An Analysis of Simultaneous Online GC Measurements of BTEX Aromatics at Three Selected Sites in the Greater Munich Area

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ABSTRACT

During two field campaigns in 1993 and 1994, measurements of aromatic compounds [benzene, toluene, ethylbenzene, m-/p-/o-xylenes (BTEX)] were carried out at urban and rural sites in the greater Munich area. These field campaigns represent a unique study using quasi-continuous gas chromatography/flame ionization detection methods concurrently at various sites. The impact of Munich’s urban plume on photochemical processes downwind from the urbanized area was observed. Most BTEX compounds showed good correlation with other primary species such as nitrogen oxides and carbon monoxide at the rural site. High mixing ratios of primary compounds at the rural site were always correlated to transport of polluted air masses from the urban area. In addition, every time the rural site encountered the urban plume, selected BTEX ratios changed significantly and the formation of ozone and peroxyacetyl nitrate occurred. This fact demonstrates that BTEX compounds play an important role in regional photochemical smog formation. BTEX ratios may be a useful tool to assess the anthropogenically driven nonmethane hydrocarbon photochemistry in future air quality studies.

1. Introduction

Besides nitrogen oxides (NOx) and carbon monoxide (CO), nonmethane hydrocarbons (NMHCs) are important precursors for ozone and other secondary photooxidants in the sunlit lower troposphere (Chameides et al. 1992; Bowman and Seinfeld 1994). The NMHC aromatic compounds benzene, toluene, ethylbenzene, and m-/p-/o-xylenes (BTEX) compose a unique group, as outlined in earlier publications (e.g., Wathe 1983; Derwent and Jenkin 1991; Field et al. 1992; Simpson 1995). Their only known degradation pathway is reaction with the hydroxyl radical (OH) during the daytime. Yet, the reaction rate toward OH is significantly different for each BTEX compound (Table 1). This property makes them an ideal NMHC class for photochemical investigations in the urban–rural transition zone. Some of the BTEX aromatics (e.g., toluene and m-xylene) are important species with respect to both their urban atmospheric mixing ratios and their reactivity-based concentrations (Chameides et al. 1992). Together with alkenes BTEX compounds yield the highest formation potentials for both ozone (O3) and peroxyacetyl nitrate (PAN) (Derwent and Jenkin 1991). According to model calculations, up to 30% of the ozone production in an urban plume may be attributed to the impact of the BTEX compounds (Hough and Derwent 1987). In particular, xylene isomers may convert significant amounts of nitrogen monoxide (NO) to nitrogen dioxide (NO2) (Simpson 1995).

Results of hydrocarbon measurements have been documented for various places throughout the world (Chameides et al. 1992). NMHC measurements have already been carried in numerous urban areas (e.g., Bruckmann et al. 1988; Aronian et al. 1989; Lanzerstorfer and Puxbaum 1990; Tsujino and Kowata 1993). These measurements were carried out discontinuously with canister sampling methods and subsequent analysis in the laboratory. Often these NMHC datasets comprise only a few samples and display little temporal resolution, so that knowledge on hydrocarbon behavior in urban areas is still limited. For this reason a more sophisticated measurement technique is required with a low NMHC detection limit and at reasonable time resolutions in order that results may be compared with other air chemical and meteorological data. To our knowledge only a few measurements have met these requirements (e.g., Dommöse and Figge 1988; Staehelin et al. 1991; Kramp et al. 1994; Rappenglück et al. 1998).

The greater Munich area (GMA) with its population of about 1.3 million inhabitants has become an important center for Germany’s high-tech industry over the last decades (e.g., Siemens, Bayerische Motorenwerke (BMW), Messerschmidt-Bölkow-Blohm (MBB), Maschinen Turbinen Union (MTU), München-Augsburg-
TABLE 1. Rate constants $k_{\text{OH}}$ for the gas-phase reactions of OH with BTEX compounds according to Atkinson (1990).

