

Residue levels of polynuclear aromatic compounds in urban surface soil from Japan

Torsten Spitzer*

Environmental, Industrial and Food Analysis, Leipziger Strasse 68, 3330 Helmstedt (Germany)

Shozo Kuwatsuka

Department of Soil Science, Faculty of Agriculture, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464 (Japan)

ABSTRACT

Samples of surface soil from urban areas of Japan were analysed for polynuclear aromatic hydrocarbons (PAHs). Concentrations of benzo[*a*]pyrene were in the range 12–225 $\mu\text{g}/\text{kg}$. Profiles of polynuclear aromatic materials were obtained by glass capillary gas chromatography. The overall distribution of PAHs is similar to the distribution of PAHs in air particulate matter and combustion sources. Benzantrhene is found at concentrations ranging from 10 to 160 $\mu\text{g}/\text{kg}$. The presence of benzantrhene and other polynuclear aromatic ketones also indicates that polynuclear aromatic materials in surface soil have originated from combustion sources. A comparison with air particulate matter showed that the concentrations of PAHs in air particulate matter are about 100-fold higher than in surface soil. Perylene seems to be more resistant to degradation in the soil environment than in air particulate matter. Subsurface layers of soil contained PAHs at concentrations below 2 $\mu\text{g}/\text{kg}$, which was the detection limit.

INTRODUCTION

Organic substances in soil can be translocated into plants. Therefore, knowledge of the presence of toxic or carcinogenic substances in soil is important [1]. Polynuclear aromatic hydrocarbons (PAHs) have been found in soil and soil-related samples like sediments, and the occurrence of PAHs in soil-plant systems has been investigated extensively [2–4].

Previous work has shown that PAHs released into the air with particulate matter from combustion sources occur together with polynuclear aromatic ketones (PAKs) and other derivatives of PAHs [5–8]. Since air particulate matter settles out and will be incorporated into the soil environment, polynuclear aromatic substances are transferred into surface soil by this process [9].

PAKs are more polar than PAHs and may be more rapidly dissipated by leaching and degradation. PAHs, however, are lipophilic and almost insoluble in water. They should be only slightly translocated from surface layers of soil by leaching. In order to obtain data on the fate of PAHs and PAH-related compounds, samples of surface soil obtained from urban areas in Japan are investigated in this work. Polynuclear aromatic compounds were isolated by clean-up on XAD-2 [10] in order to obtain unique information about PAKs occurring together with PAHs.

EXPERIMENTAL

Chemicals

n-Pentane was purchased from Nakarai (Kyoto, Japan). Ethanol and toluene were purchased from Wako (Osaka, Japan). All solvents were of chromatographic grade and used as supplied. Polycyclic aromatic hydrocarbons, 1-nitropyrene and benzan-

* Corresponding author.

throne (7-*H*-benz[de]anthracene-7-one) were also purchased from Wako and used as supplied.

Samples

Sampling sites were chosen in park areas in downtown Nagoya, Tomakomai and Sapporo, and on a field near Nagoya Airport. One sample was taken from each site at a depth of 0–3 cm. Further samples were taken from surface soil in a forest inside Nagoya University campus. The soil was then separated from residues of vegetation (grass). Samples were dried in a desiccator over silica gel at room temperature for 24 h, and transferred into glass fibre extraction thimbles. They were extracted by the Soxhlet method with a mixture of ethanol and toluene. Total carbon contents of the samples were determined after drying at 110°C using a Yanaco MT-500 C-N-corder (Yanagimoto, Kyoto, Japan).

Isolation of polynuclear aromatic compounds

Extracts were concentrated to 0.5 ml and subjected to clean-up on XAD-2. Sample extracts were transferred to the top of a column of XAD-2 (50–100 µm particle size, Serva Feinbiochemica, Heidelberg, Germany). The column had an internal diameter of 1.4 cm, and the height of the resin packing was 9 cm. The packing of the column was done with a slurry of XAD-2 in ethanol. Stepwise elution was carried out with ethanol, *n*-pentane and toluene. Polycyclic compounds were eluted with the toluene fraction, which was concentrated to 0.5 ml under vacuum (water aspirator) using a rotary evaporator. The concentrated extracts were directly subjected to capillary GC. Details of the analytical procedure are published elsewhere [11,12].

