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Polycyclic Aromatic Hydrocarbons in the Occupational Environment during Exposure to Bitumen Fumes

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Abstract

Bitumens are produced and commonly used in paving, roofing and flooring operations, as well as corrosion-protective materials in Polish industry. During these processes bitumens, heated to the temperature range from 140°C to 200°C, emit multicomponent mixtures of toxic substances into the workplace air. Assessment of workers' exposure to polycyclic aromatic hydrocarbons (PAHs) during road paving and production of roofing papers, asphalt-rubber blend and lute was the aim of this study.

The results indicated that PAHs were detected in the breathing zone of all workers. Especially dangerous to human health was the process of roofing paper production. Exposure factors for PAHs (benzo [a] pyrene, benzo [a] anthracene, anthracene, dibenzo [a, h,] antracene, benzo [b] fluoranthene, benzo [k] fluoranthene, indeno [1,2,3-c, d] pyrene, chrysene, benzo [g, h, i] perylene) went up to 20.88 μg/m^3.

Keywords: bitumens, asphalt, occupational exposure, carcinogenic compounds, polycyclic aromatic hydrocarbons, PAHs

Introduction

Bitumens comprise a range of products, derived from crude oil by refinery processes, which are essentially mixtures of hydrocarbon-type molecules and are thermoplastic in nature. Frequently, they are mixed with suitable volatile solvents such as a petroleum distillate to obtain more fluid for ease of handling. Bitumen mixes may contain different types of bitumen and bitumen derivatives, and they are classified according to appropriate tests that relate to the requirements of the intended application.

Bitumens are used mainly in road and airfield paving, roofing, flooring and the corrosion protection of metals. Road paving is an extensive industry involving nearly 15,000 workers in Poland. More than 80% of bitumens are used in the many different forms of road construction and maintenance.

Epidemiological studies of occupational exposure to bitumens have indicated an increased cancer risk in road paving workers and roofers [1-4]. These studies have limitations, and the conclusions on the specific causes of the observed excess cancer risk of the lung, oral cavity, larynx, oesophagus, stomach, skin and bladder and for leukaemia are not explicitly verified. The excess cancer risk cannot be attributed specifically to bitumen, because the workers may be exposed not only to bitumen but also to coal-tar pitches and other materials. Also, the relation between bitumen exposure and cancer was not determined [1, 2]. The American Conference of Governmental Industrial Hygienists (ACGIH) has established a threshold limit value – time-weighted average (TLV-TWA) for asphalt (bitumen) fume – 0.5 mg/m^3, as a benzene-soluble aerosol with a notation A4, which means that bitumen fumes are not classifiable as

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a human carcinogen [3]. Instead, the International Agency for Research on Cancer (IARC) [4] also has not classified bitumen as a human carcinogen (group 3), but extracts of steam-refined is classified as possibly carcinogenic for humans (Group 2B). This category is used for agents, mixtures and exposure circumstances for which there is limited evidence of carcinogenicity in humans and less than sufficient evidence of carcinogenicity in experimental animals. Although irritation effects of bitumens have been reported [5-7], a few studies have indicated a consistent association between exposure to bitumen fumes and lung function [8, 9].

Bibliography data indicate that during processes of bitumens under high temperature range from 140°C to 200°C are emitted multicomponent mixtures of toxic substances into workplace air. As bitumens consist essentially of hydrocarbons and their derivatives, the emitted mixtures contain organic compounds, among others – small quantities of polycyclic aromatic hydrocarbons (PAHs). The type and the quality of the substances in emitted mixtures is dependent of the crude oils from which bitumes were manufactured and especially on the temperature of liquefaction processes. In field studies under similar conditions, higher material temperatures have been found to lead to higher volatile compounds, fumes and particulate matter concentrations in the working environment.

Bitumen workers are exposed mainly through the inhalation of toxic substance fumes and vapours, and also through the skin. In the case of polycyclic aromatic hydrocarbons, skin penetration is an important route of entry into the body, especially in the handling of coal tar products. The significance of the dermal route is still unclear among bitumen workers [10].

Respiratory occupational exposure to bitumens has been studied by determining the following agents: total particulates, bitumen fumes as cyclohexane- or benzene-soluble matter, volatile organic compounds and PAHs, in gas-phase and particle form [10-14].

