STUDY OF AIR CONTAMINATION BY HEAVY METALS AT FIRING RANGES

KAREL LACH[1], ŠÁRKA BERNATÍKOVÁ[2], LENKA FRIŠHANSOVÁ[3], KAREL KLOUDA[3] & VLADIMÍR MIČKA[1]
[1]Institute of Public Health Ostrava, Czech Republic
[2]VŠB – Technical University of Ostrava, Czech Republic
[3]Occupational Safety Research Institute, Czech Republic

ABSTRACT

The study of air contamination by heavy metals and dust emissions was conducted on indoor (ISR) and outdoor shooting ranges (OSR) using various firearms – gun, shotgun and submachine gun. Dust particles were collected using a Nano-ID® Select fractioning sampler for both chemical analysis and a scanning electron microscope (SEM) analysis. The total emission of ultrafine particles (UFP) was evaluated including the size distribution during shooting by various equipment (FMPS, SMPS, OPS, Aerotrak). According to expectations, the air was particularly contaminated with lead and partly by antimony, tin, and copper. Observations with SEM show that lead occurs as primary spherical particles, but more often in agglomerates that contain in addition lead, zinc, antimony, and barium. Within the study, air contamination was compared on police shooting ranges by using both traditional ammunition and so-called "green ammunition" not containing lead or antimony in the igniter. When shooting with a handgun in the ISR, the total values of the concentration of lead when using traditional ammunition was about 80 μg/m^3, and with the use of "green ammunition" the value of only 2 μg/m^3 was measured. The total average concentration of lead at ISR after series of firings with shotgun, submachine gun and pistol reached 1,795 μg/m^3. The study has shown that during shooting, especially in indoor shooting ranges with insufficient ventilation, there is a short-term but high burden of heavy metals especially by lead on the persons present. From the long-term view, there is a health risk of lead intoxication especially for trainers and supervisors on shooting ranges. It is important to note that, in this study, health effects on staff and employees of firing ranges were not studied.

Keywords: air emission, shooting range, solid aerosols, nanoparticles, scanning electron microscopy, size resolved sampling, heavy metals, lead.

1 INTRODUCTION

The air and soil contamination by heavy metals at shooting ranges and in their vicinities, as well as attendant health risks, is still paid considerable attention. Shooting and post-firing gases generate heavy metal nanoparticles, which pose a health risk. These particles enter human organism principally as a result of inhalation and skin absorption. This ability stems above all from the nanoparticles' small size, which allows them to penetrate physiological barriers and spread via the blood stream to other organs and even cells [1]. A high-quality scoping study focusing mainly on environmental lead contamination and potential health problems has been presented by Laidlaw et al. [2]. In the review, Laidlaw states that blood lead levels (BLLs) > 10 μg/dL were reported in some shooters, 18 studies reported BLLs > 20 μg/dL, 17 studies > 30 μg/d, and 15 studies BLLs > 40 μg/dL. The BLL value is dependent on multiple factors, chiefly ammunition and a gun calibre used, the number of gunshots and, not least, the quality of ventilation in the case of indoor shooting ranges (ISR). The principal sources of dust emissions containing lead and other toxic metals (antimony) are the primer and the projectile. Primers in use today very often comprise lead styphenate as a sensitive explosive ingredient in combination with antimony sulphide and barium nitrate. Moreover, bullets and gunshot pellets are increasingly made from lead. As a result of the intense friction and heat erosion acting on the bullet as it is moving down and then exiting the barrel under

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the pressure of the hot gases produced by the combusted gunpowder (the propellant), there occurs a post-firing emission of the combustion gasses together with submicron particles with a high content of lead. The bullet fragments and the combustion products (organic, inorganic, soot) of the spent gunpowder are forced out of the barrel under the pressures of 124 to 128 MPa, dispersing on exiting the barrel at right angles to the direction of the gunshot. As a consequence, the shooter is directly exposed to the inhalation risk of these post-firing combustion products, the residue of which is deposited also on the shooter's skin and clothing. Not negligible is also the soil contamination at firing ranges and in their vicinities [3]. The half-life of lead in soil is estimated at 700 years. Without a suitable remediation treatment, the soil contaminated by lead thus becomes a hazardous waste for many generations to come. Lead is released from soil only gradually, mainly in the form of hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) [4], [5].