Gas chromatography

A Hitachi 263-50 gas chromatograph equipped with a flame ionization detector and adapted for capillary columns was used. Nitrogen was used as a carrier gas. The injection port was maintained at a temperature of 260°C, and the detector temperature was 300°C. A temperature programme from 110 to 260°C was chosen throughout the work, and the heating rate was 5°C/min. A fused-silica capillary column coated with SE-54 (25 m × 0.3 mm I.D., Gaskuro Kogyo, Tokyo, Japan) was used for all determinations by GC. The injection port was

glass-lined and allowed split or splitless injections. All injections were done in the splitless mode.

RESULTS AND DISCUSSION

Polynuclear aromatic compounds were isolated by clean-up on XAD-2. This method allows a selective isolation of PAHs, PAKs and nitro- and other derivatives of PAHs [13]. Further determination of polynuclear aromatic compounds was carried out by capillary GC, and profiles of polynuclear aromatic compounds were obtained. One of these profiles from the surface soils is displayed in Fig. 1.

PAHs and PAKs were not detected in the sub-surface layers of soil in urban areas. These data, however, do not prove that polar metabolites of PAHs cannot be translocated to deeper soil layers, which remains to be investigated in the future. PAHs and PAKs were also not detectable at concentrations above 2 µg/kg in surface soil from a forest in the Nagoya University campus grounds.

The qualitative compositions of polynuclear aromatic materials in the four soils analysed are similar. Several PAHs and benzantrone are present in higher concentrations and are visible as major peaks in the gas chromatograms. There also are a large number of minor peaks present.

The patterns of polynuclear aromatic compounds found in the samples resemble the pattern of polynuclear aromatic compounds in air particulate matter. In the soils from downtown Nagoya and Sapporo, benzo[*a*]pyrene is present in a smaller amount than benzo[*e*]pyrene. This fact indicates a more rapid decomposition of benzo[*a*]pyrene than benzo[*e*]pyrene as both isomers are released in a ratio of 1:1 from most combustion sources. A ratio of benzo[*a*]pyrene and benzo[*e*]pyrene close to 1:1 is encountered in the soil sample from Nagoya Airport, and this ratio is also found in aircraft turbine particulate emissions [14].

Another remarkable result is the presence of benzantrone among polynuclear aromatic compounds in all four surface soil samples. This indicates an origin of polynuclear aromatic compounds from combustion processes, where benzantrone always accompanies PAHs.

Table I lists the absolute concentrations of some PAHs found in the four samples of surface soil investigated. Concentrations of PAHs in the sample

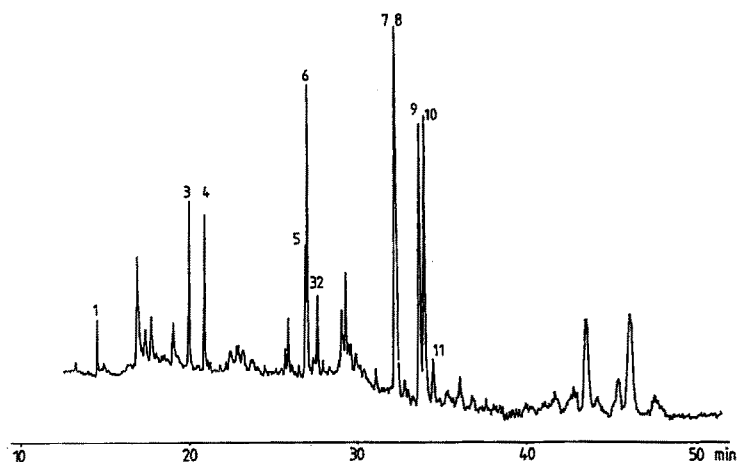


Fig. 1. Gas chromatogram of polynuclear aromatic substances found in surface soil from Nagoya Airport. GC conditions: stationary phase, SE-54; carrier gas, nitrogen; temperature programme, 110–260°C, 5°C/min; column, fused silica, 25 m × 0.3 mm I.D.; stationary film thickness, 0.2 μm. Peaks: 1 = phenanthrene; 3 = fluoranthene; 4 = pyrene; 5 = benz[*a*]anthracene; 6 = chrysene; 7, 8 = benzo[*a*]fluoranthenes; 9 = benzo[*e*]pyrene; 10 = benzo[*a*]pyrene; 11 = perylene; 32 = benzanthrone.

TABLE I

CONTENT OF SOME POLYCYCLIC AROMATIC COMPOUNDS IN SURFACE SOIL

Numbers in italics are relative amounts based on benzo[*e*]pyrene = 1.

