



AFRL-SA-WP-TR-2018-0012

Ventilation Assessment and Particle Clearance in an Enclosed Firing Range



Christin Grabinski

June 2018

**Final Report
for January 2016 to December 2016**



**DISTRIBUTION STATEMENT A. Approved
for public release. Distribution is unlimited.**

**Air Force Research Laboratory
711th Human Performance Wing
U.S. Air Force School of Aerospace Medicine
Aeromedical Research Department
2510 Fifth St., Bldg. 840
Wright-Patterson AFB, OH 45433-7913**

NOTICE AND SIGNATURE PAGE

Using Government drawings, specifications, or other data included in this document for any purpose other than Government procurement does not in any way obligate the U.S. Government. The fact that the Government formulated or supplied the drawings, specifications, or other data does not license the holder or any other person or corporation or convey any rights or permission to manufacture, use, or sell any patented invention that may relate to them.

Qualified requestors may obtain copies of this report from the Defense Technical Information Center (DTIC) (<http://www.dtic.mil>).

AFRL-SA-WP-TR-2018-0012 HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION IN ACCORDANCE WITH ASSIGNED DISTRIBUTION STATEMENT.

//SIGNATURE//

DARRIN OTT, PhD
CRCL, Force Health Protection

//SIGNATURE//

DR. RICHARD A. HERSACK
Chair, Aeromedical Research Department

This report is published in the interest of scientific and technical information exchange, and its publication does not constitute the Government's approval or disapproval of its ideas or findings.

REPORT DOCUMENTATION PAGE			<i>Form Approved</i> <i>OMB No. 0704-0188</i>		
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 7 Jun 2018		2. REPORT TYPE Final Technical Report		3. DATES COVERED (From – To) January 2016 – December 2016	
4. TITLE AND SUBTITLE Ventilation Assessment and Particle Clearance in an Enclosed Firing Range			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Christin Grabinski			5d. PROJECT NUMBER 15-067		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) USAF School of Aerospace Medicine Aeromedical Research Dept/FHOF 2510 Fifth St., Bldg. 840 Wright-Patterson AFB, OH 45433-7913			8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-SA-WP-TR-2018-0012		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION / AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A. Approved for public release. Distribution is unlimited.					
13. SUPPLEMENTARY NOTES Cleared, AFIMSC/PA, Case # 2018-0230, 3 Aug 2018.					
14. ABSTRACT Air Force small arms firing ranges began using lead free frangible ammunition in the early 2000s due to environmental and health concerns related to the use of lead ammunition. In spite of this step, range instructors continue to report respiratory symptoms. However, exposure assessments routinely detect chemicals and particulate matter (PM) in amounts much lower than their respective occupational exposure limits. The objective of this research was to investigate this issue in a closed firing range by characterizing the ventilation and byproducts from firing lead free frangible ammunition using both the M9 pistol and M4 rifle. The ventilation system was assessed by measuring air velocity and flow patterns in each firing stall. Personal sampling was conducted in the breathing zone of instructors using the standard mass-based measurement of copper, in addition to a novel real-time measurement of particle number concentration. Area sampling was conducted just upstream from the firing line for advanced PM analysis of size distribution, morphology, and elemental composition. Results indicated that the ventilation system was inadequate for clearing firing byproducts and included points of stagnant, turbulent, and backwards flow. The mass of key metals in the breathing zone was at least an order of magnitude below mass-based occupational exposure limits. Real-time measurements in the breathing zone showed sharp peaks in ultrafine PM concentration during firing. Area sampling indicated complex PM in the ultrafine size range with distinct morphologies for the M9 compared to the M4. The results of this study highlight that ventilation design and assessment standards must be revised to ensure adequate clearance of firing byproducts. Further, exposure standards must be updated to include an endpoint that is related to instructor symptoms. Real-time particle counting in the breathing zone of instructors is a promising avenue to consider, although further validation is required.					
15. SUBJECT TERMS Lead free frangible ammunition, small arms firing ranges, firing byproducts, personal exposure, occupational exposure limit, ventilation					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Christin Grabinski, PhD
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (include area code)
			SAR	34	

This page intentionally left blank.