<table>
<thead>
<tr>
<th>BTEX compound</th>
<th>$10^{-12} \times k_{\text{OH}}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>1.23</td>
</tr>
<tr>
<td>toluene</td>
<td>5.96</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>7.1</td>
</tr>
<tr>
<td>o-xylene</td>
<td>13.7</td>
</tr>
<tr>
<td>p-xylene</td>
<td>14.3</td>
</tr>
<tr>
<td>m-xylene</td>
<td>23.6</td>
</tr>
</tbody>
</table>

Nürnberg (MAN), and most of Germany’s publishing houses have their seats in Munich]. Air quality data have been well documented for the GMA (e.g., Georgii and Neuber 1986; Rappenglück et al. 1993; Fabian et al. 1994; Jakobi 1994; Suppan 1996). Maximum ozone values of up to 150 ppbv have been reported in these studies. The Verein Deutscher Ingenieure (VDI), in its function as a national institution that approves guidelines for indoor and outdoor mixing ratios of various species that are harmful to human health, set an MIK (Maximale Immissionskonzentration; maximum outdoor mixing ratio) value for ozone of 60 ppbv as the upper limit for 30-min exposure (VDI 1989). The MIK value is exceeded frequently during the spring and summer months in the GMA. The first measurements of PAN in Munich were reported by Rappenglück et al. (1993). PAN is a well-known specific indicator for NMHC photochemistry (see, e.g., Altshuller 1993). Recent work in the GMA includes the analysis of NMHC datasets (Rappenglück and Fabian 1999). The results showed that BTEXs are an important fraction of the NMHC burden in Munich’s ambient air. Moreover, BTEXs were found to be ubiquitous in the GMA. Previous measurements of primary species, including BTEX and secondary compounds such as ozone and PAN at a rural site downwind of the urbanized area of Munich, suggested the importance of BTEX in photochemical processes of an urban plume (Rappenglück 1994); enhanced values of ozone and PAN did not occur on the last day of a pollution episode as might have been expected due to persisting favorable meteorological conditions, but rather on a day before when the maximum BTEX precursor mixing ratios were observed.

Here we will report about photochemical processes in the urban–rural transition zone analyzing simultaneous gas chromatography (GC) measurements of BTEX aromatics at three selected sites in the GMA for the first time.

2. Experimental setup

a. Measurement sites

Three sites were chosen for quasi-continuous online BTEX measurements in the GMA (Fig. 1): UMW (Umweltschutzreferat der Landeshauptstadt München), MIM (Meteorologisches Institut der Universität München), and EIT (Eitting). These sites compose a selection of locations where NMHC measurements have been carried out in recent years (Rappenglück and Fabian 1997). All sites were equipped with commercial analyzers for nitrogen oxides (Monitor Labs ML 8840), ozone (Monitor Labs ML 8810), and PAN (Scintrex LPA-4). At UMW and EIT, CO analyzers (Horiba Ambient CO Monitor APMA 350E) were also installed. At the EIT site a total NMHC analyzer (Horiba Ambient HC Monitor APHA 350E) completed standard air chemical measurements. In addition to air chemical data, meteorological parameters (solar radiation, temperature, humidity, wind velocity, and wind direction) were registered on a routine basis at all sites.

Sites UMW and MIM are urban sites. UMW is a ground-based site located in a small park in the vicinity of the completely electric main railway station of Munich. UMW is not exposed to direct traffic emissions. MIM is located downtown on top of a 30-m university building, at the height of the average downtown urban roof level. At MIM, there also are no direct emissions nearby. As a downtown measurement site, however, ground-based traffic emissions play a dominant role in
this area as major traffic roads are located nearby. At MIM the impact of traffic emissions are likely to be detected, although due to vertical dilution pollutant mixing ratios are expected to be lower at this site than at surface level. Haustein von Haustenau (1993) carried out concurrent measurements of NO, CO, total NMHC, and traffic density in downtown Munich. All three pollutants exhibited a very good correlation with the temporal variation of traffic density. Also, Haustein von Haustenau applied model calculations using MUKLIMO (Microscale Urban Climate Model), as described by Sievers and Zdunkowski (1986), for Munich street canyons. In all cases minimum pollutant levels were found at the average urban roof level.

Emission inventories reveal that on the whole Munich is not very affected by industrial emissions (ULM 1993). With the exception of a BMW factory (6 km northwest of UMW and MIM) there is no heavy industry located in the GMA. According to investigations carried out by the Bavarian environmental protection agency (Bayerisches Landesamt für Umweltschutz; BayLfU), about 17.2 thousand metric tons (kt) of NMHC are emitted annually by traffic in the GMA, whereas industrial releases of NMHC are about 4.0 kt annually in the GMA (BayLfU 1992). Inventory data for benzene and toluene show that 1.05 kt of each are annual traffic-related emissions. Main traffic emissions occur in the center of Munich (ULM 1993). UMW and MIM are located within a road circle surrounding the downtown area. About 100 000 cars of all types pass this cycle in both directions every day. Yearly industrial emissions account only for 0.02 kt for benzene and 0.17 kt for toluene.

