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Capillary GC of Indicator Compounds of Degradation of Polycyclic Aromatic Hydrocarbons in Airborne Particulate Matter

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Abstract

Profiles of polycyclic aromatic compounds (PACs) are determined in several samples of urban airparticulate matter. The distribution of PACs in these samples is compared with their distribution in an emission profile from a combustion source. Cyclopenta(cd)pyrene, benzo(ghi)fluoranthene and benzo(a)pyrene are found to show largely variable ratios to benzo(e)pyrene and are used as indicator compounds for the degradation state of a mixture of PAHs from combustion sources. The validity of the method is demonstrated with the distribution profiles of PACs in samples of urban airparticulate matter. The effect of oxidative degradation on mutagenicity is being discussed.

Keywords : Cyclopenta(cd)pyrene, Benzo(ghi)fluoranthene, Benzo(a)pyrene, Degradation, PACs, PAHs

1. Introduction

Polycyclic Aromatic Compounds (PACs) are formed during incomplete combustion of fossil fuels. They consist of Polycyclic Aromatic Hydrocarbons (PAHs) and keto-, nitro- and other derivatives of these compounds. Since very large amounts of fossil fuels are being burned for heating and transportation, their release into the environment is quite substantial.

Particulate matter absorbs these compounds and is primarily released into the air with the exhaust gas of a combustion process. The particulate matter will reside in air for a certain time and will finally be precipitated onto the surface soil. Much research done on degradation of these compounds therefore deals with their fate in soil [1–5], where the dissipation occurs during microbial reactions. The overall chemical environment during dissipation reactions will be oxidising or aerobic in air and in the upper layer of surface soil, and anaerobic with an increasing depth of the soil. Chemical oxidation will therefore degrade PAHs in addition to microbial degradation in an oxidising soil environment. [6].

PACs are a major class of chemical carcinogenes in the environment. Prior to a full development of their carcinogenic poten-

tial, they need to be activated [7], and the activation includes the biogenic oxidation to diols. Chemical oxidation of anthracene was investigated at the air–aqueous interface and yielded anthraquinone [8]. Polar groups introduced into PAHs by chemical oxidation result in metabolites of increased water solubility [9, 10]. Such metabolites are supposed to undergo a more rapid biogenic degradation than the almost insoluble parent PAHs. The present research studies the disappearance of compounds from the profile of PACs. The disappearance of compounds is identified by a decrease of their quantitative ratio to benzo(e)pyrene.

2. Experimental

Sampling of airparticulate matter

A commercial vacuum cleaner is being employed in the suction of air through a glass fiber or membrane filter. Total precipitation of particulate matter on the filter surface varied from 5 mg to 1000 mg depending on the duration of the sampling interval. Sampling intervals ranged from 10 hours overnight in wintertime to 100 hours continuous sampling in summertime.

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Origin of samples

Airparticulate matter was sampled at urban sites in Germany since 1980. Samples A–F are typical samples of this sampling period. Furthermore, particulate matter from combustion sources was sampled. Sample K results from the combustion of kerosene in Pratt and Whitney JT 3 gas turbines.

Extraction of PACs

Soxhlet extraction with toluene of particulate loaded filters yielded a brown solution. This solution was concentrated with a rotary evaporator and adjusted to a volume of 1 mL with toluene (analyte solution). Standard compounds were a gift of Professor G. Grimmer. They were dissolved in toluene.

Solvents and glassware

Solvents were glass-distilled through a 30 cm Vigreux column. Glassware was washed with hot detergent solution followed by chromic-sulfuric acid as the final cleaning solution. Final sample solutions were stored in 1.5 mL glass vials with Al-lined screw-caps.

Clean-up of PACs

Adsorption chromatography on XAD-2 was performed with sequential elution by ethanol, n-pentane and toluene. The final column eluate containing the PAC fraction was concentrated to 0.5 mL. Dryness was avoided and the final volume readjusted to 1 mL with toluene.

High resolution gas chromatography

Glass capillary columns were made of borosilicate glass and coated with silicone solutions (OV-1, OV-25, SE-54, Dexsil-300) by the static method after deactivation. Performance was equal or better when compared with commercial fused silica columns. Carrier gas was hydrogen or helium. Carlo Erba 4130 and 4160 gas chromatographs with a flame ionization detector were used. Injection port and detector were maintained at 280 °C. A temperature program of 110–280 °C with a heating rate of 5 °C/min was selected, and injections were performed with a Grob type split-splitless injector in the splitless mode. The split was opened after 60 sec manually using a stopwatch.

