Atmospheric trace gas and aerosol particle concentration measurements in Eastern Lapland, Finland 1992–2001

Taina M. Ruuskanen[1], Anni Reissell[1], Petri Keronen[1], Pasi P. Aalto[1], Lauri Laakso[1], Tiia Grönholm[1], Pertti Hari[2] and Markku Kulmala[1]

[1] *University of Helsinki, Department of Physical Sciences, P.O. Box 64, FIN-00014 University of Helsinki, Finland*

[2] *University of Helsinki, Department of Forest Ecology, P.O. Box 27, FIN-00014 University of Helsinki, Finland*

Trace gases (SO_2, NO_x, O_3) and aerosol particles alongside with meteorological parameters have been measured continuously since 1992 in a remote Arctic station in Värriö, Finnish Lapland. In this background region there are practically no local sources of pollution. The goal of this study was to investigate the transport of gaseous pollutants and aerosol particles to a remote area. The seasonal, diurnal and long-term behaviour of trace gases and aerosol particles is presented as well as their correlation with each other and with local wind direction. A slightly diminishing trend was observed for low summertime ozone (O_3) concentrations from 1995 to 2001. No distinct long-term trends for other species were noted. The monthly-medium concentrations were highest for SO_2 and NO_x in the winter, for ozone in the spring and for aerosol particles in the summer. The cleanest air seemed to arrive with northwesterly local winds, whereas the most polluted air was associated with easterly local winds and occurred as short episodes.

Introduction

The chemical reactions and physical processes taking place in the unique conditions of the Arctic that change remarkably with the seasons have both local and global impacts. The interest in the Arctic area and its atmosphere is continuously increasing. This is illustrated by research that includes the formation and transport of Arctic haze (Rahn 1981, Barrie 1986, Baskaran and Shaw 2001), the observation of rapid springtime reduction in ozone concentrations in the lower atmosphere (Barrie *et al.* 1988), polar ozone depletion (Farman *et al.* 1985, Chipperfield and Jones 1999), the intrusion of stratospheric air to the troposphere during tropopause

folding (Strunin *et al*. 1997, Helmig *et al*. 2002) and the pollution and the chemistry of Arctic air (Barrie 1986, Yokouchi *et al*. 1996, Vinogradova 2000).

The Arctic area is characterized by the pronounced difference in conditions between the long winter and short summer. The lack of solar radiation and heating during the cold winter months suppresses photochemical reactions. At the same time precipitation is at its lowest and thus deposition is hindered. This leads to accumulation of anthropogenic emissions in the winter in contrast to the summer period of continuous light and more rain (Barrie and Platt 1997, Jaeschke *et al*. 1997, Harrison *et al*. 2000). During wintertime the polar front typically lies more to the south than during summertime and this results in a larger source area of pollutants that are carried to the Arctic in winter (Arya 1999). The cold and snow-covered ground during wintertime promotes frequent temperature inversions (stable conditions). Unstable conditions can however occur during summertime. Although the northern Finnish and Norwegian areas are generally considered unpolluted, it is impacted by emissions from the industry such as the Nikel and Montchegorsk smelteries in the Kola Peninsula (Kashulina and Reimann 2002).

Anthropogenic emissions account for approximately 75% of total sulphur emissions (excluding sea salt) in the Northern Hemisphere. A major natural source of SO_2, in addition to volcanic activity, is the ocean (Seinfeld and Pandis 1998). It has been estimated that 25% of the dimethyl sulfide (DMS) emitted from the Arctic Ocean is oxidized to SO_2, non-seasalt aerosol sulfate and methane sulphonate (Nilsson and Leck 2002).

The emissions of pollutants in Northern Fennoscandia (Lapland) are typically very small. The closest source of emissions is the mining industry in the Kola Peninsula east of Finnish Lapland. These copper and nickel smelteries are point sources for SO_2, CO, NO_x, hydrocarbons, dust particles and trace metals. The SO_2 emissions from Europe and Finland have declined in the 1990s, while only minor reductions have been seen for NO_x emissions. Sulphur dioxide (SO_2) emissions from the Kola Peninsula area have been twice as large as the total emissions

from Finland (Kashulina and Reimann 2001). Emissions of nitrogen oxides (NO_x) from the Kola area have been considerably smaller than SO_2 emissions, but even so, they have been twice as large as the NO_x emissions from Finnish Lapland area (Laurila *et al*. 1991).

Metallurgical complexes in Nikel and Montchegorsk have contributed to over 80% of the SO_2 emissions from the Kola region. Instantaneous pollutant concentrations in the air may momentarily reach high values at considerable distances downwind from the initial emission source. Emissions from the Kola region can be detected in the otherwise clean arctic air as far away as Alaska (Polissar *et al*. 1999).

In this paper we present long-term continuous measurements of SO_2, NO_x, ozone, aerosol particles and meteorological data at Värriö in 1992–2001. This will include the trends of concentrations over the last ten years, seasonal and diurnal patterns as well as the behaviour of the species of interest under occasional pollution episodes and different wind directions.

Numerous studies in the Finnish Arctic area have been carried out (e.g. Laurila *et al*. 1991, Raitio *et al*. 1995, Kerminen *et al*. 1997, Virkkula 1997, Virkkula *et al*. 1999). Results from the SMEAR I station (Station for Measuring Forest Ecosystem–Atmosphere Relation) in Värriö have been presented in publications concerning the station itself (Hari *et al*. 1994), aerosol formation events (Aalto *et al*. 1995, Pirjola *et al*. 1998), variations in trace gas and aerosol particle concentrations (Ahonen *et al*. 1997) and back trajectory analysis (Kulmala *et al*. 2000b). However, all those studies have focussed on relatively short periods. This work is the first one in which results from continuous measurements covering ten years are presented from Värriö.

Experimental description

Station

The Värriö measurement station SMEAR I (69°46´N, 29°35´E) (Hari *et al*. 1994) is located in Värriö nature park in eastern Lapland, less than 10 km from the border of Russia (Fig. 1).

The measurements were done from different heights of a measurement tower located on top of a hill 390 m above sea level. The range of Värriö fjelds continue from north to south and the tower is surrounded by these fjelds. Most of the trees are about 50-year-old Scots pines (*Pinus Sylvestris* L.). The height of the trees is about 8 m and their mean diameter is approximately 8 cm. The station is located below the alpine timberline (400 m a.s.l.) but some of the fjeld tops nearby are above it. The distance from the nearest small road to the station is approximately 8 km and from the nearest major road about 100 km. There are no towns or industry close by. Because there is practically no local pollution, transported pollutants are easy to detect. The nearest major pollution sources are Montchegorsk located 150 km to the east of station and Nikel located 190 km to the north of the station. Värriö measurement station and Montchegorsk are separated by a line of mountains on the Russian side, which ranges from north to south.

Fig. 1. Map of the location of Värriö measurement station and most important emission locations.

