Polycyclic Aromatic Hydrocarbons Distribution in Fine and Ultrafine Particles Emitted from Diesel Engines

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Abstract

This paper presents the results of PAH determination adsorbed on fine and ultrafine particles emitted to the air from diesel exhaust, with a special emphasis on sample preparation procedure prior to HPLC-FL analysis. Samples were taken with a personal environmental monitor and personal cascade impactor in order to ensure size-segregated sampling of air particulate matter (in the range of the following particles' diameters <0.25, 0.25-0.5, 0.5-1.0, 1.0-2.5, and 2.5-10 μm). Application of solid phase extraction with a BakerBond PolarPlus column and mixture of acetonitrile/isopropanol (1:1 v/v) for PAH's elution ensures recovery values of 94%. The mean content of total PAHs collected at the Diesel engine came to (68.0 ± 3.4) and (78.1 ± 3.9) ng·m^{-3} in $PM_{2.5}$ and PM_{10} fractions, respectively. The sum of pyrene, fluoranthene, and benzo(a)anthracene contributed to 74% in the $PM_{2.5}$ and 66% in PM_{10} fraction of total PAH content. Average total PAH's concentrations in smaller fractions of 0.5-1.0 μm, 0.25-0.5 μm, and <0.25 μm separated with PCI sampler were determined at the level of (15.5 ± 0.7), (2.05 ± 0.1), and (40.9 ± 2.1) ng·m^{-3}, respectively. In the ultrafine particles' fraction (diameters below 0.25 μm), such compounds as phenanthrene, fluoranthene, pyrene, benzo(*a*)anthracene, benzo(*k*)fluoranhene, and benzo(*ghi*)perylene were identified and determined. The percentage of PAH's input in $PM_{0.25}$ fraction came to the level of 52% on average, in comparison to total PAH concentrations in the PM_{10} fraction.

Keywords: polycyclic aromatic hydrocarbons, particle size distribution, diesel exhaust fumes, solid phase extraction

Introduction

Motor vehicles fuelled with gasoline or diesel are important source of pollutant emissions, particularly toxic compounds with potential health impact, in ambient and working environments. The emitted exhaust from heavy-

and light-duty engines is a mixture of gases, vapours, semi-volatile compounds, and particulate matter. These particles, which contain mainly elemental carbon, represent a good sorption surface for the hundreds of organic and inorganic compounds produced after incomplete combustion in diesel engines. Particulate matter (PM) is currently the most severe air contaminant, causing approximately 300,000 deaths annually in Europe [1, 2]. Epidemiological studies

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indicate that increases in ambient PM concentrations lead to short-term morbidity and mortality. Exhaust fumes from petrodiesel are one of the most important sources of fine and ultrafine PM. The size of airborne particles determines parts of the respiratory tract that they are deposited in. PM with aerodynamic diameter (dp) smaller than 10 micrometers (PM_{10}) are associated with respiratory responses, while those of diameters below 2.5 micrometers ($PM_{2.5}$) are associated mainly with cardiovascular diseases [3, 4]. Several epidemiological and toxicological studies indicate that fine PM (dp < 2.5 μm) causes pulmonary inflammation as well as systemic effects in humans [5]. There are also studies indicating that ultrafine particles (0.1 μm) are more toxic than larger ones. Combustion-derived ultrafine particles could be a true driver of adverse effects of particulate air pollution. Epidemiological and toxicological research suggests that there is a statistically significant increase in neoplastic diseases in the case of workers exposed to this kind of PM [3]. However, the process of cancer transformation under the influence of PM, especially its fine fractions (dp <2.5 μm) containing mixtures of xenobiotics, is not fully explained. Chemical information has an important role to play in the study of diesel emissions, as it can provide insight into a variety of problems related to PM emissions.

Most of the research concerning motor vehicle exhaust fumes has been focused on mass concentrations in particles, either a total mass concentration [6-9] or both PM_{10} and $PM_{2.5}$ fractions [10-13]. Particle size distribution affects the particulate matter's transport in the air, dry or wet deposition from the atmosphere onto natural surfaces. Data on particle size distribution of organic compounds is crucial in order to estimate their input into the ecosystems and deposition into the human respiratory system [14]. Furthermore, small particles can penetrate deeply in the lungs and cause direct health problems since the threat to humans connected with inhalation of organic aerosols depends on its size [15].

Polycyclic aromatic hydrocarbons (PAHs) are widespread contaminants formed during incomplete combustion of organic matter in the air. In cities, vehicular traffic is considered to be the most significant contributor to the atmospheric PAH's load [16]. Dunbar et al. [17] suggested, on a per vehicle basis, that busses and trucks (the majority of which run on diesel fuel) emit greater amounts of particle-bound PAHs than passenger vehicles. Since several PAHs and some of their degradation products (oxygenated and nitrated PAHs) are known to have high carcinogenic and mutagenic potential [18, 19], they consequently have been included in the European Union priority lists of pollutants [20, 21]. Benzo(a)pyrene (a 5-ring PAH) is considered as one of the most carcinogenic PAH's and has been used as an indicator of environmental PAH's exposure.

