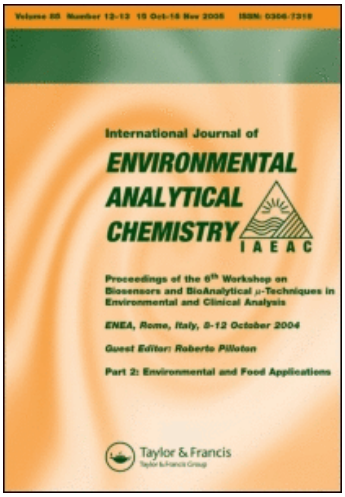
This article was downloaded by:
On: *19 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Comparison of the Profiles of Polycyclic Aromatic Hydrocarbons in Different Areas of a City by Glass-Capillary-Gas-Chromatography in the Nanogram-Range

G. Grimmer[a]; K. W. Naujack[a]; D. Schneider[a]
[a] Biochemisches Institut für Umweltcarcinogene, Ahrensburg, F.R.G.

To cite this Article Grimmer, G. , Naujack, K. W. and Schneider, D.(1981) 'Comparison of the Profiles of Polycyclic Aromatic Hydrocarbons in Different Areas of a City by Glass-Capillary-Gas-Chromatography in the Nanogram-Range', International Journal of Environmental Analytical Chemistry, 10: 3, 265 — 276
To link to this Article: DOI: 10.1080/03067318108071550
URL: http://dx.doi.org/10.1080/03067318108071550

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Environ. Anal. Chem. 1981, Vol. 10, pp. 265–276
0306-7319/81/1004-0265 $06.50/0
© Gordon and Breach Science Publishers Inc., 1981
Printed in Great Britain

Comparison of the Profiles of Polycyclic Aromatic Hydrocarbons in Different Areas of a City by Glass-Capillary-Gas-Chromatography in the Nanogram-Range†

G. GRIMMER, K.-W. NAUJACK and D. SCHNEIDER
Biochemisches Institut für Umweltcarcinogene, Sieker Landstraße 19, D-2070 Ahrensburg, F.R.G.

(*Received June 18, 1980; in final form January 23, 1981*)

Downloaded At: 09:04 19 January 2011

Since the PAH-mixture of different emittants such as coal heatings, oil heatings or gasoline engines are different and therefore characteristic, it is to be expected, that these PAH-profiles are helpful to recognize the main sources of an air pollution. Furthermore, this investigation compares the local concentrations of several selected PAH and records the temporary variation in PAH-profiles of different areas in a city during the year.

The collecting system consists of a low volume air sampler, connected with a glass fibre filter (490 cm^2). To separate the mixture of PAH glass-capillary-gas-chromoatography is used and 15 PAH are selected for this investigation (splitless injection, Silicone OV 17). The repeatability of the total collecting procedure and for the analysis is satisfactory.

Four areas have been selected inside the city: I. area with hand-stoked residential coal heatings, II. area with oil heatings preferentially, III. stations in a tunnel with automobile traffic, IV. area surrounding a coke plant.

The PAH-profiles differ in many cases from area to area and the concentrations of all PAH regarded (including benzo(a)pyrene) vary strongly during the day, week and year on the same place, even during the heating period for the 16 collecting stations investigated monthly (e.g. in case of BaP at the same place from 1.6 ng/m^3 to 299 ng/m^3).

Especially the distribution pattern of 4 PAH (BcPH, CYC, BghiP, COR) is completely different from the other PAH's recorded in the city. The first one correlates to the automobile traffic in the tunnel.

KEY WORDS: PAH-profiles, domestic coal heatings, oil heatings, automobile traffic, coke plant.

†Paper presented at the 10th Annual Symposium on the Analytical Chemistry of Pollutants. May 1980. Dortumnd, GFR.

INTRODUCTION

The purpose of the investigation was to compare

1) *the local variation in the city:* the variation of the concentration of each of 15 polycyclic aromatic hydrocarbons (=PAH) in different areas of the city,

2) *the temporary variation:* the variation of the concentration of each of these compounds on a selected collection station in the city during the day, the week, and the year. For this reason the collecting time was limited to 1 hour.

