

Ozone in Remote Areas: Seasonal Cycles and trends

A contribution to Photooxidants, Particles, and Haze across the Arctic and North Atlantic: Transport, Observations and Model.

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Seasonal cycles and trends in ozone in Sweden are studied within the frame of "Tropospheric Ozone and Precursors – TRends, Budgets and Policy (TROTREP)", a project of the Thematic Programme for Environment and Sustainable Development within the Fifth Framework Programme. The project is also a part of the subproject "Tropospheric Ozone Research" in EUROTRAC-2. The main objective of TROTREP is to evaluate, validate and predict the effectiveness of past and future EU air quality legislation with respect to ozone and its precursors.

Data quality is crucial when trend calculations are based on observations. One way to deal with this problem is to compare time series of daily averages of ozone from neighbouring sites. Data from Esrange in Northern Sweden have been compared with the corresponding data from two other sites in Northern Scandinavia, one in Norway, Jergul (in 1997 replaced by Karasjuk) and the other in Finland, Pallas. The result indicates a good agreement in terms of seasonal cycles and the day to day variation. However, for some years one of the three sites (which one differs among years) has values that are systematically different compared to the other two, see **Figure 1**. For one period, a malfunctioning monitor may have caused the divergent results, but in most cases we have not yet been able to explain the discrepancies.

At sites situated close to large source areas, NO₂ can act as a temporary sink for ozone. In this case Ox (O₃+NO₂) would be a better parameter to study. NO₂ amounts to about 12 % of the winter average and about 5 % of the summer average of Ox at Rörvik (year 2000). However, at a remote site like Esrange the concentration of NO₂ is insignificant in relation to ozone (**Figure 2**).

Trajectory integrated NO_x emissions have been used to segregate ozone monitoring data from a number of European monitoring sites (Solberg, 2001). The integrated NO_x emissions were combined with ozone monitoring data from EMEP (European Monitoring and Evaluation Programme) for the years 1988-1996. Daytime averages of the ozone data were allocated to each of 10 percentile classes of integrated NO_x emissions (calculated as 30-day running averages through the year). The lowest percentile class (< 10-percentile) of integrated NO_x emissions is considered to represent the European background air. A clear relationship was found between the integrated NO_x-emissions and the ozone observations at the Swedish sites (**Figure 3**), with increasing amplitude of ozone with increasing NO_x-emissions. The estimated background seasonal cycle is similar for the different sites. In polluted air masses the differences are more pronounced and indicate latitude dependence. The seasonal cycle shows an ozone deficit in winter and a surplus in summer compared to the background. The difference in ozone concentration between the lowest and the highest percentile class of integrated NO_x emissions is a measure of the "controllable" ozone.

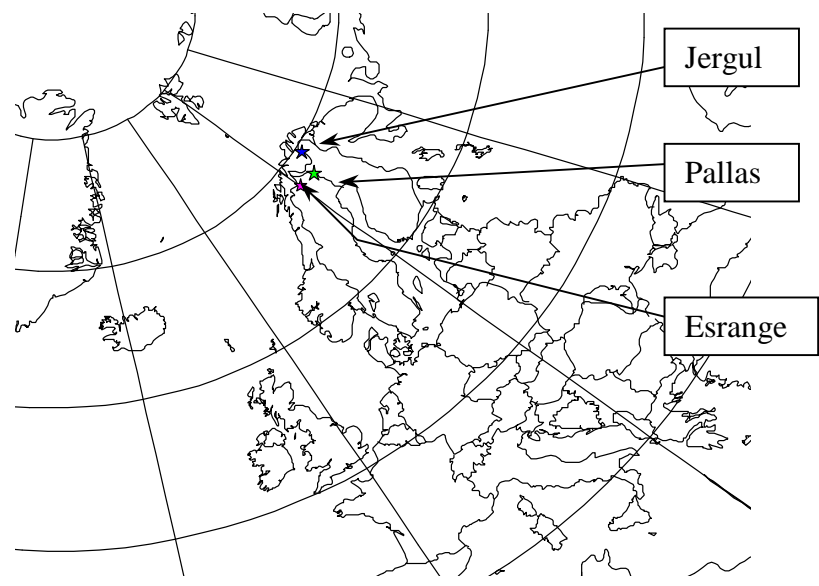
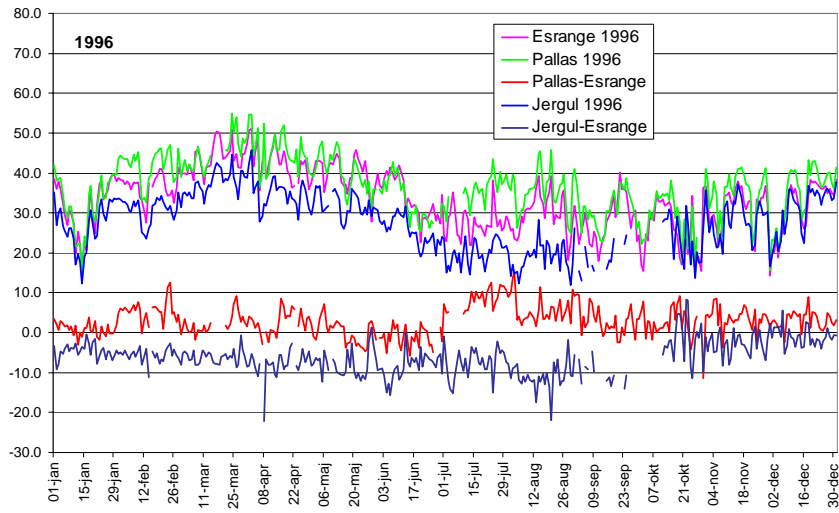
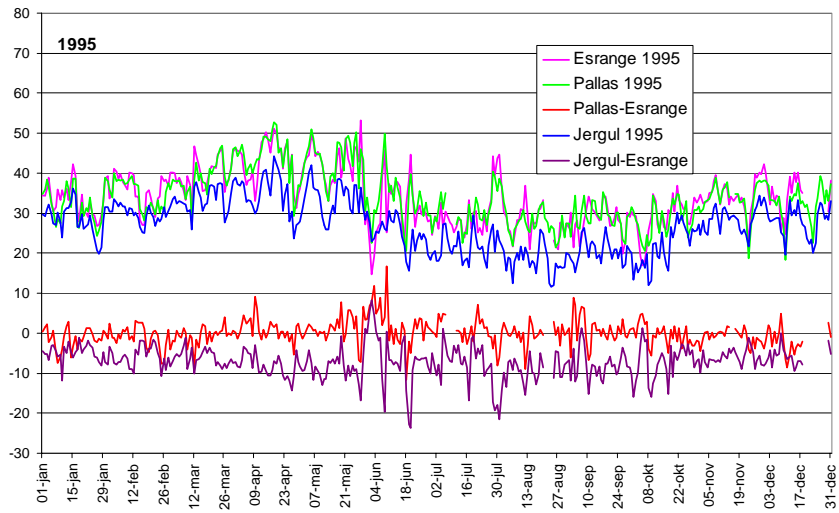


Figure 1. Daily averages of ozone in ppb and the differences in ozone concentrations between neighbouring sites.

