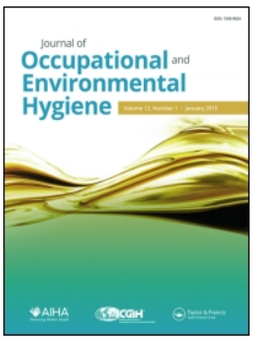

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Characterization of exposure to byproducts from firing lead-free frangible ammunition in an enclosed, ventilated firing range

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ABSTRACT

U.S. Air Force small arms firing ranges began using copper-based, lead-free frangible ammunition in the early 2000s due to environmental and health concerns related to the use of lead-based ammunition. Exposure assessments at these firing ranges have routinely detected chemicals and metals in amounts much lower than their mass-based occupational exposure limits, yet, instructors report work-related health concerns including respiratory distress, nausea, and headache. The objective of this study at one firing range was to characterize the aerosol emissions produced by weapons during firing events and evaluate the ventilation system's effectiveness in controlling instructor exposure to these emissions. The ventilation system was assessed by measuring the range static air pressure differential and the air velocity at the firing line. Air flow patterns were near the firing line. Instructor exposure was sampled using a filter-based air sampling method for metals and a wearable, real-time ultrafine particle counter. Area air sampling was simultaneously performed to characterize the particle size distribution, morphology, and composition. In the instructor's breathing zone, the airborne mass concentration of copper was low (range = <1 μg/m^3 to 16 μg/m^3), yet the ultrafine (nanoscale) particle number concentration increased substantially during each firing event. Ultrafine particles contained some copper and were complex in morphology and composition. The ventilation assessment found that the average velocity across all shooting lanes was acceptable compared to the recommended guideline (20% of the ideal 0.38 m/s (75 ft/min). However, uniform, downrange airflow pattern requirements were not met. These results suggest that the mass-based occupational exposure limits, as applied to this environment, may not be protective enough to eliminate health complaints reported by instructors whose full-time job involves training personnel on weapons that fire lead-free frangible ammunition. Using an ultrafine particle counter appears to be an alternative method of assessing ventilation effectiveness in removing ultrafine particulate produced during firing events.

KEYWORDS

Direct reading instruments; occupational exposure limits; small arms, ultrafine particles; wearable ultrafine particle counters; ventilation

Introduction

In the early 2000s, the United States Air Force (AF) small arms firing ranges began replacing lead-based ammunition with copper-based lead-free frangible (LFF) ammunition in response to environmental and health concerns related to the use of lead ammunition. However, the introduction of LFF ammunition did not eliminate health concerns. Following the change, instructors began reporting health complaints such as headache, sore throat, cough, eye irritation, trouble breathing and metallic taste, during and after firing exercises.[1–2] Several exposure assessments that measured air contaminants in the breathing zone of instructors during small arms firing of LFF ammunition have found the concentrations of chemicals and particulate matter (PM) to be well below mass-based, applicable occupational exposure limits (OELs).[1–3]

Weapons emissions are composed of a complex mixture of chemicals and PM. Expected chemical byproducts from firing LFF ammunition include combustion gases

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(e.g., carbon monoxide, carbon dioxide, nitrogen oxides, hydrogen cyanide), acid gases and volatile and semi-volatile organic compounds.[6] Expected PM include soot and metals. Metal-based particles are generated by abrasion between the bullet and the rifled barrel,[2,4] in addition to nucleation of vapors emitted under high temperature and pressure conditions.[5] According to the safety data sheet for the ammunition being used at these ranges, copper is the primary metal that makes up the projectile (along with a small amount of zinc). Furthermore, previous exposure assessments have confirmed that copper is the most prevalent metal in the aerosol.[1–3]

Characterization of emissions produced when firing LFF has shown to include high number concentrations of PM in the ultrafine size range.[2] This finding was consistent with a Swedish Defense Department study that showed firing LFF ammunition using a rifle produced PM with 90% of the particle number <30 nm.[6] This is important for two reasons. First, ultrafine particles do not contribute significantly to the mass of an aerosol, which is generally used as the metric for PM OELs. Furthermore, the size of PM plays a major role in health effects. For example, PM ≤2.5 µm (PM2.5) is considered the key size fraction associated with cardiopulmonary disease in areas with high levels of air pollution.[7] Moreover, ultrafine PM (≤0.1 µm) has been shown to be more toxic than fine PM (0.1–2.5 µm) of similar composition when exposure occurs by inhalation.[8–17] Concerns related to ultrafine PM include the ability to deposit in the gas exchange region of the lungs, migrate to lung interstitial spaces and the blood stream, be internalized by cells, as well as deposit on the nasal membrane and translocate through the olfactory nerves to the brain.[18–20]

Engineering controls are often used to mitigate exposure to chemical and PM hazards. Ventilation, in particular, is the primary engineering control used to remove weapons emissions within an enclosed firing range. There are several performance requirements and recommendations associated with the ventilation system used in an enclosed firing range. These requirements have been described in documents published by the U.S. Navy Environmental Health Center, National Institute for Occupational Safety and Health (NIOSH), U.S. AF Civil Engineer Center and the American Conference of Governmental Industrial Hygienists (ACGIH).[4,21–23] First, the air flow should be evenly distributed (uniform) across the firing line.[4,21,22] Uneven flow can result in recirculation or backflow of contaminated air into the breathing zone of a shooter or instructor. Second, the minimum volumetric flow rate supplied to or exhausted from the range should be 102 L/s/m^2 (20 ft^3/min/ft^2) of the cross-sectional area of the room.[23] Third, the recommended velocity at the face of the supply air, radial-style diffusor located behind the firing line is 2–3 m/s (400–600 ft/min). Downrange, air velocity at the bullet trap exhaust should range from 13–15 m/s (2500–3000 ft/min). The air velocity at the firing line, where weapons emissions are produced, should be 0.38 m/s (75 ft/min).[4,21–23] The guidelines for air velocity at the firing line are based on a study conducted by NIOSH and the America Air Filter Company for controlling airborne lead exposure. This document was published in 1975 and its recommendations are still considered appropriate.[4,21,22] Finally, 3–7% more air should be exhausted than supplied to maintain at a slight negative pressure inside the range relative to adjacent areas.[4,21,22]

The objectives of this research study were to characterize the aerosol emission produced during weapons firing events, measure instructor exposure to the emissions, and measure the effectiveness of the ventilation system in removing air contaminants from the breathing zone of instructors.

Materials and methods

Sampling environment

Sampling was conducted at the indoor small arms firing range at Wright Patterson AFB. The range was designed to meet the specifications in the Engineering Technical Letter on Small Arms Range Design and Construction.[22] Shooters fire from behind the firing line, and instructors move between the firing line and ready line, interacting with shooters throughout each exercise (Figure 1A).

