A decade of trace gas measurements using DOAS in Finnish Lapland

Aki Virkkula[1], Kimmo Teinilä[1], Risto Hillamo[1] and Andreas Stohl[2]

[1] *Finnish Meteorological Institute, Air Quality Research, Sahaajankatu 20 E, FIN-00880 Helsinki, Finland*

[2] *Department of Ecology, Technical University Munich, D-85354 Freising-Weihenstephan, Germany*

Trace gas concentrations have been measured at Sevettijärvi in Finnish Lapland from 8 January 1992 to 10 July 2002. The maximum hourly SO_2 concentrations decreased from around 500 μg m^{-3} in the first two years of the monitoring to 200–300 μg m^{-3} in the mid 1990s. The annual average SO_2 concentrations decreased from about 5 μg m^{-3} to 3–4 μg m^{-3} during the same period when taking into account the years for which the data coverage was above 85%. For NO_2 and O_3 no clear trends were observed. The sources of all three trace gases were investigated using wind measurements and in the case of NO_2 also using back trajectories. The analysis indicated that the source areas of NO_2 and SO_2 are to the east and north-east of the site, i.e., at Nikel-Zapolyarnyj industrial areas in Kola Peninsula, Russia. In addition to these, NO_2 transported from other industrial and urban areas in Europe can also be observed at Sevettijärvi.

Introduction

At the end of the 1980s and beginning of the 1990s Finns were seriously concerned about whether the Ni-Cu smelters in the Kola Peninsula, especially at Nikel and Zapolyarnyj, could have serious effects on the nature of Finnish Lapland. There was a good reason to be concerned because these two smelters emitted more than twice the amount of SO_2 emitted by the whole of Finland (Tuovinen *et al.* 1993) and because they are located close to Finnish territory. In addition in Monchegorsk, somewhat further from the Finnish border, there is another big smelter that affects Lapland. In summer 1991 the Finnish Meteorological Insti-

tute (FMI) built a station for measuring atmospheric aerosols and trace gases at Sevettijärvi (69°35´N, 28°50´E, 130 m above sea level) in order to study pollution coming from the Russian industrial areas in the Kola Peninsula to Finnish Lapland. The goal was to provide information on air quality for The Lapland Forest Damage Project, a multidisciplinary effort to determine the effects of Kola emissions on the health of the forests in Lapland (Tikkanen and Niemelä, 1995; www.metla.fi/julkaisut/muut/elproj/). The site is essentially as near to the large pollution sources in Kola Peninsula as possible in Finland (Fig. 1). The distance to Nikel is approximately 60 km. The site is also close to the Barents Sea
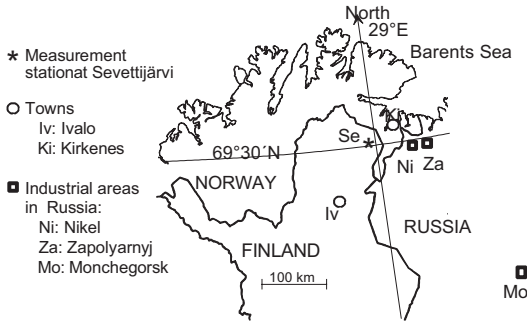
Fig. 1. Location of the measurement site and nearest sources of pollution.

which is a part of the Arctic Ocean. The distance to the nearest fjord is approximately 40 km. The nearest important population centres are Kirkenes in Norway and Ivalo in Finland.

In addition to investigating fresh pollution from the Russian smelters, the site can be used to study other sources as well. As shown by Virkkula *et al*. (1995, 1997, 1999), the site is exposed to air coming from sources other than the Kola Peninsula for most of the time. Pollution episodes from the Kola Peninsula arrive typically at Sevettijärvi two or three times per month, while the rest of the time either continental air masses from other parts of Europe or cleaner air from the North Atlantic and Arctic Ocean arrive at the site. The most frequent wind sectors S and SW bring air from continental Europe, so the site gives a good description of the polluted European air that leaves the continent and goes into Arctic areas. A significant fraction of time the air is coming from the Norwegian Sea and the Arctic Ocean, so data on background concentrations is obtained as well. The fact that the site is north of the Arctic Circle makes it possible to investigate the effects of polar night and polar sunrise. An example of this is the relation between the SO_2 and particle number concentration, being clearly different between the dark winter months and spring/summer period (Virkkula *et al*. 1997). This relation has demonstrated that a large fraction of the aerosol observed during pollution episodes from Nikel is of secondary origin. Studies on aerosol chemistry at Sevettijärvi have been presented, e.g., by Kerminen *et al*. (1997, 1999), Maenhaut *et al*. (1999a, 1999b), Fridlind *et al*. (2000) and Ricard *et al*. (2002a, 2002b).

In Norway there are measurement stations closer to the smelters. The Norwegian Institute for Air Research (NILU) has measured air pollution in the border areas of Norway and Russia and studied the dispersion of both gaseous and particulate air pollutants from Nikel and Zapolyarnyj for over a decade. The Norwegian results have been published regularly and extensively in several annual reports. In a recent report describing the results from the border stations it was shown that after a clear decrease of SO_2 concentrations from the 1980s to 1990s, the average concentrations have remained approximately at the same level (Hagen *et al*. 2002).

The aim of this paper is to investigate how the concentrations of SO_2, NO_2 and O_3 have varied during the decade of measurements, and whether there are any trends in the peak and average concentrations of these compounds. Virkkula *et al*. (1995, 1997) presented a source analysis for aerosols and SO_2. The only component for which no source analysis has been presented is NO_2 and therefore some attention is paid here for making a similar analysis for that compound.

