Ground-Based and Airborne Measurements of Nonmethane Hydrocarbons in BERLIOZ: Analysis and Selected Results

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Abstract. During the Berlin Ozone Experiment BERLIOZ in July–August 1998 quasi-continuous measurements of C_2–C_{12} nonmethane hydrocarbons (NMHCs) were carried out at 10 sites in and around the city of Berlin using on-line gas-chromatographic systems (GCs) with a temporal resolution of 20–120 minutes. Additional airborne NMHC measurements were made using canister sampling on three aircraft and an on-line GC system on a fourth aircraft. The ground based data are analyzed to characterize the different sites and to identify the influence of emissions from Berlin on its surroundings. Benzene mixing ratios at the 4 rural sites were rather low (<0.5 ppbv). Berlin (and the surrounding highway ring) was identified as the main source of anthropogenic NMHCs at Eichstädt and Blossin, whilst other sources were important at the furthermost site Menz. The median toluene/benzene concentration ratio in Berlin was 2.3 ppbv/ppbv, agreeing well with measurements

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in other German cities. As expected, the ratios at the background sites decreased with increasing distance to Berlin and were usually around one or below. On 20 and 21 July, the three northwesterly sites were situated downwind of Berlin and thus were influenced by its emissions. Considering the distance between the sites and the windspeed, the city plume was observed at reasonable time scales, showing decreasing toluene/benzene ratios of 2.3, 1.6 and 1.3 with increasing distance from Berlin. Isoprene was the only biogenic NMHC measured at BERLIOZ. It was the most abundant compound at the background sites on the hotter days, dominating the local NMHC reactivity with averaged contributions to the total OH loss rate of 51% and 70% at Pabstthum and Blossin, respectively. Emission ratios (relative to CO and to the sum of analysed NMHCs) were derived from airborne measurements. The comparison with an emission inventory suggests traffic-related emissions to be the predominating source of the considered hydrocarbon species. Problems were identified with the emission inventory for propane, ethene and pentanes.

Key words: nonmethane hydrocarbons, pollution roses, toluene/benzene ratio, city plume, isoprene, NMHC/CO ratios, emission inventory.

1. Introduction

Nonmethane hydrocarbons (NMHCs) as a subset of volatile organic compounds (VOCs) are, together with oxides of nitrogen, the major precursors of photochemically produced secondary pollutants such as ozone and peroxyacetyl nitrate (PAN) (Atkinson, 2000; Chameides *et al.*, 1992).

Emissions of NMHCs comprise a broad spectrum of compounds, originating from natural (e.g. Kesselmeier and Staudt, 1999) and anthropogenic sources such as road transport (exhaust gases and gasoline evaporation) and solvent use (mainly in connection with paints, degreasing agents, dry cleaning and varnishes) (Field *et al.*, 1992; Friedrich and Obermeier, 1999). Between 1990 and 1996 German VOC emissions decreased significantly from 3178 kt yr^{-1} to 1868 kt yr^{-1} due to emission control and the shutdown of many industrial plants in eastern Germany after the German Unification (Umweltbundesamt, 1998). According to the CORINAIR emission inventory (Friedrich and Obermeier, 1999), however, Germany is still the largest VOC emitter in Europe, followed by the United Kingdom, France and Italy.

Nonmethane hydrocarbons have been measured in many field experiments all around the world. Measurements in Europe are predominantly focussed on the central or northwestern regions and comprise either solely the light hydrocarbons C_2–C_5 (e.g. Klemp *et al.*, 1997; Lindskog and Moldanová, 1994) or a greater hydrocarbon spectrum (Derwent *et al.*, 2000; Fenneteaux *et al.*, 1999; Koppmann *et al.*, 1998; Lewis *et al.*, 1999; Rappenglück and Fabian, 1999; Thijsse *et al.*, 1999).

The objective of the Berlin Ozone Experiment (BERLIOZ) was to obtain a as complete as possible characterization of the Berlin city plume and to improve our understanding of the chemical and physical processes involved in the formation of photooxidants such as ozone, peroxides and PAN (Becker *et al.*, 2002).

This paper presents results of measurements of C_2–C_{12} NMHCs that were made during the BERLIOZ field experiment in July–August 1998 with different *in situ* instruments at 10 surface sites located in and around the city of Berlin, Germany.

The ground based measurements are compared with each other in order to derive the influence of the emissions from Berlin on the surrounding environment and to identify possible local influences at different sites. The relevance of biogenic VOC emissions, i.e., isoprene, to oxidant formation is also investigated for the different sites. In the second part of the paper, data obtained from airborne measurements are utilized to estimate the NMHC emissions of Berlin relative to those of CO and to the sum of analysed NMHCs. The results are compared with an emission inventory.

2. Experimental

2.1. SITE DESCRIPTION

Figure 1 shows a map of the area where the BERLIOZ field experiment was conducted. The city of Berlin (3.4 mio. inhabitants) lies in the northeast of Germany. It is surrounded by a sparsely populated agricultural and forested area. The entire federal state of Brandenburg has a very small population density of only 88 inhabitants km^{-2}, compared to the 3882 inhabitants km^{-2} of Berlin. As the strong anthropogenic emissions of Berlin should produce a well-defined plume on a relatively low background, this makes the region an interesting place for studying the impact of human activities on tropospheric chemistry (Becker *et al.*, 2002).

The terrain in Brandenburg is almost flat and consequently wind patterns are supposed to reflect the general weather conditions without pronounced influence of local orography, such as valley wind systems or land-sea breezes. However, during hot summer episodes thermally induced small scale flows between the heated urban area and the cooler surroundings within the boundary layer may not be entirely ruled out. In addition, enhanced horizontal dilution processes that are likely to occur over flat areas complicate the interpretation of the data set.

The surface stations were aligned along an axis extending from Blossin in the southeast to Menz in the northwest with the city of Berlin in the center. NMHC measurements were carried out at all sites marked by wind roses in Figure 1. For the downtown stations only one wind rose is shown which is representative for the entire city.

2.2. ANALYTICAL EQUIPMENT

An overview of the various gas chromatographic systems (GCs) used for NMHC measurements is given in Table I. As discussed in detail by Volz-Thomas *et al.* (2002), all instruments were quality assured by interlaboratory tests with synthetic gas standards and (except the three Chrompack GCs at Berlin and the airmoVOC GC at Neukölln) by an ambient air intercomparison, to ensure the homogeneity of the NMHC dataset and to prevent the occurrence of several sub-sets. The ambient air intercomparison took place at Schönhagen (Figure 1) just before the main campaign. The HP 5890 (Hewlett-Packard, Palo Alto, CA, U.S.A.) instrument of the FZJ group served as the reference method to which the other GCs were compared.
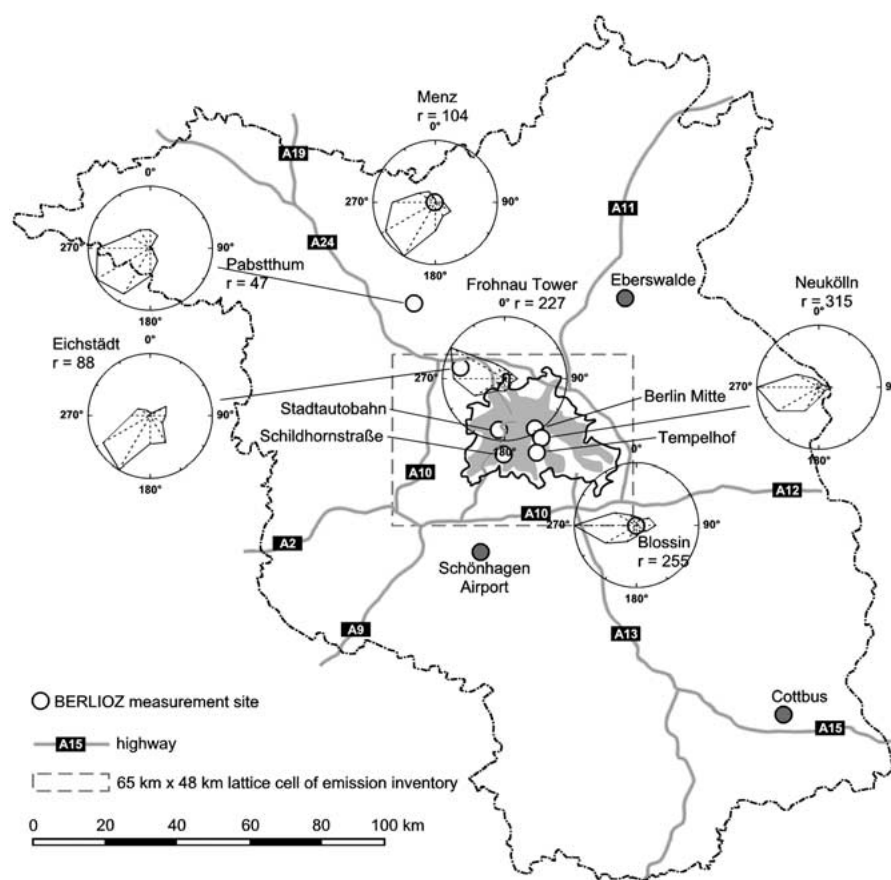
Figure 1. Map of the federal state of Brandenburg with the city of Berlin, the major highways and the surface sites of BERLIOZ. The roses (note the varying radius *r*) show the number of NMHC samples in each wind sector.

The reference GC (Schmitz *et al.*, 2000) has an absolute random error (bias) of ± 7 pptv and a random relative (concentration dependant) error of $\pm 7\%$ (Volz-Thomas *et al.*, 2002). The limit of detection (LOD) is around 5 pptv for the most compounds (cf. Table I).