Contrary to UMW and MIM, the EIT site represents a rural site in the agricultural plains north of Munich. The instrumental equipments were housed in the uppermost floor of an hydroelectrical power plant. The only towns in this area are Erding (about 16 000 inhabitants) located about 7-km southeast of EIT, and Freising (30 000 inhabitants) 10-km northwest of EIT. The urbanized area of Munich is about 20 km to the southwest. There are no significant emission sources between Munich and EIT. At EIT ambient air quality is likely to be influenced by transport and/or dilution from the surrounding region and, under particular meteorological conditions, by the superimposed transport from the Munich area. During daytime photolysis will play another important factor. According to Atkinson (1990) nighttime chemistry involving the nitrate (NO₃) radical will have an impact on only alkenes and terpenes; NO₃ reacts very slowly with alkanes. Reactions with aromatics are unknown. Aromatics are stable during the nighttime.

In our study we will present the results of measurements carried out from 8 August–2 May 1994 and from 12–26 August 1993 at UMW; from 28 April–24 May 1994 at MIM; and from 28 April–2 May 1994 and 12–26 August 1993 at EIT. Special attention will be given to the characteristics of the urban plume at the rural EIT site.

b. Instruments for BTEX measurements

At EIT and MIM identical GC systems (Siemens RGC 402) were used. At UMW, a GC Airmotec HC1010 was used. Thorough specifications of these instruments are given elsewhere (Rappenglück and Fabian 1998; Rappenglück et al. 1998). Here we will provide only a brief description.

1) Siemens RGC 402

The Siemens RGC 402 is able to obtain online BTEX measurements within a cycle time of 30 min. Its measurement technique consists of quasi-continuous ambient air sampling (sampling time 20 min, sample volume about 0.7 L), a double-stage preconcentration procedure onto an adsorbent (Poropak Super Q), and a cryofocusing step (+5°C; refrigerant ethanol) for the sample. Afterward, the compounds are thermally desorbed rapidly at 140°C and injected into two different columns mounted in series (column A: WCOT-CP-Wax-CB, length 25 m, i.d. 0.25 mm, film thickness 0.2 µm; column B: WCOT-CP-Sil-CB, length 25 m, i.d. 0.32 mm, film thickness 1.2 µm) for multidimensional temperature-programmed separation of the different hydrocarbon species. The carrier gas was nitrogen with a purity of 99.999%. Column A separates all higher aromatic compounds beginning with toluene, whereas column B is used for benzene. At first the sample passes through column A for about 4 min. During this time all higher volatile hydrocarbons already enter column B, where they are retained. After 4 min both columns are disconnected from each other and flushed separately with the nitrogen carrier gas. Now the separation processes continue simultaneously and independently in columns A and B. Finally the hydrocarbon components elute and are detected by flame ionization detectors (FID) and identified by their individual retention times. The detection limit is 0.01 ppbv for each BTEX compound. The detection limits were taken as three times the standard deviation of the corresponding blank values. The estimated overall accuracy was about ±20% and the precision was ±10%–15%, depending on the specific hydrocarbon compound. For calibration, dynamical dilution methods were applied using calibration gas cylinders containing benzene, toluene, ethylbenzene, p-, m-, and o-xylene in the range of 10 ppmv (obtained from Messer-Griesheim).

2) Airmotec HC1010

The Airmotec HC1010 is also able to obtain online BTEX measurements within a cycle time of 30 min. The measurement consists of quasi-continuous ambient air sampling (sampling time 28 min 55 s, sample volume
about 1.5 L), a preconcentration procedure onto an adsorbent (Carbosieve SIII 60/80 mesh/Carbotrap), and a cryofocusing step (−20°C; refrigerant CO₂; adsorbent Carbopack 60/80 mesh) for the sample. Afterward the compounds are thermally desorbed rapidly at 350°C and injected into a DB-5 column (length 9 m, i.d. 0.2 mm, film thickness 1.0 μm). Hydrogen with a purity of 99.999% was used as a carrier gas. The temperature program is as follows: 40°C for 445 s, then ballistically to 175°C for 360 s. The BTEX compounds are detected by FID and identified by their individual retention times. The detection limit is about 0.1 ppbv. As with Siemens RGC 402, the detection limits were taken as three times the standard deviation of the corresponding blank values. The estimated overall accuracy was about ±20% and the precision ±10%–15%. The same calibration procedures as for the Siemens RGC 402 were applied.

