Measurements of Carbon Monoxide and Nonmethane Hydrocarbons During POPCORN

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Abstract. During the field campaign POPCORN (Photo oxidant formation by plant emitted compounds and OH radicals in North-eastern Germany) in Pennewitt (Mecklenburg-Vorpommern, Germany) in August 1994, carbon monoxide and nonmethane hydrocarbons were measured over a large maize field by in-situ gas chromatography. Throughout the campaign CO and NMHC showed, even for a remote rural area, unexpectedly low mixing ratios. Except a few episodes, CO mixing ratios were around 120 ppb. Ethane was the only hydrocarbon showing mixing ratios exceeding 1 ppb. The mixing ratios of all other NMHC ranged between several hundred ppt and the lower limit of detection which was between 20 and 5 ppt depending on the compound. During three frontal passages CO and NMHC mixing ratios increased significantly, while between August 13 and 16, 1994, polar air masses were encountered with CO and NMHC mixing ratios dropping to values which are typical for North Atlantic background air. During this period average CO mixing ratios were 85 ppb and ethane as the most abundant hydrocarbon decreased to 650 ppt. The large-scale meteorological situation is reflected in an unusual frequency distribution of CO. The distribution shows three maxima which can be assigned to the periods of the frontal passages, to the observation of polar air masses and the rest of the campaign. Two-day backward trajectories were calculated in order to obtain information about the origin of the air masses transported to the site. The observed NMHC and CO data can be attributed to the origin of the air masses and the air mass trajectories. NMHC and CO mixing ratios were well correlated indicating that these compounds originated from similar mostly anthropogenic sources. An exception was isoprene which showed no correlation with CO. With values below 100 ppt the mixing ratio of isoprene, which is emitted by terrestrial vegetation, was also unexpectedly low during the first half of the campaign although the maximum temperatures were around 35°C.

Key words: carbon monoxide, nonmethane hydrocarbons, photochemistry, air mass characterization.

1. Introduction

Nonmethane hydrocarbons (NMHC) are subject to photochemical transformation reactions which produce ozone and other oxidants. These reactions also lead to a variety of different secondary compounds (aldehydes, ketones, etc.) which react further and also contribute to the formation of photo-oxidants. The knowledge of the atmospheric distribution of NMHC is necessary for the understanding of photochemical processes, especially the HO_x cycle, but can also be used to determine transport and dilution effects. NMHC have been previously measured in a large number of different field experiments at many locations around the world, also at remote continental sites. An overview of such measurements and the compounds investigated so far is given by Singh and Zimmerman (1992) and Atlas *et al.* (1995). An overview over previous field campaigns concerning the measurement of OH radicals and a detailed description of the POPCORN campaign tasks are given by Plass-Dülmer *et al.* (this issue). In this paper the measurements of CO and nonmethane hydrocarbons are presented. The variation in the CO mixing ratios and changes in the NMHC pattern together with meteorological data and backward trajectories based on ECWMF (European Center for Medium Weather Forecasts, Reading, Great Britain) data are used to characterize the air masses encountered during the campaign. A characterization of the air masses and the CO and NMHC mixing ratios are necessary for an interpretation of the OH measurements, and a comparison between measured and modelled OH.

2. Experiment

During POPCORN, carbon monoxide and NMHC were measured by in-situ gas chromatography. The surrounding of the measurement site and the location of the individual experiments is shown in detail by Plass-Dülmer *et al.* (1998) (cf. Figure 3 therein). Our instruments were installed in a laboratory container (GC) in the center of the maize field. The sample inlet (the same for both instruments) was located at mast #2 about 10 m south of the laboratory container at 6 m altitude above the ground and 4.5 m above the maize canopy. The inlet line (stainless steel tube, 10 mm ID, 15 m length) was continuously flushed with ambient air at a flow rate of 40 L/min in order to minimize wall losses or contaminations. Carbon monoxide was measured with a reduction gas analyser (RGA3, Trace Analytical Inc.). The time for one measurement was 2.5 minutes. The calibration of the instrument was done with reference air of known CO mixing ratio by alternately measuring reference air and sample air in order to eliminate possible drifts in the sensitivity of the instrument. Thus, one measurement of ambient air was made every 5 minutes. The detection limit was 2 ppb, the reproducibility 1%.

NMHC (C_2–C_7 alkanes, alkenes, acetylene and aromatics) were measured by FID/ECD gas chromatography. The samples were preconcentrated at liquid nitrogen temperature on a stainless steel tube packed with glass beads from 1.5 to 3.5 L (STP) of air. After preconcentration the sample loop was heated to 120°C and the sample was injected into the gas chromatograph. The hydrocarbons were separated into a light fraction (C_2–C_3) and a heavy fraction (C_4–C_9) using a 7 m RTX-1 capillary column (Restek, 0.53 mm ID) and a 10 m porous layer open tubular column (J&W, Poraplot Q, 0.53 mm ID). The light fraction was then separated on a 30 m aluminium oxide/KCl capillary column (J&W, 0.53 mm ID) after passing through a 10 m capillary column (Quadrex CW-20M, 0.53 mm ID) which retained the water from the sample. The heavy fraction was separated on a 105 m RTX-1 capillary column (Restek, 0.32 mm ID). The time for one complete analysis was 3 h 20 min. Figure 1 shows a schematic drawing of the gas chromatographic system.

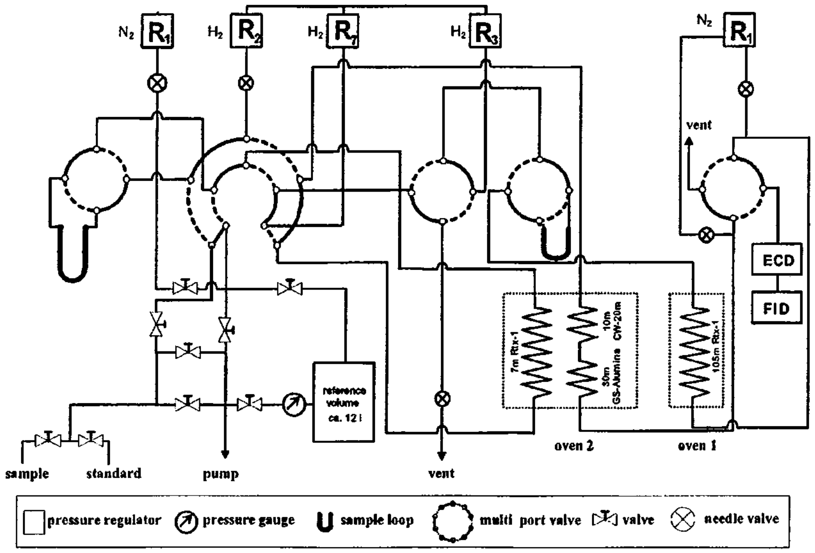

Figure 1. Schematic of the gaschromatographic system as used during the POPCORN campaign.

