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Ozone Exposure Indices for ICP-Forest Observation Plots within the Nordic Countries

Final project report

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Final project report
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Project summary

The project aim was to develop methods to estimate local ozone exposure indices that could be applied to forest sites in the Nordic countries.The project dealt with 3 different possibilities for site ozone measurements and three different ozone exposure indices, according to the matrix below:

Ozone measurements/ exposure index	**24-h mean concentrations**	**daylight AOT40**	**cumulative ozone uptake to leaves**
No measurements at all			
Passive sampler measurements, 14-day periods	n.a.		
Hourly measurements with instruments	n.a.	n.a.	n.a.

n.a. indicates that the combination was not applicable for the present project.

It was recognized early on in the project that it was convenient to estimate ozone exposure in 14-day periods. This was presumably because the 14-day periods were long enough to include several different weather conditions, while they were short enough not to be influence by seasonal changes. Furthermore, ozone measurements with passive (diffusive) samplers are recommended to be made in 14-day periods in the ICP Forest manual. However, in this project we did not use passive sampler measurements. Instead, 14-day 24-h average ozone concentrations were calculated from hourly concentrations measured with ozone instruments.

The major conclusion from the project were:

- The 14-day mean ozone concentration might be predicted with an interpolation method using existing ozone instrument measurements, for any forest site at southern and middle latitudes of the Nordic countries, with an uncertainty of +/- 3.7 ppb for the 24-h mean and +/- 3.1 ppb for the 12-h mean ozone concentrations, and with a 67% probability.

- The EMEP model can simulate the daily maximum ozone concentrations for Nordic forest sites relatively well. However, the 14-day 24-h mean ozone concentrations may not be so well predicted by the EMEP model at all sites. It is possible, however, that part of this problem may be that measurement sites located in clearings show a more pronounced diurnal ozone concentrations cycle than is appropriate for the forest canopy itself.

- Comparison of a the new dry deposition module of the EMEP model for ozone deposition against field micro meteorological data shows that the performance of this module looks promising. There is, however, still more development and evaluation needed before the modeled estimates of stomatal ozone flux should be used to compare with effect parameters such as crown thinning etc.

- There exists a strong relationship between daylight AOT40 and the 24-h average ozone concentrations for 14-day periods, which is specific for a certain site.

- If a certain site can be assigned into one of three categories, then it seems as if the 14-day daylight AOT40 can be estimated from the 14-day 24-h average ozone concentrations with an accuracy of +/- 20% for most sites and +/- 30% for the Nordic sites.

- A generalized scheme for assigning a category for an unknown site is presented.

- The EMEP modeling studies suggest that there are good relationships between modeled 6-monthly mean ozone concentrations and stomatal ozone uptake for Nordic sites. This is, however, when using both modeled ozone concentrations and modeled stomatal ozone uptake. These relationships are much poorer for shorter time-periods, for example 2-weekly or daily.

Content

1. Introduction

The impact of tropospheric ozone on the vegetation has become a major concern in Europe (Fuhrer et al., 1997) as well as in North America (Samuelson and Kelly, 2001). Ozone concentrations are, according to recent model calculations, expected to increase over mid and high latitudes over the entire atmosphere (Johnson et al. 2001). A critical level for the impact of ozone on forest trees has been adopted and defined as an AOT40 (Accumulated exposure Over Threshold 40 ppb) of 10 ppm h, during daylight hours over a six months growing season (Kärenlampi & Skärby, 1996). This level was intended to protect the most sensitive receptors. In e.g. southern Sweden this critical level for ozone is often exceeded (Pleijel & Kindbom, 1999).

Evidence for negative effects of ozone on the biomass production of young trees have been provided by several experiments (reviewed by Skärby et al., 1998). However, the impact of ozone on natural forests has been difficult to determine (Sandermann et al., 1997), although the ozone-induced degradation of the forests in the San Bernadino Mountains in southern California is well documented (Miller et al., 1997).

One way of establishing the ozone impact on mature forest trees in the field is to correlate ozone exposure with some effect parameter, such as stem growth or crown density. This approach has been applied for the stem growth of mature Loblolly pine in USA (McLaughlin & Downing 1995) as well as for the stem growth of mature beech trees in Switzerland (Braun et al. 1999). In both cases a statistically significant impact of ozone exposure on the growth of the trees was established. In a Swedish study, stem circumferences of mature Norway spruce trees have been measured at approximately weekly intervals during the vegetation season since 1993 at Asa Experimental Forest in south Sweden. In parallel, ozone levels, weather and soil moisture have been measured. A multiple regression analysis demonstrated a strongly significant impact of ozone exposure on the yearly stem growth (Karlsson et al., in preparation). Thus, there are several studies showing correlation between ozone exposure and negative impacts on the growth of mature trees. However, as there is always a potential problem with co-linearity between independent variables in field studies, these statistical studies need to be further confirmed.

The growth and vitality of forest trees in the Nordic countries is assessed through the large number of ICP-Forest observation plots. However, a major problem when trying to establish correlation between ozone exposure and some effect parameter is the low density of sites where ozone concentrations are measured in the Nordic countries (Figure 1, Table 1) together with a relatively large local variation in ozone exposure (Table 2).

Thus, there is a need to establish a database with relevant ozone exposure values with a high spatial resolution covering a long time period (>10 years). A relatively inexpensive method to measure ozone levels is to use passive, diffusive samplers. This method has been used at irregular intervals at many sites e.g. in Sweden. However, a major difficulty is that the passive samplers gives a 24-h mean value for the ozone concentrations during the time that it is exposed (usually 2 or 4 weeks), while the exposure – response index presently used is the daylight AOT40 (see above). Thus, in order to be related to effects, the 24-h mean ozone concentrations need to be converted to the daylight AOT40 ozone index.

In order to come closer to a realistic description of a critical dose in relation to an effect, the ozone impact should be described as a leaf uptake dose (ozone flux), rather than an air concentration based exposure dose. It is at present uncertain which type of ozone exposure index that will be used for the next revision of the UNECE CLRTAP Gothenburg protocol around 2005, but it can be expected that within a few years all ozone research concerning dose-response relationships will be based on this flux approach.

Not only the ozone exposure to forests, but also the forest ozone uptake dose varies over Europe. Long, light days and high humidity in air and soil are typical for the situation in large parts of the Nordic countries. The consequence is that in spite of lower ozone concentrations in the Nordic countries, the stomatal conductance is high and therefore the ozone uptake can be as high or higher as compared to the continental and south Europe. This was illustrated for European beech in Emberson et al. (1998, Table 3). The ozone exposure expressed as AOT40 during the vegetation season was 3 times higher in central Europe as compared to Sweden. If the dose is instead expressed as ozone flux, this was equally high in all parts of Europe. Thus one aim of the present project was to investigate the possibilities to establish an ozone flux based exposure index over the Nordic countries.

At the beginning, the project was focussed on establishing ozone exposure index for the ICP Forest level II plot. However, the aim was later expanded to include ozone exposure at any forest site in the Nordic countries.

2. Project aims

- To develop methods to estimate local ozone exposure indices that could be applied to forest sites in the Nordic countries.
- The ozone exposure indices under consideration were 24-h mean ozone concentrations, daylight AOT40 and cumulative ozone uptake to leaves and needles.

3. General approaches

In principle, the project dealt with 3 different possibilities for site ozone measurements and three different ozone exposure indices, according to the matrix below:

Ozone measurements/ exposure index	**24-h mean concentrations**	**daylight AOT40**	**cumulative ozone uptake to leaves**
No measurements at all			
Passive sampler measurements, 14-day periods	n.a.		
Hourly measurements with instruments	n.a.	n.a.	n.a.

n.a. indicates that the combination was not applicable for the present project.

It was recognised early on in the project that it was convenient to estimate ozone exposure in 14-day periods. This was presumably because the 14-day periods were long enough to include several different weather conditions, while they were short enough not to be influenced by seasonal changes. Also, it was assumed that ozone measurements with passive (diffusive) samplers were made in 14-day periods, as is recommended in the ICP Forest manual (www.icp-forests.org). However, in this project we did not use passive sampler measurements. Instead, 14-day 24-h average ozone concentrations were calculated from hourly concentrations measured with ozone instruments. Thus, in this project we did not deal with the accuracy of the passive sampler method.

14-day periods with data-loss >10% were not used. When summing up AOT40 from 14-day periods to the vegetation period 1 Apr - 30 Sep, years with 3 or more 14-day periods lacking were excluded.

According to the UNECE definition, the daylight hours are those hours having a clear-sky global radiation greater than 50 W m^{-2} (Fuhrer et al., 1997). Within the European Union this is approximated by the fixed period of 08:00–20:00 Central European Time (CET), which definition we adopted for simplicity here.

Trees are, in general, less sensitive to ozone exposure compared to e.g. agricultural crops. Thus, there need to be relatively large differences in ozone exposure in order to detect differences in impacts. Consequently, we regarded an accuracy of +/- 20% as acceptable when estimating ozone exposure indices.

We needed to define which leaves or needles that the ozone exposure indices should concern:

1. All ozone molecules have an effect => exposure index should cover all leaves during the whole life span
2. The important ozone damage is on photosynthesis => exposure index should cover upper, sunlit canopy

3. Ozone induced pre-mature leaf/ needle senescence => exposure index should cover all leaves during the whole life span

Although not altogether proven, the general view is that the primary effect of ozone is on photosynthesis. Thus, we aimed to consider the ozone exposure at the upper, sunlit part of the canopy.

The project made use of ozone monitoring sites in the Nordic countries where hourly ozone concentrations have been measured with instruments under long time periods. They are described in Figure 1 and Table 1.

4. Considering sites with no ozone measurement; estimating 24-h mean ozone concentrations and daylight AOT40

There are in principle two possibilities to obtain information about the ozone 24-h mean concentration and daylight AOT40 at sites where no measurements are made:

- Interpolation between existing measuring sites
- Modelling with the EMEP model

4.1. Interpolation

PORG (1997) states that during the afternoon, a period with effective vertical mixing, the ozone concentrations measured with instruments at a certain site might be representative for large regions.

This approach was tested for the two neighbouring sites Rörvik (now moved to nearby site Råö) and Östad, where there was assumed to be a coast to inland gradient, and on a gradient in south Sweden, from Vavihill, though Asa and Norra Kvill, ending at Aspvreten (see Figure 1). Finally it was tested on all sites, with the exception of extreme northerly sites.

4.1.1. The Rörvik – Östad comparison

In PORG (1997) it is stated "... expect a difference in the exposure to ozone between the coast and inland during on-shore flow, with essentially a constant value of concentration at the coast throughout the 24-h period, but a pronounced diurnal variation inland, with an amplitude which increases with the distance from the coast".

Rörvik is situated about 1 km from the coast, south of Göteborg, while Östad is situated 45 km inland, NE from Göteborg. Thus, these two sites should be suitable to test the coast to inland difference in the diurnal cycle ozone concentrations.

The hourly ozone concentrations at Rörvik and Östad are illustrated with 10 days in July 1994, Figure 2. The nighttime ozone concentrations are more strongly reduced at Östad most days, while the daytime concentrations are more similar. The average diurnal ozone concentration curves for Östad and Rörvik showed more similar values

during daytime, compared to nighttime (Figure 3), but the difference was not large. 14-day period mean ozone concentrations were calculated for both Östad and Rörvik, on a 24-h and a 6-h (12:00-18:00) basis, respectively. When comparing Östad and Rörvik, the 6-h mean concentrations did not show much greater similarity, compared to the 24-h mean concentrations, Figures 4 and 5.

The difference in diurnal ozone concentrations and weather conditions between Östad and Rörvik was further analysed in a preliminary study using the local meteorology model TAPM for eight days in July - Aug 1999, Figure 6. TAPM, The Air Pollution Model, was developed by Australian CSIRO Atmospheric Research Division. It is a 3-D meteorological and chemical model for air pollution studies. The meteorological component of TAPM is an incompressible, non-hydrostatic, primitive equation model with a terrain-following vertical coordinate for three-dimensional simulations. Investigations have shown that the model performs well in simulating air temperature and wind, which are the two most important fields to drive air pollution modelling.

During the first four days the pattern of the diurnal ozone concentrations were similar between Östad and Rörvik, with very low nighttime concentrations. The weather during these four days was characterised by relatively steady, westerly winds and the night time temperature differences between 10 and 100 m height were low. During the following four days the nighttime ozone concentrations at Östad still went down almost to zero, while the nighttime ozone concentrations at Rörvik remained at around 20 ppb. The nighttime temperature difference between 10 and 100 m height was considerably larger during this period, especially for Rörvik. The TAPM model predicted that there was a nighttime landbreeze at Rörvik, coming from the inland east of Rörvik, while the nighttime wind direction at Östad remained from the west. Thus, these very preliminary meteorology simulations indicated that the shift in the night time ozone concentration patterns, when comparing Östad and Rörvik, was associated with a shift in the weather conditions. The relatively high nighttime ozone concentrations at Rörvik during the last four day was associated with the occurrence of a land breeze from the east inland. This easterly land breeze was not predicted for Östad. The weather conditions when the night time ozone concentrations went down close to zero at both Östad and Rörvik seemed to be associated with steady, westerly winds. These preliminary findings need to be confirmed by further investigations.

Thus, the coast to inland difference in diurnal cycle ozone concentrations described by PORG (1997) for the UK sites Mace Head - Lough Navar and Weyboume - Sibton could not be confirmed here. The afternoon ozone concentrations at Östad and Rörvik were not so similar and the difference in nighttime concentrations depended on the prevailing weather conditions.

4.1.2. The Vavihill-Asa-NorraKvill-Aspvreten comparison

The hourly ozone concentrations at Vavihill, Asa, Norra Kvill and Aspvreten are illustrated with 7 days in July 1994, Figure 7. Nighttime decrease in ozone concentration is pronounced at Asa and Aspvreten, while not at Vavihill and Norra Kvill. This is also shown in the average diurnal ozone concentrations curves, where Vavihill and Norra Kvill show very similar patterns, while Asa show a much greater amplitude in the diurnal variations, Figure 8.

The s.d. for the 24-h mean, the 12-h mean and the 6-h mean ozone concentrations for all four different sites were compared for each14-day period during Apr – Sep 1993 - 1999, for those 14-day periods when there were data for all sites. The average 24-h s.d. was 3.8 ppb, the 12-h s.d. 2.8 ppb and finally the 6-h s.d. 2.8 ppb. Thus, there was a reduction in the s.d. for the four sites, when going from the 24-h to the 12-h mean concentrations, but not from the 12-h to the 6-h mean ozone concentrations.

4.1.3. The comparison of all sites, except extreme northerly sites

The interpolation method was tested for all Nordic sites, except the extreme northerly sites. The 14-day mean ozone concentrations were calculated on a 24-h and 12-h basis for each 14-day period. This is illustrated for two years 1994 and 1995 in Figure 9.

In order to investigate how much a certain site differed from the rest, the standard deviations of the 14-day mean ozone concentrations were calculated for each 14-day period, with different number of sites included (Table 4). This was done using the 24-h and 12-h averages. The average s.d. for all 14-day periods during 1993-1998 was then calculated. It was found that removing the sites Utö and Vindeln considerably reduced the average s.d. Removing the other sites made little difference. It is interesting that using the 14-day 24h average ozone concentration as the ozone exposure index, then Utö was the worst ozone polluted site in the Nordic countries during most of 1995 (Figure 9). However, the explanation is that the variation in the diurnal ozone concentrations at Utö is very small.

Conclusions:

- **Comparing two sites, we found little evidence for a clear-cut coast to inland gradient in the diurnal ozone concentration patterns. For the coastal site the diurnal pattern was very much governed by wind-direction - whether it was from the sea or land, so that the average diurnal pattern was only partly "coastal".**
- **The standard deviation for mean ozone concentrations between different sites at southern and middle latitudes of the Nordic countries, excluding Utö, for 14-day periods was around 3.7 ppb for the 24-h average and 3.1 ppb for the 12-h average.**
- **Thus, the 14-day mean ozone concentration might be predicted for any forest site at southern and middle latitudes of the Nordic countries, using existing ozone instrument measurements, with an uncertainty of +/- 3.7 ppb for the 24-h mean and +/- 3.1 ppb for the 12-h mean and with a 67% probability.**

4.2. Modelling

4.2.1 Introduction

This chapter reports briefly on some results on ozone concentration and ozone uptake modelling, performed within the EMEP photo-oxidant model. The new version of this model contains a deposition module, which enables explicit calculation of the stomatal component of surface fluxes. The module has previously been examined and tested mainly in an offline mode, but recently calculations have been presented made with the module implemented in the full 3-D oxidant model. A brief description of the new model version, presenting preliminary stomatal uptake calculations for all of Europe, can be found in Simpson et al. (2002a,b).

This modelling is capable of differentiating between stomatal and non-stomatal ozone flux, and as such enables estimates of the absorbed ozone dose to be made for different vegetation types as a component of total ozone deposition. Stomatal ozone flux (or ozone uptake) is calculated with consideration of vegetation-specific phenology and physiological responses to environmental conditions and as such should improve spatial and temporal assessments of the possible risks of ozone damage to vegetation across Europe.

The deposition module within the EMEP model estimates the ozone deposition towards the ground using a number of serial and parallel resistances. One of the important resistances is the stomatal resistance and the deposition module contains a simulation model for stomatal conductance (inverse resistance). This means that ozone uptake into the leaves/ needles forms a part of the estimation of local ozone concentrations. A complication arises with mixed-species forests. In this case, the local ozone concentrations will have to be estimated using an average stomatal resistance estimate for the whole canopy. Then, the deposition module may have to be run again, now to estimate the ozone uptake for the separate tree species.

