Effects of Environmental Conditions and Transport on Surface Ozone Concentrations in Finland

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Abstract

    Widespread ozone production takes place over Central Europe during the period April-September. Embedded in the background concentration of about 30 ppb, long-range transport episodes to southern parts of Finland are frequent. In northern parts of Finland, elevated concentrations are mainly observed in spring, when background concentrations of precursor species are higher, and lower dry deposition velocities favour a long-range transport of ozone. At the Finnish sites, the highest 1-hour ozone concentrations are between 75 and 90 ppb. In southern parts of Finland over 80 ppb concentrations have been observed. Both statistically and in the cases of high ozone concentrations studied, the concentration of the sum of gaseous nitric acid and particulate nitrate, which are oxidation products of nitrogen oxides, shows elevated levels. The anthropogenic origin of these elevated ozone concentrations was further confirmed by trajectory analysis, which shows that on these occasions the trajectories passed through areas of Europe having a high emission density of nitrogen oxides and volatile organic compounds. Based on observations at Utö, located in the northern Baltic Sea, the ozone production efficiency per NO_x molecule emitted seems to be high. These observations show that in northern Europe anthropogenic emissions of ozone precursors act as a source of tropospheric ozone in April-September but as a sink in October-February. The seasonal cycle of ozone production should be taken into account when climate effects of changing tropospheric ozone concentrations due to anthropogenic ozone precursors are estimated.

Key words: ozone, troposphere, photochemical pollution, long-range transport, trajectories, radiative forcing

1.   Introduction

    The chemical mechanism by which ozone is produced in urban air pollution was first described by *Leighton* (1961). Since then it has been found that there are decennial trends both in background and tropospheric ozone concentrations (*Penkett* and *Brice*, 1986; *Logan*, 1985; *Staehelin et al.*, 1994; *Marenco et al.*, 1994; *Volz-Thomas*, 1993). Substantial   increases   have   occurred   in   both   the   average   and   high   episodic

concentrations; the rate of increase has probably steepened after 1950 (*Staehelin et al.*, 1994; *Marenco et al.*, 1994). However, *Logan* (1994) reports that the increase has leveled off during recent years. Changes in ozone concentrations reflect general changes in both the photochemical processes and the oxidising capacity resulting from anthropogenic emissions (*Crutzen* and *Zimmermann*, 1991). Ozone is a powerful oxidising agent and high ozone concentrations have detrimental effects on human health and on vegetation (*PORG*, 1993). Ozone concentrations are also likely to have effects on ecosystems in Finland (*Laurila* and *Lättilä*, 1994). More recently, the importance of ozone as a greenhouse gas has been pointed out (*Wang et al.*, 1993; *Marenco et al.*, 1994).
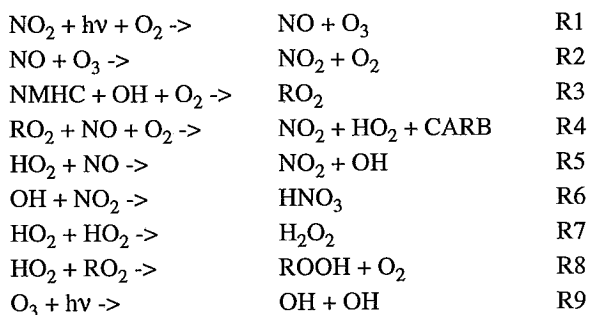
In Finland, routine surface-layer ozone concentration measurements began in the mid-1980's (*Hakola, et al.*, 1991). The measurements have been made as part of the international Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants (EMEP) and Global Atmospheric Watch (GAW), as well as to serve national needs. In the Finnish Meteorological Institute (FMI) scientific activities were boosted by participation in the European EUREKA project EUROTRAC (see e.g. *Borrell et al.*, 1994) and its subproject Tropospheric Ozone Research (TOR). A great deal of work has been carried out to measure (*Lindskog et al.*, 1993; *Laurila et al.*, 1994a; *Laurila et al.*, 1994b, *Laurila et al.*, 1995; *Laurila* and *Hakola*, 1996) and model (*Lindfors et al.*, 1995a) the concentrations and photochemistry of volatile organic compounds (VOC) in Finland. VOCs emitted by vegetation are in many parts of the world very important compounds in photochemical processes (*Chameides et al.*, 1992). The role of biogenic VOCs emitted from the boreal forests (*Lindfors et al.*, 1995b) is the subject of special scrutiny. The vast forest areas in Finland and the photochemical activity of biogenic species (*Hakola et al.*, 1993; *Hakola et al.*, 1994) also make this a high-priority research area in the future.

This presentation concentrates on the seasonal and diurnal behaviour of ozone concentrations using the ozone measurements conducted at the FMI. Special emphasis is placed on the photochemical formation of ozone and advection processes using trajectories and weather maps and the sum of gaseous nitric acid and particulate nitrate as a tracer of anthropogenic photochemical pollution. The seasonal cycle of ozone production efficiency is studied because it has implications on the anthropogenic perturbation of the concentrations of tropospheric ozone which is one of the most important greenhouse gases.

2.   *Basis of the ozone production in the troposphere*

The ozone formation mechanism (*Liu et al.*, 1987) is now shortly described. The presence of nitrogen oxides $NO_x = NO_2+NO$ is essential to get net photochemical ozone formation in the troposphere. In sunlight, NO_2 is photolysed to form O_3 and NO (reaction R1, see below), after which NO reacts with ozone (R2). A photostationary steady state is rapidly reached in which ozone concentrations remain unchanged. To

have net production, radicals capable of reacting with NO are needed. First, the photochemical processes produce OH radicals which react rapidly, for example, with non-methane hydrocarbons (NMHC) or methane to produce radicals (RO_2) (R3). These radicals react with NO (R4). Thus, less NO molecules are left to react with ozone molecules (R2), giving rise to a net increase in the ozone concentration. The catalytic nature of the process is established in reaction R5, where the HO_2 produced is converted back to OH which is needed at the beginning of the cycle. The most important sink of NO_2 from this cycle is its photochemical conversion (R6) to gaseous nitric acid (HNO_3) which may be taken up by aerosols and dissolved as nitrate (NO_3^-). Reactions (R6 - R7) lead to loss of radicals while the photolysis of ozone summarised as (R9) is the most important source of radicals.

$NO_2 + h\nu + O_2 \rightarrow$	$NO + O_3$	R1
$NO + O_3 \rightarrow$	$NO_2 + O_2$	R2
$NMHC + OH + O_2 \rightarrow$	RO_2	R3
$RO_2 + NO + O_2 \rightarrow$	$NO_2 + HO_2 + CARB$	R4
$HO_2 + NO \rightarrow$	$NO_2 + OH$	R5
$OH + NO_2 \rightarrow$	HNO_3	R6
$HO_2 + HO_2 \rightarrow$	H_2O_2	R7
$HO_2 + RO_2 \rightarrow$	$ROOH + O_2$	R8
$O_3 + h\nu \rightarrow$	$OH + OH$	R9

If nitrogen oxides are not present, other photochemical processes, such as the photolysis of ozone, result in a slow net depletion of ozone. When concentrations are low, as in rural or remote locations, the ozone production rate depends on the concentrations of NO_x (the NO_x-sensitive region). However, in conditions typical of metropolitan areas, enough NO_x is always present and ozone production is critically dependent on the concentrations of reactive volatile organic compounds in addition to the concentration of NO_x.

The concentrations of nitrogen oxides NO_x and the concentrations of all odd-nitrogen species NO_y (the sum of NO_x, gaseous nitric acid, particulate nitrate, and organic nitrate species) have been used to calculate their difference $NO_z = NO_y - NO_x$ (*Volz-Thomas et al.*, 1993). The amount of NO_z is a measure of the fraction of NO_x that was originally emitted but is no longer in an active form for producing ozone. Plotting ozone against with NO_z has been used to estimate how many molecules of ozone are formed in an air mass for each NO_x molecule emitted (*Volz-Thomas et al.*, 1993).