In addition, canister samples were collected during the main campaign at the surface sites and compared to the *in situ* GCs. The canister samples were analysed by IFU with a dual column GC (Varian 3600 CX, Varian, Darmstadt, Germany), for which an accuracy of 1% for mixing ratios >1 ppbv, 3% for mixing ratios >100 pptv, and 20% for mixing ratios >30 pptv is reported (Habram *et al.*, 1998). The LOD is 20 pptv for the most hydrocarbons (cf. Table I).

The two reference methods compare with a relative error of $\pm 10\%$ and a somewhat larger absolute error of 60 pptv, which may be addressed to problems arising

Table I. Survey of gas chromatographic systems used during the BERLIOZ campaign

	Blossin –1 [a] ZUF [f]	Eichstädt +1 [a] TU-M1 [g]	Pabstthum +2 [a] FZJ [h]	Pabstthum +2 [a] FZJ [h]	Menz +3b [a] BUGH [i]
Gas chromatograph					
Type	airmoVOC HC-2010	Siemens P-Sichromat 2/8	Hewlett Packard HP 5890	airmoVOC HC-1010	airmoVOC HC-2010
Location	*In situ*	*In situ*	*In situ*	*In situ*	*In situ*
Column(s)	BGB-2.5	CP-Wax-CB CP-Sil-CB	DB 1	DB 5ms	BGB-2.5
Preconcentration/cooling	Ads. tubes/CO_2	Ads. tubes/EtOH	Cryogenic/N_2	Ads. tubes/–	Ads. tubes/CO_2
Time resolution (min.)	30	30	80	20	30
Sampling time (min.)	21	20	20	19	18
Performance and data quality					
C-range	C2–C10	C4–C12	C2–C10	C5–C10	C2–C10
Number of analysed compounds	59	46	63	50	41
Lit. reference	m	n	o	p	m
Accuracy	± 16% + 16 pptv	± 20%	± 7% + 7 pptv	± 14% + 10 pptv	± 15% + 26 pptv
Precision	8%	10–15%	3–7%	5%	8%
LOD (pptv)	10–35	10–80	5	2–8	14–26
Number of quality assured compounds [d]	19	5	63	28	21
Samples	1066	391	247	308	508

	Berlin 0 [a] TU-M0 [g]	Berlin [b] 0 [a] Senat [j]	Berlin [c] 0 [a] Senat [j]	Canister aircraft IFU [k]	Eco-Dimona aircraft Metair [l]
Gas chromatograph					
Type	Siemens P-Sichromat 2/8	Chrompack CP 7001	airmoVOC HC-1010	Varian 3600 CX	airmoVOC HC-1010
Location	*In situ*	*In situ*	*In situ*	Laboratory	*In situ*
Column(s)	CP-Wax-CB CP-Sil-CB	CP-Wax-S2-CB	DB 624	DB 1	BGB-2.5
Preconcentration/cooling	Ads. tubes/EtOH	Ads. tubes/–	Ads. tubes/–	SS-aircans electropolished	Ads. tubes/–
Time resolution (min.)	30	30	30	–	10
Sampling time (min.)	21	20	29	0.5	9
Performance and data quality					
Number of analysed compounds	22	2	2	50	40
Lit. reference	n	–	–	q	–
Accuracy	± 20%	± 5%	± 5%	± 20%	± 10% + 10 pptv
Precision	10–15%	5%	5%	1–4%	5%
LOD (pptv)	10–80	7	7	20	2–8
Number of quality assured compounds [d]	10	e	2	50	32
Samples	429	3615	4503	134	155

[a] Short cut for BERLIOZ ground stations. At southeasterly flows the negative numbers correspond to the sites upwind of Berlin (lee), the positive numbers indicate downwind station (luff). The greater the number, the larger the distance to the city.
[b] Three sites: Stadtautohobahn/Lerschpfad, Berlin Mitte, Schildhornstraße.
Four sites: Neukölln, Tempelhof, Frohnau Tower Ground, Frohnau Tower Top.
[d] Identity of quality assured compounds: cf. Volz-Thomas *et al.*, 2002.
[e] Instrument did not participate at the field intercomparison.
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[g] Lehrstuhl für Bioklimatologie und Immissionsforschung, TU München.
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[i] Physikalische Chemie, Bergische Universität Gesamthochschule Wuppertal.
[j] Senatsverwaltung für Stadtentwicklung, Umweltschutz und Technologie, Berlin.
[k] Fraunhofer Institut für Atmosphärische Umweltforschung, Garmisch-Partenkirchen.
[l] MetAir AG, Illnau, Switzerland.
[m] Winkler *et al.*, 2001.
[n] Rappenglück *et al.*, 1999; Rappenglück and Fabian, 1999.
[o] Schmitz *et al.*, 2000.
[p] Konrad and Volz-Thomas, 2000.
[q] Habram *et al.*, 1998.

from the canisters and/or short term fluctuations in the ambient air (Volz-Thomas *et al.*, 2002).

The accuracy limits of the NMHC measurements for mixing ratios above 100 pptv were set individually for alkanes, alkenes, aromatic compounds and alkynes to 10%, 20%, 10% and 15%, respectively. At lower mixing ratios, the data quality objectives allowed a relaxed accuracy limit of 50% at 50–100 pptv and of 100% below 50 pptv for all compounds. The data quality was checked for every hydrocarbon individually and the results are given in Volz-Thomas *et al.* (2002). For some instruments further information about the data quality is available. The reference to literature, the stated accuracy, precision (repeatability) and LOD is included in Table I, if available.

The number of quality assured substances varies remarkably amongst the different sites and instruments (see Table I). This strongly hampers evaluation of the NMHC data set, since the overlap of quality assured substances for the respective sites is very small. Thus, despite the large NMHC spectrum analysed, we restrict our evaluation mainly to benzene and toluene. In some cases, data of species are presented, which did not pass quality assurance in Schönhagen. The airmoVOC HC-2010 GCs showed considerable blanks after transportation and quantitative analysis of benzene, toluene and the methylheptanes was not possible. However, at least the canister crosschecks conducted at the respective sites during the campaign showed good agreement between *in-situ* method and canisters (Volz-Thomas *et al.*, 2002), and we thus believe that the measurements of benzene and toluene are accurate as stated in Table I. The three Chrompack GCs and the airmoVOC HC-1010 at Neukölln are part of the quality assurance (QA) procedures of the monitoring network routinely operated by the Senat. Their data quality is thus comparable to the quality assured airmoVOC HC-1010 instruments of the Senat.

During 6 days (20 and 21 July and 3, 5, 6, and 8 August) whole air samples were collected aboard of three aircraft. Electropolished stainless steel canisters were pressurized to about 3 bar using metal bellow pumps and analysed within 3 days by two laboratories. The results from samples collected in July which were analysed by BTU had to be discarded as the laboratory did not meet the data quality objectives. The samples from August were analysed by IFU (see Table I and Habram *et al.* (1998) for details of the technique). These samples were also analysed for CO by GC separation and HgO detection (Seiler *et al.*, 1980), using a reduction gas analyser (Trace Analytical RGA-3, Menlo Park, CA, U.S.A.). The instrument was calibrated by a set of gas mixtures referenced to the NOAA CMDL standard (Novelli *et al.*, 1991). The uncertainty of the CO measurements was less than 5 ppbv.
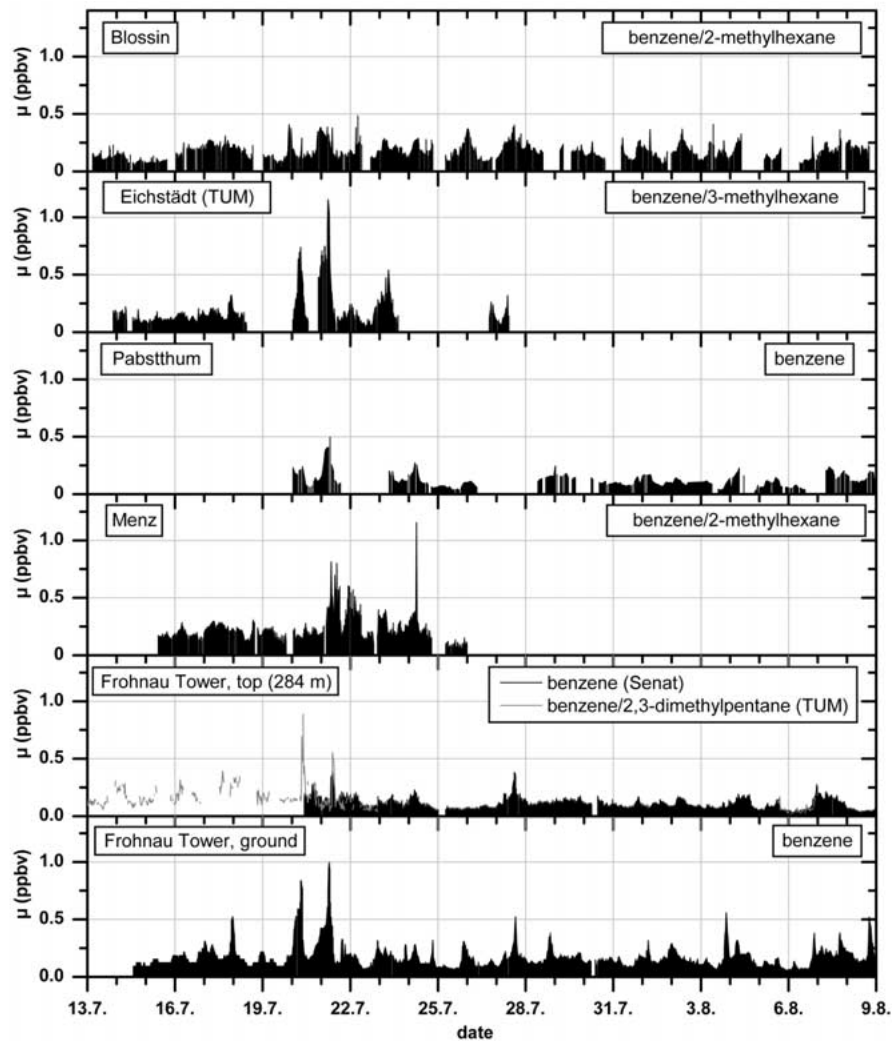
Figure 2a. Time series of benzene mixing ratio μ (ppbv) for the whole campaign (13 July to 8 August 1998) at the background sites and the suburb Frohnau.