GC/MS

GC/MS was performed with a Hewlett Packard 5890 machine operated with EI ionization at 70 eV. The separation column was a fused silica capillary of 0.3 mm ID coated with OV 1.

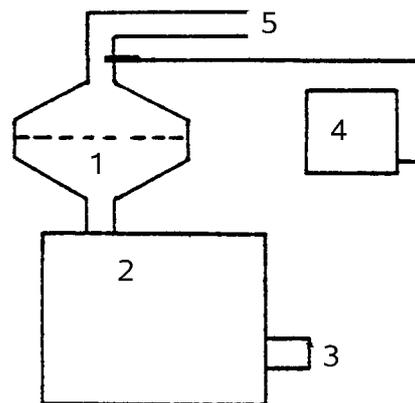


Figure 1. Sampling device for emission samples. 1 membrane filter, 2 high volume sampler, 3 air outlet 4 temperature gauge, 5 air inlet

3. Results and Discussion

The analysis of PACs includes the sampling, clean-up and determination by chromatographic methods. The sampling method chosen in this investigation was high volume sampling, and the amounts of particulate matter collected on each filter ranged from 5–1000 mg.

High volume sampling allows the precipitation of a relatively large amount of particulate matter within a short time. This facilitates the further analytical procedure, since a sufficient amount of analytes will be present. A schematic drawing of the sampling apparatus is given in Fig. 1. PACs with molecular weights above 226 are almost quantitatively absorbed on airparticulate matter. The filter material was cellulose acetate [11].

The isolation of absorbed organic materials was done by Soxhlet extraction with toluene. The toluene extract was evaporated and adjusted to 1 mL. Dryness was avoided during the process of evaporation in order to avoid losses of volatile PAHs.

Mass spectra of PACS largely contain the molecular ion as the base peak and have no further distinctive fragmentation patterns. GC/MS is useful in order to distinguish PAHs from other compound classes like polycyclic aromatic ketones. Thus, the coelution of benzo(e)pyrene (molecular ion 252) with benzo(cd)pyrene(6)one (molecular ion 254) on the stationary phase OV-1 was confirmed by GC/MS. On the other hand, GC/MS cannot distinguish isomeric PAHs like benzo(a)fluoranthene or benzopyrenes.

Most analytical work on polycyclic aromatic compounds concentrates on the isolation of PAHs only [12, 13]. The ratios of stable compounds are used for a source identification of immisions, and cyclopenta(cd)pyrene and benzo(ghi)fluoranthene are rarely reported. These compounds are less stable and are not found due to degradation prior or during sampling. Degradation of these compounds can also take place during the analytical procedure.

The limitation of determination on parent PAHs is a result of analytical procedures, which are mostly based on a clean-up using

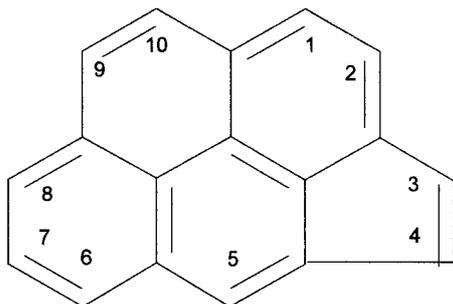


Figure 2. Structural formula of cyclopenta(cd)pyrene. Positions of H atoms are numbered

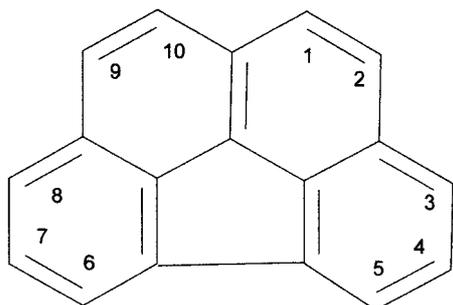


Figure 3. Structural formula of benzo(ghi)fluoranthene. Positions of H atoms are numbered

silica columns. Such a clean-up separates compounds according to their polarity. Polar derivatives of PAHs are being separated from parent PAHs and must be determined by other procedures, because they will no longer be present among the isolated PAHs. However, oxo- and nitro- derivatives of PAHs are among primary emissions of combustion processes. A compound class selective method of clean-up [14, 15] was therefore chosen in this investigation.