In addition to the just-described simplified photochemical cycle, other processes in the troposphere also control ozone concentrations. These include advection from the stratosphere, dry deposition to the surface of the earth as well as wet chemical processes which influence the concentrations of both the oxidants and of the nitrogen species critical for ozone formation. According to a recent three-dimensional modelling study of the global troposphere by *Müller* and *Brasseur* (1995), the most important sources of

ozone are photochemistry and import from the upper domain (the stratosphere), 4550 and 550 Teragrams per year, respectively. This production is balanced by photochemical sinks and dry deposition to the surface of 4000 and 1100 Teragrams per year, respectively.

3.   Ozone as a climate gas

Ozone contributes to the radiative forcing of the atmosphere because it strongly absorbs long wave thermal radiation of the atmosphere and solar UV radiation. Thus, both short- and long-term changes in its concentration change the radiative balance. Absorption of solar radiation takes place mainly in the stratosphere. Observed ozone depletion since the late 1970s in the stratosphere has lead to a negative radiative forcing which is estimated to be -0.1 W m-2 as a global mean (*IPCC*, 1995).

Increasing tropospheric ozone concentrations induce a positive radiative forcing. Based on observations the ozone concentrations at the surface level at the end of the 19th century were close to 10 ppb (*Volz* and *Kley*, 1988; *Marenco et al.*, 1994) and at higher level mountain stations in the Alps about 20 ppb in the 1950's (*Staehelin et al.*, 1994). As pointed out by *Staehelin et al.*, the highest concentrations were less than 40 ppb. Since then, a steady exponential increase (1.6 % yr^{-1}) in the average (*Marenco et al.*, 1994) and high ozone concentrations (*Staehelin et al.*, 1994) has occurred. The highest rate has been after the second world war but the increasing trend has declined during 1980s (*Logan*, 1994). An increasing trend of tropospheric ozone concentrations has been observed also in Japan and the U.S. In Canada, a declining trend during 1980s was reported by *Tarasick et al.* (1995).

The estimation of the long-term change of radiative forcing of ozone is difficult because concentrations of ozone are temporally and regionally changing. Compared to ozone concentration changes in the boundary layer those in the high troposphere are roughly 10 times more efficient in terms of radiative forcing (*Chalita et al.*, 1996). There are very few historical ozone sounding records. Using observed ozone concentration changes from soundings between 1971-1980 and 1981-1990 *Wang et al.* (1993) estimated that the radiative forcing of ozone is comparable to that of methane. A two-dimensional radiative-dynamical-chemistry model study by *Hauglustaine et al.* (1994) indicated a global mean radiative forcing change of 0.55 W m^{-2} since preindustrial times. Based on a global three dimensional model *Chalita et al.* (1996) calculated increased radiative forcing of 0.8 W m^{-2} over the Northern Hemisphere industrialised regions in summer. In winter and over the Southern Hemisphere the radiative forcing of ozone has increased roughly 0.2 W m^{-2} since preindustrial times. Thus, the radiative forcing of changing tropospheric ozone concentrations is of the same order of magnitude as that of methane.

4.   Measurements and trajectory calculations

The Finnish Meteorological Institute monitors ozone concentrations on a routine basis in Finland. Data from the sites (depicted in Fig. 1) are transferred daily to Helsinki. Ozone is monitored continuously using commercial monitors based on UV-absorption. The ozone data used covers the period 1989-1994 except at Oulanka, Tvärminne, and Pallas, where measurements were begun in October 1989, June 1991, and September 1991, respectively. In addition, daily filter-pack samples of gaseous nitric acid and particulate nitrate, which are analysed by ion chromatography, are used in interpretation. More detailed information on the measurements and locations are to be found in *Leinonen* (1994) and *Laurila et al.*, (1994c).
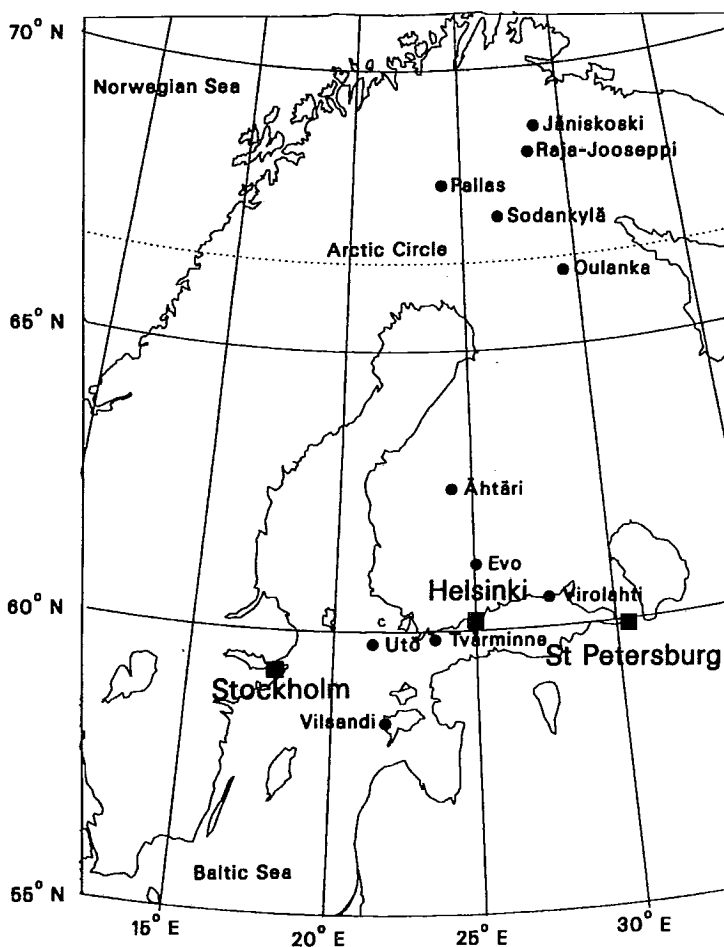
Fig 1. Locations of the ozone monitoring sites and major cities in the study area. Jäniskoski is a Russian and Vilsandi an Estonian EMEP site from which data are also daily transferred to the FMI.

Trajectories were obtained from three sources. Trajectories for the three episodes presented are three-dimensional, calculated either with the Royal Netherlands Meteorological Institute (KNMI) trajectory model (*Reiff et al.*, 1986) and meteorological data from the European Centre for Medium-range Weather Forecasts (ECMWF) analyses at a T106 spectral resolution, or with the trajectory model by *Eerola* (1990) and meteorological data from the high-resolution limited area model of the FMI.

The trajectories employed to calculate statistical source areas for the elevated ozone concentrations at Utö originate from the EMEP acid deposition model calculations reported by *Tuovinen et al.* (1994). Briefly, the wind data were obtained from the LAM50E weather prediction model at the Norwegian Meteorological Institute. The trajectories were calculated on the 150-km horizontal EMEP grid at a terrain-following normalised pressure level of $\sigma=0.925$, which corresponds to 945 hPa if the surface pressure is 1013 hPa. Trajectories are 96 h long and are set to arrive at the measurement sites four times a day (0600, 1200, 1800, 2400 UTC).

5.   Seasonal and diurnal cycles of ozone concentrations

In regions with considerable emissions of ozone precursors, high ozone concentrations are frequently observed in summer. On the other hand, in clean background locations in the Northern Hemisphere the spring maximum is dominant (*Logan*, 1985). In Finland, the availability of solar radiation divides the year into three photochemical seasons (*Laurila et al.*, 1993). In April-September photochemical production prevails when precursors of ozone are present. The highest ozone concentrations are observed in this period. In October-February ozone concentrations are depleted in polluted air masses. March and September are transition months when neither production nor depletion is dominant.