3. Results and Discussion

3.1. COMPARISON OF THE MEASUREMENT SITES

In order to compare the 10 measurement sites, the time series of benzene mixing ratios μ (ppbv) are shown in Figure 2 for the entire field campaign from 13 July through 8 August. Since all measurements were made at surface pressure, the volume mixing ratio μ can be taken to be equivalent to concentration. Benzene is primarily emitted by motor vehicles (e.g. Derwent *et al.*, 2000) which makes it a suitable NMHC-tracer of the urban plume.
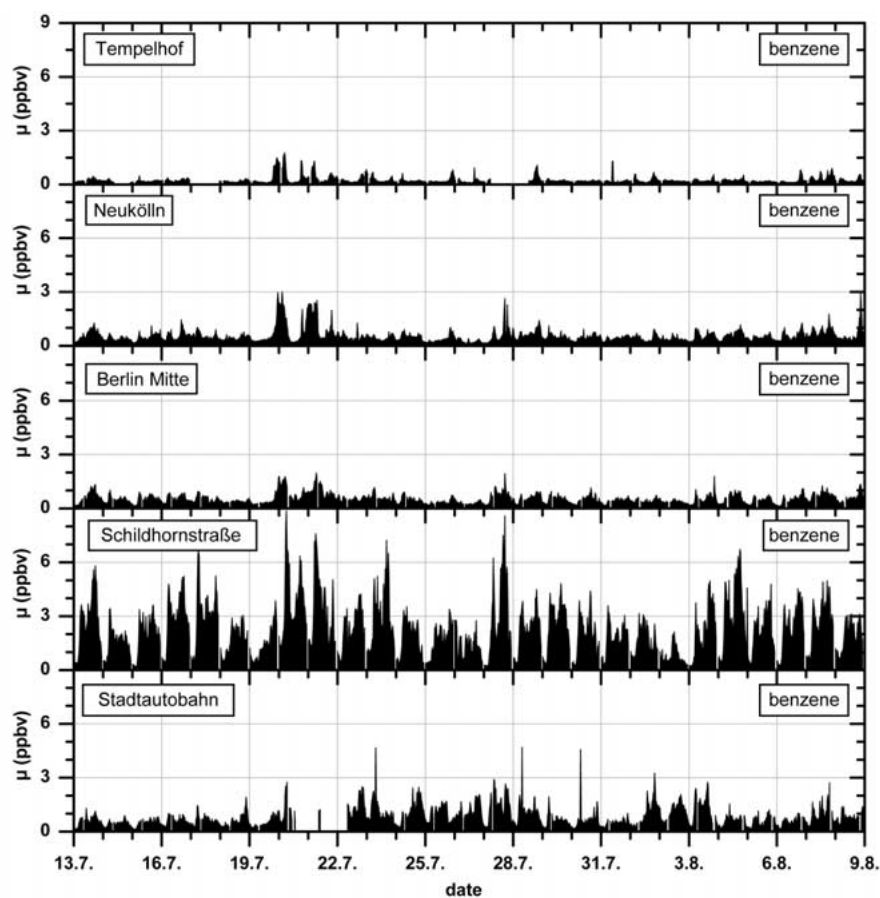
Figure 2b. Time series of benzene mixing ratio μ (ppbv) for the whole campaign (13 July to 8 August 1998) at the Berlin city sites (note the changing scales).

At the sites equipped with airmoVOC HC-2010 GCs (Blossin, Menz) benzene coeluted with 2-methylhexane, at Eichstädt (TUM) with 3-methylhexane and at Frohnau Tower (TUM) with 2,3-dimethylpentane. In order to correct the benzene data, the contribution of the various alkanes to the benzene peak was estimated from the average concentration ratios of alkane/(alkane+benzene) measured at Pabstthum. The gaschromatograph of FZJ separates benzene from 2-methylhexane, 3-methylhexane and 2,3-dimethylpentane without coelution. In addition, the data from the HC-1010 GC aboard the MetAir aircraft were analysed. The results are summarized in Table II.

The aircraft data from Metair were collected on 20 and 21 July and 8 and 9 August, in the planetary boundary layer (altitude <1000 m) above and within a radius of ∼70 km around Berlin. The alkane/(alkane + benzene) ratios are in good agreement with the surface levels. Likewise, Glaser *et al.* (2000) did not find a distinct gradient in the NMHC vertical profiles at Pabstthum within the

Table II. Average relative contribution of coeluting compounds, standard deviation sd and number of available data n

Coeluting alkane	Relative contribution	sd (1σ)	n
Pabstthum			
2,3-dimethylpentane	6%	±6%	63
2-methylhexane	8%	±8%	160
3-methylhexane	10%	±10%	173
Metair aircraft			
2,3-dimethylpentane + 2-methylhexane	14%	±7%	87
3-methylhexane	12%	±5%	96

planetary boundary layer in the afternoon of 20 and 21 July. Hence the ratio of alkane/(alkane + benzene) at Pabstthum is comparable to and representative for the other surface sites and it is possible to derive the necessary correction for coelution with reasonable accuracy (cf. Table II: sd $= \pm 6$–10%) from the ratios shown in Table II.

The largest benzene mixing ratios of up to 9 ppbv were observed at the downtown site Schildhornstraße, whereas the concentrations at the rural sites were usually below 0.5 ppbv. The time series show a diurnal pattern with higher pollution levels during the night and lower concentrations during the day. This is most likely due to the vertical stabilization of the nocturnal boundary layer associated with low wind speeds. Under these conditions, pollutants emitted near ground level even at small rates may accumulate during the night and reach high concentrations in the early morning. At some sites the morning rush hour around 07 universal time (UT) coincides with this accumulation peak (Schildhornstraße, Tempelhof, Neukölln, at the base of the Frohnau Tower and occasionally at Blossin), leading to an enhancement of the peak mixing ratios. The latter stations usually show a second maximum around 15 UT, most likely associated with the evening rush hour. These patterns are most pronounced at sites nearby source areas and diminish with increasing distance to Berlin because of dilution effects and photochemical degradation during transport. Short spikes as observed e.g. in Menz on 24 July suggest the occasional influence of local sources.

3.2. IDENTIFICATION OF LOCAL INFLUENCES

In order to provide insight in the source distribution of anthropogenic hydrocarbons in the BERLIOZ area, the concentration roses of benzene (coelution corrected) are shown in Figure 3. To avoid the influence of photochemical degradation on the

pollution roses, one could consider nighttime values only. However, the source distribution of a species can only be inferred from the concentration roses when there is an unequivocal wind field, which is not often the case at night. Thus, we included both day and nighttime data, but discarded measurements at wind speeds <0.5 m s^{-1}, to investigate the source distribution from a statistical point of view. Due to its relatively low photochemical reactivity (Atkinson, 1994), the influence of photochemistry on the benzene mixing ratios is small on local to regional scales. The stations Schildhornstraße and Stadtautobahn are located directly at major roads and the roses would not allow further interpretation in this context. For comparison, only the concentration rose of Schildhornstraße is shown.

The wind roses plotted in Figure 1 reveal that westerly to southwesterly winds prevailed during the BERLIOZ campaign at all sites, whereas the number of measurements is rather limited for northeasterly flow. This applies especially for the stations Menz, Pabstthum and Eichstädt (TUM) which have larger gaps in the time series. Therefore, measurements for northeasterly flow are not representative at these sites.

Assuming that the origin of an observed air mass is traced by the local wind direction at the measurement site, one would expect the highest mixing ratios towards Berlin, whereas the west sector should be representative for background conditions, since no major anthropogenic NMHC sources exist within a distance of 200 km, with the exception of Magdeburg (251.000 inhabitants), located about 130 km southwest of Berlin. The observations in Figure 3 are in general agreement with this expectation: The largest differences between the median mixing ratios of the Berlin and background sectors are found at Eichstädt (TUM) and Pabstthum with factors of 4 and 2, respectively. As expected from the distance to Berlin, the difference at Pabstthum is smaller than at Eichstädt. At Frohnau Tower the median concentrations at ground level are about 30% higher than at top level (284 m above ground). Both data sets show the same difference of a factor of 1.5 between the two sectors. The distinction is less pronounced than at Eichstädt and Pabstthum, which might be due to the nearby motorway (A111) or the Berlin district Henningsdorf in the west.

Besides the median mixing ratios, the influence of Berlin is clearly evident in the much larger difference between medians and 75-percentiles in the Berlin sector of the measurement sites. At Blossin, the median for the Berlin sector is only slightly enhanced (factor 1.1). The northwesterly peak could also be related to the Spreeau motorway junction (A10/A12) or the small town Friedersdorf (5 km distance, 1700 inhabitants).

