

Risk of cancer from the use of tar bitumen in road works

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ABSTRACT Tar bitumens are increasingly being used as a binder in road works. They consist of a standard product of about 70% bitumen and 25-30% tar. Tar bitumens are classifiable as the pyrolysis products of organic materials and are applied hot. Depending on the temperature used there are emissions of various intensities of polycyclic aromatic hydrocarbons (PAH), some of which are carcinogenic. A total of 250 one hour air samples was taken at breathing height on 20 days at 11 road works sites. The region of road paving operations in the immediate neighbourhood of the finishing machine operator and the screedmen were the chosen sampling points. A total of 19 unsubstituted PAH in the PAH complex present in the air samples was quantitatively determined by means of gas chromatography/mass spectrometry. These included benzo[b]fluoranthene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-cd]pyrene, all of which are carcinogenic. The median concentrations of chrysene and of benzo[b,j + k] fluoranthenes (determined en masse) were 9.3 and 2.8 $\mu\text{g}/\text{m}^3$ respectively. The median concentrations of benzo[a]pyrene (BaP) and indeno[1,2,3-cd]pyrene were 0.7 and 0.2 $\mu\text{g}/\text{m}^3$ respectively. Dibenzo[a,h]anthracene had the lowest median concentration with about 0.03 $\mu\text{g}/\text{m}^3$. Of the resulting shift means, the BaP concentration was over 1 $\mu\text{g}/\text{m}^3$ in about 50% of the cases, over 2 $\mu\text{g}/\text{m}^3$ in 35%, and over 5 $\mu\text{g}/\text{m}^3$ in about 15%. Even when the temperature of the paving mix was only between 120° and 135°C, 4.8% of the concentrations (\equiv 3 samples) were greater than 2 μg BaP/ m^3 ; this value was exceeded in 34.9% of the determinations (\equiv 30 samples) when the temperature of the tar bitumen was between 135° and 150°C. The highest concentration measured here was 17.8 μg BaP/ m^3 . The recommended maximum paving temperature of the paving mix of 150°C was exceeded in about 23% of all cases. The maximum concentration determined under any condition was 22 $\mu\text{g}/\text{m}^3$. Thus the employment of tar bitumen as a binding material during road paving operations must be regarded as causing a considerable risk to health. The primary task is to ascertain whether tar bitumen can be replaced as a binder in paving for roads and what safety measures are practicable.

The places of work where the air contains polycyclic aromatic hydrocarbons (PAH) include the production and processing of high boiling residues of the dry distillation (pyrolysis) of fossil fuels. Those worthy of mention include coke works, gas works, iron foundries, and the manufacture of aluminium.¹⁻⁴ Here it is mainly preparations based on coal tar or pitch that are used.

The risk of cancer to people inhaling such substances has been established^{5,6} whereas in animal experiments tars and pitches are among the classic carcinogenic materials.⁷⁻⁹

Tar bitumen is used as a binder for bituminous

mixes used in road works or the laying of load bearing, binding, and surface layers. Under experimental conditions it has been possible to record the evaporation of measurable amounts of PAH emissions from tar bitumen even at temperatures of about 100°C.¹⁰

Thus there is a presumption that PAH including carcinogenic substances will be emitted during hot paving. Tar bitumen is a standardised product containing about 70% road bitumen and 25-30% of "special coal tar pitch."¹¹ This pitch is produced from coal tar by a specialised process. Its PAH content corresponds to that of the tar bitumens of earlier years.¹² A tar bitumen binder known as Carbobitumen 70 has been used in road laying for some time.

The aim of our investigation was to analyse the

PAH profile in air samples taken at road works and to estimate the risks to health of those engaged in using Carbobitumen. We also wished to determine the benzo[a]pyrene concentrations achieved at the maximum paving temperature of 150°C recommended by the manufacturers.

Material and methods

DESCRIPTION OF WORK AND SAMPLING METHOD

The most important work areas of the paving machine using bituminous mixtures were included in the investigation. The air samples were made, according to the regulations, at breathing height and in the immediate neighbourhood of the machine operator and the rakerman on the screed distributor with heated flattening equipment and thus correspond to measurements made for a particular person. The driver sits on his paver about 1.50 m over the asphalt mix on the finishing machine platform and controls the individual functions of the machine. Whether the covered cabin is open at the sides depends on the weather. There is normally a worker to the left and another to the right of the finisher to carry out any subsidiary tasks, such as removing asphalt mix that has fallen sideways from the finisher or flattening small areas of paving. The rakerman also monitors the thickness of the paving being laid and controls the supply of new asphalt mix from trucks reversing up to the finisher.

