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Carbonyls and Nonmethane Hydrocarbons at Rural European Sites from the Mediterranean to the Arctic

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Abstract. Results of regular measurements during 1992–1995 of hydrocarbons and carbonyl compounds for a number of rural European monitoring sites are presented. The measurements are part of the EMEP programme for VOC measurements in Europe. In addition, several years of regular measurements are included from the Norwegian stations Birkenes at the south coast, and Zeppelin Mountain on Spitsbergen in the Arctic. The sampling frequency has been about twice per week throughout the years, implying that a substantial amount of measurement data are available. Almost all the chemical analyses have been performed by one laboratory, the EMEP Chemical Co-ordinating Centre located at NILU, which avoids problems of intercomparison and intercalibration among different laboratories. For the measured concentrations both seasonal and geographical variations are shown and discussed. The diurnal cycles of the hydrocarbon concentrations were studied in detail at one site, where the grab samples by EMEP where compared with a parallel continuous sampler, operated by EMPA, Switzerland. Hydrocarbons linked to natural gas and fuel evaporation become well mixed into the Arctic in the winter, whereas combustion products show a latitudinal gradient. The sum of oxygenated species constitutes about 5–15% of the sum of C_2–C_5 hydrocarbons in winter. In summer they are almost equal in magnitude, consistent with an increasing oxidation of hydrocarbons.

Key words: hydrocarbons, carbonyl compounds, measurements, European concentrations, rural sites.

1. Introduction

Volatile organic compounds (VOC) play a central role in many aspects of tropospheric chemistry. Anthropogenic emissions of hydrocarbons (R–H) in combination with nitrogen oxides (NO_x) lead to the formation of ozone, PAN and other oxidants when there is sufficient UV-radiation. Moreover, through the hydrocarbons' primary reaction with the OH radical, and through the subsequent degradation of the organic compounds, the concentration of the OH radical will be altered, which in turn causes a general perturbation of the tropospheric chemistry (Isaksen, 1988).

A wide range of aldehydes (R–CHO) and ketones (R–CO–R) are formed when the primary hydrocarbons are decomposed in the troposphere. The carbonyl compounds (aldehydes and ketones) are themselves successively broken down by reaction with OH and by photodissociation to simpler carbonyls, before they form CO and ultimately CO_2. If the NO_x concentration exceeds a critical value of a few

10's of ppt, ozone molecules are formed during the degradation process (Crutzen, 1988). The concentration and distribution of carbonyl compounds are therefore, to some extent, indications of the previous oxidation of hydrocarbons in the air mass, and have been proposed suitable for validation of photochemical models (Chatfield *et al.*, 1987).

Simultaneous measurements of hydrocarbons and carbonyl compounds are a particularly powerful tool, because the relative distributions between the primary pollutants and the secondary formed products give a picture of the photochemical history of the air mass. The interpretation is, however, complicated in many ways. Some of the carbonyl compounds are themselves emitted in considerable amounts, and the carbonyls may be so short lived that they are decomposed during the transport.

Another application of VOC measurements is to validate emission inventories. In this context, measurements of hydrocarbons alone are limited by the fact that by the time of measurement many of the emitted hydrocarbons may have reacted, and a large share of the emitted components may have been converted to aldehydes and ketones. The sum of hydrocarbons and carbonyl compounds is therefore a more conservative quantity, although a significant fraction of the carbonyls also may have been lost.

Based on the recommendations from the EMEP (Co-operative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe) Workshop on Measurements of Hydrocarbons/VOC in 1989, a pilot programme on light hydrocarbons, aldehydes and ketones was initiated within EMEP. This programme aimed at collecting VOC data as a support to the ongoing modelling of photochemical oxidants. The hydrocarbon measurements within EMEP started in the autumn of 1992, while the analysis of carbonyls were initiated during spring 1993. The measurements have previously been presented in EMEP reports (Solberg *et al.*, 1993; 1994; 1995a).

In the EUROTRAC sub project TOR (Tropospheric Ozone Research) hydrocarbons have been measured at an increasing number of sites since 1987. The co-operation between EMEP and the TOR project has allowed an exchange of measurement data. Some results from the combined EMEP and TOR hydrocarbon measurements have been published by Lindskog *et al.* (1995).

This paper presents the EMEP VOC measurements from the start until the beginning of 1995, financed by EMEP, as well as the VOC measurements at the two Norwegian TOR stations, Birkenes at the south coast of Norway and Zeppelin Mountain on Spitsbergen in the Arctic, financed by NILU (Norwegian Institute for Air Research). Measurements of hydrocarbons at the latter sites have previously been presented by Hov *et al.* (1984, 1989, 1990, 1991, 1995), Isaksen *et al.* (1985), Hov and Schmidbauer (1992) and Solberg *et al.* (1995b). An important objective with this paper is to provide modellers with applicable measurement data of VOC concentrations in Europe. In addition the representativity of the grab samples is

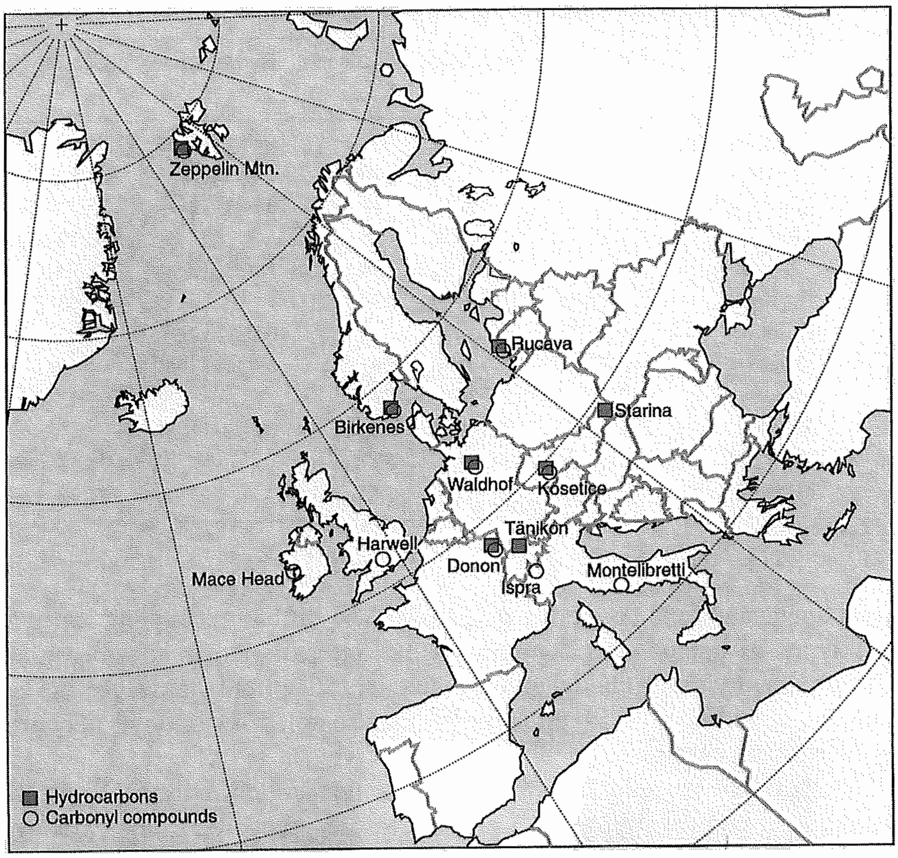


Figure 1. Map showing the location of the EMEP VOC measuring stations and the Norwegian TOR sites (Birkenes and the Zeppelin Mountain). The symbols mark what type of compounds are measured at the different sites.

discussed by comparison with continuous measurements, and the geographical and temporal variations are presented.

2. Instrumentation, Sampling Procedures and Site Locations

2.1. SAMPLING TIMES AND SITES

Figure 1 shows the location of the EMEP VOC stations presented here, as well as the two Norwegian TOR sites. The different symbols mark the types of measurements performed at the different locations. Table I gives the names of the stations, geographical coordinates, altitudes and the type of measurements.

The hydrocarbons and carbonyl compounds are normally sampled on the same days twice per week, mostly on Mondays and Thursdays. The canisters for spot sampling of hydrocarbons are normally filled about noon during a time of 10–20 min. (as described in more detail below), while the 8 hours sampling of carbonyl

Table I. The measurement data which this work is based on

Station	Latitude	Longitude	Altitude (m a.s.l.)	Hydrocarbons	Carbonyls
Zeppelin Mtn.	78°55′ N	11°54′ E	474	09/89–12/94	04/94–09/94
Birkenes	58°23′ N	8°15′ E	116	01/88–12/94	03/93–05/95
Rucava	56°13′ N	21°13′ E	18	09/92–12/94	05/93–06/95
Mace Head	53°10′ N	9°30′ W	15		10/93–04/95
Waldhof	52°48′ N	10°45′ E	74	10/92–12/94	05/93–04/95
Harwell	51°25′ N	1°19′ W	137		08/93–06/94
Kosetice	49°35′ N	15°05′ E	633	08/92–12/94	04/93–04/95
Starina	49°03′ N	22°16′ E	345	09/94–12/94	
Donon	48°30′ N	7°08′ E	775		06/93–04/95
Tänikon	47°29′ N	8°54′ E	540	09/92–12/94	
Ispra	45°48′ N	8°38′ E	209		04/93–04/95
Montelibretti	42°06′ N	12°38′ E	48		07/93–02/95

compounds are done centred around noon. The different sampling times for the two types of components complicates the interpretation of the measurements. During situations with changing wind directions, like frontal passages, the canister samples of hydrocarbons and the DNPH tube samples of carbonyls may originate from different air masses.

Furthermore, if the hydrocarbon concentrations follow a diurnal cycle, the spot sampling at noon will produce a bias in the data compared to the carbonyl data. However, at rural sites, local anthropogenic emissions should be small and as the dry deposition of hydrocarbons is negligible, one should not expect a large diurnal cycle. It is therefore of interest to investigate how representative the spot sampling of hydrocarbons at noon are. The representativity depends both on the site location, time of year etc., and is therefore not easy to estimate on an average basis. Section 3 presents a comparison between the spot samples from Tänikon and the continuous measurements performed at the same location by EMPA.

Particularly in central Europe, rural sites are on occasions exposed both to advection of polluted air masses from the nearest cities, and episodically contaminated by nearby emissions. Table II gives an idea of the influence of regional anthropogenic sources at the different sites. This table shows the average and 95 percentile NO_2 concentration observed during December 1992 to February 1993 at sites with daily filter samples of nitrogen and sulphur compounds in the EMEP monitoring network (Lövblad *et al.*, 1995). Also given is the 50×50 km^2 and 150×150 km^2 grid square emission flux of NO_x, based on recent estimates (Berge *et al.*, 1995). There are large differences in the observed NO_2 concentrations with Birkenes and Rucava showing the smallest anthropogenic influence and Ispra the highest. Birkenes, Rucava, Mace Head, Waldhof, Kosetice, Starina and Donon all have fairly low emission rates in the 50×50 km^2 grid square, whereas several of

Table II. Average ($\overline{C}$ winter) and 95 percentile (P_{95}, winter) of daily measured NO_2 concentrations for December 1992–February 1993, as well as the 50 × 50 km^2 ($E_{NO_x,\,50}$) and 150 × 150 km^2 ($E_{NO_x,\,150}$) grid square emission flux of NO_x

	$\overline{C}$ winter (μg N m^{-3})	P_{95}, winter (μg N m^{-3})	$E_{NO_x,\,50}$ (1000 tonnes y^{-1})	$E_{NO_x,\,150}$ (1000 tonnes y^{-1})
Birkenes	0.84	2.61	1.1	13
Rucava	1.62	3.82	1.3	12
Mace Head			0.1	42
Waldhof	5.31	11.70	3.6	123
Harwell			44.2	286
Kosetice	3.32	10.18	1.9	74
Starina			4.2	60
Donon			3.3	94
Tänikon	7.34	12.60	16.8	119
Ispra	12.51	19.90	29.5	181
Montelibretti			10.8	173

these sites are located in areas with high emission fluxes in the 150 × 150 km^2 grid square. This indicates that the sites are not located in the vicinity of major source areas, but may be situated in high emission regions. Montelibretti, Tänikon, Ispra, and Harwell are exceptions to this. They are all located in 50 × 50 km^2 grid squares with high emission rates reflecting more densely populated areas, and are possibly more subject to fresh anthropogenic plumes.