The signals of both instruments were digitized and aquired by a personal computer using a commercial chromatography software package. The atmospheric mixing ratios of the individual NMHC were calculated by comparing the samples with a reference air of known composition. The mixing ratios of the different hydrocarbons in the reference air were in the range of a fraction of a ppb to a few ppt and thus comparable with the levels in ambient air. The detection limits were between 5 and 20 ppt for the C_2 and C_3 hydrocarbons and about 1 ppt for the higher NHMC. The reproducibility was between 10% and 30% depending on the compound.

The CO instrument was operated continuously during the whole campaign providing CO data from 2 to 25 August 1994. The NMHC instrument suffered from a number of technical problems during the campaign. As a consequence there are gaps in the data. Mixing ratios of C_2 and C_3 hydrocarbons are available from 5 to 24 August 1994. During some periods ethene and ethane were not well separated on the aluminium oxide column due to high humidity in the air samples. In these cases only the sum of both compounds is available. Due to a breakdown of some parts of the instrument, no measurements of C_4–C_9 NMHC were possible after August 16. Therefore, C_4–C_9 data are available only for the period from 5 to 16 August 1994. In order to close some gaps in the data base, whole air samples were taken at the same inlet line in 2 L evacuated stainless steel canisters. With a stainless steel capillary (0.5 mm ID) the flow into the canisters was reduced.

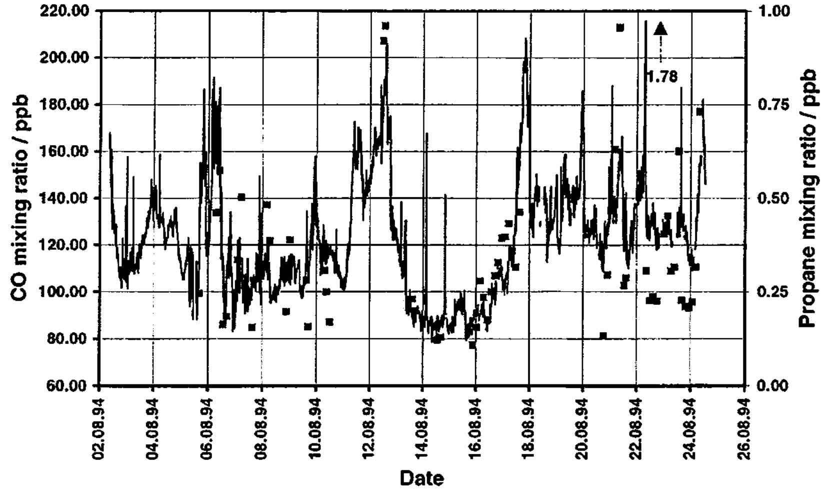

Figure 2. Time series of CO mixing ratios measured during the POPCORN campaign (solid line). Also included are the propane mixing ratios (filled squares).

The time for filling the canister was about 20 minutes and thus comparable to the time for the sample preconcentration of the in-situ instrument. The canister samples were analysed for C_2–C_9 hydrocarbons in the laboratory in Jülich after the campaign by a similar technique as described above (cf. Rudolph *et al.*, 1986).

3. Results and Discussion

3.1. CARBON MONOXIDE

Figure 2 shows a time series of the mixing ratios of CO, included are the propane mixing ratios which are discussed below.

Even for a remote continental site the CO mixing ratios were relatively low during the entire campaign. Except a few episodes the mixing ratios were around 120 ppb between 2–13 August and 17–24 August. The three episodes of higher CO mixing ratios on 5–6 August, 12–13 August, and 17–18 August were correlated with frontal passages. The spikes which can be observed sporadically in the data set consist of several data points. The corresponding reference gas measurements show no anomalous behaviour, thus these mixing ratios are real. They may be due to emissions of local sources such as agricultural equipment working near to the site. Between 13 and 16 August, CO mixing ratios decreased to values below 90 ppb, which is close to the northern hemispheric background concentration (see below). A diurnal variation was not observed for CO during the campaign indicating that local sources with a pronounced diurnal cycle did not influence the CO abundance. The mixing ratios of long-lived atmospheric trace gases such as CO are considerably

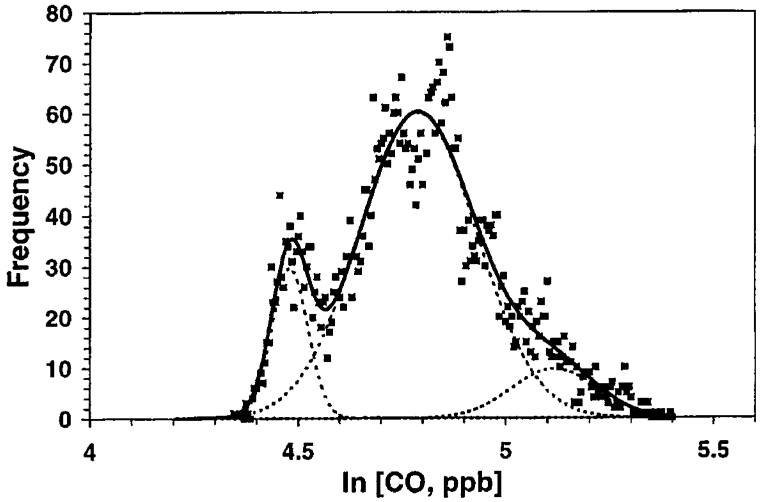

Figure 3. Frequency distribution of the measured CO mixing ratios. The squares are the data points in 1 ppb intervals, the dotted lines are individual Gaussian profiles, the solid line is the least squares fit of the sum of the three Gaussian profiles to the data points.

influenced by atmospheric dilution processes. Owing to these processes the trace gas concentrations show an exponential evolution with time. Thus, the logarithm of the mixing ratios should govern a Gaussian normal distribution (Bencala and Seinfeld, 1976; Ott, 1990).