3. Results and discussion

a. Period I: April–May 1994

During the time period from 8 April–24 May 1994, an approximately four-week BTEX dataset was obtained at UMW (1112 samples) and MIM (937 samples). As a representative surrogate for BTEX the time series of toluene are plotted for all sites (Fig. 2). The lower panel shows a higher resolution for the period 28 April–2 May when BTEX data were also available from the rural site EIT. In addition, this period is marked by the maximum BTEX mixing ratios throughout the total time period of
FIG. 3. Median diurnal variations of toluene at UMW and MIM during corresponding measurement periods in April and May 1994, respectively. Bars indicate standard deviations.

April and May 1994. Henceforth, we will focus on these four days.

Although both urban sites differ (UMW is a ground-based site; MIM is a roof-level site) their toluene series are well correlated. The Spearman’s rank correlation coefficient for toluene$_{UMW}$ ↔ toluene$_{MIM}$ is 0.83 for 28 April–2 May (level of significance: 99%; number of data points: 155). The time series (April–May 1994) of median diurnal variations of toluene for both sites are shown in Fig. 3. The same urban structures are discernible with maxima during rush hour from 0600 until 0900 LT (local time). Diurnal minima occurred during the afternoon, mainly due to enhanced atmospheric mixing processes that overcompensate traffic emissions that still continue, though at emission rates slightly lower than during early morning hours. Finally, evening mixing ratios increased due to lower urban boundary layers. Traffic can be identified as the predominant emission source affecting the downtown area where UMW and MIM are located by the toluene/benzene ratio. Unlike acetylene, which is exclusively emitted by exhaust, the toluene/benzene ratio takes into account various traffic-related processes such as evaporation, storage, and exhaust (e.g., Dulson 1981; Volkswagen AG 1988; Mousisopoulos 1993; QUARG 1993). This ratio shows typical urban values (e.g., Wathne 1983; Roberts et al. 1984; Singh et al. 1985) for both sites (MIM: 2.0; UMW: 1.7). As demonstrated in Fig. 3, toluene values at MIM are typically less by a factor of 2.5 compared to the corresponding values at UMW. Lower values at MIM at the average urban roof-level compared to ground-level values are to be expected because main (i.e., traffic) emissions are found at the ground level (see section 2a). MIM can be regarded as a site that well meets the requirement for representative measurements of urban background NMHC pollution in Munich because this site is away from single-point plumes and it measures area air pollution. Since UMW only differs in absolute values from MIM and not in trends, UMW also can be regarded as a first-order approximation of mean NMHC pollution typical for the downtown Munich area.

At the rural site EIT different phenomena were observed, with toluene mixing ratios much lower at EIT than at both urban sites (Fig. 2). Median toluene mixing ratios from 28 April to 2 May were 4.61 ppbv for UMW, 1.82 ppbv for MIM, and 0.27 ppbv for EIT. Toluene values from EIT are typical for southern Bavarian rural areas (Rappenglück and Fabian 1997). Toluene also exhibits different diurnal variations at the three sites (Fig. 2). In contrast to the urban sites, toluene maxima at EIT generally appear some hours later. However, this specific diurnal variation at EIT may not be attributed to different diurnal traffic variations at EIT. Traffic peaks are unlikely to occur shortly after midnight at rural locations. Thus, these toluene enhancements at EIT likely are not caused by nearby emissions. Both the nocturnal boundary layer and transport processes lead to an accumulation of toluene at EIT. However, the peak time lag observed between EIT and the urban sites suggests that transport processes play an important role at EIT. Since no OH exists during the nighttime, BTEX aromatics are very stable then. Provided there are no emission sources, only dilution processes would have impacted BTEX mixing ratios, leaving BTEX ratios unaffected. During the nighttime, transport processes for BTEX compounds may be observed unambiguously because no photochemistry affects these species.