2.2. ANALYSIS OF HYDROCARBONS

Air samples are collected manually by filling evacuated electropolished, stainless steel canisters of 0.8 l volume, during a time of 10–20 min. The bottles are then shipped to the laboratory, and the chemical analyses normally take place within a week after the time of sampling. Most of the hydrocarbon measurements in EMEP have so far been analysed by the Chemical Co-ordinating Centre (CCC) located at NILU. Samples from September to December 1994 from Donon, Ispra and Montelibretti were analysed by the JRC–Ispra in Italy, but are not presented here. The laboratory at NILU was accredited according to EN 45001 in September 1993.

The air samples are now analysed for C_2–C_7 alkanes, C_2–C_5 alkenes, as well as aromatics (benzene, toluene and xylenes), isoprene and acetylene. Until 1991 (before the start of the EMEP VOC programme), only C_2–C_5 compounds were analysed at the TOR sites Birkenes and the Zeppelin Mountain. This paper mostly presents the C_2–C_5 compounds. Note that due to problems in integrating the chromatograms for propene after July 1993 for Birkenes and the Zeppelin Mountain, no propene data have been obtained after this time for these two sites. Note also that due to local contamination, the hydrocarbon samples from Rucava in the period June–November 1994 had to be discarded.

The laboratory analysis at NILU is done by gas chromatography with flame ionisation detection by an automated Chrompack VOC-AIR instrument. A detailed documentation of the instrumentation and analysis procedure is given in EMEP/CCC (1995), and by Schmidbauer and Oehme (1986). A NIST certified standard gas mixture containing 10 ppb n-butane and benzene is used every day to calibrate the instrument. A response factor calculated for 1 ppbC together with the carbon number is then applied to all hydrocarbons. Except for acetylene, this approach has been shown to be valid for most hydrocarbons. The acetylene concentrations reported by NILU in intercalibration exercises are, however, often in the upper range, which could indicate that the applied response factor derived from n-butane may be too low for acetylene. The cleaning of the canisters, checking of their blank-values, sample stability studies and a record of every canister are very important parts of the analysis. There are no corrections made for any possible deviations of the detector response due to differences in the molecular structure. In the EC intercomparison reported by De Saeger and Tsani-Bazaca (1992) the accuracy of the results from NILU compared very well with the gravimetric determination by Partridge (1992). An intercomparison of analytical methods for VOC organised within EMEP in 1993 revealed that most of the labs analysed a wide range of hydrocarbons within an accuracy of ± 10–15% (Romero, 1995).

In addition to the JRC-Ispra, the laboratories at the hydrometeorological institutes in the Czech Republic and in Slovakia have started their own analyses of hydrocarbons. Both institutes participated in an exercise where the same canister samples were first analysed by their own laboratories, and then shipped to the lab at NILU and re-analysed. After a certain time of intercalibration and exchange of standards to establish response factors for their instruments, very encouraging results were obtained. Figure 2 shows the comparison of ethene analysed by NILU and the Slovak Hydrometeorological Institute. Ethene is often claimed not to be stable in canister samples. The agreement between the results is excellent and the time series correlate very well. There is no evidence for problems of sample stability or integrity over long periods of storage. As the ethene concentration at Starina mostly was above 500 ppt, these observations do not, however, contradict the hypothesis that ethene contamination in steel canisters may be a problem at low concentrations. Furthermore, the good agreement between the two labs' analyses is only indicative of the stability between the times of these analyses. Possible processes occurring in the first few hours after sampling would not be detected by this type of comparison.

2.3. CONTINUOUS SAMPLING AND ANALYSIS OF HYDROCARBONS

Tänikon, located in the north-eastern part of Switzerland, was established as an EMEP VOC site in August 1992 and is also part of the Swiss federal air pollution

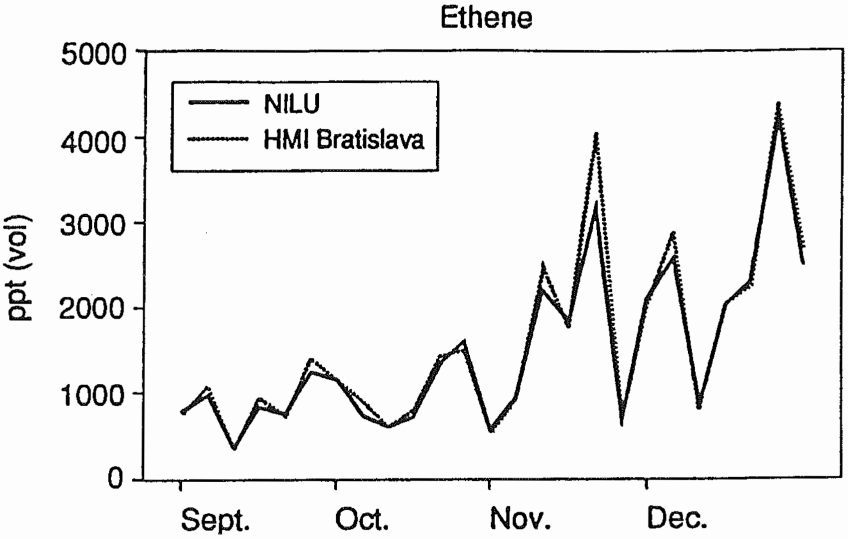


Figure 2. Ethene at Starina, Slovakia, as analysed from the same canister samples by two laboratories during four months in 1994. The labs were NILU and the Hydrometeorological Institute, Slovakia.

network (NABEL). Since July 1994 hydrocarbons have been measured continuously by EMPA (Swiss Federal Laboratories for Material Testing and Research). The fully automated measurement system for hydrocarbons is based on a Varian 3400 gas chromatograph (Varian Inc., CA, USA), equipped with a flame ionisation detector (FID) and a Varian SPT system (sample preconcentration trap). Varian software is used for data collection and peak integration. The spectrum of the analysed C_2–C_8 compounds corresponds to that of the EMEP VOC programme with the exception of ethane and n-heptane.

The ambient air is aspirated inside the station cabin from a well ventilated glass manifold (40 m^3 h^{-1}) by a mass flow controller (Bronkhorst High-Tech BV, Ruurlo, The Netherlands) and a pump. Sampling is performed 12 times a day with a sampling duration of 30 min at a flow rate of 20 ml min^{-1}. Each analysis cycle consists of the following steps: At the initial stage, the stainless steel trap (2 mm i.d., 3 mm o.d., 30 cm long), packed with two adsorbents (29 cm HayeSep D 60/80 mesh and 1 cm activated charcoal 60/80 mesh) is precooled with liquid CO_2 to −45 °C. Then, by activating two Valco valves (type -WT; 6-port and 10-port,) dehydrated ambient air passes through the trap (Valco Instruments Co. Inc., Houston, U.S.A.). Still at −45 °C, the trap is purged with carrier gas (99.999% N_2 cleaned with activated charcoal and molecular sieve filters) for 0.5 min at a rate of 7.5 ml min^{-1} to remove residual oxygen. Then the trap is isolated from the gas stream and rapidly heated to 145 °C (conduction heat) and held for 0.9 min to desorbe the components. Without further focusing the sample is then injected into the analytical column (PLOT, Al_2O_3/KCl, 50 m long and 0.53 mm i.d., Chrompack, Middelburg, The Netherlands) by flushing carrier gas through the trap at a rate of 7.5 ml min^{-1}. For the purpose of trap cleaning the gas flow in the trap is maintained until the end of the analysis. The oven temperature program is as follows: 5 min at 40 °C then 190 °C with 4 °C min^{-1}, held 10 min, 200 °C with 15 °C min^{-1}, held 15 min. Prior to analytical preconcentration humidity is selectively removed from the sample air by passing it through a nafion dryer, model MD–125–48(S) (Perma Pure Products, Farmingdale, N.J.). To prevent excessive moisture build-up and memory effects in the dryer, an automated clean-up procedure that involves periodically heating the dryer (100 °C) while being purged with zero air is installed (Pleil and Oliver, 1987).

For calibration two Scott Environmental Technology, Inc. pressurised cylinders containing a mixture of 15 ppmv of the following compounds in nitrogen are used as working standards: Cylinder 1: all n-alkanes up to n-hexane, cylinder 2: i-butane, 2,2-dimethylpropane, i-pentane, 2,2-dimethylbutane, 2-, and 3-methylpentane. For calibration runs, appropriate amounts of the standards are dosed to humidified zero air with a gastight syringe to reach a nominal concentration of about 1–1.5 ppb. The results are taken as a basis for calculation of carbon-number-response. The estimated error (standard, dilution) is about 20%.

The EMPA laboratory participated in two intercalibration exercises in 1994. For the compounds discussed in this paper the results of the EMEP intercalibration (Romero, 1995) are –3% for propane and +13% for ethene compared to NILU, whereas the results of the second EU intercalibration reported by De Saeger (1994) agreed very well with the gravimetric standard.

2.4. ANALYSIS OF CARBONYL COMPOUNDS

The sampling of carbonyl compounds is done by drawing air through a cartridge which contains silica coated with 2,4-dinitrophenylhydrazine (2,4-DNPH) packed in a polyethylene tube. The aldehydes and ketones react with the acidified 2,4-DNPH to form the corresponding hydrazones. The sampling time is about 8 hours, and the total air sample volume is 750 litres. The tubes are then shipped to the laboratory where the subsequent analyses of the hydrazones are performed. All the chemical analyses of carbonyl compounds have been done by the CCC of EMEP at NILU.

The cartridges are eluated with acetonitrile, and the sample extract is analysed by reversed phase high-performance liquid chromatography by UV detection, using a Hewlett Packard 1050 modular system equipped with a diode array detector. The detection limits of the carbonyl compounds are in the range of 0.01–0.05 μg m^{-3}. This method is a modification of the method presented by Slemr (1991), and it is described in detail in EMEP/CCC (1995).

Parallel sampling, using two samplers simultaneously, was performed at Birkenes twice a week for a period of 8 months. The results for formaldehyde, acetaldehyde and acetone are shown in Figure 3. In general the two time series agree very well with a few exceptions. At day 100 in 1995 there was a deviation of about 35% for all three compounds. This was most likely caused by technical problems in volume recording. Apart from this the measured acetaldehyde concentrations also show a marked deviation at day numbers 26, 30 and 37 in 1995. At the moment the reason for these discrepancies is not clear. A possible explanation could be the formation of syn- and anti-isomers of the acetaldehyde hydrazone, which makes it more difficult to integrate the chromatograms.

The analytical method was capable of identifying a wide spectrum of individual compounds, but the number of compounds actually detected was often limited by concentrations dropping below the detection limit. The carbonyl compounds reported to the EMEP VOC database include aldehydes up to C_6 (hexanal), a number of ketones including methylethylketone and methylvinylketone, as well as aromatic carbonyls (benzcarbaldehydes etc.). For many of the higher order carbonyls the measurement data are, however, rather sparse at many of the sites, because the compounds were not detectable. Note that the samples of carbonyls from Rucava in the period from mid September 1993 to the end of the year had to be discarded due to technical problems.

A standard gas meter was used for the volume determination, with no correction for possible changes in pressure or temperature inside the instrumentation. The pressure will not change, but there may be a slight heating of the air causing a slight change in the volume. The carbonyl concentrations are initially reported as $\mu g\ m^{-3}$, and the uncertainty in the volume determination thus introduces an uncertainty in the reported gas concentrations. This uncertainty will, however, be at most 10%. This is less than the overall uncertainty of the measurement method, which is 15% according to the accreditation. In this paper all carbonyl concentrations were transformed from $\mu g\ m^{-3}$ to volume mixing ratios (ppt or ppb) by assuming a temperature of 288 K and a pressure of 1013 hPa. This will not raise the uncertainty of the concentration values significantly, and an uncertainty of 15% is still valid.

