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Preface

The measurements of nine light nonmethane hydrocarbons (NMHC) at Birkenes from January 1988 - June 1993 are presented. Except for propene, all components showed a minimum in summer, but the winter to summer ratio was not anticorrelated to the lifetime as one would expect. The time of the decline in the concentrations in spring started first for the most reactive components.

Sector analysis based on trajectories for the whole period 1988-1993 are presented. The highest average concentrations were from the south sector for all the components when all data were taken into account, but there were seasonal modifications in this pattern.

The distribution of the individual NMHC indicates a higher fraction of long lived components when the transport was from NW to NE, consistent with more unpolluted air masses in these directions.

The fraction of alkenes of the total sum of NMHC increased in the summer, probably due to biogenic emissions from nearby ocean surfaces. Trajectories indicated the Skagerrak to be an important source area.

Trend analysis for the individual NMHC are presented, and there are large differences among the components. Acetylene, propane and iso-butane showed upward trends from 1988-1993 of several per cent per year, while the alkenes showed a decline of 5-7%/a. The long-time trends are to some extent explained by changes in the air transport at Birkenes, as described by calculated trajectories.

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Summary

Regular measurements from 1988-1993 of nine light nonmethane hydrocarbons (NMHC) at Birkenes have been presented. Except for propene, all the components showed a clear seasonal cycle, with a minimum concentration in the summer. The seasonal cycle was most pronounced for the long lived components acetylene, propane and ethane.

A least squares sine fit indicated that the average time of the winter maximum was linked to the lifetime and occurred later in winter for the long lived components. This reflects that components with a long lifetime, as ethane, reach an equilibrium concentration between emission rates and photochemical loss in the background troposphere later in the winter than the short lived components. Furthermore, the decline in the concentrations in the spring started in the order of reactivity: The most short lived NMHC first dropped in concentration.

Comparison with the average sum of observed NMHC at the Arctic station Zeppelin Mountain at Spitsbergen from 1989-1993, revealed a much more pronounced seasonal variation at the Arctic station, while the sum of NMHC was similar at the two stations in winter. The episodic nature was much larger at Birkenes during the whole year than on the Zeppelin Mountain.

Sector analysis based on trajectories from 1988-1993 showed that the highest average concentrations were from the south when averaging all data, but that there were seasonal variations for the different components. In spring the long lived components were more uniformly distributed for all the sectors, indicative of meridional mixing in the troposphere.

We found indications of nearby emissions of alkenes in summer, and the sector analysis indicated strong sources in SE in that season, possibly biogenic emissions from Skagerrak.

The average distribution of the individual NMHC from the different sectors, revealed that the fraction of the long lived components increased from south to north in all the seasons, indicating "chemically older" air masses. However, the fraction of the short lived components was higher in summer than in spring in all the sectors, consistent with a less pronounced seasonal cycle. This suggests that the photochemical activity in summer is sufficiently strong to oxidize most of the remotely emitted reactive components before the air mass arrives at Birkenes. A large fraction of the observed summer concentrations of the reactive components must therefore be linked to nearby sources.

Episodes with high concentrations of NMHC in winter from the different sectors showed a high fraction of butanes and pentanes in NW, and a high fraction of the alkenes in S. The highest acetylene fraction was in sector SE.

The trend in the long term running average concentrations of the individual components at Birkenes for the period 1988 - 1993 showed large differences between the components. Acetylene showed an upward trend of several %/a, while the alkene concentrations showed a decline of 5-8%/a. Analyses of the frequency of trajectories from different sectors indicated that at least part of the observed trends in concentrations was linked to large scale changes in the transport pattern during the five and a half years period. There is, however, no obvious explanation for the almost linear decline in the ethene concentration observed at Birkenes from 1988-1993.

Non-methane hydrocarbons (NMHC) measured at Birkenes in South Norway, 1988 - 1993

1. Introduction

Nonmethane hydrocarbons (NMHC) contribute to the formation of photochemical oxidants, notably ozone (O_3), hydrogen peroxide (H_2O_2), and peroxyacetyl nitrate (PAN). NMHC are precursors of carbon monoxide (CO) and carbon dioxide (CO_2). Both directly and indirectly (through CO), the nonmethane hydrocarbons influence the atmospheric hydroxyl radical (OH) concentration. NMHC are therefore linked to a range of atmospheric environmental issues: acid deposition through OH, H_2O_2 and O_3 , photooxidant formation which takes place when nitrogen oxides ($NO_x=NO+NO_2$) and NMHC react under the presence of sunlight, and global tropospheric change through the influence on the OH radical concentration, CO and CO_2 .

The quantitative role of the NMHC in photooxidant formation or global change is not settled, for many reasons. The sources of anthropogenic and natural hydrocarbons are complex and variable in time and space and the knowledge of the atmospheric concentration distribution of the individual nonmethane hydrocarbons can at best be characterized as fragmentary.

Until 1980 measurements of NMHC referred almost exclusively to urban air, and the emphasis was put on the concentration level and the specific sources in cities. Later the focus changed to the rural and background troposphere, and several campaigns and measurement activities have taken place related to NMHC in the background troposphere. Singh and Salas (1982) measured NMHC at different latitudes in the Pacific Ocean, Rudolph and Ehhalt (1981) investigated the latitudinal variation of NMHC over the North Atlantic Ocean. One focus of the Polarstern Cruise of the Atlantic Ocean in 1988 (Ehhalt and Harris, 1992) was on NMHC concentrations and oceanic emissions.

For the rural continental atmosphere a large part of the measurements around 1985 referred to North America, and fewer to the European continent (Colbeck and Harrison, 1985).

In the subproject Tropospheric Ozone Research (TOR) in Eurotrac, a large amount of individual hydrocarbons have been measured in a systematic way at several background sites in Europe for many years, in conjunction with the measurement of related trace species like ozone, nitrogen oxides, PAN, carbon monoxide and hydrogen peroxide.

Measurements of ozone and its precursors have been carried out since 1989 at Schauinsland (1250 m a.s.l.) in the Black Forest near Freiburg. Volz-Thomas et al. (1993), Kley et al. (1993) and Klemp et al. (1993) show how measurements of

light hydrocarbons can be used both to establish the climatology of these compounds with time of day and season, and when used in conjunction with meteorological information, anthropogenic and biogenic sources can be identified as well as their role in ozone formation.

At Rörvik on the southwest coast of Sweden continuous measurements of nonmethane hydrocarbons have been carried out for several years as a part of the TOR project (Lindskog and Moldanová, 1994, Mowrer and Lindskog, 1991; Lindskog and Mowrer, 1993; Lindskog et al., 1992). These measurements have been analysed both in terms of daily and seasonal variability, to identify the speciation of anthropogenic urban emissions and to identify biogenic sources.

At Birkenes near the south coast of Norway and at Ny Ålesund on Spitsbergen, spot samples of nonmethane C₂-C₆ hydrocarbons have been taken approximately every second day since 1987 at Birkenes and since 1989 at Ny-Ålesund in pressurized steel canisters. The measurements show that the winter maximum in total nonmethane hydrocarbons is quite similar at Ny-Ålesund and Birkenes, in spite of the 20° latitude difference, while the summer minimum at the Arctic site is lower than further south. Furthermore, the concentrations of more reactive hydrocarbons are lower in the Arctic air masses. The measurements as well as model interpretations have been reported in Hov et al. (1984, 1989, 1990, 1991, 1994), by Isaksen et al. (1985) and by Hov and Schmidbauer (1992).

Since the beginning of 1992, a TOR site has been in operation at Porspoder at the seashore of the western tip of Brittany, France, with a fully automatic analysis of C₂-C₉ hydrocarbons by a Chrompack instrument. The first results about the climatology of the hydrocarbon composition in terms of seasonal variation in different synoptic transport sectors, are just being published (Boudries et al., 1994).

Free tropospheric and boundary layer individual hydrocarbons over the British Isles and the North Atlantic have been reported by Lightman et al. (1990) and Penkett et al. (1993). A large number of flights were carried out so that seasonal cycles of the light hydrocarbons could be established. For the C₂-C₆ alkanes, acetylene, benzene and toluene, there was a marked seasonal variation with a winter maximum and a summer minimum. For the more reactive alkenes, the seasonal variation is less clear. From the seasonal cycles as well as from changes in hydrocarbon ratios as air masses moved away from the anthropogenic European sources, there were indications of oceanic sources of both alkenes and some alkanes, and preferential removal of branched-chain (iso isomers) hydrocarbons compared to the straight-chain molecules.

No attempt will be made here to review the measurements of nonmethane hydrocarbons in North America or off the the North American continent. Reference is made to Parrish et al. (1992) for examples of the application of nonmethane hydrocarbon measurements in conjunction with measurements of other trace constituents in the atmosphere, to estimate the photochemical age of different air masses. Jobson et al. (1994) provide information on seasonal trends in nonmethane hydrocarbons in rural Canada.

The main objective of this report is to present a climatology of NMHC concentrations at a rural background station. Data from the rural site Birkenes in South Norway are presented with emphasis on averaged annual cycles of concentrations of total NMHC and several individual components. Regular measurements have been made at Birkenes for more than 5 years.

It has also been an aim to explore differences in concentration and composition in different regions (sectors), and to detect possible time trends.

Knowledge of the annual cycle in NMHC concentrations in the background European troposphere is crucial for evaluating the photochemical activity and oxidant formation in the troposphere, and thereby crucial for making decisions of emission control strategies.

2. Instrumentation, sampling and calibration

Manual samples were taken in stainless steel bottles (SS 304) of 0.8 l volume with a metal-bellow pump every second day, although there have been irregular intervals due to practical difficulties. The subsequent analysis was made in the laboratory at NILU using gas chromatography equipped with a flame ionization detector. A detailed description of the sampling technique and analytical method is given in Schmidbauer and Oehme (1986), Hov et al. (1989 and 1991) and Hov and Schmidbauer (1992).

A NIST certified standard gas mixture containing 10 ppb n-butane and benzene is used for calibration. A response factor calculated for 1 ppbC together with the carbon number is then applied to all hydrocarbons. There are no corrections made for any possible deviations of the detector-response due to differences in molecular structure. The analytical technique together with this type of calibration, has been used in the first hydrocarbon intercalibration organized by Joint Research Centre Ispra (De Saeger and Tsani-Bazaca, 1992). The relative deviation of the measurements from the gravimetric standard was 5.3% as a mean over all compounds. The relative bias was 1.9% as a mean. The overall deviation as a mean for all participating laboratories was 36.3%, the overall mean bias 20.2%.

Data from Norwegian sites in publications up to 1992 were calibrated with individual response factors obtained by Scott Calibration Mixtures. There are some important deviations from the theoretical response, especially for C₃ compounds, and all data have been recalibrated against the NIST certified n-butane and benzene standard. The following factors have been used in recalculating concentrations based on Scott Calibration Mixtures to NIST-certified standard: ethane 1.00 (reference gas), ethene 0.87, propane 0.54, propene 1.05, i-butane 0.79, acetylene 0.73, n-butane 0.72, i-pentane 0.80, n-pentane 1.04.

The stability of the individual hydrocarbons in pressurized steel bottles which are stored over some time before analysis, has been questioned. The experience at NILU is that species up to C₇ (including toluene) are quite stable even after

several months. The xylenes may be adsorbed on the inner surface of the bottle, in particular if the bottle is exposed to cold (freezing) temperatures. In Table 1 are shown the results of repeated analysis of the composition of the same pressurized air sample in a stainless steel bottle over a 10 weeks time period.

A part of the reference gas mixture from IFU was filled into one of NILU's bottles, but since there was only some air left for this exercise, it was not possible to follow normal sampling procedure, which involves up to 10 times pressurizing and depressurizing of the bottle. This procedure normally ensures that there is enough time for equilibration. But since this standard mixture (RGM) was a rather dry sample and our steel canister was filled without repeated flushing, it is not very surprising that changes happen in the first hour after filling. From 10% for C₆ compounds up to 35% of C₈ compounds were adsorbed to the inner surface within the time period from filling the can until the first analysis (Table 1). When the normal sampling procedure is followed, effects of adsorption to canisters will be much less.

It is seen that for C₂ and C₃ hydrocarbons, the ratio of the standard deviation over the mean measured concentration over a storage period from 1h to 68d is 2 or 3%. There is no significant difference between the alkanes and the alkenes or acetylene, in contradiction to a common assumption that ethene and propene are subject to severe change with time in pressurized air samples stored in stainless steel bottles. For butene the stability is slightly poorer, but if analysed within a few weeks after sampling, there are no significant adsorption problems for this compound either. This also applies to C₅ and C₆ alkanes and alkenes and for benzene and toluene, while for the xylenes the ratio of the standard deviation to the mean is 10-14% (which is for the xylenes about the precision of the method).

This is not the final proof of the stability of C₂-C₇ hydrocarbons in pressurized air samples stored in stainless steel canisters, since this may vary from bottle to bottle and with environmental parameters, but the results are acceptable. The experience reported by Partridge (1992) should be kept in mind, however, where the gas cylinders chosen for the EC VOC intercomparison reported by De Saeger and Tsani-Bazaca (1992) were found to behave very differently from previous experience.

These gas cylinders were not passivated stainless steel canisters like ours, and it was found that higher molecular weight hydrocarbons from C₆ and upwards, decreased steadily with time after filling of the cylinders, and the rates were different for each cylinder. The decrease was due to adsorption onto the walls, because when the cylinders were heated overnight to about 50 °C the original hydrocarbon concentrations were restored for all compounds except acetylene. For acetylene the concentration was not reversible and there was indication of an irreversible chemical reaction with the cylinder walls at a rate which varied strongly from one cylinder to another.

Table 1: Stability of the composition of the pressurized air sample in a stainless steel bottle stored at laboratory temperature at NILU. The sample is identical to the second round of the intercalibration in the TOR project 1992. The concentrations are given in pptv.

	RGM*	1 hour	1 hour/ RGM	1 day	10 days	17 days	37 days	43 days	68 days	Mean (1h-68d)	Std. (1h-68d)	Std./mean (%)	1 hour/ mean
ethane	2943	2 891	0.98	2 886	2 810	2 858	2 971	2 815	2 812	2 863	55	2	1.01
ethene	3638	3 565	0.98	3 546	3 451	3 451	3 592	3 558	3 447	3 516	58	2	1.01
ethine	3610	3 588	0.99	3 577	3 503	3 514	3 685	3 478	3 366	3 530	93	3	1.02
propane	1686	1 650	0.98	1 636	1 595	1 607	1 690	1 617	1 566	1 623	37	2	1.02
propene	6552	6 551	1.00	6 498	6 350	6 336	6 617	6 312	6 161	6 404	147	2	1.02
n-butane	1053	1 010	0.96	1 014	991	996	991	971	973	992	15	2	1.02
propane, 2-methyl	630	641	1.02	634	618	623	604	597	597	616	16	3	1.04
1-butene	250	236	0.95	237	240	233	265	251	227	241	12	5	0.98
propene, 2-methyl	340	297	0.87	315	311	335	333	331	281	315	19	6	0.94
2-butene, trans	73	70	0.96	73	73	69	72	71	66	71	2	3	0.99
2-butene, cis	77	77	1.01	74	73	73	73	76	72	74	2	2	1.04
1,3-butadiene	77	77	1.01	74	73	73	73	76	72	74	2	2	1.04
n-pentane	591	547	0.93	555	546	539	543	549	533	544	7	1	1.00
butane, 2-methyl	1156	1 151	1.00	1 160	1 134	1 108	1 108	1 117	1 093	1 124	23	2	1.02
1-pentene	82	76	0.93	73	74	66	72	75	67	72	4	5	1.06
isoprene	28	29	1.03	31	30	30	32	32	30	30	1	3	0.96
n-hexane	229	206	0.90	213	205	204	207	197	195	204	6	3	1.01
benzene	906	726	0.80	785	732	667	774	756	731	739	36	5	0.98
n-heptane	1197	841	0.70	1 002	942	857	959	927	893	917	53	6	0.92
toluene													
n-octane	338	236	0.70	270	238	216	223	191	233	229	22	10	1.03
ethyl benzene	1201	771	0.64	897	781	704	756	637	813	766	76	10	1.01
m/p xylene	527	343	0.65	401	329	272	292	262	345	321	45	14	1.07

* RGM is the reference gas mixture supplied by Institut für Umweltforschung (IfU), Garmisch-Partenkirchen, Germany (organizing laboratory for the TOR intercomparison).