In contrast to the other background sites, Menz has no significant enhancement of benzene mixing ratios in the Berlin sector. The benzene rose shows the largest median (0.229 ppbv) at 120°, were several small towns are located, including Zehdenick (26 km), Gransee (14 km) and Dannenwalde (12 km). The site has the largest distance to Berlin (71 km) and, thus is less influenced by the emissions
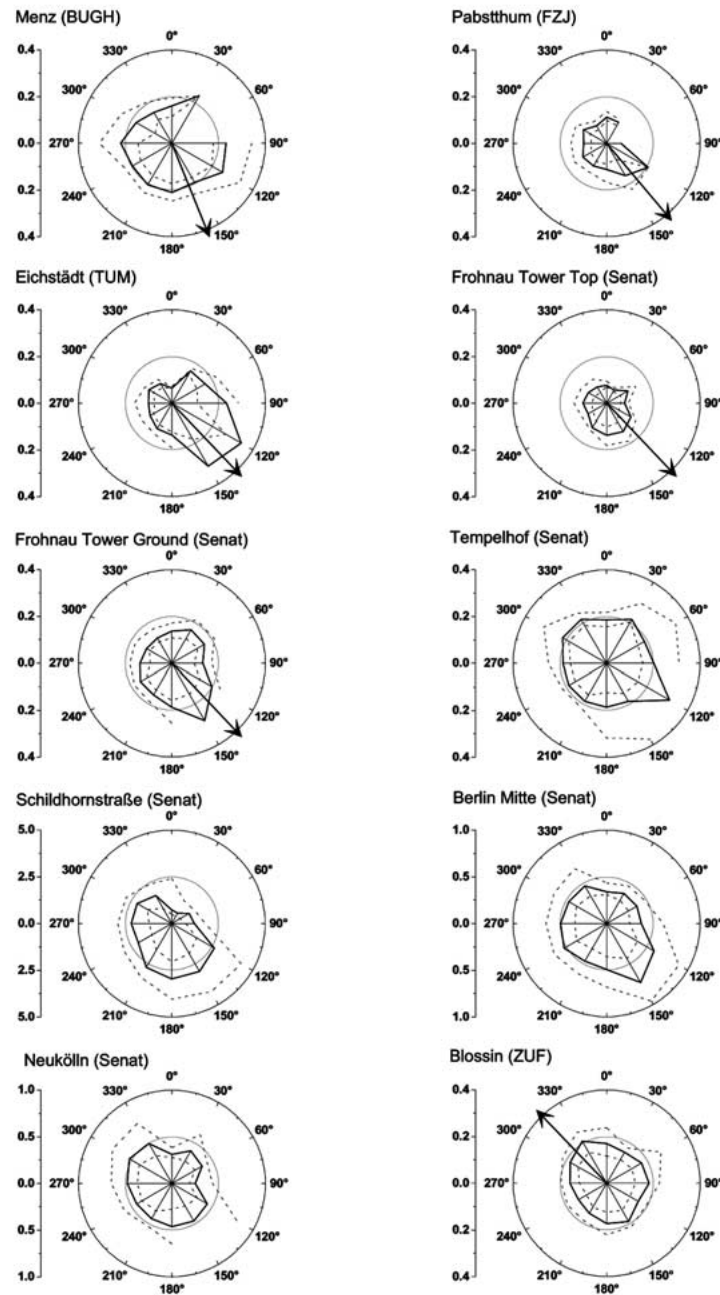
Figure 3. Benzene concentration roses. Solid line indicates median mixing ratio (ppbv), broken lines denote 25- and 75-percentiles. The sites are aligned according to their latitudinal position. Note that the scale changes for the three downtown sites Schildhornstraße, Berlin Mitte and Neukölln. The arrows indicate the direction of Berlin.

of the city because of dilution and photochemical degradation during transport. Therefore small nearby sources gain in relative importance.

The downtown sites Tempelhof, Berlin Mitte and Neukölln show maxima in southeasterly directions. A possible explanation is that the two days (20 and 21 July) with southeasterly winds had also the highest temperatures. Since evaporative emissions of NMHCs follow the increase in temperature (Kourtidis *et al.*, 1999), their contribution on these days should be larger than during the rest of the campaign. Other reasons for the higher concentrations on 20 and 21 July close to the source region are the low mixed layer heights in conjunction with low wind speeds.

The comparison of the benzene mixing ratios at the different stations with respect to winds from Berlin and west is summarized in Table III. The background mixing ratios of benzene, as given by the medians in the west sector of Eichstädt (TUM, 91 pptv), Pabstthum (98 pptv), Frohnau Tower Top (101 and 126 pptv) are in excellent agreement both, with each other and with the value of 116 pptv reported by Koppmann *et al.* (1998) for a remote site in Mecklenburg-Vorpommern, 130 km northwest of Berlin.

By far the highest benzene pollution levels were found at the downtown station Schildhornstraße with a median of 2.1 ppbv. This site is located next to a road with a traffic load of 55.000 vehicles/day. The influence of the local traffic pollution at this site is enhanced by the micrometeorological conditions of a street canyon with low ventilation. As expected from the pollution rose (Figure 3), the road passes the station right in the southwest.

The concentration ratios of two hydrocarbons with common sources but different atmospheric lifetimes can provide further insight into the influence of nearby or distant sources on the hydrocarbon concentrations at a measurement site (Rappenglück and Fabian, 1999a, 1999b). With the less reactive species in the denominator, the smaller the ratio, the less important are nearby sources and the more important becomes long-range transport.

Toluene/benzene concentration ratio roses are presented in Figure 4. The benzene mixing ratios were corrected for coelution as described above. At Blossin and Menz toluene coelutes with 4-methylheptane. Judging from the Pabstthum data set, however, the contribution is less than 1% (sd = ± 0.5%; $n = 16$) and can thus be neglected.

As shown above, the measurement site Schildhornstraße is strongly influenced by local traffic and thus its toluene to benzene ratio can be considered typical for Berlin traffic emissions. The median toluene/benzene ratio of 2.3 ppbv/ppbv (upper and lower quartiles are 2.1–2.4 ppbv/ppbv) is in good agreement with the average ratio measured in different German cities, which amounts to 2.2 ± 0.5 ppbv/ppbv ($n = 122$) as calculated from the TFS-VOC reference-list (Mannschreck *et al.*, 2002). Kurtenbach *et al.* (2002) report slightly lower ratios of 2.0 ± 0.6 ppbv/ppbv from measurements in a traffic tunnel at Wuppertal, Germany.

Table III. Statistical results of benzene measurements for wind from Berlin and from the west. Number of samples per sector n, mean, standard deviation, median and 25–/75-percentiles. Data of the stations affected by coelutions were corrected by a factor according to Table II

Station	Operator	Factor	Berlin sector					West sector				
			n	Mean (ppbv)	sd (ppbv)	Median (ppbv)	25–75% (ppbv)	n	Mean (ppbv)	sd (ppbv)	Median (ppbv)	25–75% (ppbv)
Blossin	ZUF	0.92	57	0.173	0.067	0.164	0.120–0.216	253	0.149	0.056	0.144	0.107–0.179
Eichstädt	TUM	0.90	44	0.385	0.255	0.372	0.142–0.545	26	0.105	0.045	0.091	0.070–0.149
Pabstthum	FZJ	1	8	0.199	0.134	0.185	0.139–0.208	40	0.109	0.055	0.098	0.064–0.151
Menz	BUGH	0.92	30	0.177	0.031	0.176	0.155–0.194	72	0.231	0.135	0.201	0.133–0.284
FrTwr, top	TUM	0.94	18	0.241	0.173	0.191	0.146–0.276	158	0.137	0.070	0.126	0.092–0.171
FrTwr, top	Senat	1	39	0.156	0.063	0.149	0.101–0.191	186	0.106	0.048	0.101	0.065–0.140
FrTwr, gnd	Senat	1	62	0.287	0.206	0.189	0.156–0.338	331	0.146	0.066	0.136	0.093–0.179
Tempelhof[a]	Senat	1	1086	0.254	0.207	0.186	0.155–0.248	–	–	–	–	–
Neukölln[a]	Senat	1	1296	0.548	0.380	0.464	0.340–0.618	–	–	–	–	–
B-Mitte[a]	Senat	1	1233	0.533	0.272	0.464	0.340–0.649	–	–	–	–	–
Schildhstr[a]	Senat	1	1229	2.260	1.439	2.132	1.112–3.059	–	–	–	–	–
Stadtautob[a]	Senat	1	1153	0.826	0.551	0.680	0.464–1.051	–	–	–	–	–
All[b]			3872	0.440	0.324	0.371	0.217–0.556	1066	0.142	0.074	0.131	0.093–0.175

