**Ozone, VOC and Nitrogen Species Concentrations in Ambient Air in the Boreal Region of Europe**

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**Introduction**

The European boreal regions are characterised by extensive forest areas with large biomasses providing potential for biogenic VOC emissions. According to recent emission estimates, the annual biogenic and anthropogenic VOC emissions in this region are of the same order of magnitude (Simpson et al., 1998). A major part of the annual load of biogenic VOCs is emitted during warm sunny summer days when photochemistry is most active and elevated ozone concentrations are observed.

There are three factors which strongly influence the atmospheric composition and chemical processes over the northern parts of Europe. First, the large forests areas provide the lower atmosphere with reactive compounds of biogenic origin, while also acting as an effective sink of many chemical species, e.g. ozone, by dry deposition. Second, the anthropogenic emissions of nitrogen oxides and VOCs take place mainly in the central parts of the European continent, i.e. in the southern parts of the boreal zone, which creates a strong north-south gradient between the more densely populated areas and the clean arctic areas. Third, the strong seasonal cycle of solar radiation gives rise to a photochemically active summer when the biogenic emissions are most intense.

In this report we will discuss the atmospheric composition in the boreal region, based on ambient air measurements. We will show the levels of ozone concentrations, the potential for ozone production, and the biogenic VOC composition with its seasonal cycle.
In the high northern latitudes, there is a spring maximum of background tropospheric ozone due to the high ozone concentrations in the lower stratosphere and due to the photochemical oxidation of ozone precursors which have accumulated in the northern atmosphere during winter (Penkett and Brice, 1986; Laurila and Hakola, 1996). As an example, we present in Figure 1 the 30-day running median of ethyne concentrations at Pallas (67°58’ N, 24°07’ E), showing the autumn-winter accumulation of this VOC which mainly originates from anthropogenic traffic emissions. During spring, the ethyne concentrations are decreased by photochemical oxidation, down to the summer minimum level in July. These photochemical oxidation processes are driven by the strong seasonal cycle of the UV-B and UV-A radiation. Within BIPHOREP, the photolysis rates of NO$_2$ and the photolysis rates of ozone to produce O$_1^\text{D}$ were measured, in order to study the daily and seasonal variability of the photolysis rates, and the effects of clouds on them (Laurila et al., 1998). Figure 1 also shows the 30-day running median of the isoprene concentration at Pallas. This biogenic compound is observed in ambient air during the growing season which is June-September at these latitudes.

The daily maximum ozone concentrations are shown in Figure 2 at monitoring stations in the northern (Oulanka, 66°19’ N, 29°24’ E) and southern (Utö, 59°47’ N, 21°23’ E) parts of the study region. In spring, both the episodic and background levels of ozone are relatively simi-
lar in the whole region. In summer, the effective dry deposition of ozone restricts the range of long-range transported ozone episodes and there is also less local production in the northern parts of the area. The highest concentrations are observed in the southern parts of the region.

**Ozone exposure to vegetation**

Elevated ozone concentrations have detrimental effects on vegetation and human health. The estimation of the effects of ozone on vegetation within the framework of the UN-ECE critical level studies has been done using the ozone exposure index AOT40 (Kärenlampi and Skärby, 1996; Laurila and Lättilä, 1994) which accumulates the hourly ozone concentrations exceeding 40 ppb. In a new draft for the daughter ozone directive by the European Commission it is proposed to estimate the exceedances of critical loads of ozone for crops and forests using the AOT40 index. In this work, we have calculated the AOT40 indices for the May-July period. This period is used instead of April-September, which is the accumulation period for the estimation of ozone effects on forests, because the proposed critical levels are based solely on experiments conducted on deciduous trees. In the boreal region, April is still a dormant period for these species. According to the May-July AOT40 exposure index at the Finnish ozone monitoring stations, which are shown in Figure 3, high (over 40 ppb) ozone

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**Figure 2.** Daily 1-hourly ozone concentration maxima at Utö and Oulanka.
Figure 3. Ozone exposure index AOT40 at background monitoring stations in the European boreal region. The index is calculated for the daylight hours over the May-July period (Kärenlampi and Skärby, 1996).