Work is still required to improve many of the input databases to the new model, and to deal with soil moisture effects, before proper estimates of ozone uptake can be made. However, the basic features of the ozone uptake modelling are now in place and the results presented here are believed to represent a reasonable first estimate of the spatial and temporal patterns of ozone concentrations and ozone uptake that exist across Europe.

4.2.2 Brief description of module

The deposition module has been described and evaluated in a series of publications (Emberson et al, 2000a,b,c, 2001, Simpson et al., 2001, Tuovinen et al., 2001). The deposition flux of ozone at a particular height z is calculated as the product of the ozone concentration at height z and the deposition velocity, $V_{g,z}$, at that height. $V_{g,z}$ is calculated using a standard resistance approach, where the resistances used are

(1) R_a -- aerodynamic resistance between z and the top of the vegetation canopy;
(2) R_b -- the quasi-laminar layer resistance to ozone transfer;
(3) R_c -- the surface (canopy) resistance to ozone.

For the regional ozone modelling, we calculate fluxes to a number of land-cover classes within each grid square, using a sub-grid (mosaic) approach, similar to that used previously for the MADE model (Jakobsen et al., 1997). Stability and turbulence are first calculated over each land use, based upon the vegetation characteristics (roughness length, height, LAI). Deposition velocities are then calculated, which can be multiplied by the oxidant model's O_3 concentrations (both estimated at the same reference height) to estimate both total O_3 flux and the stomatal component.

The surface resistance is controlled by various parameters associated with the ground and external leaf surfaces, and by the stomatal conductance of the leaves. It is the stomatal conductance, G_{sto}, which governs the flux of ozone into the leaf itself, and thus controls ozone uptake to the plant. G_{sto} is calculated using a multiplicative model, which has been parameterised for a number of different vegetation types, accounting for light, temperature, vapour pressure deficits and soil moisture. For details of the functions used see Emberson et al, 2000c.

4.2.3 Input Data

In order to perform preliminary calculations of ozone flux as presented below, simplified input data have been used. More details of this are given in Simpson et al. (2002), but one change was made for this study. Vegetation height and leaf area indices (LAIs) were reduced north of 60 deg. N using a linear function, in order to generate more realistic values for Nordic conditions (e.g. Tuovinen et al. 2002).

4.2.4 The calculations

Here we present calculations from the EMEP model for the year 1999. It should be noted that soil moisture deficits have not been included in the current modelling scheme, this may generate overestimations of stomatal flux for some vegetation types, although this is likely more important in southern Europe. It should be noted that the calculations of stomatal uptake of ozone (SUO_3) are given as nmol $O_3/m^2/s$ on a ground area basis.

4.2.5 Comparison with measurements

Figures 10 illustrate the performance of the EMEP model for some Nordic sites, comparing the daily maximum values from January to November, for 1999. These plots show that the model performs rather well, and correlation coefficients for 34 sites studied range from about 0.6 to 0.8. The seasonal cycles are generally well reproduced, as are many of the episodic ozone events with high elevations. These results are in line with those found in earlier EMEP model runs, and confirm that the new unified EMEP model is functioning well also for the Nordic sites.

A detailed comparison of the hourly ozone concentrations at the Swedish Asa site, measured with ozone instruments and predicted with the EMEP model (Figure 11), showed that in this case the daily maximum concentrations are relatively well

predicted, but the low nighttime ozone concentrations are not well predicted by the EMEP model. This confirms that the 14-day 24-h mean ozone concentrations may not be so well predicted by the EMEP model at all sites, although such discrepancies are of course expected when comparing model results with a single site. In contrast, Jonson et al. (2002) found that the EMEP model reproduced the diurnal patterns of two UK sites very well during summertime, so clearly further work is needed to evaluate this aspect of model performance. It is also important to note that the diurnal variation given by either model or measurements depends on the assumed or actual underlying ground surface. Surface with high roughness (e.g. Forests) should have a much smaller diurnal cycle than smooth surfaces (e.g. Grasslands). In the case of Asa, the model results are taken for forest surfaces, whereas the measurements are made in a clearing within the forest, and are thus partly representative of grasslands. These factors may explain the discrepancy shown in Figure 11.

Conclusions:

- **The EMEP model seems to simulate the daily maximum ozone concentrations for Nordic forest sites relatively well.**
- **The 14-day 24-h mean ozone concentrations may not be so well predicted by the EMEP model at all sites. Although such discrepancies are unavoidable in any comparison of a model with measurements at one point, it can also be noted that diurnal cycles seen by measurements at 5m above ground in forest clearings may partly reflect underlying grassy surfaces.**

5. Considering sites with no ozone measurement; estimating cumulative stomatal ozone uptake

5.1 Validation against micro-meteorological measurements

As part of the project, the EMEP-model deposition module has been validated in a first step, using the data on ozone concentrations, local meteorology and measured ozone deposition rates. The measurement data are for two coniferous forests (Scots pine in Finland, Norway spruce in Denmark), covering a period of one to few weeks depending on the site.

On average, the model performs well for the Scots pine forest in Finland, if local input data are used (Figures 12, A-C). There is a slight tendency for over-predicting the deposition rate, except for highest rates, which are under-predicted. A similar but somewhat larger over-prediction is obtained for the bulk canopy stomatal conductance (Figure 12, C).

The daytime deposition rates are somewhat over-predicted at the Danish site with Norway spruce, especially in the afternoon (Figure 13). The difference between the modelled and observed surface conductance correlates with VPD. This may point out to a too weak VPD response in the model, even though the maximum VPD values are not higher than about 1 kPa, or to an inadequate representation of the actual leaf-to-air VPD within the canopy.

It is important to distinguish between the site-specific performance on a local scale and that in the context of a regional-scale transport model. In the former case, the model predicts, on average, reasonably accurate deposition parameters for the sites considered here, although there are unexplained differences, probably indicating limitations in some process parameterisations. For a regional application of the module, significant uncertainties originate from the large variability in the canopy characteristics within a land cover class. This was observed for the low Scots pine forest in Finland, where the default LAI value for coniferous forests causes a significant over-prediction, even though the model compares favourably with observations when adjusted to local parameters. The results for this site also show that, based on standard observational data, it is much more difficult to validate individual modelled deposition pathways than the total flux. The regional-scale meteorological input data may also be a significant source of uncertainties (Tuovinen et al., 2001).

5.2 Modelling stomatal ozone uptake for diffrerent Nordic sites

Figure 14 shows the results of the stomatal uptake modelling, both on a 24 h basis and using two-weekly averages. All stomatal uptake rates (SUO3) have been given in terms of nmole/m2/s. The calculations in this case are for coniferous forests. These figures confirm that during the first few months of the year there is hardly any stomatal uptake. In fact this uptake really commences around 1st April at southern sites (e.g. Birkenes, Frederiksborg), but much later at northern sites such as Oulanka. Between April and September the uptake correlates quite well with changes in the daily mean ozone, except on some occasions when SUO3 values fall suddenly, presumably in response to stomatal limitations caused by high temperatures and vapour pressure deficits.

Conclusions:

- ♣ This first step of comparison of a new dry deposition module for ozone against field micro meteorological data shows that the performance of this module looks promising.
- ♣ Evaluation of the modelling of stomatal ozone uptake to coniferous forests using flux measurements at a few sites suggests that the EMEP model can yield reasonable result if appropriate input data (especially leaf-area index, LAI) are properly characterised.

6. Considering sites with passive sampler ozone measurements; estimating daylight AOT40

6.1. General approach

The general approach was to develop statistical methods to estimate the daylight AOT40 from 24-h mean ozone concentrations for 14-day periods between 1 Apr and 30 Sep, using hourly ozone concentrations measured with instruments. Data from 24 sites in Denmark, Sweden, Norway and Finland was used to parameterise the methods (Table 1).

We have used two different statistical methods:

- Polynomial curve-fit for the relation between daylight AOT40 and 24-h mean concentration
- Functions based on the assumption that there is a close to Gaussian distribution for the hourly ozone concentrations and based on knowledge about 24-h means and s.d for the 14-day periods (Tuovinen 2001).

6.2. General features of the 24-h average – daylight AOT40 relationships

There exist surprisingly strong relationships between daylight AOT40 and 24-h mean ozone concentrations for most sites investigated (Figure 15, Table 5). Polynomial curve-fit, estimated for 14-day periods when 24-h mean concentration was >23 ppb, yields coefficients of determination from 0.62 to 0.98.

6.3. Temporal variation

The relations between 24-h mean concentrations and the daylight AOT40 were very stable over time within each site, i.e. the temporal variation was low when regarded on a yearly basis. This was obvious from the fact that the analyses of the 24-h mean - daylight AOT40 relations covered several years (Table 5). It was also illustrated in Figure 16, where six years of data from Asa, Sweden, were analysed. Comparing measured and predicted daylight AOT40 (predicted from 24-h mean concentrations using the fitted polynomial functions, see further below) showed a deviation for 14-day periods of up to +/- 1000 ppb h. However, when summing up over the growing season, this tended to even out. Thus, there was a very strong correlation between measured and predicted daylight AOT40 for the Apr-Sep periods for all years analysed.

6.4. Spatial variation

The polynomial curve-fit functions for the relation between 24-h mean and daylight AOT40 for the different sites are illustrated in Figure 17. In the 24-h mean concentration range between 30 and 40 ppb, the sites tended to divide into three different categories, as illustrated with black, red/yellow/green and blue symbols. The polynomial curve-fit for all 14-day periods from all sites within each category is

illustrated in Figure 17, with continuous black, dotted black and red lines, respectively.

6.5. A statistical model based on Gaussian distribution of hourly ozone concentrations.

It is possible to estimate an AOT value based on a measured mean concentration only, if a reasonable estimate of the standard deviation is available and the concentration distribution can be approximated by the Gaussian distribution (Tuovinen, 2001).

We obtain the AOT index (A_G) as

$$A_G = T\left[\sigma\varphi\left(\frac{\mu - c_0}{\sigma}\right) + (\mu - c_0)\Phi\left(\frac{\mu - c_0}{\sigma}\right)\right] = \sigma T\left[\varphi(\hat{\mu}) + \hat{\mu}\Phi(\hat{\mu})\right], \quad (1)$$

where c_0 is the cut-off concentration (e.g. 40 ppb for AOT40), T is the integration period, $\hat{\mu} = (\mu - c_0)/\sigma$ is the normalised mean exceedence of c_0, φ is the standard Gaussian distribution having $\mu = 0$ and $\sigma = 1$,

$$\varphi(x) = \tfrac{1}{\sqrt{2\pi}} e^{-x^2/2}, \quad (2)$$

and Φ is the corresponding cumulative density function,

$$\Phi(x) = \int_{-\infty}^{x} \varphi(y)dy . \quad (3)$$

Examples of the 14-day 24h AOT40 as a function of the 24h mean concentration for different 24h standard deviations are shown in Figure 18.

It is possible to estimate 12-h (daylight) AOT40 (A_{12}) as a function of the 24-h AOT40 (A_{24}). One can expect that these two quantities are strongly related, but also that there exists no universal relationship. As the AOT40 data considered here extend to the origin, we assume a first-order relationship with a zero intercept and define an additional parameter, α, to be determined for each location from the regression equation

$$A_{12,i} = \alpha A_{24,i} \quad (4)$$

The 12-h and 24-h AOT40 values integrated over 14-day periods are very strongly correlated (Table 5), with coefficients of determination ranging 0.96-0.99. This indicates that it would be possible to reliably estimate the 12-h AOT40, if the site-specific proportionality factor, α, was known.

Tuovinen (2002) showed that the assumption of the Gaussian distribution provides a good estimate of AOT40 at sites representing widely differing pollution climates in Europe, even in the case of a strongly skewed concentration distribution. For a

practical application, the model must be calibrated for each monitoring site. This can be accomplished by calculating the 24-h s.d. and the proportionality factor from the hourly measurements taken with a co-located concentration monitor. The overall accuracy of the calibrated model has proved to be generally acceptable when compared against independent data not used for the calibaration (Tuovinen, 2002). If no hourly-resolved data are available, the statistical parameters must be estimated from general site characteristics.

The average and s.d. for the different 14-day s.d. and proportionality factors, α, for the different monitoring sites, divided into the three different categories described under section 6.4 above, is shown in Table 6. The differences in 14-day s.d. and proportionality factors, α, between the three categories is clear. However, it should be noted that in the present application, the classification of the sites is based on the differences in the polynomial curve-fit functions and may not be optimal for the Gaussian model.

6.6. Predictions of 14-day daylight AOT40 from 14-day 24-h mean ozone concentrations, based on the two statistical methods.

The two different statistical methods, described above were used to predict 14-day daylight AOT40 from 24-h mean ozone concentrations. The 24 sites were divided into the three different categories described in section 6.4 above.

For the curve-fit based method, one curve-fit function was constructed for each of the categories based on all 14-day periods for all sites in that category (Figure 17). This single function was thus used to predict the 14-day daylight AOT40 for all sites within the category (Figure 19). The predicted 14-day AOT40 were then summed up for the period 1 Apr - 30 Sep for each year. This was compared with the summed measured daylight AOT40 for the same periods (Figure 20).

For the Gaussian distribution based method, 14-day 24-h AOT40 were calculated using functions 1 and 4 above. Values for 14-day, 24-h s.d. and the proportionality factors, α, were used for the different categories, according to Table 6. The predicted 14-day daylight AOT40 were compared to measured (Figure 21) and the summarised values 1 Apr - 30 Sep were also compared (Figure 22).

The average, max and min discrepancy between predicted and measured vegetation period daylight AOT40 are shown in Table 7, for the two methods and for the different sites.

Comparing measured and predicted daylight AOT40 showed deviations for 14-day periods of up to +/- 1200 ppb h (Figures 19 and 21). However, when summing up over the vegetation season this tended to even out, so that there were relatively good correlation between measured and predicted daylight AOT40 for the vegetation period for most sites (Figures 20 and 22). It should be noted that in relatively few cases the predicted daylight AOT40 was below the present critical levels for ozone, 10000 ppbh, while the measured daylight was above 10000 ppb h, and *vice versa*.

Another important conclusion from the analysis from the Asa site, was that the precision for estimating vegetation period daylight AOT40 was twice as good when using 14-day period 24-h average ozone concentrations compared to 28-day periods (data not shown).

As an average for the different years analysed, the errors between predicted and measured vegetation period daylight AOT40 were below 20% for most sites for both methods (Table 7), except Norra Kvill, Virolahti, Jelöya, Birkenes and Sandve. These are all category 2 sites. This maybe indicates that this category should be divided further. However, the error for these sites were not above 30%, except for the Sandve site, were it was 40-50%. Data for the Sandve site were only available for two vegetation periods.

6.7. How to assign a category for any site ?

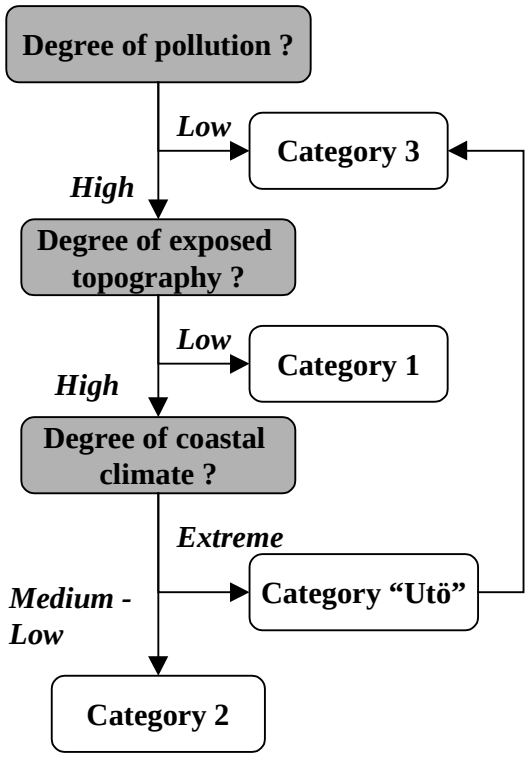
The challenge with this methodology is to be able to determine which category any forested site in the Nordic countries belongs to.

According to PORG 1997, "As windspeeds and turbulent mixing processes are enhanced on hills, it follows that surface depletion effects are smaller on hills that at sheltered lowlands".

Furthermore it is stated in PORG 1997 that "surfaces with greatly reduced uptake (e.g. open water) also show small diurnal cycles, especially if they are relatively windy exposed sites such as the coast".

A third important factor is the general pollution climate, with a south to north gradient in the Nordic countries.

We could then characterise the three different categories, and the special case of Utö, of sites according to the following scheme:



An alternative method, not using the three categories, is illustrated in Figure 22, where the average s.d. of all hourly ozone concentration values within a 14-day period is plotted against the "alpha factor", α. α was introduced in section 6.5 above and is the factor that's connects the daylight 12-h AOT40 to the 24-h AOT40 for a certain site:

$A_{12,i} = \alpha A_{24,i}$

An α value close to one means that all AOT40 is accumulated during daylight hours, while a value close to 0.5 means that equally much AOT40 is accumulated day and night. By identifying the different sites in figure 22 and comparing the unknown site with the site characteristics in Table 4, it might be possible to make an assumption of the values for the 14-day 24-h s.d. and the alpha value for the site in question.