[a] All data included in Berlin sector.
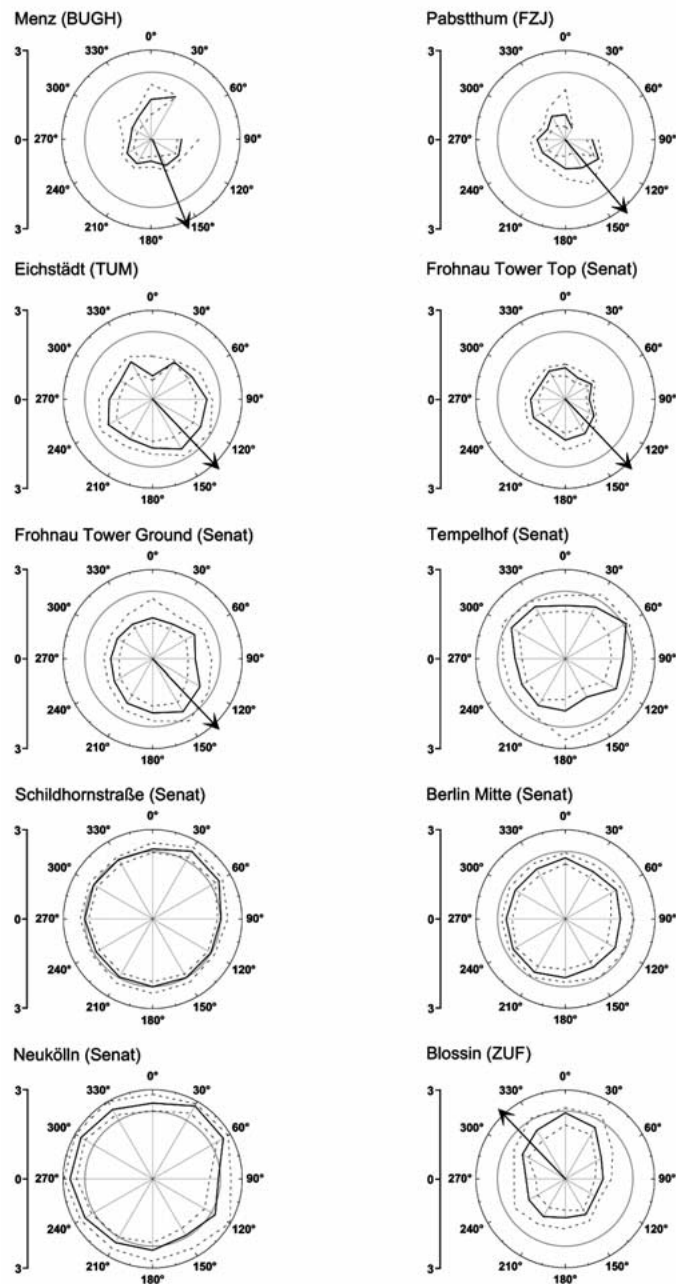[b] Data from Schildhornstraße and Stadtautobahn not included.

Figure 4. Wind roses for toluene/benzene concentration ratios. Solid line indicates median ratio (ppbv/ppbv), broken lines denote 25- and 75-percentiles. The sites are aligned according to their latitudinal position. The radius of the circles stands for a ratio of 3. The typical Berlin ratio of 2.3 is indicated by the grey circle. The arrows indicate the direction of Berlin.

The median toluene/benzene ratio is always <3 at all sites. At the downtown stations Schildhornstraße, Neukölln and Berlin Mitte and to some extend at Tempelhof, the toluene to benzene ratio is rather uniform around the value of 2.3. At Eichstädt and the base of the Frohnau Tower it is slightly smaller than 2.3, and finally, at Menz and Pabstthum it is much lower (mostly <1), reflecting the greater distance to Berlin. At these sites the toluene/benzene ratio is dominated by long-range transport. This is also the case for Frohnau Tower Top, which is 284 m above the ground. The small ratios indicate that the site is not affected by the Berlin plume, but usually receives aged air masses influenced by the free troposphere.

While the benzene concentration roses generally showed elevated pollution levels towards Berlin, the toluene/benzene ratio roses are more complicated. Higher ratios in direction of the city are even less pronounced and are obvious only at the nearest sites Frohnau Tower, Eichstädt and, to a lesser extend, at Pabstthum. The maximum ratios at Menz and Blossin point to other directions than Berlin, suggesting the importance of other emission sources such as small towns or frequented roads (Berlin highway ring) in the neighbourhood of these sites.

In Figure 5 the toluene/benzene ratio (ppbv/ppbv) is plotted against the benzene mixing ratio. As indicated by the solid line, the median ratio is distinctly smaller at the background sites (Menz, Pabstthum, Eichstädt, Blossin) than at the sites in the city (Stadtautobahn, Schildhornstraße, Berlin Mitte, Neukölln). The smallest median toluene/benzene ratios of 0.9 were found at Menz, Pabstthum and the top of Frohnau Tower (1.1).

As indicated by the scatter of the data points, the best correlation between the two hydrocarbons is observed at the sites closest to the sources, i.e., Schildhornstraße, Stadtautobahn and to some extend Berlin Mitte. Despite the large variation of benzene concentration (three orders of magnitude), the variation of the toluene/benzene ratio is rather small at these three sites and the 25-/75-percentiles almost equal the median. At the background sites the toluene/benzene ratio is more variable, reflecting the importance of other sources, as is also indicated by the toluene/benzene-roses.

The toluene to benzene ratio of 2.6 at the urban background site Neukölln is remarkably high. The higher ratio may be addressed to the slower driving conditions of the vehicles in that part of the town (Heeb *et al.*, 2000).

Because of the prevailing westerly winds during BERLIOZ, the influence of Berlin on the remote sites is only barely recognizable from the statistical data. However, on 20 and 21 July, the impact of Berlin was visible at the northwesterly sites Eichstädt, Pabstthum and even at the most distant station Menz.

In Figure 6 the diurnal variation of benzene (coelution corrected) and toluene on 20 July is shown. A description of the meteorological conditions on this day is given by Corsmeier *et al.* (2002). Briefly, the maximum temperature was 30 °C at 14:30 UT, the wind direction was southeast in the morning and turned to southwest later in the day and thus Blossin represents background measurements upstream of
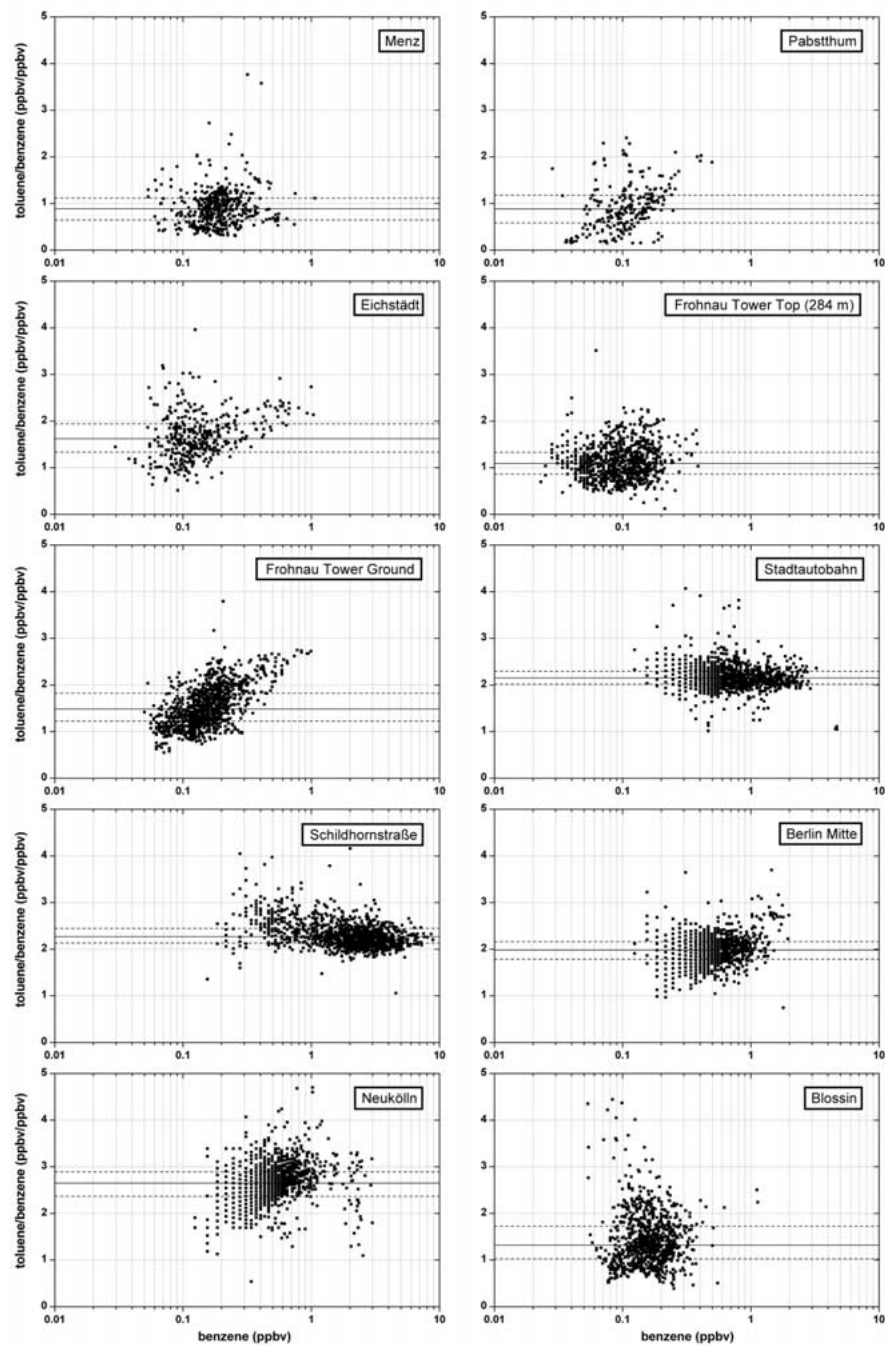
Figure 5. Toluene/benzene mixing ratio (ppbv/ppbv) plotted against benzene concentration (ppbv). The solid line indicates median toluene/benzene ratio, the broken lines give the 25-/75-percentiles.
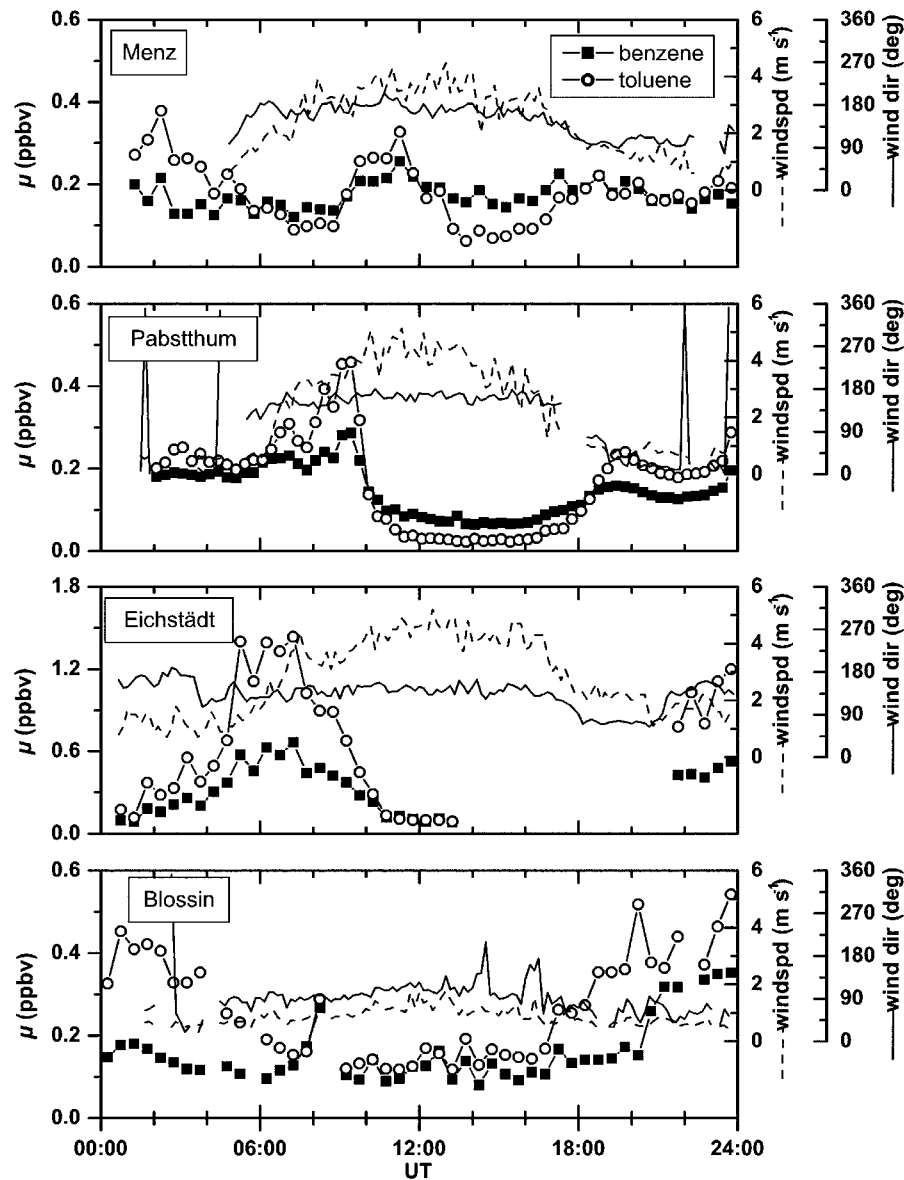
Figure 6. Diurnal variation of benzene and toluene mixing ratio μ (ppbv), windspeed (values < 0.5 m s^{-1} were discarded; broken line) and wind direction (grey line) for 20 July at the background stations Menz, Pabstthum, Eichstädt and Blossin.