The risk of the possible exposure to heavy metals gains in importance when one considers that there are between 16,000 and 18,000 indoor shooting ranges in the United States employing tens of thousands of staff [6]. The paper [7] demonstrates the significance of the chemical composition monitoring and characterization of emitted inorganic particles and post-firing gases (the characterization of air emissions from open burning and open detonation) for the army during shooting practice sessions with infantry guns, but also with howitzers. The authors of the paper worked out a way of collecting samples of combustion products in the immediate proximity to a howitzer's muzzle and conducted sampling both outdoors and in a specially adapted indoor environment preventing the dispersal of the plume of contaminants after firings. The paper's findings concern the chemical analysis of the air samples, the distribution and composition of the particulate matter. The aim of the above study was to produce a more detailed protocol to establish the correlations between the military guns and ammunition used and possible health risks.

One of the metals present in dust emissions is antimony, which comes almost exclusively from primers, where it is most often found in the form of antimony sulphide. In their paper, Nechvátal and Senčík [8] explore antimony and its toxicity when it exists as nanoparticles that can negatively impact cellular metabolism even at very small doses.

In the current study, we focus on establishing more detailed information regarding dust emission size distribution, heavy metal weight distribution in dust samples, total fine particles count and the correlation between guns and ammunition used and a shooting range type (indoor or outdoor).

2 MEASUREMENT AND SAMPLING

The objective of the present paper is to provide a complex characterization of an ultra-fine solid aerosol encountered at shooting ranges for small arms training (pistols, submachine guns and shotguns). This paper compares the measurement values obtained during the firing of various guns in order to determine to what extent the used ammunition and firearms can influence the measurements of total emissions, particle size distributions and the concentrations of selected heavy metals. Our measurement and sampling device was always positioned immediately behind shooters at an ISR and approx. 2 m behind shooters at an OSR. In the first part of the study, a series of measurements was made using a pistol (always using the same weapon (Luger, 9 mm)) at police shooting ranges (both an ISR and an OSR); in the second part of the study, which took place at an ISR, we tested three weapons: a submachine gun, a shotgun and a pistol. During the course of the conducted measurements, we were able to amass a comparatively large volume of knowledge and data. This paper presents only a small portion of the results with the intention of illustrating the possibilities of contemporary technical apparatus for the characterization of solid aerosols and the

demonstration of potential hazards resulting from the presence of toxic substances in workplace and outdoor air. Prior to each post-firing sample collection, we obtained a reference sample of blank, unpolluted ambient air.

2.1 Instruments used

A Fast Mobility Particle Sizer (FMPS, Model 3091, TSI Inc., St. Paul, MN) was used for particle size distribution and total number concentration measurements. Size distributions were measured from 5.6 to 560 nm (16 channels per decade with one-second shortest scan time). Size resolving sampling was carried out by means of a wide-range aerosol sampling system – Nano-ID® Select, (Naneum Ltd., UK). The samples of all 12 stages (from 1 nm to 35 μm) collected by the Nano-ID® Select were analysed both for heavy metal content by ICP-MS (Perkin Elmer, model NexION 350D, Waltham, MA 02451 USA) and also SEM (FEI QUANTA 450 FEG, FEI Company, WA) was used for observing the morphology of particles, equipped with back scattered electrons (BSE) and Everhardt Thornley (ETD) detectors with EDS and WDS modules for energy-dispersion element analysis and wave-dispersion element analysis respectively. Accessories to this SEM include the module for the so-called "scanning transmission electron microscopy" (STEM). In order to determine the surface of deposited dust particles in the tracheobronchial (TB) and alveolar (A) part of the respiratory tract, the mobile equipment Aerotrak 9000 (TSI Inc., St. Paul, MN, USA) was used. With respect to the measurements conducted at indoor shooting ranges, apart from observing the effect of various weapons on the quality and quantity of emitted particles, we monitored the concentrations of solid aerosol particles utilizing the synergic connection of NanoScan (SMPS) Nanoparticle Sizer 3910 and Optical Particle Sizer 3330 (OPS) (TSI Inc., St. Paul, MN, USA). The indicated simultaneous deployment of the two instruments made it possible, through the sophisticated software MULTI-INSTRUMENT MANAGER (MIM-2™), to link the measured distribution values from both instruments in the size range of ≤ 10 nm to 10 μm.