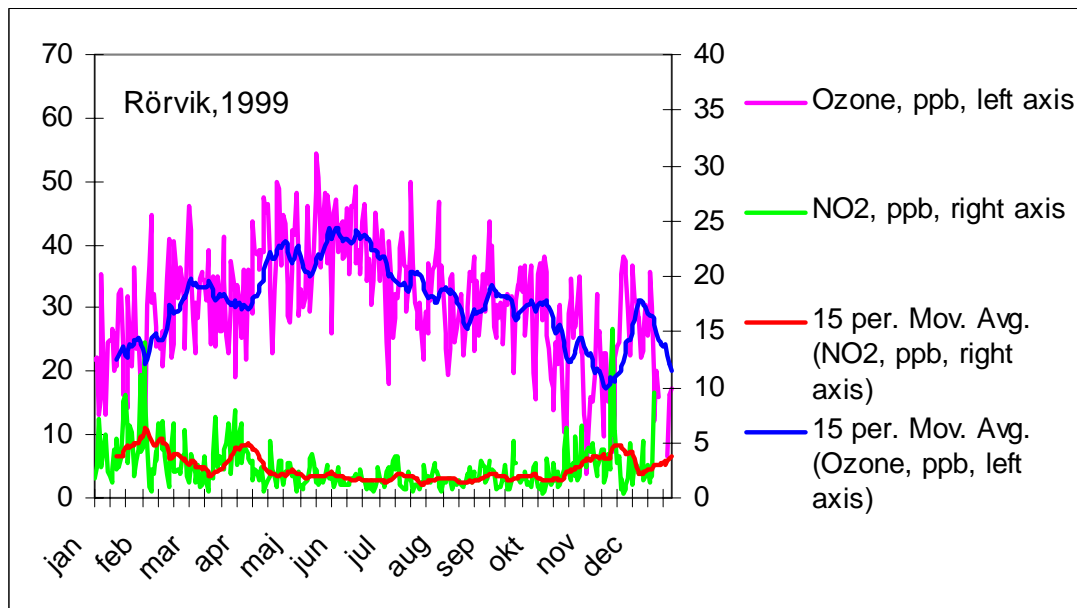
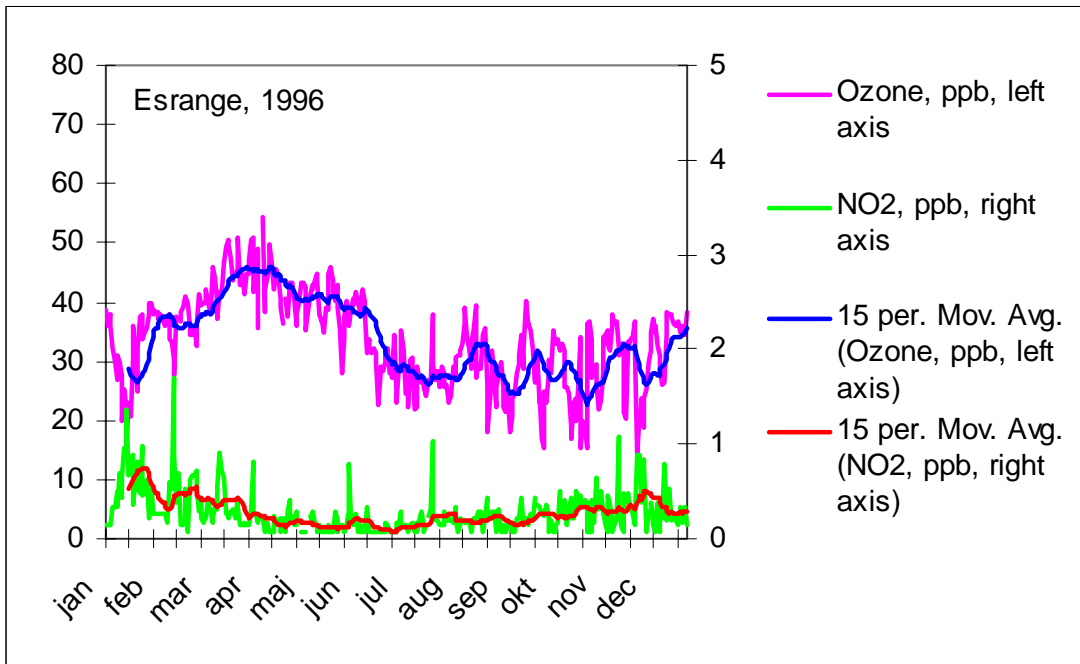


Figure 2. Daily averages and 15-day moving averages of ozone and NO₂ in ppb at Esrange (upper panel) and Rörvik.