3) *the profile-variation within the city:* that means the ratio of these 15 PAH, e.g. to BeP, the so-called profile of the PAH.

The aforementioned analytical data are the precondition for an evaluation of the carcinogenic burden for man by air pollution and may give an answer to the question: Does the PAH concentration of an area correlate with the lung cancer incidence there?

Downloaded At: 09:04 19 January 2011

ARRANGMENT OF THE COLLECTING STATIONS IN THE CITY

In a German industrial city of 700000 inhabitants, 4 areas have been selected inside the city and one outside. These areas are polluted by typical emittants:

i) a residential area preferentially heated by domestic coal heatings,
ii) a residential area preferentially heated by oil heatings,
iii) stations in a tunnel with automobile traffic,
iv) an area surrounding a coke plant.

Each area is surrounded by 4 collecting stations. Measuring planning and sampling were achieved by the Landesanstalt für Immissionsschutz in Essen.

COLLECTING SYSTEM AND THE ANALYTICAL METHOD

The collecting system consists of a low volume air sampler, equipped with a flow meter, which collects about $10\,m^3/hr$ (Sartorius/Ströhlein GmbH & Co, Düsseldorf, type Porticon). Figure 1 shows the PAH-collecting system.

The air sampler is connected with a container for the filter. The glass fibre filter with a collecting area of $490\,cm^2$ is not impregnated since no impregnation is necessary in case of low-flow-rates. The break-through of PAH was controlled by a second filter arranged at the rear.

The PAH, collected on the filter, are extracted by toluene. Before

heating, 300 ng benzo(b)chrysene as a internal standard are added to the solution. Since the ratio of desorption/adsorption of PAH from particulate matter is disadvantageous in case of non-aromatic solvents, such as methanol, acetone, dichloromethane or cyclohexane, toluene is used for the extraction of the *loaded* filter. A total recovery of the 300 ng benzo(b)chrysene from the loaded filter is achieved by toluene extraction (1 hr, 110°C).

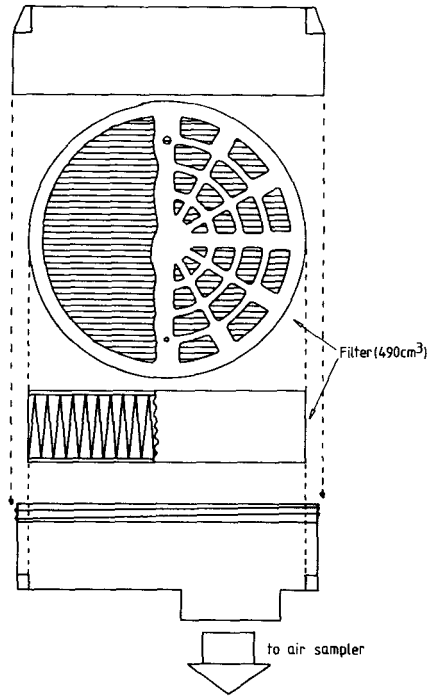


FIGURE 1 Collecting arrangement for air suspended matter.

For the enrichment of PAH chromatography using a SEPHADEX LH 20 column (10 g) with isopropanol is necessary. The fraction from 48–180 ml contains only PAH with more than 3 rings.

To separate the mixture of PAH, glass-capillary-gas-chromatography is used. The capillaries (0.27 mm × 25 m) are coated with Silicone OV 17.