Instrumentation

The measurement station is equipped with both gas and aerosol measurement instruments. The aerosol instrumentation has been described by Virkkula *et al*. (1997, 1999) and it includes both physical measurements and filter sampling for chemical analyses. In this paper we do not discuss aerosol measurements but concentrate on gaseous pollutants.

Gas measurements

Concentrations of O_3, SO_2 and NO_2 were measured using a commercial Differential Optical Absorption Spectrometer (DOAS), model AR 500, manufactured by Opsis AB, Lund, Sweden. A detailed description of the instrumental setup at Sevettijärvi has been presented by Virkkula (1997), so only a brief summary is given here.

The instrument consists of a broad-band light source, receiver at a distance of 1021 m from the light source, and spectrometer. An approxi-

mately 40-nm band of the whole spectrum of the light from the lamp is measured for each gas. For O_3 the band is from 265.7 to 304.4 nm, for SO_2 it is from 280.7 to 319.3 nm and for NO_2 it is from 406.2 to 444.2 nm. Within the 40-nm window, 1000 samples corresponding to 1000 channels are taken in 10 ms. The scanning lasts a user-defined integration time, typically one to five minutes. The gas concentrations are determined from the measured light spectrum. The procedure that is close to that described by Edner *et al.* (1993), includes a fitting of premeasured absorption spectra of the selected gases to the measured ambient spectrum. The more light from the lamp which arrives at the analyzer, the better the fitting i.e., the better are the visibility and alignment of the source-receiver combination. The procedure applies the Beer-Lambert law to all 1000 channels, which results in 1000 concentration values. As an output, the instrument gives the mean and standard deviation of these values. Both concentration and standard deviation are given in selected units under ambient conditions, in this case in μg m^{-3}.

Calibration

During the first three years of the measurements the instrument was calibrated three or four times per year by using two calibration cells of a known length and three different concentrations of SO_2 or NO_2 (delivered by AGA AB) mixed in N_2, and pure N_2 (Fig. 2). This gave a total of seven calibration points. The instrument proved to be very linear in the range in use. The slopes of the calibration lines varied by less than 10% between the calibrations. Therefore, during the rest of the years the calibration was conducted only once a year after changing the lamp.

Determining the offset was more difficult, especially for NO_2. When leading the light directly from the calibration unit to the spectrometer, the offset was often around 1 μg m^{-3} even though no absorbing gas was present. For SO_2 the offset obtained in a similar way was usually in the range 0.5–1 μg m^{-3}. However, if the obtained offset was set to the calculation routine of the instrument, it gave negative values during periods of clean air. It appears that the offset
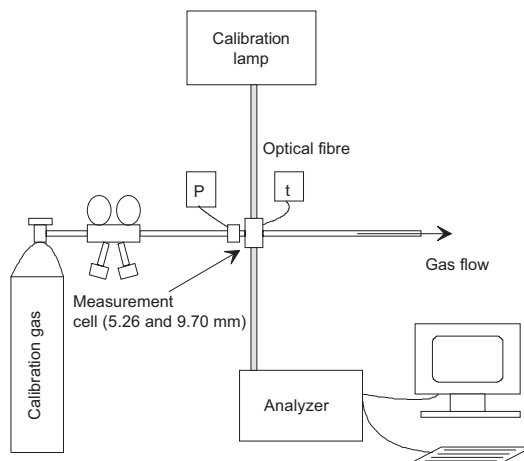

Fig. 2. DOAS calibration setup.

was due to the high light intensity when the light was lead from the calibration unit. This of course raises doubts on the span measurements as well. However, the span and the linearity were also checked using a method of standard addition during some clean days, i.e., when the NO_2 and SO_2 concentrations were close to the instrumental detection limits. The light from the actual measurement light path was taken through the calibration cell and it was filled with calibration gases just as when using the setup shown in Fig. 2. The slopes remained the same as when using the calibration lamp.

Due to the difficulties mentioned above in determining the offset, another approach was used: after collecting a whole year of data, a subset of summer days was selected, during which the wind blew directly from the cleanest sectors (W, NW or N) and both gas and aerosol measurement instruments showed very low concentrations. The offset was set in such a way that NO_2 and SO_2 concentrations became zero in these days, after which this same offset was used for the rest of the year.

The chosen approach has some drawbacks. NO_2 and SO_2 concentrations are not zero in clean marine air. For example, Beine *et al.* (1996) measured an average NO_x concentration of 27.7 ppt (≈ 0.057 μg m^{-3} as NO_2) at Spitsbergen, and Berresheim *et al.* (1995) reported an average SO_2 concentration of 20 ppt (≈ 0.05 μg m^{-3}) in the marine boundary layer. However, these concentrations are clearly lower than the detection
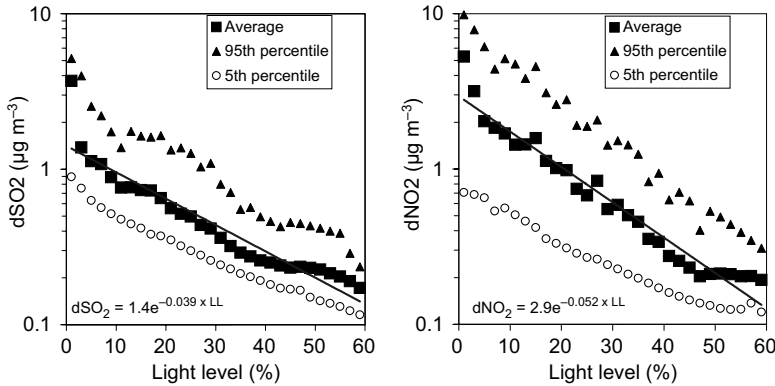
Fig. 3. Standard deviation of the concentration calculated from the 1000 wavelength channels in the wavelength windows for SO_2 and NO_2 at various light levels in 1992 through 2002.

limits of the DOAS, which supports the applicability of our approach. The detection limits will be discussed below.