Measurement set-up

The measurements were done for concentrations of SO_2, O_3 and NO_x (trace gases), for the number concentration of aerosol particles (14 nm–3 μm) and meteorological data such as temperature, humidity, radiation (PAR and global), pressure and wind direction and speed. Measurements of gas and aerosol particle concentrations and meteorological data were performed continuously at the measurement station. The operation of the system is monitored and checked at least twice a week and the gas analysers were calibrated at least once a year. The gases and aerosol particles were measured at different heights, inside the canopy and above it. All the data presented in this study are from measurements at the nine-meter level. The measurement cycle lasted 20 minutes for gases and particles and five minutes for meteorological data. One hour means were calculated from the measurements. Sampling lines were changed in the autumn of 1993 from stainless steel to Teflon. There were only short time breaks for the monitoring system, usually in the late summer due to thunderstorms. O_3 measurement data from October 1993 to December

1994 was excluded from data analysis due to instrument malfunction.

SO_2 was measured with a fluorescence analyser (Model 43S, Thermo Environmental Instruments, Inc., detection limit 0.1 ppb), O_3 with a photometric analyser (Model 49, Thermo Environmental Instruments, Inc., detection limit 1 ppb), and NO_x with a chemiluminescence gas analyser (Model 42C TL, Environmental Instruments, Inc., detection limit 0.1 ppb). The chemiluminescence method has been designed for NO_x ($NO + NO_2$) measurements, but the catalytic converter measuring NO_2 after reduction to NO partially reduces other oxidized nitrogen species as well. Therefore the term NO_x, used in this paper, refers to the detection of NO, NO_2 and partial detection of HONO, HNO_3, PAN and some other organic nitrates. Aerosol particles were measured with a condensation particle counter (CPC; TSI 3760, detection limit 10^{-3} particles cm^{-3}). Calibration errors and losses in sampling lines, for example, account for measurement errors. The measurement system and instrumentation have been presented in more detail by Hari *et al.* (1994) and Ahonen *et al.* (1997).
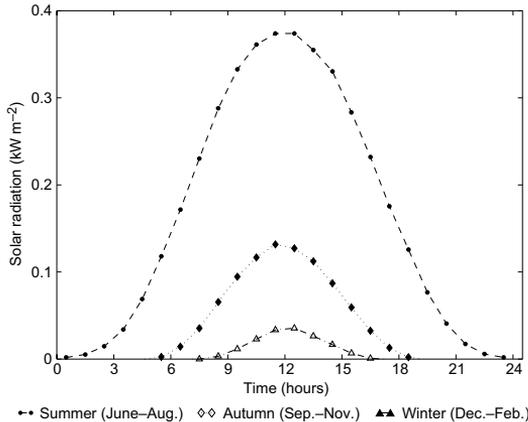
Fig. 2. Diurnal variation of global radiation in different seasons (winter from December to February, spring from March to May, summer from June to August, autumn from September to November).

Results and discussion

Meteorology

The Värriö area has a characteristic polar nature: winters are dark and long, summers short and light. The polar night at Värriö lasts from 19 to 24 December and the polar day lasts from 29 May to 15 July. During the polar day the sun never goes under the horizon but the solar radiation has a clear diurnal behaviour with a distinct maximum at midday and a minimum at midnight when it is nearly at zero kW m^{-2}. This seasonal behaviour of solar radiation can be clearly seen in the seasonal behaviour of global radiation (Fig. 2). Freezing of the global radiation measurement instrument can cause some problems. This happens especially in the spring, so results from this period are not used. The wind direction is the same as for the rest of Finland and for most of Scandinavia. The wind blows mainly from southwest, especially during winter, in the summer it is more evenly distributed to all directions (Fig. 3). The mean temperature throughout the measurement period was –1.1 °C. During the coldest winter months from December to February it was –10.6 °C and for the warmest summer months from June to August it was 10.8 °C (Table 1). The measurement station is located at the top of a hill and the temperatures in the valleys were characteristically lower during the coldest winter period. The temperature difference can be more than 10 °C, so –15 °C temperature on top of the hill might correspond to –25 °C in the valley below, hence indicating stable inversions.

Long-term variation

Sulphur dioxide, ozone, nitrogen oxides and aerosol particle concentrations were presented as one-hour means and running monthly means (Fig. 5) to make a rough estimate on a long-term variation. A more detailed trend analysis of trace gases in Finnish Lapland has been carried out by Virkkula *et al.* (2003).

Sulphur dioxide did not have a clear trend (Fig. 4a). Momentary high concentration pollution events that break usual low concentration measurements can be observed from the ten year measurements. Monthly-mean concentrations were less than five ppb, while hourly means were sometimes over 50 ppb. Monthly-mean concentrations were slightly higher during the late 1990s. This trend in the concentration could be due to decreasing winter temperatures during that time (Table 1), which led to hindered deposition and accumulation of pollutants.

Monthly-mean ozone concentrations were between 25 and 45 ppb (Fig. 4b). O$_3$ mixing ratios in the remote clean lower troposphere are in the range of 10–50 ppb, depending on latitude and season (Logan 1985). Hourly-mean concentrations displayed a diurnal variation and had values from 15 to 75 ppb. A clear seasonal variation was also seen. The slightly higher values in the beginning of the 1990s as compared with the rest of the measurement period might be due to the change in a measurement setup, which took place in 1994. A slightly decreasing trend in the summertime lows was seen from 1995 to 2001.

NO$_x$ measurements started in 1997 (Fig. 4c). The four-year measurement period is too short for observing long-term trends. Monthly-mean concentrations were below one ppb and the highest hourly means were over five ppb.

The hourly-mean aerosol particle concentrations were most frequently between 400 and 1200 particles cm^{-3}, the highest values being
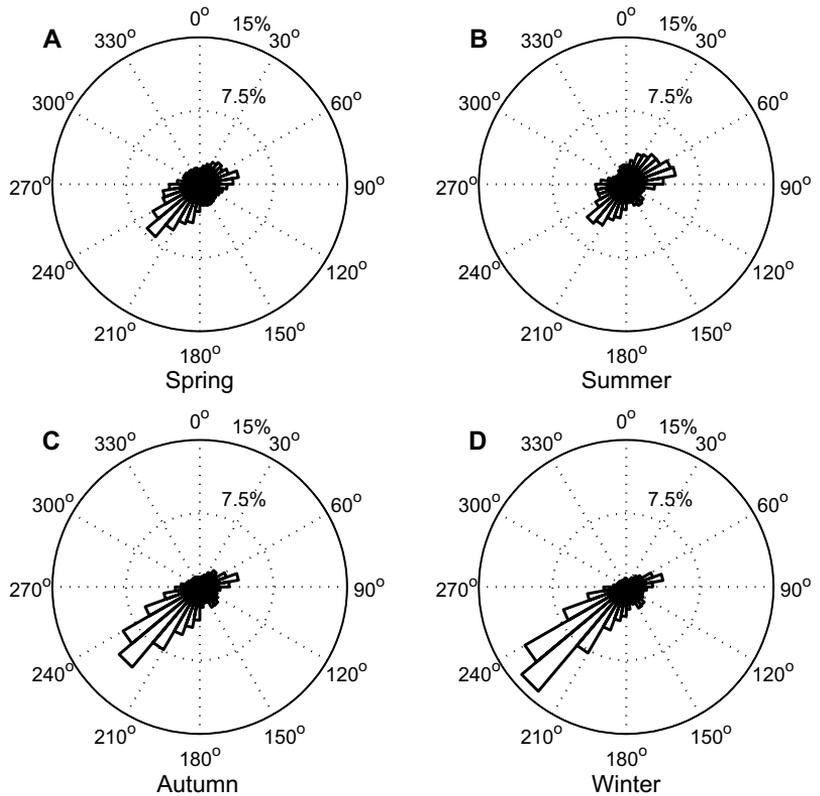
Fig. 3. Distribution of measured local wind direction in different seasons (winter, spring, summer, autumn), occurrence is presented in percents, numbers on the circle indicate the wind direction in degrees.

over 14 000 particles cm^{-3} (Fig. 4d). Low concentrations of only tens of particles cm^{-3} were measured monthly. During the ten years of measurements there was a significant variation, usually about 1000 particles cm^{-3}, mostly due to seasonal fluctuations. Monthly-mean aerosol particle concentrations were highest in 1996.

