

# Determination of Benzo[a]pyrene Diones in Air Particulate Matter with Liquid Chromatography Mass Spectrometry

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The formation of the benzo[a]pyrene (B[a]P) diones (B[a]P-1,6-dione, B[a]P-3,6-dione, B[a]P-6,12-dione) as the main products of oxidative degradation of B[a]P has been observed under atmospheric conditions in air particulate matter. Samples were collected at two different sites in Munich, Germany. Total B[a]P dione concentrations were determined by APCI/LC–MS and ranged between 8 and 605  $\text{pg m}^{-3}$ . The formation of the direct mutagen B[a]P-epoxide was not observed. B[a]P dione concentrations did not correspond with B[a]P and total carbon concentrations, but showed a correlation with solar irradiation. B[a]P dione concentrations were higher on daytime filters compared to filters collected during the night. Lower concentrations of B[a]P diones were observed at the site with higher traffic contributions, suggesting a major role of atmospheric transport. Rapid, high-volume sampling indicates that the B[a]P dione formation is not dependent on B[a]P concentrations, but on photochemical conditions.

## Introduction

Polycyclic aromatic hydrocarbons (PAH) are known as strong, ubiquitous carcinogens and mutagens, formed by natural diagenetic processes or anthropogenic (e.g., burning of fossil fuels in power and heat generation, industry, or traffic) processes (1). PAHs occur in fossil fuels, tobacco smoke, sediments, automobile exhausts, and airborne particulates (2–5). Among the PAHs, benzo[a]pyrene (B[a]P) has been studied extensively because of its strong carcinogenicity (IARC). Particle-adsorbed B[a]P formed in combustion processes is exposed to a variety of gaseous pollutants in urban atmospheres. The degradation of PAH in the troposphere can lead to toxic derivatives which contributes to the carcinogenic potential of particulate organic matter (POM). These compounds are formed in gas phase or heterogeneous processes by nitrogen oxides, ozone, hydroxy radicals, or solar irradiation. Among these possible degradation pathways, the reaction of PAH with  $\text{NO}_x$  has been studied the most; by far less data are available on the influence of ozone, radical reactions, or solar irradiation. The pattern of polar degradation products of PAH collected near the emission

sources is somewhat different from extracts of particles collected from ambient air. During the atmospheric transport, chemical reactions between the organic components and gaseous pollutants change the composition of the organic phase of tropospheric particles.

Despite the fact that considerable investigations on the degradation of B[a]P under simulated atmospheric conditions have been made (6–8), there is a lack of knowledge about the composition and fate of B[a]P degradation products adsorbed on particles under atmospheric conditions. The B[a]P degradation by ozone or irradiation leads to B[a]P quinones (B[a]P-1,6-dione, B[a]P-3,6-dione, B[a]P-6,12-dione) as the main products (6, 9, 10). They can be considered as oxygenated PAH intermediates that undergo further degradation. This compound class is of concern because of their genotoxic effects. The occurrence of B[a]P diones in suspended particulate matter has been reported (11–15), but investigations of atmospheric degradation products of B[a]P over a longer period with regard to atmospheric conditions have not been made yet.

It has been demonstrated that the LC–MS technique is a very sensitive tool for the determination of B[a]P derivatives (11, 12), in particular for B[a]P-diones, which cannot be quantified satisfactorily by GC–MS because of their low volatility. In this paper we report about the determination of B[a]P diones, using LC–MS, as the main degradation products of B[a]P in air particulate matter. The aim of this work was to prove the applicability of LC–MS for the analysis of polar degradation products of particle-bound B[a]P and to examine different atmospheric conditions that could be important for the formation of polar degradation products such as the analyzed B[a]P diones.

## Experimental Section

**Materials.** HPLC-grade water, methanol, dichloromethane, and ethyl acetate were obtained from Merck (Darmstadt, Germany). Benzo[a]pyrene was obtained from Sigma (St. Louis, MO). B[a]P-1,6-dione, B[a]P-3,6-dione, B[a]P-6,12-dione, B[a]P-7,10-dione, and B[a]P-4,5-epoxide were purchased from Midwest Research Institute (Kansas City, MO). Triphenylene was obtained from Ehrenstorfer (Augsburg, Germany).

**Apparatus.** LC was performed with a Hewlett-Packard 1090 liquid chromatograph (Palo Alto, CA). A Rheodyne injector (Cotati, CA) 7125 equipped with a 20  $\mu\text{L}$  loop was used. For the LC separation, a Nucleosil (4.0  $\times$  125 mm, 3  $\mu\text{m}$ ) RP 18 column (Macherey & Nagel, Düren, Germany) with a (4.0  $\times$  17 mm) precolumn of the same material was used. Methanol/water (85:15, v/v) was used as the eluent with a flow rate of 1  $\text{mL min}^{-1}$ .

**Atmospheric Pressure Chemical Ionization (APCI).** A VG platform from Fisons Instruments (Manchester, U.K.) equipped with a standard atmospheric pressure ionization (API) source was used. The APCI interface consists of a heated nebulizer probe and a standard atmospheric pressure source equipped with a corona discharge pin. The source and probe temperatures were set to 180  $^{\circ}\text{C}$  and 500  $^{\circ}\text{C}$ , respectively. The corona discharge voltage was 2.5 kV, the cone voltage was 20 V, and the HV lens voltage was set to 0.2 kV. Analysis was performed in single ion recording (SIR) mode with  $m/z = 282$ .