Ozone calibration would require a separate calibrator that was not available. Therefore an intercomparison was conducted with a conventional ozone monitor during the winter 1993–1994 (Virkkula 1997). This calibration yielded a "calibration" line O_3(true) = 1.148 × O_3(DOAS) – 16 μg m^{-3}. No other intercomparison or calibration was conducted for ozone after that. The ozone data shown in this paper are based on this single intercomparison, so uncertainties in O_3 concentrations are clearly higher than those in SO_2 and NO_2 concentrations. In spite of this, there is one argument that supports the use of the ozone data for at least a qualitative discussion. The calibration of the other two gases did not vary much between the lamp changes and the instrument and the method used for ozone measurement was the same as for the other two gases, only the analyzed wavelength range was different. If a significant drift had been present in any gas data, this should have had some clear technical reason which would then have been present for the other gas measurements as well.

Performance of the instrument with varying visibility

In addition to the concentration and standard deviation, the instrument also outputs a value called light level (LL) that is directly proportional to the amount of light arriving at the receiver. It is expressed in percents and a detailed description of this concept has been given by

Virkkula (1997). Briefly, the light level is < 20% when the visibility is low and > 40%–50% when the visibility is high.

The relation between the light level and the standard deviation of ozone measurements was analyzed by Virkkula (1997). For light levels > 20% it was shown to be approximately $stdO_3$ = 10 × exp(–0.067 × LL) μg m^{-3} for one-hour averages. For a light level of 30% this results in a noise level of 1.3 μg m^{-3}. For SO_2 and NO_2 measurements the corresponding relation has not been discussed. To analyze the performance of the instrument, the std data for SO_2 and NO_2 from years 1992 to 2002 were classified into 2% "LL bins". The averages and 5th and 95th percentiles of the respective bins demonstrate that at a given light level, the std of the concentration varies significantly (Fig. 3). This is due to (1) the variability of visibility during an hour and (2) different integration times during the whole decade of measurements. In the present paper all measurements were handled as one-hour averages, although in the actual measurements the integration times were not always the same. As in the case of ozone, the std for SO_2 and NO_2 decreased exponentially with LL (Fig. 3). For the one-hour average data in 1992–2002 a regression fit to the averages gave: dSO_2 = 1.4 × exp(–0.039 × LL) μg m^{-3} and dNO_2 = 2.9 × exp(–0.052 × LL) μg m^{-3}. These numbers can be used for a rough calculation of the detection limits of the instrument at various light levels, since the actual noise of the data is not exactly the same as the standard deviation of the spectrum fits. For instance, during a clean air period the standard deviation of SO_2 concentrations could be 0.15 μg m^{-3} even though the noise
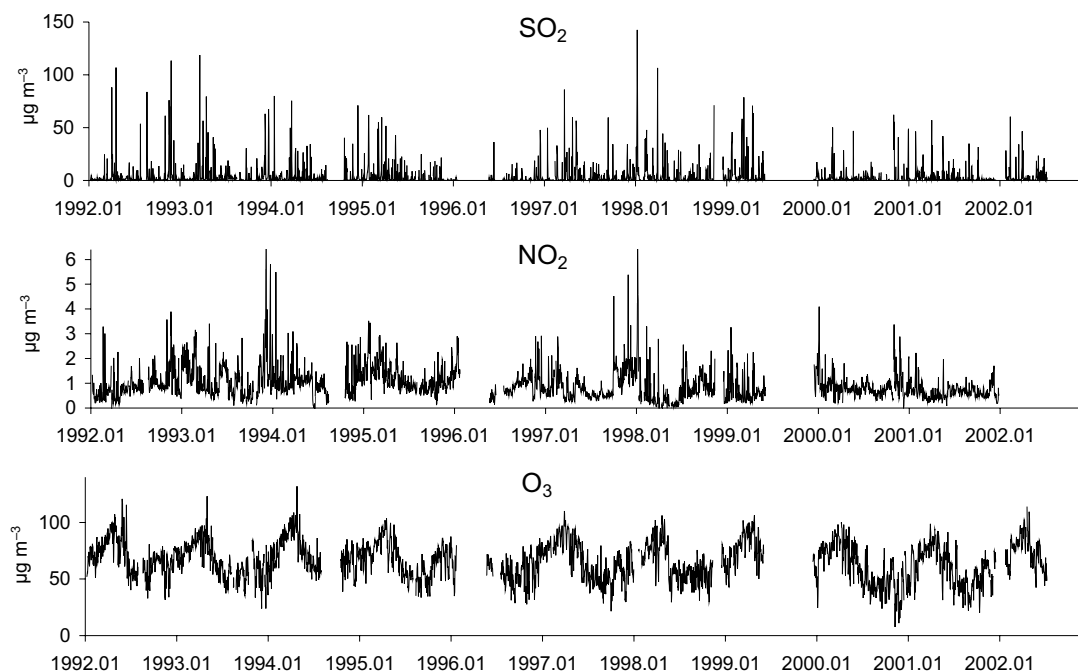
Fig. 4. 24-hour average concentrations of SO_2, NO_2, and O_3 at Sevettijärvi from 8 January 1992 to 10 July 2002.

reported by the instrument's fitting routine was 0.2 μg m^{-3}. In general the noise reported by the instrument was slightly higher than the noise of the actual data. No statistical analysis was done to do this comparison, though, and thus the noise discussed here can be regarded as a conservative estimate of the noise.