The values for RGM are NILU's results from the TOR intercomparison of this gas mixture (5 analyses performed by direct use of this cylinder)

In the EC intercomparison reported by De Saeger and Tsani-Bazaca (1992), 15 individual hydrocarbons were sufficiently stable in the cylinders sent out for intercomparison to almost 20 European laboratories to permit an evaluation. The sampling, preconcentration, analysis and calibration procedures were the same as normally used by each individual laboratory. The accuracy of the results from NILU compared very well with the gravimetric determination by Partridge (1992) and the conclusion of De Saeger and Tsani-Bazaca is worth noting: "The best results were obtained in those laboratories which are involved consistently and for longer periods of time in routine ambient air hydrocarbon measurements".

In 1993 a small intercomparison of VOC analytical methods was organized within EMEP (European Monitoring and Evaluation Programme). One bottle was analysed 4 times by 3 different groups (NILU, Partridge at National Physical Laboratory in England, and Bottenheim at Atmospheric Environment Service in Toronto, Canada). The experiment took about 3 months, including the shipping time of the bottle. The results are shown in Table 2. The composition of the bottle was quite stable during the 3 months of the intercomparison, and the agreement among the laboratories is very good.

Table 2: VOC intercomparison within EMEP, summer 1993, organized by the Institute of Applied Environmental Research at Stockholm University. Each laboratory analysed 4 samples of air from the same pressurized bottle.

	NILU	NPL*	AES**
C ₂ H ₆	2 429	2 840	2 513
C ₂ H ₄	4 323	4 130	4 498
C ₃ H ₈	1 335	1 430	1 404
C ₃ H ₆	2 393	2 350	2 497
n-C ₄ H ₁₀	1 262	1 400	1 247
i-C ₄ H ₁₀	528	460	526
C ₂ H ₂	1 940	1 530	1 688
Sequence of analysis	2	3	1

* National Physical Laboratory, England (R.H. Partridge)

** Atmospheric Environment Service, Toronto (Jan Bottenheim)

It is also worth to mention that an intercalibration of C₂-C₈ hydrocarbons was carried out in Scandinavia in the first two months of 1992. NILU, the University of Stockholm and the Finnish Meteorological Institute were visited by a representative from IVL who had prepared 3 replicate samples of an NBS propane standard plus 3 replicate samples of ambient air. It was concluded that the majority of the hydrocarbons were analysed within $\pm 10\%$ of the median value by the 3 laboratories (Lindskog and Mowrer, 1992).

3. Observed concentrations of individual hydrocarbons

3.1. Actual observations, 1988-1993

In this report we present measurements from the period January 1988 - June 1993. Figures 1-2 show the daily observations for nine components together with their sum during these years. The Figures show that there was a substantial scatter in the observed concentrations especially for short lived components like propene, i- and n-butane and i- and n-pentane. Episodes with elevated concentrations mostly occurred in winter except for propene which reached high concentrations also in summer.

The solid curves in Figures 1-2 are the least squares fit to the function:

$$C = c_0 + c_1 \text{ sine } (c_2 + (t-1988) 2\pi) + c_3 (t-1988) \quad (1)$$

where t is the time (in years). The calculated concentration function C is a sine function, which represents the seasonal variation, with a linear term added, representing a long time trend in the concentration. The coefficients c_0 , c_1 , c_2 and c_3 were calculated by the least squares method. Table 3 gives the calculated coefficients c_0 (the "average" concentration), c_1 (the amplitude of the seasonal variation), the julian date of maximum concentration (deduced from c_2), and c_3 , the linear trend. The dashed curves in Figures 1-2 are the least squares sine fit for each year (from summer to summer) without the linear term. Differences between the dashed and solid curves indicate anomalies in the concentration between specific seasons and years.

For ethane, ethene and propane the sine fit for each year is close to the overall linear+sine fit, indicating only small variations from one year to another for these components. For the other components the yearly sine fit shows a higher value in 1992, consistent with the numerous episodes in the same year.

Table 3: Calculated coefficients in equation (1) by the least squares fit.

	c_0	c_1	c_2	c_3
	"mean" (ppt)	Amplitude (ppt)	Julian day of max value	Trend (ppt/year)
C_2H_6	2 060	920	49	-59
C_2H_4	670	260	6	-51
C_2H_2	520	400	17	+33
C_3H_8	820	540	33	-16
C_3H_6	180	30	1	-14
n- C_4H_{10}	550	340	352	+41
i- C_4H_{10}	250	170	342	+39
n- C_5H_{12}	270	120	356	-15
i- C_5H_{12}	270	200	330	-28
Σ NMHC	15.4 ppbC	7.5 ppbC	9	+132 pptC/year

The relative amplitude c_1/c_0 expresses the seasonal variation. It was largest for acetylene with a value of 0.77, and smallest for the most short lived components

propene (0.17) and ethene (0.39). Zander et al. (1991) investigated the seasonal cycle of acetylene at Jungfraujoch by a least square sine fit and found a yearly mean of 0.26 ppb, and an amplitude of 0.13 ppb. The smaller relative amplitude at Jungfraujoch than at Birkenes can be taken as indications of sources of acetylene closer to the Jungfraujoch station than at Birkenes.

The maximum concentration was found to be in the winter for all the components. However, while the curves fitted for *i*- and *n*-butane and *i*- and *n*-pentane have maximum values in the last part of the year, the time of the maxima for the other components was calculated to be in the first two months of the year. The calculated date of maxima for the short lived components ethene and propene were close to the beginning of the year, while ethane, the most long lived one, was calculated to have a maximum late in the winter. This relation between life time and seasonal cycle reflects that short lived components are mostly controlled by the rate of chemical decomposition determined by the UV-radiation, while long lived components continue to grow in concentration in the first part of the year because of an imbalance between the emission rate and the photochemical loss at this time of year.

The calculated trends were quite different for the components. Ethene and propene were calculated to decrease with approximately 51 ppt/year and 14 ppt/year respectively, or approximately 8%/year, while acetylene was calculated to increase by 33 ppt/year or 6%/year. The long time trends are further discussed in section 6.

In Table 4 is given the monthly average concentrations of the nine components and their sum with all data from 1988-1993, and Table 5 shows the seasonal average concentrations, together with the ratio of the winter to summer average concentrations and the lifetimes in winter and summer. Seasonal averages were defined as three months averages (Dec-Feb, Mar-May, June-Aug, Sep-Nov). The lifetimes were calculated by the reaction rate constants of Atkinson (1990), assuming temperatures of 0 °C and 15 °C, and OH average concentrations of $2 \cdot 10^5$ and $1 \cdot 10^6$ molecules/cm³ in the winter and the summer, respectively. The ozone concentration, for the alkene reactions, was set to $1 \cdot 10^{12}$ molecules/cm³ (~40 ppb) in both seasons.

The Tables 4 and 5 show that ethene, acetylene, propane and *n*-pentane had a maximum average concentration in the winter season, ethane had a maximum average in spring, while the others had the highest averages in autumn. The spring maximum of ethane was shown also by the date of maximum calculated by the sine fit above, and can be explained by the lifetime through the OH reaction. If the lifetime is sufficiently long, there will not be an equilibrium between the emissions rate and the chemical decomposition, and the concentration will continue to rise until the UV-radiation becomes sufficient to cause a large enough increase in OH.

Table 4: Monthly average concentrations of nine NMHC and their sum observed at Birkenes in the period January 1988-June 1993. Values are given in pptv, except the sum which is in ppbC.

	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	C ₃ H ₈	C ₃ H ₆	n-C ₄ H ₁₀	i-C ₄ H ₁₀	n-C ₅ H ₁₂	i-C ₅ H ₁₂	Σ NMHC
Jan.	2588	761	919	1214	157	819	423	348	436	21.5
Feb.	2661	781	890	1291	185	784	408	259	336	20.8
March	2801	630	926	1279	154	892	462	278	367	21.7
April	2681	480	770	1070	114	594	305	202	250	17.3
May	1939	323	415	514	97	267	137	98	139	10.0
June	1268	271	207	288	97	249	130	91	138	7.2
July	1085	346	194	319	139	317	192	116	197	8.2
Aug.	966	299	229	304	112	432	287	150	257	9.1
Sept.	1153	336	313	415	99	609	382	197	375	12.0
Oct.	1725	769	827	741	185	1079	589	379	663	21.3
Nov.	1895	735	829	883	184	987	492	322	546	20.4
Dec.	2088	636	826	1013	131	826	412	275	437	19.0

Table 5: Annual and seasonal average concentrations of nine NMHC and their sum observed at Birkenes in the period January 1988-June 1993. Values are given in pptv, except the sum which is in ppbC. Ratio of winter to summer average concentrations (w/s) are also given. τ_w and τ_s are lifetimes in winter and summer, based on reaction rate constants by Atkinson (1990), and $[OH] = 2 \cdot 10^5$ molecules/cm³ in winter, and $1 \cdot 10^6$ molecules/cm³ in summer and $[O_3] = 1 \cdot 10^{12}$ molecules/cm³ in both seasons. The temperature was set to 0°C for winter and 15°C for summer.

	Year	Winter	Spring	Summer	Autumn	w/s	τ_w (days)	τ_s (days)
C ₂ H ₆	1972	2363	2506	1125	1585	2.1	296	49
C ₂ H ₄	530	705	489	302	611	2.3	4	1
C ₂ H ₂	627	877	723	209	654	4.2	80	14
C ₃ H ₈	805	1124	983	302	676	3.7	61	11
C ₃ H ₆	136	145	124	114	155	1.3	1	0.3
n-C ₄ H ₁₀	652	822	608	323	890	2.5	26	4.8
i-C ₄ H ₁₀	348	418	313	194	488	2.2	27	5.1
n-C ₅ H ₁₂	226	315	200	116	299	2.7	16	3.1
i-C ₅ H ₁₂ *	337	436	261	190	528	2.3	16	3.1
ΣNMHC	15.9	20.4	16.7	8.1	17.8	2.5		

* The temperature dependency of i-pentane was assumed to be equal to that of n-pentane.

3.2. Comparison with other measurements

In Table 6 is shown the median concentrations of the nine NMHC for winter and summer for the period 1988-1993 at Birkenes, compared to the winter and summer median concentrations in a period in 1992-1993 at four European sites: Rucava (56°N, 21°E) in Latvia, Langenbrügge (52°N, 10°E) in N. Germany, Tänikon (47°N, 9°E) in Switzerland, and Kosetice (49°, 15°E) in the Czech republic (Solberg et al., 1993). The average of the measurements at a remote marine location in the Pacific (Greenberg and Zimmerman 1984) are shown as well.

Table 6: Median concentrations of nine NMHC at Birkenes 1988-1993 in winter (w) and summer (s), compared with winter and summer medians of the NMHC at four European locations 1992-1993 and average concentrations in the remote Pacific. All values are in ppb.

	Birkenes ¹		Rucava, Latvia ²		Langenbrügge, Germany ²		Kosetice, Czechia ²		Tänikon, Switzerland ²		Remote marine ³
	w	s	w	s	w	s	w	s	w	s	
C ₂ H ₆	2.4	1.1	2.5	1.7	2.9	1.5	2.9	1.6	3.2	1.5	1.8
C ₂ H ₄	0.58	0.27	0.8	0.19	1.4	0.22	1.8	0.30	3.3	0.52	0.46
C ₂ H ₂	0.73	0.19	1.2	0.43	1.6	0.50	2.0	0.63	4.0	0.79	0.51
C ₃ H ₈	1.1	0.28	1.4	0.35	1.6	0.45	1.5	0.50	1.7	0.52	0.72
C ₃ H ₆	0.12	0.09	0.17	0.06	0.33	0.05	0.34	0.07	0.68	0.11	0.22
n-C ₄ H ₁₀	0.67	0.21	0.66	0.17	0.87	0.21	0.76	0.28	1.5	0.61	0.17
i-C ₄ H ₁₀	0.34	0.12	0.33	0.09	0.46	0.11	0.41	0.14	0.67	0.22	0.11
n-C ₅ H ₁₂	0.24	0.09	0.21	0.06	0.28	0.06	0.31	0.11	0.44	0.22	0.03
i-C ₅ H ₁₂	0.31	0.12	0.26	0.07	0.42	0.11	0.44	0.21	1.1	0.57	0.02
	w	s	w	s	w	s	w	s	w	s	

1) This report.

2) Solberg et al., 1993.

3) Greenberg and Zimmerman, 1984

In winter the median concentrations of the five C₂-C₃ components were lower at Birkenes than at the other European sites, while the median concentration of n- and i-butane and n- and i-pentane was similar at Birkenes and at Rucava. In summer the median concentration of the alkenes was higher at Birkenes than at Rucava and Langenbrügge. The median concentrations of the C₄ and C₅ alkanes were close to the medians at Langenbrügge.

This comparison indicates that there are sources of butanes and pentanes closer to Birkenes than for acetylene and the other alkanes. There must also exist sources of ethene and propene close to Birkenes in summer.

At Birkenes the concentrations of ethane, propane and acetylene are lower than at the other European stations, and this shows that Birkenes is more remote from the major emission areas of these components than the other European sites shown.

3.3. Average seasonal variation

In Figure 3 is shown the 30 days' running average concentration and standard deviation during an annual cycle of the nine NMHC and their sum, averaged from 1988-1993. The running average was calculated each date from the observations in the period ± 15 days around that date in all the years. The standard deviation was calculated by the expression:

$$\sigma_j = \sqrt{\frac{\sum(c_i - x_i)^2}{N-1}}, \text{ for } i = j - \frac{n}{2}, \dots, j + \frac{n}{2} \quad (2)$$

where c_i is the actual observation on date i one year, X_i is the n ($=30$) days' running average on the same date i , the same year, and σ on date j was calculated from all the $i=1, N$ observations in the ± 15 days period that year. The resulting values were then averaged for the same date in the different years from 1988-1993. The vertical bars in Figure 3 marks the \pm one σ levels, and are shown with one week's interval. This definition of σ expresses the average episodic nature of the components during the annual average cycle, while differences from one year to another, due to e.g. different prevailing transport patterns, or different start times of the spring degradation are eliminated. The variations between the years have already been shown in Figures 1-2.