Figure 2 shows a glass-capillary-gas-chromatogram of the PAH-profile from an area burdened with automobile exhaust (area III). Of this chromatogram, 15 PAH are selected: benzo(b)naphtho(2,1-d)thiophene (BNT), benzo(c)-phenanthrene (BcPH), benzo(ghi)fluoranthene (BghiF),

Downloaded At: 09:04 19 January 2011

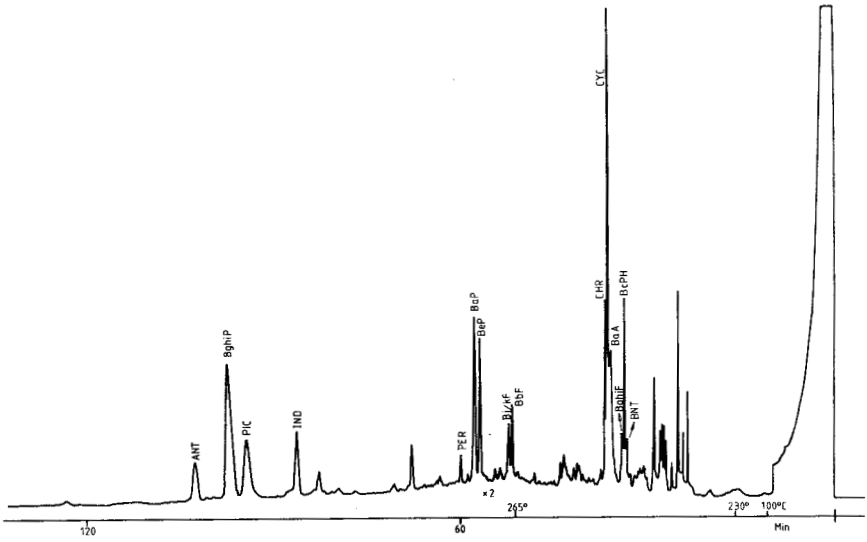


FIGURE 2 Area in a city burdened with automobile exhaust; glass-capillary-gas-chromatogram (0.28 mm × 25 m, OV 17).

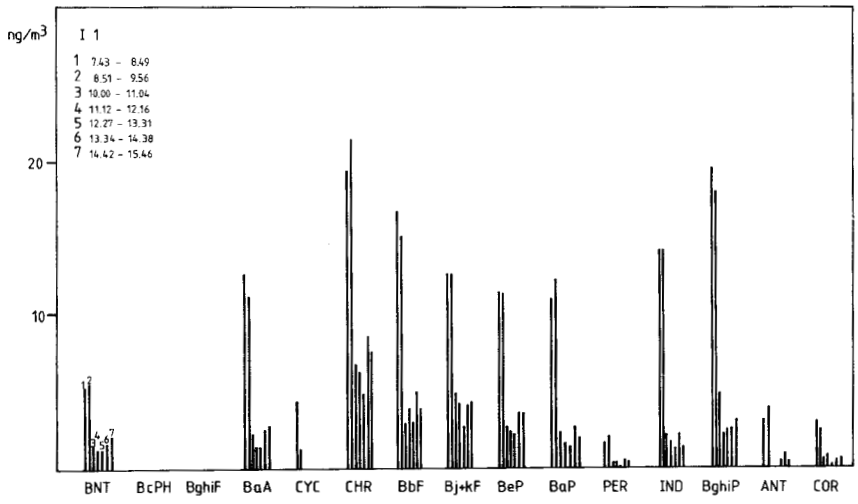


FIGURE 3 Residential area (I), preferentially heated with domestic coal heatings. The lines represent the collecting-hours during the day.

Downloaded At: 09:04 19 January 2011

benz(a)anthracene (BaA), cyclopenta(cd)pyrene (CYC), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(j)fluoranthene + benzo(k)fluoranthene (Bj + k)F, benzo(e)pyrene (BeP), benzo(a)pyrene (BaP), perylene (PER), indeno(1,2,3-cd)-pyrene (IND), benzo(ghi)perylene (BghiP), and Coronene (COR).

RESULTS AND DISCUSSION

Temporary variation

Figure 3 shows the variation of the concentration during a day for several PAH in a residential area, preferentially heated with domestic coal heatings. The concentration of the PAH is plotted on the left side. The 7 lines represent the collecting-hours, explained in the corner of the figure.