Conclusions:

- **There exists a strong relationship between daylight AOT40 and the 24-h average ozone concentrations for 14-day periods, which is specific for a certain site**
- **If a certain site can be assigned into one of three categories, then the 14-day daylight AOT40 can be estimated from the 14-day 24-h average ozone concentrations with an accuracy of +/- 20% for most sites and +/- 30% for all sites**
- **A generalised scheme for assigning a category for an unknown site is presented**
- **It should be emphasised that the validation of the statistical methods is not based on independent data. Thus, further validation studies are needed.**

7. Considering sites with passive sampler measurements; estimating cumulative ozone uptake

7.1 Relation between 14-day mean ozone concentration and the 14-day stomatal ozone uptake

As noted in section 3 it was an early choice of this project to assess the relationship between two-weekly measurements of mean ozone concentrations and stomatal uptake, in order to assess the usefulness of employing passive sampling devices in forest areas. The plots shown in Figure 14 illustrate that at least on a daily basis the correlation between these two parameters is only moderate, with stomatal ozone uptake, SUO_3, rates being much more variable than mean O_3 concentrations at Nordic sites. The plots of 2-weekly means shown in Figure 14 above suggest a stronger relationship, but in general we have not found strong correlation between mean O3 and mean SUO_3. Over all sites, correlation coefficients ranged from some negative values (-0.34 at Voss was the worst) to quite high positive (0.66 at Frederiksborg). It thus seems at first sight as though no simple and reliable relationship exists between 2-weekly data which could be collected by passive samplers and SUO_3, although a combined use of stomatal uptake model and measured 2-weekly concentrations may overcome this problem to some extent.

However, if we investigate these relationships over a longer time-scale, namely April-September of 1999, much better correlations are found. Figure 24 shows a number of scatter plots which have been constructed from the collection of all 6-monthly (modelled) data from 34 Nordic stations. (In these plots we make more explicit use of the model's predicted concentrations and SUO_3 values for either sub-grid vegetations or the grid-average). Considering firstly the top-left plot, this shows a very good correlation between SUO_3 over forests and the mean O_3 levels calculated over forests. From this plot, it seems that simple 6-monthly means of ozone concentration could indeed provide a good surrogate for SUO_3 differences. The equivalent plot for grassland does not show quite as good a correlation, but the relationship is still reasonable.

Figure 24, bottom-left, shows the relationship between modelled SUO3 over forests and the model's mean O_3 over grassland (in the same grid-square). This relationship is interesting in practice, because many measurement sites, which are intended to monitor ozone levels in forests, are actually located in nearby grassland areas or large clearings. The model results suggest that such a mixing of data from forests and grasslands leads to a less robust relationship than one obtains from using data which is really representative of the forest.

Finally, the bottom right figure 24 illustrates the relationship between SUO_3 and the simple grid-average ozone produced by the model. This relationship is in fact quite reasonable, but at least for forests it seems better to use the forest-specific outputs of the EMEP model directly.

The data which went into these figures are listed for each station in Table 8. This table also shows the quite large differences found for different land-covers at the same site. Grasslands always show lower mean O_3 concentrations, because of their different aerodynamic properties compared to forests. This leads directly to very large

differences in AOT40, which can be very different over Grassland compared to Forest. The results for SUO3 are more complicated, because grasslands also have different stomatal conductances than forests, so that SUO_3 values are generally greater to grassland vegetation than to forests.

7.2 Caveats

It should be noted that all of the results presented in this section for stomatal uptake and the relationships to mean O_3 and AOT40 are derived from model simulations. Such predictions are hard to verify, but as noted in previous sections a considerable amount of model evaluation has already been performed for this model. There are difficulties however in extracting the stomatal uptake rates from available measurements and more work is needed to improve our knowledge and predictive power for this component.

The EMEP model as used here does not yet include soil moisture effects in the modelling of SUO_3. Inclusion of such effects would lead to reduced SUO_3 in some periods, and probably lower correlations between mean O_3 and SUO_3. This will be investigated further when soil moisture modelling has been implemented.

Conclusions:

♣ The modelling studies outlined in this chapter suggest that:

1. There are good relationships between modelled 6-monthly mean, stomatal ozone uptake and AOT40 for Nordic sites.

2. These relationships seem to be much poorer for shorter time-periods, for example 2-weekly or daily, something that should be further investigated.

3. It is likely that some combination of measured O_3 concentration and modelled stomatal uptake rate will give the most accurate estimate of SUO_3. This hypothesis needs further study in order to identify and evaluate the most promising methodologies for such an integrated approach.

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Tables

Table 1. Characteristics of 24 Nordic forest sites where ozone concentrations have been measured on an hourly basis for long time periods.

Station	Samp-ling height (m)	Altitude (m)	Local topography	Vegetation
Asa	5	150	field	grassland surrounded by forest
Aspvreten	5	20	small hill	forest land
Birkenes	2	190	low land	65% forest
Esrange	4	475	hill	few spruce trees
Hurdal	2	300	middle elev	95% forest
Jelöya	2	5	coastal	forest,grass,heather
Karasjok	2	333	middle elev	40% forest, 40% heather
Kårvatn	2	210	middle elev	60% forest
Norra Kvill	5	261	large hill	grassland close to forest
Osen	2	440	high elev.	70% forest
Oulanka	5	310	inland, rolling hills	70% con. for., 25% bog/heather
Pallas				
Prestebakke	2	160	low land	70% forest
Rörvik	5	10	coast, flat	coastal grassland
Sandve	2	40	low land	forest. cultivated
Tustervatn	2	439	high elev.	50% forest
Ulborg	18	10	flat low land	forest
Utö	5	7	rocky island, sea	treeless island
Vavihill	5	175	ridge,south side	grassland spot in beech forest
Vindeln	3	225	hill slope	forest land
Virolahti		8	low coastal	50% con. for., 40% grasland
Voss	2	500	high elev.	heather 40%, 20% cultivated
Ähtäri	5	162	inland, rolling hills	50% con. for.,20% bog/heather, 20% water
Östad	5	62	field	grassland surrounded by forest

Table 2. The importance of local variations in ozone exposure is illustrated in the table below, where the calculated daylight AOT40 Apr-Sep is compared for four different monitoring stations with ozone instruments. Rörvik (10 km S Göteborg) and Östad (45 km NE Göteborg) are approx 60 km apart and illustrates the "coast-to-inland" effect on ozone exposure. Asa (20km N Växjö) and Norra Kvill (100 km NE Växjö) illustrates the difference between "sheltered" and "exposed" local topography. The present critical level for ozone impact on trees is 10000 ppb h Apr-Sep.

daylight AOT40, Apr-Sep, ppb h					
	1994	**1995**		**1993**	**1994**
Rörvik	14864	8407	**Norra Kvill**	10630	14864
Östad	8813	4372	**Asa**	7915	6842

Table 3. Comparison of two different ozone exposure indices, calculated for European beech (*Fagus sylvatica)* at four different sites in Europe for one growing season (1994). AOT40GS, accumulated ozone exposure over 40 ppb over the growing season, and Flux GS, accumulated ozone flux to the leaves over the growing season (from Emberson et al, 1998).

	AOT40 GS nl l *hours	**Flux GS** mmol m^{-2} (leaf area)
Sweden	4.5	6.6
UK	4.9	6.7
Central Europe	15.2	7.0
Spain	3.9	6.9

Table 4. For each separate 14-day period, Apr – Sep 1993-1998, the mean ozone concentration was calculated for sites from the southern part of the Nordic countries. Then, for each separate 14-day period a mean ozone concentration was calculated, from the site-specific 14-day mean ozone concentrations, for all sites included. Each of these mean values have a standard deviation. The mean value for all standard deviations, for all sites included, was then calculated for all 14-day periods where there were data from all sites. This procedure was done using both the 24-h and 12-h mean ozone concentrations. This table shows the mean value for the s.d., with different number of sites included.
AS, Asa; ÖS, Östad; VA, Vavihill; RÖ, Rörvik; AP, Aspvreten; NK, Norra Kvill; UL, Ulborg; PR, Prestebakke, BI, Birkenes; VI, Virolahti; UT, Utö; ÄH, Ähtäri; JE, Jelöya; OS, Osen, VN, Vindeln.

	AS	ÖS	VA	RÖ	AP	NK	UL	PR	BI	VI	UT	ÄH	JE	OS	VN	s.d. 24-h mean	s.d.. 12-h mean
Sites included	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	4.4	3.6
Sites included	■	■	■	■	■	■	■	■	■	■		■	■	■	■	3.8	3.3
Sites included	■	■	■	■	■	■	■	■	■	■		■	■	■		3.7	3.1

Table 5. Some different parameters used for the statistical methods for the 24 sites used for parameterisation. Category refers to section 6.4. Time period means time when hourly ozone data were available. Polynomial curve-fits are for the relation between 14-day 24-h mean ozone concentrations and 14-day daylight AOT40 estimated for periods when the 24-h mean ozone concentrations exceeded 23 ppb. Average 14-day s.d. refers to the average of the standard deviations of all hourly ozone concentrations within each of the 14-day periods. Regression, 14-day AOT_{12} vs AOT_{24} refers to the linear regression analysis (assuming a slope though origo) of the relation between 14-day AOT40 accumulated 12-h (08:00 – 20:00) per day and the 14-day AOT40 accumulated 24-h per day, where α is the slope.

Site	Cate-gory	Time-period	Polynomial curve-fit, $y=ax^2+bx+c$, 24-h mean >23 ppb					Average 14-day s.d.	Regression, 14-day AOT_{12} vs AOT_{24}	
			a	b	c	r2			α	r^2
Östad	1	1994-95	11.0	-579.0	7777	0.64		13.1	0.87	0.99
Asa	1	1993-99	8.6	-442.1	5866	0.75		13.0	0.81	0.99
Virolahti	2	1993-98	2.7	-106.6	1083	0.76		11.5	0.79	0.97
Birkenes	2	1994-98	0.1	67.7	-1711	0.67		11.1	0.84	0.98
Rörvik	2	1992-98	4.0	-184.3	2096	0.83		11.1	0.75	0.99
Aspvreten	2	1992-98	5.4	-284.9	3858	0.87		11.1	0.74	0.98
Kårvatn	2	1994-98	1.4	-31.7	-10	0.83		11.0	0.69	0.97
Ähtäri	2	1993-98	1.8	-53.1	258	0.73		10.9	0.77	0.98
Osen	2	1994-98	0.0	63.9	-1493	0.77		10.6	0.82	0.98
Vavihill	2	1992-98	2.6	-100.9	846	0.98		9.9	0.65	0.98
Prestebakke	2	1994-98	2.5	-93.0	825	0.67		9.9	0.77	0.97
Vindeln	2	1992-98	4.1	-215.4	2886	0.76		9.4	0.75	0.98
Voss	2	1994-98	2.1	-88.9	964	0.83		9.1	0.63	0.96
Jelöya	2	1994-98	3.5	-164.0	1927	0.84		9.1	0.71	0.97
Sandve	2	1996-98	0.6	25.2	-1170	0.62		8.9	0.66	0.96
Ulborg	2	1993-98	8.2	-452.2	6225	0.86		8.8	0.71	0.98
Hurdal	2	1997-98	0.2	37.3	-1040	0.70		8.7	0.74	0.98
Norra Kvill	2	1992-98	3.0	-135.7	1496	0.96		8.5	0.61	0.99
Utö	3	1993-98	3.3	-168.5	2050	0.91		7.6	0.56	0.97
Tustervatn	3	1994-98	3.6	-205.2	2969	0.92		6.7	0.53	0.99
Oulanka	3		2.6	-132.0	1703	0.91		6.6	0.56	0.99
Esrange	3		3.7	-211.8	3003	0.91		6.2	0.54	0.99
Karasjok	3	1997-98	1.7	-79.8	924	0.94		6.0	0.53	0.99
Pallas	3	1992-98	4.1	-240.3	3520	0.94		5.7	0.52	0.99

Table 6. The average values and s.d. for the three site categories, for some parameters used in the statistical method based on normal distribution, see section 6.5.

Average for sites within category	**14-day period Average 24h S.D.**	**14-day period AOT12h = α * AOT24h**	**14-day period AVG12h = α * AVG24h + β**	
		Average α	**Average α**	**Average β**
Category. 1	**13.0**	**0.84**	**1.15**	**2.65**
Category. 2	**10.0**	**0.73**	**1.03**	**3.18**
Category. 3	**6.5**	**0.54**	**0.94**	**3.14**
Standard deviation for sites within category	**14-day period Average 24h S.D.**	**14-day period AOT12h = α * AOT24h**	**14-day period AVG12h = α * AVG24h + β**	
		Average α	**Average α**	**Average β**
Category. 1	**0.0**	**0.04**	**0.03**	**1.22**
Category. 2	**1.0**	**0.07**	**0.06**	**3.04**
Category. 3	**0.7**	**0.02**	**0.05**	**2.16**

Table 7. Discrepancies, in % of the measured values, between predicted and measured daylight AOT40 summed for the vegetation period 1 Apr - 30 Sep, for both statistical methods, based on curve-fit and based on Gaussian distribution.

Site	**Curve-fit method, % error**			**Gaussian distribution method, % error**		
	avg	max	min	avg	max	min
Östad	-6	-4	-8	4	23	-16
Asa	0	5	-9	10	41	-12
Vavihill	2	13	-9	3	9	-12
Norra Kvill	**21**	45	3	**23**	44	5
Rörvik	-6	27	-18	-9	18	-21
Aspvreten	-12	4	-21	-13	-1	-23
Vindeln	12	35	-5	13	32	-3
Virolahti	**-27**	-13	-43	**-29**	-15	-44
Ähtäri	-16	10	-31	-16	13	-32
Ulborg	18	45	-5	15	37	-6
Jelöya	**25**	60	5	**21**	52	6
Prestebakke	-8	19	-20	-12	16	-23
Hurdal	14	15	12	11	11	10
Osen	-14	-9	-26	-15	-10	-28
Birkenes	**-20**	-3	-39	**-24**	-7	-42
Sandve	**50**	87	14	**43**	77	8
Voss	15	27	7	16	26	13
Kårvatn	-1	31	-16	2	30	-10
Esrange	2	38	-16	-6	24	-20
Tustervatn	4	16	-2	-8	6	-26
Karasjok	15	15	15	-9	-9	-9
Oulanka	-7	0	-12	-19	-9	-26
Pallas	14	28	-1	8	19	-2
Utö	-10	0	-20	-17	-4	-32
Average (absolute values)	13.3			15.8		

Table 8. Modeled 6-monthly mean ozone, AOT40f and stomatal uptake (SUO3) for Nordic Sites. Data are presented for Grid Averages, Coniferous Forests, and Grasslands at the Location of the Site.

	Mean O3 (ppb)			AOT40f (ppm h)			SUO3 (kgO3/ha)	
	Grid	Conif.	Grass	Grid	Conif.	Grass	Conif.	Grass
Ahtari	35.9	36.9	29.1	5.4	6.5	2.0	20.8	31.7
Ammarnas	34.5	35.8	28.8	2.7	3.5	1.1	14.8	20.9
Asa	39.0	39.4	26.2	8.4	9.1	0.5	18.6	13.0
Aspvreten	39.1	41.1	33.9	9.4	12.5	6.2	24.8	39.1
Birkenes	39.6	40.6	31.9	9.0	10.4	2.9	23.3	20.4
Esrange	32.6	33.7	26.9	1.6	2.1	0.5	13.8	21.2
Flarkfen	31.7	32.4	26.1	1.1	1.3	0.3	12.3	22.7
Frederiksborg	36.9	41.0	34.1	11.2	15.7	8.3	27.2	40.9
Hoylandet	35.1	37.2	30.9	3.8	5.0	1.9	18.6	25.0
Jeloya	38.9	41.3	33.7	9.9	12.7	6.5	26.9	34.8
Jergul	31.8	33.7	27.6	1.4	2.0	0.5	11.1	22.3
Kaarvatn	34.7	39.8	28.1	3.7	7.5	1.5	17.0	17.6
Mekrijarvi	34.7	36.1	27.9	3.6	4.9	1.1	19.5	28.3
Nordmoen	36.8	39.8	32.1	6.6	9.4	4.1	23.9	29.1
Norra Kvill	37.9	42.0	34.1	7.0	12.8	5.9	23.9	35.2
Osen	37.0	39.6	32.0	5.6	7.8	2.8	21.7	25.2
Ostad	37.6	41.8	33.7	7.4	13.5	5.9	24.3	32.5
Oulanka	32.9	33.9	27.1	2.2	2.8	0.5	15.6	24.2
Petsikko	31.1	32.3	26.4	0.9	1.2	0.3	11.1	22.0
Prestebakke	41.0	42.3	34.5	12.2	14.1	7.1	27.1	36.7
Rorvik	36.0	39.6	29.3	5.8	10.7	1.8	21.1	18.0
Sandve	36.4	40.9	33.1	4.4	9.9	2.5	22.4	18.9
Sannen	42.0	44.5	36.5	15.7	19.3	10.9	28.9	43.4
Sogne	40.7	41.1	32.5	10.8	11.4	3.5	24.4	21.4
Storulvsjon	36.2	37.8	30.8	5.3	6.7	2.7	21.6	30.1
Svanvik	30.5	32.1	26.2	0.8	1.1	0.2	11.1	22.4
Tustervatn	35.3	37.2	30.4	3.3	4.5	1.3	13.6	21.5
Ulborg	35.6	42.8	35.6	8.5	16.2	8.8	26.5	35.9
Valle	36.1	41.4	33.7	4.5	10.9	4.4	20.3	23.2
Vavihill	37.8	43.3	35.2	10.6	17.8	9.3	26.7	40.1
Velen	37.5	41.9	33.9	8.1	13.1	6.0	25.1	35.3
Vindeln	34.0	36.0	29.3	3.6	5.0	2.0	19.0	28.0
Virolahti	36.5	36.8	25.2	6.0	6.4	0.7	18.7	15.2
Voss	37.5	41.3	30.1	7.0	10.8	3.0	21.3	20.2