TABLE OF CONTENTS

	Page
LIST OF FIGURES	ii
LIST OF TABLES	ii
ACKNOWLEDGMENTS	iii
1.0 EXECUTIVE SUMMARY	1
2.0 INTRODUCTION	2
3.0 BACKGROUND	3
4.0 METHODS	5
4.1 Sampling Approach	5
4.2 Ventilation Measurements	6
4.3 Exposure Characterization	7
5.0 RESULTS	8
5.1 Ventilation Assessment.....	8
5.1.1 Velocity Measurements	8
5.1.2 Smoke Tests	9
5.1.3 Range Pressure.....	9
5.2 Exposure Assessment.....	11
5.2.1 Personal Sampling	11
5.2.2 Area Sampling – Background PM	12
5.2.3 Area Samples – Firing Byproducts	15
5.2.4 Surface Dust.....	20
6.0 DISCUSSION	21
7.0 CONCLUSION.....	23
8.0 REFERENCES	23
LIST OF ABBREVIATIONS AND ACRONYMS	26

LIST OF FIGURES

	Page
Figure 1. Schematic of the firing range.....	6
Figure 2. Image of the velocity measurement approach	7
Figure 3. Average velocity at the firing line using the nine-point method	9
Figure 4. Images from smoke tests.....	10
Figure 5. Particle number concentration in the breathing zone of firing range instructors.....	11
Figure 6. Background PM concentration over time	12
Figure 7. Average air velocity and particle concentration at the firing line in individual stalls.	13
Figure 8. Morphology of PM in background air	14
Figure 9. Morphology and composition of PM in background air.....	15
Figure 10. Particle size distribution measured in the area sample	16
Figure 11. Morphology of PM emitted during firing of the M9 pistol (A-C) or M4 rifle (D-F).	17
Figure 12. Morphology and composition of PM emitted during M9 firing.....	18
Figure 13. Morphology and composition of PM emitted during M4 firing.....	19
Figure 14. Surface dust accumulated on the floor of the range during firing, about 10 feet downrange from the firing line	20

LIST OF TABLES

	Page
Table 1. Constituents and Expected Firing Byproducts for LFF Ammunition.....	3
Table 2. Summary of Sampling Methods	8
Table 3. Pressure Measurements in the Range and Building.....	10
Table 4. Particulate Matter Mass Based Measurement Data	12
Table 5. Average Background Particle Concentration on Different Days.....	12

ACKNOWLEDGMENTS

We would like to acknowledge the technicians who assisted with ventilation assessment and air sampling, including TSgt Jeremiah Jackson, SSgt Alexander Moore, and Ms. Laura Flory. We would also like to acknowledge Captain Mark Methner, a key collaborator at the National Institute for Occupational Safety and Health, who provided advice throughout this project. Finally, we would like to thank Dr. Saber Hussain for loaning instrumentation and his research assistants Ms. Cassandra Mankus and Mr. Trevor Tilly for completing transmission electron microscopy analysis of samples collected during firing.

This page intentionally left blank.

1.0 EXECUTIVE SUMMARY

The 711th Human Performance Wing Research, Studies, Analysis, and Assessments Council supported this study to evaluate current ventilation and exposure assessment standards in Air Force (AF) small arms ranges firing lead free frangible ammunition and develop recommendations for updates to these standards considering state-of-the-art technologies. We conducted all of the testing at the indoor small arms firing range at Wright-Patterson Air Force Base in Dayton, OH.

The first objective was to test the ventilation conditions. First, we took velocity measurements at nine points in each of the firing stalls, according to ventilation assessment guidance published by the Navy Environmental Health Center. Velocity averages were consistent over the course of several days, indicating that the range may pass a regular inspection using this standard method. However, plotted velocity measurements indicated highly variable flow within and among stalls, which suggests that the flow was not laminar. Smoke tests verified this and identified points of stagnant, turbulent, and backwards flow. Next, we investigated whether the range was at slight negative pressure, which is required to prevent firing byproducts from infiltrating the building enclosing the firing range. A combination of measurements using a barometric pressure sensor and smoke tests indicated that the range was at positive pressure on all of the days tested.