PAHs with two or three aromatic rings are mostly detected in the vapor phase, whereas those between four and seven fused rings are generally associated with particulate matter [22]. Due to the complexity of aerosol and low concentration levels of PAHs, enrichment and clean-up procedures are usually required prior to the final chromatographic analysis. Solid phase extraction (SPE) is widely applied in polycyclic aromatic hydrocarbon analysis [23-27]. One of the benefits of using SPE is that only small volumes of solvent are required and purification time is short. It also allows for a wide variety of extraction conditions that may be used to achieve the desired separation and preconcentration.

The literature review clearly indicates that there have been relatively few studies reported on any aspects of chemical composition of ultrafine particles in the diesel exhaust fumes. Moreover, mostly for such type of analysis samples are taken directly from the exhaust pipes at specially constructed stands in conditions simulating urban driving conditions. Simultaneously, there is a lack of measurements indicating how many particles are transferred to the air of people working directly with the diesel engines. Due to a great interest in the contribution of fine and ultrafine particles in exposure assessment, research was undertaken in order to assess the distribution of PAH's concentration in dust fractions emitted from diesel exhaust fumes, which are common dangerous agents in the working environment.

Presented results confirmed that PAHs included in the particles emitted from diesel engines are mainly present in its ultrafine fraction that penetrates the human respiratory tract down to the gas exchange regions [3]. If a mass of particles suspended in the air is comprised mainly of fine particles, they penetrate into the lungs till pulmonary alveolus. These particles do not return when they reach the trachea, but part of fine dust gets through directly inside the human body and thus may cause cardiovascular diseases. Organic compounds transmitted on the surface of particles are dissolved owing to the humidity of respiratory systems and quickly reach the organism. Therefore, health effects are different for both direct respiratory system and other internal organs. The smaller particles, the smaller mass of dust, and thus major potential damages they can cause. The probability of inhalation, exhalation, and depositing of particles inside the human body, as well as reaction to this deposition differ among individuals. However, the establishment of rules for determination and exposure assessment with respect to particle size in order to assess their influence on human health is possible and desired. For example, in Ireland, occupational exposure limit value (OELV) for 8 hours reference period for diesel exhaust particles < 0.1 μm is established for 0.15 mg/m³ [28].

Experimental Procedures

Chemicals and Materials

PAH's standard mixture and the corresponding individual compounds were obtained from Supelco. The standard PAH's mixture (EPA 610 Polynuclear Aromatic Hydrocarbons Mix 100-2000 μg·ml⁻¹ MEOH:CH_2Cl_2 (1:1)) contains: naphthalene (NA), acenaphtene (AC), fluorene (FL), phenanthrene (PH), anthracene (AN), fluoranthene (FLR), pyrene (PY), benzo(*a*)anthracene (B*a*A); chrysene

(CH), benzo(*b*)fluoranthene (B*b*F), benzo(*k*)fluoranthene (B*k*F), dibenzo(*ah*)anthracene (DBA), benzo(*a*)pyrene (B*a*P), benzo(*ghi*)perylene (B*ghi*P), and indeno(1,2,3-*cd*)pyrene (IN). A standard reference material, SRM 2975 Diesel Particulate Matter (Industrial Forklift), from the National Institute of Standards and Technology (NIST), U.S. Department of Commerce: in Gaithersburg MD was used for validation of the method.

Acetonitrile, dichloromethane, and methanol of analytical grade were purchased from Sigma-Aldrich (UK), and *iso*-propanol was purchased from J.T. Baker (Deventer, Netherlands). Milli-Q water obtained with a Milli-Q system (Millipore, Bedford, MA, USA) was used for analysis. A Sigma-Aldrich SPE 12 vacuum system (Visiprep™ SPE Vacuum Manifold) was used for extraction, and a number of Bakerbond SPE columns (J.T. Baker (Deventer, Netherlands)) were tested as described below.

To determine PAH's content in the size-segregated dust fractions, especially the smallest fraction of diameters below 0.25 μm, the EPA 610 Polynuclear Aromatic Hydrocarbons Mix standard was applied. This standard contains 15 congeners, including 9 PAHs for which the exposure assessment of workers is carried out in relation to the MAC-NDS value of -0.002 mg·m^{-3} established by Polish law. This value covers time-weighted average concentrations calculated as a sum of time-weighted average concentrations ratio for particular PAHs (that means for dibenzo(*a,h*)anthracene, benzo(*a*)pyrene, benzo(*a*)anthracene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, indeno(1,2,3*c,d*)pyrene, chrysene, anthracene, and benzo(*g,h,i*)perylene) and appropriate carcinogenic factors calculated based on B*a*P.