The seasonal variation in both the 30 days' running average and the standard deviation was very similar for ethane and propane. The difference between ethane and propane compared to the other components, indicates that the regulating factors of these two groups are different. The measured concentrations at a remote site like Birkenes is controlled by the photochemical activity, the transport and the mixing with the free troposphere. For two components with similar lifetimes, such as propane and acetylene, the magnitude of the episodes and the seasonal variation should be similar if the sources were similar. The different seasonal cycle of acetylene and propane then implies that their sources are different. This is consistent with the investigations of NMHC source profiles (Nelson et al., 1983; Field et al., 1992; Harley et al., 1992). The standard deviation, σ_j , which expresses the episodic nature, was much lower for ethane and propane than for the other components, indicating a well mixed mid latitude northern hemisphere for C_2H_6 and C_3H_8 .

Peaks in the 30 days' running average and in the standard deviation in October/November were observed for the alkenes, acetylene, and C_4 and C_5 alkanes, but not for ethane and propane. The high average concentrations in autumn were a result of frequent episodes with high concentrations of the C_4 and C_5 alkanes and acetylene, as seen in Figures 1-2. The sector analyses (section 4) show that these episodes were linked to transport from south.

Figure 3 shows that there was an average local maximum concentration in July for propene. The seasonal amplitude of ethene was also less than what one should expect from its reactivity. The peak in the propene concentration seen in summer and the higher concentration than expected of ethene in the same season, can probably not be attributed to anthropogenic sources. Biogenic emissions from

coastal areas upwind of the site (Hov et al., 1989), or from the North Sea may contribute. The short lifetimes of these components in the summer (Table 3) reduce the chances for long range transport.

In a review of the global distribution of light hydrocarbons in the oceans, Rudolph et al. (1993) found that oceanic emissions of light hydrocarbons (C_2 - C_4) were reported in the range 10^8 - 10^{11} molecules/(cm^2s). The emissions are highest for light alkenes, and generally lower for the alkanes. Light alkenes are mainly formed by photochemically induced reactions of dissolved organic carbon (DOC). It seems that only a part of the total pool of DOC in the oceans is a potential precursor for alkenes. Budget considerations indicate that in ocean surface water, for alkenes the most important loss mechanism is emission to the atmosphere.

On a German-Soviet cruise in the North Atlantic in April-May 1991 Ratte et al. (1993) found that the emission rate of ethene was about $1 \cdot 10^8$ molecules/(cm^2s), of propene and 1-butene about 40 % of this rate. There was strong evidence that the presence of dissolved organic matter was necessary. Dissolved organic matter may be released from algae and then transformed photochemically to alkenes.

Bonsang (1993) found from measured depth profiles of ethene, propene and acetylene in seawater that ethene and propene are the two major hydrocarbons present with a minimum in winter and in the spring and fall the water column concentration is a factor of two-five higher. There is some fall off with depth below the surface layer of ethene and propene, while acetylene has a quite constant concentration with depth down to approx. 1500m with no seasonal variability, and it is concluded that the production of acetylene could result from a mechanism independent of biological processes.

Rudolph et al., (1989) showed that in the remote marine troposphere in Antarctica the annual average mixing ratios of 0.36 ppbv of ethene and 0.21 ppbv of propene was dominantly caused by oceanic biogenic emissions.

In Figure 4 is shown the 30 days' running average concentration of each component, scaled by its annual average concentration. In this figure only n-butane is shown, but the scaled seasonal variation of the other three C_4 and C_5 alkanes were almost identical to n-butane.

In the spring, when the rate of chemical loss increases, there was a clear tendency that the most short lived components declined first. The decline in the ethene concentration in spring started in the first part of March, followed by C_4 and C_5 alkanes, and then acetylene and propane were reduced. That the curves for propane and acetylene in spring are similar, is in good agreement with the lifetime which is similar for these two components. The average spring decline in ethane, the most long lived component, did not start until mid of April and the summer minimum concentration in acetylene and propane was reached 1-2 months before the minimum in the ethane concentration.

In Figure 5 is given the 30 days' running average concentration and standard deviation of the sum of the nine NMHC observed at Birkenes from 1988-1993

(same as in Figure 3) compared to the sum of the same components observed on the Zeppelin Mountain on Spitzbergen from September 1989-June 1993. The running average and standard deviation was calculated as described above.

The seasonal variation was much greater at the remote Arctic station than at Birkenes, but in January and February the sum of the concentrations were similar at the two stations, around 20 ppbC. The standard deviation, expressing the frequency and magnitude of episodes, was several times higher at Birkenes than at the Zeppelin Mountain. The fact that the average sum of NMHC in winter were similar at the two locations illustrates the importance of long range transport and the slow decomposition of the NMHC during that time of the year.

4. Sector analyses

Differences in the observed hydrocarbon concentrations due to transport from different geographical areas, were studied using trajectories arriving at Birkenes for the period 1988 - May 1993. Four days' back trajectories were calculated every 6 hours for horizontal winds on the 925 hPa isobaric surface given for the EMEP grid as described by Hov et al. (1989) and Hov and Schmidbauer (1992). Meteorological data were supplied by the Norwegian Meteorological Institute. The 360° geographical circle around Birkenes was divided into 5 sectors, NE, SE, S, SW, and NW, as shown in Figure 6. A transport sector was then allocated for each day with NMHC measurement if more than 50% of all the trajectory coordinate points between 150 and 1500 km that day were inside one sector. The meteorological data for 1993 were preliminary, with missing data some days resulting in a number of days without calculated trajectories.

Figure 7 shows the average sector concentrations for the four seasons and for the entire year, with all the data from 1988-1993. The number of trajectories allocated to each sector for each season is given in Table 7.

Table 7: Number of trajectories allocated to the different sectors.

	NE	SE	S	SW	NW	Undef
Winter (Dec-Feb)	5	18	12	83	55	21
Spring (March-May)	19	34	12	63	64	48
Summer (June-Aug)	5	13	3	56	67	18
Autumn (Sept-Nov)	10	21	11	51	52	23
Total	39	86	38	253	238	110

The highest annual average sector concentration of the sum of the hydrocarbons was from the south (24 ppbC), and the second highest from SE (18 ppbC). All the individual components also had the highest average concentration from S for the whole year, but this changed for the different seasons. The minimum annual average sum of the NMHC was from the NW (13 ppbC).

The difference between the components became pronounced in spring, when the C₄ and C₅ alkanes had the highest average concentration from SW and the alkenes had the highest averages from S, while the three long lived components, ethane, propane and acetylene were more uniformly distributed in all sectors. The uniform distribution of these components indicates that the long lived components are well mixed throughout the lower troposphere in the spring.

In summer all components had low concentrations, but the maximum average propene concentration from sector SE was pronounced, which may be an indication of biogenic emissions from the ocean in that direction (Skagerrak). Notice that the concentrations from S should be interpreted with care, as only 3 trajectories originated from this sector in summer (Table 7).

Figure 7 shows that a large part of the episodic occurrence of elevated concentrations in the components in October/November is explained by transport from south. The autumn average in the sum of the NMHC in this sector was 30 ppbC. The average acetylene and ethene concentrations were higher from S in autumn compared to the winter, while the average concentrations for the C₄ and C₅ alkanes were higher from all the three sectors SE-SW in autumn than in the winter.

5. The distribution profile of the individual hydrocarbons

The concentration of individual NMHC relative to each other (the NMHC distribution profile), has been proposed as an indicator of the chemical age and history of an air mass (Nelson et al., 1983; Roberts et al., 1984; 1985). The term *chemical age* refers to the fact that due to the photochemical decomposition the fraction of slowly reacting components will increase compared to the reactive compounds in an air mass without new emissions.

However, when measuring at a remote site like Birkenes, the observed distribution profile is the result of many sources, and each component has its own chemical lifetime, which is a function of time and position. Furthermore, the emissions of hydrocarbons vary in composition in space and in time in a complex way, and vary even with time.

It is therefore very difficult on the basis of data presented in this report, to determine the origin of an air mass arriving at Birkenes, from the "fingerprint" of the NMHC distribution profile using only single day measurements. On the other hand, when averaging over a number of days, and over larger source regions, as in the method of the sector analysis described, some general features of the distribution of the NMHC emissions in different geographical areas emerge.

5.1. NMHC in different seasons

Figure 8 shows the 30 days' running average through an annual cycle of the relative fraction of the individual hydrocarbons as per cent of the sum when all

data from 1988-1993 were included. The fractions were calculated on a ppbC basis for each component.

The distribution was nearly uniform through the winter and the early spring with approximately 25% ethane, 19% propane and 15% n-butane as the three most abundant components when given in ppbC. In April/May the average ethane fraction rose to a peak above 40% and then decreased gradually through the summer and reached a minimum value in October/November. The accompanying decrease in the fraction of other components during spring was not observed for the alkenes, which increased to a maximum in the summer - an indication of biogenic emissions as explained above.

The maximum in the ethane fraction is consistent with the slow chemical degradation of ethane by the OH radical in the spring. As seen from Figure 4 the chemical degradation of the NMHC in spring occurs in the same order as of the reactivity - the most volatile components drop in concentration first. This implies that the fraction of the most long lived component, which is ethane, will increase for a period in the spring.

5.2. NMHC distribution in different sectors

The NMHC distribution profile from different sectors has also been analysed. The analyses have been made for each season separately, and the results averaged for 1988-May 1993 are shown in Figure 9. The Figure shows the percentage of each component on a ppbC basis relative to the total sum in each sector for the four seasons and for the entire year. The components are arranged with decreasing lifetime from the bottom to the top. As mentioned, due to the low number of allocated trajectories (Table 7), some of the columns in Figure 8 are not representative, these are the NE sector in winter (5 trajectories), and the NE and S sectors in summer (5 and 3 trajectories, respectively).

In all the seasons the fraction of the short lived components increased from the northerly to the southerly sectors, as expected from the difference in the chemical age of air masses (Roberts et al., 1984; 1985 and Parrish et al., 1992). However, in all the sectors the fraction of the long lived components ethane, acetylene and propane was highest in spring and lowest in autumn. Compared to spring, the fraction of the most short lived components, ethene and propene, increased significantly in the summer in all the sectors, while there was a pronounced decline in the fraction of propane and acetylene. This is just the opposite of what one should expect from the idea of chemical ageing of air masses polluted by anthropogenic, continental sources. The presence of closer, biogenic emissions of the alkenes in summer provide an explanation for this, but this cannot explain why there was a rise in the fraction of the C₄-C₅ alkanes from spring to summer in all the sectors as well.

In the autumn the influence of a number of high episodes from the S sector can be seen. The fraction of ethene and acetylene was especially high in this sector in the autumn, and there was a minimum of 17% in the ethane fraction. In the same

season the fraction of C₄-C₅ alkanes was high in all the sectors. This indicates that the episodes were caused by a combination of high emissions and fast transport.

The increase in the fraction of the short lived components in summer and autumn in all sectors is consistent with the larger seasonal variation observed for the long lived species (Figures 1-2, Tables 3-5). It shows that there is not necessarily a simple inverse proportionality between the relative fraction of volatile compounds and the photochemical lifetime except maybe at very remote sites, or in the case of just one dominant source influencing the measurements. More often the measuring site, like Birkenes, is influenced by a lot of sources at different distance from the site. Then the fraction of the short lived components may even *increase* with increasing photochemical activity, when a larger part of the observed concentrations originate from the closest sources.

The high fraction of short lived components observed at Birkenes in summer, and the smaller seasonal variation of these components, may therefore be attributed to several source areas, ranging from areas nearby to the large emission areas in central Europe. In summer a high fraction of the emissions in central Europe is decomposed before arriving at Birkenes, and a larger part of the observed concentrations originates from closer source areas with lower emission rates.

The average sector concentrations in Figure 7 for the short lived components therefore reflect the geographical distribution of the emission areas close to the site in summer and the more remote emission areas in winter.

5.3. Interpretation of emission sources from the distribution of NMHC

If the source strength of nearby emission sources is less than the source strength of more remote sources for Birkenes, the speciation of the NMHC sources is best expressed by the average sector concentrations in winter, as argued above. Figure 9f shows the average fractions of the nine NMHC in the cases when the sum of the NMHC in each sector was equal to or larger than the 75 percentile of all the observations in winter in that sector. Figure 9f is based on 1, 4, 3, 20 and 14 observations in sector NE, SE, S, SW and NW respectively. The profile for sector NE is therefore not representative with only one case, while the other profiles are averages of several independent episodes although the number of cases is small.

Figure 9f shows large differences between the sectors. The fraction of C₄-C₅ alkanes in these pollution events was especially large in sector NW, but also sector SW and SE had a high fraction of these components. The acetylene fraction was large in sector SE as well, while sector S had a higher fraction of ethene and propene than the other sectors.

Anthropogenic NMHC is emitted from a variety of sources, with different NMHC distribution profiles depending on the type of source. A major part of the emissions is due to the distribution and use of vehicle fuel, either as combustion products or as vapours from evaporation in the engine, from unburned fuel during filling of vehicles, gas distribution etc. and from spillage and leaks. Another important source is leaks from pipelines and wells of natural gas. Also from

industrial processes NMHC are emitted, and the use of solvents is an important source (~30% of the total anthropogenic NMHC emission).

The NMHC emission from traffic and other combustion processes is known to contain a large portion of acetylene, ethene, propene and the higher order alkanes and aromatics including xylenes (Nelson et al., 1983; Bailey et al., 1990; Field et al., 1992; Harley et al., 1992). Ethane and propane, and to a lesser extent butanes and pentanes, are emitted more from natural gas distribution and application (Nelson et al., 1983; Mayrsohn and Crabtree, 1976). Evaporation of gasoline and unburnt fuel contains a high fraction of butanes and pentanes with smaller amounts of the other alkanes (Nelson et al., 1983; Harley et al., 1992).

The large fraction of alkenes in the high episodes during winter from sector S suggests that automotive combustion emissions are important, which is consistent with the high load of traffic in central Europe, but it is not clear why the acetylene fraction then is not more pronounced in this sector. All of the anthropogenic acetylene (and ethene) emissions have been related to exhaust from vehicles (Nelson et al., 1983). The low number of episodes from S Figure 9f was based on, could be one explanation for this result, but the distribution profiles in Figure 9f did not show major changes when the number of winter episodes were expanded to include all cases above the 50 percentile in each sector instead of the 75 percentile in each sector as in Figure 9f.

The maximum in the acetylene fraction in sector SE is an indication of large vehicle emissions in the eastern part of the continent as well. The difference between the episode profiles in sector S and SE in Figure 9f may then be explained by a slow, but still important photochemical activity even in the winter. The lower ratio of ethene and propene to acetylene in sector SE than in S is then an indication of a longer "photochemical time" (OH concentration multiplied by the travel time) for the emissions to reach Birkenes for transport from SE compared to S.

In the NMHC distribution profiles in Figure 9f none of the sectors show clear indications of emissions from natural gas leaks (ethane and propane). Müller (1992) estimated that the (once) "centrally planned" countries contributed 60% of the world's total natural gas emissions of NMHC. This may not be reflected in Figure 9, because of the long distance to the major natural gas emission areas and because ethane and propane are quite well mixed in the troposphere.

6. Trends in NMHC concentrations

6.1. Trends in observed concentrations and transport direction

Individual NMHC have been measured at only a few sites in Europe and the time series are usually short. Little is therefore known about the trend in the background tropospheric concentrations. A growth rate of several per cent/a has been reported for long lived anthropogenic components like acetylene (Guicherit, 1988), but the numbers are uncertain and there is reason to believe that the concentration changes according to the rising number of cars equipped with catalytic converters and other engine developments.