Sector classification of measured species

The connection between the local wind direction and mean concentration distributions of sulphur dioxide, ozone, nitrogen oxides and aerosol particles were calculated for all the seasons (Figs. 5–8). The concentration means were calculated as a function of local wind direction in ten-degree sectors and presented in a compass circle where zero degrees correspond to north. Three different source areas can be seen: the Kola industrial area in the east, the Arctic Ocean and Barents Sea in the north to north-west, and the

national and European transport from southwest to southeast. Air masses coming from the Arctic Ocean are thought to be the cleanest ones (Harrison *et al.* 2000).

The highest SO$_2$ concentrations were measured when the local winds were northerly or easterly, whereas the lowest concentrations were associated with the south-westerly local wind directions during all the seasons (Fig. 5). The main source area for high SO$_2$ concentrations measured in Värriö was the Kola Peninsula. Highest momentary concentrations were measured during northerly and easterly winds. Local easterly winds attribute to the emissions from smelteries and ore refineries in the Kola Peninsula, namely from Montchegorsk, located less than 150 km from Värriö. High concentrations measured during northerly winds might be due to the smeltery in Nikel located north, less than 200 km, of Värriö in the Kola Peninsula. The Arctic Oceans natural SO$_2$ emissions may also contribute to it. Due to the proximity of these large industrial complexes, in contrast to the

Table 1. Monthly median, minimum and maximum values of temperature (°C) and median values of relative humidity (RH in %) in Värriö 1992–2001.

	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	RH
January	−9.6	−7.2	−12.3	−8.5	−8.4	−13.4	−10.6	−15.3	−10.6	−7.9	87.8
	(−17.8/1.3)	(−23.8/−0.8)	(−27.4/−1.8)	(−19.5/0.1)	(−18.6/−1.9)	(−20.4/−0.3)	(−21.6/−1.1)	(−37.5/−2.0)	(−22.8/−0.7)	(−16.7/2.2)	
February	−6.2	−9.3	−11.9	−9.7	−13.8	−12.7	−18.9	−11.4	−9.8	−14.7	84.6
	(−15.8/1.5)	(−21.4/2.3)	(−24.5/−0.5)	(−19.5/−1.0)	(−21.9/−1.2)	(−22.0/0.9)	(−28.5/−0.6)	(−28.9/−0.8)	(−19.2/−0.7)	(−25.8/−0.4)	
March	−3.7	−6.1	−6.9	−5.6	−5.9	−7.2	−11.3	−7.0	−6.3	−11.0	83.6
	(−16.4/2.5)	(−20.1/2.6)	(−16.3/2.9)	(−14.5/1.9)	(−12.4/3.6)	(−15.9/3.3)	(−20.5/2.8)	(−18.3/0.8)	(−18.2/6.0)	(−21.7/0.5)	
April	−6.7	−3.5	0.1	−2.2	−4.2	−5.9	−5.5	−0.9	−1.5	−2.2	75.1
	(−16.6/6.9)	(−13.8/9.2)	(−9.4/11.5)	(−8.5/5.3)	(−12.3/4.7)	(−14.4/3.1)	(−20.5/9.7)	(−13.6/13.8)	(−12.2/6.9)	(−15.7/8.3)	
May	3.3	2.7	0.5	1.1	−0.4	1.4	1.3	−0.7	2.9	1.1	67.9
	(−3.0/23.8)	(−3.4/17.6)	(−4.8/13.2)	(−6.4/15.7)	(−8.3/12.1)	(−4.4/11.2)	(−3.1/11.3)	(−11.0/10.8)	(−6.2/16.3)	(−5.5/15.0)	
June	10.8	7.0	7.9	10.3	7.0	9.8	6.3	12.4	9.0	11.5	67.5
	(0.6/25.6)	(−0.9/17.2)	(0.5/21.3)	(−1.1/21.3)	(−2.8/18.1)	(−2.1/26.7)	(−3.3/19.2)	(−2.8/26.4)	(−0.4/26.2)	(0.0/22.6)	
July	–	13.9	12.9	9.8	11.4	13.2	13.5	12.2	14.6	12.7	74.2
	(–/–)	(1.9/21.8)	(2.7/24.5)	(2.3/24.4)	(1.6/20.6)	(4.2/26.1)	(4.5/24.0)	(1.6/25.4)	(3.5/27.8)	(4.0/25.7)	
August	6.5	9.7	11.4	8.5	13.1	12.5	8.7	8.5	10.0	9.5	84.1
	(1.8/12.6)	(3.1/21.8)	(3.1/25.0)	(3.3/24.3)	(2.1/22.9)	(3.4/23.0)	(−0.9/15.0)	(1.9/17.6)	(4.4/19.3)	(1.9/18.3)	
September	7.6	0.7	3.3	4.2	3.4	6.8	4.7	6.7	6.0	8.2	88.6
	(−0.2/15.2)	(−4.4/6.6)	(−2.3/10.8)	(−2.0/17.7)	(−3.6/17.1)	(−2.0/16.8)	(−4.2/13.3)	(−1.2/19.4)	(−2.4/12.3)	(−3.7/15.1)	
October	−9.4	−3.9	−0.8	−0.5	0.3	−1.7	−0.9	0.2	4.2	−1.7	93.7
	(−18.4/7.0)	(−13.7/6.8)	(−10.1/8.6)	(−13.7/10.3)	(−9.1/7.4)	(−12.0/3.7)	(−9.6/4.8)	(−4.7/6.8)	(−15.2/9.9)	(−8.9/6.3)	
November	−10.4	−6.2	−7.5	−10.3	−4.1	−6.8	−10.6	−5.3	−2.1	−7.9	92.2
	(−21.0/0.2)	(−15.2/−0.4)	(−15.0/0.9)	(−19.7/−1.1)	(−19.5/3.3)	(−21.1/2.2)	(−18.3/−0.2)	(−12.9/3.0)	(−15.2/3.2)	(−16.7/−1.6)	
December	−4.7	−10.0	−5.6	−12.0	−10.9	−10.2	−10.2	−11.3	−8.2	−12.6	90.9
	(−14.6/1.2)	(−18.3/−2.3)	(−15.5/−0.7)	(−26.7/−0.3)	(−21.3/−0.2)	(−21.6/4.0)	(−24.4/2.2)	(−22.6/−1.5)	(−24.8/2.2)	(−22.5/−0.1)	

Fig. 4. Hourly means (grey) and running monthly mean (black) of (**A**) sulphur dioxide, (**B**) ozone , (**C**) nitrogen oxides, and (**D**) aerosol particle concentrations.

more remote source areas in Finland and Europe, minimal dilution and oxidation of SO_2 occurs, especially during winter. The effect of dilution can be seen as lower sulphur dioxide concentrations with local northeasterly winds. A line of mountains on the Russian side prevents a direct movement of polluted air masses. Seasonal variations in SO_2 emissions from the Kola area are probably minor, since the smelters are in more or less full operation all year around. National and European emissions are slightly higher in the winter when the need for heating is largest.