Sampling Site and Sampling System of PAHs

The work stand used for the generation of diesel exhausts was prepared in a garage of ca. 5×4×2 m size. A diesel common rail engine system (from the car Skoda Fabia Combi) of 2.0 L volumetric capacity with 59 kW of power at 4,000 rpm manufactured in 2007 was used for the presented studies. During the experiment, the diesel engine ran at 900 rpm·min^{-1}. The engine was mounted on a portable trolley.

Diesel fuel was EKODIESEL PLUS 50 of cetane number not smaller than 51, density of 820-845 kg·m^{-3}, and sulphur content not higher than 50 mg·kg^{-1}.

The air samples were collected at 0.5 m distance from the exhaust pipe of the working diesel engine and 1 m from the floor for 5-6 hours.

The particles were trapped on the 25 mm polytetrafluoroethylene (PFTE) filters by use of the personal cascade impactor (PCI), consisting of four impaction stages. They were separated in the following order of the particles' aerodynamic diameter: < 0.25, 0.25-0.5, 0.5-1.0, 1.0-2.5, and 2.5-10 μm. Particles of dp smaller than 0.25 μm were collected on a 37 mm after-filter made of PTFE (2 μm pore). The air flow was regulated in the range of 9 L·min^{-1} by a Leland Legacy pump. Due to the small mass of collected particles of diameters higher than 0.25 μm, for further preparation and analysis the appropriate fractions were col-

lected simultaneously from four parallel PCI samplers and analyzed together. Samples were taken at a flow rate of 9 L·min^{-1}. About 2,700-3,240 L of air was passed through the four samplers in the case of the PCI sampler.

Airborne particles also were collected using a personal environmental monitor (PEM) with 37 mm PTFE filters for PM$_{10}$ and PM$_{2.5}$ fractions. When PEM samplers were used, samples were taken with a flow rate of 10 L·min^{-1} for 6 hours.

After collection, in both cases filters were stored in darkness at 4ºC.

The gaseous phase was not sampled in the presented investigation since it was shown that more than 95% of analytes were associated with the particulate material in vehicle emissions [7].

Sample Preparation

After sampling, PAHs were extracted from filters with cold dichloromethane (below 5ºC) to prevent its loss by volatilization. A sonic bath with closed vials was used for 30 min. SPE method was applied in order to clean up samples before further HPLC analysis. The standards were prepared by spiking known amounts of the EPA 16PAH mixture from Supelco onto the filters, therefore no blank correction was applied.

Sample Extraction and Optimization of SPE Procedure

The clean-up of extracts is a very important step in determination of PAHs in diesel particulate matter due to the complexity of a matrix. For this purpose, due to the low polarity of PAHs, SPE has been used mainly with C$_{18}$-bonded silica columns. Taking into consideration suggestions made by various authors [23-27, 29, 30], the SPE optimization process was based on a choice of columns, selection of eluent, the effect of eluent volume, and sorbent preconditioning step.

Several octadecyl sorbents (J.T. Baker (Deventer, Netherlands)) were tested, including Separcol C-18, PreSep C-18, BondElut C-18, BakerBond PolarPlus, BakerBond PAHs, and BakerBond C-18. The highest level of recoveries were observed with columns filled with non end-capped C$_{18}$ (BakerBond PolarPlus). Such results were explained in the literature [31] by spherical orientation of a flat PAH molecule in a well-oriented surface structure of the stationary phase, especially these located in the pores.

Sorbents were pre-conditioned with 3 mL of methanol followed by washing, twice with 3 mL of water and 2 propanol mixture (9:1, v/v). Then a 10 mL sample solution was loaded onto the SPE column under vacuum pressure.

Solvent used for PAH's elution should be strong enough to elute the analyte and simultaneously strongly bind the pollutants. In the presented study such solvents as methanol, 2-propanol, acetonitrile, dichloromethane, and the mixture of 2-propanol with acetonitrile (1:1, v/v) were tested. Fig. 1 presents the recovery values of individual PAHs when these solvents were used for their elution from

the Baker Bond PolarPlus column. The best results were obtained for a 2-propanol-acetonitrile mixture, particularly for PAHs of larger mass. Columns were washed twice with 1.5 mL of the selected eluent.

While 2-propanol/acetonitrile eluent was used for other octadecyl columns mentioned above, lower recovery values were observed (from 20% in case of BakerBond C-18 and BakerBond PAHs columns, up to about 50% for the PreSep C-18 SPE column). It was probably caused by different properties and surface topography (porosity, density of coverage) of these materials.

Since the control of flow rate is critical for maintaining reproducible extractions, the flow through the cartridge was established to ca 2 mL·min^{-1}.

