

ORIGINAL PAPER

International Journal of Occupational Medicine and Environmental Health 2016;29(4):667–682 http://dx.doi.org/10.13075/ijomeh.1896.00693

EXPOSURE TO DIESEL EXHAUST FUMES IN THE CONTEXT OF EXPOSURE TO ULTRAFINE PARTICLES

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Abstract

Objectives: Diesel exhaust fumes emission is a significant source of ultrafine particles, the size of which is expressed in nanometers. People occupationally exposed to diesel exhaust particles include mainly workers servicing vehicles with engines of this type. This article presents the analysis of measurements of ultrafine particle concentrations occurring in the bus depot premises during the work connected with everyday technical servicing of buses. Material and Methods: The measurements were carried out in the everyday servicing (ES) room of the bus depot before, during and after the work connected with bus servicing. Determinations included: particle concentrations in terms of particle number and particle surface area, and mass concentrations of aerosol. Results: Mean value of number concentration of 10- to 1000-nm particles increased almost 20-fold, from 7600 particles/cm³ before starting bus servicing procedures to 130 000 particles/cm³ during the bus servicing procedures in the room. During the procedures, the mean surface area concentration of particles potentially deposited in the alveolar (A) region was almost 3 times higher than that of the particles depositing in the tracheo-bronchial (TB) region: 356.46 µm²/cm³ vs. 95.97 µm²/cm³, respectively. The mass concentration of the fraction of particulate matter with aerodynamic diameter 0.02-1 um (PM,) increased 5-fold during the analyzed procedures and was 0.042 mg/m³ before, and 0.298 mg/m³ while the procedures continued. Conclusions: At the time when bus servicing procedures continued in the ES room, a very high increase in all parameters of the analyzed particles was observed. The diesel exhaust particles exhibit a very high degree of fragmentation and, while their number is very high and their surface area is very large, their mass concentration is relatively low. The above findings confirm that ultrafine particles found in diesel exhaust fumes may be harmful to the health of the exposed people, and to their respiratory tract in particular.

Key words:

Occupational exposure, Ultrafine particles, Diesel engine exhaust, Particles number concentration, Particles surface area concentration, SEM/EDS analysis

This work was supported under the grant agreement of Ministry of Science and Higher Education No. 5052/B/P01/2010/38 "Indicators of the exposure to nanoparticles in the workplace and their impact on the respiratory system function." Grant manager: Prof. Irena Szadkowska-Stańczyk. Received: May 26, 2015. Accepted: October 5, 2015.

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INTRODUCTION

Exposure to diesel exhaust fumes affects primarily workers of several occupational groups, but may also occur as a result of air contamination in urban environments. These exhaust fumes occur both in atmospheric air, where they become dispersed mainly by transport vehicles such as buses, railway engines, cars and especially trucks, and in the atmospheres of indoor workplaces where equipment and vehicles provided with compression-ignition engines are serviced or operated. The group of workers occupationally exposed to solid particles from exhaust fumes produced by self-ignition engines includes operators of various types of machines (excavators, cranes, forklift trucks, etc.), workers of bus depots, car mechanics, railwaymen, miners, and workers servicing machines with such engines.

Unlike the engines with spark-ignition combustion, where the combusted mixture is rather homogenous, combustion in diesel engines is strongly non-homogeneous. In selfignition engines, diesel oil is injected into a cylinder filled with high-temperature compressed air. The high temperature causes that the mixture of fuel and air is self-ignited. The composition of exhaust fumes produced during that process largely depends on the composition and properties of the diesel oil, conditions prevailing during its combustion or the engine wear. Total combustion of fuels containing hydrocarbons produces exclusively carbon dioxide (CO_2) and hydrogen oxide (H_2O) as the only products. However, although contemporary diesel engines exhibit a high efficacy of combustion – at least 98%, yet incomplete combustion in such engines results in a number of toxic products. The diversity of these products is huge, and their estimated number may be as high as several thousand different chemical compounds occurring as gas or in the form of solid particles.

The basic gaseous components of exhaust fumes emitted by compression-ignition (diesel) engines are: carbon oxides, nitrogen and its compounds, oxygen, steam, sulfur compounds and a vast number of hydrocarbons, mainly aromatic ones.

Nitrogen oxides include 2 compounds: nitrogen monoxide (NO) and nitrogen dioxide (NO₂), most toxic being nitrogen dioxide, i.e., a brown gas emitting an irritant smell. Incomplete combustion of carbon gives rise to carbon monoxide which, due to its high affinity to hemoglobin, inhibits the systemic transport of oxygen which leads to death. As a result of incomplete combustion of hydrocarbons, these compounds are also found in diesel engine exhaust fumes.