Monthly averages of ozone concentrations at selected Finnish and European sites are shown in Fig 2. The sites are all situated in either marine, coastal, or elevated locations to eliminate local effects which show up in low-lying continental sites as a diurnal cycle due to nocturnal inversions. The spring maximum and late summer minimum at Pallas indicate that this site is photochemically less polluted than Utö where the spring maximum extends into the summer. This conclusion is supported by the very low concentrations of the sum of gaseous nitric acid and particulate nitrate found in northern Finland compared to concentrations in south-western Finland (*Leinonen*, 1994). However, long-range transport episodes also reach the northern parts of Finland (*Rummukainen et al*, 1996). The seasonal cycle at Zeppelin shows similarities with Pallas, but spring-time ozone depletion episodes (*Solberg et al.*, 1994), typical for the Arctic Sea areas (*Barrie et al*, 1988), decrease the monthly averages in spring. Schauinsland is in the heart of a photochemically polluted region of Europe (*Simpson*, 1993). The highest monthly average is in August as is typically the case for very polluted sites. Part of the high average level of the concentrations at Schauinsland is due to the

higher elevation of the site. The coastal region of the north-western part of Spain is often exposed to subtropical marine air masses which have low concentrations of ozone.
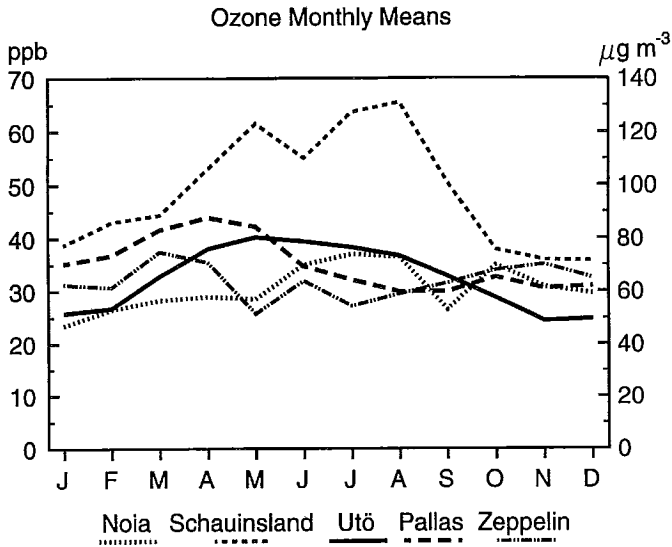
Ozone Monthly Means

Fig. 2. Monthly averages of ozone concentrations at Noia (1993-1994) in Spain, Schauinsland (1990-1992) in Germany, Utö (1989-1994), Pallas (1991-1994), and Zeppelin (1990-1992) in Spitzbergen. Data from Noia (42°N, 8°W, elevation 685 m a.s.l.), Schauinsland (47°N, 7°E, elevation 1205 m a.s.l) and Zeppelin (78°N, 11°E, elevation 474 m a.s.l) are from *Hjellbrekke* (1995) and *Hjellbrekke* (1996).

The diurnal cycle at selected sites of the FMI is illustrated in Fig 3 for summer when the amplitude of the diurnal cycle is highest (*Laurila* and *Lättilä*, 1994). For the comparison of the ozone behaviour in Finnish urban areas, diurnal cycles are shown for Luukki, Tikkurila, and Töölö, which are monitoring stations run by the Environmental Office of the Helsinki Metropolitan Area Council. Detailed description of these sites and measurements may be found in *Hämekoski et al.* (1991).

The effect of the diurnal cycle of mixing conditions can be seen in the surface ozone concentrations at continental sites. The high dry-deposition velocity of vegetative surfaces enhances this phenomena. In addition, NO_x emissions from local sources deplete ozone because NO_x emissions are emitted mostly as NO. Each NO molecule depletes one ozone molecule according to the reaction (R2). Both effects show up clearly in nocturnal conditions when the ozone transport from aloft is restricted. At the marine station, where there is no diurnal cycle of wind speed, ozone concentrations follow closely the boundary layer concentrations. At Pallas, the nocturnal surface inversion is below the site. On the average, a maximum is observed in the late afternoon hours. Luukki lies in forested terrain some 20 km from the centre of Helsinki. The site is not directly affected by heavy traffic emissions. The ozone concentrations are very close to those observed at the FMI sites in the coastal region. Tikkurila is located in the

suburban area of Helsinki where there is substantial traffic around the site while less vegetation than at Luukki. Lower average concentrations at Tikkurila may be due to the direct titration reaction (R2) from NO emissions. Töölö site is in a street canyon with high daytime traffic density. The daytime ozone concentration maximum has leveled off. The relatively high nocturnal maximum may be due to low traffic density after midnight and the closer proximity of the coastline compared to Tikkurila and Luukki.
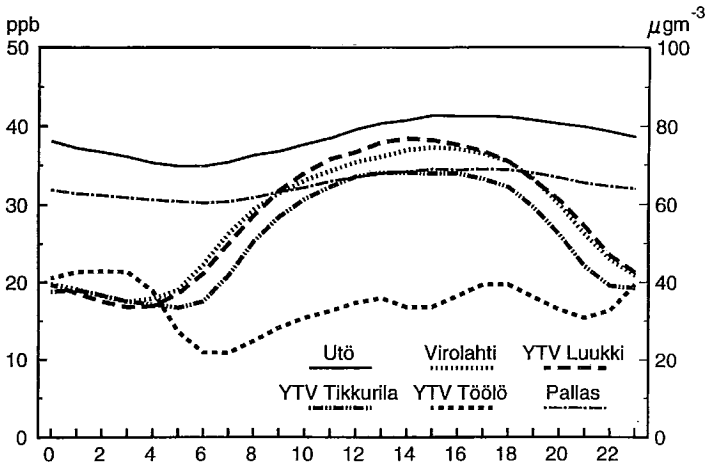

Fig. 3. Diurnal cycles of ozone concentrations in June-August 1992-1994 at Utö, Virolahti, Pallas, and three stations in the Helsinki Metropolitan Area: Luukki, Tikkurila, and Töölö.

To regionally compare the ozone in the boundary layer, the seasonal cycle of daily maximum 1-hour average ozone concentrations is used, because daily maximum concentrations are not affected by ozone depletion in the nocturnal inversion (Fig. 4). In winter, there is a south-north gradient of ozone concentrations. In spring, ozone concentrations are at their highest, especially in the northern parts of the country. The geographical scale of the long-range transport of photochemical air pollution diminishes in summer, resulting in a north-south gradient of average ozone concentrations in the boundary layer. Using the EMEP oxidant model *Simpson* (1995) calculated the April-September (1989) average field of daily maximum concentrations from European emissions of ozone precursors. The calculated average concentration gradient between northern and southern parts of Finland was 15 ppb. The minimum of the yearly cycle is in late summer in the northern parts, and in late autumn in the southern parts of the country.
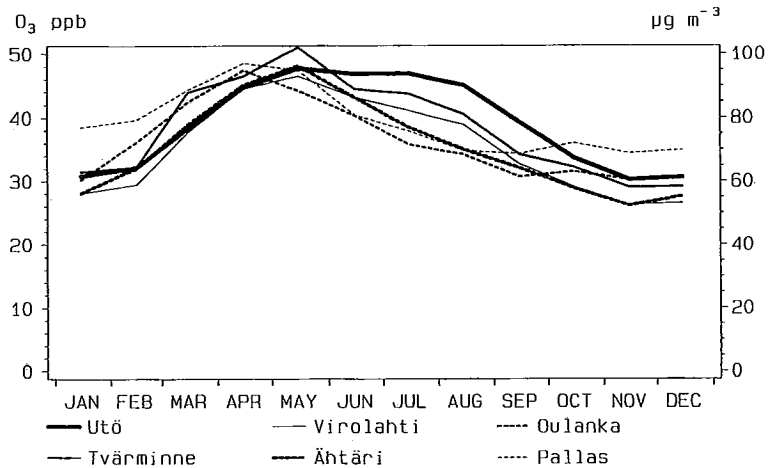
Fig. 4. Monthly averages of daily maximum 1-hour concentrations at Utö, Tvärminne, Virolahti, Ähtäri, Oulanka, and Pallas.

