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Identification and determination of polycyclic aromatic hydrocarbons (PAHs) in Diesel exhaust in the working environment and assessment of workers' occupational exposure to these suspected human carcinogens were the aim of this experimental investigation.

The range of exposure factors calculated on the basis of 9 individual PAH concentrations determined in personal air samples shows that time-averaged concentration of these compounds did not exceed the Polish Maximum Admissible Concentration (MAC) value for PAHs, that is, 2 $\mu g \cdot m^{-3}$. The highest concentrations of PAHs were determined in the breathing zone of forklift operators. The maximum exposure factor was 0.427 $\mu g \cdot m^{-3}$ (about 1/4 of MAC).

Diesel combustion exhaust   occupational exposure   workplace air
carcinogenic compounds   PAHs

1. INTRODUCTION

Diesel exhaust is a complex mixture of combustion products of Diesel fuel. The composition of this mixture depends on the type of engine, the speed and

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load at which it is run, and the composition of the fuel used. In general, the organic compounds identified in Diesel exhaust emission contain hydrocarbons (aliphatic and aromatic), hydrocarbon derivatives, polycyclic aromatic hydrocarbons (PAHs), PAH derivatives, heterocyclic compounds, and heterocyclic derivatives. The organic fractions consist of soluble organic compounds such as aldehydes, alkanes, alkenes, and high-molecular weight PAHs and PAH derivatives. Diesel exhaust contains mutagenic and carcinogenic chemicals, both when it is in the vapour phase and when associated with respirable particles (Cantrell &Watts, 1997; IARC, 1989; Leberchert & Czerczak, 1997).

The International Agency for Research on Cancer (IARC, 1989) has classified whole Diesel exhaust as probably carcinogenic to humans. Epidemiological studies have shown that Diesel emissions cause increased incidence of lung cancer in occupationally exposed workers. Elemental carbon particles are considered likely to account for human lung cancer because they can penetrate the entire lung, and also because they adsorb different chemical substances including PAHs and nitroarenes.

Diesel exhaust is a chemically complex mixture containing a few hundred different chemical compounds. This complexity makes it impossible to monitor all exhaust pollutants to determine exposure. That is why some measure of exposure must be selected. In general two methods have been used for monitoring occupational exposure to Diesel exhaust. In the first one, Diesel particulate matter (DPM) is measured: Submicrometer particulate mass is measured with the gravimetric method, whereas respirable combustible dust is measured both with the gravimetric method and with elemental carbon (Cantrell &Watt, 1997; Dahman & Bauer, 1997; National Institute of Occupational Safety and Health, 1998). The other method consists in measurements of specific polycyclic hydrocarbons in the working environment (Davies, Bartle, Williams, & Andrews, 1988; Dridi, Driss, Sabbah, & Bouguerra, 1998; Mar et al., 1999; Schilhabel, Winkeler, & Levsen, 1989; Tancell, Rhead, Pemberton, & Braven, 1995). DPM is emphasised because it is a major component of Diesel exhaust, it is suspected of contributing to a health hazard, and it is measurable. PAHs are closely associated with DPM and are suspected of having a role in cancer initiation.

Assessment of occupational exposure to Diesel exhaust has not been solved, because limit values for this mixture of chemical compounds and particulate matter in the working environment have not been established. Recently the American Conference of Governmental Industrial Hygienists (ACGIH) has proposed a Threshold Limit Value (TLV) of 0.15 $mg{\cdot}m^{-3}$ for Diesel particulates and a designation of a suspected human carcinogen.

Another proposition is a TVL of 0.02 $mg \cdot m^{-3}$ for elemental carbon in Diesel respirable particulates (ACGIH, 1997, 2001).

Of Diesel-associated PAHs, it is only in Polish regulations (Rozporządzenie, 2001) that a Maximum Admissible Concentration (MAC) has been established for a mixture of 9 gas-phase and particle PAHs: anthracene, chrysene, benzo-[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenzo[a,h] anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-c,d,i,]pyrene. This MAC value of 2 $\mu g \cdot m^{-3}$ refers to the sum of the concentrations of particular PAHs multiplied by their relative carcinogenic factors (Niebst & LaGoy, 1992). That is why identification and determination of PAHs in Diesel exhaust in the working environment and assessment of workers' occupational exposure to these suspected carcinogens to human were the aim of an experimental investigation.