PAHs along with their polar derivatives were isolated by absorption chromatography on XAD-2 [16]. The toluene eluate from the XAD-2 column containing PACs was further investigated by capillary gas chromatography without further fractionation. A typical gas chromatogram obtained by this procedure is displayed in Fig. 4. The applicability of hydrogen as a carrier gas was confirmed by performing control determinations with helium as a carrier gas. These experiments confirmed the absence of any chemical reactions, e.g. hydrogenation, between the carrier gas hydrogen and the analytes.

The sample displayed in Fig.4 originates from urban airparticulate matter after a sampling period of 60 h in summertime. The average ambient temperature during sampling was 23 °C. The baseline rise is an indication of polycyclic aromatic degradation products being present besides PAHs. The relatively low amounts of peaks 2, 3 and 7 are an indication of some degradation that has occurred with PAHs either during the relatively long sampling time or during atmospheric exposure. Figure 5 displays the profile of PACs in particulate emissions of kerosene combustion. The absence of a

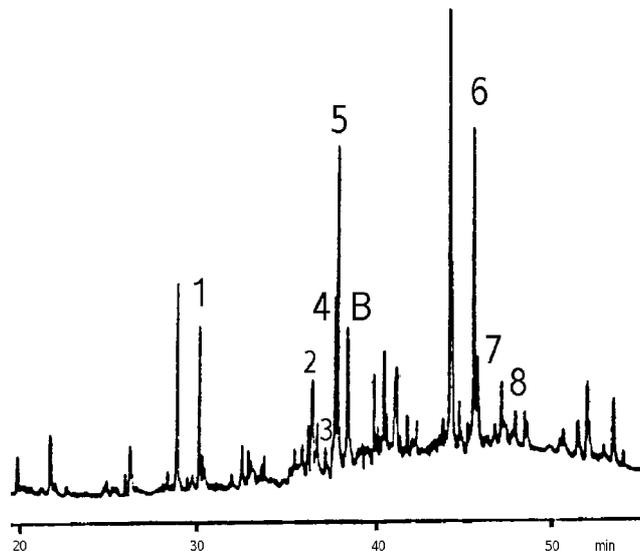


Figure 4. FID trace of PAHs in urban airparticulate matter isolated by clean-up on XAD-2. Column : glass capillary 30 m x 0.25 mm, stationary phase : OV-1, injection : splitless (60 sec), carrier gas : hydrogen, temperature program : 110 –260 °C, 5 °C/min, peak numbers : 1 pyrene, 2 benzo(ghi)fluoranthene, 3 cyclopenta(cd)pyrene, 4 benz(a)anthracene, 5 chrysene, 6 benzo(e)pyrene, 7 benzo(a)pyrene, 8 perylene, B : benzanthrone

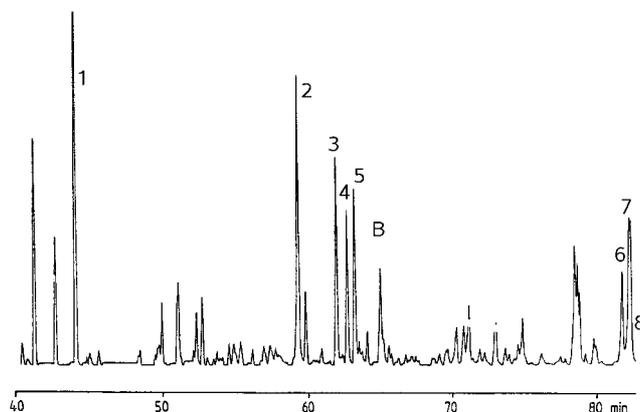


Figure 5. FID trace of PACs in particulate emissions of kerosene combustion isolated by clean-up on XAD-2. Column : glass capillary 90 m x 0.35 mm, stationary phase : SE-54, injection : splitless (60 sec), carrier gas : hydrogen, peak numbers and temperature program : same as Fig. 4

baseline rise indicates that no polycyclic aromatic degradation products were accumulated in this sample. Compounds 2,3 and 7 display relatively high concentrations. They are clearly major components in emissions of PACs. Since SE-54 was the stationary phase, there is partial coelution of benzo(a)pyrene (molecular ion 252) with 6-H-benzo(c, d)pyrene-6-one (molecular ion 254), which is a polycyclic aromatic ketone being present in the emissions from most combustion sources along with PAHs [17].