2.2 Results from FMPS

The very quick response (1 sec) of a measured signal allows for the display of even short transition states during the UFP concentration change. We corroborated the logical assumption that the total number of emitted particles is conditioned, first and foremost, by whether a shooting range is of the indoor or outdoor type. Regarding the OSR, the quality of air is influenced by the direction of airflow and the current weather; at the ISR, the main factor controlling air quality is the intensity of ventilation. Test firings conducted by the police using both classic and "green" (NON-TOX) ammunition always prominently ramped up the total count of UFPs. The UFP number and size distribution during firing at the OSR are shown in Fig. 1 and Fig. 2. After each series of shootings, the parameters of the air environment quickly returned to its default values. Concerning the ISR, the return to the normal air state took a slightly longer time, depending above all on the quality of ventilation at the shooting range. The highest total particle counts reached $2x10^6$ N.cm^{-3} for the OSR, where N is the number of particles, and the size mode of the particles detected at the moment of firing was in the range of 30 to 35 nm.

A more or less similar situation was detected with respect to the ISR. The total UFP count at the moment of firing again reaches up to $4x10^6$ N.cm^{-3}. This means that, despite the closed environment of the ISR, the maximum counts for the OSR and the ISR hardly differ at all.

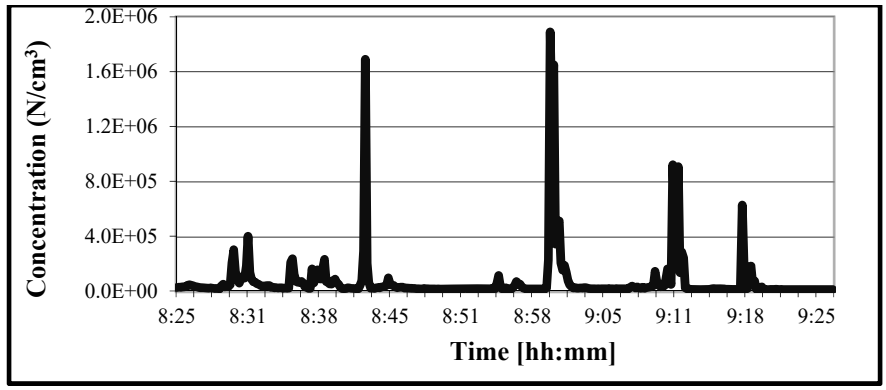


Figure 1: OSR: total concentration of UFP during firing measured by FMPS (1 sec averaging).

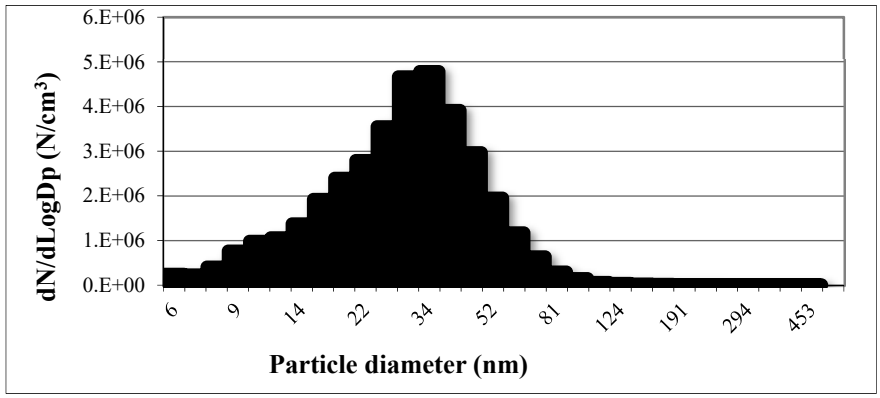


Figure 2: OSR: particle number size distribution at the moment of pistol firing.

There is a difference, however, in the average time the gas plume lingers in the proximity of the shooter and in the related total count of particles deposited in the lungs of the shooter. Fig. 3 shows the particle distributions for pistol firing at the ISR. The size mode of these particles was 60 nm (Fig. 4).