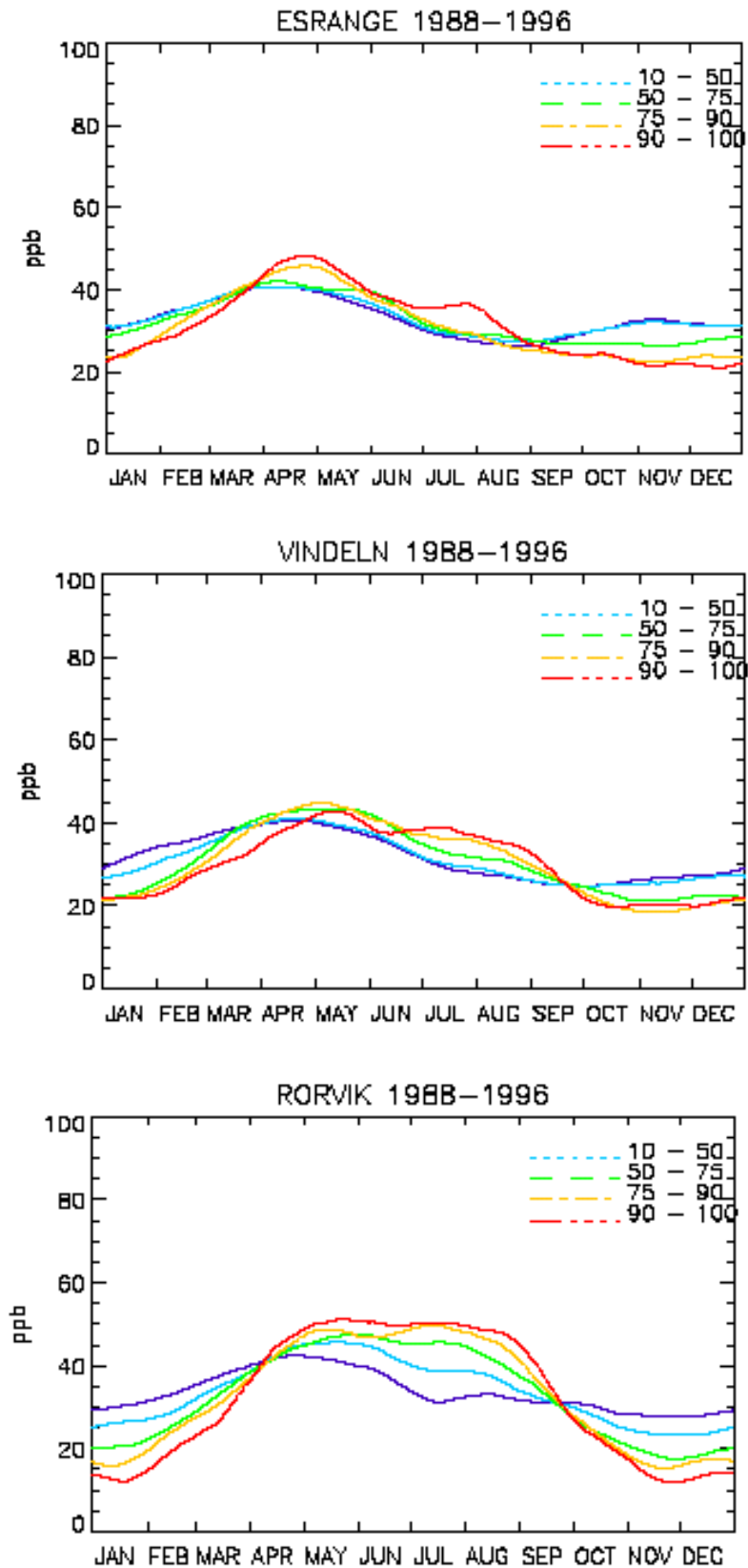


Figure 3. The seasonal cycles of ozone for different percentile classes of trajectory integrated NO_x emissions. The estimated background seasonal cycle (10-percentile of NO_x-emission) is given with the purple line (from Solberg, 2001).

Seasonal cycles have been calculated using all the data and daytime data (10:00 – 17:00 local time) from three monitoring sites in Sweden, Esrange (67°53'N; 21°04'E) 1991-2000, Vindeln (64°15'N; 19°46'E) 1986-2000, and Rörvik (57°23'N; 11°55'E) 1987-2000. In addition, sector analysis has been applied on the ozone data (1988-1996), using the 2D back trajectories calculated by NILU.

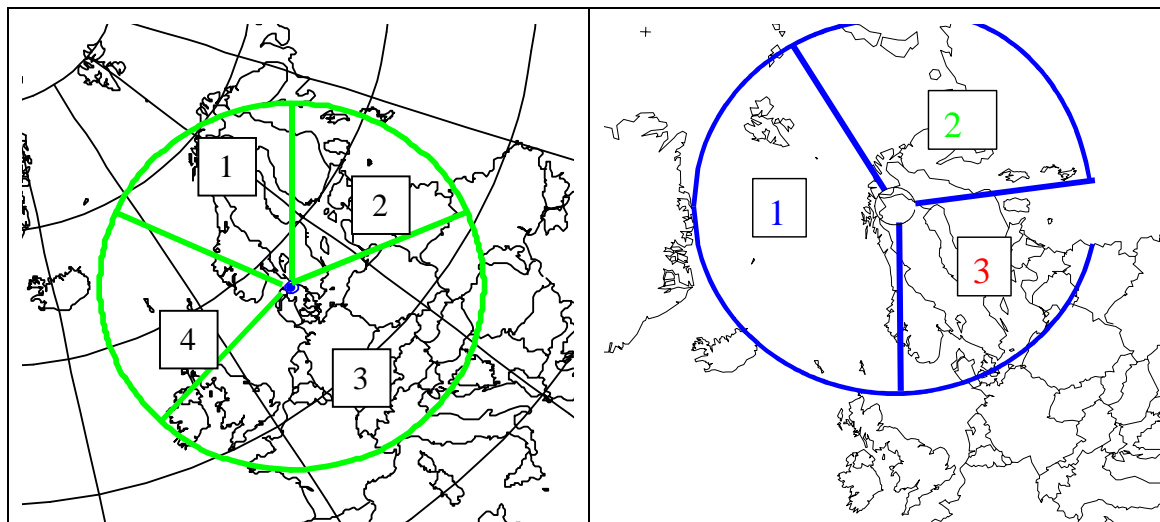


Figure 4. Trajectory based sectors for Rörvik (left panel) and Esrange.

A comparison among the different years points to a large interannual variation with a clear dislocation in time of the spring maximum. The average seasonal cycle at both Esrange and Vindeln has a maximum in April and a minimum in late summer. At Rörvik the maximum occurs in May and the minimum in November.

The number of observations in each sector differs considerably among months, seasons and years, which has an obvious impact on the seasonal cycle. At Esrange the largest difference is obtained between sector 2 (22.5° – 135°), where the spring peak occurs in March and the minimum in September, and sector 3 (135° – 232.5°) with a maximum in April and a minimum in October (**Figure 5**). The results from Vindeln (**Figure 6**) are similar (Lindskog and Kindbom, 2001).

At Rörvik 4 sectors are used. Sector 3 (112.5° – 270°) contains trajectories from Continental Europe and UK and thus representing polluted air. This is clearly demonstrated by the trajectory integrated NO_x emission data. In this sector a first ozone peak is obtained in May and a second one in July (**Figure 5**). The minimum occurs in November. The lowest concentration of ozone precursors is found in sector 4 (270° – 337.5°) with air masses originating from W and NW. In this sector a spring maximum is obtained in April. If one considers sector 4 as a proxy for background, an ozone deficit is seen in the “polluted” sector in winter, most likely due to a reaction with NO, and a surplus in summer as a result of photochemical production in the boundary layer. This is in consistence with the results obtained by NILU using the trajectory integrated NO_x emissions (**Figure 3 and 7**).

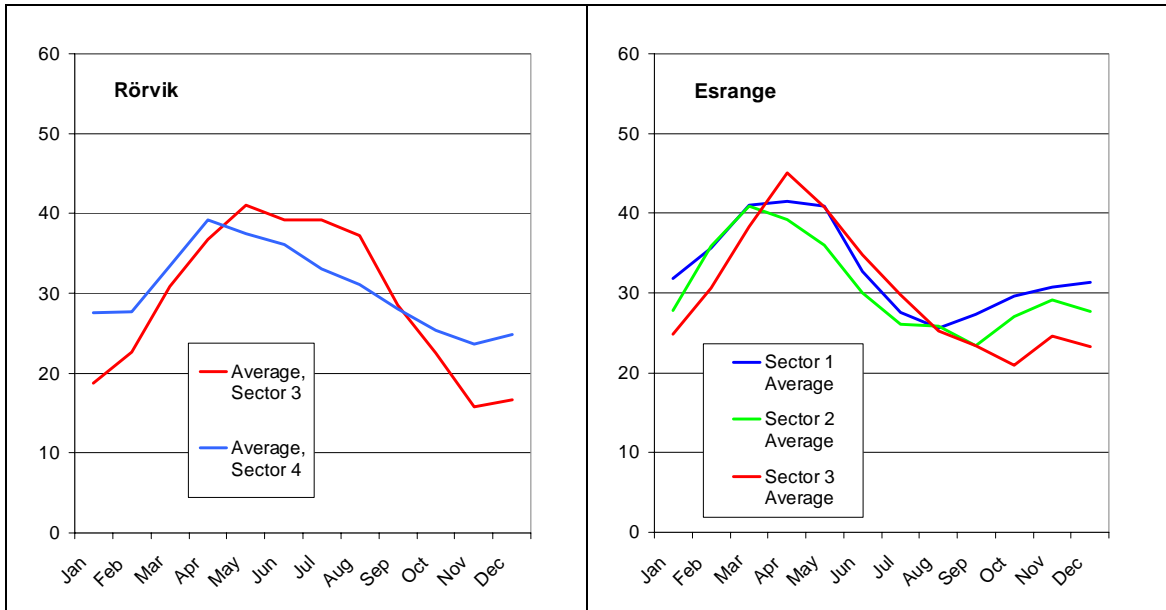


Figure 5. Ozone seasonal cycles in two different sectors averaged over 9 years (1988-1996) at Rörvik (left panel) and in three different sectors averaged over 6 years (1991-1996) at Esrange (right panel).