Weapons fired during this assessment included the M9 pistol and M4 rifle. The M9 pistol is a single-round semi-automatic weapon with a barrel length of 125 mm (4.9 in). The M4 rifle can be operated as a single-round or three-round burst semi-automatic weapon and has a barrel length of 370 mm (14.6 in). The LFF ammunition fired by both weapons was supplied by the Federal Cartridge Company. The main difference between ammunition is the size of the bullet: 9 mm in diameter for the M9 pistol and 5.56 mm for the M4 rifle.

Sampling events

Sampling was completed during four weapons qualification exercises: two with the M9 pistol and two with the M4 rifle. During each exercise, 10–20 firing events were completed. Before each firing event, shooters were instructed to load a specific number of rounds in a magazine. During each firing event, shooters were allowed to fire all of the rounds, which generally took 1–2 min. The total number of rounds fired was 90 for exercises using the M9 pistol and 196 for exercises using the M4 rifle. There

were 10–13 shooters per exercise. The duration of the exercises was 162 min for the first M9 exercise and 72 min for the second M9 exercise. The duration of the M4 exercises was 146 min and 192 min. For the first M9 exercise, the shooters were split into two groups, and the entire exercise was completed twice, since only half the range was operational on that day. Additional differences in exercise duration was due to variation in time required for instruction, which is based most heavily on shooter skill level.

Hazard controls

The personal protective equipment worn by the shooters and instructors included a bullet proof vest, safety glasses and double hearing protection: foam ear plugs and ear muffs. Engineering controls in the enclosed firing range included a push-pull style ventilation system and a bullet trap. Air was supplied to the range via a bank of radial-style perforated diffusers located at the junction between the ceiling and wall and running the entire length of the back wall behind the firing line. Air exiting these diffusers was directed towards the shooting lanes with the intent of moving downrange towards the exhaust plenum (see Figure 1A). The distance from the radial diffusers to the firing line was approximately 5 m (16 ft), which meets the NIOSH recommendation.[21] The height from the floor to the bottom of the radial plenum was about 2.2 m (7 ft). Air was exhausted downrange at the bullet trap through a series of horizontally arranged slot hoods. The bullet trap captured major fragments and dust generated upon impact.

Ventilation assessment

The range ventilation was assessed using the following techniques described in the Navy Environmental Health Center Indoor Firing Ranges Industrial Hygiene Technical Guide:[4]

- perform a smoke test to observe airflow patterns;
- calculate the volumetric air flow rate in the range;
- measure the air velocity at the supply, exhaust, and firing line; and
- measure the static air pressure difference between the range and adjacent areas.

Smoke tests were completed using the FlowMarker Fog Generator (Degree Controls, Inc., Milford, NH). For observation of airflow patterns near the firing line, the smoke generator was held at hip height, and video was recorded as the instrument was walked slowly past each firing stall, just upstream from the firing line. Range dimension measurements were made using a tape measure (Supplemental Information, Table SI). The percent open area of the air supply was calculated using image processing software (see Supplemental Information). The air velocity measurements and static pressure measurements were completed using a VelociCalc anemometer (TSI, Inc., Shoreview, MN). Air velocity measurements were completed at 189 points in a grid pattern in front of the air supply and also at 69 points along the length of the

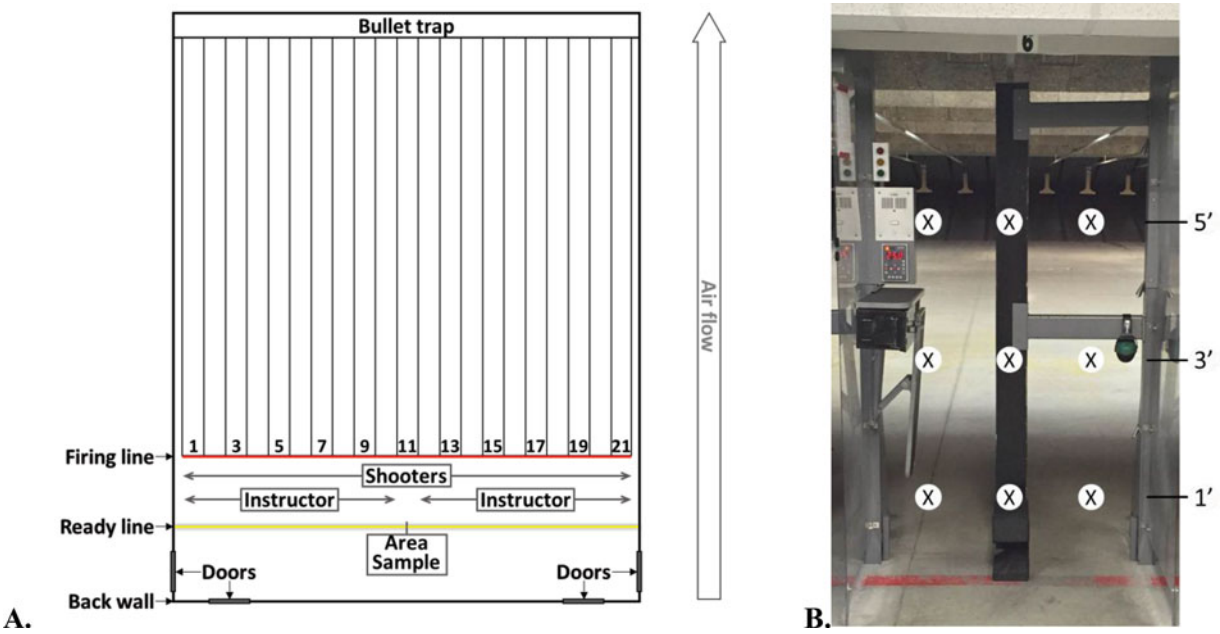

Figure 1. Enclosed, ventilated firing range overview. A. Schematic of the firing range; B. Image of one stall with labels indicating the nine points where velocity measurements were made.

Table 1. Summary of sampling methods.

Measurement	Instrument	Analysis	Sample Type
metal concentration	pump, cassette, MCE filter	ICP-MS (modified NIOSH 7300)	personal & area
particle number concentration	PUFP	RT data	personal
particle size distribution	SMPS	RT data	area
particle morphology & composition	ESP	TEM-EDS	area

slot hood exhaust inlets at the bullet trap. For volumetric air flow calculations, the average air velocity at the supply or exhaust was multiplied by the cross-sectional area of the respective duct opening, then divided by the cross-sectional area of the range. Air velocity measurements were completed at nine points in a grid pattern within each firing stall (Figure 1B). Smoke tests were used to visualize the direction of airflow at door openings to confirm static pressure measurements made using the Velocicalc.

