Ministry of
the Environment

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NERI Technical Report No. 35
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December 1991

Data sheet

Title:	Rural Ozone measurement in Denmark, 1985-1989
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Department:	Department of Emissions and Air Pollution
Serial title and no.:	NERI Technical Report No. 35
Publisher:	National Environmental Research Institute
Year of Publication:	December 1991
Technical assistance:	Axel Egeløv
Fieldwork	Holst Jørgensen
Laboratory assistance:	Axel Egeløv, Tom Rasmussen, Kenneth Vinther, Bjarne Jensen
Typist:	Lene Thorsted
Please quote:	Hertel, O., Hovmand, M.F. (1991): Rural Ozone measurements in Denmark, 1985-1989. National Environmental Research Institute. 23 p. - NERI Technical Report No. 35.
	Reproduction permitted only when quoting is evident.
Uncontrolled terms:	Ozone Monitoring, Rural Measurements
ISBN:	87-7772-040-7
ISSN:	0905-815X
Printed by:	Grønager's Bogtryk & Offset
Number of pages:	23
Circulation:	125
Price (incl. 22% VAT excl.freight):	DKK 45.00
For sale at:	National Environmental Research Institute Department of Emissions and Air Pollution Frederiksborgvej 399, 4000 Roskilde Denmark Tel: + 45 46 30 12 00 Fax: + 45 46 30 11 14

Contents

Abstract

Ozone measurements were performed at two forest sites in Denmark. The sites were 250 km apart.

From a station in West Jutland (56°17', 8°26') ozone results from the period mid 1985 -1989 were obtained and are reported here. One year measurements, 1989, were obtained from a station in North Zealand (55°57', 12°21'), and results from this site are highly correlated with the other site.

The measurements show a pronounced maximum in ozone concentrations during spring and summer with highest one hour mean concentrations between 80 and 100 ppb.

The diurnal variation shows a maximum ozone level between 1400 h and 1800 h, most pronounced during spring and summer.

The obtained results are in agreement with earlier reported data from other European locations and confirm that ozone levels with phytotoxic potentials are exceeded at Danish monitoring sites.

1. Introduction

The objective of this project was to establish a serie of measurements of ozone concentrations in Danish forests over a long span of time. In this way daily and seasonally variations in the ozone concentration can be documented.

It is important for the ongoing research in photochemistry to have long series of well documented background measurements.

Two forests were chosen: Ulborg, West Jutland, where the measurements started in 1985, and Frederiksborg, North Zealand where measurements started in 1988.

Natural ozone in the troposphere is due partly to intrusion from the stratosphere and partly to formation by natural processes. "Anthropogenic" ozone is emitted to the troposphere as a secondary pollutant formed in photolytic reactions with emissions of nitrogen oxides ($NO_{x)}$ and volatile organic compounds (VOC) mainly hydrocarbon from combustion reactions for example from traffic exhaust.

At these reactions many different compounds are formed among which ozone is the most abundant and best documented. Other compounds formed are hydrogen peroxide, epoxides, organic peroxides and peroxyacetyl nitrate (PAN).

All these constituents of polluted air have - like ozone - great oxidizing capability. This explains the phytotoxic potential, which ozone is generally used as an indicator for. A wide range of plant species are affected by ozone concentrations often found in polluted air.

At the UN ECE Bad Harzburg workshop in 1988, the critical level of ozone was defined as the ozone concentration above which direct adverse effects on sensitive plants, plant communities and ecosystems may occur according to present knowledge (*Guderian, 1988*).

The amount of leaf damage rises progressively with rising ozone concentration. (*Hech, 1966, Davis, 1973*). Exposure to high concentrations during a short period of time causes more plant damages than exposure to moderately elevated ozone concentration over a longer period.

2. Photochemistry of ozone

About 90% of atmospheric ozone is found in the stratosphere. Downward transport of atmospheric ozone through the tropopause is a major source of natural ozone in the troposphere, while deposition on the ground is a major sink of ozone.

Intrusions of stratospheric ozone through events called "tropopause foldings" seam to be the main source of global tropospheric ozone (*Seinfeld, 1986*).

A second source of ozone in the clean remote troposphere is believed to result from the following sequence of reactions:

1. $OH + CO \rightarrow CO_2 + H$

2. $RO_2 + NO \rightarrow RO + NO_2$

3. $NO_2 + h\nu \rightarrow NO + O^*$

4. $O^* + O_2 (+M) \rightarrow O_3 + (+M)$ ($M = N_2$ or O_2)

This formation of ozon seem to be in equilibrium with the following ozone destroying photochemical reactions:

5. $O_3 + h\nu \rightarrow O^* + O_2$

6. $2O^* + H_2 \rightarrow 2OH$

7. $OH + O_3 \rightarrow HO_2 + O_2$

8. $HO_2 + O_3 \rightarrow 2\ O_2 + OH$

As can be seen from 1. and 2. nitrogendioxid, NO_2, can be formed without the presence of ozone. In areas with a surplus of NO_2 there will be a net production of ozone during daytime (3. and 4.). During nighttime there will be a reduction in the ozone concentration (7. and 8.).