Figure 3 shows a plot of the frequency of CO mixing ratios versus the natural logarithm of the CO mixing ratios. At the first glance, the distribution seems to be characterized by two maxima. It turns out, however, that the best fit to the data points is achieved considering three modes. Conducting a least squares fit of the sum of three Gaussian profiles the position of the maxima and the standard deviation of the CO mixing ratios can be calculated. The broadest distribution has a maximum at ln [CO] = 4.78 corresponding to a mean CO mixing ratio of 119 ppb. One smaller distribution peaks at ln [CO] = 4.48 corresponding to a CO mixing ratio of 88 ppb. The third mode appears to be at ln [CO] = 5.12 corresponding to a mean CO mixing ratios 167 ppb. The standard deviation for all modes and the ranges in terms of mixing ratios are given in Table I.

Comparing these results with the time series of CO (cf. Figure 2) the mode with a mean CO mixing ratio of 88 ppb can be assigned to the period between 13 and 16 August, where fast transport of air masses from the North Atlantic dominated the large scale meteorological situation. The mode with a mean CO mixing ratio of 167 ppb includes all data measured during the three periods of relatively high CO mixing ratios around 6 August, 12 August, and 17 August. The mode with a mean CO mixing ratio of 119 ppb includes all other measurements. To confirm

Table I. Results of the fits to the complete and separated data sets of the frequency distribution of the CO mixing ratios.

Mode No.	Center of mode		1 σ range	
	ln[CO]	[CO], ppb	ln[CO]	[CO], ppb[a]
All data				
1	4.48	88.2	0.051	83.8 / 92.2
2	4.78	119.1	0.167	100.8 / 140.8
3	5.12	167.3	0.121	148.3 / 188.9
Separate data sets[b]				
1	4.49	89.1	0.063	83.7 / 94.4
2	4.79	120.3	0.161	102.4 / 141.3
3	5.07	159.2	0.133	139.4 / 181.2

[a] Given are the mixing ratios for the mean $- \sigma$ / mean $+ \sigma$.

[b] For this calculation the data were devided into separate sets according to the episodes discussed in the text, i.e. mode #1 for 13–16 August, mode #2 for 7–11 August and 18–24 August and mode #3 for 5–6 August, 12–13 August, and 17–18 August.

this classification the CO data were divided into separate data sets corresponding to the periods discussed above. Each individual data set was fitted with a Gauss profile. The results which are also given in Table I are in excellent agreement with the results of the fit to the complete data set confirming that the modes can be assigned to the different meteorological situations. The broadest of the three modes may consist of two maxima. However, if the fit procedure is forced to fit an additional fourth Gauss profile to the data, the maximum and 1 σ range of the broad distribution does not change significantly. In this case an additional profile appears at $\ln [CO] = 4.85$ which corresponds to a mean CO mixing ratio of 127 ppb. This distribution cannot be assigned to any of the meteorological situations discussed above. The data contributing to this mode are distributed over the whole campaign. Therefore, we assume that the distribution is trimodal and the the fourth mode is not significant. The observations for CO are in agreement with the measurements of PAN mixing ratios. Schrimpf *et al.* (1998) report a bimodal log-normal distribution with one mode corresponding to measurements made during the period of 13–16 August, the second mode corresponding to nearly all other measurements. Even the third mode with the highest mixing ratios is indicated in the frequency distribution of PAN.

As discussed above, the three frontal passages encountered during the campaign are associated with an increase in CO and NMHC mixing ratios (see below). Analysis of the back trajectories and the meteorological data reported by Brauers *et al.* (1998) shows an increase in the mixing ratios after the passage of two cold fronts on 5 August. A similar situation is observed for the frontal passage on 17 August, when a warm front was immediately followed by a cold front. The increase of the mixing ratios occurred with the passage of the cold front. However, the situation was different on 13 August when the mixing ratios increased before the front reached the measuring site. This increase of CO and NMHC mixing ratios can be partly explained by changes in the wind direction and thus changes in the origin of the air masses associated with a frontal passage. Such a situation can be seen for 5–6 August, where wind direction changed from north-west to south-west (cf. Figures 7 and 8). For the other two frontal passages on 13 and 17 August the back trajectories do not change significantly with the frontal passages (cf. Figures 9–11). The cause for an increase of CO and NMHC mixing ratios during these episodes is not fully understood.

3.2. NONMETHANE HYDROCARBONS

Similar to CO, the NMHC mixing ratios were unexpectedly low throughout the campaign. The individual measurements are given in Table II. Table III. gives a synopsis of the CO and NMHC data.

For ethane, the most abundant nonmethane hydrocarbon, mixing ratios around 1 ppb were measured. The mixing ratios of the other NMHC rarely exceeded 1 ppb. The mixing ratios of the alkanes follow the pattern shown for CO indicating that these trace gases originated from similar, mostly anthropogenic, sources. As an example, the time series of propane has been included in the plot of the time series of CO mixing ratios (Figure 2). Light alkenes which have also natural sources do not show this distinct behaviour. Between 5 and 11 August NMHC mixing ratios were low with some variability depending on the impact of continental emissions. On 12 August NMHC concentrations increased by more than a factor of two which coincides with an increase in CO mixing ratios to about 200 ppb. Between 13 and 16 August NMHC follow exactly the behaviour of CO with a sharp decrease on 13 August and extremely low values until 16 August. During this episode the mixing ratios of all NMHC dropped dramatically. Ethane was around 600 ppt and benzene and toluene mixing ratios were about 60 and 10 ppt. From 16 to 18 August NMHC mixing ratios increased again. There are no data for the period between 18 and 21 August due to problems with the capillary column. During the last week of the campaign the NMHC mixing ratios remained rather low.

Figure 4 shows a plot of acetylene versus CO mixing ratios. The data set has been divided into the episodes corresponding to the different CO modes: the periods of the frontal passages, the period of 13–16 August with extremely low CO mixing ratios the periods between 7–11 August and 20–24 August with CO mixing ratios around 120 ppb. The two latter periods have been plotted separately for the correlation. As expected, the plot shows that acetylene and CO are well correlated. However, no significant difference can be seen in the correlations for the different meteorological situations. Calculation of a linear regression to the data gives an intercept at [CO] = 78 ppb, which is very similar to the value of 71.8 ppb which was found for the North Atlantic during a ship cruise in 1988 (Koppmann *et al.*, 1992).