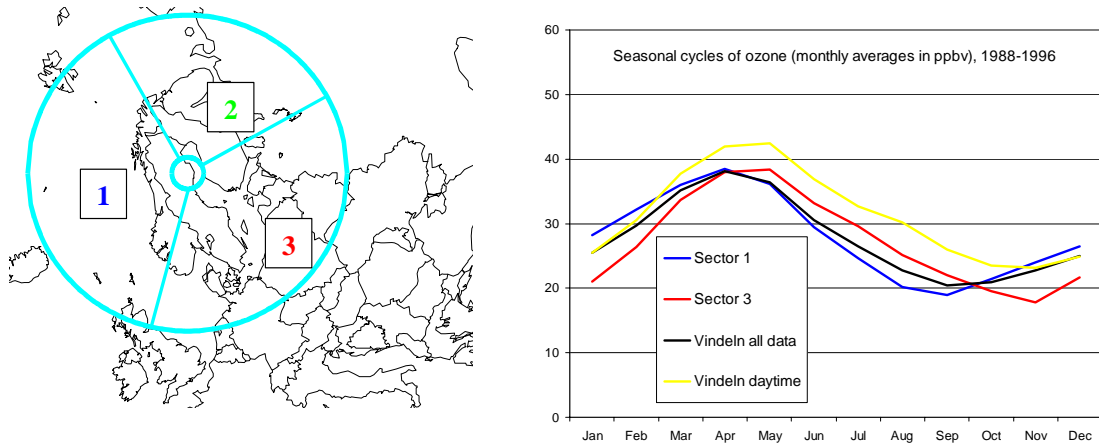


Figure 6. Trajectory based sectors for Vindeln (left panel) and ozone seasonal cycles in three different sectors averaged over 9 years (right panel).

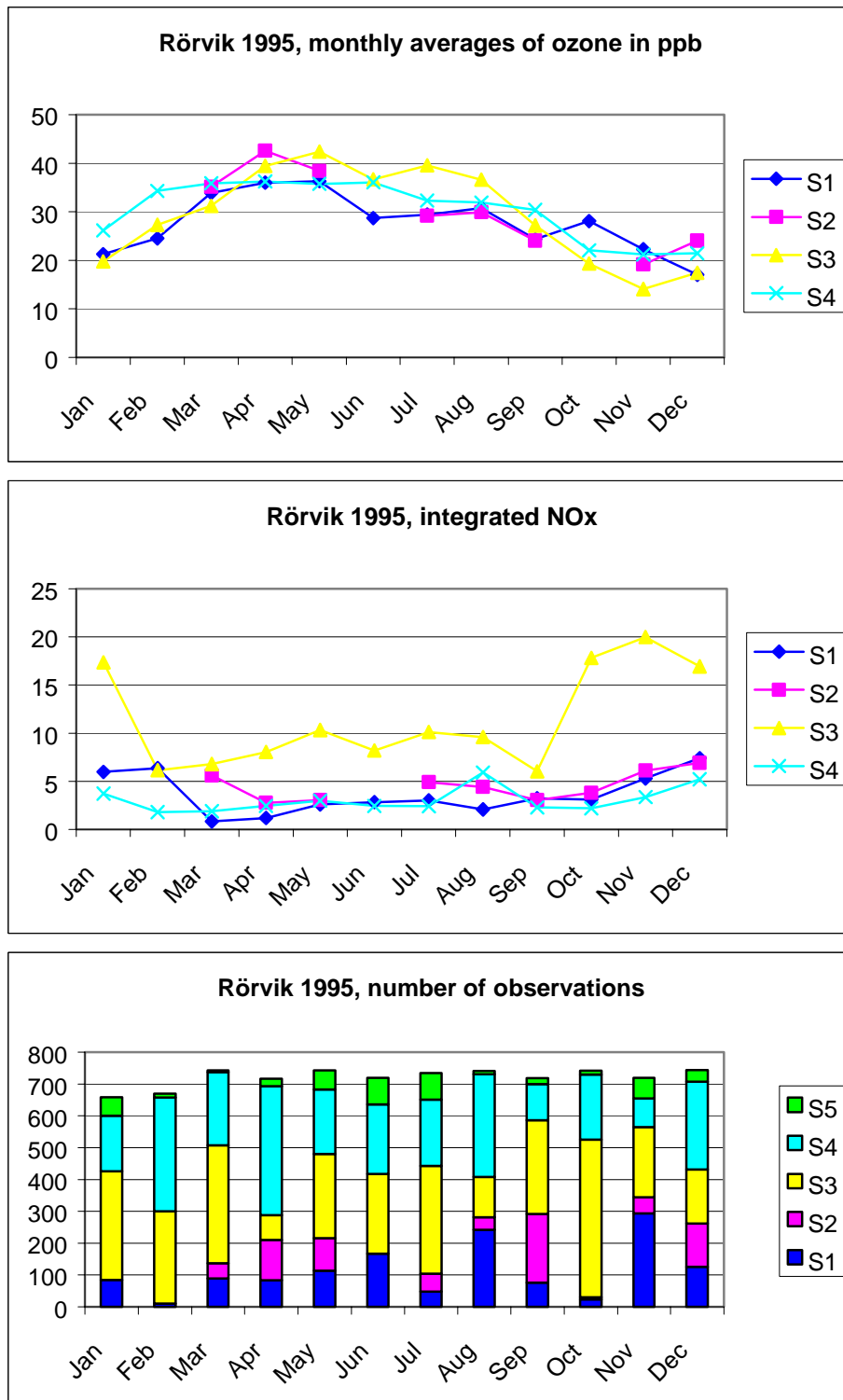


Figure 7. Ozone seasonal cycles in four different sectors (upper panel), seasonal cycles of integrated NOx emission in the different sectors (middle panel) and the number of observations in the different sectors (lower panel). S5="undefined".

Over the last 10 – 15 years a significant decrease in nitrogen dioxide concentrations during the winter half-year has taken place in Sweden, both in urban air and in background air (**Figure 8 and 9**).