For validation of the method, the standard reference material SRM 2975 (Diesel Particulate Matter) was used. Table 1 summarizes the data obtained for the proposed SPE procedure of the studied PAH group. There is no significant difference (confidence interval at 95% using *t*-test) between achieved results and the certified content. The obtained results show that SPE treatment using BakerBond PolarPlus column could purify extracts of fine dust particles emitted from diesel engines and protect the chromatographic column in subsequent HPLC-FL analysis.
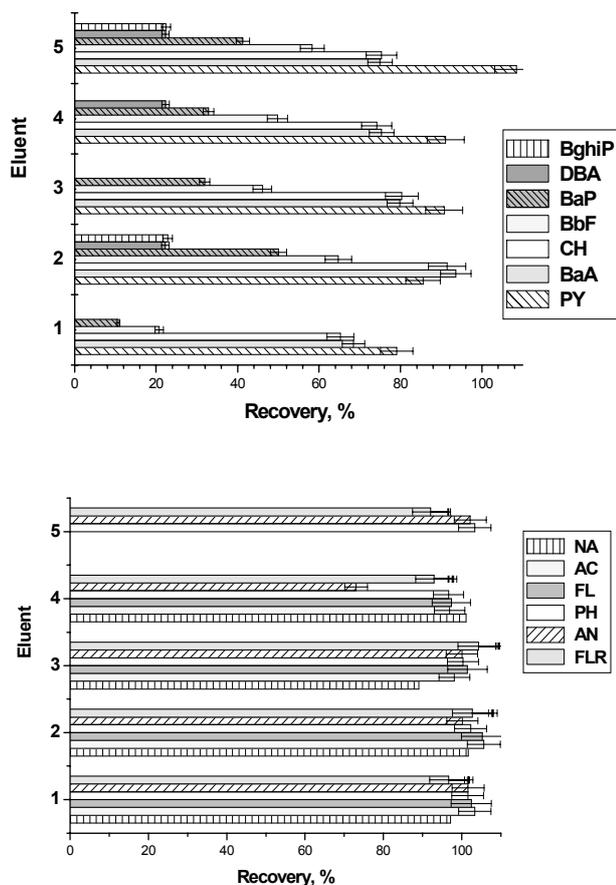
Table 1. Certified and measured concentrations (µg·g^{-1}) of exemplary PAHs in the NIST reference material SRM 2975.

PAHs	Certified values	Determined values
PH	17±2.8	16.24±0.16
FL	26.6±5.1	23.58±2.33
PY	0.9±0.24	0.83±0.02
CH	4.56±0.16	4.29±0.09

Mean±SD (standard deviation), n=5

HPLC Analysis

Separation and identification of PAHs were achieved using HPLC (EliteLaChrom, Merck Hitachi) with fluorescence detection (FL) according to the methods described in the PN-Z-04240-5/2006 standard [30]. A reversed-phase HPLC column (Pinnacle II PAH, 150×3.2 mm, 5 µm particle size) from Restek was used with a pre-column (20×3.2 mm). The flow rate was 0.97 mL·min^{-1} and the injection volume was 10 µL. Elution was performed with a gradient starting from an eluent composition of 50% acetonitrile in water (up to 5 min).

The acetonitrile concentration was increased up to 100% in 25 min, and maintained at 100% for 5 min. The wavelength of the fluorescence detector was altered for each PAH as it was defined in the previous publication of the authors [29]. Data was collected and processed with HP ChemStation software. Limit of detection (LOD) results for selected PAHs, determined based on blanks analysis, did not exceed 0.1 ng·m^{-3}. Relative standard deviation (±RSD) was calculated for 6 samples (n = 6).

Results and Discussion

Application of the sample preparation method established above allowed us to determine the content of PAHs in fine dust particles.

Samples were collected using PEM samplers, which allow us to separate the airborne particles in several ranges of their diameters. The mean content (n=6) of total PAHs collected at the diesel engine during one shift (6 h) was (68.0±3.4) and (78.1±3.9) ng·m^{-3} in PM$_{2.5}$ and PM$_{10}$ fractions, respectively. The concentrations of ten identified and determined in these fractions individual compounds are presented in Table 2. The most abundant PAHs in these fractions were pyrene (PY) and benzo(*a*)anthracene (B*a*A), followed by fluoranthene (FLR) and chrysene (CH). The sum of PY, FLR, and B*a*A contributed to 74% and 66% of total PAHs content in the PM$_{2.5}$ and PM$_{10}$ fractions, respectively. Exemplary chromatogram of PAHs emitted in the fraction of 10 µm diameter is shown in Fig. 2. The obtained results are different from those by Chao et al. [32], where the emission concentrations of total PAHs of diesel fuel were within the range of 18.8-54.4 µg·m^{-3}. However, the authors used other diesel fuel (100% fossil diesel) and a