Aerosol characterization

Personal air samples were collected in the breathing zone of the instructors while simultaneous area sampling was conducted at a stationary location behind the ready line (see Fig. 1A). Sampling pumps (GilAir Plus, Sensidyne, St. Petersburg, FL) were set to 3.0 L/min and connected to an open face 37-mm cassette that contained a 0.8-micron mixed cellulose ester (MCE) membrane (SKC, Inc., Eighty Four, PA). Each filter was analyzed using inductively coupled plasma mass spectrometry (ICP-MS) in accordance with NIOSH Method 7300 by an accredited analytical laboratory (ALS Environmental, Salt Lake City, UT). The filter analysis was limited to copper and zinc because they are the primary metals expected to be present in the air during weapons firing using copper-based, LFF ammunition.[1–2] Personal sampling of particle number concentration was achieved using a data logging, portable ultrafine particle counter (PUFP) from Enmont, LLC (New Richmond, OH) which has a detection range of ≥4.5 nm (50% cut-off) up to about 10 microns and 0–200,000-#/cm^3. This instrument is unique in that the working fluid is water and the orientation does not affect the performance, allowing it to be wearable.[24]

The particle size distribution was characterized at a stationary location behind the firing line using a scanning mobility particle sizer (SMPS; NanoScan, TSI, Inc., Shoreview, MN), which can separate PM according to size (range from 10–420 nm in 13 size bins) and number concentration (range from 0–1,000,000#/cm^3). For transmission electron microscopy (TEM) examination, particles were collected for the duration of each exercise using an electrostatic precipitator (ESP; NanoSampler, TSI, Shoreview, MN) at a flow rate of 1.0 L/min and voltage of −10 kV. The collection substrate was composed of a nickel grid coated with a formvar (thermoplastic)-carbon film (Electron Microscopy Sciences, Hatfield, PA). The PM collected on each grid was examined for size, morphology and composition using TEM with energy dispersive X-ray spectroscopy (EDS). All EDS identification peaks were marked using the software 4pi revolution (4pi Analysis, Inc.) and confirmed using data available from Deslattes et al.[25]

A summary of the sampling methods is shown in Table 1. Data collected from direct reading instruments (PUFP and NanoScan) were exported to Excel (Microsoft Corporation, Redmond, WA) for analysis and plotting.

Results

Ventilation assessment

The average velocity across all firing stalls was 0.25, 0.41, 0.45, and 0.42 m/s (50, 81, 89, and 82 ft/min) on days 1–4, respectively. All values were at or above the minimum 0.24 m/s (50 ft/min) NIOSH guideline. On days 2–4 when both sides of the range were operating, the velocities were within 20% of the ideal 0.38 m/s (75 ft/min) guideline.

The average air velocities were not uniform across firing stalls, and coefficient of variation calculations indicated a large amount of variability within each stall (Figure 2). On the first day, the right side of the range (stalls 12–21) had no airflow moving downrange (Figure 2A). Further investigation revealed the air handling units supplying air to this side of the range were not functioning. Given this finding, firing (M9 pistol) was only conducted on the side of the range with operating ventilation (stalls 1–10), which required the course to be conducted twice to accommodate all shooters. For the remaining days of sampling (days 2–4), the range ventilation system was fully operational (Figure 2B–D). However, on these days, a pronounced decrease in air velocity at stall 11 was noticed, and the variability on the right side of the range (stalls 12–21) appeared to be slightly less than the left. Smoke tests at the firing stalls showed airflow patterns sometimes moving uniformly downrange. However, there were multiple areas and stalls that exhibited stagnant or backwards airflow patterns (Figure S1). According to the ACGIH, the volumetric flow rate per cross-sectional area of an enclosed firing range should be a minimum of 102 L/s/m^2 (20 ft^3/min/ft^2) of the room cross-sectional

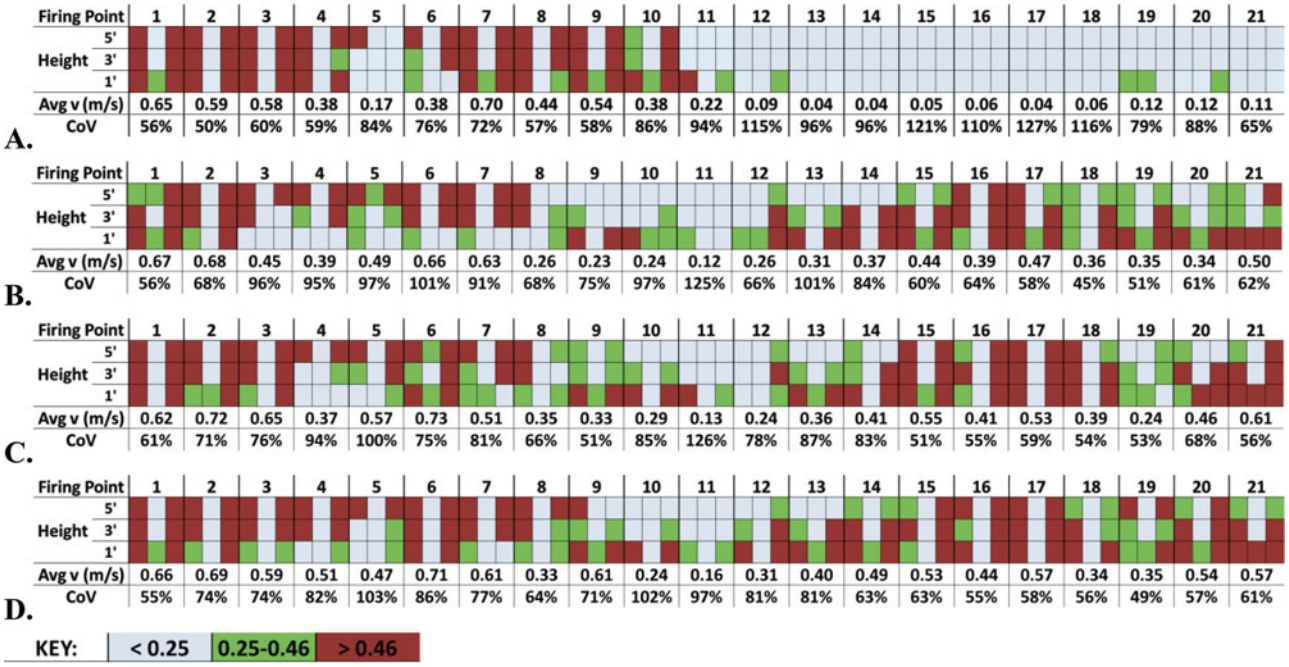

Figure 2. Heat map for air velocity at the firing line using the nine-point method (see Fig. 1B). A. M9 pistol exercise, day 1; B. M4 rifle exercise, day 1; C. M9 pistol exercise, day 2; D. M4 rifle exercise, day 2. The block corresponding to each measurement is shaded blue for velocities less than the minimum acceptable velocity of 0.25-m/s (50-ft//min), green for velocities that fall within the acceptable range of 0.25–0.46-m/s (50–90-ft/min) and red for velocities that are greater than the maximum acceptable velocity of 0.46-m/s (90-ft/min). The average velocity (Avg v) and the coefficient of variation (CoV) are shown for each firing stall.