Ambient air concentrations of biogenic VOCs

The biogenic VOC emissions are active during the growing season. A good approximation for the growing season in the boreal region is the period when the daily average air temperatures constantly exceed +5 °C. On the average this period is from the end of April to the end of October and from the end of May to the end of September in the southern and northern parts of the boreal region, respectively.
During the two BIPHOREP campaign years, ambient air samples were collected regularly on a fjeld top at Pallas in the northern boreal zone and on a hill top at Mekrijärvi (63° 07’ N, 31° 04’ E) in the border area between the southern and middle boreal zones. In addition, light hydrocarbon data from the Utö Island on the Baltic Sea were used as reference concentrations in the southern border of the boreal region. Light hydrocarbons were collected in canisters at noon and analysed by GC/FID after two-stage preconcentration (Laurila and Hakola, 1996). Monoterpenes were sampled using TENAX tubes at Pallas and Mekrijärvi and analysed by GC/MS (Hakola et al., 1998). Carbonyl compounds were collected on DNPH cartridges at Mekrijärvi and Pallas and analysed at the University of Stockholm (Janson et al., this volume). At Pallas, the sampling took place on a fjeld top which is about 250 m above the surrounding terrain (Rummukainen et al., 1996) and at Mekrijärvi the samples were collected on a hill top, about 60 m above the surrounding terrain. Both sites are in a remote area. Utö is an island station on the Baltic Sea, where regular ambient air monitoring and sampling is carried out by the Finnish Meteorological Institute (Laurila, 1996).

The average summer concentrations of light hydrocarbons at the three sites are presented in Figure 4. They show an increase of the anthropogenic species towards south, which is typical
Figure 5. 30-day running medians of isoprene and total monoterpene concentrations (in pptv, left axis) and temperature (in °C, right axis) at noon at Mekrijärvi in 1997.

Figure 6. 30-day running averages of isoprene concentration at Mekrijärvi in 1996, 1997, and 1998.
for the North European regions. The isoprene concentrations are highest at Mekrijärvi, which is the more southern terrestrial site, and lowest at the marine site of Utö.

It is generally assumed that the intensity of biogenic emissions is a function of temperature. In addition, many species also show a light dependence of the emissions (Guenther, 1993; Kesselmeier et al., 1996; Steinbrecher et al., 1997; Hauff et al., 1999; Schuh et al., 1997). The noon temperature and the 30-day running medians of the ambient air isoprene and total monoterpene concentrations at Mekrijärvi, which are presented in Figure 5, indeed show that monoterpenes are observed from May to September. The total monoterpene concentration follows the noon temperatures more closely than the isoprene concentration. In spring, the isoprene concentrations appear a few weeks later than the monoterpenes, and this lag is maintained with respect to the maximum concentrations around midsummer. Compared to the onset of leafing and the photosynthetic activity, isoprene emissions have been observed to be delayed a few weeks also in cuvette emission measurements (Grinspoon et al., 1991; Hakola et al., 1998).

Observations at Mekrijärvi and Pallas suggest that in the boreal region the ambient air isoprene concentrations are very low until June. Thus, isoprene has a significant influence on tropospheric chemical processes in the June-September period only, unlike monoterpenes, which have significant concentrations also in May. The interannual variation of biogenic VOC concentrations is substantial due to the changing weather conditions. This is shown in Figure 6, as the 30-day average concentrations of isoprene at Mekrijärvi in 1996, 1997, and 1998. Generally, 1996 was the coolest and 1997 the warmest of these three years. Statistical analysis of light hydrocarbon concentrations at these background areas (Laurila et al., 1998) indicates that a substantial part of the ethene, propene and 1-butene concentrations are also of biogenic origin.

Seasonal changes have been found in the monoterpene composition of birch (Hakola et al., 1998) and Norway spruce (Janson et al., this volume) emissions. The monoterpene composition in ambient air at Mekrijärvi shows also systematic changes according to season. The monthly relative isoprenoid concentrations in 1997 are presented in Figure 7. The results show that $\alpha$-pinene is highly dominating in May. The camphene and sabinene concentrations are highest in July. Hakola et al. (this volume) have observed elevated sabinene and ocimene
Figure 7. Monthly relative isoprenoid concentrations at Mekrijärvi in 1997.

emissions from birch during this period. Birch is common in the vicinity of the measurement site, thus it could be the source of the elevated ambient air concentrations. Ocimenes are not observed in ambient air, probably due to their high reactivity. The limonene concentrations are relatively high in autumn. The relative concentrations of 3-carene, β-pinene, and camphene vary less during the summer. The isoprene concentrations are relatively low in the
beginning of the growing season but they increase during the summer, constituting 25 % of the total isoprenoids in August.