Incomplete combustion of hydrocarbons usually results from too low oxygen/fuel ratio, or from too low temperature in the combustion chamber. Gaseous hydrocarbon components of diesel exhaust include: aliphatic and cyclic hydrocarbons, saturated and unsaturated, containing up to 19 carbon atoms per particle, aldehydes (e.g., formaldehyde, acetic aldehyde, acryl aldehyde), benzene, 1,3-butadiene, polycyclic aromatic hydrocarbons (PAH) and their nitro-derivatives (nitro-PAH) [1,2].

Apart from numerous compounds occurring in the form of gases and vapors, exhaust fumes emitted by diesel engines contain very small solid particles. Emission of ultrafine particles is a phenomenon characteristic of this type of engines. Particles in diesel engine exhaust fumes are largely differentiated both in respect of their physical properties, such as shape or size, and their chemical composition.

Indices describing size and structure of diesel exhaust particles, such as mass, surface area, number, and proportions of particles with different size ranges (size distribution) are essential physical characteristics, both in respect of the feasibility of limiting their emission and their detrimental effects to human health. Those characteristics determine how deep the particles penetrate into the respiratory tract, and thus how much they impair the respiratory function.

Increased emission of ultrafine particles occurs when the engine is not warmed up, especially during its cold start-up, idle running, or when operated at a low load. Particles released by diesel engines are usually fine particles identified as particulate matter fraction with aerodynamic diameter $\leq 2.5 \ \mu m \ (PM_{2.5})$, containing a very high proportion of ultrafine particles with diameters below 0.1 μm . Ultrafine particles are emitted directly from the engine or may arise from condensation of the exhaust gas. In the environment they combine very fast into larger groups and aggregate, and thus their lifetime as independent particles is short [3,4].

Typical diesel particles are usually agglomerates consisting of approx. 15–40 nm diameter basic particles [5]. As the particles are very small, their overall surface area is very large, thus enabling adsorption of various compounds. Furthermore, due to their small size, the particles very easily get into the respiratory tract, reaching the fine pulmonary alveoli [6].

The main component of ultrafine particles in the exhaust fumes of self-ignition engines is elemental carbon in form of soot particles capable of absorbing numerous organic and inorganic compounds on their surface, e.g., hydrocarbons and their derivatives, inorganic compounds of sulfur, nitrates or metals such as lead, platinum, aluminum, calcium [1,7,8].

The chemical composition of ultrafine particles in the exhaust fumes of diesel engines, their number and size, are affected by several factors, including: engine operating conditions, use of solid particles filter, technical condition of the engine, as well as the type of engine fuel [9–12].

The accessible information indicates that exhaust fumes from diesel engines may produce very adverse health effects, including cancer. Health risks manifested by various symptoms may result from acute or chronic exposure. Following acute or short-lasting exposure, diesel exhaust fumes may cause a strong irritation of eyes, throat or bronchi, neurophysiological disorders (dizziness, nausea), and respiratory tract symptoms, e.g., coughing. Chronic exposure may result both in non-neoplastic diseases (e.g., obstructive disorders of pulmonary ventilation) and cancer [1,6,13]. In 2012, the International Agency for Research on Cancer (IARC) classified diesel exhaust fumes as carcinogenic to humans (group 1 of IARC classification). The results of epidemiological studies demonstrate that a chronic exposure to exhaust fumes emitted by selfigniting engines is connected with an increased risk of the development of lung cancer (sufficient evidence) and urinary bladder cancer (limited evidence) [14].

The main factors indicated as a cause of cancer are nanometer-sized particles, on the surface of which some of the organic compounds mentioned above are adsorbed (e.g., PAH), exhibiting carcinogenic or mutagenic effects. This study attempted to asses the concentration of the ultrafine particles released to workplace atmosphere by diesel engines during the maintenance works performed in the bus depot.

MATERIAL AND METHODS

The measurements were carried out in the room with everyday servicing channel (ES channel). Such a channel serves for everyday inspection of the technical condition of vehicles coming back to the depot after their whole day use. In each vehicle, every day (among other things) the braking system, steering wheel, power transmission system and fluid levels are checked. Then the buses are washed and cleaned inside. There were 2 parallel lines in the room, through which vehicles were passing continually, stopping at consecutive stands. The gates to the room with ES channels were opened when the next bus came in and immediately closed behind it. Two hundred buses were stationed in the depot and 2 hundred buses passed every day through the ES channel.