The concentrations of total particular matter ranged from 0.1 to 18.7 mg/m^3 and the solvent fraction – from 0.1 to 16.6 mg/m^3 [11, 12]. Brandt et al. [13] have identified in the paving workers' breathing zone fourteen polycyclic aromatic hydrocarbons: phenanthrene, anthracene, dibenzo [a, h] anthracene, fluoranthrene, pyrene, chrysene, benz [a] anthracene, perylene, benzo [a] pyrene, benzo [g, h, i] perylene, anthanthrene, dibenzopyrene, coronene. PAH$_S$ represented a small fraction of the benzene – soluble matter in selected air samples. The amount of these compounds in the breathing zone would appear to be directly associated with the amount of solvent fraction. Time-weighted average concentration of total PAHs over 8 h ranged from 0.004 to 2.971 µg/m^3.

As indicated, Finnish research [10] of bitumen worker exposure to total particulates showed low results, below – 0.1 mg/m^3. Only at the breathing zone of manual mastic pavers did the average concentration of total particulates exceed 1 mg/m^3. Approximately 75% of the total particulate results were below the TLV-TWA value of bitumen fumes (0.5 mg/m^3). The highest bitumen fume concentrations were also determined during manual mastic paving (2.65 mg/m^3). HPLC analysis showed that the arithmetic mean concentrations of total PAHs and PAHs of greater than four aromatic rings were 5.03 and 0.11 µg/m^3, respectively. The determining PAH concentrations during road paving were lower in comparison to other industries [4].

Biomonitoring of the metabolite of pyrene, 1-hydroxypyrene in urine has usually been used to determine workers' exposure to PAHs, also in pavers and roofers handling bitumens. Numerous studies have confirmed that 1-hydroxypyrene (1-OHP) is a good exposure indicator in occupational exposure to all PAHs [14,15]. However, a recent study of occupational exposure during road paving in Finland [10] has indicated that a reliable assessment of individual pavers exposed to PAHs only on the basis of urinary metabolite of pyrene is precluded. The results of this investigation have not indicated a significant difference between the postshift and preshift concentrations of 1-OHP in the road pavers' urine, in spite of the high correlation of pyrene concentrations on workplace air with urinary 1-OHP, which may suggest other PAH sources besides bitumen, like food and smoking habits or delayed adsorption of pyrene through the skin.

Assessment of occupational exposure to fifteen PAHs frequently appearing in industrial fields is very difficult because there are no limit values available for all individual PAH concentrations in workplace air, also in biological material, like blood, urine etc.

Of industries associated with PAHs, it is only in Polish regulations that a Maximum Admissible Concentration (MAC) has been established for a mixture of nine gas-phase and particle PAHs: benzo [a] pyrene, benzo [a] anthracene, anthracene, dibenzo [a, h,] antracene, benzo [b] fluoranthene, benzo [k] fluoranthene, indeno [1,2,3-c, d] pyrene, chrysene, benzo [g, h, i] perylene. This MAC value of 2 µg/m^3 refers to the sum of the concentration of particular PAHs multiplied by their relative carcinogenic factors (Table 1) proposed by Niebst and LaGoy [16].

Occupational risk connected with the appearance of a carcinogenic agent, also PAHs in workplace air, even if the exposure is lower than MAC value, is always assessed as high. That is why identification and determination of PAHs in bitumens fumes and assessment of workers' exposure to these suspected carcinogens to humans were the aim of an experimental investigation.

The objective of this study was to assess occupational exposure to PAHs during road paving and roofing paper, asphalt-rubber blend and lute production, taking in consideration nine of them, for which a Polish MAC value has been established.

Materials and Methods

Instrumentation

Gynkotek GINA 50 HPLC system, equipped with fluorescence detector and autosampler; a laboratory shaker;

ultrasonic bath, solid phase extraction-apparatus – Supelco; personal SKC and TWO-MET AP-2 pumps.

Chemicals

Dichlormethane, toluene, acetonitrile for HPLC (produced by Riedel de Haën); polycyclic aromatic hydrocarbons, and ORBO-43 tubes (Supelco), glass fibre filters of pore diameter 0.8 μm (Whatman).

PAH_s Measurement

Separation of polycyclic aromatic hydrocarbons and the adequate sensitivity of determination were ensured by the column: Supelcosil™LC-PAH column with gradient mobile phase acetonitrile: water (50: 50/5 min/100: 0/20 min/50: 50/2 min), flow rate 2 ml/min, and fluorescence detector programmed excitation (246-300 nm) and emission (370-500 nm).