Figures

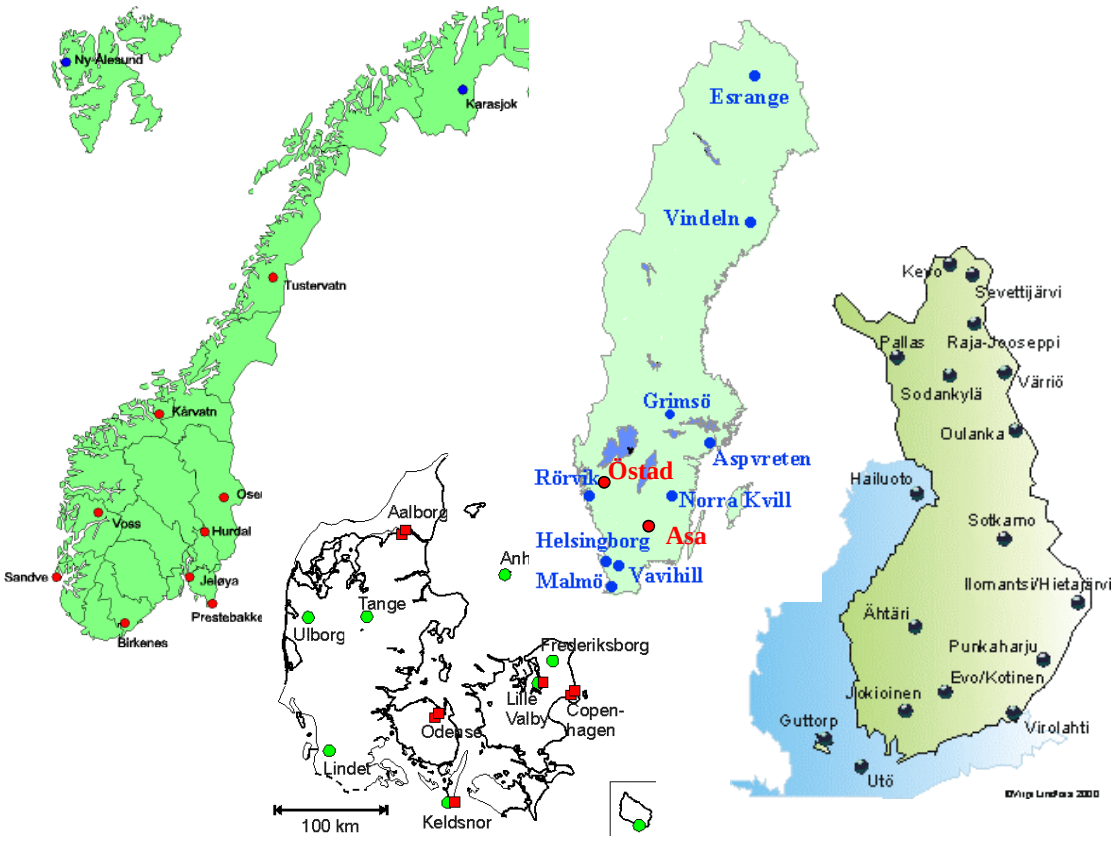


Figure 1. The location of ozone monitoring sites in the Nordic countries, where hourly ozone concentrations have been measured with instruments under long time periods, see also Table 1. Note that not all sites on this map are included in the present study.

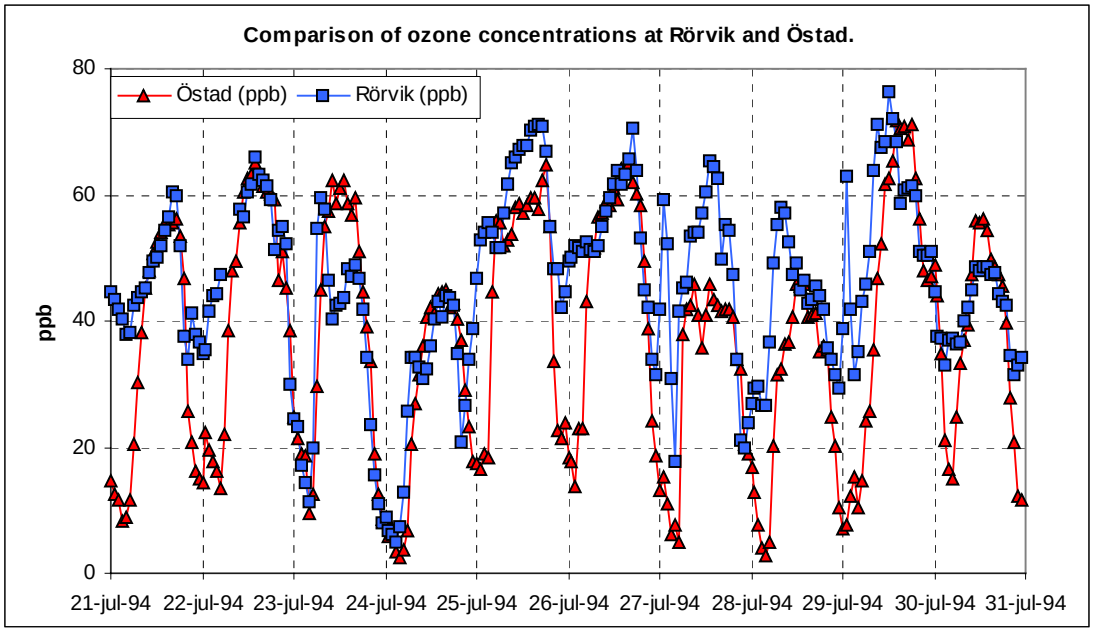


Figure 2. Comparison of hourly ozone concentrations, measured with ozone instruments, at the two neighbouring sites Rörvik and Östad, where there was assumed to be a coast to inland gradient in ozone concentrations. Rörvik is situated about 1 km from the coast, south of Göteborg, while Östad is situated 45 km inland, NE from Göteborg.

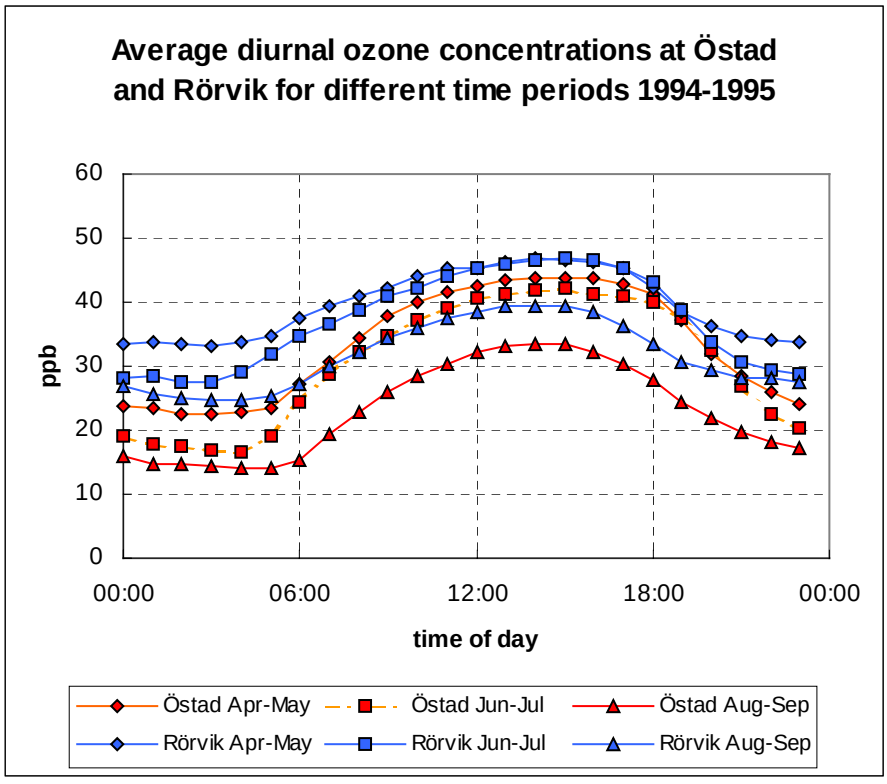


Figure 3. Comparison of mean hourly diurnal ozone concentrations, measured with ozone instruments, for different time periods during the growing seasons (Apr – Sep) 1994 and 1995, at the two neighbouring sites Rörvik and Östad, where there was assumed to be a coast to inland gradient in ozone concentrations.

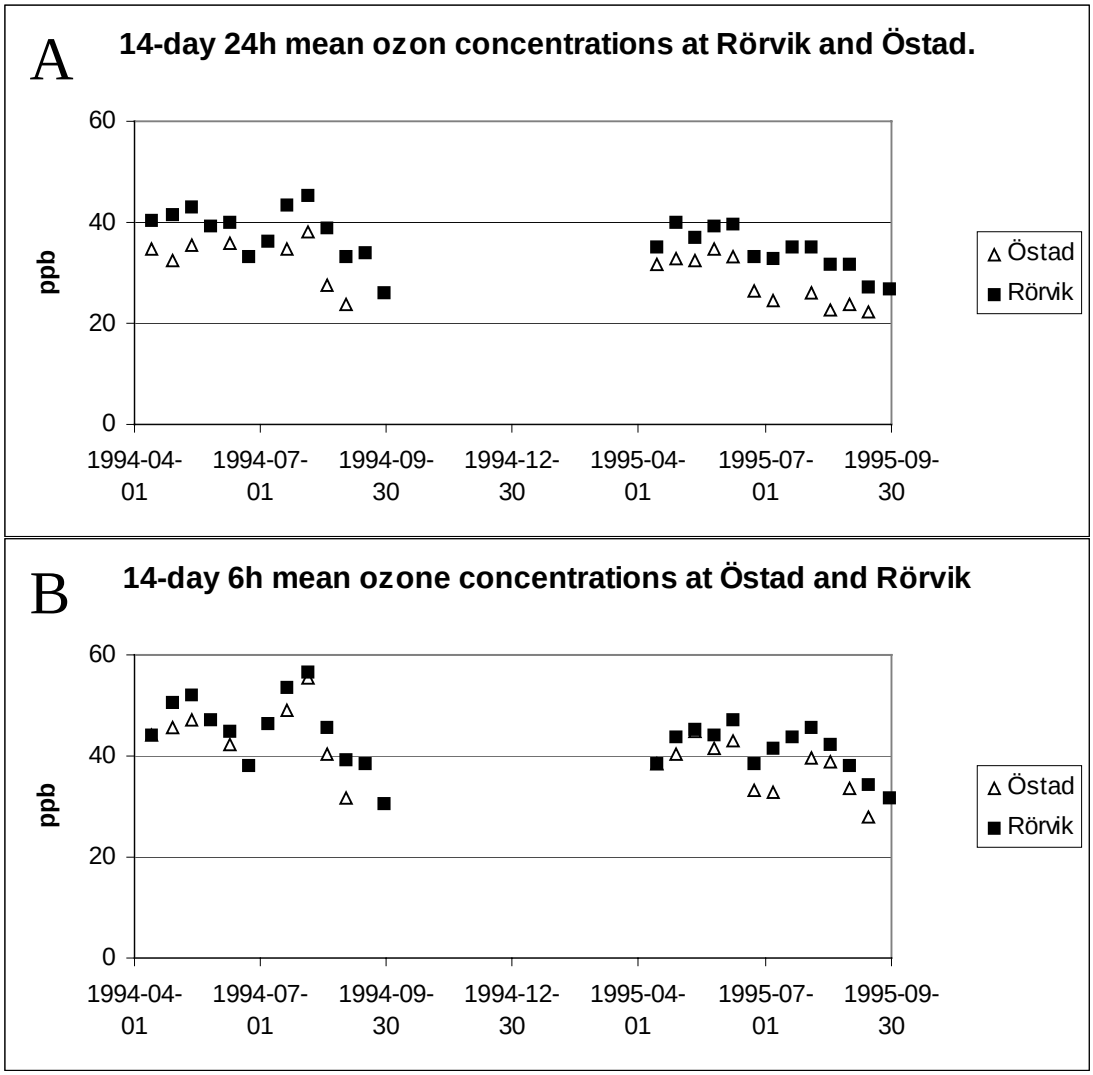


Figure 4. Comparison of 14-day mean ozone concentrations, measured with ozone instruments, during the growing seasons (Apr – Sep) 1994 and 1995, at the two neighbouring sites Rörvik and Östad, where there was assumed to be a coast to inland gradient in ozone concentrations. A, 24-h mean ozone concentrations; B, 6-h (12:00-18:00) mean ozone concentrations.

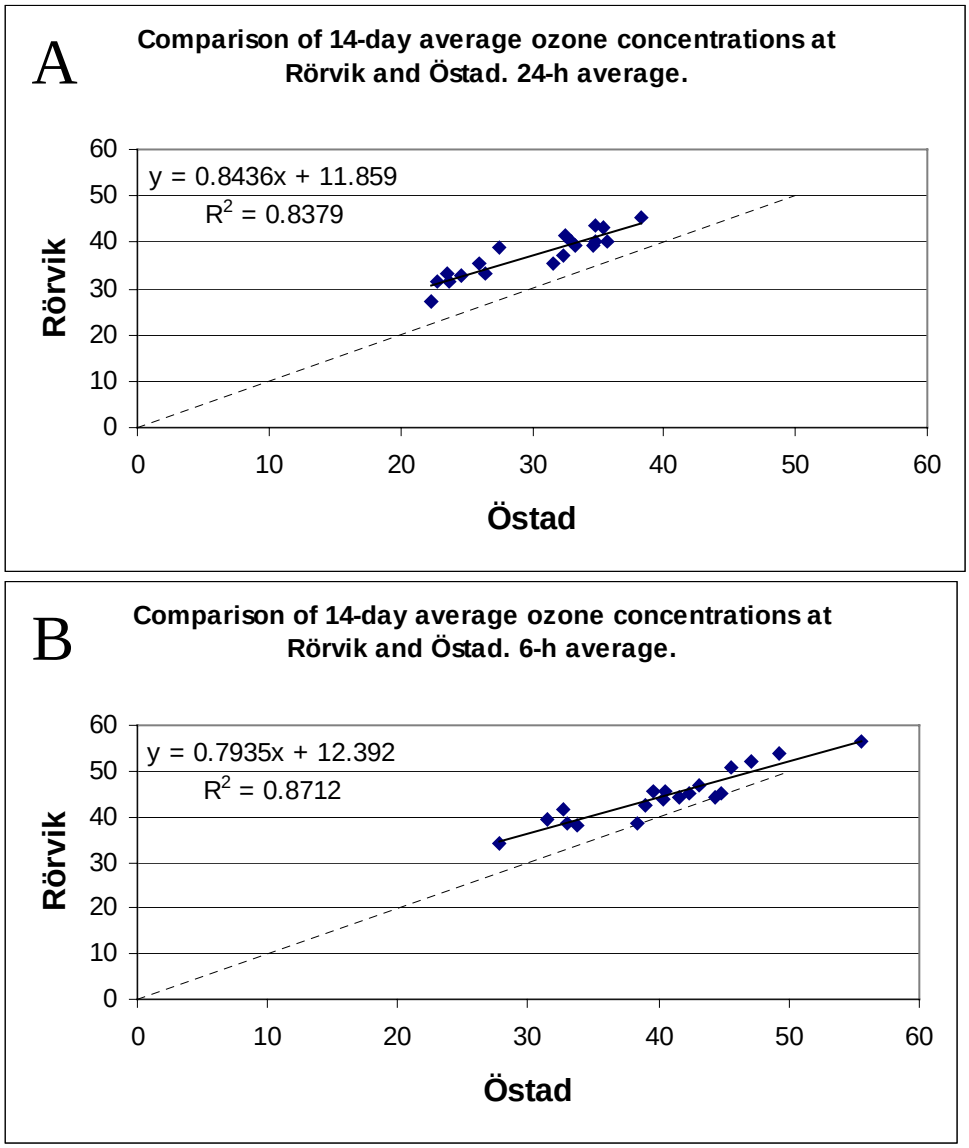


Figure 5. Linear regression analysis of 14-day mean ozone concentrations, measured with ozone instruments, during the growing seasons (Apr – Sep) 1994 and 1995, at the two neighbouring sites Rörvik and Östad, where there was assumed to be a coast to inland gradient in ozone concentrations. A, 24-h mean ozone concentrations; B, 6-h (12:00-18:00) mean ozone concentrations.