The second objective was to characterize the firing byproducts. Ultrafine particle counts measured in the breathing zone of the instructor indicated sharp peaks in concentrations with firing. Copper was detected in personal and area samples for respirable (50% cut-off of 4 μm) and total particulate matter during one M9 exercise and all M4 exercises. However, concentrations were well below the time-weighted average 8-hour occupational exposure limit for copper dust (1.0 mg/m^3) as well as copper fume (0.1 mg/m^3). Analysis of the size distribution in the area sample indicated that ultrafine particles dominated the aerosol number concentration and that these particles reached smaller sizes during firing of the M4 rifle *versus* the M9 weapon. Particulate matter morphology and composition were complex and unique when generated by each weapon.

The results from this study highlight issues with ventilation standards and assessment technologies. We met with the local Bioenvironmental Engineer shop to discuss recommendations for updating the ventilation requirements and assessment protocols. We also shared our findings with the Occupational and Environmental Health Department at the U.S. Air Force School of Aerospace Medicine to support a fact sheet submitted to bioenvironmental engineers AF wide. We presented the results on a poster at two meetings in October 2015: the American Association for Aerosol Research Conference in Minneapolis, MN, and Wing Tech Day at Wright-Patterson Air Force Base, OH.

Most importantly, the results from this study guided the identification of key research gaps to improve our understanding of ventilation and clearance of firing byproducts in AF firing ranges. A key success in the present project includes the demonstration of wearable direct reading ultrafine particle counters by instructors during firing exercises for dynamic measurement of byproducts. Future work is required to identify the acceptable limits for ultrafine particle concentrations recorded. Further, to update exposure assessment technologies and standards, it is essential to understand the underlying cause (e.g., copper mass, ultrafine particles) for respiratory effects in firing range instructors.

2.0 INTRODUCTION

Air Force (AF) small arms firing ranges began using lead free frangible (LFF) ammunition in the early 2000s due to environmental, health, and safety concerns related to the use of lead ammunition. In spite of this step, instructors continue to report health symptoms, including sore throat, cough, eye irritation, and metal taste, during firing exercises [1,2]. However, three key studies involving exposure assessment at small arms firing ranges using LFF ammunition found chemicals and metal-based particulate matter (PM) in firing byproducts at levels that were much lower than their respective occupational exposure limits (OELs) [1-3].

One possible cause for the discrepancy between reported symptoms and low-level exposures in the case of PM is the limitations of mass-based measurement methods. As the size of PM decreases, there is a drastic reduction in the contribution to mass-based measurements. Furthermore, the size of PM plays a major role in health effects. PM $\leq 2.5 \mu\text{m}$ (PM_{2.5}) is the key size fraction associated with cardiopulmonary disease in areas of air pollution [4]. Moreover, ultrafine PM ($\leq 0.1 \mu\text{m}$) has been shown to be more toxic than fine PM (0.1-2.5 μm) of similar composition when exposed by inhalation [5-14]. Concerns related to ultrafine PM include the ability to deposit in the gas exchange region of the lungs, translocate to 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 [15-17]. Therefore, characterization of ultrafine PM concentration may provide important information to support exposure assessments.

Regardless of whether the exposure hazard is understood, engineering controls are essential to mitigate exposure. Ventilation is the primary engineering control in the firing range and functions to move air downstream from the firing line to the bullet trap. The National Institute for Occupational Safety and Health (NIOSH) identified a flow rate of 75 feet per minute (fpm) for controlling lead exposure in 1975, which was set as the standard still used today. The approach for ventilation assessment in the AF is to measure the velocity at nine points in the firing stall, average the velocities, and then assess whether they meet the NIOSH standard [18]. However, velocity measurements do not indicate the direction of flow, so this approach can be misleading. Flow must be laminar and even across the width of the firing range to move firing byproducts consistently downrange. Turbulence (i.e., swirling motions) and stagnation will recirculate and accumulate contaminants, resulting in unwanted exposures. Therefore, it is important that that flow patterns be seriously considered in a ventilation assessment strategy.

