6.00 h.

The different diurnal O_3 profiles for Ulborg and Lille Valby may partly be due to the higher NO_x levels at Lille Valby titrating relatively more of the ozone However, also the diurnal variation of O_x (O_3+NO_2) was weaker at Ulborg than at Lille Valby.. This may be due to that the Ulborg station, located 10 km from the North Sea influenced by the meteorological conditions over the sea with less diurnal variations in mixing height and thereby in ozone concentrations.

Winter

During the winter the maximum ozone concentrations of 19 ppb at Lille Valby and 23 ppb at Ulborg were reached around 13.00 h (Figure 4.11). The minimum concentrations at Lille Valby appeared during the rush hours i.e. 6.00 - 10.00 h and 15.00 - 18.00 h, when the titration of ozone by NO was significant. A third minimum was observed at night. The Ulborg station showed lowest concentrations around midnight, but also lower concentrations during the rush hours. The wintertime O_x profiles were not significantly different at the two stations.

Seasonal Variation

Distinct seasonal ozone variation

The ozone and O_x levels showed a distinct seasonal variation with the highest monthly concentrations in spring and summer and lowest monthly concentrations during autumn and winter (Figure 4.12). The two stations Ulborg and Lille Valby, located approximately 300 km apart, showed in general the same seasonal patterns indicating that the ozone concentrations in Denmark are determined by large scale phenomena.

Spring-summer maximum

For Ulborg 1985-1994 (Figure 4.9) the maximum of the monthly mean ozone concentrations during the spring-summer ranged from 39 to 52 ppb and the autumn-winter minimum ranged from 11 to 20 ppb. The annual monthly maxima at Ulborg and Lille Valby respectively, were 43 and 46 ppb in June 1992 , 38 and 44 ppb in May 1993 and 44 and 44 ppb in July 1994. Thus, the seasonal maxima changed from year to year, but the stations showed the same overall seasonal fluctuations. However, most of the year the monthly average ozone concentrations at Lille Valby were lower than at Ulborg due to the higher NO titration at Lille Valby. The seasonal O_x variations were not very different at Lille Valby and Ulborg.

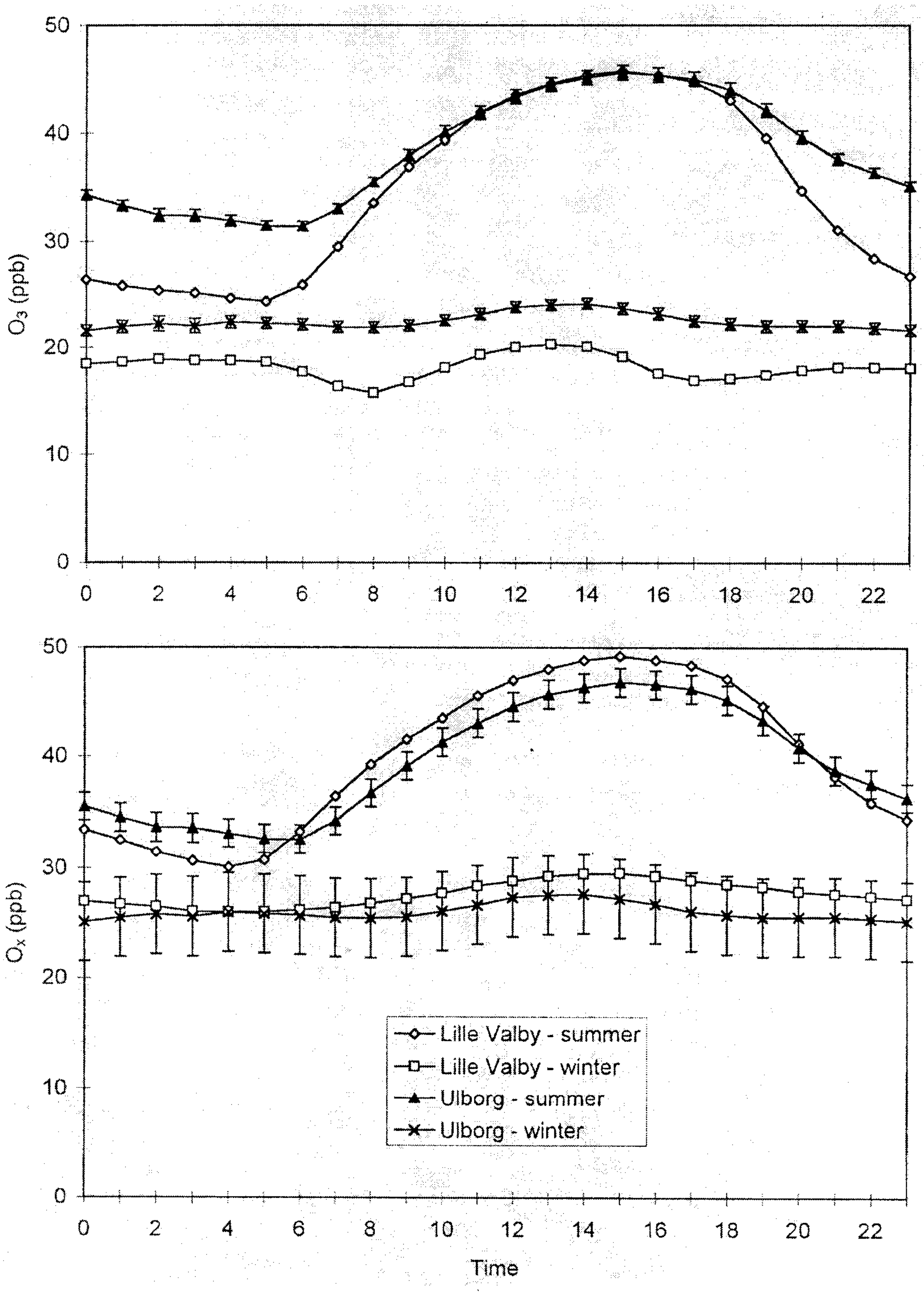


Figure 4.11.
a) Average diurnal variations for O_3 calculated for hourly mean values. The error bars represent the standard diviations divided by the square root of number of measurements at each hour. The error bars are not drawn for the Lille Valby measurement, but they are almost equal to those for Ulborg.
b) Average diurnal variations for O_x calculated for hourly mean values. The error bars represent the standard deviations for O_3 divided by the square root of number of measurements plus the diurnal average values for NO_2 (see text).

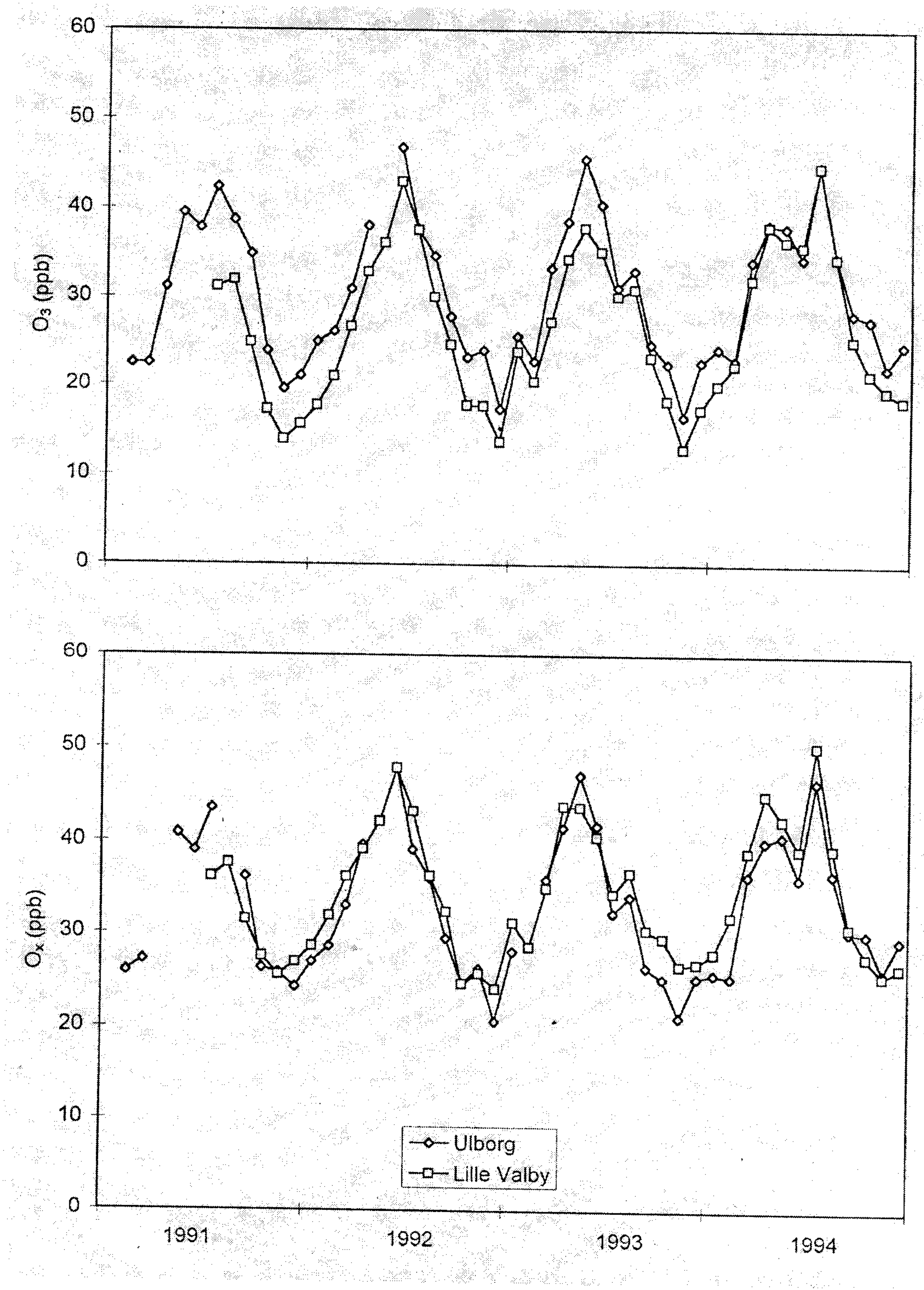


Figure 4.12. Monthly average O_3 and O_x concentrations, 1991 - 1994, measured at Ulborg and Ll. Valby.

Influences from Continental and background areas

In order to interpret the origin of ozone the dependence of ozone and O_x on wind direction in Figure 4.7 have been classified with respect to pollution conditions in the following.

'Continental+regional' (40-160°)

The sector 40-160°, i.e. from Northeast to South-Southeast, is at all stations influenced by air from the continent and at Lille Valby by air from the Greater Copenhagen area (1.340.000 inhabitants with the centre located 30 km east of the station). The sector is defined as a sector with 'continental+regional' influence. However, from the distribution on wind direction in Figure 4.7 it appears that the distributions from different parts of Denmark were very much alike. Thus, the influence of pollution from Copenhagen on the ozone concentrations found at Lille Valby was minor compared to the transport of ozone from the continent.

'Continental' (180-240°)

The sector 180-240°, is influenced by continental air and to a minor extent from the city of Roskilde (40,000 inhabitants) located 6 km south southwest of Lille Valby.

'Background' (260-20°)

Finally, conditions close to the northern hemispheric background is defined as the sector 260-20°. This sector is characterised by air from relatively unpolluted areas (the North Sea and Kattegat marine areas). No industries or major cities influence air in this wind sector.

The seasonal variation in ozone and O_x classified in 'continental+regional', 'continental' or 'northern hemispheric background' areas are shown in Figure 4.13 as monthly averages from August 1991 - December 1994.

Weak seasonal 'background' variation

In 1992 and 1993 the time evolution of 'continental+regional' and the 'continental' seasonal ozone profiles were rather similar, whereas the 'northern hemispheric background' showed much weaker seasonal variations due to the relatively high concentrations during the winters, when the NO_x concentrations arriving in this sector are low. In the spring and summer 1994 the ozone concentrations for the southerly to westerly ('continental') directions were relatively low. This may be due to frequent cold, windy and overcasted weather which gave low ozone levels for this sector.

Little difference in O_x between sectors

The differences in O_x concentrations during the winters between the 'continental+regional', the 'continental' and the 'northern hemispheric' conditions were less distinct. The largest seasonal variations with both the highest summer O_x concentrations and the lowest winter O_x concentrations were found for the 'continental+regional' air, i.e. from wind directions from northeast to south-southeast. As argued above long range transport from the continent is believed to determine the O_x concentrations for this sector.

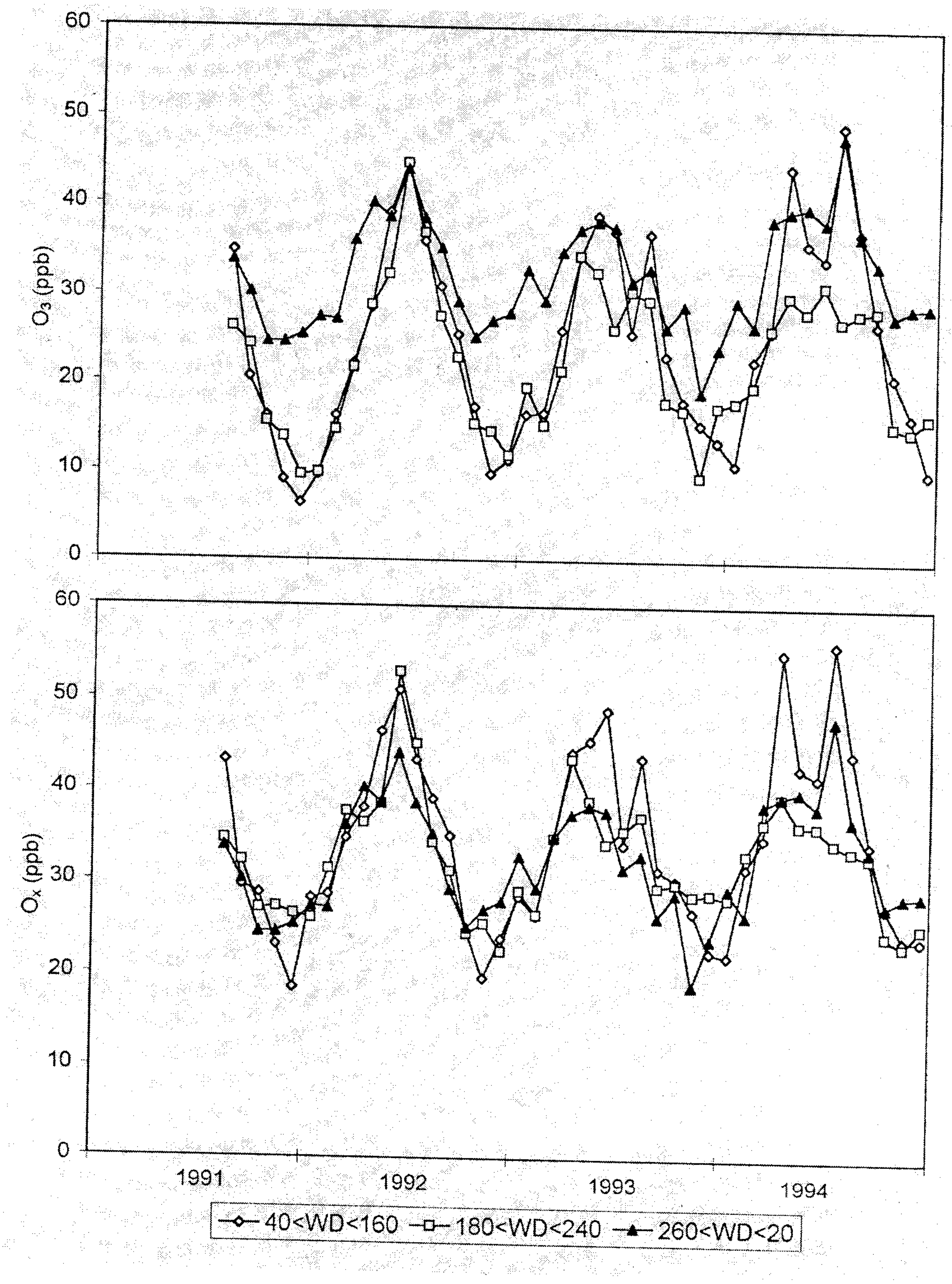


Figure 4.13. Monthly average O_3 and O_x concentrations at Lille Valby corresponding to the wind direction sector 40°-160° (local urban, east continental), 180°-240° (south and south-west continental) and 260°-20° (hemispheric background).

Ozone and meteorological parameters

The ozone concentrations depend strongly on meteorological parameters, which determine not only the transport of ozone and the precursors, but also the physical conditions for the chemical reactions. The correlations between ozone and global radiation, temperature, wind velocity and pressure are illustrated by ozone measurements at Lille Valby from August 1991 to December 1994 (Figure 4.14).

Global radiation

A significant correlation is observed between the ozone and the global radiation (GR), but it does not seem to be a simple linear relation. It is remarkable that the highest ozone values were found at medium values for the GR. The ozone concentrations are only slightly above the mean value, when the GR was at a maximum. This can partly be explained by the gradual increase in ozone during daytime with a maximum in the afternoon, while the GR has a maximum around noon.

Temperature

High ozone concentrations (i.e. above 75 ppb) were only observed at temperatures above 22°C. Apart from the correlation at high ozone concentrations and high temperatures the relationship was poor. Almost zero ozone has been observed at temperatures around 20°C and levels exceeding 40 ppb occurred at temperatures down to -5°C.

Pressure

The medium or low ozone concentrations are not correlated with the atmospheric pressure, but the high ozone concentrations occurred at pressures around the average (1000-1020 hPa). The relation between high ozone and global radiation, temperature and pressure can be explained assuming that transport of heavily polluted hot continental air from Central and Eastern Europe takes place, when a summer high pressure gradually moves towards east. The high temperature and the almost clear sky along the transport path will favour the formation of ozone. The haze due to the pollution in the air reduce the global radiation at ground level. This is illustrated for a single episode in section 4.5.

Wind speed

The relation between ozone and wind speed was characterised by an almost constant ozone value of around 35 ppb for wind speeds above 8 m/s. The high wind speed favour mixing in the planetary boundary layer with more air from the free troposphere where the ozone concentration is almost constant. Furthermore, when the wind speeds approach zero and the NO_x emissions are less mixed, no high ozone concentrations occurred.

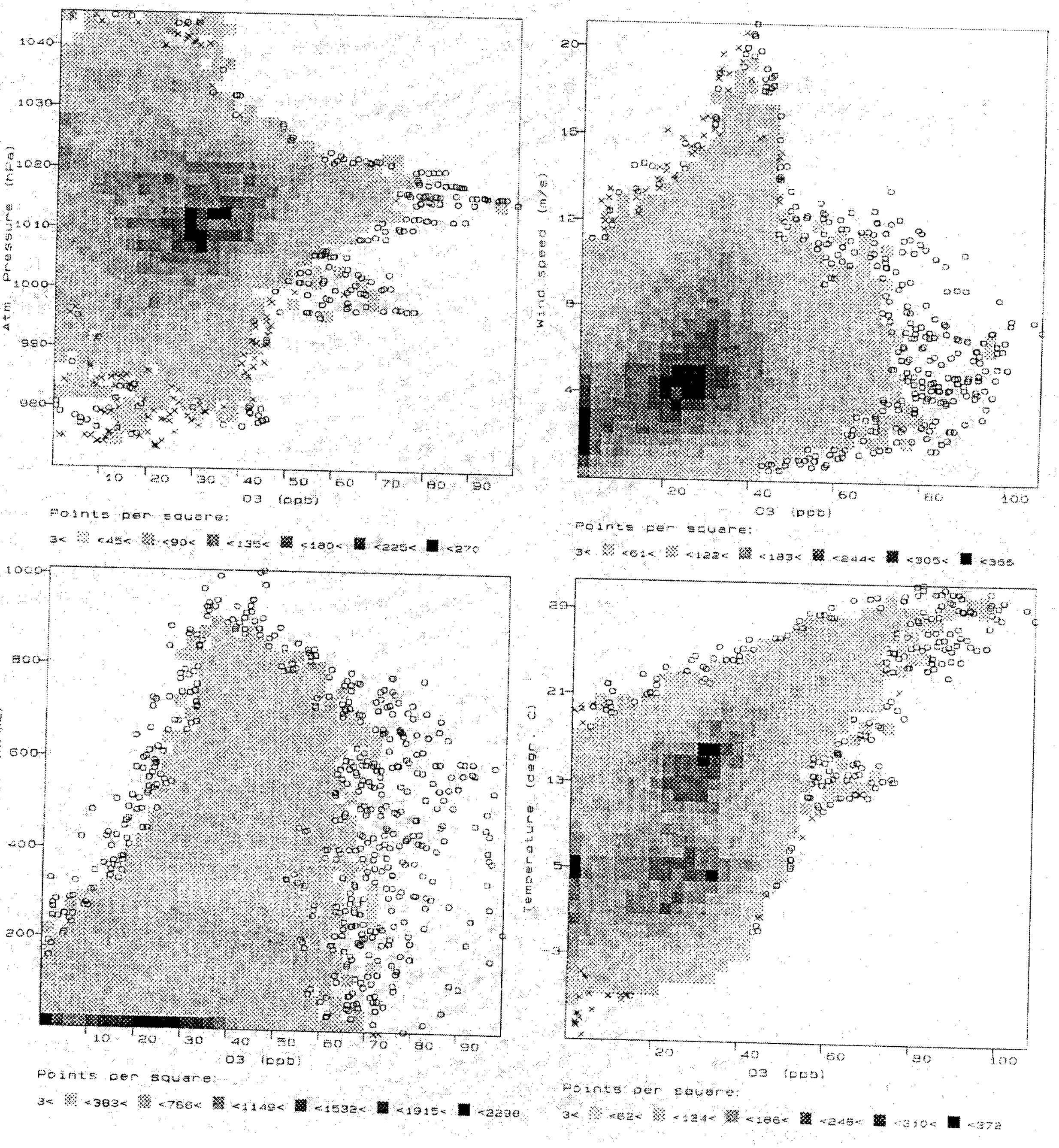


Figure 4.14. Scatterplots for ½-hourly O_3 concentrations vs. different meteorological parameters measured at Lille Valby from August 1991 to December 1994. The plot area is divided into 40 x 40 squares, which are shaded according to the scale below the figures. If the number of points in a square is ≤ 3 the single points are drawn as x for night measurements and o for day measurements. the total number of points is above 50,000 on each of the figures.

4.5 Ozone at street level and in the urban background

Ozone in urban air

One of most important reactions in urban air is the reaction of O_3 with NO (Section 7.2):

$$O_3 + NO \rightarrow O_2 + NO_2$$

The reaction is very fast (less than a minute) and is important for depletion of ozone and simultaneous formation of NO_2 in street canyons. It means that ozone is the limiting component for formation of NO_2 in streets with high traffic intensity and consequently large emission of NO. At some distance from the sources, i.e. urban background, all NO is often converted so no more ozone will be depleted.

Weekly variation

Figure 4.15 shows the weekly variation of ozone at Copenhagen (street), Copenhagen (urban background) and Lille Valby (regional background). The ozone concentration at the urban background shows nearly the same pattern as the rural background with highest levels early in the afternoon and lowest levels early morning before sunrise. The minimum at the urban background is lowest due to some influence from the morning rush hours. The patterns are more similar at the weekends, when the traffic density is small. The ozone concentration at the street site during day time on weekdays is lower and more constant, because ozone is consumed by oxidation of NO emitted from the traffic in the street. The ozone level during rush hours is very small at the street due to consumption by reaction with NO. During weekends it is more similar to the urban background, but still lower.

O_3 dependence on wind direction

Figure 4.16 shows the relations between the O_3 concentrations and the wind direction in the street and urban background. The concentration of ozone is much lower in the street and it depends more on the wind direction than at the urban background site. This corresponds to the opposite wind direction dependence of NO in the same figure. It is also seen that the urban background of NO is very small indicating that NO here is the limiting component for formation of NO_2.

$O_x = O_3 + NO_2$

If no other processes are important, and if the direct emission of NO_2 is relatively small, the sum of O_3 and NO_2 (O_x) will be the same at street sites and at urban background sites. Figure 4.16 shows the wind direction diagrams for O_x at the two sites. They are, as expected, nearly isotropic and the concentration levels for every wind sector are nearly the same at the two sites. The results also indicate that no other processes are significant in general, and that the direct emission of NO_2 is small.

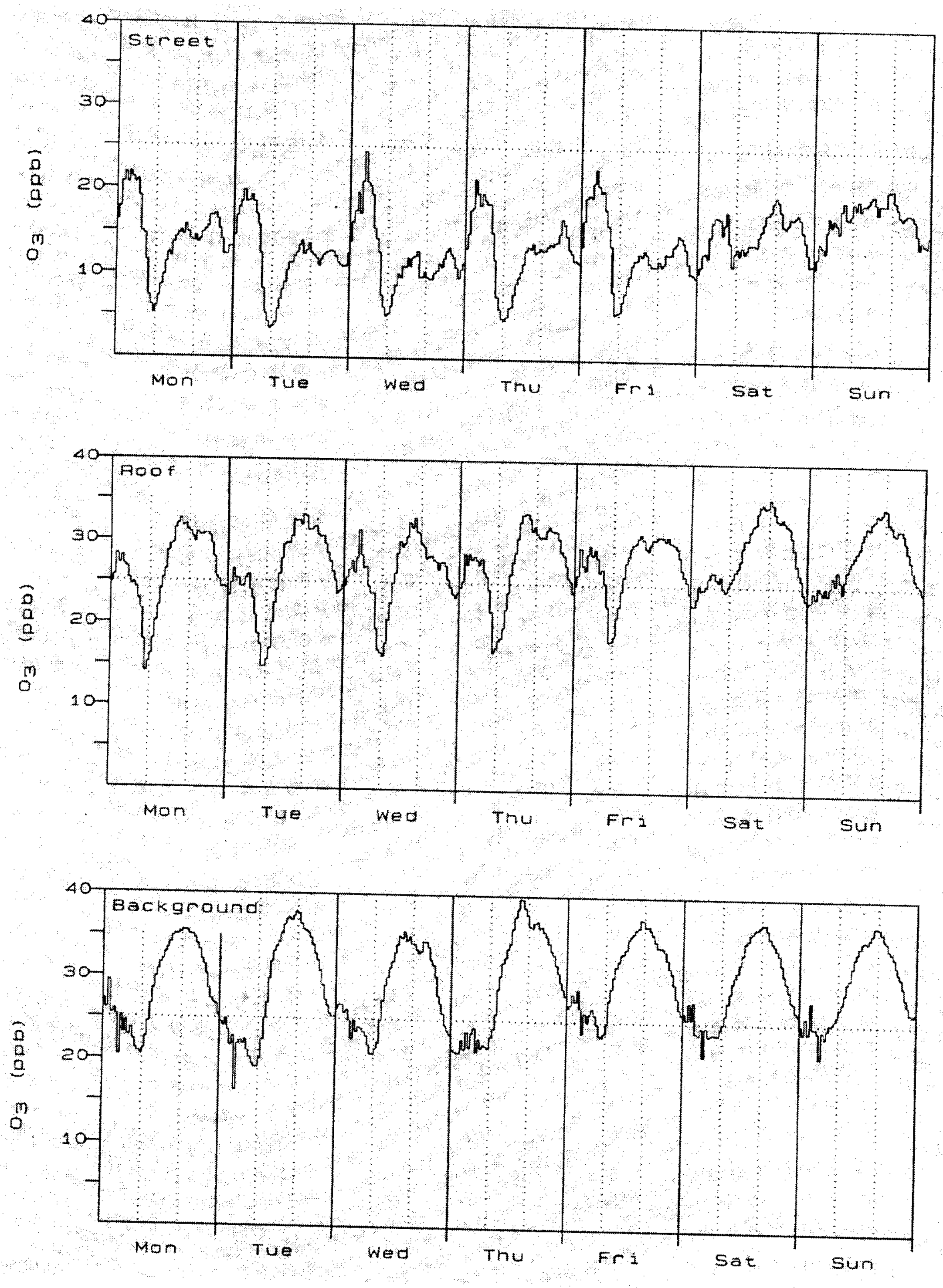


Figure 4.15. Weekly variation of ozone measured at street level in Jagtvej (Copenhagen), at the roof of the H.C. Ørsted Institute (urban background) and at the semirural site Lille Valby, April-December 1994.

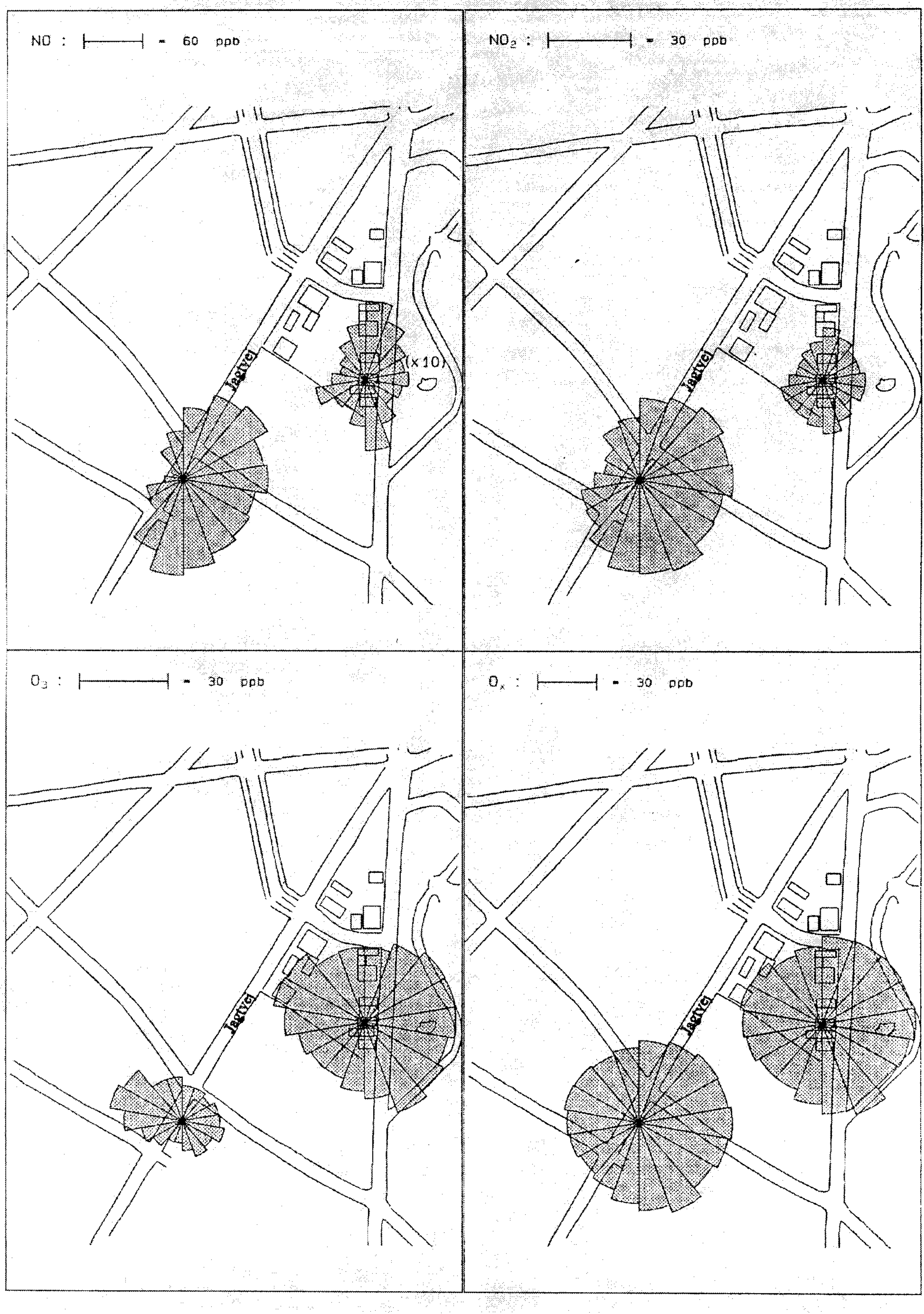


Figure 4.16. NO, NO_2 , O_3 and O_x concentration wind direction distributions at street level in Jagtvej and at the roof of the H.C. Ørsted Institute (urban background) in Copenhagen, averages of hourly means 1994.

OH-radicals

Ozone is the most significant source of tropospheric OH-radicals, which are considered a trigger for the complex reaction chain leading to formation of oxidized species. OH radicals, which are very reactive species, carry a perturbation in the photochemical cycle of NO, NO_2 and O_3. This makes ozone to build up as well as other pollutants including e.g. peroxyacetyl nitrate (PAN) and formaldehyde. NO_2 is removed by photolysis, oxidation by OH-radicals and heterogeneous reactions with water to generate nitrite and nitrates.

$$NO_2 + OH \rightarrow HNO_3$$

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

Such processes are most important in Southern European urban areas, but may also be significant for Denmark on a regional scale and also in urban areas during photochemical high pressure summer episodes with warm weather and low wind speeds.

4.6 Threshold values, episodes

EU-directive

Ozone has potential damaging effects on living organisms including humans and plants (Chapter 6). Based on threshold values recommended by the World Health Organisation (WHO 1987), the EU Commission has adopted a Directive (EEC 1992). The member states shall report all exceedances of the threshold values to the EU Commission and inform the population if the hourly mean concentration exceeds 180 $\mu g/m^3$ or give a warning if the concentration exceeds 360 $\mu g/m^3$ (Table 4.2). The information or warning shall include the following information:

- Date, hour and place of the occurrence of concentrations in excess of the above mentioned threshold values.
- Reference to the type(s) of community values exceeded (information or warning).
- Forecasts of the change of concentrations, geographical area concerned and the duration.
- Population concerned.
- Precautions to be taken by the population concerned.

The EU Directive do not at present impose the member states to comply with the threshold values since the measures to be taken for abatement of ozone in the atmosphere are not very well known and they have to be implemented on a regional scale.