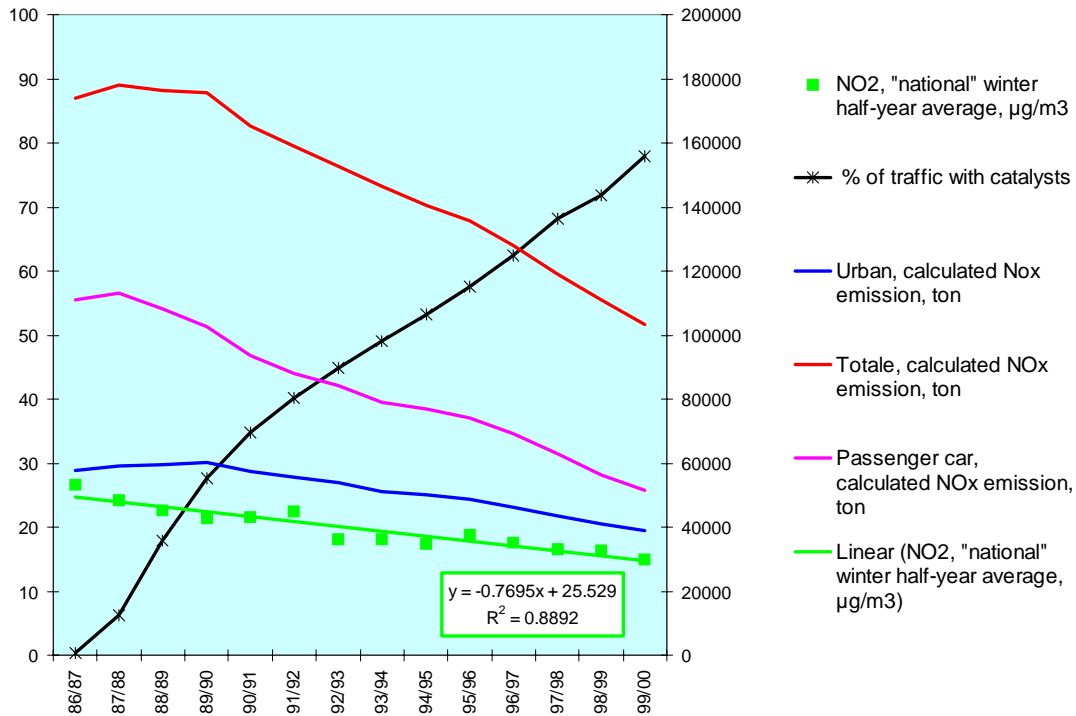


Figure 8. Calculated yearly emissions in tonnes of NO_x in Sweden from passenger cars, from the entire road traffic, and in urban areas (right value axis). "National" winter half-year averages of NO₂ in µg/m³ calculated as an average of 15 urban areas in Sweden (left value axis) and percentage of traffic using catalyst (left value axis). (From Svanberg and Lindskog, 2000).

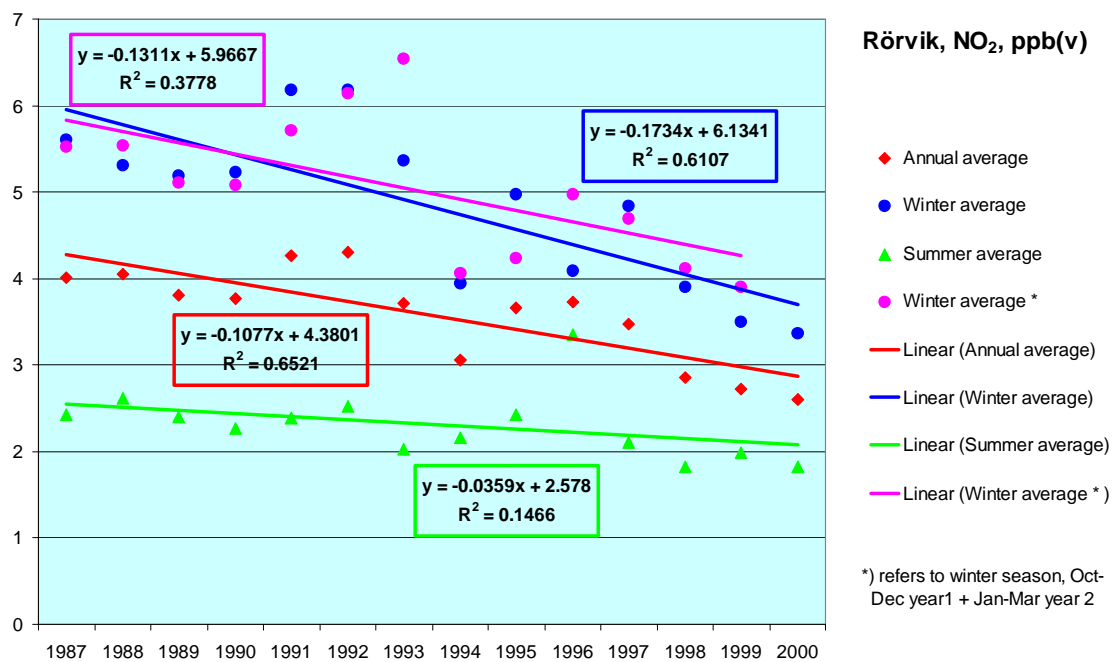


Figure 9. Yearly NO₂ concentrations at Rörvik between 1987 and 2000.

During the same period the ozone level as yearly average seems to have remained the same, in spite of the measures taken in Europe to reduce the emissions of ozone precursors.

A decrease in emissions could affect the regional ozone levels in two different ways. In winter, a reduction of NO_x emissions and the subsequent reduced titration by NO may result in an increase of ozone. In summer, the reduction would lead to a reduced photochemical production of ozone in the boundary layer, primarily affecting the peak values.

The Mann-Kendall test was applied to ozone observations from five background monitoring stations in Sweden for the period 1985-1998/1999. Increasing ozone levels were found at most of the stations in February and March (**Figure 10**). For Vindeln the most pronounced increase is found in April. The linear regression analysis using all data for the period 1990-1998 indicated an increase of about 1.1 ppb/year (at the 99% confidence level) at Rörvik for February and March and about 1 ppb/year at Vindeln for April. The annual change of the April averages was reduced to 0.8 ppb/year when data from 1999 was included. A decrease of about 0.6 ppb/year was obtained at Norra Kville (the most southern of the sites) for September.

