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Contents

Summary

In this report is presented measurements of ozone, non-methane hydrocarbons, sulphate, ammonium, halocarbons and meteorological parameters from Spitsbergen in the Norwegian Arctic. The presented data cover the spring period for several years. The focus of this study is the rapid depletion of ozone in the lower troposphere in spring observed in Ny-Ålesund and on the nearby Zeppelin Mountain. Such depletion is also observed in other parts of the Arctic. It has been an aim to explore the physical and chemical environment in which the ozone depletion is taking place, and thereby to make statements about mechanisms which can cause the depletion. It has also been important to get an indication of the magnitude of the ozone loss process, at least in a qualitative sense.

Analyses based on trajectory calculations are presented, which show that the episodes with low ozone concentrations on the Zeppelin Mountain are closely linked to the transport direction. Most of the episodes occur when air masses are transported from NW-N-NE.

A correlation between ozone and local temperature was found, probably because air depleted in ozone is trapped in the cold boundary layer when the vertical temperature stratification is stable and mixing with the free troposphere is suppressed. No temperature threshold value for the ozone depletion was found.

Relative humidity and the concentration of sulphate aerosols seem to be linked with the ozone depletion. The measurements indicate that the low ozone episodes occur mostly when both the relative humidity and the concentration of the sulphate particles exceed a certain level. This is consistent with chemical mechanisms where heterogeneous reactions on ice crystals and on sulphate aerosols are required for the depletion process to be efficient.

The concentration of several individual C_2-C_5 hydrocarbons was much lower during episodes of low ozone than for the average conditions. The change in ratio between the individual NMHC gives a strong indication of another oxidizing mechanism for the C_2-C_5 NMHC than the normal OH chemistry. Linear regression of the change in NMHC composition showed that a hypothesis of oxidation by *chlorine* atoms was significant on a 90% significance level in all the episodes with NMHC measurements and an observed low ozone concentration. In many of the low ozone episodes, chlorine oxidation alone could explain close to 95 % of the variance in the NMHC data.

The concentration of acetylene, however, was much lower during the episodes than what could be explained by Cl oxidation alone. This is an indication of active Br chemistry in the low ozone episodes, since acetylene is quite reactive with Br.

No clear relationship between wind speed and the low ozone episodes is seen. During some periods the episodes occurred when the winds were weak, but air with very low ozone was also observed at times with strong winds.

Periods of several days with ozone concentrations close to zero have been observed on the Zeppelin Mountain. This indicates that the air masses depleted in ozone are not confined to small areas, but occur on a horizontal scale of several hundred kilometres.

The vertical extent of the ozone depleted layer was investigated by ozone soundings in Ny-Ålesund and also from Bear Island 500 km further south. The soundings show that the ozone depleted air may reach up to 3-4 km above the ocean surface.

The vertical and horizontal extent of the air masses with reduced ozone concentrations, indicate that the responsible chemical mechanism is an important loss process for tropospheric ozone in the Arctic basin in spring and thereby is important for the ozone budget in the northern hemisphere in general.

Tropospheric ozone depletion in the Arctic during spring

Measurements on the Zeppelin Mountain on Spitsbergen

1. Measurements

Measurements of trace gases and meteorological parameters have been performed by NILU on Spitsbergen in the Norwegian Arctic since the early 1980's. From 1988-September 1989 the measurements were made close to the small settlement at Ny-Ålesund, near sea level (79° N, 12° E). From September 1989 the measurement instruments were moved to the new research station on the nearby Zeppelin Mountain, 474 m above sea level, accessible from Ny-Ålesund by cable car. The location of the station is given on Figure 1.

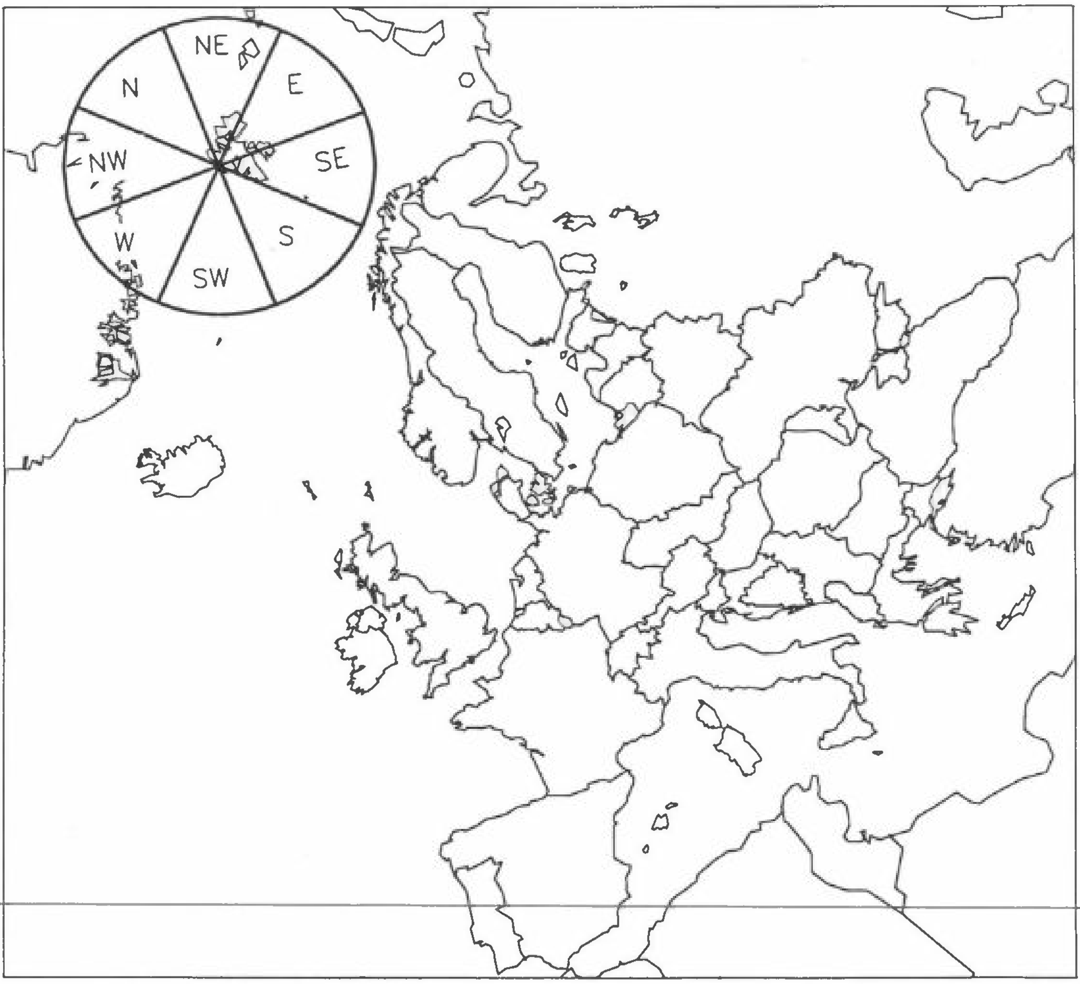


Figure 1: Map showing the location of the Norwegian TOR station Zeppelin Mountain and the sector boundaries used in the frequency distribution calculation.

The measurement program at the Zeppelin station has gradually been extended. At the end of 1993 it covered the analyses of 26 non-methane hydrocarbons (NMHC), 5 chlorofluorocarbons, N_2O and methane in pressurized air samples collected 2-3 times/week (sometimes even daily), automatic monitoring of NO_2, SO_2, sulphate, nitrate and ammonium by daily filter samples, continuous registration of ozone by UV-absorption, and occasional measurements of PAN, NO_y and CO. In addition there is continuous registration of wind speed, wind direction, temperature, pressure, and humidity. Table 1 summarizes the measurements in Ny-Ålesund and on the Zeppelin Mountain included in this report. Some of the components mentioned above were left out due to few valid data, either because the values were below the detection limit or as the result of instrument problems.

Table 1: Measurements from Ny-Ålesund and the Zeppelin Mountain presented in this report.

Component	Time resolution	Period with measurements	Sampling frequency	Method of analysis
O_3	Hourly average	1989-1993	Continuous	UV-absorption
Wind speed	"	1991-1993	"	
Wind gust	"	"	"	
Wind direction	"	"	"	
Temperature	"	"	"	
Relative hum.	"	"	"	
Pressure	"	"	"	
Total SO_4	24h average	1989-1993	"	Ion chrom.
$NH_3(g)+NH_4(s)$*	"	"	"	"
NMHC**	Spot sample	1991-1993	2-3/week	GC-FID
CFC	"	1991-1992	"	GC-EC

* total ammonia plus ammonium

** 9 analyzed components in 1991 (C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6, $i\text{-}C_4H_{10}$, $n\text{-}C_4H_{10}$, $i\text{-}C_5H_{12}$, $n\text{-}C_5H_{12}$), 26 later.

Details of the measurement techniques for NMHC are documented by Schmidbauer and Oehme (1986) and by Solberg et al. (1993), for chlorofluorocarbons by Müller and Oehme (1990), for the filter samples in Chemical Co-Ordinating Centre (1977).

The meteorology is described by two sets of data. The first is the continuous measurements made on the Zeppelin station already mentioned and listed in Table 1. The other set was calculated from analyzed fields given every six hours on the 925 hPa EMEP grid. The analyzed field parameters were wind speed, temperature, relative humidity, mixing height and vertical velocity (the vertical velocity for the 850 hPa level).

For the period March-June in the years 1989-1993 a 24h isobaric back trajectory arriving on the Zeppelin Mountain was calculated every six hour in the same way as described by Hov and Schmidbauer (1992). The analyzed parameters changed every second hour, except for the mixing height which changed every 12h, and were then averaged over the resulting 12+1 values along the 24h back trajectories for the years 1989-1993. The resulting data we refer to as the "regional meteorological data set", as opposed to the measured "local meteorological data". The regional data are believed to be more representative of the meteorological conditions in a larger region around the Zeppelin Mountain and not affected by local conditions at the measuring site. This is especially important for the wind speed and wind direction, as these are often influenced by the location of the measuring site. On the Zeppelin Mountain the topography surrounding the station tends to channel the wind into either a N- or a S-direction. Table 2 lists the calculated regional meteorological parameters.

Table 2: Calculated regional meteorological parameters.

Parameter	Type of data	Years of data	Frequency
Mixing height Temperature Relative humidity Wind speed Vertical velocity**	Average along a 24h back trajectory*	1989-1993	Every 6 hour
Transport sector	See text	1989-1993	Every 6 hour

* Isobaric trajectories (925 hPa) on the EMEP-grid.

** Given for 850 hPa.

For the regional data set, the transport sector was calculated instead of the wind direction. Eight 45° wide sectors from NE, E and clockwise to N was defined as shown in Figure 1, and a sector was allocated to a trajectory if at least 50 % of the 24h back trajectory was inside one of the sectors, otherwise it was characterized as "undefined" (Hov et al., 1989; Hov and Schmidbauer, 1992).

The time series for all measured compounds and calculated parameters for the spring months March-June in the years 1989-1993 are given in Appendix A. All continuous data are connected by curves in the diagrams. Spot samples on successive days were also considered as continuous in this context. The symbols mark the mid time of the observation for the filter samples and the grab samples. The calculated transport sectors are numbered clockwise from NE, so that sector 1 is NE, 2 is E, 3 is SE, 4 is S, 5 is SW, 6 is W, 7 is NW, 8 is N and 9 means that the sector was undefined.

The time series show that each year the ozone concentration is fairly constant during the first part of the time period, then suddenly large fluctuations and low concentrations are found, normally in late March, as for instance in 1990. The last episodic low ozone concentration is normally seen in early June, but in 1992 there was an episode later in that month, on 17-18 June, when the ozone concentration dropped to 10-15 ppbv.

The duration of each of the low ozone episodes varied from a few hours to a long period in late April 1993, when the concentration was between zero and 10 ppbv for several days. This episode is described in detail in the last section of this report.

Of the parameters shown in Appendix A, perhaps the most striking correlation is found between temperature and ozone. The diagrams indicate a distinct positive correlation between ozone and temperature. Low ozone episodes almost always come together with a temperature minimum. During some periods the reduced ozone concentration is accompanied by low wind speeds as well, as in some periods in 1992, but there are several exceptions also.

Due to the rapid fluctuations it is not easy to compare the ozone concentration with the other measured trace compounds just based on the plotted time series, but low NMHC concentrations during the episodes of low ozone are seen in many cases. This was particularly pronounced in 1993.

The time series of ozone, local temperature, wind speed, sulphate and acetylene in the period April-May 1991 are shown in Figure 2 as an example of how the air composition develops in the spring. In addition to the relationships noted above, the sulphate concentration was above "normal" in several of the low ozone episodes seen in Figure 2, but not in everyone.

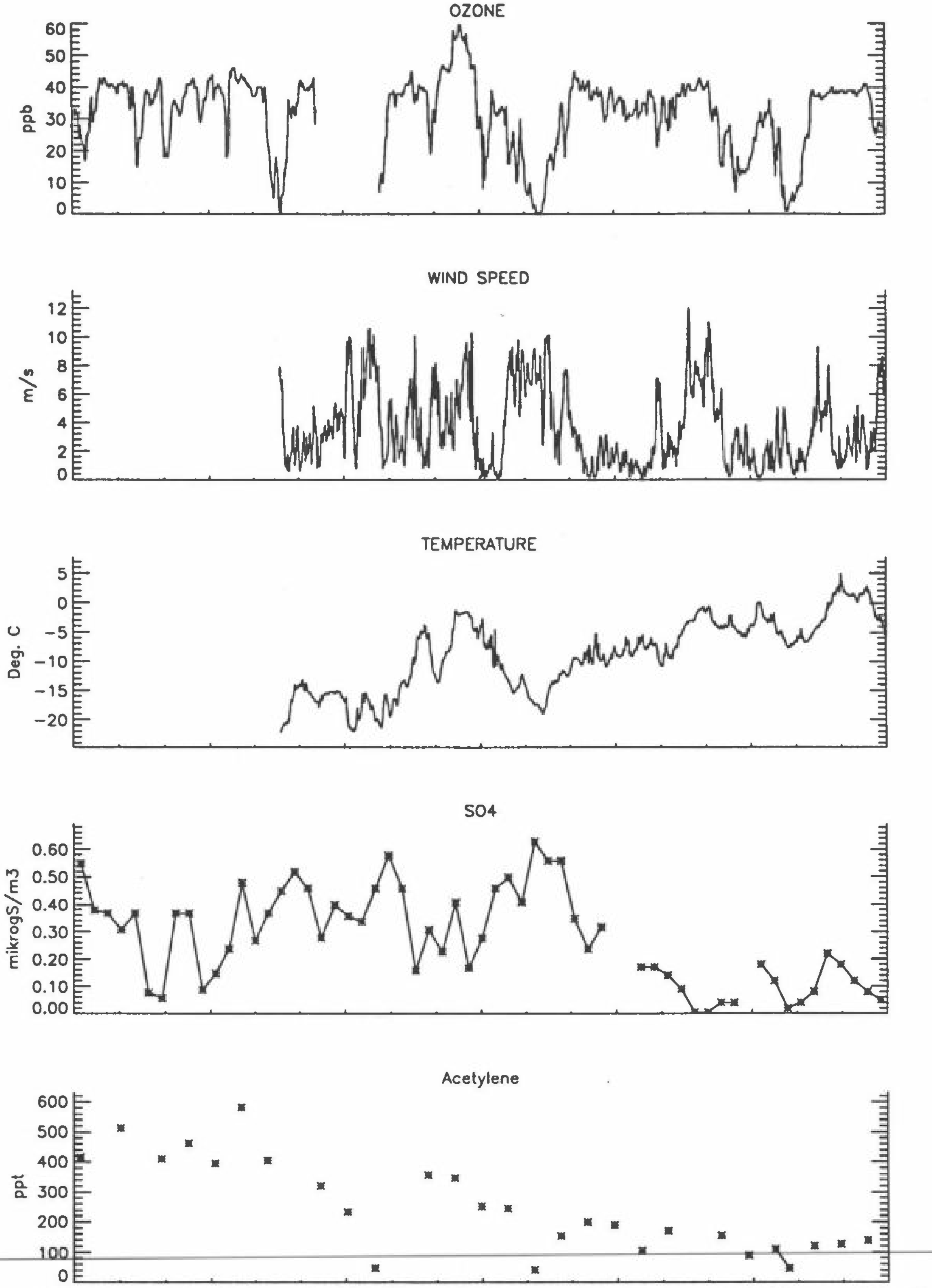


Figure 2: Time series of ozone (ppb), wind speed (m/s), temperature (° C), sulphate aerosols (µg S/m³) and acetylene (ppt) measured on the Zeppelin Mountain, April-May 1991.

2. The relationship between low ozone episodes and meteorology

Episodes with low ozone are found under special meteorological conditions. Both at Alert in Canada and Barrow in Alaska, the low ozone episodes have been found in air masses from N at low temperatures, in a stable surface layer above an ice covered surface (Bottenheim et al., 1986; Barrie et al., 1989; Bottenheim et al., 1990).

Several questions are unanswered regarding the meteorology during these episodes however, and the link between the documented meteorological modulation and the proposed chemical mechanisms responsible for the ozone loss is unclear. The strong anti-correlation between O_3 and filterable Br found by some authors (Barrie et al., 1988, 1989; Oltmans et al. 1989; Bottenheim, 1990) has been proposed to be due to the formation of Br through the photolysis of bromoform (CH_3Br) which is produced biologically in the Arctic Ocean, and subsequent catalytic destruction of O_3 through reaction with Br. Also elevated concentrations of sulphate aerosols during the low ozone episodes have been reported (Bottenheim et al., 1990). Both these findings should indicate that there is some open sea upwind during the episodes and not only ice covered surface.

It is important to see whether the meteorological conditions during low ozone episodes are the same on the Zeppelin station as found at Barrow and Alert, because the Zeppelin station is in several ways different from these latter two.

The Zeppelin station is situated on a mountain top 474 m above sea level, and is therefore expected to be above the surface inversion layer on many occasions. The station is surrounded by ocean in the half circle to the west, and also - at a distance of 250-350 km - to the east. As opposed to Alert and Barrow, all wind sectors around the Zeppelin Mountain are to some extent oceanic.

2.1. Transport sector

In Table 3 is given the total number of 24h back trajectories from the different sectors as defined in the previous section, the number of trajectories arriving during low ozone episodes, and the resulting percentage of trajectories in each sector associated with low ozone episodes. The numbers are based on one trajectory every six hours in March-June for the years 1989-1993, but only for the time period between the first and the last low ozone episode each year. The total number of trajectories in the table refers to the number of all trajectories between the first and the last observed low ozone episode each year, summed over all years, 1989-1993. A low ozone episode was defined by averaging the hourly ozone measurements over six hours centred around the time of the trajectory arrival (0, 6, 12, and 18 UT), and if this average concentration was less than or equal to 10 ppbv it was called an episode.

The trajectory analysis shows that the low ozone episodes observed on the Zeppelin Mountain are linked to the transport sector. About 80 % of the episodes occurred when the one-day back trajectory originated from the W-NW-N sectors, while most of the other episodes were associated with an undefined transport direction. Sector N had the highest fraction of episodes, approx. 30 %, and nearly no episodes occurred with transport from E-SW.

Table 3: The number of trajectories from different sectors during low ozone episodes compared to the total number of trajectories from the same sectors in March-June 1989-1993, and the corresponding fraction in per cent.

	NE	E	SE	S	SW	W	NW	N	Un-def.	Σ
Total no. of trajs.	75	26	59	45	85	90	150	148	91	769
Traj.s, $\overline{O}_3 \leq 10$ ppb	3	0	1	0	2	19	27	42	18	112
Fraction (%)	4	0	2	0	2	21	18	28	20	15

It is interesting to note the large difference between transport from NE and from NW: There were only 3 low ozone episodes out of 101 trajectories from the sectors E-NE, as opposed to 46 out of 240 from W-NW. This is surprising, since large longitudinal gradients at 80° N in chemistry or meteorology were not really expected. This finding may indicate that the distance to the Arctic Ocean is crucial, as the ocean is close to the measuring site to the west and northwest, while the air has passed over several hundreds of kilometres of continent when transported from NE. The distance to the Arctic Ocean would be of significance if it were the region where ozone depletion takes place. The rugged topography will induce significant vertical mixing of surface air (which may be depleted in ozone), and free tropospheric air with higher ozone concentration during transport from NE.

Another explanation for the difference between the number of low ozone episodes from NW and NE, is the extent of ice coverage and open sea. The Greenland Sea, between Greenland and Spitsbergen, is ice-free a much longer time of the year than the ocean north and east of Spitsbergen. If the ozone depletion depends on ocean areas with both ice and open sea in April/May, then low ozone concentrations would be most likely in air from the W-NW sector.

In Figure 3 is shown the ozone frequency distribution for the different sectors. All hourly ozone concentrations (from the same time periods as above) were divided into subranges (bins) of 5 ppb, ranging from 0-60 ppb. The curves give the number of hourly ozone concentrations in each bin, relative to the total number of hourly ozone values inside each sector.

Except for sector S, the number frequencies in Figure 3 show a bimodal distribution with one peak around 35-45 ppb, and a secondary peak at 5-25 ppb, depending on the sector. Sector S has no secondary peak at low ozone concentrations.

The peak at 35-45 ppb is most pronounced for the E and S sectors, and there are very few values below 10 ppb from the sectors in the eastern half circle. The frequency distribution for the W, NW and N sectors are clearly different from the other sectors, and have a much higher frequency of ozone concentrations below 10 ppb.

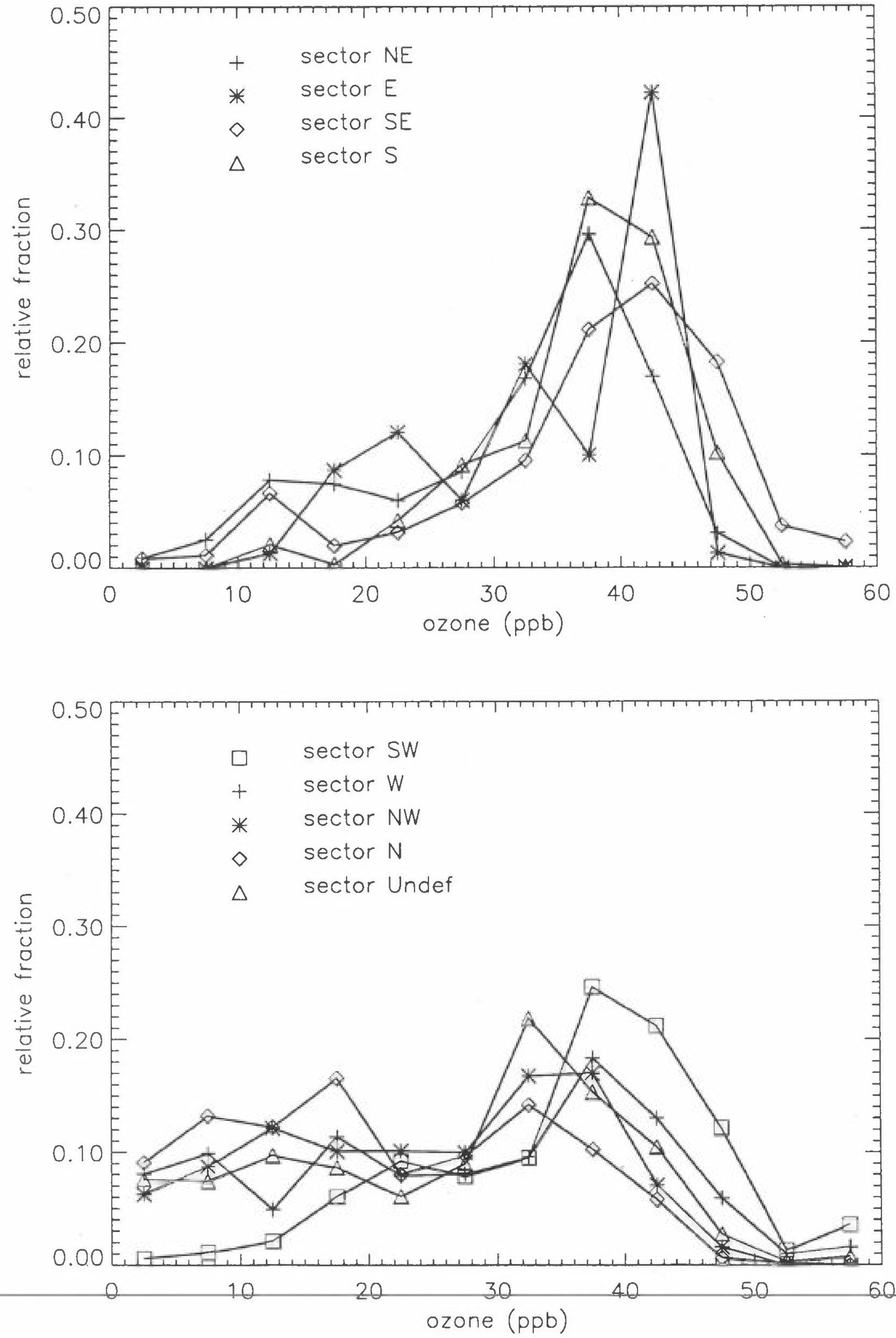


Figure 3: Number frequency of hourly ozone concentrations divided into bins of 5 ppb (0-5 ppb, 5-10 ppb, etc.) for 8 transport sectors. All data between the first and the last occurrence of a low ozone episode each of the years 1989-1993 were used.