Due to the scatter in the data and the large seasonal cycle, a trend detection based on a straight forward regression of daily measured concentrations against time is known to be uncertain and produce errors for many atmospheric trace constituents (Gilbert, 1987). Several approaches have been attempted for sorting out the often minor time trends from the daily and seasonal variability in such data sets. In this work we used three different methods: One was a linear regression of monthly 365 days' running median concentrations, another was a least squares fit to a linear + sine function as described in Chapter 3, for monthly median concentrations, and the third method was non parametric, named seasonal Kendall slope estimation, which is suited for short time series with seasonally dependent data (Gilbert, 1987).

The basic idea in the last method is to count the positive and the negative forward time differences between all combinations of different years for each month separately, and then average over the months. If the resulting averages give a high number of either negative or positive differences, then it is probable that there is a significant trend in the data. This trend may then be estimated and is called the seasonal Kendall slope estimator which is the median of all the forward time differences described (using all months). The Kendall slope estimation method is explained in detail in Appendix 2 and in statistical textbooks, e.g. Gilbert, 1987.

In Figure 10 is shown the 365 days' running median concentration each month of each of the observed NMHC at Birkenes from 1988-1993 and the trends calculated by the linear regression of these values. The monthly median concentrations were only calculated if there were observations at least on 25% of the 365 days. The monthly values shown in Figure 10 are the monthly median concentrations scaled by their average values.

Table 8 gives the calculated trends by the three different methods. Only the trends significant on a 95% significance level are listed in the table, and the values are transformed to %/a. The numbers in Table 8 are given as $a \pm b\%/year$, where the probability that the trend is within $a-b$ and $a+b$ is 95% ($\pm 2 \sigma$, where σ is the standard deviation of the slope. For the Kendall slope estimation the upper and lower calculated 95% confidence limits are given, see Appendix 2).

The least squares sine fit was the most conservative of the three trend calculation methods, since a significant trend was found by this method for only two of the components, ethene and acetylene. A negative trend in the ethene concentration

and a positive trend in the acetylene concentration were found by all the three methods, and the estimated Kendall slopes were very close to the least squares sine fit for both of these components. The trends for propene and n-butane were calculated to be significantly negative with a decline of 7-8%/a, both by the linear regression of the 365 days' running medians and by the Kendall slope estimation.

The differences between the trends calculated by the three methods reflect the uncertainties and the limitations in the different methods. The monthly 365 days' running medians rule out the seasonal cycle. But these medians are indeed not independent values, and episodes of high concentrations may influence the median value for half a year before and after such episodes. The monthly median concentrations used in the other two methods of trend estimation are independent values, but while the least squares' sine fit depends on the assumption of an equal seasonal variation every year, the Kendall slope estimation is based on an assumption of a similar trend each month. If the real trend is upward in some months and downward in other, the Kendall slope estimate will be misleading.

Table 8: Calculated trends in the concentration of nine NMHC at Birkenes from 1988-1993. Unit: %/a.

	Linear regression of 365 days running medians	Least squares sine fit	Kendall slope		
			Estimated slope	95 % limits	
C ₂ H ₆	-	-	-1.7	-0.1	-3.2
C ₂ H ₄	-5.4 ± 1.2	-8.4 ± 5.8	-8.4	-3.9	-15
C ₂ H ₂	10.1 ± 2.1	5.9 ± 4.7	5.4	1.9	7.7
C ₃ H ₈	4.8 ± 1.7	-	-	-	-
C ₃ H ₆	-7.0 ± 3.3	-	-8.8	-4.4	-13
n-C ₄ H ₁₀	-	-	-	-	-
i-C ₄ H ₁₀	3.7 ± 2.0	-	-	-	-
n-C ₅ H ₁₂	-7.3 ± 2.5	-	-8.1	-4.0	-11
i-C ₅ H ₁₂	-	-	-	-	-
ΣNMHC	2.6 ± 1.5	-	-	-	-

The opposite trends found between acetylene and ethene (and propene except for the sine fit) are surprising, and there is no obvious reason for the result. As described in Chapter 5, the anthropogenic sources of these components are mostly the same. One reason for the opposite trends between acetylene and the alkenes may be that the alkenes are highly reactive compounds, while acetylene has a rather long lifetime (2-3 weeks). A small change in the atmospheric oxidation would therefore cause a much larger change in the alkene concentrations measured at Birkenes than for acetylene. A change in the atmospheric oxidation could be due to either a change in the meteorological transport pattern, or a rise in the tropospheric background concentration of OH or ozone. Whereas the alkenes are oxidized by both OH and O₃, acetylene only reacts with OH.

Another possible explanation for the opposite trends in acetylene and the alkenes could be a reduction in the biogenic emissions of the alkenes. In any event, an interpretation is quite uncertain, since the time series are relatively short, and the

data scattered, and therefore influenced by episodes. The yearly trends in NMHC measured at Birkenes are a result of many effects: Large scale changes from one year to another in meteorological parameters like wind speed and direction, boundary layer mixing, cloudiness etc., changes in the concentration of OH and O₃ and changes in the emissions.

As discussed in Chapter 5, the concentration of individual NMHC relative to each other may provide indications about the oxidation in the air mass during the time from the species were emitted to the measuring site (the chemical age). In Figure 11 is shown the time series of the monthly median values of the concentration ratio n-butane/n-pentane and n-butane/i-pentane from 1988-1993. A linear regression was performed for the monthly medians of the concentration ratio n-butane/n-pentane, shown by the dashed line. For n-butane/i-pentane a least squares linear + sine fit (Equation 1) was performed. The ratios were calculated from concentrations given on a carbon basis (pptC).

A pronounced increase in the n-butane/n-pentane ratio is seen. The seasonal variation in this ratio was very small, the upward trend was statistically highly significant and the linear correlation coefficient, *r*, was as high as 0.78. For the time series of n-butane/i-pentane on the other hand (Figure 11), no significant trend was found, while the seasonal variation in this ratio was larger than for n-butane/n-pentane.

As indicated in Table 5, the reactivity of the pentanes with OH is expected to be similar (Atkinson, 1990) and is faster than the reactivity of the butanes with OH. Based on the different time series in Figure 11, no obvious trend in the OH oxidation therefore can be detected. The increase in the n-butane/n-pentane ratio may instead indicate a change in the emission pattern. In Harley et al. (1992) the specification of n-butane for exhaust and fuel evaporative emission is similar to that for i-pentane, while for n-pentane less amounts are found in the evaporated unburnt fuel. This may indicate an increase in the emission from evaporated fuel in the air mass reaching Birkenes. However, the upward trend in acetylene must be due to engine exhaust, as almost 100% of acetylene is emitted from that source type.

In order to compare the trend in the concentrations with large scale changes in the transport patterns, the frequency of trajectories from the different sectors was calculated. Figure 12 shows the 365 days' running average frequency of trajectories arriving at Birkenes from the different sectors. Only the trajectories arriving at days with NMHC measurements were counted.

The Figure shows that there were large changes in the trajectory frequencies over the period 1988-1993. From 1988 until 1990 the frequency of trajectories from sector SW rose to a maximum of 45% of all the trajectories, while the number of unallocated trajectories dropped from 15 to 5%. The dominating transport sector SW was then reduced to approximately 25% from 1990 to 1991, and at the same time the frequency of trajectories from SE increased from below 10% to 18%. Also the less frequent sectors S and NE showed peak frequencies in 1991. From the last part of 1991 to 1993 this changed back again, and the frequency of

trajectories from SE dropped to a few %. The large increase in unallocated trajectories at the end of the period was due to the missing values in the preliminary meteorological data for 1993, influencing the 365 days' running average frequencies.

The fluctuations in the monthly values of the 365 days' running average concentrations in Figure 10 show similarities with the frequencies in Figure 12. The major decline in trajectories from sector S and SW in 1990 and 1991 coincided with a drop in the average concentration of acetylene, and C₄-C₅ alkanes and the following rise in the frequency of trajectories from sector SW in 1992 was correlated with the rise in the average concentration of acetylene and propene.

Except for the peak in the average concentration of propene in 1992 there is no obvious link between the changing transport directions and the general decline in the alkenes from 1988-1993, so it is an open question why the average alkene concentration drops. Although a part of the alkenes probably is due to biogenic emissions which may be highly variable in time, this is thought to be important only during a limited time of the year.

6.2. Trends in emissions into the air arriving at the Birkenes site

Mylona (1989) showed that in the years 1979-1986 there was a trend in the transport pattern which gave rise to a smaller reduction in airborne SO₂ and SO₄⁻ in NW Europe than the reduction in the SO₂ emissions. As explained above, changes in the transport pattern may explain some of the observed trends in the NMHC concentrations at Birkenes. If the integrated emissions along trajectories to Birkenes change during the time period studied, the concentrations at the Birkenes site should also change.

The spatial and temporal distribution of the anthropogenic and biogenic NMHC emissions over Europe is not so well known. Comparison of the trends in the integrated emissions of NMHC along a 96 h trajectory together with the trends in the observations, can give indications of the accuracy of the emission field.

In Figure 13 is shown the 365 days' running average of the integrated emissions (IE) of NMHC along 96 h trajectories calculated for every 6 h throughout all years, scaled by the average values for the period 1988-1992 (there was not sufficient meteorological data processed for 1993). The IE values were calculated from a time independent emission field along the 96 h, 925 hPa trajectories, taking into account the effect of the dilution due to varying mixing heights through the equation:

$$IE = \sum_0^{96h} \frac{E}{H} \Delta t, \quad (3)$$

where E is the emission as a function of position along the 96h trajectory, and H is the mixing height which is a function of location, at 12 GMT, derived from the radiosonde network over Europe, and analysed objectively to obtain the H field.

The two diagrams in Figure 13 show the 365 days' running median IE each month, with all days included (left Figure) and with only the days with NMHC measurements at Birkenes included (right side). The numbers in both Figures were scaled by their average values. Both Figures show major fluctuations in the IE, but there was no significant upward or downward trend in the period.

The peak in the 365 days' running average IE coincided with a peak in the frequency of trajectories SE-S in 1991 (Figure 12). However, there is no clear correlation between the 365 days' running average IE (Figure 13) and the 365 days' running average concentrations or trajectory frequencies (Figure 10 and 12). The IE does not take into account neither any mixing processes, nor the photochemical activity, which is controlling the NMHC concentrations measured at Birkenes during a large part of the year.

Furthermore, because Figure 10, 12 and 13 are based on 365 days' running averages, any correlation between the time series are difficult to judge, and may even be spurious.

This implies that an evaluation of the trends in observed NMHC at Birkenes due to trends in emissions along the trajectories, probably requires a detailed photochemical model calculation for the whole time period. This is beyond the scope of this report.

7. Episodes

Below we show a few examples of episodes with high observed NMHC concentrations at Birkenes. The episodes illustrate the variability of the observed concentrations, both with respect to the individual components and the total.

We have focused on two episodes, on the following dates:

I) 15 - 19 October 1989

II) 24 - 26 July 1989

7.1. Episode I: 15-19 October 1989

The middle and late part of October 1989 was characterized by a stable high pressure system extending all the way from the Azores high eastward to Southeast Europe. Further north, from 55°N to 65°N, frontal systems were passing through with the associated low pressure systems, with the lows located mostly far west in the Atlantic Ocean, some of them very intense.

The upper and surface wind at the south coast of Norway was generally strong, and the direction changed from SSW to N, depending on the position of the fronts. The polar front was located E-W across the south coast of Norway on the 17 October.

The calculated trajectories arriving at Birkenes on the 15, 17, and 19 October are shown in Figure 14. Four trajectories each day are shown (arriving at 0, 6, 12, and 18 GMT).

The frontal passage on 17 October caused a marked change in the trajectory patterns. On 15 October the trajectories all came from the north, around the back side of the old frontal system, now located in western-Russia. As the new front was passing, the trajectories changed to westerly on 17 October and to southwest on 19 October. The general wind speed at the surface was approximately 10 m/s.

The NMHC concentrations were measured on 15, 17, and 19 October 1989. The observed concentrations on these days are given in Table 9, together with the calculated 30 days' running average concentrations (data from all years). In Figure 15 is shown the actual observations for all components in October 1989. At Rörvik, Sweden, this episode was also observed, most pronounced on 19 - 20 October (Lindskog 1991). The episode has also just recently been studied with photochemical model calculations by Hov et al. (1994).

Table 9: Observed concentrations at Birkenes in the October episode 1989, and the 30 day's average of data from all years (centered around the dates of observations). All values in ppbC.

	15/10	17/10	19/10	30 d average (1988-1993)
ethane	2.8	3.0	8.1	3.5
ethene	1.7	2.4	6.0	1.6
acetylene	2.8	6.8	4.8	1.6
propane	1.5	2.2	7.0	2.2
propene	1.2	1.2	1.2	0.55
n-butane	5.9	15.1	10.0	4.0
i-butane	2.4	6.6	5.1	2.2
n-pentane	2.5	5.4	4.1	1.8
i-pentane	4.1	9.5	7.4	3.1
Σ NMHC	25.9	52.2	53.6	20.5

In Figure 15 it is seen that the concentrations of acetylene, the butanes and pentanes were high on 15-19 October (the three high cases in the middle of the month), most pronounced on 17, when the n-butane concentration exceeded 15 ppbC. There were, however, differences in the composition of the NMHC between the individual days.

On 15 October, with transport from NW-N, the propene concentration was the highest in the month, and the other components, except ethane and propane, were also significantly higher than the average level.

On 17 October, the transport shifted to westerly, and propene was slightly less, while a peak was observed in the other components except for ethane and propane. The ethane and propane concentrations were close to the 30 d average values.

On 19 October, the transport was from SW, and the ethane and propane concentrations increased significantly with ethane exceeding 8 ppbC, the third highest concentration that year. At the same time the other components were still high, but less than on 17 October (except for propene which was almost the same).

This episode illustrates that the source composition changes with sector. It also supports the general feature, that ethane and propane follow each other closely, and have sources which are different from those of the other components.

7.2. Episode II: 24-26 July 1989

This episode is linked to a quite different meteorological situation. In the mid summer of 1989 an extensive high pressure system was located in NE-Europe/S-Scandinavia and it gave clear and warm weather over large areas. An approaching cold front pressed the high pressure system eastwards in this period. The meteorological observations in south Norway indicated a weak wind field from SE, and ground temperatures of 22-30° C. The trajectories on 24 and 26 July are shown in Figure 16.

The 4 d trajectories on 24 July are very short because of weak winds, and they come from Skagerrak and south Sweden. On 26 July the trajectories are longer, extending further into Sweden, Finland and the Baltic states.

The observed NMHC concentrations in July 1989 are shown in Figure 17, and the values on 24 July and 26 July are given in Table 10.

On 24 July the concentration of propene and ethene were very high, the propene concentration of 2.5 ppbC was the second highest in 1989. The n-pentane concentration was also significantly higher than the average value (Table 10). But the concentrations of the other components on this date were close to their average levels.

The surface wind speed was a few m/s. Furthermore, the concentrations of the longer lived anthropogenic components were about average and as the lifetime of propene and ethene are a few hours to a few days (Table 6), emission from anthropogenic sources is not a probable explanation for the elevated concentrations of propene.

Since the trajectories are largely oceanic, the emission from algae in the summer warm Skagerrak Sea is a more probable explanation. Both the high temperature, the presence of sunlight to stimulate biological activity in the sea water, and the direction of the transport give rise to conditions which may produce the summer peak seen in the alkene concentrations.