Evaluation of the degree of releasing nanometric-size particles at the workstations included determination of concentrations (in terms of particle number and their surface area) of nanoparticles potentially deposited in the tracheo-bronchial (TB) or the alveolar (A) regions, and determination of aerosol mass concentration. The following devices were used to determine the parameters enabling evaluation of concentrations at workplaces located in the bus depot:

- Condensation Particle Counter (CPC, model 3007-2, TSI, USA) to determine the number of 10- to 1000-nm particles in air volume unit (particle number concentration). The number of particles sized below 100 nm in a given air volume was determined by an indirect method, using the pre-selector for CPC (model 376060) which enables counting by the apparatus of particles above a specific diameter (in this case 100 nm). The number concentration of particles with 10–100 nm diameter was determined as a difference between the number of all counted particles (10–1000 nm) and the number of particles counted using the selector (100–1000 nm) in unit volume of air.
- Monitor of Nanoparticles AeroTrak 9000 (TSI, USA) to determine the surface area concentration (particles surface area in unit volume of air) of the particles depositing in tracheo-bronchial region – TB or in pulmonary alveoli – A. The range of the measured particles was 10–1000 nm.
- Monitor of Aerosol Concentration DustTrak (model 8534, TSI, USA) – to determine the mass concentration of aerosol, including dimensional fractions (particles in dimensional range 0.1–15 μ m, fractions PM₁, PM_{2.5}, respirable, particulate matter with aerodynamic diameter 2.5–10 μ m (PM₁₀), total particulate matter).

The measurements were made twice during 2 different measuring days (that were not consecutive working days). The measurement strategy comprised sampling before the procedure connected with technical servicing of vehicles (in the room where there were no buses yet), during the servicing procedure (i.e., with running bus engines), and when it was over. Air was sampled about 1.5 m above the floor level, in the area corresponding to the workers' breathing zone. Air sampling was performed each time in the same way: for 16 min with 2-min time intervals. The number of samples collected on particular measuring days was 12 samples on the first day and 16 samples collected on the second day of the measurements. The measurements were made in the room through which buses were passing in cycles. Two entrance gates led to the room, opened when the bus was running into it and closed right away.

Simultaneously, air samples were collected at the workplaces by aspiration method onto filters to obtain the samples for scanning electron microscopy and energy dispersive X-ray spectroscopy analysis (SEM/EDS) of the airborne particles. Microscopic analysis SEM/EDS of the filter surface was carried out using the scanning electron microscope VEGA 3 (Tescan, Czech Republic) with an X-ray microanalyzer EDS INCA (Oxford Analytical Instruments, UK), equipped with a monocrystalline silicon lithium (SiLi) detector for the detection of the elements of composite material surfaces from beryllium (Be) to uranium (U) with the maximal spectral resolution 128 eV for Mn-K α lines. Three magnifications of 1000×, 10 000× and 20 000× were used.

The statistical analysis included determination of arithmetic means, standard deviations, and minimal and maximal values observed during measurements. The statistical significance of differences was assessed using the ANOVA Kruskal-Wallis test and Mann-Whitney U test.

RESULTS

Detailed results of measurements carried out in the everyday servicing room, including the data from individual measurement days and mean values, are presented in Tables 1–3.

The mean concentration of the number of particles in specified air volume in the room without particle emission source (before the first bus rides in, where there were no vehicles at all for the whole day) reached 7.6×10^3 particles/cm³, with observed variation

Measurement day	Number concentration of particles [particles/cm ³]						
and process step	10-1 00	00 nm	10–100 nm				
	AM±SD	minmax	AM±SD	minmax	[%]		
1st day							
before the activity	8900 ± 400	8 400–9 800	6500 ± 400	6 000–7 300	73		
during activity	$138\ 400^{*}\pm 30\ 000$	96 800-205 300	$116\ 000^{*} \pm 31\ 000$	62 300-186 000	83		
after activity	8 560*,**±10 400	64 400-102 300	67 200*±12 100	49 400-83 700	78		
2nd day							
before the activity	6300 ± 200	5 900-6 600	4500 ± 200	4 200–4 900	72		
during activity	121 700*±29 200	61 700–186 800	77 600*±25 500	14 700–149 700	63		
after activity	88 600*,**±28 200	46 700-151 000	69 600****±28 600	26 900-134 800	77		
1st and 2nd day together							
before the activity	7600 ± 300	7 200-8 200	5500 ± 300	5 100-6 100	72		
during activity	$130\ 000^* \pm 29\ 600$	79 300–196 100	96 800*±28 300	38 500-167 900	73		
after activity	87 100*,**±19 300	55 600-126 600	$68\ 400^{*,**}\pm 20\ 400$	38 200-109 200	77		

Table 1. The number concentration of particles from diesel engines exhaust

AM - arithmetic mean; SD - standard deviation; min. - minimal value; max - maximal value.