The objective of this study was to estimate occupational hazards of forklift operators and workers in bus garages by monitoring 15 PAHs in their breathing

TABLE 1. Physical and Chemical Properties of Determined Polycyclic Aromatic Hydrocarbons (PAHs) and Their Carcinogenic Factors

PAHs	Molecular Weight	Number of Rings	Boiling Point (°C)	Relative Carcinogenic Factor (Niebst & LaGoy, 1992)
Naphthalene	128.2	2	217.7	0.001
Acenaphthene	154.2	3	96.2	0.001
Fluorene	166.2	3	295.0	0.001
Phenanthrene	178.2	3	340.0	0.001
Fluoranthene	202.3	4	375.0	0.001
Pyrene	202.3	4	404.0	0.001
Chrysene*	228.3	4	448.0	0.010
Benzo[g,h,i]perylene*	276.3	6	500.0	0.010
Anthracene*	178.2	3	342.0	0.010
Benzo[a]anthracene*	228.3	4	437.5	0.100
Benzo[b]fluoranthene*	252.3	5	481.2	0.100
Benzo[k]fluoranthene*	252.3	5	480.0	0.100
Indeno[1,2,3-cd]pyrene*	276.3	6	530.0	0.100
Benzo[a]pyrene*	252.3	5	310.0–312.0	1.000
Dibenzo[a,h]anthracene*	278.4	5	269.0–270.0	5.000

Notes. *—PAHs for which a Polish Maximum Admissible Concentration (MAC) value has been established (Rozporządzenie, 2001).

zone and assessing exposure taking into consideration 9 of them, for which a Polish MAC value has been established (Table 1).

2. EXPERIMENTAL

2.1. Apparatus

A Gynkotek (Germany) GINA 50 HPLC system, equipped with a fluorescence detector; a Hewlett-Packard (USA) HP 6890 gas chromatograph, equipped with a mass spectrometer; a computer containing the Wiley mass spectral library; a laboratory shaker; an ultrasonic bath; a Supelco (USA) solid phase extraction-apparatus; personal SKC (USA) and TWO-MET (Poland) AP-2 pumps.

2.2. Chemicals

Dichlormethane; benzene, acetonitrile for HPLC (produced by Riedel de Haën, Germany); PAHs and ORBO-43 tubes (Supelco, USA); glass fibre filters of pore diameter 0.8 µm (Whatman, USA).

2.3. Measurement of PAHs

Separation of PAHs and adequate sensitivity of determination were ensured by the Supelcosil™LC-PAH column (Supelco, USA) with gradient mobile phase—acetonitrile:water (50:50/5 min/100:0/20 min/50:50/2 min), flow rate 2 ml·min^{-1}, and a fluorescence detector programmed in the range 246–300 nm. Identification of particular PAHs was accepted by GC MSD-SIM with HP-5MS Ultra-low Bleed (5%-diphenyl (95%)-dimethylpolysiloxane copolymer column (30 m × 0.32 mm, film thickness 1 µm), in programmed temperature in the range 40–280 °C.

For sampling PAHs, glass fibre filters and ORBO-43 tubes with the flow rate below 100 L·min^{-1} were used. Prior to sampling, the filters were extracted ultrasonically in benzene. They were conditioned in a desiccator for about 24 hrs at ambient temperature and constant humidity. Personal breathing-zone samples were collected according to Polish Standard PN-89/Z-04008/07 (Polski Komitet Normalizacji, Miar i Jakości, 1989).

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 min. The extract was then evaporated to dryness in nitrogen atmosphere. Purification of PAHs was achieved by the use solid phase extraction method on a Supelco-SPE Instrument.

The lowest detection limit for each of the 15 PAHs was 0.001 $\mu g{\cdot}m^{-3}$ during sampling of about 0.8 m^3 of air.