The structural formulas of cyclopenta(cd)pyrene and benzo

Table 1. Ratios of 7 Polycyclic Aromatic Hydrocarbons (PAHs) to benzo(e)pyrene (relative amount=1.0) in urban airparticulate matter (samples A–F) and particulate emissions of kerosene combustion (sample K)

PAH	A	B	C	D	E	F	K
Pyrene	2.45	1.45	1.10	2.25	1.43	0.63	8.6
Benzo(ghi)fluoranthene	0.95	0.22	0.55	0.56	0.53	0.32	2.0
Cyclopenta(cd)pyrene	1.64	0.52	0.34	0.06	0.31	0.0	1.24
Benz(a)anthracene	1.25	1.0	0.74	0.81	0.86	0.58	0.74
Chrysene	1.68	1.64	1.48	1.5	1.65	1.32	2.06
Benzo(a)pyrene	1.03	0.88	0.71	0.44	0.78	0.47	0.80
Perylene	0.15	0.14	0.12	0.06	0.12	0.0	0.30
Benzo(e)pyrene	1.0	1.0	1.0	1.0	1.0	1.0	1.0

(ghi)fluoranthene are displayed in Fig 2 and 3. Both compounds have one ring structure with 5 carbon atoms. The sterically strained nature of such a ring can be one reason for their higher reactivity and degradation in particulate matter, which occurs more rapidly than the dissipation of benzo(a)pyrene [6, 18].

The compound class selective isolation procedure on XAD-2 is the method of choice whenever ratios of different compound classes are to be determined. Unlike other separation methods PAHs are coeluted with oxo-, nitro- and other polar derivatives, and a capillary gas chromatogram will then directly show compound ratios of interest. The chemical degradation of PAHs will lead to large numbers of isomers being present as a non-separated peak cluster in capillary chromatography, and a baseline elevation will be the result. 7-H-Benz(de)anthracene-7-one and 6-H-benzo(cd)pyrene-6-one are the most abundant polycyclic aromatic ketones, and their concentrations are comparable to benzo(e)pyrene in primary emissions. The coelution of the later compound with benzo(e)pyrene leads to an abnormally high peak-height for benzo(e)pyrene in Fig.2. The coelution is directly visible by a molecular ion of mass 254 in GC/MS. Application of other stationary phases like SE-54 or OV-25 will also solve this problem, because coelution will then occur with benzo(a)pyrene or perylene, respectively. Another important feature is the low concentration of cyclopenta(cd)pyrene in this chromatogram, although this PAH is a major compound released from internal combustion engines [17]. The ratio of different PACs was further investigated in a number of samples of urban particulate matter. The sampling was done over short or long periods and under different total dust concentrations and weather conditions. Results are listed in table 1.

Concentrations of cyclopenta(cd)pyrene show a large variation from high to almost absent. The high concentration occurred in particulate matter A, which was sampled overnight for 10 hours at a high concentration of total dust ($220 \mu\text{g}/\text{m}^3$) in the wintertime. It is therefore assumed that the profile of PAHs in sample A was not altered by atmospheric degradation. Lower concentrations of 2, 3, and 7 were always found over longer sampling periods covering

Table 2. Sampling parameters

Sample	average temperature ()	sampling duration (h)	total dust ($\mu\text{g}/\text{m}^3$)
A	-12	10	220
B	-8	144	120
C	-1	160	105
D	+4	110	23
E	+5	80	90
F	+9	75	40

intervals of daytime and lower total dust concentrations. This applies to samples B–F. It is therefore concluded that cyclopenta(cd)pyrene is a major component of primary emissions, but disappears rapidly after atmospheric exposure.

Particulate matter A also displayed high concentrations of benzo(a)pyrene and benzo(ghi)fluoranthene, which are comparable to the concentrations of these compounds in primary emissions. Both compounds are also present in all other samples, but their ratio to benzo(e)pyrene is decreased. The decrease in the ratio to benzo(e)pyrene is an indicator of degradation, since the rather stable compound benzo(e)pyrene is degraded at a much slower rate.

