

Quasi-continuous measurements of hydrocarbon immissions

B. RAPPENGLÜCK, Freising-Weihenstephan

Summary. Within the framework of the research programme titled "Air pollution and human health" the Lehrstuhl für Bioklimatologie und Immissionsforschung (LfBIM) is responsible for the subproject "Measurements of various hydrocarbons being precursors for photooxidants of human-bioclimateological relevance" (KOVVOX). Priority is given to the measurements of aromatics of anthropogenic origin such as benzene, toluene, ethylbenzene and *m*-/*p*-/*o*-xylenes (BTEX) which play an important role in photochemical processes. In addition some of these species are regarded to be hazardous to human health. The investigations are carried out on a quasi-continuous basis by two different gas-chromatographic systems that make it possible to obtain on-line 30-minute averages of the hydrocarbon concentrations in ambient air. One system is installed in a mobile laboratory which is used for campaign measurements at various places in southern Bavaria. The other gas-chromatograph is set up at a stationary measurement site in the vicinity of the institute and serves as a reference. At both measurement facilities additional air chemical (NO_x , CO, SO_2 , ozone, PAN) and meteorological data is provided by other research programmes of the LfBIM. This enables comprehensive investigations of photochemical processes and their potential effects on human health. First results of two different measurement sites will be described in details.

Quasi-kontinuierliche Messungen von Kohlenwasserstoffimmissionen

Zusammenfassung. Im Rahmen des Forschungsvorhabens „Luftverunreinigung und menschliche Gesundheit“ zeigt sich der Lehrstuhl für Bioklimatologie und Immissionsforschung (LfBIM) verantwortlich für die Durchführung des Unterprojektes „Erfassung verschiedener Kohlenwasserstoffe als Vorläufersubstanzen für human-biometeorologisch relevante Photooxidantien“ (KOVVOX). Der Schwerpunkt wird hierbei auf die Messung von aromatischen Verbindungen anthropogenen Ursprungs wie Benzen, Toluol, Ethylbenzen und *m*-/*p*-/*o*-Xylen gelegt. Diese spielen eine wichtige Rolle in photochemischen Prozessen. Überdies werden einige von ihnen als gesundheitsschädlich angesehen. Die Untersuchungen werden mittels zweier verschiedener gaschromatographischer Systeme, die es ermöglichen, quasi-kontinuierlich 30-Minuten Mittelwerte der Kohlenwasserstoff-Konzentrationen in der Umgebungsluft on-line zu erhalten, durchgeführt. Ein System ist in einem mobilen Meßlabor, welches für Meßkampagnen an verschiedenen Orten in Südbayern herangezogen wird, untergebracht. Der andere Gaschromatograph ist an einer festen Station in der Nähe des Institutes aufgestellt und dient als Referenz. An beiden Meßstellen stehen zusätzliche luftchemische (NO_x , CO, SO_2 , Ozon, PAN) und meteorologische Daten anderer Forschungsvorhaben des LfBIM zur Verfügung. Dies ermöglicht umfassende Untersuchungen photochemischer Prozesse und ihrer möglichen Auswirkungen auf die menschliche Gesundheit. Erste Resultate von zwei verschiedenen Meßorten werden im Detail beschrieben.

1 Introduction

In the development of photochemical smog episodes non-methane volatile hydrocarbon compounds (VOCs) play a crucial role in the formation of photooxidants such as ozone and PANs (FINLAYSON-PITTS and PITTS 1986). This mechanism was investigated in several smog chamber experiments and applied in various model calculations (e.g. ANDERSSON-SKÖLD et al. 1992, HOUGH and DERWENT 1987). Up to this moment there already exist results of hydrocarbon measurements throughout the world (CHAMEIDES et al. 1992), but there is a lack of on-line hydrocarbon measurements for longer periods. For this purpose a more sophisticated measurement technique is required that allows to detect a variety of VOCs with a low detection limit at reasonable time resolutions in order to be compared with other air chemical and meteorological data. To our knowledge only a few measurements have met these requirements so far (STAEHELIN et al. 1991, BAYER, LANDESAMT F. UMWELTSCHUTZ 1991, DOMMRÖSE and FIGGE 1988).

Hydrocarbons consist of different classes with specific properties regarding their origins, chemical structure, chemical reaction pathways, reaction kinetics, atmospheric mixing ratios and atmospheric life-times. In our investigations we paid special attention to the aromatics benzene, toluene, ethylbenzene and the *m*-/*p*-/*o*-xylenes, the so-called BTEX-compounds.