area. Our results indicated values of 200 L/s/m^2 at the air supply and 20 L/s/m^2 at the air exhaust (Table S1). Therefore, the values calculated for the air supply did meet the guideline, but the exhaust did not.

The static pressure measured between the range and in the building corridor outside the range on each of the four sampling days is shown in Table 2. The building air pressure always equaled the outdoor air pressure. However, the range was at positive pressure relative to the building corridor on two days and neutral on the other two days. Smoke tests conducted each day at door openings showed air flowing out of the range into the building corridor.

Exposure characterization

Air sampling results are presented in Table 3. Copper was detected in the breathing zone of instructors during both M4 rifle exercises, while M9 pistol firing exercises produced a detectable amount in only one instructor. Zinc was not detected in any sample during M9 firing; however, low levels were found on personal and area air samples during M4 firing exercises. The airborne mass concentration for copper was always about an order of magnitude higher than zinc when it was present, which is expected since copper is more prevalent than zinc in the bullet. The 8-hr time-weighted average (TWA) was calculated assuming zero exposure to copper or zinc during non-firing time (instructors left the range) in order to compare to the most protective OEL. No detectable levels of copper and zinc (minimum detectable concentrations; 1 µg/m^3 for copper, 2 µg/m^3 for zinc) were found in background area air samples collected inside the range on days when no firing occurred. Copper concentrations in the breathing zone of instructors were low (<1% of the copper dust OEL of 1000 µg/m^3 and <5% of the copper fume OEL of 100 µg/m^3) regardless of the weapon fired.

Particle number concentrations measured in the breathing zone of the instructor using the PUFP showed clearly defined, sharp increases that corresponded to firing events (Figure 3). These increases were approximately 1–5 orders of magnitude higher than background number concentrations, but were of short duration (a few seconds).

The median particle size that correlated with peaks in particle number concentration during the M9 firing events measured in the area sample tended to be between 40–80 nm (Figure 4A). The median particle size that correlated with peaks in particle number

Table 2. Static pressure measurements.

Day	1	2	3	4
Range Pressure (kPa)	102.404	101.930	102.574	102.337
Building Pressure (kPa)	102.371	101.896	102.574	102.337
Pressure Differential (data)	+	+	neutral	Neutral
Pressure Differential (smoke)	+	+	+	+

Table 3. Airborne concentrations of copper and zinc during firing exercises.

Weapon		M9 pistol				M4 rifle			
Day		1		2		1		2	
Shooters		13		13		12		10	
Exercise duration (min)		162		72		146		192	
Element		Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn
Exercise	*MDC*[a] (μg/m³)	*1.0*	*1.0*	*2.3*	*2.3*	*1.1*	*1.1*	*0.9*	*0.9*
	Instructor-1 mass (μg/m³)	2.0	ND	ND	ND	15.8	1.8	13.2	1.4
	Instructor-2 mass (μg/m³)	ND	ND	ND	ND	7.7	ND	11.2	1.4
	Area mass (μg/m³)	1.4 ± 0.2	ND	ND	ND	2.3 ± 1.1	ND	11.4 ± 0.1	1.2± 0.1
8 h TWA	*MDC (μg/m³)*	*0.3*	*0.3*	*0.3*	*0.3*	*0.3*	*0.3*	*0.3*	*0.3*
	Instructor-1 mass (μg/m³)	0.7	ND	ND	ND	4.9	0.5	5.3	0.6
	Instructor-2 mass (μg/m³)	ND	ND	ND	ND	2.4	ND	4.5	0.5
	mass (μg/m³)	0.5 ± 0.1	ND	ND	ND	0.7 ± 0.3	ND	4.6 ± 0.1	0.5 ± 0.1

Note. ND = not detected.
[a]The minimum detectable concentration (MDC) was calculated by dividing the analytical method limit of detection (expressed as mass per sample) by the total air volume sampled during each task.

concentration during the M4 firing events were much lower, with the majority of peaks between 30–40nm (Figure 4B). Interestingly, the concentration of particles that reached the area sample during M4 exercises was an order of magnitude lower compared to M9 exercises.

PM collected using the ESP for subsequent characterization by TEM-EDS showed complexes of singular and agglomerated particulate with both high and low density regions (Figure 5). In some cases, there appeared to be very small sub-10 nm high density particles embedded in a less dense matrix (Figure 5AB,F). However, the particle morphology was unique for the M9 when compared to the M4. The particles emitted during M9 firing were highly irregular (Figure 5A–C), while the particles emitted during M4 firing appeared to contain one or more dense sub-100 nm spherical particles surrounded by a low-density matrix (Figure 5D,F).