Using the above formulas at 40% light level, the noise is equal to about 0.3 μg m^{-3} for SO_2 and to about 0.4 μg m^{-3} for NO_2 at a one-hour averaging time. These values are clearly higher than the background values of these gases and therefore the procedure for determining the offsets described above can be defended. However, when averaging the data further, the noise and thus the detection limit reduces inversely proportional to the square root of the averaging time. Therefore, when taking longer averages, the error produced by assuming a zero concentration in marine air may become significant.

Between 8 January 1992 and 10 July 2002, the instrument produced data approximately 84% of the time. The missing data were caused by total power breaks at the station, lamp failures, and maintenance by the manufacturer. A light level of 30% was set as a lower limit for

accepted data. Approximately 95% of the instrument working hours had light levels exceeding this limit for each of the measured species.

Meteorological measurements

The temperature, pressure, and relative humidity were monitored at a two-meter height, whereas the wind speed and direction were monitored at a 7.5-meter height. The data were stored as five-minute averages into a computer. Using the temperature and pressure measurements, the concentrations given by the DOAS were finally transformed to corresponding values at 1013 mbar and 273 K.

Concentration data

The time series of 24-hour average SO_2, NO_2, O_3 concentrations revealed a decreasing trend for SO_2 but no clear trend for NO_2 or O_3 (Fig. 4). A statistical summary of measured concentrations is presented in Table 1. When interpreting the results, it has to be kept in mind that the number of hours during which the instrument produced

data varied between the different years. One should therefore avoid using the years 1996, 1999 and 2002 when calculating trends from the annual averages. Furthermore, it has to be emphasized that all ozone data were handled using the result of the winter 1993/1994 inter-comparison, as discussed above.

High SO_2 concentrations appeared as short peaks and there was no clear seasonal cycle, contrary to what has been observed at more remote arctic sites (e.g. Barrie 1986, Tuovinen *et al.* 1993). The seasonal cycle typical for more remote sites is caused by higher emissions and limited oxidant concentrations during the winter (Feichter *et al.* 1996, Lohmann *et al.* 1999), as

well as by different meteorological conditions between the winter and summer (e.g. Raatz 1989, Barrie *et al.* 1989).

The highest NO_2 concentrations were also observed as short-term peaks. However, for NO_2 there was a fairly clear seasonal cycle, the concentrations being higher in winter and lower in summer. The seasonal cycle was clearest for O_3, with high concentrations observed in spring and low concentrations observed in late summer and autumn. In addition to this there was a clear diurnal cycle for O_3. Both these ozone cycles are well-known (e.g. Finlayson-Pitts and Pitts 1986) and will not be discussed here in more detail.

Peak SO_2 and NO_2 concentrations were

Table 1. Annual averages, maximum hourly concentrations and percentiles of hourly averaged concentrations from 8 January 1992 to 10 July 2002. N_{hrs} = number of hours in the respective year, N_{mhrs} = number of hours the instrument was working, $N_{(LL > 30)}$ = number of hours the light level of the respective gas was above 30%. The data points with LL > 30% are accepted to the statistics.

|	Year										
	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002
N_{hrs}	8784	8760	8760	8760	8784	8760	8760	8760	8784	8760	4570
N_{mhrs}	8027	8364	7154	8402	5135	8429	7482	3759	7728	8484	3559
% of time	91.4	95.5	81.7	95.9	58.5	96.2	85.4	42.9	88.0	96.8	77.9
SO_2											
$N_{(LL > 30)}$	7885	7737	6993	8218	5056	8218	7319	3472	7333	7289	3184
Average	4.8	5.0	4.1	4.2	2.0	3.9	5.5	7.0	2.9	2.8	4.1
Max	552	455	346	259	158	337	242	212	223	176	192
Percentiles											
99	98	88	79	80	47	75	93	101	62	51	84
90	5.8	8.6	7.2	6.8	2.4	6.2	9.5	14.4	3.8	4.4	6.1
50	0.8	0.8	0.6	0.6	0.3	0.5	0.4	1.1	0.4	0.6	0.6
NO_2											
$N_{(LL > 30)}$	7853	7948	7010	8274	5033	7468	4391	3302	7974	7837	
Average	0.4	1.2	1.3	0.8	0.6	0.5	0.5	0.4	0.9	0.7	
Max	17.4	13.0	18.2	19.9	5.2	8.5	9.5	5.8	5.2	7.1	
Percentiles											
99	4.0	5.7	4.0	3.2	2.8	3.0	4.8	3.1	3.2	2.0	
90	1.2	2.4	2.2	1.7	1.3	1.4	1.5	1.5	1.4	1.1	
50	0.3	1.0	1.4	0.7	0.5	0.3	0.2	0.1	0.8	0.6	
O_3											
$N_{(LL > 30)}$	7875	7636	6662	8212	5059	8301	6976	3402	7879	6633	3441
Average	69	66	73	68	58	66	63	75	60	58	74
Max	142	143	156	113	101	122	123	114	117	104	127
Percentiles											
99	118	101	111	102	86	103	104	106	100	95	107
90	91	87	94	88	76	90	87	95	87	82	93
50	69	67	74	68	59	66	63	75	60	58	76
10	48	43	53	46	37	41	41	53	32	34	53
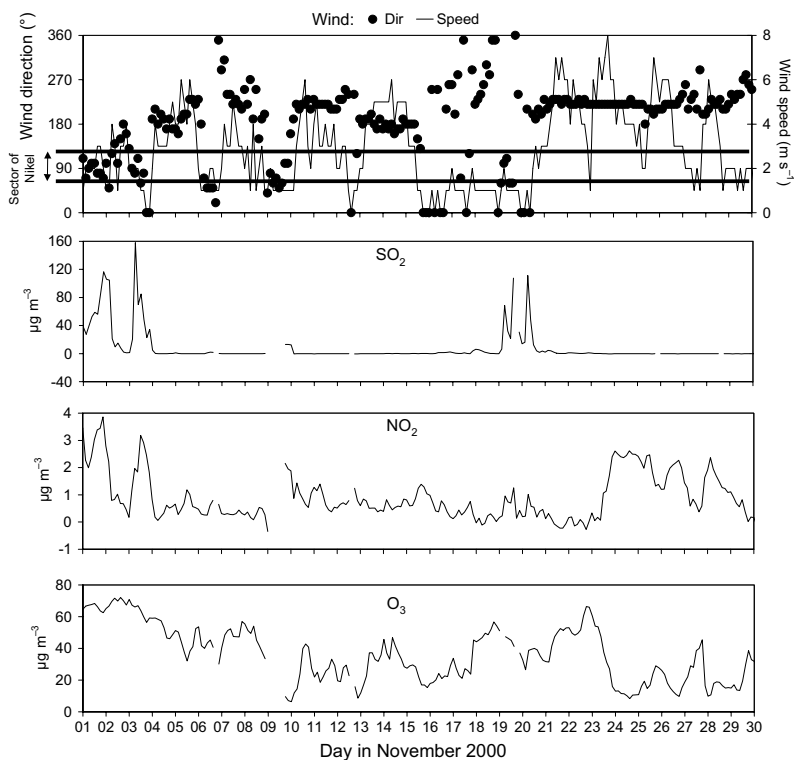
Fig. 5. Three-hour average SO_2, NO_2 and O_3 concentrations and momentary wind measured every three hours in November 2000.