Table 10: Observed NMHC concentrations at Birkenes in the July episode 1989, and the 30 day's average of data from all years (centred around the dates of observations). All values in ppbC.

	24/7	26/7	30 d average (1988-1993)
ethane	1.9	5.3	2.1
ethene	2.7	2.5	0.65
acetylene	0.44	0.33	0.39
propane	0.71	3.7	0.95
propene	2.5	0.53	0.41
n-butane	0.81	0.87	1.2
i-butane	0.40	0.50	0.72
n-pentane	1.6	0.53	0.55
i-pentane	1.2	0.55	0.82
Σ NMHC	12.3	14.8	7.8

But the concentrations, at least for propene, are remarkably high, which may indicate that the biogenic emission is highly variable both in time and space. The elevated concentration of n-pentane is another interesting feature, suggesting a biogenic source for this component as well.

On the next day of NMHC observations, 26 July, the composition of the hydrocarbons has changed radically. The propene concentration was reduced to the average value, while ethane and propane now were very high. Ethene was almost constant. At the same date there was no increase in acetylene or the C₄-C₅ alkanes. This suggests that the hydrocarbons measured at Birkenes on 26 July originated from anthropogenic emissions.

8. Acknowledgement

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Appendix 1

Figures

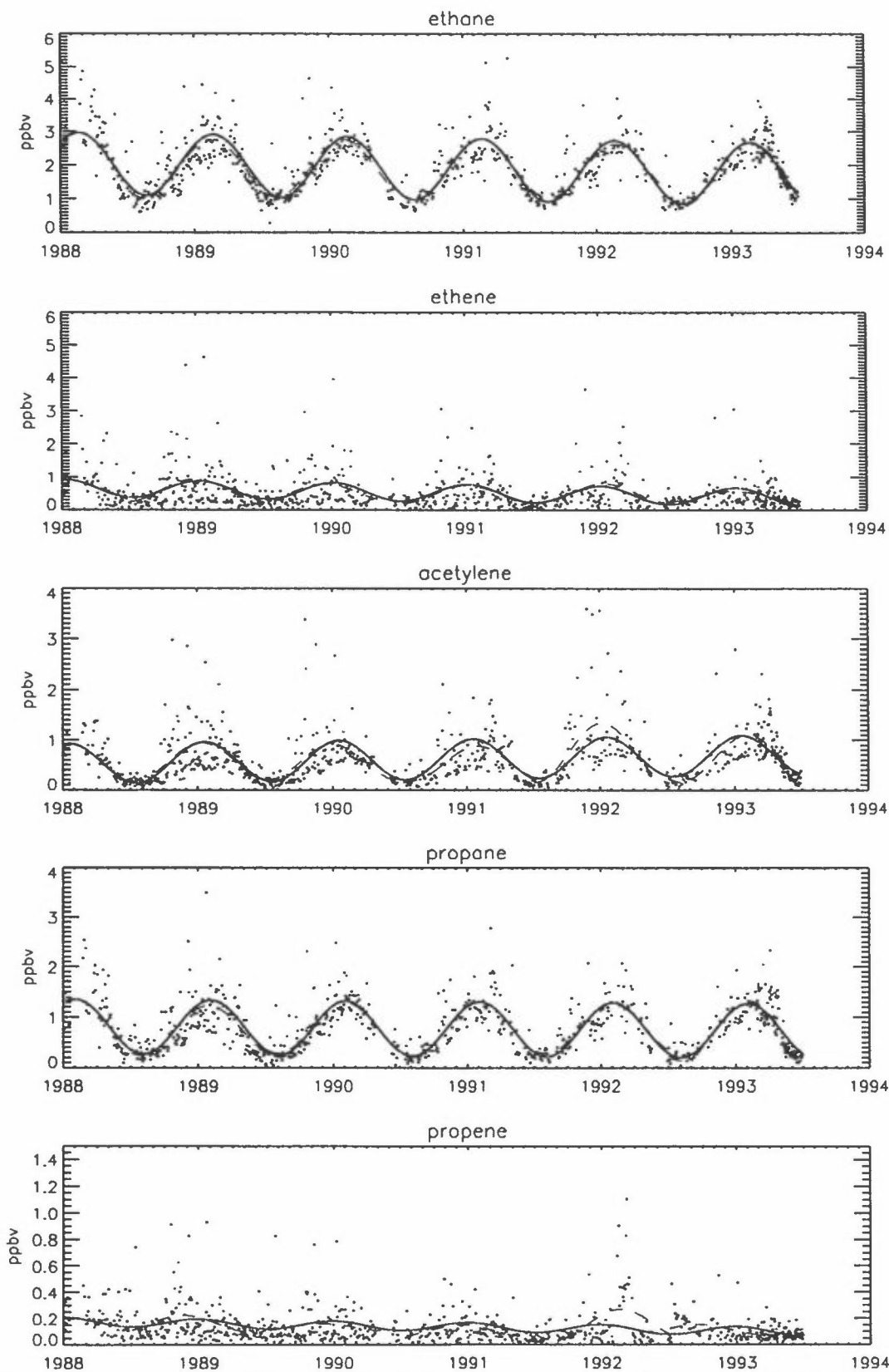


Figure 1: Daily measurements of ethane, ethene, acetylene, propane and propene at Birkenes 1988-1993 in ppbv (dots). The solid curve is the least squares fit to a linear + sine function, and the dashed curve is a least squares sine fit each year.

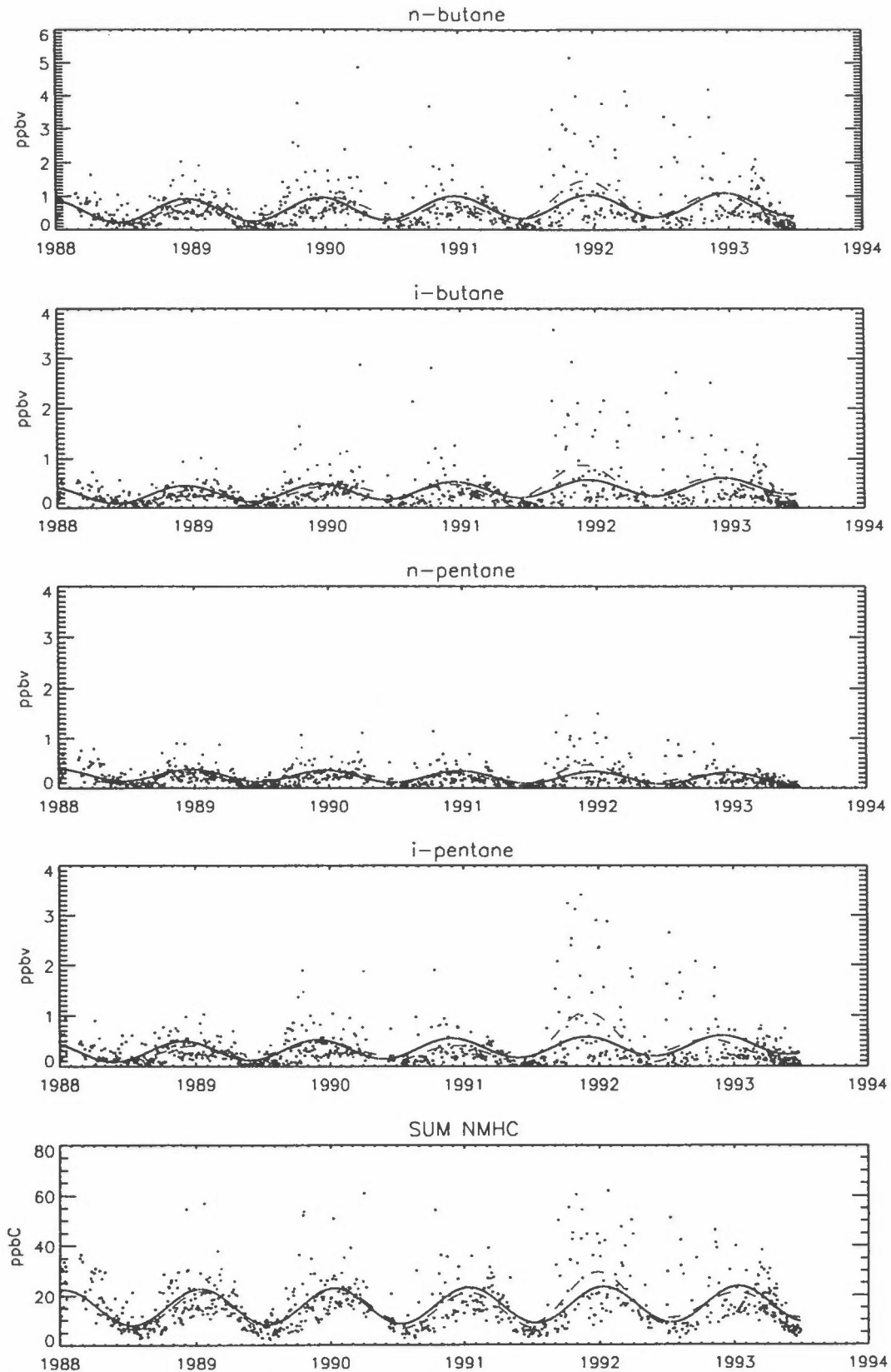


Figure 2: Same as Figure 1 for the C_4 - C_5 alkanes and the sum (in ppbC) of the nine NMHC.

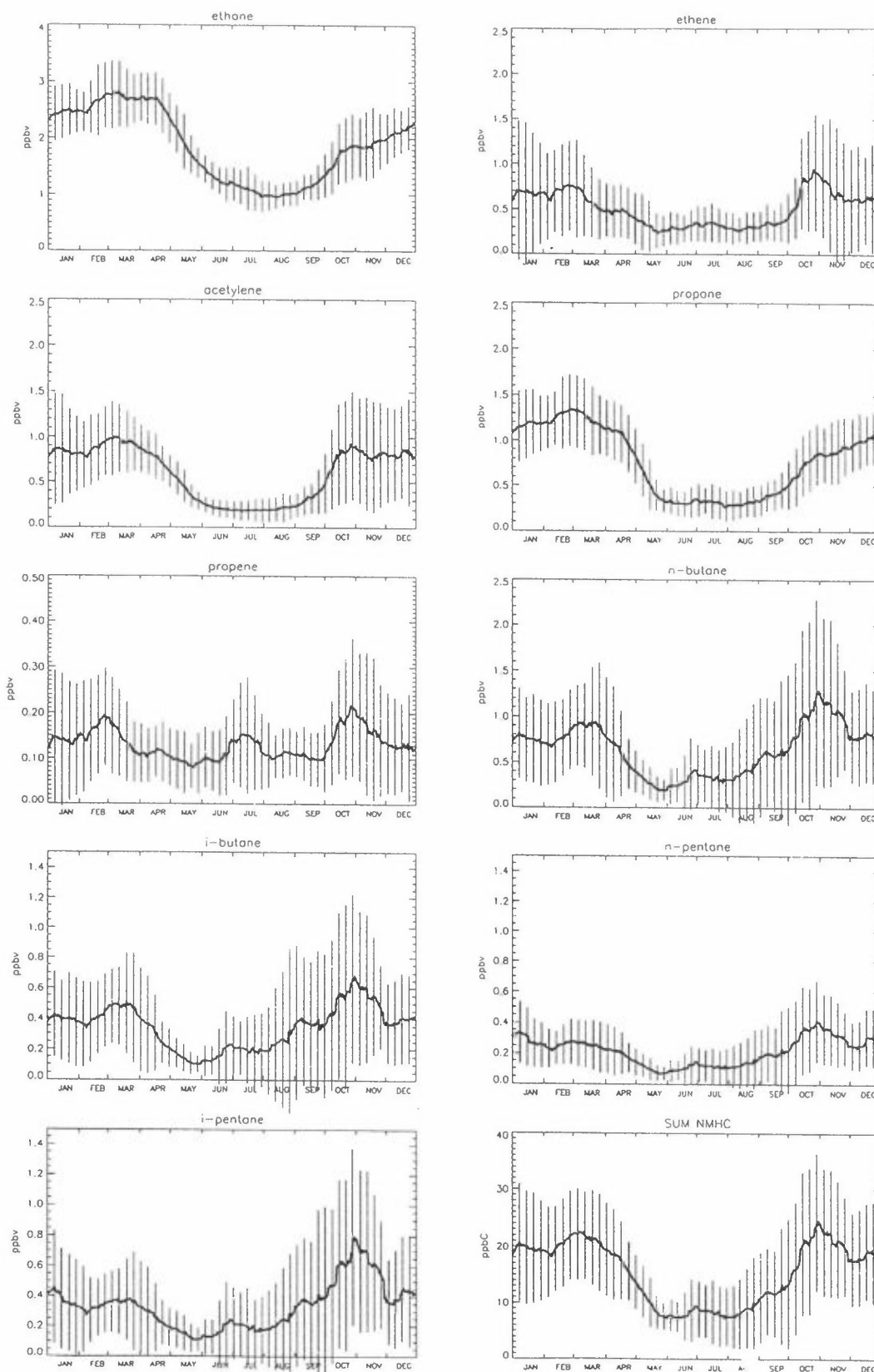


Figure 3: 30 days' running average concentrations and standard deviation bars (see text for definition) of nine NMHC in ppbv and the sum in ppbC with measurements from 1988-1993.

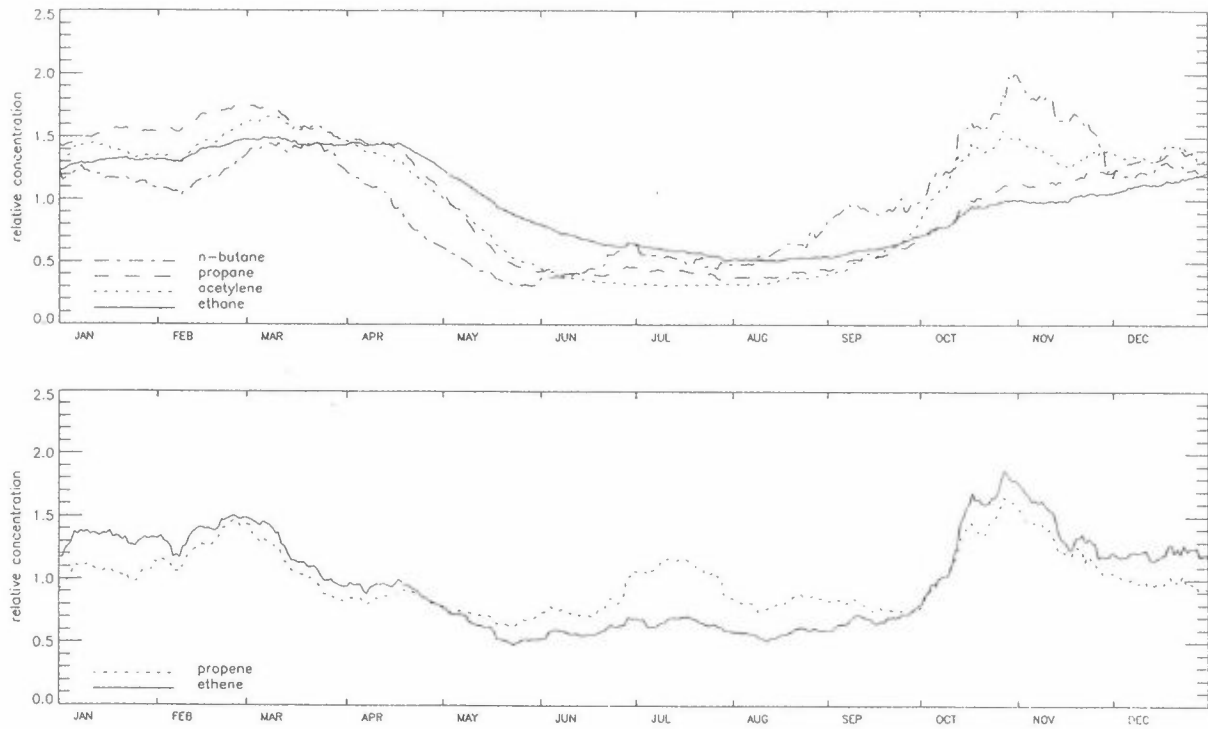


Figure 4: Scaled 30 day's running average concentrations of ethane, acetylene, propane and n-butane (upper diagram), and for ethene and propene (lower diagram).