Berlin, while the downwind sites Eichstädt, Pabstthum and Menz were temporarily influenced by the Berlin plume.

As expected, highest mixing ratios are found in Eichstädt, decreasing from Pabstthum to Menz. Eichstädt has its maximum toluene concentrations ($\sim$1.4 ppbv) around 05–07 UT, Pabstthum (0.450 ppbv) around 09 UT and Menz (0.300 ppbv)

around 11 UT. At the luff site Blossin, the toluene mixing ratio is below 0.300 ppbv during daytime. At a windspeed around 3.5 m s^{-1} the theoretical transport time of an air parcel from Eichstädt to Pabstthum or from Pabstthum to Menz is ~2 h. This theoretical transport time agrees well with the observed time shifts of the plume at the downwind stations. Compared to the other sites, Pabstthum observed the Berlin plume for the shortest period of time, suggesting that due to its westernmost position, probably only the boarder of the plume was detected.

Likewise the absolute concentrations, the maximum toluene to benzene ratio within the plume decreases from 2.3 at Eichstädt, 1.6 at Pabstthum to 1.3 at Menz, showing the photochemical aging and mixing of the plume with background air during transport.

3.3. BIOGENIC HYDROCARBONS

Although a comprehensive set of biogenic VOCs is not available for the BERLIOZ campaign, there are measurements of isoprene (2-methyl-1,3-butadiene) available at three sites (Blossin, Pabstthum and Menz). Isoprene is known to be released as the dominant hydrocarbon by many plant species (e.g. Kesselmeier and Staudt, 1999), but was also observed as a minor constituent of traffic emissions (Jemma *et al.*, 1995; McLaren *et al.*, 1996; Derwent *et al.*, 1995; Reiman *et al.*, 2000).

Generally, highest isoprene mixing ratios in conjunction with a pronounced diurnal variation were observed on the hottest days of the campaign (20–23 and 27 July) with daily mean temperatures above 24 °C. Maximum values occured during noontime on 21 July with 1.9 ppbv at Menz and 5.6 ppbv at Blossin. At Pabstthum isoprene peaked on 23 July (1.6 ppbv) while on 21 July values of up to 0.9 ppbv were reached. During the remaining days, isoprene levels were mostly <0.5 ppbv.

The high isoprene mixing ratios are in good agreement with recent emission calculations by Richter *et al.* (1998), which revealed that apart from deciduous trees also coniferous trees are important isoprene emitters in eastern Germany, due to their high biomass. Blossin is located at the edge of a large coniferous forest, extending 5 km to the northwest. Additionally, the sampling inlet of the GC was only 4.5 m high, topped by the surrounding trees, thus the local influence of nearby conifers is most likely responsible for the enhanced isoprene levels at noon. At Pabstthum only a small coniferous forest is situated in the west, whilst in the southeast an agricultural area (mainly consisting of grassland) extends 6 km towards Berlin. Hence, Pabstthum is only slightly influenced by isoprene emissions. As Pabstthum, Menz also lies east of a forest and agricultural areas extend into the direction of Berlin in the immediate vicinity (<30 km).

In Figure 7 the isoprene mixing ratios (ppbv) at the background sites Blossin, Pabstthum and Menz are shown for 20 and 21 July. At Blossin isoprene shows its typical temperature and light dependent (Guenther *et al.*, 1991, 1993) diurnal variation. As indicated by pentane, the diurnal variation of the other NMHCs is

quite uniform. It shows only slightly enhanced concentrations during the night. Comparing the concentration of NO_w ($= NO_x$ + unknown amount of NO_z; cf. Kanter *et al.*, 2002, this issue) with NO_x at the other sites, relatively unpolluted air reached Blossin throughout these two days.

At Pabstthum and Menz the typical diurnal variation of isoprene is only obvious at 21 July. In the afternoon the wind shifts from southeast to west, transporting fresh natural emissions to the sites. On 20 July the main wind direction was southeast and, as discussed above, the Berlin plume could be observed in the morning (cf. also NO_x). As no greater forests lie in the direction of Berlin, isoprene levels remain low at this day. The concentration maximum is in the evening. As the isoprene mixing ratio increases between 17 and 20 UT more steeply as the pentane concentration, atmospheric mixing can not be responsible for this increase alone. The buildup might be caused by continueing natural emissions from the nearby forests in the early evening. During the night the isoprene level again falls below pentane.

In order to assess the relative impact of the anthropogenic and biogenic hydrocarbon fractions on the oxidant formation at the sites, the OH reactivity ([NMHC] $\times k_{OH}$) is shown in Figure 8 for 20 July at Blossin and Pabstthum. The OH loss rate is a simple indicator of a compound's photochemical activity. As expected, isoprene accounts for a large part of the total OH reactivity at both sites with an averaged contribution of 70% at Blossin and 51% at Pabstthum. The values are similar to the fractions found in other studies at rural sites (Goldan *et al.*, 1997; Lamanna and Goldstein, 1999).

The substantial higher NMHC reactivity at Blossin is almost exclusively caused by the much higher isoprene mixing ratios (see Figure 7), which is particularly obvious around noontime. During the passage of the city plume at Pabstthum (represented by the sample at 08:30 UT) the contributions of isoprene (46%) and the remaining anthropogenic NMHCs (54%) to the NMHC reactivity are almost equal, however the total reactivity never reaches as high values as in Blossin.

Because other biogenic compounds with similar or even greater reactivity (terpenes or unsaturated carbonyls) could not be considered here, the overall impact of the biogenic hydrocarbon fraction on the OH loss rate is much greater than Figure 8 suggests. Additionally, as the simple OH reactivity scale considers only the first step of photooxidant formation, and not the reaction mechanisms of the products of the OH radical attack, this leads to a further underestimation, compared to the more elaborated scales as photochemical ozone creation potentials (POCP; e.g. Derwent *et al.*, 1998) or the maximum incremental reactivity concept (MIR; e.g. Carter *et al.*, 1995).