* Statistical significance of differences between mean values (before-during activity; before-after activity) (p < 0.05).

** Statistical significance of differences between mean values during-after activity (p < 0.05).

Table 2. Surface area concentration of particles potentially deposited in the alveolar (A) and tracheo-bronchial (TB) region, emitted by the vehicles with diesel engine

Measurement day	Surface area concentration [µm ² /cm ³]					
and process step	alveolar	fraction	tracheo-bronc	chial fraction		
	AM±SD	minmax	AM±SD	min.–max		
1st day						
before the activity	29.0±1.3	27.6-31.4	6.1 ± 0.20	5.9–6.5		
during activity	$279.6* \pm 226.1$	125.1-1 374.4	$67.1^{*} \pm 38.20$	27.9-178.5		
after activity	$145.2^{*,**}\pm 61.7$	73.0-283.5	$52.0^* \pm 28.40$	30.8-119.1		
2nd day						
before the activity	18.6 ± 0.3	18.2–19.2	4.3 ± 0.05	4.3–4.4		
during activity	433.3*±197.9	54.4-863.8	$124.8*\pm 56.70$	25.3-269.9		
after activity	133.1****±62.7	83.7-240.6	16.8*,**±3.10	12.8–22.5		
1st and 2nd day together						
before the activity	23.8 ± 0.8	23.0-25.3	5.2 ± 0.10	5.1–5.5		
during activity	$356.5* \pm 212.0$	89.8-1 119.1	$96.0^{*} \pm 47.40$	26.6-224.2		
after activity	139.2*,**±62.2	78.4–262.1	34.4*,**±15.80	21.8–70.8		

Abbreviations as in Table 1.

Measurement dav				Si	ze segregated mas [mg/m	s concentratio	E			
and process step	PM		PM		respiral	ole	PM		particles < 1:	5 000 nm
	AM±SD	minmax	AM±SD	minmax	AM±SD	minmax	AM±SD	minmax	AM±SD	minmax
1st day										
before the activity	0.053 ± 0.004	0.050 - 0.060	0.054 ± 0.004	0.050-0.060	0.054 ± 0.004	0.050-0.060	0.058 ± 0.006	0.050-0.070	0.058 ± 0.006	0.050-0.070
during activity	$0.114^* \pm 0.039$	0.060 - 0.240	$0.116^* \pm 0.040$	0.060-0.250	$0.119^{*}\pm0.042$	0.060-0.260	$0.138^* \pm 0.057$	0.070-0.360	$0.138^{*}\pm0.057$	0.070-0.360
after activity	$0.144^{*,**}\pm 0.033$	0.090 - 0.220	$0.145^{*,**}\pm 0.033$	0.090-0.220	$0.146^{*,**}\pm 0.033$	0.090-0.220	$0.155^{*,**}\pm 0.034$	0.100 - 0.230	$0.155^{*,**}\pm 0.034$	0.100 - 0.230
2nd day										
before the activity	0.030 ± 0.002	0.030 - 0.030	0.030 ± 0.002	0.030-0.030	0.030 ± 0.002	0.030-0.030	0.032 ± 0.002	0.030 - 0.040	0.032 ± 0.002	0.030-0.040
during activity	$0.482^* \pm 0.197$	0.100 - 0.840	$0.488^{*}\pm0.200$	0.100 - 0.850	$0.494^* \pm 0.202$	0.100 - 0.860	$0.515^* \pm 0.207$	0.110-0.910	$0.515^* \pm 0.207$	0.110-0.910
after activity	$0.224^{*,**}\pm0.064$	0.160 - 0.330	$0.229^{*,**}\pm 0.064$	0.160-0.340	$0.236^{*,**}\pm0.065$	0.170-0.350	$0.269^{*,**}\pm0.069$	0.190 - 0.380	$0.269^{*,**}\pm0.069$	0.190-0.380
1st and 2nd day together										
before the activity	0.042 ± 0.003	0.040-0.045	0.042 ± 0.003	0.040-0.045	0.042 ± 0.003	0.040-0.045	0.045 ± 0.004	0.040-0.055	0.045 ± 0.004	0.040-0.055
during activity	$0.298^* \pm 0.118$	0.080-0.540	$0.302^* \pm 0.120$	0.080-0.550	$0.307^* \pm 0.122$	0.080-0.560	$0.327^* \pm 0.132$	0.090-0.635	$0.327^* \pm 0.132$	0.090-0.635
after activity	$0.184^{*,**}\pm 0.048$	0.125-0.275	$0.187^{*,**}\pm 0.048$	0.125-0.280	$0.191^{*,**}\pm 0.049$	0.130-0.285	$0.212^{*,**}\pm 0.051$	0.145-0.305	$0.212^{*,**}\pm 0.051$	0.145-0.305