The large frequency of high ozone concentration from S, E and SE corresponds to transport from the European continent, where a maximum in the surface ozone concentration is observed in spring.

The high fraction of ozone concentrations around 10-20 ppbv for several of the sectors suggests numerous episodes where the surface ozone "hole" has been partly filled.

2.2. Local meteorological measurements

Measurements of wind speed, wind direction, wind gust, temperature, relative humidity and pressure started in summer 1990 at the Zeppelin Mountain station on a continuous basis. The wind measurements are taken 10 m above the ground, while the other parameters are measured at an elevation of 2 m. For the period of the spring time ozone depletion, three years (1991-1993) of data at the moment exist, and are given as hourly values. There are some periods with instrumental problems and with lower data cover.

When comparing the meteorological data with the ozone measurements, all the data were averaged over 6h, to avoid too many dependent time points since the persistence of the meteorological parameters, at least pressure and temperature, is greater than the persistence of ozone. The data were averaged in the same way as mentioned above for ozone, i.e. the 6h averages were centred around 0, 6, 12, and 18 UT. A low ozone episode was, as before, defined if the 6h average concentration was less or equal to 10 ppbv.

For the years with meteorological measurements, 1991-1993, the different meteorological parameters were then averaged into two groups: One consisting of all measurements taken during low ozone episodes, and a second group consisting of all the other measurements, but only for the time period between the first and the last occurrence of a low ozone episode each year. This was to avoid bias due to different sampling seasons.

As discussed above, a clear link between regional transport from W-NW-N, and low ozone concentrations was discovered, and different average values of a meteorological parameter like temperature could be expected when averaged during and outside the low ozone episodes. However, it is important to distinguish the effects on the calculated average values that are just the result of sampling more Arctic air masses, from effects that are directly linked to the chemical depletion of ozone.

To do so, the averaging of the meteorological parameters as described above (during and outside the low ozone episodes), was in addition also performed for the cases when the transport was from the Arctic region only. For this last purpose, 80 % or more of a *four*-days back trajectory arriving at the Zeppelin station, had to be inside the northern half circle around the station (270°-90°) for the measurements to be counted. These cases are referred to as cases with *Arctic air masses* in the following text. Although most of the four-days back trajectories from this Arctic sector hit the grid boundaries due to the location of Spitsbergen in the EMEP grid (Figure 1), this method of sorting the measurements provides more homogenous air mass samples than when all measurements are lumped together.

The resulting average values are given in Table 4. The first line for each parameter gives the average, the sample variance and the number of data points during and outside the low ozone episodes when all the data were used. The second line gives the same parameters calculated when only Arctic air masses were counted.

Table 4: Average values of measured meteorological parameters during low ozone episodes ($\overline{O}_3 \leq 10$ ppb) and outside ozone episodes ($\overline{O}_3 > 10$ ppb), $\overline{x}$ mean and s_x standard deviation, n_x number of cases (1991-1993). Z is a standard normally distributed statistic for the hypothesis that the two populations of data have the same mean value. Values in brackets mark non-significant numbers.

	$\overline{O}_3 \leq 10$ ppb			$\overline{O}_3 > 10$ ppb			
Parameter	$\overline{x}$	s_x	n_x	$\overline{x}$	s_x	n_x	|Z|
Local wind speed (m/s)	3.5	2.2	64	3.5	2.4	252	(0.23)
" 1)	4.1	2.3	44	2.8	2.1	124	3.7
Local temperature (C)	-14.4	4.9	64	-7.2	4.4	252	8.9
" 1)	-15.6	4.9	44	-10.1	3.8	124	6.1
Local RH (%)	85	4	49	87	7	127	3.6
" 1)	83	4	30	84	9	45	2.2
Local pressure (hPa)	945	10	64	952	8	252	4.7
" 1)	947	10	44	955	7	124	4.7
Local windgust (m/s)	6.4	3.0	64	7.0	4.2	245	(0.4)
" 1)	7.1	3.0	44	5.2	3.0	121	3.6

1) Arctic air only.

In the last column of the table is given the standard normally distributed Z-statistic for the hypothesis that the two data sets (during and outside the episodes) are sampled from two populations with the same mean. The hypothesis of equal means was tested by a standard Mann-Whitney test (also known as Wilcoxon's rank sum test), which is a non-parametric rank method, where the distributions don't have to be normal, but the shapes (approximated by the variance) must be similar (Gilbert, 1987). In this test all the values are sorted and assigned ranks. If the average rank of one data set is sufficiently different from the other data set, it is probable that the two data sets belong to populations with different mean values.

As seen from Table 4, the average local wind speed was similar during and outside the low ozone episodes, when averaging over all data. When only Arctic air masses were considered, however, the average wind speed was higher during the episodes of depleted ozone than otherwise. Local wind speed is plotted against the ozone concentration in Figure 4 (all values are 6h averages).

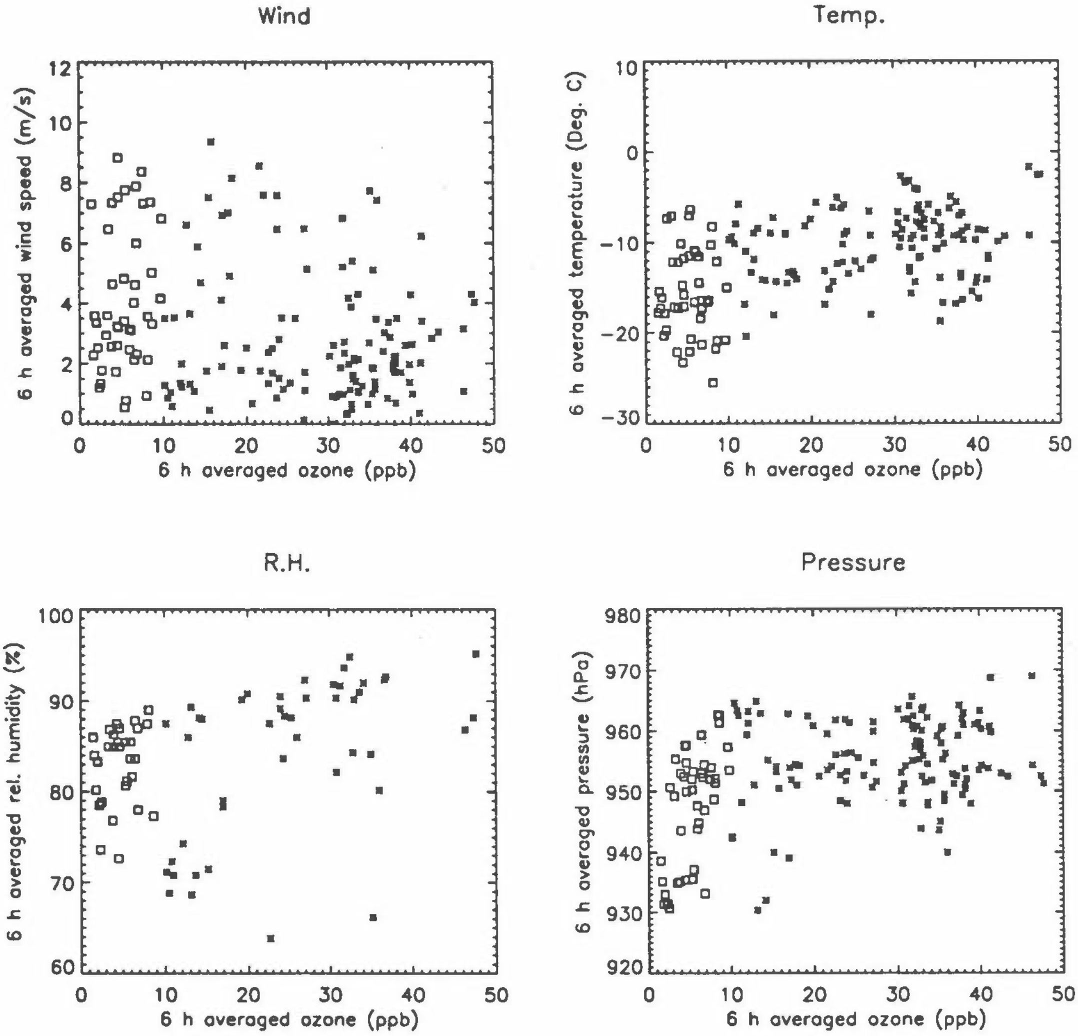


Figure 4: Scatter plots of 6h averaged ozone concentrations vs. 6h averaged meteorological parameters based on hourly measurements on the Zeppelin Mountain 1991-1993. Only data between the first and the last low ozone episode each year are shown, and only for Arctic air masses (see text for explanation). Open boxes mark low ozone episodes.

No clear correlation between ozone and wind speed is seen, but the spread of the data is large, independent of the ozone concentration. Figure 4 shows that very low ozone concentrations occur even at the highest average local wind speeds of 8-10 m/s. This finding indicates that the depletion of ozone is not a small scale, local phenomenon since mechanical mixing increases with the wind speed.

The average measured wind gust also shows the same pattern. Using all data, the numbers look similar, but when sampling only Arctic air masses, the average wind gust was higher during the low ozone episodes than otherwise. This is reasonable, since the wind gust is closely connected to the mean wind speed.

The average measured temperature was much lower during episodes of low ozone concentrations than for all data kept together. As argued above, this difference is partly due to the higher fraction of Arctic air masses during the episodes, and we found this effect to be a few degrees. However, even when sampling only Arctic air, the average temperature was 5.5° C lower during the episodes than outside of the episodes.

Figure 4 shows that there is a positive correlation between the measured temperature and the ozone concentration, when the Arctic air masses only are considered. Furthermore, there is an indication that the link between ozone and temperature is "physical" and not "chemical", since there does not seem to be any threshold temperature for the low ozone episodes to occur. It is more reasonable to link ozone and temperature in a physical way: Low surface temperature is associated with strong inversions and only a weak coupling between the boundary layer and the free troposphere, with only little vertical mixing. Under such conditions, the ozone depleted air is trapped in a layer near the surface and is recognized as a low ozone episode, even at mountain stations like the Zeppelin Mountain. The chemical ozone loss may well take place independently of the temperature, but in a less stable boundary layer the reduced surface ozone will be more easily replenished with higher concentrations from above.

For relative humidity many data were missing, and it should be noted that at low temperatures the concentration of water vapour has to be very low, giving less reliable measured relative humidities. The numbers in Table 4 show small differences, although the sample variance is larger for measurements taken outside the low ozone episodes. This is better illustrated in Figure 4, where the average ozone concentration is plotted against the relative humidity for Arctic air masses only. The relative humidity is confined to a narrower range during the ozone episodes than otherwise.

Table 4 and Figure 4 also indicate that the pressure at the Zeppelin station on an average was lower during the low ozone episodes than otherwise. This is, however, mostly due to the long period in late April 1993 with low ozone concentrations, when a low pressure system was located near Spitsbergen for several days (see also section 4).

2.3. Regional meteorology

In Table 5 is given the average values of the calculated regional meteorological data in the same way as for the local data in Table 4. These data do not cover exactly the same time period as the local measurements on the Zeppelin station, but were calculated for the years 1989-1993. As for the local measurements, the ozone concentrations were averaged over six hours, centred around 0, 6, 12, and 18 UT (the trajectory arrival times), and the regional meteorological parameters were averaged during the low ozone episodes and outside. The analysis was made for all data, and for the data with Arctic air masses only, as above.

The first parameter in Table 5 is the mixing height. It is not really a diagnostic parameter, since it is held constant for 12h along the trajectory, and is often given discrete values, so that many of the one-day average mixing heights for different times became equal. This distorted the analysis of equal means in Table 5. Anyhow, the average mixing heights during the low ozone episodes are not significantly lower than outside of the episodes, which may be contrary to the expected.

Table 5: Average values of calculated meteorological parameters during low ozone episodes ($\overline{O}_3 \leq 10$ ppb) and outside of ozone episodes ($\overline{O}_3 > 10$ ppb), $\bar{x}$ mean and s_x standard deviation, n_x number of cases (1991-1993). Z is a standard normally distributed statistic for the hypothesis that the two populations of data have the same mean value. Values in brackets mark non-significant numbers.

	$\overline{O}_3 \leq 10$ ppb			$\overline{O}_3 > 10$ ppb			
Parameter	$\bar{x}$	s_x	n_x	$\bar{x}$	s_x	n_x	$\lvert Z \rvert$
Hmix (m)	926	319	112	887	432	658	2.5
" 1)	958	147	81	912	291	346	3.1
W (mm/s) (850 hPa)	1.1	5.9	112	0.7	5.5	658	(0.02)
" 1)	0.3	5.8	81	-2.1	3.6	346	3.0
RH (%) (925 hPa)	85	12	112	77	17	658	4.1
" 1)	85	13	81	74	16	346	6.1
T (°C) (925 hPa)	-14.6	5.7	112	-10.2	7.5	658	6.3
" 1)	-15.7	5.1	81	-14.8	6.2	346	(1.4)
Wind speed (m/s) (925 hPa)	8.1	3.6	112	7.5	3.5	658	(1.2)
" 1)	8.5	3.8	81	6.9	2.9	346	2.9

1) Arctic air only.

Figure 5 shows the regional meteorological parameters plotted against ozone concentration for Arctic air only. There is a fan-like relationship between ozone and the mixing height, implying a larger spread of values outside of the episodes than during the episodes.

The average vertical velocity (w) was close to zero during the low ozone episodes, while negative outside of the episodes when sampling Arctic air masses only. This reflects that transport from north is most often associated with a slow subsidence of cold air.

The vertical velocity is plotted against the ozone concentration in Figure 5 (Arctic air masses only). The highest values of w, above 10 mm/s, shown in Figure 5, are all from 1993. Most of the cases with these high values of w occurred when the 6h average ozone concentration was below 10 ppb during April and May 1993. It is surprising that high values of w, indicating pronounced upward mixing, occurs at the same time as the low ozone concentration. The process depleting ozone are believed to take place near the surface in a shallow mixed layer "decoupled" from the free troposphere.

Due to the sparse station network, meteorological data for the Arctic are always quite uncertain. This concerns derived quantities like mixing height and vertical velocity in particular, which should be interpreted with care.

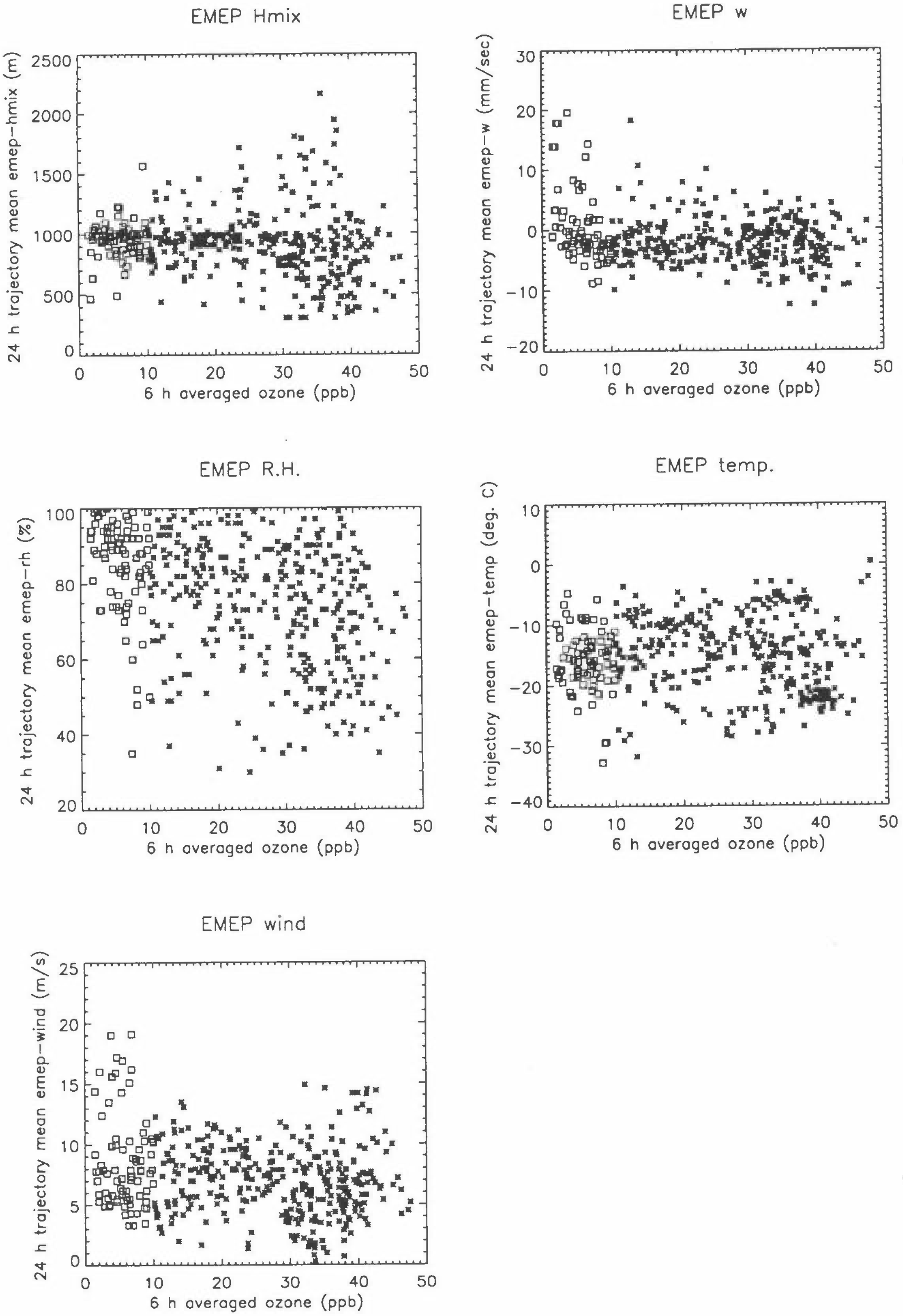


Figure 5: Scatter plots of 6h averaged ozone concentrations vs. averages along 24h backwards trajectories of regional meteorological data. The met. data are analyses on 925 hPa on the EMEP grid given every six hours. The parameters are mixing height (m), vertical velocity at 850 hPa (mm/s), relative humidity (%), temperature (° C) and wind speed (m/s). Only data between the first and the last low ozone episode each year are shown, and only for Arctic air masses (see text for explanation). Open boxes mark low ozone episodes.

On the other hand, the soundings from Ny-Ålesund during the episode of low ozone in April 1993 (Section 4) indicate a well mixed layer from the surface up to 2-3 km. This is therefore not in conflict with the high values of w which are calculated at 850 hPa, or approx. 1.5 km.

The calculated regional relative humidity (Table 5) was significantly lower outside the low ozone episodes than during the episodes. During all the episodes when the 6h average ozone concentration was below 6-7 ppbv, the regional relative humidity was above 70 %, otherwise it could drop to 30-40 % (Figure 5). This may support the chemical mechanism proposed by Mc Connell et al. (1992), where the scavenging of HBr and brominated organic compounds by ice crystals and aerosols releases Br_2, which is required to maintain a sufficiently high concentration of Br in the daytime atmosphere to produce the rapid ozone destruction observed.

Contrary to the local measurements, the average regional temperature was not significantly lower during the ozone episodes than outside the episodes, when the Arctic air was sampled (Table 5 and Figure 5). There are several possible explanations for this result:

The local and regional calculations did not cover the same time period, and therefore not the same episodes. Furthermore, the regional temperature data are one-day averages backwards along one trajectory, while the local measurements are averaged over 6h at one location.

Another explanation is that the regional temperatures refer to a fixed pressure surface, 925 hPa, and not a height level. A systematic relationship between surface pressure and ozone concentrations could therefore complicate the analyses based on temperature on a pressure surface. Such a relationship is observed, but the effect is small. An average pressure difference during and outside the low ozone episodes of at most 10 hPa (Table 4) corresponds to a vertical displacement of around 80 m of the pressure surface. With a constant potential temperature over this vertical distance, the temperature difference is only about 1° C, insufficient to explain why the average local temperature difference during and outside the episodes is 6° C, while there is no difference in the regional temperatures.

A third explanation is that the difference between the local and the regional temperatures reflects an inversion or stable boundary layer. The Zeppelin Mountain station is almost always below the 925 hPa surface. The average temperature data in Tables 4 and 5 then indicate that the average vertical temperature gradient was close to zero and even slightly positive during the low ozone episodes, whereas outside the episodes it was negative, which is the normal situation. This is consistent with the finding of a physical relationship between temperature and ozone as argued above, indicating a stable stratification.

The average regional wind velocity was slightly higher when sampled during than outside of the low ozone episodes (Table 5). In Figure 5 is shown the plot of the wind velocity against the ozone concentration for Arctic air only. A number of very high average wind speeds, above 15 m/s, occurred at times with 6h average ozone concentrations below 10 ppb. As for the high w-values, these cases all belong to the April 1993 episode (Section 4).

On the other hand, no low ozone episodes occurred when the average regional wind speed was below 3 m/s, whereas such low velocities were quite frequent for ozone concentrations between 30 and 40 ppbv. This indicates that the low ozone episodes measured on the Zeppelin Mountain are advected into the station so that a minimum wind is required to find a low ozone episode there.

3. Low ozone episodes and the link to other trace constituents

The theoretical explanation of the chemical mechanism causing the rapid surface ozone depletion in the Arctic in spring is not yet firmly established. A negative correlation between ozone and filterable bromine has been linked to the depletion process (Barrie et al., 1988, 1989). It was proposed that Br was produced in spring by photolysis of bromoform (CH_3Br), which is emitted from algae in the Arctic Ocean and which has been seen to accumulate over polar ice during winter (Bottenheim, 1990).

Reactions of NO_2 and N_2O_5 with Br components and sea-salt particles (NaBr) can also give rise to reactive Br (Finlayson-Pitts et al., 1983, 1990; Fan and Jacob, 1992). Release of Br^- originating from the snow pack, conversion to HBr and later formation of Br_2 by aerosols and ice crystal scavenging is another proposed mechanism (Mc Connell et al., 1992). A correlation between sulphate aerosols, NO_2, and ozone has been reported by some authors (Li et al., 1990).

Between ozone and some light hydrocarbons, a correlation has been found for some periods (Bottenheim et al., 1990; Jobson et al., 1993). The hydrocarbon measurements indicate an active chlorine chemistry during the events with ozone depletion (Jobson et al., 1993).

In Section 2 in this report was discussed the physical conditions for episodes with low surface ozone on the Zeppelin station. A similar description can be given of the chemical environment during such episodes, and provide some clues about the chemical process responsible for the ozone depletion. The measurement programme at the station includes several components that have been linked to the ozone depletion process, like sulphate aerosols and individual light hydrocarbons.

Compared to the meteorological data, however, a firm link between ozone and other chemical trace constituents is harder to establish. None of the other components are available as hourly values, and the lower frequency of the spot samples reduce the number of simultaneous measurements of ozone, NMHC (non-methane hydrocarbons) and chlorofluorocarbons.

Table 1 gives the measurements presented in this report, together with the period of measurements, the sampling frequency and the type of data. Total sulphate (not corrected for sea-salt) and sum ammonium are measured as 24h filter samples throughout the year, whereas the non-methane hydrocarbons and the freons are analysed in spot samples of air collected in the pressurized steel canisters.

The time series (Figure 2 and Appendix A) already discussed, showed in a qualitative way correlation between ozone and other components during certain time periods. In this section we analyse the chemical data in much the same way as the meteorological data, by defining days with low ozone episodes, and comparing the concentration of the other chemical components during low ozone episodes with the chemical composition outside of the episodes.

The filter samples of sulphate and ammonium normally refer to the 24h period from 8 UT to 8 UT the following day. Since many of the low ozone episodes lasted for shorter time periods than 24h, and we wanted to include those in the data analyses, a day with a low ozone episode was defined if a 6h running average concentration of ozone equal or below 10 ppbv in the period 8 UT-8 UT was found that day. This means that an unknown and perhaps significant part of the sulphate and ammonium concentrations found on days with low ozone episodes, has been collected outside of the low ozone event in time.

For the spot samples of CFCs and NMHC, we used another definition of days with a low ozone episode. A manual spot sample is collected in about 20 min., but the time of day when the sampling is done varies from day to day, in most cases it is between 8 am and 1 pm. Therefore, a low ozone episode was defined if the 6h average ozone concentration between 8 am and 1 pm that day was equal or below 10 ppbv. Using these definitions, the trace constituents were averaged into two groups: During and outside of days with low ozone episodes.

As for the meteorological parameters, we wanted to sort out effects due to sampling of different air masses. For sulphate and ammonium this was done in the same way as described above, by using only measurements on days when the Zeppelin mountain received Arctic air. For the NMHC and CFCs, the number of simultaneous measurements of ozone and these components was too small to sort the data in this way.

For all the trace components, only measurements on days between the first and the last occurrence of a low ozone episode each year were used.

3.1. Sulphate and ammonium

Although sulphate and ammonium have been measured since 1989 (Table 1) we chose to use observations only from the Zeppelin Mountain station, which was established in the autumn of 1989, to ensure a comparable set of data. Before September 1989 all measurements were taken near the sea surface close to the small settlement in Ny-Ålesund.