Substance	Content (μg/kg)				
	Air particulate matter	Nagoya centre	Nagoya Airport	Sapporo centre	Tomakomai industry
Fluoranthene	7800 <i>4.9</i>	38 <i>2.1</i>	128 <i>0.58</i>	160 <i>1</i>	375 <i>2.3</i>
Pyrene	54000 <i>3.4</i>	31 <i>1.7</i>	118 <i>0.5</i>	160 <i>1</i>	570 <i>3.5</i>
Benz[<i>a</i>]anthracene	1500 <i>0.93</i>	118	99 <i>0.45</i>	160 <i>1</i>	203 <i>1.2</i>
Chrysene	7400 <i>4.6</i>	6.5	225 <i>1</i>	320 <i>2</i>	345 <i>2.1</i>
Benzo[<i>a</i>]fluoranthenes	27000 <i>1.7</i>	70 <i>0.25</i>	278 <i>1.3</i>	440 <i>2.8</i>	329 <i>2</i>
Benzo[<i>e</i>]pyrene	16000 <i>1</i>	18 <i>1</i>	220 <i>1</i>	160 <i>1</i>	165 <i>1</i>
Benzo[<i>a</i>]pyrene ^a	7000 <i>0.43</i>	12 <i>0.7</i>	225 <i>1</i>	100 <i>0.63</i>	120 <i>0.73</i>
Perylene	500 <i>0.03</i>	<2	34 <i>0.15</i>	20 <i>0.13</i>	38 <i>0.23</i>
Benzanthrone	2000 <i>0.13</i>	10 <i>0.55</i>	60 <i>0.27</i>	160 <i>1</i>	45 <i>0.27</i>

^a Benzo[*a*]pyrene is co-eluted with 6-*H*-benzo[*cd*]pyrene-6-one on SE-54, and quantitative values are the sum of both compounds.

from downtown Nagoya are as low as 10% of the concentrations found in the other three samples. The range of concentrations encountered was 10–500 $\mu\text{g}/\text{kg}$. This is 100 times lower than concentrations of PAHs in air particulate matter. This reduction in the concentrations of PAHs in surface soil compared with air particulate matter indicates that PAHs are not accumulated, but degraded in surface soil.

The concentrations of PAHs in air particulate matter were obtained by high-volume sampling and extraction of precipitated matter with toluene and clean-up on XAD-2 [15]. The quoted concentrations are average values encountered in urban air particulate matter, and individual values can be 10 times higher or lower [7,16,17].

Degradation of PAHs is also indicated if an excess of benzo[e]pyrene over benzo[a]pyrene is found in PAH profiles. While these isomeric benzopyrenes are released from most combustion sources in ratios close to 1:1, benzo[a]pyrene is less stable and disappears more rapidly in an environment where degradation of PAHs can take place. Perylene occurs in rather low concentrations in air particulate matter compared with benzo[e]pyrene, whereas in soil the ratio of perylene to benzo[e]pyrene is higher. This may indicate that perylene is more resistant to degradation in the soil environment than in air particulate matter. There was also a large number of minor polynuclear aromatic compounds present, many of which were not resolved as single components by capillary GC. Such components are probably isomeric or otherwise structurally related derivatives formed during primary degradation of PAHs in soil. Primary derivatization of PAHs can be the well known epoxide/diol formation [18]. Another interesting finding is the presence of PAKs among PAHs in the samples investigated. Their half-lives in soil are therefore similar to those of PAHs.

The concentrations of PAHs found in samples investigated here are of the same order of magnitude as concentrations of PAHs found in other samples of surface soil from Japan [19] or Norway [20]. Much higher concentrations of PAHs are found in surface soil from waste disposal sites [21] or railway ditches [22]. The concentrations of PAHs directly near a road with heavy automobile traffic in Great Britain were 10 times higher than the concen-

TABLE II

RELATIVE RETENTION (α) OF IDENTIFIED COMPOUNDS BASED ON BENZO[e]PYRENE

Substance	α
Penanthrene	0.432
Fluoranthene	0.569
Pyrene	0.623
Benz[a]anthracene	0.800
Chrysene	0.804
Benzofluoranthenes	0.957
Benzo[e]pyrene	1.000
Benzo[a]pyrene	1.011
Perylene	1.025
Benzanthrone	0.821

trations of PAHs reported here [23,24]. It should also be pointed out that present-day concentrations of PAHs are the result of a higher intake of PAHs by precipitation of air particulate matter, and overall concentrations of PAHs in surface soil are higher nowadays than they were 100 years ago [25–27].