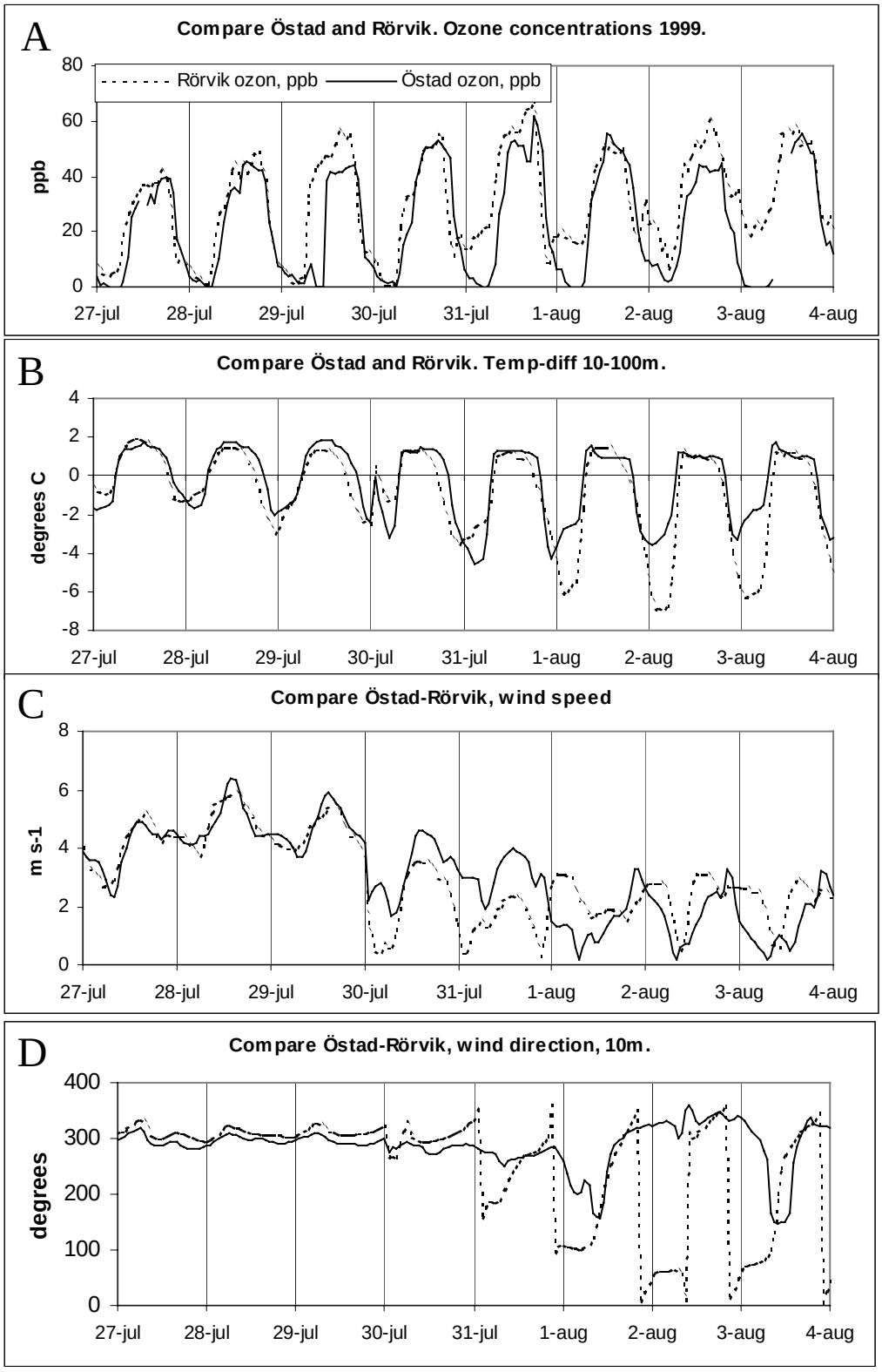


Figure 6. The difference in diurnal ozone concentrations and weather conditions between Östad and Rörvik as analysed using the local meteorology model TAPM, The Air Pollution Model developed by Australian CSIRO Atmospheric Research Division, during eight days in July - Aug 1999. A, Hourly ozone concentrations, measured with ozone instruments; B, Modelled temperature difference 10 – 100m above ground; C, Modelled wind speed at 10m above ground; D, Modelled wind direction at 10m above ground. Solid line, Östad; broken line, Rörvik.

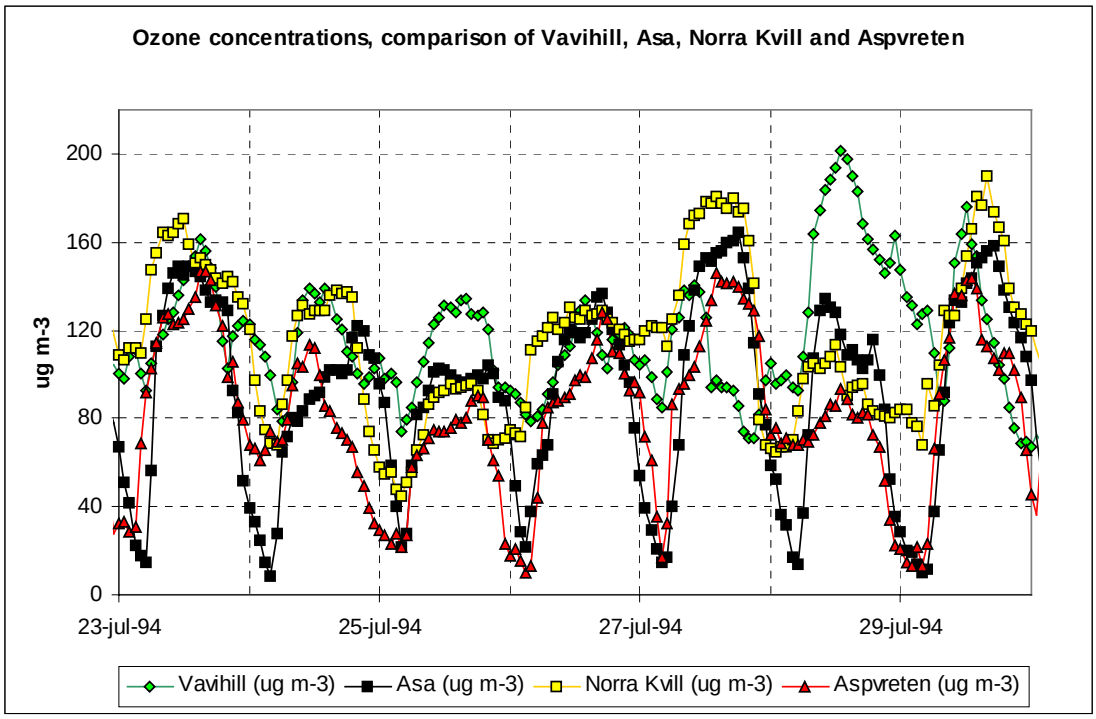


Figure 7. The hourly ozone concentrations at Vavihill, Asa, Norra Kvill and Aspvreten, measured with ozone instruments, during a 7-day period in July 1994

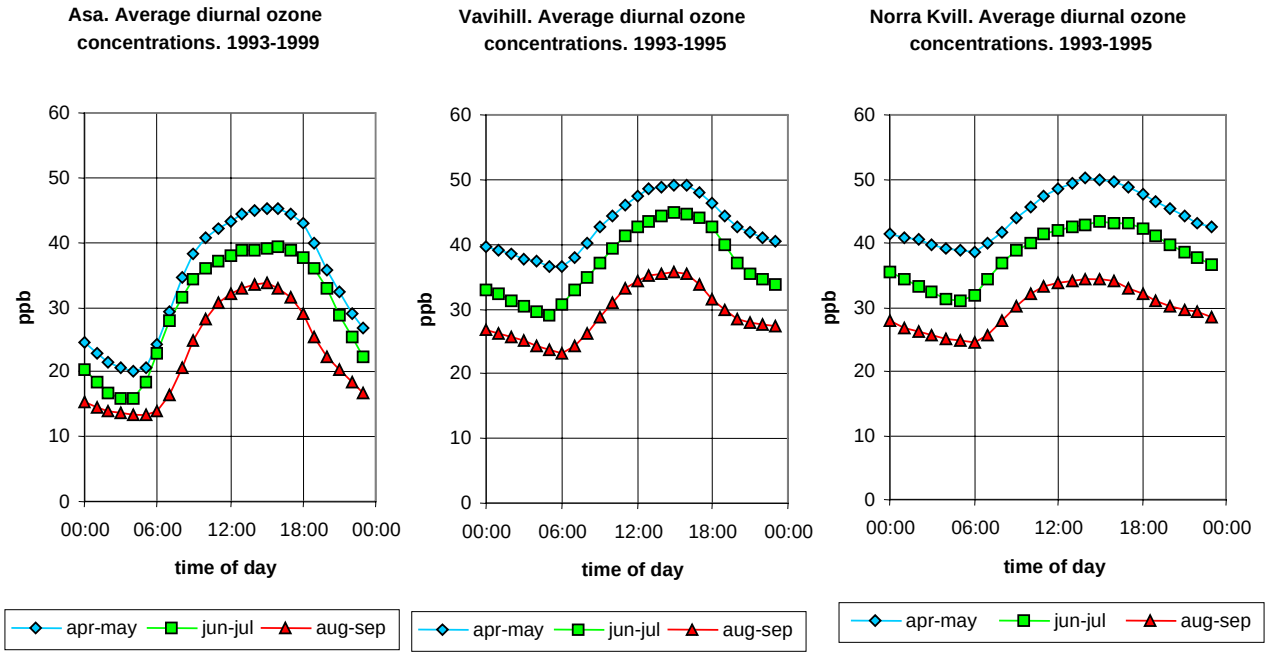


Figure 8. The mean hourly diurnal ozone concentrations at Vavihill, Asa and Norra Kvill during different time periods 1993-1999, measured with ozone instruments.

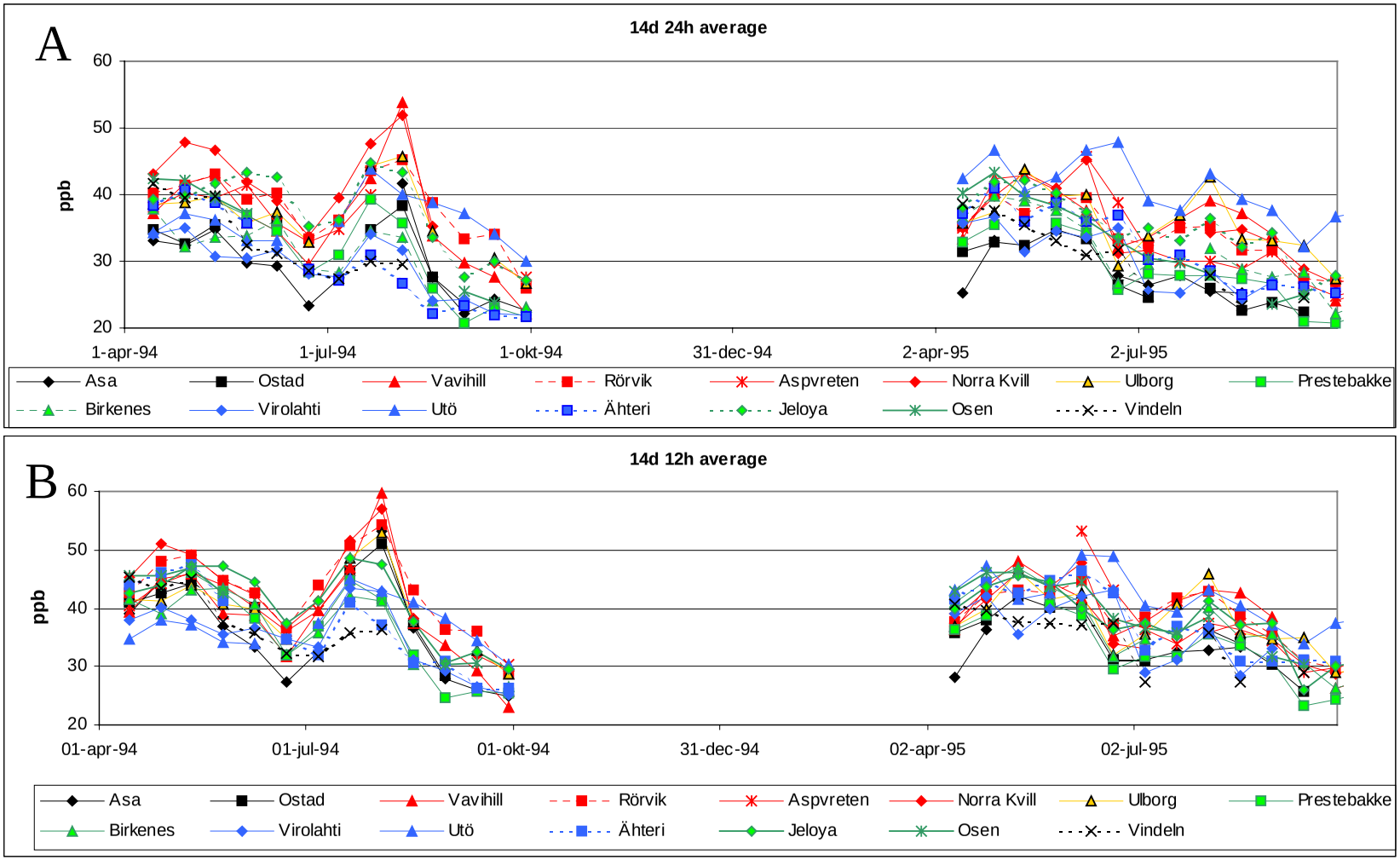
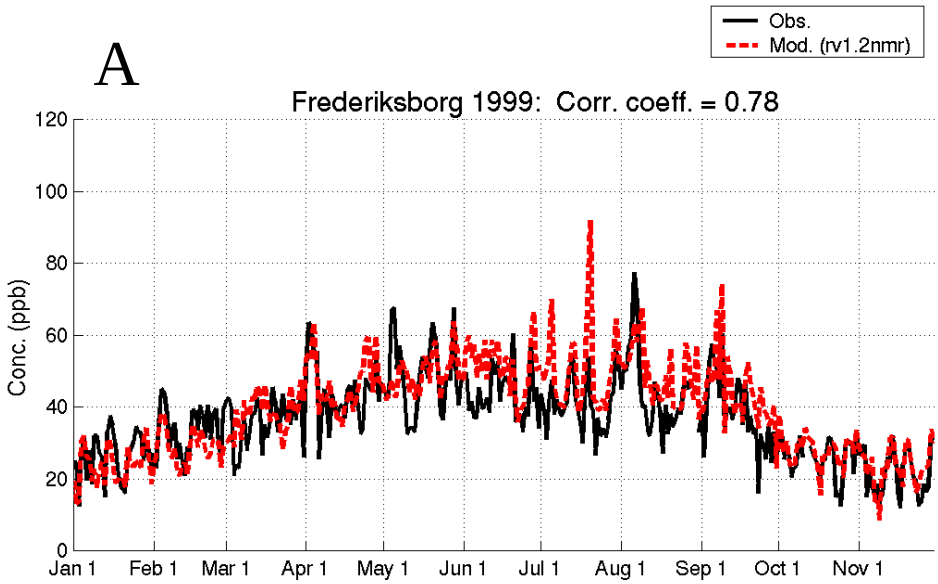
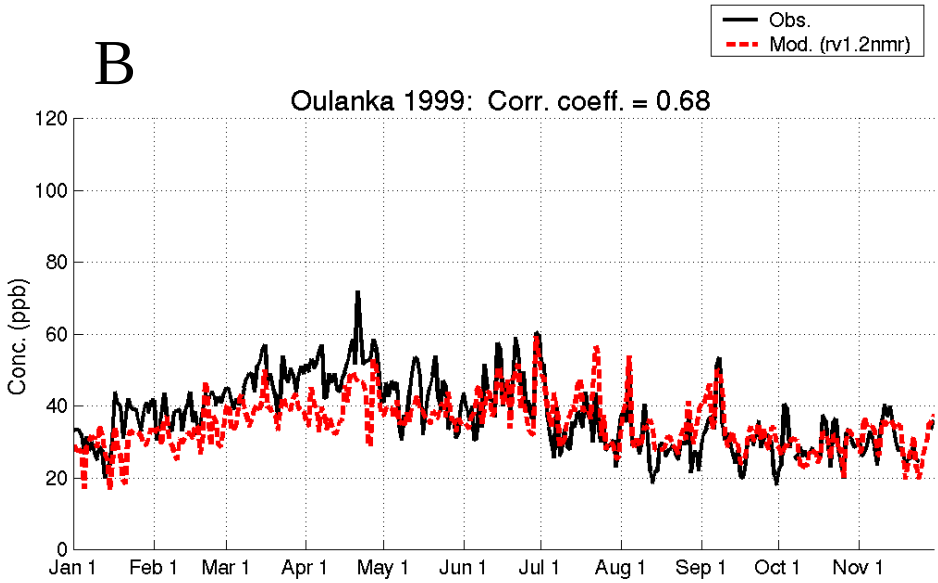


Figure 9. The 14-day mean ozone concentrations, Apr-Sep, calculated on an 24-h (A) and 12-h (B) basis, for two years 1994 and 1995 for all Nordic sites, except the extreme northerly sites.