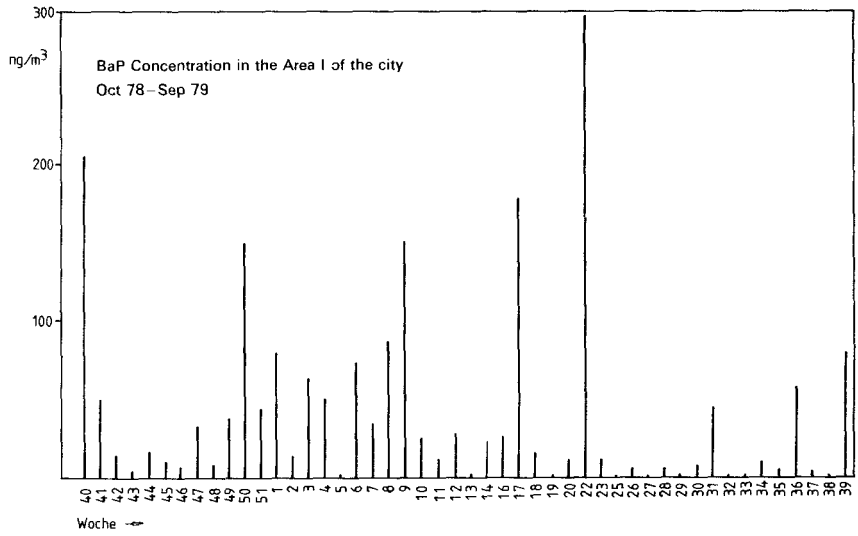


FIGURE 4 Benzo(a)pyrene-concentration in area I of the city from October 1978 to September 1979.

For example in case of BaP, the difference in the concentration between the first two hours in the morning and the next hours is more than five times. Between 7.43 and 10.00 a.m., for the most PAH the concentration is 3 to 4 times higher than from 10.00 a.m.–15.46 p.m. This is confirmed by long period measuring.

Figure 4 shows the variation for the BaP-concentration, measured each week at the same area during 12 months. The height of the lines represents

Downloaded At: 09:04 19 January 2011

the concentration of BaP. In the horizontal direction the number of weeks in 1978 and 1979 are plotted. The highest BaP-concentration of 300 ng BaP/m^3 is recorded in the twenty-second week of 1979, the last week of May. The lowest concentration is detected two weeks later, in June.

Local variation of the PAH-concentration and the profile variation

The second question is the local variations in different areas of the city. The Figure 5 shows the map of the city in which the 4 areas are labeled.

The areas I–IV were previously explained (arrangement of the collecting stations in the city). Once a week, a sample of 10 m^3 air was collected during 1 hour. To get a representative sample, the day of the week as well as the time during the day (daytime) was changed randomly. The Figure 6 shows the average concentration of BaP in the 4 areas, burdened by typical sources.

In each area, about 50 samples were collected during the period of October 1978 and September 1979. This Figure 6 demonstrates the results for BaP.

Area I. The area was burdened preferentially by domestic coal heatings. The average value of 50 weeks was 15.4 ng BaP/m^3. The range is demonstrated below the line: 0.3–72.5 ng BaP/m^3.

Area II. Preferentially central oil heating. Average 6 ng BaP/m^3, range: 0.2–66.2 ng BaP/m^3.