Some diurnal cycles of TENAX samples were collected at Mekrijärvi. The VOC measurement site is located on a hilltop, north of the research station. This site is better suited to ambient air concentration measurements of ozone and VOCs. The diurnal cycle of ozone at the elevated site is smooth because the site is partly above the nocturnal surface inversion. The relative average concentration profile on June 10-11, 1998 is presented in Figure 8. It shows significant concentrations of many oxygenated species in addition to monoterpenes of which α–pinene, carene, β-pinene, and camphene have highest concentrations. The observation of these oxygenated species, which most probably are of biogenic origin, stresses that their sources and behaviour should be studied in more detail. These species may be very important for the biogenic aerosol formation because they are more water soluble than for example the monoterpenes.
To estimate the participation of biogenic VOCs in ozone formation the OH-reactivity- scaled concentrations were calculated, according to Chameides et al. (1992). Each hydrocarbon species (J) is represented by a propene equivalent concentration given by

\[ \text{Propy-Eq} (J) = C_J \frac{k_{OH}(J)}{k_{OH}(C_3H_6)}, \]

where \(C_J\) is the concentration of hydrocarbon species J in ppbC, \(k_{OH}(J)\) is the rate constant for the reaction between species J and OH, and \(k_{OH}(C_3H_6)\) is the rate constant between propene and OH. Since hydrocarbon oxidation is usually initiated by a reaction with OH, these Propy-Eq concentrations should provide a better estimate of the relative contribution of each hydrocarbon species to the flux of organic carbon being oxidized in the study area. Figure 9 shows the monthly mean concentrations of the species grouped into monoterpenes, isoprene, light alkenes, and other light hydrocarbons. In forested regions, the ambient air concentrations of alkanes and other less reactive species are relatively high. However, in summer the biogenic monoterpenes and isoprene dominate the reactive mass due to their high reactivity. Our statistical analysis and the cuvette emission measurements suggest that in remote areas a large amount of other light alkenes are emitted by vegetation. Thus, in addition to the isoprenoid compounds, biogenic emissions are also an important source of a number of other
reactive species. Unfortunately, aromatic compounds were not analysed and it is therefore not possible to assess the importance of these reactive anthropogenic species. In this region, elevated ozone concentrations are observed in spring and summer. According to Figure 9, biogenic VOCs are very important for local ozone production and photochemical processes in summer but in spring anthropogenic species constitute most of the reactive VOC mass.

**Concentrations of nitrogen oxides**

Areas of high NOx precursor emission densities are not extensive in the study region. As a consequence, the NOx concentrations are so low that in the rural and background areas of the North European boreal zone ozone production may be assumed to be NOx limited.

As NOx plays a key role in the photochemical processes, a considerable effort was made to obtain high quality NOx measurements in the remote northern areas of the boreal region. It turned out that the intended instrument, the ECOPHYSICS CLD770 /PLC760, was not sensitive enough for summer measurements. Thus, a more sensitive model CLD780TR/PLC762 was purchased. Unfortunately, the system was still in test use at Pallas during the summer 1997, and representative summer NOx data was only obtained in 1998, when the BIPHOREP Project was ending.

The NO mode was calibrated automatically by adding ppm-level NO calibration gas (by Messer-Griesheim) to the sampling line to get a 4.8 ppb increase to the observed NO concentration. In May-June 1998, the NO$_2$ mode was not active and the system measured NO continuously. The NO$_2$ concentration was calculated using the photostationary state assumption (e.g. Ridley et al., 1992), measured J(NO$_2$) photolysis frequencies, and measured ozone concentrations.