**Capillary Gas Chromatography Mass Spectrometry.** A Fisons GC 9000 gas chromatograph (Micromass, Manchester, U.K.) connected to a Fisons MSD 800 mass selective detector was used for the B[a]P analysis, 30 m  $\times$  0.25  $\mu\text{m}$  i.d. (0.25  $\mu\text{m}$

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film thickness) HP-5 column (Hewlett-Packard, Palo Alto, CA). The MS was operated in the electron impact mode with an electron energy of 70 eV. SIR was performed with  $m/z = 252$ . The initial oven temperature was 150 °C, immediately ramped to 310 °C at 10 °C/min and held for 10 min. The temperature of the splitless injector and the GC-MS interface was 270 °C. The injection volume was 1  $\mu$ L.

**Capillary Gas Chromatography High-Resolution Mass Spectrometry.** A Hewlett-Packard HP 5890 Series II gas chromatograph (Hewlett-Packard, Palo Alto, CA) was connected to a VG AutoSpec mass spectrometer (Micromass, Manchester, U.K.) with a resolution of 10 000 using a 60 m  $\times$  0.25  $\mu$ m i.d. (0.25 mm film thickness) DB-5 column (J&W Scientific, Folsom, CA). The MS was operated at the electron impact mode with an electron energy of 40 eV and a trap current of 800  $\mu$ A. A mass scanning range of  $m/z = 100-350$  was set at 1.1 scan/s. The carrier gas used was ultrahigh purity helium (grade 5.6). The initial oven temperature was 90 °C, immediately ramped to 220 °C at 15 °C/min and to 310 °C at 2 °C/min and held for 20 min. The temperature of the splitless injector and the GC-MS interface was 270 °C.

**Sample Collection and Preparation.** Real samples of particulate matter were collected on kiln-fired (450 °C for 12 h) glass fiber filters (GF/C Whatman, Springfield Mill, U.K.) with a low-volume sampler GS 050 (Derenda, Berlin, Germany) at a flow rate of 2.3 m<sup>3</sup> h<sup>-1</sup>. High-volume samples were collected on glass fiber filters (Macherey & Nagel, Düren, Germany) with a high-volume sampler (Staplex TFIA2, Brooklyn, NY) at a flow rate of 36 m<sup>3</sup> h<sup>-1</sup>. All samplers were placed on a container at a height of three meters.

Samples in wintertime at Grosshadern were collected for 24 h; samples in summertime at Grosshadern and Luise-Kiesselbach-Platz were collected for 11.5 h. High-volume samples at Luise-Kiesselbach-Platz were collected for 1 h.

Triphenylene was used as internal standard for B[a]P (25 ng per filter), and B[a]P-7,10-dione was used as internal standard for the B[a]P diones (5 ng per filter) and added on the filters after collection. The recoveries of the four B[a]P-diones were checked by analysis of spiked soot filters and found to be almost quantitative (90–95%). The occurrence of B[a]P-7,10-dione was not observed in POM. The compound is formed only in the enzymatic metabolism under physiological conditions. Filters were extracted in 4 mL dichloromethane (low volume filters) or 50 mL dichloromethane (high volume filters) in an ultrasonic bath for 15 min. The extracts were evaporated to dryness by a gentle stream of nitrogen, and the residue redissolved in 50  $\mu$ L ethyl acetate.

Particle distributions were characterized with a commercial differential mobility particle sizer (DMPS), which combines an electrostatic classifier (EC) (TSI model 3071, TSI Inc., St. Paul, MN) and an ultrafine condensation particle counter (UCPC) (TSI model 3025). The ozone concentration was measured with a commercial O<sub>3</sub> analyzer based on an UV absorption based system (Ansyco, Karlsruhe, Germany). Elemental carbon data were obtained with a coulometer after combustion (Coulomat 702 DR/C, Ströhlein, Karst, Germany) according to a German standard guideline (16). Two identical filters were collected for the analysis of the organic compounds and the carbon data, respectively.

Black carbon measurements were carried out with an aethalometer (GIV, Breuberg, Germany). Specific absorption coefficient data (12.5 m<sup>2</sup> g<sup>-1</sup> for Grosshadern and 15.4 m<sup>2</sup> g<sup>-1</sup>) for the correction of black carbon were obtained by coulometry.