A comprehensible overview of the measured results with respect to the values of exposure and the deposition of individual heavy metals in the respiratory tract have been previously described in a study [9] and are reproduced here in Table 1. On the basis of the statistical assessment of the values of concentration, the authors of the publication conclude that it is evident that in the case of OSR very sharp peaks arising during firings do not significantly affect the median and the firings have a more significant impact in the ISR environment.

The second part of the present study was conducted at the shooting range called “Patriot”, located near the centre of Ostrava. The objective was to compare the measurements of air contamination after firing three different guns: a submachine gun, a shotgun and a pistol. Again, the measurements were made among other using the FMPS instrument. The first

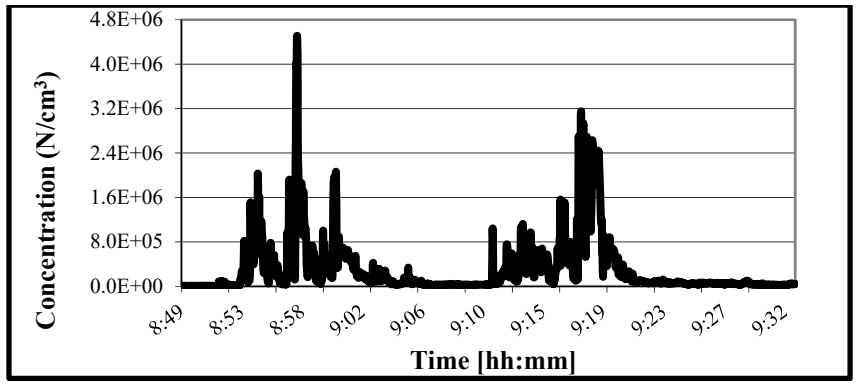


Figure 3: ISR: total concentration of UFP during pistol firing measured by FMPS (1 sec averaging).

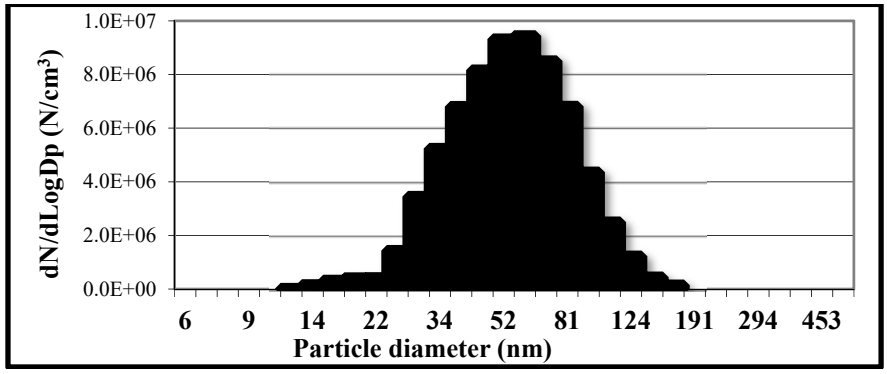


Figure 4: ISR: number size distribution at the moment of pistol shooting.

Table 1: Summary of airborne exposures at the police shooting ranges[a]. *(Source: Lach et al. 2014.)*

Type of measuring stage	MED (cm^{-3})	MAD	GM (cm^{-3})	GSD	MAX (cm^{-3})
OSR TOX, shooting period	1.88E+04	7.50E+03	2.67E+04	2.75	3.64E+06
OSR, background	2.71E+04	1.70E+03	2.72E+04	1.10	3.66E+04
OSR TOX, shooting period	2.63E+04	4.10E+03	3.92E+04	2.68	6.07E+06
OSR, background	2.62E+04	5.00E+02	2.63E+04	1.03	3.04E+04
ISR NON-TOX, shooting period	3.56E+05	2.66E+05	3.79E+05	3.83	1.78E+07
ISR NON-TOX, background	6.43E+03	3.20E+02	6.47E+03	1.08	9.54E+03
ISR TOX, shooting period	7.98E+04	5.65E+04	1.01E+05	4.60	4.51E+06
ISR TOX, background	5.85E+03	6.85E+02	5.83E+03	1.15	7.82E+03