The average diurnal cycles of the measured NO and calculated NO$_2$ concentrations show that the NOx concentrations at this remote site are very low. At noon, the average NO concentrations were $18 \pm 11$ ppt and $23 \pm 11$ ppt in May and June, respectively. The noontime calculated NO$_2$ concentrations were $25 \pm 20$ ppt and $61 \pm 48$ ppt in May and June, respectively. During these measurements, the air masses were advected to the Pallas area from the Norwegian Sea and Barents Sea and from northern continental regions where the NOx emission densities are very low. Thus, these NOx concentrations are in the lower limit of the summer concentrations in the northern boreal region.
Figure 10. Monthly averages of total nitrate at Utö (60°N) and Oulanka (66°N).

Under these low NOx conditions, net photochemical ozone production is very low or absent. However, the NOx concentrations are not low enough for photochemical ozone destruction, and an urban or continental plume carried to the area may trigger ozone production. During northerly advection, air masses with the very low NOx concentrations may be transported to the southern parts of the boreal region, where the average NOx concentrations are generally higher. Previous NOx measurements at Utö (Laurila et al., 1993) have shown that the average background NOx concentration is about 1 ppb in the southern areas of the boreal zone. It is quite evident that in the rural and background areas of the boreal region there is high variability of NOx concentrations and potential for tropospheric ozone production, depending on the air mass origin.

Photochemical ozone production efficiencies

The primary source of tropospheric ozone is the oxidation of VOCs, CH₄ and CO in the presence of NOx and sunlight, with NOx acting as a catalyst. NO₂ is further photochemically oxidised to HNO₃ and may be present as HNO₃ or particulate NO₃⁻. Total nitrate, which is the sum of these two compounds, characterises the level of nitrogen compounds in ambient air. According to the monthly averages of the total nitrate concentrations, which are shown in Figure 10, there is a strong north-south gradient of total nitrate concentrations reflecting the large scale European distribution of NOx emissions.
The concentrations of oxidised nitrogen species and ozone have been used to estimate the photochemical ozone production in photochemically ageing air masses (Volz-Thomas et al., 1993). It is assumed that the ratio of total oxidised nitrogen species (NOz=NOy-NOx) to ozone reveals how many photochemical ozone production cycles, on the average, each emitted NO molecule has taken part in before it is further oxidised, mainly to HNO3. It is assumed that there are no other sink processes present. However, the dry and wet scavenging of these species is not similar during the transport, which complicates the interpretation. Photochemical ozone production efficiencies about 4 to 5 have been observed in the central parts of Europe (Volz-Thomas, 1993) while Trainer et al., 1993; Kleinman et al., 1994; and Olszyna et al., 1994 have reported ratios between 8.5-12.3 in the rural areas of eastern U.S.A.

We calculate the monthly ozone production efficiency using the total nitrate concentration, i.e. the sum of gaseous nitric acid and particulate nitrate, as a surrogate for the NOz, assuming that organic nitrate concentrations are relatively low. The monthly linear regression between the 24-hourly concentrations of ozone and total nitrate is presented in Figure 11. These results show that on the average there is photochemical ozone production between March and October. During winter ozone is oxidised by air pollutants. Ozone production is efficient in May-August when the solar radiation intensity is highest. This is also the high season of bio-
Figure 12. The 96-h three-dimensional trajectories ending at the 300 m height at Pallas, calculated using the wind fields of the high resolution limited area weather prediction model (HIRLAM) of the Finnish Meteorological Institute. The date indicates the time of arrival at Pallas.

genic VOC emissions. At Utö, the summer average slope between ozone and total nitrate is about 11. In a more clean northern environment at Oulanka the monthly ratios are between 40 and 70, indicating high ozone production efficiency in this low NOx environment. These estimates are rather uncertain because transport distances are long and it is probable that the sink processes of ozone and the nitrogen species are not similar between the source area and the measurement site. Qualitatively we may conclude that in the boreal region photochemical ozone production is very sensitive to the NOx concentrations, and that in the clean northern parts of the region, any NO molecules present in the atmosphere are very efficiently used for ozone production. This is expected, based on the nonlinear dependence of ozone production on the NOx concentrations (Lin et al., 1988).
VOC concentrations during an ozone episode at Pallas