On the other hand ozone will react with NO and form NO_2:

9. $NO + O_3 \rightarrow NO_2 + O_2$

Nitrogen oxide, NO, hydrocarbon, CH, and carbon monoxide are all characteristic compounds emitted from combustion of fossil fuels e.g. from traffic, power plants or industry. In consequence hereof pollution with these substances will at first deplete ozone and later reform ozone and built up enhanced ozone concentrations during daytime (eqs. 3, 4 and 9).

2.1 Ozone episodes

As mentioned high ozone concentrations in the troposphere will be found either as a consequence of natural formation or as a secondary pollutant of photochemical smog formation.

Photochemical smog episodes are big scale processes that occur during high pressure periods. This is why a division of the phenomena into local formation and remote transformation can be discussed. It is convenient, though, to make this division in order to illustrate the problem.

Local formation is not common in Denmark because of the topography of the country, the windy climate and the status as an agricultural nation and not a nation with heavy industry. The alarmingly high pollution levels reported in other countries are not reached in Denmark.

On the contrary episodes of remote transported polluted air do bring high levels of ozone concentrations. During high pressure over Central Europe, low wind speed and intense solar radiation the photochemical smog is built up day for day and transported with the air to Denmark.

Thus the highest ozone concentrations are found in air masses passing over polluted areas in Central Europe during high pressure situations and transported to Denmark (*Christensen et al., 1990*).

3. Measurement

3.1 Location of sites

In order to get information and documentation of the yearly and diurnal variation in ozone concentrations at nonpolluted areas, ozone monitoring was started in mid 1985. Ozone monitors were installed in open places in two Danish forests (Fig 1).

The first site was at Ulborg (West Jutland), where monitoring started in mid 1985. The second site was at Frederiksborg (North Zealand), where measurements started in mid 1988. This report shows the result from Ulborg measurements 1986 - 1989 and discusses these in the light of similarly measurements made in Europe. The results from Frederiksborg are in accordance with the Ulborg results, but are not further discussed in this report.

West-Jutland

The Ulborg station is situated at 56°17', 8°26', 40 m above sea level. The monitoring station is placed in Ulborg Forest District in West Jutland, 20 km east of the North Sea coast line. The nearest town is 15 km NE of the station. There is no industry in this area. The monitor hut is placed in a forest clearing (25 x 25 m), surrounded by trees of 5-6 m height. The gas inlet is 5 m above the ground.

North-Zealand

The Frederiksborg station is situated at 55°57', 12°21', 40 m above sea level. The monitoring station is placed in Frederiksborg Forest District 20 km south of the Kattegat coast. The nearest town is 3 km SW from the station. The monitor stands in a clearing (25 x 50 m) surrounded by trees of 10 m height. The gas inlet is 3.5 m above the ground. Canopy effects on measurements can not be excluded at this station.

3.2 Measurement method

Monitor Lab. Model 8810 ozone monitors based upon ultraviolet (UV) absorption photometry are used. Ozone has an intense absorption band in the UV at 253.7nm. A sequential intake of scrubbed and unscrubbed ambient air is lead to the cuvette for absorption measurements. A reference light intensity of the UV light source is determined from ozone free air (scrubbed). The UV-absorption in ambient air gives an indirect measure of the ozone concentration, using the Lambert-Beer absorption law. An ozone concentration is measured every 10 s and stored in the computer. One hour average values are derived from these readings.

To adjust for the drift of zero and span a daily check is performed running a internal zero and span cycle. Three times a year a laboratory check is performed using an external ozone calibration unit.