3.4. NMHC EMISSIONS OF BERLIN

Concentration ratios of individual hydrocarbons to CO measured in the plume of Berlin should, after subtracting the background concentrations and after correction
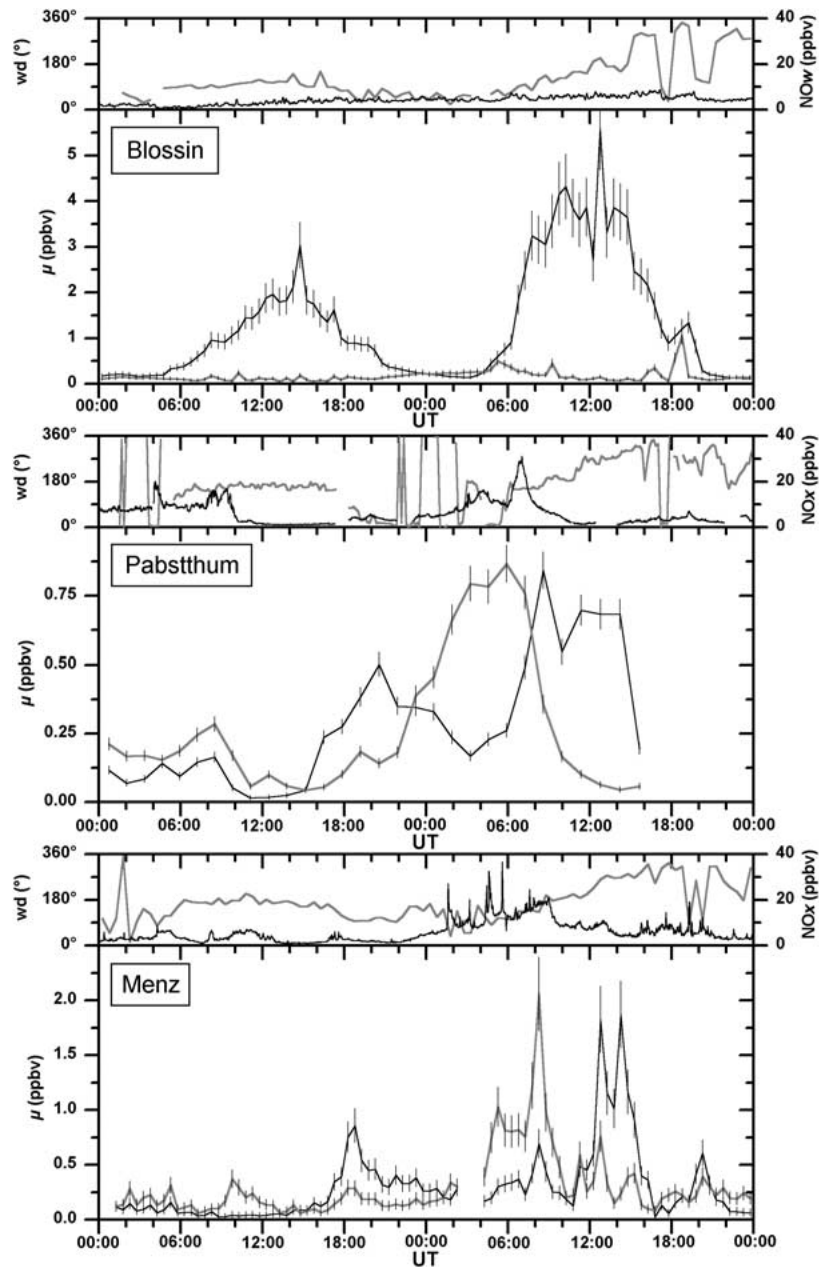
Figure 7. Mixing ratios μ (ppbv) of isoprene (black line) and pentane (grey line) at the background sites Blossin, Pabstthum and Menz at 20 and 21 July. The error bars correspond to the accuracies denoted in Table I. Wind direction wd (grey) and concentration of NO_x (black) are plotted in the small graphs, respectively. For Blossin only NO_w measurements are available (see Kanter *et al.*, 2002).
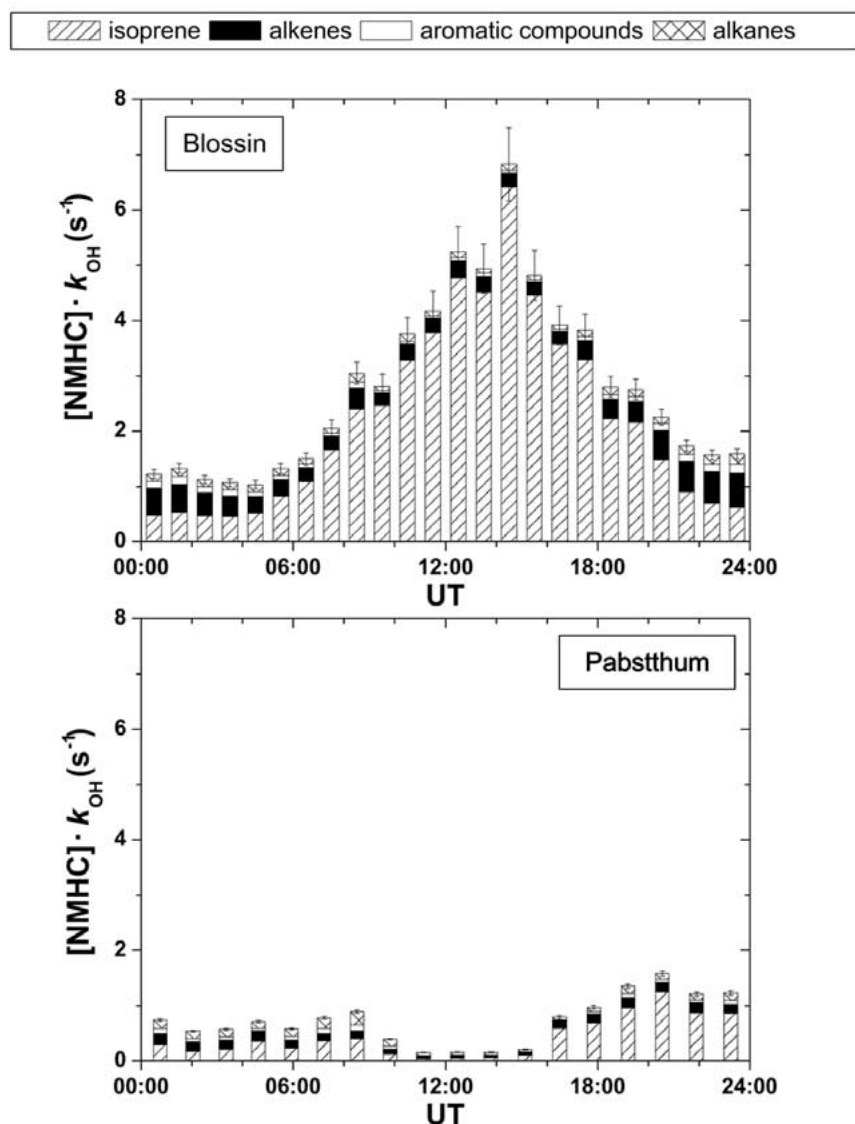
Figure 8. Total OH loss rate (s^{-1}) and relative contributions for isoprene and the anthropogenic hydrocarbons (lumped) at Blossin and Pabstthum for 20 July. Nighttime values are included for comparison reasons only, since no significant OH loss may occur at this time of the day. The hydrocarbon classes comprise: Alkanes (ethane, propane, i-butane, n-butane, i-pentane, n-pentane, 2,2-dimethylbutane, 3-methylpentane, n-hexane, methylcyclopentane, 2,4-dimethylpentane, 3-methylhexane, methylcyclohexane, 2,3,4-trimethylpentane, 2-methylheptane, 3-methylheptane, n-octane), alkenes (propene, i/1-butene, trans-2-butene, cis-2-butene, 2-methyl-2-butene) and aromatic compounds (benzene, toluene, ethylbenzene, styrene, o-xylene, m/p-xylene).

for chemical transformations, provide information about their emission strength relative to the emission of CO in the city of Berlin. Emission ratios can be derived from measurements at the surface or aboard aircraft (Slemr *et al.*, 2002, this issue; Klemp *et al.*, 2001). As discussed in the previous section, however, the ground based measurements are often influenced by nearby sources and consequently in this section we will rely on the aircraft canister data set only. The airborne on-line GC measurements by Metair were not considered because concurrent CO measurements were not available on this aircraft.

Afternoon flights on 3 and 8 August provide a suitable data basis for the determination of the emission ratios since all samples were taken within the boundary layer containing fresh city emissions. On 3 August, the samples taken downwind of the city of Brandenburg were not considered leaving 17 samples for the determination of the emission ratios. On 8 August all 46 samples were taken to determine the emission ratios. The measured mixing ratios of NMHCs and CO were linearly correlated. Assuming constant background concentrations for the NMHCs and CO during the measurement, the slopes of the resulting regression lines and their statistical uncertainties represent the emission ratios and their uncertainties, respectively. The intercept of the regression line provides an information about the background concentrations. Orthonormal regression was preferred to usual least square fit because it considers both CO and NMHC measurements to be independent and takes into account the uncertainties in both measurements (for more details see Slemr *et al.*, 2002, this issue). In addition, emission ratios of individual hydrocarbons to the sum of all NMHCs measured by the canisters were determined in the same way. The emission ratios were corrected for removal by OH, assuming an hydroxyl radical concentration of 3×10^6 molecules cm^{-3} (Platt *et al.*, 2002) and an average transport time of 2 h.