The objective of this study was to characterize the ventilation system and methods for evaluating the ventilation system. The acquired knowledge is essential for recommending updates to the AF ventilation guidance for closed firing ranges to better control the clearance of firing byproducts. We also aimed to evaluate real-time (RT) PM as an indicator for clearance of firing byproducts using a state-of-the-art wearable condensation particle counter capable of logging particle number concentration in 1-second intervals. We evaluated whether particle-counting technology could be used in place of or to supplement compliance mass-based measurements in exposure assessments. Finally, we used advanced instruments in area samples to characterize the size distribution of PM during firing and collected PM for offline analysis of morphology and composition.

3.0 BACKGROUND

Key components of LFF ammunition used by the AF include cartridge composed of brass; jacket composed of copper; projectile containing primarily packed copper powder and a nylon binder; propellant composed of nitrocellulose, nitroglycerine, and diphenylamine; and primer composed of nitrocellulose, nitroglycerine, diazodinitrophenol, tetracene, barium nitrate, and aluminum. When a bullet is fired, the trigger ignites the primer, which burns without the presence of oxygen. The primer ignites the propellant, which forces the projectile out of the barrel toward the target. Key byproducts expected include metal-containing PM and decomposition gases of the various bullet components (Table 1).

Table 1. Constituents and Expected Firing Byproducts for LFF Ammunition

Component	Constituents	Firing Byproducts
Primer	aluminum, Al barium nitrate, Ba(NO ₃) ₂ nitrocellulose, C ₆ H ₇ O ₂ (OH) ₃ nitroglycerin, C ₃ H ₅ N ₃ O ₉ diazodinitrophenol, C ₆ H ₂ N ₄ O ₅ tetracene, C ₁₈ H ₁₂	aluminum oxide fume barium oxide fume carbon monoxide, carbon dioxide, nitrogen oxides
Propellant	nitrocellulose, C ₆ H ₇ O ₂ (OH) ₃ nitroglycerin, C ₃ H ₅ N ₃ O ₉ diphenylamine, C ₁₂ H ₁₁ N	carbon monoxide, carbon dioxide, nitrogen oxides
Projectile core	copper powder, Cu zinc stearate, C ₃₆ H ₇₀ O ₄ Zn tin, Sn Zytel® nylon resin (DuPont) ^a	copper oxide fume carbon monoxide, carbon dioxide, zinc oxide fume tin oxide fume hydrogen cyanide, ammonia, phosgene, hydrogen chloride
Projectile jacket	brass (alloy of copper and zinc)	zinc oxide fume, copper oxide fume
Cartridge case	brass (alloy of copper and zinc)	zinc oxide fume, copper oxide fume

^a~76% polyhexamethylene adipamide, (C₁₂H₂₂N₂O₂)_n and ~24% proprietary toughener, lubricants, stabilizers, colorants.

Exposure assessments generally compare concentrations of detected compounds to OELs, which originate from an enforceable standard set by the Occupational Safety and Health Administration (OSHA) or recommended standard set by NIOSH or the American Conference of Governmental Industrial Hygienists (ACGIH). OSHA establishes OELs in the form of an enforceable permissible exposure limit (PEL), which is a time-weighted average (TWA) for an 8-hour workday in a 40-hour workweek. NIOSH sets recommended exposure limits (RELs), which are TWA concentrations for up to a 10-hour workday during a 40-hour workweek. ACGIH sets threshold limit values (TLVs), which are a TWA for an 8-hour workday in a 40-hour workweek. Recommended OELs are based on health factors instead of economic or technical feasibility. Since recommended OELs are not enforceable, they can be updated more regularly and are generally more conservative.

In addition to being expressed as PELs, RELs, and TLVs, OELs are sometimes expressed in the form of a short-term exposure limit, which is a TWA over 15 minutes that should never be exceeded during a workday, and a ceiling limit, which is a maximum peak exposure that should never be exceeded. Both enforceable OSHA and recommended NIOSH OELs are found in the NIOSH Pocket Guide to Chemical Hazards, which is available online [19]. ACGIH OELs are found in publications that can be purchased through the ACGIH website (<http://www.acgih.org/home>).