Concurrent observations of toluene as a specific
NMHC of anthropogenic origin and of the sum of NMHCs at EIT revealed additional information: although the total NMHC analyzer did not have a good detection limit (100 ppbC ± 50 ppbC), the selected time period 28 April–2 May permitted correlation analysis because in most cases total NMHC values were above the detection limit. Total NMHC and toluene showed a good relationship (Spearman’s rank correlation coefficient for toluene ↔ total NMHC: 0.74; level of significance: 99%; number of data points: 169). Correlation analysis for BTEX ↔ total NMHC yielded the same results. Although toluene represents only about 5% of the total NMHC (BTEX about 10% of the total NMHC), the good correlation allows us to take toluene as a surrogate for most NMHCs at EIT. Usually in urban areas, the percentages of toluene and BTEX of total NMHCs are higher (e.g., Nelson et al. 1983; Blake et al. 1993). On a ppbC basis, BTEX aromatics were found to account for about 52.4% and toluene alone for about 21.7% of C₆-C₉ NMHC measured at UMW with the Airmotec HC1010 system (Rappenglück and Fabian 1997). Recent investigations showed that C₆-C₉ NMHC patterns in the urbanized area of Munich are similar to those obtained in other cities worldwide (Rappenglück and Fabian 1999). These findings also suggest that the BTEX fraction of total NMHCs lie in the range that is mentioned in the works of Nelson et al. (1983) and Blake at al. (1993). Lower percentages, such as the ones we found at the rural site EIT, indicate faster degradation processes for these aromatic compounds.

Biogenic NMHCs were not likely to contribute significantly to total NMHCs at the EIT site, at least during this time of the year. Emissions of biogenic NMHC strongly depend on sunlight and temperature (see, e.g., Guenther et al. 1993) and are most likely to occur during the growing season in summer. Investigations carried out over the last decade in coniferous forest areas in southern Bavaria, the most abundant forest type in this region, showed that maximum concentrations of biogenic NMHCs in ambient air occur in the month of August (Kreuzig and Korte 1986; Kreuzig et al. 1986; Schürmann 1993). Recent results from model studies for the area of eastern Germany (Richter et al. 1998) revealed that biogenic NMHC emitted by coniferous forests make up more than 75% of the total biogenic NMHC budget. Ambient air mixing ratios of biogenic NMHC usually display diurnal variations that are different from anthropogenic hydrocarbons (see, e.g., Rappenglück et al. 1999). According to online NMHC results made from 27 July–26 September 1995 in a large coniferous forest east of Munich (Rappenglück and Fabian 1997) mean diurnal variations for toluene, benzene as surrogates for anthropogenic NMHCs, and α-pinene and β-pinene as surrogates for biogenic NMHCs showed that maximum diurnal mixing ratios of both pines occurred during nighttime hours, while toluene and benzene displayed slightly elevated values during the daytime. No correlation between the diurnal behavior of anthropogenic and biogenic NMHCs could be identified. As outlined above, the correlation between toluene and total NMHC at EIT was good regardless of daytime or nighttime data. It is therefore plausible to assume that anthropogenic NMHCs were the most important fraction of total NMHC at EIT during our investigations. This assumption can be supported by taking into account measurements of nitrogen oxides and CO. These species are known to be predominantly emitted by anthropogenic activities in urban areas (e.g., Goldan et al. 1995). Table 2 lists the results of the correlation analysis between BTEX compounds and nitrogen oxides for all three sites. For UMW and EIT there are also correlation analyses for BTEX compounds and CO (at MIM no CO analyzer was installed). In all cases the best relationships exist between BTEX compounds and CO, followed by BTEX compounds and NOₓ. This suggests similar emission sources for BTEX, CO, and NOₓ. Correlation results between BTEX compounds and NO exhibit very different values from NO₂ and NOₓ at all three sites: in all cases correlation coefficients for correlations between aromatic compounds and NO yielded lower values than corresponding correlation analysis for NO₂ and NOₓ. Among the correlation coefficients between BTEX compounds and NO the corresponding values for EIT were the lowest ones. These results can be explained by the short lifetime of NO (about 40 s): sites that are closer to emission sources (e.g., urban sites such as MIM and UMW) will have higher correlation coefficients between NO and anthropogenic NMHCs such as BTEX compounds.

The impact of major emission sources on the rural receptor site can be identified by plotting air pollution roses. Such investigations have been previously published for the EIT site (Rappenglück and Fabian 1997) for the period 2 February–10 July 1993. This dataset comprises more than 5000 samplings (30-min values), which is enough to establish representative air pollution roses. For April and May 1994 no air pollution roses were constructed due to limited datasets. However, assuming that both neither severe climatological nor emission changes took place between 1993 and 1994 the air pollution rose of 1993, as presented in Rappenglück and Fabian (1997), may also apply in 1994. Figure 4 shows the corresponding results both for all samples and for nighttime samples only at the EIT site. From Fig. 4 it is clear that southerly and southwesterly winds transport enhanced levels of aromatic compounds. This is true for all measurements, as well as for nighttime measurements only. In other field studies carried out in the northeastern GMA including the EIT site, it was found that also high amounts of other precursors such as nitrogen oxides were usually associated with southwesterly winds (Suppan et al. 1992; Suppan 1996). By far the major portion of the precursor pool observed at EIT must be attributed to the transport of polluted air masses originating southwest from the urban area of Munich.