A
Obs.
Mod. (rv1.2nmr)
Frederiksborg 1999: Corr. coeff. = 0.78
Conc. (ppb)
0
20
40
60
80
100
120
Jan 1
Feb 1
Mar 1
Apr 1
May 1
Jun 1
Jul 1
Aug 1
Sep 1
Oct 1
Nov 1


B
Obs.
Mod. (rv1.2nmr)
Oulanka 1999: Corr. coeff. = 0.68
Conc. (ppb)
0
20
40
60
80
100
120
Jan 1
Feb 1
Mar 1
Apr 1
May 1
Jun 1
Jul 1
Aug 1
Sep 1
Oct 1
Nov 1

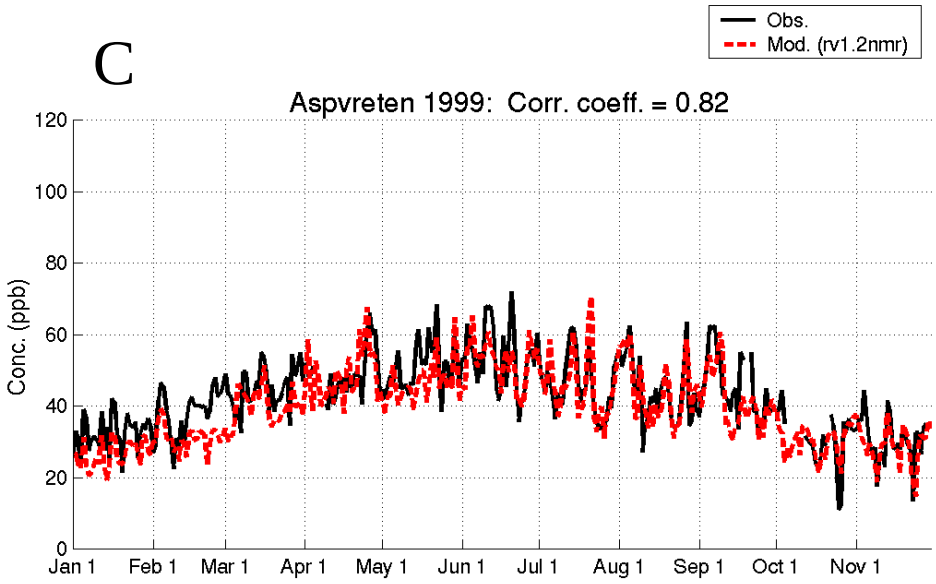


Figure 10. Modelled *versus* observed daily maximum ozone concentrations for 1999. **A**, Frederiksborg (Denmark); **B**, Oulanka (Finland); **C**, Aspvreten (Sweden).

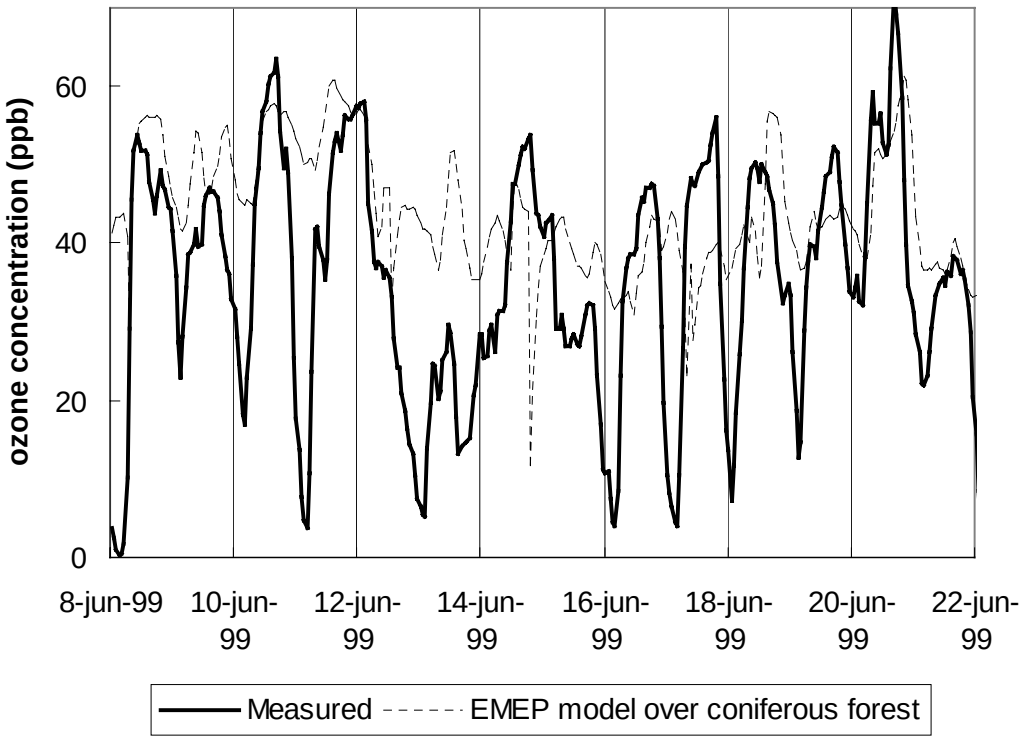


Figure 11. Example of hourly ozone concentrations at the site Asa, Sweden during 14 days 1999. The solid line shown ozone concentrations measured with an instrument at 5m above ground in an open grassland area in the forest landscape. The broken line shown the ozone concentrations estimated with the EMEP model (hourly time scale) for above a coniferous forest in the same EMEP grid.

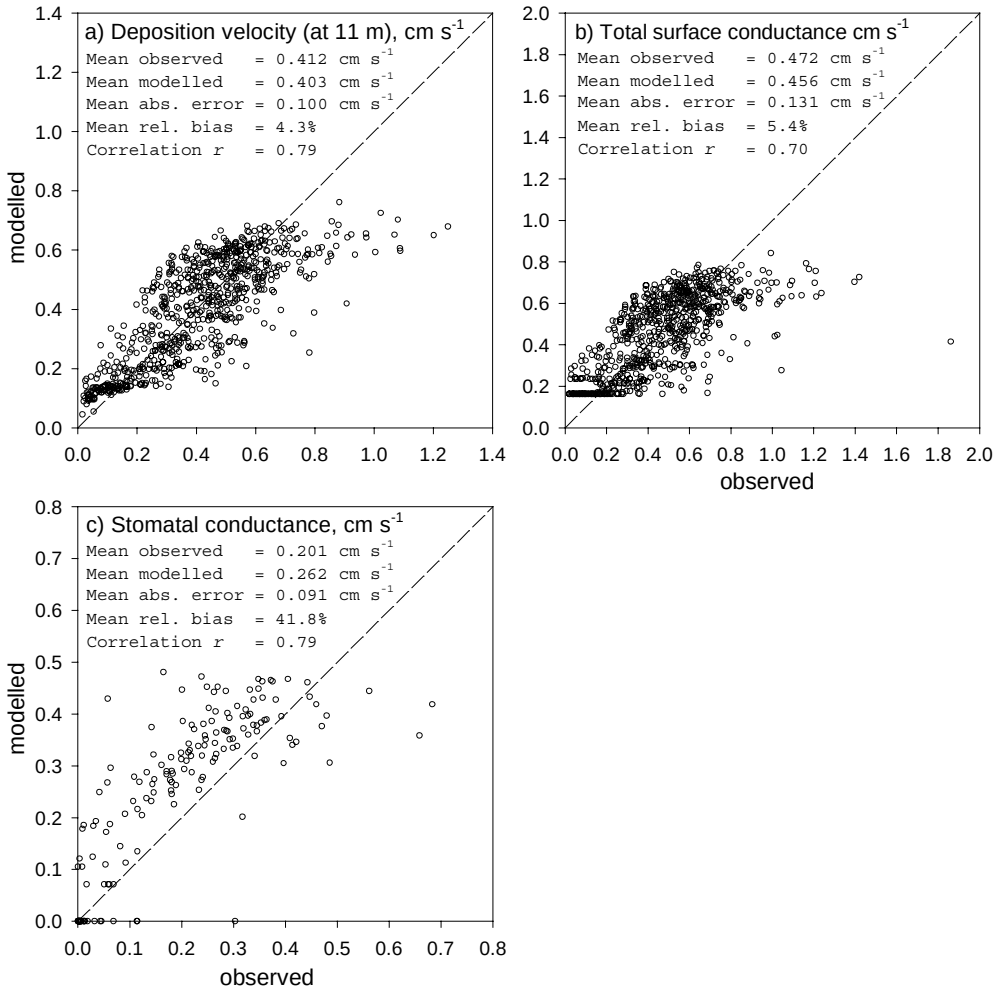


Figure 12. Comparison of the modelled dry deposition velocity (a), total surface conductance (b) and canopy stomatal conductance (c) for ozone, with those derived from O_3 and H_2O flux measurements at Mekrijärvi in July 1995 (23–27 July for G_{sto}); mean abs. error = arithmetic mean of |xmod–xobs|, where xmod and xobs are the modelled and observed quantity in question, respectively; mean rel. bias = arithmetic mean of 2(xmod–xobs)/(xmod+xobs) for non-zero xmod and xobs.

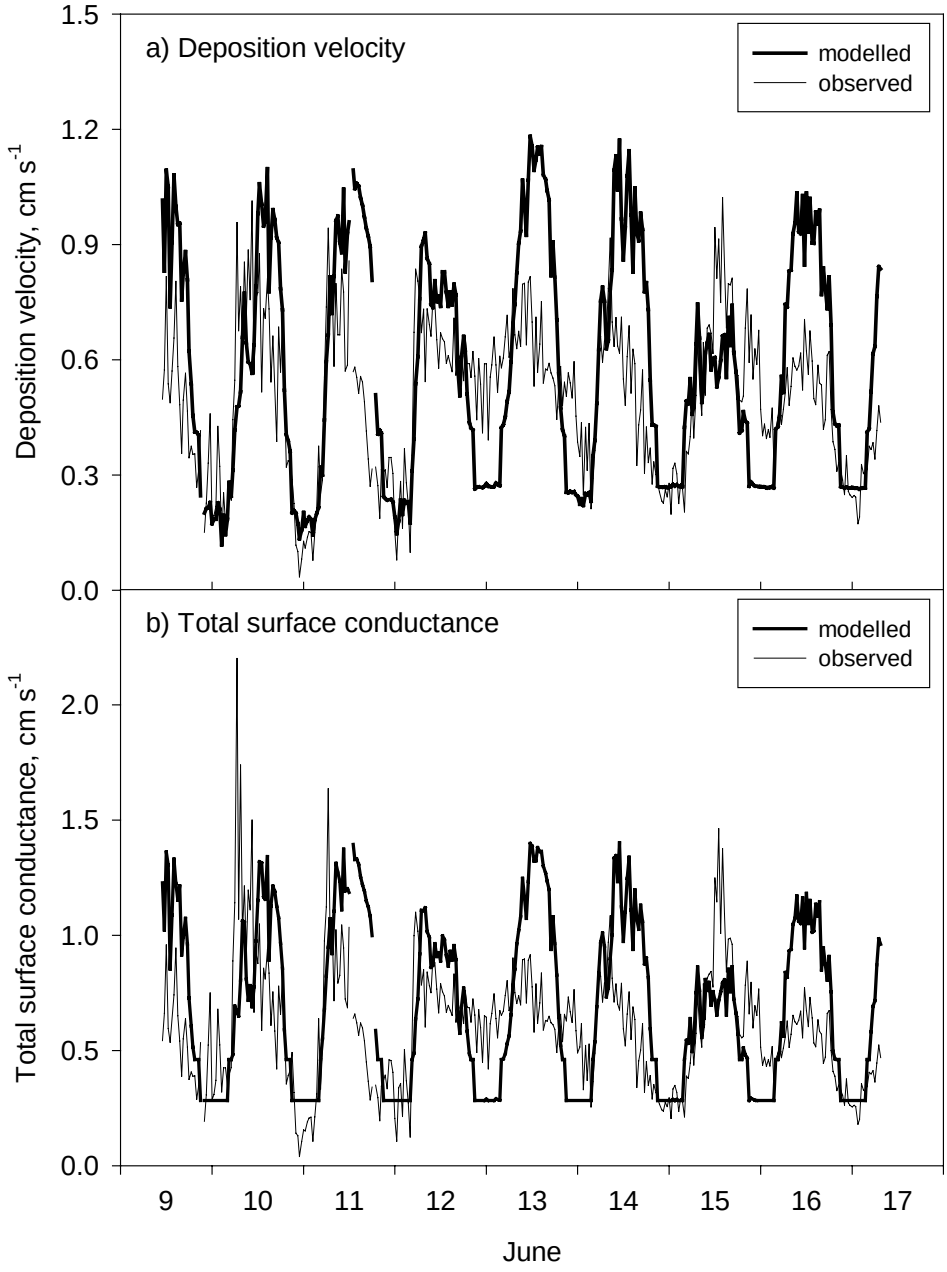
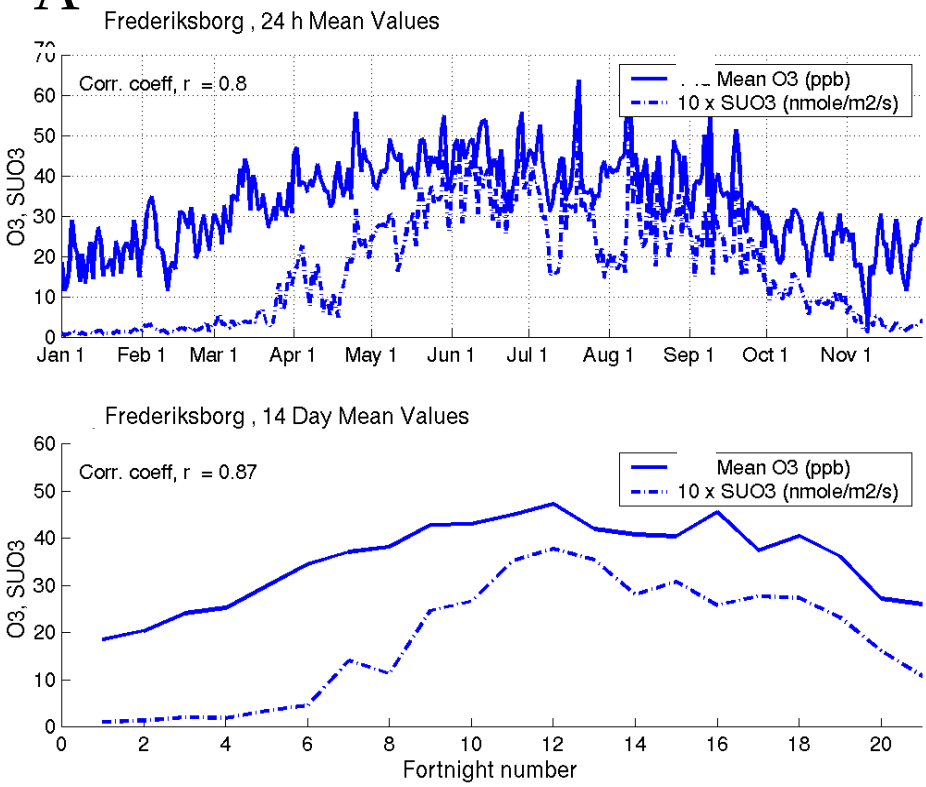
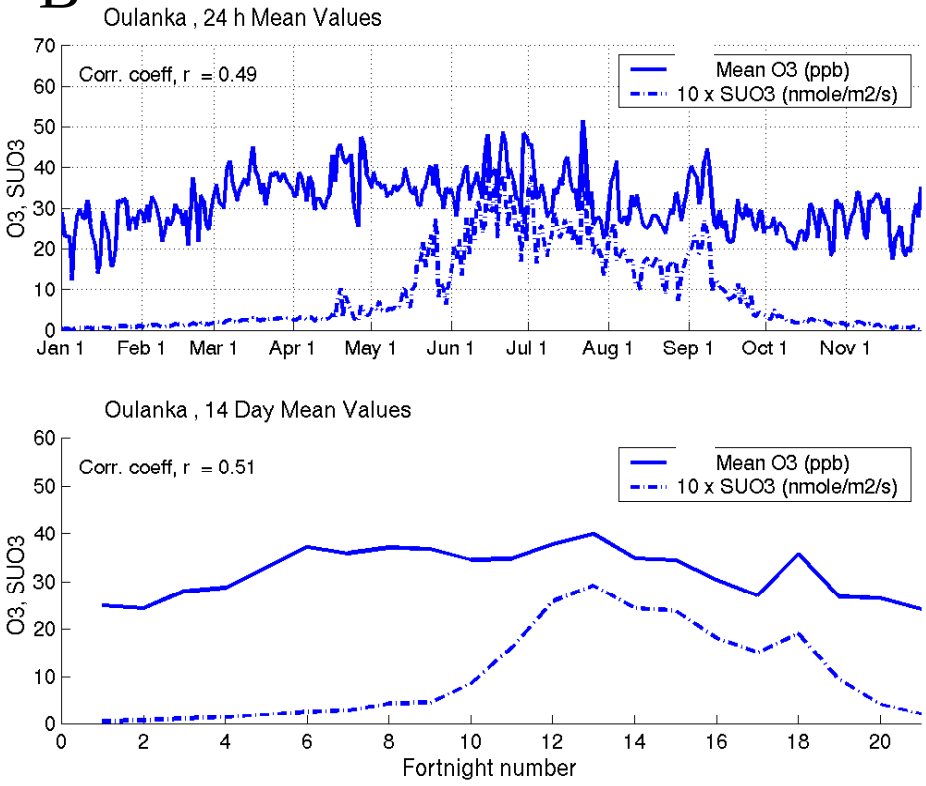


Figure 13. Observed and modelled dry deposition velocities at 21 m (a) and total surface conductances (b) from 9 to 17 June 1994 in a Norway spruce forest at Ulborg, Denmark.