For PAH sampling, glass fibre filters and ORBO-43 tubes with the flow rate below 100 L/h were used. Prior to sampling, the filters were prewashed ultrasonically in toluene and conditioned in a desiccator for about 24 h at ambient temperature and constant humidity. After sampling the filters were transported in the dark and stored at -20°C. The filters and solid sorbent from ORBO-43 tubes were extracted ultrasonically with dichloromethane (5 mL) for 20 minutes. The extract was then evaporated to dryness in nitrogen atmosphere. Purification of PAHs was achieved by using the solid phase extraction method of Supelco-SPE Instrument.

The method was developed and validated with accordance to general requirements for the performance of procedures for the measurement of chemical agents concentrations in workplace air, including in PN–EN 482 [18]. The overall precision was in the range 5.0-7.5%, instead overall uncertainty: 11.1-16.0%. The detection limits and others validating data of the methods for the select measuring PAHs are presented in Table 2.

Description of Plant Activity

Assessment of occupational exposure to toxic substances emitted in thermal plasticization processes of bitumen was carried out in three kinds of plants – roofing paper production, asphalt-rubber blend and lute production and road paving. The selection of processes was

Table 1. Toxicological properties of the determinated PAHs and their carcinogenic factors.

PAHs	Classification as dangerous substances [17]	Relative carcinogenic factor [16]
Naphthalene	Carc. cat.3 R40, Xn R22, N R50/53	0.001
Acenaphthene	Nc	0.001
Fluorene	Nc	0.001
Phenanthrene	Nc	0.001
Fluoranthene	Nc	0.001
Pyrene	Nc	0.001
Chrysene*	Carc. cat.2 R45, Muta. cat. cat.3, R68, N R50/53	0.01
Benzo[g,h,i]perylene*	Nc	0.01
Anthracene*	Nc	0.01
Benzo[a]anthracene*	Carc. cat. 2 R45, N R50/53	0.1
Benzo[b]fluoranthene*	Carc. cat. 2 R45, N R50/53	0.1
Benzo[k]fluoranthene*	Carc. cat. 2 R45, N R50/53	0.1
Indeno[1,2,3-cd]pyrene*	Nc	0.1
Benzo[a]pyrene*	Carc. cat. 2 R45, Muta. cat. 2, R46, R43, N R50/53	1.0
Dibenzo[a,h]anthracene*	Carc. cat. 2 R45, N R50/53	5.0

Abbrevation: *) PAHs for which Polish MAC value are established; nc -Not classified as hazardous agents; Carc. cat. 2 – classified as carcinogenic agent categorie 2 (possible human carcinogen); Muta. cat. 2 – classified as mutagenic agent categorie 2 (possible mutagenic to human); Xn – harmful; N – dangerous for the environment; R22 – Harmful if swallowed. R40 – Limited evidence of carcinogenic effects. R43 – May cause sensitisation by skin contact. R45 – May cause cancer. R46 – May cause hereditery genetic damage. R68 – Possible risk of irreversible effects. R61 – May cause harm to fetus. R50/53 – Very toxic to aquatic organisms.

made by taking into account different the materials and processes involved.

Roofing Paper Production

Determination of fifteen PAHs in workplace air for 27 workers employed during processes of roofing paper production was performed. Roofing paper is produced in the impregnation process of the cardboard by proofing asphalt PS 40 heated to about 185°C. At the next step of production, both sides of impregnated cardboard are protected by asphalt – PS 75 at the same temperature.

Air samples were taken in the breathing zone of asphalt pump operators, proofing tank operators, plating tank operators, pasting machine operators, coiler operators, workers transporting the product, and five other operators.

Asphalt – Rubber Blend and Lute Production

Asphalt D 175, latex and unicor 53 are the main components used in the production of two kinds of isolation materials: asphalt-rubber blend and lute. They are heated to 80°C and mixed with bentonite, p-cumenephenol and dioctyl adipate during blend manufacturing, and – in the case of lute – with bentonite, sylimic and talc. Final products are loaded into plastic containers by hands. Personal air samples in the breathing zone of workers producing these products were taken.

Road Paving

The air was sampled during road surface coating with asphalt. Asphalt D 50 is mixed with grinding aggregate at about 130-180°C in a paving plant. After that process the hot blend was transported to the roadside and was overloaded to tar spraying tanker by which the asphalt layer was applied to the road surface. Behind the tanker, the roller hardens and smoothes the asphalt layers.

Assessment of exposure to chemical compounds, especially to PAHs, was carried out on 11 workers of paving teams: tar spraying tanker operators, roller drivers and pavers.

Results and Discussion

Forty-one full-shift personal samples were collected. The range of concentrations of individual PAHs and descriptive statistic are presented in Table 3.