The importance of the BTEX-hydrocarbons which are mainly of anthropogenic origin (FIELD et al. 1992) is partly based on their reactivity to the OH-radical. Among the hydrocarbon classes the reactivity of the aromatics is in the medium-range only. But in contrast to many other hydrocarbons that contain double-bonds such as highly reactive alkenes and terpenes the aromatics do not take part in additional reactions with ozone (WARNECK 1988). Moreover the BTEX-species may be encountered in sufficient concentration levels in ambient air even in rural areas (KHALIL and RASMUSSEN 1992, ISIDOROV 1990), so that they can have an effective influence on photochemical processes.

Regarding the medical aspects of the aromatics in question, besides their role in producing photooxidants of human-bioclimateological relevance, they may in itself display hazardous effects on human health (BRODZINSKY and SINGH 1983). Especially benzene is well known for its cancerous property and is likely to be controlled by future governmental regulations in Germany.

At present the University of Munich pursues an interdisciplinary study that is part of the research programme "Air pollution and human health". Within this framework the Lehrstuhl für Bioklimatologie und Immissionsforschung (LFBIM) works on two projects, "Measurements of human-biometeorological relevant photooxidants in a conurbation" (PHOTOX) (JAKOBI et al. 1993) and "Measurements of various hydrocarbons being precursors for photooxidants of human-bioclimateological relevance" (KOVOX) (RAPPEGLÜCK and FABIAN 1993).

These results are the basis for the interpretation of medical data obtained by the study of the Institute and Outpatient Clinic of Occupational Medicine "Effects of elevated ozone concentrations on the lung function of different groups of the population" (OLIM) (HÖPPE 1993).

Various measurements sites in southern Bavaria were chosen which should be as close as possible to the locations where the test persons live or work. For these measurements campaigns a mobile laboratory was used. For the longer-extended reference measurements of the hydrocarbon species a stationary site in the vicinity of the LFBIM was chosen.

This paper reports first results of BTEX-measurements obtained at the stationary measurement site as well as at one location of the measurement campaign.

2 Experimental setup

For measuring hydrocarbons two different commercially available gas-chromatographic-systems were used. In the mobile laboratory a gaschromatograph HC1010 developed by Airmotec AG was installed, whereas at the stationary measurement site the gas-chromatographic-system RGC202 (Siemens AG) was set up.

In both cases principally the same measurement technique was applied: quasi-continuous air-sampling, followed by a double-stage preconcentration procedure on adsorbent and a cryofocusing step of the sample. Afterwards the compounds are rapidly thermally desorbed and injected into a specific column for temperature-programmed separation of the different hydrocarbon species. Finally they are detected by a flame-ionisation-detector (FID) and identified by the compounds individual retention times.

The measurement procedure can be divided into two pathways: the preconcentration and the desorption pathway. Both are integrated in these instruments and performed for two air samples independently at the same time: whilst one air sample is adsorbed the other one is thermally desorbed and gas-chromatographically analyzed.

Differences between the instrumentations exist in their hardware configurations (size, weight, power and maintenance requirements) and in their analytical capabilities (detection limit, range of the VOC-spectrum, separation capabilities). Further information about the gas-chromatographic systems are given elsewhere (RAPPEGLÜCK and FABIAN 1993, RIEMSCHNEIDER 1992).

Calibration procedures were performed with gas-cylinders

containing specified volume mixing ratios of BTEX-aromatics (RAPPEGLÜCK and FABIAN 1993).

The additional analyzers for the other trace substances and the meteorological instrumentation is described in details by other authors (JAKOBI et al. 1993, SUPPAN and FABIAN 1993).

3 Measurement sites

Measurements described in this paper were carried out at two locations, the Ebersberger forest area (1 April–18 April 1993 and 29 May–22 June 1993) and near the village Eitting (11 February–22 June 1993) in the vicinity of the LFBIM.

The Ebersberger forest has an extension of approx. $15 \times 15 \text{ km}^2$ and lies about 25 km to the east of the Munich agglomeration area. It is an almost homogeneous forest and mainly consists of spruce trees. The measurement site itself was located in a spacious clearing. In the south-eastern part of this clearing at a distance of 100 m away from the measurement site there is situated a small open-air restaurant that is mainly visited by excursionists on Sundays and festival days during the warmer summer period. Therefore limited traffic at the parking lot must be taken into account on a few days especially during the late afternoon and evening. But on the whole in most cases this measurement site can be considered as an almost unpolluted forest site where it is possible to investigate specific effects regarding the chemistry and meteorology in a forest area. At times these effects may be superimposed by lee side effects of the urban area of Munich.