## Results and Discussion

**Analytical Procedure.** For the analysis of PAH in environmental samples, often GC-MS is used. However, problems can occur with more polar degradation products. Thermally

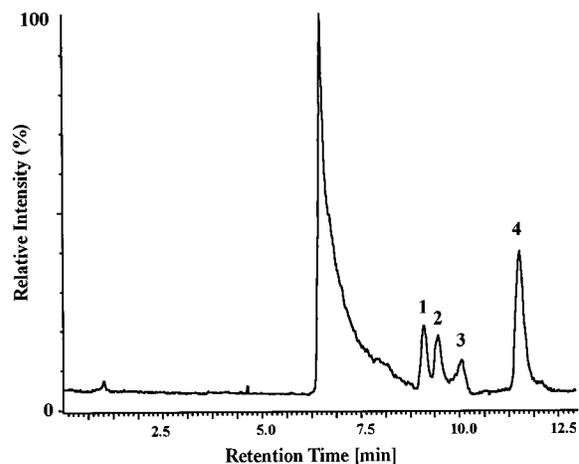


FIGURE 1. Detection of the B[a]P diones in real samples of air particulate matter with APCI/LC-MS. (1) B[a]P-3,6-dione, (2) B[a]P-1,6-dione, (3) B[a]P-6,12-dione, (4) B[a]P-7,10-dione (internal standard).

unstable compounds can undergo decomposition or very polar substances are trapped by the stationary phase material of common gas chromatography columns. In the case of the B[a]P-diones, poor detection limits at the low nanogram range and a small dynamic range were observed with GC-HRMS. This is due to the low volatility of these compounds, which is indicated by their high melting points of 261 °C (B[a]P-7,10-dione), 278 °C (B[a]P-1,6-dione), 282 °C (B[a]P-3,6-dione), and 315 °C (B[a]P-6,12-dione) with subsequent decomposition. The responses of the different isomers decrease in this order.

By application of APCI/LC-MS, the detection limits of the B[a]P-diones are 2 to 3 orders of magnitude lower compared to those of GC-MS (11), i.e., in the low picogram range. Recent experiments show that the use of the newest LC-MS instruments with orthogonal interface orientation leads to an even better sensitivity by increasing the signal-to-noise ratio by a factor of 5. In contrast to electron impact ionization (EI), only molecular ions are observed. The HPLC separation was performed with an isocratic elution of methanol/water (85:15). The matrix is sufficiently separated from the analytes (see Figure 1). Thus, no previous fractionation or cleanup of the filter extracts is required.

The presence of the direct mutagen B[a]P-4,5-epoxide, which was reported to be present in filter extracts in laboratory experiments of ozonolysis of B[a]P (17), was not confirmed in the filter extracts despite a detection limit of 10  $\mu$ g m<sup>-3</sup>. This supports results which report that the formation of the epoxide is only observed in the presence of a dioxirane formed in the reaction of tetramethylethylene with ozone (18).

The developed LC-MS method provides good sensitivity with the possibility of rapid sample preparation and analysis time.

**Sampling Location and Procedure.** Two sampling campaigns have been carried out for several weeks in February 1997 and July 1997 at two sampling sites in Munich, Germany, to consider different meteorological and seasonal conditions. The two sampling sites represent also different air pollution conditions. Sampling site Munich-Grosshadern is situated at the southwestern outskirts of Munich, characterized by air masses from rural areas in the southwest and west of Munich. The sampling site Luise-Kiesselbach-Platz is a heavily polluted junction in Munich, where one highway, two city highways, and three city roads cross. It is dominated by fresh particle emissions with only minor contributions coming from other sources. In Figure 2, the influence of the

Munich-Grosshadern

Luise-Kiesselbach-Platz

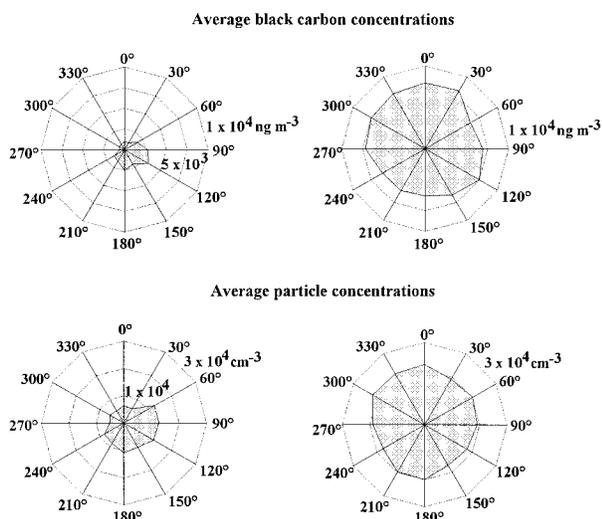


FIGURE 2. Correspondence of black carbon and particle concentration with wind direction at both sampling sites. Higher concentrations at Munich-Grosshadern are observed with south-eastern winds, whereas Luise-Kiesselbach-Platz as a high polluted site with a lot of fresh emissions shows no relation to wind direction.