3. Comparison between Grab Sampling and Continuous Measurements of Hydrocarbons

The total data set of the continuous hydrocarbon measurements comprises a spectrum of 19 analysed C_2–C_8 compounds or compound groups for the time period between 1 August and 31 December 1994. Seven compounds with different sources and reactivities were selected for the comparison with the grab samples: Ethene, propane, *i*-butane, *i*-pentane, *n*-pentane, benzene and toluene. To investigate seasonal differences, the data set was divided into a summer period (1 August to 15 September) and a winter period (16 September to 31 December).

Every single measurement consists of a half-hourly value, sampled every two hours between hh:30 and [hh+1]:00 exactly, except during the summer season when the starting time could vary ± 20 min or even shift for a whole hour. The

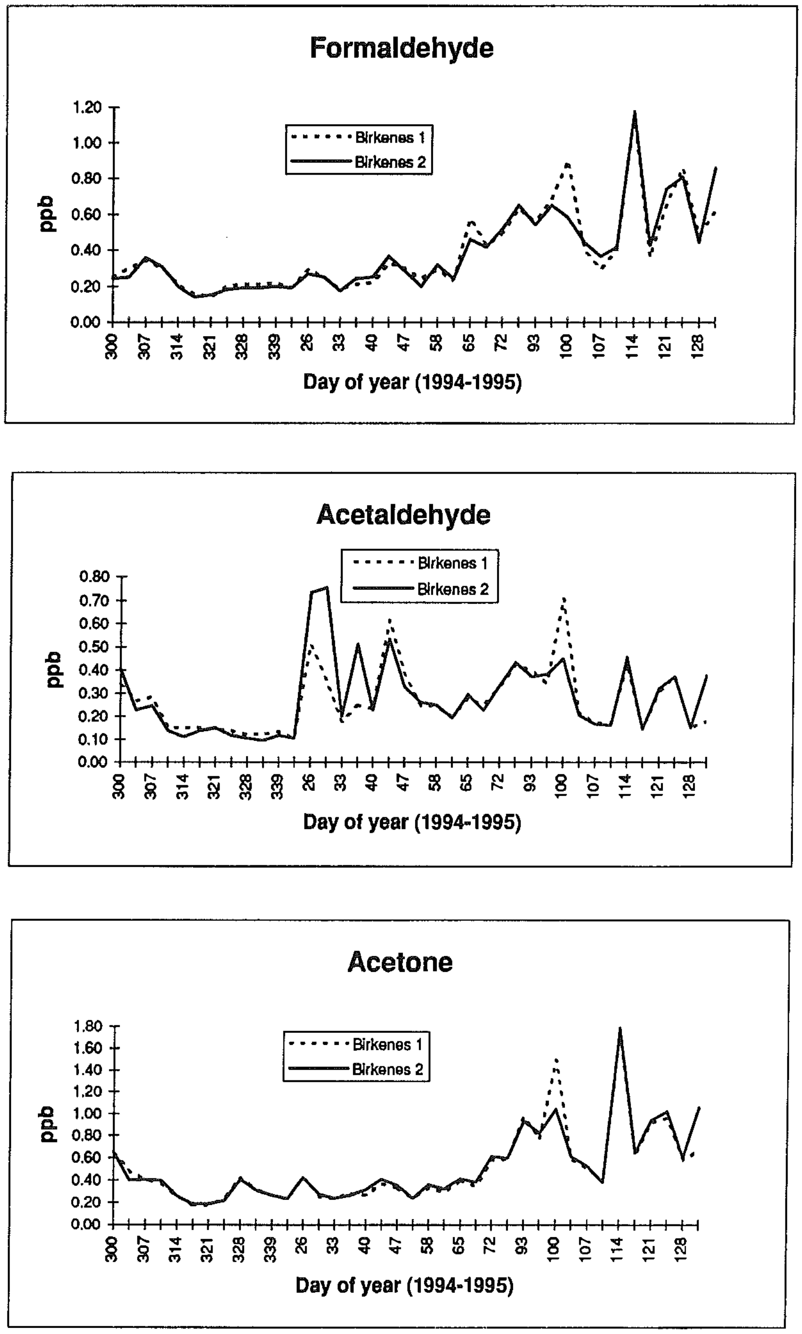


Figure 3. Time series from two parallel measurements of carbonyls at Birkenes in an eight months period during autumn 1994 to spring 1995. The x-axis gives the day of year in 1994 and 1995. All values are in ppb.

Table III. Comparison of grab samples (NILU) and continuous measurements (EMPA) sampled in parallel: Mean values $\overline{x}_{\text{grab}}$, $\overline{x}_{\text{cont}}$, linear regression $x_{\text{cont}} = a \cdot x_{\text{grab}} + b$, correlation coefficient r, standard deviation of the slope s_a, standard deviation of the intercept s_b and number of data pairs n

	$\overline{x}_{\text{grab}}$ [ppt]	$\overline{x}_{\text{cont}}$ [ppt]	a	b [ppt]	s_a	s_b [ppt]	r	n
Ethene	1460	1780	1.139	110	0.132	244	0.907	18
Propane	770	780	0.963	40	0.079	77	0.952	17
i-Butane	390	380	0.860	40	0.081	41	0.940	17
i-Pentane	900	880	0.952	20	0.122	134	0.895	17
n-Pentane	390	340	0.923	–20	0.060	29	0.970	17
Benzene	480	340	1.004	–140	0.107	57	0.921	18
Toluene	710	690	0.933	30	0.071	59	0.957	18

measured concentrations were attributed to the full hour in which the sampling took place. To ease the discussion of diurnal cycles, an additional data set consisting of hourly values was prepared, in which the missing hour between two consecutive measurements was interpolated. Gaps of more than two hours were not interpolated but treated as missing values. Most data gaps were caused by instrumental failure or reconstruction problems of the adsorption tube. Totally 861–907 measurements exist for each species.

Differences in concentrations between the continuous measurements and the grab sampling could either be due to different analytical methods or due to the different time periods covered by the two methods. In Section 3.1 below we discuss the differences which could be ascribed to the different analytical methods, by comparing the noon values from the continuous measurements with the grab samples (which are all performed around noon). Then, in Section 3.2, diurnal cycles in the concentrations are discussed to elucidate the differences between noon concentrations and concentrations at other times of the day.

3.1. COMPARISON OF THE NOON CONCENTRATIONS OBTAINED BY THE CONTINUOUS MEASUREMENTS AND THE GRAB SAMPLING

As the sampling by the two methods were not performed exactly simultaneously, the values closest in time, or in some cases the mean value of the two measurements before and after the grab sampling, were used for the comparison. The results of the comparison are presented in the form of a linear regression analysis in Table III.

For propane, i-butane, i-pentane, n-pentane and toluene the agreement of the mean noon values between the grab samples and the continuous measurements was very good. The regression analysis shows that neither the slopes differ significantly from 1 nor the intercepts from 0. However, the standard deviations are in some cases considerable. One explanation for this could be, that the sampling for the two compared methods was not covering exactly the same time periods as mentioned above.

Higher differences in the mean noon concentrations of benzene and ethene were obtained between the two methods, indicating systematic differences in the analytical procedure, though only the intercept of benzene was significantly different from 0 (on the 95% confidence level). For ethene similar differences between NILU and EMPA were already observed in the EMEP intercalibration (Romero, 1995).

3.2. DIURNAL CYCLES IN HYDROCARBON CONCENTRATIONS

The continuous measurements were used to calculate the diurnal cycles in the components. To suppress an undue influence of days with high concentrations, relative diurnal cycles were calculated by dividing every single observation by the average concentration of that day. Furthermore, the observations were classified into two groups of data, according to the daily average wind speed at the station: Below 1 m s^{-1} and above 1.8 m s^{-1}, approximately equal to the 30 and 70 percentile of the wind speed distribution, respectively. At low wind speeds the influence from local sources should be visible, whereas at high wind speeds the more regional characteristics should be reflected.

The resulting average relative diurnal cycles are shown in Figure 4. Measurements sampled during the low wind speeds show an influence from local traffic with peak emissions in the rush hours. The diurnal cycle of propane is an exception to this, indicating a different source for this compound. The diurnal cycles of the components during the higher wind speeds are less pronounceed, consistent with a more thorough mixing which reduces the local influence. The diurnal cycles at days with high wind speeds reflect the influence from different regional sources at different distances, occasionally superimposed by local events. This analysis shows that the measuring site at Tänikon is exposed to local traffic emissions, but the grab sampling around noon seems to be a well chosen time due to the absence of traffic peak emissions at this time of the day.

The relationship between the noon values and the daily means, using the continuous measurements only, was investigated by linear regression analysis, and the results are given in Table IV. All slopes in Table IV are less than 1, implying that the noon values were lower than the daily means, consistent with the calculated diurnal cycles in Figure 4. The correlation coefficients for i-butane, i-pentane and n-pentane are relatively low, and, as shown in Figure 5, they are affected by three encircled events when the noon values were much higher than the daily means. Rejecting these values improved the correlation significantly, as given in Table IV. Butanes and pentanes are related to fuel evaporation and spillage (Harley *et al.*, 1992) in contrast to propane.

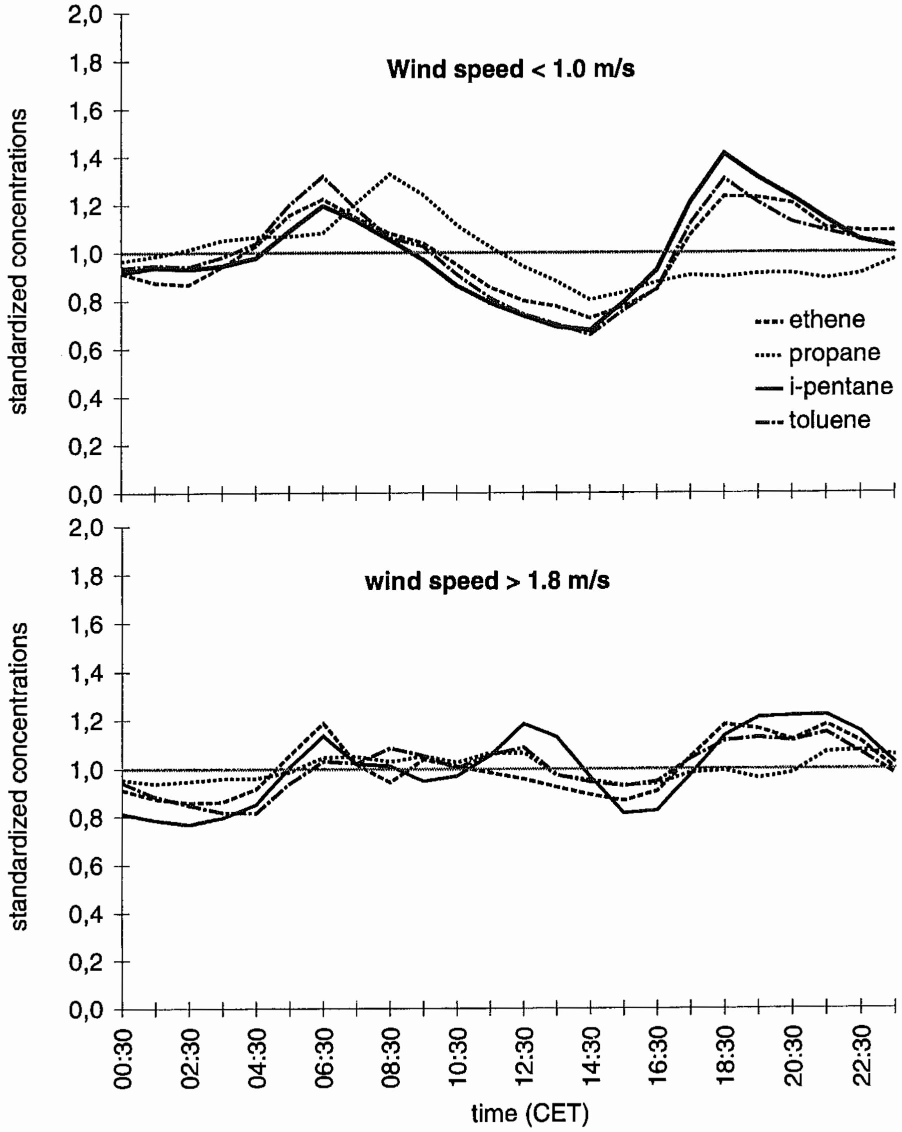


Figure 4. Diurnal cycles of standardized hydrocarbon concentrations at Tänikon for wind speeds below 1 m s^{-1} (upper diagram) and above 1.8 m s^{-1} (lower diagram). The hydrocarbon concentrations were standardized by dividing every value by the daily mean concentration.