The average concentrations of sulphate and ammonium during and outside of the days with low ozone episodes are given in Table 6. Nearly all the sulphate measurements were above the detection limit, while several of the ammonium samples were below the detection limit of 0.05 μg (N)/m^3. All values below the detection limit were set equal to half of the detection limit.

Table 6: Average concentration of sulphate and sum ammonium ($NH_3 + NH_4^+$) during days with low ozone episodes and outside the episodes. $\bar{x}$ mean and s_x standard deviation, n_x number of cases (1991-1993). Z is a standard normally distributed statistic for the hypothesis that the two populations of data have the same mean value. Values in brackets mark non-significant numbers.

Parameter	$\overline{O}_3 \le 10$ ppb			$\overline{O}_3 > 10$ ppb			
	$\bar{x}$	s_x	n_x	$\bar{x}$	s_x	n_x	$\lvert Z \rvert$
Sulphate	0.35	0.18	40	0.26	0.18	102	2.6
" 1)	0.38	0.16	27	0.34	0.16	53	(1.0)
NH_3 (g) + NH_4^+ (s)	0.11	0.06	39	0.11	0.08	101	(0.4)
" 1)	0.10	0.03	27	0.11	0.05	53	(1.4)

Unit of sulphate and ammonium: µg (S)/m^3 and µg (N)/m^3

1) Arctic air only.

No detectable difference is seen between sum ammonium during or outside of the low ozone episodes, but the average sulphate concentration was significantly higher on a 5 % significance level during the episodes when using all measurements. When taking into account only measurements in Arctic air masses, the difference became smaller and was not statistically significant, because the average sulphate concentration was higher in air of Arctic origin than the average for all directions. The numbers in Table 6 therefore indicate that the negative correlation seen in some periods between sulphate aerosols and ozone is to some extent explained by the differences in transport directions during the low ozone events, compared to the average situation. These findings therefore do not support in a decisive way a cause-effect relationship between low ozone and high concentrations of aerosol sulphate.

Figure 6 shows the plot of daily averaged ozone vs. the daily average sulphate concentration for days with Arctic air only. The open boxes represent days with a low ozone episode (defined by a 6h average concentration less or equal to 10 ppbv during the day). It is interesting to note that of all the days with a *daily* ozone average concentration of 10-12 ppbv or less, the sulphate concentration was above a level of 0.25 µg (S)/m^3, except for one single case when an extremely small sulphate concentration was observed.

This may indicate that the chemical process that deplete surface ozone in the Arctic requires a certain amount of sulphate aerosol particles in order to proceed, and when this limit is exceeded the sulphate concentration is unimportant. Model calculations by Fan and Jacob (1992) showed that heterogeneous chemistry including Br on sulphuric acid particles could produce a very rapid depletion of surface ozone, but no sensitivity calculations for the dependence of the ozone loss on different particle concentrations or size distributions were made. McConnell et al. (1992), as mentioned above, argued that ice crystals and aerosol particles were required for rapid ozone loss to occur.

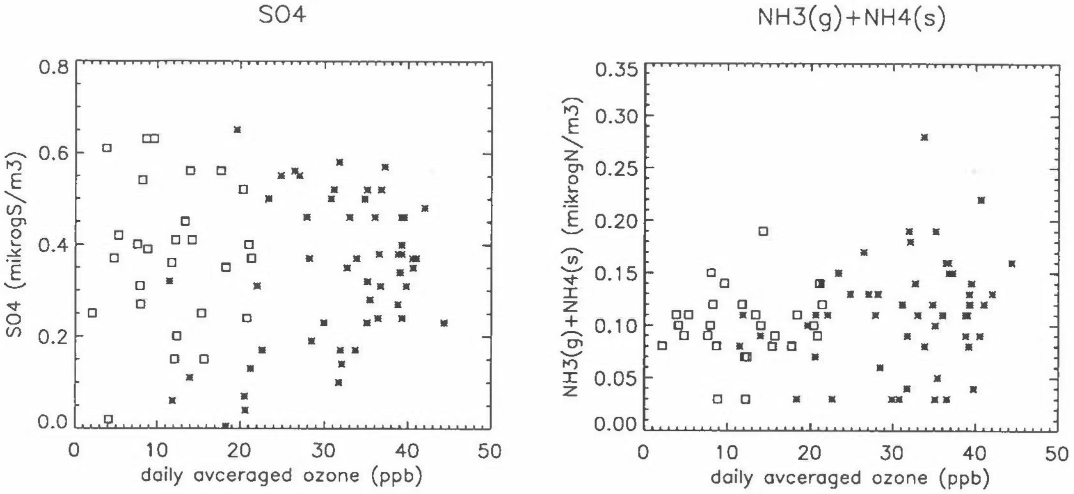


Figure 6: Scatter plots of daily averaged ozone concentrations (ppb) vs. daily average filter samples of total sulphate ($\mu g\ S/m^3$) and sum ammonium, NH_3 (g) + NH_4 (s) ($\mu g\ N/m^3$), on the Zeppelin Mountain 1990-1993. Only data between the first and the last low ozone episode each year are shown, and only for Arctic air masses (see text for explanation). Open boxes represent days with a low ozone episode.

3.2. Halocarbons

The measurements of halocarbons at the Zeppelin Mountain are scattered. Two years of data (1991-1992) was available for this study. The averaging of the measurements into two groups, during and outside days with a low ozone episode, was made as described above, by defining a low ozone episode on the basis of the 6h average from 8 am-1 pm.

The resulting average values are given in Table 7. Due to the low number of data, no attempt was made to consider Arctic air masses only. As shown by the table, there were only 3 days with simultaneous measurements of ozone and halocarbons during events with low ozone. Although the number of data is small, the averages indicate no difference in the concentrations of these halocarbons during and outside of the low ozone episodes.

Table 7: Average concentration of halocarbons (ppt) during and outside of low ozone episodes (1991-1992). $\bar{x}$ mean and s_x standard deviation, n_x number of cases.

	$\overline{O}_3 \le 10$ ppb			$\overline{O}_3 > 10$ ppb		
	$\bar{x}$	s_x	n_x	$\bar{x}$	s_x	n_x
CFC-11	287	15	3	289	19	24
CFC-113	54	3	3	54	3	26
Triclorethane	228	6	3	233	17	26

$\overline{O}_3$ means the average ozone concentration between 8 UT and 13 UT.

These compounds are very stable in the troposphere, and the measured surface concentrations only reflect the degree of mixing from the emission areas. The mean concentrations of halocarbons observed on the Zeppelin Mountain inside and outside of the low ozone episodes indicate that these anthropogenic substances are not suitable to distinguish between air with low and "normal" ozone.

3.3. Non-methane hydrocarbons

Some of the NMHC at Spitsbergen show a very pronounced seasonal cycle, with a strong decline in the concentration during spring. This can be seen from the time series in Figure 2 and Appendix A. When comparing NMHC measured during episodes of low ozone with measurements made at other times in spring, it is therefore crucial to sort out the seasonal variation in some way. Instead of tabulating just the concentration averages during and outside of the episodes, the relative deviation from the 14 days' running mean concentration was calculated for each day for each component.

The 14 days' running mean concentration for day number i was defined by:

$$\bar{c}(i) = \frac{1}{n} \Sigma\, c(j),\ j = i-7, \ldots, i+7$$

Only the days without a low ozone episode was used in the calculation of this running mean.

The relative deviation from the running mean on day i was then (in %):

$$x(i) = 100\left(\frac{c(i) - \bar{c}(i)}{\bar{c}(i)}\right)$$

where *c(i)* is the actual observed concentration on day *i*.

These data (the x's) were then analysed in two groups as before: During and outside of episodes with low ozone. The resulting average values are listed in Table 8.

Although the number of NMHC measurements during low ozone episodes is limited (6 for benzene, 8 for the rest), the difference between the average values during and outside of the episodes, was remarkably large for many of the NMHC. I- and n-butane, i- and n-pentane, acetylene and propane on an average had 50-70 % lower concentrations than the running mean on days with a low ozone episode. During the episodes the average deviation from the running mean concentration was more than one sample variance from the running mean for all of the non-methane hydrocarbons except for ethene, propene and benzene. This indicates that the lower NMHC concentrations observed during the events of low ozone are highly significant for these compounds.

Table 8: Per cent deviation of NMHC from the mean NMHC concentration during and outside of low ozone episodes. See text for definition. $\bar{x}$ *mean and* s_x *standard deviation,* n_x *number of cases (1991-1993).*

	$\overline{O}_3 \le 10$ ppb			$\overline{O}_3 > 10$ ppb		
	$\bar{x}$	s_x	n_x	$\bar{x}$	s_x	n_x
C_2H_6	-31	6	8	0.2	10	42
C_2H_4	-20	30	8	-3	45	42
C_2H_2	-66	11	8	0.2	18	42
C_3H_8	-55	7	8	-0.3	19	42
C_3H_6	-11	34	8	-4	48	42
n-C_4H_{10}	-65	9	8	-1	24	42
i-C_4H_{10}	-56	10	8	-2	22	42
n-C_5H_{12}	-63	18	8	-3	49	42
i-C_5H_{12}	-63	16	8	-5	36	42
C_6H_6	0	7	6	-2	17	21

For ethene and propene the concentrations were lower than the running mean during the ozone episodes, but since the sample variances in the data are large, which indicates that there is a wide range of measured concentrations, it cannot be concluded that these deviations are significant.

The average benzene concentration did not change during the ozone episodes compared to outside of the episodes. This is an important point, since it excludes the possibility that the lower NMHC concentrations seen during the events of low ozone, were due to very clean air masses in these periods. No significant biogenic sources of benzene are known, while a large fraction of the anthropogenic sources of benzene are the same as for e.g. acetylene, and the chemical lifetimes with regard to OH are similar for these two compounds (Harley et al., 1992, Nelson et al., 1983).

This is evidence for another removal process for NMHC than OH oxidation which removes ethane, propane, acetylene, the butanes and pentanes simultaneously with the depletion of surface ozone. The NMHC depletion during episodes of low ozone concentrations has been reported at other Arctic sites (Jobson et al., 1993; Bottenheim et al., 1990), and it has been argued that oxidation by free chlorine radicals could explain the observed loss of some of the NMHC. The large reduction in the above mentioned components compared to the unaffected benzene concentration is consistent with the large difference in reactivity of these compounds with respect to Cl.

In Figure 7 the relative deviation of the NMHC from the running mean is plotted vs. the daily average ozone concentration. The open boxes represent days with a low ozone episode. For e.g. acetylene and i- and n-butane the episode days cluster in the lower left corner of the diagrams, expressing large deviations from the running mean concentration, whereas between ozone and benzene no link is seen.

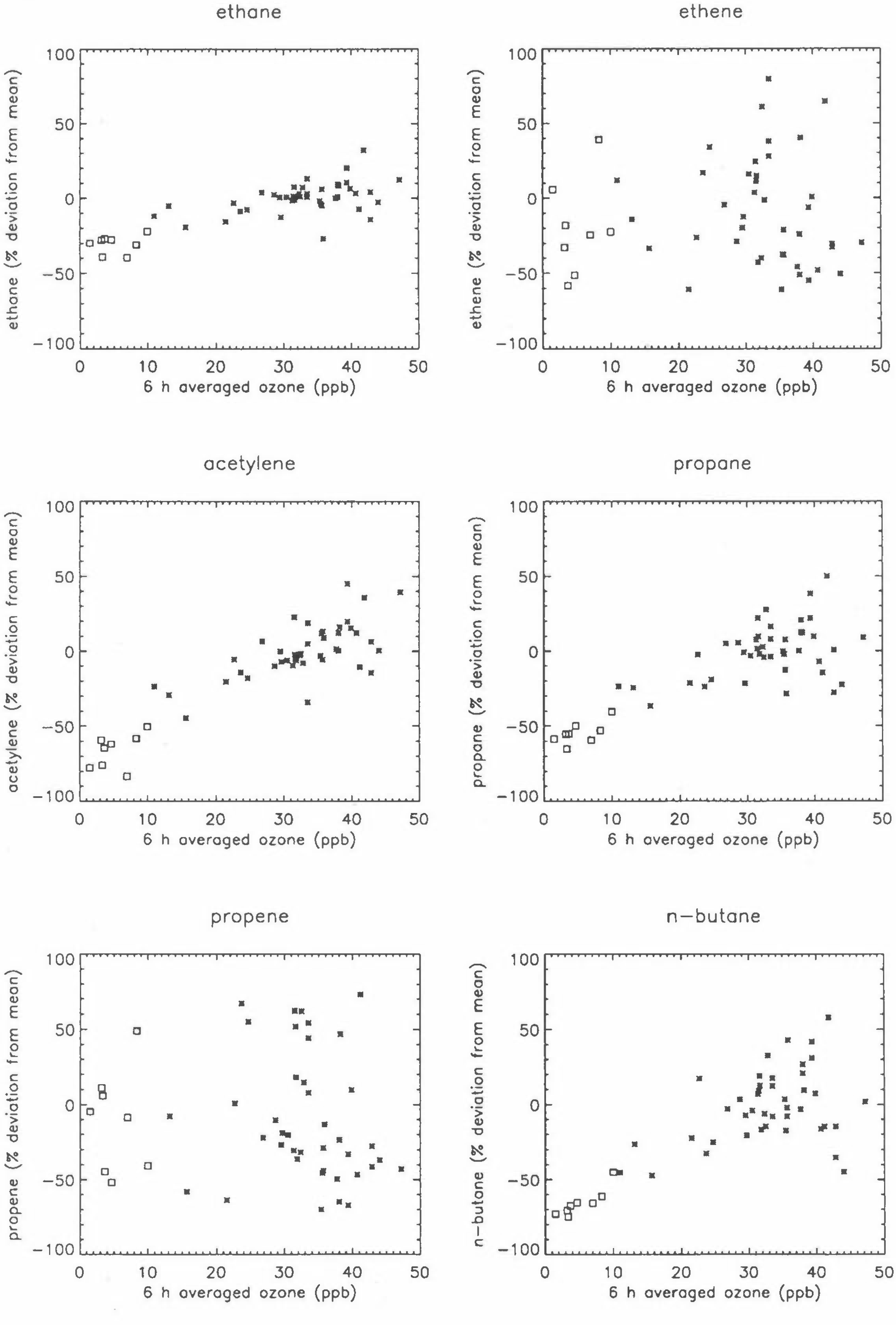


Figure 7: Scatter plots of the 6h average concentration (8 a.m.-1 p.m.) of ozone (ppb) vs. the percentage deviation of hydrocarbons from the 14 days' running mean concentration. Data include measurements from 1992-1993 for benzene, and 1991-1993 for the other hydrocarbons. Only data between the first and the last low ozone episode each year are shown, and only for Arctic air masses (see text for explanation). Open boxes represent days with a low ozone episode.

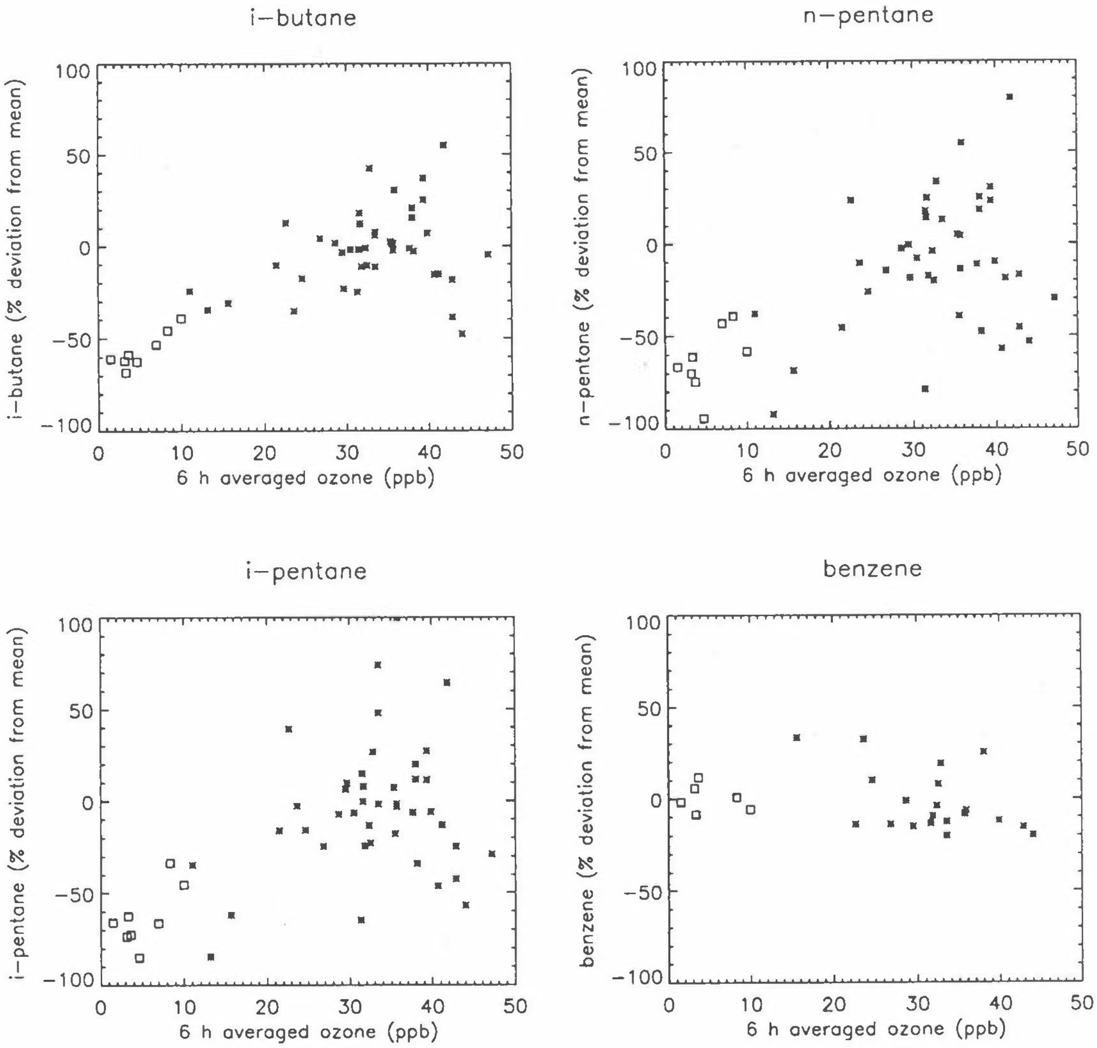


Figure 7, cont.

It is also interesting to note a tendency of a linear relationship between the daily average ozone and the NMHC concentration deviation. In other words, the sign of the process seen in Figure 7 is not observed in a few episodes only, but is apparent for a large fraction of the measurements. This indicates that related chemical processes are depleting both ozone and many of the non-methane hydrocarbons in the Arctic spring.

For a further confirmation of the different chemical environments acting, the concentration ratios between different compounds can be analysed (Roberts et al., 1984, 1985). Jobson et al. (1993) plotted i-butane/n-butane vs. i-butane/propane and found two clusters of data points: One indicating air masses with OH controlled chemistry, with a constant ratio i-butane/n-butane, and another indicating air masses with Cl controlled chemistry, where the ratio i-butane/propane was constant. I-butane and n-butane are almost equally reactive with regard to OH, while propane and i-butane have similar reaction rate coefficients with respect to Cl.

The same analysis was attempted for the Zeppelin data, but the resulting picture was not very clear. Instead, in Figure 8 is shown the plot of i-butane/n-butane vs. the ratio i-butane/benzene. The reactivity with OH is similar for i- and n-butane, while n-butane is about 50 % more reactive with respect to chlorine than is i-butane, and benzene is almost non-reactive with respect to Cl.

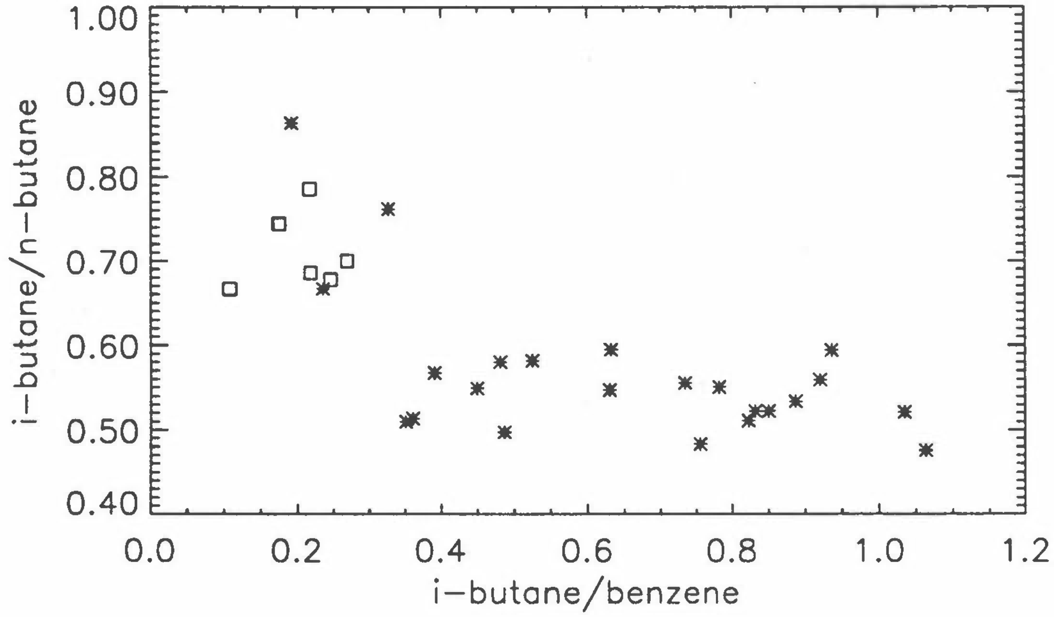


Figure 8: Scatter plot of the concentration ratio i-butane/benzene vs. the concentration ratio i-butane/n-butane. Only data between the first and the last low ozone episode (1992-1993) are shown, and only for Arctic air masses (see text for explanation). Open boxes represent days with a low ozone episode.

The measurements on days with a low ozone episode is marked as open boxes in Figure 8. It is obvious that for the measurements taken on the episode days, the i-butane/n-butane ratio is much larger (about 0.7) than compared to the other measurements (about 0.55), which is in agreement with the faster reaction rate coefficient of n-C_4H_{10} + Cl compared to i-C_4H_{10} + Cl. The i-butane/n-butane ratio of 0.55 as a "normal" value is close to what is found at other locations (Jobson et al. 1993).

Three of the data points marking "normal ozone" days cluster together with the data points for the low ozone days. The 6h average ozone concentration for two of these three cases was 14-16 ppbv, which is far below the normal value of 30-40 ppb, although not low enough to be counted as a low ozone episode ($\leq$ 10 ppbv).

For the oxidation of non-methane hydrocarbons we can write the following expression for each of the measured NMHC components when the effects of mixing are ignored:

$$c_i = c_{0,i} \cdot e^{-(k_i \int x dt)} \quad \textit{for component } i$$

where c_i is the measured concentration
$c_{0,i}$ is the initial concentration before the oxidation started
k_i is the reaction rate coefficient
x is the concentration of the oxidant, like Cl or OH

Then ln (c_i/c_0) should be linearly dependent on k_i and the slope should be equal for all the components.

For each of the eight low ozone episodes with measurements of NMHC, we performed a regression calculation between k_i and ln (c_i/c_0) based on the measurements of ethane, acetylene, propane, n-butane, i-butane, n-pentane, i-pentane and a dummy value for benzene. The initial concentrations $c_{0,i}$ of each component was estimated by the 14 days' running median concentration (based on observations outside low ozone episodes only), which was slightly lower than the running mean concentration. Benzene was only analysed in the last six episodes, but in all these episodes the ratio c_i/c_0 was between 0.9 and 1.1, and since the reactivity with Cl is low, this small deviation may well reflect other processes than the ineffective chlorine oxidation. A ratio of 0.95 for benzene was therefore applied in the analyses of all the 8 episodes.

Since acetylene turned out to be an outlier in the regression analysis, another regression analysis was made where acetylene was taken out. The regression without acetylene was named "case B". In "case A" all the components were included.

Table 9 lists the resulting parameters. r is the linear correlation coefficient, and p is the probability that the regression is not significant. The analysis was made for the OH reaction rate coefficient as well as for the Cl reaction rate coefficient (although extensive oxidation with OH is unlikely due to the observed behaviour of benzene).

When acetylene was included, the regression was significant for half of the cases when Cl chemistry was assumed, while the regression for OH was less significant. However, when acetylene was left out of the analysis, the significance improved dramatically, and Table 9 shows that about 95 % of the variance in the data, estimated by r^2, was solely explained by chlorine oxidation in 5 of the 8 episodes. Furthermore, the regression was statistically significant on a 90 % significance level in all the episodes. The regression calculations without acetylene are shown in Figure 9. The calculated negative values of the constant term, a_0, indicate that the initial concentrations generally were slightly too high. This may reflect the somewhat lower NMHC concentrations in Arctic air compared to the overall average.