wind direction on black carbon and particle concentration is demonstrated. The data for the sampling site Luise-Kiesselbach-Platz show that these parameters are independent of wind direction and transport, nearly only direct emissions are observed. Although Munich-Grosshadern is characterized by predominantly southwest to west winds, higher particle concentrations are observed with southeast winds, because of emissions from a highway southeast of this sampling site. Meteorological data (such as temperature, humidity, wind velocity, and wind direction) were recorded directly at these sites or were provided by the Bavarian State Agency for Environmental Protection (Bayerisches Landesamt für Umweltschutz). At Munich-Grosshadern, ozone and particle concentrations were tracked; at the Luise-Kiesselbach-Platz, trace gas concentrations of NO, NO<sub>2</sub>, CO, CO<sub>2</sub>, and SO<sub>2</sub> were recorded additionally. For the sampling site Munich-Grosshadern, the dependence of the ozone concentration on the wind direction can clearly be determined; higher ozone concentrations are resulting from western winds coming from rural areas. At the sampling site Luise-Kiesselbach-Platz, which is located near the center of the city, this effect is not observed. Extremely high ozone concentrations, which are typical for photochemical conditions, have not been observed. Absolute concentrations of total carbon (TC, the total amount of organic and inorganic carbon), nonextractable carbon (NEC, the proportion of soluble organic compounds), nonvolatilizable carbon (NVC, the proportion of carbon after thermodesorption of volatile organic carbon) and elemental carbon (EC, graphitic carbon), are given in Table 1. Relatively high values for NEC, NVC, and EC indicate a high contribution of traffic emissions to the collected samples of POM. The average value of EC at the Luise-Kiesselbach-Platz in July 1997 with 9 μg m<sup>-3</sup> is higher than the new German immission standard of 8 μg m<sup>-3</sup>, which are effective from January 1998 (19). B[a]P concentrations were determined with GC-MS, B[a]P diones were determined with LC-MS. B[a]P concentrations show no correlation to carbon data and fine dust concentrations. However, high particle concentrations seem to correspond with higher B[a]P concentrations. The average B[a]P concentrations are in a good agreement to results which have been determined in previous samplings (20).

TABLE 1. Absolute Concentrations of Carbon Fractions TC, NEC, NVC, and EC in Particulate Matter During the Different Sampling Periods

| sampling site                     | data points (n) |     | value                    |                           |                           |
|-----------------------------------|-----------------|-----|--------------------------|---------------------------|---------------------------|
|                                   |                 |     | av (μg m <sup>-3</sup> ) | max (μg m <sup>-3</sup> ) | min (μg m <sup>-3</sup> ) |
| Grosshadern (02/1997)             | 22              | TC  | 5.99                     | 11.70                     | 2.72                      |
|                                   |                 | NEC | 3.75                     | 6.51                      | 1.94                      |
|                                   |                 | NVC | 2.92                     | 6.01                      | 1.47                      |
|                                   |                 | EC  | 2.09                     | 3.31                      | 1.15                      |
| Grosshadern (07/1997)             | 18              | TC  | 8.68                     | 17.70                     | 4.90                      |
|                                   |                 | NEC | 6.12                     | 9.48                      | 3.34                      |
|                                   |                 | NVC | 3.36                     | 6.82                      | 0.84                      |
|                                   |                 | EC  | 2.64                     | 5.05                      | 0.83                      |
| Luise-Kiesselbach-Platz (07/1997) | 22              | TC  | 20.85                    | 29.98                     | 11.48                     |
|                                   |                 | NEC | 15.75                    | 27.26                     | 7.98                      |
|                                   |                 | NVC | 12.54                    | 21.23                     | 5.56                      |
|                                   |                 | EC  | 9.70                     | 17.01                     | 5.47                      |

**Low-Volume Sampling. Sampling in Wintertime.** During the sampling period in February 1997, the concentrations of the B[a]P-diones ranged between 5 and 334 pg m<sup>-3</sup> for single components and 43 and 605 pg m<sup>-3</sup> in total. (see Figure 3). The ratio of the three diones (B[a]P-1,6-dione, B[a]P-3,6-dione, B[a]P-6,12-dione) was approximately constant over this period, showing values of approximately 1:0.8:0.5, respectively. The weather conditions can be divided into three periods. The first week (Feb. 3–10) was characterized by sunny weather, followed by a week (Feb. 11–18) of rain and clouded sky. The third week showed a moderate weather improvement. Dione concentrations imply a link between their formation on particles and the corresponding weather conditions. In Figure 4, the dione concentrations are depicted versus the ozone concentration and solar irradiation. Whereas the dione formation does not show a significant parallelism with ozone, radiation seems to play an important role in the formation of diones. The low dione value on February 13, despite high irradiation, is presumably attributable to the very low concentrations of particles TC and B[a]P recorded on that day. B[a]P concentrations ranged from 0.3 to 2.8 ng m<sup>-3</sup> (average: 1.0 ng m<sup>-3</sup>), showing no correlation with the B[a]P diones or the TC concentrations. No significant correlation was observed between the B[a]P diones and the meteorological data or ozone concentrations except for the solar irradiation (Figure 5). B[a]P concentrations are normalized to TC concentrations in order to exclude the impact of high particle concentrations. A normalization to B[a]P does not seem appropriate. First, there is another pathway leading to B[a]P diones via photochemical reaction of nitro-B[a]P (21). Second, in laboratory experiments the amount of formed B[a]P diones is not proportional to B[a]P concentrations (12). It can be assumed that reactions take place only at the surface of the particles, deeper layers are not affected. High-particle concentrations are characteristic of small, fresh particles, whereas lower particle concentrations imply less emitted, and possibly also aged, agglomerated particles. This behavior was confirmed by data of the differential mobility particle sizer (DMPS) system operated during this sampling period. During periods of lower emissions, fresh particles are able to agglomerate which reduces the specific surface area of the particles and their adsorbed organic matter (e.g., B[a]P). This results in fewer active centers accessible to transformation processes.