4. Seasonal and Geographical Distribution of VOC

The concentration of hydrocarbons at a given location is determined by the emission source strength, the mixing with background air due to advection and turbulent diffusion, and the chemical loss. Thus, the time scale of transport from the emission areas compared to the chemical life time, determines how much of each individual

Table IV. Comparison of noon samples vs. daily means, with and without three special events. Slope of linear regression $\overline{x}_{\text{noon}} = a \cdot x_{\text{mean}} + b$ at Tänikon, correlation coefficient r and number of compared data pairs n

	All values				3 Events rejected			
	a	b [ppt]	r	n	a	b [ppt]	r	n
Ethene	0.890	–68	0.952	71	0.886	–70	0.947	68
Propane	0.893	36	0.968	69	0.887	36	0.967	66
i-Butane	0.918	25	0.886	72	0.828	35	0.939	69
i-Pentane	0.826	64	0.781	73	0.730	76	0.922	70
n-pentane	0.851	19	0.892	73	0.823	11	0.947	70
Benzene	0.824	14	0.934	69	0.824	3	0.945	66
Toluene	0.739	93	0.848	69	0.727	87	0.847	66

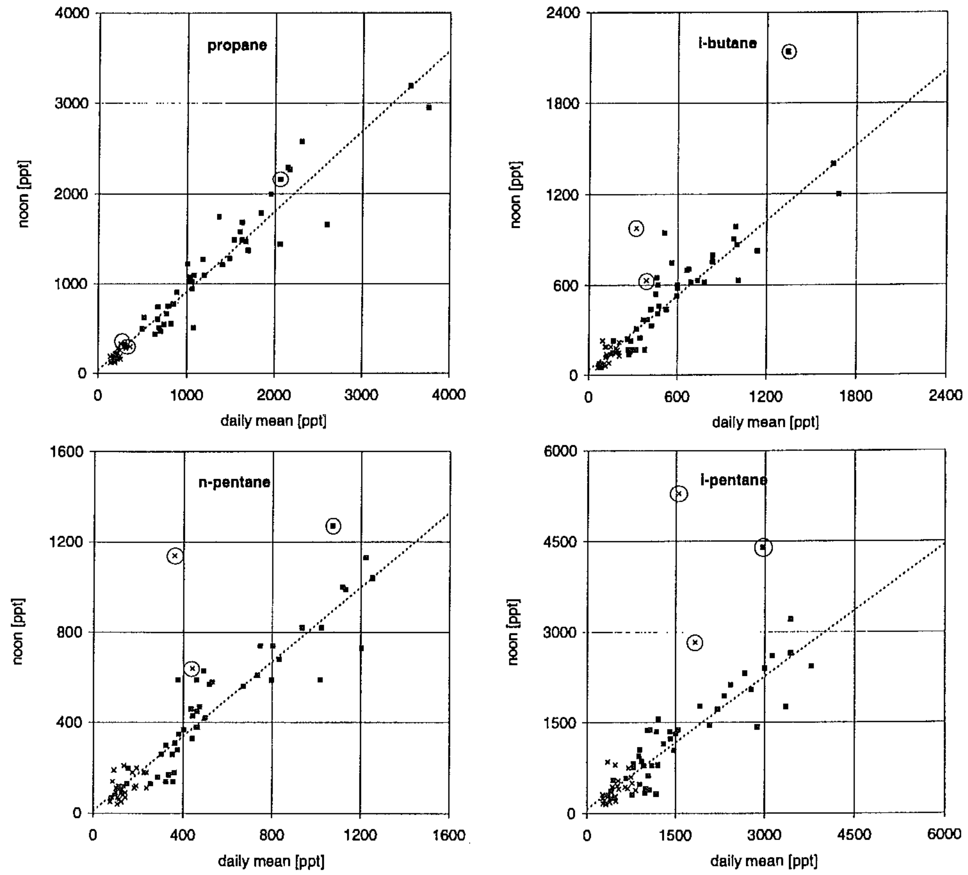


Figure 5. Noon concentrations as a function of the daily means for a number of hydrocarbons based on the continuous sampling at Tänikon. Samples from 1 August–15 September are marked by x'es, whereas samples from 16 September–31 December are marked by filled squares. The dotted lines mark the linear regression lines, calculated when the encircled values were not included.

Table V. Chemical lifetimes of VOC in winter and summer (days). The values were based on [OH] $= 2 \cdot 10^5$ molecules cm^{-3} in winter, [OH] $= 2 \cdot 10^6$ molecules cm^{-3} in summer, [O_3] $= 1 \cdot 10^{12}$ molecules cm^{-3}, $T = 273$ K in winter and $T = 298$ K in summer. Reaction rate constants from Atkinson (1990), Atkinson *et al.* (1992) and Wirtz *et al.* (1994)

	Lifetime, winter (d)	Lifetime, summer (d)
Ethane	311	23
Ethene	4	0.6
Acetylene	71	6.5
Propane	62	5
Propene	0.9	0.2
n-Butane	24	2.3
i-Butane	27	2.5
n-Pentane	16	1.5
i-Pentane	16	1.5
Isoprene	0.4	0.05
Formaldehyde	6	0.6
Acetaldehyde	3	0.4
Acetone	307	26

component of the original plume will survive the transport. Reactive components may be totally lost, and the concentration measured at a rural site may only reflect local emissions.

Table V shows typical chemical lifetimes of a number of VOC based on the reaction with OH and ozone for winter and summer conditions, respectively. These life times were calculated by assuming an OH concentration of $2 \cdot 10^5$ and $2 \cdot 10^6$ molecules cm^{-3} in winter and summer, respectively, T = 273 K and 298 K in winter and summer, respectively, and an ozone concentration of $1 \cdot 10^{12}$ molecules cm^{-3} in both seasons. Reaction rate constants from Atkinson (1990), Atkinson *et al.* (1992) and Wirtz *et al.* (1994) were applied. Note that photolysis was not considered, which implies that the actual chemical life times of the carbonyl compounds in Table V are shorter than the tabulated values.

In winter the chemical lifetimes of hydrocarbons are prolonged due to the low concentration of OH and the weaker UV-radiation compared to in summer. Furthermore, the height of the mixed boundary layer are often lower in winter than in summer. Thus, if the emission strength is fairly constant during the year, a pronounced seasonal cycle with high concentrations in winter and low in summer is expected for the hydrocarbons, which is indeed observed.

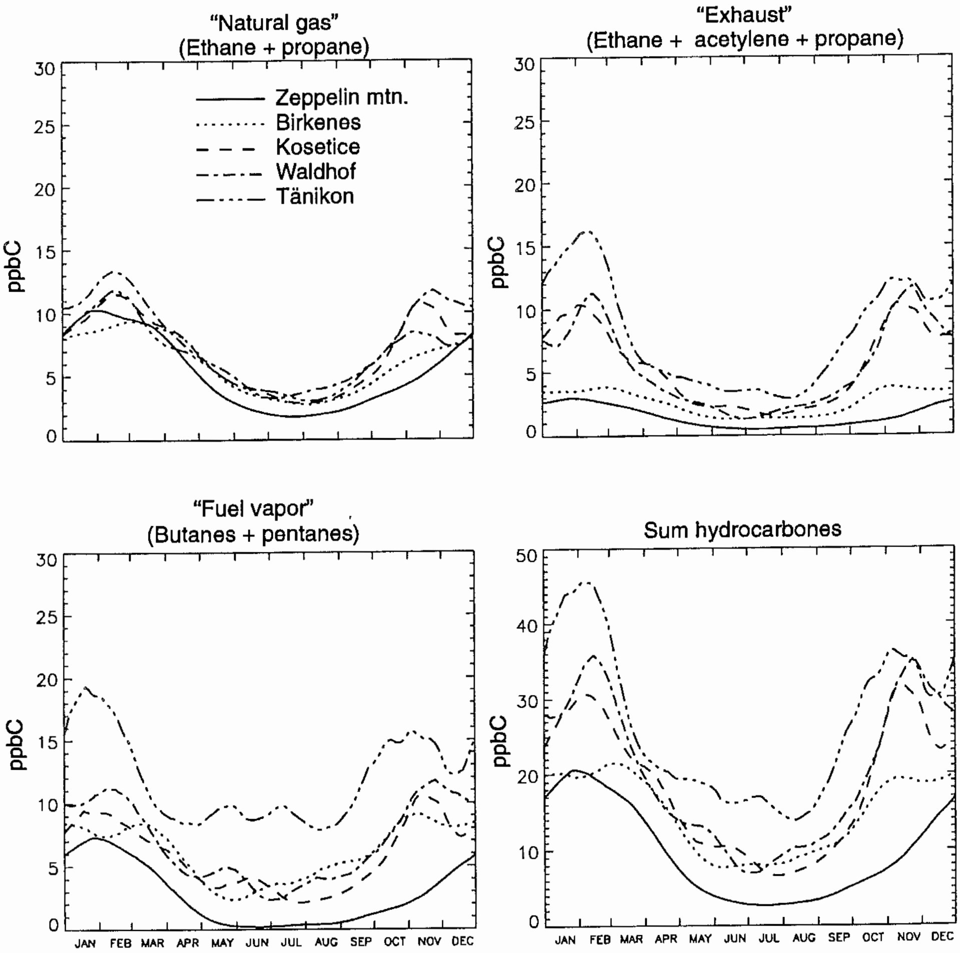
Isaksen *et al.* (1985) discussed the transport of organic gases into the Arctic, and found that in summer the chemical lifetime of most components (except ethane) is shorter than the characteristic transport time from Europe into the Arctic, whereas in winter, the transport time from 40–60° N to 80° N is comparable to, or shorter than the chemical lifetime (Table V) of a number of hydrocarbons. The characteristic time of transport from mid Europe (50° N) into the Arctic (80° N) in winter was estimated to be of the order of 10 days in a 2-d model calculation by Isaksen *et al.* (1985), whereas an annual average value of 1.8 months (assuming a meridional eddy coefficient, Kyy, of $1 \cdot 10^6$ m^2 s^{-1}) is given by Warneck (1988). Iversen (1989) calculated a frequency of high meridional index of 10–30% in winter for the longitudes 10° W to 20° E. The high meridional index corresponded to a poleward geostrophic wind of at least 10° latitude/(1.5 days). For a latitudinal span of 20°, approximately the distance from Birkenes to Ny-Ålesund, and assuming a 20% frequence of high meridional index, this would indicate a transport time of the order of 15 days in winter. The chemical lifetimes of ethane, propane and acetylene in winter are much longer than 10–15 days, while the chemical lifetime of butanes and pentanes is of the same order as this transport time. One would therefore expect a gradual build-up of many components in the northern troposphere (north of 50° N) during the winter months.