PM – particulate matter. Other abbreviations as in Table 1.

Table 3. Size segregated mass concentration in the bus depot

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for respective measurement days within: 8.9×10^3 particles/cm³ on the first day and 6.3×10^3 particles/cm³ on the second day of measurements. After the start of the work in the ES room, the particle concentration was higher and its mean value during that stage reached: 130×10^3 particles/cm³ (138.4×10^3 particles/cm³ and 121.7×10^3 particles/cm³ on the first and second day of the measurements, respectively). Once the work in the ES room was completed, the mean number concentration of particles gradually returned to its initial state and during the measurement reached 87.1×10^3 particles/cm³ and was contained within the range from 85.6×10^3 particles/cm³ to 88.6×10^3 particles/cm³ during the first and second day of the research.

The observed changes were statistically significant (p < 0.05). The mean percentage of ≤ 100 nm particles in the total pool of particles was not changed significantly during consecutive stages of the research and in most cases constituted over 70% of all measured particles, whereas changes during particular measurement days did not exceed 10% (Table 1).

Figure 1 depicts the trends of changes in the level of number concentration of 10–1000-nm and 10–100-nm particles during the measurement on the selected measurement day. An increase in the mean number concentration of particles for all particles counted by means of CPC and the particles having diameters < 100 nm, observed when the work in the ES room started, was over 17-fold.

Significantly increasing was also the surface area concentration of the particles when buses traveled along the everyday servicing channel. Variation resulting from the data in this range within 2 different days is presented in Table 2. Before the activities connected with inspection of vehicles started, the mean values of particles surface area concentration was 23.8 μ m²/cm³ for the fraction potentially deposited in pulmonary alveoli and 5.2 μ m²/cm³ for the tracheo-bronchial fraction, respectively. Once the work started, i.e., while the buses were in the everyday servicing



Fig. 1. Number concentration of particles emitted from diesel engines

room, these concentrations were at a significantly higher level: 356.4 μ m²/cm³ for fraction A and 95.9 μ m²/cm³ for the TB fraction.

As results from the above data, this parameter, very often acknowledged as the most significant index of exposure, increased over 15-fold in the room while the vehicles were present on ES stands. When the work was over in the ES room, the surface area concentration of the particles was lower, as compared to the status when the vehicles were shifted from one location to another in the ES channel. It was 139.1 μ m²/cm³ for fraction A and 34.3 μ m²/cm³ for fraction TB. The observed changes were statistically significant. Irrespective of the level of concentrations of both fractions and the stage of the testing process, the surface area concentration of the particles potentially deposited in pulmonary alveoli was on average 3–4 times higher than the concentration of the fraction deposited in the tracheobronchial part. While the buses were translocated through the ES room, the dynamically changing levels of concentrations related to 2-min time intervals were observed. Figure 2 illustrates the variability of the levels of surface area concentration for the particles released from running diesel engines noted during an exemplary measurement day.

The mass concentration of the particles released with exhaust fumes of running bus engines was determined for respective measurement fractions: PM_1 , $PM_{2.5}$, respirable fraction, PM_{10} and the fraction of all particles in a measurable range of the apparatus, i.e., 100–15 000 nm (total fraction of particles). The results of the measurements of mass concentrations of particles including their dimensional fractions and differentiation of results related to different measurement days are presented in Table 3. Before the work was started in the everyday servicing room, the mean mass concentration of aerosol of fraction PM_1 , corresponding to particles < 1000 nm was 0.042 mg/m² (with daily mean



A - alveolar; TB - tracheo-bronchial.

Fig. 2. Surface area concentration of particles emitted by the vehicles with diesel engine

values 0.053 mg/m³ and 0.03 mg/m³ on the first and second day of measurements, respectively) and increased 7-fold, to value 0.298 mg/m³ (0.114 mg/m³ on the first day, and 0.482 mg/m³ on the second day) at the time when buses were systematically moving through the room.