Notes: MED: median; MAD: median absolute deviation; GM: geometric mean; GSD: geometric standard deviation; MAX: maximum measured value; TOX: classic ammunition; NON-TOX: so called "green" ammunition not containing lead etc. [a]The background level was measured just before shooting started. All statistical calculations are based on total concentration data from FMPS with 1 second averaging interval.

tested weapon was a submachine gun. A total of 14 rounds were fired in series of three shots. The total UFP concentration and size distribution is shown in Fig. 5 and Fig. 6. The UFP concentration rose to extreme values and did not lower below $8x10^5$ N/cm^3, not even during a pause. The distribution curve is asymmetrical and gradually increases towards higher values. The size mode of the distributed particles is 40 nm with the maximum concentration of $3x10^6$ N/cm^3. The resulting total UFP number concentration and size distribution values for shotgun shooting (10 rounds were fired in series of two shots) are depicted in Fig. 7 and Fig. 8. In contrast with the measurements taken at the police shooting ranges, we notice a truly massive increase in the emissions of solid aerosol particles, which was even perceptible by ordinary senses. Besides fine particles, firing a shotgun also released into the air relatively coarse particles, most likely the residues of unspent gunpowder. An intentional interruption in ventilation had no significant effect on the total UFP concentration. The size distribution mode (Fig. 5) at the moment of reaching the maximum concentration UFM corresponds to the particle size of approx. 35 nm; the maximum short-term concentration of the particles was almost $5x10^6$ N/cm^3.

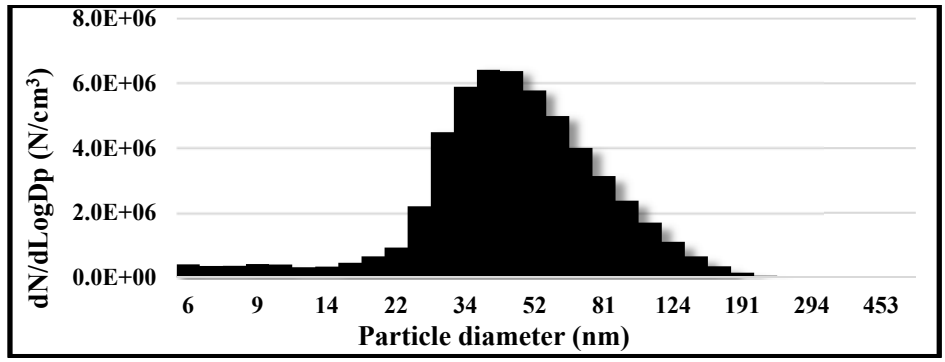


Figure 5: "Patriot" shooting range: number size distribution during submachine gun shooting.

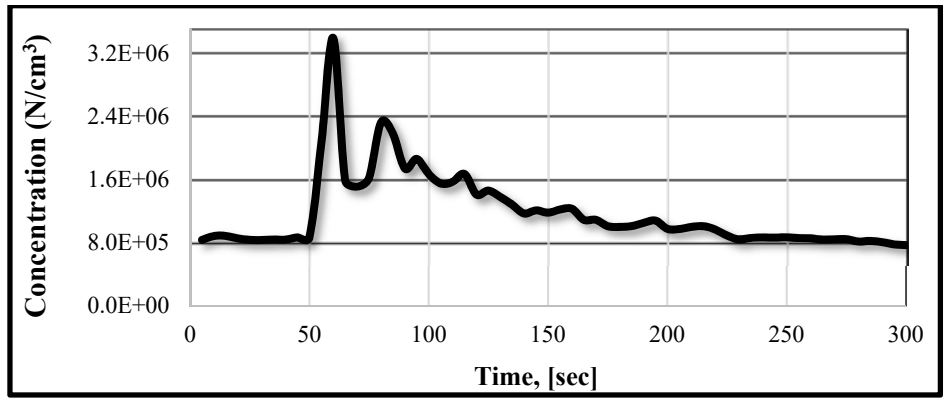


Figure 6: "Patriot" shooting range: total concentration of UFP during submachine gun firing measured by FMPS (5 sec averaging).