PM OEL classifications include dust and mist, fume, total, and respirable. Dust refers to total PM. Fumes are produced when a solid is heated to gas phase, then cooled until condensed into solid or liquid PM. Due to the conditions that produce fumes, fume PM is usually $<1\ \mu\text{m}$. Total PM includes all PM present. Respirable PM reaches the respiratory region of the lungs, defined as 50% cut-point at $4\ \mu\text{m}$. Not all PM has an OEL for all fractions. For example, particles not otherwise regulated have OELs for total and respirable size fractions, while copper has OELs for dust and fume categories. OELs are often mass-based and are generally lower for PM designated as fume or respirable compared to dust or total. The reason for this is that smaller size fractions contribute less to mass-based measurements and more to health effects.

Several studies have been published regarding the use of LFF ammunition in small arms firing ranges. The first is a review of available literature for toxicological and environmental information associated with expected byproducts from firing LFF ammunition, which was conducted in 1999, before LFF was introduced across the AF [20]. The authors confirmed that LFF projectile alternatives, including copper with a nylon binder, were preferred over lead ammunition from human health and environmental perspectives. Regardless, it was recommended to train instructors and shooters that the hazard is not eliminated and should still be controlled.

One of the first studies measuring byproducts generated from firing LFF ammunition in AF firing ranges was conducted in 2001 at Randolph Air Force Base (AFB), TX [21]. Levels of copper, lead, nickel, zinc, and tungsten were measured in both personal and area samples. All concentrations were well below their respective OELs. Copper was the most prevalent metal and was $<34\%$ of the OEL for fume and $<3.4\%$ of the OEL for dust. A similar evaluation was conducted in 2001 at Columbus AFB, MS [22]. Levels of copper, lead, nickel, zinc, and tungsten were measured in area samples. Copper was again the most prevalent metal and reached up to 85% of the copper fume OEL and 8.5% of the copper dust OEL. Nylon combustion byproducts ammonia and hydrogen cyanide were also sampled and found to be well below their respective OELs.

Due to continued reports of symptoms experienced by instructors, a student at the Air Force Institute of Technology conducted a study in 2005 in collaboration with the Air Force Institute for Operational Health at several firing ranges using LFF ammunition [3]. These studies found that copper was 1.3% of the copper dust OEL and zinc was 0.04% of the zinc dust OEL. Ammonia and phosgene were 1.1% of their respective OELs. Aluminum, barium, hydrogen chloride, hydrogen cyanide, nitrogen oxide, and nitrogen dioxide were all less than 1.0% of their respective OELs.

A follow-up study was conducted from 2005-2007 by the Air Force Institute for Operational Health at four ranges using LFF ammunition [2]. Gaseous byproducts, including ammonia, hydrogen cyanide, and phosgene, were $<2\%$ of their OELs. The firing range with the highest levels of copper was Whiteman AFB, which is a partially enclosed range. However, the levels were still $<20\%$ of the copper dust OEL. Symptoms reported by instructors included sore

throat (55%), cough (52%), itchy/watery eyes (41%), runny nose (36%), trouble breathing (27%), and tight chest (21%). The symptoms were not statistically different between instructors exposed to byproducts from firing lead and LFF ammunition and there were only minor differences in byproduct composition. It was observed in this study that symptoms were more prominent in closed *versus* open ranges.

Representatives from NIOSH completed an additional follow-up study in 2012 [1]. The report confirmed that copper concentrations in AF firing ranges did not exceed OELs during firing exercises. They also found that the ventilation system was not operating according to the standard and recommended updating. Electron microscopy confirmed the presence of copper particles in the ultrafine size range. Symptoms reported by instructors included headache (92%), metallic taste (42%), sore throat (33%), shortness of breath (25%), and nasal/sinus irritation (25%)

The studies summarized here highlight that there are ongoing exposure issues at U.S. AF ranges firing LFF ammunition. Similar concerns regarding the use of LFF ammunition have also been raised by the Norwegian and Swedish militaries. The exposure concerns are centered on the fact that byproducts are often found to be below OELs in AF firing ranges, but symptoms are still reported. Although updated engineering controls were often identified as an essential means to mitigate exposure, they were not characterized in the AF exposure assessments concurrent to exposure data [1-3]. The next step is to continue investigation into exposure issues in AF firing ranges using state-of-the-art technologies to assess new methods for characterizing firing byproducts and examine potential solutions for engineering control assessment for efficient clearance of firing byproducts.