observed at winds blowing directly from Nikel (*see* e.g. Fig. 5). However, increases in the SO_2 concentration were not always accompanied by concomitant increases in the NO_2 concentration. A possible explanation for this is that the sources of these two pollutants are different: SO_2 originates from the industrial emissions of the Ni-Cu smelters, whereas the main source of NO_2 is traffic. The Nikel-Zapolyarnyj industrial area has local traffic and the smelters are not necessarily in full use at the same time as the traffic intensity is highest. Furthermore, SO_2 is released mainly from 100 to 160-m-high stacks in Nikel and Zapolyarnyj (Tuovinen *et al*. 1993), whereas NO_x emissions from automobiles take place on the surface. This altitude difference may occasionally result in different transport routes of emissions from the two sources caused, for example, by surface inversion and wind shear.

Another interesting observation can be made from the time series of November 2000 (Fig. 5). After the second major Nikel episode in 18–21 Nov. 2000 the winds turned to the south, and on 23 Nov. 2000 NO_2 concentrations rose and O_3 concentrations dropped significantly. During

the months when sunlight is available, ozone is produced by photochemical reactions of volatile organic compounds and NO_x. On the other hand, when no sunlight is available, NO_2 destroys ozone via the reaction $NO_2 + O_3 \rightarrow NO_3 + O_2$ (e.g. Seinfeld and Pandis 1998). The episode following 23 Nov. 2000 is an example of the latter phenomenon. No anticorrelation between NO_2 and O_3 could be seen during the first Nikel episode (1–4 Nov. 2000). This remains to be explained because the reaction between ozone and NO_x is expected to be so fast that the ozone concentration should have been reduced within the few hours required for air to arrive from Nikel at Sevettijärvi. One possible explanation is that there was still enough sunlight available in the beginning of November, since the Arctic night begins on 22 November at Sevettijärvi.

The fairly clear positive correlation between NO_2 and SO_2 during the dark months (Fig. 6) demonstrates that even though these two gases may not have a common source, they still are likely to have a common geographical source area, at least for high concentrations. The less clear positive correlation between NO_2 and SO_2
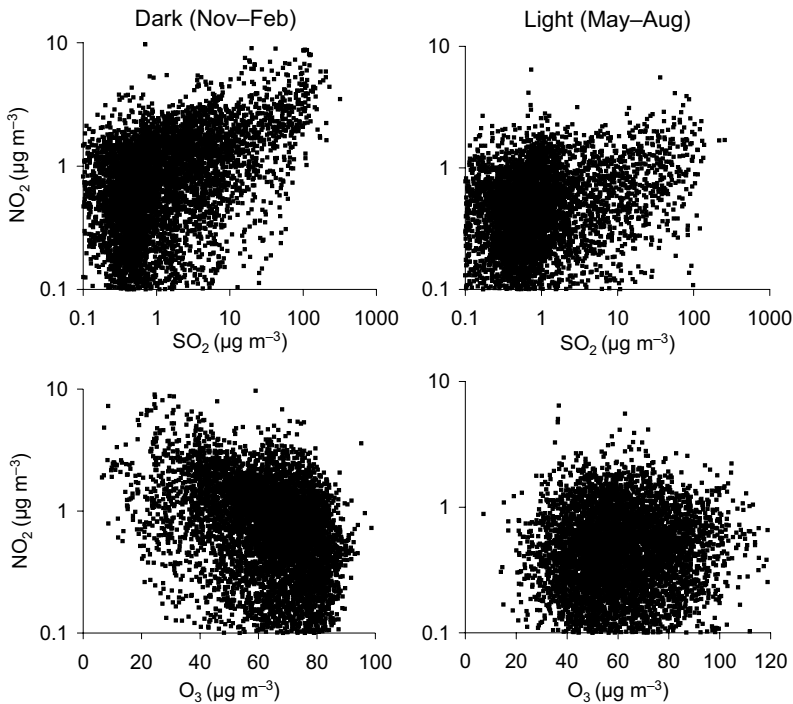
Fig. 6. NO$_2$ concentration against SO$_2$ and O$_3$ concentrations during the dark (November, December, January, and February) and light (May, June, July, August) months.

during the light months may partly be explained by a rapid photochemical destruction of NO$_x$ at the presence of sunlight. Between NO$_2$ and O$_3$, no relation during the light months could be seen (Fig. 6). This may be partially explained by the diurnal cycle of ozone and low NO$_2$ concentrations, even though also other reasons are possible such as the few calibrations of the ozone measurements. The decrease in ozone concentrations with increasing NO$_2$ concentrations is similar to what was observed in the time series shown in Fig. 5. This feature is also in agreement with the studies of Laurila (1999), Simmonds *et al.* (1997) and Scheel *et al.* (1997) which have shown that ozone is depleted in polluted air masses during the winter.