For occupational exposure assessment to PAHs during road paving, roofing paper, asphalt-rubber blend and lute production exposure factors were calculated. Only seven PAHs – benzo [a] pyrene, dibenzo [a, h] antracene, benzo [b] fluoranthene, benzo [k] fluoranthene, chrysene, benzo [g, h, i] perylene, and anthracene – were taken into account in the calculated exposure factors, because none of the samples contained benzo [a] anthracene and indeno [1,2,3-c, d] pyrene.

Exposure factors (C) in µg/m^3 for determining PAHs were calculated according to:

$$C = (x_1 \times w_1) + (x_2 \times w_2) + (x_3 \times w_3) + (x_4 \times w_4) + \\ + (x_5 \times w_5) + (x_6 \times w_6) + (x_7 \times w_7) + (x_8 \times w_8) + (x_9 \times w_9)$$

where:

$x_1 \ldots x_9$ – time weighted average concentrations of particular PAHs, µg/m^3

$w_1 \ldots w_9$ – carcinogenic factors for PAHs listed in Table 1.

The calculated exposure factors for determining PAHs are introduced in Table 4.

Table 2. Validating data of PAH methods.

No.	PAH	Determination limit [µg/m^3]	Relative standard deviation [%]	Correlation coefficient	Overall precision [%]	Overall uncertainty [%]
1	Chrysene*	0.008	6.2	0.9797	6.5	15.8
2	Benzo[g,h,i]perylene*	0.010	5.1	0.9899	5.8	14.3
3	Anthracene*	0.010	6.2	0.9770	7.5	15.5
4	Benzo[a]anthracene*	0.015	7.5	0.9878	6.0	11.1
5	Benzo[b]fluoranthene*	0.010	5.8	0.9800	6.5	12.5
6	Benzo[k]fluoranthene*	0.012	5.5	0.9878	5.0	12.0
7	Indeno[1,2,3-cd]pyrene*	0.012	10.2	0.9981	6.9	13.8
8	Benzo[a]pyrene*	0.007	6.4	0.9899	6.6	13.2
9	Dibenzo[a,h]anthracene*	0.010	5.8	0.9784	6.4	15.4

The investigations indicated that every one of forty-one participants of our experiments were exposed to polycyclic aromatic hydrocarbons, but in the above 50% workplaces only a few (three to seven) from 15 determined PAHs were found. Only acenaphthene, fluorene and naphthalene, which are not classified as human carcinogenic agents, existed in all investigated air samples.

Benzo [a] pyrene was detected in the air of the 25 workplaces. The highest exposure factor for this compound was 0.05 µg/m^3 and it was 40 times lower than the Polish MAC value established for this compound: 2 µg/m^3. Dibenzo [a, h] anthracene, the most carcinogenic of the 15 PAHs determined, was present in the breathing zone of 16 workers. The time-averaged

Table 3. Average concentrations of individual PAHs (µg/m^3) in the workers' breathing zone.

PAH	Concentration (µg/m^3)								
	Paper roofing			Asphalt blend and lute packing			Road paving		
	Concentration range	Average n=25	SD	Concentration range	Average n=3	SD	Concentration range	Average n=13	SD
Naphthalene	0.090 –3.220	0.614	0.815	0.390 – 0.75	0.630	0.208	0.1 – 5.5	1.736	2.62
Acenaphthene + fluorene	0.050 – 3.050	0.888	0.869	0.230 – 0.50	0.340	0.140	0.2 – 17.3	4.465	6.46
Phenanthrene	n.d. – 0.480	0.078	0.158	0.050 – 0.12	0.09	0.035	n.d. – 5.17	0.764	1.58
Anthracene**	n.d. – 0.120	0.014	0.022	0.008 – 0.01	0.009	0.001	n.d. – 0.27	0.038	0.08
Fluoranthene	n.d. – 0.140	0.039	0.049	0.030 – 0.04	0.036	0.006	n.d. – 0.35	0. 038	0.10
Pyrene	n.d. – 0.170	0.053	0.082	n.d. – 0.010	0.003	0.006	n.d. – 0.24	0.043	0.08
Benzo[g,h,i]perylene**	n.d. – 0.559	0.037	0.113	n.d. – 0.100	0.030	0.058	n.d. – 0.048	0.005	0.010
Indeno[1,2,3-cd]pyrene**	n.d.			n.d.			n.d.		
Benzo[a]anthracene**	n.d.			n.d.			n.d.		
Chrysene**	n.d. – 0.076	0.048	0.196	0.002* - 0.008	0.005	0.003	n.d. – 0.03	0.003	0.010
Benzo[b]fluoranthene**	n.d. – 0.117	0.014	0.037	n.d. – 0.010	0.004	0.005	n.d. – 0.066	0.006	0.020
Benzo[k]fluoranthene**	n.d. – 0.060	0.009	0.023	n.d. – 0.007	0.002	0.004	n.d. – 0.064	0.005	0.020
Benzo[a]pyrene**	n.d. – 0.480	0.006	0.012	0.003* - 0.013	0.007	0.005	n.d. – 0.034	0.006	0.010
Dibenzo[a,h]anthracene**	n.d. – 4.160	0.272	0.860	n.d. – 0.03	0.010	0.017	n.d. – 0.076	0.007	0.020
Average ofTotal PAHs	-	2.070	-	-	1.170	-	0.300	7.12	-