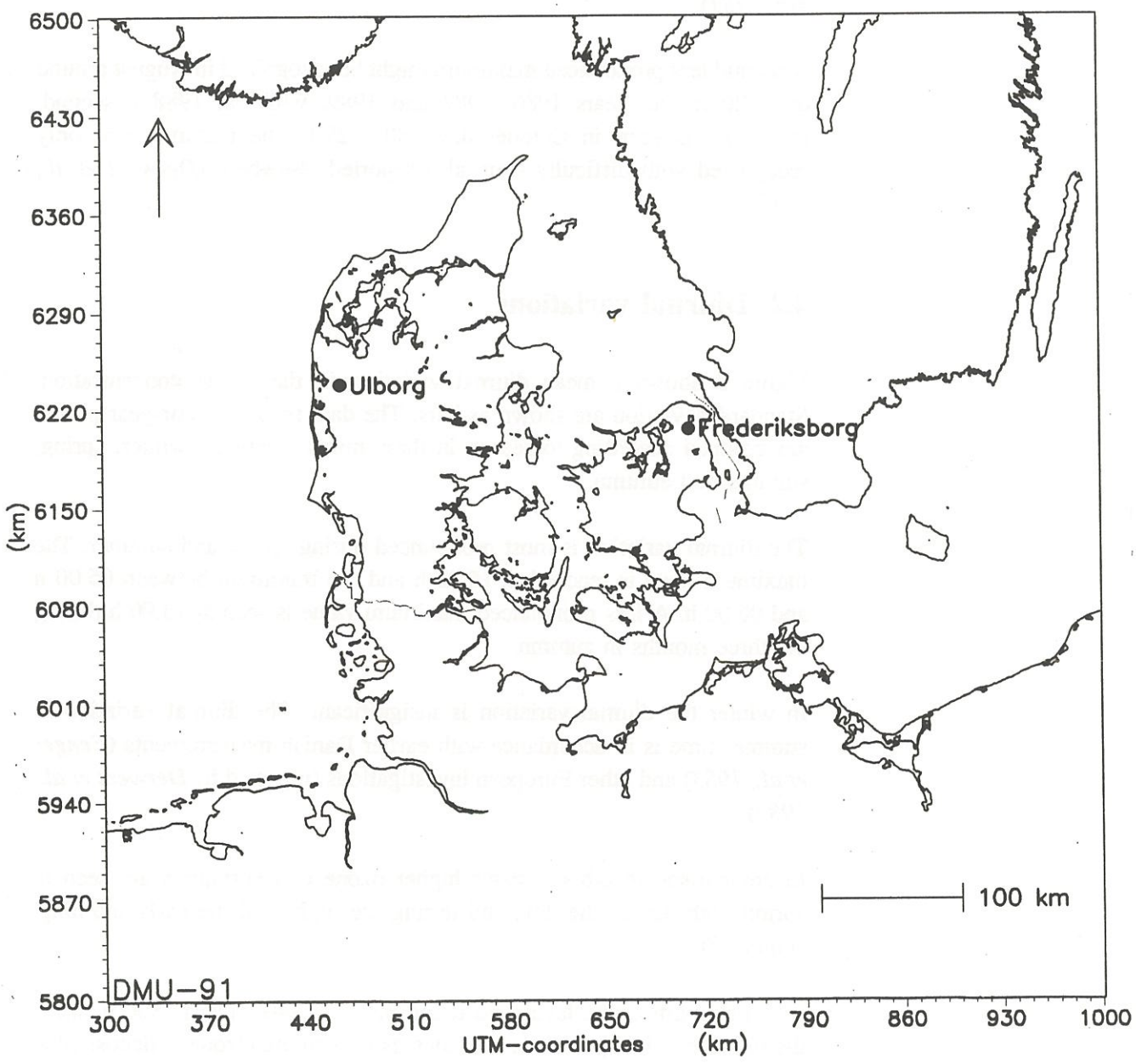

Figure 1
Locations of Danish ozone monitoring stations

4. Results and discussion

4.1 Yearly variations

In Figure 2 daytime (9.00 h - 17.00 h) mean values obtained at the Ulborg station are shown for each of the years 1986 to 1989. A curve is fitted in between the daily values using a smoothing program.

A pronounced maximum is seen all four years in April day 100 - 130. This is in accordance with other North European data (*Greenfelt and Schjoldager, 1984*).

A second less pronounced maximum might be recognized in August around day 220 in the years 1986, 1987 and 1989, while in 1988 a second, maximum is seen in October day 280 - 290. The maxima here only recognized with difficulty - are also reported elsewhere (*Derwent et al., 1990*).

4.2 Diurnal variations

Figure 3 shows a mean diurnal variation in the ozone concentration. Standard deviation are shown as bars. The data from the four-year period are grouped according to season in three months periods: winter, spring, summer and autumn.

The diurnal variation is most pronounced during spring and summer. The maximum level is reached at 16.00 h and the minimum between 05.00 h and 06.00 h. A less pronounced maximum value is seen at 15.00 h during the three months in autumn.

In winter the diurnal variation is insignificant. The diurnal variation in summer time is in accordance with earlier Danish measurements (*Fenger et al., 1983*) and other European investigations (reported by *Derwent et al., 1987*).

In comparison to other seasons higher ozone concentrations are seen in spring both during the day, and during the night and the early morning, (Figure 2).

The maximum ozone levels are found between 1400 h and 1800 h, when the photochemical production reaches its maximum. Ozone is deposited at the ground. During the day ozone concentrations at ground level are maintained by vertical turbulent transfer throughout the mixing layer, while during the night thermal stratification can cause a reduction in the

downward transport of ozone leading to relatively low levels at ground level.

This is often the case during spring and summer. The ratio between the daytime maximum and the night time minimum is 1.7 during the summer period compared to 1.5 in the spring. This is probably a result of the more instable atmospheric conditions in the spring with abundant turbulent mixing during night and day.