Transport analyses

Wind roses

The simplest way of analyzing sources statistically using meteorological data is to combine wind and concentration measurements. The measured concentrations were classified according to wind direction and speed (Fig. 7). Since wind data existed at a three-hour time resolution, all concentrations were first averaged for three hours. The most common wind direction was SSW which prevailed approximately 21% of the time between 1992 and 2002 (Fig. 7A). These winds bring continental air to the site, as shown earlier by Virkkula *et al.* (1997, 1999). Winds blew rarely (~7% of the time in 1992 to 2002) from the sectors pointing to Nikel (E to ESE). The average NO$_2$ and SO$_2$ concentrations were highest in these sectors. Another, smaller peak sector for NO$_2$ was S to SW pointing to central Europe. The lowest average concentrations of both NO$_2$ and SO$_2$ were observed in the sectors W to NNW bringing the cleanest marine air to the site. Winds from these clean sectors prevailed approximately 20% of the time between 1992 and 2002. Some statistical values of the concentrations in the three distinct wind sectors were also calculated (Table 2).

Since ozone has a very clear seasonal cycle (Fig. 4) together with a diurnal cycle in summer (Virkkula 1997), it cannot be presented using concentration wind roses similar to SO$_2$ or NO$_2$. Another approach was therefore used to combine ozone data with wind measurements. First, a running 30-day average (denoted by <>)

$<[O_3],30d>$ was calculated for the O_3 concentration. Second, a deviation from this average was calculated as $devO_3 = [O_3] - <[O_3],30d>$, where $[O_3]$ is the three-hour average O_3 concentration. This deviation is a value that fluctuates around zero: during the transport of high ozone concentrations it is positive and during O_3 destruction it is negative. Since ozone reactions in the dark differ from those in sunlight, the wind statistics for $devO_3$ was calculated twice, once for the dark period from November to February and another time for the light period from May to August. For the light months the diurnal ozone cycle was taken into account by using only values measured between 12:00 and 16:00 when the ozone concentrations at Sevettijärvi are at their highest (Virkkula 1997). The two periods yielded a very different wind rose for the ozone deviation (Fig. 7C and Table 3). During the dark months the highest concentrations came from the clean oceanic sector, whereas other sectors and no-wind class displayed negative values indicative of ozone destruction. During the light months the highest positive concentration deviations came from the continental sector, being suggestive of the transport of ozone from continental Europe. This is consistent with the result of Laurila (1999) who demonstrated that continental Europe acts as a source for ozone in summer and as a sink in winter.

The quantitative values of the above analysis of ozone concentrations suffer from the lack of calibrations. However, in the wind classification of the ozone data, the deviation of the actual concentration from the 30-day average concen-
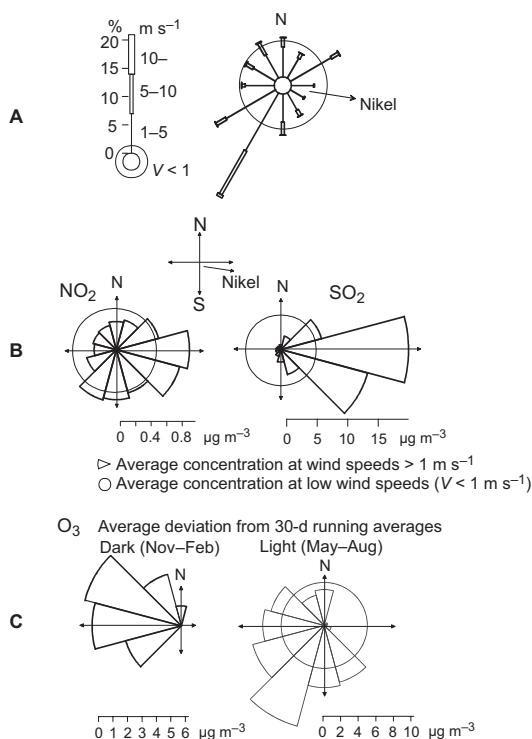

Fig. 7. Wind directional distributions of (**A**) wind speed, (**B**) average NO_2 and SO_2 concentration, and (**C**) average deviation of three-hour average O_3 concentration from the running 30-day average O_3 concentrations in the dark and the light months. For the light months only daytime (12:00–16:00 local time) concentrations are taken into account.

tration was applied. This procedure makes the analysis less sensitive to calibration errors, since possible changes in calibration slope and offset are slow. Calibration errors may influence the deviation mainly in two ways:

Table 2. SO_2 and NO_2 concentrations (µg m^{-3}) in major wind sectors.

Sector	Average	S.D.	Percentiles		
			10	50	90
SO₂					
E	19.9	31.0	0.2	4.8	62.2
S–SW	1.4	4.6	< 0.2	0.5	2.8
W–NW	1.0	5.4	< 0.2	0.4	1.2
NO₂					
E	0.9	1.1	< 0.2	0.6	2.4
S–SW	0.7	0.7	< 0.2	0.5	1.6
W–NW	0.3	0.4	< 0.2	0.3	0.9

Table 3. Deviation of daytime (12:00–16:00 local time) three-hour average O_3 concentration (µg m^{-3}) from the running 30-day average O_3 concentrations in the dark and the light months in major wind sectors.