Table VI gives the monthly mean and median concentrations of the C_2–C_5 hydrocarbons as well as formaldehyde, acetaldehyde and acetone for the different stations calculated by taking measurements from all available years together. The tabulation of monthly data is included to ease the application of the measurements e.g. among modellers. Mean values are most often presented in the literature, but median values are also essential when studying components with a large spread in the concentrations. For the two Norwegian TOR stations, Zeppelin Mountain and Birkenes, the number of hydrocarbon observations were between 40 and 100 for each month except for propene. For the other sites (the EMEP VOC stations) there was between 12 and 25 observations for each month. Rucava was an exception to this with only 6–9 observations in each of the months June–September, due to the contamination problem in 1994 as explained in Chapter 2. The monthly carbonyl values were mostly based on 13–18 measurements.

4.1. SEASONAL AND MERIDIONAL GRADIENTS IN HYDROCARBONS

Figure 6 shows the average seasonal cycle at different stations of the sum of the C_2–C_5 alkanes, alkenes and alkyne (on carbon basis), as well as the sum of three groups of components, representative of different source categories: Ethane + propane ('natural gas'), ethene + acetylene + propene ('exhaust') and C_4–C_5 alkanes ('fuel vapour'). The curves in Figure 6 show the 30 days' running average applied twice to the data for all years taken together. The effect of the second averaging was only to reduce the small scale noise which results when calculating running averages of scattered data.

The build-up of hydrocarbons during winter is clearly visible from Figure 6 when comparing the sum of hydrocarbons at Birkenes and the Zeppelin Mountain. The sum of hydrocarbons reaches an equilibrium level of about 20 ppbC at Birkenes in winter, while on the Zeppelin Mountain, 2000 km further north, there is a gradual



"Natural gas" (Ethane + propane)

"Exhaust" (Ethane + acetylene + propane)

"Fuel vapor" (Butanes + pentanes)

Sum hydrocarbones

Figure 6. Average seasonal cycles of the sums of different groups of hydrocarbons for several measuring sites. All components were summed on a carbon basis. The lower right diagram shows the total sum of the three other groups shown in the other diagrams (ethane + propane + ethene + acetylene + propene + n-butane + i-butane + n-pentane + i-pentane). The seasonal cycles were calculated by a 30 days' running average applied twice and using all available data.

rise in concentration during autumn and winter, which peaks at the same level in late January. The winter value of 20 ppbC compares well with 2-dimensional (Strand and Hov, 1994) and 3-dimensional model calculations (Berntsen and Isaksen, 1994). For 60° N Strand and Hov (1994) calculated a nearly constant value of about 20 ppbC for the first 50 days of the year, and about 5 ppC for the summer. The summer value is lower than the observed summer average for Birkenes, but this is explained by regional transport episodes which is not captured in a 2-d model. Berntsen and Isaksen (1994) applied a global 3-dimensional model with detailed photochemistry, based on a chemical tracer model with grid squares of 8° latitude by 10° longitude. For the grid square containing Spitsbergen they calculated a sum of hydrocarbons of 20–25 ppbC from January to the start of March and a drop in concentration to approximately 5 ppbC in summer, which is in good accordance with our observations.

When the EMEP sites are considered, quite large differences in the sum of C_2–C_5 hydrocarbons were found among the stations in winter. However, except for Tänikon, these differences are largely explained by differences in components linked to vehicle combustion, indicated by the sum of ethene, acetylene and propene, the 'exhaust' category. The average seasonal cycles of both the natural gas category and the fuel vapour category were similar for Birkenes, Waldhof and Kosetice. In late winter (February) the differences from the Zeppelin Mountain in the Arctic to Kosetice in central Europe become small, except for the exhaust category compounds. Tänikon differed from this because the components linked to fuel vapour were substantially higher than the other stations, probably due to local emissions. However, the average seasonal cycle in the sum of ethane and propane at Tänikon agreed well with the other sites.

The difference in seasonal cycles of the VOC groups could be explained in several ways. One possible explanation is that the three continental sites were influenced by more local sources from combustion than from other sources in winter. On the other hand, the observations could also be explained by non-constant emission source strengths over the year. Urban hydrocarbon measurements in Switzerland indicate a summer maximum in evaporative fuel compounds and a winter maximum in combustion products (ATAL, 1994). Estimates by Bailey *et al.* (1990) indicate that emissions of acetylene, ethene and propene are higher during 'cold starts' of the vehicles compared to 'hot starts', whereas the opposite is the case for i-butane, n-butane and i-pentane. A summer maximum in the fuel evaporation and a winter maximum in the emission of combustion products is qualitatively in agreement with the observed seasonal cycles shown in Figure 6.

Figure 7 and Figure 8 show the mean, median, 10-, 25-, 75- and 90-percentile for ethane, ethene, acetylene, propane, n-butane and i-pentane for winter and for summer. Winter was defined as December through February, and summer was defined as June through August. The stations are arranged from north to south. In winter there is a general increase in the ethene and acetylene concentration from the northern to the southern sites, which is consistent with the increase in observed NO_2 and in the regional NO_x emission as discussed in Section 2 and Table II. The average ethane and propane concentration is highest at Waldhof, suggesting a maximum in the leakage of natural gas in this region. Figure 7 shows that the meridional concentration gradients become small even for n-butane and i-pentane, when comparing the winter medians, except for Tänikon. This shows that the hydrocarbons build up in the remote northern troposphere during winter. The measurements suggest that alkanes from C_2 to C_5 become quite well mixed from central Europe into the Arctic.

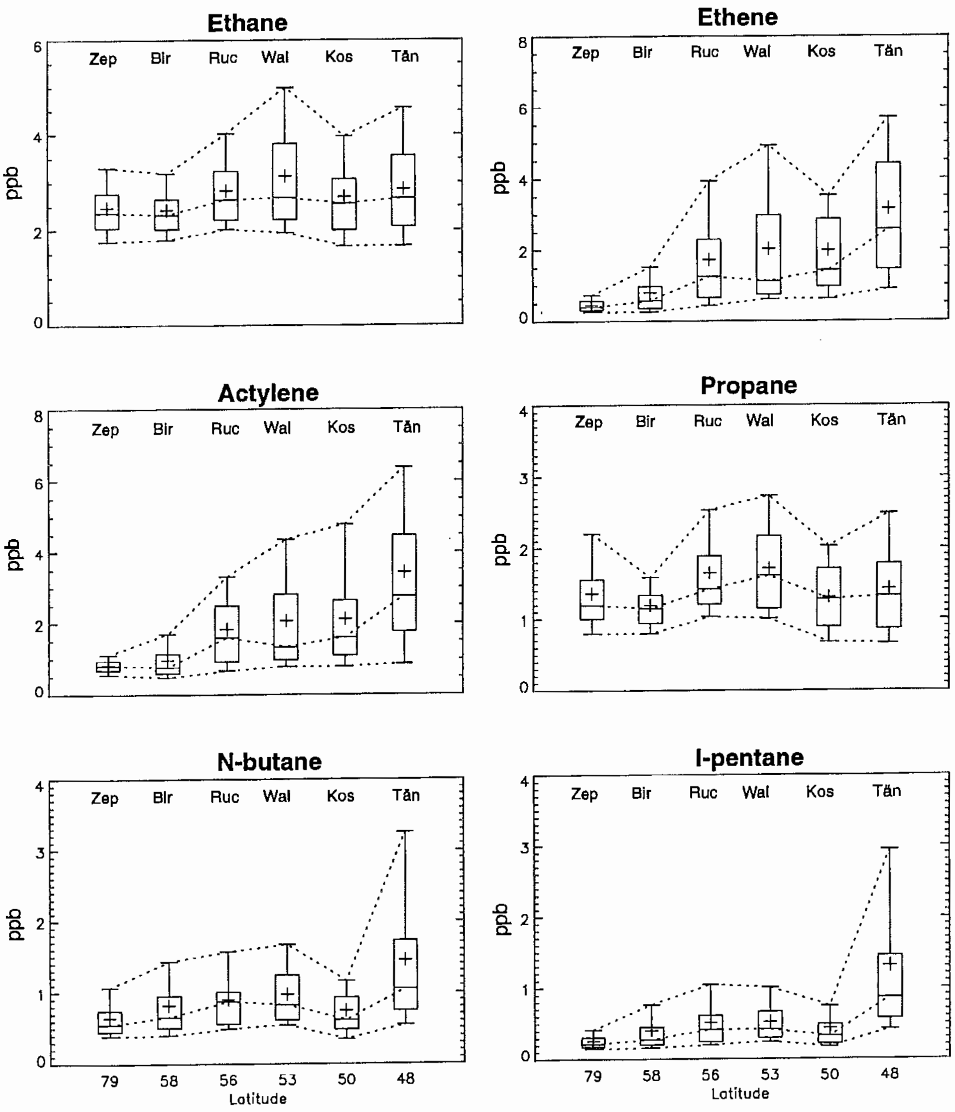


Figure 7. Box- and whisker-diagrams showing percentiles and mean concentrations of observed hydrocarbons in three winter months (December–February) at the Zeppelin Mountain, Birkenes, Rucava, Waldhof, Kosetice and Tänikon. The stations are arranged from north to south. The markers indicate the 10- and 90-percentiles (lower and upper bonds), 25- and 75-percentiles (lower and upper boundaries of boxes), medians (horizontal line inside boxes) and means (crosses). The dotted lines connect the 10- and 90-percentiles and the medians for clarity. All values are in ppb.

In summer the situation is quite different, as seen by Figure 8. *N*-butane and *i*-pentane almost disappear on the Zeppelin Mountain. At the other sites the spread in the summer data values is larger than in winter, indicating a low background concentration superimposed by episodes of high concentrations. Ethane is the only compound which still show a fairly even meridional distribution from Europe into the Arctic, and the concentration on the Zeppelin Mountain is about 80% of the concentration in Europe. The corresponding ratios for propane and acetylene are about 25–30%. These numbers would indicate an average time scale for the exchange between Europe and 79° N, of only around 7 days based on photochemical decay only and assuming no sources in between. As the actual time scale for this process is considerably longer on average in summer, closer sources could also contribute.

The alkenes are certainly not subject to long range transport in summer. The lifetimes of ethene and propene are less than one day in summer, still these compounds show a small gradient from north to south (Figure 8 and Table VI). The only explanation for this is the presence of local sources near the measuring sites. Propene has a chemical lifetime of only a few hours in summer, implying that concentrations exceeding a value of the order of 10 ppt are most likely caused by emissions near the measuring site. It is almost impossible to avoid that minor local emissions on occasions affect rural monitoring sites, but the contribution will be negligible most of the year, as long range transport from the major source areas will dominate the observed concentrations. In summer, however, short lived hydrocarbons may be totally depleted during long range transport, and the observations will only reflect the scattered minor emissions near the site. Local emissions could be due to a small anthropogenic source, but ethene and propene is also released by biogenic sources in summer, both from the ocean (Rudolph *et al.*, 1993; Ratte *et al.*, 1993), and from vegetation (Volz-Thomas *et al.*, 1993).

At Tänikon, where local traffic is known to influence the concentrations, there is a substantial spread in the summer data for all compounds, in contrast to the observations on the Zeppelin Mountain where propene show a much larger spread in observed concentrations than compared to acetylene and the C_4 and C_5 alkanes. This is an indication that the local sources influencing the Zeppelin Mountain are not anthropogenic, but more likely of biogenic origin. However, this has to be analysed in more detail to draw firm conclusions.