Sampling time, UT	Ethane	Ethene	Ethane + Ethene	Ethyne	Propane	Propene	i-Butane	1-Butene	n-Butane	n-Pentane	Isoprene	n-Hexane	Benzene	n-Heptane	Toluene
Aug. 5, 1994 14:05											0.47		0.14		
Aug. 5, 1994 16:05				0.27	0.25	0.08		0.09	0.18	0.39	0.56	0.17	0.28		0.12
Aug. 6, 1994 06:55				0.67	0.46	0.09		0.06	0.62	0.25	0.11	1.05	0.63	0.02	0.30
Aug. 6, 1994 10:01				0.52	0.57	0.05		0.06	0.60		0.11	2.15	0.36	0.02	0.01
Aug. 6, 1994 13:19	0.51	0.31	0.81	0.16	0.16	0.04	0.21	0.04	0.10	0.14	0.74	0.16	0.12	0.02	0.05
Aug. 6, 1994 16:29	0.41	0.34	0.76	0.11	0.18	0.02	0.21	0.04	0.11	0.44		0.30	0.10	0.02	0.01
Aug. 7, 1994 02:04			1.36	0.16	0.34	0.07	0.10	0.05	0.16	0.26	0.06	0.18	0.11	0.03	0.07
Aug. 7, 1994 05:14			1.20	0.21	0.50	0.08	0.13	0.05	0.22	0.32	0.04	0.19	0.13		0.08
Aug. 7, 1994 08:25						0.01	0.15	0.12	0.15		0.08	0.49	0.02	0.12	
Aug. 7, 1994 12:08				0.14	0.23	0.02	0.06	0.05	0.11	0.08	0.07	0.04	0.15	0.01	0.05
Aug. 7, 1994 15:03			0.90	0.15	0.16	0.02	0.02	0.02	0.07	0.09	0.06	0.05	0.08	0.01	
Aug. 8, 1994 03:59			1.49	0.15	0.48	0.09	0.11	0.05	0.18	0.11	0.01	0.08	0.13	0.01	0.11
Aug. 8, 1994 06:50			1.14	0.18	0.39	0.06	0.07	0.07	0.12			0.09	0.13	0.01	
Aug. 8, 1994 21:24				0.22	0.20	0.07	0.08	0.03	0.12	0.07	0.02	0.14	0.10	0.01	0.05
Aug. 9, 1994 00:34	1.08	0.19	1.20	0.37	0.28	0.26	0.15	0.06		0.15	0.02	0.04	0.26	0.02	0.12
Aug. 9, 1994 16:51			1.03	0.18	0.16	0.12			0.01	0.01	0.02	0.19		0.07	
Aug. 10, 1994 07:29				0.34	0.31	0.13	0.11	0.14	0.20	0.10		0.15	1.38		1.55
Aug. 10, 1994 08:45			1.01	0.26	0.25	0.05				0.03	0.06	0.12	0.01	0.03	
Aug. 10, 1994 11:57			0.95	0.20	0.17	0.03			0.05	0.03	0.03	0.11	0.01		
Aug. 12, 1994 11:30	1.58	0.70	2.28	0.65	0.92	0.16		0.04	0.44	0.31	0.04	0.14	0.23	0.05	0.30
Aug. 12, 1994 12:55	1.60	0.56	2.16	0.72	0.96	0.11			0.49	0.30	0.05	0.12	0.29	0.07	0.21
Aug. 13, 1994 14:40	0.87	0.14	1.01	0.14	0.23	0.09			0.04	0.06	0.02	0.04	0.04	0.02	0.01
Aug. 13, 1994 17:15	0.82	0.15	0.97	0.13	0.20	0.07			0.03	0.03	0.07	0.03	0.04	0.02	0.02
Aug. 14, 1994 13:14	0.62	0.33	0.94	0.10	0.12	0.03	0.09	0.04	0.07	0.02	0.00		0.08	0.01	
Aug. 14, 1994 16:25			0.99	0.15	0.13	0.04	0.03		0.03	0.04	0.02	0.00		0.04	
Aug. 15, 1994 17:53			0.94	0.11	0.14	0.03	0.04		0.10		0.00				
Aug. 15, 1994 21:03			0.94	0.14	0.11	0.03	0.02	0.01	0.00		0.00	0.01	0.01		0.01
Aug. 16, 1994 00:14			0.97	0.13	0.16	0.03	0.02		0.00	0.02	0.00	0.02	0.02		
Aug. 16, 1994 03:23			1.10	0.15	0.28	0.03	0.07	0.02	0.08	0.03	0.00		0.03		
Aug. 16, 1994 06:34			1.11	0.17	0.24	0.05	0.02	0.03	0.07	0.02	0.00		0.03	0.01	0.01
Aug. 16, 1994 10:11	0.61	0.28	0.88	0.11	0.18	0.02	0.02	0.01	0.03	0.02	0.00	0.01	0.06	0.01	0.10
Aug. 16, 1994 13:22			1.19	0.19	0.25	0.02	0.10	0.01	0.19	0.07	0.00	0.05	0.11	0.01	0.06
Aug. 16, 1994 16:33			1.28	0.22	0.29	0.03	0.08	0.01	0.15	0.05	0.00	0.04	0.04	0.01	0.02
Aug. 16, 1994 19:44			1.38	0.29	0.33	0.05	0.07	0.04	0.15	0.07	0.00	0.05	0.12	0.01	0.22

Table II. *Continued.* Due to the technical problems discussed above there are only data for light NMHC available for the period between August 16 and August 24.