6.   Episodes of high ozone concentrations

As examples of three kinds of transport and pollution source areas, the three cases having the highest concentrations are presented. These episodes are: the highest ozone concentrations observed in April at Oulanka, and in May in the northernmost parts of Scandinavia, and the record highest concentration observed in the south coastal region.

6.1   The episode in April 1990

The first episode occurred in April 1990. The ozone concentrations at four stations are depicted in Fig. 5. Between 21.-26.4.1990, a ridge of high pressure with low wind speeds and sunny weather affected the southern parts of Finland. Warm daytime temperatures, close to 15°C, were observed in the central parts of Finland. Accumulation of the air pollutants related to ozone photochemistry was observed (Fig. 6). In the Baltic Sea region, elevated concentrations of PAN (*Laurila et al.*, 1992) provide strong evidence of the anthropogenic photochemical origin of the elevated ozone concentrations. On the 26th, northward transport was initiated due to the approach from the west of low pressure system (Fig. 7). Ozone concentrations at Oulanka fell on the evening of the 27th when a front connected with the low passed the station. On the 28th clean air masses prevailed with westerly winds.
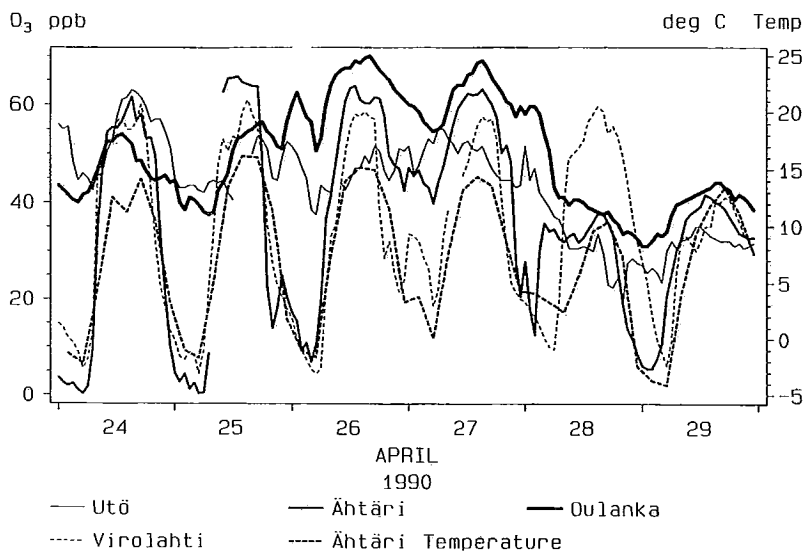
Fig. 5. Ozone concentrations for 24.-29.4.1990 at four monitoring stations, and temperature at Ähtäri.
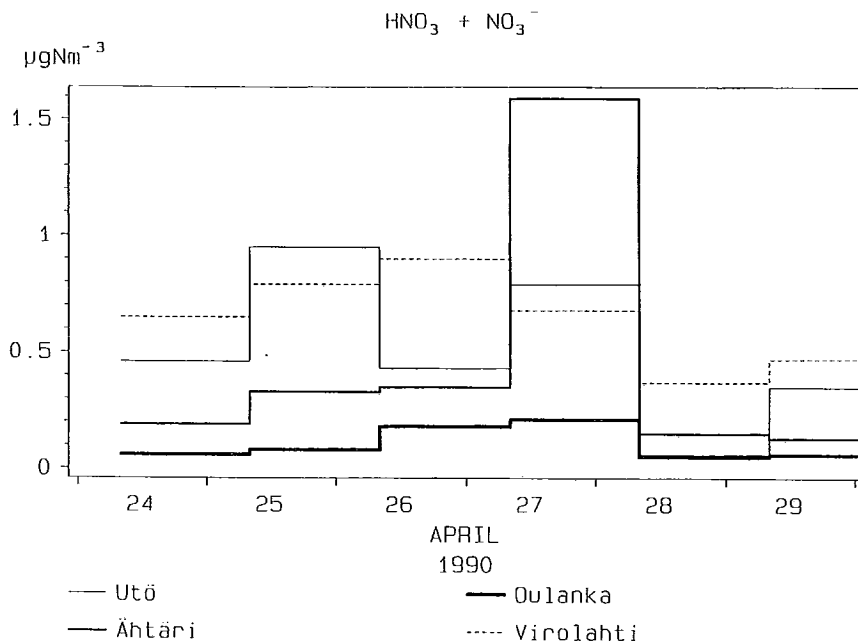

Fig. 6. The sum of gaseous nitric acid and particulate nitrate concentrations in the air at four monitoring stations.
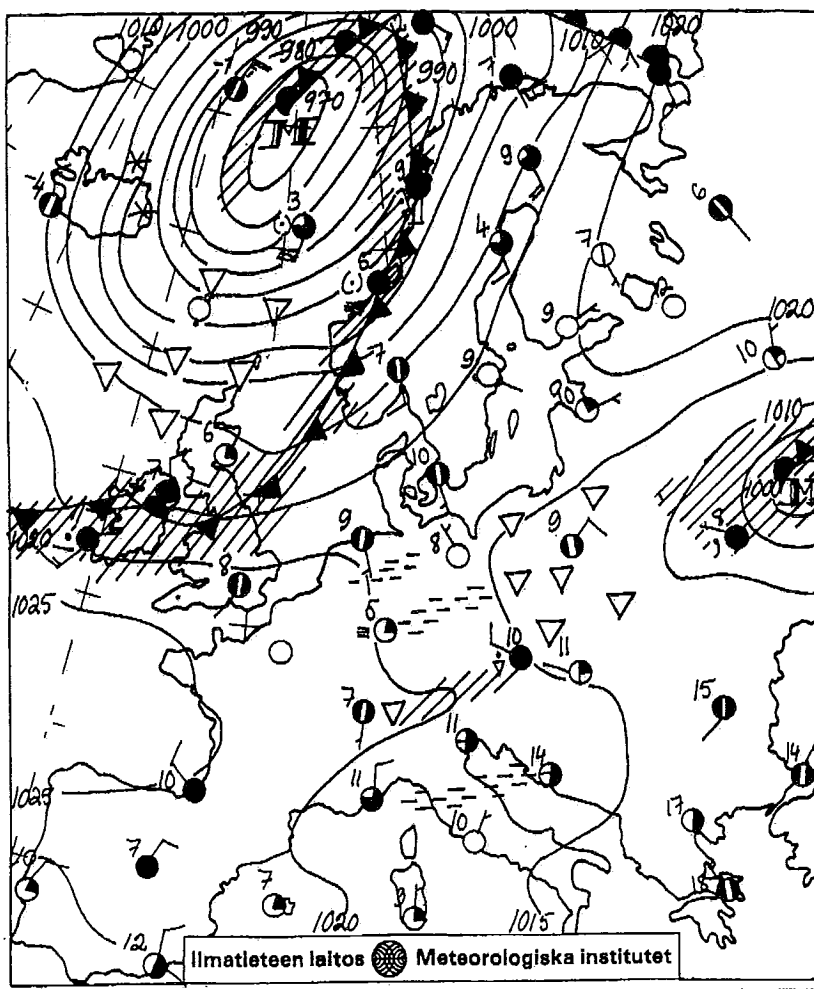
Fig. 7. The surface weather map at 06.00 UTC, April 26th, 1990.