The two monitoring stations Ulborg and Frederiksborg are 250 km apart. Frederiksborg is situated in a more populated area. Compared to Ulborg the Frederiksborg station is also exposed to more pollution from Central Europe transported by south-westerly winds. This also affects the levels of NO_2 and SO_2 being twice as high at Frederiksborg compared to Ulborg (*Hovmand and Bille-Hansen, 1988*). In Figure 6 one hour ozone levels monitored at the two stations are correlated, the best linear fit forced through 0.0 is shown. The slopes of the lines computed for the four seasons are between 0.8 and 1.2, probably not significantly different from 1. The two stations do not exhibit significant differences in ozone concentration patterns through the four seasons of 1989.

4.3 Critical levels

Ozone levels recommended not to be exceeded for the protection of sensitive plants and ecosystems are shown in *Table 1*.

Table 1. Some critical exposure duration values, adapted at the UN ECE Workshop at Bad Harzburg 1988. In part from (*Derwent et al., 1990*).

Period of exposure (hours)	Ozone Concentration (ppb)
1	75
8	30
7 (0900-1600h) Growing season	25

The critical 8 hour value is exceeded at the Danish stations during the growing season every year as seen from *Figure 2*. *Figure 4* and *5* gives the daily maximum 1 hour values. Hourly concentrations of 75 ppb are often exceeded at the Ulborg stations during the spring and summer season in 1987, 1988 and 1989. The few results from the Frederiksborg station, also exhibit one hour average ozone concentrations above 75 ppb.

The number of hours per year, where ozone concentration exceeds 80 ppb, are shown in *Table 2*. As indicated in *Figure 2* and *4* in particular during 1988.

According to *Derwent et al., (1990)* the ozone concentration at most European monitoring stations exceeded the critical 8 hour ozone daily average value during spring and summer time.

Table 2. Numbers of hours per year, where the average ozone concentration exceeds 80 ppb.

Year	1986	1987	1988	1989
Station				
Ulborg	0	8	37	12
Frederiksborg	-	-	-	26

- no measurements or incomplete data set

Table 3 gives the 50, 95 and 99 percentiles for three month periods; spring (March, April, May), summer (June, July, August), autumn (September, October, November) and winter (December, January, February). Highest percentile values are spring 1988 followed by summer 1989 and spring 1987.

Table 3. Ozone concentrations one hour mean, ppb. Percentiles for 3 months 50% (median), 95% and 99%. Number of one hour observations per 3 months.

Year	1985		1986				1987				1988				1989			
Period	A	W	Sp	Su	A	W	Sp	Su	A	W	Sp	Su	A	W	Sp	Su	A	W
median	27	28	34	31	25	21	35	32	17	16	47	25	19	24	36	32	21	19
95%	44	42	53	53	38	37	56	48	36	34	72	50	37	36	51	61	36	32
99%	47	46	61	62	41	39	68	64	40	38	84	56	39	38	65	76	42	34
one hour observations x 100	15	19	19	19	11	20	17	21	21	11	18	19	9	19	20	17	21	7*

A = autumn, W= winter, Sp = spring, Su = summer
* one months observations

5. Conclusion

Ozone was monitored continuously during the years 1985 to 1989 at a Danish forest site to reveal whether ozone levels exceeded phytotic levels or not.

Diurnal variations showed maximum levels between 1400 h and 1800 h most pronounced in spring and summer. Variations during the year showed highest values in April and May.

Though the two monitoring stations are 250 km apart, the results from the two stations are highly correlated, confirming earlier reports of ozone as being long range transported.

In 1988 the one hour ozone level of 80 ppb were exceeded 37 times according to the measurements. 1987 and 1989 had somewhat lower numbers of exceedings.

The eastern part ot the country seems to have more high level periods compared to the western part.

In conclusion the ozone concentrations at both Danish stations reach phytotoxic levels nearly every year.