Sampling time, UT	Ethane	Ethene	Ethane + Ethene	Ethyne	Propane	Propene
Aug. 16, 1994 22:54			1.42	0.33	0.39	0.07
Aug. 17, 1994 02:05			1.31	0.24	0.40	0.06
Aug. 17, 1994 05:16			1.36	0.35	0.43	0.07
Aug. 17, 1994 08:31	0.77	0.52	1.30	0.31	0.36	0.05
Aug. 17, 1994 11:38			1.30	0.49	0.32	0.03
Aug. 17, 1994 14:51			1.61	0.38	0.46	0.05
Aug. 20, 1994 18:36			0.75	0.32	0.13	0.07
Aug. 20, 1994 21:46			1.26	0.40	0.30	0.12
Aug. 21, 1994 00:55			1.70	0.46	0.47	0.12
Aug. 21, 1994 04:04			2.09	0.50	0.63	0.17
Aug. 21, 1994 08:07			2.54	0.61	0.96	0.25
Aug. 21, 1994 12:49			1.42	0.28	0.27	0.02
Aug. 21, 1994 14:33			1.37	0.32	0.29	0.03
Aug. 22, 1994 08:26			1.50	0.34	0.31	0.03
Aug. 22, 1994 11:36			1.17	0.34	0.23	0.01
Aug. 22, 1994 14:45			1.19	0.36	0.24	0.02
Aug. 22, 1994 17:55			1.26	0.28	0.23	0.06
Aug. 22, 1994 21:04	1.50	0.33	1.93	0.39	1.78	0.09
Aug. 23, 1994 00:13			1.55	0.34	0.40	0.07
Aug. 23, 1994 03:23			1.47	0.40	0.45	0.06
Aug. 23, 1994 06:32			1.26	0.30	0.31	0.04
Aug. 23, 1994 09:42			1.32	0.87	0.32	0.04
Aug. 23, 1994 12:55			1.12	0.37	0.63	0.02
Aug. 23, 1994 16:01	0.43	0.74	1.18	0.35	0.23	0.02
Aug. 23, 1994 19:11			1.15	0.36	0.21	0.05
Aug. 23, 1994 22:20			1.10	0.29	0.21	0.04
Aug. 24, 1994 01:30			1.18	0.30	0.22	0.05
Aug. 24, 1994 04:39			1.42	0.44	0.32	0.08
Aug. 24, 1994 07:55			2.17	0.74	0.73	0.27

This agrees with the assumption that during the advection of polar air masses the CO mixing ratios were typical for North Atlantic air masses.

Figure 5 shows a plot of the propane versus the CO mixing ratios with different result. The larger scatter is due to the variation in the slopes and especially in the CO axis intercept representing the different episodes indicated in the plot. Due to the limited alkane measurements the number of data are not sufficient to plot a meaningful frequency distribution as for CO. However, because alkanes are correlated with CO as discussed below one can expect a similar behaviour for the alkanes during the campaign. Table IV gives the correlation coefficients for CO, alkanes, alkenes, acetylene, aromatics and isoprene.

Table III. Synopsis of the CO and NMHC data sets. The mixing ratios for CO are given in ppb, the mixing ratios for all other compounds are given in ppt.

	No. of measure-ments	Mean	Standard deviation	Median	5%	16%	84%	95%[a]
CO	5429	122	25	120	87	96	145	168
Ethane + ethene	57	1320	399	1256	813	953	1614	2167
Propane	63	364	269	294	130	170	483	925
i-Butane	24	78	55	70	14	18	112	205
n-Butane	31	168	160	121	5[b]	42	223	491
n-Pentane	32	121	120	74	15	23	263	322
n-Hexane	30	195	415	69	14	27	184	564
n-Heptane	25	18	14	14	6	6	22	52
Acetylene	63	318	179	299	110	140	458	717
Propene	63	72	61	50	17	25	115	246
1-Butene	26	48	35	42	7	14	64	138
Isoprene	29	70	166	24	5[b]	5[b]	66	564
Benzene	33	148	137	116	19	36	260	356
Toluene	27	95	85	71	14	90	206	297

[a] Percentiles.
[b] Lower limit of detection.

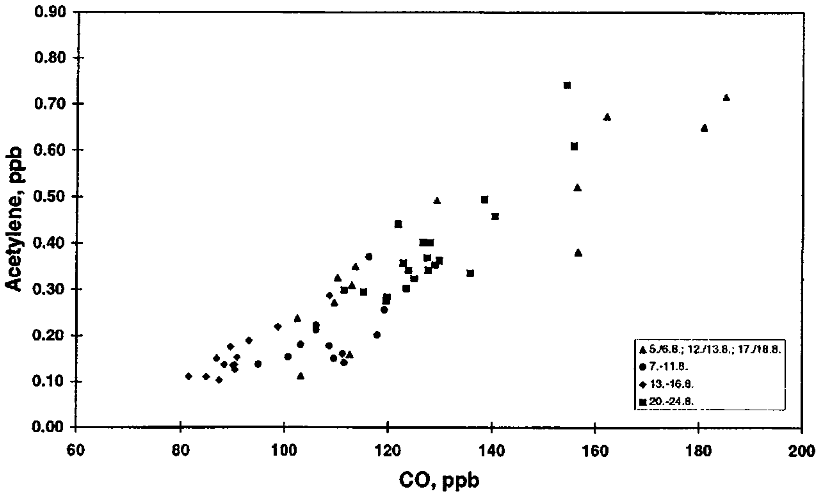

Figure 4. Plot of acetylene versus CO mixing ratios for the different episodes (see text).

	CO	Ethane + ethene	Propane	n-Butane	n-Pentane	n-Hexane	n-Heptane	Acetylene	Propene	1-Butene	Benzene	Toluene
Ethane + ethene	0.80											
Propane	0.78	0.89										
n-Butane	0.70	0.65	0.65									
n-Pentane	0.40	0.26	0.41	0.54								
n-Hexane	0.14	0.10	0.29	0.34	0.98							
n-Heptane	0.61	0.62	0.69	0.57	0.96	0.20						
Acetylene	0.91	0.74	0.68	0.65	0.25	0.30	0.49					
Propene	0.45	0.71	0.61	0.50	0.13	0.12	0.50	0.50				
1-Butene	0.15	0.21	0.25	0.20	0.29	0.28	0.26	0.24	0.62			
Benzene	0.59	0.49	0.21	0.41	0.93	0.19	0.37	0.37	0.39	0.77		
Toluene	0.60	0.74	0.20	0.22	0.83	0.19	0.70	0.28	0.36	0.58	0.91	
Isoprene	0.02	0.24	0.17	0.15	0.03	0.58	0.09	0.11	0.23	0.22	0.31	0.06