A


Frederiksborg , 24 h Mean Values
Corr. coeff, r = 0.8
Mean O3 (ppb)
10 x SUO3 (nmole/m2/s)
O3, SUO3
Jan 1
Feb 1
Mar 1
Apr 1
May 1
Jun 1
Jul 1
Aug 1
Sep 1
Oct 1
Nov 1
Frederiksborg , 14 Day Mean Values
Corr. coeff, r = 0.87
Fortnight number

B


Oulanka , 24 h Mean Values
Corr. coeff, r = 0.49
Mean O3 (ppb)
10 x SUO3 (nmole/m2/s)
O3, SUO3
Jan 1
Feb 1
Mar 1
Apr 1
May 1
Jun 1
Jul 1
Aug 1
Sep 1
Oct 1
Nov 1
Oulanka , 14 Day Mean Values
Corr. coeff, r = 0.51
Fortnight number

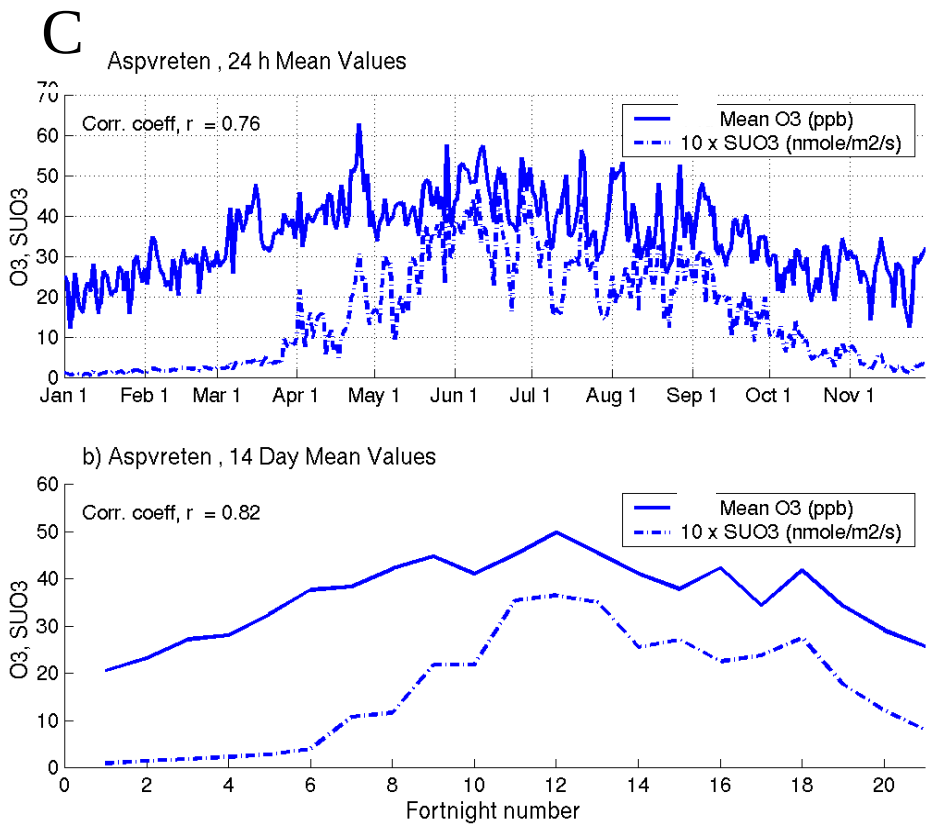


Figure 14. Modelled ozone concentrations and stomatal uptake rates (SUO3) for coniferous forests. Plots show results for daily averages (upper pane) and two-weekly averages (lower pane). A, Frederiksborg (Denmark); B, Oulanka (Finland); C, Aspvreten (Sweden).

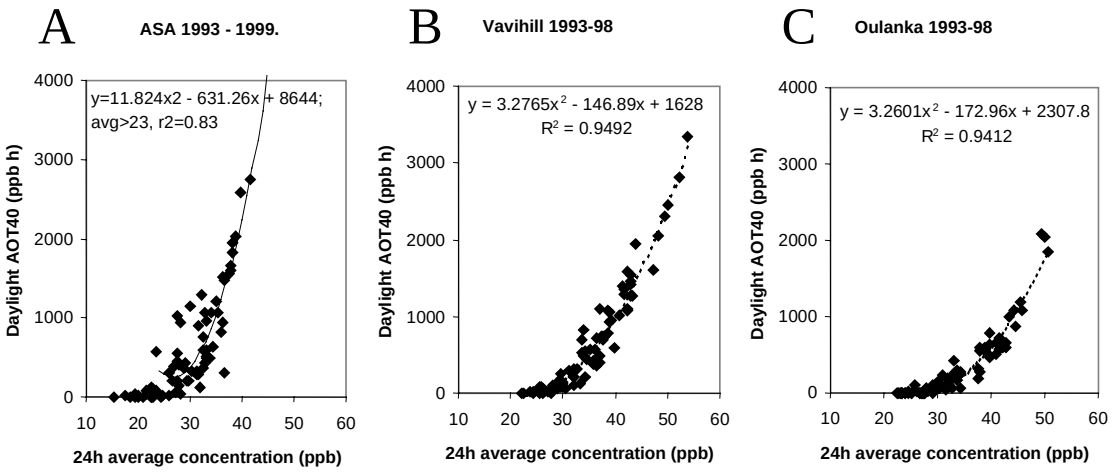


Figure 15. Relationships between daylight AOT40 and 24h average ozone concentrations during 14-day periods Apr – Sep, 1993 – 1997, for three Nordic sites belonging to three different categories (see section 6.4). A, Asa (Sweden); B, Vavihill (Sweden); C,Oulanka (Finland).

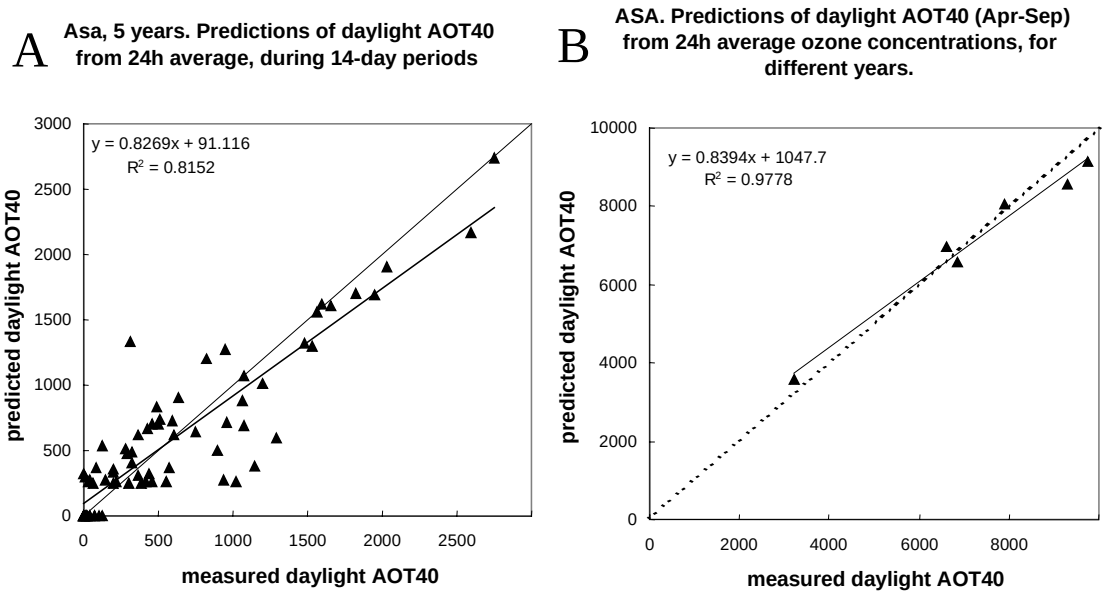


Figure 16. Comparing measured and predicted daylight AOT40 during 14-day periods Apr – Sep, 1993 – 1998 for the Asa site. Predictions were made from 24-h average concentrations using the fitted polynomial function in Figure 15 A. A, For 14-day periods; B, For growing seasons Apr –Sep each year, as cumulated from the 14-day periods within each growing season.

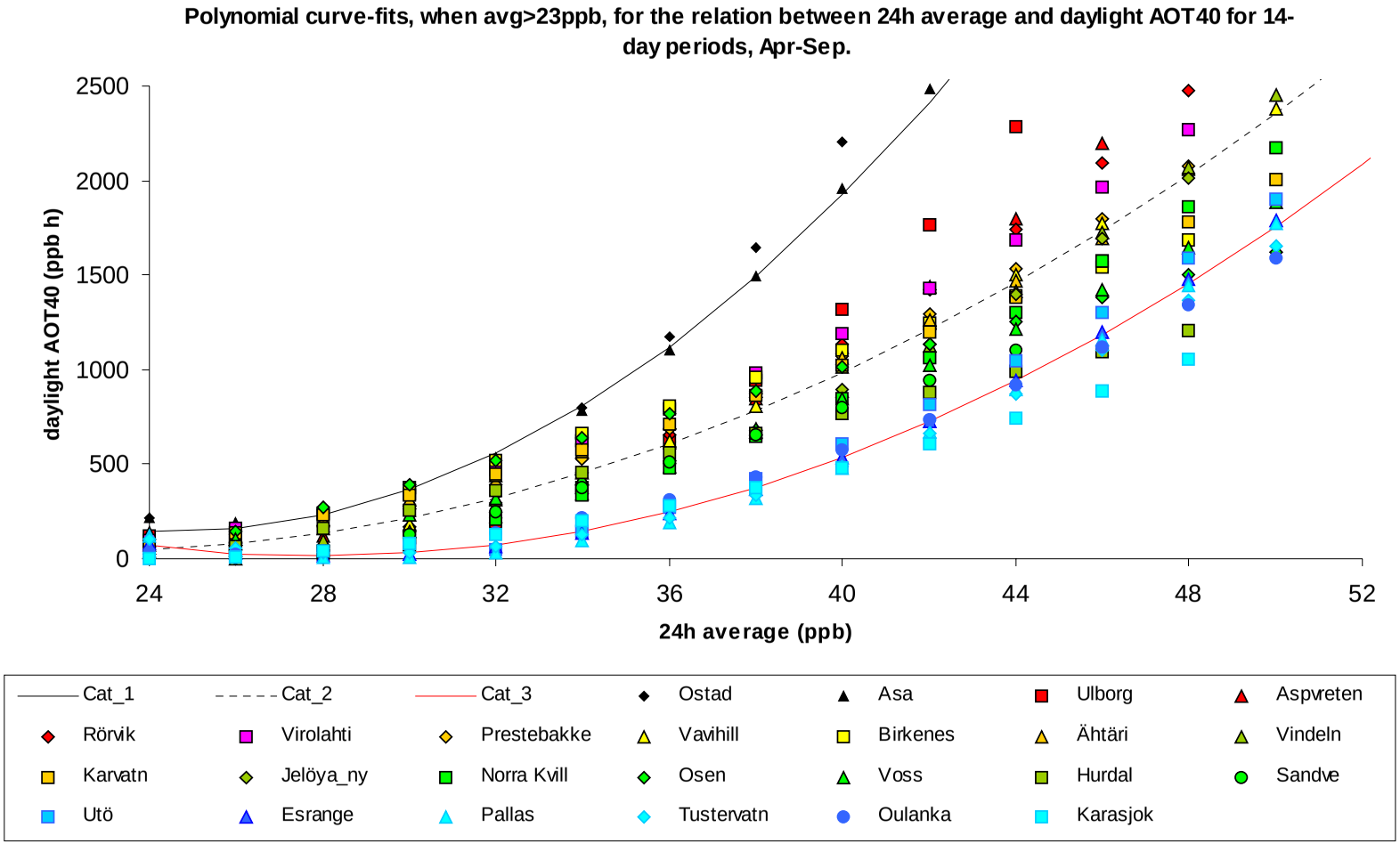


Figure 17. The polynomial curve-fit functions for the relation between 24-h mean and daylight AOT40 for 14-day periods covering several years for the different Nordic sites. The markers do not represent individual datapoint, but are used to illustrate the different curve-fits. The polynomial curve-fit for all 14-day periods from all sites within each different category (see section 6.4) is illustrated with continuous black, dotted black and red lines, respectively.

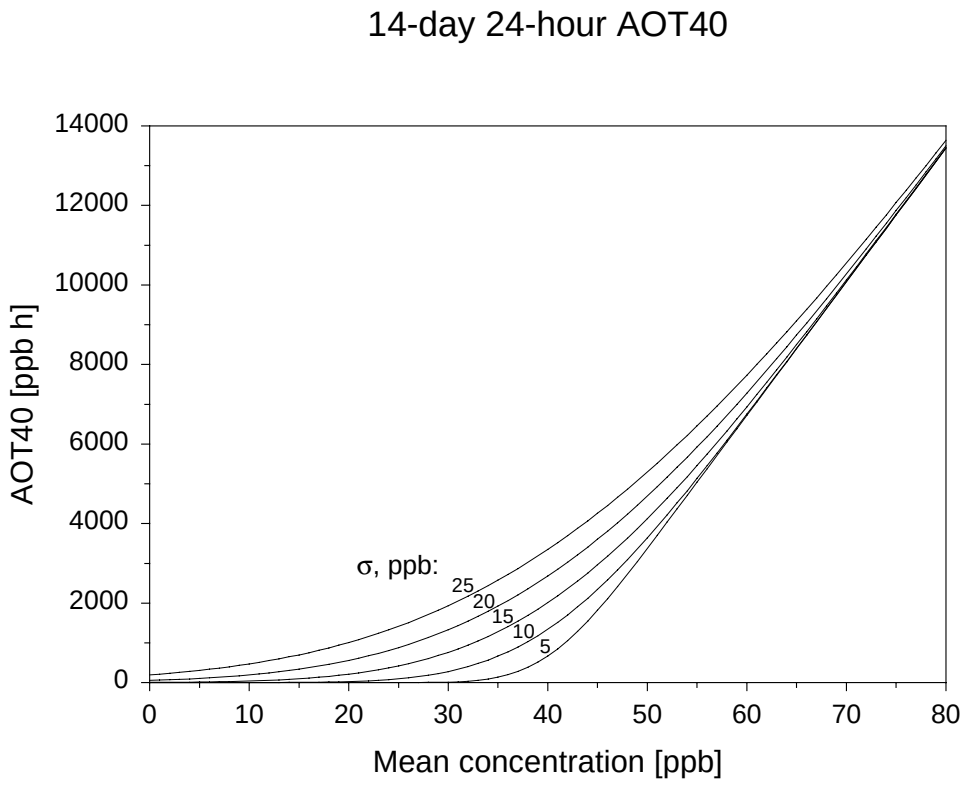


Figure 18. The accumulated exposure AOT40 as a function of the mean concentration for different standard deviations (ρ). The concentrations are assumed to follow a Gaussian probability distribution. The integration period is 14 days.

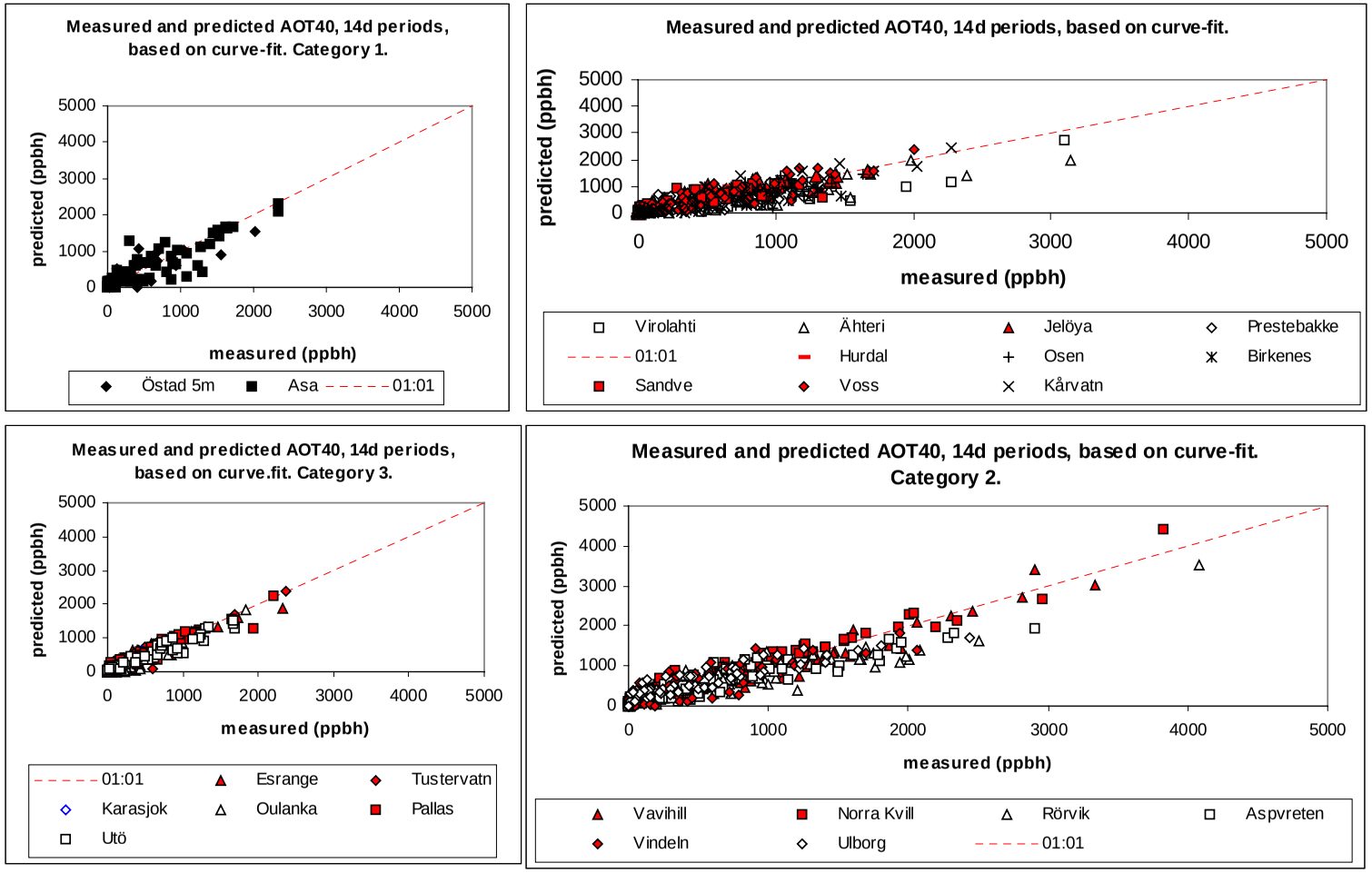


Figure 19. Comparison of 14-day daylight AOT40 predicted from 14-day 24-h mean ozone concentrations, using one single curve-fit function for each site category, with the true daylight AOT40 calculated from the hourly measurements.