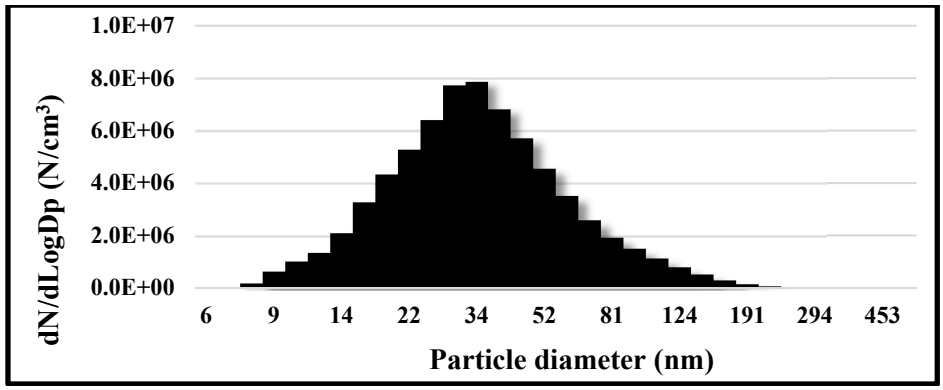


Figure 7: "Patriot" shooting range: number size distribution during shotgun shooting.

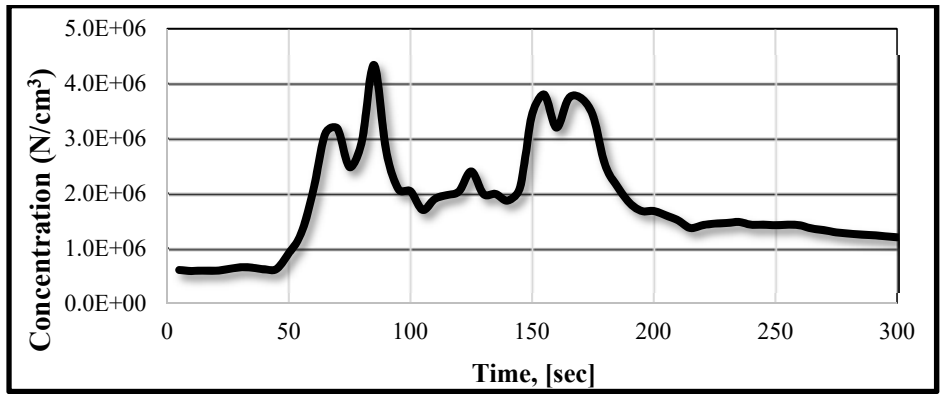


Figure 8: "Patriot" shooting range: total concentration of UFP during shotgun firing measured by FMPS (5 sec averaging).

2.3 Particle sample collection

The aerosol samples were collected using a wide-range sampler Nano-ID® Select [10] in the size range from 1 nm up to 35 μm. Particles are collected simultaneously due to inertial and diffusion deposition and separated into 12 size channels. This sampler enables sufficient amounts of the nano and micron region particulate matter to be collected for further analysis of chemical composition by ICP-MS and scanning electron microscopy. Polished glass microscope slides were used as sampling media for the impactor (0.25–35 μm), while Nylon screens with mesh openings from 20 to 125 per μm were used for diffusion cell (1–250 nm).

2.4 Chemical analysis of samples collected

The samples of all 12 stages collected by the Nano-ID® Select were analysed for metal content by ICP-MS, THERMO XSeriesII and Perkin Elmer NexION 350D. Prior to analysis, samples were mineralized using a microwave system (Milestone MLS 1200 Mega, Milestone Inc., CT). Digestion was carried out in closed vessels preventing loss of volatile elements

like As or Sb. Once the digestion was complete, the samples were allowed to cool and then samples were diluted with high-purity water up to a volume of 50 ml. The analysis by ICP-MS was performed under normal conditions i.e. without using so called collision cells and internal standards. For each element a five-point calibration curve plus blank were used. Results were corrected by values from the blank samples (slide or net).