The mean mass concentration of 100–15 000 nm particles, constituting a fraction of all particles counted by DustTrak, reached 0.045 mg/m³ (0.058 mg/m³ on the first day and 0.032 mg/m³ on the second day) before the work started in the ES room, whereas during the works connected with buses moving through the room it was increasing, similarly as in case of PM₁, 7-fold, to the 0.327 mg/m³ level (0.138 mg/m³ and 0.515 mg/m³ on the first and second day, respectively). Once the activities carried out in everyday servicing room were over, the mass concentration of individual fractions of particles varied depending on the measurement day; on the first day of the measurements that concentration still remained at a high level, or was even slightly higher, whereas on the second day it was lower by over 50%. In case of fraction PM_1 , the mean daily concentration values after the end of the work in the ES room was 0.144 mg/m³ on the first day and 0.224 mg/m³ on the second day of the measurements. The same values determined for all 100–15 000-nm particles were: 0.155 mg/m³ during the first measurement and 0.269 mg/m³ during the next one. The mean value of mass concentration of fraction PM_1 reached then 0.184 mg/m³ and that of all 100–15 000-nm particles reached 0.212 mg/m³. All changes in mass concentration observed during the study were statistically significant.

Figure 3 presents the development of the levels and trends of changes in mass concentration of fraction PM₁ particles and total particles fraction, i.e., all particles counted by the apparatus, during the whole exemplary measuring period.

Figures 4–6 present the comparisons of consecutive parameters, depicting the relations between ongoing





Fig. 3. Mass concentration of PM, and total particles < 15 000 nm in the bus depot





Fig. 4. Number and surface area (fraction A) concentration of 10–1000-nm particles





Fig. 5. Number (10-1000 nm) and mass (PM₁) concentration of particles



A – alveolar; PM₁ – particulate matter with aerodynamic diameter $0.02-1 \,\mu m$.

Fig. 6. Surface area concentration (fraction A) and mass concentration (PM₁) of particles

changes in tested factors and their trends on the selected measuring day. The comparison below shows that with high dynamics of changes going on during the process, we can observe that an increase in the number concentration of particles ≤ 1000 nm is almost simultaneous with an increase in surface area concentration of the alveolar fraction (A) of particles emitted by diesel engines (Figure 4). It was also found out that with increasing number concentration of 100-1000 nm particles, the mass concentration of fraction PM₁ was also increasing, as presented in Figure 5. Graphical presentation of the variation of surface area concentration of fraction A particles and fraction PM₁ mass concentration is given in Figure 6. Also in this case the surface area concentration increase was accompanied by increased mass concentration of 100-1000-nm particles.

Results of SEM analysis

Photo 1 shows the SEM images of the filter surface.

energy dispersive X-ray spectroscopy (EDS) analysis showed the presence of the following elements: carbon (C), oxygen (O), sodium (Na), aluminium (Al), silicon (Si) and sulphur (S) (Table 4). It was found that the presence of Al and Si has a local character (Spectrum 1). Other elements are present in all tested areas (Spectra 1–5).

DISCUSSION

The occurrence of a number of various hazards and adverse health effects resulting from exposure to individual components of diesel exhaust fumes is particularly important in the case of workers servicing the devices or vehicles with such engines, performing their occupational activities in rooms, workshops, or other indoor locations. The principles of carrying out the measurements and methods used in evaluation of occupational exposure to harmful agents, including carcinogens, were comprehensively described in scientific literature and also in legal provisions and standards [15,16]. The value of the highest admissible

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A – agglomerates of particles with diameter $< 0.1 \,\mu m$.

Photo 1. Scanning electron microscopy (SEM) images of the filter surface: magnification a) 1 000× and b) 20 000×

Spectrum		Element [wt%]					
	С	0	Na	Al	Si	S	[wt%]
1	46.17	53.19	0.18	0.11	0.14	0.21	100
2	47.02	52.59	0.19	-	-	0.20	100
3	49.74	49.84	0.21	-	-	0.21	100
4	52.36	47.22	0.24	-	-	0.18	100
5	53.07	46.55	0.20	-	-	0.18	100
Minmax	46.17-53.07	46.55-53.19	0.18-0.24	0.11-0.11	0.14-0.14	0.18-0.21	_

Table 4. The weight percentage of the elements on the tested filter surface

C – carbon; O – oxygen; Na – sodium; Al – aluminium; Si – silicon; S – sulfur. Min. – minimal value; max – maximal value.

concentration of respirable fraction of solid particles in diesel engine exhaust fumes is 0.5 mg/m^3 [1,17].