2.4. Description of Plant Activity

Assessment of occupational exposure to chemical substances included in Diesel exhaust was carried out in two kinds of workplaces: for mechanics in bus garages and for forklift operators.

2.4.1. Bus garages

Determination of 15 PAHs in workplace air for 23 workers employed in bus depots was performed. Workstations were located in halls of about 200 m^2, equipped with a mechanical ventilation system.

Air samples were taken in the breathing zone of 5 mechanics working in inspection pits, 5 electromechanics, and 13 mechanics-locksmiths. About 60 buses were inspected during one workshift.

2.4.2. Forklift operators

Three or four forklifts with Diesel engines moved in commercial and customhouse warehouses, whose area was about 250 m^2. Those warehouses were equipped with ventilation systems. Personal air samples were taken in the breathing zone of 24 drivers during transport and handling of products.

3. RESULTS

Forty-seven full-shift personal samples were collected. Tables 2 and 3 present the range of concentration of individual PAHs and descriptive statistics.

To assess occupational exposure to PAHs, exposure factors were calculated for 9 PAHs: benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, benzo[g,h,i]perylene, anthracene, and indeno[1,2,3-c,d]pyrene (Table 4).

TABLE 2. Average Concentrations of Individual Polycyclic Aromatic Hydrocarbons (PAHs) in the Breathing Zone of Bus Garage Workers

PAHs	Concentration (µg m^{-3})								
	Mechanic (Inspection Pit)			Electromechanic			Mechanic-Lockmith		
	Minimum--Maximum	Arithmetic Mean (n = 5)	*SD*	Minimum--Maximum	Arithmetic Mean (n = 5)	*SD*	Minimum-Maximum	Arithmetic Mean (n = 13)	*SD*
Naphthalene	0.35900–9.94000	3.75100	4.2200	0.22900–20.29400	8.3726	8.2890	0.1060–22.2390	5.52140	8.24190
Acenaphthene	0–23.20700	9.97700	8.5270	0.80500–27.20600	10.4650	9.9890	2.7130–55.9700	20.92900	23.87200
Fluorene	0.00330–0.06100	0.01600	0.0250	0.00200–0.13800	0.0300	0.0600	0.0020–0.1080	0.03200	0.05100
Phenanthrene	0.00200–0.01300	0.00820	0.0045	0.00200–0.06100	0.0200	0.0230	0.0100–0.0620	0.02800	0.02350
Anthracene	0.00005–0.01500	0.00720	0.0066	0.00100–0.01800	0.0080	0.0080	0.0020–0.0270	0.01120	0.01130
Fluoranthene	0.00500–0.02300	0.01300	0.0079	0.00400–0.44100	0.0930	0.1940	0.0090–0.1860	0.06250	0.08310
Pyrene	0–0.07700	0.03940	0.0288	0.00200–0.13400	0.0530	0.0510	0.0280–0.1240	0.06570	0.04100
Benzo[g,h,i]perylene	0.00100–0.00900	0.00460	0.0030	0.00100–0.11500	0.0270	0.0490	0.0020–0.0110	0.00550	0.00400
Indeno[1,2,3-cd]pyrene	0.00200–0.32200	0.06600	0.1430	0.00200–0.33600	0.0690	0.1490	0.0020–0.2320	0.05950	0.11500
Benzo[a]anthracene	0.00200–0.01800	0.00590	0.0069	0.00100–0.01200	0.0056	0.0047	0.0020–0.0290	0.01450	0.01400
Chrysene	0.00100–0.00500	0.00240	0.0017	0.00030–0.00900	0.0029	0.0035	0.0010–0.0150	0.00650	0.00645
Benzo[b]fluoranthene	0.00100–0.01900	0.00660	0.0074	0.00100–0.01100	0.0660	0.0048	0.0004–0.0110	0.00735	0.00500
Benzo[k]fluoranthene	0.00100–0.00280	0.00136	0.0008	0.00030–0.00500	0.0023	0.0021	0.0004–0.0030	0.00185	0.00135
Benzo[a]pyrene	0.00100–0.02800	0.01320	0.0124	0.00100–0.01600	0.0101	0.0058	0.0050–0.0310	0.01500	0.01160
Dibenzo[a,h]anthracene	0–0.01100	0.00370	0.0047	0.00009–0.00300	0.0029	0.0041	0.0001–0.0050	0.00180	0.00220