It proved possible to determine representative PAH concentrations for a shift on 20 days at 11 road work sites. A total of 250 air samples was taken. Of these, 58 determinations were made in the driving cab of the finisher and 192 samples were taken in the working area around the screed distributor. The samples were collected for one hour.

The technical conditions were those laid down for the analysis process in the TRGS 402* criteria. The points these cover include the method of analysis, number, and spatial and temporal distribution of the samples to be taken together with their analytical determination.¹³

The analyses of the bituminous mixtures being used at a particular site for their PAH contents may, under certain conditions, allow conclusions to be made concerning the concentration of the emitted PAH. For this purpose 21 material samples were taken and included in the investigation.

ANALYTICAL PROCEDURES

The sampling equipment comprised a special filter

holder containing a glass fibre filter connected to a controlled sampling pump.

It has been shown experimentally that, despite their high boiling points, the saturated vapour pressures of some PAH are considerable.^{14,15} This can have an appreciable effect on the results obtained even at temperatures that are to be expected at the workplaces involved. Thus if the samples are collected on filters alone losses must be expected even from particularly bound PAH, particularly when the size of the ring system is small as a result of re-evaporation from the filter. Losses caused by this blow off effect together with the gaseous PAH components present in the emissions, which are not, or not completely, retained, may be adsorbed on a collection phase comprising XAD-2 or Tenax resin connected after and in series with the filter system. We have already reported elsewhere on the reliability of this combined system.¹⁶ It makes it possible to differentiate between the PAH associated with the particulate matter collected on the glass fibre filter and the total PAH concentration of the air sample.

The material samples, the glass fibre filters used for sampling, and the Tenax or XAD-2 adsorption resins were subjected to Soxhlet extraction with boiling toluene for four hours. Further sample preparation steps were then applied to the PAH containing extracts.¹⁷⁻¹⁹ The qualitative and quantitative analysis of the PAH was made by capillary gas chromatography. Indeno[1,2,3-cd]fluoranthene was used as an internal standard. The individual components were identified by comparing their gas chromatographic retention times with those of reference PAH and by their mass specific detection exploiting the substance specific individual molecular masses (SIM = selected ion monitoring).

CHOICE OF PAH

The choice of the PAH used as reference substances was made on the basis of toxicological criteria and the possibility of their presence in the air at the place of work.⁶ The PAH included in the investigation, the abbreviations used for them in the text, melting points and boiling points, and their carcinogenic and mutagenic properties as shown in animal experiments and the Ames test respectively are listed in table 1.

The five compounds marked with an asterisk are included in the list of maximum workplace concentrations and biological tolerance values for substances at the place of work of the Deutsche Forschungsgemeinschaft.⁵ These substances have been unequivocally proved to be carcinogenic in animal experiments and under conditions that are comparable with those obtaining for man at the place of work.

*Technische Regeln für Gefahrstoffe (Technical rules for hazardous materials).

Table 1 The 19 polycyclic hydrocarbons (PAH) chosen for an estimate of the risk involved in the work areas of road works during the use of tar bitumen as a binder. The table includes the abbreviations, the melting and boiling points, and biological activities according to animal experiments and the Ames test; the PAH are divided according to the ring system

	Abbreviation	MP (°C)	BP (°C)	Carcinogenicity (animal studies)	Mutagenicity (Ames test)
4 Ring systems					
Fluoranthene	FLU	111	383	-; CC	+
Pyrene	PYR	150.4	393	-; CC	-
Benzo[a]fluorene	BAFL	190	407	-	+/-
Benzo[b]fluorene	BBFL	208-209	401-402	-	-
Benzo[c]phenanthrene	BCPH	66.1	435	++; TI	++
Benzo[a]anthracene	BAA	160-161	438	±/+; TI	+
Chrysene*	CHR	256	441	±/+; TI	+
5 Ring systems					
Benzo[b]naphtho[2,1-d]thiophene	BNT	185.8	429.9	-	+
Benzo[ghi]fluoranthene	BGHIF	149	431.8	-	-
Benzo[b+j+k]fluoranthene*	BBJKF	165-217	480-481	+/+ +/+ +/+; TI	++/+ +/+ +
Benzo[e]pyrene	BEP	178.7	493	-/+	+
Benzo[a]pyrene*	BAP	178.1	496	+++ +/+ +/+ +/+; TI	+++ +
Perylene	PER	273-274	497†	-	+
Dibenzo[a,j]anthracene	DAJA	197	531†	++	+
Dibenzo[a,h]anthracene*	DAHA	266.6	535†	+++ +/+ +/+ +/+; TI	+++ +/+ +/+ +
6 Ring systems					
Indeno[1,2,3-cd]pyrene*	IND	163.6	534†	+/+ +/+; TI	++
Benzo[ghi]perylene	BGHIP	278.3	542†	+/-; CC	+/-
Anthanthrene	ANT	264	547†	±/+ +	+
7 Ring systems					
Coronene	COR	438-440	590†	+/-; TI	+

*Unequivocally shown to be carcinogenic in animal experiments.⁵

†Estimated from the gas chromatographic retention time.