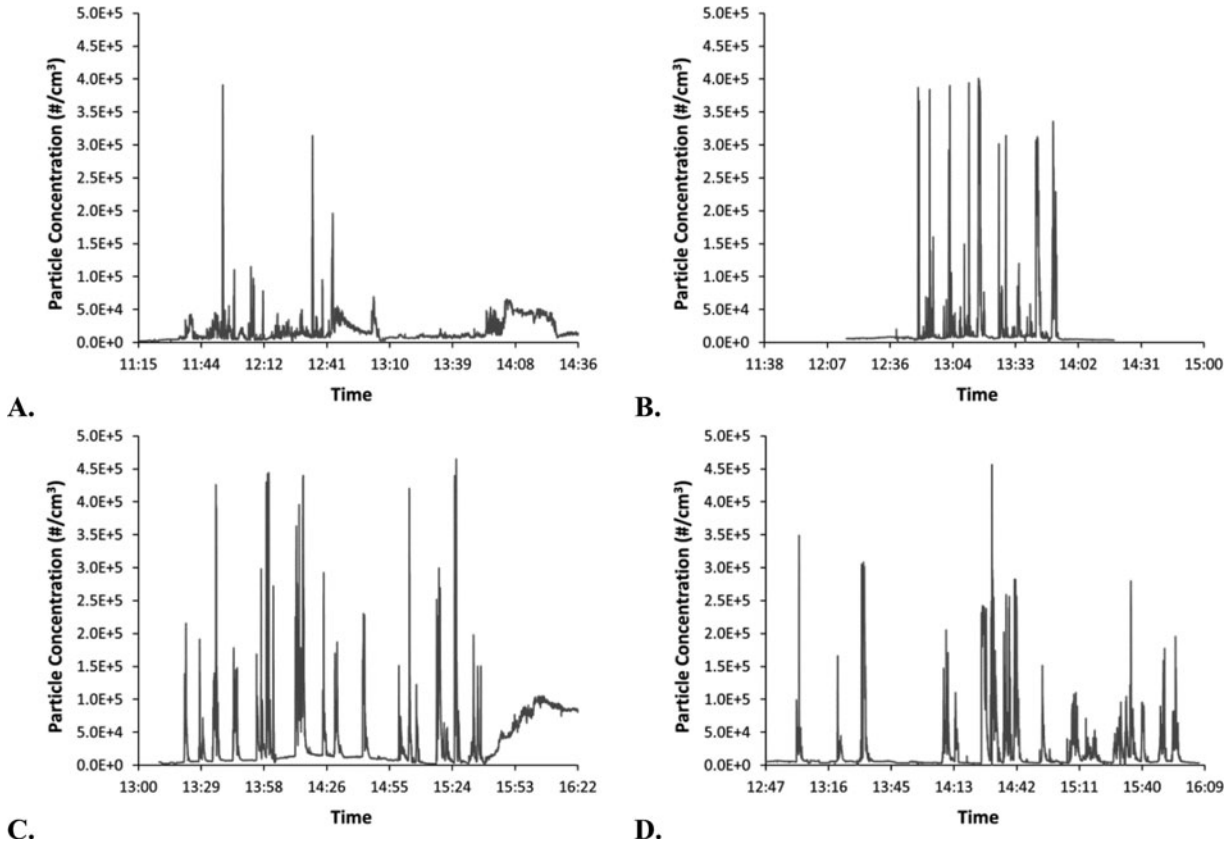

Figure 3. Particle number concentration in the breathing zone of firing range instructors. A. M9 pistol exercise, day 1; B. M9 pistol exercise; day 2; C. M4 rifle exercise, day 1; D. M4 rifle exercise; day 2.

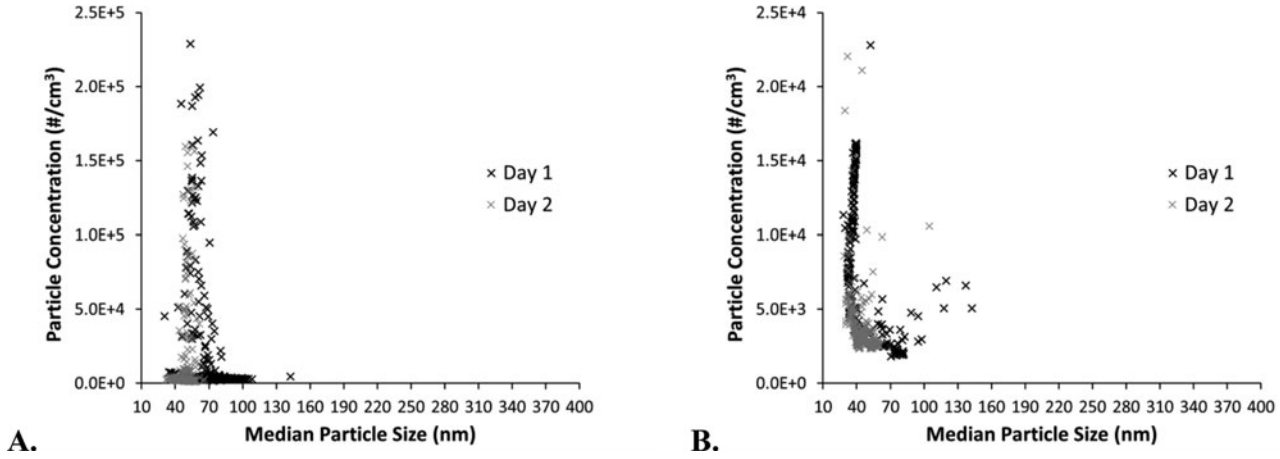

Figure 4. Particle concentration *versus* median size measured in the area sample. A. M9 training exercises; B. M4 training exercises.

Elemental analysis (using EDS) of PM collected during M9 firing indicated the presence of aluminum, sulfur, calcium, iron, copper, zinc, and lead (Figure 6). Three regions were characterized for one of the samples (Figure 6B). Lead was found to be present in the densest region, while aluminum was the dominant metal in the less dense regions. Iron was primarily present near the edge of the composite.

Key elements found in particles emitted during M4 firing were slightly different than those present in the emissions produced by the M9 and included silicon, sulfur, sodium, potassium, copper, zinc, and bismuth (Figure 7). The EDS analysis on the different portions of the particles emitted during M4 firing showed dense spherical nanoscale particles composed primarily of bismuth, while the copper was found in the region containing smaller sub-10 nm particles (Figure 7B).

Background PM air samples were also collected during days when no firing occurred. Two common particle types were observed; an amorphous soot-like particle and a porous particle (Figure S2). The chemical composition of these two common background PM morphologies are shown in Figure S3). The amorphous soot-like particle was carbonaceous with traces of silicon while the porous particle was composed primarily of potassium with traces of silicon, phosphorous, sulfur, copper, and zinc. Neither of the distinct morphologies observed during weapons firing were observed in background samples. However,