Fig. 9 shows the comparison of the weight distributions of lead during pistol shooting, using classical ammunition (TOX), for the outdoor and indoor shooting ranges. The solid line represents the lead weight distribution in relation to the particle size at the ISR while the dashed line stands for the lead distributions at the OSR. The lead concentration values for the ISR are several times higher than those measured for the OSR. The dotted line represents blank sample values. In comparison, Fig. 10 shows the lead distribution at the "Patriot" shooting range for pistol shooting (the last tested in the sequence), during which the mean concentration of lead grew to 1795 μg/m^3. The measurement, taken during the last shooting series in a row, attests to the substantial deterioration of the ambient air conditions during intensive firing in short successive series. The measurement value poses an immense health hazard under prolonged exposure. In contrast, the lead concentrations for pistol shooting measured at the police shooting range (ISR) averaged out at 75 μg/m^3, probably due to better ventilation. During pistol shooting, lead is predominantly concentrated in particles that range in size from 100 nm to 2,000 nm. For shotgun shooting, the size range of particles containing most lead is narrower, their size varying between 250 nm and 1,000 nm.

2.5 SEM observation

The UFP samples obtained through size-dependent sampling were examined using SEM in order to determine the particles' morphology, shape and elemental composition. According to the findings, lead was present primarily as a metal in the form of spherical particles; it was very often accompanied by other metals (antimony, tin, zinc) and formed metal alloys. The greatest portion of the spherical particles that included a majority content of lead did not exceed the size of 500 nm. The appearance of these lead particles is shown in Fig. 11. Fig. 12 demonstrates the results of the EDX elementary analysis of the discovered particles. Discounting the metal microparticles, we found that a high proportion of the airborne dust particles were those with a majority content of carbon. These are presumably the unburnt

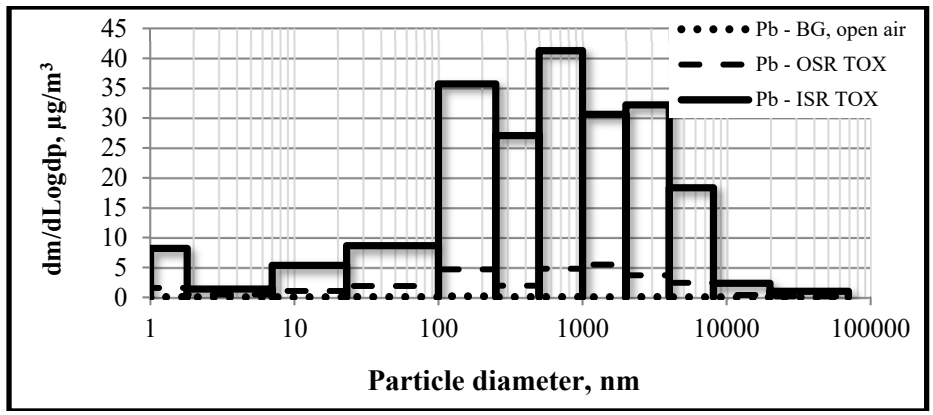


Figure 9: Lead-size distribution and concentration comparison, μg/m^3: ISR TOX vs OSR TOX.