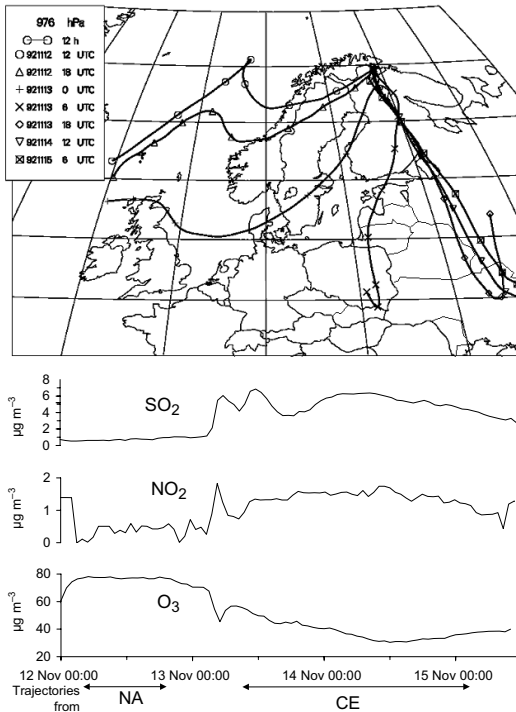| Sector		Average	S.D.	Percentiles		
				10	50	90
Light	E	0.3	12	−15.3	0.1	11.4
	S–SW	11.7	13	−4.5	10.8	28.7
	W–NW	3.5	11	−10.1	3.5	15.9
Dark	E	−4.9	10.7	−20.1	−5.2	6.6
	S–SW	−3.3	9.8	−18.5	−1.4	7.1
	W–NW	6.9	11.4	−7.4	7.2	19.7

Fig. 8. One-hour average SO_2, NO_2, and O_3 concentrations between 12 and 15 November 1992, along with associated 96-hour back trajectories arriving at Sevettijärvi at 50-m altitude every six hours. (Source areas NA: North Atlantic, CE: Continental Europe).

1. A wrong offset would affect the result only in case the offset changed during the 30-day period. This is not very probable. For the other gases the offset remained close to same during a year and nothing in the ozone time series suggests that this would not be the case for ozone as well.
2. A wrong slope does affect the deviation. However, based on experience on calibrations of the other two gases, it may be assumed that during a month the slope remains close to constant. If the deviation at a given moment is positive, the momentary deviation will increase the average measured deviation during winds from the sector and if it is negative, it will decrease the respective average deviation.

Based on these arguments, the quantitative values of the deviations may be erroneous but qualitatively they remain the same. Therefore the interpretations of the different average deviations in the different wind sectors are not changed.

Trajectory analyses

A better approach for studying the sources of gases is to use back trajectories. Three or four three-dimensional 96-hour back trajectories arriving at ground level, at 950 hPa and at 900 hPa were calculated for each day during the first three years of the measurements, from January 1992 to June 1994. Most trajectories were calculated using the TRADOS model of Finnish Meteorological Institute. For the year 1992, three-dimensional trajectories were calculated using the FLEXTRA trajectory model described in detail by Stohl and Wotawa (1995). The set of trajectories used in this work are the same as described and used for the source analyses of aerosols and SO_2 by Virkkula *et al.* (1997).

The trajectories were first applied to single episodes (Fig. 8). At the beginning of the period, on 12 Nov. 1992, air flew from the north Atlantic (NA) and northern Scandinavia to Sevettijärvi. Both SO_2 and NO_2 concentrations fluctuated around the detection limits of the instrument. On 13 Nov. 1992 the air mass origin moved to continental Europe (CE) and both SO_2 and NO_2 concentrations increased clearly. Ozone behaved the opposite way, decreasing as soon as the polluted continental air arrived at the station.

In addition to looking at episodes, trajectory data can be used in a statistical way. Stohl (1996) presented a trajectory statistical method for analyzing the sources of observed concentrations. This procedure calculates the geometric mean concentration that is observed at the receptor site when trajectories have crossed each cell of a geographical grid which is superimposed on the domain of the trajectory computations. The geometric mean is weighted by the residence time of the trajectory in each grid cell according to the formula:

$$\log\left(\mathrm{GMC}_{m,n}\right) = \frac{\sum_l \log\left(C_l\right)\tau_{m,n,l}}{\sum_l \tau_{m,n,l}} \,, \qquad (1)$$

where $\mathrm{GMC}_{m,n}$ is the geometric mean concentra-

tion, m and n are the indices of the horizontal grid, l is the index of the trajectory, C_l is the concentration observed on the arrival of trajectory l and $\tau_{m,n,l}$ is the time spent in grid element (m, n) by the trajectory l. Log($GMC_{m,n}$) serves as a first-guess field that is treated by an iterative redistribution and smoothing procedures.

For Sevettijärvi measurements, the trajectory statistical method has been applied to sulphate, ammonium and sodium concentrations, aerosol number concentration, aerosol scattering coefficient, and SO_2 concentration (Virkkula *et al*. 1995 and 1997, Lupu and Maenhaut 2002). Here we extend this analysis for NO_2 (Fig. 9). The trajectories used for the statistics were the ones arriving at 950 hPa level above the site during the years 1992–1994, so Fig. 9 does not represent the whole decade of measurements. The one-hour average NO_2 concentrations were first averaged over six hours, since trajectories were available for every six or eight hours. The six-hour average was assigned to the respective trajectory.