Table 4.2. WHO guideline values and a simplified set of EU threshold values. A warning implies a more detailed information about the possible precautions. Concentrations are in ppb (the threshold values in $\mu g/m^3$ are shown in brackets).

Averaging period	WHO	EU	Inform the population	Warning of population	Protection of
24 hour		32.5 (65)			plants
Moving 8 hour	50-60	55 (110)			health
Hour	76-100	100 (200)	90 (180)	180(360)	health/plants

Danish exceedances

All the EU threshold values, except the alarm value, were regularly exceeded in Denmark. Table 4.3 gives an overview of the number of exceedances at Lille Valby and Ulborg. Similar statistics applied for all the other stations. The exceedances were of course most frequent during the summer. The 24-hour threshold was exceeded at all times of the year and in average every third day. The 8-hour moving average value has only been exceeded from March to September, whereas hourly concentrations higher than 90 ppb were observed only in the summer month from May to August. Concentrations above 90 ppb occurred on average every second year. It can be concluded that the concentrations found in Denmark are harmful for plants and may affect humans with respiratory diseases (WHO 1987).

Table 4.3. Number of days per year the threshold values were exceeded at Ulborg and Lille Valby (Ll.V.).

Period	Threshold ppb ($\mu g/m^3$)	1986 Ulborg	1987 Ulborg	1988 Ulborg	1989 Ulborg	1990 Ulborg	1991 Ulborg	1992 Ulborg/ Ll.V.	1993 Ulborg/ Ll.V.	1994 Ulborg/ Ll.V.
24 h mean	32.5 (65)	101	93	96	98	37	146	142/119	129/96	154/122
8 hour moving	55 (110)	8	9	39	20	6	22	27/29	15/11	23/27
1 hour	100 (200)	0	0	0	0	1	0	2/1	0	0
1 hour	90 (180)	0	1	1	2	1	0	2/4	0	0/1

An ozone episode

The highest ozone concentrations occur in summer, when the temperatures are high. A period at the end of July 1994 has been chosen as illustration of an ozone episode. Figure 4.17 shows simultaneous values for ozone, temperature, atmospheric pressure and global radiation at Lille Valby during the hot period in July-August 1994. It is evident that the high global radiation in the first part of the period, when the pressure was high, was not sufficient to induce extremely high O_3 concentrations. However, when the high pressure moved towards east, hot continental air masses was transported to the measuring site. Ozone was long range transported or partly produced from the precursors in the polluted air mass during the transport.

Critical levels (AOT40)

The term "critical levels" are often used for impact studies on plant growth. Critical levels of O_3 are defined as concentrations above which adverse effects may occur according to the present knowledge (Führer, Achermann 1994). The proposed long term critical level is expressed as cumulative exposure over the threshold concentration of 40 ppb. This exposure index is referred to as AOT40 (Accumulated exposure Over a Threshold of 40 ppb). It is calculated as the sum of the difference between hourly O_3 concentrations in ppb and 40 ppb for each hour, when the O_3 concentration exceeds 40 ppb. Critical levels have been defined for agricultural crops and forest vegetation.

Danish AOT40 values

The AOT40 for crops is calculated only for daylight hours in May, June and July, when daylight hours are defined as hours with global radiation of 50 W/m^2 or more. As a rule of thump it may be assumed that a AOT40 value of 2.6 ppm·h gives a reduction of the relative yield of the crops of around 5%, whereas 10.5 ppm·h gives around 20% reduction (Führer, Achermann 1994). For the protection of forest trees, a provisional AOT40 value of 10 ppm·h is proposed. This cumulative exposure is calculated for 24 hours every day from April to October. Compared to these values the results from Ulborg (Table 4.4) indicate that significant plant damages must have occurred due to the long term exposure to O_3.

AOT40- acute

A short term critical level has tentatively been defined for the development of acute (visible) O_3 injuries on crops as an AOT40 of 700 ppb·h over three consecutive days, during daylight hours. This critical level applies to periods, when the soil moisture does not limit the growth. As seen from Table 4.4 visible injuries can be expected nearly every season. Figure 4.18 shows the variation of the AOT40 acute values during the 1992 season.

The assessment of plant damages due to O_3 in the atmosphere is complex. Numerous factors, which influence the O_3 impact, have to be accounted for (Skärby et al., 1994). However, the above considerations show that the problem is serious. For a more detailed discussion see Chapter 5.

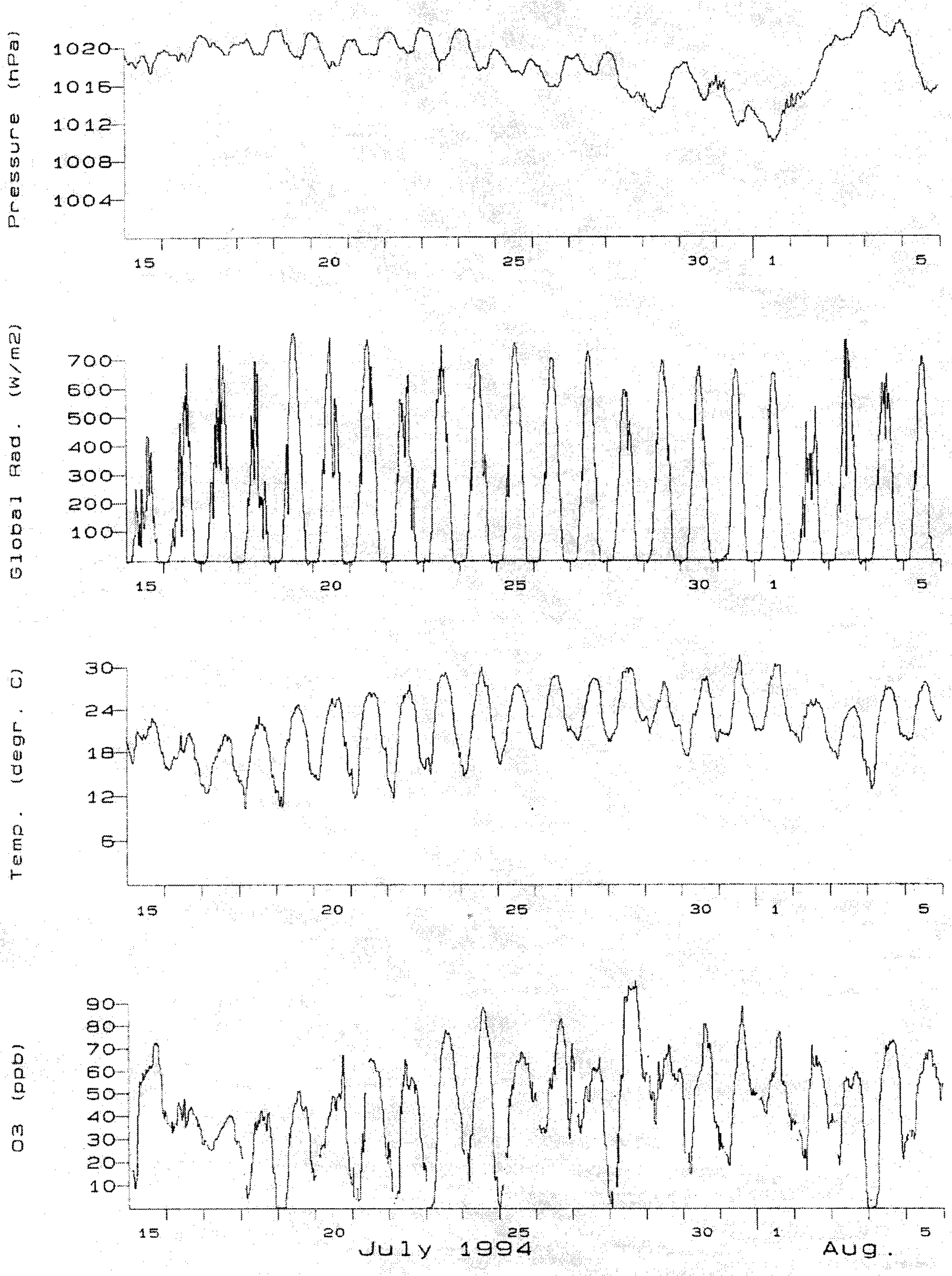


Figure 4.17. ½-hourly O_3 concentrations and different meteorological parameters measured at Lille Valby, during the "ozone episode" in July and August 1994.

Table. 4.4. AOT40 values calculated for measurements at Ulborg. The values are corrected for missing data by multiplying the calculated results with the ratio between possible and valid measurements. Except for the number in () all results are based on more than 70% of the possible measurements. The last column shows the number of days, when the AOT40 acute value was greater than 700 ppb·h from April to August.

Year	AOT40 - trees (all day, May-Jul.) (ppm·hours)	AOT40 - crops (daylight hours, Apr.-Sep.) (ppm·hours)	AOT40 - acute no. of days>700
1986	10.7	5.1	0
1987	8.6	4.5	0
1988	24.1	12.2	21
1989	11.6	8.0	5
1990	5.1	1.9	0
1991	11.7	6.4	4
1992	15.8	12.1	16
1993	10.1	(7.1)	3
1994	12.9	7.8	6

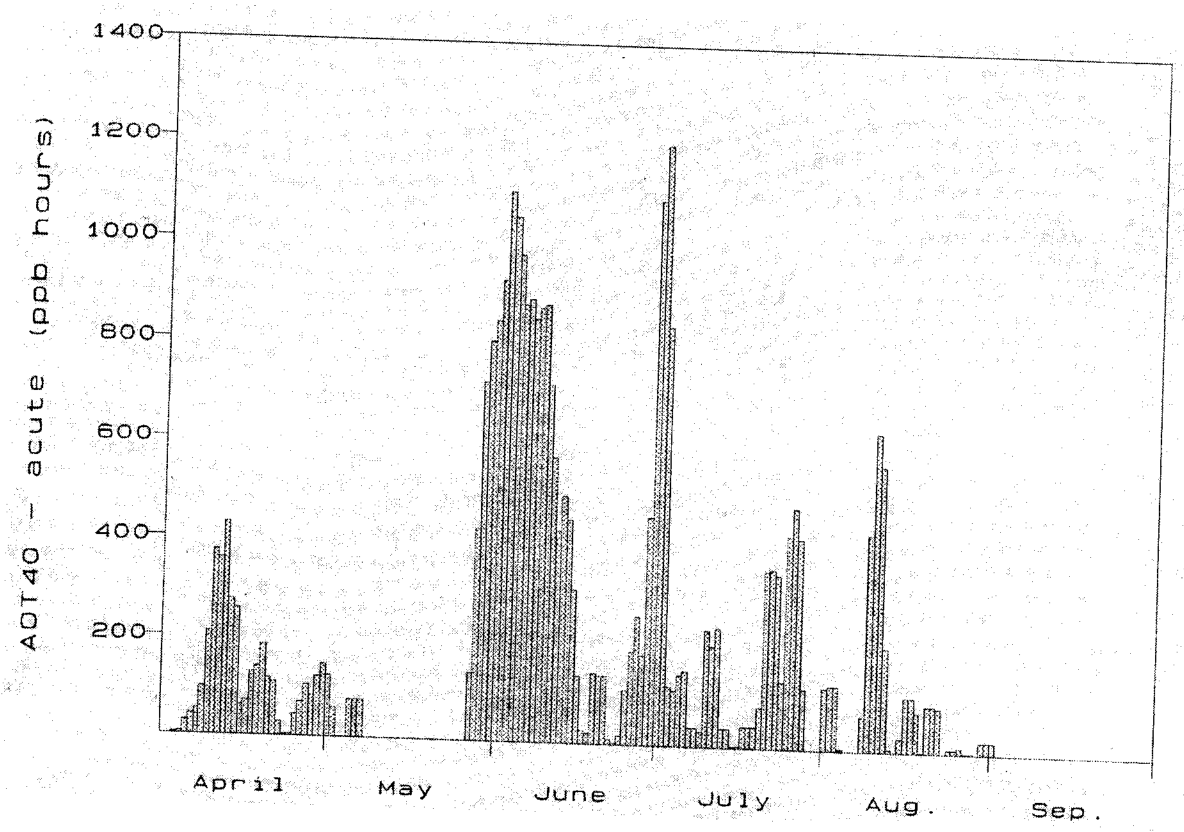


Figure 4.18. The AOT acute values measured at Lille Valby during the summer 1992.

4.7 Deposition of ozone

The aim of monitoring the deposition is to determine the flux of ozone into a forest canopy in order to calculate the chemical and physiological potential per time unit of the ambient ozone. Simultaneously, the activity of the canopy is investigated by measuring different physiological parameters.

Gradient method

The ozone flux has been determined by the so-called gradient method. This method requires measurements of ozone concentrations at different heights over the vegetation cover and simultaneous measurements of micrometeorological parameters. If a flux of ozone from the atmosphere into the forest canopy is to be expected, the ozone concentration close to the canopy is lower compared to the concentrations at higher altitudes. This is a result of the constant depletion of ozone from the air masses in contact with the canopy.

Gradient measurements

Ozone gradient measurements were performed at a 36 m high tower in the Ulborg forest. Results of measurements made in June 1994 are shown in Figure 4.19. For the season, the ozone concentration level was relatively low, probably due to the low temperatures during that period.

Concentration differences

Differences in ozone concentrations at 36 and 18 m's height were determined. The forest canopy had an average height of 12 m during that period. The concentration differences varied between 0 and 5 ppb with an average around 1 ppb. The depletion of ozone from the atmosphere close to the canopy was a result of three mechanisms:

- stomata uptake of ozone
- absorption of ozone to the vegetation surfaces
- chemical reactions with substances emitted from the forest floor

Flux determinations

Estimates for ozone fluxes to the canopy were calculated from the gradient values and from micrometeorological determinations of momentum fluxes of heat and wind. The work was carried out in cooperation between NERI, Risø National Laboratory and the University of Copenhagen (Ro-Poulsen *et al.* 1995).

4.8 Field studies of photochemistry

The troposphere contains a variety of natural and anthropogenic compounds, which are oxidized by ozone or reactive radicals (e.g. $OH\cdot$, $HO_2\cdot$, $NO_3\cdot$) forming photochemical products. A few examples of field studies of photochemical precursors and products will be presented in the following. The photochemical mechanisms are described in chapter 3.

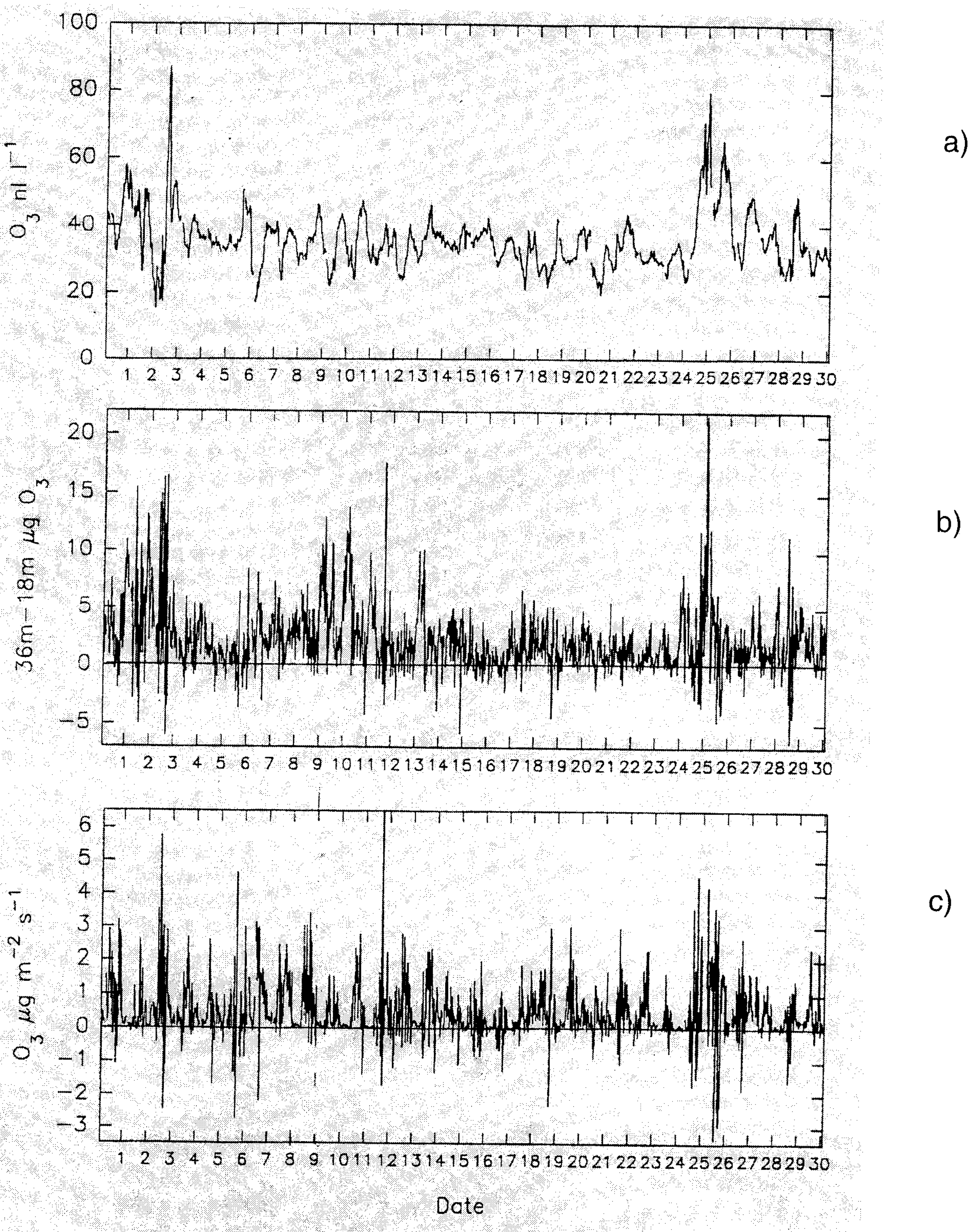


Figure 4.19. Ozone measured over a spruce forest (Ulborg), June 1994.
a) mean ozone concentrations,
b) differences in concentration levels between 36 m and 18 m,
c) ozone flux to the canopy in ug m^{-2} s^{-1} .

Oxygenated hydrocarbons

By the photochemical oxidation processes, reactive hydrocarbons, particularly alkenes, are transformed into oxygenated hydrocarbons i.a. carbonyls and carboxylic acids.

Carbonyls

Carbonyls can be formed by reactions of OH·, O_3, NO_3· or HO_2· with reactive alkenes of biogenic origin (e.g. isoprene) or anthropogenic origin (e.g. ethene, propene, buthene). Radical reactions with alkanes will also produce carbonyls. Furthermore, direct emissions from combustion processes, e.g. automobile exhaust, is an important source of especially formaldehyde. Removal processes may be reaction with OH·, photolysis and dry and wet deposition. Thus carbonyls may be considered as intermediate products in the photooxidation of hydrocarbons.

Semirural observations

Formaldehyde, acetaldehyde and acetone were studied at the semirural site Lille Valby (Christensen 1994; Granby *et al.* 1996). Concentrations of the gas phase carbonyls were determined by collection on 2,4-dinitrophenylhydrazin coated silica tubes and HPLC analyses (Tejada 1986). For the period 7-27 April 1994, the average concentrations were for formaldehyde 0.8 ppb, acetaldehyde 0.5 ppb and acetone 1.0 ppb (Figure 4.20). The concentrations were lowest during the nights. The strong correlations between the carbonyls suggest a common source: formaldehyde/acetaldehyde (r = 0.91, n = 50), formaldehyde/acetone (r = 0.75), acetaldehyde/acetone (r = 0.84). The carbonyls were as well correlated with the carboxylic acids (r = 0.70-0.84), O_3 (r = 0.33-0.47), O_x (r = 0.57-0.66) and NO_y (r = 0.44-0.62).

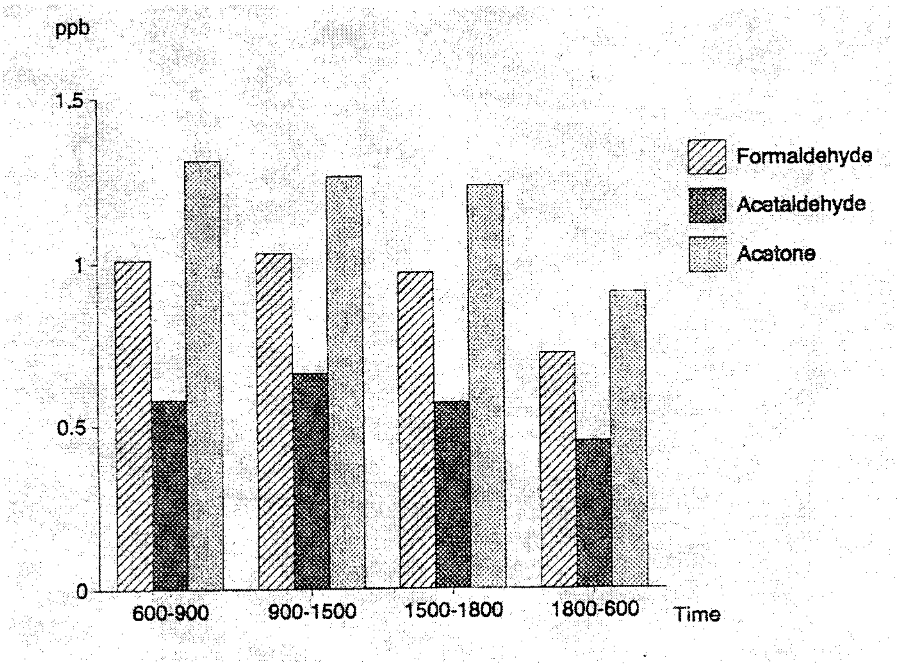


Figure 4.20. Average concentrations of formaldehyde, acetaldehyde and acetone, Lille Valby 7-27 April, 1994 (after Christensen 1994).

Carbonyl sources

The concentrations of the carbonyls and the other photochemical products were highest, when the air mass originated from Central-Eastern Europe. Thus, oxydation of anthropogenic or biogenic hydrocarbons during long range transport of photochemically polluted air is probably the main carbonyl source in the present case study. However a contribution from production of locally emitted biogenic compounds may have occurred.

Carboxylic acid sources

The important sources of the most common carboxylic acids in the atmosphere; formic and acetic acid are suggested to be products of reactions between ozone and biogenic or anthropogenic alkenes (Calvert, Stockwell 1983), reactions between peroxyacetyl radicals and RO_2 radicals (Moortgat *et al.* 1989), oxidation of hydrated aldehydes to aqueous carboxylic acids in the clouds (Chameides, Davis 1983) or direct emissions from natural or anthropogenic sources.

Seasonal variation

The carboxylic acids were measured in 1993-1994 at Lille Valby (Granby *et al.* 1996) by collection on sodium carbonate filters and analyses by ion chromatography. The results show that during the winters (1993,1994) the acetic acid dominated over formic acid (the formic acid/acetic acid ratio was 0.6) but the correlation between the carboxylic acids is fair (r = 0.87) (Figure 4.21). During the summers formic and acetic acid showed equal and highly correlated concentrations up to 3 ppb (r = 0.95).

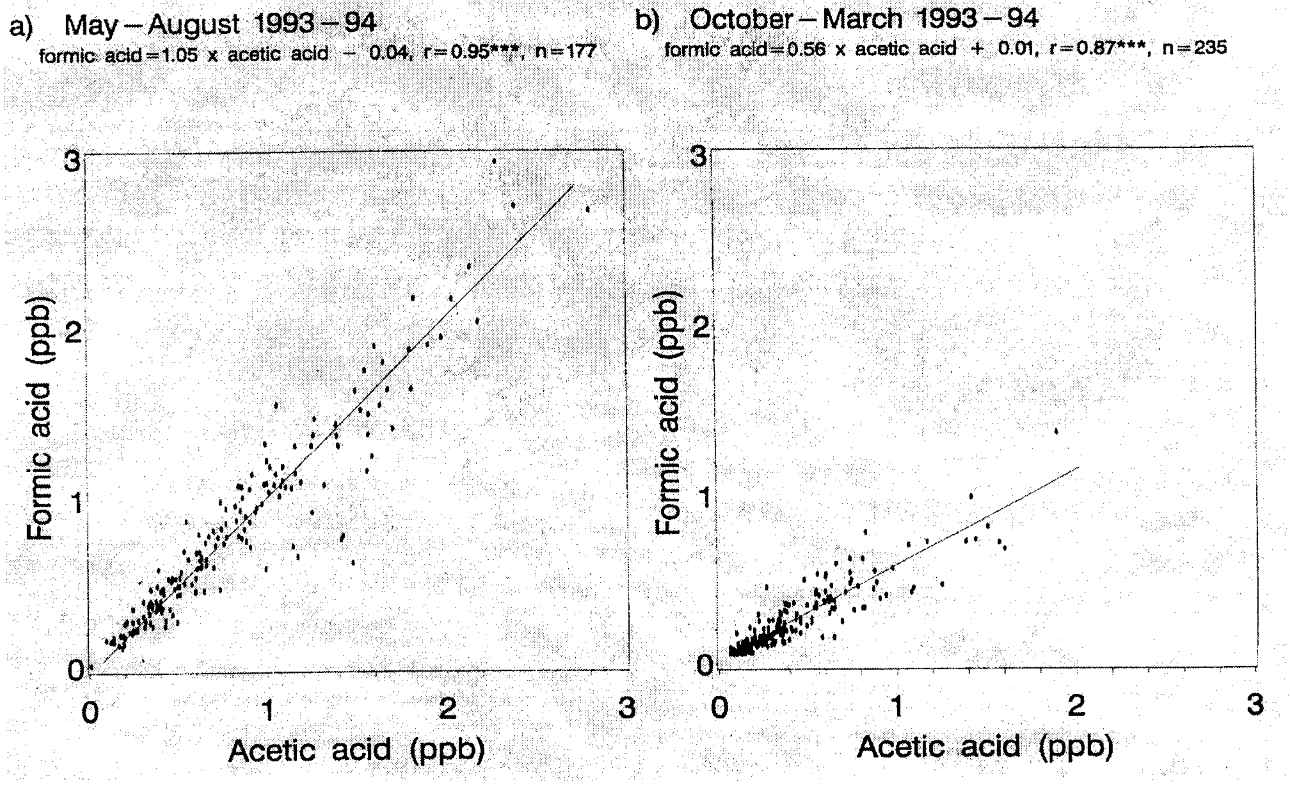


Figure 4.21. Formic acid versus acetic acid concentrations measured at Lille Valby May-Aug. 1993-94 and Oct.-Mar. 1993-94 (from Granby et al. 1996).

Correlation with photochemical products

In April-June 1993 e.g. formic acid correlated with the photochemical products O_3 (r = 0.58), O_x (r = 0.70), HNO_3 (r = 0.71) and PAN (r = 0.62). The highest concentrations were present, when the air arrived from east-south (Figure 4.22), which indicates long transport or production by oxidation of rective hydrocarbons during transport from Eastern or Central Europe. When the air mass arrived from the more rainy and windy westerly directions (marine areas), the concentrations were lower.

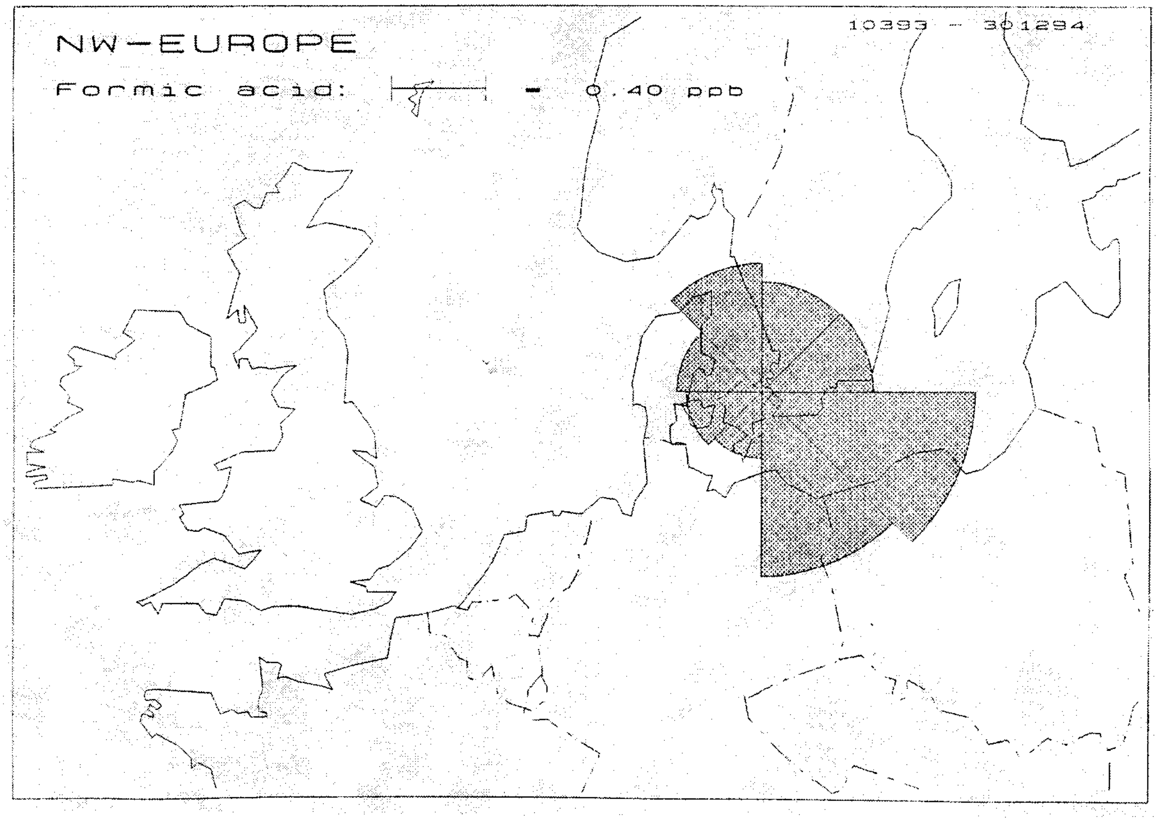


Figure 4.22. Concentration of formic acid (averages of daily means in ppb) at Lille Valby as a function of wind direction.

Nitrogen compounds

NO_x as catalyst for O_3 formation

The potential for ozone formation in the troposphere is limited by the availability of NO_x as catalyst. The atmospheric lifetime of NO_x in the planetary boundary layer depend on the temperature, but is mostly less than a day because of conversion to e.g. less active photochemical products as nitric acid or nitrate. However, the product PAN may be transported over long distances before it decomposes thermally into peroxyacyl radicals and NO_2, which then can act as an ozone catalyst in remote areas (Crutzen 1979).

$NO_z = NO_y - NO_x$

During a measuring campaign at Lille Valby, 25 May- 30 June 1993, NO_x, NO_y, and the oxidation products nitric acid, nitrate, PAN, and PPN (peroxypropionyl nitrate) were determined in addition to ozone. NO_y is the sum of all odd-nitrogen species. The difference between the NO_y and NO_x is defined as NO_z. NO_z is a measure of the NO_x proportion that was originally emitted into the troposphere, but no longer is in the active form to produce ozone, i.e. the photochemical nitrogen products (HNO_3, NO_3^-, PAN, PPN, organic nitrates etc.). The NO_x cycle and the coupling with oxydized nitrogen compounds, hydrocarbons and ozone formation is shown in Figure 4.23.

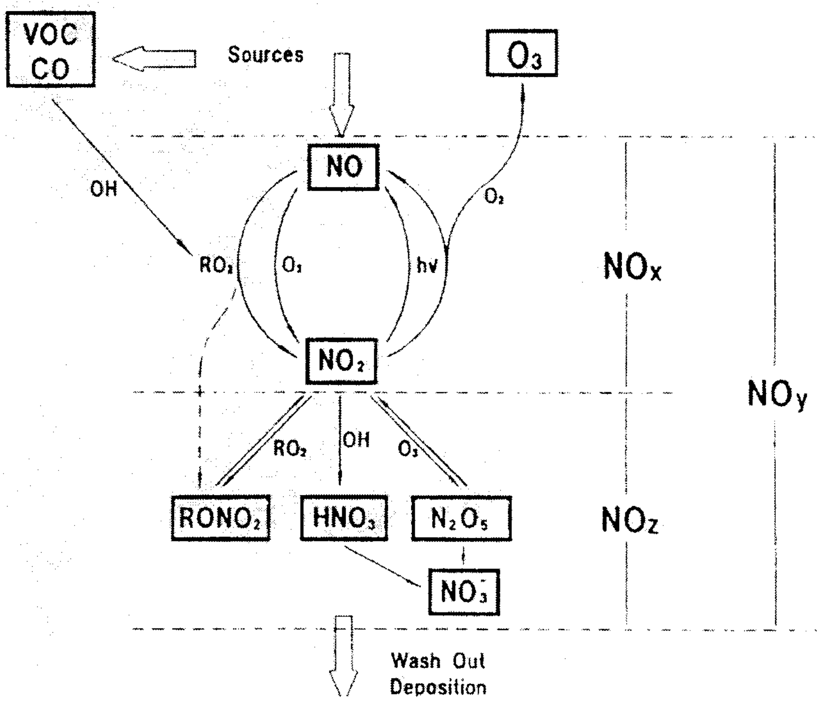


Figure 4.23. Major pathways in the NO_x cycle and the couplings with CO and hydrocarbons and ozone (from Volz-Thomas et al, 1992).

Composition of NO_y

Figure 4.24 shows the NO_y composition at different levels of ozone. The mean NO_y concentration was almost similar for the four levels being 5.0, 4.2, 4.2 and 5.3 μgN m^{-3} at 20-30, 30-40, 40-50 and 50-60 ppb ozone, respectively. The residual gas NO_y consisted of various NO_z compounds, which were not speciated in the investigation (e.g. organic nitrates). The Figure shows that the proportion of NO_z increased from 21 % at 20-30 ppb ozone to 67 % at 50-60 ppb ozone. The amounts of NO_z compounds, which cannot be accounted for (residual gas NO_y), also increased with increasing ozone concentrations (Nielsen *et al.* 1996).