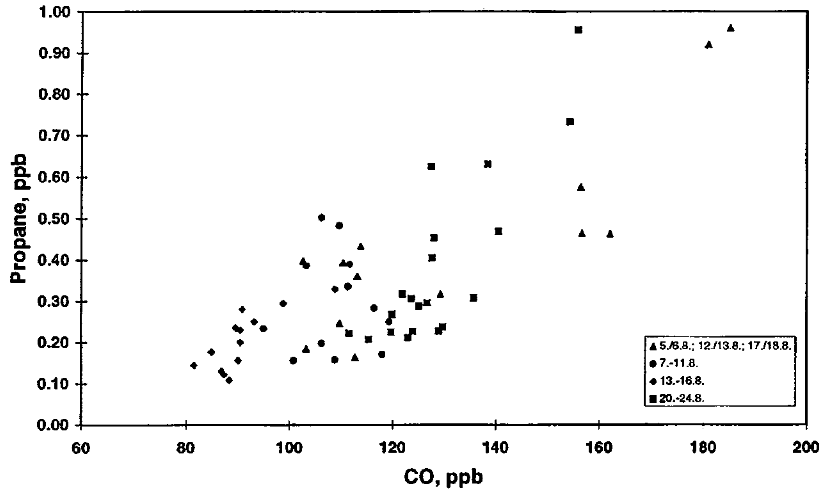

Figure 5. Plot of propane versus CO mixing ratios for the different episodes (see text).

The individual NMHC are rather well correlated within their homologs. The correlation between alkanes and alkenes is weak due to their different sources, source distributions, and atmospheric lifetimes. As expected, isoprene as a biogenic compound shows no significant correlation with any of the other anthropogenic components, or with CO. Except for propene, for all other NMHC no diurnal variation was observed. Including all measurements, propene showed a diurnal variation between average mixing ratios of 30 ppt during local noon and about 60 ppt during local midnight.

One of the main purposes of the POPCORN campaign was the investigation of the influence of locally emitted volatile organic compounds of biogenic origin (see Plass-Dülmer *et al.*, 1998). Besides light nonmethane hydrocarbons special interest was placed on isoprene and monoterpenes. Measurements of the latter were done with a GC-MS system and are reported by Wedel *et al.* (1998). With our GC we were able to measure isoprene as one of the predominantly biogenically emitted compounds. Except two individual measurements in the first two days of the campaign, when mixing ratios of 560 and 740 ppt were observed, isoprene levels were extremely low and never exceeded 110 ppt during the first two weeks of the campaign. The low mixing ratios of isoprene were somewhat suprising because the temperatures, especially during the first half of the campaign, were very high with maximum values around 35°C (Brauers *et al.*, 1998). This finding indicates that the contribution of local biogenic emissions to the atmospheric concentration of organic trace compounds must have been very low. This is also confirmed by measurements of the emission rates of light NMHC from the maize plants (Parusel, 1996). However, despite the rather low mixing ratios of isoprene, it's contribution to the turnover with OH radicals is larger than for the C_2–C_5 alkanes and the C_2–C_4 alkenes (Wedel *et al.*, 1998).

3.3. CHARACTERIZATION OF THE AIR MASSES

In remote areas the atmospheric trace gas mixing ratios are related to their sources, dilution processes and the photochemical history. Thus, for the interpretation the meteorological conditions and the knowledge of the origin of the air masses is necessary. The local meteorological parameters, which have a direct influence on the fate of the investigated air mass within the planetary boundary layer, have been measured during the whole campaign and are reported in detail by Brauers *et al.* (1998). To get information about the origin of the air masses two day isentropic backward trajectories were calculated at potential temperature levels of 300, 304, 308, 312, 316, and 320 K based on a dynamical method described by Danielsen (1961) and Bleck (1967). For the calculation of the backward trajectories ECMWF analysis data of wind, temperature and geopotential height four times per day (0000, 0600, 1200, 1800 UTC) were used. Within the planetary boundary layer non negligible processes such as turbulence and friction prohibit the calculation on isentropic levels. Therefore, trajectories below 850 hPa were omitted. Thus, back trajectories can give only a hint to the origin of the air sampled during the campaign and can only give a rough indication of local and regional pollution. For this purpose the local wind data are more suitable. The backtrajectories indicate that except for a few episodes air masses were advected from westerly directions during most of the POPCORN campaign. Thus the air passed over the North-Western to South-Western parts of the European continent and was at least partly under the influence of continental emissions from Great Britain or the Western European countries. For an analysis of the fate of the air masses on their way to the measuring site at Pennewitt the campaign (August 1994) period is divided into different episodes according to the individual large scale meteorological situations. These cases are then compared with the CO data and the pattern of NMHC in order to characterize the air masses observed at the site.

During the period of 3–8 August, air masses influenced predominantly by continental emissions were encountered at the measuring site (Figure 6). Between 3 and 5 August air masses were transported at the beginning from southwest and subsequently from northwest passing over Northern France, the Benelux countries, Great Britain, and Western Germany. The air masses were predominantly of marine origin with contributions of continental sources only during the previous 12 hours. The influence of anthropogenic emissions on the trace gas composition can be seen in CO mixing ratios varying between 100 and 150 ppb, depending on the trajectory. NMHC mixing ratios remained low during that period, ethane never exceeded 1 ppb. Following a frontal passage with rain and variable wind directions

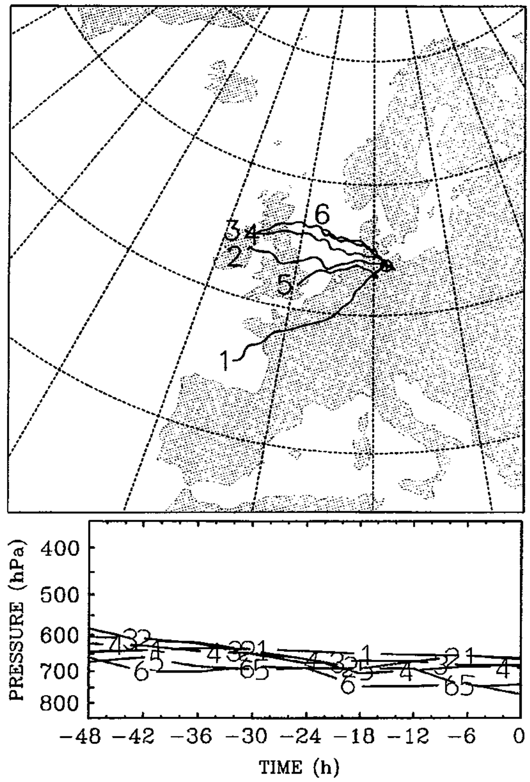

Figure 6. Two day isentropic backtrajectories calculated at 6 hour intervals for every 12 hours on the potential temperature level of 304 K between 3 August, 0000 UTC (trajectory # 1) and 5 August, 1200 UTC (trajectory # 6). The lower plot shows the altitude change of the air mass during the two days for the individual trajectories.

on 5 August, the wind changed back to southwesterly directions between 6 and 8 August (Figure 7).