Ozone concentrations did not show any local wind direction pattern (Fig. 6). This was true for all the seasons. The concentration distributions were even, indicating that there were no specific regions contributing to the formation and transport of O_3 to Värriö.
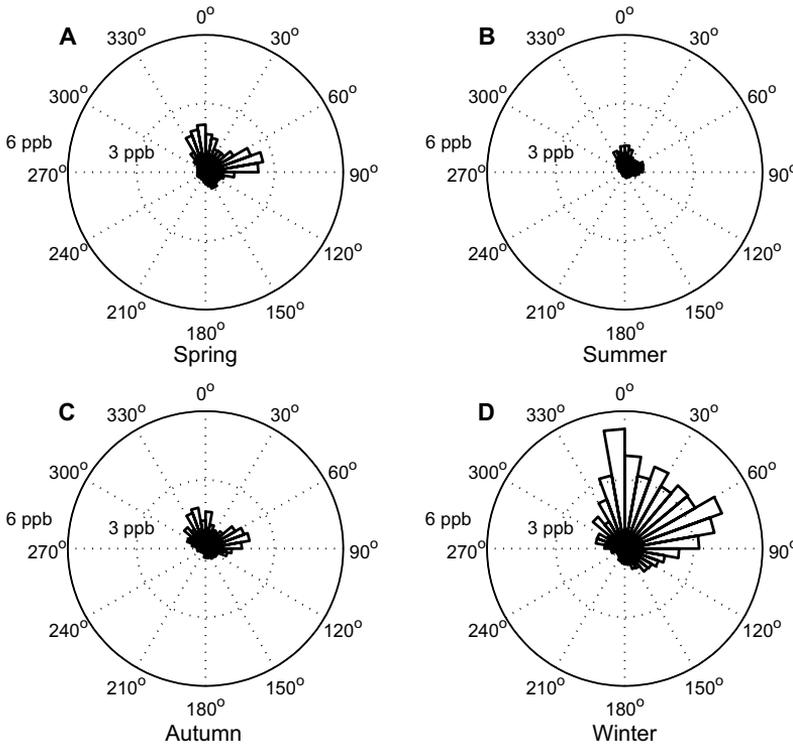
Fig. 5. Mean concentrations of sulphur dioxide, presented in ppb, as a function of local wind direction in (**A**) spring, (**B**) summer, (**C**) autumn and (**D**) winter. Numbers on the circle indicate the wind direction in degrees.
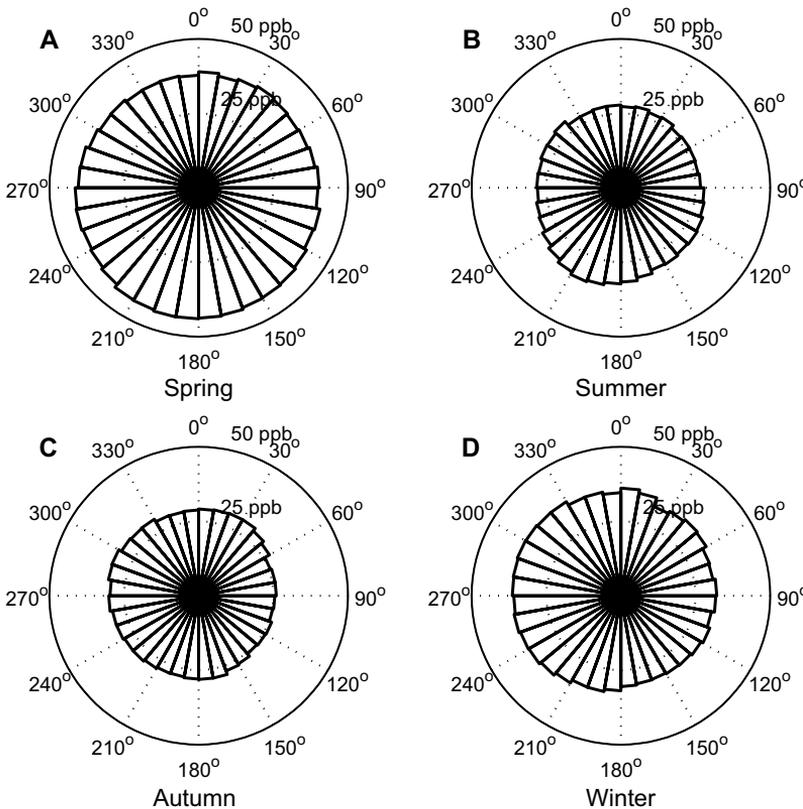
Fig. 6. Mean concentrations of ozone, presented in ppb, as a function of local wind direction in (**A**) spring, (**B**) summer, (**C**) autumn and (**D**) winter. Numbers on the circle indicate the wind direction in degrees.
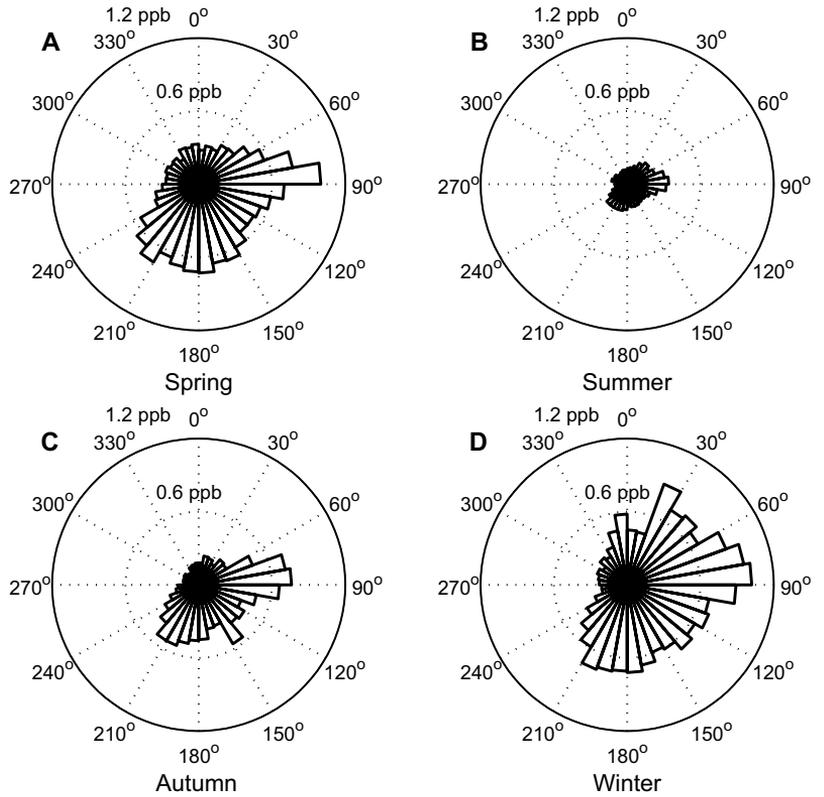
Fig. 7. Mean concentrations of NO$_x$, presented in ppb, as a function of local wind direction in (**A**) spring, (**B**) summer, (**C**) autumn and (**D**) winter. Numbers on the circle indicate the wind direction in degrees.
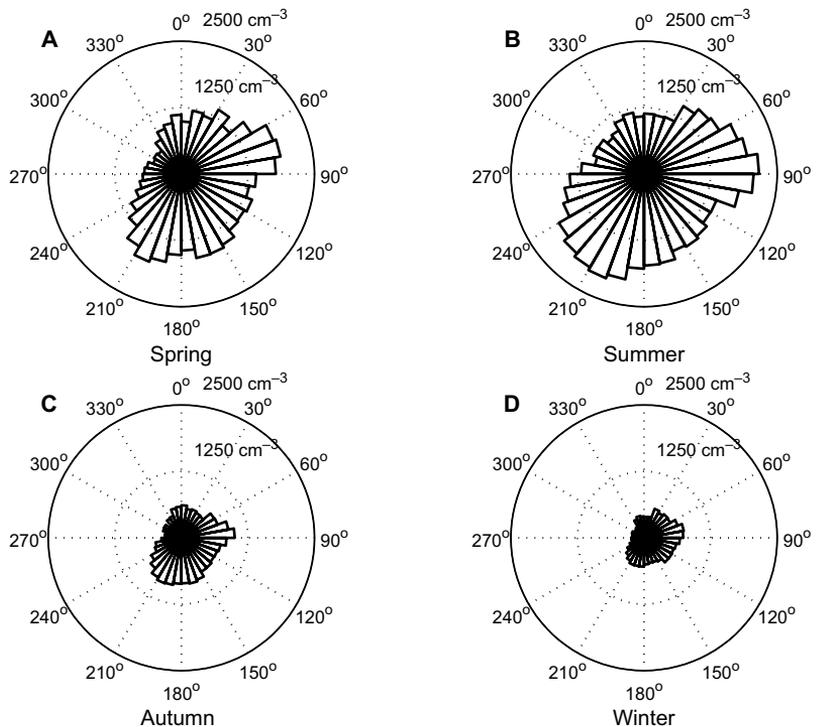
Fig. 8. Mean concentrations of aerosol particles, presented in particles cm^{-3}, as a function of local wind direction in (**A**) spring, (**B**) summer, (**C**) autumn and (**D**) winter. Numbers on the circle indicate the wind direction in degrees.