O_3 generating potential of NO_x

The correlation between gaseous NO_z and O_x appears from Figure 4.25. Measurements for June 1993, afternoons (12-17 p.m.), at temperatures above 20°C and wind speeds above 5 m/s are selected. The relationship between O_x and gaseous NO_z is: $O_x = (3.0\pm0.5)$ ppb gas $NO_z + (55\pm1)$, $r = 0.76$, $P = 0.0001$. The figure shows that at temperatures above 20°C, the NO_x emissions led to an increase in O_x. 3 ppb O_x was produced per ppb gaseous NO_z formed (NO_x destroyed) or about 2 ppb O_x per ppb 'gas + particle' NO_z (as gaseous NO_z ~0.7 "gas + particle" NO_z). At conditions with temperatures below 20°C no correlation between O_x and NO_z was found.

An investigation in the summers 1989-1991 in Schauinsland, Germany showed that the net ozone generation potential of NO_x was 4-5, but it could be up to 10. In winter, on average NO_x emissions did not result in net ozone formation (Volz-Thomas *et. al* 1992).

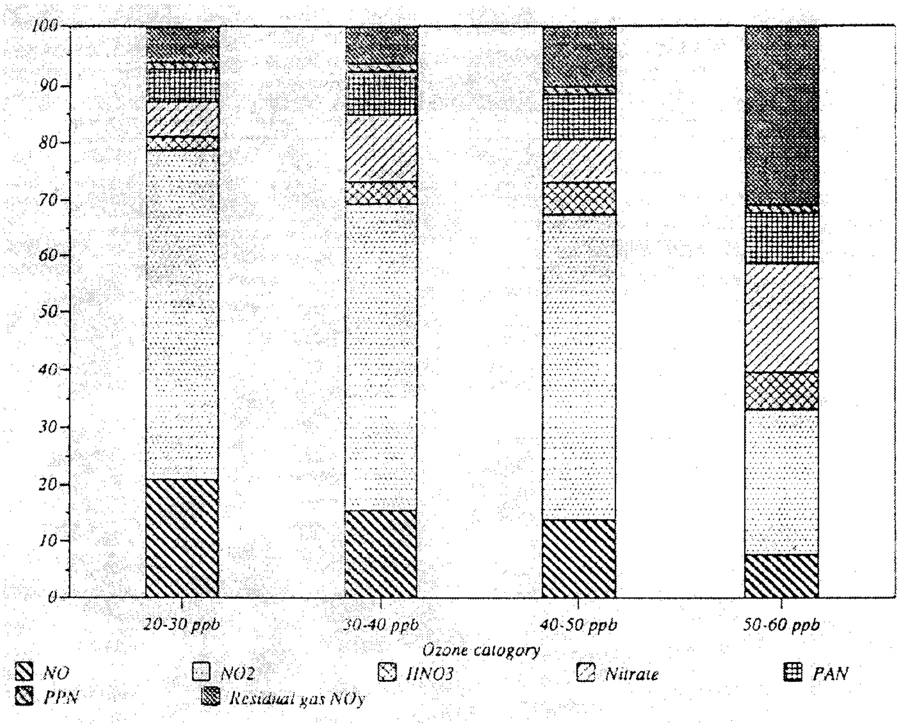


Figure 4.24. Composition of total NOy at different Ox levels at Lille Valby May-June 1993 (from Nielsen et al. 1996).

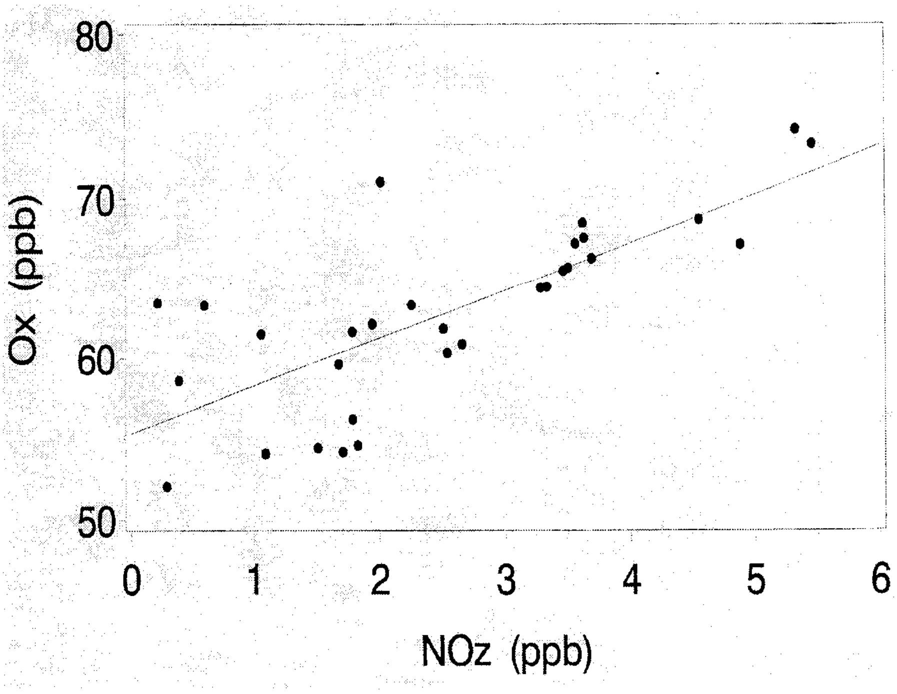


Figure 4.25. Correlation between concentrations of gaseous NO_z and O_x (ppb) at temperatures above 20°C and wind speeds above 5 m s^{-1}. O_x=(3.0±0.5)*gas NO_z+(55±1), r=0.76, p=0.0001.

Hydrogen peroxide

Hydrogen peroxide is primarily formed as a product of radical photochemistry through recombination of HO_2 radicals. Thus, it terminates photochemical radical reactions. Another important role of the hydrogen peroxide is as the dominant oxidant of sulphur dioxide in the atmosphere forming sulphuric acid. The hydrogen peroxide was measured by a diffusion scrubber technique (Dasgupta *et al.* 1988).

H_2O_2, measured

Hydrogen peroxide and ozone measured during a high pressure period from 30 June-8 July 1992 are shown as a case study in Figure 4.26 (Granby *et al.* 1994). The temperature was high the first two days 28-29°C and 19-23°C the rest of the period. Both ozone and hydrogen peroxide showed a diurnal pattern typical for photochemical products during high pressure periods. The highest concentrations occurred in the afternoons with generally highest photochemical production and highest mixing heights, whereas in the nocturnal boundary layer the deposition of the products and depletion of ozone and HO_2 radicals by NO caused a reduction of H_2O_2 and O_3. Thus the night-time concentrations were relatively low. The hydrogen peroxide concentrations reached 2 ppb during the first 3 days of the measuring period and 1.0-1.3 ppb the rest of the period. The ozone concentrations were 100-110 ppb the first 2 days and then they dropped to maximum values of 40-60 ppb.

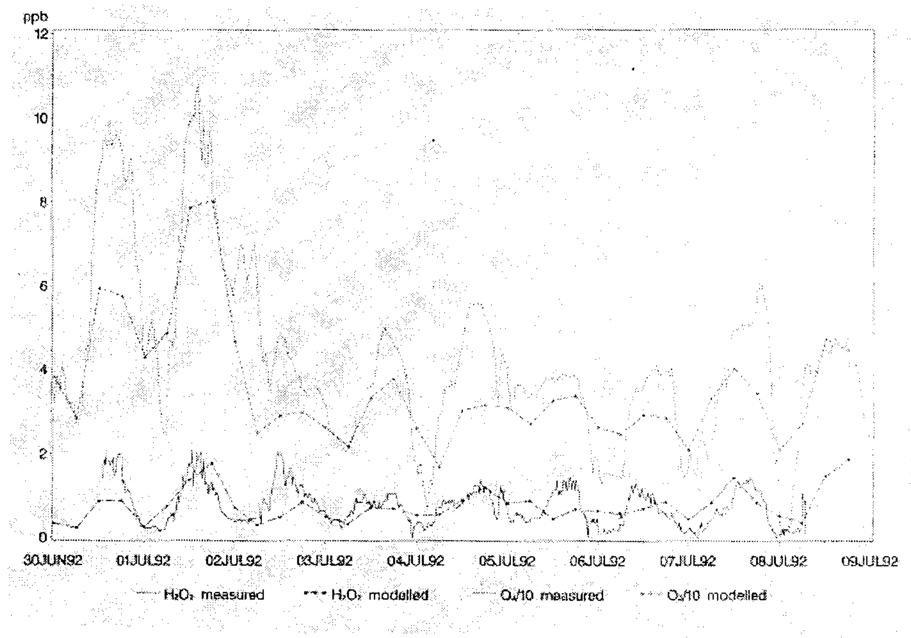


Figure 4.26. Comparison between results of a trajectory model and measurements of ozone and hydrogen peroxyde (ppb) at Lille Valby 30 June-8 July 1992 (Granby et al. 1994).

Long range transport

The relatively high photooxidant concentrations the first two days may partly be due to long range transport of photochemical pollution from southerly directions, which was reflected in the increased sulphur dioxide concentrations. On 2 July the hydrogen peroxide concentrations were still high in spite of a decrease in ozone concentrations, probably because the hydrogen peroxide formation depends strongly on the relative humidity, which was the double at 2 July (55%) compared to the following days (25-30%).

Modelled and measured concentrations H_2O_2

The measurements of hydrogen peroxide and ozone were compared with results from a one dimensional trajectory model (Atmospheric Chemistry and Deposition (ACDEP) model), which includes chemical reactions, dry and wet deposition and vertical transport described by eddy diffusion (Hertel *et al.* 1995). The model calculates along trajectories 96 hour backwards and shows point results every 6 hours. The measurements and model results are about the same level, but the model shows smaller fluctuations. This may be explained by fewer data points for the model, locally increased NO emissions at the measuring site (the model estimate emissions from 15x15 km^2 grids) or locally more stable boundary layer, causing higher nighttime depletion, than predicted by the model.

4.9 Conclusion

Ozone is transported over long distances and the levels found in Denmark reflect the pollution and/or weather situation over a larger geographical scale.

The European levels of O_3 have more than doubled within the last century, especially within the latest 3 decades. However, recently the situation has changed so the increase now is less than previously. An ongoing monitoring of O_3 is important to follow the trend in the future.

The EU threshold values for human exposure are regularly exceeded in Denmark. Also the critical levels for development of plant injuries are exceeded. The episodes with high O_3 concentrations mostly occur when the air mass arrives from Central-Eastern Europe, that is at east-southerly winds. In contrast when the air is blowing from westerly winds the level is closer to the European background concentration of about 34 ppb.

Field studies have revealed that in addition to O_3 the Danish ambient air contains many different photochemical products (HNO_3, H_2O_2 , PAN, carbonyls, carboxylic acids, unidentified NO_z components etc.).

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5 Effects of ozone on vegetation

Annemarie Bastrup-Birk, Lisbeth Mortensen

5.1 Introduction

Ozone (O_3) is quantitatively the dominating oxidant in photochemical air pollution. Other compounds like hydrogen peroxide, aldehydes, formate, peroxyacetyl nitrate (PAN) and nitrogen dioxide are present too, and several of these are known to be phytotoxic, but under Danish conditions the concentration of these gasses are without significance for direct effects on vegetation. Therefore, only the effects of O_3 will be described.

First recognition of O_3 leaf injury

Oxidant damage on plants was first recognised in the late 1940's in California. O_3 was found to cause leaf injury on grape in California and tobacco in Eastern USA. Also O_3 was found to inhibit photosynthesis, and thus growth, without the presence of visible leaf injury.

The toxicity of O_3 is related to its oxidizing power, but although the effects of O_3 have been extensively studied during the last 30-40 years, the mechanisms behind O_3 toxicity are still not well understood.

Economic losses due to O_3

O_3 is believed to be one of the main responsible air pollutant causing reductions in yield in agriculture and silviculture. In the USA O_3 alone or in combination with SO_2 and NO_2 is estimated to cause more than 90% of the reductions in yield due to air pollutants (Heck et al. 1982). In the Netherlands, it was estimated that for 1983 air pollution reduced crop production with 5% of which 70% is caused by O_3 (Tonneijck 1989). A Swedish survey based on O_3 concentrations between 1986-88 concluded that the economic value of the reductions in crop yield for the whole country was between 0.97 and 3.3 billion SKR in 1988 prices (Hasund et al. 1990).

Start of European studies

In Europe O_3 effect studies commenced in Germany in the late 1960's with the use of tobacco as indicator plant. This technique was soon used all over Europe including Denmark (Ro-Poulsen et al. 1982). O_3 concentrations in Europe were high enough to injure sensitive indicator plants. As a consequence continuous measurements of O_3 and effect studies were initiated in many countries.

OTC-networks

Effects of O_3 on vegetation can be investigated as dose-response experiments where vegetation is fumigated by known concentrations of O_3. These experiments can be performed in the laboratory, in climate regulated chambers, in greenhouses, or under semi-controlled conditions in Open Top Chambers (OTC's). Most effects studies on vegetation have been performed in OTC's (Figure 5.1). A range of important crop species has been investigated in the National Crop Loss Assessment Network (NCLAN) in the USA and in the CEC OTC network in Europe.

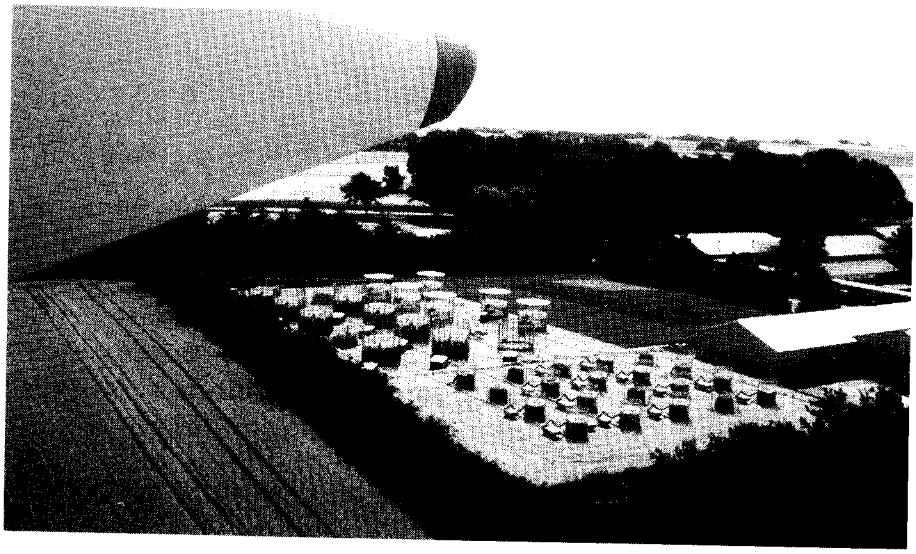

Figure 5.1. An overview of the Danish OTC facility at the National Environmental Research Institute, Risø.

5.2 O_3 uptake

O_3 must be taken up by the plants in order to affect them, and the uptake takes place through small apertures on the leaves, the stomata (Figure 5.2). From the free troposphere O_3 is transported to vegetation cover by turbulent diffusion. The surface of the leaves is surrounded by a thin layer of laminar air where O_3 is transported by molecular diffusion. The degree of stomata opening is dependent on external as well as internal mechanisms linked to the water and nutrient status of the plant, and is very sensitive to changes in the environment (Figure 5.3). The opening of stomata determines the O_3 flux into the leaf.

O_3 flux

The total flux of O_3 onto and into the leaf has traditionally been treated as a result of the concentration difference between the surrounding air (C_a) and the sink site in the leaf (C_i) plus the overall resistance to gas movement, as a resistance analogue model, see also Chapter 2. Usually C_i is assumed to be negligible, and this has been confirmed for leaves of sunflower which were exposed for short periods with O_3 concentrations up to 1500 ppb (Laisk et al. 1989). The total flux of ozone can thus be expressed as,

$$F_{total} = (C_a - C_i) / r_{total}$$

where $r_{total} = r_b + ((r_s + r_i)^{-1} + r_p^{-1}))^{-1}$ is the total resistance which comprises of resistances in series and parallel. Each leaf is surrounded by the boundary layer, a layer of laminar air in which gas transport is by gaseous diffusion; the resistance to this transport is r_b. The other resistances relate to diffusion through stomata (r_s) and to sorption and reaction on the leaf surface (r_p). The resistance analogue model is appropriate for gas-phase processes only; the resistances of the part of the pathway that involve internal gas-phase diffusion, partition in the liquid phase, diffusion in the liquid phase, and quasi resistance of any chemical reaction that a pollutant enters into, are combined into residual or internal resistances in the mesophyll (r_i) (Runeckles 1992).

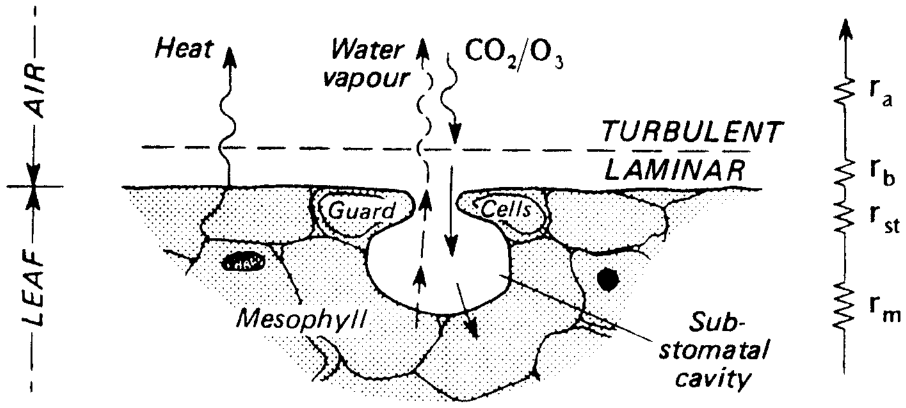

Figure 5.2. Schematic presentation of a leaf stomata.

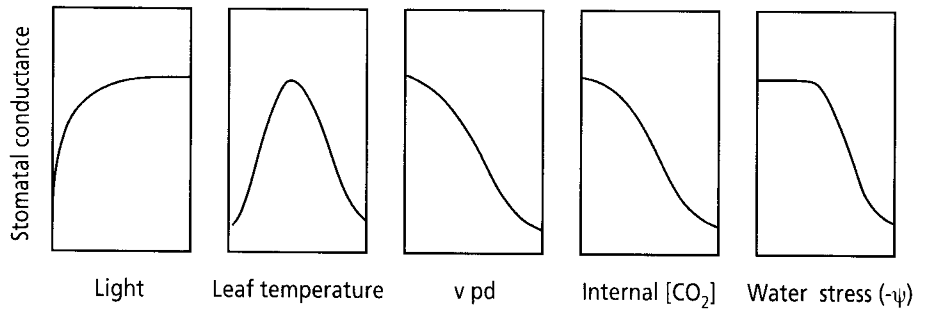

Figure 5.3. The response of stomata opening to different environmental factors.

Boundary layer resistance

The size of r_b is inversely related to wind speed and characteristics of the leaf surface, such as dimensions and roughness. In the field r_b is often regarded as negligible in relation to r_s. However, under many experimental conditions, r_b can be high because of low wind speed and thus may lead to conclusions of too high threshold concentrations for effects. The opposite can also be the case in OTC's where the turbulence is high.

Stomatal resistance

The size of r_s changes during the day and during the growth season and is dependent on radiation, temperature, relative humidity, the water and nutient status of the soil, and the age and physiological status of the plant (Figure 5.3) Further O_3 can influence the size of r_s. At concentrations below 200 ppb (a concentration very high in Denmark) the response is variable, but the stomata close at higher concentrations (Darrell 1989) and thus increase r_s and decrease the flux of O_3 into the leaves.

Of the total O_3 flux reaching a plant canopy, some O_3 may react with chemical constituents in the canopy air or be destroyed on surfaces e.g. soil, stems and leaves. Leuning et al. (1979) estimated that 50 to 60% of the O_3 reached the soil in a tobacco field. The uptake into the leaves is regulated by the stomata and no uptake through cuticle takes place (Kerstiens, Lendzian 1989).

Reactions between O_3 and organic compounds?

Plants emit different volatile organic compounds e.g. ethylene and terpenes which easily react with O_3. Such reactions may take place in the air around the leaf and in the air spaces within the leaf. Based on chemical reaction kinetics, half-lives for O_3 in such reactions have been calculated to range from more than 1 hour to around 0.01 minutes, which is a long time in comparison with calculated turn-over rates of 0.1 - 0.4 seconds for O_3 within the leaves. It is thus assumed that this reaction is not of high importance for changes in O_3-flux into the leaves.

Is it O_3 or its reaction products that are toxic?

Inside the leaves, O_3 or its reaction products must dissolve in the apoplast and diffuse through the cell wall to reach plasmalemma. It is not known whether it is O_3 itself, or its reaction products from reactions within the air spaces in the leaves or between the cell wall constituents and the cell membrane, that are directly responsible for many of the various phytotoxic effects attributed to O_3. Some effects may be caused directly by O_3, while others may be caused by its reaction or decomposition products.

5.3 Sensitivity to O_3

Species sensitivity

Plant sensitivity to O_3 differs not only between species, but also within cultivars. In screening tests, where several plant species were exposed to O_3 and evaluated for visible injury, it was found that some plant families (e.g. *Papilionacea*) have a higher proportion of sensitive species than others (e.g. *Compositae*) (Ashmore 1984). Further, species characteristics of calcareous habitats and cultivated land tend to be more sensitive than those of acid, nutrient-poor habitats.

Cultivar sensitivity

Different sensitivity among cultivars is e.g. found in spring wheat, beans, tomatoes, tall fesque, and in populations of *Plantago major* L. in Britain. A study comparing 10 cultivars of wheat, *Triticum aestivum* L. and *Triticum durum* L. introduced in Greece between 1932 and 1980, showed an inverse relationship between the year of introduction and O_3 sensitivity, indicating that breeding for high yield produces O_3 sensitive plants (Velissariou et al. 1992).

Differences in sensitivity

The reason for the differences in sensitivity to O_3 is not fully understood. Some plants close the stomata during fumigation, thus preventing an O_3 uptake. In other plants, the difference between sensitivity and resistance can be traced to levels of, or ability to generate, antioxidants (e.g. ascorbate and gluthatione).

Life cycle

Biotic and abiotic factors can modify the sensitivity to O_3. Among the biotic factors, the plant genetic make-up is the most important (see above). It gives plants the possibility of tolerating or avoiding the pollutant. The sensitivity to O_3 changes during the life-cycle of the plant and the organs. Periods of fast growing and high metabolic activity seem to correspond with periods where the plants are most sensitive. A range of agricultural species is highly sensitive during early growth stages and again during flowering and grain filling. Fully expanded leaves are more susceptible to leaf injury than young growing leaves.

Pathogens

Certain pathogens may lessen the sensitivity of the plant to O_3, but this is often restricted to the infected part of the plant. On the other hand some aphids prefer O_3 exposed plants (Kristiansen 1992). This may be due to an increase in, or a changed composition of, amino acids in the leaves.

Abiotic factors

Dose, climate and edaphic factors are all abiotic factors which modify the sensitivity to a given dose. These factors have an effect on the uptake of O_3 (see Section 5.2) and on the physiological stage of the plants and thus on their sensitivity.

Pollution climate

The pollution climate of a plant is charaterized by: the composition of the dose, the frequency of exposures, the duration of each exposure, the time span between the episodes of the diurnal fluctuations and chronology of concentrations during the day and growth season. It varies from one region to another. Therefore extrapolation or generalization from single biological experiments may be hazardous.

The disagreement between authors in rating plant sensitivity might be due to the fact that the absorbed doses differ among the experiments and are very difficult to quantify. Because of these difficulties the dose is mostly described as the external dose - as an hourly mean or a sum accumulated during the exposure period.

5.4 Damage pattern following O_3 exposures

Visible injury

At episodic high O_3 concentrations, plants may respond with visible leaf injury caused by cell death. Such injury is white to tan flecks on tobacco (Figure 5.4) and clover, or dark small spots seen on bean and potatoes. In conifers, this kind of damages is seen as apical needle necrosis. This acute injury does not necessary lead to reductions in yield, but is important for crops as letture and spinach where the economic value lies in their leaf appearance. At lower levels of O_3 over longer periods, accelerated leaf senescence and premature leaf drop are seen, by which leaf area duration decreases and thus shortens the growth season. Inhibition of net photosynthetic rate (Saxe 1991) and growth are found in many plants without visible injury. It is believed that different mechanisms are responsible for the different damage symptoms.

Figure 5.4. Damaged tobacco leaf exposed to ambient conditions at a rural site in Denmark.

Growth reductions

Growth reductions following O_3 exposures are often followed by changed assimilate partitioning. In plants that have not flowered or set fruit, and at low O_3 levels, the remaining available assimilate is generally diverted to leaves and stems at the expense of roots and crown. When plants mature, flower and develop seeds, these sinks receive a relatively high proportion of the available assimilate. Therefore reductions in harvest index or biomass are for most plant species only seen at high O_3 concentrations. The altered assimilate partitioning in spring wheat is not due to a change in translocation velocity, and it is concluded to be due to less amount translocated assimilates (Mortensen, Engvild 1995).

5.5 Effects of O_3 on agricultural crops

Crop loss assessment studies

In 1984, the Commission of European Communities (CEC) initiated an experimental programme to evaluate crop loss due to air pollution in Europe. As in the corresponding NCLAN in the USA initiated in 1980, open-top chambers (OTC´s) were used, and various crops were exposed to different levels of O_3. In the European OTC network, mostly leguminous and cereal species were exposed.

Danish land use

The Danish agricultural area is about 2.8 mill. ha. Cereals are grown on more than half of the area (around 1.5 mill. ha). Clover and grass mixtures cover about 17%, oil seed rape 7%, root crops 6%, and leguminous 4%. Barley and wheat are the most important Danish crops covering about 49% of the cultivated land.

Cereals

Barley

Both spring and winter wheat have been extensively studied for O_3 effects and have proven to be sensitive. Barley seems more resistant than wheat to moderate O_3 concentrations. Temple et al. (1985) found that two barley cultivars were resistant to O_3 below 60 ppb. A Swedish study with one cultivar showed that yield reductions were not likely to occur at 45 ppb (Pleijel et al. 1992).

Wheat

For many years, the response of wheat to O_3 has been studied in 7 European countries. Both field-grown and potted plants were exposed in OTC´s. Based on Danish results it was found that both potted and field-grown plants were negatively affected by O_3 (Mortensen et al. 1991). However, the field grown plants reacted with higher yield reductions to comparable concentrations than the potted plants (Skärby et al. 1992).

Injured leaves on wheat cultivars

During exposure to O_3 wheat leaves get visibly injured with chlorotic and necrotic areas. These symptoms start on older leaves at the leaf tip and progress to the base. Accelerated senescence caused by O_3 is found in many studies using different cultivars of wheat. The ultrastructural changes in the flag leaf during accelerated senescence were studied in the cultivar Drabant. Chloroplasts became smaller and contained more plasto-globuli. Vesicles were formed between the grana thylacoids, the plasmalemma separated from the cell wall and convoluted (Ojanperä et al. 1992).

Photosynthesis in wheat cultivars

Flag leaf photosynthetic rate (P_n) is inhibited by O_3, (Table 5.1.) In the cultivar Ralle, this reduction is related to the senescence of the flag leaf. Grandjean, Fuhrer (1992) measured P_n of the flag leaf of spring wheat (cv. Albis) from full expansion to complete senescence, and found a reduction with increasing O_3 levels. In young leaves, O_3 affected stomata directly and thus reductions in P_n were due to decreased diffusion. In older leaves the effects of O_3 were mainly on carboxylation. In the same cultivar ^{14}C was used to demonstrate effects of O_3 on photosynthesis of flag leaves (Lehnherr et al. 1988). O_3 seemed to affect photosynthesis mostly during anthesis. The decrease was not due to limitations in diffusion, but rather in the pentose-phosphate reductive cycle.

Table 5.1. Effects of O_3 on flag leaf net assimilation rate (μmol m^{-2} s^{-1}) before and after anthesis in the cultivar Ralle exposed to charcoal-filtered air (CF, 16 ppb O_3), non-filtered ambient air (NF, 28 ppb O_3), or NF with addition of O_3 8 hour day^{-1} (NFO 61 ppb O_3) (Mortensen, Engvild 1994).

	CF	NF	NFO
Before anthesis	17.3	16.6	17.4
After anthesis	13.6	11.7	2.4

Yield in wheat cultivars

The effects of O_3 on wheat yield in the European OTC-network are summarised by Skärby et al. (1992). Wheat grain yield in OTC´s is reduced between 5 and 15% at current O_3 levels in Europe. This reduced grain yield is primarily caused by smaller grains and to a lesser extent to fewer grains.

At the higher O_3 levels straw yield is less reduced than grain yield resulting in reduced harvest indeks (Table 5.2).

Table 5.2. The relative biomass and seed dry weight in relation to charcoal filtered air, and harvest index of spring wheat (*Triticum aestivum* L. cv. Ralle) exposed to different levels of O_3 in OTC's. CF = charcoal filtered air, NF = non filtered air, NFO = non filtered air added O_3 8 hour day^{-1} during day light.

	Biomass % of CF			Yield % of CF			Harvest index		
Year	CF	NF	NFO	CF	NF	NFO	CF	NF	NFO
1989	100	112	73	100	93	67	45	38	42
1991	100	93	80	100	89	73	44	42	40

Oat

Oat showed no effect on grain yield after exposure in OTC's to filtered and unfiltered air from anthesis to maturity (Pleijel et al. 1994).

Pasture and forage crops

Yield quality

Managed and unmanaged pasture cover large areas in many European countries, and occupy about 17% of the Danish arable land. The plant mixtures of grass and clover are common species. The share of clover species in relation to grasses is important for the quality of the harvested or eaten biomass. Further, clover species are part of many natural ecosystems. Many clover species have proved to be very sensitive to O_3 and exhibit visible leaf injury (Pihl Karlson et al. 1995) as well as decreases in biomass after exposures to O_3 (Mortensen, Bastrup-Birk 1996a). The sensitivity of clover species is used in the ICP-Crops (International Co-operative Project on crops).

Clover species

A Danish study in OTC's showed that the shoot dry weight of white clover decreased with increasing O_3 concentration after 8 weeks of exposure, the stolons being mostly affected (Mortensen, Bastrup-Birk 1996a), (Figure 5.5.) Exposure of the cultivar Grassland Huia for 15 weeks to 40 ppb O_3 with two 1-hour peaks of 80 ppb twice a week and one 1-hour peak of 110 ppb once a week resulted in a 44% reduction of total biomass dry weight, roots being the most affected with 57% and shoots with 39% (Ashenden et al. 1995). After 16 days of exposure in OTC's to filtered, non-filtered or non-filtered added episodic O_3 concentrations (200 ppb for 6 hours on four sunny days), the. shoot dry weight of red clover was reduced compared to plants from filtered air. Nitrogen fixation was reduced during fumigation, but recovered after the end of the treatment (Ensing, Hofstra 1982).

Differences in sensitivity among white clover cultivars were studied in relation to visible injury following O_3 exposure in OTC's or in controlled environments. The sensitivity was related to stomatal density, but not to activity of the enzymes superoxide dismutase and peroxidase (Becker et al. 1989). Agricultural crops are relative homogeneous and thus adaptation to O_3 is not very likely. In white clover - tall fescue mixtures exposed for two years in OTC's, surviving clover plants from the high O_3 treatments (2 times ambient) contained a higher amount of plants resistant to acute O_3 levels than in the filtered treatment (Heagle et al. 1991).

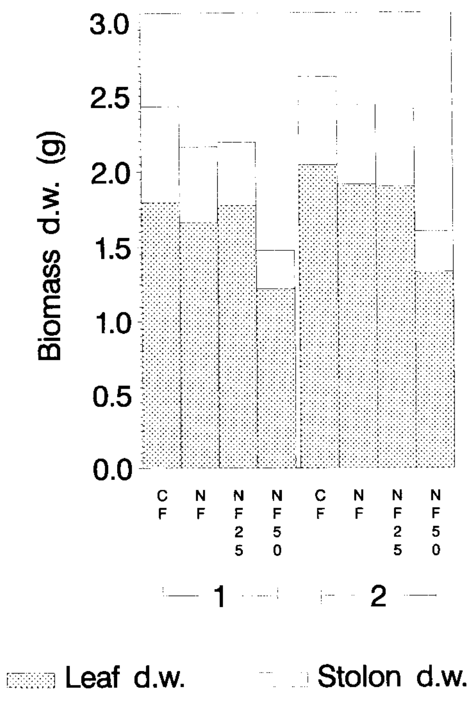

Figure 5.5. The biomass of white clover after 8 weeks of exposure in OTC's (relative to control) for experiment 1 and experiment 2 (Mortensen, Bastrup-Birk 1996a).

Grass-clover mixtures

The sensitivity of clover species to O_3 may contribute to the observed decline of clover species in pastures, as well as management practise, fertilizer application and cutting regime.

Swiss mixture

A Swiss pasture mixture containing mainly white and red clover and different grasses (orchard grass, perennial ryegrass, and meadow fescue) was exposed for two seasons in OTC's to four levels of O_3 and harvested several times each year. After two growth seasons, the yield of clover decreased and that of grasses increased with increasing O_3 concentrations. During the second year, no O_3 was added to half of the chambers that have received additional O_3 the previous year. Some of the clover population did recover (Fuhrer et al. 1994).

White clover - perennial ryegrass

A perennial ryegrass white clover mixture in the field was fumigated with O_3 (50 to 70 ppb above ambient) in August and September. Plants were harvested more or less frequently, simulating grassing or silage production. O_3 reduced the production, but the cutting frequency had no effects and there was no interaction between O_3 and cutting frequency. The reduced production was mainly due to reduction in clover. In the spring following fumigation, the stolon as well as the tiller frequency were determined, and it was found that a decrease in stolon density persisted during the winter. O_3 had the opposite effect on tiller density of the grass as it increased (Wilbourn et al. 1995).