TABLE 3. Average Concentrations of Individual Polycyclic Aromatic Hydrocarbons (PAHs) in the Breathing Zone of Forklift Operators

PAHs	Concentration (μg·m^{-3})		
	Minimum-Maximum	Arithmetic Mean (*n* = 24)	*SD*
Naphthalene	0–84.3720	15.2890	21.8590
Acenaphthene	0.1920–17.2770	6.7770	5.0160
Fluorene	0–0.1990	0.0160	0.0420
Phenanthrene	0.0070–0.1520	0.0350	0.0390
Anthracene	0.0020–0.0410	0.0130	0.0080
Fluoranthene	0.0030–0.3200	0.0530	0.0640
Pyrene	0–0.3860	0.1330	0.0820
Benzo[g,h,i]perylene	0–0.0450	0.0150	0.0100
Indeno[1,2,3-cd]pyrene	0 –0.0320	0.0047	0.0091
Benzo[a]anthracene	0–0.0710	0.0200	0.0190
Chrysene	0.0030–0.0320	0.0100	0.0080
Benzo[b]fluoranthene	0.0040–0.0590	0.0130	0.0120
Benzo[k]fluoranthene	0.0020–0.0075	0.0160	0.0080
Benzo[a]pyrene	0.0080–0.0630	0.0220	0.0160
Dibenzo[a,h]anthracene	0–0.0110	0.0027	0.0028

TABLE 4. Comparison of Exposure Factors of All 9 Polycyclic Aromatic Hydrocarbons (PAHs) and Benzo[a]pyrene

Workplaces	Number of Work-places	All 9 PAHs (μg·m^{-3})		Benzo[a]pyrene (μg·m^{-3})	
		Range of Exposure Factors (Minimum-Maximum)	Median	Range of Exposure Factors (Minimum-Maximum)	Median
Mechanics in inspection pits	5	0.008–0.045	0.024	0.001–0.025	0.012
Electromechanics	5	0.006–0.084	0.057	0.001–0.016	0.008
Mechanics-locksmiths	13	0.009–0.161	0.036	0.001–0.038	0.019
Forklift operators	24	0.011–0.427	0.072	0.008–0.063	0.031

4. DISCUSSION

The investigation indicated that all 47 participants of our experiments were exposed to PAHs and in more than 90% of workplaces, there were all 15 of the determined PAHs.

The total concentration of PAHs (without naphthalene) in the breathing zone air of forklift operators and workers in bus garages ranged from 1.588 to

17.505 µg·m^{-3}. The investigations indicated that naphthalene and acenaphthene were the most abundant hydrocarbons in Diesel exhaust.

As shown in Tables 2 and 3, there is a wide variability in the determined concentrations of individual PAHs. Dridi et al. (1998) also reported high individual variability in PAH emission from Diesel car engines, but their results refer only to hydrocarbons adsorbed on glass fibre filters.

The range of exposure factors calculated on the basis of 9 individual PAH concentrations determined in personal air samples (Table 4) shows that time-averaged concentrations of these compounds did not exceed Polish MAC for PAHs. The highest concentrations of PAHs were determined in the breathing zone of forklift operators. The maximum exposure factor was 0.427 µg·m^{-3}, which is about one quarter of the MAC value (2 µg·m^{-3}).

Benzo[a]pyrene, for which the relative carcinogenic factor is 1, was detected in the air of all workplaces. The highest exposure factor (time-averaged weighed concentration) for this compound was 0.063 µg·m^{-3} and it was about 30 times lower than the Polish MAC value for benzo[a]pyrene.