The major origins of the observed NO_2 at Sevettijärvi were the regions of heavy traffic in Europe (Fig. 9). A clear difference between northern and southern Finland can also be seen, which is in agreement with the higher population density in the south of the country. Yet another detail is the "hot spot" in Norway, which is probably an artifact from the calculation. In spite of this, the obtained map is in qualitative agreement with the NO_2 emission maps produced by EMEP (e.g. Berge 1997).

The obtained concentration values are comparable with the wind sector statistics in Table 2. According to the trajectory statistics, NO_2 concentrations in air coming from the oceans was in the range 0.2–0.5 μg m^{-3}. According to the wind statistics the average concentration in the W–NW sectors was 0.3 μg m^{-3} and 90% of the concentrations were < 0.9 μg m^{-3}. These values are about an order of magnitude higher than the average NO_x concentration of 27.7 ppt ($\approx$ 0.057 μg m^{-3} as NO_2) measured at Spitsbergen (Beine *et al*. 1996). This may be a true result, even though part of this difference might be due to the higher noise and detection limit of DOAS compared with the NO_x analyzer used by Beine *et al*. (1996). On the other hand, the median NO_x

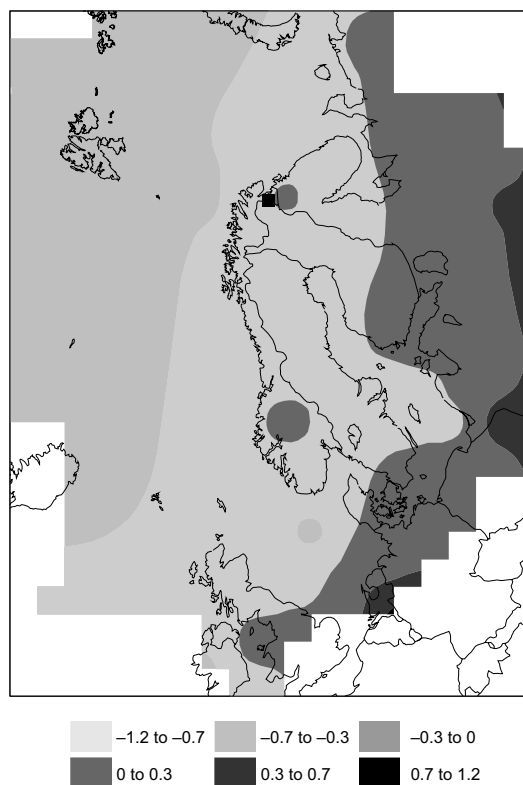| –1.2 to –0.7 | –0.7 to –0.3 | –0.3 to 0 |
| 0 to 0.3 | 0.3 to 0.7 | 0.7 to 1.2 |

Fig. 9. Geometric mean nitrogen dioxide concentrations at Sevettijärvi when trajectories have passed each grid square. The concentrations are expressed in log (gmNO$_2$) where gmNO$_2$ is the geometric mean NO$_2$ concentration. The lower limits of the contours are thus 0.06, 0.2, 0.5, 1.0, 2.0, and 5.0 μg m^{-3}. The white areas are those grid squares, which have been crossed by less than 20 trajectories. The data used for the statistics is from 1992 to 1994 only.

concentrations measured at Värriö measurement station located approximately 200 km south of Sevettijärvi and run by the University of Helsinki varied between 0.1 and 0.2 ppb ($\approx$ 0.2–0.4 μg m^{-3} as NO_2) when trajectories originated from the Arctic Ocean (Kulmala *et al*. 2000). These values are comparable with those given by the wind and trajectory statistics for Sevettijärvi.

The wind sector statistics shows that 90% of the NO_2 concentrations measured during winds from the south were < 1.6 μg m^{-3}. On the other hand, the trajectory statistics in Fig. 9 show that the geometric mean NO_2 concentrations at Sevettijärvi varied between 1 and 5 μg m^{-3} when air

comes from continental European sources south of Finland and Sweden. Kulmala *et al.* (2000) reported median NO_x concentrations of around 1 ppb ($\approx$ 2 μg m^{-3} as NO_2) in Värriö for air masses originating from Western, Central and Eastern Europe. These values are again comparable with each other.

Although the highest NO_2 concentrations were observed during pollution episodes from Nikel, the trajectory statistics do not assign the highest values there. This discrepancy can probably be explained by the area-averaging of the trajectory statistical procedure: the industrial area in Nikel is not very large and the statistics averages also the neighboring areas with low NO_x emissions into the same grid cell.

Conclusions

The DOAS instrument was used for a decade to measure the concentrations of gaseous SO_2, NO_2 and O_3. The instrument worked quite reliably during the whole time, even though there were some long discontinuities in the data which made a quantitative trend analysis difficult. Anyhow, our data show that the maximum hourly SO_2 concentrations decreased from around 500 μg m^{-3} during the first two years of the monitoring to 200–300 μg m^{-3} in the mid 1990s. The annual average SO_2 concentrations decreased from about 5 μg m^{-3} to 3–4 μg m^{-3} during the same period when taking into account the years for which the data coverage was above 85%. These values are lower but basically in agreement with measurements conducted by Norwegians. It has been observed that SO_2 emissions from Nikel, and thereby concentrations measured at Svanvik, have remained more or less at the same level after a clear decrease from the 1980s to the early or mid 1990s. For NO_2 and O_3 concentrations no clear trend was observed in this study.

The sources of the three trace gases were studied using wind measurements and in the case of NO_2 also using back trajectories. The trajectory analysis is an extension to our earlier source analyses that have given a good picture on the transport of both gases and aerosols to Sevettijärvi. Since the pollutant sources are hundreds, even thousands, of kilometers away, the obtained results are applicable to most of northernmost Fennoscandia. This can be seen, for example, when comparing NO_2 concentrations measured in Sevettijärvi with NO_x concentrations measured at a site 200 km south of Sevettijärvi.

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