At the small village Eitting the reference measurement site was set up in a vacant room of a hydroelectrical power station. Air samples were taken at the third floor (15 m height above ground level) the meteorological parameters were measured at the roof (20 m above ground level). The power station is located in the vicinity of the new Munich airport (approx. 5 km to the west). In the close surroundings there are no significant emitters to the south and to the west. In the north a small road (500 m away from the site) runs to the village Eitting that is situated in the east of the power station. Some traffic can be observed during the morning and evening hours.

4 Results

In this section three examples of significant diurnal variations of the BTEX-hydrocarbons in conjunction with other relevant trace gas species will be described.

4.1 Site Ebersberger forest

Fig. 1 depicts the diurnal variation of the chemical compounds on 4 April 1993. On this day the general weather situation exhibited only weak pressure gradients. In the course of the day some bright periods occurred during the

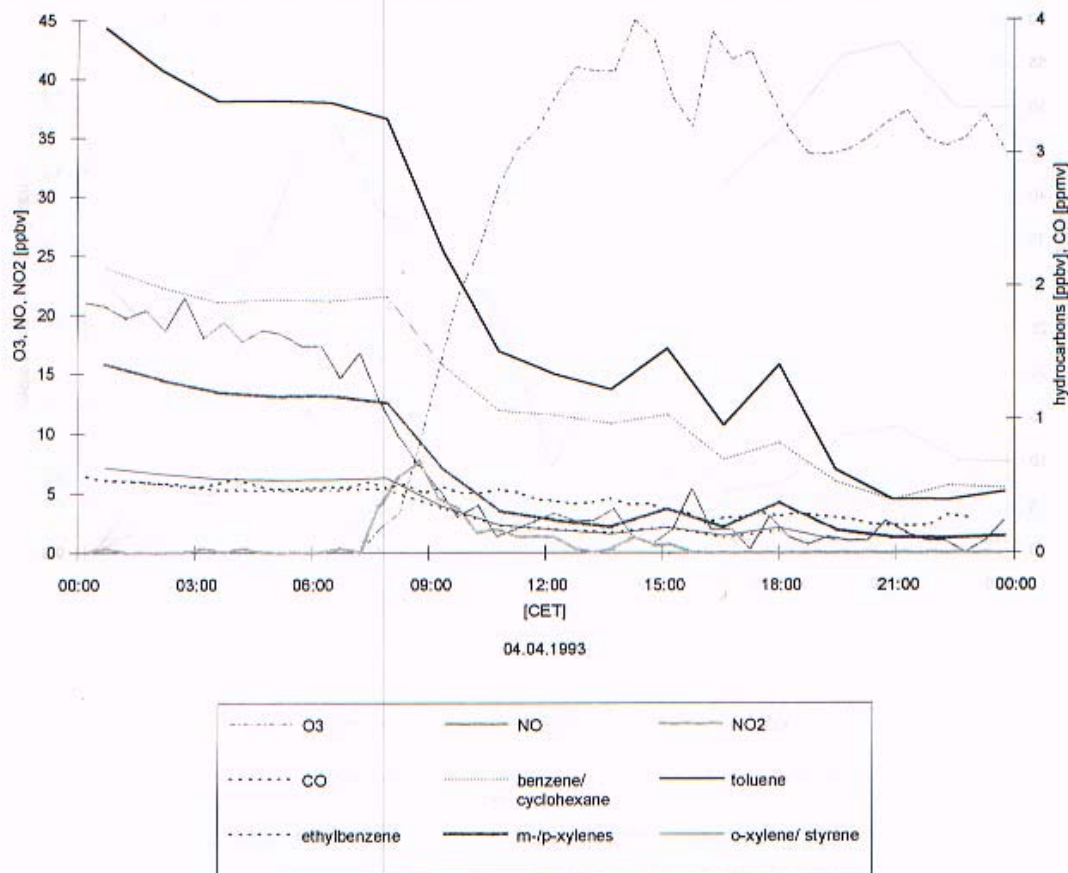


Fig. 1. Temporal variation of the mixing ratios of hydrocarbons along with ozone, NO, NO₂ and CO at the measurement site Ebersberger forest on 4 April 1993 (30-min averages).