Highest NO_x concentrations were measured at local easterly winds (Fig. 7), being suggestive of an immediate transport from the industrial areas in Kola, especially Montchegorsk, and possibly also from other areas in Russia. The smelter located in Nikel, north of Värriö, might be responsible for the high SO_2 concentrations associated with northerly winds, even though it does not seem to be a very important source of NO_x. This might be due to the fact that there is an ore refinery in Montshegorsk but not in Nikel, making the emissions from these complexes different in composition (Kashulina and Reimann 2002). During local southerly winds, especially in winter and spring season, elevated concentrations were measured for NO_x but not for SO_2. Sulphur dioxide is a reactive gas and it will eventually be converted into sulphuric acid and other reaction products in the atmosphere. If the emission source is located far enough, the transport time will be sufficient for SO_2 to be converted into other compounds. On the other hand, the measured NO_x includes the reaction products of emitted nitrogen oxides. PAN (peroxyacetyl nitrate) is a product of atmospheric reactions of nitrogen oxide pollution and may often make up for a large fraction of measured NO_x in remote areas. The lowest NO_x concentrations were measured when the wind was from the west or north. Those sectors do not contain any significant pollution sources.

Similar to SO_2 and NO_x, the highest aerosol particle concentrations were measured during easterly winds (Fig. 8). Also in accordance with SO_2 and NO_x, the lowest aerosol particle concentrations were measured in the clean air masses brought by northwesterly winds from the Arctic Ocean. These air masses contain also sea-salt particles. High aerosol particle concentrations were also measured during southerly and southwesterly winds, except in winter, suggesting a southern aerosol particle source that is not related to polluted air masses. Aerosol particles from different regions have characteristic chemical compositions that can be identified with chemical analysis. The Kola Peninsula smelters, central Europe and Arctic Ocean have been determined as sources for aerosols in Finnish Lapland (Virkkula *et al.* 1999). We will next have a more detailed look at the differences in seasonal variation between aerosol particles and SO_2, as all the sources for these two species seem to not be the same.

Possible source regions for aerosol particles and SO_2 measured at Värriö during the three different types of episodes were previously studied with a trajectory analysis (Ahonen *et al.* 1997, Kulmala *et al.* 2000b). When the local wind direction was west or northwest and low aerosol particle and SO_2 concentrations were measured, the trajectory analyses showed that the air mass came from the Arctic Ocean and went then over the Barents Sea and sparsely-populated areas in Finland and Norway. When the local wind direction was from northeast or northwest and low aerosol particle concentrations together with high SO_2 concentrations were noted, the air came from the Arctic Ocean, over the Barents Sea and then over the Kola area. One episode having high aerosol particle and SO_2 concentration associated with south-west winds was analyzed. Trajectories showed that the air mass came from the Arctic Ocean and Kola area and south of the mountains between Montchegorsk and Värriö. It can be seen from the trajectory analyses that the events with high SO_2 concentration together with high aerosol particle concentrations were typical for air masses coming from the Kola Peninsula. Situations with high aerosol particle concentration and SO_2 concentrations smaller than 0.1 ppb were associated air masses coming from the Arctic Ocean (Ahonen *et al.* 1997). These analyses support the conclusion that only a small amount of SO_2 measured in Värriö is of marine origin and that a major fraction of it comes from non-local anthropogenic emissions, mainly from the Kola areas.

Local wind directions can be related to the direction of nearby source areas. Therefore, comparing concentration differences of measured species based on wind direction is to some extent justified, even though more accurate information could be obtained with the trajectory analysis.

Diurnal variation

The diurnal pattern of sulphur dioxide, ozone, nitrogen oxides, and aerosol particle concentrations changed with the season (Fig. 9). In gen-
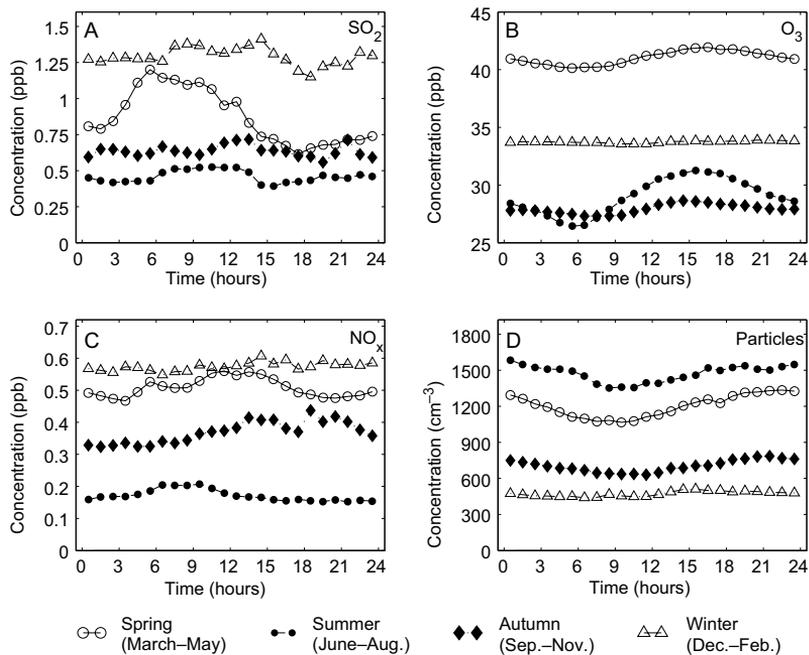
Fig. 9. Diurnal pattern of hourly mean (**A**) sulphur dioxide, (**B**) ozone, (**C**) nitrogen oxides, and (**D**) aerosol particle concentration averages during different seasons (winter, spring, summer and autumn).

eral, the diurnal variation was least notable in the dark and cold winter, and most notable in spring or summer when the radiation was stronger.