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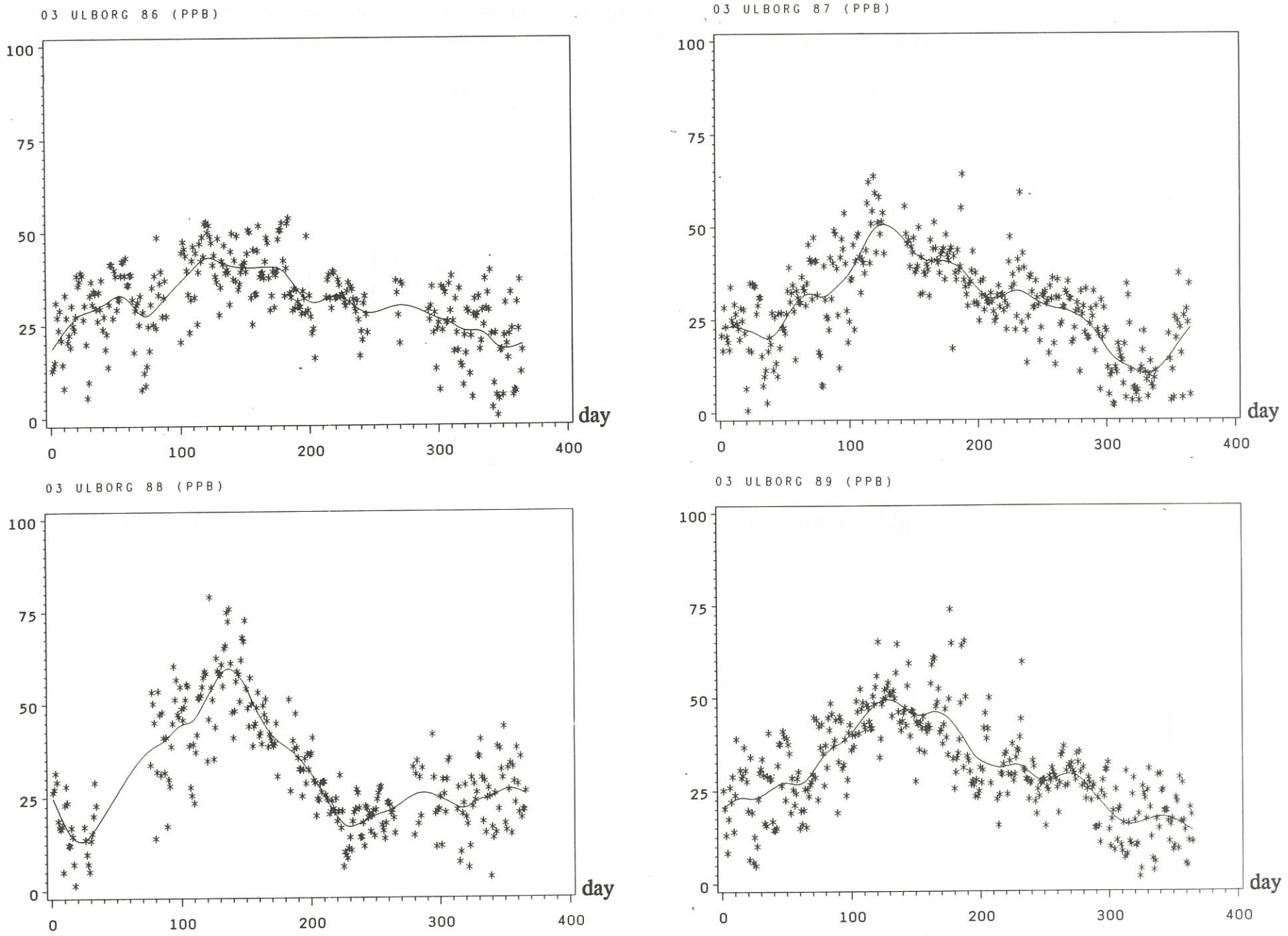

Figure 2. Daytime (900 h to 1700 h) mean ozone concentrations from 1986-89 monitored at the Ulborg stations