White clover and tall fescue

White clover cv. Regal and tall fescue (*Festuca arundinacea* Schreb. cv. Kentucky 31) were exposed for two seasons in OTC's to six different levels of O_3 and two soil moisture levels. Plots were harvested when plants reached a height of 20 to 25 cm (6 times the first year and 7 times the second year). Both O_3 and water stress did reduce the yield, but there were no interactions on total yield. During the two years of the experiment, the total production was reduced by 10% at a seasonal mean 12-hour O_3 concentration of 46 ppb. The reduction was mainly caused by a 19% reduction in clover growth and an increase in fescue growth (Heagle et al. 1989). In some studies the invasion of weeds was also investigated. The results showed that weeds and grass often compete and replace clover (Fuhrer et al. 1994; Heagle et al. 1989).

Red clover and timothy grass

A mixture of red clover and timothy grass was exposed in OTC´s to four different levels of O_3 for one year. The experiment was repeated the following year. After the first year the total amount of biomass was reduced with increasing O_3 levels, and this was due to a decrease in the share of clover. The next year, however, no significant effect was found, although the number of episodes was higher (Kohut et al. 1988). A mixture of white clover and perennial ryegrass is commonly used in Denmark, but no investigations on its sensitivity to ozone have been carried out. Other crops used for husbandry are alfalfa and corn, both of which are sensitive to O_3 (Temple et al. 1988).

Industrial seeds

Rape

Five Danish spring rape cultivars were exposed during vegetative growth for 5 weeks to three levels of O_3 above ambient concentrations in OTC´s. As for many other crops large differences in sensitivity were found, and the primary effect of O_3 was an early leaf drop. Potted spring rape was exposed in a three-year study in OTC´s to two or three levels of O_3. Seed yield decreased with increasing O_3 concentrations (5 ppb to 60 ppb seasonal 8-hour means). This was primary due to smaller seeds, and to a smaller extent to fewer seeds per silique and siliques per plant (Adaros et al. 1991).

Root crops

Potatoes

Because O_3 can change the partitioning of assimilates of plants, an effect of O_3 on root crops is to be expected. However, only very few investigations in Europe have been carried out on the effect of O_3 on these crops. In Sweden, potatoes were exposed over two years in OTC´s to three levels of O_3 (29 to 43 ppb the first year, and 31 to 51 ppb the second year). At the highest concentration, the weight of tubers decreased with 34% the first year and 20% the second year (Jönsson, Skärby 1985).

In the US several experiments have been carried out on the sensitivity of potatoe cultivars to O_3. High O_3 exposures have lead to visible injury (Voss et al. 1982). Potatoes are sensitive to ozone with reduced percentage of dry matter, reduced tuber weight and tuber amount, reduced dry weight of leaves and roots and reduced amount of total sugars. Ozone exposure thus affects both the yield and the quality of potatoes (Pell et al. 1988).

Turnips

Turnips was exposed over two years in OTC´s to five levels of O_3 (14 to 97 ppb 7-hour seasonal mean). Both the first year potted and field-grown plants were placed in each chamber. Potted plants had less leaf injury, and the reduction in root yield was less than in field grown plants. The second year, different cultivars were exposed in the chambers. All cultivars reacted to increasing O_3 with reductions in above as well as in below ground biomass. The roots were however more affected than shoots (Heagle et al. 1985).

Consequences for Danish agriculture

O_3 exposures

The results of many of the above mentioned studies have been expressed in terms of dose-response functions. Many plants react stronger to episodic high concentrations than to the same dose given as lower concentrations over longer time. Therefore dose expressions should take account of high concentrations. The published doses are, however, in most cases expressed as either a 7-hour mean, 8-hour mean, 10-hour, or a 12-hour mean averaged over the growth season. The number of hours used in the dose expression reflects most often the period in which O_3 addition had taken place in the above ambient O_3 treatments. Danish values of O_3 measured at the OTC-facility in a height of 1.2 m are shown in Table 5.3. These values are assumed to be representative of the O_3 levels in Denmark. The doses vary from year to year, being lowest in 1991 and highest in 1995.

Table 5.3. Seasonal (May to August) average O_3 concentrations at the OTC facility at NERI, for the period 1990 to 1995. 7-hour mean is between 10^{00} and 16^{59}, 8-hour mean is between 9^{00} and 16^{59}, 10-hour mean is between 9^{00} and 18^{59} and 12-hour mean between 8^{00} and 19^{59} (GMT + 1).

Mean period	1990	1991	1992	1993	1994	1995
7-hour	39	33	37	33	40	42
8-hour	38	32	36	32	39	40
10-hour	38	32	36	32	40	41
12-hour	37	31	35	32	39	40

Dose-response relationships

Dose-response relationships for different crops important to the Danish agriculture are shown in Table 5.4 and Figure 5.6. The curves for wheat and clover are from the Danish OTC-experiments. The sensitivity of crops varies: spring wheat being the most sensitive and barley the most resistant crops, Figure 5.6. Based on the seasonal O_3 concentrations in Table 5.3 and on the dose-response relations in Table 5.4, the reduction in yield for each crop is calculated (Table 5.5).

Growth conditions

The percentage of yield reductions caused by O_3 may exceed 10% for many of the crops. However, the dose-response relations are based on OTC-experiments, where crops are grown under optimal conditions in relation to water, fertilizer and pest control. Further, high O_3 concentrations often coincide with weather conditions where drought is likely to occur in the field. During water stress plants close their stomata and less O_3 is taken up. When crops develop water stress, the calculated reductions in Table 5.5 are therefore likely to be smaller.

Table 5.4. Dose-response functions for some agricultural crops. x_7, x_8,x_{10}, and x_{12} are 7, 8, 10, and 12 hour seasonal mean O_3 concentrations respectively.

Crop	Function	Reference
Spring wheat	$y=\exp(-(x_8/79)^{2.315})$	This work
White clover	$y=\exp(-(x_8/142)^{1.756})$	Mortensen, Bastrup-Birk 1996a
Pasture	$y=\exp(-(x_{12}/72)^{4.032})$	Kohut et al. 1988[1]
Pasture	$y=1 - 0.00425X_{12}$	Heagle et al. 1989[2]
Sugar beet	$y=\exp(-(x_7/93)^{2.74})$	Heagle et al. 1985
Alfalfa	$y=\exp(-(x_{12}/152)^{2.26})$	Temple et al. 1988[3]
Spring rape	$y=1.02 - 0.00589*x_8$	Adaros et al. 1991[3]
Potato	$y=1 - 0.00396*x_{10}$	Pell et al. 1988
Barley	$y=1 - 0.001027*x_7$	Temple et al. 1985[4]

[1] Red clover - timothy mixture
[2] White clover - tall fescue mixture
[3] Recalculated
[4] Recalculated by Naf , Fuhrer, 1993.

Table 5.5. Reduction in yield of different crops for the last 6 years (in percent). Values based on calculations from functions in Table 5.3 and values in Table 5.4.

Crop	1990	1991	1992	1993	1994	1995
Spring wheat	17	12	15	12	18	19
Barley	4	3	3	3	4	4
Potato	15	13	14	13	16	16
Sugar beet	9	6	8	6	9	11
Spring rape	20	17	19	17	21	22
Alfalfa	4	3	4	3	5	5
White clover	9	7	9	7	10	10
Pasture 1	7	3	5	3	8	9
Pasture 2	16	13	15	13	17	17

Many of the dose-response relationships used to calculate the percentage of reduction are for cultivars, not used in Denmark. Danish cultivars may not have the same response to O_3. Further, the relationships are based on experiments performed under other climatic and pollutant conditions than those prevailing in Denmark (see Section 5.3). The relation for wheat is based on work with spring wheat, but in Denmark winter wheat is more common than spring wheat. Work with winter wheat is primarly performed in the USA, and data indicate that it is sensitive to O_3.

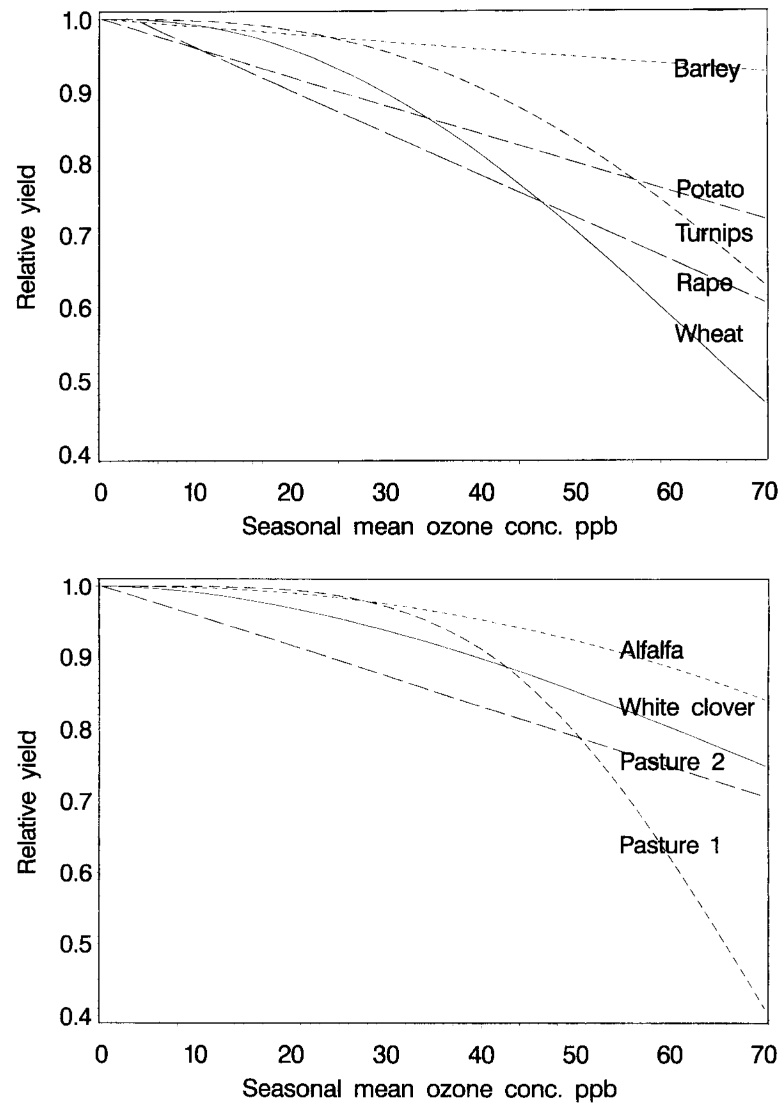

Figure 5.6. Dose-response relationships for important crops in Denmark, based on Table 5.5.

Economy of crops

Cereals are the most important crops in Denmark. Root crops and industrial seeds play only a minor role. From an economic point of view cereals are still the most important crops, but potatoes, beets and rape seeds are also important. Whole crop and forage occupy 18% of the arable land. When air pollutants reduce the production or quality of these crops, fewer animals can be supported by the area. The area must be increased, futter must be imported, or farmers must decrease their livestock.

Economic losses

Table 5.6 shows the reduction in the agricultural production value caused by O_3 during the years 1991 to 1994. The reductions vary between 6 and 8%. These figures are, however, only valid if the above mentioned assumptions are justified and thus represent the worst case. An analysis taking into account farmers practice in rotation of crops, effects on husbandry, determination of prices, and agricultural policy is needed in order to determine the effects of O_3 on the single farmer and consumer.

Table 5.6. The production value of some important Danish agricultural crops in brackets, and the calculated reduction in production value caused by O_3. Values in millions of DKR. The calculations are based on data in Tables 5.5 and Statistisk Årbog, 1995.

Crop	1991		1992		1993		1994	
Wheat	(3516)	479	(3551)	627	(3750)	509	(2918)	641
Barley	(3851)	119	(2583)	80	(2133)	66	(2203)	92
Sugar beets	(1068)	68	(1007)	88	(1136)	73	(1040)	103
Potatoes	(864)	129	(979)	159	(673)	101	(839)	160
Industrial seeds	(1957)	401	(575)	135	(665)	136	(676)	180
Total	(17910)	1196	(14987)	1089	(14585)	885	(13972)	1076
% of total production value		6.7		7.3		6.1		7.7

5.6 O_3 and forest decline

New forest decline

The appearance of severe diebacks of European forests in the beginning of the 1980's was for a long time attributed to acid rain. Many experiments have shown that ambient concentrations of O_3 may lead to visible damages on sensitives forest species. The possibility that air pollution could limit forest productivity on a regional scale has received much attention since a new type of damage or decline in forests throughout Europe was recognised during the 1970's. This new forest decline is characterised by occurring over large geographical areas and by affecting several or all forest tree species at the same time though to a varying degree. The growth of trees in forest ecosystems can be modified by several environmental variables (light, humidity, ambient CO_2 concentrations, gaseous pollutants) and other biological factors (leaf age, plant water status, nutrient status, respiration rate) in addition to genotype (see Section 5.3).

Dieback at stand-level in forests is a natural phenomenon which apart from fire and flooding is mainly caused by biotic factors as pests, insects, fungal or bacterial attacks. Long-term subtle climatic change is also suggested as a cause of stand-level die-back as seen from pollen spectrum records, Figure 5.7. Forest damages in this century may also be explained by local air pollution. Stand-level tree mortality is enhanced by air pollution from nearby smelters or other industrial emissions. The main air pollutants responsible for this toxification are sulphur dioxide, nitrogen oxides while photochemial oxidants have had a minor role.

Forest conditions in Denmark

In the Nordic countries forest decline has only been seen very close to industrial factories where the emissions are or have been high as in Finland and in Norway. The changes were registered over large forested areas and concern on the future of the forest have grown also in Scandinavia. As in the other European countries, a widespread monitoring of forest damages based on estimations of needle and leaf loss was initiated. Results of these observations are shown on Figure 5.8 showing the needle/leaf losses from common coniferous and deciduous trees in Denmark 1988-1994 (Skov- og Naturstyrelsen 1995). The needle loss of more than at least 25% from Norway spruce trees has increased from 9% to 24% in the period. The other conifers have a higher levels of needle loss which seemed to have stabilised in 1994. Beech trees have a lower leaf loss which have stabilised around 9% since 1992. On the other hand, oak trees have experienced an increased amount of lost leaves from 25% in 1989 to 33% in 1994.

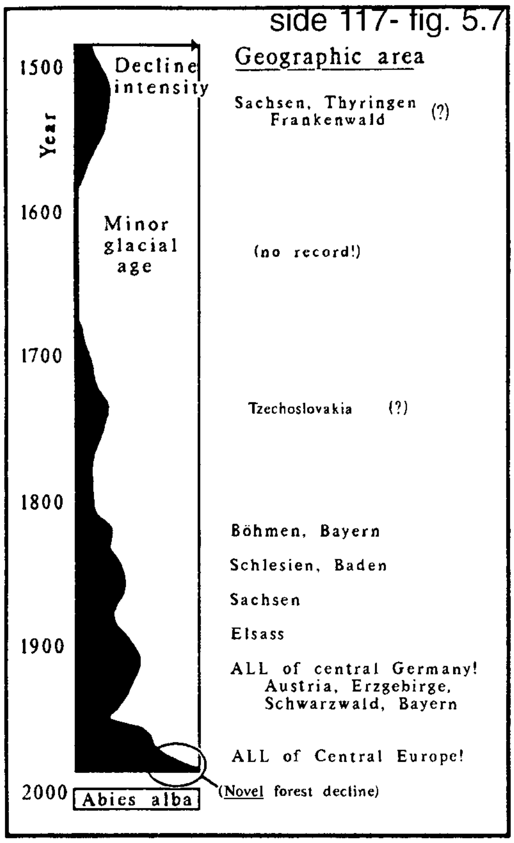

Figure 5.7. The history of the dieback of Silver Fir *Albies Alba*; pollen spectrum records (Larsen 1986).

Observations in the Nordic countries show similar results. In Denmark, an increasing amount of trees has died especially in Jutland on soils experiencing nutrient deficiencies. In 1994, about 3% of the Danish Norway spruce trees died. Damages are also seen in broad-leaved trees. The loss of leaves from birch trees is estimated to be larger than the needle loss in Sweden and Norway from spruces. In Denmark and in the southern part of Sweden similar phenomena are registered for beech and other deciduous trees.

Direct effects

Many hypothesis have been put forward on the causes of this continuing forest decline: 1) soil acidification and aluminium toxicity, 2) O_3 injury, 3) magnesium deficiency 4) excess nitrogen 5) growth-altering organic chemicals and 6) general stress (Hinrichsen 1986). In this context only the hypothesis on O_3 injury is taken up. The O_3 hypothesis has been advocated by Prinz et al. (1987) based on extensive field observations and measurements of O_3 in West Germany.

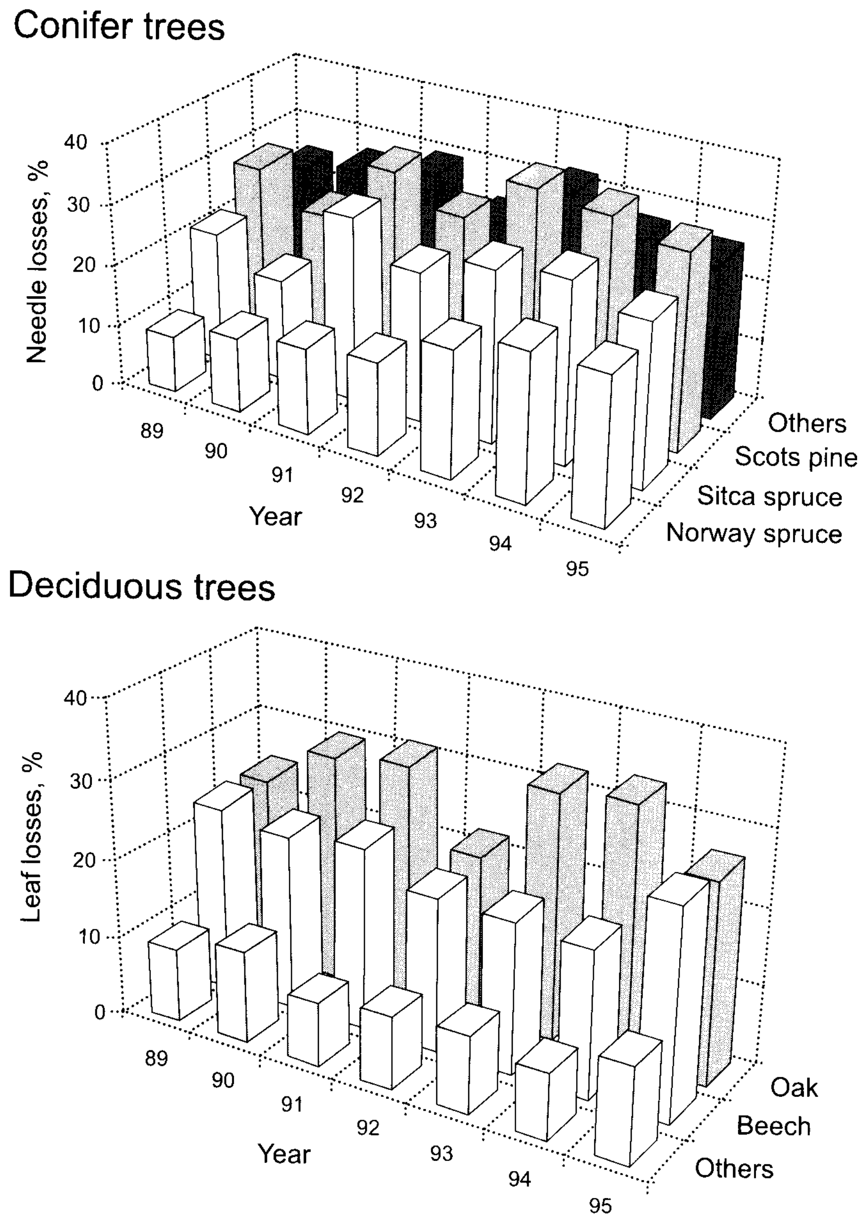

Figure 5.8. Needle/leaf losses in Denmark 1988-1994 (Skov- og Naturstyrelsen 1995).

Causes

O_3 causes only direct effects on vegetation by entering the needles/leaves through the stomata. Concentrations of O_3, above or close to O_3 levels known to cause effects on many species, are registered in Denmark. The ambient concentrations of O_3 (daylight, summer) vary between 30-40 ppb with episodes reaching up to 110-120 ppb usually occurring in spring and summer. The question is then whether O_3 is of importance as a pollutant reducing the productivity and the recreation value of forests in Denmark.

Visible injury

Episodic acute exposures to photochemical oxidants, especially O_3, can result in visible injury to leaves or needles of sensitive tree species. Leaf yellowing, premature senescence and necrosis may appear. Symptoms of O_3 injury such as chlorotic and necrotic flecking and emergence of tip-burn have been observed. Conifers seem to be more susceptible to O_3 than broad-leaved trees especially in the late spring and early summer. Acute O_3 injury appears as death of the needle tip or the entire needle. In less severe cases chlorotic patches of tissues turning yellow and brown, alternating with green and healthy patches of tissue are observed. As for other air pollutants premature defoliation may occur. On broad-leaved trees O_3 injury appears as stipples or flecks of necrosis.

Danish effect studies on trees

Since the middle of the 1980's, research on direct effects of O_3 on Danish trees has been conducted in open top chambers (OTC´s) at the National Environmental Research Institute in close collaboration with the Risø National Laboratory and the Institute of Plant Ecology at the University of Copenhagen. Growth chamber and OTC-studies have also been conducted at the Royal University of Veterinary and Agricultural Sciences, Copenhagen/Hørsholm.

OTC-studies

In all OTC-experiments the trees were exposed to O_3 fumigation. The main purpose was to reproduce O_3 symptoms on healthy plants under controlled conditions within realistic levels of O_3, thereby confirming O_3 as a causal or contributory agent in tree dieback. Still, the mechanisms of O_3 injury and/or stress repair on trees are not well understood. The experiments use mainly young trees and the results may not be transposed to mature trees. Also the O_3 sensitivity of these young trees has up to now mostly been tested in short-term exposure experiment varying from few weeks to few years. More knowledge on the effects of long-term exposure is needed to assess the sensitivity of trees to O_3 (Skärby et al. 1994). Moreover experiments have been performed on shoots with cuvesters on 35-year old Norway spruce trees at the Ulborg site, Denmark. No experiments on the effects of O_3 have been carried out in open sites in Denmark.

Norway spruce,
European beech and
Scots pine

Most research on effects of photochemical oxidants on trees has concentrated on Norway spruce (*Picea abies*) and European beech (*Fagus sylvatica*) which are both of economical and ecological importance in Denmark. Both tree species are considered as rather tolerant to O_3 stress by Chappelka and Chevone (1992). However, this classification is based on investigations using high concentrations of O_3 in combination with short-term exposures in relation to the life-span of the needles. Reich (1987) demonstrated that when photosynthesis and growth are concerned, the uptake of O_3 and the duration of the exposure in relation to the life-span of the needles/leaves are important in determining the responses. Some research has also been conducted on Scots pine (*Pinus sylvestris* (L.)) among conifers, poplar, birch, beech and alder among broad-leaved trees in Scandinavia.

Biomass and growth

Norway spruce

If the O_3 dose is sufficiently high and the repair mechanisms of the tree have been overloaded, O_3 effects are observed. That leads to cellular injuries that may cause changes in growth. A study by Mortensen et al. (1988) showed a delay of 1 week in the time of bud-break and shoot growth and a reduction in the needle length in young Norway spruce trees after two seasons of O_3 exposure (ambient air added 30 ppb during day-time).

Scots pine

Only few studies on biomass and growth have been conducted on Scots pines. Skeffington et al. (1985) found that 50 ppb O_3 during two months resulted in reduced dry weight of new needles and a decreased production of new fine roots in Scots pine. Mortensen (1994) found that an O_3 exposure of 70 ppb (8 hours/day) in 85 days decreased the relative growth rate in one of three provenances and increased the shoot/root ratio in all of them. Too little is still known about the O_3 sensitivity in Scots pine to draw any conclusions.

Deciduous trees

Mortensen and Skre (1990) exposed birch and alder trees to 30-40 ppb, 7 hours a day for 56 days in controlled growth chambers and experienced a significant decrease in growth. At 50 ppb, 7 hours a day, all three species developed visible yellow spots (birch) and brown spots (alder) on the oldest leaves. Stem diameter increment of beech seedlings was found to be significantly reduced with increasing O_3 concentrations when exposed to high episodes in spring and early summer (Mortensen et al. 1995).

Photosynthesis

Photosynthesis is one of the physiological parameters affected most negatively by O_3 (Saxe 1991). O_3 can inhibit the rate of net carbon assimilation in a variety of coniferous and deciduous tree species (Figure 5.9). Photosynthetic responses to O_3 can occur almost immediately or only after prolonged exposure depending on the concentration.

Norway spruce

For Norway spruce photosynthesis rates are reduced in older but not in current year needles in OTC´s (Wallin et al. 1990) and in growth chambers (Saxe, Murali 1989). The response of the photosynthesis rate in Norway spruce seemed to depend on whether the measurements were made before during or after fumigation. The maximal net photosynthesis measured before and after the daily fumigation showed a non-significant increase for the trees fumigated with O_3 in OTC´s. First late in the afternoon at high light intensities a significant depression between 36 and 54% was experienced in the rate of photosynthesis. The effects seemed to be partly reversible (Mikkelsen 1993). The net photosynthesis was increased to the same level as the control as soon as the O_3 addition treatment was stopped each day. After the fumigation stopped in September, the current year needles of the fumigated trees exhibited an increased photosynthesis (21%) as compared to the controls.

This increase in net photosynthesis in current year needles are in agreement with other investigations of Norway spruce (Eamus et al. 1990; Wallin et al. 1990), but physiological explanation is still lacking. Mikkelsen and Ro-Poulsen (1995) on the other hand have used cuvettes on mature 35-year old Norway spruce trees in the field thereby eliminating differences in morphology and soil conditions compared to studies in growth chambers, but still manipulating with the microclimate. Results show a significantly reduced photosynthesis in current year needles when O_3 is added and the light intensities are high (Figure 5.10) Wallin et al. (1990 and 1992) exposed Norway spruce grown in OTC´s to three levels of O_3 (CF (charcoal filtered air), NF (non filtered air) and NF+30 (non filtered air added 30 ppb O_3). O_3 was found to stimulate the rate of net photosynthesis in current year shoots, significantly only in the first year study (Wallin et al. 1990). In 1- to 3 year old shoots, the light-saturated rate of net photosynthesis decreased with increasing shoot age and O_3 concentration. The photosynthetic rate in the current shoots was highest in the non-filtered air treatment. In older shoots the rate decreased with increased O_3 concentration and shoot age. This effect was accompanied by a decrease in carboxylation efficiency in the 2- and 3-year old shoots from the ambient and elevated O_3 treatments.

The results indicated that O_3 disturbed the stomatal regulation or ability of stomata to close which may result in a higher loss of water per given amount of carbon gain. This reduction in photosynthesis has also been related to structural changes in the cells (Sutinen et al. 1990). They found that the chloroplasts were the first organelles affected by O_3. The chloroplasts became shorter with increasing O_3 concentration. The mechanisms are not fully explained, but it is probable that O_3 causes disturbances in the lipid parts of the cell-membranes. Wallin et al. (1990) found that the decrease in net photosynthesis was accompanied with a significant decrease in leaf conductance. Mikkelsen (1995) found that stomatal conductance was higher in charcoal filtered treatments than in O_3 treatments. But no evidence exists at present to support a direct effect of O_3 on guard cell function. It can be concluded that O_3 interferes more with chloroplast function than with stomatal function.

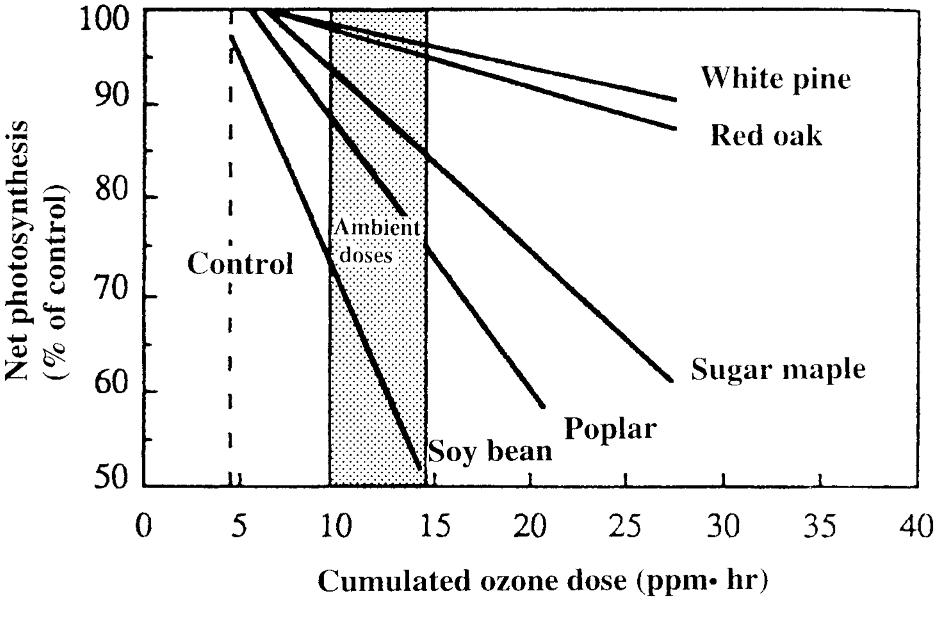

Figure 5.9. Effects of O_3 on the net photosynthesis response of different species (Reich, Amundson 1985).

Scots pine

Scots pine trees (*Pinus sylvestris*) have been studied in Sweden (Skärby et al. 1987). Current year shoots of 20 year old pine trees exposed to 60-200 ppb O_3 during 1 month showed no change in photosynthesis but a significant increase in respiration as well as an increase in the night time transpiration were detected.

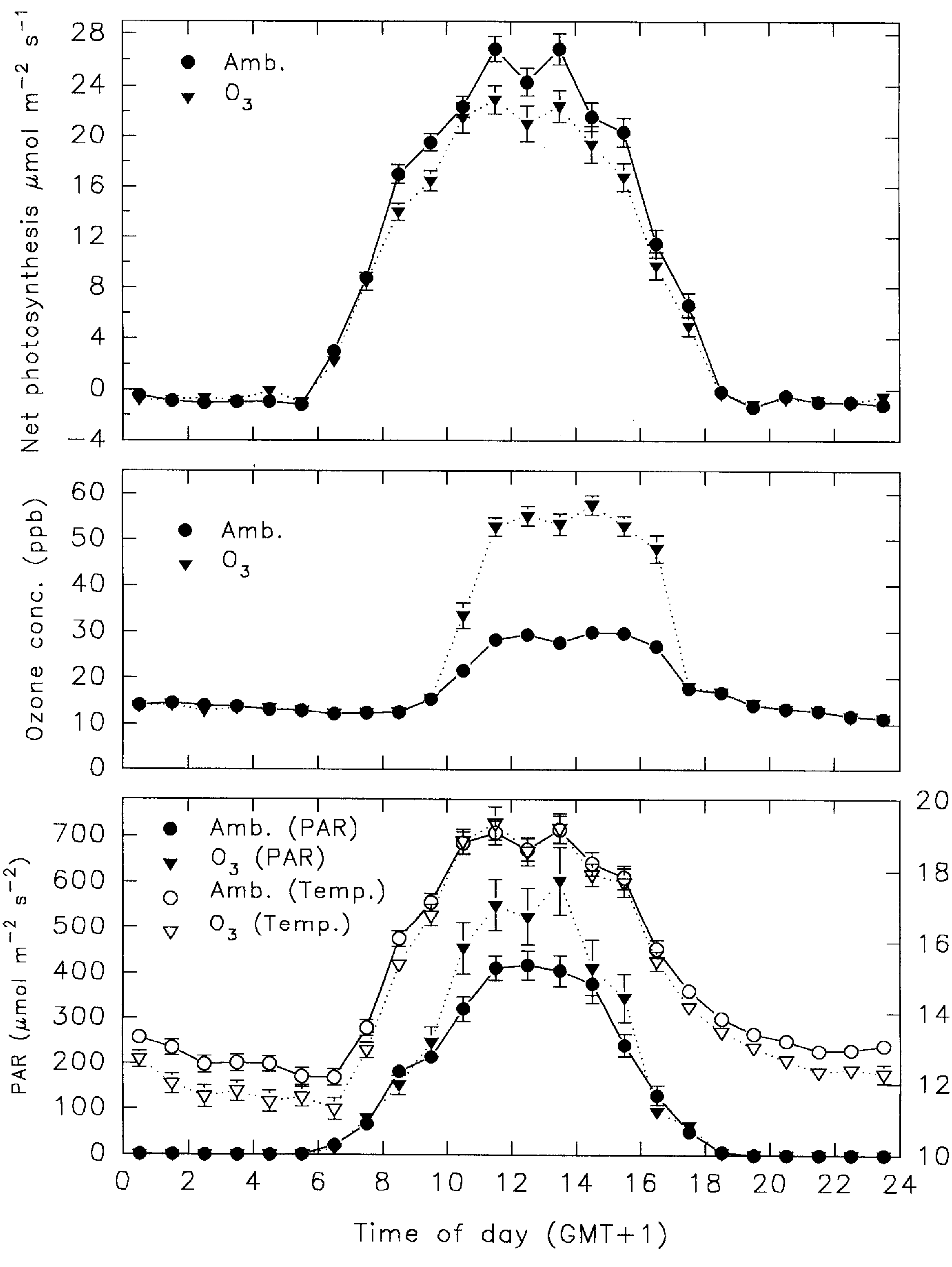

Figure 5.10. Significant decrease in the photosynthetic activity of current-year needles (Mikkelsen, Ro-Poulsen 1995).