The concentrations of PAHs are affected by the sampling depth, since concentrations in deeper layers of soil will be much lower. However, some accumulation of PAHs in deeper soil layers under exceptional circumstances has been reported [28]. The ratio of benzo[a]pyrene to benzo[e]pyrene in air particulate matter is often less than 1, since during atmospheric exposure benzo[a]pyrene is degraded more rapidly than benzo[e]pyrene. The concentrations of benzo[a]pyrene were also lower than concentrations of benzo[e]pyrene in all samples of surface soil investigated here.

Table II lists relative retention times of some compounds based on benzo[e]pyrene, which had a retention time of 33.5 min.

CONCLUSION

The profiles of PAHs in surface soil from urban areas in Japan show a distribution of polynuclear aromatic compounds similar to air particulate matter. PAKs are also present, which indicates that half-lives of such compounds in surface soil are similar to those of PAHs. Perylene seems to be more resistant to a degradation in the soil environment than in air particulate matter.

REFERENCES

- 1 M. Sakamoto, S. Kobayashi, M. Nakano and T. Negishi, *Sci. Total Environ.*, 37 (1984) 247.
- 2 R. C. Sims and M. R. Overcash, *Residue Rev.*, 88 (1983) 1.
- 3 J. T. Coates, A. W. Elzerman and A. W. Garrison, *J. Assoc. Off. Anal. Chem.*, 69 (1986) 110.
- 4 I. Blankenkorn, D. Meijer and R. V. Delft, *Fresenius Z. Anal. Chem.*, 343 (1992) 497.
- 5 T. Spitzer and S. Kuwatsuka, *Environ. Pollut.*, 62 (1989) 63.
- 6 F. R. Guenther, S. N. Chesler, G. E. Gordon and W. A. Zoller, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 761.
- 7 J. J. Gether and K. E. Thrane, *Anal. Chim. Acta*, 184 (1986) 99.
- 8 J. Schulze, A. Hartung, H. Kiess, J. Kraft and K. H. Lies, *Chromatographia*, 19 (1984) 391.
- 9 E. Aamot, Y. Krane and E. Steinnes, *Fresenius Z. Anal. Chem.*, 328 (1987) 569.
- 10 T. Spitzer and S. Kuwatsuka, *J. Chromatogr.*, 435 (1988) 489.
- 11 T. Spitzer, *J. Chromatogr.*, 237 (1982) 273.
- 12 T. Spitzer and S. Kuwatsuka, *J. Chromatogr.*, 358 (1986) 434.
- 13 T. Spitzer and W. Dannecker, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 301.
- 14 T. Spitzer and W. Dannecker, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 98.
- 15 T. Spitzer, *Anal. Chem.*, 55 (1983) 2226.
- 16 S. A. Wise, B. A. Benner, S. W. Chesler, L. R. Hilpert, C. R. Vogt and W. E. May, *Anal. Chem.*, 58 (1986) 3067.
- 17 Y. Suzuki and S. Imai, *Analyst*, 110 (1985) 907.
- 18 J. K. Selkirk, *Adv. Chromatogr.*, 16 (1978) 1.
- 19 H. Matsushita, *Igaku to Seibutsugaku*, 103 (1981) 315.
- 20 B. Vogt, F. Brakstad, K. Thrane, I. Nordenson, J. Krane, E. Aamot, K. Kolset, K. Esbensen and E. Steinnes, *Environ. Sci. Technol.*, 21 (1987) 21.
- 21 B. Davani, J. Ingram, L. Gardea and G. A. Eiceman, *Water, Air, Soil Pollut.*, 27 (1986) 267.
- 22 T. Wan, *J. Environ. Qual.*, 20 (1991) 228.
- 23 V. Butterworth, S. C. Kellow and H. G. Robinson, *Sci. Total Environ.*, 33 (1984) 75.
- 24 S. Y. N. Yang, D. W. Connell, D. W. Hawker and S. Y. Kayal, *Sci. Total Environ.*, 102 (1991) 229.
- 25 K. C. Jones, J. A. Tidridge, K. S. Waterhouse and A. E. Johnston, *Environ. Pollut.*, 56 (1989) 337.
- 26 K. C. Jones, J. A. Stratford, K. S. Waterhouse, E. Furlong, W. Giger, R. A. Hites, C. Schaffner and A. E. Johnston, *Environ. Sci. Technol.*, 23 (1989) 95.
- 27 K. C. Jones, J. A. Stratford, K. S. Waterhouse and A. E. Johnston, *Trace Subst. Environ. Health*, 21 (1987) 140.
- 28 M. Besteigne, J. Lefevre and C. Rose, *Eur. J. For Pathol.*, 18 (1988) 310.