Figure 5 gives a survey of various meteorological
Parameters and trace gas mixing ratios obtained at UMW, MIM, and EIT from 28 April to 2 May 1994. The upper two panels reveal that elevated toluene levels at EIT appear when two conditions are fulfilled: (a) the wind direction must be southwesterly (where the urbanized area is located) and (b) toluene peaks at EIT are preceded by corresponding peaks at the urban site UMW. These phenomena usually occur after midnight at EIT. Toluene peaks at EIT usually occur about 2 h later than at UMW and MIM. Mean wind velocity values from 28 April to 2 May 1994 were approximately 2.2 m s⁻¹. As a first-order assumption this corresponds to an upwind distance of about 16 km. This can be regarded as a lower limit for the distance to the urban plume. Calculations were based on meteorological measurements taken on a pole atop of the 30-m hydroelectrical power plant building at EIT. Wind velocity increases with increasing height within the boundary layer. This allows the urban plume to progress faster to the EIT site than the near-surface measurements predict. Thus, it is plausible to assume the GMA as the dominant emission source that affects the EIT site.

Figure 5 also exhibits the times series of secondary compounds. From 28 April to 2 May 1994 there is a continuous day-to-day increase of the diurnal maximum of ozone at all sites, with ozone values at EIT always being the highest each day. This is due to the absence of nearby NO emissions. Better indicators of photochemical processes are PAN, a specific indicator for hydrocarbon driven photochemistry, and Oₓ ([Oₓ] = [O₃] + [NOₓ]) (third and fourth panels in Fig. 5). Maximum Oₓ values do not differ much between UMW and EIT. However, at both sites, photochemical processes become stronger with each passing day from 28 April to 1 May. The lowest panel of Fig. 5 exhibits some selected BTEX ratios. For both sites the time series of toluene/m&p-xylene are plotted. Primarily due to the fast reacting m-xylene, this ratio represents a sensitive marker of photochemistry, where high ratios indicate strong photochemical processes. In Fig. 5 the toluene/benzene ratio is given only for UMW. For the EIT site no data were available for this ratio because the benzene peak could not be evaluated. The toluene/benzene ratio usually is taken as a surrogate for the influence of traffic emissions. At the urban site UMW both BTEX ratios were almost constant throughout the four days. This suggests that, contrary to the EIT site, emission processes were dominant and overcompensating concurrent photochemical processes. By contrast, prevailing photochemical processes would lead to diurnal variations in these BTEX ratios. At first this would apply to the toluene/m&p-xylene ratio, in case of very strong photochemistry also the less sensitive toluene/benzene ratio should be affected. At EIT the results are different than at UMW: significant diurnal variations occurred in the toluene/m&p-xylene ratios. During nighttime the toluene/m&p-xylene ratio was in the same range as observed at UMW for corresponding times, while during the morning this ratio at EIT rapidly increased and then disappeared by noon due to strong photochemistry (at this time the xylene mixing ratios fell below the GC detection limit). This is in contrast to the UMW site where the toluene/m&p-xylene ratio remained unaffected even during the daytime. At EIT photochemical
Fig. 4. Air pollution roses for aromatic compounds at EIT [according to Rappenglück and Fabian (1995)]. Values are given in ppbv. Cases of calm winds, that is, horizontal wind speeds less than 0.2 m s⁻¹, are not considered.
Fig. 5. Time series of meteorological parameters and trace gas mixing ratios at UMW, MIM, and EIT during 28 April–2 May 1994.
processing that consumes hydrocarbon and nitrogen oxide precursors was observed. These processes finally led to the enhancement of secondary compounds, as can be seen on the second and third day: during the morning increases of toluene/m&p-xylene and PAN at EIT occurred concurrently. On these days increasing toluene/p&m-xylene ratios at EIT were always preceded by toluene peaks at UMW. Winds were from the south and southwest, and transport of urban air masses from the area of Munich occurred. The impact of the nocturnal boundary layer also may have favored the enhancement of primary precursors. During the events on 29 and 30 April air masses at EIT during the night were marked by toluene/m&p-xylene ratios that were similar to those concurrently observed at the urban site UMW. Particularly during the nighttime when BTEX compounds are not subject to photochemistry, toluene/m&p-xylene ratios are likely to be similar in the GMA and at EIT. However, the combination of transport of high BTEX precursor mixing ratios from the GMA to EIT and the subsequent photochemistry during the daytime on the same day within the urban plume will affect the BTEX ratios. By contrast, against a low background of BTEX precursors variations of BTEX ratios would not be that effective in terms of NO–NO$_2$ conversion. On the first and the last days there were also increases in the toluene/m&p-xylene ratio; however, there were no increases in the PAN mixing ratios. The main reason for this different behavior was different wind patterns. On the first and last days mainly westerly to northwesterly winds prevailed. Air masses originating from these areas were photochemically aged air masses.