4.2. SEASONAL AND GEOGRAPHICAL GRADIENTS IN CARBONYL COMPOUNDS

Figure 9 shows the average seasonal cycle of formaldehyde, acetaldehyde, acetone and the carbon sum of all analysed carbonyl compounds for Birkenes, Rucava and Mace Head (left diagrams) and Waldhof, Kosetice, Donon, Ispra and Montelibretti (right diagrams). The curves were calculated by a 30 days' running average applied twice, as for the hydrocarbons explained above. The results from Harwell and the Zeppelin Mountain are not included in the figures, due to the less frequent sampling and poorer data coverage at these locations. For Montelibretti the number of samples were too few to calculate a representative seasonal average in spring, and for Mace Head the number of samples from May to September were too few

Table VI. Monthly mean and median concentrations (1st and 2nd line, respectively) of hydrocarbons and carbonyl compounds at EMEP and Norwegian TOR sites, based on several years of measurements. Unit: ppt

	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
						Ethane						
Zeppelin	2715	2702	2726	2215	1492	1054	809	808	997	1222	1558	2049
	2468	2576	2690	2251	1484	1090	802	771	1000	1216	1498	1993
Birkenes	2566	2630	2780	2622	1922	1292	1052	958	1158	1646	1994	2117
	2441	2528	2657	2560	1825	1260	978	915	1103	1485	1863	2004
Rucava	2604	2897	3114	2555	1982	1297	1038	915	1233	1812	2258	2946
	2403	2713	2735	2551	2017	1219	950	924	1082	1788	2056	2781
Waldhof	2753	3906	3132	2541	1969	1329	1137	1222	1490	1958	3164	2864
	2288	3284	2817	2504	1990	1185	1017	1017	1464	1913	2880	2498
Kosetice	2498	3440	2859	2829	1894	1343	1049	1034	1609	1858	3026	2371
	2529	3068	2599	2800	1826	1364	985	980	1398	1675	2294	2115
Tänikon	2833	3362	2808	2317	1809	1275	1109	1002	1525	1950	2301	2567
	2748	3014	2526	2350	1780	1265	1146	1033	1452	1767	2058	2227
						Ethene						
Zeppelin	515	408	232	147	118	102	96	143	139	181	284	410
	452	360	216	140	106	96	93	128	117	175	221	375
Birkenes	792	815	614	468	335	266	321	307	340	675	811	764
	571	659	455	393	251	224	272	274	313	519	591	530
Rucava	1163	1288	845	656	300	260	202	308	442	1070	1131	2468
	739	1050	794	489	267	160	134	231	344	992	1277	1911
Waldhof	1379	2734	979	611	382	295	262	467	658	961	2788	1952
	793	2290	949	497	291	191	170	293	625	652	1913	1119
Kosetice	1722	2479	986	930	390	447	232	331	539	1089	2195	1825
	1228	2055	779	812	325	389	227	297	473	849	1831	1281
Tänikon	3447	3554	1594	897	691	610	589	530	1258	1687	2611	2710
	2463	3491	1020	720	497	531	538	518	1190	1016	2338	2226
						Acetylene						
Zeppelin	908	884	846	576	267	120	85	103	175	263	482	719
	890	861	850	599	264	123	82	96	166	263	400	678
Birkenes	994	1001	942	780	431	215	207	267	334	780	929	922
	781	849	824	707	378	198	176	211	288	537	731	679
Rucava	1038	1814	1620	1189	577	365	249	332	508	1124	1203	2425
	1008	1612	1405	1019	486	246	223	320	483	971	1138	2109
Waldhof	1288	3008	1579	1202	706	368	390	498	743	994	2607	1948
	1003	2586	1075	1029	673	294	377	346	742	768	2056	1319
Kosetice	1819	2797	1632	1574	739	565	382	481	809	1228	2071	1862
	1741	2313	1226	1645	639	528	320	401	835	980	1794	1439
Tänikon	2395	4137	2357	1447	1210	844	939	771	1520	1942	2624	3606
	2025	4241	1406	1311	1094	747	1024	714	1366	1486	2261	2582

Table VI. *(Continued)*

	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
						Propane						
Zeppelin	1580	1456	1324	789	261	97	60	100	242	398	608	1055
	1370	1288	1279	782	230	94	50	82	198	374	519	998
Birkenes	1241	1308	1286	1032	499	300	301	298	410	698	911	1042
	1182	1284	1189	949	419	262	274	260	348	625	835	984
Rucava	1406	1664	1562	938	587	223	250	259	411	728	1151	1803
	1373	1525	1341	932	591	153	187	236	333	691	1046	1445
Waldhof	1639	1999	1510	928	611	477	370	531	702	959	1816	1567
	1250	1754	1373	893	583	322	274	396	589	832	1607	1377
Kosetice	1296	1670	1281	974	557	453	268	330	582	755	1463	1096
	1405	1628	1156	930	512	450	230	294	482	656	1054	992
Tänikon	1379	1707	1212	852	563	459	445	379	679	972	1199	1280
	1401	1649	1091	824	582	387	411	388	612	809	986	1050
						Propene						
Zeppelin	70	116	61	55	51	59	120	84	51	54	-	80
	64	78	50	48	48	54	141	85	39	52	-	83
Birkenes	157	185	154	114	97	96	139	112	99	185	184	131
	104	121	100	88	75	71	83	103	83	114	110	97
Rucava	260	246	209	157	114	85	66	93	107	258	215	485
	180	174	159	127	131	66	62	98	79	232	223	381
Waldhof	309	438	212	126	129	120	80	133	172	260	546	470
	252	381	178	144	130	115	76	99	173	187	333	356
Kosetice	372	336	179	176	115	123	84	197	232	247	373	390
	317	326	168	159	128	123	73	111	138	270	328	285
Tänikon	681	571	299	203	194	186	149	144	379	403	576	727
	463	521	274	200	170	167	149	137	316	325	490	525
						N-butane						
Zeppelin	744	673	543	256	53	25	30	33	100	156	282	501
	605	574	505	244	46	15	17	25	69	148	236	451
Birkenes	866	791	864	575	255	260	320	428	506	864	857	793
	674	626	751	468	208	202	183	208	287	523	587	630
Rucava	780	901	900	481	243	109	116	185	230	412	642	1002
	635	881	909	377	261	61	128	114	196	372	664	915
Waldhof	899	1059	806	443	334	298	237	335	421	580	1118	962
	742	897	672	414	288	181	168	256	368	508	999	794
Kosetice	820	840	733	457	273	314	163	206	343	452	818	646
	613	809	520	344	240	280	155	174	269	419	651	539
Tänikon	1403	1608	983	886	768	638	818	659	941	983	1234	1379
	885	1507	736	679	647	583	707	605	815	708	1053	847
						I-butane						
Zeppelin	377	341	281	143	28	9	25	26	55	80	142	268
	316	297	268	142	23	7	15	14	34	80	116	237

Table VI. *(Continued)*

	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Birkenes	452	419	452	306	134	138	199	287	323	480	445	403
	349	325	384	242	113	101	102	113	149	257	295	309
Rucava	585	464	491	264	130	65	65	68	104	233	335	510
	366	470	480	211	128	35	61	56	99	222	341	453
Waldhof	601	552	424	253	178	151	133	186	234	295	577	521
	429	453	362	214	158	95	88	117	207	259	570	482
Kosetice	466	456	322	276	163	178	80	130	197	258	460	366
	319	438	274	241	135	154	71	101	173	215	368	298
Tänikon	1167	740	432	319	279	229	264	202	347	436	559	630
	523	750	350	291	281	187	216	182	280	332	441	441
						N-pentane						
Zeppelin	270	248	173	66	15	7	12	13	39	56	98	182
	227	208	155	64	11	6	7	9	21	53	80	164
Birkenes	342	262	267	190	92	90	109	141	158	294	276	267
	243	228	229	145	66	63	68	73	101	209	212	213
Rucava	344	498	459	208	117	52	53	57	127	228	322	547
	226	366	381	195	108	32	43	49	104	197	330	429
Waldhof	338	414	250	161	254	110	110	169	176	286	545	372
	244	318	227	114	104	59	68	101	170	215	431	284
Kosetice	300	325	199	197	155	191	66	120	164	212	379	275
	202	326	176	155	96	146	56	85	142	185	368	202
Tänikon	488	513	321	217	330	242	260	250	361	427	500	505
	314	470	287	204	214	216	252	230	287	267	377	345
						I-pentane						
Zeppelin	297	271	186	74	12	7	13	10	35	54	105	203
	258	225	176	69	9	6	7	8	20	52	86	190
Birkenes	449	346	354	244	131	143	201	265	297	509	450	415
	300	276	296	177	96	88	99	101	139	300	309	270
Rucava	446	526	629	273	149	73	71	73	142	304	352	559
	267	463	477	263	108	44	67	66	120	241	402	547
Waldhof	455	571	374	230	280	176	169	247	270	366	790	532
	348	452	342	181	178	99	115	160	257	307	592	427
Kosetice	477	449	294	286	195	271	109	169	274	317	508	399
	305	480	227	223	163	224	96	152	209	288	420	264
Tänikon	1292	1319	763	618	786	685	819	693	1049	1004	1142	1320
	630	1136	575	485	656	555	756	662	816	828	1015	748
						Formaldehyde						
Zeppelin	-	-	-	153	276	271	-	197	144	-	-	-
	-	-	-	134	272	229	-	158	138	-	-	-
Birkenes	229	386	347	526	827	728	967	671	468	341	292	288
	221	299	339	496	753	658	898	654	418	315	284	260
Rucava	614	788	519	991	720	788	899	754	706	710	612	665
	607	737	504	946	607	804	796	607	741	607	500	686

Table VI. *(Continued)*

	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
MaceHead	-	378	284	442	-	-	-	-	-	-	426	230
	-	268	244	307	-	-	-	-	-	-	370	236
Waldhof	408	720	533	870	1155	1051	1714	1448	894	750	868	460
	398	552	406	745	930	906	1600	1162	788	670	796	398
Kosetice	873	1053	973	1132	1418	1616	1737	1872	1206	894	972	743
	1024	898	697	1028	1273	1387	1647	1730	1111	890	954	733
Donon	571	706	760	887	1322	1289	1372	2143	738	946	792	452
	544	638	630	823	1210	1217	1245	2329	753	804	713	410
Ispra	2344	2036	2394	1888	2064	3439	4248	3400	2054	1737	2017	2026
	1946	1887	2616	1915	2013	3018	3861	3570	2029	1552	2364	1946
Montelibretti	1162	1278	-	-	-	-	2948	5903	2487	1359	-	-
	957	1308	-	-	-	-	2746	6233	2273	1379	-	-
							Acetaldehyde					
Zeppelin	-	-	-	168	316	98	-	80	81	-	-	-
	-	-	-	167	236	81	-	78	83	-	-	-
Birkenes	221	317	214	280	385	275	483	243	212	240	176	210
	158	253	207	236	328	231	441	255	210	220	145	145
Rucava	357	457	298	446	334	301	399	351	309	413	314	433
	344	411	247	438	306	279	242	253	290	371	236	352
MaceHead	-	207	160	217	-	-	-	-	-	-	240	106
	-	124	129	118	-	-	-	-	-	-	199	116
Waldhof	310	519	356	439	407	325	476	439	391	460	640	343
	247	419	301	414	392	258	381	406	352	419	543	293
Kosetice	554	586	557	545	577	728	744	787	540	541	662	373
	387	561	419	537	567	763	661	733	513	510	669	328
Donon	319	420	472	477	734	556	647	789	454	565	524	288
	269	344	414	414	685	518	580	827	398	484	430	263
Ispra	1344	1282	1320	1055	991	1309	1484	1383	1027	1086	1229	1276
	1238	1330	1386	1015	881	1198	1343	1373	981	908	1418	1144
Montelibretti	672	664	-	-	-	-	979	1504	887	699	-	-
	548	639	-	-	-	-	981	1370	776	731	-	-
							Acetone					
Zeppelin	-	-	-	538	624	548	-	552	494	-	-	-
	-	-	-	473	652	518	-	505	534	-	-	-
Birkenes	-	333	406	1120	1481	1248	1220	886	829	562	390	327
	-	338	381	791	1300	1050	1198	779	831	583	408	310
Rucava	397	499	525	1085	835	773	1029	823	803	700	651	395
	351	520	399	1109	774	701	852	762	803	591	465	416
Mace Head	-	384	-	-	-	-	-	-	-	-	486	237
	-	277	-	-	-	-	-	-	-	-	473	224
Waldhof	1167	1283	1119	1325	1318	1176	1629	1528	1227	1153	1112	669
	609	1068	717	1048	1090	1011	1280	1553	1007	958	1154	534
Kosetice	678	904	1161	1476	1771	1775	1897	1720	1261	1009	884	507
	622	752	730	1329	1561	1687	1594	1561	1162	917	858	509

Table VI. *(Continued)*

	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Donon	738	903	1108	1308	1657	1847	1724	2019	1125	1085	969	563
	487	856	734	1282	1641	1473	1551	1981	1015	925	848	461
Ispra	1875	1997	2184	1970	1793	1650	1739	1566	1495	1592	2025	1837
	1704	2097	2095	2005	1586	1459	1476	1427	1437	1308	2152	1732
Montelibretti	822	855	-	-	-	-	1781	-	1357	1080	-	-
	823	974	-	-	-	-	1728	-	1349	1168	-	-

for this calculation. It is important to bear in mind that the average seasonal cycles presented in Figure 9 are based on a varying number of observations from site to site and from month to month, and that the time period covered by the measurement programme is still rather limited, implying that the results could be biased by random effects.