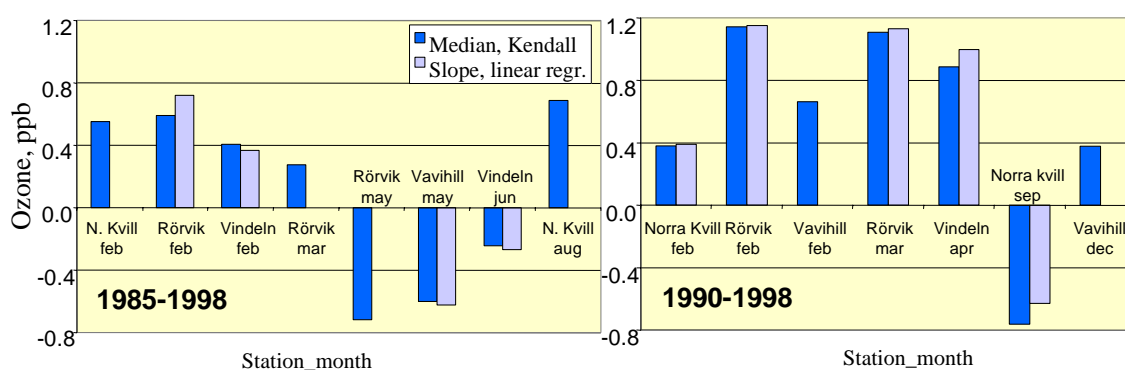


Figure 10. Magnitude of annual change of monthly averages where the change was at least 95% statistically significant. The median change according to the Mann-Kendall test, as well as the slope from linear regression analysis is presented. (From Kindbom and Lindskog, 2001)

Any tendency in observed concentrations of ozone as a result of measures taken to reduce the emissions of ozone precursors is expected to be traceable at Rörvik, since this site is quite frequently exposed to polluted air masses from Continental Europe. However, as indicated in **Figure 11**, no significant downward trend was observed in the yearly averages for the period 1987-2000. Instead, a significant ($p=0.05$) upward trend of 0.25 ppb/year in background ozone is obtained. This increase in ozone is even more pronounced (0.36ppb/year, $p=0.005$) when only daytime data is considered (**Figure 12**). In this case also the 50%-ile is increasing, 0.26 ppb/year ($p=0.02$). The changes differ with season. The winter half-year average has increased with 0.36 ppb/year ($p=0.001$) (**Figure 13**). If this increase is driven mainly by the general increase in large scale background levels and/or the reduction in precursor emissions remain uncertain. Sector analyses performed on seasonal values (1988-1996) indicate a significant ($p=0.01$) increase of the winter half-year 10th percentile (0.69 ppb/year) in the polluted sector (**Figure 14**). In addition, an increase in the winter average values is found (0.34

ppb/year, $p=0.1$). These results support the hypothesis that the increase in ozone is due to a reduced NO titration. In the clean sector the only significant ($p=0.05$) increase was obtained for the winter 95th percentile, 0.45 ppb/year. No tendency was found in the sector analyses performed on monthly bases.

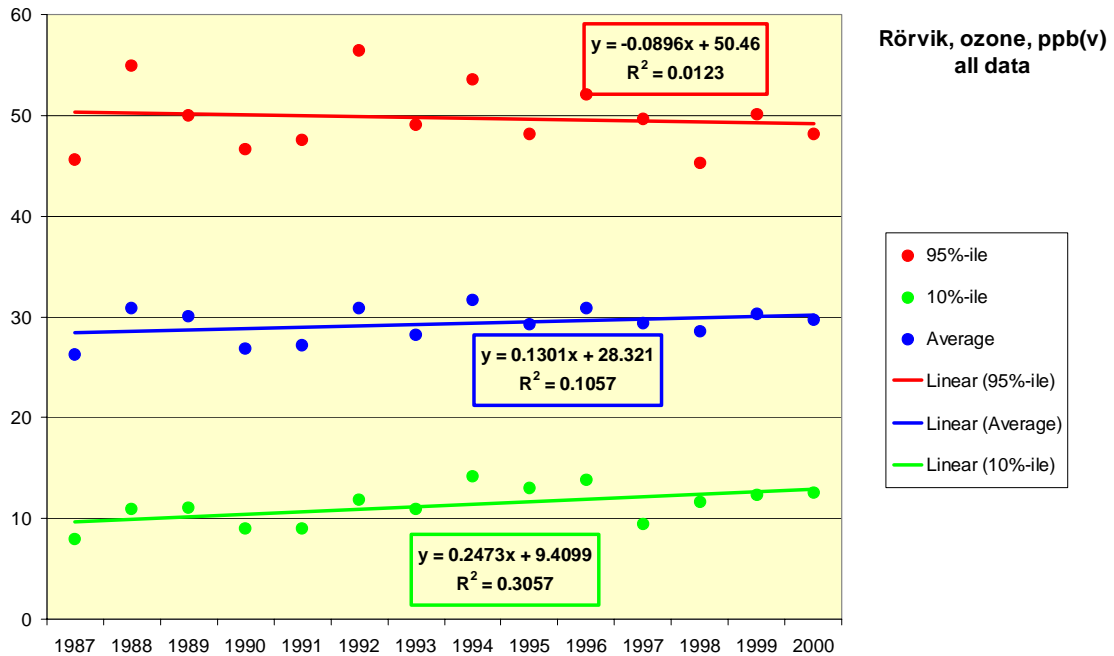


Figure 11. Annual averages, 95th- and 10th- percentiles calculated on ozone observations at Rörvik, 1987-2000.

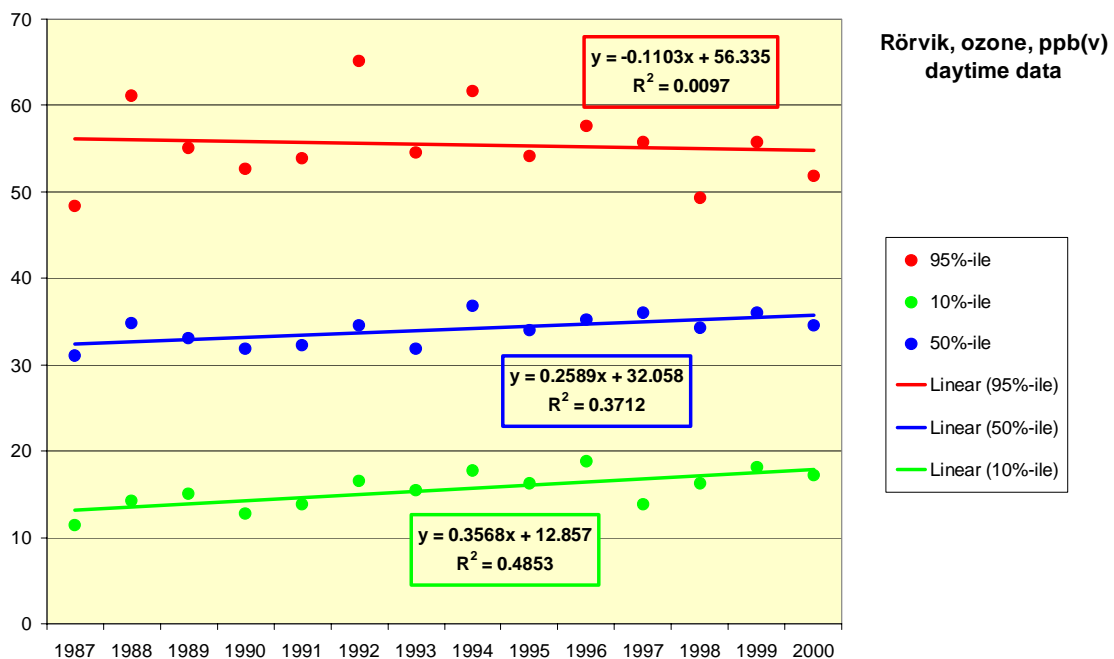


Figure 12. Annual averages, 95th- and 10th- percentiles calculated on ozone daytime (10 a.m.-5 p.m., local time) observations at Rörvik, 1987-2000.