4.0 METHODS

4.1 Sampling Approach

Sampling was completed 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 [23]. The main engineering controls include a ventilation system and bullet traps. The ventilation system pushes air downstream from the firing line and pulls air from a location near the bullet trap located at the back wall. The amount of air pulled should be 3-7% greater than the amount pushed to maintain a slight negative pressure in the range. The bullet trap is designed to capture major fragments and dust generated upon impact. Shooters fire from behind the firing line, and instructors move around between the firing line and ready line, interacting with shooters throughout each exercise (Figure 1).

Weapons included the M9 pistol and M4 rifle. The M9 pistol is a single-round semiautomatic with a barrel length of 125 mm, while the M4 can be operated as single-round or three-round burst semiautomatic and has a barrel length of 370 mm. The ammunition for both weapons was LFF ammunition from Federal Premium Ammunition, formerly called Federal Cartridge Corporation (Anoka, MN). The ammunition differed mainly in size: 9 mm for M9 pistols and 5.56 mm for M4 rifles.

The personal protective equipment worn by the shooters and instructors during each exercise included a bulletproof vest and double hearing protection: foam earplugs and earmuffs. During each exercise, 10-20 tests were completed. For each test, the students were instructed to load a certain number of rounds and then fire. Each test took about 2 minutes, during which the

students were allowed to expire all of the rounds designated for that test. The total number of rounds was 90 during M9 exercises and 196 during M4 exercises.

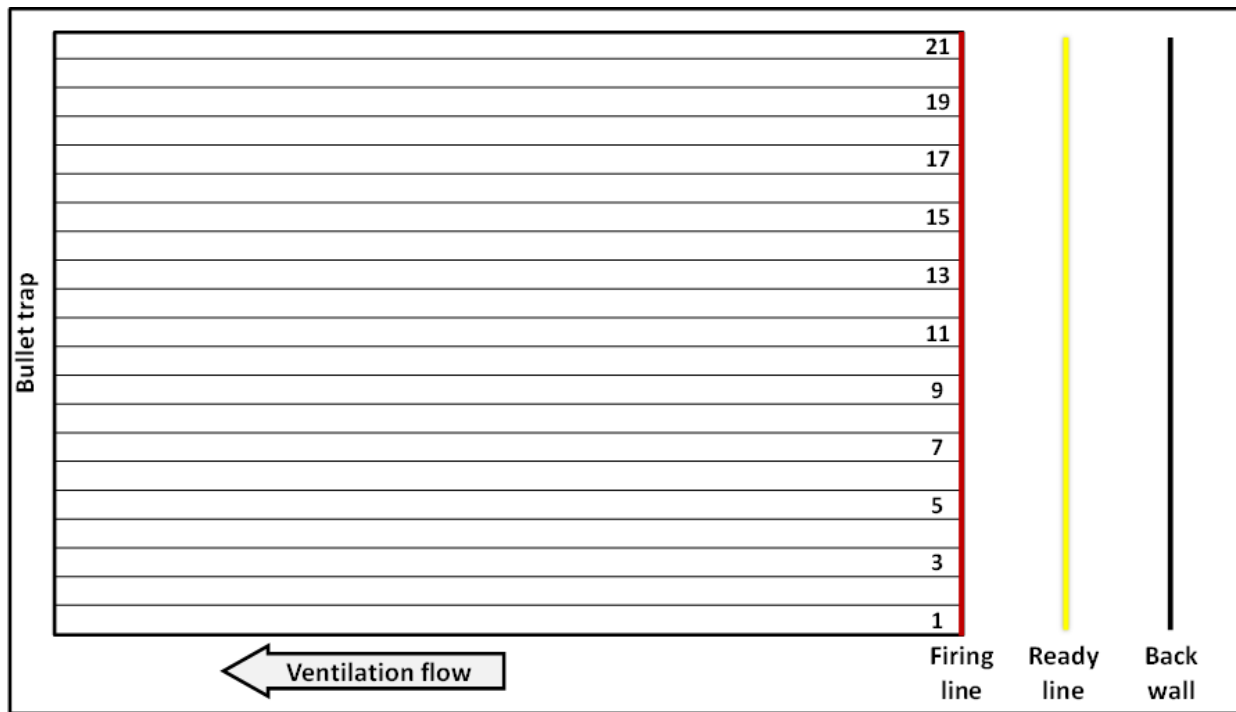


Figure 1. Schematic of the firing range.