The sulphur dioxide concentration did not have a clear diurnal variation, except in the spring when it had a small maximum in the morning and a minimum in the late afternoon (Fig. 9a). This feature might be due to changes in the mixing and dilution of SO_2 as the sun heats up surface air and increases the mixing of air masses.

The diurnal variation of the ozone concentration varied with the time of the year (Fig. 9b). This can be explained by the changing diurnal solar radiation in Värriö from the long dark winter nights to the one and a half-month-long polar day in the midsummer. In December the radiation was at its annual minimum with only minor diurnal variation. Diurnal ozone variation is also at its minimum. The turning point is the polar night when the sun does not come up for a few days. During the summer the solar radiation has a clear diurnal behaviour with maximum intensity at midday and a minimum at five in the early morning (Fig. 2). Ozone reached its maximum four hours later (at around 16:00) than solar radiation, and the minimum appeared between 05:00 and 07:00 in the morning (Fig. 9b). Ozone

had the highest diurnal variation during the summer months, with some variation seen also during the spring and autumn.

Ozone is formed as a result of photochemical reactions of CO and non-methane hydrocarbons in the presence of NO and NO_x (Seinfeld and Pandis 1998). Especially during springtime in Arctic areas, ozone is transported from the stratosphere (Levy *et al.* 1985). Ozone is depleted from the atmosphere by reactions with other gas phase compounds, reactions on surfaces and by photolysis that at the same time contributes to the formation of OH-radicals (Seinfeld and Pandis 1998). During the night a stable boundary layer is formed and the ozone concentration decreases due to a constant dry deposition and chemical reactions. After sunrise photochemical reactions start to produce more ozone and a mixed boundary layer grows to its maximum (Helmig *et al.* 2002). The formation of a stable boundary layer with a steady deposition sink to the surrounding forest can be momentarily disturbed by intrusions of air from the free troposphere. This is attributed to the location of the measurement station relatively high on top of a hill.

Over half of the global NO_x emissions are from anthropogenic sources (Seinfeld and Pandis 1998). Included in this estimation is
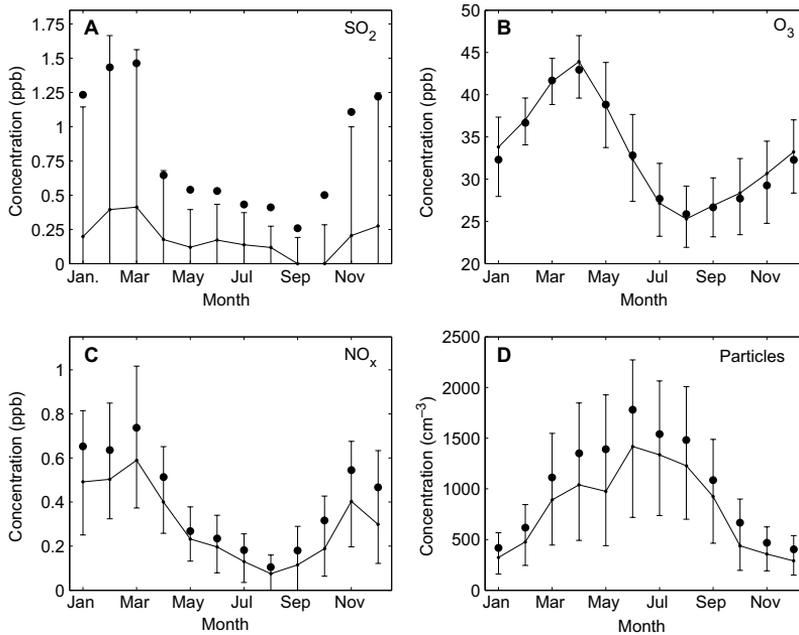
Fig. 10. Monthly averages (circles), medians, 25 and 75 percentiles (solid line and bars) of (**A**) sulphur dioxide, (**B**) ozone, (**C**) nitrogen oxides, and (**D**) aerosol particle concentrations.

NO, NO_2, and all atmospheric compounds that are their oxidation byproducts as well as HNO_3. Anthropogenic emissions are derived primarily from the combustion of fossil fuels and biomass burning. Natural emissions include soil releases of mostly NO, NO_2 and N_2O, as well as lightning during which inert atmospheric N_2 is oxidized in a high-energy reaction. The soil activity in Värriö is small and presumably does not release notable amounts of nitrogen compounds. Measured NO_x was from pollution episodes that were most notable in winter when the mixing of air masses is at its smallest (Fig. 9c). Summer concentrations were lower than those in other seasons, and winter concentrations were the highest. Similar to SO_2, NO_x did not have a clear diurnal behaviour. Minimum NO_x concentrations appeared after midnight and maximum ones after noon.

The diurnal variation of aerosol particle concentration was season dependent, being at its greatest in the summer and least noticeable in the winter (Fig. 9d). The minimum concentrations appeared around 08:00 in the morning in the spring, a few hours later at about 10:00 in the summer and at midday in the autumn. The concentration maximums were during the night, at midnight in the summer and a few hours earlier in the spring and autumn. The diurnal variation was connected to new particle formation, which

has been observed at different measurement stations in Lapland and also in other Nordic countries (Kulmala *et al.* 2000b, Tunved *et al.* 2003).

Sulphur dioxide is regarded as a participant in aerosol particle formation (Laaksonen *et al.* 2000). High SO_2 concentrations with high aerosol particle concentrations came usually with easterly winds from the Kola industrial area. High aerosol particle concentrations were also frequently measured during the moments of low SO_2 concentrations, especially in the summer season. This implies that aerosol particle formation does not acquire high SO_2 concentrations.

Seasonal variation

Sulphur dioxide, nitrogen oxides, ozone and aerosol particle concentrations had a characteristic seasonal variation (Fig. 10). Calculated monthly averages and medians followed the same patterns at different concentration levels.

Sulphur dioxide concentration had a seasonal variation but it was not as regular as that of ozone (Fig. 10a). Highest concentrations were measured in the winter, usually in January or February, and minimum concentrations appeared in the summer or early autumn. This behaviour was most likely due to seasonal differences in

the wind direction, mixing height and variations in emission rates. In the winter the wind direction was more often from the southwest than in the summer (Fig. 3), which might be expected to result in lower pollutant concentrations in the winter, since the nearest and most significant emission sources are in the northeast. A snow and ice cover on surfaces may also slow down the dry deposition of gases in the winter, leading to high measured concentrations (Barrie 1986, Barrie and Platt 1997, Jaescheke *et al*. 1997, Vinogradova 2000).