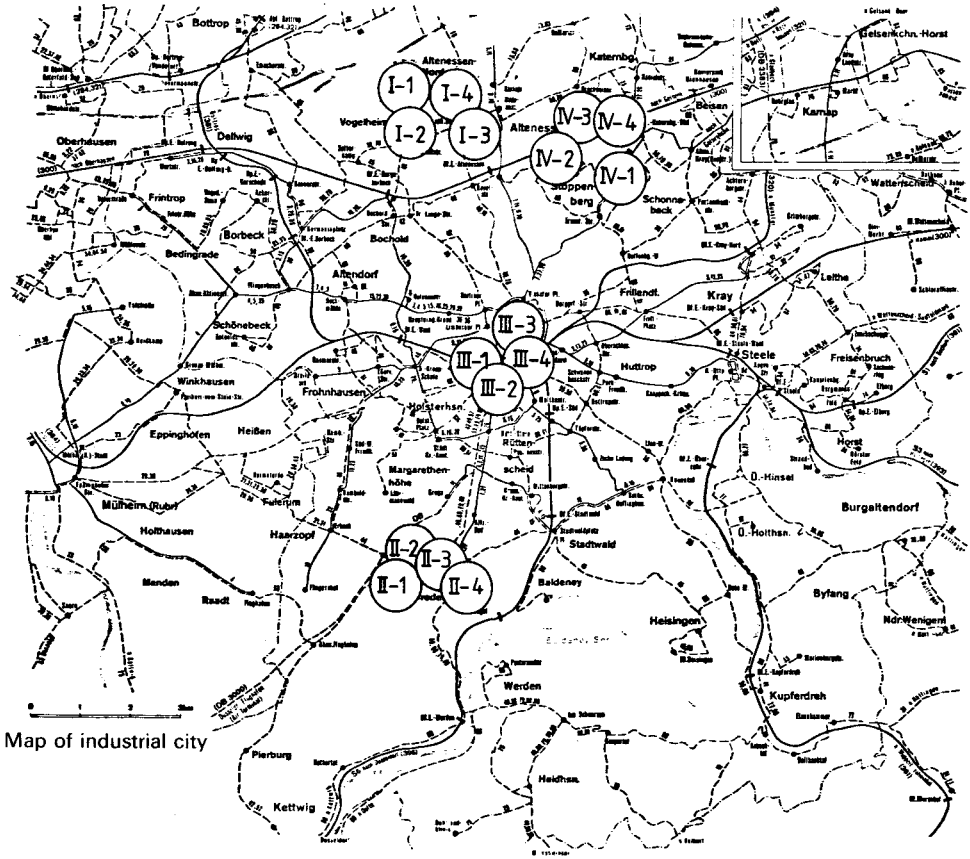
Area III. The tunnel with automobile traffic. Average 31 ng BaP/m^3, range: 1.1–109 ng BaP/m^3.

Area IV. Area around the coke plant; Average 40.4 ng BaP/m^3, range: 1.4–299 ng BaP/m^3.

This distribution-pattern of BaP in the city is completely different to the pattern of cyclopenta(cd)pyrene, a PAH especially produced by gasoline driven automobiles (Figure 7). As was to be expected, the tunnel with automobile traffic shows the highest annual concentration of cyclopenta(cd)pyrene. (Average: 88 ng CYC/m^3, range 0.1–440 ng/m^3). It is very surprising, that within a distance of about 4 km, the concentration drops to 1.6 ng CYC/m^3. This is about one fiftieth of the concentration in the tunnel. The same holds true for other areas.

It can not be generally expected that the ratio of the PAH is constant within the city since the different emittants produce different PAH-profiles. A

Downloaded At: 09:04 19 January 2011



Map of industrial city

FIGURE 5 Map of an industrial city in which 4 areas polluted by typical emittants are labeled: I. The residential area preferentially heated by domestic coal heatings; II. a residential area heated preferentially with oil heatings; III, a tunnel with automobile traffic; IV. an area surrounding a coke plant.