While the biogenic degradation of PAHs activates their carcinogenic potential and leads to a limited number of isomers, the chemical degradation occurring mainly in the atmosphere seems to be a rather unspecific degradation process leading to a very large number of isomeric dissipation products that are indicated by a baseline rise in capillary gas chromatograms. It is therefore unlikely that the overall carcinogenic potential of PAH emissions will be activated or increased by such a degradation. However, atmospheric reaction products with some carcinogenic potential have been identified [18], and primary metabolites of atmospheric degradation are further metabolized to secondary degradation products [19]. These reaction products were found at much lower concentrations than primary emissions of PAHs. Cyclopenta(cd)pyrene was identified as the most rapidly degraded PAH among major PAHs in undegraded primary emissions in this investigation. The amount of

this compound correlates well with mutagenicity [20], and this also supports the assumption that the disappearance of this compound from partially degraded PAH mixtures in particulate matter rather reduces the overall mutagenicity of the sample. Underivatized PAHs also had a major, nitro derivatives a minor contribution to the overall mutagenicity of urban particulate matter in Genoa [21], which also supports the assumption of a decrease of mutagenicity by chemical dissipation of PAHs in the atmosphere, which leads to large numbers of different or isomeric reaction products. The concentrations of the three indicator compounds of PAH degradation, (benzo(a)pyrene, cyclopenta(cd)pyrene and benzo(ghi)fluoranthene, can thus give a qualitative approximation of the mutagenic potential of polycyclic aromatic compounds found in particulate matter.

While there are many reports on the abundance of more stable PAHs like benzo(ghi)perylene [22, 23, 24, 25], benzo(ghi)fluoranthene and cyclopenta(cd)pyrene are not even mentioned in most investigations covering profiles of PAHs in the environment. The determination of stable PAHs is easier, and quantitative ratios of stable PAHs provide an information on the source of PAHs. Cyclopenta(cd)pyrene is degraded faster than benzo(ghi)fluoranthene in the environment. The impact of cyclopenta(cd)pyrene on the environment may be underestimated, since the accurate sampling of this compound may require an oxidant denuder [26].

Degradation of PAHs in the environment proceeds simultaneously by biotic and non-biotic mechanisms, and chemical oxidation may be a first reaction before additional microbial reactions take place [27, 28, 29, 30, 31, 32]. Anaerobic degradation proceeds slower and may not contribute to the rapid dissipation of cyclopenta(cd)pyrene [33].

Finally, polycyclic aromatic ketones seem to be degraded rather rapidly at a rate comparable to benzo(a)pyrene.

4. Conclusion

Benzo(ghi)fluoranthene and cyclopenta(cd)pyrene occur at ratios to benzo(e)pyrene of 1.0 or higher in emissions and undegraded immissions of PAHs. This is found in samples A and K. Low ratios of the three PAHs cyclopenta(cd)pyrene, benzo(ghi)fluoranthene and benzo(a)pyrene to benzo(e)pyrene (less than 0.5) in emission samples of different origin can be attributed to a degradation of these compounds proceeding at a faster rate than with benzo(e)pyrene. Accordingly, it is obvious that a lower ratio is found in samples with a long atmospheric exposure time. This is found in samples B – F. The ratio is also lower after exposure to daylight or elevated summer temperature when compared to darkness or lower temperature in winter. Very long sampling intervals produce degraded PAH profiles that are similar to each other even at distant sampling sites. This is attributed to a secondary dissipation of PAHs on the filter surface by the airstream passing by, and

this effect is the subject of a separate investigation being undertaken. Benzo(a)pyrene is a well known carcinogenic compound. Since this compound is rather rapidly decomposed, a decrease in carcinogenic potential of airparticulate matter with degradation by atmospheric exposure can be expected. The results reported here have an impact on all sampling experiments done over extended time intervals with atmospheric exposure. It must be assumed that all such sampling leads to PAH-profiles that were altered by degradation in the course of the sampling procedure, whenever benzo(ghi)fluoranthene, benzo(a)pyrene and cyclopenta(cd)pyrene are found at unusually low ratios to benzo(e)pyrene.

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