A clear seasonal variation in ozone concentrations can be seen (Fig. 10b). The highest monthly-average concentrations appeared always during the spring months, peaking in April. The minimum concentrations occurred in July and August. This feature is typical for a remote site (Levy *et al*. 1985, Logan 1985), and it can be concluded that the ozone concentration was closely linked to its formation rate by photochemistry. The spring maximum in ozone concentrations can be explained by the accumulation of ozone precursors during the wintertime. This is due to the low level of photochemical activity, the transport of ozone rich air from the stratosphere coupled with the accumulation of ozone precursors, and the increase in solar radiation (Jaeschke *et al*. 1997).

The height of the boundary layer increases during summertime. This might lead to better mixing, deposition and lower concentrations. Removal of ozone in the luminous seasons, spring and summer, could be due to catalytic photochemical reactions with BrO_x radicals of biological origin from the Arctic Ocean (Barrie *et al*. 1988, Barrie and Platt 1997). The snow cover usually melts in Värriö in late May along with the start of the growing season. An uncovered canopy and stomatal activity increase the deposition velocity and thereby lead to lower concentrations of trace gases. Ozone concentrations are at maximum in the summer near populated and industrialized regions as this is where ozone is produced photochemically from hydrocarbons and NO_x originating mainly from traffic (Levy *et al*. 1985). Ozone concentrations in Värriö had a clear minimum in the late summer months.

NO_x concentrations have been measured in Värriö from 1997 to 2001. NO concentra-

tions have also been measured but they were constantly lower than the detection limit of our instrument. Although the pollution events were not as dominant as in the case of SO_2, NO_x had a clear seasonal cycle similar to SO_2. It is likely that the seasonal behaviour of NO_x and SO_2 are due to the same reasons. High monthly NO_x concentrations (median values 0.5–0.6 ppb) were measured in winter, with highest values appearing in March, early spring. The concentrations were at the minimum in the late summer (median values less than 0.2 ppb) and an increase in concentrations began around September. The seasonal concentration variability of NO_x was larger than that of ozone. This suggests that photochemical reactions do not dominate the seasonal behaviour of NO_x concentrations. Lowest measured concentrations were less than 0.2 ppb and the highest concentrations were over 10 ppb.

Aerosol particle concentrations had a distinct seasonal variation (Fig. 10d). The concentration minimum was in the midwinter in December or January. In the spring and summer concentrations were clearly higher. Sources of aerosol particles have been suggested to be more of an anthropogenic origin in winter than in summer (Barrie 1986, Vinogradova 2000). This conclusion is supported by our study. It has also been suggested that the dense air and low precipitation in the winter would lead to the accumulation of aerosol particles (Jaeschke 1997). The dry deposition of aerosol particles is not likely to be hindered by the snow cover, since the texture of the deposition surface is less critical for particles than for gases (Seinfeld and Pandis 1998). The maximum in aerosol particle concentrations could be seen in midsummer, and the increase in concentrations began in spring. The activity of aerosol particle formation events in Värriö and Pallas stations in Finnish Lapland, southern Finland, and in other Nordic countries was studied by Tunved *et al*. (2003). Events occur most frequently at the continental boundary layer in spring and autumn, one probable reason being the suitable meteorological conditions at that time (Nilsson *et al*. 2001). The importance of a biological factor in aerosol particle formation events has also been suggested in a study where measurements from SMEAR I and from SMEAR

II stations were analyzed (Kulmala *et al.* 2000a, Kulmala *et al.* 2001). The lowest monthly-mean aerosol particle concentrations were below 50 particles cm^{-3}, and during the annual minimum in the winter concentrations were generally under 200 particles cm^{-3}. The momentary concentration maxima were usually around 1400 to 1900 particles cm^{-3}, even though concentrations higher than 10 000 particles cm^{-3} were measured on a few occasions. The highest measured momentary concentration was 17 400 particles cm^{-3}. The lack of photochemistry in the winter might inhibit aerosol particle formation, while the bare canopy might enhance it in the summer.

Conclusions

A ten-year period (1992–2001) of continuous measurements of SO_2, O_3, NO_x and aerosol particles at Värriö showed no obvious long-term trend for the concentration of sulphur dioxide, nitrogen oxides or aerosol particles in view of monthly moving averages of hourly-mean data. A slight decreasing trend was observed for low summertime ozone concentrations during 1997–2001.

The main sources for SO_2 appeared to be non-local anthropogenic emissions, mainly from the Kola industrial area. Also NO_x concentrations were controlled by anthropogenic emissions from Finland and Europe. Ozone formation seemed to be controlled by photochemistry. Aerosol particle concentrations were likely to be dominated by anthropogenic point-source emissions in the winter and by natural formation over larger areas in the summer. Emissions of sulphur dioxide from the large industrial complexes in the Kola Peninsula were observed as periodically high SO_2 concentrations at Värriö. A similar feature has also been reported in Sevettijärvi, north of Värriö (Virkkula *et al.* 2003). Episodes with high SO_2 concentrations lasted, in general, only a few hours and otherwise the concentrations remained low. The highest momentary concentrations were measured during local northerly and easterly winds. Also aerosol particle and nitrogen oxide concentrations peaked with easterly winds. Contrary to SO_2, high NO_x concentrations were measured during southerly winds, especially in winter and spring.

A distinct seasonal behaviour was observed for all the compounds studied. The overall seasonal variations in trace gas concentrations were similar to each other, showing high concentrations in winter and spring. The seasonal variation in aerosol particle concentration was different, being usually highest during the summer. We attribute these seasonal features to the main source areas for these compounds, primary emissions opposed to secondary formation processes, prevailing meteorological conditions and atmospheric chemistry.

The diurnal variation of the SO_2 concentrations was most notable in springtime with higher levels in the morning and before noon. For O_3 the largest diurnal variation was seen in summer when its concentrations increased from the early morning low to a maximum in the afternoon. The diurnal variation of the aerosol particle concentration was also greatest in the summertime. Maximum particle concentrations appeared before midnight and minimum concentrations in the morning before noon.

References

Aalto P., Kulmala M. & Nilsson E.D. 1995. Nucleation events in the Värriö environmental measurement station. *J. Aerosol Sci*. 26: S411–S412.

Ahonen T., Aalto P., Rannik Ü., Kulmala M., Nilsson E.D., Palmroth S., Ylitalo H. & Hari P. 1997. Variations and vertical profiles of trace gas and aerosol concentrations and CO_2 exchange in Eastern Lapland. *Atmos. Environ*. 31: 3351–3362.

Arya S.P. 1999. *Air pollution meteorology and dispersion. Atmospheric system and pollutant transport,* Oxford University Press, Oxford, 310 pp.

Barrie L.A. 1986. Arctic pollution: an overview of current knowledge. *Atmos. Environ*. 20: 643–663.

Barrie L.A., Bottenheim J.W., Schnell R.C., Crutzen P.J. & Rasmussen R.A. 1988. Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere. *Nature* 334: 138–141.

Barrie L.A. & Platt U. 1997. Arctic tropospheric chemistry: an overview. *Tellus* 49B: 450–454.

Baskaran M. & Shaw G.E. 2001. Residence time of arctic haze aerosols using the concentrations and activities of ^{210}Po, ^{210}Pb and ^7Be. *J. Aerosol Sci*. 32: 443–452.