Fig. 1. PAHs recoveries obtained with application of different eluents: (1) methanol, (2) acetonitrile: 2-propanol (1:1, v/v), (3) 2-propanol, (4) acetonitrile, (5) dichloromethane. Bars correspond to mean ±RSD (n = 4).
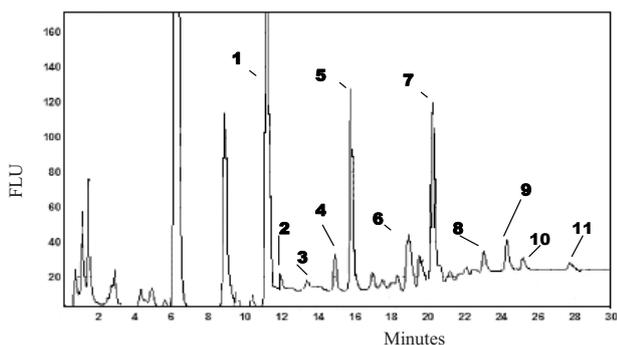
Fig. 2. Chromatogram of PAHs emitted in the particles fraction of 10 μm diameter, collected at the diesel engine. Peak identification: 1 – FLR, 2 – PA, 3 – AN, 4 – FL, 5 – FL. 6 – B*a*A, 7 – CH, 8 – B*b*F, 9 – B*k*F, 10 – B*a*P, 11 – B*ghi*P.

direct injection, turbocharged EURO II diesel engine. The authors also used a different collection method of particle-phase PAHs. They had taken samples on fibreglass filters, a gas sample was drawn directly from the tailpipe and then diluted in an ejection dilutor. Time for sampling was not given.

The concentrations of B*a*P in the analyzed $PM_{2.5}$ and PM_{10} samples were found to be 0.4 and 0.72 ng·m⁻³, respectively. Benzo(*a*)pyrene has been commonly used as a good index for the whole PAH's carcinogenicity [33]. The European Union defined a target value for B*a*P as 1 ng·m⁻³ for total content in the PM_{10} fraction [34]. This may indicate that its contamination in fine particles emitted from the tested diesel engine is below the EU legal limit.

In order to determine more in detail, the distribution of PAHs in the particles' phase emitted from a diesel engine, the personal cascade impactor sampler was used. The particles were separated into fractions of the following ranges of aerodynamic diameter: <0.25, 0.25-0.5, 0.5-1.0, 1.0-2.5, and 2.5-10 μm. Filters for collection of fractions of higher particle diameter (1.0-2.5 and 2.5-10 μm) contained such a small content of dust, that it was impossible to measure its PAHs concentration. Whereas the average total concentration of PAHs in the fractions of dp 0.5-1, 0.25-0.5, μm and < 0.25 μm were 15.5±0.7, 2.05±0.1, and 40.9±2.1 ng·m⁻³,
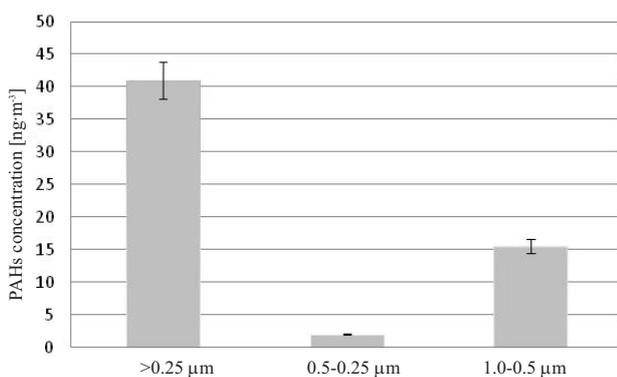
respectively (Fig. 3). These results indicate that total PAH's concentrations in diesel exhaust particles fraction of diameters smaller than 0.25 μm were higher than concentrations of these chemical substances in other remaining fractions. The size distribution of PAHs may be affected by such factors as e.g. sulphur content, as it may nucleate to provide a surface for PAHs to condense on. The fuel applied characterized over seven times smaller sulphur content with reference to the EU requirements. The percentage PAH's input in particle fractions with diameters smaller than 0.25 and 0.5-1.0 μm on average came to 52% and 20% of total PAH's concentration in the PM_{10}, respectively. Presented results also are confirmed by Di Filippo et al. [35]. The authors also received the highest content of PAHs in particle fractions of diameters below 1.0 μm. It should be emphasized, however, that the authors applied low pressure impactor (DLPI) to collect the aerosol samples and separate lower fractions, even down to 0.03 μm, and they have tested urban aerosol, not diesel exhaust fumes.