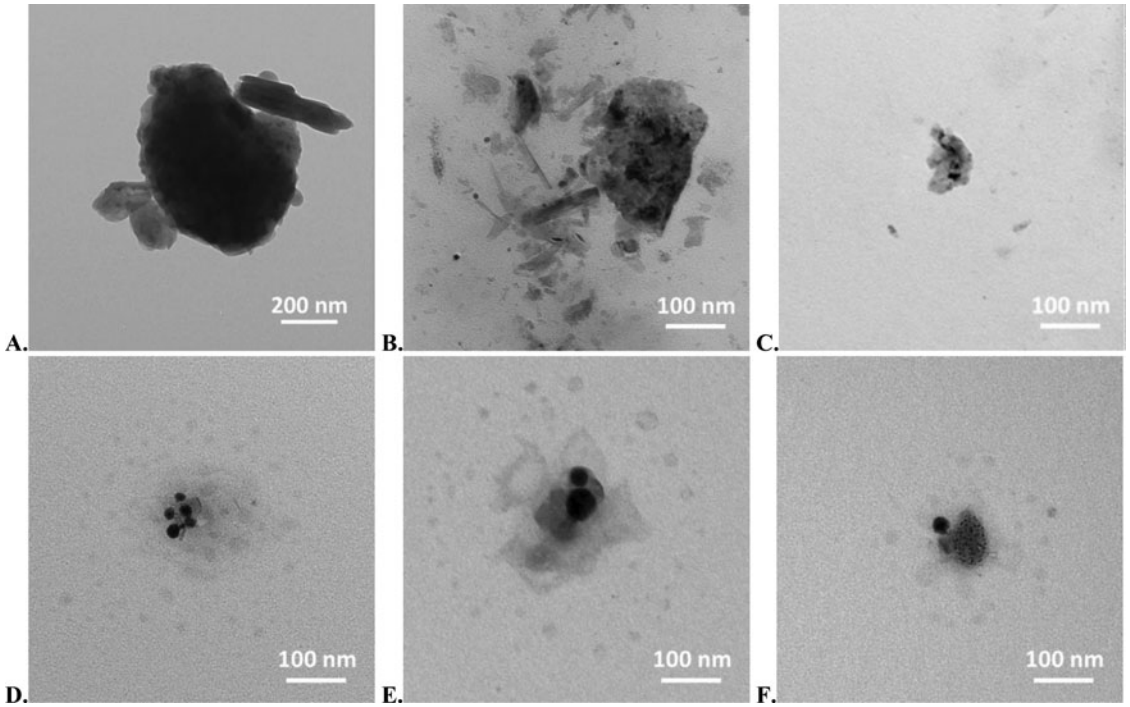

Figure 5. Morphology of particulate matter emitted during firing of the M9 pistol (A–C) or M4 rifle (D–F).

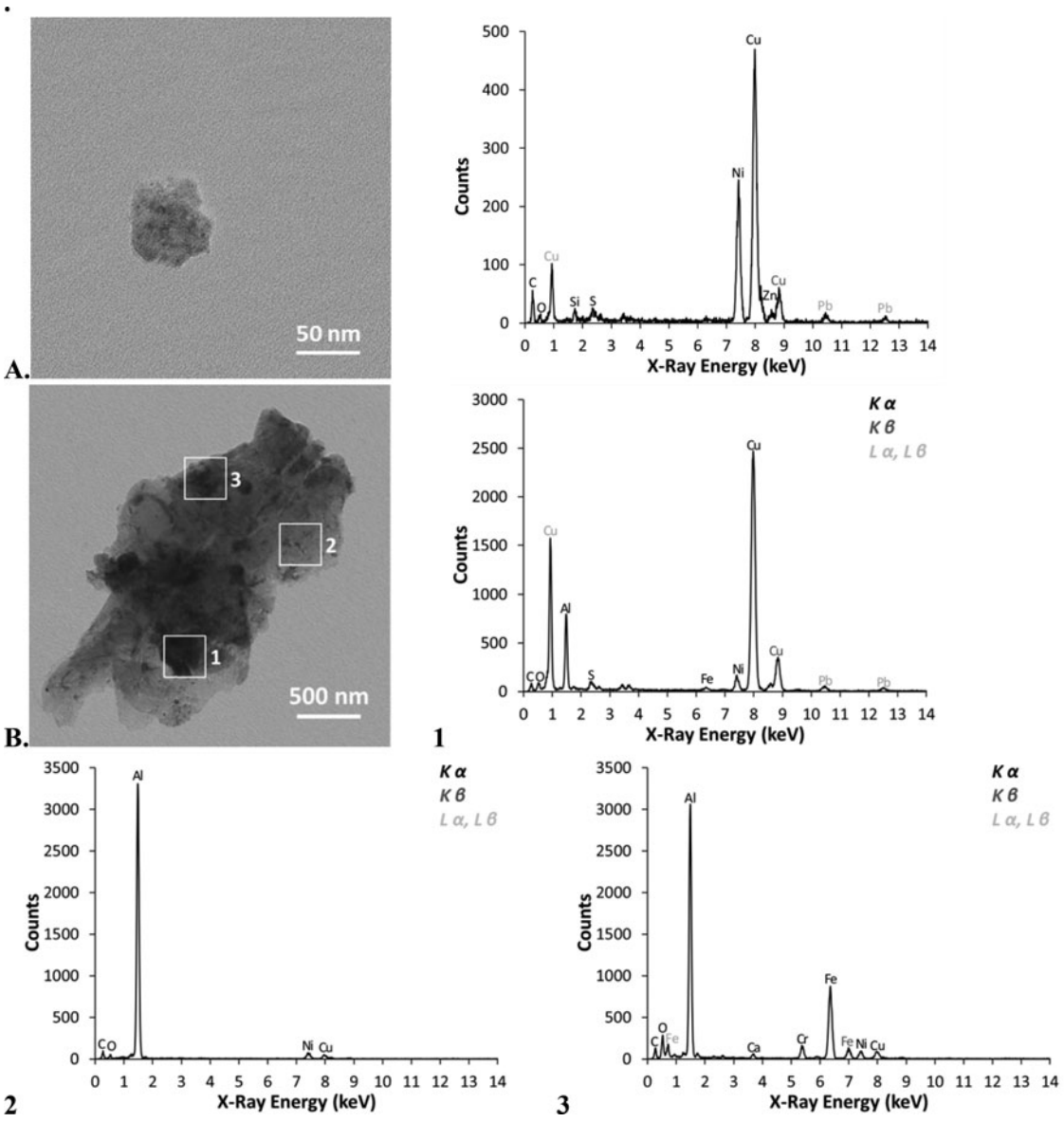

Figure 6. Morphology and composition of particulate matter emitted during M9 firing. A. Single particle with whole area scan results from EDS; B. Single particle with three small area scan results from EDS. Elements identified include carbon (C), oxygen (O), aluminum (Al), sulfur (S), calcium (Ca) silicon (Si), chromium (Cr), iron (Fe), copper (Cu), and lead (Pb).

particles observed in background samples were found in samplings collected during both M9 and M4 firing.

Discussion

Over the last 15 years, instructors at AF small arms firing ranges have been reporting adverse health effects, such as respiratory irritation, headache, and nausea.[1–2] These reported symptoms coincide with the introduction of LFF ammunition.[1–2] Given this finding, our primary objective was to characterize the range ventilation system and instructor exposure to byproducts from firing LFF ammunition in an enclosed firing range using both conventional and advanced technologies.