The average seasonal cycles of the carbonyl compounds are quite different from the hydrocarbons. The sum of carbonyl compounds show a maximum in summer at all the sites, but the seasonal amplitude and the absolute concentrations vary. The comparison of the sum of carbonyl compounds is complicated by the fact that each date with measurements may consist of a varying number of components included in the summation due to concentrations below the detection limit. Although this means that the concentration is low, the sum of a large number of compounds below the detection limits may contribute to the sum, especially when they are summed on a carbon basis.

In winter the sum of carbonyl compounds is about 12 ppbC at Ispra, a factor of 3–10 higher than for the sites further north, and even twice the value for Montelibretti. Birkenes and Mace Head show the lowest concentrations of 1–1.5 ppbC in these months. The sum of carbonyls have a broad maximum from May to July at Kosetice and Donon, while at Birkenes the highest average value is found in May. The spring peak in the sum of carbonyls at Birkenes is mostly due to a peak in the acetone concentration. Acetone shows a pronounced seasonal variation at all sites, except at Ispra, while a slight maximum is found in summer for formaldehyde and acetaldehyde at most of the sites.

The seasonal cycle of the carbonyl compounds at Ispra differs substantially from the other sites. The sum of carbonyls at Ispra is the result of a pronounced peak in the formaldehyde concentration in mid summer of 4 ppb, compared to an almost constant value of approximately 2 ppb in other parts of the year, and a minimum in the acetone concentration in the summer. Although the number of samples from Montelibretti is fewer, the measurements indicate a peak in the formaldehyde concentration in summer, similar to at Ispra, but later in the year. In winter the concentrations are, however, much less than at Ispra.

The higher carbonyl concentrations at the two Italian sites could possibly reflect a combination of a more efficient oxidation of precursors and higher biogenic

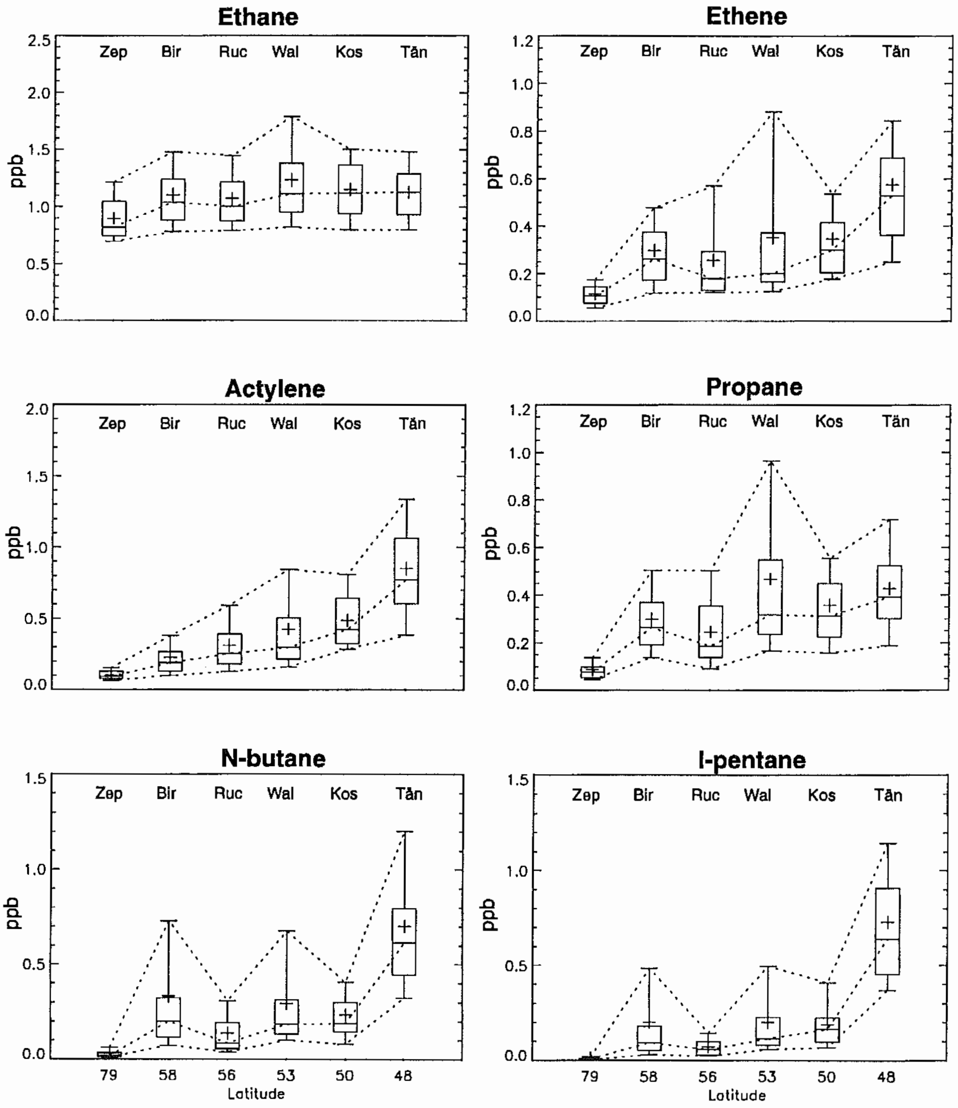


Figure 8. Same as Figure 7 for the three summer months, June–August.

emissions of VOC. It cannot, however, be ruled out that the measurements from the Italian sites are influenced by anthropogenic emissions near the stations as discussed in Chapter 2 and indicated in Table II. In November and December 1994 the average concentrations of ethene and acetylene (analysed by JRC – Ispra) were about twice the monthly average concentrations at Kosetice, and for the C_4 and C_5 alkanes the difference was larger, about a factor of 3–4 compared to Kosetice. Until a more detailed study of the relationship between carbonyl and anthropogenic

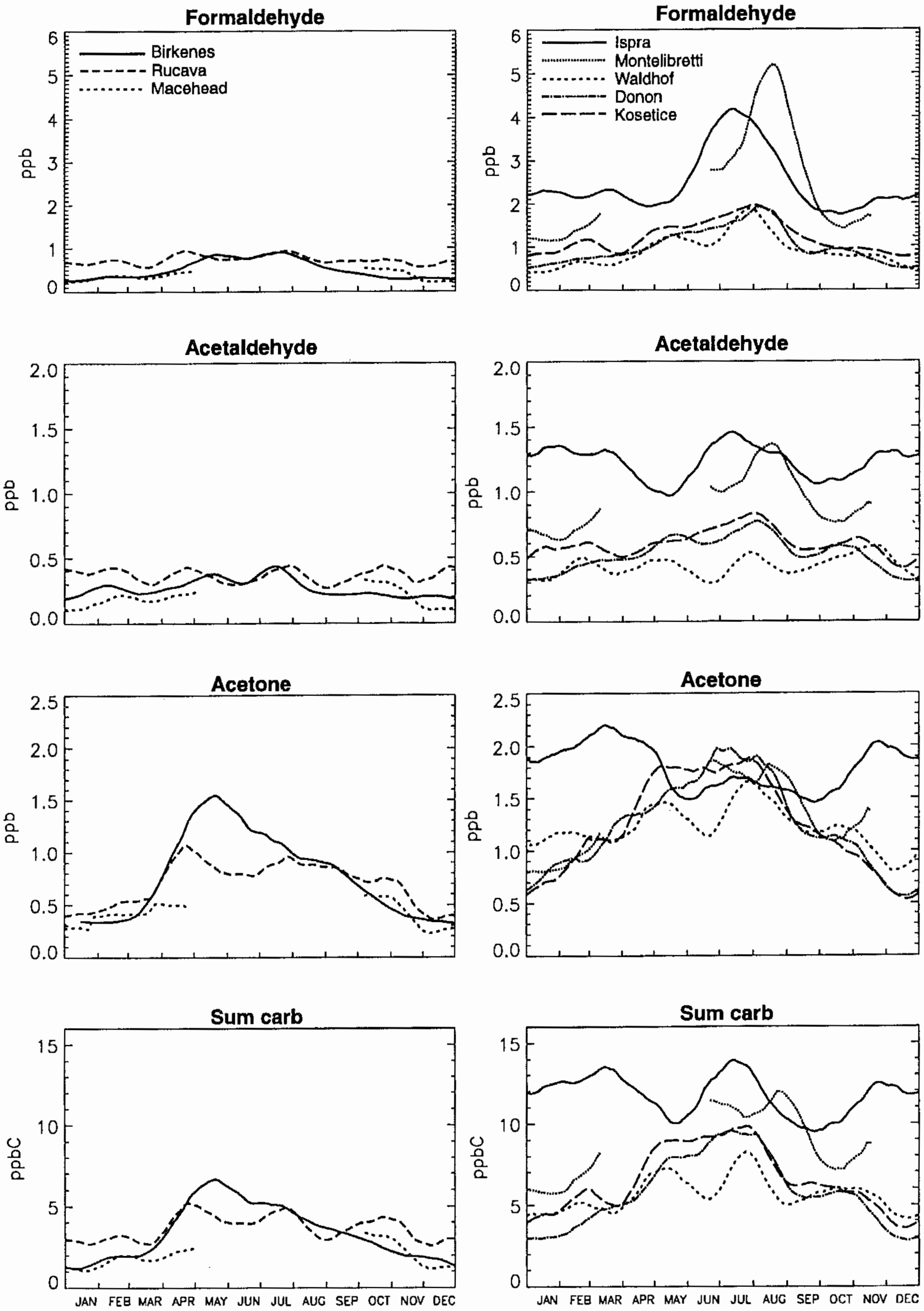


Figure 9. Average seasonal cycles of the sum of all measured carbonyl compounds (ppbC) and of formaldehyde, acetaldehyde and acetone (ppb) for Birkenes, Rucava and Mace Head (left diagrams), as well as for Waldhof, Kosetice, Donon, Ispra and Montelibretti (right diagrams). The seasonal cycles were calculated by a 30 days' running average applied twice and using all available data.

tracers is performed, the results from Ispra and Montelibretti should be used with care.

Formaldehyde, acetaldehyde and acetone constitutes most of the sum of measured carbonyl compounds. These three compounds contribute on the average 85–95% of the total carbon sum of carbonyls through the year, and no seasonal cycle was found for the fraction of these compounds compared to the sum. Analysis of the higher order carbonyls is still important, because these compounds are more specific tracers of certain reaction pathways, and of the oxidised species, than the low-weight carbonyls.

Figure 10 shows the box and whisker diagrams for the winter and summer seasons for the carbonyls, similar to Figure 7 and 8 for the hydrocarbons. Measurements from May were included in the summer season for the carbonyls. The carbonyls were measured on a daily basis from April to September on the Zeppelin Mountain in 1994, so the Zeppelin Mountain is included in the figure for the summer season.