Abb. 1. Zeitlicher Verlauf der Mischungsverhältnisse von Kohlenwasserstoffen zusammen mit Ozon, NO, NO₂ und CO an der Meßstelle Ebersberger Forst am 4. April 1993 (30-min Mittelwerte).

morning hours. In the afternoon weather patterns changed slightly, the formerly southerly winds turned to west and wind velocities reached 6 m/s. Some rain could be observed for a short time during this time of the day. The highest temperature achieved almost 10 °C.

On account of the low wind velocities photochemical processes are dominant in the beginning. All the primary substances decrease almost simultaneously throughout the day. Regarding the BTEX-species toluene is the predominant aromatic followed by benzene and both m-/p-xylene isomers. Ethylbenzene and o-xylene have the lowest mixing ratios of the investigated hydrocarbons and exhibit quite similar diurnal variations. Relevant information about the hydrocarbons specific reactivity to the OH-radical may be indicated by the slope of the BTEX-decay in the morning hours. Toluene appears to diminish more rapidly than benzene and m-/p-xylene. In the late evening benzene that is supposed to have the lowest chemical reactivity of the hydrocarbons investigated has about the same mixing ratio as toluene. Shortly after sunrise at 9.00 h the sharpest decline

of these substances appear. Synchronously this gives rise to an NO₂-peak by the oxidation processes of NO and the VOC. In consequence a rapid increase of the ozone mixing ratio begins. Further diminishing of the primary species including NO that plays an important role in the destruction mechanism of ozone can be observed from late afternoon on. This effect may be considered as a dilution effect on account of the growing wind velocity. This phenomena is also reflected in the behaviour of ozone that remains on a relatively high level for the lack of NO, especially in the evening and night. Similar dependencies of ozone on wind velocity were already investigated in more details in the Munich area (RAPPEGLÜCK et al. 1993).

Another example for simultaneous photochemical decay of BTEX-hydrocarbons and enhancement of ozone may be illustrated in Fig. 2 depicting the diurnal variations of these relevant species on 11 June 1993:

On this day overall summer conditions could be observed caused by a high-pressure situation over southern Germany. There were mostly sunny skies and the tempera-