The record highest 1-hour average ozone concentration (70 ppb) at Oulanka for April was observed on 26.4.1990. Trajectory calculations show that the air that arrived at Oulanka at 12 UTC on the 26th at the 950 hPa level, was on the 25th over Ähtäri and between the 21st and 24th of April over the south-western parts of Finland and near the station of Utö (Fig. 8). The 24-hour net increase of ozone concentration along the trajectory was 3 ppb between 25.-26. and 5 ppb between 26.-27. The air that arrived at Oulanka on the 27th, was on the previous day near the station of Virolahti. The ozone concentration increased by 10 ppb between 26.-27. along the trajectory arriving at Oulanka on the 27th of April. The sum of gaseous nitric acid and particulate nitrate concentrations was between 0.4 and 1.0 μgNm^{-3} in the southern coastal region but was

less in the central and northern parts of the country. Accumulation and transport of the sum of gaseous nitric acid and particulate nitrate in the air closely follow the meteorological advection and ozone concentrations. The decrease of the sum of gaseous nitric acid and particulate nitrate concentrations along the trajectory is probably due to the shorter life times of the sum of gaseous nitric acid and particulate nitrate compared to ozone.
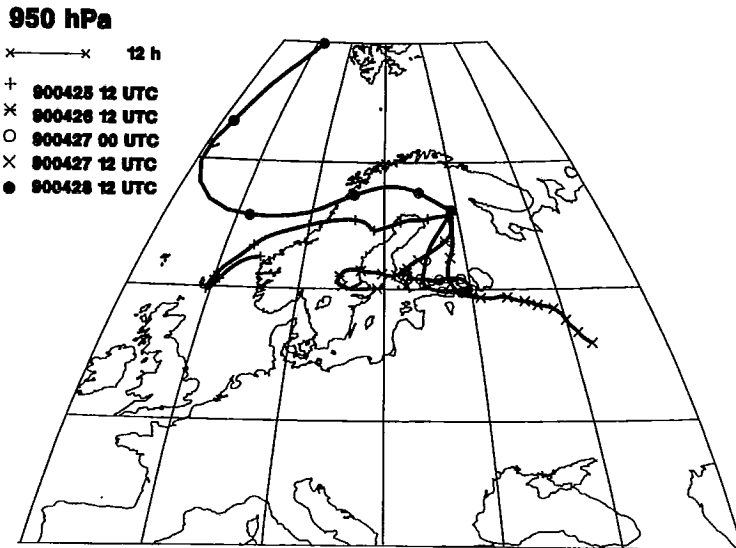

Fig. 8. The 120-hr three-dimensional back-trajectories ending at the 950 hPa level at Oulanka. The date indicates the time of arrival at Oulanka. The trajectories were calculated using the ECMWF wind fields.

6.2   The episode in May 1992

An episode of regionally-elevated ozone concentrations took place in Northern Scandinavia at the end of May 1992 (Fig. 9). The highest ozone concentrations were observed at the Russian EMEP station of Jäniskoski (*Tuovinen* and *Laurila*, 1994). At the Norwegian EMEP-station of Jergul, located 160 km north of Pallas and 170 km west of Jäniskoski, ozone concentrations also reached 70 ppb on the 27th of May (*Hjellbrekke*, 1995). The concomitantly increasing sum of gaseous nitric acid and particulate nitrate concentrations at Jergul and Oulanka show the anthropogenic origin of the elevated ozone concentrations.
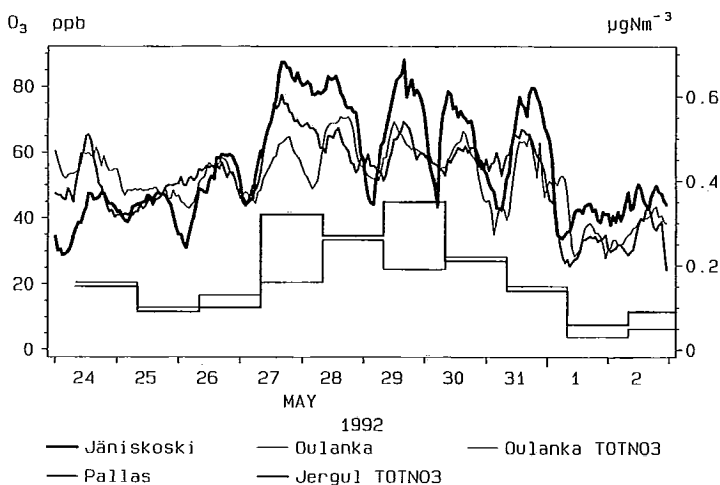
Fig. 9. Ozone concentrations (left axis) at Jäniskoski, Pallas and Oulanka in May 1992, and 24-hour average of the sum of gaseous nitric acid and particulate nitrate concentrations at Jergul and Oulanka (right axis).

Ozone concentrations increased on the 27th when a high pressure area, centred over Scandinavia (Fig. 10), advected air anticyclonically from the western parts of Europe (Fig. 11). The air mass was very warm for May in Northern Scandinavia, daytime temperatures increasing from 10°C on the 26th to 20°C on the 27th. Cloudless conditions during the transport and very low dry deposition over the North and Norwegian Seas were ideal for the long-range transportation of high ozone concentrations. In Finland, the most northern parts experienced the highest concentrations during this episode because the central and southern parts of the country only impacted the effect of more local emissions.

6.3   The episode in June 1992

The third episode represents the highest ozone concentration measured in 1990 - 95 in Finland by the FMI. It took place at the station of Tvärminne on June 12th, 1992. A high pressure area in Northern Europe (Fig. 12) was centred over Northern Russia, resulting in westward advection over the southern parts of Finland (Fig. 13), where ozone concentrations were generally close to 60 ppb. However, at Tvärminne concentrations increased sharply on June 12th, the highest values were observed in the evening. As the trajectory calculations suggest, the air had passed over the Moscow region during the morning of June 10th. The reason for the short duration of the episode is unclear. The mixing conditions on the coast of the Gulf of Finland may be one reason. Another may be that the air arriving on the evening of 12th at Tvärminne had experienced two photochemically-productive daytime cycles but only one nocturnal