Table 9: Calculated regression parameters for the equation

$$ln\left(\frac{c_i}{c_0}\right) = a_0 + b \cdot k_i$$

Date	Case A				Case B					
	OH		Cl		OH		Cl			
	r	p	r	p	r	p	r	p	a_0	b
5 May 1991	0.1	77	0.2	67	-0.6	18	-0.70	8	-0.2	-0.03
24 May 1991	-0.83	2	-0.84	2	-0.77	4	-0.99	0	-0.01	-0.05
11 May 1992	-0.56	20	-0.71	7	-0.67	10	-0.98	0	-0.12	-0.03
20 April 1993	-0.81	3	-0.84	2	-0.83	2	-0.97	0	-0.04	-0.05
21 April 1993	-0.85	1	-0.86	1	-0.87	1	-0.98	0	-0.01	-0.06
22 April 1993	-0.3	53	-0.38	40	-0.7	6	-0.97	0	-0.08	-0.05
29 April 1993	0.3	49	0	100	-0.1	76	-0.67	10	-0.22	-0.02
30 April 1993	-0.08	87	-0.22	64	-0.4	31	-0.82	2	-0.27	-0.04

r = linear correlation coefficient
p = probability (%) of no significant regression
c_i = measured concentration
c_0 = 14 days' running median concentration (without the low ozone days)
k_i = reaction rate coefficient ($*10^{11}$ for Cl, $*10^{13}$ for OH)
Case A: C_2H_6, C_2H_2, C_3H_8, n-C_4H_{10}, i-C_4H_{10}, n-C_5H_{12}, i-C_5H_{12}, C_6H_6
Case B: As case A, without C_2H_2.

This analysis we think gives a strong indication of chlorine oxidation acting in the same environment where ozone depletion takes place. As suggested by Jobson et al. (1993) the deviation of acetylene from the regression line, may be explained by oxidation with Br in addition to Cl, since acetylene is much more reactive with regard to bromine than the other components.

The b coefficients in Table 9 are equal to the expression: $-\int xdt$, and may be used to estimate the average concentration of the oxidizing agent, i.e. Cl, if a time constant for the depletion process can be estimated. Assuming one day exposure to the chlorine and bromine environment, an average Cl concentration of $3 \cdot 10^4$-$6 \cdot 10^4$ molecules/cm^3 was found.

The calculated regression lines in case B, without acetylene, were also used to calculate the difference between the acetylene concentration expected from Cl oxidation alone, compared to the measured acetylene concentration. If it is assumed that this difference in concentration is due to the bromine oxidation of acetylene, a concentration of Br may be calculated as well, from the expression :

$$\ln (C_2H_{2i}/C_2H_2^*) = -k \cdot Br \cdot T$$

where

C_2H_{2i} = measured acetylene concentration
$C_2H_2^*$ = expected acetylene concentration from the regression
k = reaction rate coefficient for C_2H_2 + Br
T = time constant

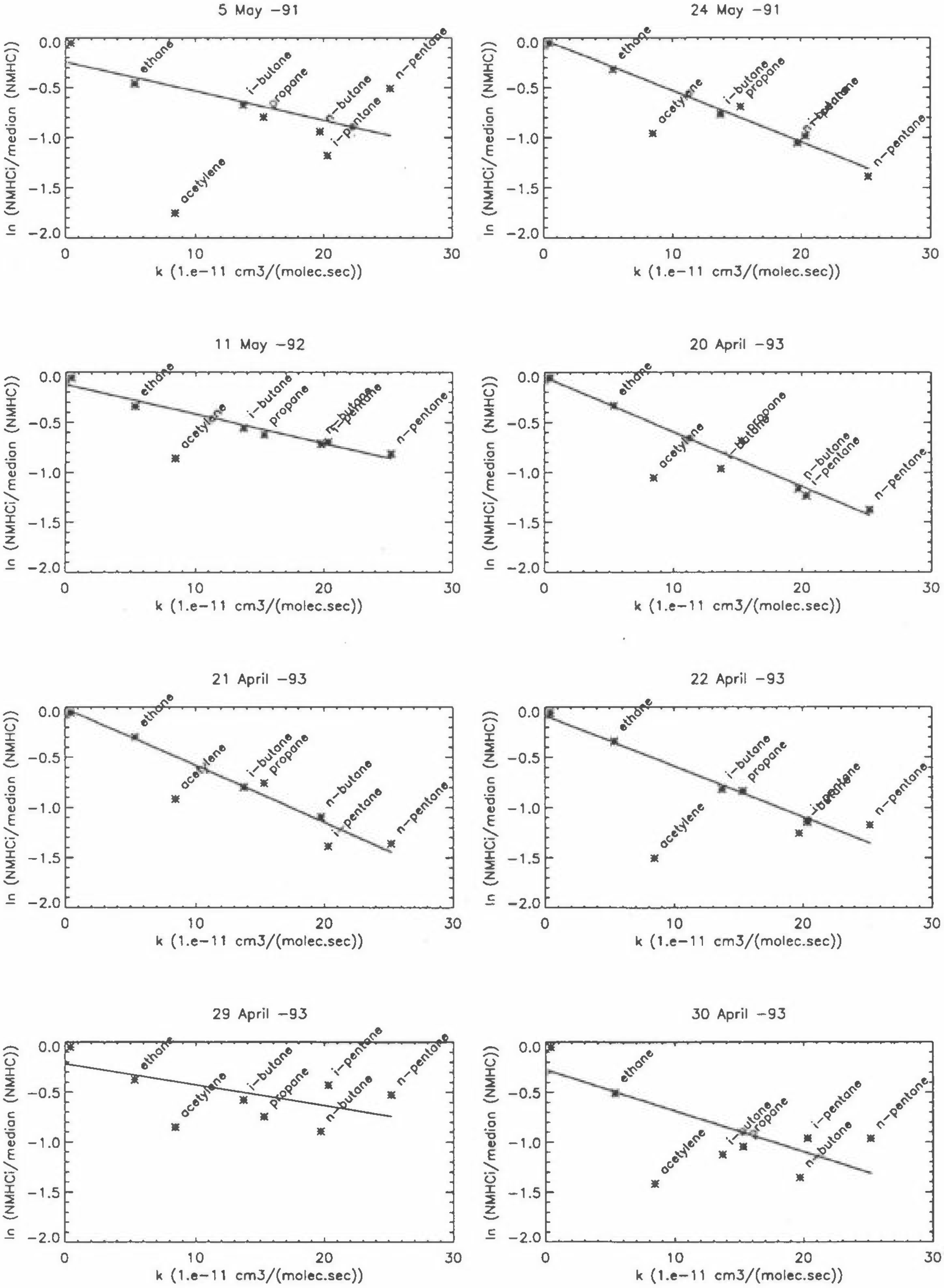


Figure 9: Linear regression of $\ln\left(\frac{c}{\text{median } c}\right)$ where c = NMHC concentration, median = 14 days running median, vs. the reaction rate coefficient with chlorine (10^{-11} cm^3 $molec^{-1}$ s^{-1}) for 7 NMHC on 8 days of low ozone episodes. Acetylene is only plotted, but was not used in the linear regression calculation. For benzene $\left(\frac{c}{\text{median } c}\right)$ was set to 0.95 in all 8 cases.

Assuming a time constant of one day as above, the (gaseous) Br concentration was calculated to vary from $3 \cdot 10^7 - 1 \cdot 10^8$ molecules/cm^3. This range of values is of the same order of magnitude as the measurements of filterable bromine (Barrie et al., 1989) and particulate excess Br (Li et al., 1990).

4. Vertical and horizontal extent of ozone depleted air during an episode

The time series of hourly ozone concentrations measured on the Zeppelin Mountain station, 474 m a.s.l. (Figure 2 and Appendix A) showed that episodes with ozone depleted air could last for several days, even with significant wind. This indicates that the boundary layer ozone "holes" occur not only on a small scale, but are regional in extent. Ozone depletion is frequently observed at the altitude of the Zeppelin station, a further indication that the ozone depleted air masses are not confined to a shallow layer close to the ocean surface. Bottenheim et al. (1990) argue that it is most likely that the O_3 destruction takes place in a boundary layer column of air and not directly at the surface. It is therefore important to identify the vertical extent of the air masses with reduced ozone concentrations.

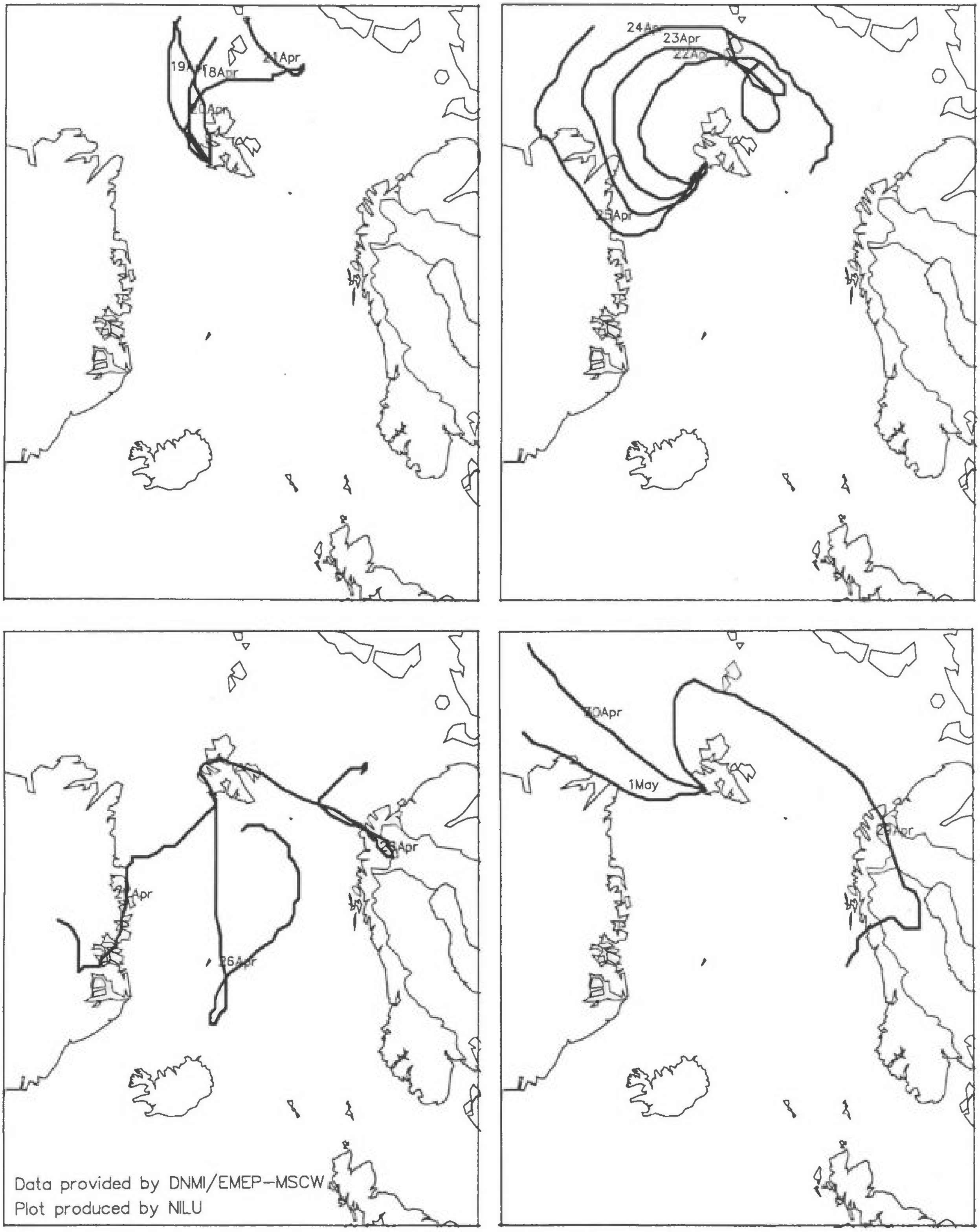
To do so, the ozone balloon soundings launched occasionally for several years at Ny-Ålesund by Alfred Wegener Institut and on Bear Island (19°E, 74.5°N) by the Norwegian Meteorological Institute and NILU were investigated. The long episode of ozone depletion measured at the Zeppelin station in late April 1993 is used to give an example of these soundings.

4.1. Meteorology and ozone sondes during the April 1993 episode

4d trajectories for the period 18 April-1 May 1993 are shown in Figure 10. From 18-25 April a low pressure system which moved from northern Finland to the Barents Sea was gradually filled. On 18 and 19 April the wind field over Spitsbergen was from N-NE and rather strong, whereas on the 23 April the low was reduced and there was only small pressure gradients over a large region from Northern Scandinavia/Russia to the North Pole. The weak cyclone was accompanied by scattered snow showers, and the surface temperature was between -8° and -20° C in the area.

From 26-28 April a new low pressure system moved up the Denmark strait from SW, over the Greenland Sea and passed directly over Spitsbergen, causing a pronounced shift in the transport direction and bringing milder air masses from the Atlantic Ocean into the station on the Zeppelin Mountain, as seen form the trajectories on Figure 10. As this low moved E of Spitsbergen on 29 April-1 May, the wind shifted back to N-NE again, accompanied by a temperature drop and more snow on the island. The pressure field on 29-30 April was sufficiently strong to produce wind speeds of about 10 m/s at the surface.

In Figure 11 is shown the result from the ozone sondes launched from Ny-Ålesund and Bear Island between 18 April and 1 May 1993. In the figure are given the wind velocity, relative humidity, potential temperature (theta) and



Data provided by DNMI/EMEP-MSCW
Plot produced by NILU

Figure 10: EMEP trajectories on 925 hPa arriving at the Zeppelin Mountain at 12 UT on 18 April–1 May 1993. The trajectories are 4 days long, but shorter if they hit the grid boundary. The arrival dates are 18, 19, 20 and 21 April (upper left), 22, 23, 24 and 25 April (upper right), 26, 27 and 28 April (lower left) and 29, 30 April and 1 May (lower right).

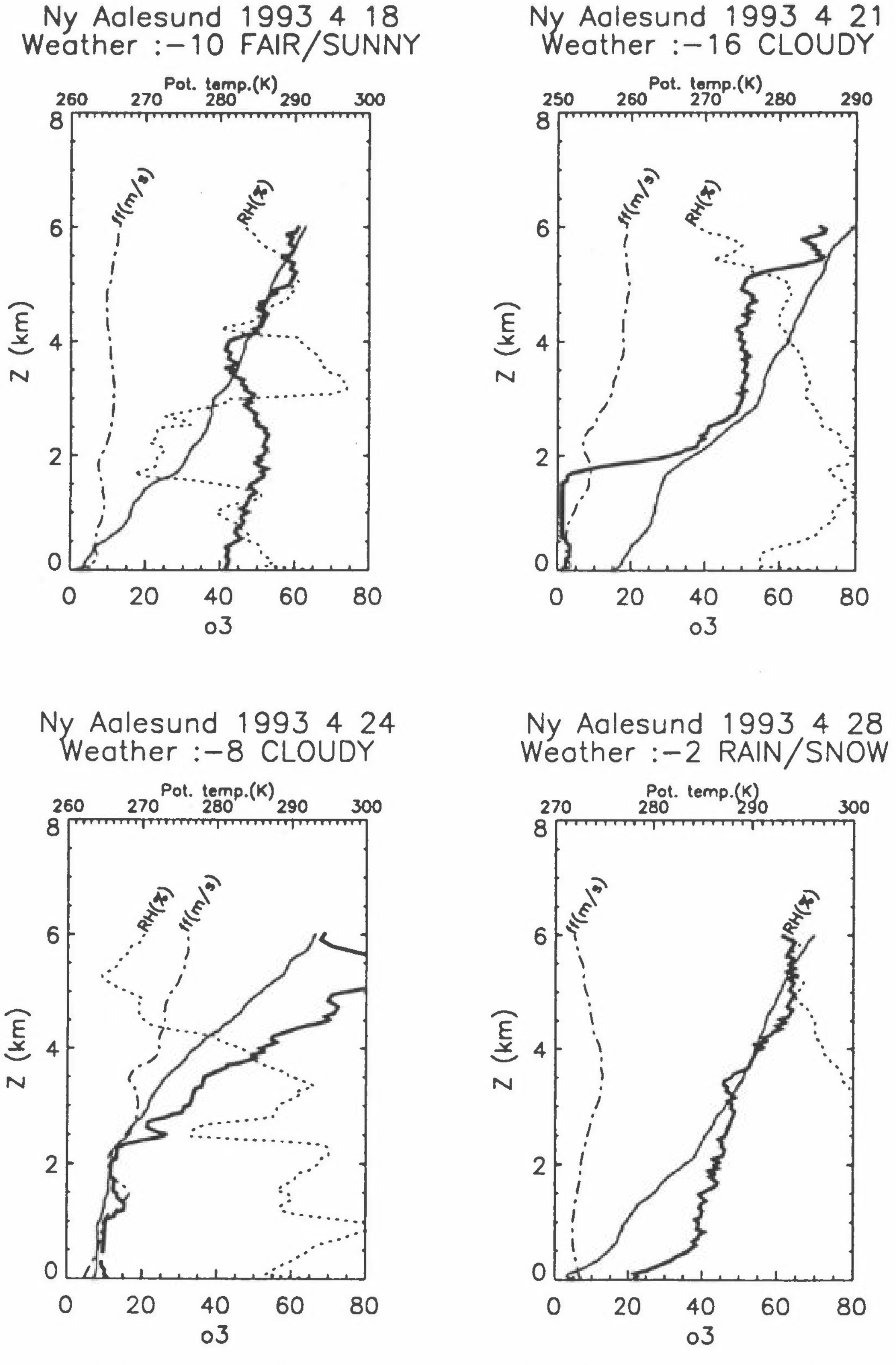


Figure 11: Measurements by ozone soundings at Ny-Ålesund and Bear Island 18 April–1 May 1993 from the surface to 6 km. Thick line is ozone mixing ratio (ppbv), thin full line is potential temperature (K), dotted line is relative humidity (%, referring to the values of the lower x-axis) and dash-dotted line is wind speed (m/s, also referring to the values at the lower x-axis). Ozone soundings in Ny-Ålesund were performed in collaboration with the Alfred Wegener Institute, and on Bear Island with the Norwegian Meteorological Institute.

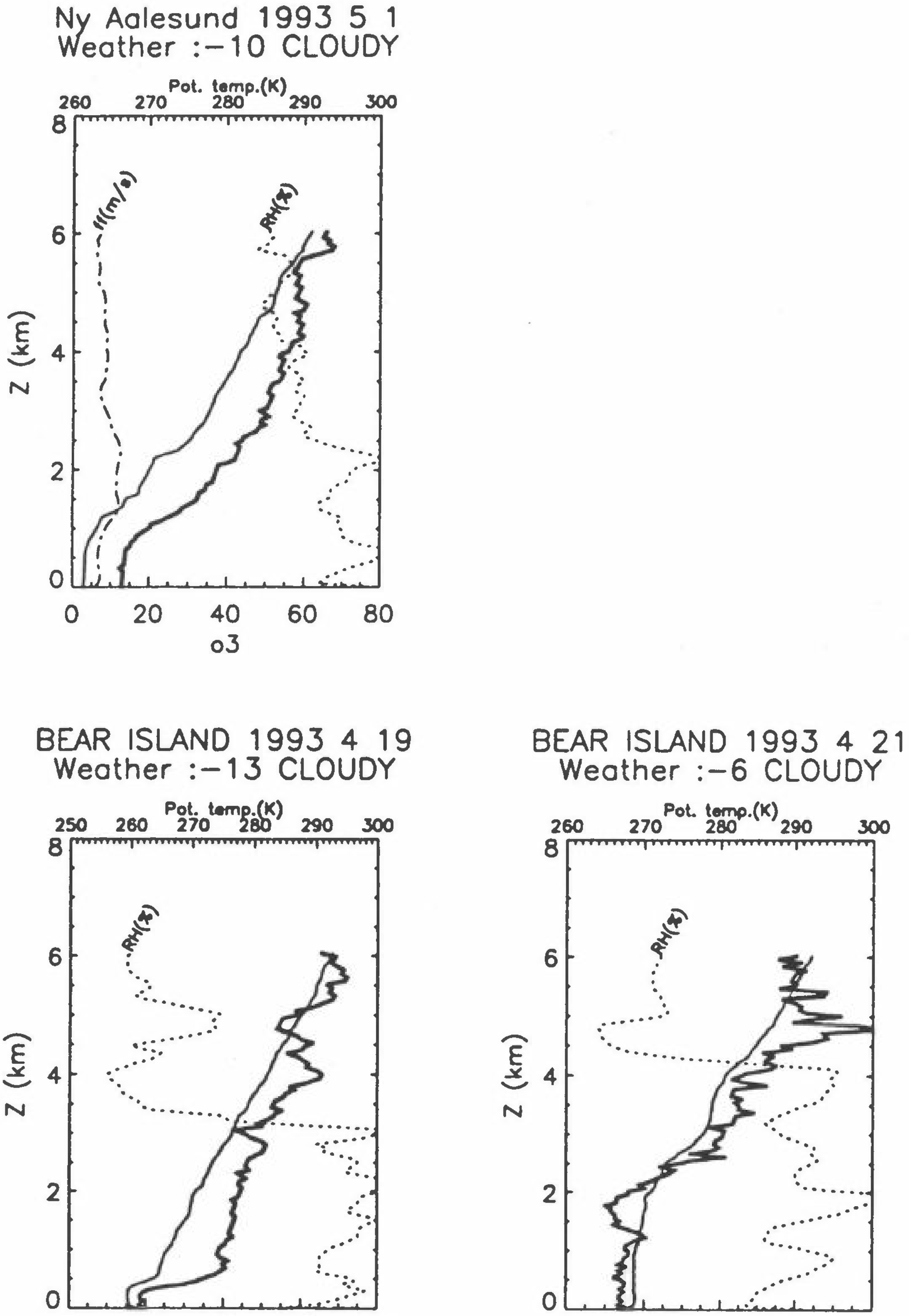


Figure 11, cont.

ozone mixing ratio from the ground (close to the ocean surface) and up to 6 km. The weather condition at the time of launch, as noted by the observer releasing the balloon, is given in the plot as well.

Neither the sounding nor the surface measurements showed any sign of ozone depletion on 18 April, although there was a steady transport from NE. As seen from the potential temperature stratification (Figure 11) a mechanically mixed layer probably existed up to 500 m above the ground, where an increase in the vertical gradient of theta must have suppressed any further vertical exchange. The air was dry, with only 40-60 % relative humidity, and the observer reported fair and sunny weather. This corresponds to the finding above that no low ozone episodes occurred while the relative humidity was below about 70 %.

The time series of ozone, meteorological parameters and other trace constituents measured on the Zeppelin Mountain given in Figure 12 show that the low ozone episode started on 19-20 April when the wind slowed down, and the relative humidity increased. Then, during a period of 4-5 days, before the new low pressure system approached, the measured ozone concentrations were close to zero most of the time.

The positive correlation between ozone and acetylene is clearly seen from Figure 12. A positive correlation between ozone and ethane, propane and n-butane and a negative correlation between ozone and sulphate is seen as well, but less pronounced.

The soundings made on 21 and 24 April show that ozone was being depleted in a layer from the ocean surface and up to a considerable height. The vertical gradient in the potential temperature on 21 April was not very different from that on the 18, but the wind speed was lower, the relative humidity was higher (60-80 %), and the observer reported cloudy weather. On this date, 21 April, almost all ozone was destroyed up to 2 km altitude, whereas above that level the concentration was normal. The sharp vertical gradient in ozone at 2 km coincided with a shift in the vertical gradient of theta, marking the top of a mixed layer.

On the 24 April, the ozone depletion had gone even further up, to 3-4 km if 40 ppbv is taken as a normal concentration. The small vertical gradient in theta probably allowed mixing up to nearly the same height. The weather was cloudy, but the relative humidity was lower than on 21 April.

The passage of the new low pressure system is clearly seen from the sounding on 28 April. The surface temperature rose to -2 °C, precipitation was falling, and the ozone concentration was almost normal, except for a shallow layer near the surface where the concentration was reduced to 20 ppbv. This reflects that a very different air mass had arrived on Spitsbergen. The surface ozone concentration measured on the Zeppelin Mountain increased to around 40 ppbv 26-28 April.