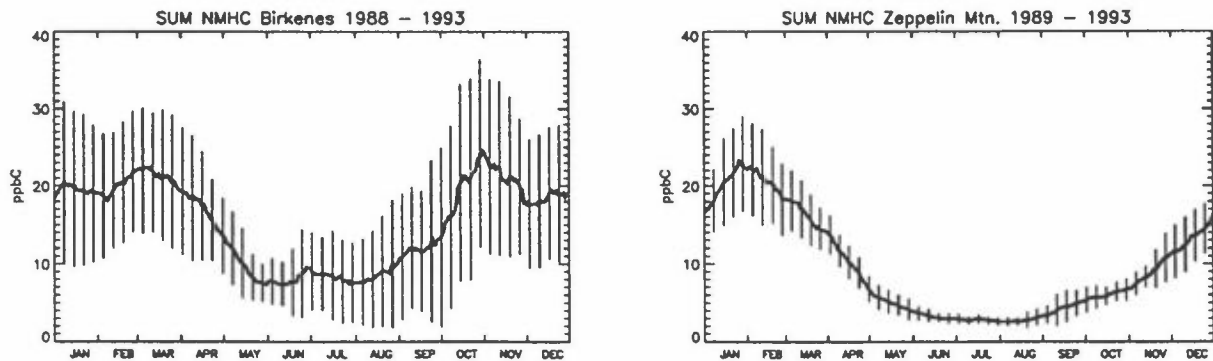


Figure 5: 30 days' running average sum of the NMHC with measurements from 1988-1993 at Birkenes (left Figure) and from 1989-1993 on the Zeppelin Mountain on Spitzbergen in the Arctic (right Figure).

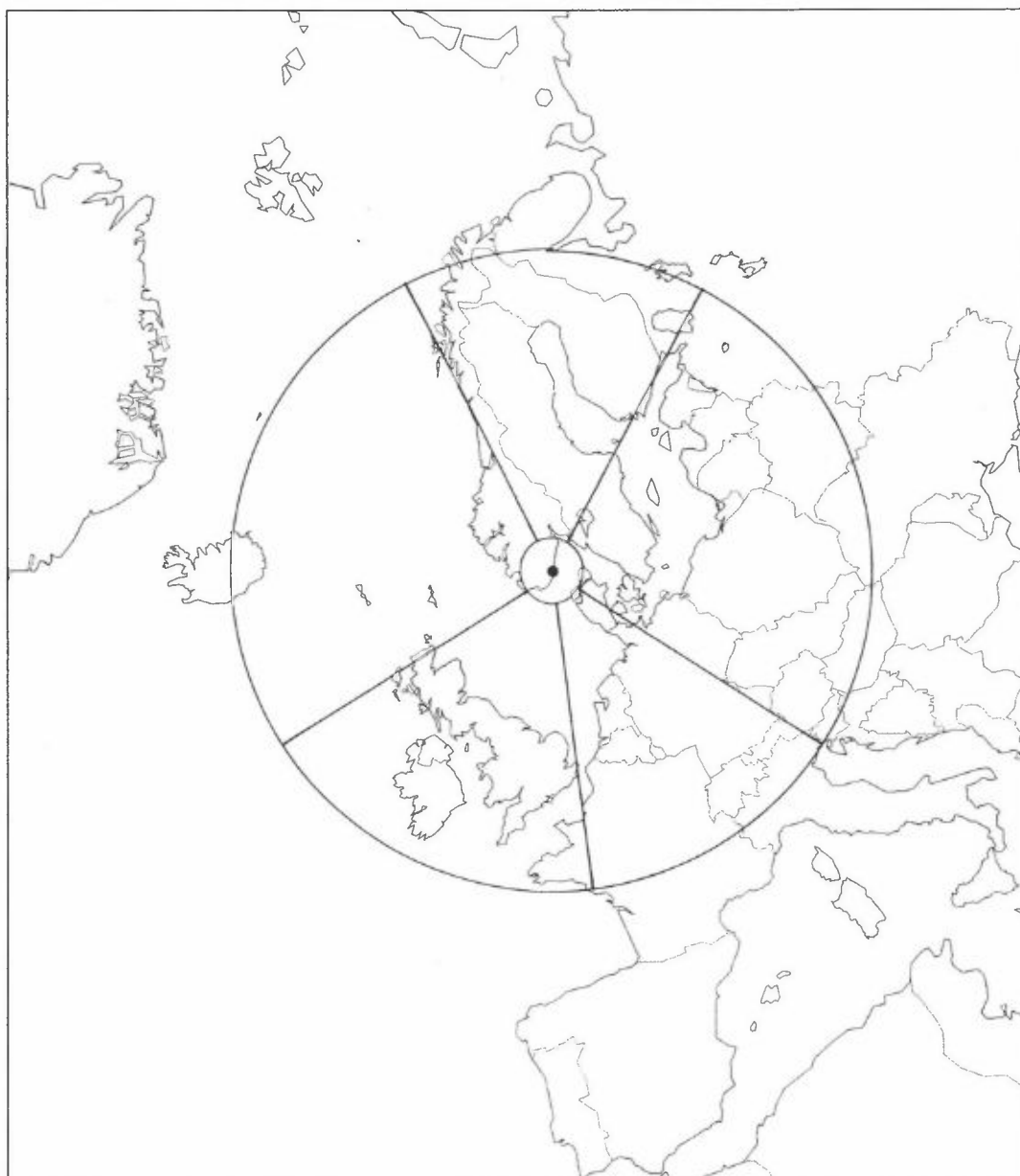


Figure 6: Map showing the location of the Norwegian TOR-station Birkenes and the sector boundaries used in the sector analyses.

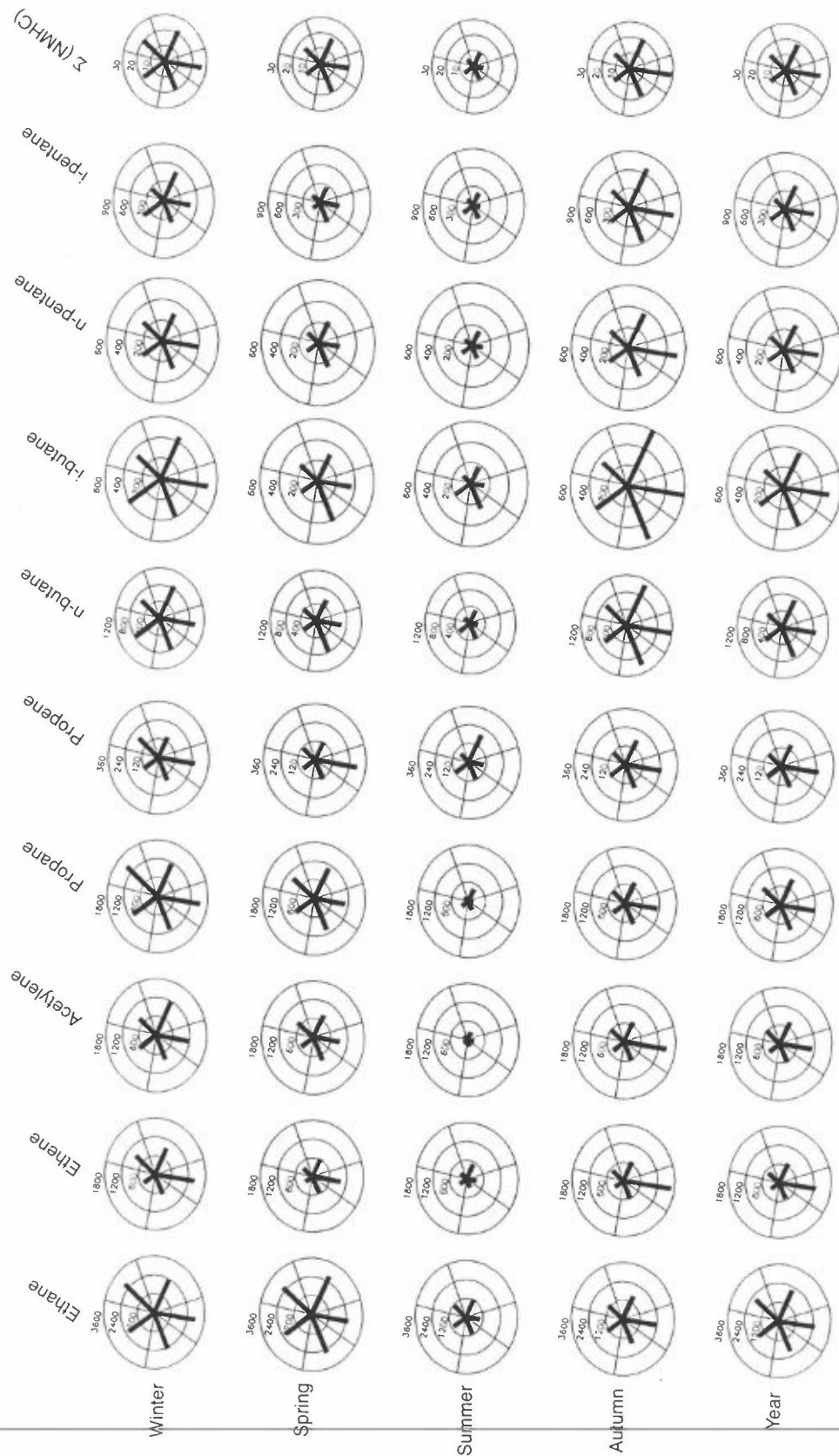


Figure 7: Average sector concentrations of the nine NMHC (ppbv) and their sum (ppbC) for the period 1988-1993 for winter, spring, summer, autumn and the year.

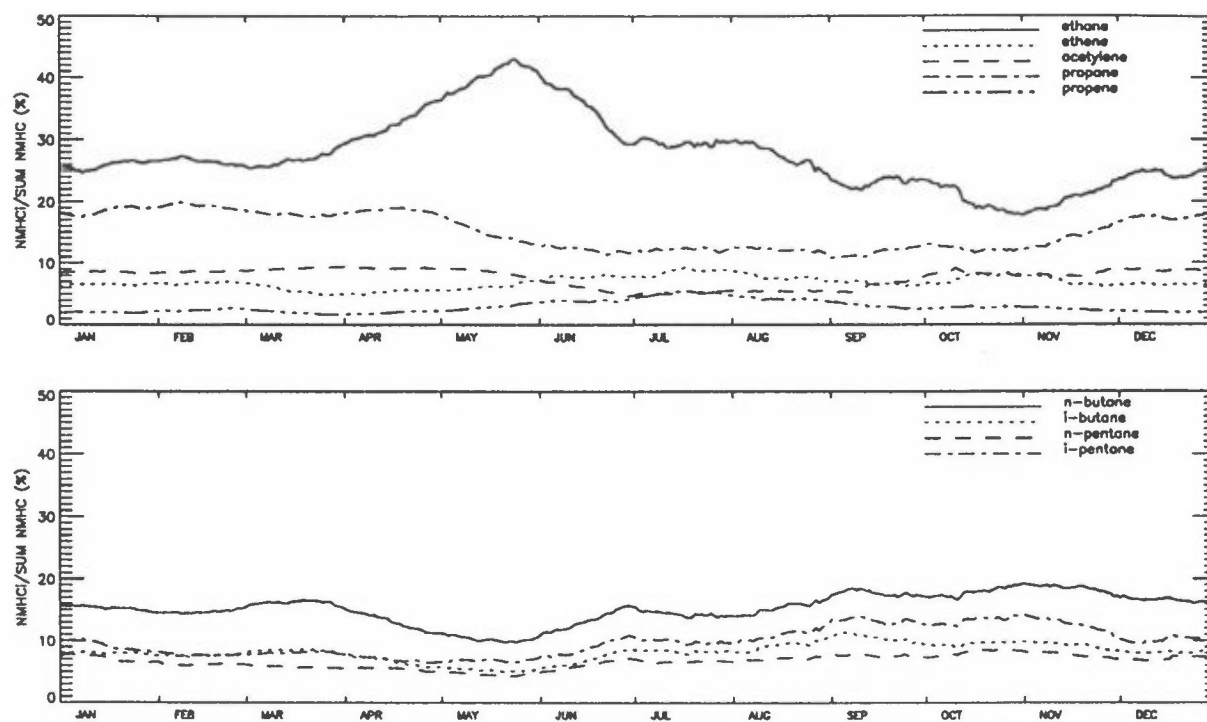


Figure 8: Fractions of nine NMHC relative to their sum (in %) during a years cycle at Birkenes. The curves show the 30 days' running average fractions with measurements from 1988-1993 included. The fractions were calculated on a ppbC basis.