Ozone shows no correlation at all, which is probably because of the very low levels (daily average values between 7 to 33 ppbv). However, it has to be stated that the exact formation process of the B[a]P diones cannot be given here. Nevertheless, it seems obvious that photochemical processes

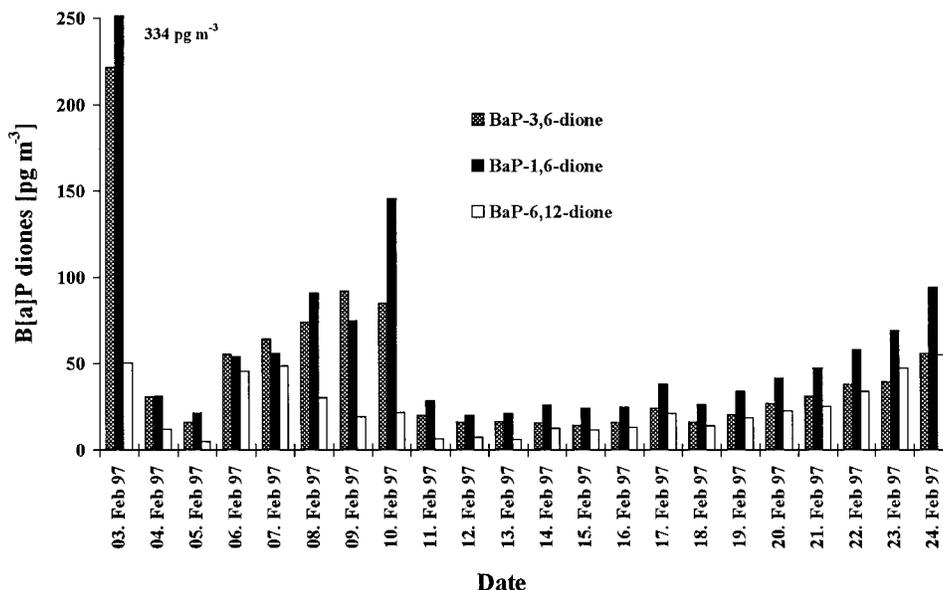


FIGURE 3. Concentrations of B[a]P-3,6-dione, B[a]P-1,6-dione, and B[a]P-6,12-dione in air particulate matter during the sampling period in February 1997 in Munich-Grosshadern.

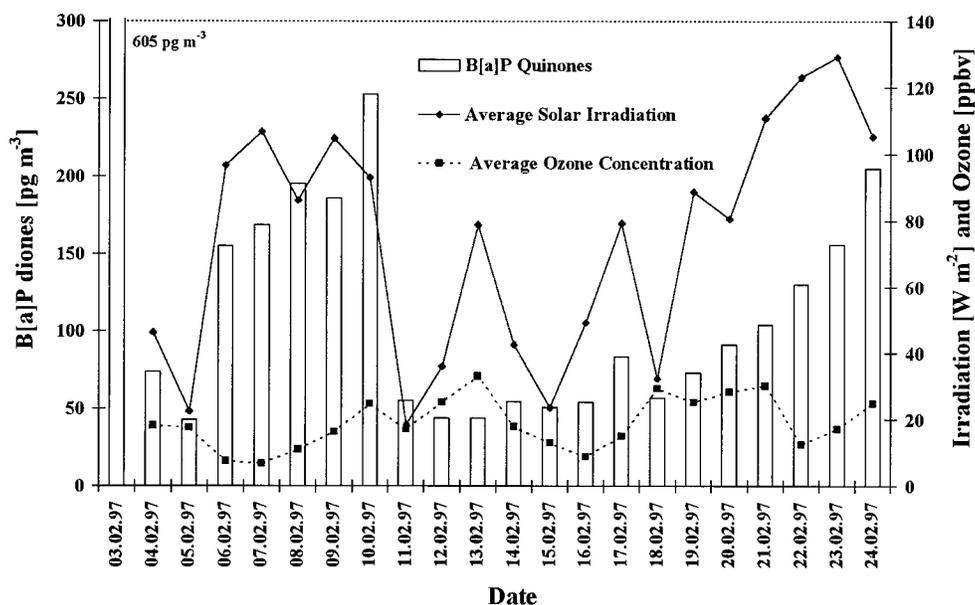


FIGURE 4. Formation of B[a]P diones versus ozone concentration and solar irradiation during the sampling period in February 1997 in Munich-Grosshadern.

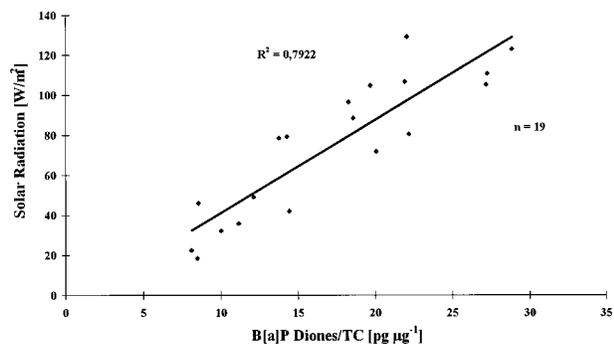


FIGURE 5. Correlation between normalized B[a]P dione concentration and solar irradiation.

have a major role on the formation of B[a]P diones in the atmosphere. It has been previously suggested that the decay constant for B[a]P on wood soot particles shows a direct

relationship between the first-order decay rate constant and the average available sunlight (22).