However, the currently used methods do not comprise determination of the concentration of ultrafine particles included in diesel exhaust fumes. This publication presents the results of analysis based on measurements of concentration of submicron particles found in exhaust fumes emitted by diesel engines. The analysis comprises not only the mass concentration which is the most frequently determined parameter in the evaluation of

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exposure to aerosols containing ultrafine particles, but also other parameters very important due to the potential health effects, such as the number concentration and surface area concentration of particles potentially deposited in the tracheo-bronchial and the alveolar regions of the respiratory tract. Measurements were carried out in the everyday servicing room of the bus depot. Air was sampled at the 1.5 m height – in the breathing zone of workers performing the works connected with on-going technical inspection of buses. The above analysis indicates that the mean number concentration in case of particles with sizes up to 1000 nm increased 17-fold during the works performed in the ES room, as compared to the value before the activities connected with buses passing through the room, and was at the level of 130×10^3 particles/cm³. The 10–100-nm particles constituted 70% of that number.

A high increase in the number concentration of the ultrafine particles, along with those sized below 100 nm, was also observed in the test carried out at the garage workstations after 5 min and 8 min from the moment the diesel engine was switched on [18]. In the study carried out in 9 warehouses where the source of particles emission were diesel engines of continually used forklift trucks, the values of the number concentrations of particles sized 0.02–1 μ m were determined. The results for the above range of particle sizes differed considerably because the measurements were carried out in different warehouses. The mean (weighted) values of number concentration of the particles noted in the study ranged from 50×10³ particles/cm³ to 218×10³ particles/cm³ [19].

In another study, which evaluated the exposure to diesel exhaust fumes of people waiting at a bus station, it was found out that at an average time of the passengers waiting for the bus, which was 4.7 min, the mean value of number concentration of the particles was 14.1×10^3 particles/cm³. Observed was also – depending on the daytime – a pattern of changes in the number of particles found in the air at the waiting stations. The highest number concentrations of particles were noted in the morning and afternoon-evening hours of the traffic peak with a clearly decreased particle concentration at the noon hours [20]. Those values were lower than ours because, in that instance, the measurements were conducted in open air.

Another parameter analyzed in this study, describing the exposure to ultrafine particles emitted from diesel engines, was the surface area concentration of the particles (i.e., concentration of particles expressed in terms of the surface area of the particles per unit volume of air). The increase in the value of this concentration during the works performed in the bus room was significant both for the fraction of particles potentially deposited in the pulmonary alveoli part and in the tracheo-bronchial portion of the lungs; however, the degree of changes was different depending on the day on which the measurements were carried out. On the first measurement day the surface area concentration of the particles of both fractions increased about 10-fold, whereas on the second day a 23-fold increase in the concentration was observed for fraction A and almost 3-fold increase for the TB fraction. Up to now, few studies on exposure to particles involve determination of surface area concentration of particles. The most frequently performed measurements, consisting in determination of mass concentration, are more and more often accompanied by determination of the concentration in terms of the number of particles emitted into the environment (as it often happens in case of determination of exposure to ultrafine particles in communal environment) [21-23]. The surface area concentration of particles is a parameter determined sporadically, usually in experimental rather than real conditions.

In the research monitoring the surface area concentration of particles deposited in the alveolar part of lungs of people staying near a busy street with frequently passing trucks and buses, the values of that parameter were found to differ considerably, depending on the day of the week in which the measurements were made. The mean values of surface area concentration of particles noted in this study ranged from 34.9 μ m²/cm³ to 89.2 μ m²/cm³; it was observed that on working days the concentration was on average twice higher than during the weekend. During that study, also high fluctuations were found in the value of fraction A particles surface area concentration during a single day, for example at the highest noted mean concentration the results obtained during the whole day ranged from 27.4 μ m²/cm³ to 510.5 μ m²/cm³ [24]. Equally high fluctuation in the value of surface area concentration of particles deposited in pulmonary alveoli was observed in this study. The corresponding results obtained within one measurement day during the works performed in the ES room ranged between 54.4 μ m²/cm³ and 863.8 μ m²/cm³.