Frequently, in different technologies where PAHs might be present, concentration of benzo[a]pyrene only is measured, and its concentration is considered an exposure factor in assessing exposure to PAHs. Figures 1 and 2 present a comparison of the concentration of benzo[a]pyrene and of the remaining PAHs in workplace air during the operation of forklifts and buses with Diesel engines.

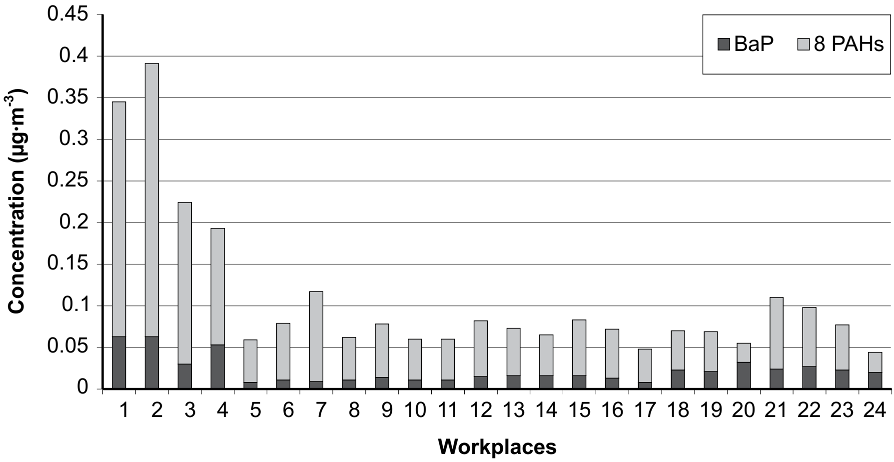

Figure 1. Forklift operators. Exposure to benzo[a]pyrene and 8 polycyclic aromatic hydrocarbons (PAHs): dibenzo[a,h]anthracene, benzo[a]anthracene, anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, benzo[g,h,]perylene, and indeno[1,2,3-c,d]pyrene. *Notes.* BaP—benzo[a]pyrene.

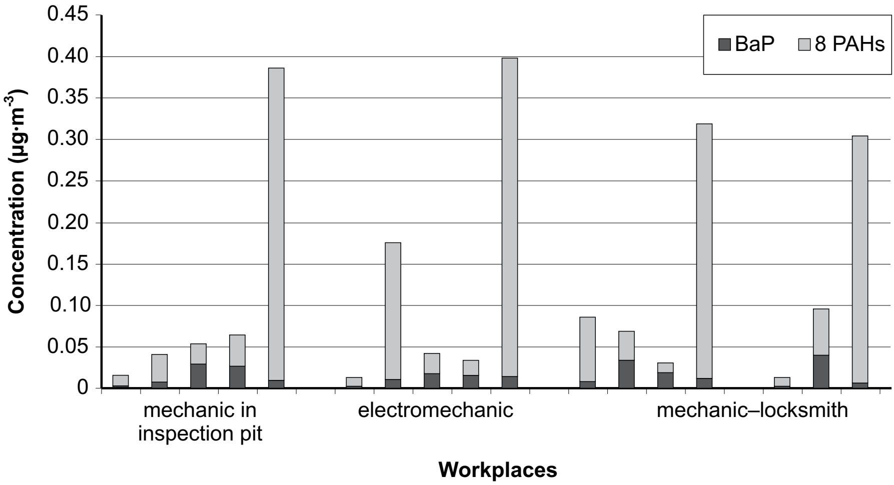

Figure 2. Workers in bus garages. Exposure to benzo[a]pyrene and 8 polycyclic aromatic hydrocarbons (PAHs): dibenzo[a,h]anthracene, benzo[a]anthracene, anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, benzo[g,h,] perylene, and indeno[1,2,3-c,d]pyrene. *Notes.* BaP— benzo[a]pyrene.

The results of our investigation confirm that measurements of only benzo[a]pyrene for occupational assessment of workers' exposure to PAHs during emission of Diesel combustion exhaust is not correct and does not indicate the hazard to human health.