In the last sounding shown from Ny-Ålesund, from 1 May, the cyclone had passed Spitsbergen and the air flow from N caused lowered ozone concentrations once again. The similarity between the curve for the potential temperature and

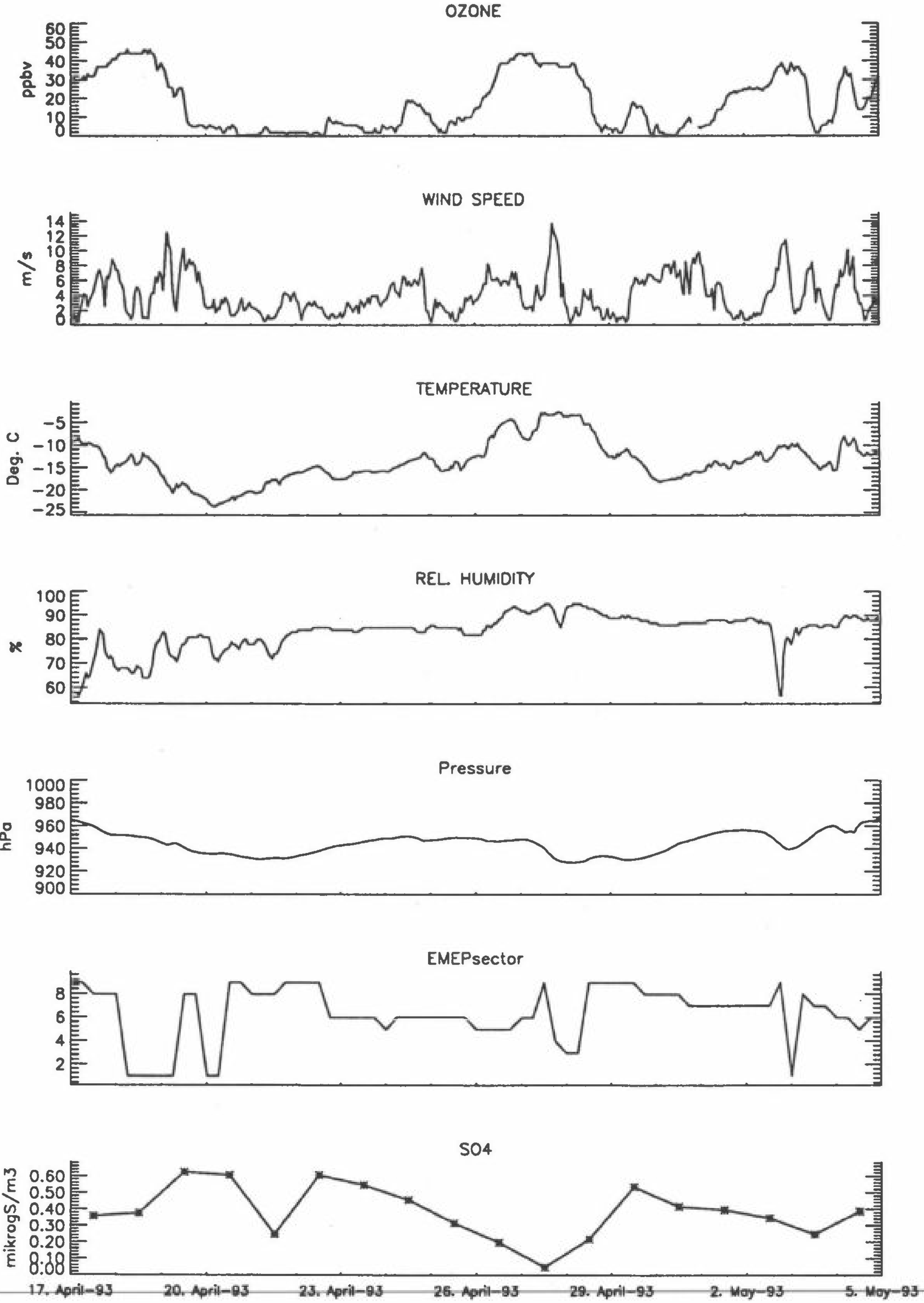


Figure 12: *Time series of ozone, meteorological parameters and other trace constituents measured on the Zeppelin Mountain. Also shown is the calculated transport sector for 17 April-5 May 1993. 8 transport sectors of 45° width was used, counted clockwise with 1 being NE, 2 E, etc. Sector 9 is the undefined sector. The sectors are shown in Figure 1.*

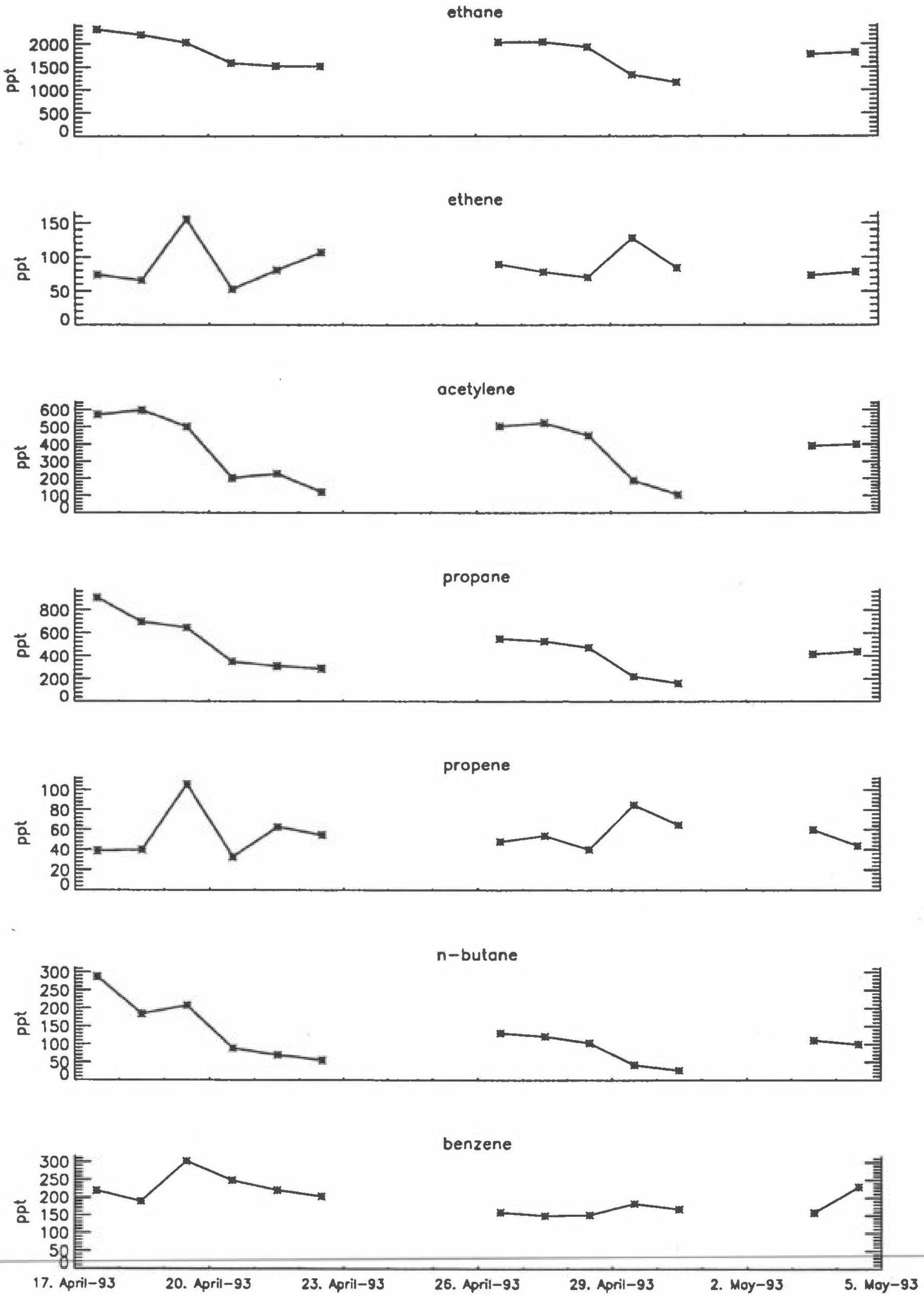


Figure 12, cont.

that for ozone concentration 1 May is striking and shows the importance of vertical stability.

In the same way as for the sounding from Ny-Ålesund 21 April, the sounding from Bear Island, 500 km to the south, for 21 April showed that the ozone concentration was significantly reduced up to about 2 km height, although the concentration was around 15 ppbv, and not zero, as in Ny-Ålesund. The potential temperature was almost constant with height in this layer above Bear Island. The higher ozone concentration on the more southerly station Bear Island than in Ny-Ålesund, may indicate mixing and a partly filling of the surface ozone hole, due to heating from the ocean, while transported from north.

The magnitude of the Arctic tropospheric ozone loss is important for estimating the influence on the tropospheric ozone budget. Whereas the vertical extent of the reduced ozone may be examined by regular balloon soundings, estimates of the horizontal scale require aircraft measurements. This has not been performed at Ny-Ålesund. The time series of ozone and the wind speed may, however, give an indication of the horizontal extent of the areas with reduced ozone.

During the April 1993 episode, the ozone concentration was below 10 ppbv continuously in the 6 d period from 20 April-25 April. The soundings reported wind speeds of 2-8 m/s in the ozone reduced layer on 21 April and 5-15 m/s on 24 April. Assuming an average wind speed of 5-8 m/s this corresponds to a horizontal distance of 2 500-4 000 km depleted in ozone.

The circular trajectories for 22-24 April (Figure 10) encompass a circle of the order of 10^3 km in diameter, or 10^6 km^2 in area. The persistent low ozone concentration on the Zeppelin Mountain could suggest that this whole area was depleted in ozone to some extent.

The low ozone concentration apparent from the sounding at Bear Island, 480 km south of Ny-Ålesund, is consistent with this.

When the depleting process stops, diffusion will gradually replenish the depleted surface ozone. The extent of ozone depletion in the area encompassed by the trajectories is therefore dependent on the size of the area where the ozone depletion takes place. The persistence of this April episode, coupled with modest wind speeds, however, strongly indicates that the areas of reduced surface ozone are of regional, and not local, extent.

If it is assumed that it takes 1d to fill in the surface ozone hole when the destruction mechanism is inactive, then the surface layer loss mechanism corresponds to an ozone loss flux of about $2\cdot10^{12}$ molecules/cm$^2\cdot$s (40 ppb x 2 km/1d). This is about 20 times the average source of ozone through the troposphere.

From the ozone soundings at Bear Island, Ny-Ålesund, Sodankylä in Finland as well as from Antarctica over several years, Taalas et al. (1993) calculated monthly average vertical profiles, and the average seasonal variation of ozone at different heights for each station. Taalas et al. noted a strong ozone inversion at the two Arctic sites (Ny-Ålesund and Bear Island) near the surface in *summer*

(June and July), which they linked to a possible remote marine sink, and a maximum in ozone in spring. There are several possible reasons why the episodes of low surface ozone are not reflected in these average profiles. These events are of an episodical nature and the the highest, as well as the lowest, surface ozone concentrations are observed in Arctic during spring. An average of many soundings will therefore easily mask out the low ozone episodes.

Taalas et al. (1993) presented several anomalies in addition to the average sonde profiles. One of these soundings, for Sodankylä in Northern Finland (67.4°N, 26.6°E) on 31 May 1989 is a situation with transport from the Arctic, with a cold surface layer up to 1.4 km with high relative humidity. The sounding showed a pronounced ozone minimum in this surface layer, and the partial pressure of ozone was below 2 mPa (20 ppb).

This case is very similar to the low ozone episodes at Ny-Ålesund, and suggests that air masses depleted in surface ozone may be transported over a considerable distance to lower latitudes.

Their finding of an ozone sink over the remote marine ocean may suggest that the chemical mechanisms which cause the pronounced ozone loss during spring in the Arctic are active during summer as well, but less pronounced or acting over a much deeper layer since the lower troposphere then is not as stratified as in the spring.

5. Acknowledgement

This work was partly funded by the Norwegian Research Council (Division for environment and development), and by the Department of Environment to the Norwegian Polar Institute for running the research station on the Zeppelin Mountain. Thanks are due to the local engineers in Ny-Ålesund, to DNMI, Oslo for meteorological data support (EMEP/MSC-W) as well as for the ozone sonde launches on Bear Island. Ozone soundings in Ny-Ålesund were performed in collaboration with the Alfred Wegener Institute, and on Bear Island with the Norwegian Meteorlogical Institute.

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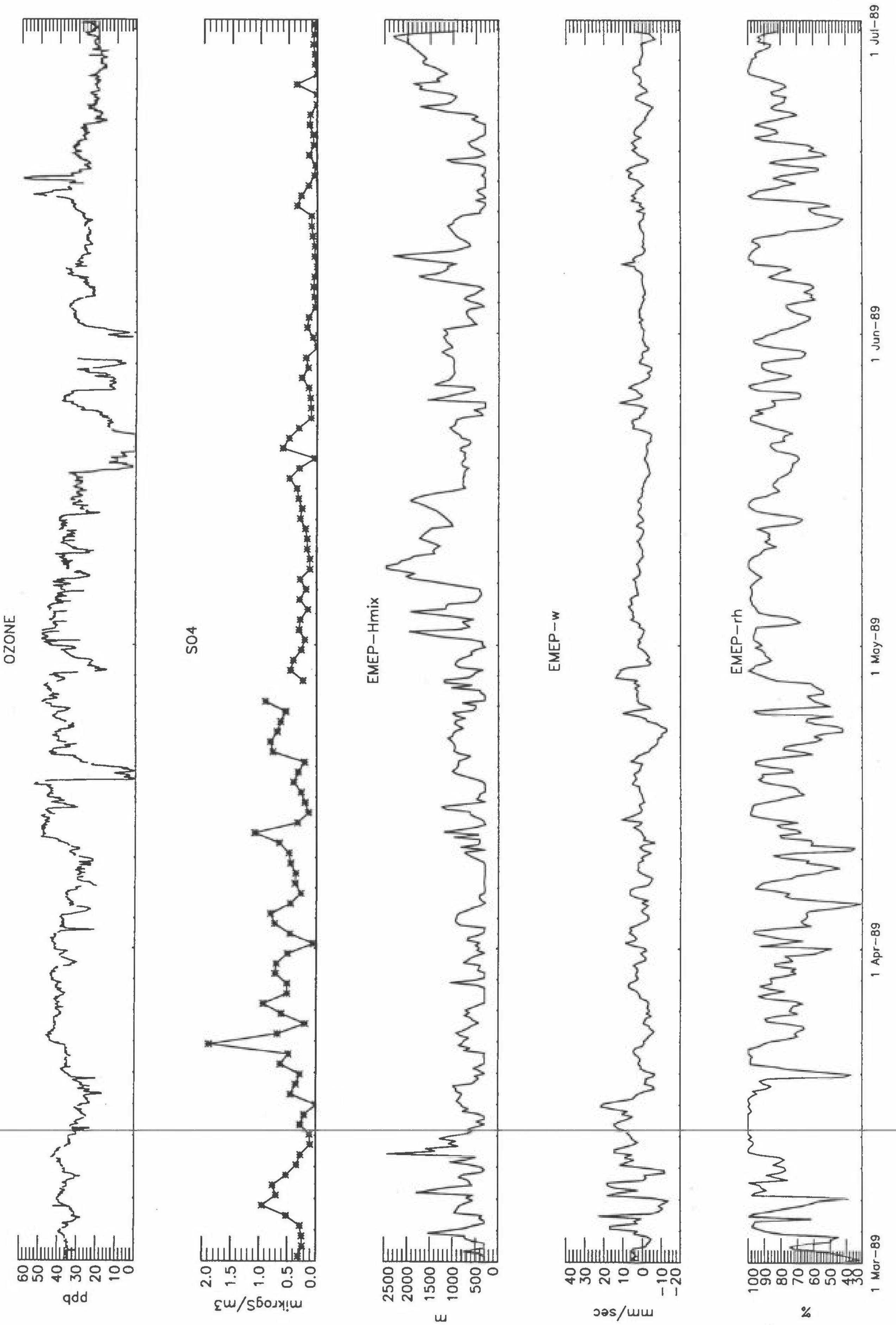
Appendix 1

Time series of ozone, total sulphate, sum ammonium, hydrocarbons, halocarbons, N_2O and meteorological parameters measured on the Zeppelin Mountain and Ny-Ålesund 1 March – 1 July in the years 1989–1993. In 1989 the measurements were done at Ny-Ålesund, near the sea surface, later the measurements are from the Zeppelin Mountain (474 m asl).

1,1,1-trichlor means 1,1,1-trichlorethane. Also shown is the calculated averages along 24h backwards EMEP trajectories of regional meteorological data. EMEP-Hmix is the average mixing height, EMEP-w is the average vertical velocity at 850 hPa, EMEP-rh is the average relative humidity, EMEP-temp is the average temperature and EMEP-wind is the average wind speed. EMEPsector is the 45° transport sector counted clockwise from NE. Sector 1 = NE, 2 = E, 3 = SE, 4 = S, 5 = SW, 6 = W, 7 = NW, 8 = N and 9 is an undefined sector.


OZONE
ppb
60
50
40
30
20
10
0
SO4
mikrogS/m3
2.0
1.5
1.0
0.5
0.0
EMEP-Hmix
m
2500
2000
1500
1000
500
0
EMEP-w
mm/sec
40
30
20
10
0
-10
-20
EMEP-rh
%
100
90
80
70
60
50
40
30
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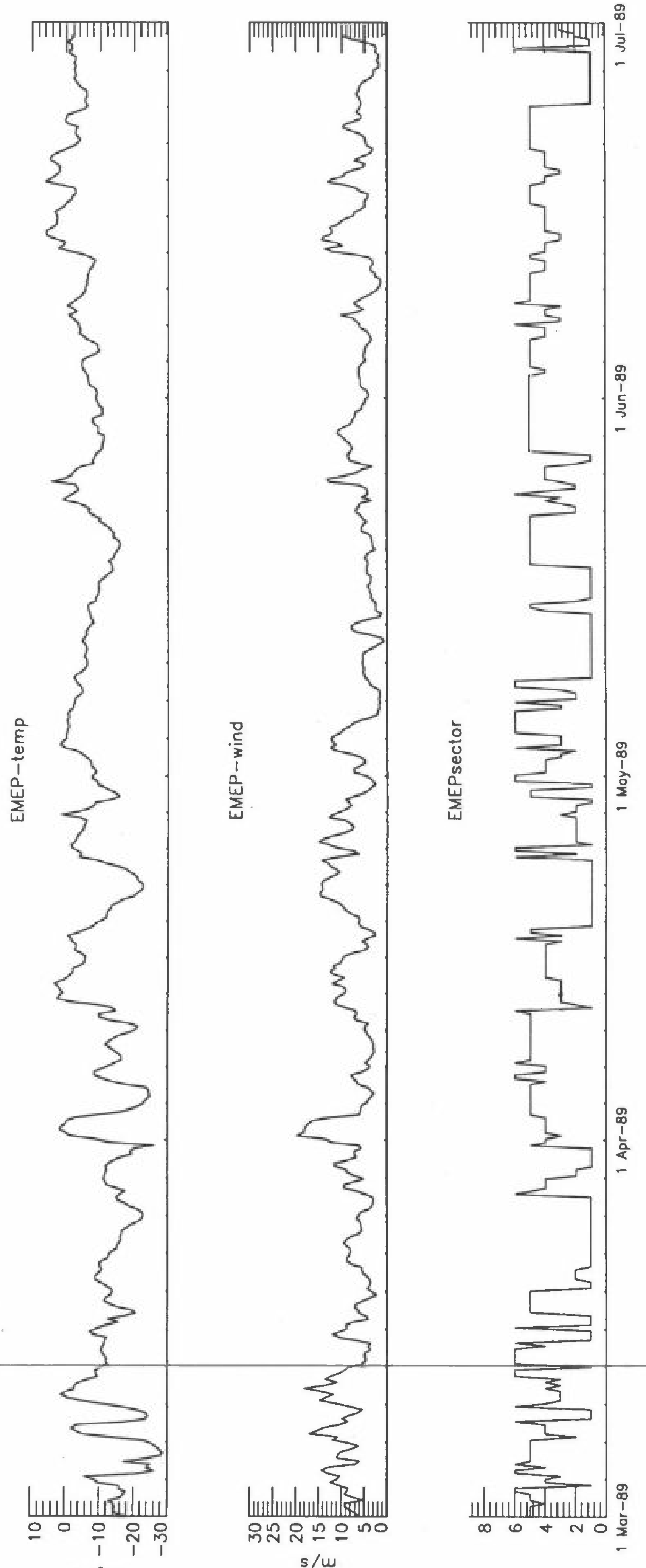
1 Apr-89
1 May-89
1 Jun-89
1 Jul-89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deg. C
10
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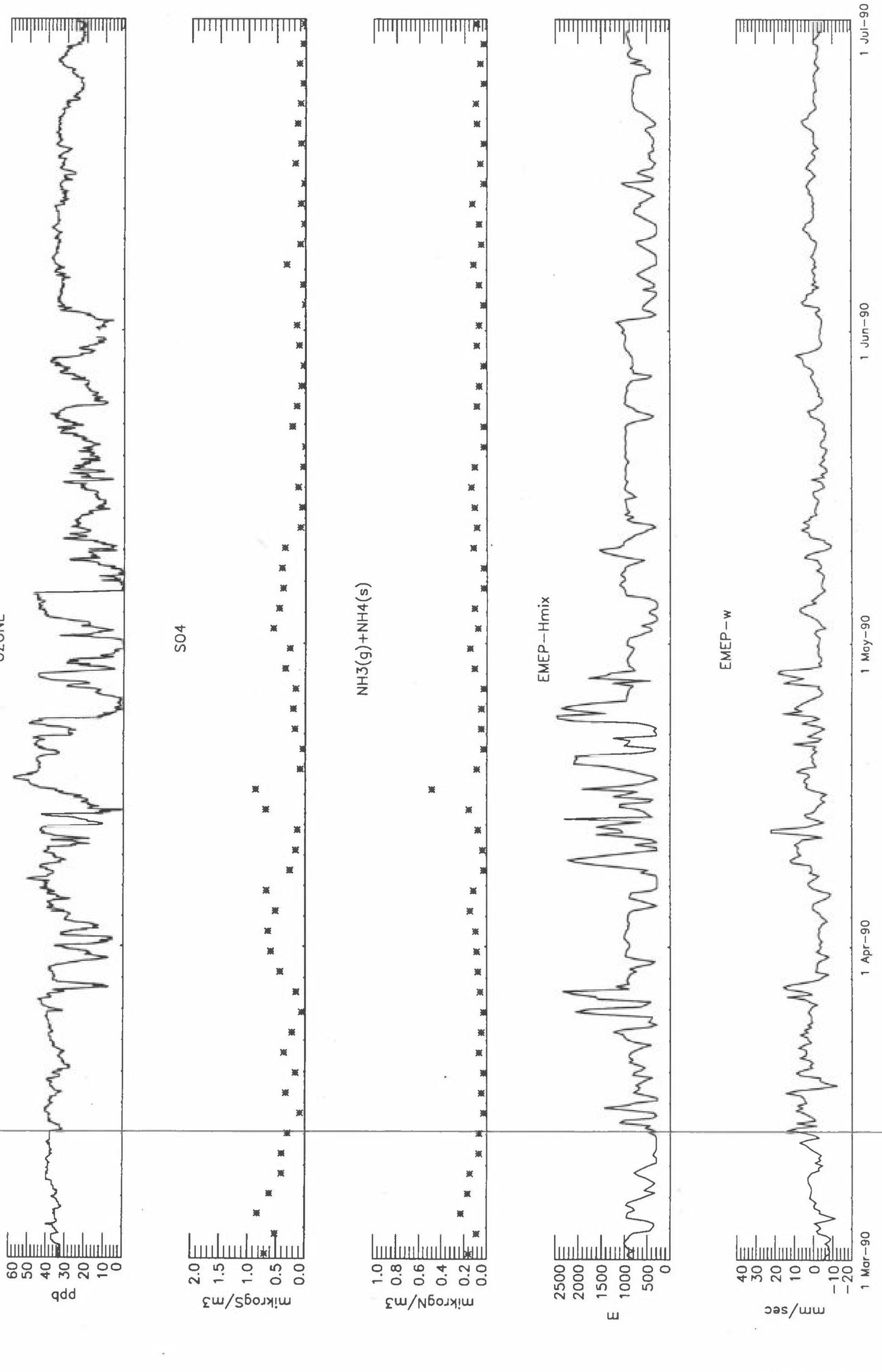
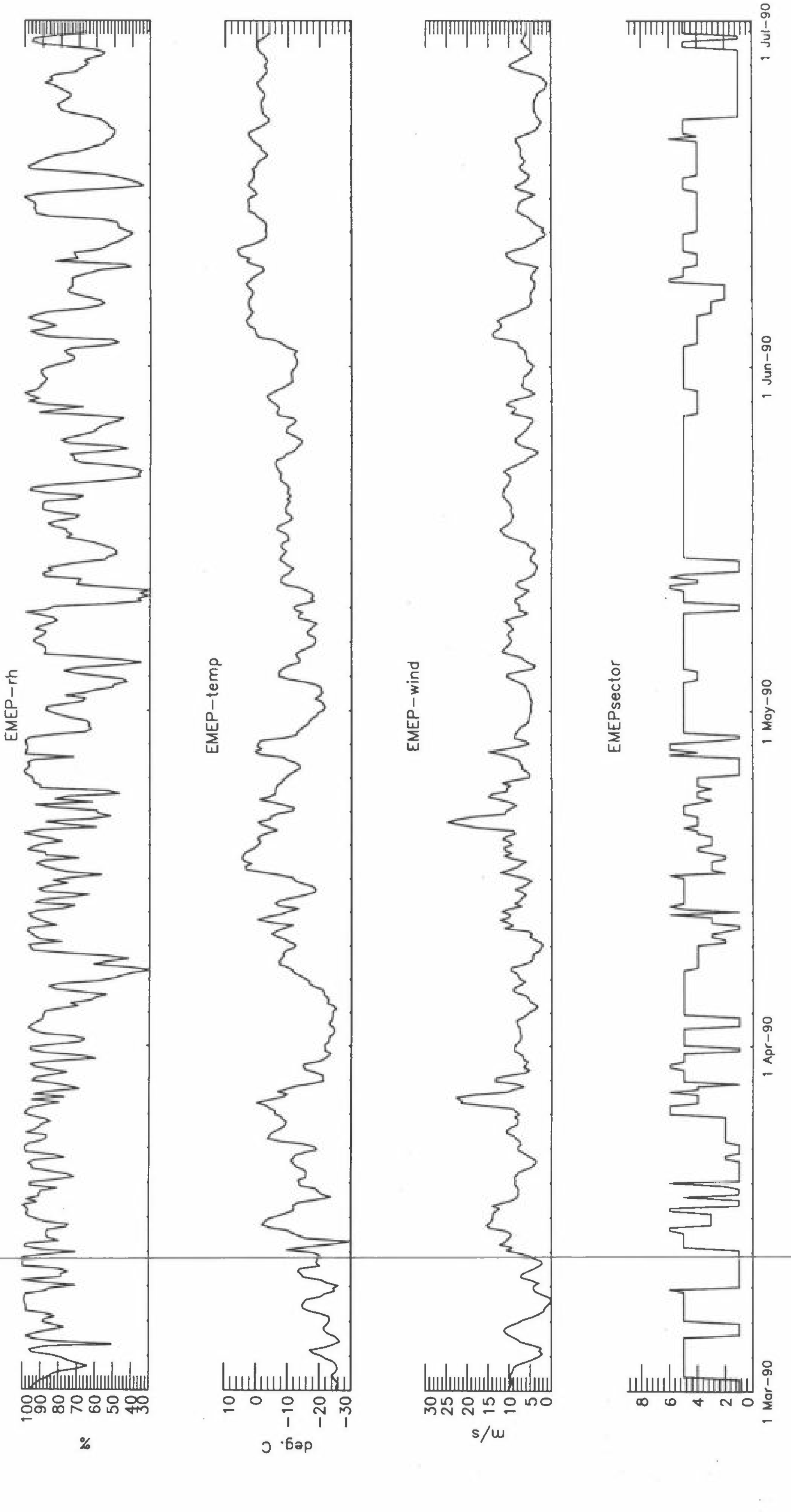
-20
-30
EMEP-wind
m/s
30
25
20
15
10
5
0
EMEPsector
8
6
4
2
0
1 Mar-89
1 Apr-89
1 May-89
1 Jun-89
1 Jul-89