period following the morning rush-hour time in the Moscow area. This idea rests on the accuracy of the trajectory calculations. The atmospheric flow field is often more complicated than the wind field products by weather prediction models.
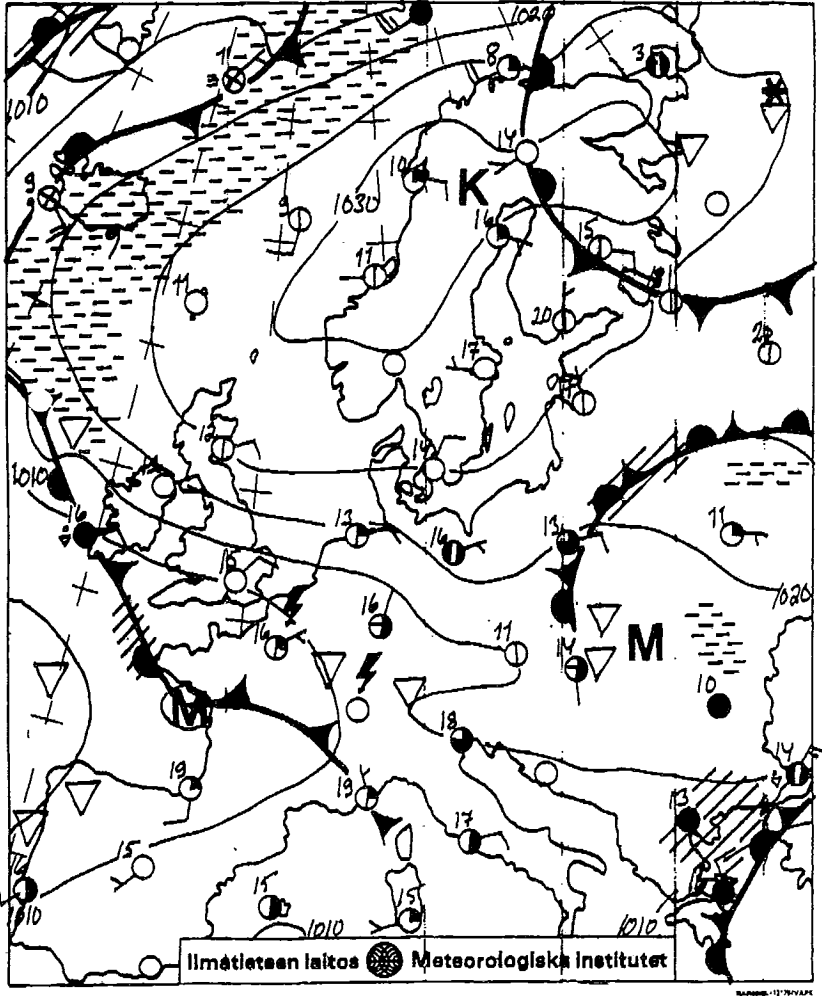

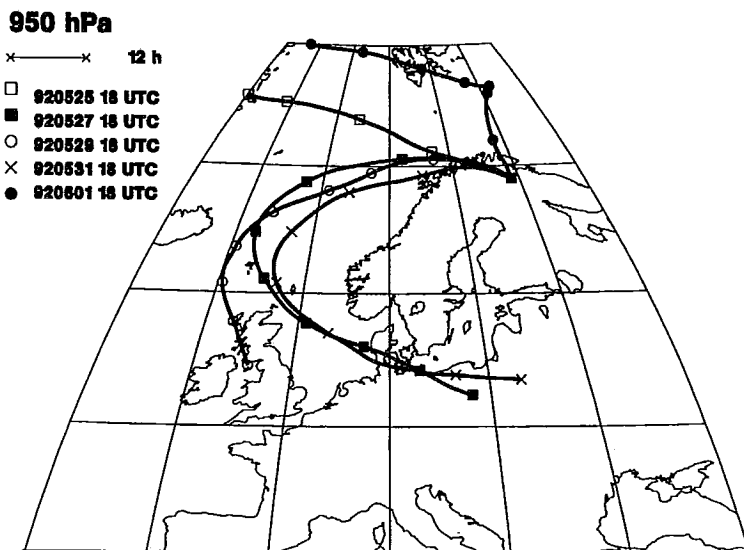Fig. 10. The surface weather map at 06.00 UTC, May 27th, 1992.

Fig. 11. The 96-hr three-dimensional back-trajectories ending at the 950 hPa level at Jäniskoski. The date indicates the time of arrival at Jäniskoski. The trajectories were calculated using the HIRLAM wind fields at the FMI.

7.   Meteorological and chemical factors affecting ozone concentration at Utö

Elevated ozone concentrations have been related to meteorological variables such as wind speed and direction, temperature (*Hakola et al.*, 1991; *Feister* and *Baltzer*, 1991; *Vukovich*, 1995), pressure fields and transport patterns (*Davies et al.*, 1992; *Vukovich* and *Fishman*, 1986), and chemical tracers (*Trainer et al.*, 1993; *Sillman*, 1995). In this chapter ·three. factors are considered: temperature as a simple meteorological parameter, trajectory climatology, and the concentration of the sum of particulate nitrate and gaseous nitric acid which is a direct by-product in photochemical ozone formation.

High ozone concentrations usually develop in stagnant anticyclonic conditions when hot sunny weather prevails (*Davies et al.*, 1992; *Vukovich*, 1995). In Finland, high ozone concentrations are often observed in continental air masses when above-average temperatures are expected. Utö data was used to test the temperature dependence of ozone concentrations. Temperature deviation from the average is used instead of absolute temperature in order to eliminate the seasonal cycle. Average temperature is calculated by taking the average of 30-day running means in the years 1989-1994. The 10, 50, and 90 ozone percentiles in ten temperature deviation classes are plotted in Fig.

15. The scatter, indicated by percentiles 10 and 90, is large compared to the small increase in the ozone concentration medians. The highest temperature deviations seem to predict high ozone concentrations slightly better than lower or average temperatures predict the corresponding concentrations.
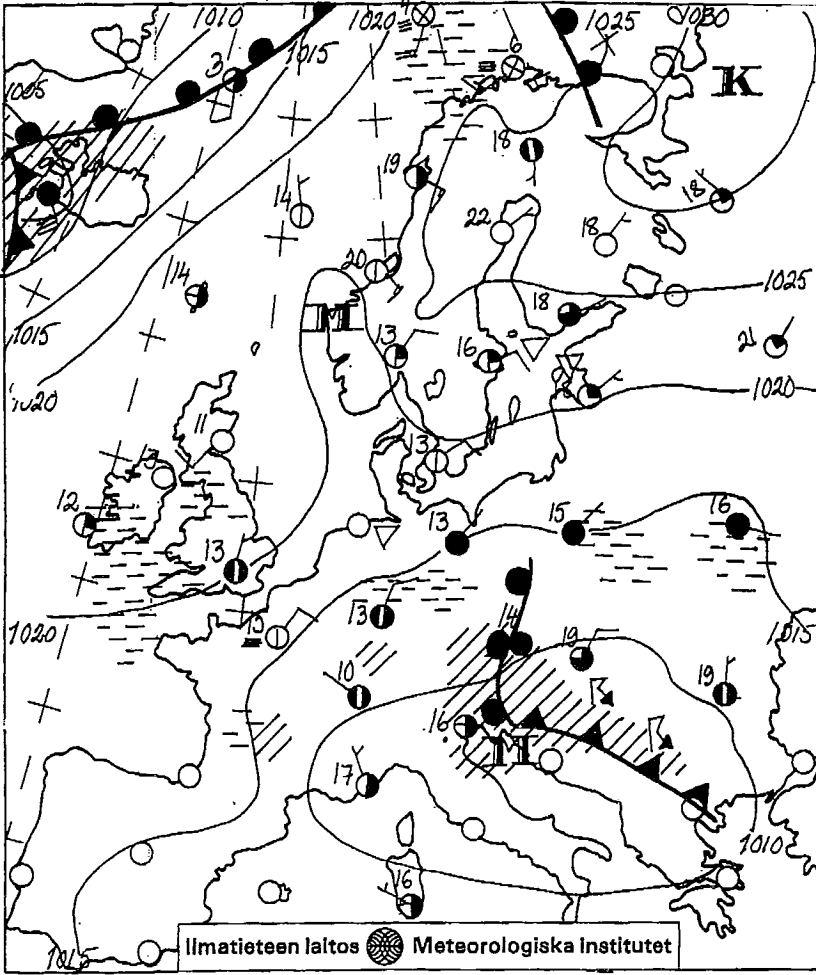

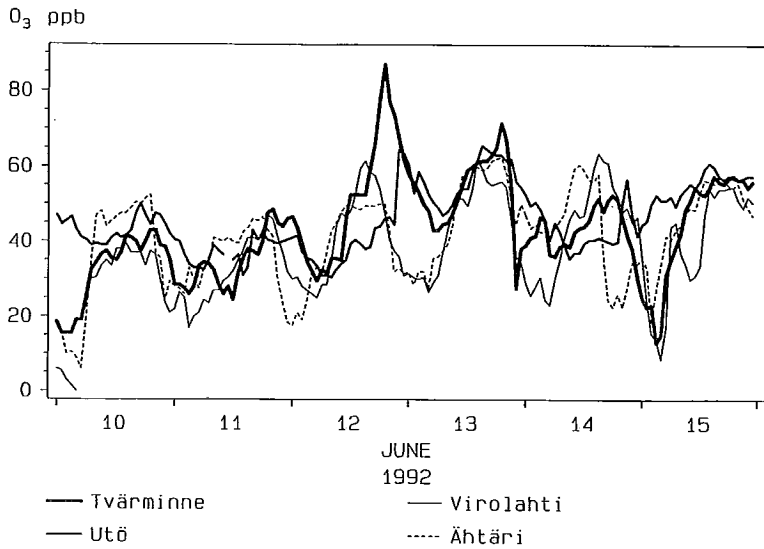Fig. 12. The surface weather map at 06.00 UTC, June 12th. 1992.