In December–February the photochemical formation of carbonyls is low, and elevated concentrations should mostly reflect direct anthropogenic emissions, rather than secondary formation. The spread of the measured concentrations in winter is low for Birkenes and Mace Head, indicating few episodes with transport of air masses polluted by carbonyl emissions. The median formaldehyde concentration at these sites is about 250 ppt, consistent with reported background values in the literature (Lowe and Schmidt, 1983). The winter values at Kosetice indicate a higher influence from emissions of formaldehyde and acetaldehyde than at the other sites (except for the measurements at the Italian sites). Based on urban measurements in Hungary, Haszpra *et al.* (1991) argue that the aldehyde emission in that region is higher than in Western Europe, possibly due to the composition of the fleet of vehicles. This is in qualitative agreement with the EMEP measurements, but longer time series are needed to clarify that this finding is really representative for the region.

In winter acetone has a chemical lifetime of a month or more, sufficient for mixing over large areas. The marked differences in acetone concentration between the sites are therefore surprising. Direct emissions of acetone are apparently much more important at Waldhof, indicated by the large spread in measured concentrations. The average acetone concentrations of 250–400 ppt in winter at the most northern sites in winter is indicative of the tropospheric background value.

The geographical variation in the carbonyl percentiles in summer resembles that in winter in many ways, with some exceptions. There is a general north to south increase in the concentration in summer, as in winter, and the northernmost stations, the Zeppelin Mountain, Birkenes, Rucava and Mace Head seem to fall in a lower concentration regime than the other sites. The formaldehyde concentration on the Zeppelin Mountain is around 250 ppt and shows almost no spread in the data during May–August. We believe this represents the general background concentration in the remote northern troposphere in summer, and the value agrees with values calculated from the assumption of a photochemical steady-state and production from methane oxidation only (e.g. Warneck, 1988). It is interesting to note that acetone apparently is mixed into the Arctic even in summer, causing an average concentration of 500–600 ppt on the Zeppelin Mountain.

The reports of carbonyl measurements at rural sites are still rather sparse. Shepson *et al.* (1991) presented carbonyl measurements from Ontario, Canada, sampled in July–August 1988. They found average concentrations of formaldehyde, acetaldehyde and acetone of about 1.7, 0.5 and 1.7 ppb, respectively. These values agree quite well with the average summer concentrations shown in Figure 10 for Kosetice and Donon. Acetone was measured over eastern Canada in July to August 1990 and reported by Singh *et al.* (1994). They found a mean value of 1.1 ppb, while the observed concentrations were in the range from 0.36 to 2.3 ppb. They estimated a representative background concentration to be around 0.5 ppb. These values are lower than the summer averages for our central European sites, but are in accordance with the concentrations at Birkenes and Rucava.

4.3. THE FRACTIONATION BETWEEN CARBONYLS AND HYDROCARBONS

The average seasonal cycles of the fraction of carbonyls compared to the total sum of VOC (hydrocarbons + carbonyls) were calculated for the Zeppelin Mountain, Birkenes, Kosetice and Waldhof and are shown in Figure 11. The percentage fraction of carbonyls to the sum of VOC shows a maximum in summer. Furthermore, the calculated contribution of carbonyls to the sum of VOC are surprisingly similar at all the sites. In winter the carbonyls contribute about 5–15% to the VOC sum, whereas this fraction rises to 40–50% in summer. At Kosetice the fraction even peaks at 60% in July.

The maximum of the carbonyl fraction in summer is consistent with an oxidation of the hydrocarbons leading to a formation of aldehydes and ketones in this season. That the sum of carbonyls is comparable in magnitude with the sum of C_2–C_5 hydrocarbons in summer is interesting, and illustrates the importance of performing carbonyl measurements especially in summer. At the moment we would not speculate why the seasonal cycle in the fraction of carbonyls to the sum of VOC seems to be that similar for the different sites. The data may still be biased by random averaging artifacts, hence more measurements are required to draw conclusions.

5. Conclusions

Several years' regular measurements of light hydrocarbons and carbonyl compounds at rural sites in Europe have been presented. The stations cover a region from the Mediterranean to the Arctic. The measurements are part of the European monitoring and evaluation programme (EMEP) and the EUROTRAC project Tropospheric Ozone Research (TOR). In addition, half a year with continuous

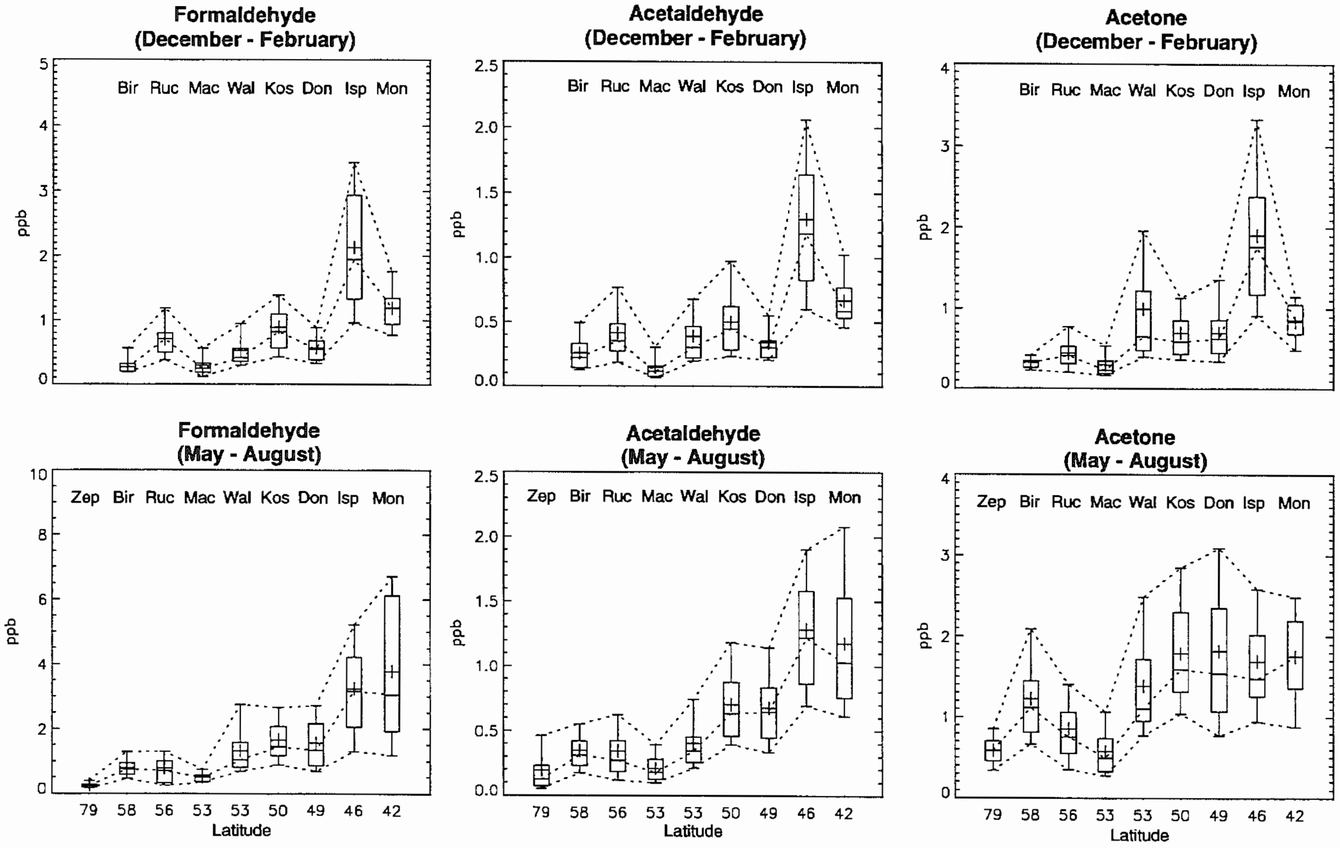


Figure 10. Box- and whisker-diagrams showing percentiles and mean concentrations of observed carbonyl compounds in three winter months (December–February) and four summer months (May–August) at the Zeppelin Mountain (summer only), Birkenes, Rucava, Mace Head, Waldhof, Kosetice, Donon, Ispra and Montelibretti. The stations are arranged from north to south. All values are in ppb. The percentiles and means are marked as explained in Figure 7.

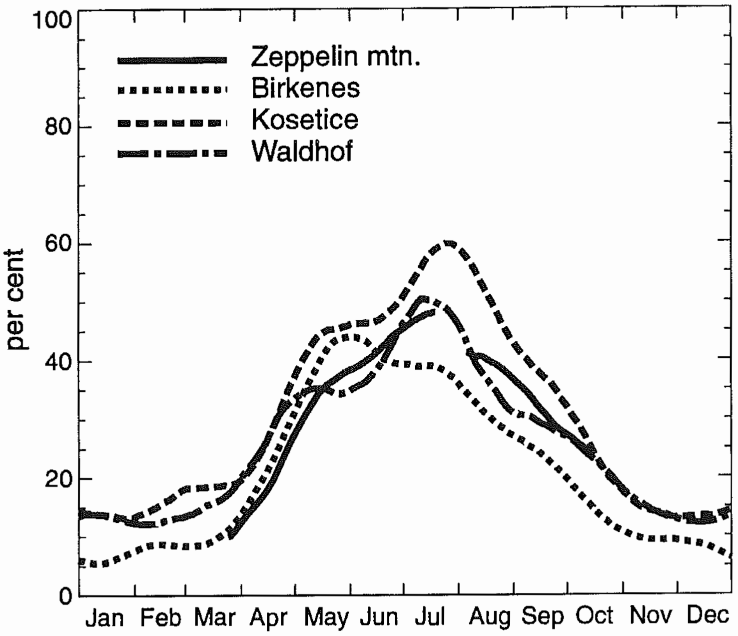


Figure 11. The percentage fraction of the sum of all carbonyl compounds to the total sum of VOC (hydrocarbons + carbonyls) for the Zeppelin Mountain (full line), Birkenes (dotted), Kosetice (dashed) and Waldhof (dash-dot).

sampling of hydrocarbons at Tänikon in Switzerland is included to elucidate the diurnal cycles in hydrocarbon concentrations at this site.

The measurements indicate that C_2–C_5 hydrocarbons are efficiently mixed from the European continent into the Arctic atmosphere during winter. This causes a gradual build-up which in late winter peaks at a sum of C_2–C_5 hydrocarbons of around 20 ppbC at 79° N on the Zeppelin Mountain, Spitsbergen, close to the average winter concentration at Birkenes, Southern Norway (58° N). The seasonal cycles in the sum of C_2–C_5 hydrocarbons vary significantly among the sites, but most of these differences were due to compounds emitted by combustion (acetylene, ethene and propene). Components related to emissions of natural gas and fuel evaporation were well mixed from central Europe to the Arctic in winter. The higher concentrations of combustion products in Central Europe than at the other stations may indicate an influence from local sources, but could also suggest that traffic emissions in general contain a larger share of combustion compounds than evaporative compounds in winter compared to in summer.

The elevated concentrations at Tänikon, with peaks in the morning and afternoon of most components, show that this site is influenced by local traffic emissions. However, the EMEP grab sampling is performed around noon, when the local influence is lower. In view of the fact that it is practically impossible to find sites in densely populated areas with no local VOC sources, methods should be developed to allow for correction of local influences.

The carbonyl measurements indicate that formaldehyde, acetaldehyde and acetone are the three dominant components, and constitute 85% or more of the total sum of carbonyls which were detected. The seasonal cycles of the carbonyl compounds are mostly opposite to the hydrocarbons, and show a maximum in spring and summer. This is most pronounced for acetone, while acetaldehyde only shows a minor variation during the year. The concentration of several carbonyls were much more abundant at two Italian sites than further north, and the seasonal cycles were quite different. It is not clear, however, whether this is due to a local anthropogenic influence at the sites, or if it is representative of a larger region.

In summer the carbon sum of carbonyls were of the same magnitude as the carbon sum of C_2–C_5 hydrocarbons. The seasonal cycle in the percentage amount of carbonyls to the total sum of all VOC (hydrocarbons + carbonyls) were similar at all the sites, from the Zeppelin Mountain in the Arctic to Central Europe. More measurements are needed to clarify if this is a general fact.

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