Biogenic VOC emissions are especially important in ozone formation if they are mixed into a polluted air mass with elevated NOx concentrations due to anthropogenic emissions. An example of such a meteorological situation occurred in June 1997 at Pallas when the site was exposed to both continental and clean marine air masses. On June 1-6 and 16-27 air was advected to the area from the Norwegian Sea, the Barents Sea, and the northern parts of Scandinavia. The air mass trajectories to Pallas are presented in Figure 12. The observed temperatures were cool, about 10°C. The ozone concentration was about 35 ppb and the total nitrate concentrations were very low. The ozone and total nitrate concentrations, together with selected VOC data at Pallas in June 1997, are presented in Figure 13. On June 7-15, a warm continental air mass was advected to northern Scandinavia. The trajectories show that these air masses originated from areas south of and surrounding the Baltic Sea. During this period, elevated ozone and total nitrate concentrations were observed at Pallas. The VOC concentrations for this period indicate that the continental air mass had received anthropogenic emissions. Ethyne, which is emitted by traffic sources, showed elevated concentrations (see Figure 13). The temperatures were also higher during this advection period (about 23° at the top of the fjell) which gives rise to higher emission rates of biogenic...
VOCs. This is reflected as elevated isoprene concentrations, also seen in Figure 13. In the boreal region it is typical that the highest temperatures, and thus also the highest biogenic emission rates, are observed in polluted air masses which are advected from the more populated continental regions. The nitrogen oxides present in these polluted plumes provide the catalyst needed for effective ozone production from biogenic VOCs.

Conclusions
Elevated tropospheric ozone concentrations are a ubiquitous phenomenon in the European boreal areas. In the southern parts of the region the highest concentrations may exceed 180 $\mu$g m$^{-3}$, which is the information threshold for human health protection given in the ozone directive issued by the European Council. Also the critical AOT40 ozone exposure levels for the protection of vegetation are frequently exceeded. The maximum ozone concentrations and the AOT40 values decrease towards the north, but critical level exceedances may still occur.

Ozone production and ozone concentrations in the troposphere are very much dependent on the concentrations of nitrogen oxides. In clean northerly air masses the nitrogen oxide concentrations are so low that photochemical ozone production is restricted. Local emissions of nitrogen oxides may, in favourable situations, result in net ozone production. Local emissions also maintain the elevated ozone concentrations which are advected from the more southern areas, giving rise to longer transport distances of ozone episodes. The ozone production efficiencies from nitrogen species seems to be higher in the clean northern areas, as expected based on photochemical theory and the nonlinear dependence of ozone formation on the NOx concentrations.

During summer the biogenic VOCs dominate the reactive VOC mass in background areas. According to the measurements, the total monoterpene concentrations are higher than the isoprene concentrations, suggesting that monoterpene should not be neglected in photochemical studies. There are systematic differences between the ambient air concentrations of isoprene and the various different monoterpene species. Monoterpene are observed earlier in spring than isoprene, which is present in significant concentrations after May. This cycle of ambient air concentrations is in accordance with emission studies which show, on the other hand, delayed emissions of isoprene, and on the other hand, that a large share of monoterpene is emitted from storage pools inside the plant which are present already in spring. There is also systematic variability between the monoterpene species during
the growing season. α-pinene is highly dominating in May while limonene concentrations increase in autumn. At Mekrijärvi, camphene and sabinene concentrations are highest in July. These observations reflect the emissions from plants surrounding the measurement site and the relative importance of emissions from pools and de novo synthesis (Steinbrecher et al., 1998). Emissions from de novo synthesis depend on the phenology of the plant. Hakola et al., (1998) observed the onset of ocimene and sabinene emissions from birch after midsummer. Ambient air concentrations at Mekrijärvi show also an increase of sabinene concentrations after midsummer. Ocimenes are not observed in ambient air probably due to its high reactivity.

Detailed species specific information of the ambient air concentrations of monoterpenes and oxygenated species is very important for the development of photochemical oxidation schemes that take into account the effect of biogenic VOCs on ozone and aerosol production. This information is particularly vital for the estimation of aerosol production, because the aerosol production yields are very different for different monoterpenes species. Further work to characterize both the monoterpenes emission factors and mechanisms and their relation to the ambient air concentrations is needed. A more detailed analysis of the data collected during this project will provide the first very interesting results on this fascinating subject.

References