O$_3$ ppb

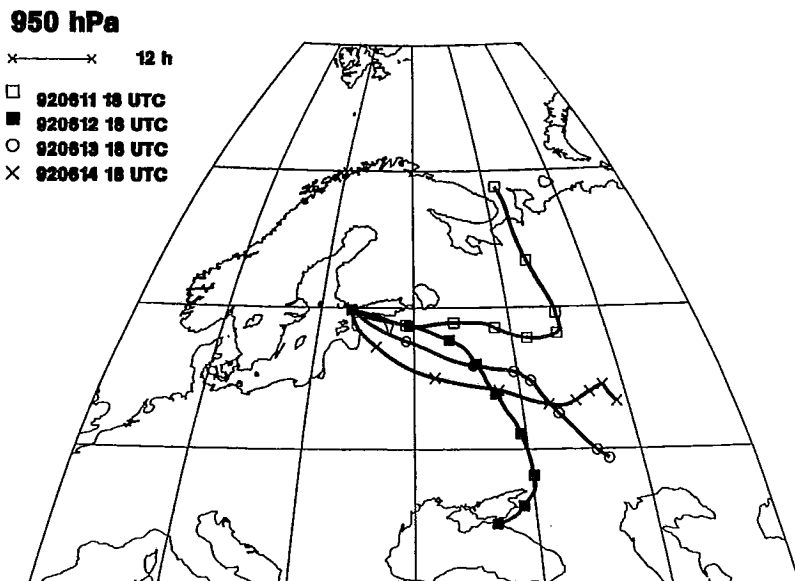Fig. 13. Ozone concentrations at Tvärminne, Utö, Virolahti, and Ähtäri in June 1992.

Fig. 14. The 96-hr three-dimensional back-trajectories ending at the 950 hPa level at Tvärminne. The date indicates the time of arrival at Tvärminne. The trajectories were calculated using the HIRLAM wind fields at the FMI.
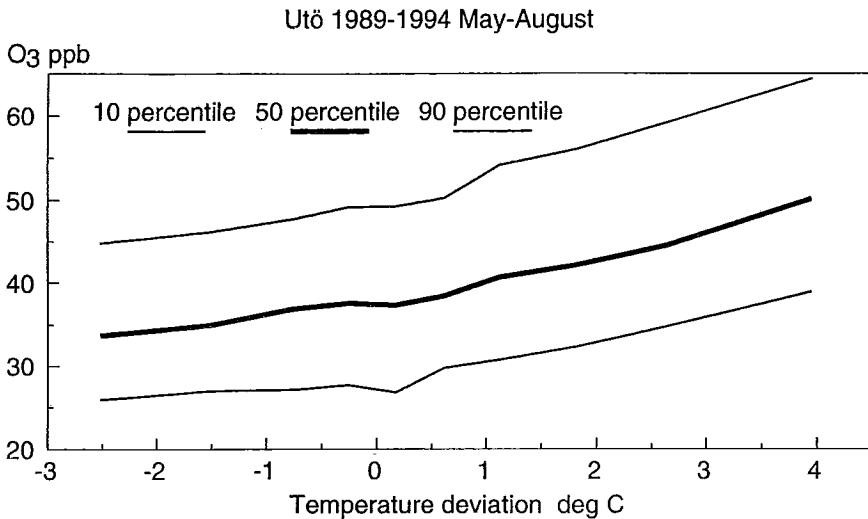
Utö 1989-1994 May-August

Fig. 15. Ozone levels as a function of the temperature deviation from the average at Utö. In addition to the median the 10 and 90 percentiles are also shown to illustrate variability.

To illustrate the probable origin of the elevated ozone concentrations, these were combined with atmospheric trajectories that describe the route of an air mass prior to its arrival at a certain location. For the May-August season in 1989-1993 those trajectories arriving at Utö corresponding to an ozone concentration higher than 60 ppb were selected. The total time spent by the ozone-rich air prior to its arrival at Utö was then mapped at each location by counting the number of the 2-hourly locations of these trajectories in the grid. This results in a geographical distribution depicting the probable source areas and the mean flow patterns related to elevated concentrations. In order to compensate for the purely geometric effect of the central tendency in the probability field produced this way, the raw distribution was weighted by the distance from the receptor site (*Poirot* and *Wishinski*, 1986). It is to be noted that the distribution as such does not display the areas over which the observed ozone is produced, but rather indicates the area over which the trajectories have passed during the most recent 96 hours.

The selection criterion threshold of 60 ppb (including 3 % of all cases) is well above the clean air background concentration of roughly 30 ppb. The distributions (Fig. 16) show that the trajectory distribution lies above an area of high emissions having a good potential for ozone production. There are some individual isoline 'spots' due to the distance weighting of the trajectories and interpolation method. There is a maximum over the North Sea because the 96-hour back-trajectories are often too short to follow transport in high pressure situations from areas south and west of the North Sea.

Fig. 16. Isolines of 96-hour back-trajectory occurrences ending at the 950 hPa level at Utö in May-August 1989-1993 when ozone concentrations exceeded 60 ppb. The distribution was weighted by the distance from Utö and the isolines are expressed in relative units. The trajectories were calculated in EMEP MSC-W using wind data from the Norwegian Meteorological Institute.

To show the anthropogenic origin of elevated ozone concentrations, daily average concentrations are divided according to the respective daily average of the sum of gaseous nitric acid and particulate nitrate concentrations (Fig. 17). The sum of gaseous nitric acid and particulate nitrate has been used to estimate NO_z, the concentration of the sum of oxidation products of NO_x, as discussed in the introduction. This sum probably estimates NO_z well because, according to measurements by *Parrish et al.* (1993) and *Atlas et al.* (1992), gaseous nitric acid and particulate nitrate represent almost all the NO_z species in rural and remote areas, the reminder being mostly organic nitrates such as peroxyacetyl nitrate (PAN). The slope in the figure gives an estimate of how many ozone molecules have been formed from each NO_x molecule emitted. For Utö in summer, the slope in the Fig. 17 gives climatologically 11 molecules of ozone formed from each NO_x molecule emitted. This number may be compared to the summer average of 4-5 molecules of ozone formed from each NO_x molecule emitted at Schauinsland in Southern Germany, as observed by *Volz-Thomas et al.* (1993). In the eastern United States ozone-to-NO_z ratios at rural sites of 8.5 in Pennsylvania (*Trainer et al.*, 1993), 11.4 in Georgia (*Kleinman et al.*, 1994), and 12.3 in Tennessee (*Olszyna et al.*, 1994) have been found. Observations of an urban plume in Birmingham, Alabama, by *Trainer et al.* (1995) indicated that 7 molecules of ozone were produced per molecule of NO_x