The ventilation assessment found that the operating conditions generally did not meet the guidelines.[4,21–23] First, volumetric flow rate measurements showed approximately ten times more air being supplied than exhausted. Second, static pressure measurements indicated that the range was operating at a positive pressure differential relative to adjacent areas during firing exercises (Table 2). The implication of such a condition is that firing emissions generated within the firing range are not effectively removed from the range and can expose instructors to emissions and contaminate other areas of the building that houses the firing range.

The ventilation system should move air uniformly downrange from the firing line.[4,21–23] Smoke tests and

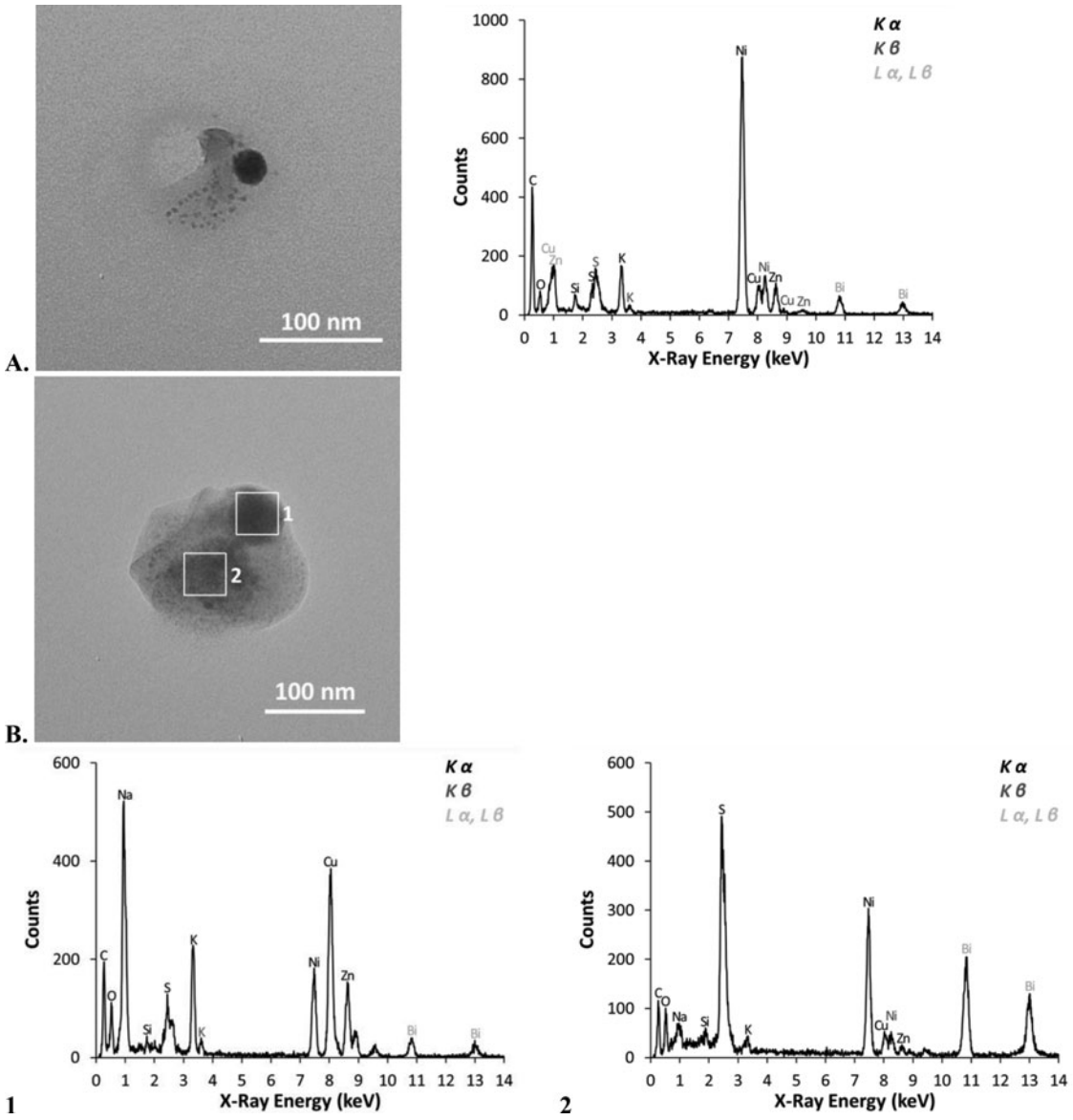

Figure 7. Morphology and composition of particulate matter emitted during M4 firing. A. Single particle with whole area scan results from EDS; B. Single particle with two small area scan results from EDS. Elements identified include carbon (C), oxygen (O), sodium (Na), silicon (Si), sulfur (S), potassium (K), copper (Cu), zinc (Zn), and bismuth (Bi).

velocity measurements at the firing line indicated that the direction and magnitude of the airflow was not uniform (Figures 2, S1). However, the air velocity values met the guideline when averaged across all of the stalls, which could provide the impression that range ventilation conditions were acceptable. It is important to note that both the smoke tests and velocity measurements at the firing line produced similar results regarding the variability of flow. However, the former took about five minutes, while the latter took about one hour to complete. The main drawback to using the smoke test alone is that the results are qualitative and may be difficult to document. Similarly, charting air velocity at each firing stall prior to each firing exercise is impractical due to the extensive time requirement. Therefore, neither approach is ideal, which indicates that new approaches may be necessary to evaluate the effectiveness of firing range ventilation systems. One approach would be to implement low-cost real-time air velocity sensors at multiple points along the firing line. Another approach might involve the use of a device, operating in real-time, to monitor weapons byproducts behind the firing line where instructors spend most of their time.

Recent studies suggest that the primary airborne hazard during firing of LFF ammunition is copper particulate, yet personal exposures are far below applicable OELs.[1–3] One plausible explanation is that the firing byproducts are dominated by ultrafine (nanoscale) PM, which do not contribute to the mass-based measurements.[6] Such a finding provided the impetus for measuring both copper mass concentration and

ultrafine particle concentration in the breathing zone of instructors.

On a mass basis, copper was detected more often in samples collected during M4 firing exercises than M9. However, none of the samples exceeded 1% of the copper dust OEL (Table 3). These values are consistent with previous exposure assessments in AF ranges firing LFF ammunition.[1–3] The copper concentration in the area sample collected during M4 rifle firing exercises was more similar to instructor exposure on day 2 than day 1. Variation between the two instructors may be related to the activity of the instructors, where one instructor may spend more time working in closer proximity to the shooters. However, the variation in the stationary area sample for copper (located behind the firing and ready line) may be related to the limited number of samples collected as well as ventilation conditions that did not consistently move emissions downrange away from shooters and instructors.