**b. Period II: August 1993**

In August 1993 concurrent BTEX measurements were carried out at UMW and EIT for about a 2-week period. No data were available for the MIM site for August 1993. However, as outlined previously, the UMW site also adequately represented an urban environment. This was demonstrated by the good correlation of toluene between UMW and MIM. Figure 6 shows the time series plots of toluene for UMW and EIT. As in 1994, the peak toluene values at EIT lagged corresponding maximum mixing ratios at UMW. Median diurnal variations of toluene are plotted in Fig. 7. The results of UMW are in good agreement with the median diurnal variations given in Fig. 3 for period I (April–May 1994). The rural site EIT exhibits a diurnal variation that is partly due to the impact of the nocturnal boundary layer. Contrary to EIT, other rural sites in southern Bavaria (Rappenglück and Fabian 1999) show only slight diurnal variations. EIT, however, shows differences between nighttime and daytime values that are even stronger than at UMW. At UMW daytime toluene values are about 50% of the nighttime values, whereas the corresponding values for EIT are less than 20% of the EIT daytime values. Maximum values are always observed during early morning hours. However, rush hour peaks as observed at UMW are not present. As stated before, traffic as a significant nearby emission source can be excluded at EIT. Moreover, the mean toluene/benzene ratio differs significantly between the UMW and EIT sites: for UMW it is 1.9 ± 0.3, whereas for EIT the value is 0.9 ± 0.5. The EIT site is not directly affected by nearby urban traffic emission sources but rather by already photochemically processed air masses. However, the greater standard deviation of 0.5 found at EIT compared to 0.3 calculated for UMW implies stronger temporal variations in the toluene/benzene ratio at EIT than observed at the urban site UMW, suggesting higher toluene/benzene ratios during the night and lower ratios during the day due to solar radiation and the presence of OH.
We will concentrate on two episodes (14–17 August 1993, denoted “episode I” and 19–22 August 1993, denoted “episode II” in Fig. 6). Episode II will be discussed first (Fig. 8). The upper panel of Fig. 8 shows that with the exception of the first day, the wind velocity and wind direction exhibited recurrent diurnal variations. In the early morning hours southerly and southwesterly winds of approximately 1–3 m s$^{-1}$ prevailed. These were ideal conditions for transport of urban air masses from the Munich area. A good example for this feature is the third day: during the daytime, the wind direction steadily moved from southwest to west and northwest. The wind velocity increased at the same time and reached maximum speeds of up to 4 m s$^{-1}$. Trace gases such as ozone, O$_x$, and PAN also exhibited recurrent behaviors from day to day, as can be seen from the third and fourth panels of Fig. 8. Maximum ozone, O$_x$, and PAN values all stayed at about the same level, not showing a day-to-day increase. Moreover, their diurnal shapes did not change very much. The BTEX ratios (lowest panel in Fig. 8) at UMW exhibited constant values for both toluene/benzene and toluene/m&p-xylene, similar to the results plotted in Fig. 5. At EIT, pronounced variations in these ratios were observed. During the daytime the toluene/benzene ratio decreased. The toluene/m&p-xylene ratio existed at least during the nighttime. During the daytime, however, this ratio rapidly disappeared because at this time the m/p-xylene mixing ratios fell below the GC detection limit. This rapid depletion of the m/p-xylene isomer is most likely to be attributed to strong photochemistry. Interestingly, during episode II nighttime values of BTEX ratios at EIT were always of the same order as found at the urban site UMW. This may be expected because wind patterns were constant overnight and suggested Munich as the origin of the air masses arriving at EIT. In addition, photochemical degradation of the BTEX compounds did not take place at this time of the day, thereby leaving BTEX ratios unaffected en route to EIT. Episode II can be regarded as a reference episode because no significant change in maximum ozone values occurred from day to day.