Downloaded At: 09:04 19 January 2011

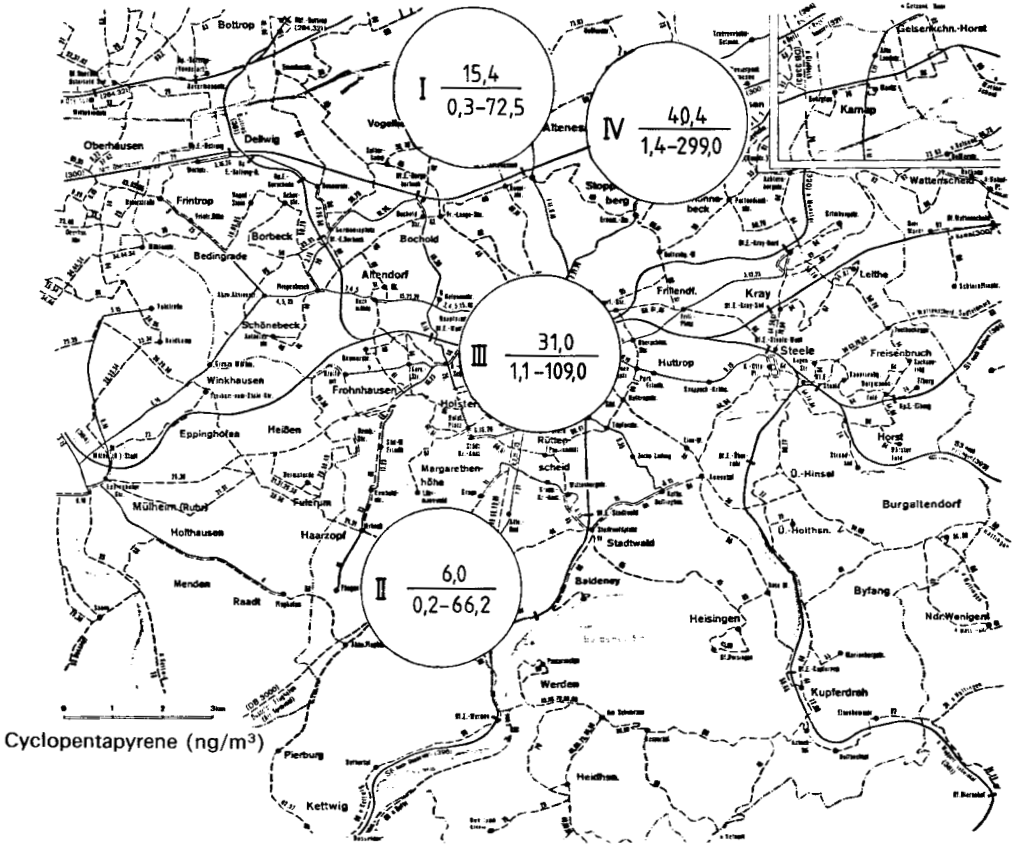


FIGURE 6 The distribution-pattern of benzo(a)pyrene (ng/m³) in the city. Averages of 50 weeks, and below the line the range (ngBaP/m³).