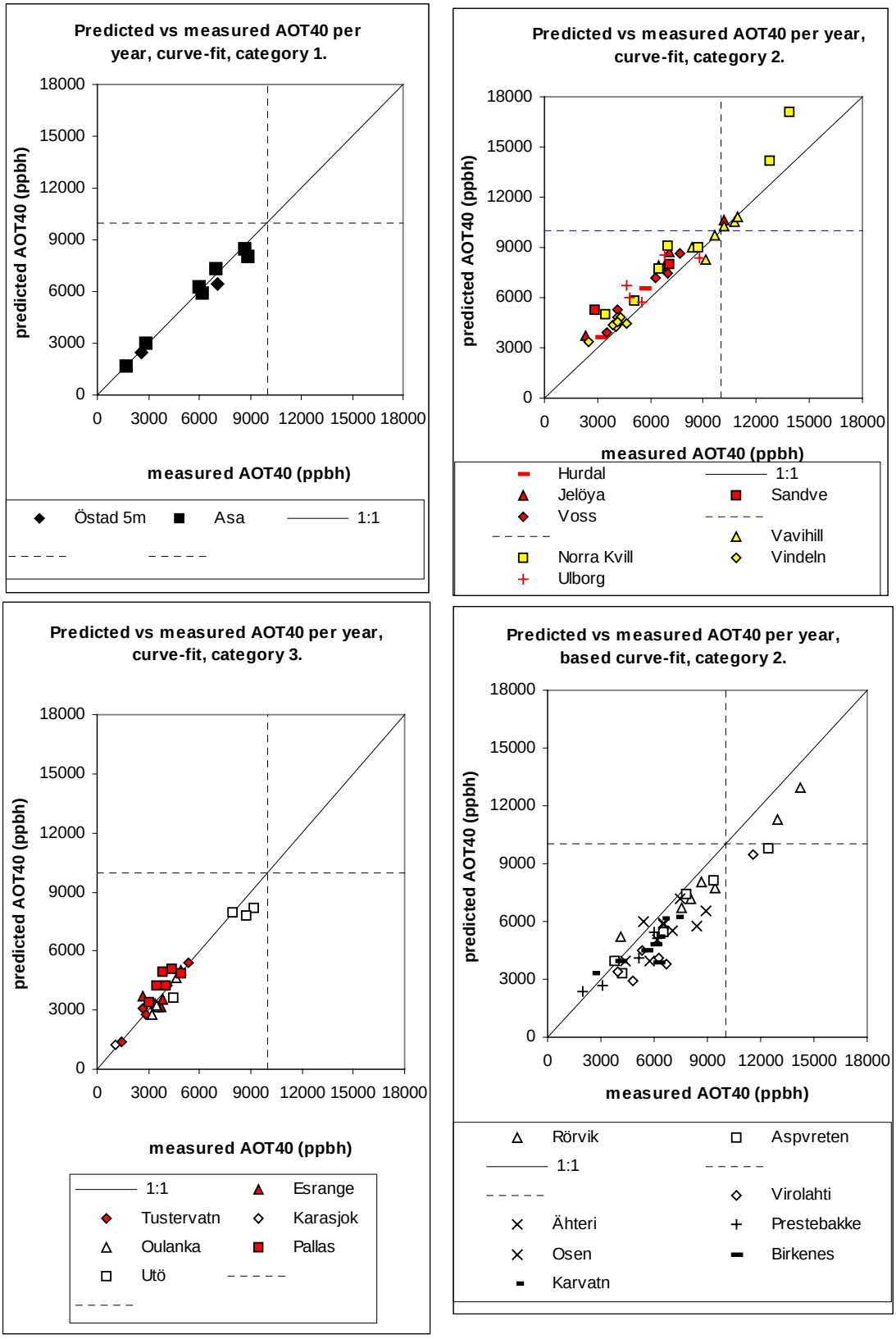


Figure 20. Comparison of 14-day daylight AOT40 predicted from 14-day 24-h mean ozone concentrations, using one single curve-fit function for each site category, with the true daylight AOT40 calculated from the hourly measurements. Summed up for the period 1 Apr - 30 Sep for each year.

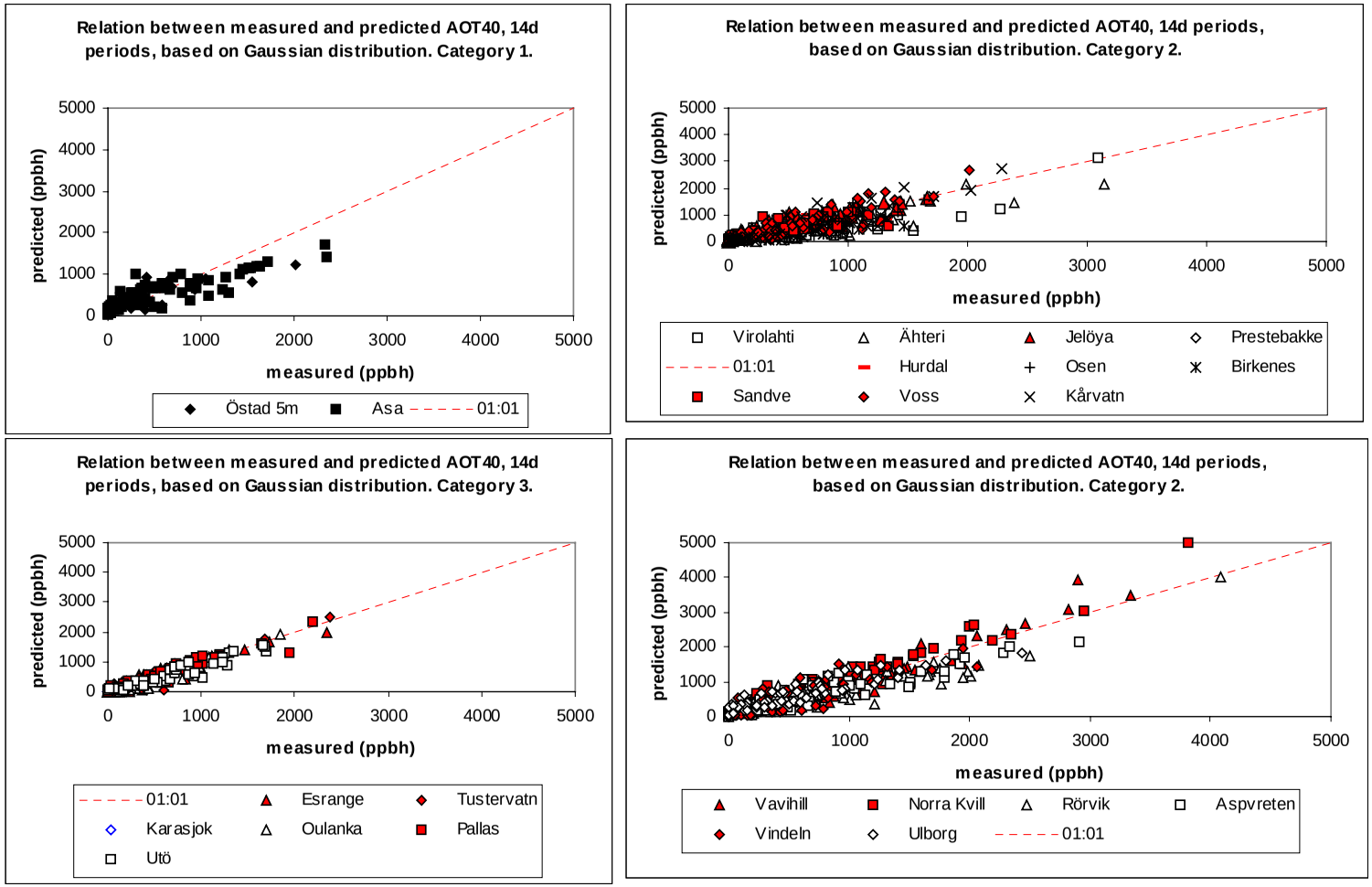


Figure 21. Comparison of 14-day daylight AOT40 predicted from 14-day 24-h mean ozone concentrations, using functions based on a Gaussian distribution of hourly ozone concentrations and with parameters for each site category, with the true daylight AOT40 calculated from the hourly measurements.

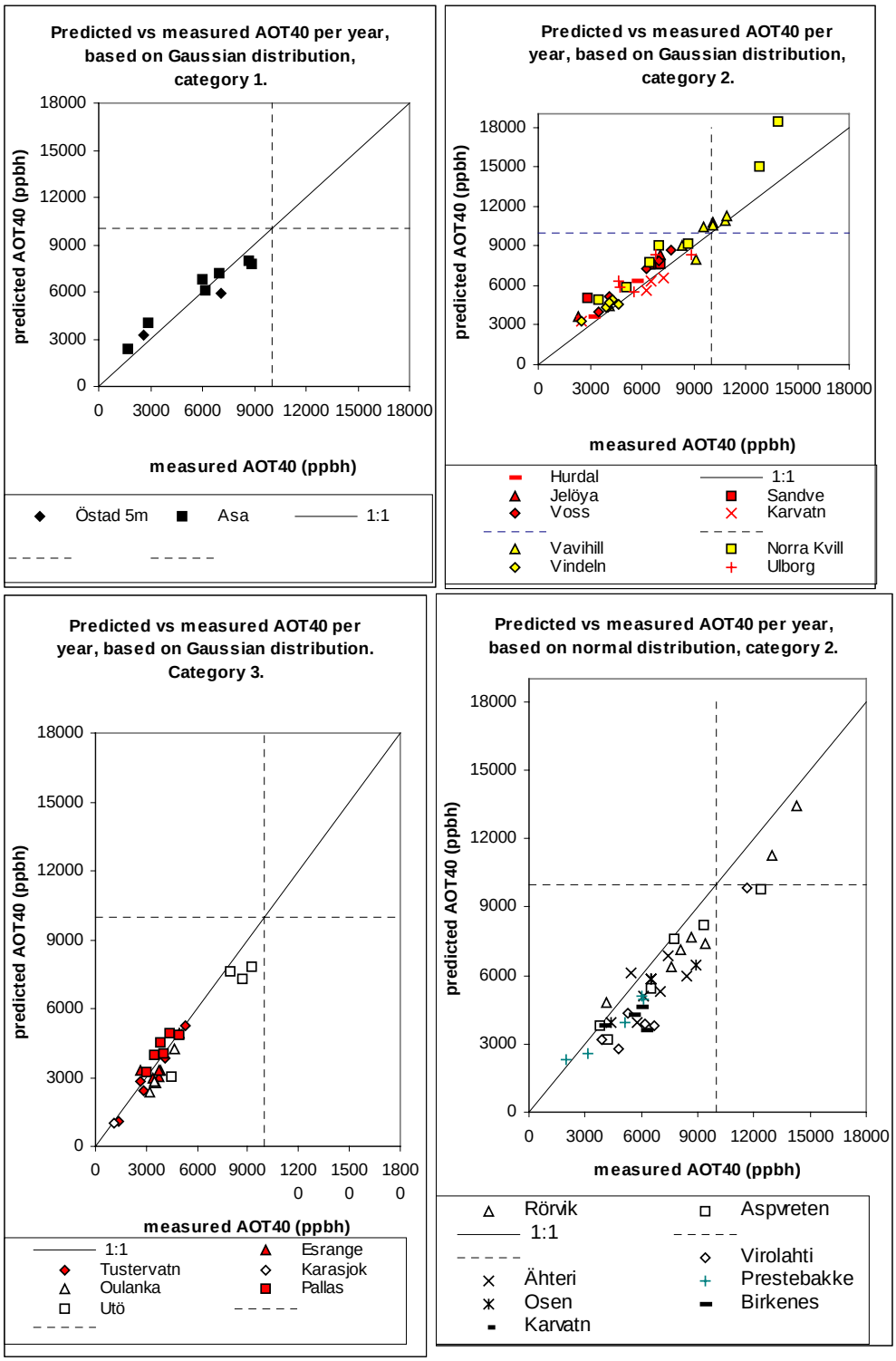


Figure 22. Comparison of 14-day daylight AOT40 predicted from 14-day 24-h mean ozone concentrations, using one single curve-fit function for each site category, with the true daylight AOT40 calculated from the hourly measurements. Summed up for the period 1 Apr - 30 Sep for each year.

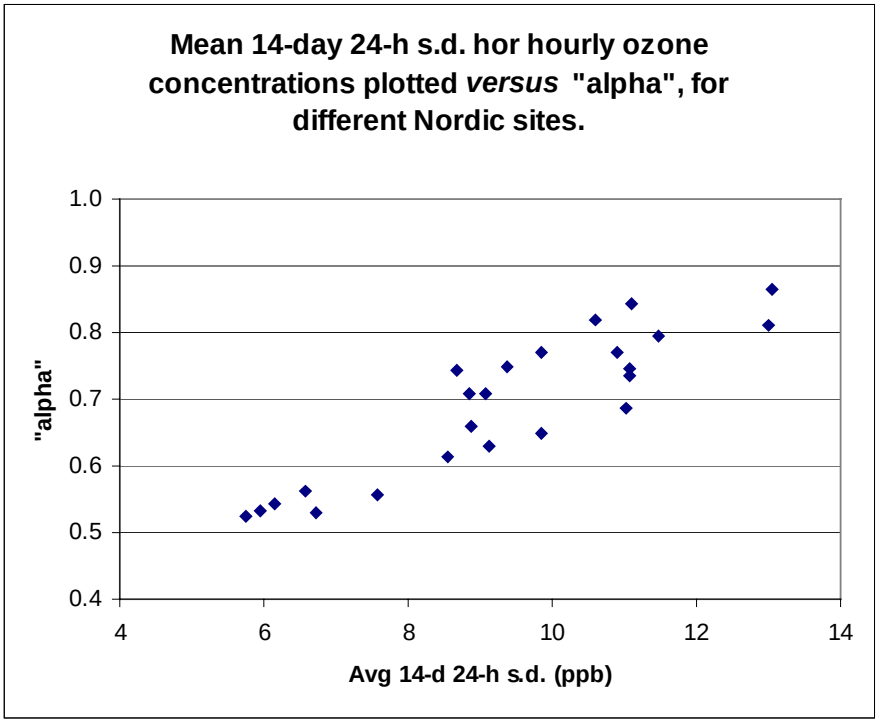


Figure 23. The average s.d. of all hourly ozone concentration values within a 14-day period is plotted against the "alpha factor", α. α was introduced in section 6.5 and is the factor that's connects the daylight 12-h AOT40 to the 24-h AOT40 for a certain site. Each datapoint represents one Nordic site.

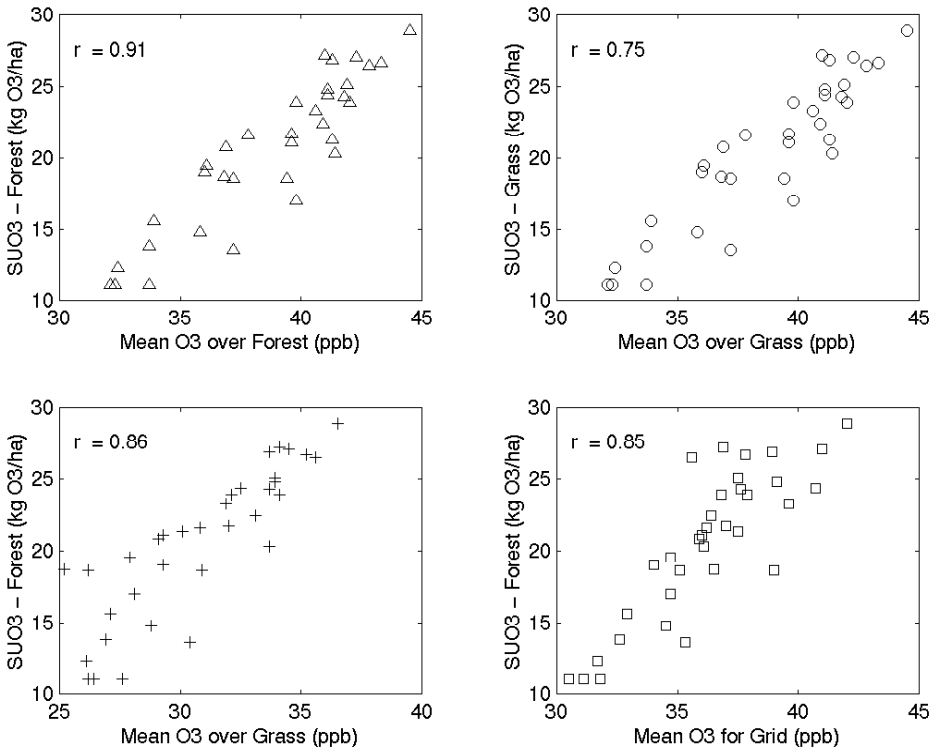


Figure 24. Relationships between simulated 6-monthly means of ozone concentration and integrated SUO3 (cumulated stomatal uptake of ozone) values. Each point represents the location of a Nordic measurement site. Concentrations and SUO3 values have been extracted from the model's simulations for either different vegetation surfaces (here, coniferous forest or grassland) or from the grid-average model result.

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