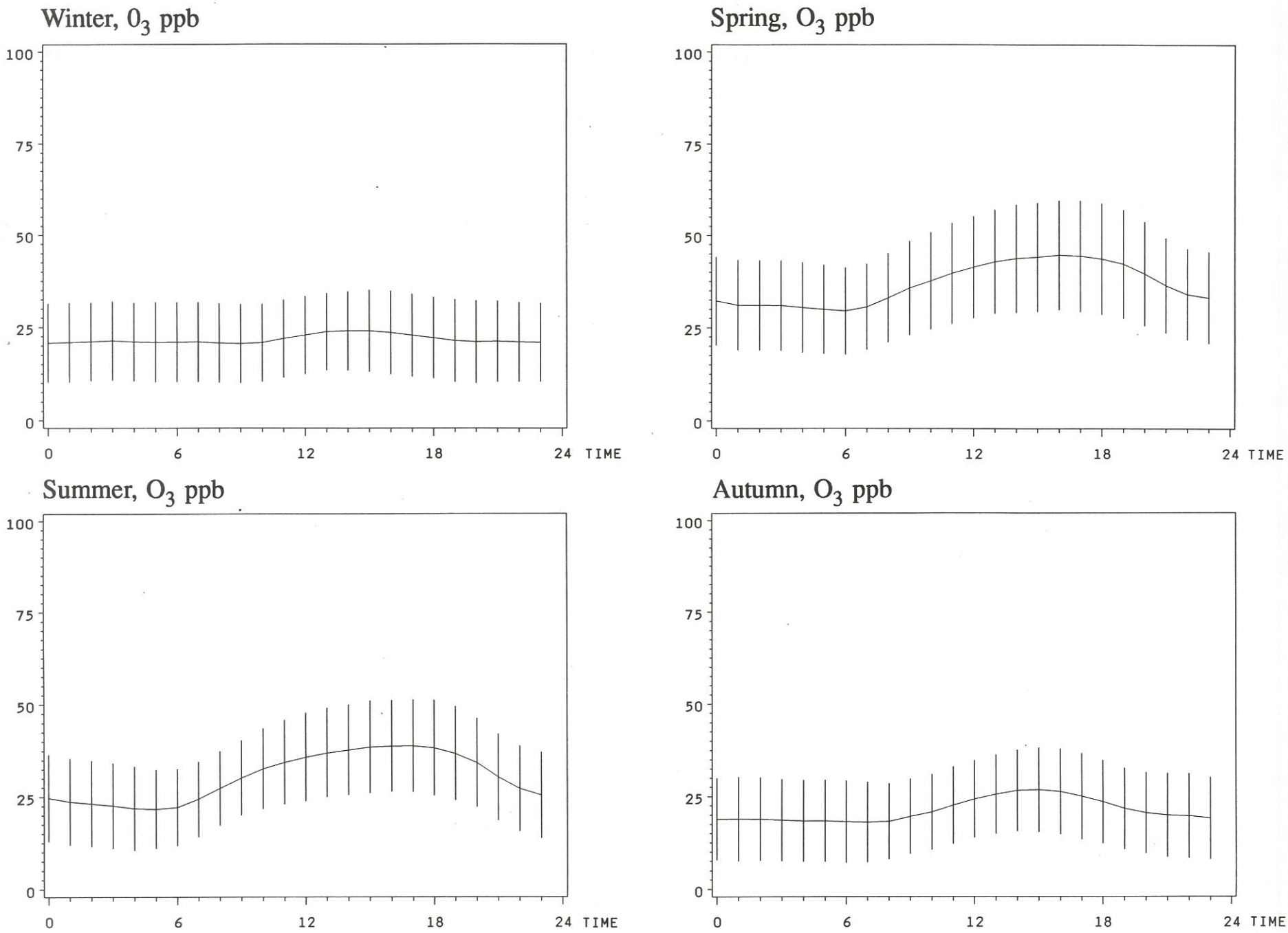

Figure 3. Mean diurnal variation in ozone concentrations at Ulborg. Mean hourly values from four years are grouped into four seasons. Plus minus on standard deviations shown as bars.