Beech

Beech seedlings were grown in OTC's and exposed to 3 levels of O_3 (charcoal filtered air (CF), non-filtered air (NF), and non-filtered air added 30 ppb O_3 (NF+)) during two seasons (1988 and 1989) in OTC's 8 hours per day (Mikkelsen 1993). Net photosynthesis was reduced by 25-40% of charcoal-filtered treatments (20 ppb) during fumigation of appr. 75 ppb. There was no difference in net maximum photosynthesis detected before and after the fumigation. The effect of O_3 on photosynthesis after several months of fumigation is almost momentarily reversible. In another 1-year study on beech (Paludan-Müller, Zeuthen 1994) showed a decrease of the net photosynthesis of 33% from mid-august after 50 ppb O_3 concentration was added to ambient levels. The reduction was attributed to an inhibition of the carboxylation processes through the effect on the Rubisco activity and indirect effect on the cell membranes. An enhanced respiration could also explain the reduction in net photosynthesis.

Birch

Mortensen and Nilsen (1992) tested 23 wild species for O_3 sensitivity and found that birch belonged to the most sensitive species. Five clones of birch (*Betula pendula*) were exposed to slightly elevated levels of O_3 in OTC over 2 growth seasons (Pääkönen et al. 1993). There was a clear difference in sensitivity between clones. The most sensitive clone reacted with decreased height growth and leaf biomass and increased visible injury. Three clones showed intermediate reactions while one clone was unaffected. O_3 caused decreased stomatal conductance but an increased stomatal density in emerging leaves.

Other effects

Beech - Senescence

Mikkelsen (1993) and Paludan-Müller, Zeuthen (1994) found that O_3 accelerates the senescence processes in beech leaves by app. 3 weeks. An important mechanism under senescence is the production of free radicals and the peroxidation of lipids. O_3 is thought to lead to direct oxidative damages and production of radicals. Probably O_3 has accelerated senescence through such reactions in the beech leaves. O_3 may also be involved in the aging of the antioxidative systems. With a lower activity in the antioxidative systems, the concentration of O_3 and radical may increase in the leaves thereby creating oxidative damages and early senescence. Senescence can also be due to increased ethylene production in the leaves (Kimmer, Koslowski 1982).

Norway spruce - Antioxidative system

In order to study the effects of two seasons of O_3 exposure on a clone of Norway spruce, measurements of a large number of potentially detoxifying enzymes and antioxidative compounds were investigated (Nast et al. 1993). No systematic relation between O_3 and the degree of enzyme activities or levels of antioxidants was found.

Pigments

O_3 significantly reduced the concentration of chlorophyll a and b, and alpha- and beta-carotene in 1- and 2-year old needles of Norway spruce, but increased the concentration of antheraxanthin (Mikkelsen, Ro-Poulsen 1994; Wallin et al. 1990).

Genotype

Mortensen (1990) found in a growth chamber experiment that the biomass of top shoots and roots of Norway spruce was reduced in four out of six provenances after an exposure of 80-100 ppb, 7-8 hours daily one season. The exposure is unrealistic, but shows that O_3 causes significant dry weight reductions in Norway spruce.

Frost resistance

In another experiment (Skre, Mortensen 1991), two different Norway spruce clones were exposed to 0, 40, 80 and 160 ppb O_3, for 10 hours a day during shoot elongation (2 months). The trees were also tested for frost resistance during the dormancy induction period. O_3 increased frost sensitivity in one of the clones. At the 40 ppb level shoot growth increased significantly relative to control plants. At 80 and 160 ppb a significant reduction in all growth parameters was detected. There was also a reduction in the formation of new roots already at 40 ppb. Six clones of Norway spruce were exposed to O_3 (50, 100, 200 ppb) 8 hours per day during one season showed no general changes in either foliar nutrient concentrations or concentrations of terpenes (Ogner 1993a, 1993b). It was concluded that variations in these factors mainly were due to genetic and climatic variations.

Modelling efforts

Process-based models

Modelling has become an important tool in the study of air pollution effects. Process-based models are useful in the study of forest responses to stress. They are based on the mechanisms and incorporate processes by which both human-made and natural stresses may origin. These models are useful for simulating combinations of conditions that could not be studied empirically. Many of the physiologically based models are modular and have a detailed code for photosynthesis to simulate the effect of stresses on the carbon acquisition.

The following allocation of photosynthate and partitioning of dry matter use general source-sink relationships and species-specific phenology to distribute carbon and nutrient allocation throughout the plant. These models have shortcomings like an inadequate descriptionof the processes below-ground level, due to the relatively poor understanding of the physiology and biochemistry of the roots. Another weakness is the description of the response of net photosynthesis when many experiments show unchanged photosynthesis under chronic levels of O_3 and even increased photosynthesis. The TREGRO model (Weinstein at al. 1991) has been initialised with OTC data at NERI, Denmark and used for the simulation of the effects of O_3 on Norway spruce (Leonardi et al. 1997).

Conclusions

Research on the effects of O_3 on trees in Denmark as well as in the Nordic countries in the last 10 years confirms that the O_3 damages the physiological functioning and the growth of trees significantly. But the role of tropospheric O_3 on nature trees is still not quantified. An economic analysis of the reductions in productivity caused by O_3 would be relevant. Many of the experiments have been conducted on young trees under controlled conditions in OTC´s and growth chambers. There is a need for translation of these results to field conditions and to mature trees. Only few experiments in Denmark is performed under field conditions and there is still a lack of data on effects on forest production.

Multi-factors

Many of the air pollution studies have emphasized the impact of single pollutants, focusing on the individual effects of O_3. In the forests these pollutants occur at the same time and at low levels (Johnson, Lindberg 1992). A lot of different factors can alter the response functions at the level of individual tree, stand or community and includes other air pollutants, CO_2, water stress, temperature, radiation, competition among species and biotic pathogens.

Interactions

On-going experiments in Denmark are also dealing with the interactions of O_3 with other stress factors. An experiment is conducted at the OTC facility at the National Environmental Research Institute. The effects of O_3 and soil nitrogen content on the growth, physiology, anatomy and biochemistry of Norway spruce seedlings are studied over two growth seasons. Other experiments in Denmark are investigating the interactions between O_3 and drought, enhanced winter temperatures, climate changes, frost hardiness (the Forest Section of the Royal University of Veterinary and Agricultural Sciences). The importance of the provenance to resist O_3 stress is studied. Several provenances of both Norway spruce and European beech are exposed to elevated O_3 concentrations of ambient air added 50 ppb and 100 ppb in closed-top chambers (CTC´s) over three growth seasons.

The importance of the interactions in governing the response of trees and the high variability in space and time of multiple interactions are two of the reasons why traditional single or multiple factors experiments in air pollution studies have not been successful in improving the understanding of the long-term consequences of air pollution stress on forest productivity.

In the future one might expect that these stress interactions are going to be reanalyzed. Methodologies are going to be developed and applied in order to account for the impact of stress interactions in space and in time. A promising approach includes ecological modeling at several scales: from individual trees, over forest stands to community and landscapes. Thereby a link to ecological risk assessment is provided.

5.7 Critical levels for O_3 - Concluding remarks

Definition

For trees as for crops, critical levels have been defined as the critical exposure dose below which significant adverse effects on vegetation do not occur. The work in defining critical levels has primarily been done within the framework of UN-ECE (United Nation-Economic Corporation Europe). The concept of critical levels has become very useful for policy-makers being a tool in negotiations on abatement strategies and mapping of areas at risk. The definition of critical levels must therefore be transparent and easy to use without loosing the biological sense.

Development in critical levels for O_3

Critical levels for O_3 were first defined in 1988 (Guderian 1988) based on mean concentrations during day-light hours. Plants exposed to the same O_3 dose given as low concentrations or as peaks react stronger to the dose given as peaks. In 1992 a new concept was introduced, where only O_3 concentrations over a threshold (AOT) were cumulated, the suggested cut-off concentration was 40 ppb (AOT40) (Ashmore 1992). In 1993, a critical level for O_3 to protect agricultural crops was defined as 5300 ppb-hours summed up during day-light hours (global radiation $\geq 50\ W/m^2$) and three months (May to July). This value is related to 10% reduction in yield (Fuhrer, Ackerman 1994), and is based on data from the European OTC wheat study (Table 5.8). For forests a provisional critical level for O_3 was set to 10000 ppb-hours calculated as an AOT40 based on a 24-hour basis over 6 months corresponding to a 10% reduction in biomass.

Table 5.8. Relationship between relative yield reduction in wheat and AOT40. The regression line y = 99.6 - 0.00170 x AOT40, R^2=0.889 (Fuhrer 1996).

Relative yield reduction (%)	AOT40 (ppb-hour)
5	2700
10	5600
15	8600
20	11500

The Kuopio meeting in 1996

In 1996, at the Kuopio workshop, a critical level for protecting crops was redefined to be 3000 ppb·hour accumulated during three months and during day light hours. More European and America data on wheat have become available and have been included in the regression analysis. Further the critical level was defined for a 5% yield reduction. Nordic data on spring wheat, white clover, and European beech have shown that under Nordic conditions a cut-off concentration of 30 ppb did fit the data best (Mortensen, Bastrup-Birk 1996a, 1996b).

For visible leaf injury in agricultural crops a short term AOT40 value is defined as 3000 ppb·hour cumulated during day light hours over 5 days when vapour pressure deficit conditions are low and 5000 ppb·hour when vapour pressure conditions are high (Table 5.9).

Table 5.9. Critical levels for O_3 (AOT40-values) as defined at the Kuopio meeting in 1996. O_3 concentrations above a cut-of concentration of 40 ppb are cumulated during day-ligth hours where global radiation > 50 W/m^2 . VPD is the vapor pressure deficit.

Vegetation and effect	AOT40	Remark
Tree species (annual increment)	10.000 ppb·hour	Cumulated for 6 months (April-October)
Crop species (yield)	3.000 ppb·hour	Cumulated for 3 months (May-July)
(Visible injury)	500 ppb·hour	high VPD 5 days
	300 ppb·hour	low VPD 5 days

For forests the critical level of 10000 ppb·hour was redefined based on the accumulated O_3 during daylight (> 50/W m^2) over a 6 months growth season (April-September). This value is based on available data on beech and corresponds to 10% reduction in annual increment. For natural vegetation no values are defined so far, as experimental data are almost lacking, and it is suggested that the value for crops will be sufficient to protect wild flora. When calculating the AOT40 values an average of 5 years should be used (Table 5.9).

Uncertainties

The critical level concept has been based on OTC-experiments. In OTC´s the climate is changed in relation to ambient conditions, the windspeed is constant and defined by the blowers, the temperature is increased, and radiation decreased. How these changes affect plant uptake of and response to O_3 is not well known. There are special problems with the trees, because it is not clarified how effects on young trees are related to old mature trees. Further, the accepted 10% reduction in annual increasement is a lot taking into account the life span of trees, so it could be questioned whether biomass is the right measure in this context. The discussion on critical levels is still ongoing.

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6 Relationships between emission sources and excess ozone concentrations

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6.1 Introduction

The aim of mathematical models

In the troposphere has ozone damaging effects on plants, animals and humans, when the concentration exceeds certain critical levels. Therefore it is necessary to carry out three tasks:

- Determination of sufficiently accurate critical levels of the ozone concentrations,
- Reductions of ozone concentrations to below the critical levels
- Development of reliable and robust control strategies by which the ozone concentrations can be kept under the critical levels.

Both the second and third task are very expensive. Therefore the high ozone concentrations must be reduced to the critical levels, but not more. Furthermore, it is necessary to reduce (as much as possible) the economical costs of these actions. Mathematical models can be used in the search of an optimal solution.

Danish Eulerian Model

A mathematical model for studying air pollution levels in Europe (the Danish Eulerian Model) will be shortly discussed. The model consists of a system of 35 partial differential equations and leads to huge computational requirements, when it is handled numerically. Therefore it is necessary to use big modern highspeed computers (with vector and/or parallel capabilities).

The Danish Eulerian Model has been used to run various scenarios in order to study some of the relationships between emissions in Europe and high ozone concentrations. Modern visualisation techniques have been applied to illustrate the effects of different emission reductions used in the scenarios on the ozone concentrations and to draw some conclusions.

6.2 Long-range transport of air pollutants

Air Pollution in background areas

Air pollutants can be transported over long distances, mainly by advection due to the wind (but diffusion phenomena and chemical transformations under the transport also play an important role). This means that high concentrations and depositions may be detected also in areas without strong emission sources. This explains why the long-range transport of air pollutants is an important process, which must be studied carefully in order to understand fully all phenomena that lead to high concentrations of air pollutants in areas far away from big emission sources.

Critical levels

The pollutants, both when they are dispersed in the atmosphere and when they are deposited on surfaces, can be harmful for plants, animals and humans, if their concentrations are over certain levels (called either acceptable or critical levels; the term critical levels will be used in this paper). This may impose a requirement to reduce the concentrations that exceed the critical levels. However, it must be stressed that the reduction of the air pollution is often an expensive process. Therefore it is necessary to define exactly what kind of reduction is wanted and where it is necessary to achieve reductions. The critical levels of the concentrations and the depositions must be determined precisely and the air pollution must be reduced to these levels but not more, because the extra efforts may be very expensive.

Mathematical models of air pollution phenomena (and, first and foremost, of long-range transport phenomena) are indispensable tools in the efforts to solve the problems sketched above. Moreover, many problems connected with an optimal reduction of the air pollution to critical levels can successfully be solved only if reliable mathematical air pollution models are used (see Birkhoff 1983).

Chemical reactions

Ozone is one of the harmful air pollutants. High ozone concentrations can damage the plants during their growth period. Therefore it is necessary to study the ozone concentrations and to understand the source-receptor relationships in connection with the distribution of ozone concentrations over large areas. This is not easy, because ozone reacts with many chemical species. Therefore advanced chemical schemes, which contain sufficiently many chemical species must be used in the models. The problem of finding an optimal chemical scheme for a large air pollution model is still an open problem. It is commonly accepted, however, that a good chemical scheme must contain a series of chemical species (nitrogen pollutants, sulphur pollutants, many radicals, and many hydrocarbons).

The number of species

The number of chemical species used in different large air pollution models varies from 20 to about 200 (see e.g. Borrell et al. 1990, Carmichael and Peters 1984, Carmichael et al. 1986, Chang et al. 1987, Ebel et al. 1991, Hass et al. 1993, Peters et al. 1995, Stockwell et al. 1990 and Venkatram et al. 1988). The use of less than 20 chemical species requires crude parameterization of some chemical processes and is not advisable, if the accuracy requirements are not very crude. On the other hand, the use of more than 200 chemical species is connected with huge tasks that cannot be handled on the computers available at present without imposing a sequence of simplifying assumptions. This leads to a crude parameterization of the other physical processes involved in the air pollution models (advection, diffusion, deposition and emission) and/or to discretizations of the models on coarse grids. It should be pointed out that even the use of 100-200 chemical species leads to the necessity both to apply certain simplifying assumptions and/or to use coarse grids (since, the computers become faster and faster, such actions will probably not be necessary in the near future).

The above discussion shows clearly that a good chemical scheme for studying in an adequate way the distribution of the ozone concentrations on large areas must comprise a considerable number of species. This leads to huge computational tasks, which can successfully be solved only if fast (and sufficiently accurate) numerical methods are used, and if the air pollution models are run on big high-speed computers.

The Danish Eulerian Model

The use of a particular mathematical model, the Danish Eulerian Model (Zlatev 1995), in the solution of the tasks sketched above will be discussed in this chapter. A short description of the Danish Eulerian Model will be presented in Section 6.3. The concept of "excess ozone concentrations" will be introduced following a definition given in Simpson 1993 in Section 6.4. The difficulties, which arise when the excess ozone concentrations over large areas are to be studied, will be discussed in Section 6.5. Some of the results obtained by using several carefully chosen emission scenarios will be presented in Section 6.6. Finally some concluding remarks concerning the future plans will be given in Section 6.7.

6.3 Mathematical description the Danish Eulerian Model

Basic equations

The long-range transport of air pollutants over Europe is described by a system of partial differential equations (PDE's):

$$\begin{aligned}
\partial c_s / \partial t = & - \partial(u c_s) / \partial x - \partial(v c_s) / \partial y - \partial(w c_s) / \partial z \\
& + \partial(K_x \partial c_s / \partial x) / \partial x + \partial(K_y \partial s_s / \partial y) / \partial y + \partial(K_z \partial c_s / \partial z) / \partial z \\
& + E_s(x, y, z, t) + Q_s(c_1, c_2, \ldots, c_q) \\
& - (k_{1s} + k_{2s}) c_s(x, y, z, t), \\
s = & \ 1, 2, \ldots, q . \qquad (6.1)
\end{aligned}$$

Many air pollution models can be described mathematically by using the generic formulae (6.1). The particular model that will be studied in this paper is the Danish Eulerian Model. This model is fully described in (Zlatev 1995).

Reliability

It is very important to check carefully the reliability of a mathematical model that has to be used in meaningful simulations. The reliability of the algorithms implemented in the Danish Eulerian Model as well as the reliability of the results obtained by this model have been discussed in several papers. In the latter case it is necessary to check separately the reliability of the concentrations calculated over land and the reliability of the concentrations calculated over water (during the transport over seas and oceans). The reliability of the concentrations calculated over land has been studied by Zlatev (1995) and Zlatev et al. (1993, 1992); concentrations calculated by the Danish Eulerian Model have been compared with measurements taken at EMEP stations in different European countries (EMEP, European Evaluation and Monitoring Programme, is a common European environmental project in which nearly all European countries participate). The reliability of the concentrations calculated over water has been studied by Harrison et al. (1994); concentrations calculated over the North Sea have been compared with measurements in this paper (the measurements have been collected onbord R. R. S. Challenger over the Southern Bight of the North Sea during seven cruises in the period March-October 1989). The performance of different numerical algorithms used in the model as well as their accuracy have been studied in (Brown et al. 1995; Zlatev 1995; Zlatev et al. 1993, 1992, 1994).

Parameters in the model

The number, q of equations is equal to the number of species that are involved in the model and varies in different studies. Until now the model has mainly been used with a chemical scheme containing 35 species (it may be necessary to involve more species in the future; experiments with chemical schemes containing 56 and 168 species have recently been carried out). The chemical scheme with 35 species is the well-known CBM IV scheme (described by Gery et al. 1989) with a few enhancements which have been introduced in order to make it possible to use the model in studies concerning the distribution of ammonia-ammonium concentrations in Europe as well as the transport of ammonia-ammonium concentrations from Europe to Denmark.

The different quantities that are involved in the mathematical model have the following meaning:

- the concentrations are denoted by c_s;
- u, v and w are wind velocities;
- K_x, K_y and K_z are diffusion coefficients;
- the emission sources in the space domain are described by the functions $E_s(x,y,z,t)$;
- κ_{1s} and κ_{2s} are deposition coefficients;
- the chemical reactions are described in the model by the non-linear functions $Q_s(c_1, c_2, \ldots, c_q)$.

The non-linear functions Q_s are of the form:

$$Q_s\left(c_1, c_2, \ldots, c_q\right) = -\sum_{j=1}^{q} \alpha_{si} c_i + \sum_{i=1}^{q} \sum_{j=1}^{q} \beta_{sij} c_i c_j \qquad (6.2)$$

This is a special kind of non-linearity, but it is not obvious how to exploit this fact during the numerical treatment of the model.

It follows from the above description of the quantities involved in the mathematical model that all five physical processes (advection, diffusion, emission, deposition and chemical reactions) can be studied by using the above system of PDE's. The most important processes are the advection (the transport) and the chemical reactions. Kernels for these two parts of the model must be treated numerically by using accurate algorithms.

Splitting the model

It is difficult to treat the system (6.1) of PDE's directly. This is the reason for using different kinds of splitting. A simple splitting procedure, based on ideas discussed in Marchuk 1985 and McRae et al. 1984 can be defined, for s = 1, 2, ..., q, by the following sub-models:

$$\partial c^{(1)} / \partial t = - \partial (uc^{(1)}) / \partial x - \partial (vc^{(1)}) / \partial , y, \quad (6.3)$$

$$\partial c^{(2)} / \partial t = + \partial (K_x \partial c^{(2)} / \partial x) / \partial x + \partial (K_y \partial c^{(2)} / \partial y) / \partial y, \quad (6.4)$$

$$dc^{(3)} / dt = + E_s(x,y,z_0,t) + Q_s(c_1^{(3)}, c_2^{(3)} \ldots, c_9^{(3)}), \quad (6.5)$$

$$dc^{(4)} / dt = - (k_{1s} + k_{2s}) c^{(4)}, \quad (6.6)$$

$$\partial c^{(5)} / \partial t = - \partial (wc^{(5)}) / \partial z + \partial (K_z \partial c^{(5)} / \partial z) / \partial z, \quad (6.7)$$

The horizontal advection, the horizontal diffusion, the chemistry, the deposition and the vertical exchange are described with the systems (6.3 - 6.7). This is not the only way to split the model defined by (6.1), but the particular splitting procedure (6.3 - 6.7) has three advantages: the physical processes involved in the big model can be studied separately, it is easier to find optimal (or good) methods for the simpler systems (6.3 - 6.7) than for the big system (6.1) and if the model is to be considered as a two-dimensional model (which often happens in practice), then one should just skip system (6.7).

Space discretization

Assume that the space domain is a parallelepiped which is discretized by using an equidistant grid with $N_x \times N_y \times N_z$ grid-points, where N_x, N_y and N_z are the numbers of the grid-points along the grid-lines parallel to the O_x, O_y and O_z axes. Assume further that the number of chemical species involved in the model is $q = N_s$. Finally, assume that the spatial derivatives in (6.1) are discretized by some numerical algorithm. Then the system of PDE's (6.1) will be transformed into a system of ODE's (ordinary differential equations)

$$dg/dt = f(t,g) \quad (6.8)$$

where g(t) is a vector-function with $N_x \times N_y \times N_z \times N_s$ components. Moreover, the components of function g(t) are the concentrations (at time t at all grid-points and for all species. The right-hand side f(t,g) of (6.8) is also a vector function with $N_x \times N_y \times N_z \times N_s$ components which depends on the particular discretization method used and of the concentrations of the different chemical species at the grid-points. If the space discretization method is fixed and if the concentrations are calculated (at all grid-points and for all species), then the right-hand side vector in (6.8) can also be calculated.

As mentioned above, the large air pollution models are not discretized directly. Some kind of splitting is always used. If the model is split into sub-model as in the previous sub-section, then the application of discretization methods (normally different methods for the different sub-models) will lead to the following ODE systems:

$$dg^{(1)}/dt = f^{(1)}(t,g^{(1)}) \tag{6.9}$$

$$dg^{(2)}/dt = f^{(2)}(t,g^{(2)}) \tag{6.10}$$

$$dg^{(3)}/dt = f^{(3)}(t,g^{(3)}) \tag{6.11}$$

$$dg^{(4)}/dt = f^{(4)}(t,g^{(4)}) \tag{6.12}$$

$$dg^{(5)}/dt = f^{(5)}(t,g^{(5)}) \tag{6.13}$$

where $g^{(1)}$ and $f^{(1)}$, $i = 1, 2, 3, 4, 5$, are again vector-functions with $N_x \times N_y \times N_z \times N_s$ components. The right-hand-side functions $f^{(1)}$, $i=1, 2, 3, 4, 5$, depend on the discretization methods used. Some particular numerical methods that can be used in the discretization of the five sub-models (6.3 - 6.7) in order to obtain ODE systems of type (6.9 - 6.13) are listed below.

The discretization of the spatial derivatives in the sub-model describing the horizontal advection, the PDE system (6.3), can be carried out either by using pseudospectral expansions or by applying finite elements (Zlatev 1995; Zlatev et al. 1994). Other numerical methods can also be applied. It is important to emphasize that the resulting system (6.9) contains $q = N_s$ independent ODE systems (i.e. one such a system per each chemical species). This fact could easily be exploited on parallel computers.

The discretization of the second-order spatial derivatives in the horizontal diffusion sub-model, the PDE system (6.4), is quite similar. Both the pseudospectral algorithm and finite elements can be used. Again, other numerical algorithms can also be applied. The number of independent systems of ODE's in the resulting system (6.10) is again $q = N_s$; i.e. the same as in the previous case. It may be useful to apply different numerical algorithms in the advection and diffusion parts; see again Zlatev 1995, Zlatev et al. 1994.

The transition from (6.5) to (6.11) as well as the transition from (6.6) to (6.12) is trivial, because there are no spatial derivatives in (6.5) and (6.6). In the first case, the resulting ODE system (6.11) contains $N_x \times N_y \times N_z$ independent systems, each of them with N_s equations (because the chemical species at a given grid-point react with each other, but not with chemical species at other grid-points). In the second case, the resulting system (6.12) consists of $N_x \times N_y \times N_s$ independent ODE's (because the deposition of a given species at a given grid-point depends neither on the deposition of the other species nor on the deposition processes at the other grid-points). It is seen from the above discussion that a lot of parallel tasks arise in a natural way when the ODE systems (6.11) and (6.12) must be handled.

Finite elements can be applied in the discretization of the spatial derivatives in the vertical exchange sub-model (6.7). The resulting ODE system (6.13) consists of $N_x \times N_y \times N_s$ independent ODE systems; each of them is defined on a vertical grid-line and, therefore, contains N_z equations.

Time integration

It is necessary to couple the five ODE systems (6.9) - (6.13). The coupling procedure is connected with the time-integration of these systems. Assume that the values of the concentrations (for all species and at all grid-points) have been found for some $t = t_n$. According to the notation introduced in the previous sub-section, these values are components of the vector-function $g(t_n)$. The next time-step, time-step n+1 (at which the concentrations are found at $t_{n+1} = t_n + \Delta t$, where Δt is some increment), can be performed by integrating successively the five systems (6.9 - 6.13). The values of $g(t_n)$ are used as an initial condition in the solution of (6.9). The solution of each of the systems (6.9 - 6.12) is used as an initial condition in the solution of the next system. The solution of the last system, system (6.13) is used as an approximation to $g(t_{n+1})$. In this way, everything is prepared to start the calculations in the next time-step, step n+2 .

Predictor-corrector methods with several different correctors are used in the solution of the ODE systems (6.9) and (6.10). The correctors are carefully chosen so that the stability properties of the method are enhanced (Zlatev 1984).

Several different methods have been tried in the solution of the ODE system (6.11) (Zlatev 1995). The QSSA (quasi-steady-state approximation (e.g. Hesstvedt et al. 1978; Hov et al. 1988) is simple and relatively stable, but not very accurate (therefore it has to be run with a small time-stepsize). The classical numerical methods for stiff ODE systems (such as the Backward Euler Method, the Trapezoidal Rule and Runge-Kutta algorithms) lead to the solution of non-linear systems of algebraic equations and, therefore, they are more expensive (e.g. Hairer, Wanner 1991; Lambert 1991). On the other hand, these methods can be incorporated with an error control and perhaps with larger time-steps. The extrapolation methods (Deuflhard 1983; 1985; Deuflhard, Nowak 1986; Deuflhard et al. 1987; 1990) are also promising. It is easy to calculate an error estimation and to carry out the integration with large time-steps when these algorithms are used. However, it is difficult to implement such methods in an efficient way when all five systems (6.9 - 6.13) must be treated successively. The experiments with different integration methods for the chemical sub-model (6.11) are continuing. The QSSA will be used in most of the experiments described here. Other numerical methods for the chemical part of a large air pollution model are discussed in, e.g. (Chock et al. 1994; Hertel et al. 1993; Odman et al. 1992; Shieh et al. 1988; Verwer, van Loon 1995; Verwer, Simpson 1995).

The next ODE system, (6.12), contains, see the previous sub-section, $N_x \times N_y \times N_z$ independent ODE's. Moreover, all these ODE's are linear. Therefore they are solved exactly during the numerical treatment of the model.

The last ODE system, (6.13), can be solved by using many classical time-integration methods. The so-called θ-method (Lambert 1991) is used in the three-dimensional version of the Danish Eulerian Model (Zlatev 1995).

The need for high speed computers

The size of the systems that arise after the space discretization and the splitting procedures used to treat (6.1) numerically is enormous.

Consider the case where the model is two-dimensional, and let us assume that the model is discretized on a (96×96) grid (such a grid is used in the Danish Eulerian Model after 1993) and that $q = 35$. Then the number of equations in each of the four systems of ODE's (6.9)-(6.12) is 322,560. The time-stepsize used in the advection step is 15 min. The chemical sub-model (6.11) cannot be treated with such a large time-stepsize (because it is very stiff; especially when photochemical reactions are involved). Therefore six small time-steps are carried out for each advection time-step (this means that the chemical time-stepsize is 2.5 min.). From this description it is clear that in fact nine systems of ODE's (each of them containing 322,560 equations) are to be treated per advection step. Assume that a one-month run is to be carried with the model. This will result in 3456 advection time-steps (taking here into account that it is necessary to use five extra days in order to start up the model).

Consider now the case where the model is three-dimensional. Assume that ten layers are used in the vertical direction. Then the number of equations in every system of ODE's is 3,225,600 (i.e. ten times greater than in the previous case). The number of systems that must be treated at every time-step is increased from four to five. The number of time-steps remains the same, 3456. The chemical sub-model must again be integrated by using smaller time-steps.

It is clear that such large problems can only be solved with modern high speed computers. Moreover, it is necessary to select the right numerical algorithms (which are most suitable for the high speed computers available) and to perform the programming work very carefully in order to exploit fully the great potential power of the vector and/or parallel computers. The Danish Eulerian Model has already been successfully run on several high-speed computers (Brown et al. 1995; Zlatev 1995; Zlatev et al. 1994). However, it is still necessary to improve the performance of the different algorithms on different high speed computers. Therefore much more experiments are needed, and will be carried out in the future. High-quality software for some standard mathematical problems is now available (e.g. Anderson et al. 1992; Barrett et al. 1994) and one should try to use it extensively in large air pollution models.

6.4 Excess ozone concentrations

It is commonly accepted now that *"ozone is one of the major air pollutants that, in high concentration, can endanger health and damage plants"* (McKeen et al. 1991; Dentener, Crutzen 1993; McKeen et al. 1991; Roselle et al. 1991; Sillman et al. 1990a, 1990b; Simpson 1992). Moreover, it is also commonly accepted that the ozone concentrations (and especially the high ozone concentrations) depend non-linearly both on the NO_x emissions and on the VOC emissions (VOC: Volatile Organic Compounds); see again the above references. Some experiments, in which the NO_x emissions and/or the VOC emissions have been varied have been performed (Zlatev 1995; Zlatev et al. 1993, 1992) in order to study the effect of the emission variations on some concentrations and, first and foremost, on the ozone concentrations. The main purpose in this paper is more ambitious: we will study the effect of the emission variations on the amount of ozone that might cause damages on certain plants and on forest trees.

The first step is to define the critical quantity of the ozone in the atmosphere that will probably cause damages on the plants. Assume that:

- the time-period under consideration contains N hours,
- the ozone concentrations are measured in ppb,

c_i is the calculated by the model mean value of the ozone concentration in hour i, where i = 1, 2, .., N,

c is the critical ozone concentration which has been found relevant for the objectives of the particular study (note that if the objectives are changed, then the value of c may also change).

EXCESS.

The quantity EXCESS(c), which is defined by the following formula

$$\mathrm{EXCESS}(c) = -\sum_{i=o}^{N} \max(c_i - c, 0) \tag{6.14}$$

will be called excess ozone with regard to the critical concentration c.

The definition given above is very similar to that used in (Simpson 1993, p. 924). The only difference is that the definition here is valid for any appropriate value for the critical concentration c, while the special value c = 75 ppb is used in (Simpson 1994). This means that the definition given in this section is slightly more general and more flexible; it can be used in different studies (where as a rule c will vary when the objectives are varied; see above). The flexibility of the new definition will be illustrate with two examples in the following two sub-sections.

Effects on crops

Consider the case where harmful effects of high ozone concentrations on crops during the growth period are to be studied. Let us assume that the following conditions are satisfied:

- The time-period under consideration contains three months (May, June and July),
- The summation in (6.14) is performed only for the day-hours (or, more precisely, the period from sun-rise to sun-set),
- The critical value of the ozone concentrations is set to c = 40 ppb.

It is believed that the ozone concentrations are harmful for the crops if the value of EXCESS(40) obtained from (6.14) by using the three conditions imposed in this sub-section is greater than 5300 ppb.h; this value has recently been proposed by a large group of experts in this field in the Workshop Summary of a UN-ECE report on critical levels for ozone (Fuhrer, Achermann 1994, p. 5). The critical value 5300 ppb.h is derived by using experimental data (Ashmore 1994; Fuhrer 1994; as well as the references in these two papers).

The term "AOT40" is used in Fuhrer 1994 (AOT40: accumulated exposure over a threshold of 40 ppb); the term "excess ozone", which is used in this paper seems to be older (Beck, Grennfelt 1994; Simpson 1993). The term "excess ozone" is used also in the report of Fuhrer and Achermann (1994) see the contribution of Simpson (1994).

Effects on forest trees

Consider the case where harmful effects of high ozone concentrations on forest trees (during the summer period are to be studied). Let us assume now that the following conditions are satisfied:

- The time-period under consideration contains six months (April, May, June, July, August and September),
- The summation in (6.14) is performed both for the day-hours and for the night-hours,
- The critical value of the ozone concentrations is again set to c = 40 ppb.

It is believed that the ozone concentrations are harmful for the forest trees if the value of EXCESS(40) obtained from (6.14) by using the three conditions imposed is greater than 10,000 ppb.h. This value has been chosen as a provisional critical level for ozone in connection with forest trees at the Workshop on Critical Levels for Ozone held in Bern (Switzerland) in 1993 (e.g. Fuhrer, Achermann 1994; Skärby 1994).

It should be noted that the same notation for the excess ozone, EXCESS(40) is used both in the case where harmful effects on crops are to be studied and in the case where harmful effects on forest trees are to be studied. Of course, the values of the excess ozone are different in these two cases. However, from the context it will be clear how the excess value is calculated.