REFERENCES

American Conference of Governmental Industrial Hygienists (ACGIH). (1997). *Threshold Limit Values for chemical substances and physical agents (TLVs) and Biological Exposure Indices (BEIs)*. Cincinnati, OH, USA: Author.

American Conference of Governmental Industrial Hygienists (ACGIH). (2001). *Threshold Limit Values for chemical substances and physical agents (TLVs) and Biological Exposure Indices (BEIs)*. Cincinnati, OH, USA: Author

Cantrell B.K., & Watts, W.F. (1997). Diesel exhaust aerosol: Review of occupational exposure. *Applied Occupational Environmental Hygiene, 12*(12), 1019–1027.

Dahman, D., & Bauer, H.-D. (1997). Diesel particulate matter (DPM) in workplaces in Germany. *Applied Occupational Environmental Hygiene, 12*(12), 1028–1037.

Davies, I.L., Bartle, K.D., Williams, P.T., & Andrews, G.E. (1988). On-line fractionation and identification of Diesel fuel polycyclic aromatic compounds by two-dimensional microbore high-performance liquid chromatography/capillary gas chromatography. *Analytical Chem*istry, *60*, 204–209.

Dridi, S., Driss, M.R., Sabbah, S., & Bouguerra, M.L. (1998). Determination of aromatic hydrocarbons in airborne Diesel exhaust particulates by HPLC with UV detection and wavelenght programming. *Journal of Liquid Chromatography, 21*(4), 475–489.

International Agency for Research on Cancer (IARC). (1989). Diesel and gasoline engine exhausts. In *IARC monographs on the evaluation of carcinogenic risks to humans: Vol. 46. Diesel and gasoline engine exhausts and some nitroarenes* (pp. 41–185). Lyon, France: Author.

Leberchert, G., & Czerczak, S. (1997). Spaliny silnika Diesla [Diesel combustion exhaust]. *Wytyczne szacowania ryzyka zdrowotnego dla czynników rakotwórczych, 6*, 42–84.

Mar, L.C., Kirchstetter, T.W., Harley, R.A., Miguel, A.H., Hering, S.V., & Hammond S.K. (1999). Characterisation of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions. *Environmental Sciences Technology, 33*, 3091–3099.

National Institute of Occupational Safety and Health (NIOSH). (1998). *NIOSH manual of anlytical methods. Method 5040—Elemental carbon (Diesel particulates)* (4th ed.). Cincinnati, OH, USA: Author.

Niebst, I.C.T., & LaGoy, P.K. (1992). Toxic for polycyclic aromatic hydrocarbons. *Regulatory Toxicology and Pharmacology, 16*, 290–300.

Polski Komitet Normalizacji, Miar i Jakości. (1989). *Ochrona czystości powietrza. Pobieranie próbek powietrza. Zasady pobierania próbek powietrza w środowisku pracy i interpretacji wyników* [Air purity protection. Sampling methods. Principles of air sampling in the work environment and of interpreting the results] (Standard No. PN-89/Z-04008/07:1989). Warsaw, Poland: Wydawnictwa Normalizacyjne Alfa.

Rozporządzenie Ministra Pracy i Polityki Społecznej z dnia 2 stycznia 2001 r. zmieniające rozporządzenie w sprawie najwyższych dopuszczalnych stężeń i natężeń czynników szkodliwych dla zdrowia w środowisku pracy [Decree of the Minister of Labour and Social Policy of January 2, 2001, amending the decree on maximum admissible concentrations and intensitities of agents harmful to health in the working environment]. (2001). *Dziennik Ustaw, 4*, item 36, p. 247.

Schilhabel, J., Winkeler, H.D., & Levsen, K. (1989). Analysis of polycyclic aromatic hydrocarbons in Diesel particulate extracts by high performance liquid chromatography (HPLC). *Fresenius Journal of Analytical Chemistry, 333*, 748.

Tancell, P.J., Rhead, M.M., Pemberton, R.D., & Braven, J. (1995). Survival of polycyclic aromatic hydrocarbons during Diesel combustion. *Environmental Sciences Technology, 29*, 2871–2876.