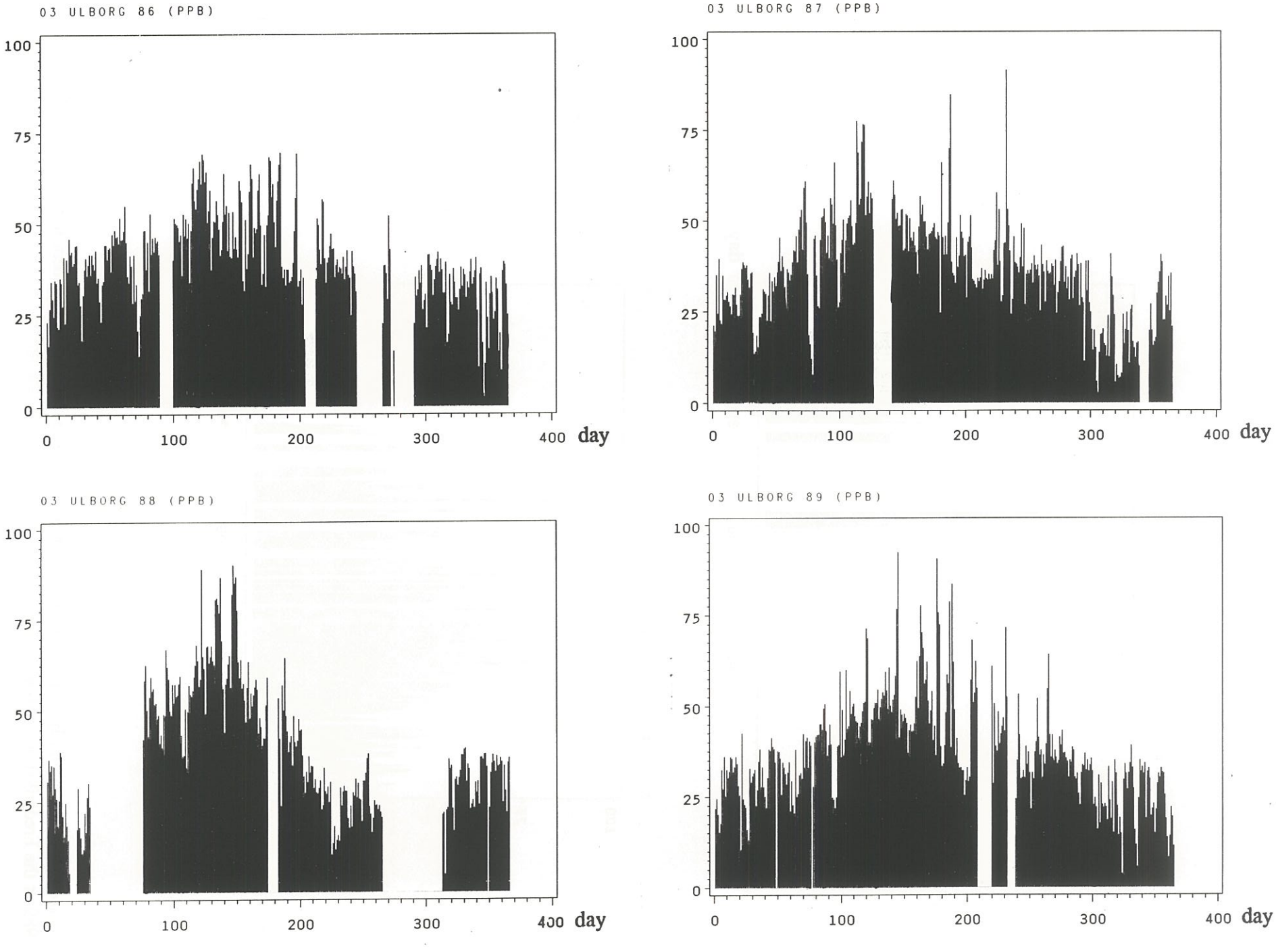

Figure 4. Maximum hourly mean ozone concentrations for each day of measurement in the period 1986-89 at Ulborg.

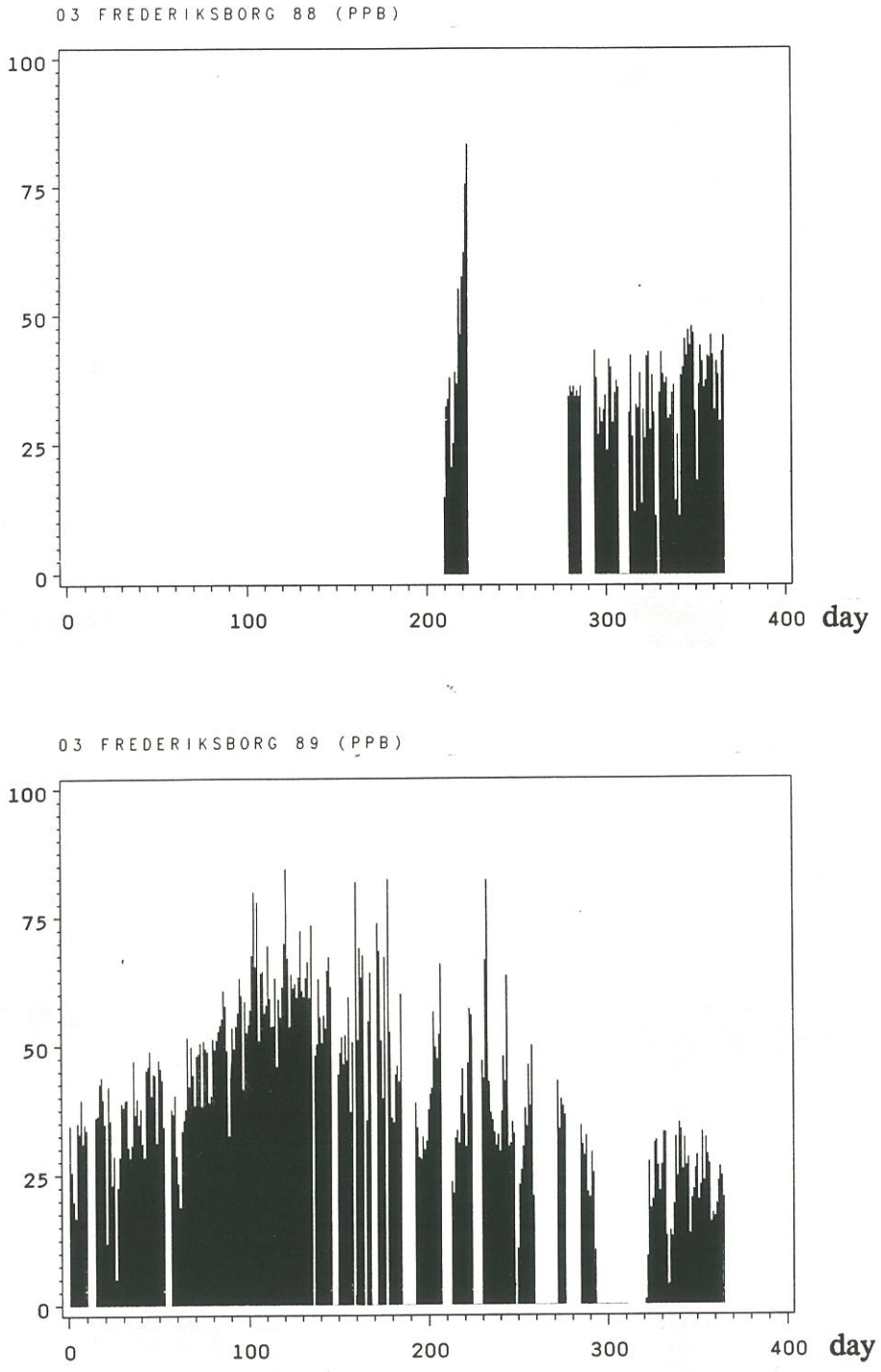

Figure 5. Maximum hourly mean ozone concentrations for each day of measurement in the period 1988-1989 at the Frederiksborg station