Downloaded At: 09:04 19 January 2011

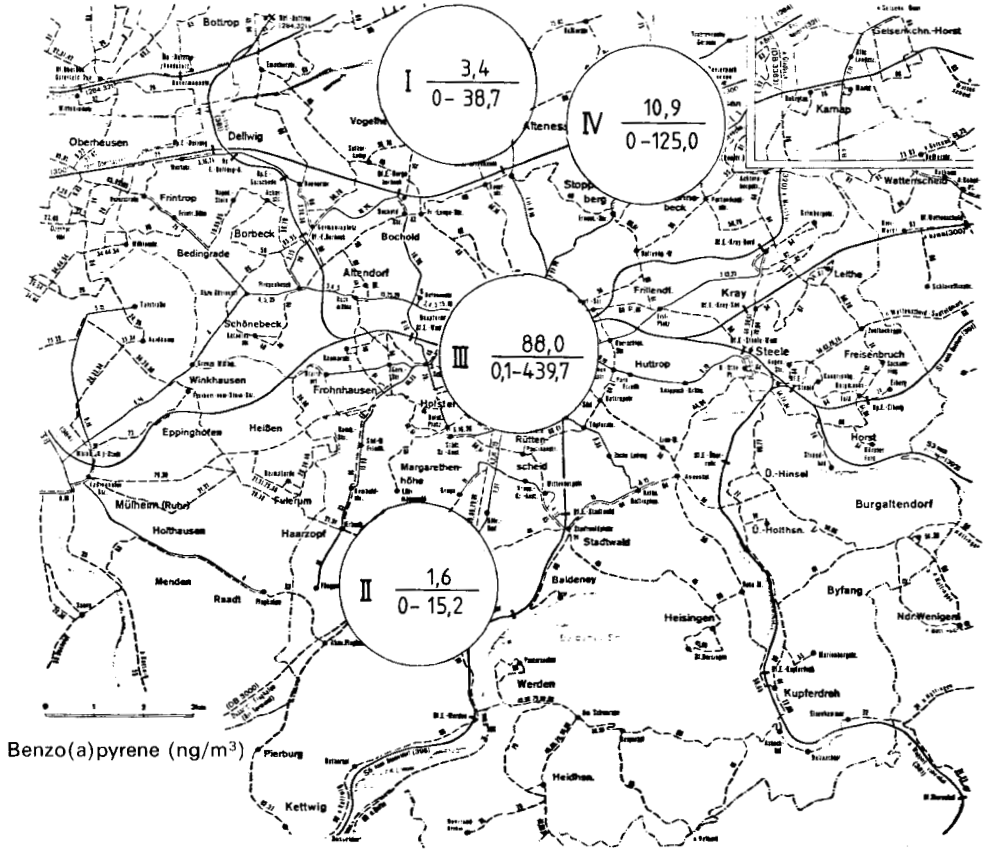


FIGURE 7 The distribution-pattern of cyclopenta(cd)pyrene (ng/m³) in the city (explanations as in Figure 6).

Downloaded At: 09:04 19 January 2011

comparison between the concentration of the 4 areas (average of October 1978–April 1979) is given in Figure 8. The ratio of the concentration within the 4 areas is clearly different in case of BcPH, CYC, BghiP and COR. These PAH predominate in area III.

Relative to the concentration of BeP, the ratios of the concentration of CHR, BbF, Bj+kF, and BaP are very similar. These PAH show the highest concentration in the area surrounding the coke plant.

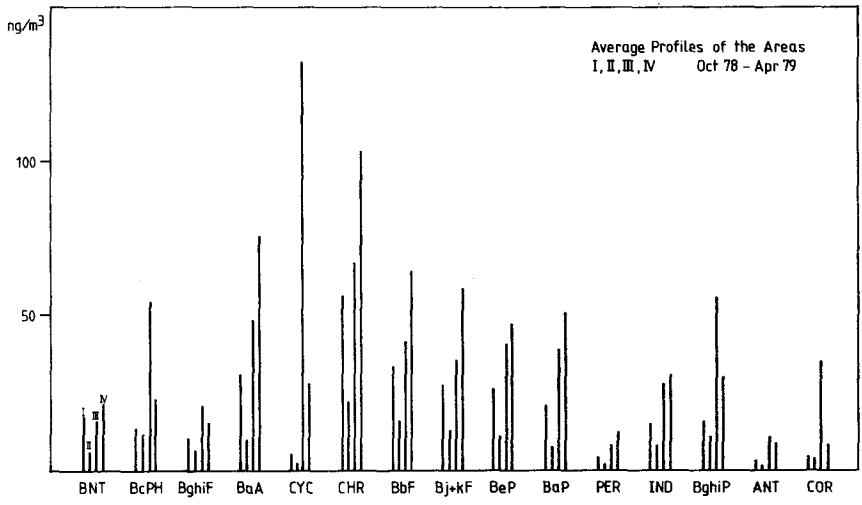


FIGURE 8 The average-profile of the areas I, II, III, and IV. Averages of about 30 weeks from October 1978 to April 1979.