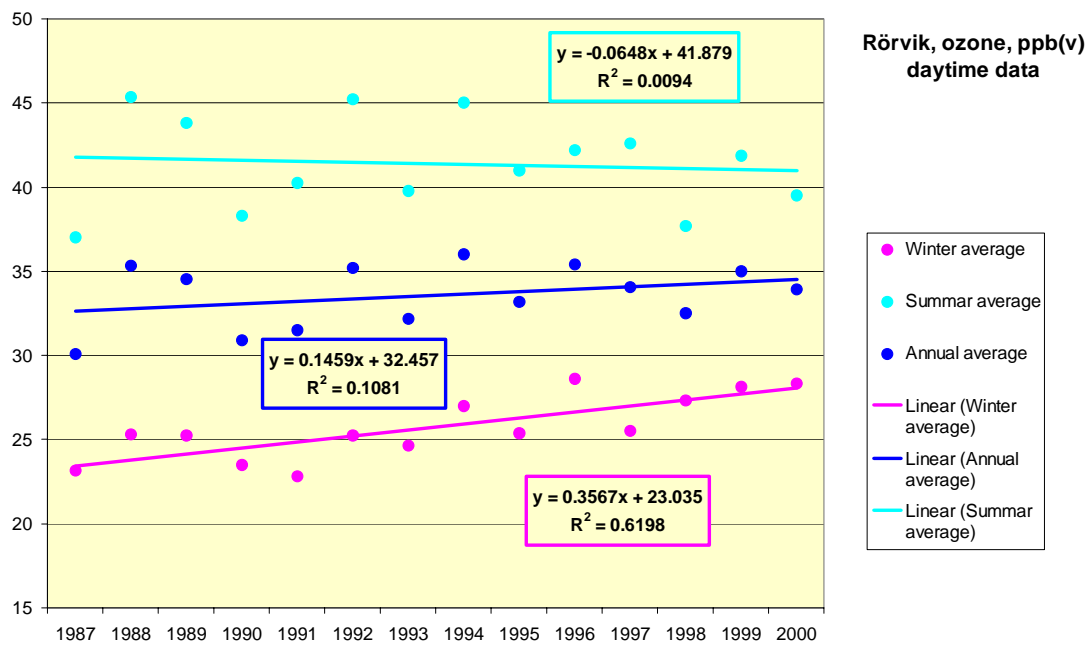


Figure 13. Annual, winter and summer averages at Rörvik, 1987-2000, based on daytime data.

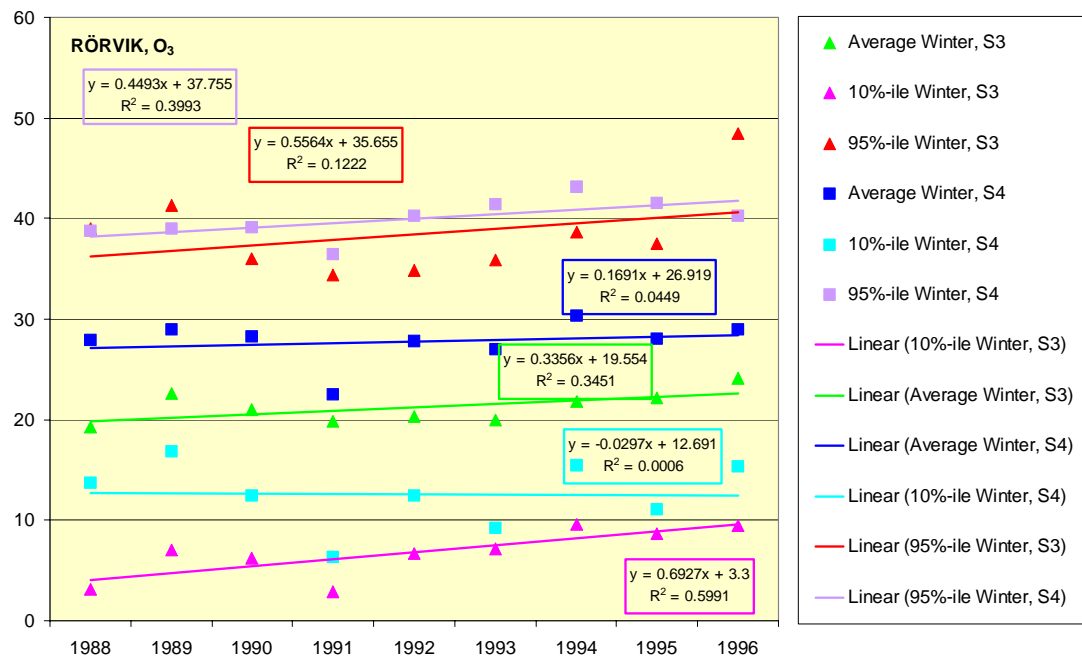


Figure 14. The development of winter half-year ozone concentrations in sector 3 (polluted) and sector 4 (clean) at Rörvik.

For Esrange only 10 years of data are available. No significant trend was obtained in the Mann-Kendall test (1991-1999). However, a linear regression analysis applied to the data showed a significant (at the 95% confidence level) increase of 0.4 ppb ozone/year in February for the period 1991-1999. When the data from year 2000 is added to the data set, the increase becomes smaller.

The same tendency of increasing ozone levels is obtained for the annual and seasonal averages (**Figure 15**). In this case the results most certainly reflect an increasing hemispheric background.

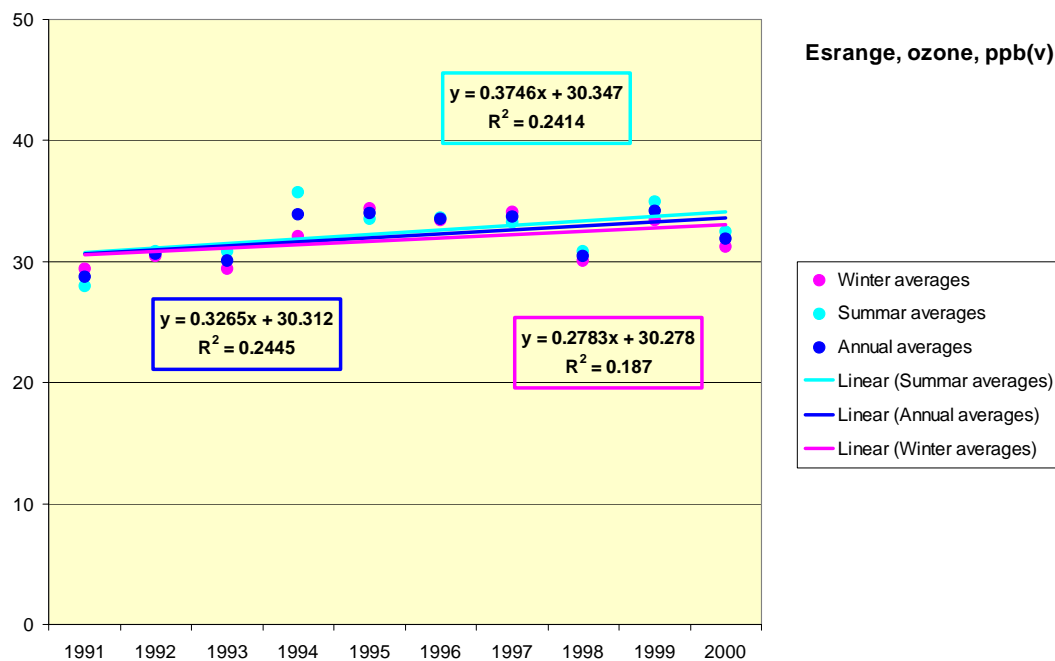


Figure 15. Annual, winter and summer averages at Esrange, 1981-2000.