OZONE
ppb
60
50
40
30
20
10
0
SO4
mikrogS/m3
2.0
1.5
1.0
0.5
0.0
NH3(g)+NH4(s)
mikrogN/m3
1.0
0.8
0.6
0.4
0.2
0.0
EMEP-Hmix
m
2500
2000
1500
1000
500
0
EMEP-w
mm/sec
40
30
20
10
0
−10
−20
1 Mar-90
1 Apr-90
1 May-90
1 Jun-90
1 Jul-90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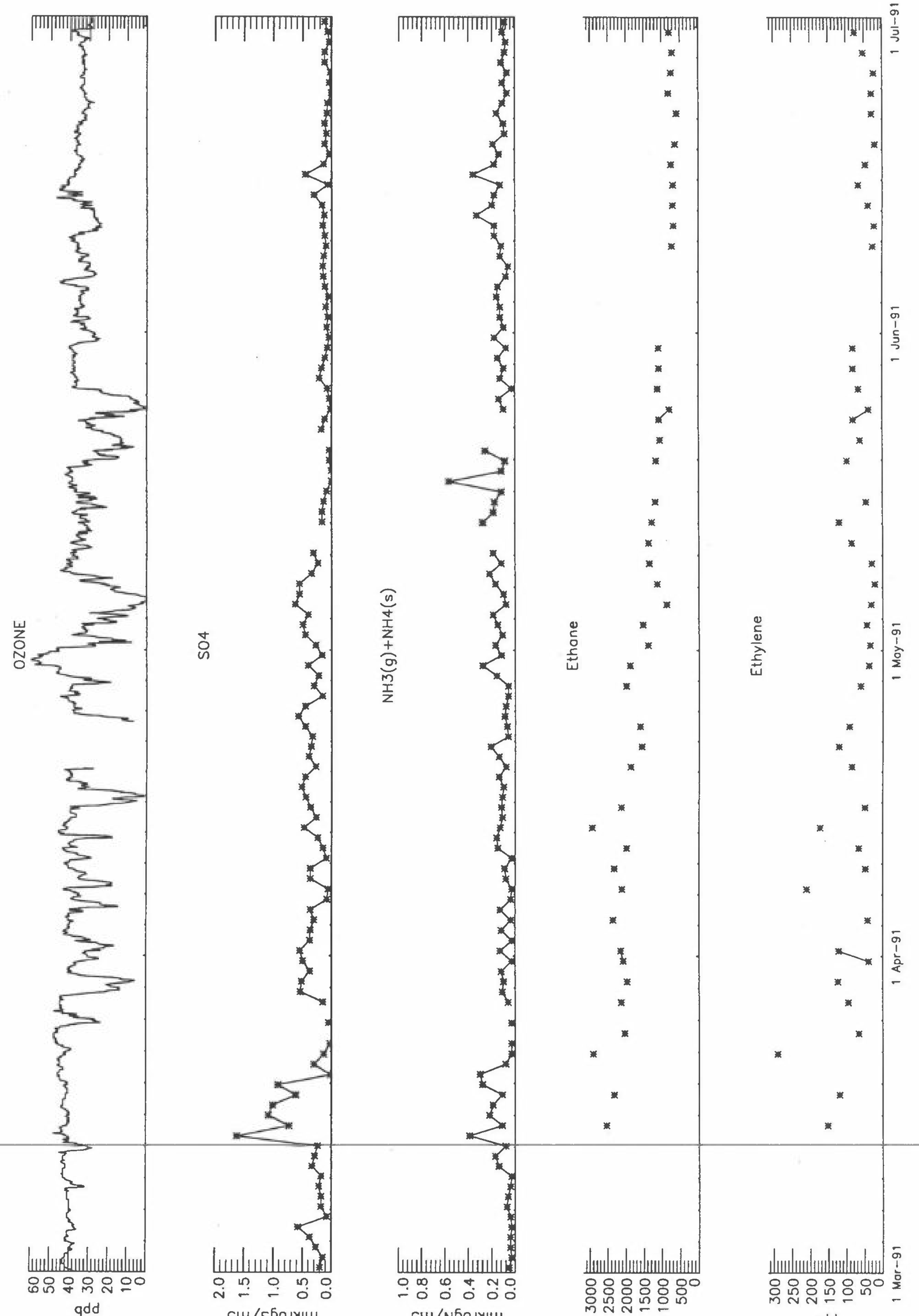
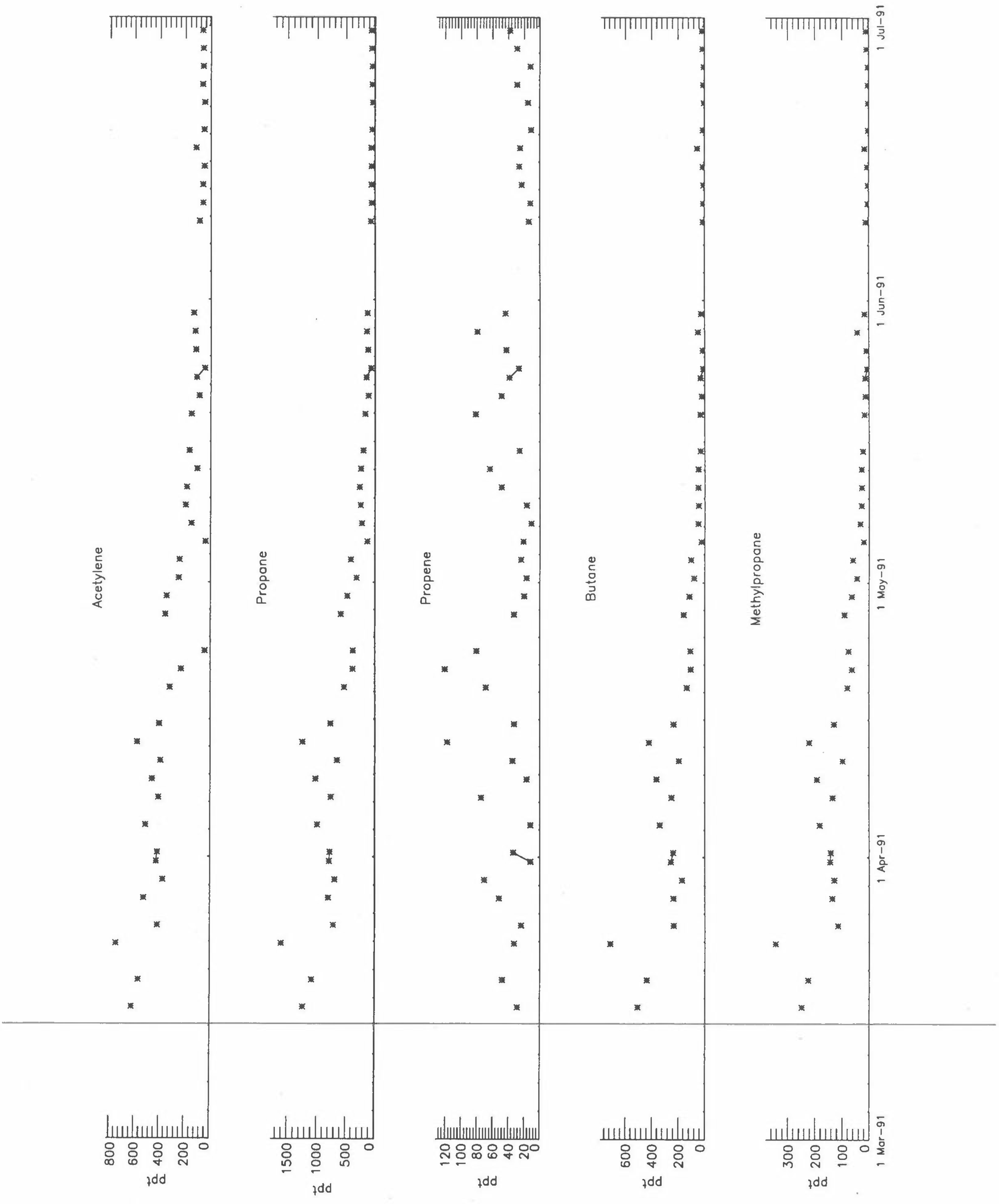
%
100
90
80
70
60
50
40
30
EMEP-temp
deg. C
10
0
-10
-20
-30
EMEP-wind
m/s
30
25
20
15
10
5
0
EMEPsector
8
6
4
2
0
1 Mar-90
1 Apr-90
1 May-90
1 Jun-90
1 Jul-90


OZONE
ppb
60
50
40
30
20
10
0
SO4
mikrogS/m3
2.0
1.5
1.0
0.5
0.0
NH3(g)+NH4(s)
mikrogN/m3
1.0
0.8
0.6
0.4
0.2
0.0
Ethane
ppt
3000
2500
2000
1500
1000
500
0
Ethylene
ppt
300
250
200
150
100
50
0
1 Mar-91
1 Apr-91
1 May-91
1 Jun-91
1 Jul-91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ppt
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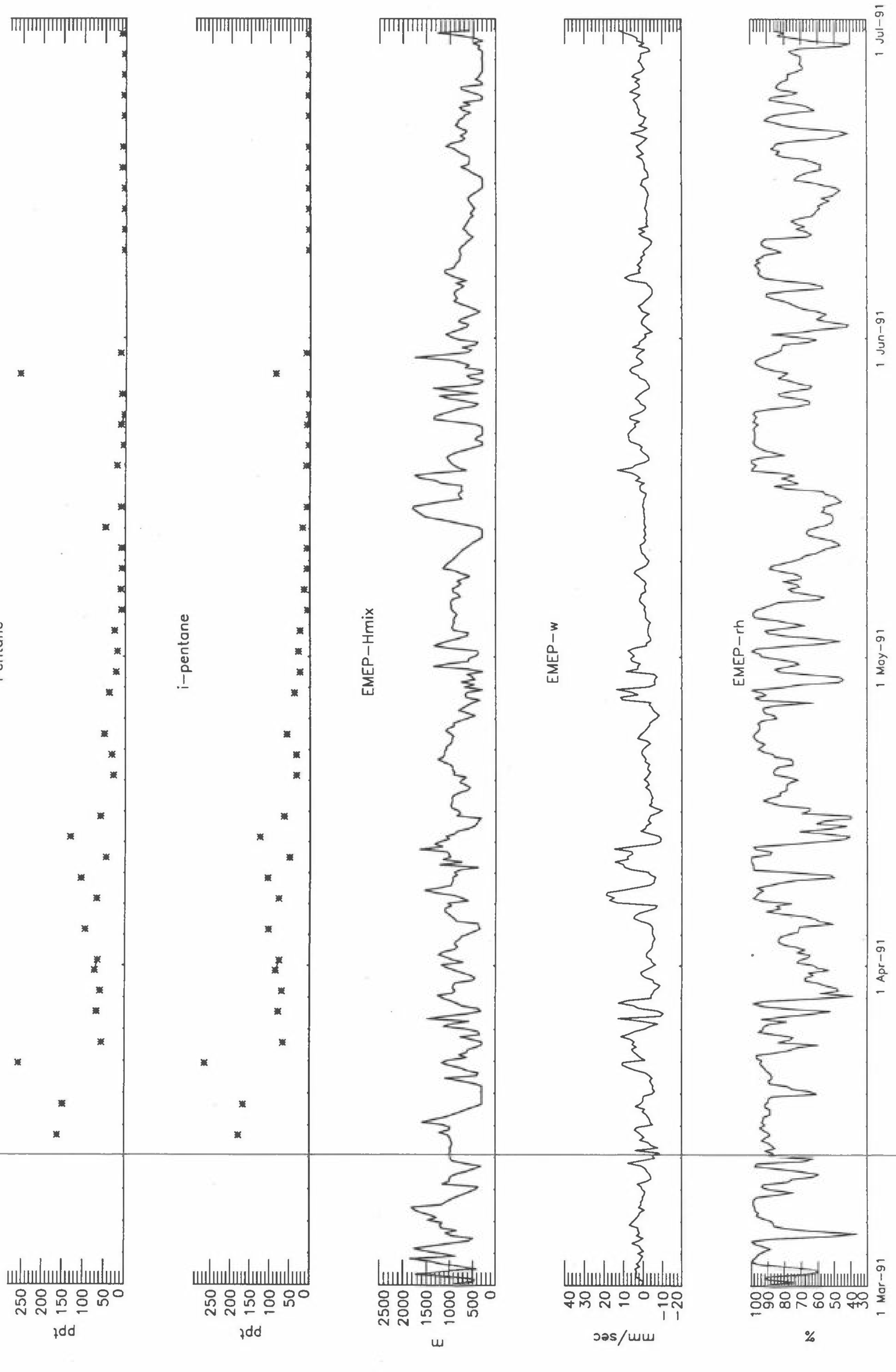
600
400
200
0
Propane
ppt
1500
1000
500
0
Propene
ppt
120
100
80
60
40
20
0
Butane
ppt
600
400
200
0
Methylpropane
ppt
300
200
100
0
1 Mar-91
1 Apr-91
1 May-91
1 Jun-91
1 Jul-91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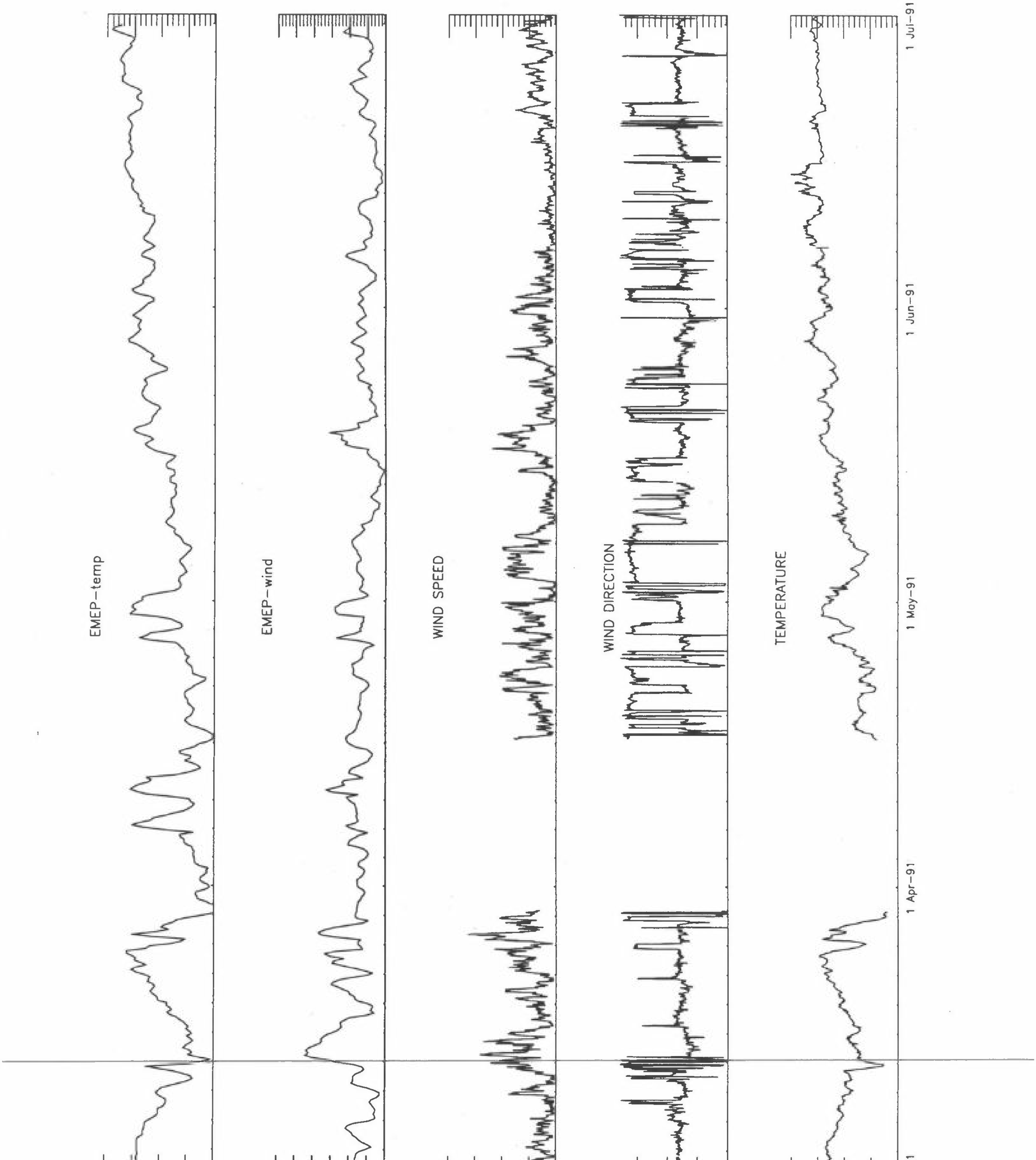
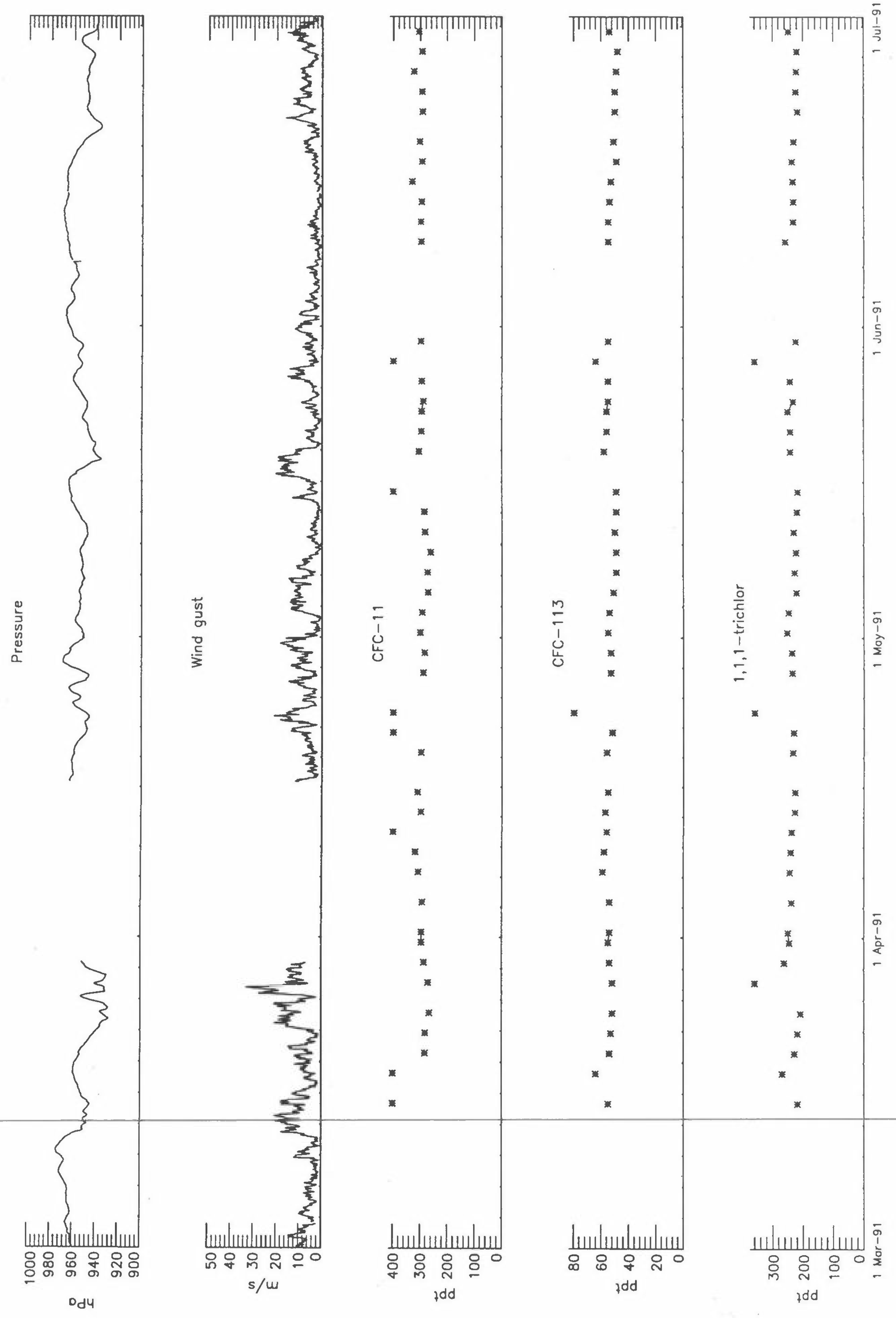
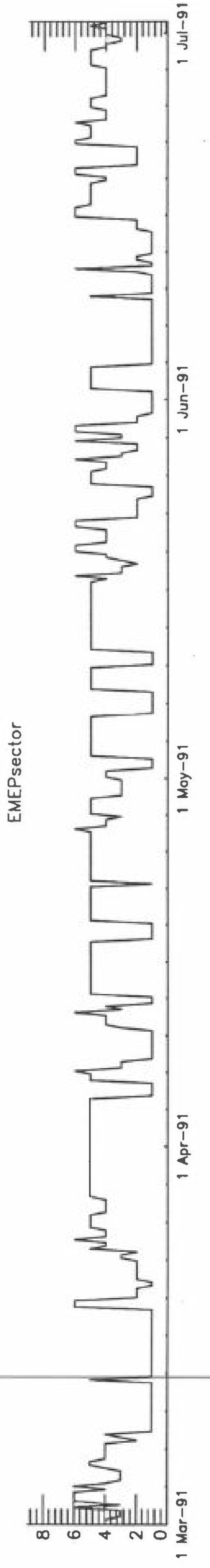
ppt
250
200
150
100
50
0
i-pentane
ppt
250
200
150
100
50
0
EMEP-Hmix
m
2500
2000
1500
1000
500
0
EMEP-w
mm/sec
40
30
20
10
0
-10
-20
EMEP-rh
%
100
90
80
70
60
50
40
30
1 Mar-91
1 Apr-91
1 May-91
1 Jun-91
1 Jul-91


EMEP−temp
deg. C
10
0
−10
−20
−30
EMEP−wind
m/s
30
25
20
15
10
5
0
WIND SPEED
m/s
20
15
10
5
0
WIND DIRECTION
deg.
300
200
100
0
TEMPERATURE
Deg. C
10
0
−10
−20
−30
1 Mar−91
1 Apr−91
1 May−91
1 Jun−91
1 Jul−91