- No evidence for animal carcinogenicity/mutagenicity.

± Very weakly active; + weakly active; ++ moderately active; +++ very active; ++++ extremely active.

TI = Tumour initiator; CC = Cocarcinogenic with benzo[a]pyrene.

Biological activities published often differ and in some cases several reports are cited.

Results

Figure 1 illustrates the gas chromatogram of an extract obtained from an air sample collected at the workplace during road works involving the use of tar bitumen. A total of 19 unsubstituted PAH in this complex pollutant spectrum were quantitatively determined.

The means of the PAH concentrations in all 250 air samples may be found in fig 2. They are presented with the mean PAH concentrations of the 21 samples of bitumen mix based on Carbobitumen which were

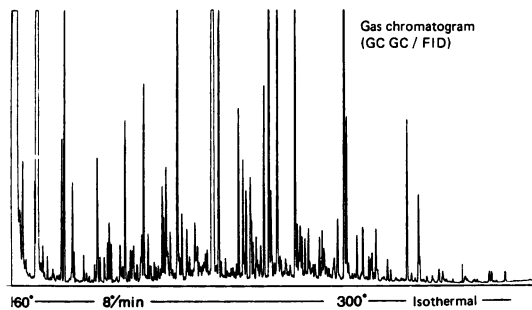


Fig 1 Glass capillary gas chromatogram (GCGC/FID) of extract of air sample taken in work area of road works during use of tar bitumen as binder.

included in the investigation. The comparable PAH profiles of both material samples are striking. On account of the differing temperature dependent volatilities of the individual PAH and the considerable scatter that this causes in the atmospheric concentrations it is not possible to draw any conclusions concerning quantitative relations. Thus the standard deviations for the PAH concentrations in the air are

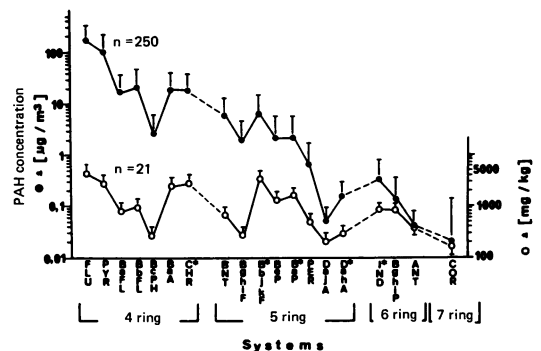


Fig 2 Means and standard deviations [$\mu\text{g}/\text{m}^3$] of PAH concentrations determined in 250 air samples from work area of road works during use of tar bitumen as binder, with means and standard deviations [mg/kg] of PAH content in 21 tar bitumen asphalt mixes. (See table 1 for abbreviations.)

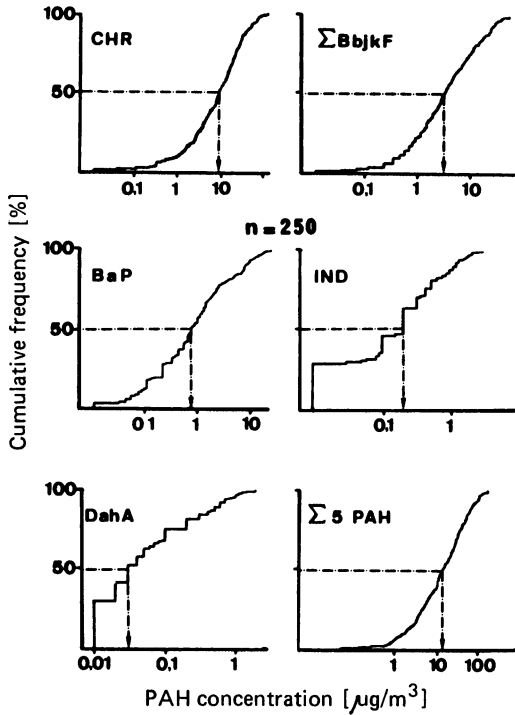


Fig 5 Cumulative frequencies of concentrations [$\mu\text{g}/\text{m}^3$] of individual PAH and of the sum of the concentrations of five carcinogenic PAH from 250 individual determinations in work area of road works during use of tar bitumen as binder. (See table 1 for abbreviations.)