6.5 Difficulties in the calculation of excess ozone

The calculation of excess ozone is a much more stringent task than the task of calculation of ozone concentrations. A model that calculates reasonable approximations to the ozone concentrations may have difficulties with calculation good approximations to the excess ozone. The two major difficulties in the calculation of excess ozone will be shortly discuss in the next two subsections.

Need of small time-steps

The diurnal time pattern, which is typical for the ozone concentrations may cause difficulties for some trajectory models. The strong diurnal variations lead to a requirement for small time-steps (one must have several instantaneous concentrations in order to calculate the desired hourly mean values of the concentrations). This requirement is always satisfied for the Eulerian models. For some trajectory models, however, this requirement is not satisfied, because in such models a few trajectories only arrive at the receptor points (typically only four trajectories: arriving at 6:00, 12:00, 18:00 and 24:00; e.g. Simpson 1992, 1993). Some interpolation rule can be used, but this produces extra numerical errors.

Need for accurate methods

Another difficulty arises because the differences c_i - c are to be used in calculation of (6.14). These differences may be in the range of uncertainty of the model, even in the case where c_i is sufficiently accurate. A simple example can be given to illustrate this statement. Consider the values of the exact concentration c^{exact} and the calculated concentration C^{calc}. Assume that

$$c^{exact} = 41, \; c^{calc} = 45, \; c = 40. \tag{6.15}$$

Then the value of the relative error of the calculated ozone concentration (in percent) is given by

$$100 \mid c^{exact} c^{calc} \mid / \mid c^{exact} \mid < 9.9 \tag{6.16}$$

which in many cases is quite acceptable.

Assume now that the contribution of hour i for the excess ozone is to be calculated. The exact contribution for hour i is

$$c^{exact} - c = 1 \tag{6.17}$$

while the corresponding calculated contribution is

$$c^{calc} - c = 5\,. \tag{6.18}$$

The relative error (in percent) of the contribution to the excess ozone for hour i is given by

$$100 \mid c^{exact} - c^{calc} \mid / \mid c^{exact} c \mid = 500 \tag{6.19}$$

It is clearly seen that although the ozone concentration has been calculated in a sufficiently accurate way, the contribution to the ozone excess for hour i is quite wrong. Of course, this is an extreme situation, but these example illustrates that more accurate methods must be used, when excess ozone is to be calculated (the same is true if excess values for some other pollutants are to be computed).

6.6 Running the model with different scenarios

The Danish Eulerian Model (Zlatev 1995; Zlatev et al. 1993, 1992, 1994) has been run by using meteorological data for five consecutive years (1989-1993) and several emission scenarios.

The meteorological data contains data files which are read at the end of every period of six hours (wind fields, precipitation fields, mixing height fields, temperature fields, cloud covers fields, humidity fields). Since the time-steps used in the model (Δt = 15 min.) are much smaller than 6 hours, linear interpolation is used to obtain the necessary values of the meteorological parameters, when these are not directly available from the data files.

Four emissions input data files are used in the model: SO_2, NO_x, anthropogenic VOC and NH_3 emissions. The first three files have been obtained from EMEP (European Monitoring and Evaluation Pro gramme), while the fourth file has been obtained from (Asman 1990). These data files contain yearly means of the emissions at the EMEP grid; simple linear interpolation rules are used to obtain variation on seasonal and (if necessary) on diurnal bases (see more details in Zlatev et al. 1993, 1992). Natural VOC emissions are also used in the model. These are calculated on hourly basis by using the procedure proposed by Lübkert and Schöp 1989; see again (Zlatev et al. 1993, 1992).

Scenarios

Four types of scenarios have been used in the attempts to establish some relationships between emissions and excess ozone:

Basic runs. These runs have been performed by using the European emissions for 1989. One run has been performed for each of the six months of interest (April, May, June, July, August and September) and for each of the five years for which we have meteorological data. This means that the total number of the basic runs is 30.

Runs with reduced NO_x emissions. All NO_x emissions in Europe have been reduced by the same amount (k%; several different values of k have been used). Then the same runs as in the previous case have been performed; the total number of runs for a given value of k is 30.

Runs with reduced VOC emissions. All anthropogenic VOC emissions in Europe have been reduced by the same amount (k%; the same values of k as in the previous case have been used). Then the same runs as in the first case have been performed; the total number of the runs for a given value of k is again 30.

Runs where both the NO_x emissions and the VOC emissions are reduced. All NO_x emissions and all anthropogenic VOC emissions in Europe have been reduced by the same amount (k%; the same values of k as in the previous two cases have been used). Then the same runs as in the first case have been performed; the total number of the runs for a given value of k is as in the previous cases 30.

Only results obtained with k = 30% will be presented in this section. However, results obtained with other values of k have been taken into account when different conclusions are drawn. In a similar way, mainly the results from 1989 (which is in a sense the worst year in this period; with greatest values of the excess ozone) will be presented, but the results from the other years have been taken into account when different conclusions are drawn.

The main purpose with these runs was to study the relationships between the emission sources and the excess ozone (including here the excess ozone in Denmark). The results from some of the runs will be discussed in this section.

Comparison with measurements

Comparisons with measurements have been carried out for 1989. At this year, measurements at 20 stations in different European countries (most of them, 10, in Germany) have been available. There are three groups of stations:

- Stations where the calculated excess ozone is considerably less than the measured excess ozone

- Stations where the measured excess ozone is considerably less than the calculated excess ozone
- Stations where the calculated excess ozone is in relatively good agreement with the measured excess ozone.

The stations from the first group are all in Germany. Some results from 1989 are given in Table 6.1. It is not very clear why the model underestimates the excess ozone in some German sites. There are no ozone measurements on hourly basis in the German stations for 1990. The following questions are to be answered in connection with the results in Table 6.1:

- Is there anything special with some of the German stations?
- Is the model underestimating large ozone concentrations?
- Are the German emissions used in the model too high?
- Are there other reasons for the discrepancies?

It is necessary to emphasize two important facts: the discrepancies are not very large, and both the calculated and the measured excess ozone concentrations are much greater (at each of these six German stations) than the critical level of 5300 ppb.h.

The stations, where the model overestimates the excess ozone, are given in Table 6.2. It is seen that the reason for the overestimation, in some of the cases, is that a large fraction of the measurements are missing (up to 75%; see the results for Offagne). If the missings are not too many, then the results could be considered as rather good for some of the stations; as Ansbach and St. Denijs.

The stations where the agreement between calculated excess ozone and measured excess ozone are reasonably good are shown in Table 6.3. These stations are in Scandinavia and Germany. The model results obtained in Northern Europe tends to be better (when compared with measurements).

It is difficult to draw detailed conclusions. However, the results for most of the stations (also for some stations in Table 6.1 and Table 6.2) are fairly good; taking into account the uncertainties in the emissions (up to 30%) and the difficulties that arise when excess ozone is calculated. Indeed, for most of the station the discrepancy between the two compared quantities is between 10% and 50%, which is comparable with the uncertainties in the emissions.

Table 1. Calculated and measured excess ozone concentrations at 1989 at six German stations. In the column under "Missings" the numbers of hours for which there are no measurements are given. Unit used: ppb.h.

Station	Country	Calculated	Measured	Missings
Westerland	W. Germany	15567 (53%)	29108	108 (5.2%)
Waldhof	W. Germany	9745 (40%)	24132	106 (7.5%)
Schauinsland	W. Germany	28283 (55%)	51184	300 (13.5%)
Deuselbach	W. Germany	24561 (57%)	43299	21 (0.9%)
Hohenwestedt	W. Germany	9371 (64%)	14680	87 (3.9%)
Bassum	W. Germany	11296 (52%)	21590	6 (0.3%)

Table 2. Calculated and measured excess ozone concentrations at 1989 in seven European stations. In the column under "Missings" the numbers of hours for which there are no measurements are given. Unit used: ppb.h.

Station	Country	Calculated	Measured	Missings
Ansbach	W. Germany	19795	11990 (61%)	123 (5.6%)
St. Denijs	Belgium	10440	5506 (53%)	294 (13.3%)
Offagne	Belgium	29480	3107 (11%)	1663 (75.3%)
Eupen	Belgium	19762	6017 (30%)	311 (14.1%)
Arkona	E. Germany	12690	5930 (47%)	166 (7.6%)
Monte Vehlo	Portugal	25064	78 (0%)	1032 (46.7%)
Ispra	Italy	38948	20700 (53%)	0 (0.0%)

Table 3 Calculated and measured excess ozone concentrations at 1989 in seven stations in North Europe. In the column under "Missings" the numbers of hours for which there are no measurements are given. Unit used: ppb.h.

Station	Country	Calculated	Measured	Missings
Ulborg	Denmark	11307	8627 (76%)	164 (7.4%)
Rørvik	Sweden	10377	7379 (71%)	0 (0.0%)
Norra Kvill	Sweden	7393	10559 (142%)	0 (0.0%)
Vavihill	Sweden	8733	11713 (134%)	471 (21.3%)
Neuglobsow	E. Germany	6435	7527 (117%)	25 (1.1%)
Rottenborg	W. Germany	24508	17446 (71%)	402 (18.2%)
Meinerzhagen	W. Germany	16334	13593 (120%)	270 (12.2%)

Comparing the results from the basic runs

The results obtained in the basic runs for the five years (1989-1993) are given in Figures 6.1 - 6.5. (all figures are placed at the end of the chapter). It is seen that, although the values of the excess ozone vary, the patterns are practically the same:

- The excess ozone in Southern Europe is high (usually more than seven times greater than the critical value of 5300 ppb.h).
- The excess ozone in Central and Western Europe is also fairly high (it normally exceeds several times the critical value).
- Only in the Northern Scandinavia and in Northern Russia the excess ozone is as a rule under the critical level.

The results in Figures 6.1 - 6.5, as well as the results in Tables 6.1 - 6.3, indicate that it is necessary to reduce the excess ozone in a large part of Europe; and in Denmark.

Runs with reduced NO_x emissions

Several scenarios with reduced NO_x emissions have been carried out. The results for 1989 in the case where all European NO_x emissions have been reduced by 30% are shown in Figure 6.6. The following conclusions can be drawn by comparing the results in Figure 6.6 with the corresponding results from the basic runs and also by using results from other experiments:

The reduction of the NO_x emissions leads in general to a reduction of the excess ozone in Europe; compare e.g. the results for 1989 from the basic run (Figure 6.5) with the results in Figure 6.6. The excess ozone in Denmark is reduced considerably.

There are, however, areas in Europe where the excess ozone is increased, when the NO_x emissions are reduced. It is difficult to see this effect by comparing the results in Figure 6.5 with the results in Figure 6.6. However, if the results obtained by reducing the NO_x emissions are related to the results from the basic run (instead of relating them to the critical value of the excess ozone), then the effect can be clearly seen. The plot in Figure 6.10 show that the ozone excess in some parts of Central and Western Europe increase considerably, when the NO_x emissions are reduced.

The distribution of the nitrogen oxide concentrations in Europe is given in Figure 6.9. Comparing Figure 6.9 with Figure 6.10 one can see that the ozone excess is increased when the NO_x emissions are reduced precisely in the areas in which the concentrations of nitrogen oxide are highest. The same conclusion can be drawn, when the results in Figure 6.10 are compared with the distribution of the NO_x emissions in Europe.

Runs with reduced anthropogenic VOC emissions

The experiments with reduced NO_x emissions were repeated with corresponding reductions of the anthropogenic VOC emissions (and by using the basic NO_x emissions). Again only results from 1989 will be presented, but the results from the other experiments are taken into account, when conclusions are drawn. The main conclusions that can be drawn from the runs are given below.

In the whole domain, excluding the Southern parts, a reduction of the anthropogenic VOC emissions seems to be more efficient than the corresponding reduction of the NO_x emissions. This is seen by comparing the results in Figure 6.7, where the distribution of the excess ozone concentrations in Europe due to the reduction of the anthropogenic VOC emissions is given, with the results in Figure 6.6, where the distribution of the ozone excess concentrations due to the reduction of the NO_x emissions is given.

The reduction of the excess ozone due to the reduction of anthropogenic VOC emissions is greatest in the areas where the nitrogen oxide concentrations are highest; compare the results given in Figure 6.7 with those given in Figure 6.5.

It should be emphasized here that only the anthropogenic VOC emissions are reduced. This means that the total VOC emissions in Europe are not evenly reduced. In areas, where the natural VOC emissions are a considerable part of the total VOC emissions, the effect of reducing the anthropogenic VOC emissions will be weaker. This is the case for some of the countries in Southern Europe, where the amount of the natural VOC emissions can (in some summer periods) exceed 50% of the total VOC emissions. The weaker effect of the reduction of the anthropogenic VOC emissions on the reduction of the critical excess ozone in the countries in Southern Europe is seen in Figure 6.11.

Reducing both the NO_x emissions and the anthropoenic VOC emissions

In the third group of experiments both the NO_x emissions and the anthropogenic VOC emissions were reduced (the reductions being the same as in the cases where only the NO_x emissions and only the anthropogenic VOC emissions were reduced; see the previous two subsections). Only results for 1989 are given, but results from other years have been used in all conclusions.

The reductions of the excess ozone obtained by the simultaneous reduction of the NO_x emissions and the anthropogenic VOC emissions are in general greater than the reductions of the excess ozone caused by reducing either only the NO_x emissions or only the anthropogenic VOC emissions; compare the results given in Figures 6.5 - 6.8.

Even the simultaneous reduction of both emissions do not result in reducing the excess ozone to the critical excess ozone level of 5300 ppb.h in a very large part of Europe. It should be mentioned here that even when all NO_x emissions and all anthropogenic VOC emissions in Europe are reduced by 95% (such an experiment has also been carried out), there are still regions in Europe where the excess ozone is greater than 5300 ppb.h.

If only the reduction of the excess ozone is important, then in some parts of Western Europe it may be better to reduce only the anthropogenic VOC emissions; compare e.g. the results in Figure 6.7 and Figure 6.8. This is only an illustration of the fact that the common reduction of the European emissions, with the same amount everywhere, will not always be the optimal solution.

Comparison of the reductions from the different scenarios

The reductions of the excess ozone in relation to the critical excess ozone level of 5300 ppb.h are given in Figures 6.6 - 6.8 for the three scenarios used. The reductions of the excess ozone in relation to the basic run can be seen in Figures 6.10 - 6.12. It is time now to try to answer the question: "What is the best scenario?" While it is obvious that different answers to this question are true for different parts in Europe, it is also obvious that other visualizations are needed in order to give more detailed answers (because the situation is not very clear when the plots mentioned above are studied). A comparison of the different scenarios is presented in Figures 6.17 - 6.19. The following conclusions can be drawn from the results presented in these figures.

The reductions obtained by using 70% NO_x emissions are compared with the reductions obtained by using 70% anthropogenic VOC emissions in Figure 6.17 (in fact, percentages are obtained by dividing the two reductions and multiplying the result by 100). It is seen that in a large part of Europe the reduction of the excess ozone achieved when the anthropogenic VOC emissions are decreased by 30% (in the whole space domain) are greater than the reductions of the excess ozone achieved when the NO_x emissions are decreased (again in the whole space domain) by 30%. The opposite is true in the Southern Europe as well as in parts of Russia, the Atlantic Ocean and Northern Scandinavia where greater reductions of the excess ozone are achieved when the NO_x emissions are decreased; in the whole space domain, by 30%. For the Northern Scandinavia and Russia this is not very important, because the excess ozone there is normally under the critical level 5300 ppb.h; see Figures 6.5 - 6.8).

The reductions obtained by decreasing, by 30%, both the NO_x emissions and the anthropogenic VOC emissions are compared with the reductions obtained by using 70% NO_x emissions in Figure 6.18 (as in the previous case, percentages are obtained by dividing the two reductions and multiplying the result by 100). It is seen that nearly in the whole of Europe the reduction of the excess ozone is greater when both emissions are reduced (by 30% in the whole space domain). This is not true only for the Southern part of Europe and a part of the Atlantic Ocean, where the reductions of the excess ozone are greater when only the NO_x emissions are reduced (by 30% in the whole space domain).

The reductions obtained by decreasing, by 30%, both the NO_x emissions and the anthropogenic VOC emissions are compared with the reductions obtained by using 70% anthropogenic VOC emissions in Figure 6.19 (percentages are again obtained by dividing the two reductions and multiplying the result by 100). It is seen that nearly in all parts of the Western and Central Europe the reduction of the excess ozone is greater if the second scenario is used (i.e. if only the anthropogenic VOC emissions are reduced by 30% in the whole space domain). This is, in fact, also true for a part of the Atlantic Ocean, but the excess ozone there is under the critical level (see Figures 6.5 - 6.8). In all other parts of the space domain of the model the reductions of the excess ozone are greater when both emissions are simultaneously reduced by 30% in the whole space domain.

The results presented in this sub-section indicate that it is not easy to design a good control strategy that can give an optimal answer to the questions where and by how much some emissions are to be reduced in order to keep the excess ozone under the critical levels. Long series of experiments with different scenarios are to be carried out in order to give an adequate answer to these questions. The models used in the simulations should be fast and reliable. Furthermore, fast and robust visualization routines, by which output data stored in enormous files could be represented in different ways, are also needed in the efforts to understand better different trends hidden behind millions and millions of numbers.

Effects of reduced European emissions on ozone excess in Denmark

The effects of the reductions of emissions in the whole of Europe on the ozone excess in Denmark will be studied in some more detail in this sub-section. Some results for 1989 are shown in Figures 6.13 - 6.16. In these figures the same data as the data in Figures 6.5 - 6.8 are used on a part of the space domain including the Southern part of Scandinavia. It is seen that:

- The excess ozone in whole of Denmark is greater than 175% of the critical excess ozone (5300 ppb.h) when the basic emissions are used. This means that the excess ozone is about twice greater than the critical level of 5300 ppb.h.
- If only the NO_x emissions are reduced by 30%, then the excess ozone in Denmark is reduced by an amount up to 30%, the reduction in the Northern Jutland being the greatest (Figure 6.14).
- If only the VOC emissions are reduced by 30%, then the excess ozone in Denmark is reduced by an amount of about 40% - 50% in nearly the whole of Denmark (Figure 6.15).
- If both the NO_x emissions and the anthropogenic VOC emissions are reduced by 30%, then the excess ozone is reduced by an amount of 48% - 56% in nearly the whole of Denmark; (Figure 6.16).
- For all three reductions of European emissions by 30% (only the NO_x emissions, only the anthropogenic VOC emissions and both the NO_x and the anthropogenic VOC emissions), the excess ozone in Denmark remains over the critical level of 5300 ppb.h. However, if both the NO_x and VOC emissions are reduced by 40%, then the ozone excess in Denmark is reduced under the critical level of 5300 ppb.h.

Effects of reducing only the Danish emissions on the ozone exces

An experiment has been carried out in order to determine the influence of the Danish emissions on the ozone excess concentrations in Denmark and in the surrounding countries. All Danish emissions have been set to zero (also the sulphur emissions and the ammonia emissions). The results obtained in this run have been compared with the results obtained in the case where the Danish emissions are not suppressed. The percentages obtained in this comparison are given in Figure 6.20. The results presented in Figure 6.20 can be summarized as follows:

- An isolated removal of the Danish emissions has only a modest influence on the levels of excess ozone in Europe; the changes vary from about - 9% to about +5%.
- The excess ozone in Denmark is slightly increased.
- The excess ozone in the surroundings of Denmark is slightly decreased.

The excess ozone in the areas far away from Denmark is practically unchanged.

6.7 Conclusions

Several experiments, in which different scenarios have been used to study the effects of varying certain emissions on the excess ozone, have been discussed in this paper. Many of the conclusions have been presented in the previous section. Some general remarks concerning such kind of experiments are given below.

Such simulations require a large number of runs with big codes. More than 720 runs have been performed in the simulation discussed in this paper. Therefore both fast numerical algorithms and fast computers are needed. Moreover, good implementation of the numerical algorithms on the modern high speed computers is absolutely necessary. Some of these problems have been discussed in Section 6.2. It should be emphasized that it was possible to perform this simulation only because the implementation of the numerical algorithms from Section 6.2 is rather efficient. However, it should also be emphasized here that further improvements are absolutely necessary. These computational problems have also been discussed in a paper written by a large group of American scientists (Peters et al. 1995).

A large air pollution model produces a lot of output data in such simulations. About one Gbyte output data have been produced in the particular simulation described here. These data have to be handled with fast visualization programs in order to represent the digital data graphically, which allows us to see better the trends hidden behind millions (and even billions) of numbers. Animation programs are in some cases giving us even better insight describing dynamically the processes that are of interest. A large set of visualization and animation programs have been prepared and used to illustrate the main conclusions from the different runs. Again, much more efforts in this direction are needed and better and faster programs have to be prepared in order to treat better similar (or even more complicated) situations.

While the difficulties related to the runs of the large air pollution models on computers and the problems related to the treatment of very large output data sets in order to visualize the results are gradually decreased because the computers become faster and bigger, the problems with high quality input data (both meteorological data and emission data) become more and more important. Any improvement of the model is unavoidably implying a requirement for better quality of the input data. The preparation of high quality input data sets for the models is one of the greatest problems when large simulation processes are to be carried out.

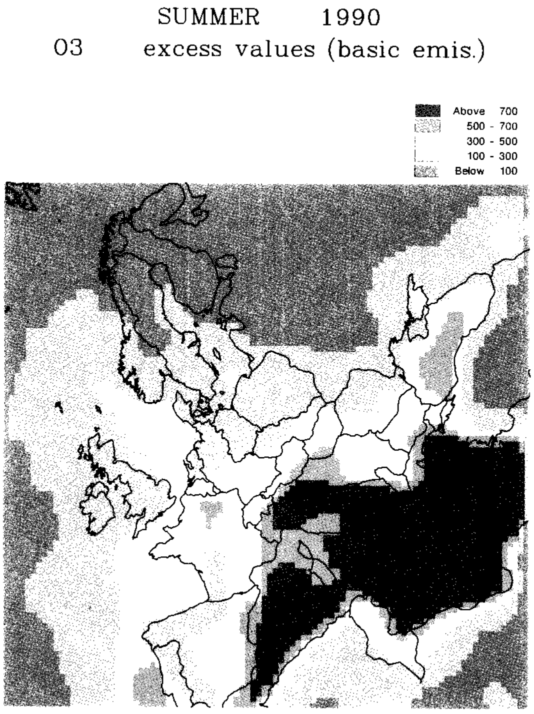
Future plans

The air pollution problem is a regional problem. Therefore it must be solved on a regional basis. Small countries, like Denmark, are not able to solve their air pollution problems by reductions of their own emissions.

The reduction of the air pollution in a large region, like Europe, by the same amount is probably not the optimal solution (an example has been discussed in Section 6.5). A careful search for optimal solutions of different air pollution problems must be carried out when the economical price of the reductions is high (and this is as a rule always the case. A more complete study of the phenomena treated in this chapter can be found in Bastrup-Birk et al. (1997). Ozone excess in a seven-year period is discussed there.

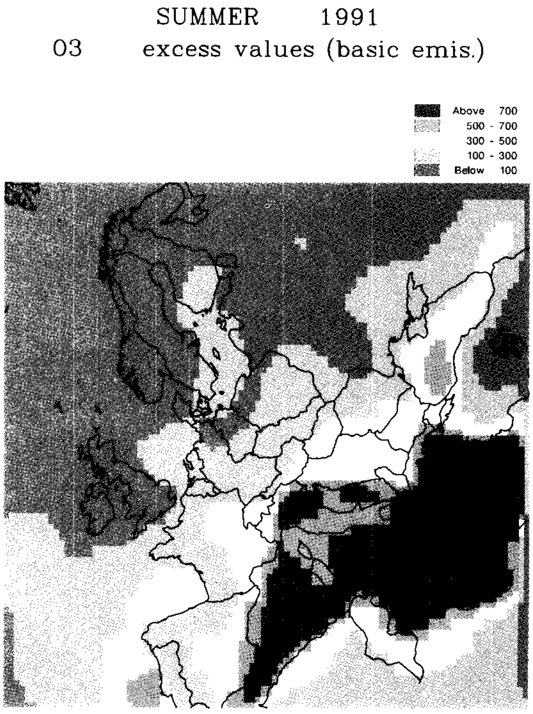
Acknowledgements

This research was partially supported by NMR (Nordic Council of Ministers), EMEP (European Monitoring and Evaluating Programme), NATO (North Atlantic Treaty Organization), SMP (Danish Strategic Environmental Programme) and the Danish Natural Sciences Research Council.


SUMMER 1990

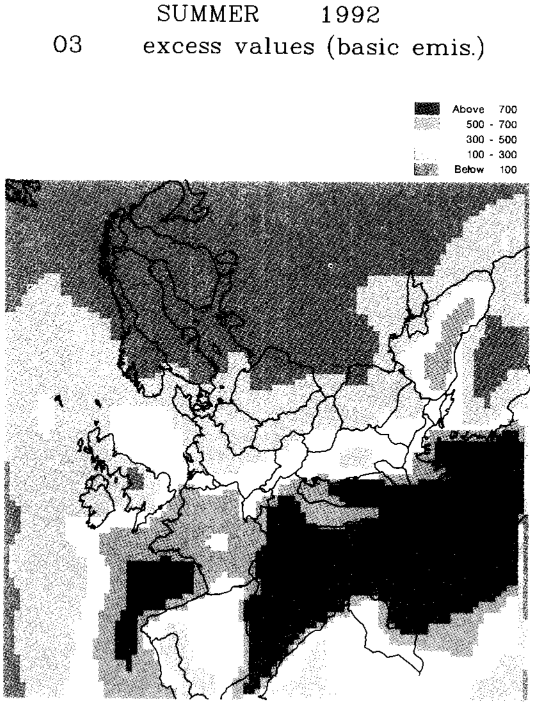
03 excess values (basic emis.)

Figure 6.1. Distribution of the excess ozone (percentages: 100 * EXCESS/5300) in 1990.


SUMMER 1991

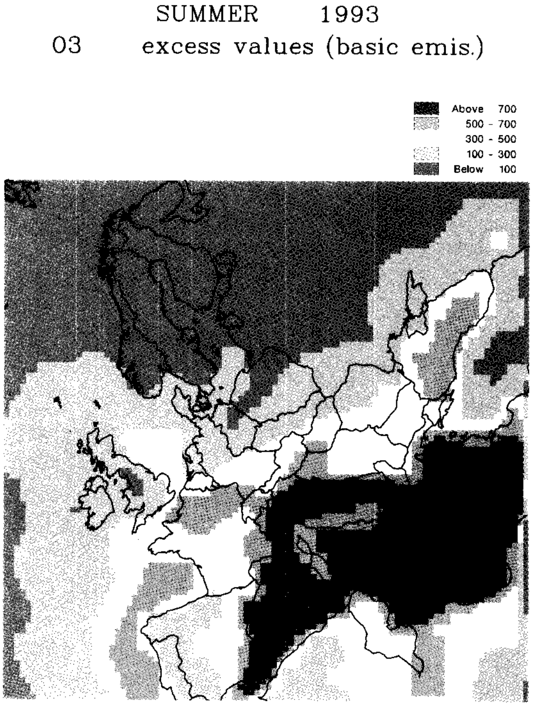
03 excess values (basic emis.)

Figure 6.2. Distribution of the excess ozone (percentages: 100 * EXCESS/5300) in 1991.


SUMMER 1992

03 excess values (basic emis.)

Figure 6.3 Distribution of the excess ozone (percentages: 100 * EXCESS/5300) in 1992.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03 excess values (basic emis.)

Figure 6.4. Distribution of the excess ozone (percentages: 100 * EXCESS/5300) in 1993.

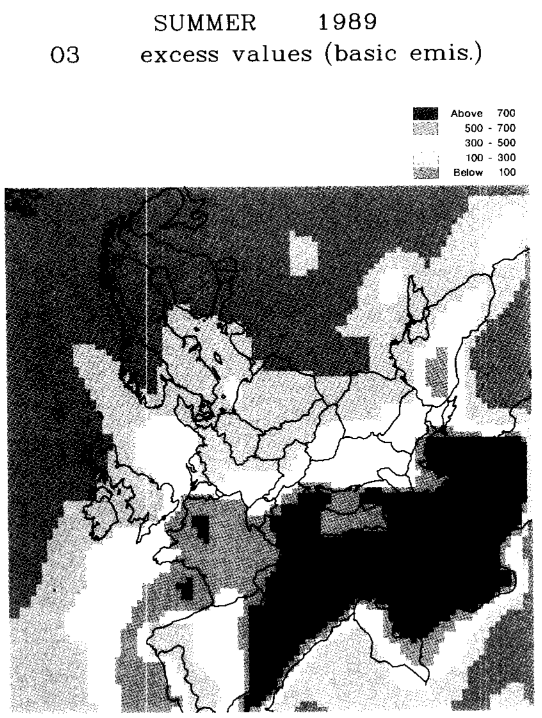

Figure 6.5. Distribution of the excess ozone (percentages: 100 * EXCESS/5300) in 1989.

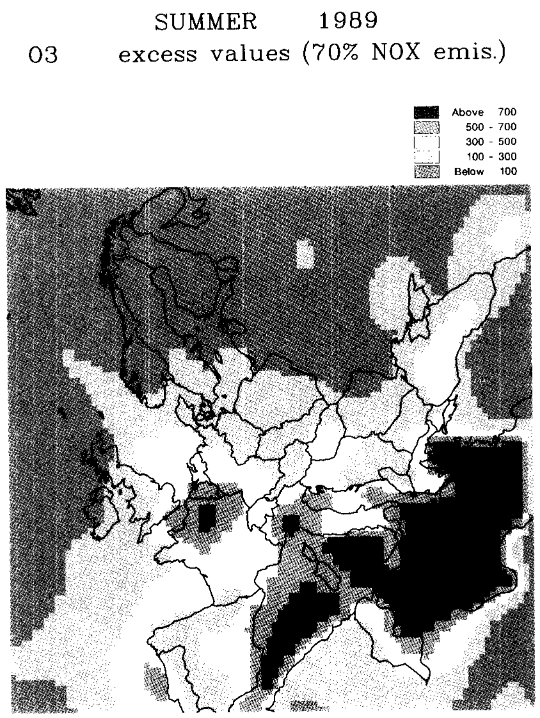

Figure 6.6. Distribution of the excess ozone (percentages: 100 * EXCESS/5300) in 1989 when the NO_x emissions are reduced by 30%.

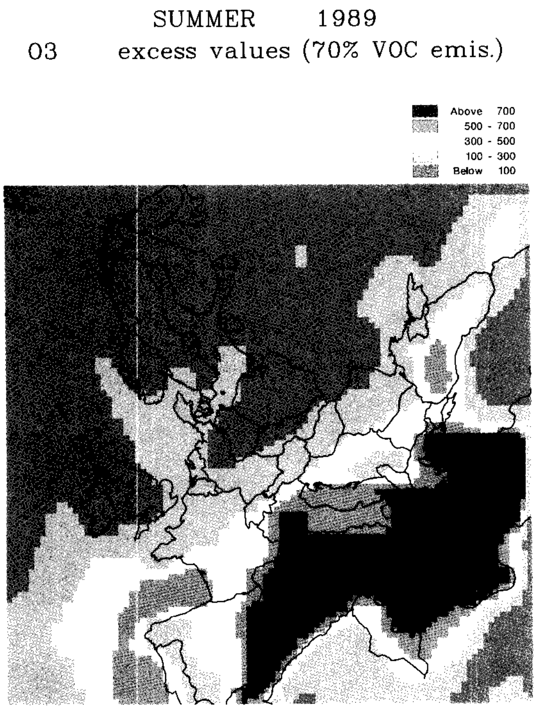

Figure 6.7. Distribution of the excess ozone (percentages: 100 * EXCESS/5300) in 1989 when the anthropogenic VOC emissions are reduced by 30%.

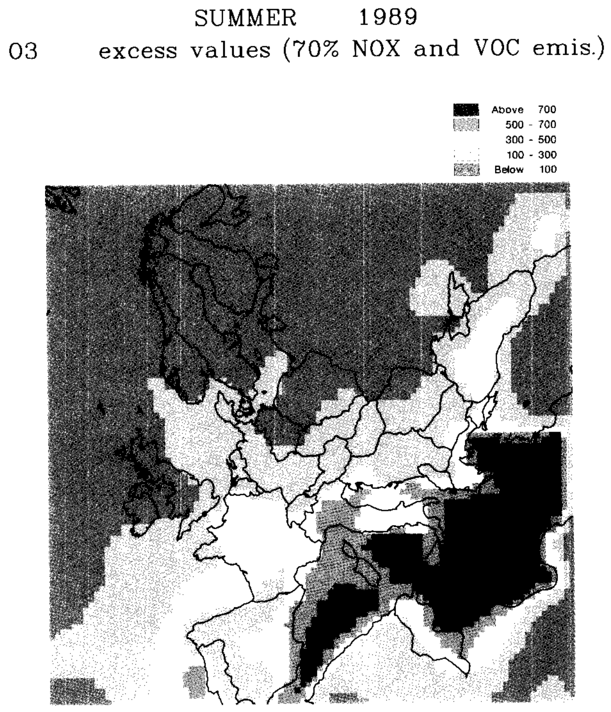

Figure 6.8. Distribution of the excess ozone (percentages: 100 * EXCESS/5300) in 1989 when both the NO_x and anthropogenic VOC emissions are reduced by 30%.

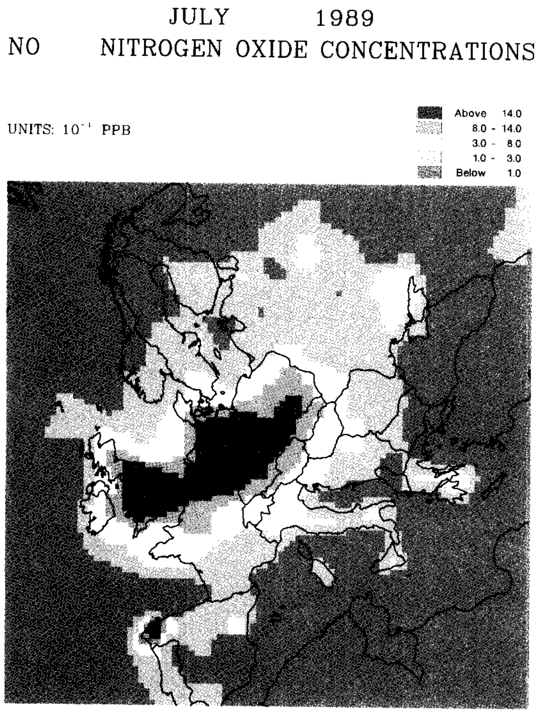

Figure 6.9. Distribution of the concentrations of nitrogen oxide in Europe in July 1989.