Pressure
hPa
1000
980
960
940
920
900
Wind gust
m/s
50
40
30
20
10
0
CFC-11
ppt
400
300
200
100
0
CFC-113
ppt
80
60
40
20
0
1,1,1-trichlor
ppt
300
200
100
0
1 Mar-91
1 Apr-91
1 May-91
1 Jun-91
1 Jul-91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8
6
4
2
0
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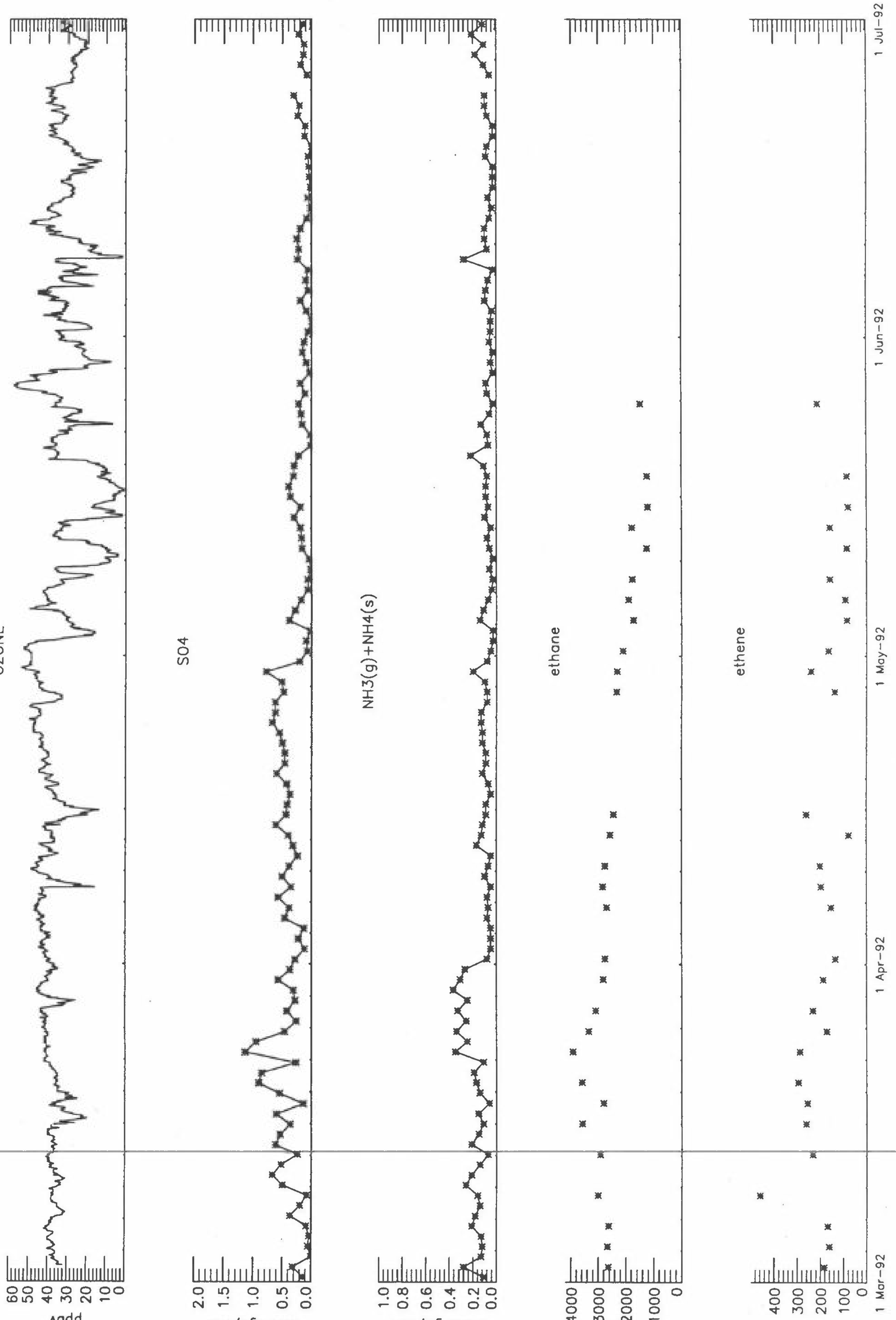
1 Apr-91
1 May-91
1 Jun-91
1 Jul-91


OZONE
ppbv
60
50
40
30
20
10
0
SO4
mikrogS/m3
2.0
1.5
1.0
0.5
0.0
NH3(g)+NH4(s)
mikrogN/m3
1.0
0.8
0.6
0.4
0.2
0.0
ethane
ppt
4000
3000
2000
1000
0
ethene
ppt
400
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200
100
0
1 Mar-92
1 Apr-92
1 May-92
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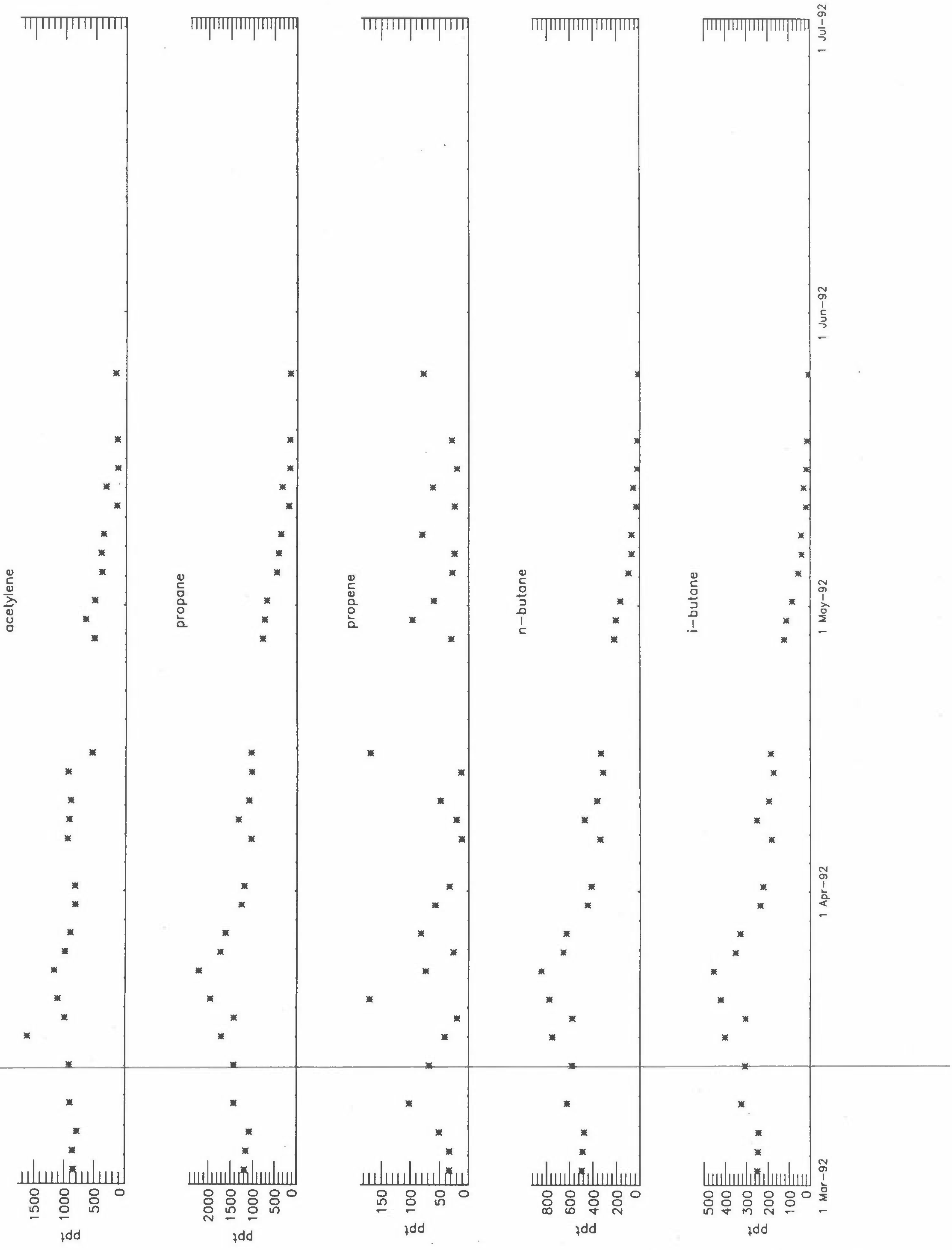
1 Jul-92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ppt
1500
1000
500
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propane
ppt
2000
1500
1000
500
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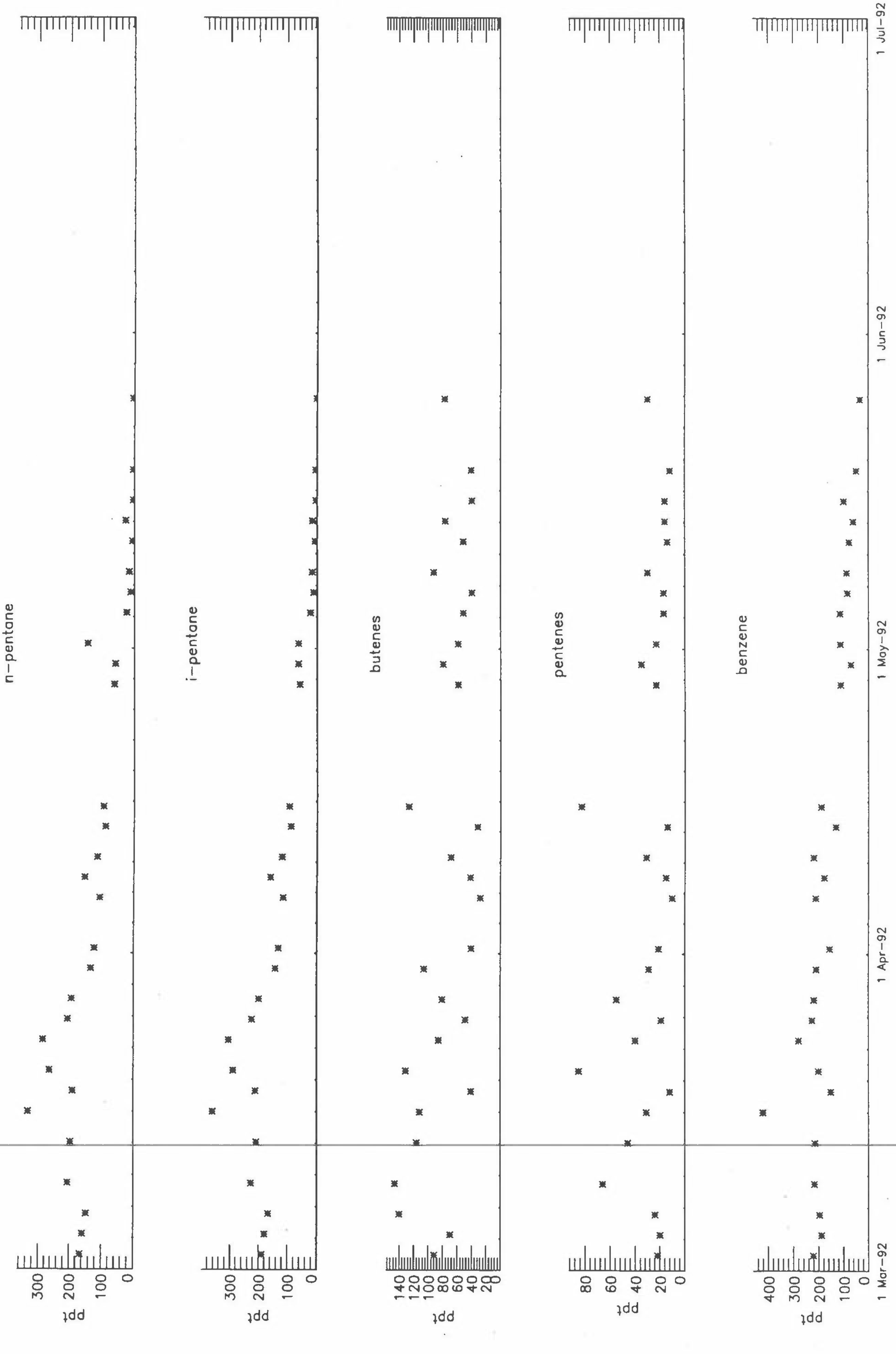
propene
ppt
150
100
50
0
n-butane
ppt
800
600
400
200
0
i-butane
ppt
500
400
300
200
100
0
1 Mar-92
1 Apr-92
1 May-92
1 Jun-92
1 Jul-92


n−pentane
i−pentane
butenes
pentenes
benzene
ppt
300
200
100
0
140
120
100
80
60
40
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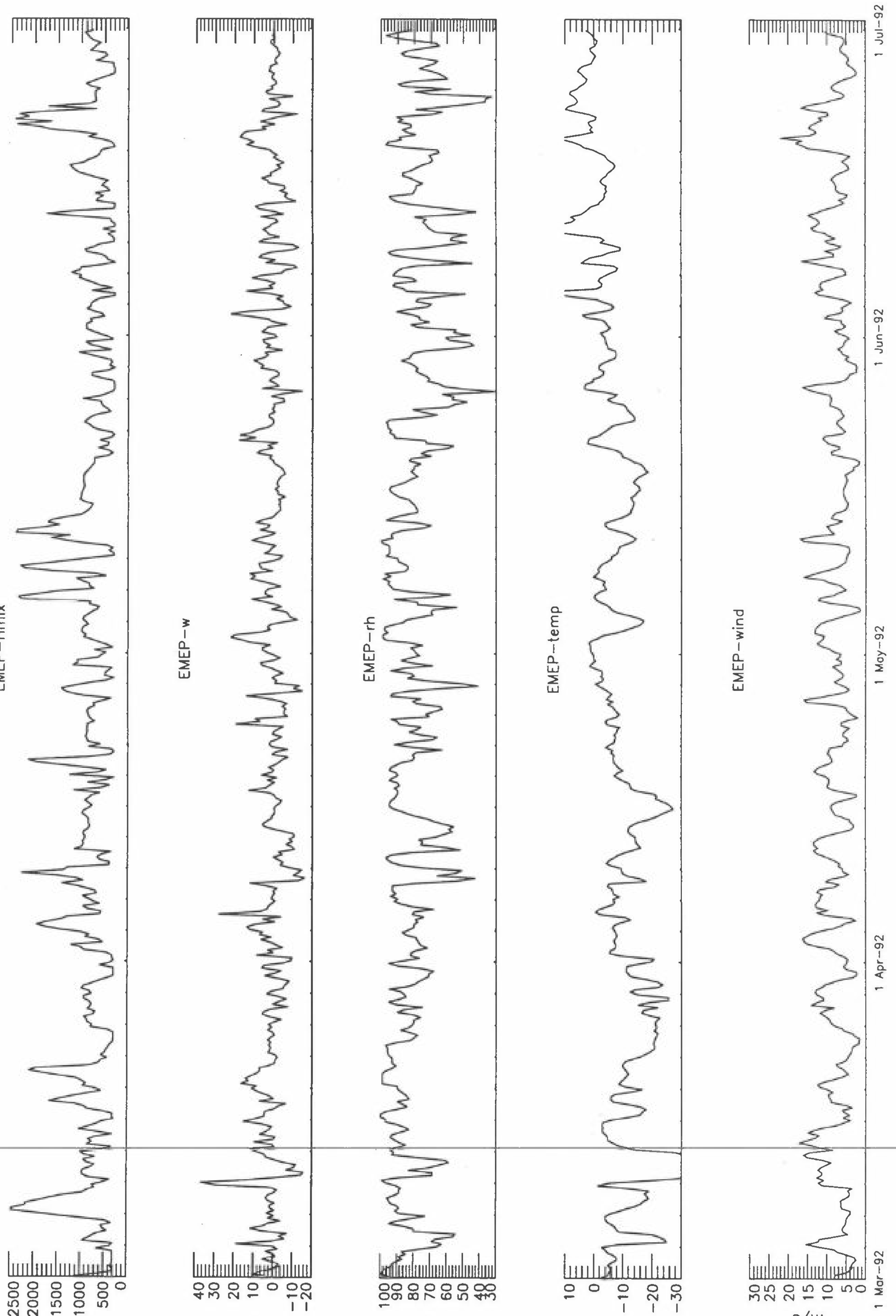
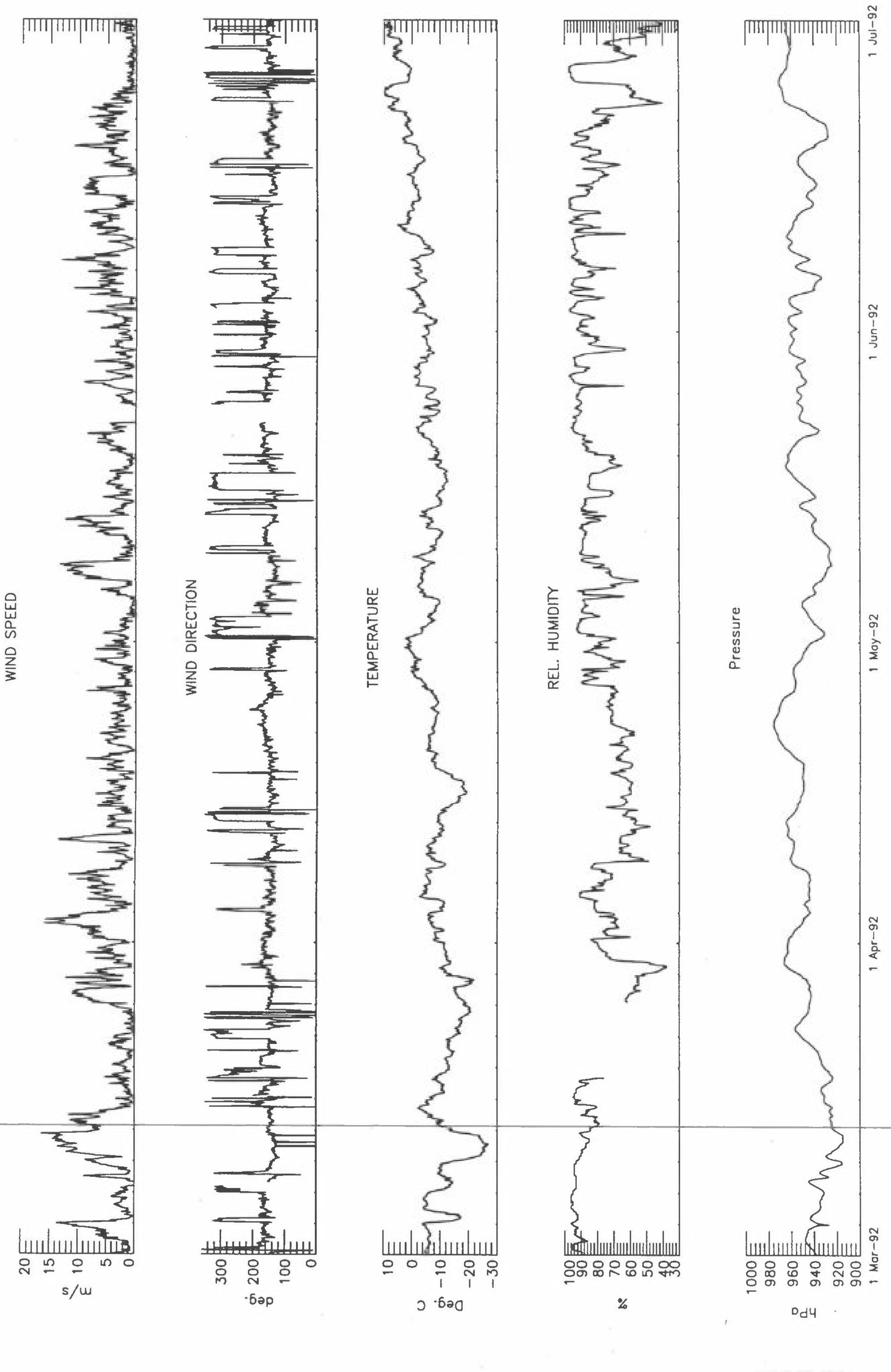
1 May−92
1 Jun−92
1 Jul−92


EMEP-Hmix
m
2500
2000
1500
1000
500
0
EMEP-w
mm/sec
40
30
20
10
0
-10
-20
EMEP-rh
%
100
90
80
70
60
50
40
30
EMEP-temp
deg. C
10
0
-10
-20
-30
EMEP-wind
m/s
30
25
20
15
10
5
0
1 Mar-92
1 Apr-92
1 May-92
1 Jun-92
1 Jul-92