The health risk for workers who are exposed to PAH may be estimated from the shift mean concentrations obtained from the eight hour day determinations of benzo[a]pyrene on the basis of a threshold for BaP of $2 \mu\text{g}/\text{m}^3$. Figure 6 shows the cumulative frequencies of the average BaP concentrations established on the 20 days during which determinations were made; more than 50% of the determined concentrations lie above $1 \mu\text{g BaP}/\text{m}^3$ air breathed. About 35% of the determinations exceed the threshold of $2 \mu\text{g}/\text{m}^3$ as the shift average. The threshold of $5 \mu\text{g BaP}/\text{m}^3$ laid down for short term exposure of one half hour per shift was exceeded in about 15% of the results obtained.

The influence of the paving temperature of the asphalt mix on the PAH may be seen in table 2 using the BaP concentration as an example. As expected, the PAH emissions increase with increasing temperature. Even at paving temperatures of $120\text{--}135^\circ\text{C}$, 4.8% of the measurements lie over the threshold of $2 \mu\text{g BaP}/\text{m}^3$. When the temperature is in the $135\text{--}150^\circ\text{C}$ range there is an appreciable overstepping of this limit of 34.9%. When the temperature is over 150°C the

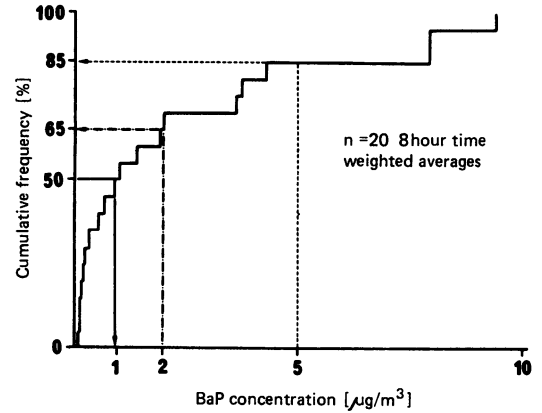


Fig 6 Cumulative frequency of mean shift benzo[a]pyrene concentrations [$\mu\text{g}/\text{m}^3$] from 20 days of determination at road works where tar bitumen was used as a binder.

emission behaviour is characterised by high, sometimes very high, BaP concentrations with a median of $3.1 \mu\text{g}/\text{m}^3$ and an absolute maximum of $22.0 \mu\text{g}/\text{m}^3$.

Discussion

Epidemiological investigations have shown an association in man between tumours and occupational contact with mixtures of PAH.²⁰⁻²² It is not possible to investigate the carcinogenic effects of individual, chemically pure PAH, or mixtures of chemically pure PAH epidemiologically because PAH at the place of work are always accompanied by other products of pyrolysis.

The carcinogenic effects of various PAH in animals have been confirmed many times^{6, 23}, the suspicion that the carcinogenic effect of particulate smokes and pyrolysates principally results from their PAH content has also been confirmed in animal experiments for coal smoke particles, particulate motor vehicle emissions, and used lubricating oils.^{24, 25} On the basis of animal

Table 2 Medians and ranges of the emitted benzo[a]pyrene concentrations ($\mu\text{g}/\text{m}^3$) and the percentages of them higher than $2 \mu\text{g}/\text{m}^3$ as a function of paving temperature of the asphalt mix for samples taken in the work area of road works during the use of tar bitumen as binder

Paving temperature of coal tar pitch/asphalt mix ($^\circ\text{C}$)	Benzo[a]pyrene ($\mu\text{g}/\text{m}^3$)		Measurements (n)	BaP $> 2 \mu\text{g}/\text{m}^3$ (%)
	Median \bar{x}	Range		
< 120	0.2	0.01–0.9	45	—
$120\text{--}135$	0.5	0.03–8.1	62	4.8
$135\text{--}150$	1.2	0.03–17.8	86	34.9
> 150	3.1	0.3–22.0	57	56.2

experiments (epicutaneous tests) it has been estimated that 70–100% of the total carcinogenic effect of these emission condensates results from their PAH content.^{25–27} A total of about 10% and 6% respectively of the carcinogenic potential of the PAH fraction of condensed coal burning and gasoline engine emissions are attributable to their benzo[a]pyrene content.^{26–28} The effect of PAH with more than three rings explains more than 80% of the carcinogenic effect of motor vehicle exhaust particles (gasoline engines), whereas the effect of benzo[a]pyrene only accounts for 2–3% of the total.²⁴ In the case of the products of combustion of coal fired plants lung implantation in rats yields results similar to those obtained from dermal application in mice.²⁹

The gene toxicity of numerous PAH has been shown in various short term test systems (see ref 30, for example.) There is usually a mutagenic effect by which the genetic constitution of cells or bacteria is altered. The extrapolation of such results to man does not, however, envisage altered genetic constitution but carcinogenic cell damage.