* below limit detection of the method; ** PAHs for which MAC values exist; n. d. not detected

Table 4. Exposure factors of PAHs.

Type of production	Workplace titles	Number of workplaces	Range of calculated exposure factors (µg/m^3)	Median
Production of roofing paper	Pump operator	3	4.22 – 20.88	5.52
	Proofing tank operator	3	0.0001 –3.12	0.0003
	Plating tank operator	7	0 – 1.61	0.0007
	Coiler operator	2	0 – 0.88	-
	Transporting operator	3	0 – 3.31	0.035
	Paster operator	4	0 – 0.66	0.0007
	other	5	0.0006 – 0.027	0.007
Production of asphalt-rubber and lute	Packers	3	0.0015 – 0.08	0.06
Road paving	Tar-spraying tanker operator	3	0.003 – 0.042	0.007
	Roller operator	2	0.0005 – 0.002	-
	Pavers	6	0 – 0.22	0.0008

weighed concentration in one case was on level 4 μg/m^3.

As shown in Table 3, there is a wide variability in determined concentration of individual PAHs. Brandt et al. [13] also reported high individual variability in PAH exposure level of paving, roofing and mastic laying workers, but their results related to the other 14 compounds with five and six rings. The authors have not determined five potential carcinogenic compounds: benzo [b] fluoranthene and benzo [k] fluoranthene.

The average concentrations of total PAHs in the breathing zone of workers during mastic production, roofing papers and road paving ranged from 1.17 μg/m^3 to 7.12 μg/m^3, similar to other reported studies [10,13]. In bitumen fumes emitted in investigated processes, volatile PAHs were present primarily in the gaseous phase: acenaphthene, fluorene and naphthalene constituted the main part of all determined PAHs, about 72-85%.

Thirty-seven workers were exposed to benzo [a] pyrene, dibenzo [a, h] antracene, benzo [b] fluoranthene, benzo [k] fluoranthene, chrysene, benzo [g, h, i] perylene, and anthracene, for which MAC values exist. The highest quantity of PAHs, taken into account in occupational exposure assessment, in all determined PAHs (nearly 18%) occured in the workplace air in roofing paper production, the lowest quantity (1%) during road paving, in spite of average total PAH concentrations three times higher than in roofing paper plants.

The calculated exposure factors as the sum of the concentration of particular PAHs multiplied by their relative carcinogenic factors ranged from 0.0001-20.88 μg/m^3. Significantly, the highest exposure factors of PAHs were determined in workplace air in the roofing paper plant. Time averaged concentrations exceed 1.5 to 20 times the Polish MAC value for PAHs at the five workplaces: at the three bitumens pump operators, planting tank operator and transporting operator (Table 4). The concentrations of benzo [a] pyrene in these workers' breathing zones were at low levels, in the range 0.01-0.05 μg/m^3 (0.005-0.025 MAC value for benzo [a] pyrene).

The concentration of benzo [a] pyrene in workplace air is a basis for assessment of exposure to bitumen fumes in Polish industry and also in other industrial technologies, where polycyclic aromatic hydrocarbons are occur. A recent study [19] has concluded that benzo [a] pyrene concentration can be used to simplify the quantification of personal exposure to a mixture of PAHs, but there may be some industrial processes with high proportion of the gaseous phase PAHs in which this concept could be less appropriate. The results of this study indicated that measurement of benzo [a] pyrene only for assessment of worker exposure to PAHs is not a good indicator of occupational exposure to carcinogenic agents in bitumen product production.

The results of occupational exposure to PAHs among workers handling bituminous fumes in Polish enterprises carried out in this study indicated that these compounds can be dangerous for worker health, especially those employed in roofing paper production plants.

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