The highest concentrations of individual PAHs in fractions of diameters in the range 0.5-1 μm and 0.25-0.5 μm were detected for dibenzo(*ah*)anthracene (DBA) and benzo(*ghi*)perylene (B*ghi*P), followed by benzo(*a*)pyrene (B*a*P) and fluoranthene (FLR). In the smallest fraction (< 0.25 μm), mostly PH, FLR, PY, B*a*A, B*k*F, and B*ghi*P were identified and determined (Fig. 4). The ratio of an individual compound's content to the sum of PAHs in three collected fractions using PCI is presented in Table 3.

The toxicities of PAHs are diversified, thus the relative contribution of individual compounds is important with regard to carcinogenic or mutagenic potential of total PAHs [32]. The fine fraction (<0.25 μm) does contain compounds of established carcinogenic factors (TEF) at the levels of 0.001 (PH, FLR, PY), 0.01 (B*ghi*P), and 0.1 (B*a*A, B*k*F) [36, 37]. The highest concentrations (12.7±1.04) and (21.2±1.02) ng·m⁻³ in ultrafine fraction were detected for B*a*A and FLR, respectively. Moreover, the compounds determined within these studies also are PAHs from a group of nine that are taken into account in the exposure assessment.


Fig. 3. Total concentration of PAHs in fractions of 0.5-1.0 μm, 0.25-0.5 μm, and < 0.25 μm diameter.
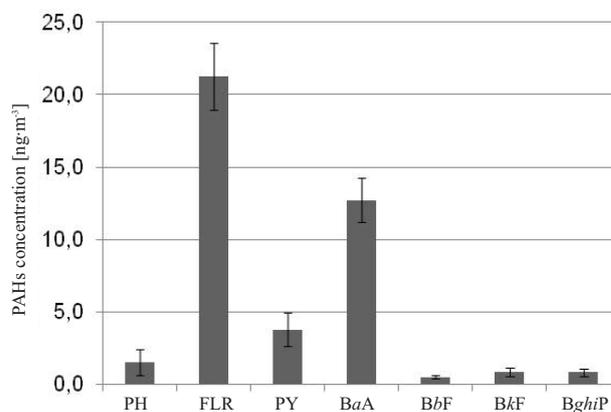
Fig. 4. Distribution of individual PAHs in ultrafine particles (<0.25 μm).

Table 2. Individual PAHs concentrations (ng·m^{-3}) collected on PM$_{2.5}$ and PM$_{10}$ (n = 10).

PAHs	PM$_{2.5}$			PM$_{10}$		
	Mean	SD	RSD [%]	Mean	SD	RSD [%]
FL	0.75	0.13	17.66	1.90	0.34	22.85
PH	3.19	1.26	32.07	6.92	1.46	26.21
AN	0.27	0.03	11.57	5.98	1.27	18.41
FLR	7.86	1.38	19.32	6.62	0.95	14.09
PY	35.64	8.66	23.75	32.57	3.58	10.65
BaA	7.14	0.42	5.31	12.35	2.43	17.67
CH	6.69	1.40	20.00	4.15	0.29	6.46
BbF	3.40	0.48	11.99	5.43	1.41	26.19
BkF	2.66	0.96	31.19	1.47	0.36	20.89
BaP	0.40	0.07	17.07	0.72	0.09	12.27

SD – standard deviation, RSD – Relative standard deviation

Table 3. The ratio of an individual compound's content to the sum of PAHs in three collected fractions using a PCI sampler.

PAHs	Fraction		
	0.5-1.0 mm	0.25-0.5 mm	<0.25 mm
PH	-	-	0.04
FLR	0.07	0.68	0.51
PY	-	-	0.09
BaA	-	-	0.31
BbF			0.01
BkF	-	-	0.02
BaP	0.11	-	-
DBA	0.30	0.07	-
BghiP	0.52	0.25	0.020

aerodynamic diameter below 0.1 μm. Such research could present a valuable input in explaning the toxicity of fine particles from diesel exhausts.

Acknowledgements

Conclusion

Thus, results of this study can be valuable data concerning PAHs content in ultrafine diesel exhaust particles of diameters smaller than 0.25 μm, which are dangerous for humans in working environments. These results will be interesting for researchers and experts involved in establishing limits in the workplace and ambient air. The correlation between particle size (mainly the smallest particles, below 0.25 μm diameter) of diesel exhausts, their chemical composition, and health hazards pose a new, interesting research direction.