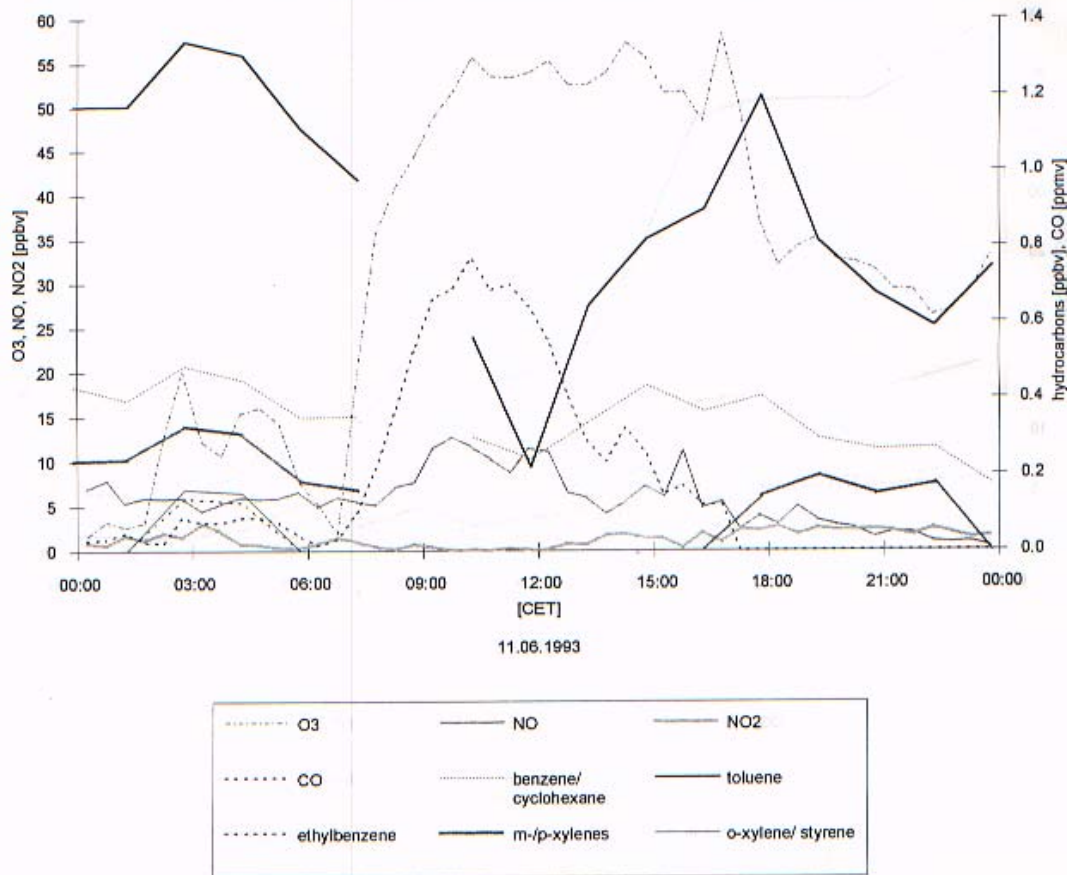


Fig. 2. Temporal variation of the mixing ratios of hydrocarbons along with ozone, NO, NO₂ and CO at the measurement site Ebersberger forest on 11 June 1993 (30-min averages).

Abb. 2. Zeitlicher Verlauf der Mischungsverhältnisse von Kohlenwasserstoffen zusammen mit Ozon, NO, NO₂ und CO an der Meßstelle Ebersberger Forst am 11. Juni 1993 (30-min Mittelwerte).

ture rose to more than 25 °C. The wind pattern showed no significant preferences for certain directions. With the exception of some strong westerly winds during a thunder storm event in the evening the wind velocity did not reach more than 3 m/s throughout the day. On the whole the diurnal variation for the chemical compounds are rather influenced by photochemical processes and the diurnal variations of the height of the inversion layer than by wind direction and wind velocity.

Therefore a distinct diurnal variation in the mixing ratios of the chemical compounds can be seen for most of them. In accordance to the features mentioned for the 4 April 1993 there is a significant photochemical decay of most of the aromatics. With the exception of toluene and benzene their concentration even fall below the detection limit. Benzene hardly shows any diurnal variation. Perhaps this is another hint to the low reactivity of benzene. In contrast to the 4 April other precursors such as NO and CO do not reflect the same diurnal variation as the BTEX-hydrocarbons. Their maximum values are reached at a time of the day when

most BTEX have their minimum mixing ratios. Therefore no correlation between BTEX and at least CO can be found at this forest measurement site as it can be observed in the vicinity of typical anthropogenic pollution sources (HAUSTEIN von HAUSTENAU 1993).

4.2 Site Eitting

For this measurement site an example of an episode lasting three days was chosen for demonstrating the possible impact of BTEX-hydrocarbons on the formation of photo-oxidants (Fig. 3). In this investigation PAN-measurements could be included. Moreover it was possible to obtain more detailed information about the m-/p-xylene isomers, because the Siemens gas chromatograph made an analytical separation of these compounds feasible.

During these three days the meteorological situation was determined by the formation of a high-pressure situation over Germany. Still the first day is influenced by the weather