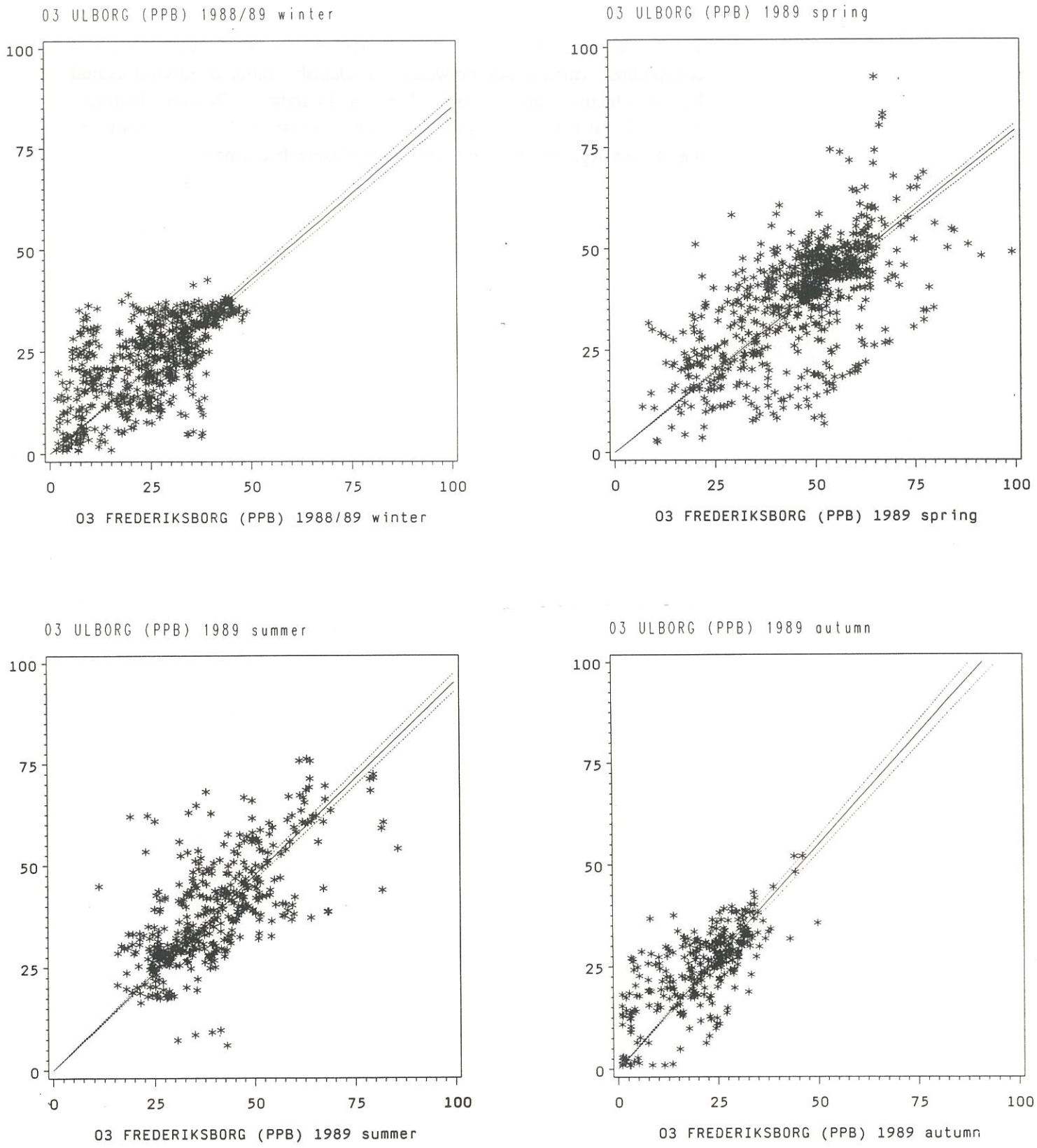

Figure 6. Correlations between hourly mean ozone concentrations measured at Ulborg and Frederiksborg respectively.

Acknowledgement

This work was a part of the cooperative project "Ionbalances in forest ecosystems" carried out between the Danish National Environmental Research Institute and the Danish Forest and Landscape Research Institute. The work was partly funded by the National Forest and Nature Agency and the Danish Agricultural and Veterinary Research Council.

National Environmental Research Institute

The National Environmental Research Institute - NERI - is a research institute of the Ministry of the Environment. Neri's tasks are primarily to do research, collect data and give advice on problems related to the environment and nature.

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