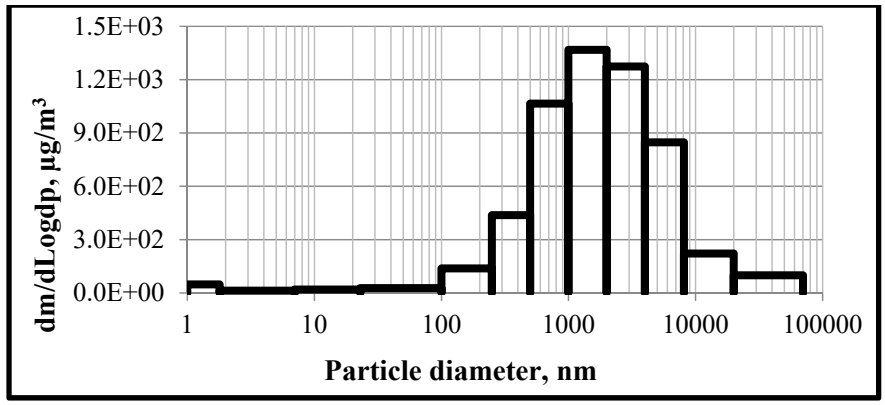
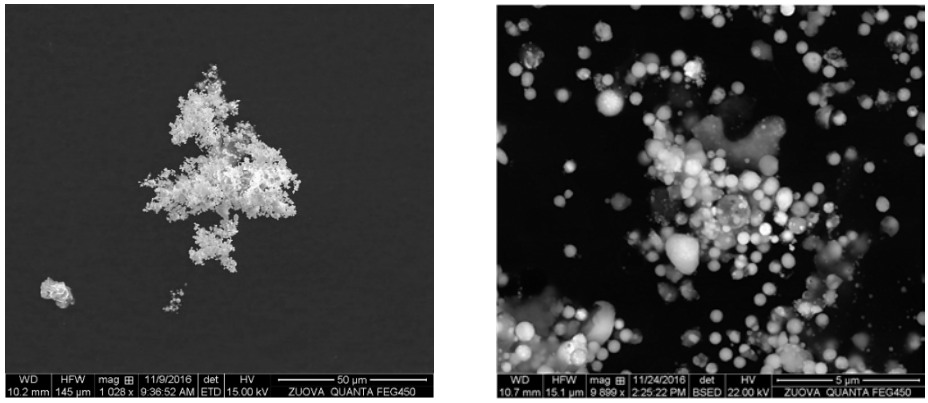


Figure 10: "Patriot" shooting range, pistol firing: lead-size dependent distribution, µg/m^3. Total mass concentration of lead reached 1,795 µg/m^3.



(a) (b)

Figure 11: Morphology of lead particles. (a) Big cluster of lead UFP; (b) Plume of spherical lead particles.

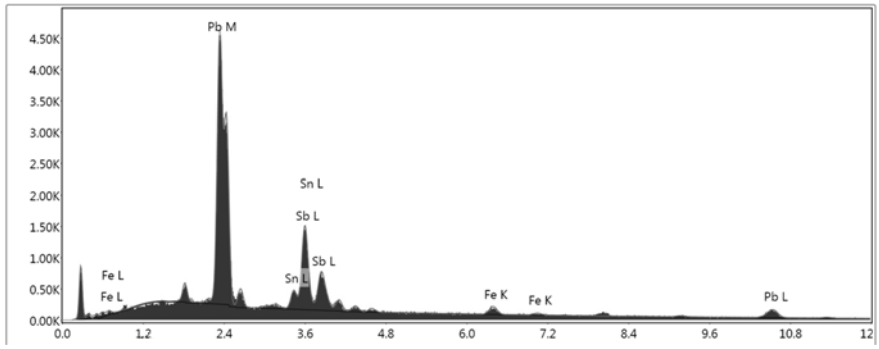


Figure 12: Demonstration of EDX elementary spectra of lead particle.

residues of gunpowder and soot. The lead particles that often no longer have spherical but rather indeterminate shapes due to abrasion (micron shavings) have a tendency to aggregate with non-metal materials (silicates, soot), creating particles with a heterogeneous nature and a size of 10 μm and greater.

3 CONCLUSION

All measurements conducted at the shooting ranges furnished proof of the not inconsiderable emissions during firing of a solid aerosol with a high content of lead and also other metals (Sb, Sn, Cu and others). The average short-term concentration of lead reached the concentration 755 $\mu g/m^3$ (shotgun, ISR), 822 $\mu g/m^3$ (submachine gun, ISR), in the case of antimony 85 $\mu g/m^3$ (shotgun, ISR), 382 $\mu g/m^3$ (submachine gun, ISR). That values correspond to the relatively high total surface of nanoparticles deposited in the alveolar part of the respiratory tract, which reached 15,000 $\mu m^2/cm^3$, while the value of the background before shooting was approximately 8 $\mu m^2/cm^3$.

Although the weight of lead is concentrated in the particles with the size range of 500 to 5,000 nm, the measurement with the FMPS confirmed the nanoparticle size mode in the range of 30 to 50 nm. Particles of this size carry a high risk of penetration into the blood stream and migration into other organs, including bones and bone marrow. It is, consequently, absolutely paramount for firing range personnel to submit to regular health checks and blood tests for lead. As a standard, indoor shooting ranges must utilize high-quality ventilation with the direction of air flow away from the shooters and towards the targets.

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