The air masses reaching the measuring site were then transported over France and the western part of Germany. During that time CO mixing ratios increased to values of 180 ppb. The mixing ratios of light NMHC and some aromatic compounds showed no significant changes but a slightly greater variability. Between 9 and 12 August, air masses above the 310 K level had their origin over the North Sea, Great Britain, Ireland and the Eastern Atlantic two days before reaching the measuring site. Below this level air masses were transported from the southern part of Great Britain and mainly from the northern parts of Germany to the site (Figure 8).

During this period wind speeds were low at these lower levels. Although these air masses can be clearly described as continental air the CO mixing ratios remained fairly low at levels around 110 ppb, while NMHC mixing ratios increased. Four

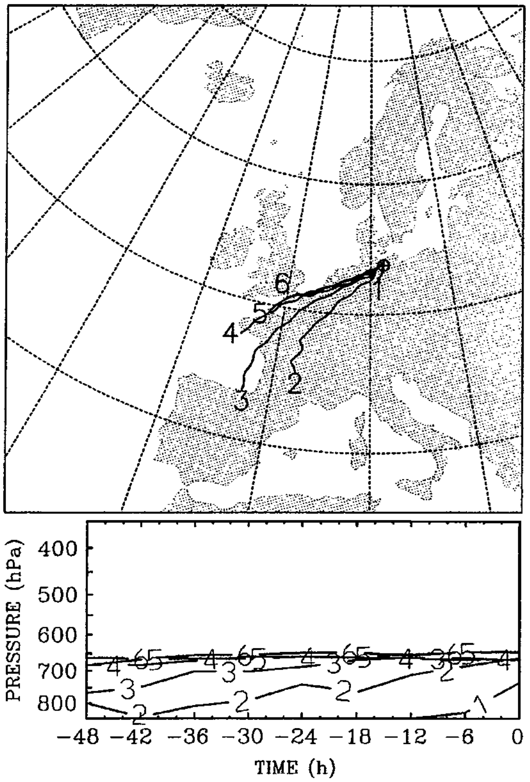

Figure 7. Two day isentropic backtrajectories calculated at 6 hour intervals for every 12 hours on the potential temperature level of 308 K between 6 August, 0000 UTC (trajectory # 1) and 8 August, 1200 UTC (trajectory # 6). The lower plot shows the altitude change of the air mass during the two days for the individual trajectories.

day backward trajectories show that lower level air masses arriving at the site on 12 August, started over Great Britain, passed over southeast Germany and were then transported to the northwest leading again to increased CO mixing ratios with peak values of more than 150 ppb. On this day NMHC mixing ratios were still rather low, but increased significantly compared to the days before. Figure 9 shows the situation between 13–16 August.

On 13 August 1994, around 12 UT a distinct cold front passed over the measuring site. The warming subpolar air lead to heavy rain in North-Eastern Germany on that day. The back trajectories show a large variability during this and the next day. Wind speeds were rather low coinciding with high CO mixing ratios of up to 200 ppb. On 14 August 1994, winds changed to north and north-west transporting polar, very clean air masses to the site. While the origin of the air masses arriving

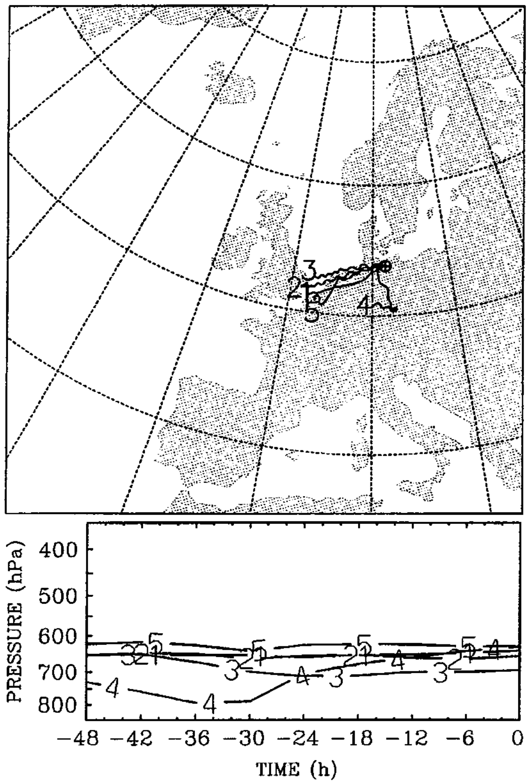

Figure 8. Two day isentropic backtrajectories calculated at 6 hour intervals for every 24 hours on the potential temperature level of 308 K between 9 August, 0000 UTC (trajectory # 1) and 13 August, 0000 UTC (trajectory # 5). The lower plot shows the altitude change of the air mass during the two days for the individual trajectories.

at the site on 15 August 1994, is over Scandinavia, on 16 and 17 August 1994, air masses were coming from the North-West and West Atlantic, respectively. During this whole period CO mixing ratios were extremely low, sometimes around 85 ppb. The NHMC mixing ratios decreased by more than a factor of two and remained at these low levels until 17 August. During 17 August CO and NMHC mixing ratios increased rapidly by almost a factor of two. On that day a cold front passed over North-Eastern Germany. Following the frontal passage air masses were transported from France over southwest Germany to the measuring site leading to the observed increase in CO and NMHC mixing ratios on 18 August (Figure 10).