Literature review indicates that particles' fraction of 0.25 μm in diesel exhausts includes a number of nanoparticles [38-40]. Therefore, research concerning PAHs concentrations should focus on their determination in particles of

References

1. POPE C.A., THUN M.J., NAMBOODIRI M.M., DOCK-ERY D.W., EVANS J.S., SPEIZER F.E., HEATH C., Particulate air pollution as a predictor of mortality in a prospective study of U.S. adults, Am. J. Respir. Crit. Care Med. **151**, (3), 669, **1995**.
2. BORM P.J.A., ROBBINS D., HAUBOLD S., T KUHLBUSCH., FISSAN H., DONALDSON K., SCHINS R., STONEV, KREYLING W., LADEMANN J., KRUT-MANN J., WARHEIT D., OBERDORSTER E. The potential risks of nanomaterials: a review carried out for ECE-TOC, Part Fibre Toxicol **3**, (11), 1, **2006**.
3. DONALDSON K., TRAN L., JIMENEZ L.A., DUFFIN R., NEWBY D. E., MILLS N., MACNEE W., STONE V., Combustion-derived nanoparticles: A review of their toxicology following inhalation exposure, Part Fibre Toxicol, **2**, (10), 1, **2005**.
4. HE CH., GE Y., TAN J., YOU K., HAN X., WANG J., YOU Q., SHAH A. N. Comparison of carbonyl compounds emissions from diesel engine fueled with biodiesel and diesel, Atmos. Environ. **43**, 3657, **2009**.
5. POPE C.A., DOCKERY D.W. Health effects of fine particulate air pollution: Lines that connect. J. Air Waste Manage. Assoc. **54**, 709, **2006**.

6. CORREA S.M., ARBILLA G. Aromatic hydrocarbons emissions in diesel and biodiesel exhaust, Atmos. Environ. **40**, 6821, **2006**.

7. BERGVALL C., WESTERHOLM R. Determination of highly carcinogenic dibenzopyrene isomers in particulate emissions from two diesel- and two gasoline-fuelled light-duty vehicles, Atmos. Environ. **43**, 3883, **2009**.

8. PORTET-KOLTAŁO F., OUKEBDANE K., DIONNET F., DESBENE P.L. Optimisation of supercritical fluid extraction of polycyclic aromatic hydrocarbons and their nitrated derivatives adsorbed on highly sorptive diesel particulate matter, Anal. Chim. Acta **651**, 48, **2009**.

9. KUUSIMÄKI L., PELTONEN K., KYYRÖ E., MUTANEN P., PELTONEN K., SAVELA K. Exposure of garbage truck drivers and maintenance personnel at a waste handling centre to polycyclic aromatic hydrocarbons derived from diesel exhaust, J. Environ. Monit. **4**, 722, **2002**.

10. GUO Z.G., LIN T., ZHANG G., HU L.M., ZHENG M. Occurrence and sources of polycyclic aromatic hydrocarbons and n-alkanes in $PM_{2.5}$ in the roadside environ of a major city in China, J. Hazard. Mater. **170**, 888, **2009**.

11. ARNODIO M., CASTELLI M., GENNARO G. DE TUTINO M. Particulate PAHs in two urban areas of Southern Italy: Impact of the sources, meteorological and background conditions on air quality, Environ. Res. **109**, 812, **2009**.

12. HAN B., BAI Z.P., GUO G.H., WANG F., LI F., LIU Q.X., LI Y.Q., HU Y.D. Characterization of PM_{10} fraction of road dust for polycyclic aromatic hydrocarbons (PAHs) from Anshan, China, J. Hazard. Mater. **170**, 934, **2009**.

13. CHIEN S.M., HUANG Y.J., CHUANG S.C., YANG H.H. Effects of biodiesel blending on particulate and polycyclic aromatic hydrocarbon emissions in nano/ultrafine/fine/coarse ranges from diesel engine, Aerosol Air Qual. Res. **9**, 18, **2009**.

14. WU S.P., TAO S., ZHANG Z.H., LAN T., ZUO Q. Distribution of particle-phase hydrocarbons, PAHs and OCPs in Tianjin, China, Atmos. Environ. **39**, 7420, **2005**.

15. HIEN T.T., THANH L., KAMEDA T., TAKENAKA N., BANDOW H. Distribution characteristics of polycyclic aromatic hydrocarbons with particle size in urban aerosols at the roadside in Ho Chi Minh City, Vietnam, Atmos. Environ. **41**, 1575, **2007**.

16. SCHAUER C., NIESSNER R., PÖSCHL U. Polycyclic aromatic hydrocarbons in urban air particulate matter: decadal and seasonal trends, chemical degradation, and sampling artifacts. Environ. Sci. Technol. **37**, 2861, **2008**.

17. DUNBAR J., LIN C., VRGUCHT I., WONG J., DURAN J., Estimating the contributions of mobile sources of PAH to urban air using real-time PAH monitoring. Sci. Total Environ. **279**, 1, **2001**.

18. TSAI P.J., SHIEH H.Y., LEE W.J., LAI S.O. Characterization of PAHs in the atmosphere of carbon black manufacturing workplaces, J. Hazard. Mater. **91**, 25, **2001**.

19. BOSTRÖM C.E., GERDE P., HANBERG M., JERNSTRÖM,B. JOHANSSON C., KYRKLUND T., RANNUNG A., TÖRNQVIST M., VICTORIN K., WESTERHOLM R. Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air, Environ. Health Perspect. **110**, 451, **2002**.