From this representation it can be concluded that there are two sources of emission in the city: (1) the pyrolysis and combustion of coal and briquets in domestic heatings, and (2) the emission of automobile exhaust especially in the tunnel. This conclusion is confirmed by Figure 9. In this figure the PAH-profile of the tunnel with automobile traffic is compared with the PAH-emission of a passenger car [1–5], driven on a chassis dynamometer during a cycle which simulates the city traffic (Regulation No 15 of the European Communities. In this case, CYC is the PAH with the highest concentration. This is in contrast to the emission of coal heatings, which produce only small amounts of CYC. Furthermore, Figure 9 demonstrates that the profile inside the tunnel is very similar to that of the bench-test. A difference can be observed in the concentration of benzo(b)naphtho(2, 1-d)-thiophene (BNT); this is absent in

Downloaded At: 09:04 19 January 2011

case of automobile exhaust from gasoline engines, because the gasoline is free of BNT or other sulphur-containing compounds. The source of BNT in the area III is not quite clear: most of the BNT originates from coal combustion. On the other hand, BNT could also originate to a small extent from DIESEL engines, which blow out thiophenes.

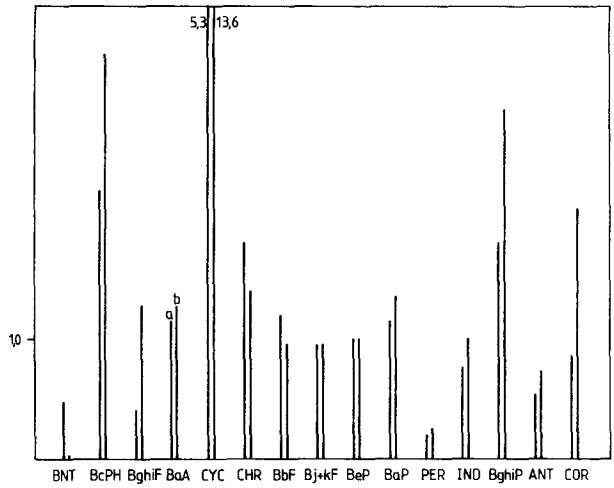


FIGURE 9 Comparison of the PAH-profiles of (a) air in the automobile tunnel and (b) emissions of a passenger car on a chassis dynamometer, simulating city-traffic (ECE-reglement No. 15).

Downloaded At: 09:04 19 January 2011

CONCLUSION

The concentration of the PAH on a selected place in the city varies strongly even in a residential area. Nevertheless, it is possible to sum up the total amount of each PAH and thus to calculate the average concentration.

The most polluted area with an annual average concentration of 40 ng BaP/m^3 surrounds the coke plant. About 3 km off this area, the annual concentration drops to one third. This means, that an average burden for a resident of this city can not be defined; e.g. for BaP, the range is 6.0–40.4 ng/m^3 in the 4 areas during the year. Furthermore, the composition of the PAH-mixture (the PAH-profile) differs in many cases from area to area within the city, e.g. in the traffic area (tunnel) CYC predominates. BNT, originating from pyrolysis or combustion of coal, shows another distribution pattern.

Acknowledgements

The authors gratefully acknowledge the operation planning of the air collecting stations and their technical organisation by Dr. Buck and Dr. Ixfeld of the Landesanstalt für Immissionschutz, Essen. The investigation was supported by the Minister für Arbeit, Gesundheit and Soziales des Landes Nordrhein-Westfalen.

References

1. G. Grimmer, A. Hildebrandt and H. Böhnke *Zbl. Bakt. Hyg., I. Abt. Orig. B*, **158,** 22 (1973).
2. G. Grimmer, A. Hildebrandt and H. Böhnke, *Zbl. Bakt. Hyg., I. Abt. Orig. B.* **158,** 35 (1973).
3. G. Grimmer and A. Hilderbrandt, *Zbl. Bakt. Hyg., I. Abt. Orig. B*, **161,** 104 (1975).
4. G. Grimmer, H. Böhnke and A. Glaser, *Zbl. Bakt. Hyg. I. Abt. Orig. B*, **164,** 218 (1977).
5. G. Grimmer, A. Hildebrandt and H. Böhnke, Gas chromatographic profile analysis of polycyclic aromatic hydrocarbons in automobile exhaust gas condensate. In *Environmental Carcinogens, Selected Methods of Analysis* Vol. 3—Analysis of PAH in environmental samples, IARC Publication No. 29, Lyon 1979.

Downloaded At: 09:04 19 January 2011