WIND SPEED
m/s
20
15
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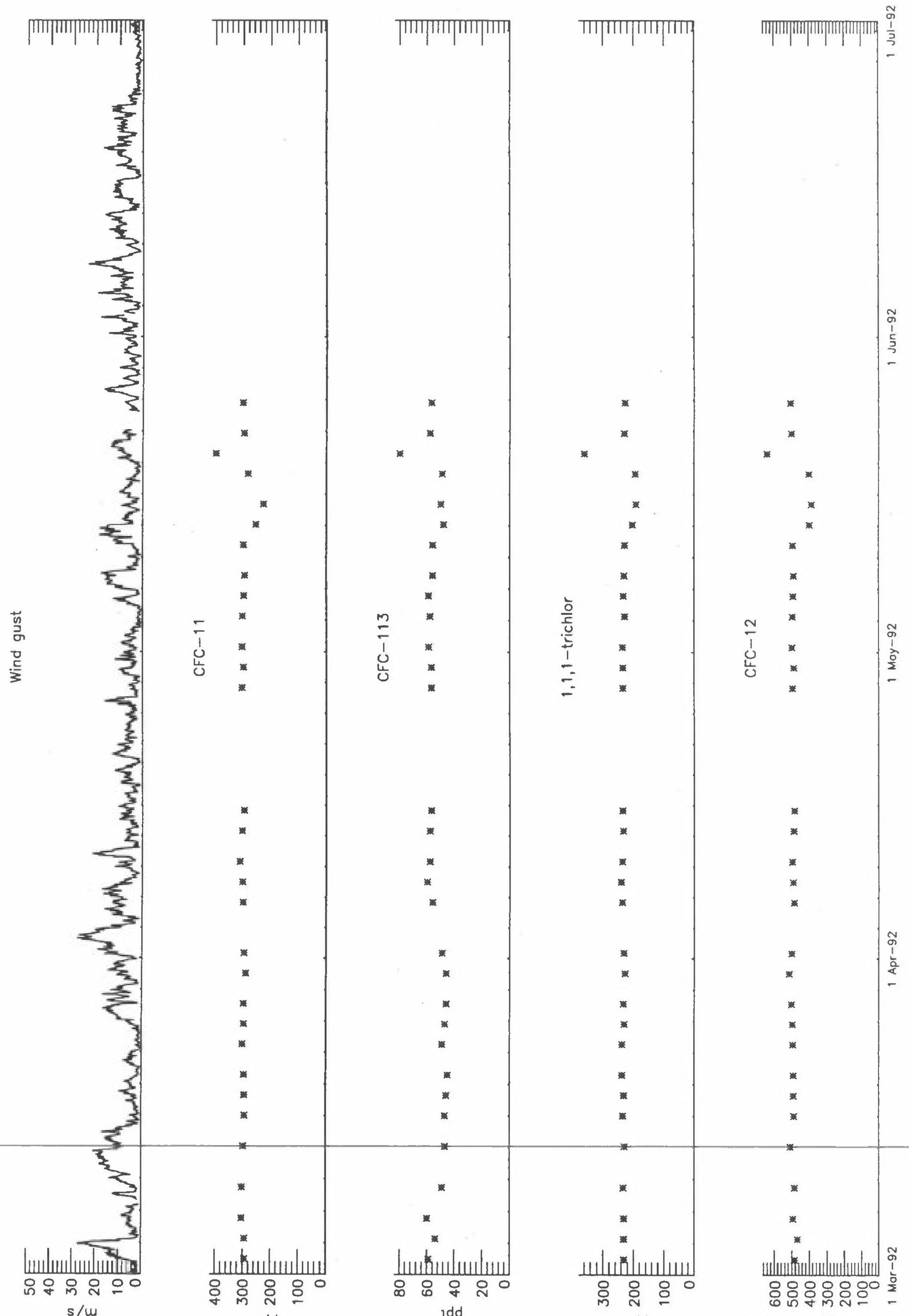
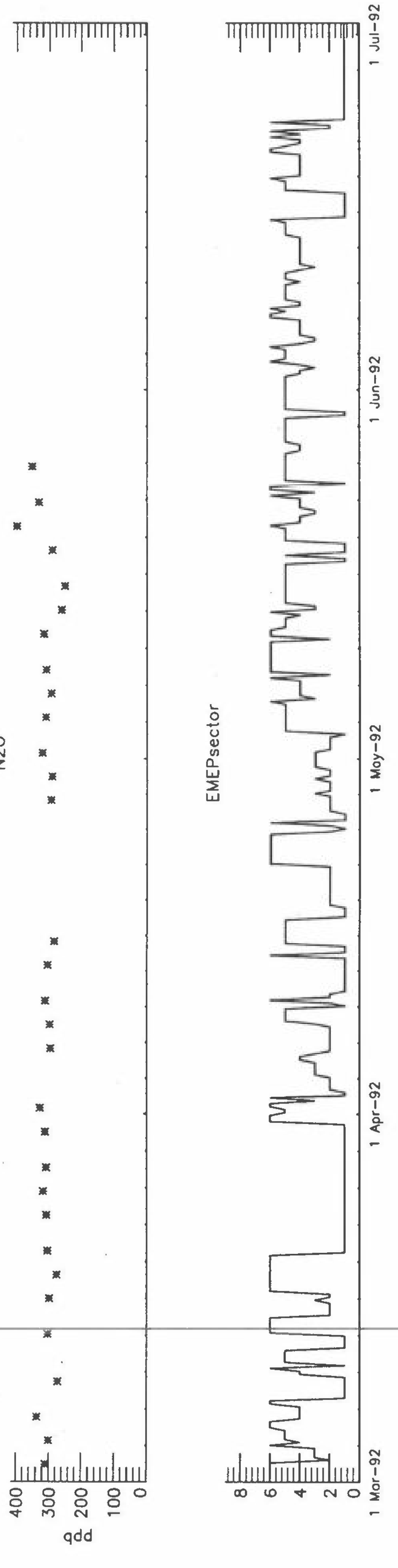
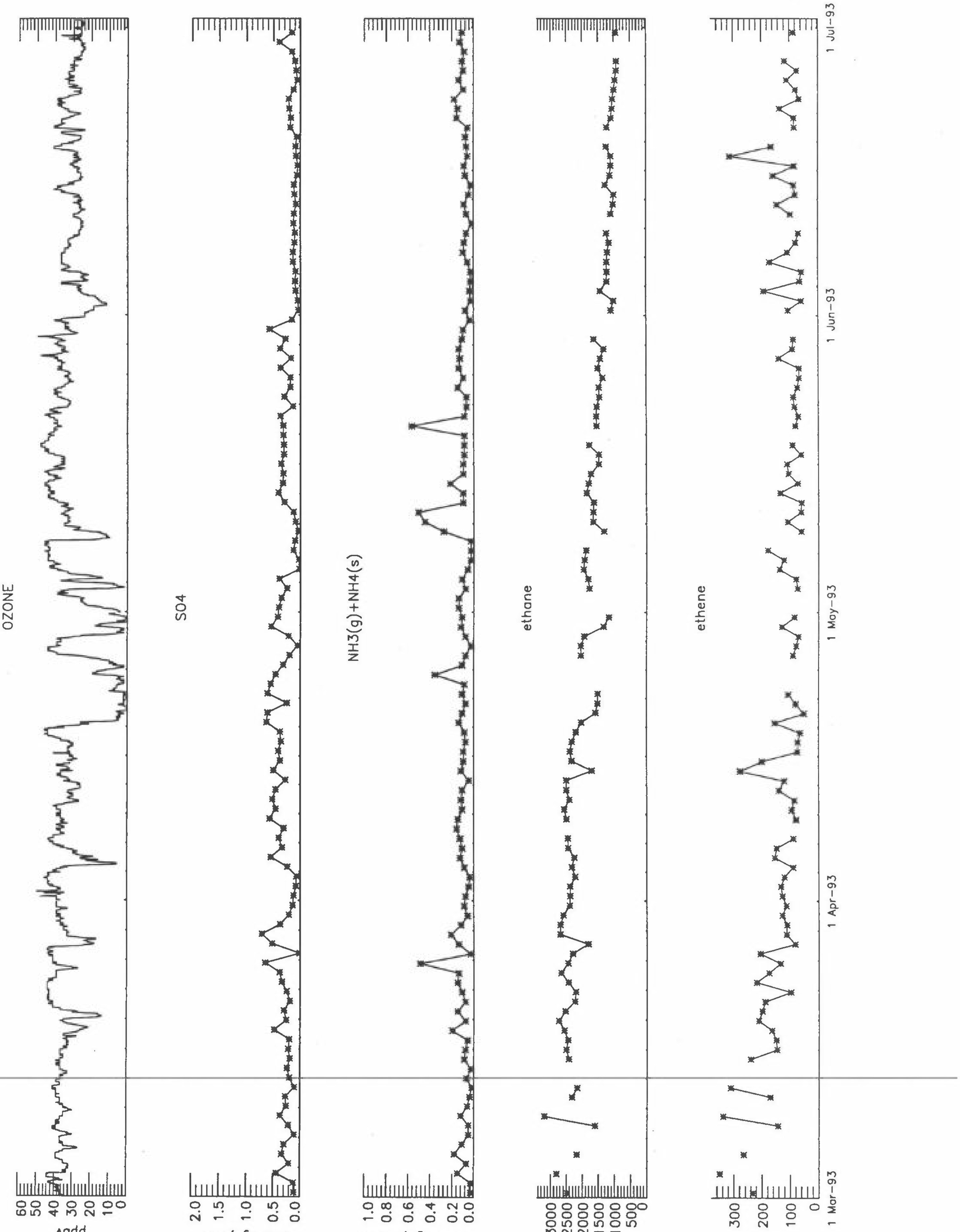
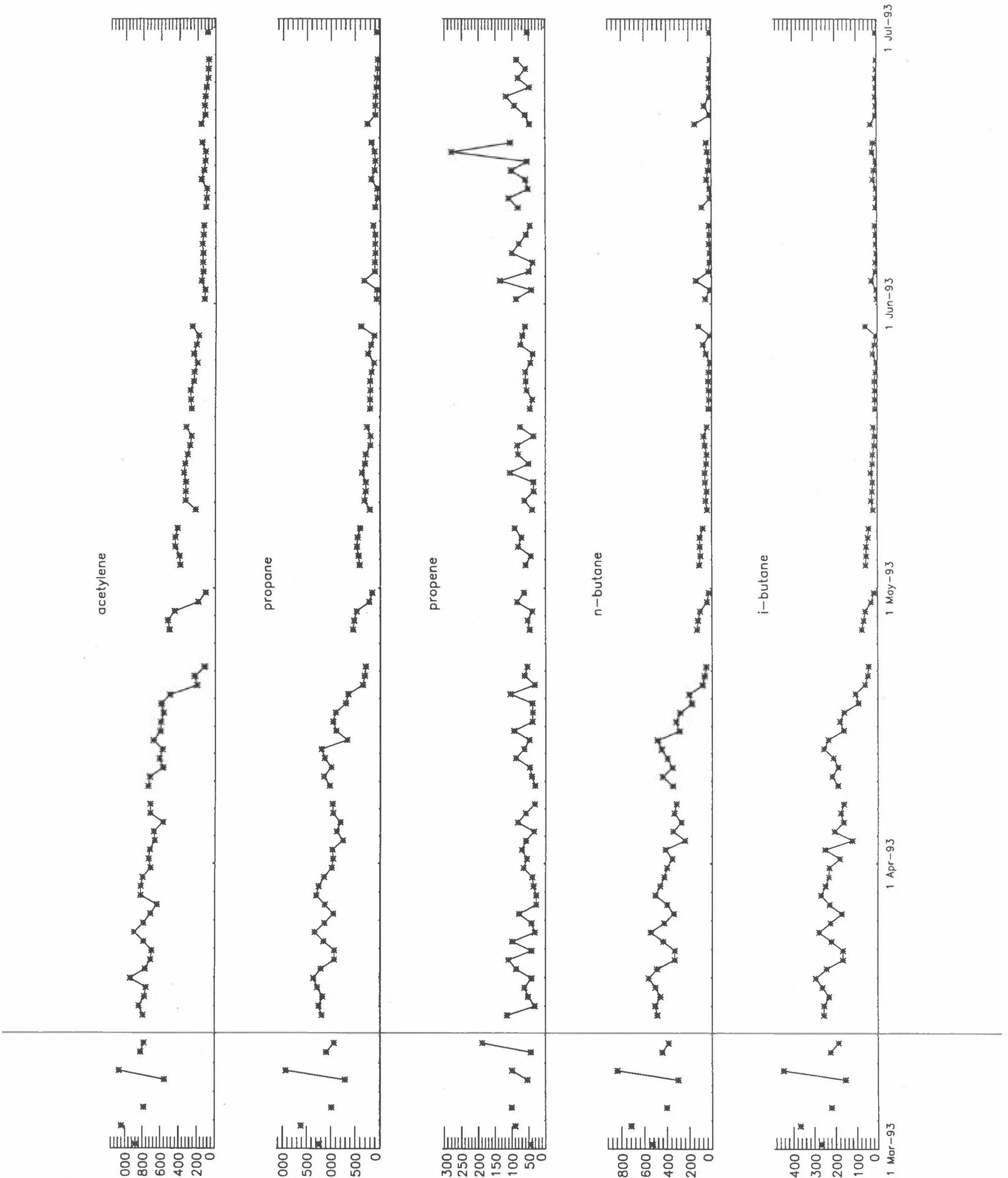
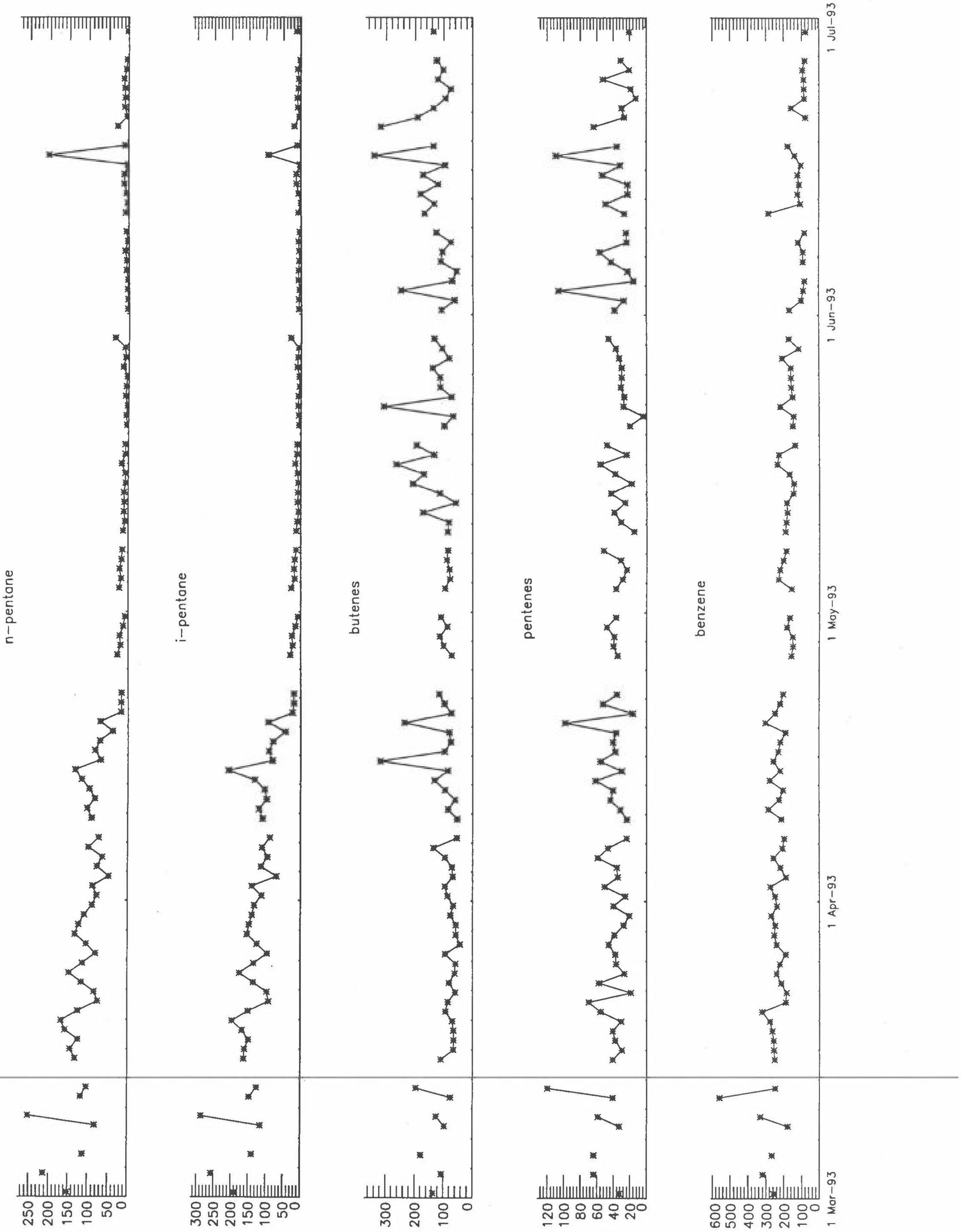
5
0
WIND DIRECTION
deg.
300
200
100
0
TEMPERATURE
Deg. C
10
0
-10
-20
-30
REL. HUMIDITY
%
100
90
80
70
60
50
40
30
Pressure
hPa
1000
980
960
940
920
900
1 Mar-92
1 Apr-92
1 May-92
1 Jun-92
1 Jul-92

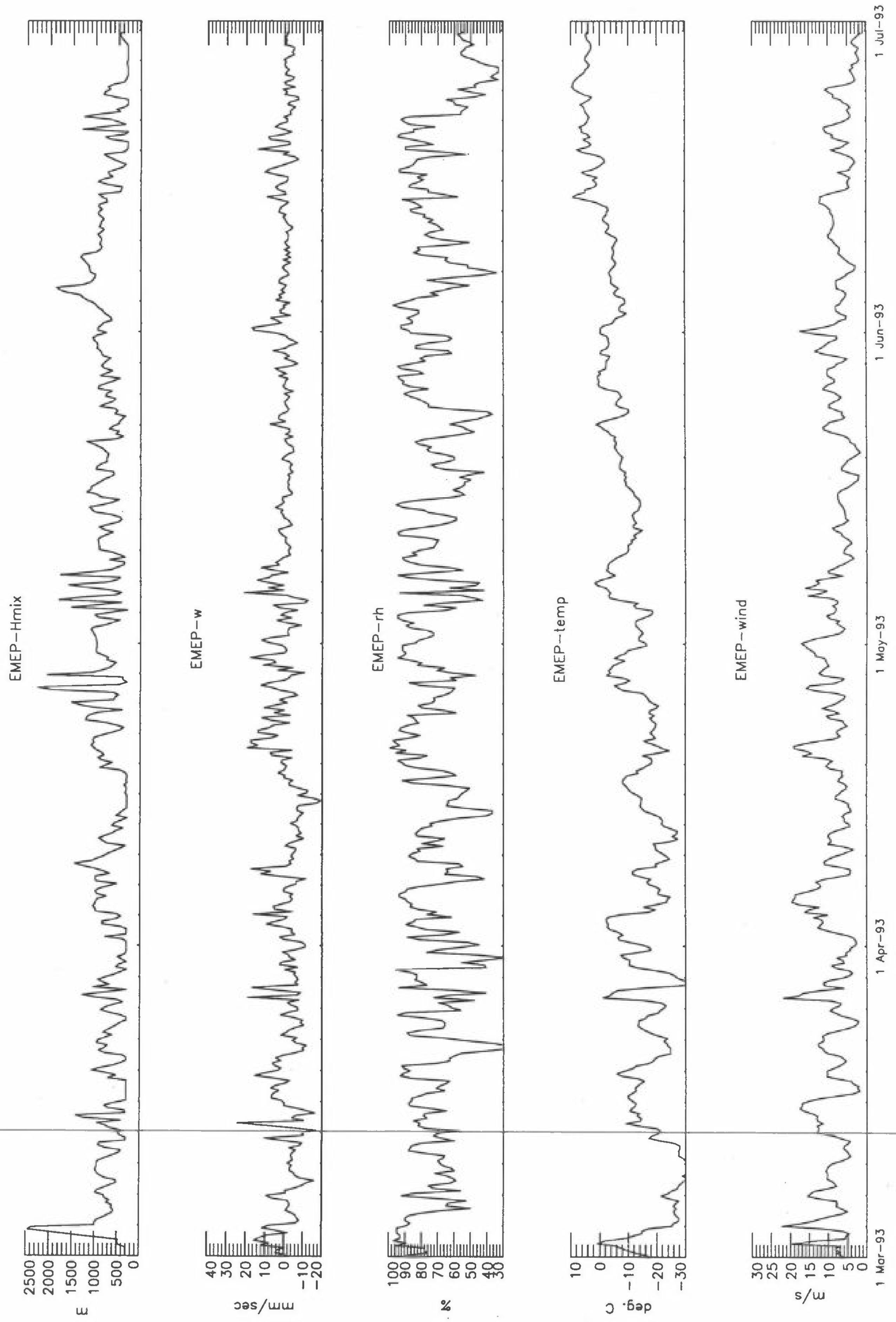

Wind gust
m/s
50
40
30
20
10
0
CFC-11
ppt
400
300
200
100
0
CFC-113
ppt
80
60
40
20
0
1,1,1-trichlor
ppt
300
200
100
0
CFC-12
ppt
600
500
400
300
200
100
0
1 Mar-92
1 Apr-92
1 May-92
1 Jun-92
1 Jul-92

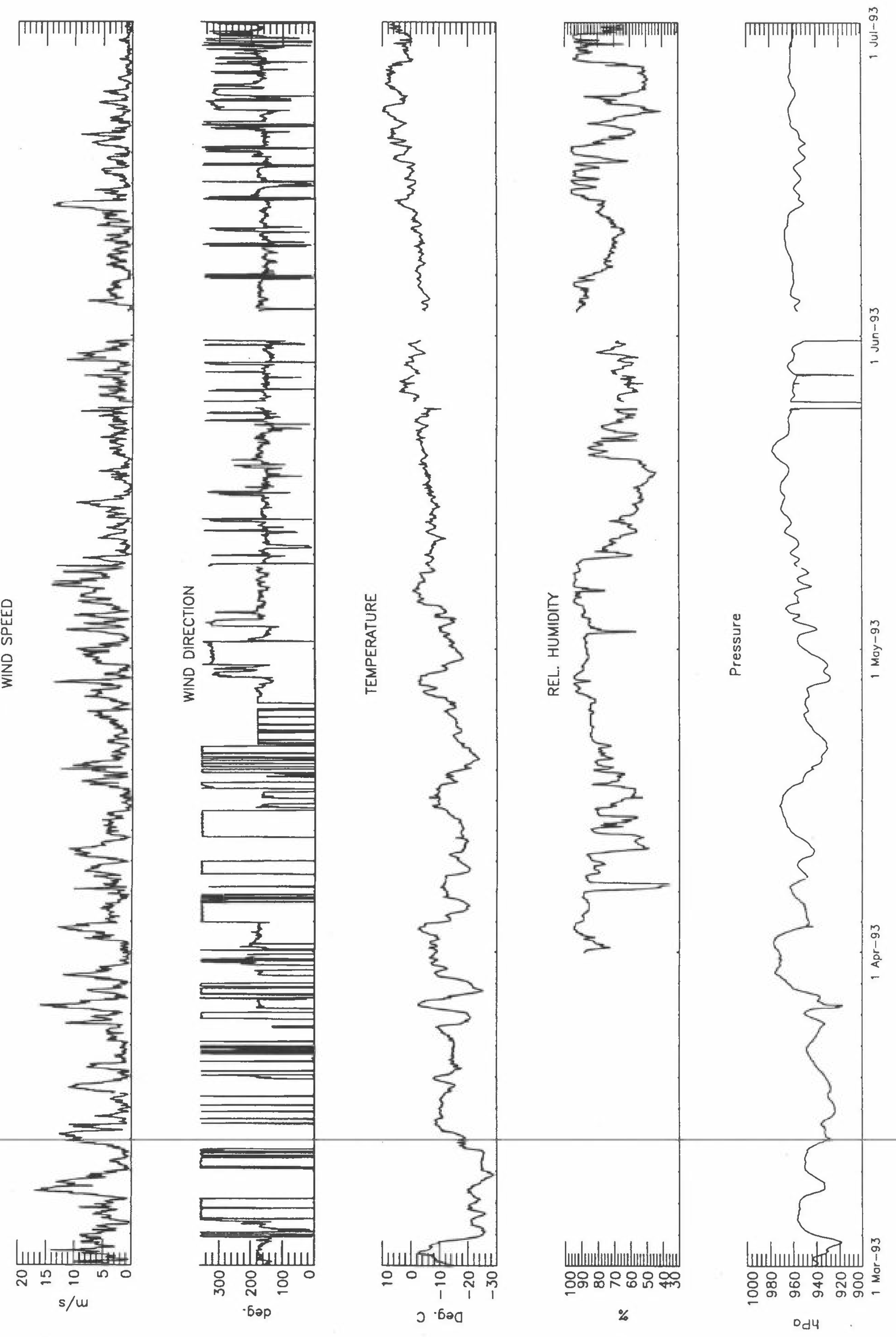

N2O
ppb
400
300
200
100
0
EMEPsector
8
6
4
2
0
1 Mar-92
1 Apr-92
1 May-92
1 Jun-92
1 Jul-92

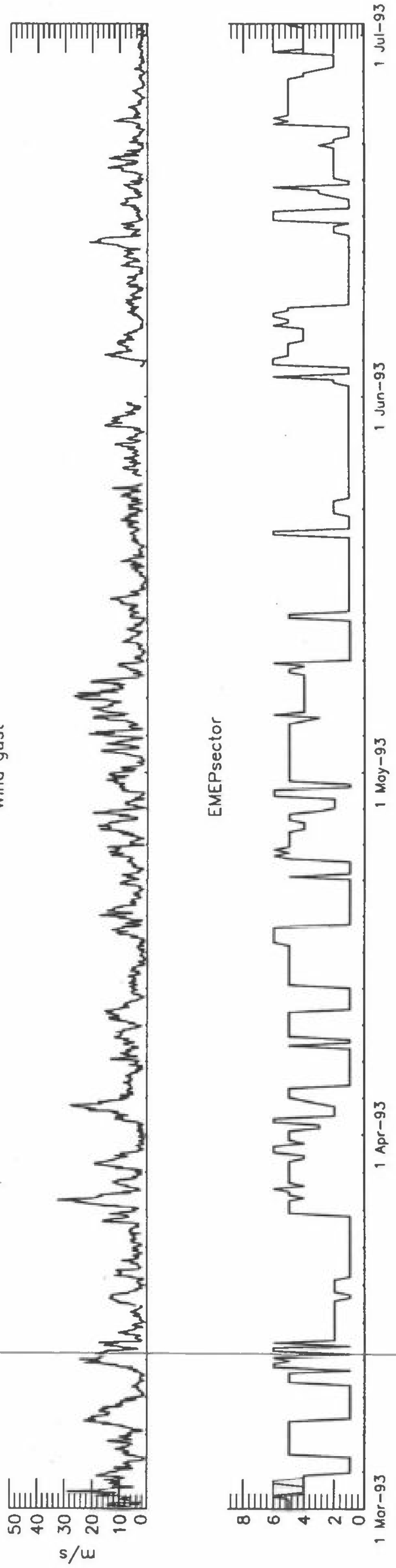

OZONE
ppbv
60
50
40
30
20
10
0
SO4
mikrogS/m3
2.0
1.5
1.0
0.5
0.0
NH3(g)+NH4(s)
mikrogN/m3
1.0
0.8
0.6
0.4
0.2
0.0
ethane
ppt
3000
2500
2000
1500
1000
500
0
ethene
ppt
300
200
100
0
1 Mar-93
1 Apr-93
1 May-93
1 Jun-93
1 Jul-93


acetylene
ppt
1000
800
600
400
200
0
propane
ppt
2000
1500
1000
500
0
propene
ppt
300
250
200
150
100
50
0
n-butane
ppt
800
600
400
200
0
i-butane
ppt
400
300
200
100
0
1 Mar-93
1 Apr-93
1 May-93
1 Jun-93
1 Jul-93


n-pentane
ppt
250
200
150
100
50
0
i-pentane
ppt
300
250
200
150
100
50
0
butenes
ppt
300
200
100
0
pentenes
ppt
120
100
80
60
40
20
0
benzene
ppt
600
500
400
300
200
100
0
1 Mar-93
1 Apr-93
1 May-93
1 Jun-93
1 Jul-93


EMEP-Hmix
m
2500
2000
1500
1000
500
0
EMEP-w
mm/sec
40
30
20
10
0
-10
-20
EMEP-rh
%
100
90
80
70
60
50
40
30
EMEP-temp
deg. C
10
0
-10
-20
-30
EMEP-wind
m/s
30
25
20
15
10
5
0
1 Mar-93
1 Apr-93
1 May-93
1 Jun-93
1 Jul-93


WIND SPEED
m/s
20
15
10
5
0
WIND DIRECTION
deg.
300
200
100
0
TEMPERATURE
Deg. C
10
0
-10
-20
-30
REL. HUMIDITY
%
100
90
80
70
60
50
40
30
Pressure
hPa
1000
980
960
940
920
900
1 Mar-93
1 Apr-93
1 May-93
1 Jun-93
1 Jul-93


Wind gust
m/s
50
40
30
20
10
0
EMEPsector
8
6
4
2
0
1 Mar-93
1 Apr-93
1 May-93
1 Jun-93
1 Jul-93

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TITLE Tropospheric ozone depletion in the Arctic during spring Measurements on the Zeppelin Mountain on Spitsbergen		PROJECT LEADER Frode Stordal NILU PROJECT NO. U-93093	
AUTHOR(S) Sverre Solberg, Ove Hermansen, Einar Joranger, Norbert Schmidbauer, Frode Stordal and Øystein Hov		CLASSIFICATION * A CONTRACT REF.	

REPORT PREPARED FOR:
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ABSTRACT

This report presents measurements of ozone, non-methane hydrocarbons, sulphate, ammonium, halocarbon and meteorological parameters from Spitsbergen in the Arctic. The focus is the rapid depletion of surface ozone in spring. Trajectories show that the ozone loss is mainly observed when the transport is from W–N. Ozone soundings and surface time series indicate that the loss process is of regional extent. The trace constituents indicate that hydrocarbons are chemically lost, as well as ozone, and that sulphate and ice particles may take part in the reactions.

NORWEGIAN TITLE

Nedbrytning av troposfæreozon i Arktis om våren. Målinger på Zeppelinfjellet på Spitsbergen.

KEYWORDS

Ozone	Hydrocarbons	Arctic

ABSTRACT (in Norwegian)

Rapporten presenterer målinger av ozon, hydrokarboner, sulfat, ammonium, freoner og meteorologiske parametere fra Spitsbergen. Tema er nedbrytning av bakkeozon om våren i Arktis. Trajektorier viser at ozontapet er knyttet til transport fra vest-nord. Ozonsonder og tidsserier av bakkedata tyder på at fenomenet er av regional utstrekning. Hydrokarboner ser ut til å bli brutt ned i tillegg til ozon, og det er indikasjoner for at sulfat og ispartikler inngår i de kjemiske reaksjonene.

** Classification*	*A*	*Unclassified (can be ordered from NILU)*
	B	*Restricted distribution*
	C	*Classified (not to be distributed)*