20. 98/83/EC Council Directive, on the quality of water intended for human consumption, European Commission, Brussels, **1998**.

21. 2006/0129 Directive of the European Parliament and of the Council on environmental quality standards in the field of water policy and amending Directive 2000/60/EC, European Commission, Brussels, **2006**.

22. LV J., XU R., WU G., ZHANG Q., LI Y., WANG P., LIAO C., LIU J., JIANG G., WEI F. Indoor and outdoor air pollution of polycyclic aromatic hydrocarbons (PAHs) in Xuanwei and Fuyuan, China, J. Environ. Monit. **11**, 1368, **2009**.

23. MARCÉ R.M., BORRULL F. Solid-phase extraction of polycyclic aromatic compounds, J. Chromatogr. A **885**, 273, **2000**.

24. OLESZCZUK P., BARAN S. Application of solid-phase extraction to determination of polycyclic aromatic hydrocarbons in sewage sludge extracts, J. Hazard. Mater. **113**, 239, **2004**.

25. BRUZZONITI M.C., FUNGI M., SARZANINI CO. Determination of EPA's priority pollutant polycyclic aromatic hydrocarbons in drinking waters by solid phase extraction-HPLC, Anal. Methods **2**, 739, **2010**.

26. ITOH N., NUMATA M., YARITA T. Alkaline extraction in combination with microwave-assisted extraction followed by solid-phase extraction treatment for polycyclic aromatic hydrocarbons in a sediment samples, Anal. Chim. Acta, **615**, 47, **2008**.

27. WANG H., CAMPIGLIA A.D. Determination of polycyclic aromatic hydrocarbons in drinking water samples by solid-phase nanoextraction and high-performance liquid chromatography, Anal. Chem. **80**, 8202, **2008**.

28. ROE R. Code of Practice for the Safety, Health and Welfare at Work (Chemical Agents) Regulations 2001 (S.I. No. 619 of 2001) H&SA, Irleand **2010**.

29. BARANIECKA J., PYRZYŃSKA K., SZEWCZYŃSKA M., POŚNIAK M., DOBRZYŃSKA E. Emission of polycyclic aromatic hydrocarbons from selected processes in steel works, J. Hazard. Mater. **183**, 111, **2010**.

30. PN-Z-04240-5:2006 Air purity protection – Tests of polycyclic aromatic hydrocarbons – Part 5: Determination of anthracene, benzo/a/anthracene, chrysene, benzo/b/ fluoranthene, benzo/k/fluoranthene, benzo/a /pyrene, dibenzo/ah/anthracene, benzo/ghe/perylene and indeno/123cd/pyrene in the workplace by high performance liquid chromatography.

31. GADZAŁA-KOPCIUCH R., WITKOWSKI S., BUSZEWSKI B. Isolation and determination of PAHs in urban particulate matter using combined analytical techniques, Air Protection **3**, 82, **1997** [In Polish].

32. CHAO H., YUNSHAN G., JIANWEI T., KEWEI Y., XIUKUN H., WANG J. Characteristics of polycyclic aromatic hydrocarbons emissions of diesel engine fueled with biodiesel and diesel, Fuel **89**, 2040, **2010**.

33. LAW R.J., KELLY C., BAKER K., JONES J., MCINTOSH A.D., MOFIAT C.F. Toxic equivalency factors for PAHs and their applicability in selfish pollution monitoring studies, J. Environ. Monit. **4**, 383, **2002**.

34. EC Directive, 2004/107/EC of the European Parliament and of the Council relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, Official Journal of the European Union L 23, **2004**.

35. DI FILIPPO P., RICCARDI C., POMATAD., BUIARELLI F. Concentrations of PAHs, and nitro-and methyl-derivatives associated with a size-segregated urban aerosol, Atmos. Environ. **44**, 2742, **2010**.

36. NISBET IC., LAGOY PK. Toxic equivalency factors (TEFs) for polycyclic aromatichydrocarbons (PAHs). Regul Toxicol Pharm., **16**, 290, **1992**.

37. USA EPA. Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. EPA/600/R-93/089; **1993**.

38. YAMADA H., MISAWA K., SUZUKI D., TANAKA K., MATSUMOTO J., FUJII M., TANAKA K. Detailed analysis of diesel vehicle exhaust emissions: Nitrogen oxides, hydrocarbons and particulate size distributions, Proceedings of the Combustion Institute, **33**, (2), 2895, **2011**.

39. LI X., HUANG Z., WANG J., ZHANG W. Particle size distribution from a GTL engine, Sci.Total Environ., **382**, 295, **2007**.

40. CHANDLER M. F., TENG Y., KOYLU U. O., Diesel engine particulate emissions: A comparison of mobility and microscopy size measurements, Proceedings of the Combustion Institute **31**, 2971, **2007**.