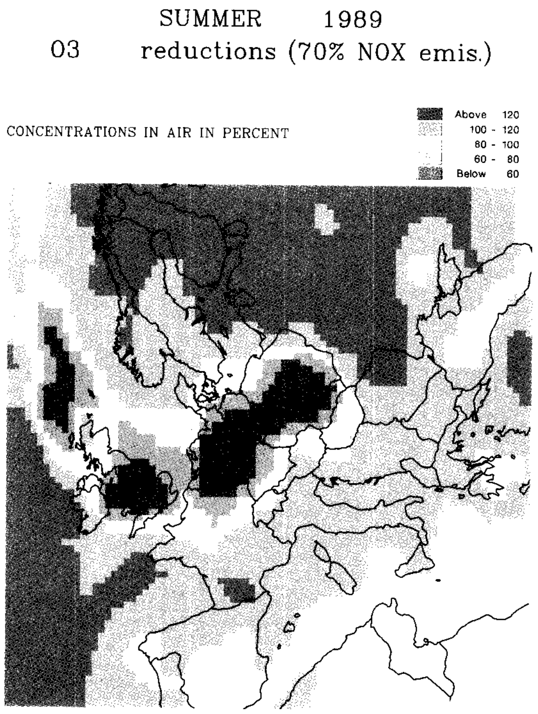

Figure 6.10. The excess ozone in 1989 (the run where the NO_x emissions are reduced by 30% related to the basic run).

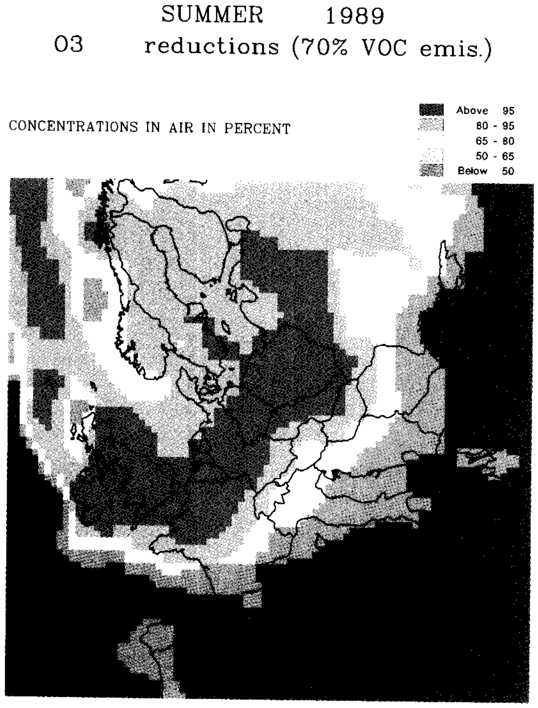

Figure 6.11. The excess in 1989 (the run where the anthropogenic VOC emissions are reduced by 30% related to the basic run).

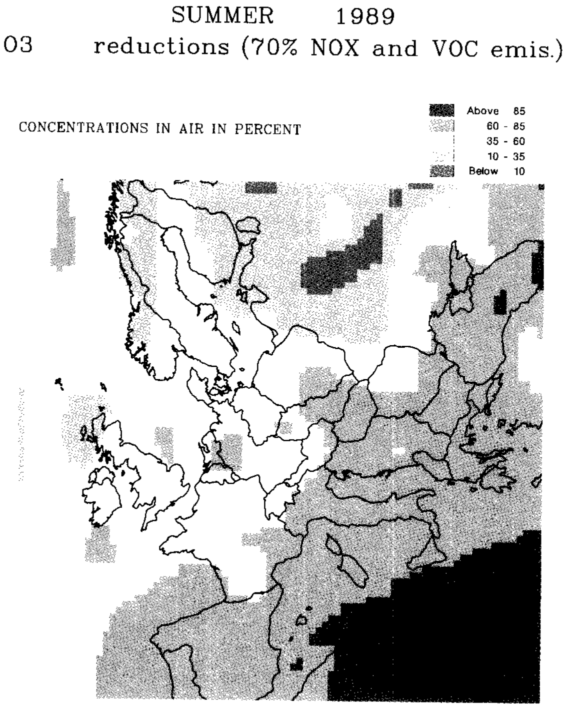

Figure 6.12. The excess ozone in 1989 (the run where both the NO_x and the anthropogenic VOC emission are reduced by 30% related to the basec run).

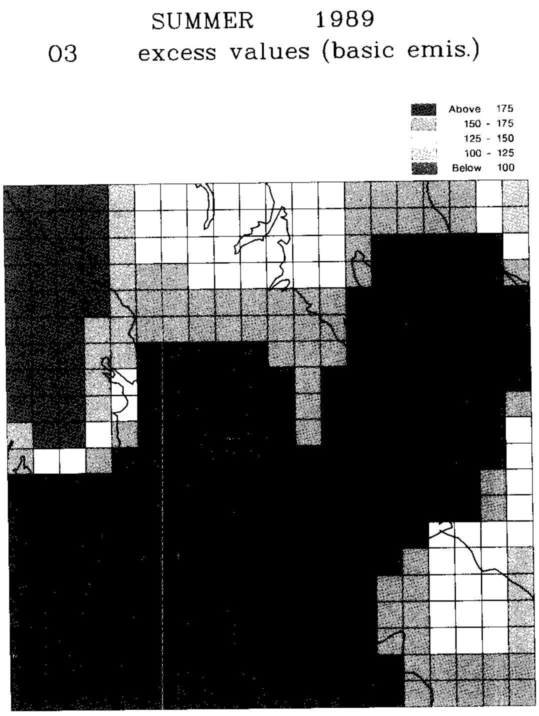

Figure 6.13. Distribution of the excess ozone (percentages: 100 * EXCESS/5300) in 1989.

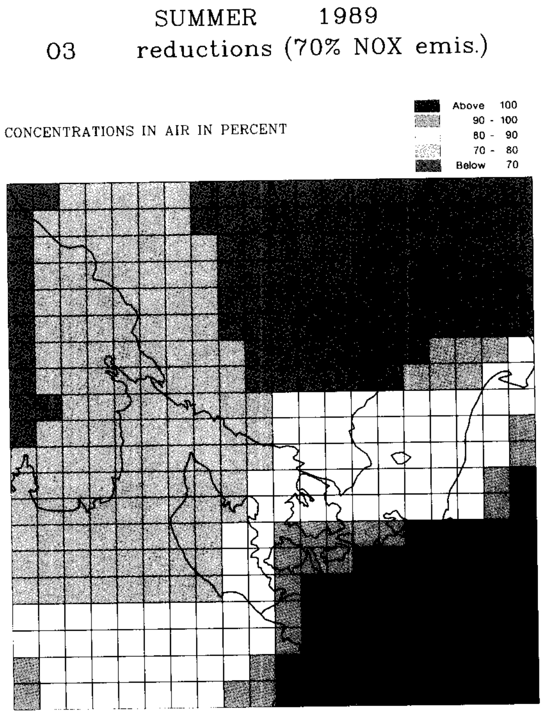

Figure 6.14. Distribution of the excess ozone in 1989 (the run where the NO_x emissions are reduced by 30% related to the basic run).

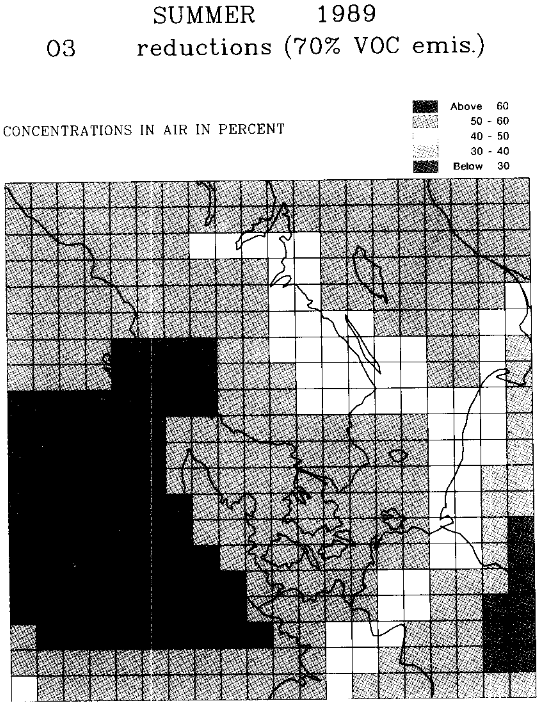

Figure 6.15. Distribution of the excess ozone in 1989 (the run where the anthropogenic VOC emissions are reduced by 30% related to the basic run).

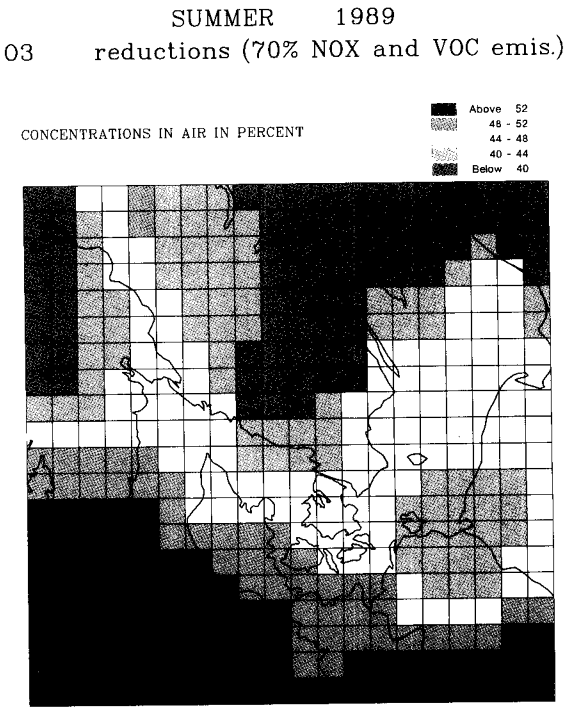

Figure 6.16. Distribution of the excess ozone in 1989 (the run where the NO_x and the anthropogenic VOC emissions are reduced by 30% related to the basic run).

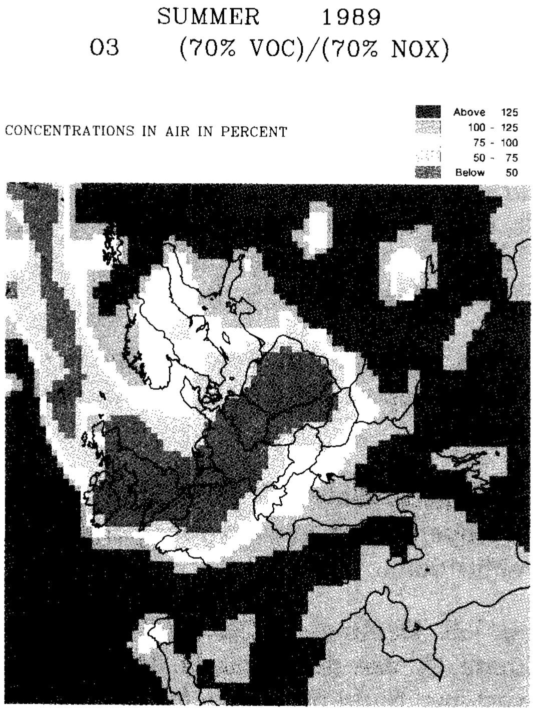

Figure 6.17. The reductions corresponding to 70% VOC emissions divided by the reductions corresponding to 70% NO_x emissions.

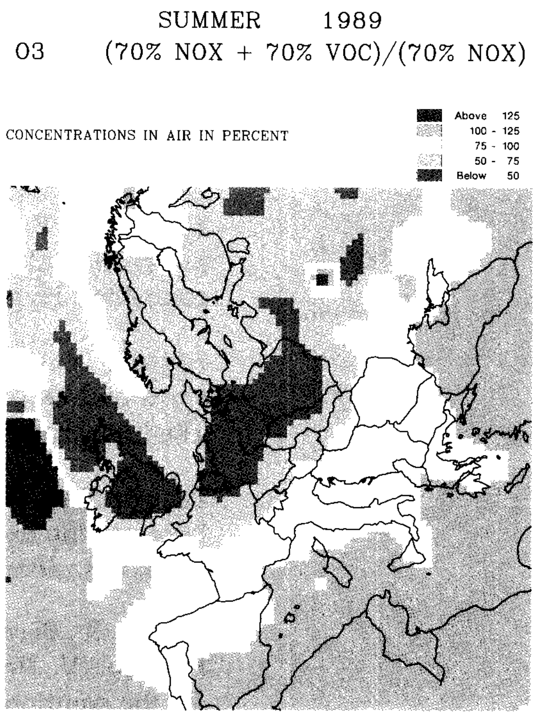

Figure 6.18. The reductions corresponding to 70% NO_x and 70% VOC emissions divided by the reductions corresponding to 70% NO_x emissions.

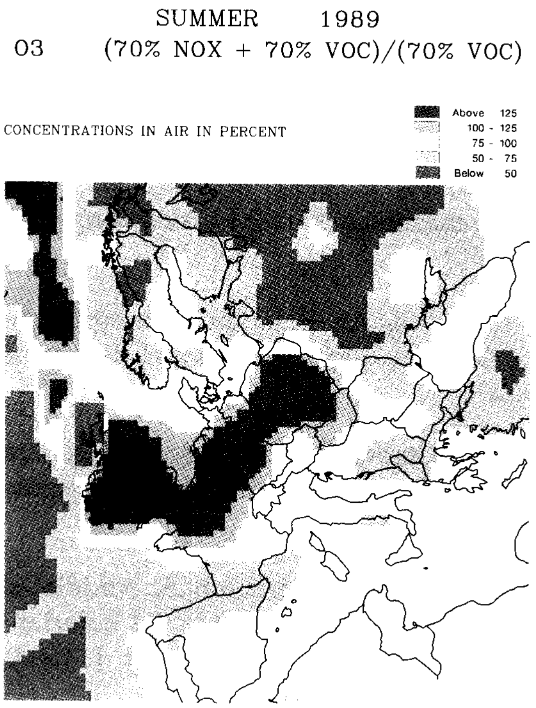

Figure 6.19. The reductions corresponding to 70% NOx and 70% VOC emissions divided by the reductions corresponding to 70% VOC emissions.

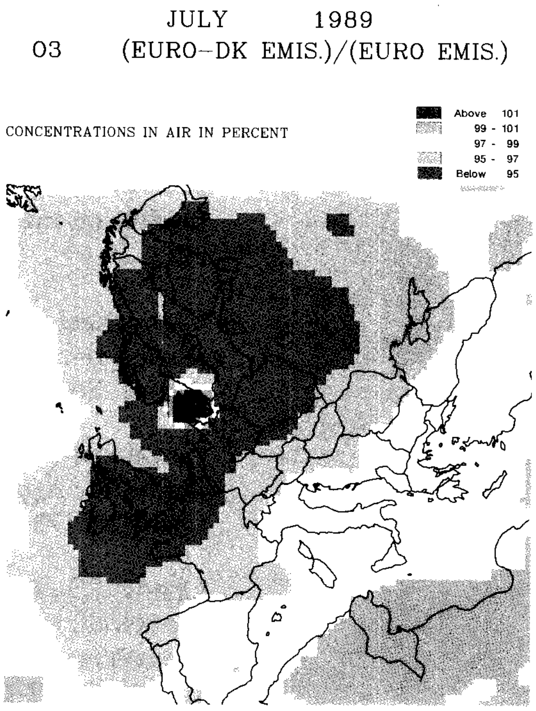

Figure 6.20. Distribution of the excess ozone in the case where all Danish emission are set to zero (percentages in relation to the basic run).

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7 Modelling photochemical air pollution in urban areas

Ole Hertel, Ruwim Berkowicz,
Elisabetta Vignati, Finn Palmgren

7.1 Introduction

High pollution levels in urban areas

Air pollution concentrations in urban areas are for many of the pollutants an order of magnitude higher, or even more, than in the rural areas. Very high concentrations of primary pollutants lead to a different chemistry than in the rural areas. The most important part of this chemistry is dominated by relatively few reactions.

Worst case situation at low wind

In urban areas the traffic density is high, and traffic is therefore the main source to air pollution. This counts especially for nitrogen oxides which are produced from atmospheric nitrogen during combustion processes. Generally the air pollution levels depend highly on the meteorological conditions. For ground level sources, like traffic, the highest concentrations occur at low wind speed.

More wind in Denmark than e.g. Milan

Characteristic for the Danish urban areas is the strong mixing due to mechanical turbulence (turbulence created by the wind friction towards the surface). Thus a comparison of the air quality in two similar streets of Copenhagen and Milan (Vignati et al. 1995), with respect to the climatological conditions, show that a much higher frequency of low wind speeds is responsible for considerably higher pollution levels in Milan than in Copenhagen. A typical residence time in Danish urban areas is 15 to 30 min, whereas in Milan it can be 1 to 2 hours and in extreme cases even more.

The high degree of mixing and the dominance of few chemical reactions mean that a box-model can be a good approximation for estimation of the urban background pollution concentrations in Danish cities.

7.2 Chemistry of nitrogen oxides in urban areas

Chemistry of nitrogen oxides in urban areas

Due to the short residence time of the air masses, the chemistry of nitrogen oxides (NO_x) in Danish urban areas can be roughly described by only two reactions: transformation of NO to NO_2 by the reaction with ozone (Equation 2.17), and the photodissociation of NO_2 (Equation 2.16). The rate of change of concentrations of NO, NO_2 and O_3 in the urban area can thus be expressed by (Hertel, Berkowicz 1989):

$$\frac{d[NO]}{dt} = -k[NO][O_3] + J[NO_2] + \frac{[NO]_v}{t} + \frac{[NO]_b - [NO]}{t} \qquad (7.1)$$

$$\frac{d[NO_2]}{dt} = k[NO][O_3] - J[NO_2] + \frac{[NO_2]_v}{\tau} + \frac{[NO_2]_b - [NO_2]}{\tau} \qquad (7.2)$$

$$\frac{d[O_3]}{dt} = -k[NO][O_3] + J[NO_2] + \frac{[O_3]_b - [O_3]}{t} \qquad (7.3)$$

where J is the photodissociation reaction rate coefficient of NO_2 and k is the chemical reaction rate coefficient for the reaction between NO and O_3.

Three govering equations

The first two terms in Equations 7.1 - 7.3 account for the transformations due to chemical reactions. Thereafter follows the contribution to the concentrations from the emission in the urban area, and the exchange rate of the air masses between the urban air and the rural background air.

Exchange with rural background

The rate of exchange between the urban and rural air is governed by the time constant τ, which is defined as D_{city}/u, where D_{city} is the effective transport length over the city centre and u is the wind speed above roof level. $[NO]_v$ and $[NO_2]_v$ are contributions to NO and NO_2 concentrations due to direct emission. The terms in Equations 7.1 to 7.3 with index b are the rural background concentrations of the respective compounds.

Urban background model

Equations 7.1 - 7.3 have been used in a numerical model for the Danish urban background concentrations (Hertel, Berkowicz 1990). The implementation was performed on data for Vesterbrogade and Stormgade in Copenhagen. The results showed average concentrations in the right range, but with a large scatter.

Example of NO, NO_3 and NO_2 in urban background

The fact that the NO_x chemistry is governed by the reaction between NO and ozone and the photodissociation of NO_2 is illustrated in Figure 7.1. The figure shows the urban background concentrations of ozone and NO_2 versus NO_x. It is seen that ozone decreases for increasing NO_x concentrations. The NO_2 concentrations increase with NO_x until the available ozone concentration is exceeded. In Figure 7.1 only daytime, hours where the traffic density is high and the concentrations of ozone arriving from the rural background areas are largest, are selected. The observed scatter is mainly due to differences in mixing conditions, but also to variations in rural background ozone levels.

in mixing conditions, but also to variations in rural background ozone levels.

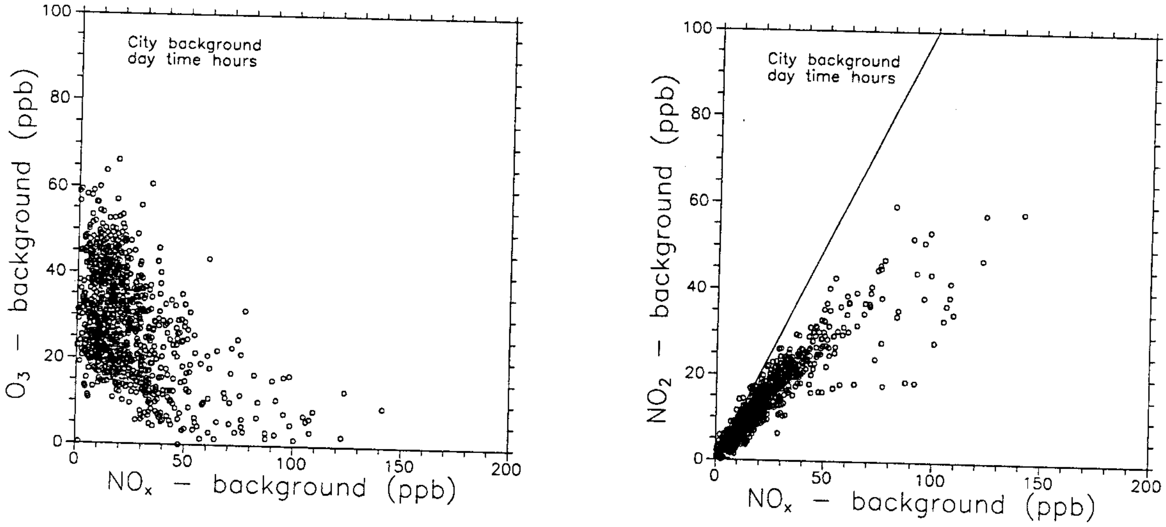

Figure 7.1. Measured urban background concentrations of ozone and NO_2 versus NO_x. The ozone concentrations decrease with increasing NO_x concentrations. The NO_2 levels increase with a one to one relation with NO_x until the ozone available is used. Measurements are hourly mean concentrations from 1993 from the SMP-Traffic station on the roof of the H.C. Ørsted institute of the University of Copenhagen.

Weekly variation in traffic

The traffic intensity varies considerably during the day, but also from day to day during the week. Figure 7.2 shows the daytime average ozone and NO_x concentrations over the week. During the working days the NO_x concentrations are relatively constant, but in the weekend, the concentrations decrease considerably due to the lower traffic density. As a result of the lower NO_x concentrations, ozone has slightly higher concentrations.

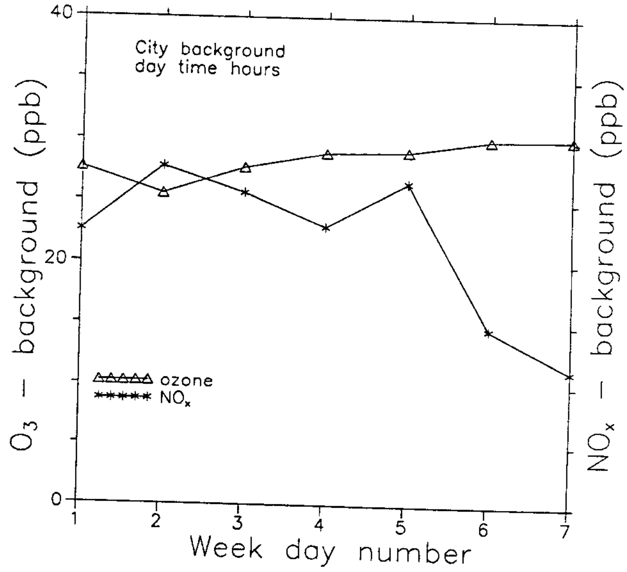

Figure 7.2. Weekly variation in the daytime ozone and NO_x concentrations in the urban background air. Measurements from 1993 from the H.C. Ørsted institute, Copenhagen. Day 1 represents Monday and day 7 Sunday.

7.3 Models for dispersion in urban streets

The OSPM developed at NERI

Measurements of urban air pollution are usually confined to a few locations in the city area. Monitoring stations are often situated in streets with significant traffic or in places where severe pollution problems are expected. Such measurements are naturally influenced by the very local conditions and care must be taken in interpretation of the results. Berkowicz et al. (1995a) described how measurements of air pollution in streets can be used for evaluation of urban air quality by means of meteorological analysis and model calculations. A model for air pollution in urban street - the Operational Street Pollution Model (OSPM) was developed at the Danish National Environmental Research Institute (Hertel, Berkowicz 1989; Berkowicz et al. 1995b). This model can be used for urban traffic planning and for policy assessment. Only a brief description of the model will be given here, however some examples of implementation of the OSPM will be given later in the Chapter.

Conditions in a street canyon

The dispersion of traffic emissions in urban areas is highly influenced by buildings. The main properties of the wind flow in a street canyon are well known. When the wind direction is perpendicular to the street direction, a vortex is generated in the street canyon, whereby the wind flow at street level is opposite to the flow above roof level (Figure 7.3).

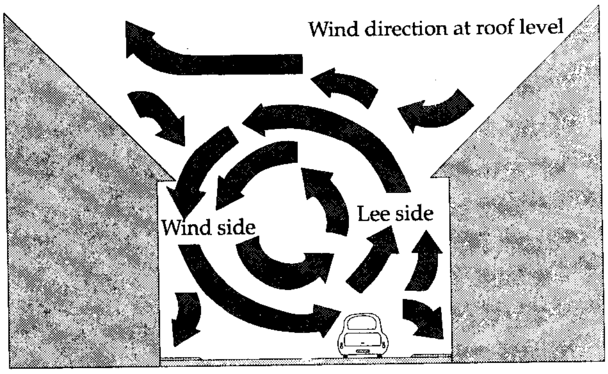

Figure 7.3. Schematic illustration of wind circulation in a street canyon. Windward and leeward sides are defined with respect to wind direction at roof level.

Other models: STREET and CPBM

This phenomenon was already taken into account in one of the first street pollution models: the STREET model (Johnson et al. 1973). A much more advanced approach was introduced by Yamartino and Wiegand (1986) in the Canyon Plume Box Model (CPBM). Results of the test of this model showed significant improvement in predictive ability compared to the simple STREET-model. A similar concept to the CPB-model is implemented in OSPM.

Three contributions to the level in a street

The OSPM calculates street concentrations as the sum of three contributions: the direct contribution from the traffic to the receptor point at the pavement on one side of the street, the contribution from recirculation inside the street and finally the contribution from the city background. The direct contribution is calculated applying a plume formula and the recirculation is simulated by a simple box model. The city background is the contribution from long range transport and from other sources inside the urban area i.a. traffic in other streets.

Comparison to streets in Copenhagen

In Berkowicz et al. (1995b) OSPM calculations were compared to measurements from three streets in Copenhagen: H.C. Andersens Boulevard, Bredgade and Jagtvej. The first two stations are operated under the Greater Copenhagen Air Pollution Monitoring Programme (HLU) and the last is operated under the National Air Quality Monitoring Programme (LMP III). The OSPM was shown to reproduce the observed dependency of the observed concentrations versus wind speed and wind direction.

Other streets than street canyons

For a long time there has been a need for improving the model in order to describe streets that cannot be categorized as street canyons. In Berkowicz et al. (1995a) the first step in this direction was made by allowing the specification of wind sectors in which there are openings between buildings along the street. By this modification, it is now possible to simulate dispersion in streets with different configurations.

Comparison to measurements at the Limfjords Bridge in Aalborg

In Hertel et al. (1995a) model calculations were performed for the street Vesterbro in Aalborg. The monitoring station at Vesterbro in Aalborg is placed on the first part of the Limfjord Bridge between Aalborg and Nørresundby. The monitoring site has a complex configuration. The street is orientated close to north-south with the monitoring station placed on the east side. At the station the street width is about 42 m. On the east side of the street the building height is about 11 m, while on the opposite side a 38 m high building is situated. Large part of the street is open.

Variation with wind speed and wind direction

Figures 7.4 and 7.5 show the observed and calculated hourly mean NO_x concentrations versus wind speed and wind direction for 1994 at Vesterbro. It appears from the figures that even with this very complex street configuration, the model is able to reproduce the observed dependency on wind speed and wind direction. Figure 7.6 shows a scatter plot of computed versus measured concentrations. In general the results are in good agreement with the observed concentrations, albeit with a slight tendency for overestimation of the low concentrations and underestimation of the high concentrations.

Some of the scatter in Figure 7.6 may be due to the uncertainties in traffic data. The traffic data used for the calculations are rather uncertain, especially with respect to fraction of the heavy traffic.

Input data from roof station

For the calculations, meteorological data and city background concentrations are obtained from a monitoring site located on a roof of a nearby building.

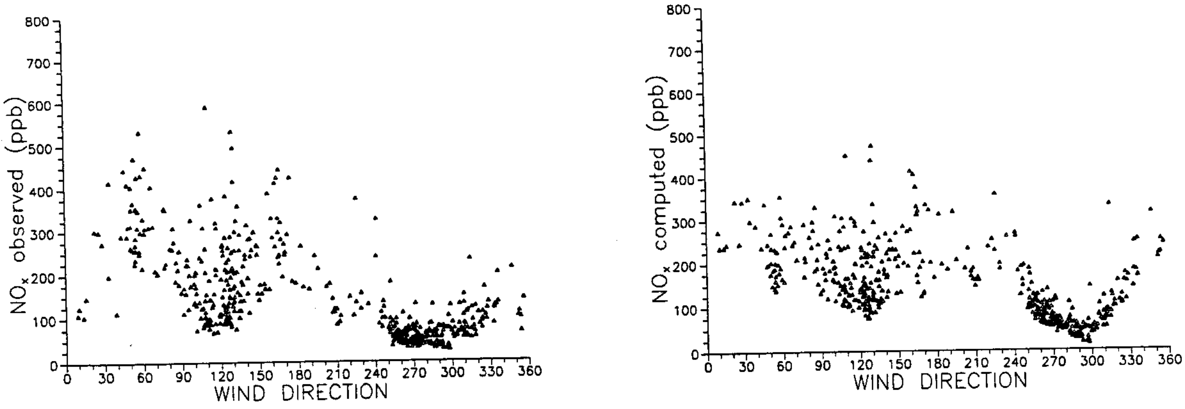

Figure 7.4. Measured and computed NO_x concentrations versus wind direction for 1994 at the east side of Vesterbro in Aalborg.

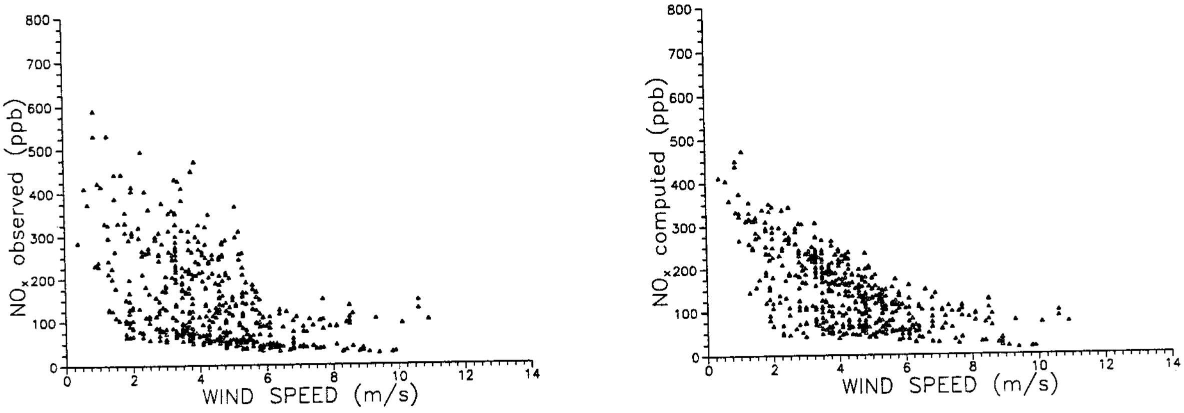

Figure 7.5. Measured and computed NO_x concentrations versus wind speed for 1994 at the east side of Vesterbro in Aalborg.

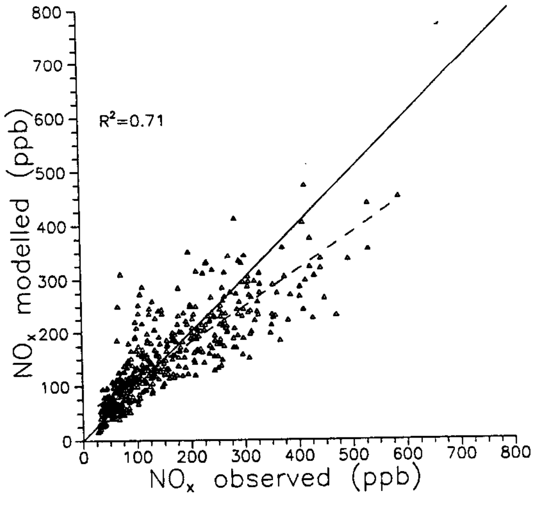

Figure 7.6. Computed versus measured NO_x concentrations for 1994 at the east side of Vesterbro in Aalborg.

7.4 Model description of NO_2 in an urban street

NO, NO_2 and O_3 in a street

Nitrogen dioxide (NO_2) concentrations in urban streets can be expressed by the same Equations 7.1 - 7.3 as for the urban background air. In this case the approximation is better than for the urban background air, since a typical residence time in an urban street is of the order of 30 s, and all other reactions than Equation 2.15 and Equation 2.16 are certainly of no importance.