Regardless of weapon fired, the particle number concentration behind the firing line rose quickly corresponding to firing events (Figure 3). There were no clear differences in particle number concentration in the breathing zone of line instructors between the M9 and M4 exercises. The maximum peak number concentrations recorded by the instrument exceeded 400,000-#/cm^3, which is above the maximum calibrated concentration of 200,000-#/cm^3. Therefore, the accuracy and precision of particle number concentration data above 200,000-#/cm^3 is uncertain. In future studies, the accuracy of peak particle number concentrations could be improved by adding a dilutor to the PUFP inlet when high particle number concentrations are expected.

There is currently no OEL based on particle number concentration. Correlations between ultrafine particle exposure in ambient environments and health effects to the general public have been explored.[27–28] However, further research is required to determine whether there is a threshold number in specific occupational environments that can be correlated with health effects and adverse health outcomes. In the meantime, particle number concentration measured in the breathing zone of instructors can be used as an indicator of not only potential exposure but also the effectiveness of the ventilation system in controlling weapons emissions.

Area air sampling data showed key differences in PM byproducts between the two weapons. First, the median particle size and concentration were both greater during M9 vs. M4 firing (Figure 4). The small particle size during firing of LFF ammunition using a rifle is consistent with other findings.[6] The difference in concentration in the area sample is unclear and may be related to differences in agglomeration rates and transport properties of PM emitted.

In addition to differences in PM size, there were differences in the morphology and elemental composition of PM generated during firing of the M9 pistol compared to the M4 rifle (Figures 5–7). The PM generated by the M9 pistol was mostly amorphous, whereas PM generated by the M4 rifle included high density spheres (Figure 5). Copper and zinc were found in PM emitted from both weapons, which was expected since copper and zinc are the primary components of the bullet. Interestingly, TEM-EDS analysis found copper and zinc were present in PM collected on background days when no firing occurred (see Figures S2–3). This suggests the possibility that a portion of weapons emissions (especially the small PM) may remain buoyant in the air after firing (especially if the ventilation system is turned off). Another possibility to account for such a finding is that particles deposited during previous firing exercises can become re-suspended during housekeeping operations or other activity in the range (such as sweeping or foot traffic).

The value of using TEM-EDS to identify components of the aerosol collected lies in the ability to confirm the presence of a particular contaminant of interest. However, because copper and zinc were identified does not mean that these metals would be detectable on a mass basis. Furthermore, additional elements identified by TEM-EDS analysis included sulfur and silicon in PM from both weapons, aluminum, iron, chromium and lead in M9 emissions, and potassium, sodium and bismuth in M4 emissions. According to the Safety Data Sheet for the ammunition fired, aluminum is a component in the primer. The remaining elements are not listed as a component, but could still be present in trace amounts or could come from other sources not related to LFF (e.g., chromium lining of the rifle barrel). Regarding lead, one possibility to account for its presence is contamination of the weapon from previous use of lead-based ammunition. Additionally, lead styphnate is suspected to be a small component of the primer used during the manufacture of LFF. A recent study by the Swedish Department of Defense also found lead, iron, chromium and potassium in LFF firing emissions.[29] The exact mechanism for differences in size, morphology and composition of PM emitted by the M9 vs. the M4 is not well-understood, as the composition of the ammunition for each weapon is identical. Differences include the size of the rounds, the amount of propellant, and the length of the barrels. The longer barrel length of the M4 leads to a greater amount of friction acting on the bullet, which leads to more abrasion and higher temperatures and pressures. Therefore, it is possible that the greater amount of friction and higher temperatures and pressures could result in the generation of unique PM by the M4 rifle compared to the M9 pistol.

Instructor health complaints and symptoms have been reported to be more significant during firing exercises using the M4 vs. M9.[1] Recently, emissions from small arms firing of LFF ammunition were collected in liquid media and delivered to *in vitro* lung cell models.[29] Emissions from a rifle were found to be more toxic than those from a pistol and was correlated to the level of copper present. However, there are additional differences between M4 and M9 firing emissions that remain to be correlated with toxicity. The toxicity of ultrafine PM is known to depend on a multitude of factors, including size distribution, shape, composition, and surface chemistry.[30] The results from this study provide evidence that differences may be related to the unique size distribution and morphology of ultrafine PM. It is also possible that additional byproducts not sampled, such as acid gases and particle-bound semi-volatile chemicals may play a role.[2] Therefore, future studies should investigate the full spectrum of emissions from firing LFF ammunition using the M4 rifle compared to the M9 pistol and evaluate toxicity outcomes.

One limitation of the present study was that the area sample was located in a stationary position just behind the ready line (Figure 1A), which is upstream from the firing line by about 2.5 m. Instructors are generally located between the ready line and the firing line and move across firing stalls during exercises. Therefore, emissions characterized in area samples were not identical to those in the breathing zone of instructor. However, if the ventilation system was completely effective in removing weapons emissions, one would expect to see no increases in particle number concentration or mass-based air samples for copper or zinc at this location. A second limitation is that the portable SMPS (Nanoscan) resolves particle size distribution on a time-scale of 60 s, which is not equivalent to the amount of time it takes for emissions to be generated during weapons firing, which is less than 1 sec. However, in this study, the overall shift in the median size of the emissions could be observed, since 10–13 weapons were fired over the course of 1–2 min, followed by a break for several minutes.

Conclusions

This study highlighted some of the key gaps in current exposures assessments conducted in firing ranges. First, PM emitted during the firing of LFF ammunition was primarily in the ultrafine (nanoscale) size range, so TWA mass-based measurement of copper dust or fume may not be the most appropriate indicator of a potential health hazard, especially since reported health complaints and symptoms repeatedly occur in instructors exposed to levels well below the OEL. The data collected in this study confirmed that ultrafine particle number concentration increases rapidly as a result of firing events and can be measured in the breathing zone of instructors in real-time using a wearable ultrafine particle counter. The ventilation system, as operated, did not fully control weapons emissions present behind the firing lines where instructors worked. Second, this study showed that the ultrafine PM emitted during firing was composed of a complex mixture of substances, which suggests that looking at one specific metal, i.e., copper, may not be adequate to fully characterize exposure. Therefore, additional work is necessary to explore other appropriate metrics for compliance sampling in ranges firing LFF ammunition.

Unfortunately, OELs that may be developed using ultrafine particle number concentrations as the measurement metric will likely require speciation of ultrafine composition. However, in the mean-time, the wearable direct reading ultrafine particle counter could be used to supplement mass-based air sampling measurements and to evaluate the effectiveness of the ventilation system in removing weapons emissions from the instructor breathing zone.

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