Episode I [14–17 August 1993 (Fig. 9)], however, is marked by strong variations in all parameters. Only the second day results are comparable to the reference episode. The other days exhibited different wind patterns, and thus, photochemical processes at both sites were decoupled and no source–receptor relationships can be established. Even on the last day when southwesterly winds occurred at least sometimes at EIT, the conditions were not ideal for observing urban plume effects at EIT. On 16 August there were only slight increases in toluene mixing ratios compared with the day before because no prominent preceding toluene peak appeared at UMW. The urban plume at EIT was not well pronounced on this day. Photochemical developments at EIT and UMW occurred independently. It is important to note that throughout episode I the BTEX ratios showed pronounced variations at both sites, indicating prevailing photochemical processes. Strong photochemical processes occurred even at the urban site UMW: high ozone and in particular high PAN values were observed. These photochemical processes were reflected by the variations in the BTEX ratios, that is, strong photochemistry overcompensated emission processes at this site. Also, at the EIT site ozone values were high; maximum PAN values, however, were relatively low compared to the UMW site. No significant day-to-day increases in max-

![Figure 7: Median diurnal variations of toluene at UMW and EIT from 12 to 26 August 1993, respectively. Bars indicate standard deviations.](image-url)
Fig. 8. Time series of meteorological parameters and trace gas mixing ratios at UMW and EIT during 19–22 August 1993 (episode II).
Fig. 9. Time series of meteorological parameters and trace gas mixing ratios at MIM, UMW, and EIT during 14–17 August 1993 (episode I).
imum ozone or O₃ mixing ratios were observed at the EIT site during the episode. During episode I the diurnal rise from nighttime to daytime ozone mixing ratios at both sites were usually accompanied by increases in the toluene/m&p-xylene ratios and decreases in toluene/benzene ratios due to daytime photochemistry (again, during daytime toluene/m&p-xylene ratios at EIT rapidly dissipate due to the fact that m/p-xylene mixing ratios fell below the GC detection limit). On the second day of episode I the diurnal maximum of O₃ was almost the same at EIT and UMW, indicating the same photochemical activity of the air masses at least with regard to ozone formation. However, this need not apply to PAN formation in the same way. According to Bowman and Seinfeld (1994) ozone and PAN formation depend in a different way on NMHC/NOₓ ratios and the NMHC mixture that is currently encountered in a given air mass. These parameters usually change with time and space. On the journey between urban areas where emission sources are located to rural areas, NMHC/NOₓ ratios tend to increase and the NMHC mixture changes according to the reactivity and the abundance of the individual species. NMHCs with high mixing ratios and low reactivity will have the longest life times and may experience long-range transports. Calculations by Bowman and Seinfeld (1994) showed in particular that aromatic NMHCs will favor PAN formation instead of ozone formation regardless of different NMHC/NOₓ ratios. However, maximum PAN formation fostered by aromatic compounds will occur at low NMHC/NOₓ ratios usually found in urban areas. During episode I, 15 August 1993 represents the only day when PAN mixing levels at EIT were significantly enhanced compared to other days of the episode. In addition, the second day was the day where a source–receptor relationship could be established: during early morning hours southwesterly winds transported the urban air masses marked by typical urban values of the toluene/benzene ratio to the rural site EIT. Moreover, 15 August is the only day during this episode when elevated toluene mixing ratios at EIT were preceded by maximum toluene values at UMW. Thus it may be concluded that under the influence of the urban plume aromatic compounds favor the formation of PAN, whereas the level of O₃ remains relatively unchanged.

4. Conclusions

An analysis of the first concurrent GC/FID measurements of aromatic compounds ever made in the greater Munich area showed that nearby rural areas are affected by elevated mixing ratios of secondary compounds when an urban plume is carried over these areas. Using BTEX mixing ratios, measurements of primary compounds (nitrogen oxides, CO, total NMHC) and selected BTEX ratios (toluene/benzene and toluene/m&p-xylene) it was found that urban air masses were transported to rural areas and led to enhanced formation of secondary compounds during the daytime. Photochemical smog episodes at urban and rural sites located in the GMA were always preceded by elevated toluene mixing ratios. Toluene is a prominent surrogate for anthropogenic NMHC. It is suggested that aromatic compounds have an important impact on the formation of PAN in the GMA. This is supported by the concurrent observations of elevated BTEX mixing ratios and simultaneous daytime increases of both the toluene/m&p-xylene ratio and PAN mixing ratios. It demonstrates that BTEX compounds, in particular fast-reacting xylenes, play an important role in the photochemical smog formation on a regional scale. Specific reduction in BTEX emissions could be an important contribution in future ozone and PAN abatement strategies in urban areas.

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