*Sampling in Summertime.* To obtain a further insight into the atmospheric processes leading to the quinone formation, the sampling period was reduced from 24 to 12 h to obtain day and nighttime variability in order to get more detailed information about the impact of solar irradiation intensity. Unexpectedly, the weather conditions along this period were characterized by above-average rainfall and a lack of photo-smog conditions. Figure 6 shows the total concentration of the three B[a]P diones. Although a clear high correlation between solar irradiation and the quinone formation could not be observed, higher dione concentrations are determined in daytime samples. Relatively high concentrations on nighttime filters can be due to high particle concentrations which are still present after the beginning of night sampling at 8 p.m. In absolute concentrations, the diones are present at lower levels than in the winter sampling period, although the B[a]P levels were found between 1.4 and 6.0 ng m<sup>-3</sup>

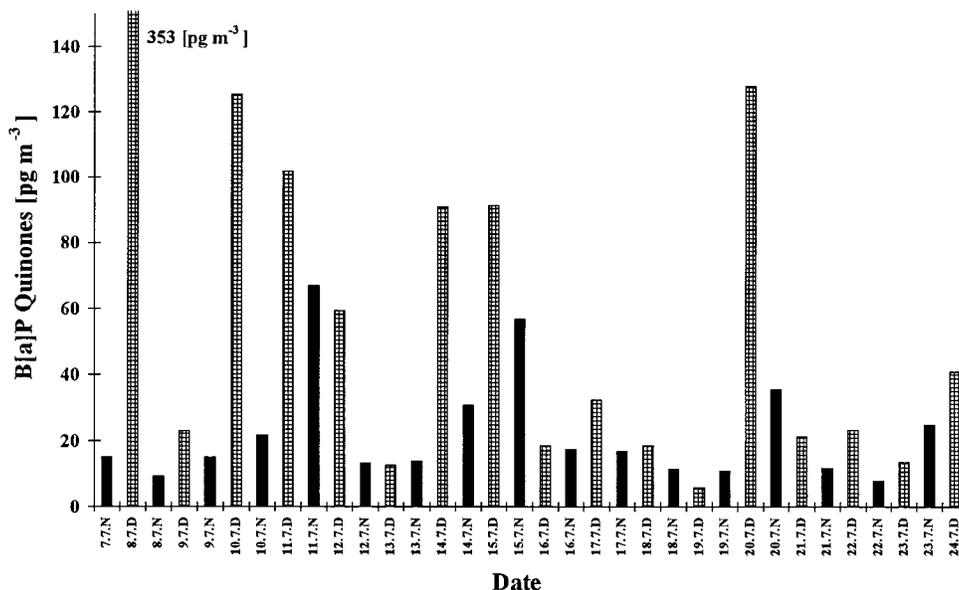


FIGURE 6. Formation of B[a]P diones in July 1997 in Munich-Grosshadern. Higher concentrations are observed on daytime filters than on nighttime filters.

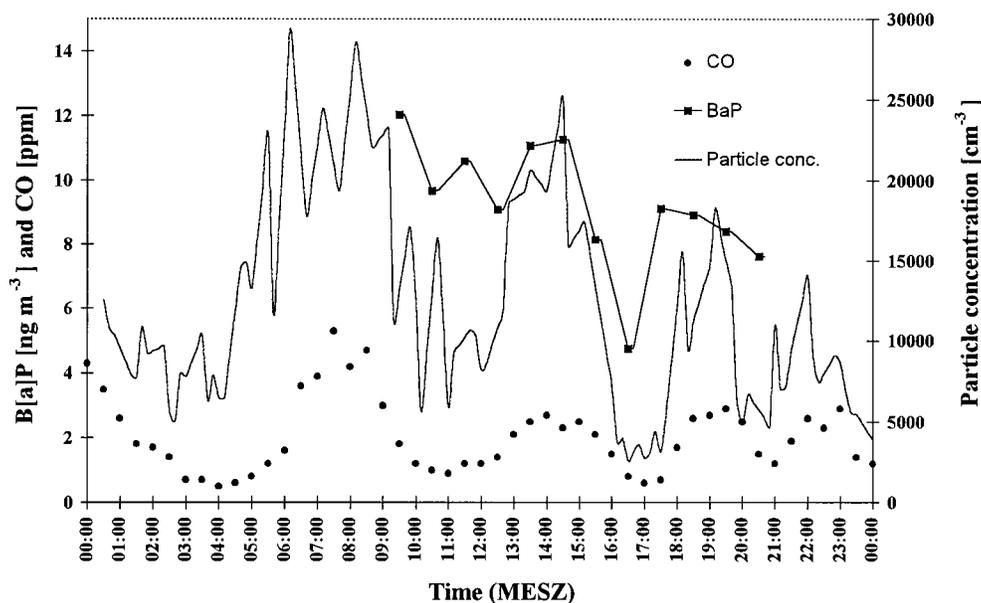


FIGURE 7. B[a]P concentrations versus particle and CO concentrations, indicating traffic activity at the highly polluted sampling site Luise-Kiesselbach-Platz on July 23, 1997.