oxidised. These numbers are in accordance with modelling studies (*Lin et al.*, 1988) that show higher ozone production efficiencies in lower rural NO_x concentrations than in urban higher concentrations. The modelling study by *Sillman* (1995) shows that ozone formation is mainly governed by NO_x concentrations when the ozone-to-NO_z ratio is greater than 9, but that when it is less than 8 ozone formation is more sensitive to concentrations of reactive organic species. High ozone production efficiency suggests that ozone production is more sensitive to NO_x than VOC concentrations in the northern Baltic Sea area. This conclusion is also supported by modelling studies by *Lindfors et al.* (1995a).
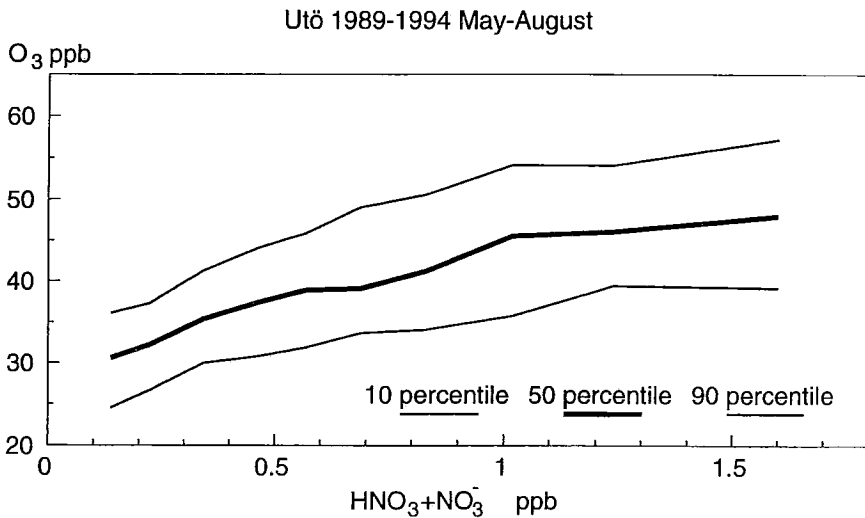
Utö 1989-1994 May-August

Fig. 17. Ozone levels as a function of the sum of gaseous nitric acid and particulate nitrate concentrations. In addition to the median the 10 and 90 percentiles are also shown to illustrate variability. The dependence was calculated using 24-hour average data.

Our value is an upper limit because all the products of NO_x oxidation were not measured. Another uncertainty is that during the transport ozone and NO_z species may be scavenged by dry and wet deposition or by mixing at varying efficiencies which means that their concentrations at the receptor point do not reflect chemical processes only. The measured surface level concentrations of HNO_3 may not represent boundary layer concentrations well because HNO_3 has a concentration gradient close to the ground due to the high dry deposition velocity. There are no representative measurements of HNO_3 at Utö because it is difficult to accurately measure HNO_3 and particulate NO_3^- separately. Using the EMEP acid deposition model *Tuovinen et al.* (1994) calculated the yearly average concentrations of HNO_3 and particulate nitrate to be roughly 0.03 and 1.0 $\mu g(N) \ m^{-3}$, respectively, in the study area. Although the ratio between these species may vary considerably it may be assumed that most of the sum is in particulate form which has a much lower dry deposition velocity.

To further study the seasonal cycle of ozone production the medians of daily average ozone concentrations, divided into four subdivisions based on the respective daily concentration of the sum of gaseous nitric acid and particulate nitrate at Utö, are plotted in Fig 18. The group of the lowest concentrations (percentiles 0-10) of total nitrate represents clean background air while the group of the highest concentrations (percentiles 90-100) represents air masses which have passed through areas of high NO_x emissions. The intermediate groups (total nitrate concentration distribution percentiles 10-50 and 50-90) represent air masses with moderate pollution. Ozone concentration in clean air is 33 ppb in spring and close to 30 ppb in summer and autumn. Photochemical ozone production takes place in spring and summer while depletion of ozone by pollutants is observed in October-February. The difference between the group representing the cleanest air and the monthly average is roughly 20 % both in summer and winter.
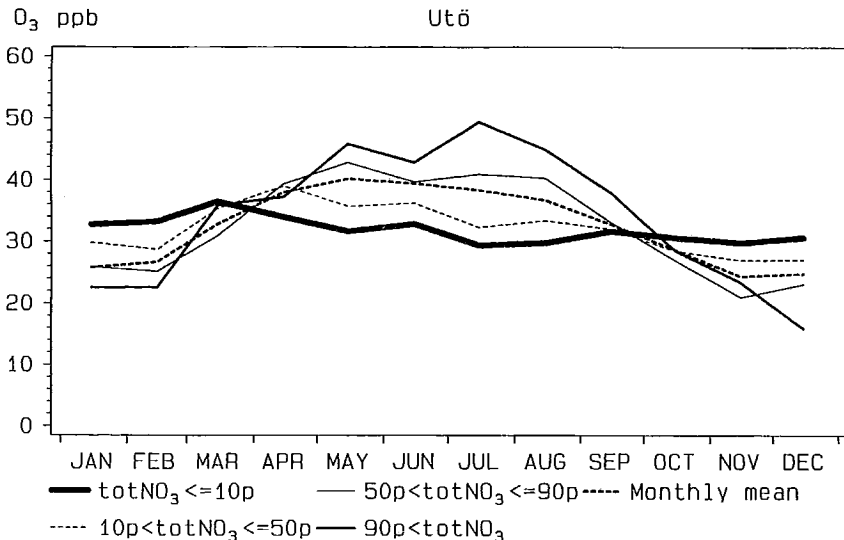

Fig. 18. Monthly medians of daily average ozone concentrations when the data is divided into subgroups based on the sum of gaseous nitric acid and particulate nitrate concentrations. The subdivision criteria were the sum of gaseous nitric acid and particulate nitrate concentrations percentiles 10, 50, and 90. Also monthly mean is shown.

8.   Conclusions

In Finland, the availability of solar radiation divides the year into three photochemical seasons (*Laurila et al.*, 1993). In April-September photochemical production prevails when precursors of ozone are present. The highest ozone concentrations are observed in this period. In October-February ozone concentrations

are depleted in polluted air masses. March and September are transition months when neither production nor depletion is dominant. During these months high concentrations are usually of short duration when there is strong advection from the south.

In the boundary layer, the present-day ozone concentration in clean background air is close to 30 ppb. High ozone concentrations are frequently observed when both long-range transport and the local weather are favourable. Cases of high concentrations also occur when the air has stayed for a longer time over Finland. Based on the trajectories and ozone concentrations at Utö, in practically all cases when clearly elevated concentrations are observed the air has passed over European areas having high anthropogenic emissions. Emitted NO_x molecules have a high efficiency producing ozone. Observations made at Utö indicate that in summer roughly 10 ozone molecules are formed from each NO_x molecule emitted. High ozone production efficiency is typical of rural and remote environments where ozone production is sensitive to NO_x rather than to VOC emissions.

The seasonal cycle of ozone production at these latitudes (60 - 70 °N) raise the idea that the radiative forcing due to the ozone precursor emissions has also a strong seasonal cycle. *Hansen et al.* (1988) assumed a linear tropospheric radiative forcing from ozone concentrations. This rough relationship was confirmed by *Chalita et al.* (1996). At Utö the average ozone concentration is about 20 % higher in summer and 20 % lower in winter compared to ozone concentration in clean air at the site. This means that the tropospheric radiative forcing due to the European anthropogenic ozone precursor emissions at high northern latitudes where there is pronounced seasonal cycle of solar radiation is positive in summer but negative in winter. This argumentation takes into account only the short term effects of anthropogenic pollutants. The slow year round average increase of ozone due to changes in background tropospheric composition of photochemically active trace species is not taken into account.

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