The averaged NMHC/CO and NMHC/sum of measured NMHCs (ΣNMHC) emission ratios measured on 3 and 8 August are summarized in Figures 9 and 10, respectively. For comparison, we also included the corresponding ratios from measurements carried out on 23–26 July 1994, at the downtown site Berlin Mitte (Stark and Lutz, 1997) and from a temporally and spatially highly resolved emission inventory made by IER specifically for the BERLIOZ campaign (Friedrich *et al.*, 2002, this issue). The inventory contained hourly emissions of CO, NO$_x$ and of about 300 NMVOC species and substance classes for the period of measurements for a rectangular area of 3120 km^2 encompassing Berlin and its circular highway as shown in Figure 1. These emissions were generated from the default TFS emission data base which has been developed and improved for ozone forecasting and evaluation purposes of chemistry and transport models (CTM) (Friedrich *et al.*, 2002, this issue). Emissions of individual NMHCs were calculated by disaggregating 50 substance classes needed as CTM input. Opposite to the Evaluation Experiment at Augsburg (EVA; Slemr *et al.*, 2002, this issue), the specific local industrial and socio-economic structure was not considered in this disaggregation. The NMHC/CO and NMHC/ΣNMHC emission ratios for Berlin Mitte were cal-
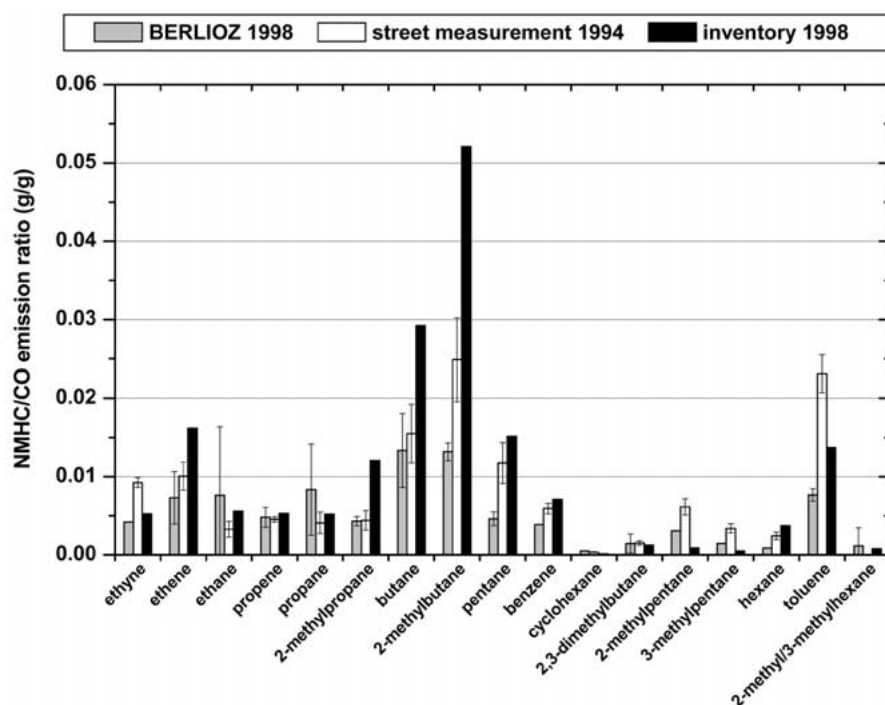
Figure 9. Average NMHC/CO emission ratios for Berlin measured on 3 and 8 August. For comparison measurements from downtown Berlin in July 1994 (Stark and Lutz, 1997) and NMHC/CO emission ratios from the inventory calculated by IER for the BERLIOZ campaign are included. The uncertainties of airborne and street measurement are the differences between the measurements on 3 and 8 August and the slope uncertainties, respectively.

culated from the original measurements in the same way as those from aircraft measurements and are thus comparable.

The NMHC/CO emission ratios from Berlin Mitte represent vehicle exhaust fingerprints (Stark and Lutz, 1997). Inspection of Figures 9 and 10 reveals that NMHC/CO and NMHC/ΣNMHC emission ratios of Berlin are generally in reasonable agreement with the measurements at the downtown site, i.e. with vehicle exhaust. The measured NMHC/ΣNMHC emission ratios are also generally in reasonable agreement with the corresponding inventory ratios whereas the modeled NMHC/CO ratios are mostly substantially larger than the measured ones. The tendency to overestimate the NMHC/CO emission ratios by the Berlin inventory can be due to an overestimation of NMHC emissions and/or an underestimation of the CO emissions. The latter was the case in Augsburg during the EVA experiment (Slemr *et al.*, 2002, this issue) and in measurements on a motorway (Vogel *et al.*, 2000), while overestimation of NMHC emissions due to overestimated emissions from solvent use was observed in Augsburg (Slemr *et al.*, 2002, this issue). Since only a few of the compounds reported here originate substantially from solvent
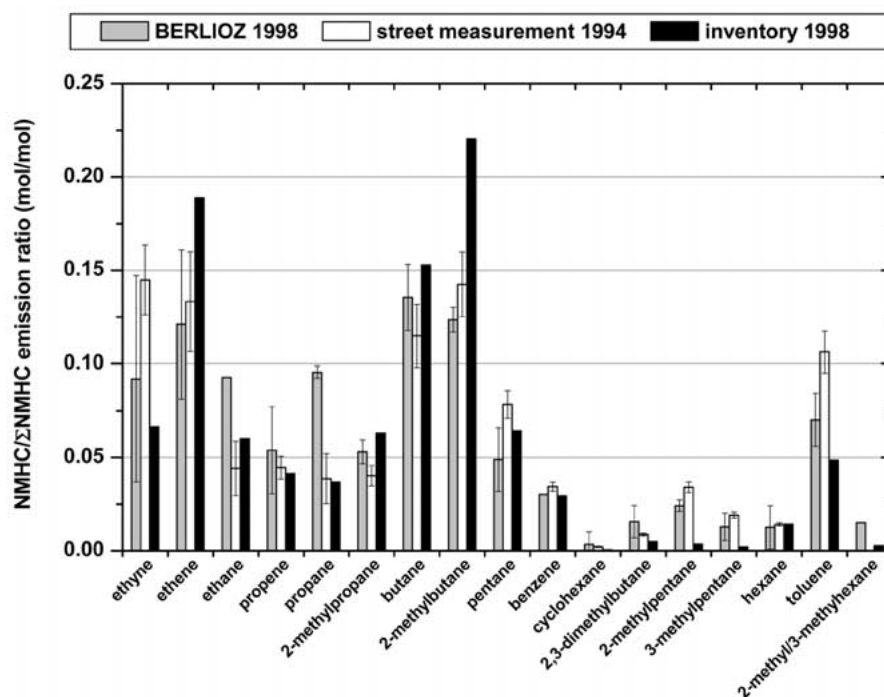
Figure 10. Average NMHC/sum of measured NMHCs (ΣNMHC) emission ratios for Berlin measured on 3 and 8 August. For comparison measurements from downtown Berlin in July 1994 (Stark and Lutz, 1997) and NMHC/ΣNMHC emission ratios from the inventory calculated by IER for the BERLIOZ campaign are included. The uncertainties for airborne and street measurement are the differences between the measurements on 3 and 8 August and the slope uncertainties, respectively.

use, more research is needed to clarify the difference between the measured and calculated NMHC/CO emission ratios.

As in Augsburg, the observed emission ratios for propane are higher than the modeled ones, most likely due to an underestimation of propane emission from liquefied natural gas. On the other hand, ethene, 2-methylbutane and pentane emissions are greater in the inventory than what is derived from the measurements in BERLIOZ and EVA. A substantial overestimation of ethene emission ratios in both cities in combination with the fact that the emissions are dominated by vehicle exhaust suggest problems with the emission factor for ethene. The overestimation of emissions of pentanes suggests that the model overestimates evaporative losses of gasoline and/or the use of gasoline as solvents.

4. Conclusions

During the BERLIOZ campaign a comprehensive NMHC dataset with high resolution in time and space was generated. The median benzene mixing ratios

reached from several ppbv at the downtown sites to values well below 500 pptv at the background sites. At westerly winds the background values were around 100 pptv. Using benzene pollution roses and toluene/benzene concentration ratio roses, the influence of the Berlin emissions on its surroundings was investigated. As expected, the greatest impact was observed at the nearest sites Blossin and Eichstädt, whilst other sources (most likely small towns or frequented roads) gain in importance at the furthermost site Menz.

The median toluene/benzene concentration ratio in Berlin was 2.3 ppbv/ppbv, which is in good agreement with measurements in other German cities. The ratios at the background sites were usually around one or below. On 20 and 21 July the Berlin plume was observed at the northwesterly sites Eichstädt, Pabstthum and Menz, showing decreasing toluene to benzene ratios of 2.3, 1.6 and 1.3 with increasing distance to the city. This decreasing ratios are also obvious in the median toluene/benzene ratios of the respective sites. On the hottest days isoprene showed a pronounced diurnal variation at the background sites, with midday maxima of several ppbv. Consequently, isoprene dominated the local NMHC reactivity on these days, with a share of more than 50% in the Berlin/Brandenburg area.

NMHC/CO and NMHC/ΣNMHC emission ratios were derived from airborne measurements and compared with earlier measurements at the downtown site Berlin Mitte and with an emission inventory. Generally, the measurements were in good agreement with the inventory, indicating that emissions of Berlin are dominated by traffic related NMHCs. Significant deviations of measured emission ratios from the calculated ones were observed for propane, ethene and pentanes, pointing to further research needs in emission modeling.

Acknowledgements

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