On the following three days wind direction turned counterclockwise from southwest to northeast and finally to northwest. The air was transported from the North-East Atlantic leading to a decrease of the CO and NMHC mixing ratios. The period

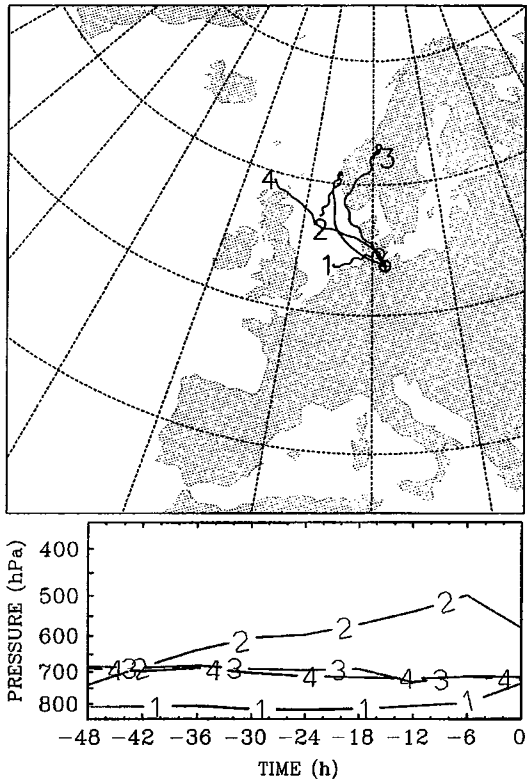

Figure 9. Two day isentropic backtrajectories on the potential temperature level of 30 K between 13 August (trajectory # 1) and 16 August (trajectory # 4). All trajectories are calculated for 1200 UTC on the individual days. The lower plot shows the altitude change of the air mass during the two days for the individual trajectories.

of 22–24 August is characterised by rather small pressure gradients over Europe. Air masses were transported from the East Atlantic (Figure 11).

CO mixing ratios varied between 120 and 150 ppb, which can be explained by urban and industrial emissions into the air masses passing over Great Britain, the North Sea and the Northern part of Germany. On 24 August the situation changed again. The air was transported from France, southern Germany and Great Britain before arriving at the measuring site leading again to increased CO and NMHC mixing ratios.

4. Summary

The nonmethane hydrocarbon and carbon monoxide mixing ratios measured during the POPCORN campaign were relatively low and can only partly be characterized

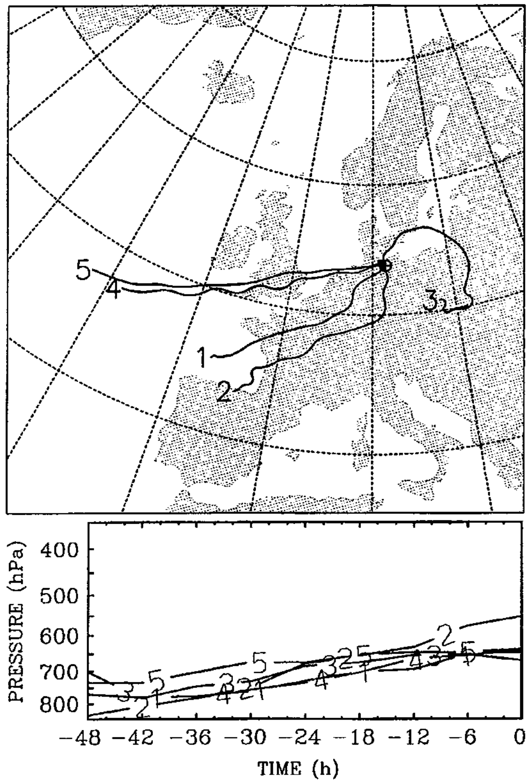

Figure 10. Two day isentropic backtrajectories calculated at 6 hour intervals for every 24 hours on the potential temperature level of 304 K between 17 August (trajectory # 1) and 21 August (trajectory # 5). All trajectories are calculated for 1200 UTC on the individual days. The lower plot shows the altitude change of the air mass during the two days for the individual trajectories.

as typical for a rural area in north-eastern Germany. CO mixing ratios showed a log-normal distribution with three modes which can be assigned to different large scale meteorological situations. One mode corresponding to a mean CO mixing ratio of 88 ppb consisted of data obtained during a period influenced by polar air masses. The second mode with a mean CO mixing ratio of 167 ppb could be assigned to three periods of high CO mixing ratios after frontal passages. The third mode included all other measurements characteristic for a remote rural area. Except ethane, NMHC mixing ratios never exceeded 1 ppb. The similar behaviour of CO and NMHC indicate that these trace gases originated from similar, predominantly anthropogenic sources and were in most cases advected by air masses of marine origin, which passed over Great Britain, the North-Western or South-Western European continent. The low mixing ratios indicate that the air

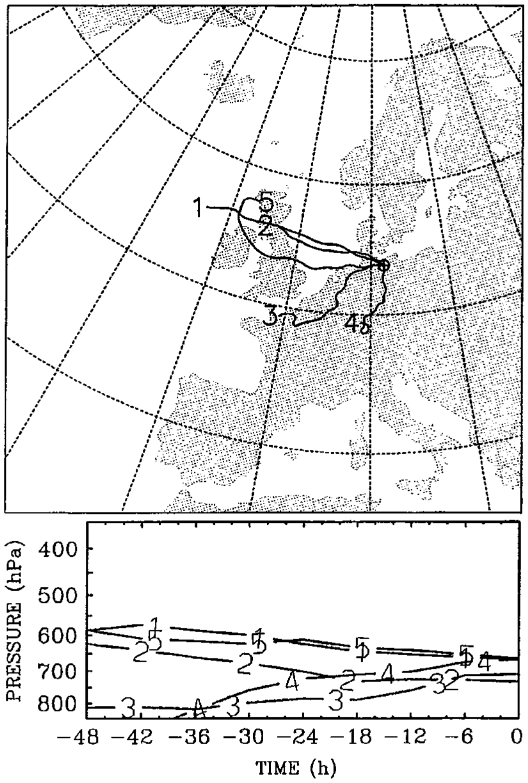

Figure 11. Two day isentropic backtrajectories calculated at 6 hour intervals for every 24 hours on the potential temperature level of 304 K between 22 August (trajectory # 1) and 26 August (trajectory # 5). All trajectories are calculated for 1200 UTC on the individual days. The lower plot shows the altitude change of the air mass during the two days for the individual trajectories.

masses were diluted with maritime background air or were photochemically aged. During the period between 14 and 16 August polar air masses were advected. During that period both CO and NMHC mixing ratios dropped to values which are normally observed over the North Atlantic (Koppmann *et al.*, 1992). The mixing ratios of isoprene, which is emitted by vegetation, were also unexpectedly low during the first half of the campaign although the maximum temperatures were around 35°C. These results indicate that the contribution of local biogenic emissions to the atmospheric concentration of organic trace compounds must have been very low.

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