In experimental studies conducted at the Lund University [25], apart from other parameters, such as particles number concentration and mass concentration, the particles dimensional distribution, morphology and size of single particles, also the surface area of diesel exhaust fume particles was determined. The surface area of the emitted particles estimated in that study, assuming the spherical particles, was 2.1×10^{-4} cm²/cm³ (21 000 μ m²/cm³). The area of the aggregates formed in the exhaust fumes was estimated at 3.5×10^{-4} cm²/cm³ (35 000 μ m²/cm³). This study estimated also the dose deposited in lungs during 3-h exposure and indicated that the surface area of particles deposited after that time would be 95.7 cm², assuming that the emitted particles are single balls, and 151.9 cm² considering the aggregates. The concentrations determined in our study amounted to 279.6 μ m²/cm³ and 433.6 μ m²/cm³, and were much lower than those obtained in laboratory conditions.

This study determined also mass concentration of particles emitted by diesel engines, including their dimensional fractions. The concentration of the finest fractions of the determined particles, i.e., PM_1 (100–1000-nm) fraction during the work going on in the ES room reached 0.114 mg/m³ on the first measuring day and 0.482 mg/m³ on the second day and was in both cases 7 times higher than before the works. A similar increase in the concentration was observed in case of all analyzed particles in size range from 100 nm to < 15 000 nm. The concentrations of that fraction at the time when the buses were moving in and out of the room was 0.138 mg/m³ and 0.515 mg/m³, respectively, depending on the measurement day.

The concentrations of respirable dust noted in the study performed in very similar conditions, in the bus depot workshop where the sources of exposure were the buses moving in and out of the inspection, repair and cleaning stands, were within $267 \,\mu g/m^3 (0.267 \,m g/m^3)$ in case of individual measurements and $211 \,\mu g/m^3 (0.211 \,m g/m^3)$ in case of the measurement conducted in the background [26]. In our study, the concentration of respirable fraction of dust on consecutive measurement days reached 0.119 $m g/m^3$ and 0.494 $m g/m^3$, and considering a high fluctuation of the analyzed parameter during a single measurement, we may assume that the value was only approximate.

In the study mentioned before [18], carried out in a garage with running diesel engine, the mass concentration of particles sized 0.1–10 μ m was at the level of 0.772 mg/m³ 5 min after the engine was switched on and 0.896 mg/m³ after 8 min.

In the research carried out in warehouse rooms where forklift trucks with diesel engines were used, the values of concentration (geometric concentration) of respirable dust determined gravimetrically (individual dosimetry) differed considerably, depending on the warehouse in which the measurements were made, ranging from < 80 µg/m³ (0.08 mg/m³) to 179 µg/m³ (0.179 mg/m³) [19]. The mean mass concentration of particles constituting fraction PM₁, determined in the study carried out in a group of 20 workers employed in the warehouse as mechanics performing repair works or other activities connected with buses and trucks, staying inside the premises, amounted to 22.8 µg/m³ (0.228 mg/m³) [27].

Scanning electron microscopy (SEM) analysis confirmed that diesel exhaust particles are agglomerates consisting of < 0.1 μ m diameter basic particles. Energy dispersive X-ray spectroscopy (EDS) analysis indicates that following elements were present in the samples: carbon, oxygen, sodium, aluminium, silicon and sulphur. In another study on particulate matter in vehicle fuels [28], exhaust SEM analysis also exhibits an agglomeration of many tiny particles. In this study it was observed that particle size ranged from $0.04 \,\mu\text{m}$ to $0.12 \,\mu\text{m}$. In the samples, the presence of carbon, oxygen and silicon was observed as in our study.

The data obtained during this study show a high differentiation of analyzed parameters, depending on the measurement day. Furthermore, even during one day, we could observe very high dynamics of changes in the values of concentrations within all analyzed parameters. This results from considerable differences in the conditions during the measurements. The considerable variation in numerical values of the analyzed parameters was affected by such unavoidable factors as: air motion caused by opening of gates when buses moved in or passed to consecutive stands in the room, diversity of vehicles in the fleet (different makes, years of production, types and wear of engines) or the time for which buses remained on the stand where they were inspected, and whether the engine was switched off or idling.

CONCLUSIONS

While the work was performed in the everyday servicing room of the bus depot, a very high increase was observed in all parameters of analyzed solid particles.

Exhaust fumes emitted by diesel engines contain a large number of very small (submicron) particles with large surface area and a relatively low mass concentration, and that is why a comprehensive evaluation of exposure should include all analyzed parameters.

Those findings confirm that ultrafine particles found in diesel exhaust fumes may be harmful to the health of the exposed people, and to their respiratory tract in particular.

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