(average:  $2.9 \text{ ng m}^{-3}$ ), which is higher than the concentrations observed in February. This can be due to the atypical weather conditions in July 1997 or to the fact that B[a]P diones are intermediates in the degradation step of B[a]P. Higher amounts of oxidative species or sunlight in summer might lead to further oxidation and to smaller molecules such as 7*H*-benz[*de*]anthracen-7-one, which showed the highest concentrations in summertime (23). Like in wintertime, no significant correlations between the chemical data and meteorological data were obtained. Samples taken at the Luise-Kiesselbach-Platz gave often B[a]P dione concentrations below the detection limit of  $5 \text{ pg m}^{-3}$ . Furthermore, several filters could not be analyzed because of heavy thunderstorms, as the filters were soaked with water. B[a]P concentrations at the Luise-Kiesselbach-Platz were between  $3.2$  and  $8.2 \text{ ng m}^{-3}$  (average:  $5.6 \text{ ng m}^{-3}$ ). The B[a]P values at the two different sites showed approximately the same ratio that was observed in February, with higher concentrations by a factor of 2 at Luise-Kiesselbach-Platz. However, dione concentra-

tions on filters collected at the same time are significantly higher at Munich-Grosshadern. Although B[a]P diones are also emitted on diesel particles (24), their formation may occur predominantly during the atmospheric transport; the higher concentrations at Munich-Grosshadern indicate this. The low dione concentrations at Luise-Kiesselbach-Platz are due to freshly emitted particles, which have only been exposed to atmospheric transformation processes for a short time. The influence of the wind direction could give evidence of the emission source. However, it seems not appropriate to relate filter data which were collected for several hours to this meteorological data which have been recorded every 30 min. The average meteorological data do not reflect rapid changes such as wind direction, for example. The averaged data for Munich-Grosshadern indicate only winds from the southwest, but as given in Figure 2, a major impact on particle concentration comes from the southeast. Hence, shorter filter collection times are required which allow a better comparison with meteorological data. The decrease

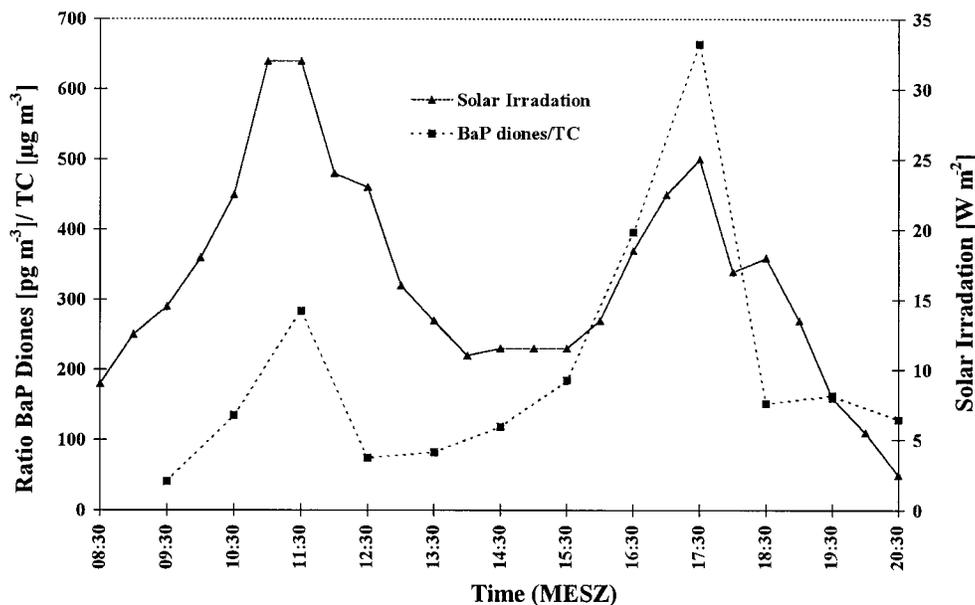


FIGURE 8. Daily distribution of B[a]P diones versus solar irradiation at the site Luise-Kiesselbach-Platz on July 23, 1997. Dione concentrations are normalized to TC concentrations.

in sample material can be avoided using high-flow high-volume sampling.

**High-Volume Sampling.** On July 23, 1997, 12 consecutive high-volume filters were taken at the Luise-Kiesselbach-Platz to examine the formation of the B[a]P diones during daytime. After a sunny morning, it turned cloudy at 11 a.m. and started to rain at 1 p.m. until 4 p.m., whereas the evening was sunny again. Particle concentrations, CO and NO<sub>x</sub> exhibit a similar profile due to traffic conditions (e.g., traffic jams during rush hours). B[a]P concentrations showed no great variability, except for the washout in the afternoon (see Figure 7), although some correspondence with particle emissions and traffic intensity can be observed. The main source of particles derived from traffic emissions is diesel engines which consist mainly (50–80%) of soot (25, 26).