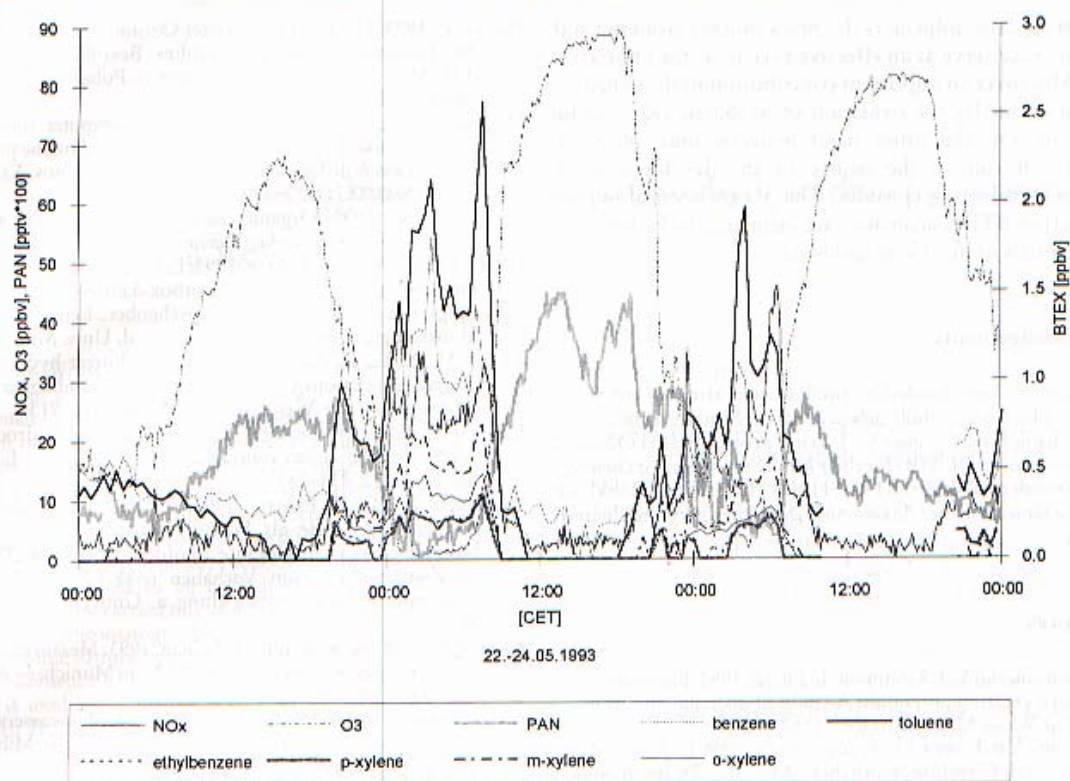


Fig. 3. Temporal variation of the mixing ratios of BTEX-hydrocarbons along with ozone, PAN and NO_x at the measurement site Eitting in the period 22–24 May 1993 (30-min averages for BTEX, apart from that 10-min averages).

Abb. 3. Zeitlicher Verlauf der Mischungsverhältnisse von BTEX-Kohlenwasserstoffen zusammen mit Ozon, PAN und NO_x an der Meßstelle Eitting im Zeitraum 22.–24. Mai 1993 (30-min Mittelwerte für BTEX, ansonsten 10-min Mittelwerte).

patterns of the rear side of a cold front that crossed southern Germany the day before. In the course of the three days the wind turned from formerly north-westerly directions to east and became weaker. Only on the first day the stronger winds influence the mixing ratios of the chemical compounds leading to smoother diurnal variations in the beginning of this episode, especially for the precursors. From the second day on there were mostly sunny skies, but the temperature only reached values about 20 °C.

As far as the chemical compounds are concerned the maximum values for the photooxidants are observed on the second day, although the meteorological conditions are supposed to be most favourable on third day (e.g. higher temperature). Regarding the mixing ratios of the relevant precursors their highest concentrations in ambient air are found in the night preceding the day with maximum ozone and PAN values. This may emphasize the precursors role during this episode. Similar to the examples mentioned above a sharp decline of the BTEX-aromatics takes place shortly after sunrise. At the same time the mixing ratios of ozone and PAN start to increase. Once again toluene is the predominant aromatic at least during the night. This is changed profoundly after sunrise. Quickly afterwards the

concentrations of almost all aromatics fall below the detection limit. Only benzene still can be found in ambient air and remains predominant during day time. Regarding ethylbenzene and the xylene isomers a certain order of their concentration levels can be discerned. The highest mixing ratios can be observed for m-xylene followed by o-xylene. P-xylene and ethylbenzene show the lowest concentration values. Moreover they are about the same order. It is important to note that mixing ratios of m-xylene that is supposed to be the most reactive xylene isomer (KILLUS and MOORE 1991) are almost double the corresponding values of p-xylene.

5 Conclusion

1. The aromatic hydrocarbons benzene, toluene, ethylbenzene and m-/p-/o-xylenes (BTEX) were measured at two different measurement sites in the vicinity of the Munich urban area in southern Bavaria. According to first results demonstrated by some episodes the BTEX-compounds seem to take part effectively in photochemical processes even in areas that are more distant to primary emitters.

2. In all cases toluene is the predominant aromatic and therefore may serve as an effective precursor for photooxidants. Moreover an important contribution to the enhancement of ozone by the oxidation of m-xylene may not be ruled out. On the other hand benzene only plays an insignificant role in the course of the development of photochemical smog episodes. The photochemical impact of the other BTEX-aromatics are estimated to be between the potentials of m-xylene and benzene.

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Dipl.-Met.

BERNHARD RAPPEGLÜCK

Lehrstuhl für Bioklimatologie

und Immissionsforschung der

Ludwig-Maximilians-Universität

München

Hohenbachernstr. 22

D-85354 Freising-Weihenstephan

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