Exchange with urban background

The exchange rate is in this case defined as $\tau = H/u_d$, where H is the building height, and u_d is the exchange velocity. $[NO]_v$ and $[NO_2]_v$ are concentrations of NO and NO_2 due to direct emission from vehicles in the street. The terms with index b are in this case the urban background concentrations of the respectively compounds.

Steady state

Assuming that a steady state is achieved, i.e. that all time derivatives become zero, we set left hand side of Equations 7.1 - 7.3 equal to zero.

Equations 7.1 - 7.3 describe thus the chemical transformations and exchange with urban background air in an urban street. They are equivalent to the following mass conservation Equations:

$$[NO_2] = [NO_2]_v + [NO_2]_b + [O_3]_b - [O_3] \quad (7.4)$$

$$[NO_x] = [NO_x]_v + [NO_x]_b \quad (7.5)$$

$$[NO_x] = [NO] + [NO_2] \quad (7.6)$$

From Equations 7.1 - 7.6 we obtain:

$$[NO_2] = 0.5\left[B - \left(B^2 - 4\left([NO_x]x[NO_2]_o + [NO_2]_n xD\right)\right)^{1/2}\right] \quad (7.7)$$

where $B = [NO_x] + R + [NO_2]_o + D$

$[NO_2]_n = [NO_2]_v + [NO_2]_b$

$[NO_2]_o = [NO_2]_b + [O_3]_b$

$R =$ J/k, is the photochemical equilibrium rate

$D =$ $1/(kx\tau)$, is the exchange rate

Help variables

$[NO_2]_n$ is the concentration of NO_2, which would be in the street in the case of no chemical transformation. $[NO_2]_o$ is the concentration, which would be in the street if all ozone was used for formation of NO_2.

Formula incorporated in OSPM

Equation 7.7 is the basic model parameterization for the formation of NO_2 in an urban street. The equation is incorporated in the Operational Street Pollution Model (Hertel, Berkowicz 1989; Hertel et al. 1990; Berkowicz et al. 1995a;b). The OSPM is developed in order to model dispersion and chemistry of pollutants from traffic in urban streets.

Comparison of calculated NO_2 with OSPM to measurements in streets

Figure 7.7 shows measured and computed hourly mean concentrations of NO_2 versus measured NO_x for Jagtvej in Copenhagen. The relationship between NO_2 and NO_x is shown for different levels of urban background ozone, and it is seen that in general the NO_2 part of NO_x increases for increasing ozone levels. This is in accordance with what was expected. The model is seen in general to reproduce the relationship between NO_2 and NO_x well.

Good agreement between model and observations

Figure 7.8 shows the modelled versus observed NO_2 concentrations for Jagtvej, Copenhagen. There is an excellent agreement between the computed and the measured concentrations.

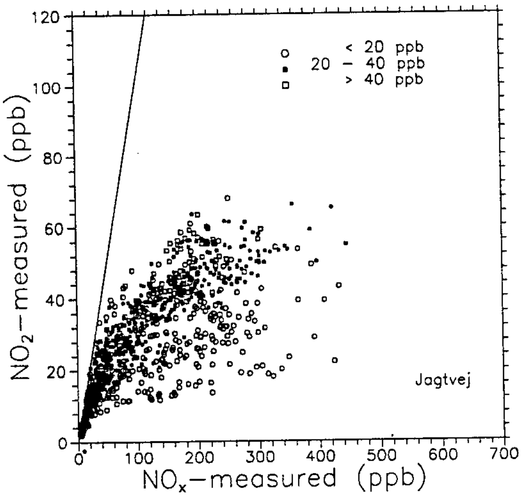

Figure 7.7. Measured and computed hourly mean concentrations of NO_2 versus measured NO_x Jagtvej, Copenhagen 1993. The relationship between NO_2 and No_x is shown for different levels of urban background ozone. The full line represents the one to one relation.

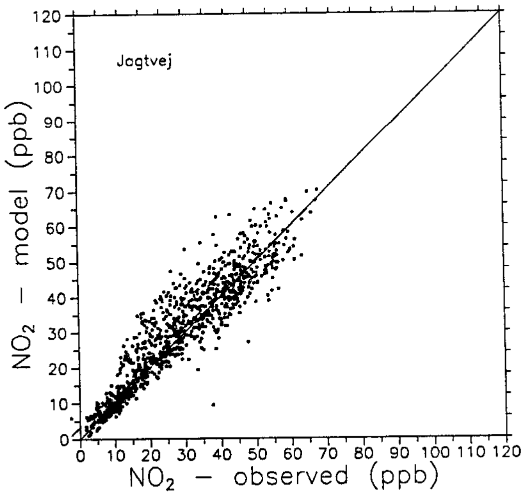

Figure 7.8. Modelled versus observed NO_2 concentrations for Jagtvej, Copenhagen 1993. The full line represents the one to one relation.

The comparisons show that NO_2 concentrations in an Danish urban street can be described well by Equation (7.7). Similarly good results have been obtained from calculations for other streets.

Ozone is not build up in Danish cities as e.g. in Los Angeles

In the case of smog episodes in e.g. Los Angeles and Athens different conditions are present. Due to frequent stagnant meteorological situations with practically no winds the residence times of the pollutants are much longer than in Danish urban areas. In this case the long residence time together with strong solar radiation and high emission intensity gives rise for a build up of ozone within the urban area. This cannot be found for Danish conditions.

7.5 Examples of model scenarios for NO_x and NO_2 calculations

Øresund scenarios

The simplified chemistry for nitrogen dioxide in urban streets, described in the previous section, is implemented in OSPM. One of the main advantages of such a model is that it can be used for prediction of future concentrations under different conditions. In Berkowicz et al. (1996) the OSPM was used for scenario calculations for the future Øresund link between Denmark and Sweden. These scenarios were based on an estimated diurnal traffic of 8 to 10,000 vehicles across the link. Calculations were performed for the traffic amount as in year 1992 and for two future situations around year 2000 assuming that 40 or 60% of the Danish cars have been equipped with catalytic converters. It was further assumed that the background pollution levels are unchanged. Calculations were performed for seven different streets on Amager island, where the link will be established in order to study the effect on pollution levels from the change in traffic amounts. The traffic data for the seven streets are given in table 7.1.

The traffic data were distributed over 24 h and split into two groups: below and above 2,5 tons, respectively.

Figure 7.9 shows the computed 98 percentiles for the present and the different scenarios year 2000 and year 2010. Also in this case it can be observed that NO_2 is considerable less affected than the NO_x concentrations by the increase in catalytic converters.

Figure 7.10 shows computed monthly averages of NO_x and NO_x for Amagerbrogade for 1992, 2000 and for year 2010 assuming 40 and 60% catalytic converters. It is seen that even though a substantial reduction in NO_x concentrations is obtained, the NO_2 levels are only little effected even in the case of 60% catalytic converters.

Table 7.1. Traffic counts for selected streets and scenarios in an investigation concerning the impact on local air pollution of the Øresund link between Denmark and Sweden. (Anders Nyvig A/S 1996, and NERI's own calculations).

Scenario year	1992	2000	2010	2010	2010
		With land construction and bridge	Without construction	With land construction	With land construction and bridge
Cars under 3,5 ton					
Njaldsgade, East of Artillerivej	6700		34000	15000	30000
Englandsvej, west of Amagerbrogade	15000		16000	19000	22000
Englandsvej, North of Følfodvej	39000		57000	26000	26000
Amagerbrogade, North of Englandsvej	20000		15000	21000	21000
Torvegade, East of Knippelsbro	31000	36000	38000	42000	44000
Vejlands Allé, West of Røde Mellemvej	44000		63000	28000	26000
Motorway, West of Amager Landevej	25000		43000	30000	46000
Vans over 3,5 ton					
Njaldsgade, East of Artillerivej	140		1200	660	680
Englandsvej, west of Amagerbrogade	660		700	780	750
Englandsvej, North of Følfodvej	1600		2600	1200	1100
Amagerbrogade, North of Englandsvej	800		850	1100	1100
Torvegade, East of Knippelsbro	1100	1400	1600	1600	1600
Vejlands Allé, West of Røde Mellemvej	1600		3000	940	940
Motorway, West of Amager Landevej	630		1800	730	1100
Busses					
Njaldsgade, East of Artillerivej	300		830	830	830
Englandsvej, west of Amagerbrogade	100		380	380	380
Englandsvej, North of Følfodvej	160		260	260	260
Amagerbrogade, North of Englandsvej	260		700	700	700
Torvegade, East of Knippelsbro	580	830	830	830	830
Vejlands Allé, West of Røde Mellemvej	36		290	290	290
Motorway, West of Amager Landevej	160		250	-	-

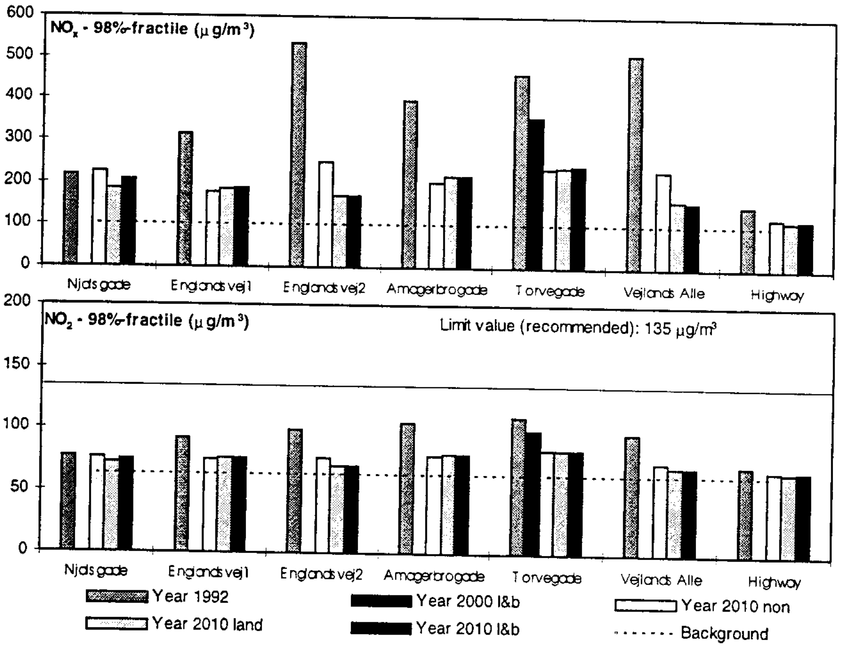

Figure 7.9. Computed 98 percentiles of 1 h mean nitrogen oxide concentrations at the south side of the seven streets for the six scenarios: 1992, 2000 with land constructions and bridge, 2010 without the link, 2010 with land construction, 2010 with land construction and bridge and the contribution from background levels.

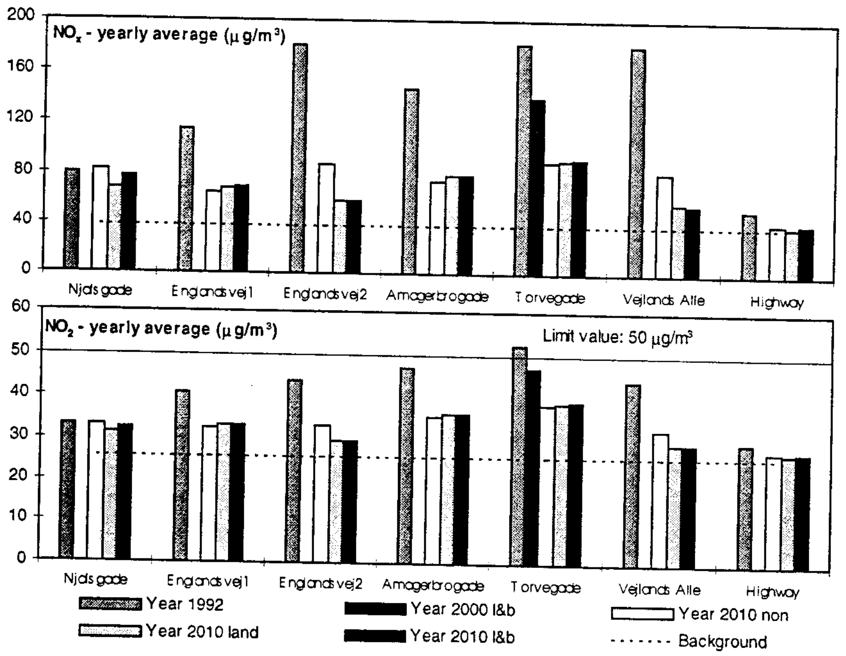

Figure 7.10. Yearly averages of NO_2 pollution levels on the south side of the seven streets for the six scenarios: . 1992, 2000 with land constructions and bridge, 2010 without the link, 2010 with land construction, 2010 with land construction and bridge and the contribution from background levels.

7.6 Modelling volatile organic compounds in urban areas

VOC in urban areas

Only few measurements of VOC concentrations have been reported for Danish urban areas. Hansen and Palmgren (1995) performed an analysis of results from campaign measurements from Copenhagen. Due to the very limited amount of available measurements, also very little has been done concerning modelling of VOC's for urban areas. At NERI it is planned to use the Atmospheric Chemistry and Deposition (ACDEP) Model (Hertel et al. 1995b) for calculating urban background concentrations. For this use the model need a very fine resolution emission inventory (grid size of 1x1 km^2 or 5x5 km^2).

Use of OSPM for estimating emission factors

The OSPM has recently been used for estimating emissions af VOC's based on analysis of campaign measurements (Palmgren et al. 1995).

Atmospheric pollution dispersion models are usually used for calculation of air quality based on known theoretical relationships between emissions, meteorology and air concentrations. On the other hand, combining model calculations with ambient pollution measurements allows in-situ determination of emissions.

Considering dispersion in streets of non-reactive or only slowly reactive car exhaust gasses, the chemical transformations can often be disregarded, and the problem can be formulated in the following way:

$$c = F(\text{meteorology}) * Q + c_{\text{background}} \qquad (7.8)$$

where c is the concentration of a particular pollutant in the street, Q is the emission from the traffic in the street and F(*meteorology*) is a function describing dispersion processes. $c_{\text{background}}$ is contribution to pollution concentrations in the street from all other sources than the traffic in the street. The dispersion function F(*meteorology*) is given by the Operational Street Pollution Model (OSPM) (Hertel, Berkowicz 1989; Berkowicz et al. 1995a,b).

Equation 7.8 can be used for calculations of hourly emissions from traffic, provided that both street and background concentrations are available. In (7.9) the index k refers to a particular hour of the day.

Results form OSPM

$$Q_k = \frac{c_k - c_{k,\text{background}}}{F_k(\text{meteorology})} \qquad (7.9)$$

In Figure 7.11 the hourly emissions of NO_x, CO and Benzene for the traffic in Jagtvej, calculated using (7.9), are shown for working days in 1994. The dots represent the single observations while the average hourly values are given by dashed lines. The scatter, compared to the average values, is due to real variations in emissions from traffic, but also to model uncertainty and uncertainty in measurements.

Diurnal pattern

The diurnal variation of emissions is mainly determined by the diurnal variation of traffic amount, its composition and driving pattern. The average diurnal variation of traffic in Jagtvej, with decomposition into light vehicles (passenger cars, vans) and heavy vehicles (trucks, buses), is shown in Figure 7.12. From comparison of emission and traffic patterns, it is evident that CO and Benzene emissions are highly correlated with the light traffic, i.e. mainly gasoline powered cars. The NO_x emissions are, on contrary, significantly influenced by the heavy traffic, which consists mainly of diesel cars.

Light and heavy traffic

Detailed traffic counts, with distribution on different vehicle categories, provides also the opportunity for estimation of emission factors for these vehicle categories. The total emission from traffic can by expressed as

$$Q_k = N_{l,k} q_l + N_{h,k} q_h \tag{7.10}$$

where q_l and q_h are emission factors for light and heavy traffic, respectively. The hourly traffic amounts for the two categories are given by $N_{l,k}$ and $N_{h,k}$. Such an equation can be written for each single observation (hour). Due to uncertainties in estimation of emissions and traffic data it is more effective to use average hourly values (an average over whole period for each day hour) what results in 24 equations with 2 unknowns: q_l and q_h. Using standard statistical methods, as e.g. the least squares method, we can estimate "the best fit" values of the emission factors q_l and q_h. The necessary condition for a successful application of this method is, however, that the traffic patterns of light and heavy vehicles are different. In the case of a correlated traffic pattern, the estimation of the emission factors for the two vehicle categories becomes very uncertain. Under such circumstances, only the average emission factor for the whole traffic can be estimated. Fortunately, the light and heavy traffic in Jagtvej have so different patterns that the outlined procedure can be used here. Due to small percentage of heavy traffic, estimations of emission factors for this category are very uncertain.

Average emission factors obtained

Emission factors for NO_x, CO and Benzene, estimated using the presented method, are shown in Table 7.1. The listed emission factors refer to 50 km/h travelling speed. For light vehicles they are furthermore given for cars without catalytic converters and also as average factors for present composition of the vehicle fleet. It is assumed here that 25% of passenger cars were equipped with catalytic converters in 1994 and that the catalists reduce emissions by 90% (this might be an overestimation for benzene). The corresponding diurnal variation of the emissions from traffic, calculated with the estimated emission factors, traffic data and taking into account the diurnal driving pattern, is depicted in Figure 7.11.

Comparison to emission factors obtained by others

The calculated emission factors for NO_x and CO, presented in Table 1, agree well with previously reported results for city traffic in Denmark (Environmental Protection Agency 1991; Sorenson, Schramm 1992; Road Directorate 1992). To our best knowledge, there exist no previous estimations of Benzene emission factors for Danish cars. Bailey et al. (1990) report on an English investigation on passenger vehicles, which were mostly 1986 market leader models.

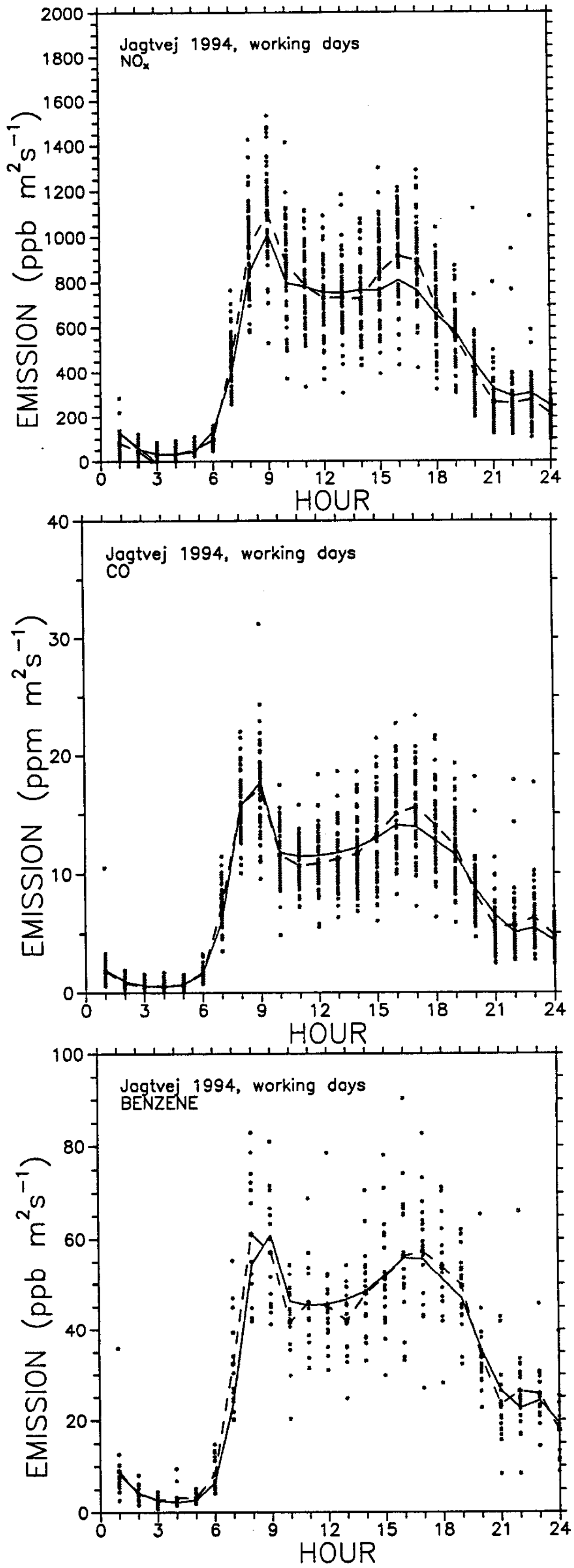

Figure 7.11. Hourly emissions of NO$_x$, CO and Benzene calculated using Equation (7.9) (dots). The average values a re given by dashed lines. Emissions calculated from traffic data are shown by solid lines.

They measured emission factors for benzene in the range 0.1 - 0.2 g/km (for travelling speed of ca. 50 km/h). These values are smaller than results from the present investigation. It is not clear, whether this is due to higher contents of benzene in the fuel used in Danish cars or to different driving pattern. The uncertainty in estimation of the emission factors using the presented method may also influence the results reported here. More work is needed in order to refine the method and get a better confidence on the estimations.

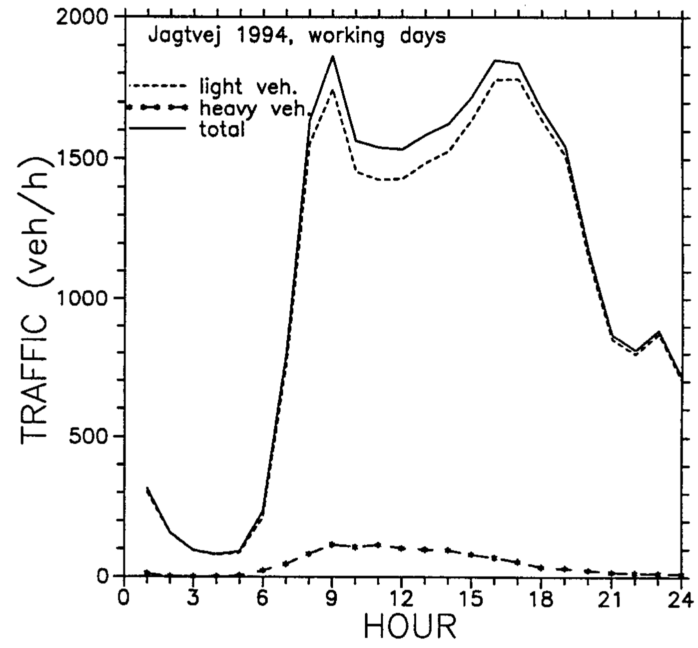

Figure 7.12. Diurnal variation of traffic in Jagtvej.

Table 7.2. Emission factors for NO_x, CO and Benzene (g/km) estimated in this work. The uncertainties are related to the mathematical procedure only.

	LIGHT		HEAVY
	non-cat	all	
NO_x	2.7 ± 0.06	2.01	15.5 ± 0.74
CO	32.5 ± 0.55	24.4	11.6 ± 6.49
Benzene	0.4 ± 0.01	0.3	-0.02 ± 0.15[1]

[1] The negative emission factor is a manifestation of the large estimation uncertainty.

7.7 Long-term concentrations of benzene

Long term calculations for Jagtvej

The presumed carcinogenic properties of Benzene require estimations of long-term exposures. The available measurements in 1994 cover, however, only few months and a reliable annual average can not be evaluated. An alternative is estimation of concentrations using dispersion models. Such calculations were performed for Jagtvej using the OSPM model. Results are shown in Figure 7.13. Monthly averages calculated using the available measurements are also shown here. Concentration levels appear to be quite high. So far no limit value are specified in Denmark, but e.g. in The Netherlands a value of 10 μg/m^3 (ca. 3 ppb) is specified as a limit value for annual average concentrations (RIVM 1991). As it follows from results shown in Figure 7.13, the benzene levels in Jagtvej are higher than this value for all months of the year. The same tendency is apparent from the available measurements.

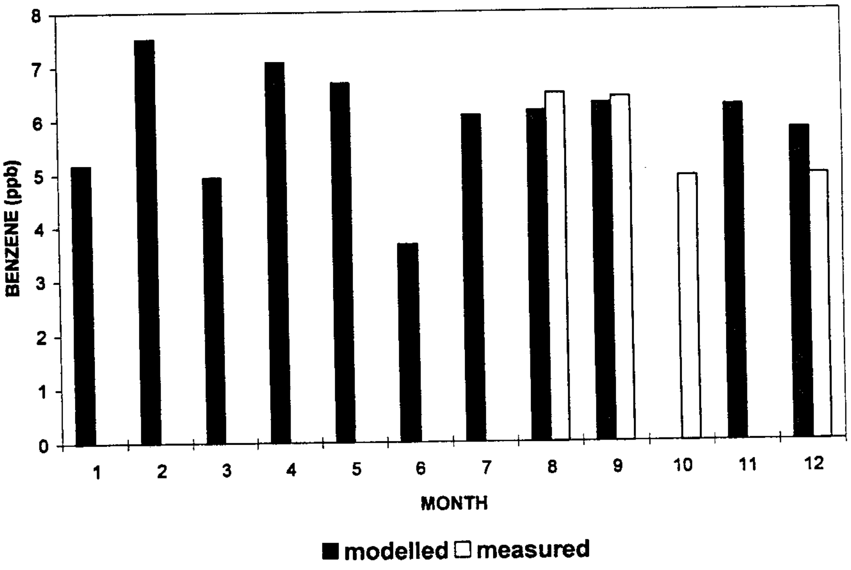

Figure 7.13. Monthly averages of benzene in Jagtvej. Measurements are available for 4 months in 1994 only.

7.8 Conclusions

Conditions in urban areas can be described by a simple box-model

The high degree of mixing and the dominance of few chemical reactions mean that a box model can be a good approximation for estimation of the urban background pollution concentrations in Danish cities.

OSPM reproduces the observations well

For the dispersion conditions in urban streets the Operational Street Pollution Model (OSPM) has shown to reproduce well the observed concentrations for a number of streets. Recent modifications have made the model able to handle complex street configurations different from typical street canyons.

NO, NO_2 and O_3 in urban areas

Nitrogen chemistry in Danish urban streets has been shown to be described very well by simply considering only two reactions: reaction between ozone and NO forming NO_2 and photodissociation of NO_2 back to NO and leading to reformation of ozone. For the urban background air the same procedure gives in average reasonable result but with a relatively large scatter.

Hydrocarbons in urban areas

The modelling of hydrocarbons in urban areas is still in the initiating phase. The OSPM has been used for estimation of traffic emissions of hydrocarbons which are in expected range.

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Danish Summary - Dansk resumé

Fotokemisk Luftforurening - danske aspekter

Faglig rapport fra DMU nr.199. Oktober 1997

Redigeret af *J. Fenger*
med bidrag fra *A. Bastrup-Birk, R. Berkowicz, A.H. Egeløv, T. Ellermann, J. Fenger. K. Granby, O. Hertel, M.F. Hovmand, K. Kemp, L. Mortensen, F. Palmgren, E. Runge, H. Skov, E. Vignati, Z. Zlatev.*

(Dette resumé er stort set en oversættelse af rapportens indledende kapitel)

Ozon - ven eller fjende?

I atmosfæren spiller ozon to helt forskellige roller. I stratosfæren, i omkring 20 km højde, beskytter det såkaldte "ozonlag" Jorden mod for meget ultraviolet stråling. Men i troposfæren, nær jordoverfladen, er fotokemisk luftforurening - eller ozonforurening efter hovedkomponenten - blevet et væsentligt miljøproblem.

Troposfærisk ozon er en såkaldt sekundær forurening, som - sammen med andre fotokemiske oxidanter - dannes i et kompliceret sæt reaktioner mellem kvælstofoxider og flygtige kulbrinter under indflydelse af sollys. Både de primære og de sekundære forureninger kan transporteres over lange afstande, og fotokemiske episoder kan derfor optræde i europæisk skala. Der er heller ikke simple relationer mellem lokale udslip og forureningsniveauer. De atmosfærekemiske reaktioner er beskrevet i rapportens kapitel 2.

Udslip af primære forureninger

De europæiske udslip af kvælstofoxider og kulbrinter er vokset med den generelle stigning i de menneskelige aktiviteter siden industrialiseringen i forrige århundrede. I de senere år synes udslippet af kvælstofoxider dog at være fladet ud.

Danske udslip af kvælstofoxider fra energisektoren er indtil de seneste år steget - i det væsentlige som følge af stigende aktivitet i transportsektoren. Udslip af flygtige kulbrinter er ligeledes steget, men med et relativt større bidrag fra rumopvarmning. Indførelsen af katalysatorer på benzindrevne biler, der er indregistreret efter 1. oktober 1990, vil dog antagelig vende tendenserne.

Kilder til - og udslip af - forureninger, der har betydning for fotokemisk luftforurening, behandles i kapitel 3.

Ozonniveauer

I Europa er niveauerne af troposfærisk ozon i landområder stort set blevet fordoblet i løbet af de sidste hundrede år, men synes nu at flade ud. I Danmark måles ozonkoncentrationen løbende i tre byer (København, Odense, Aalborg) og på fire landstationer. Foreløbig har tidsserierne dog ikke været lange nok til at påvise nogen entydig udvikling. Typiske niveauer ved landstationer er 25 ppb (50 $\mu g/m^3$) som årsmiddelværdier og med 98-percentiler på omkring det dobbelte. Tilsvarende niveauer er målt på hustage i byområder. I gadeniveau, og specielt i lukkede gaderum med meget trafik, er niveauerne meget lavere.

Oprindelsen til ozon i Danmark

Troposfærisk ozon i Danmark skyldes i det væsentlige langtransport, undertiden med episoder , der har oprindelse i Centraleuropa. I byerne er den dominerende reaktion med ozon en oxidation af kvælstofmonoxid (NO) fra biludstødning til kvælstofdioxid (NO_2). Derfor varierer niveauerne af ozon og kvælstofdioxid modsat, og stofferne kan i visse henseender opføre sig som én forbindelse. Desuden kan en reduktion af udslippet af kvælstofmonoxid medføre en forøgelse af ozonniveauerne, som det fx ses i weekender med med mindre trafik.

Danske målinger af fotokemisk luftforurening - specielt ozon - er gennemgået i kapitel 4.

Tærskelværdier

Et sæt tærskelværdier for ozon blev implementeret i Danmark i 1994. De er baseret på et EU-direktiv (92/72/EEC), som har til formål at beskytte både menneskeligt helbred og vegetation. Tærskelværdien for helbred overskrides kun få gange om året, medens værdien for vegetation hyppigt overskrides.

Skadevirkninger

Påvirkning af menneskeligt helbred er ikke behandlet i rapporten, men diskuteres i nyligt udkommet rapport fra Miljøstyrelsen, Miljøprojekt nr. 352: Sundhedsmæssig vurdering af luftforurening fra vejtrafik (P.B. Larsen, J.C. Larsen, J. Fenger, S.S. Jensen).

Ozon reagerer med overfladerne i åndedrætssystemet. Symptomerne er hoste, en fornemmelse af tørhed og en almindelig reduktion af ydeevne og velbefindende. I følge WHO kan der optræde sundhedseffekter af ozon ved gennemsnitlige niveauer over 100 $\mu g/m^3$.

Vegetation er mest følsom overfor ozon i dagtimerne. Ozon trænger ind i bladene gennem spalteåbningerne og angriber cellemembranerne. Resultatet er bl.a. en reduktion af fotosyntesen. For danske afgrødeplanter kan det svare til en 10% reduktion i udbyttet. Påvirkning af vegetation behandles i kapitel 5.

Internationale og internationale reduktionsplaner

De forenede Nationers økonomiske kommission for Europa (UNECE) etablerede omkring 1980 den såkaldte Geneve Konvention om langtrækkende, grænseoverskridende luftforurening. Den omfatter en række protokoller om reduktion af enkelte forureninger. Den gældende kvælstofdioxid-protokol forpligter de underskrivende lande til at stabilisere udslippene på 1987-niveauet. Danmark har imidlertid, sammen med 11 andre lande forpligtet sig til en reduktion på på 30% (for Danmark i forhold til 1986) før 1999. En protokol om flygtige kulbrinter opererer med en 30% reduktion i udslip i perioden 1985-1999.

Danske handlingsplaner omfatter mere langsigtede reduktioner. Således har "Tranporthandlingsplanen" som mål en 40% reduktion i de nationale udslip af kvælstofoxider og kulbrinter i perioden 1998-2000 og en 60% reduktion før år 2010.

Reduktionsscenarier

Man kan benytte modelberegninger af langtransport til vise, hvordan ændringer forureningsudslip påvirker ozonniveauerne. Det viser sig, at reduktioner i udslip af kulbrinter generelt er mere effektive end reduktioner i udslip af kvælstofoxider. Imidlertid vil ikke engang samtidige reduktioner af begge primære forureninger på en gang være nok til at forhindre, at der nogen steder i Europa kan opstå ozonniveauer, som er skadelige for vegetation.

Som diskuteret i kapitel 6 vil isolerede danske udslipsreduktioner have en forsvindende effekt i Europa som sådan, og de kan endda føre til forhøjede niveauer i Danmark.

Fotokemi i byområder

Fotokemiske reaktioner med kvælstofoxider i danske byområder kan rimeligt forenklet beskrives med kun to reaktioner: En oxidation af kvælstofmonoxid til kvælstofdioxid med ozon, og en fotodissociation af kvælstofdioxid. I kapitel 7 vises det, hvordan spredningsberegninger, der inkluderer disse to reaktioner, kan beskrive forureningsniveauerne af kvælstofdioxid i bygader.

Som en indledning til undersøgelser af byforurening med kulbrinter, er der påbegyndt modelberegninger af disse.

Konklusion

I Danmark er fotokemisk luftforurening et storskalafænomen, der kun kan påvirkes marginalt med isolerede nationale indgreb. Sammenlignet med Central- og Sydeuropa er niveauerne beskedne, og der er kun ringe påvirkning af menneskeligt helbred og velbefindende. De observerede niveauer er skadelige for vegetation og de planlagte reduktioner i udslip vil ikke fuldstændigt forhindre skader.

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