B[a]P dione concentrations exhibit a pattern with two maxima in the late morning at 11 a.m. and in the evening at 5 p.m. (see Figure 8), which show no correspondence with the B[a]P concentrations. This indicates that the dione formation is not dependent on the amount of B[a]P as mentioned above. Ozone concentrations show a similar character, but at a very low level between 10 and 25 ppbv. The solar irradiation, however, fits better to the dione curve and shows, until its first maximum, the intensity of a regular summer morning. After the rain in the early afternoon, the sun returned and increased B[a]P dione concentrations were observed. This confirms the assumption of the major contribution of photochemical processes in the formation of these B[a]P degradation products under low ozone concentrations. Again, no conclusions can be made to give the exact formation process because of the variety of photochemical parameters that are involved. However, it seems obvious that solar irradiation plays an important role in the formation process of B[a]P diones. Determination and identification of other B[a]P degradation products will require future work. Nitrated B[a]P derivatives and compounds derived by oxidative ring opening processes (2, 8) will therefore have to be examined more closely.

The applicability of the used APCI/LC-MS method is very well suited for the analysis of polar degradation products of PAH in particulate organic matter. The determination of known compounds is enhanced by the inherent chemical ionization due to little fragmentation, resulting in higher sensitivity and fewer fragment ions of coeluting compounds

which can deteriorate the quality of ion chromatograms in the SIR or MIR mode.

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#### Literature Cited

- (1) Bjorseth, A.; Ramdahl, T. *Handbook of Polycyclic Aromatic Hydrocarbons*; Dekker: New York, 1985; Vol. 2.
- (2) Allen, J. O.; Dookeran, N. M.; Smith, K. A.; Sarofim, A. F.; Taghizadeh, K.; Lafleur, A. L. *Environ. Sci. Technol.* **1996**, *30*, 1023.
- (3) Westerholm, R. N.; Almen, J.; Li, H.; Rannug, J. U.; Egeback, K. E.; Grägg, K. *Environ. Sci. Technol.* **1991**, *25*, 332.
- (4) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1993**, *27*, 636.
- (5) Lowenthal, D. H. *Atmos. Environ.* **1994**, *28*, 731.
- (6) Valerio, F.; Pala, M.; Borgogni, C. *Int. J. Environ. Anal. Chem.* **1990**, *38*, 343.
- (7) Pitts, J. N.; Paur, H.-R.; Zielinska, B.; Arey, J.; Winer, A. M.; Ramdahl, T.; Mejia, V. *Chemosphere* **1986**, *15*, 675.
- (8) Pitts, J. N. *Environ. Health Perspect.* **1983**, *47*, 115.
- (9) van Cauwenberghe, K. A. In *Handbook of Polycyclic Aromatic Hydrocarbons*; Bjorseth, A., Ramdahl, T., Eds.; Dekker: New York, 1985; Vol. 2.
- (10) Moriconi, E. J.; Racoczy, B.; O'Connor, W. F. *J. Am. Chem. Soc.* **1961**, *83*, 4618.
- (11) Koeber, R.; Niessner R.; Bayona, J. M. *Fresenius' J. Anal. Chem.* **1997**, *359*, 267–273.
- (12) Koeber, R.; Bayona, J. M.; Niessner R. *Int. J. Environ. Anal. Chem.* **1997**, *66*, 313.
- (13) Allen, J. O.; Dookeran, N. M.; Taghizadeh, K.; Lafleur, A. L.; Smith, K. A.; Sarofim, A. F. *Environ. Sci. Technol.* **1997**, *31*, 2064.
- (14) Pierce, R. C.; Katz, M. *Environ. Sci. Technol.* **1976**, *10*, 45.
- (15) König, J.; Balfanz, E.; Funcke, W.; Romanowski, T. *Anal. Chem.* **1983**, *55*, 599.
- (16) German VDI Guideline 2465/1; Beuth Verlag: Berlin, 1995.
- (17) Pitts, J. N., Jr.; Lokensgard, D. M.; Ripley, P. S.; van Cauwenberghe, K. A.; Van Vaecck, L.; Schaffer, D.; Thill, A. J.; Belser, W. L. *Science* **1980**, *210*, 1347.

- (18) Murray, R. W.; Kong, W. *Polycycl. Arom. Comp.* **1994**, 5, 139.
- (19) Verordnung zur Durchführung des Bundes-Immissionschutzgesetzes (Verordnung über die Festlegung von Konzentrationenwerten), 1996.
- (20) Petzold, A.; Niessner, R.; Project Report 94-104 02 2741994, Federal Environment Agency (Umweltbundesamt) Berlin, 1994.
- (21) Pitts, J. N., Jr. *Philos. Trans. R. Soc. London* **1978**, A290, 551.
- (22) Kamens, R. M.; Guo, Z.; Fulcher, J. N.; Bell, D. A. *Environ. Sci. Technol.* **1988**, 22, 103.
- (23) Bayona, J. M.; Casellas, M.; Fernandez, P.; Solanas, A. M.; Albaigés, J. *Chemosphere* **1994**, 29, 441.
- (24) Schuetzle, D.; Lee, F. S. C.; Prater, T. J.; Tejada, S. B. *Int. J. Environ. Anal. Chem.* **1981**, 9, 93.
- (25) McMurry, P. H.; Litchy, M.; Huang, P.-F.; Cai, X.; Turpin, B. J.; Dick, W. D.; Hanson, A. *Atmos. Environ.* **1996**, 30, 101.
- (26) Weingartner, E.; Baltensperger, U.; Burtscher, H. *Environ. Sci. Technol.* **1995**, 29, 2982.

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