From the complex spectrum of gas chromatographically and mass spectroscopically detectable PAH in the atmospheric samples from the workplace during road paving it was possible to determine quantitatively 19 PAH, some of which have decidedly carcinogenic properties. Benzo[a]pyrene is of particular importance. Special occupational protection measures are laid down from $2 \mu\text{g}/\text{m}^3$ for this substance.³¹ The tar bitumen used in road works has a mean content of 0.17% benzo[a]pyrene. This, together with the mean concentration of 2.5% of all the PAH compounds that could be determined in the investigation, explains the sometimes extremely high atmospheric concentration measured. Thus 50% of the samples yielded total PAH concentrations of more than $236 \mu\text{g}/\text{m}^3$; this included a contribution of $14 \mu\text{g}/\text{m}^3$ from the five PAH that have unequivocally been shown to be carcinogenic. In 10% of the samples these five PAH amounted to more than $100 \mu\text{g}/\text{m}^3$ and amounted to about 11% of the total PAH concentration.

Bjørseth *et al* have studied highly contaminated places of work in aluminium production and in coke works by making large numbers of determinations of PAH emission.^{32,33} According to these authors the mean total concentrations of 14 comparable PAH determined on the oven tops of a coke works are about twice as high as the corresponding mean concentrations of $366 \mu\text{g}/\text{m}^3$ determined when using tar bitumen in road works. The ratios in the work area of the "vertical pin Söderberg" plant in aluminium production are virtually reversed. Here the sums of the concentrations of 14 PAH amounted to about $194 \mu\text{g}/\text{m}^3$. It is true that at 46 and $5 \mu\text{g}/\text{m}^3$ respectively the

mean BaP concentrations at workplaces in the coke works and aluminium production plant are appreciably higher than the mean concentration of $2.2 \mu\text{g}/\text{m}^3$ determined for the road works. Nevertheless, a maximum BaP concentration of $22 \mu\text{g}/\text{m}^3$ and concentrations of over $10 \mu\text{g}/\text{m}^3$ in 10% of cases make it necessary to classify the work area in road building as just as strongly potentially carcinogenic when tar bitumen binder is used as the above mentioned places of work in coke works and aluminium production plants. The paving temperature of the asphalt mix has a decisive effect on the level of the PAH emissions. Even when the temperature was in the range 120–135°C three of 62 samples (\equiv 4.8%) had concentrations greater than $2 \mu\text{g BaP}/\text{m}^3$. The measured concentration of $8.1 \mu\text{g BaP}/\text{m}^3$ must be regarded as being particularly high. In all, 33 of the 193 results obtained at temperatures below the maximum recommended operating temperature of 150°C exceeded $2 \mu\text{g}/\text{m}^3$. It had previously been assumed on technical grounds that paving with tar bitumen using mechanical paving machines and paving temperatures $< 150^\circ\text{C}$ would lead to BaP concentrations lower than $2 \mu\text{g}/\text{m}^3$.³⁴ The BaP concentrations reported here have shown this assumption to be in need of correction. As the investigations also proved, paving temperatures higher than 150°C occur not infrequently (in 23% of the cases investigated here). This leads to intense exposure of the workers to PAH emissions.

Comparative investigations of various places of work in coke works and aluminium production plants have shown a great constancy and agreement in the PAH profiles of the characteristic PAH emissions.^{32,33,35,36} For this reason some authors have regarded it as being sufficient to determine one reference component, such as BaP, as representative of the total carcinogenic effect of the total PAH spectrum. This is not satisfactory from an occupational medical oncological point of view. The criterion of exceeding or not exceeding a BaP concentration of $2 \mu\text{g}/\text{m}^3$ taken as a reference substance does not adequately represent the carcinogenic risk in the work areas engaged in road works. Factors such as, for instance, the daily changing paving temperatures of the asphalt mix and the highly variable pitch content of the binder lead to variations in the PAH content of the daily profile which may sometimes be considerable. It thus seems to us appropriate here to at least determine the spectrum of unequivocally carcinogenic as well as of cocarcinogenic and tumour promoting PAH. It is sufficiently well known that some compounds—for example, fluoranthene and pyrene—can multiply the carcinogenic effect of benzo[a]pyrene several fold.^{37,38} The continued use of tar bitumen in road works should be questioned and consideration should be given as to whether this

product can be replaced as a binder for bituminous asphalt mix.

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