Chipperfield M.P. & Jones R.L. 1999. Relative influences of atmospheric chemistry and transport on Arctic ozone trends. *Nature* 400: 551–554.

Farman J.C., McRae G.J. & Seinfeld J.H. 1985. Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interactions. *Nature* 315: 207–210.

Hari P., Kulmala M., Pohja T., Lahti T., Siivola E., Palva L., Aalto P., Hämeri K., Vesala T., Luoma S. & Pulliainen E. 1994. Air pollution in Eastern Lapland: challenge for an environmental measurement station. *Silva Fennica* 28: 29–39.

Harrison R.M., Grenfell J.L., Peak J.D., Clemitshaw K.C., Penkett S.A., Cape J.N. & McFadyen G.G. 2000. Influence of airmass back trajectory upon nitrogen compound composition. *Atmos. Environ.* 34: 1519–1527.

Helmig D., Boulter J., David D., Birks J.W., Cullen N.J., Steffen K., Johnson B.J. & Oltmans S.J. 2002. Ozone and meteorological boundary-layer conditions at Summit, Greenland, during 3–21 June 2000. *Atmos. Environ.* 36: 2595–2608.

Jaeschke W., Beltz N., Dierssen J.P., Haunold W., Krischke U., Reinecke A., Salkowski T. & Trümbach J.V. 1997. Measurements on the distribution of trace substances in the Arctic troposphere. *Atmos. Res.* 44: 199–221.

Kashulina G. & Reimann C. 2001. Sulphur in the Arctic environment (1): results of a catchment-based multi-medium study. *Environ. Pollut.* 114: 3–19.

Kashulina G. & Reimann C. 2002. Sulphur in the Arctic environment (2): results of multi-medium regional mapping. *Environ. Pollut.* 116: 337–350.

Kerminen V.-M., Aurela M., Hillamo R.E. & Virkkula A. 1997. Formation of particulate MSA — deduction from size distribution measurements in the Finnish Arctic. *Tellus* 49B: 159–171.

Kulmala M., Hämeri K., Aalto P.P., Mäkelä J.M., Pirjola L., Nilsson E.D., Buzorius G., Rannik Ü., Dal Maso M., Seidl W., Hoffman T., Janson R., Hansson H.-C., Viisanen Y., Laaksonen A. & O'Dowd C.D. 2001. Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR). *Tellus* 53B: 324–343.

Kulmala M., Hämeri K., Mäkelä J.M., Aalto P.P., Pirjola L., Väkevä M., Nilsson E.D., Koponen I.K., Buzorius G., Keronen P., Rannik Ü., Laakso L., Vesala T., Bigg K., Seidl W., Forkel R., Hoffman T., Spanke J., Janson R., Shimmo M., Hansson H.-C., O'Dowd C.D., Becker E., Paatero J., Teinilä K., Hillamo R., Viisanen Y., Laaksonen A., Swietlicki E., Salm J., Hari P., Altimir N. & Weber R. 2000a. Biogenic aerosol formation in the boreal forest. *Boreal Env. Res.* 5: 281–297.

Kulmala M., Rannik Ü., Pirjola L., Dal Maso M., Karimäki J., Asmi A., Jäppinen A., Karhu V., Korhonen H., Malvikko S.-P., Puustinen A., Raittila J., Romakkaniemi S., Suni T., Yli-Koivisto A., Paatero J., Hari P. & Vesala T. 2000b. Characterization of atmospheric trace gas and aerosol concentrations at forest sites in southern and northern Finland using back trajectories. *Boreal Env. Res.* 5: 315–336.

Laaksonen A., Pirjola L., Kulmala M., Wohlfrom K.H., Arnold F. & Reas F. 2000. Upper tropospheric SO_2 conversion into sulfuric acid aerosols and cloud condensation nuclei. *J. Geophys. Res.* 105: 1459–1469.

Laurila T., Tuovinen J.-P. & Lättilä H. 1991. *Lapin ilmansaasteet*, Ilmatieteen laitos, ilmanlaatuosasto, 10 pp.

Levy II H., Mahlman J.D., Moxim W.J. & Liu S.C. 1985. Tropospheric ozone: the role of transport. *J. Geophys. Res.* 90: 3753–3772.

Logan J.A. 1985. Tropospheric ozone: seasonal behavior, trends and anthropogenic influence. *J. Geophys. Res.* 90: 10463–10482.

Nilsson E.D. & Leck C. 2002. A pseudo-Lagrangian study of the sulfur budget in the remote Arctic marine boundary layer. *Tellus* 54B: 213–230.

Nilsson E.D., Paatero J. & Boy M. 2001. Effects of air masses and synoptic weather on aerosol formation in the continental boundary layer. *Tellus* 53B: 462–478.

Pirjola L., Laaksonen A., Aalto P. & Kulmala M. 1998. Sulfate aerosol formation in the Arctic boundary layer. *J. Geophys. Res.* 103: 8309–8321.

Polissar A.V., Hopke P.K., Paatero P., Kaufmann Y.J., Hall D.K., Bodhaine B.A., Dutton E.G. & Harris J.M. 1999. The aerosol at Barrow, Alaska: long-term trends and source locations. *Atmos. Environ.* 33: 2441–2458.

Rahn K.A. 1981. Relative importance of North America and Eurasia as sources of Arctic aerosol. *Atmos. Environ.* 15: 1447–1455.

Raitio H., Tuovinen J.-P. & Anttila P. 1995. Relation between sulphur concentrations in the Scots pine needles and the air in northernmost Europe. *Water, Air, and Soil Pollut.* 85: 1361–1366.

Seinfeld J. & Pandis S. 1998. *Atmospheric chemistry and physics*, John Wiley & Sons, New York, 1326 pp.

Strunin M.A., Postnov A.A. & Mezrin M.Y. 1997. Meteorological potential for contamination of arctic troposphere: boundary layer structure and turbulent diffusion characteristics. *Atmos. Res.* 44: 37–51.

Tunved T., Hansson H.-C., Kulmala M., Aalto P., Viisanen Y., Karlsson H., Kristensson A., Swietlicki E., Dal Maso M., Ström J. & Komppula M. 2003. One year boundary layer aerosol size distribution data from five Nordic background stations. *Atmos. Chem. Phys. Discuss.* 3: 2783–2833.

Vinogradova A. 2000. Anthropogenic pollutants in the Russian Arctic atmosphere: sources and sinks in spring and summer. *Atmos. Environ.* 34: 5151–5160.

Virkkula A. 1997. Performance of a differential optical absorption spectrometer for surface O_3 measurements in the Finnish Arctic. *Atmos. Environ.* 31: 545–555.

Virkkula A., Teinilä K. & Hillamo R. 2003. A decade of trace gas measurements using DOAS in Finnish Lapland. *Boreal Env. Res.* 8: 351–363.

Virkkula A., Aurela M., Hillamo R., Mäkelä T., Pakkanen T. & Kerminen V.-M. 1999. Chemical composition of atmospheric aerosol in the European subarctic: contribution of the Kola Peninsula smelter areas, central Europe and the Arctic Ocean. *J. Geophys. Res.* 104: 23681–23696.

Yokouchi Y., Barrie L.A., Toom D. & Akimoto H. 1996. The seasonal variation of selected natural and anthropogenic halocarbons in the Arctic troposphere. *Atmos. Environ.* 30: 1723–1727.