The development at Vindeln is quite different. On seasonal bases, the only significant trend is observed in summer. For the period 1986-2000 the summer half-year average of background ozone, represented by the 10th percentile, has decreased with 0.31 ppb/year (p=0.02), mainly explained by decreasing concentrations in July, 0.46 ppb/year (p=0.01), see **Figure 15**. For individual months (January, February and March) significant increases of 0.3-0.4 ppb/year are obtained, also of the 50th and 95th percentiles. A small but significant increase of the 95th percentile is also found in September, 0.26 ppb/year, p=0.01.

Vindeln is the only site for which a significant trend appears in the sector analysis of monthly averages (**Figure 16**).

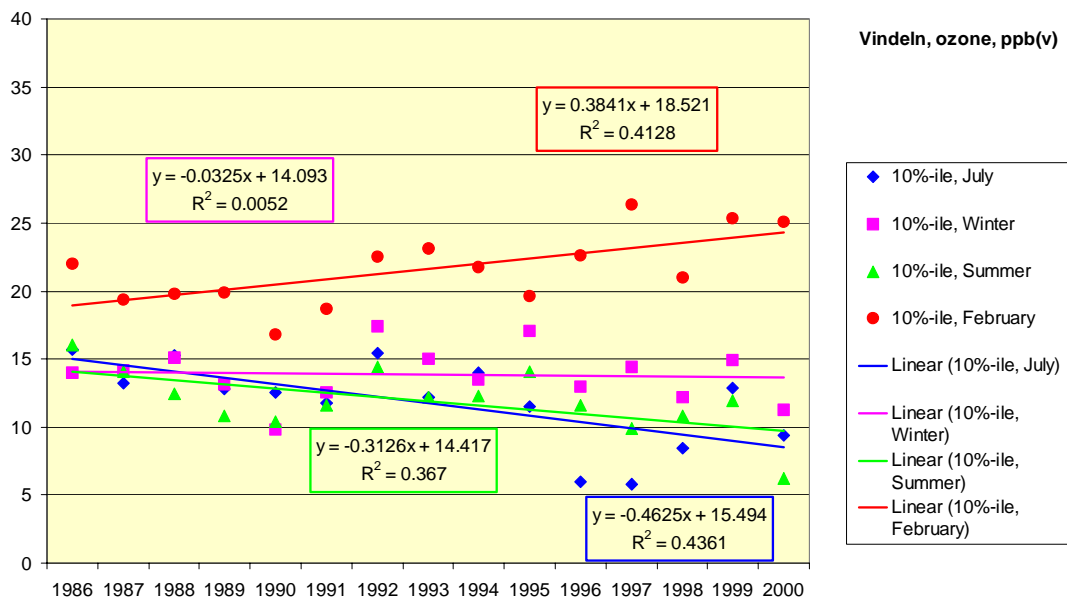


Figure 16. 10th percentiles calculated on ozone observations at Vindeln, 1986-2000.

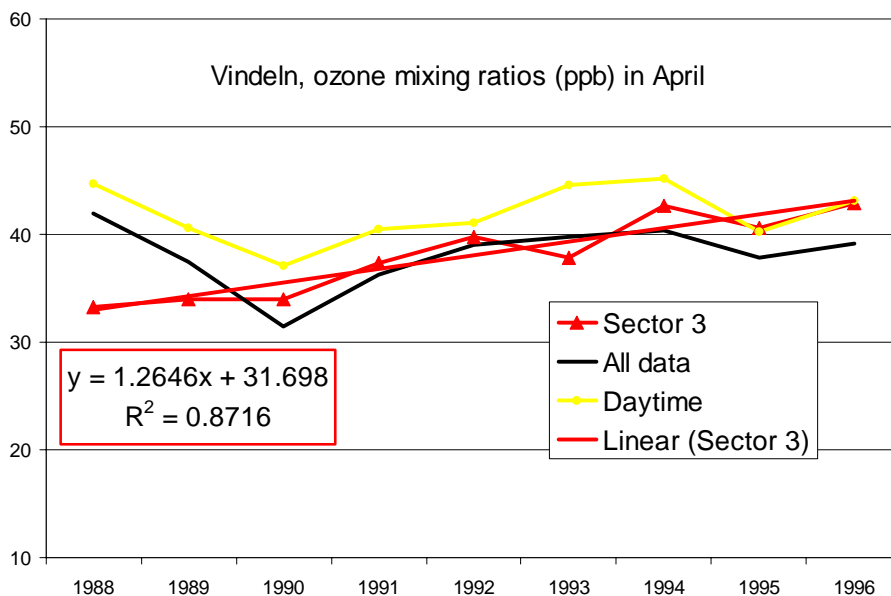


Figure 17. Average concentration of ozone for April at Vindeln. The red curve and trend line are based on all data in sector 3 (the "polluted" sector). The black curve is based on all the data and the yellow on daytime data. (From Kindbom and Lindskog, 2001.)

Conclusions

One serious problem in trend analysis, aside from data quality and site representativity, is the pronounced interannual fluctuation in observed concentrations, which can conceal the "true" trend. The variation, also manifested as alterations of the seasonal cycle, seems to be random, without any trend over the time studied. The results of the sector analyses indicate that the phenomenon may be related to the frequency and duration of transport in a certain sector and the time of the year when this transport takes place. However, the interannual variation is significant also within an individual sector. Thus, the dislocation in time of the maximum and the variability in concentration can not be explained by the sector frequency alone. The evaluation of the seasonal cycles from a few individual years indicates, as expected, that the weather conditions, e.g. the number of hours with sunshine, affect the ozone concentrations. However, for most of the monitoring sites, meteorological observations are available on rare occasions, which certainly enhance the uncertainty of the observation based trend analysis

A significant decrease in nitrogen dioxide concentrations during the winter half-year has taken place in Sweden, both in urban air and in background air, over the last 10 – 15 years. In contrast, a significant increase in winter half-year ozone is obtained at Rörvik. This is most likely the result of a reduced NO titration. The same tendency of increasing ozone levels is found at Esrange for both seasons. In this case the results most certainly reflect an increasing hemispheric background. The development for Vindeln is quite different with a significant decrease in summer ozone. Increasing levels are however found for individual months and percentiles.

Acknowledgements

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