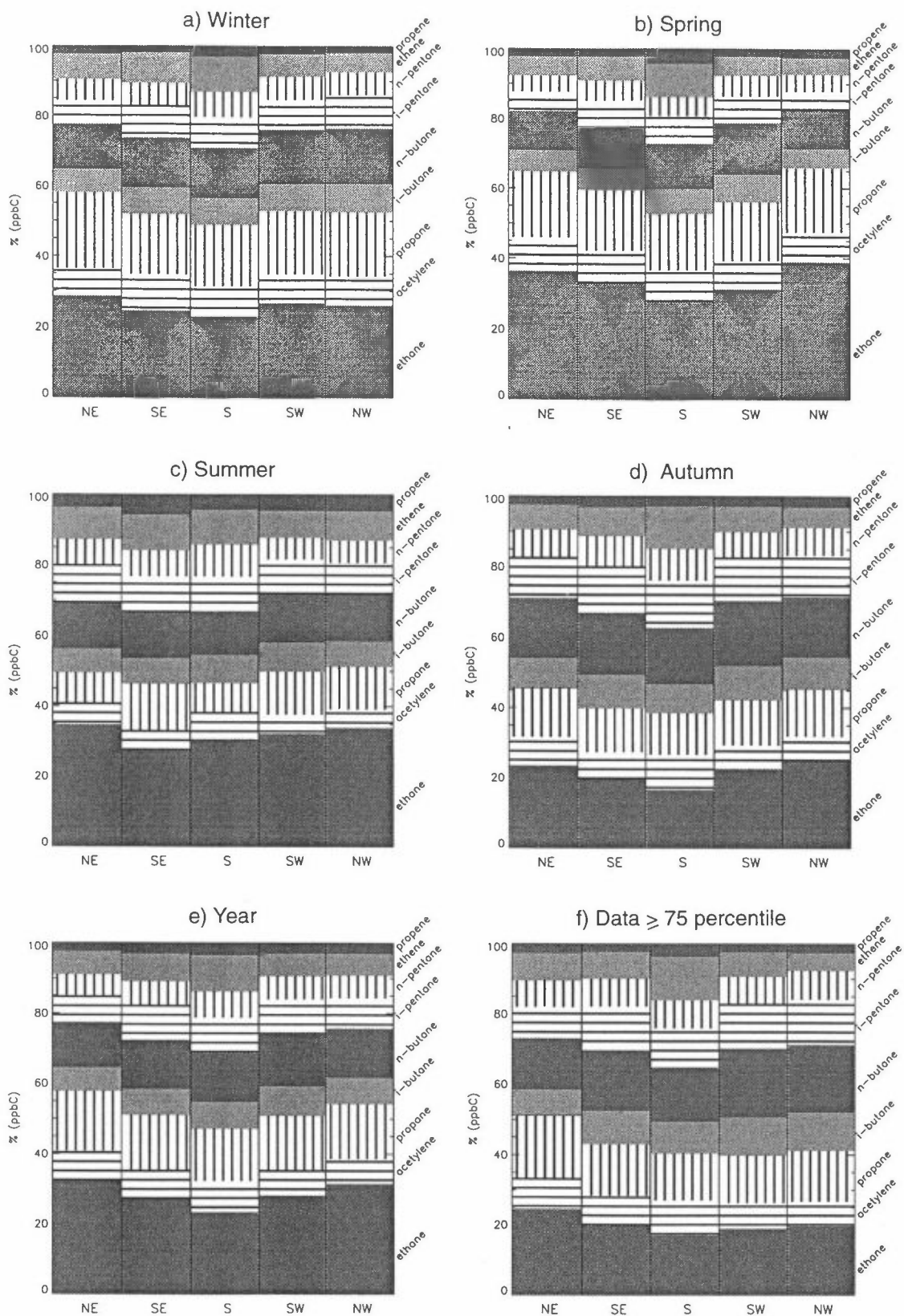


Figure 9: Average distribution profiles of nine NMHC (on a ppbC basis) in the different sectors in winter (a), spring (b), summer (c), autumn (d) and the year (e). The average distribution profiles of the episodes when the sum of NMHC was equal to or larger than the 75 percentile in each sector in winter is shown in (f).

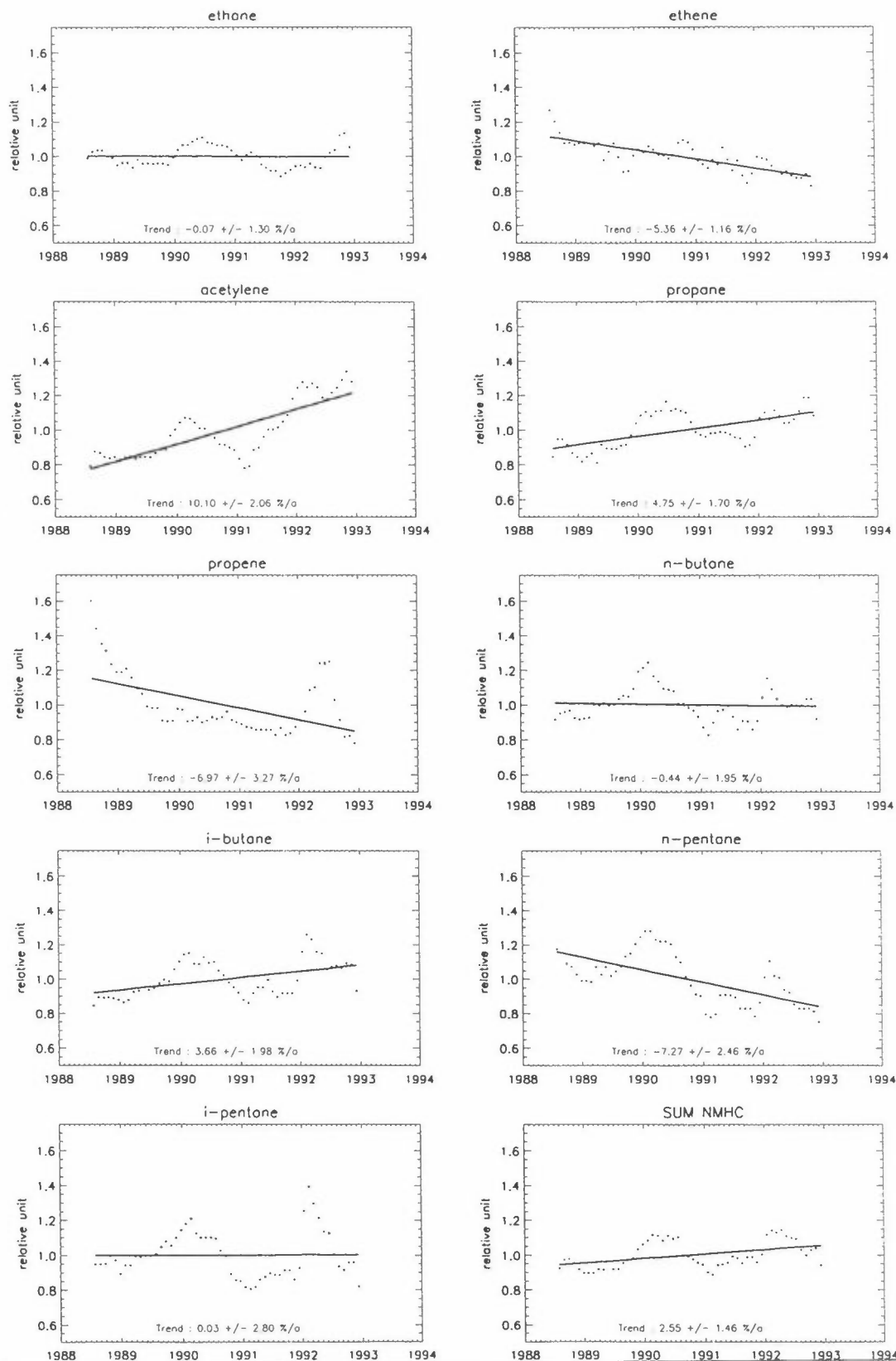


Figure 10: 365 days' running average concentrations each month in the period 1988-1993 of nine NMHC and the sum at Birkenes (dots). The straight lines show the regression lines of the same monthly 365 days' averages. The calculated trends are also given in Table 6.

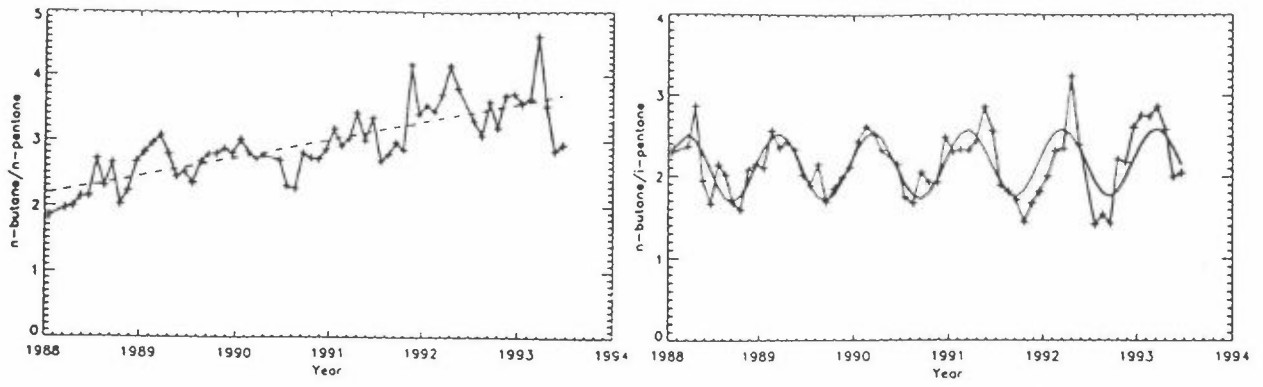


Figure 11: Monthly medians of the concentration ratio *n*-butane/*n*-pentane (left) and *n*-butane/*i*-pentane (right), 1988-1993. The dashed curve is the regression line (left) and the thick curve (right) is the fitted linear + sine function.

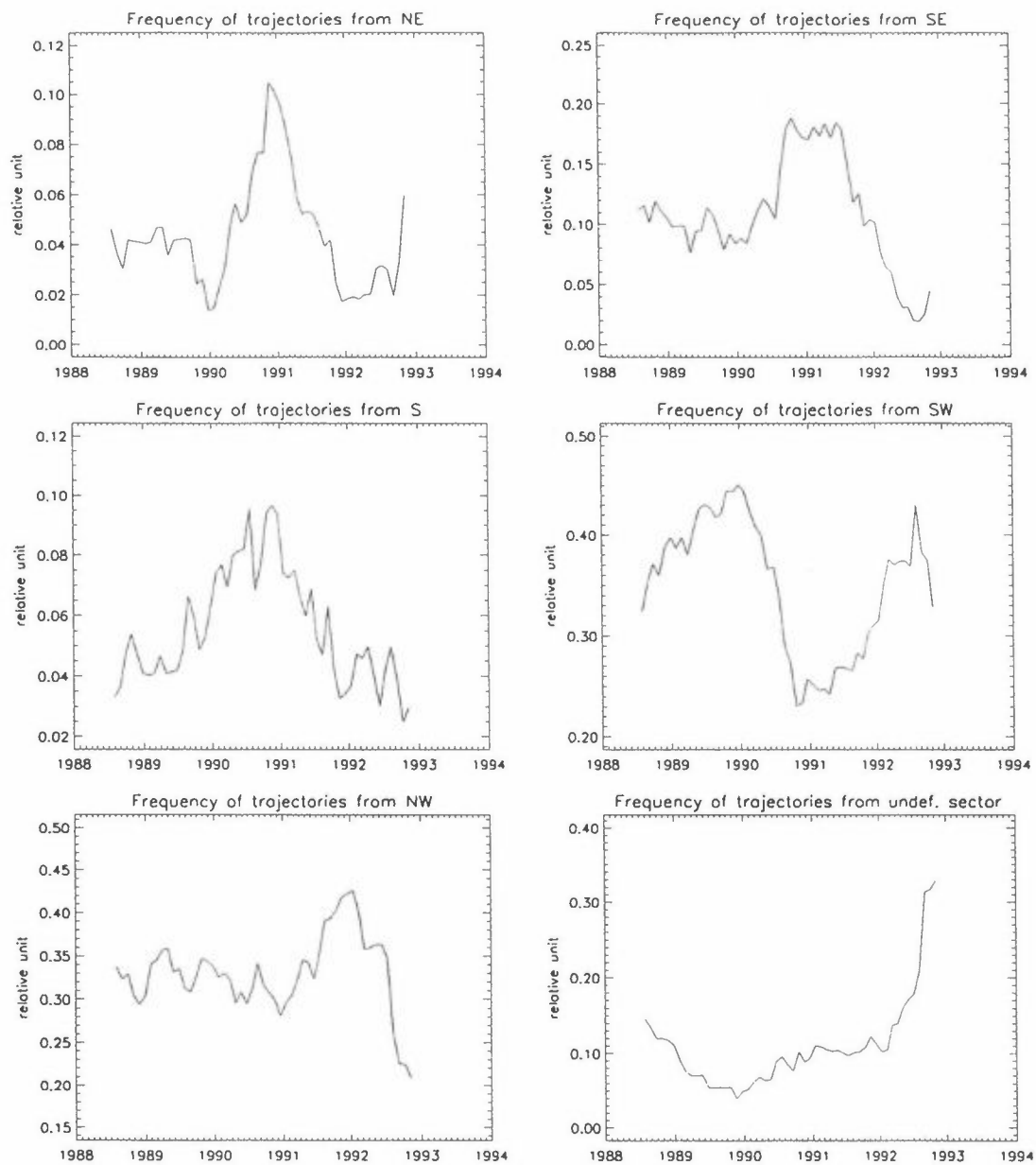


Figure 12: 365 days' running average frequencies of trajectories arriving at Birkenes from different sectors 1988-1993.

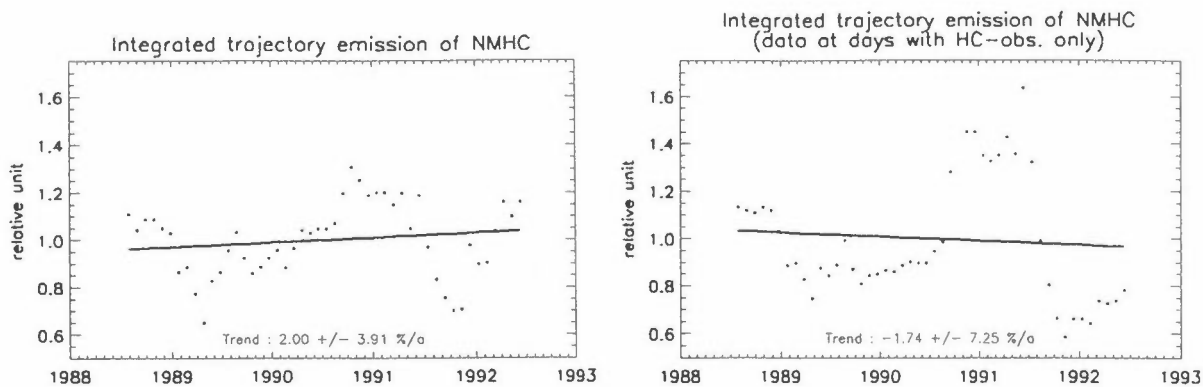


Figure 13: 365 days' running medians each month of the integrated NMHC emission along a 96 h back trajectory arriving at Birkenes (dots). The straight line is the calculated regression line of the same data points. The Figure to the left shows the results with all days included, and the Figure to the right shows the results when only the days with NMHC measurements at Birkenes were included.

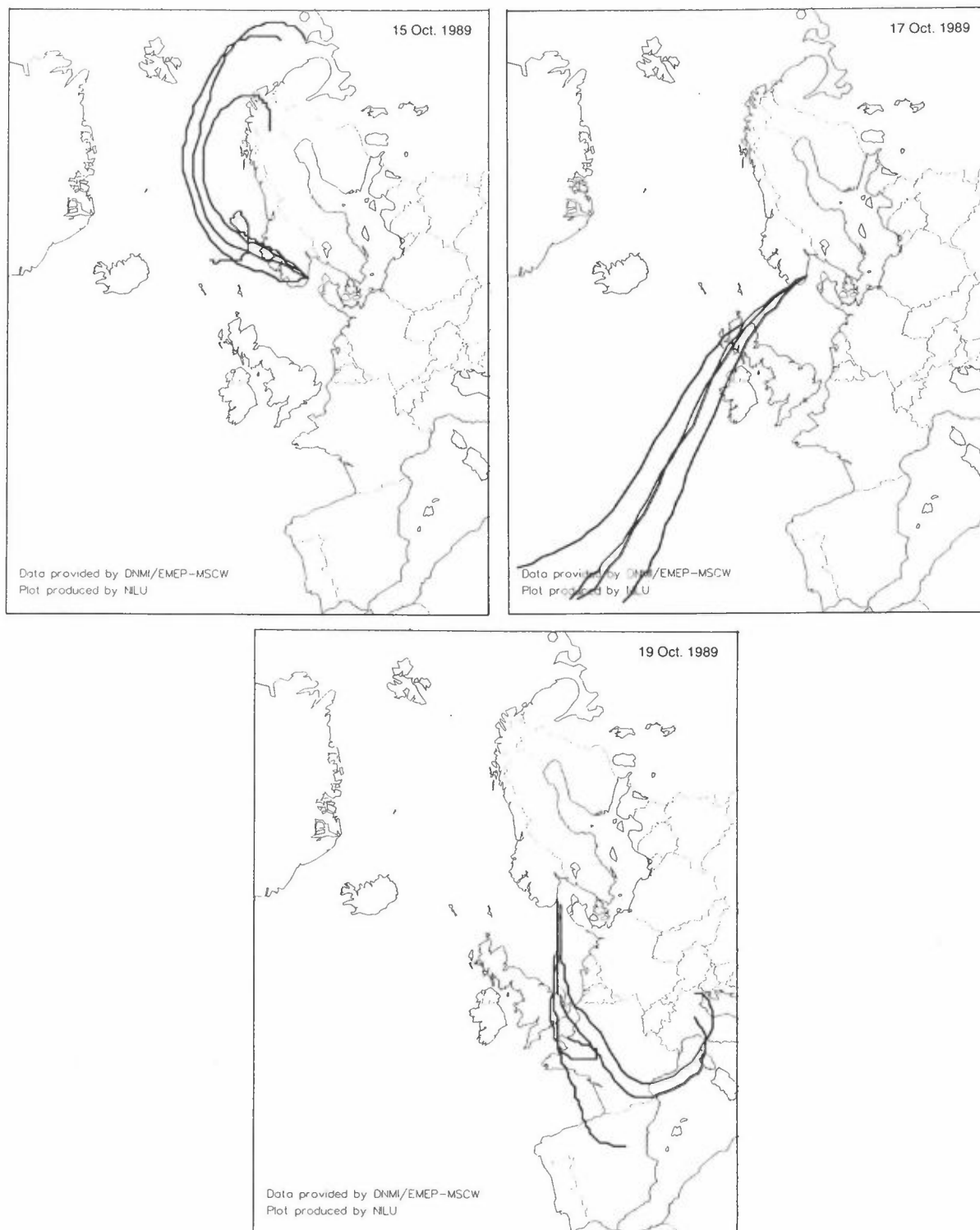


Figure 14: Calculated 4 days' back trajectories arriving at Birkenes on 15, 17 and 19 October 1989. The four trajectories each date arrived at 0, 6, 12 and 18 UT.

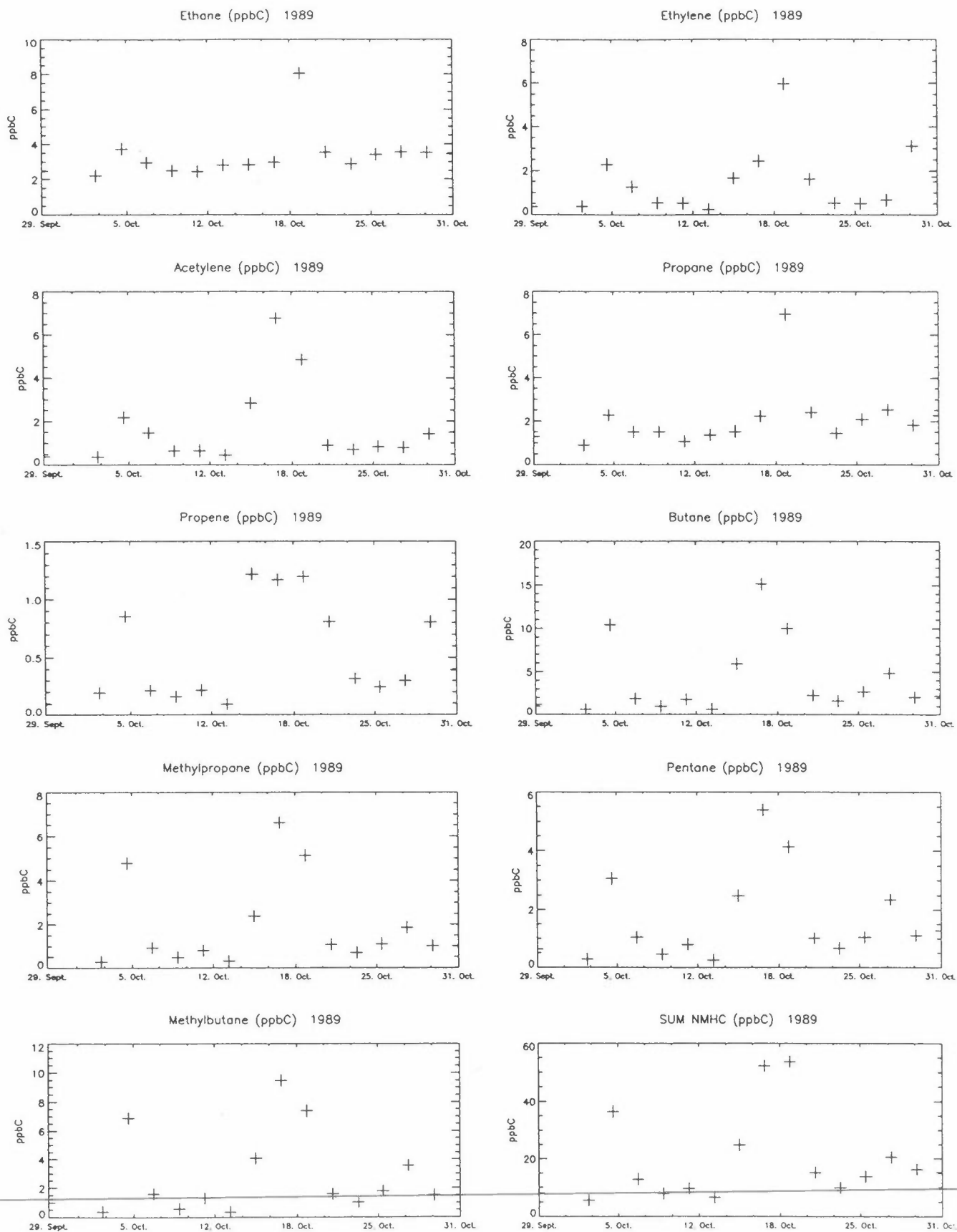


Figure 15: Observed concentrations of nine NMHC and the sum in October 1989 at Birkenes. All values in ppbC.

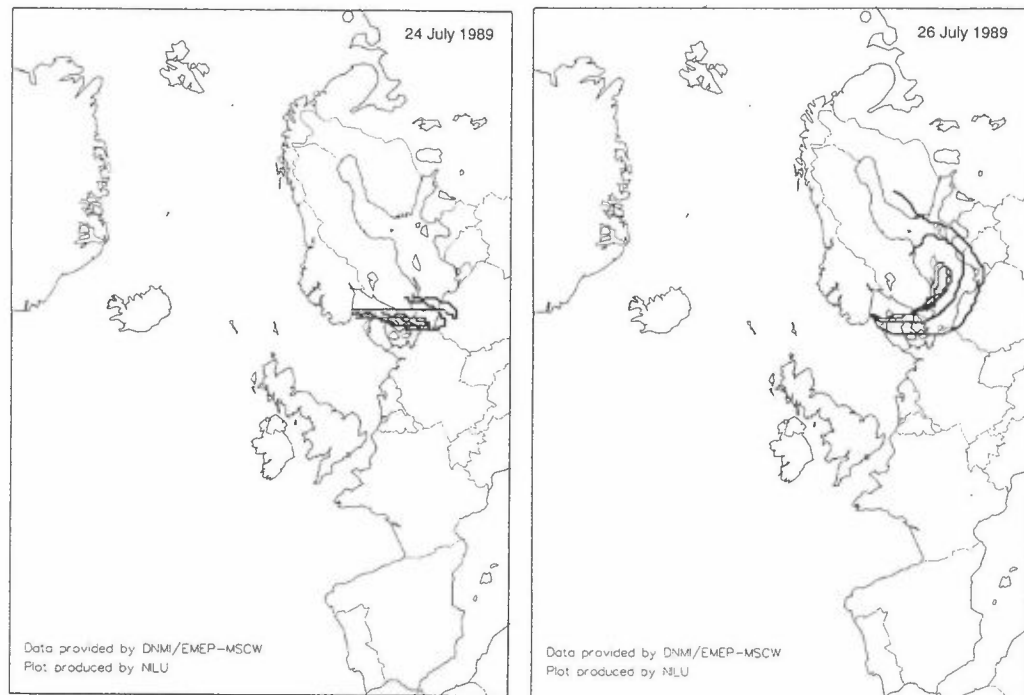


Figure 16: Calculated 4 days' back trajectories arriving at Birkenes on 24 and 26 July 1989. The four trajectories each data arrived at 0, 6, 12 and 18 UT.

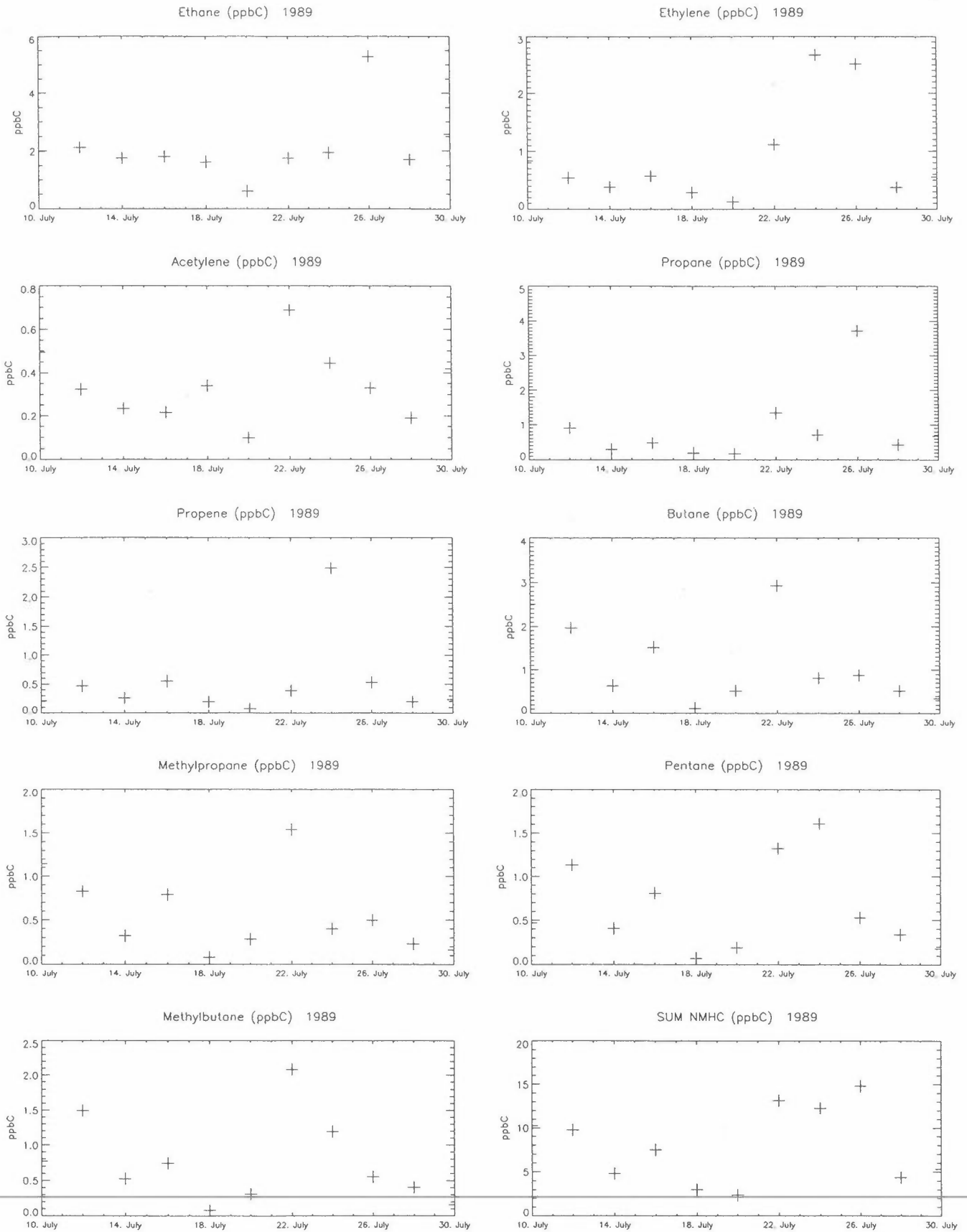


Figure 17: Observed concentrations of nine NMHC and the sum in July 1989 at Birkenes. All values in ppbC.

Appendix 2

Seasonal Kendall slope estimation

The Mann-Kendall statistic S_i is calculated for each season i :

$$S_i = \sum_{k=1}^{n_i-1} \sum_{l=k+1}^{n_i} \text{sgn}(x_{il} - x_{ik})$$

where x_{il} and x_{ik} are the values at season i , year l and k respectively, and $l > k$

n_i is the number of data (over years) for season i , and

$$\begin{aligned} \text{sgn}(x_{il} - x_{ik}) &= 1 && \text{if } x_{il} - x_{ik} > 0 \\ &= 0 && \text{if } x_{il} - x_{ik} = 0 \\ &= -1 && \text{if } x_{il} - x_{ik} < 0 \end{aligned}$$

$\text{VAR}(S_i)$ is computed as follows:

$$\text{VAR}(S_i) = \frac{1}{18} \left[n_i(n_i - 1)(2n_i + 5) - \sum_{p=1}^{g_i} t_{ip}(t_{ip} - 1)(2t_{ip} + 5) \right]$$

where g_i is the number of groups of tied (equal-valued) data in season i , t_{ip} is the number of tied data in the p th group for season i .

S_i and $\text{VAR}(S_i)$ is calculated for each season i , and then:

$$S' = \sum_{i=1}^k S_i$$

and

$$\text{VAR}(S') = \sum_{i=1}^k \text{VAR}(S_i)$$

Next, compute

$$\begin{aligned} Z &= \frac{(S' - 1)}{[\text{VAR}(S')]^{1/2}} && \text{if } S' > 0 \\ &= 0 && \text{if } S' = 0 \\ &= \frac{(S' + 1)}{[\text{VAR}(S')]^{1/2}} && \text{if } S' < 0 \end{aligned}$$

To test the null hypothesis, H_0 , of no trend versus the alternative hypothesis, H_A , of either an upward or downward trend (a two-tailed test), we reject H_0 if the absolute value of Z is greater than $Z_{1-\alpha/2}$, where $Z_{1-\alpha/2}$ is found from a table of a standard normal distribution.

If a significant value of Z is calculated, then the slope is estimated in the following way:

$$Q_i = \frac{X_{il} - X_{ik}}{l - k}$$

is calculated for all seasons and for all years where $l > k$.

The median of all these Q_i -values is the seasonal Kendall slope estimate.

A 95% confidence interval about the true slope is then obtained by calculating:

$$C_{0.05} = Z_{0.95} [\text{VAR}(S')]^{1/2}$$

$$M_1 = \frac{1}{2}(N - C_{0.05}) \quad , \quad M_2 = \frac{1}{2}(N + C_{0.05})$$

where N is the total number of forward time differences, Q_i .

Then the lower and upper confidence limits are the M_1 th largest and the (M_2+1) th largest of the N time differences.