4.2 Ventilation Measurements

The ventilation conditions were assessed using current ventilation assessment techniques, as described in the Navy Environmental Health Center Indoor Firing Ranges Industrial Hygiene Technical Guide [18]. The velocity measurements were completed using a VelociCalc® Multi-Function Ventilation Meter (TSI, Inc., Shoreview, MN). The measurements were completed at nine points in each firing stall (Figure 2). The smoke test was completed using the FlowMarker Fog Generator (Degree Controls, Inc., Milford, NH). The fog 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.

Baseline particle counts were obtained using a portable ultrafine particle counter (PUFP; Enmont, LLC, Cincinnati, OH), which was placed at the same points where velocity measurements were conducted.



Figure 2. Image of the velocity measurement approach.

4.3 Exposure Characterization

Personal sampling was conducted in the breathing zone of the instructors, and area sampling was conducted at a stationary location behind the ready line (see Figure 1). A combination of collection methods for offline analysis and direct reading methods for RT analysis was incorporated. PM metal content was assessed in both personal and area samples using the NIOSH 7300 method. Specifically, personal sampling pumps (GilAir® Plus, Sensidyne, St. Petersburg, FL) were set to 2.5 L/min and connected to a 37-mm cassette containing a 0.8- μm mixed cellulose ester membrane (SKC, Inc., Eighty Four, PA) with or without an aluminum cyclone for respirable and total PM, respectively. The filters were acid digested and analyzed offline using inductively coupled plasma mass spectrometry (ICP-MS) by ALS Global. The particle number was logged in personal samples using the PUFPP. The detection range of the Enmont PUFPP is ≥ 4.5 nm (50% cut-off) and 0-200,000 $\#/\text{cm}^3$.

In area samples, the particle size distribution was characterized using a scanning mobility particle sizer (SMPS; NanoScan, TSI, Inc.), which has a detection range of 10-420 nm in 13 size bins and 0-100,000 particle number per cubic meter ($\#/\text{cm}^3$). Also, PM was deposited onto substrates for offline analysis of morphology and elemental composition. To deposit particles, PM-laden air was introduced in electrostatic precipitator (ESP; NanoSampler, TSI, Inc.) at a flow rate of 0.3 L/min and voltage of -10 kV. The substrates included nickel grids coated with a formvar-carbon film (Electron Microscopy Sciences, Hatfield, PA). The PM was characterized for size and morphology using transmission electron microscopy (TEM) at 100 kV equipped with energy-dispersive X-ray spectroscopy (EDS) at the Materials Laboratory, Wright-Patterson AFB. The EDS peaks were marked using the software 4pi revolution® (4pi Analysis, Inc., Hillsborough, NC) and confirmed using data available from Deslattes et al. [24].

A summary of the sampling methods is shown in Table 2. Data collected from direct reading instruments were exported to Excel (Microsoft Corporation, Redmond, WA) for analysis and plotting.

Table 2. Summary of Sampling Methods

Endpoint	Instrument	Offline Analysis	Sample Type
Metals	pump, cassette	ICP-MS	personal and area
Particle number concentration	PUFPP	RT data	personal
Particle size distribution	SMPS	RT data	area
Particle morphology, composition	ESP	TEM-EDS	area

Dust accumulated on the floor of the range about 5 feet downrange from the firing line over the course of training exercises. The dust was collected into conical tubes using a metal spatula imaged on filter paper using a stereoscope (SZ-61, Olympus, Tokyo, Japan). The dust was digested in 1% nitric acid and 3% hydrochloric acid and analyzed for composition using ICP-MS (PerkinElmer Nexion 300D, Waltham, MA). The dust was also imaged using scanning electron microscopy (JEOL, Tokyo, Japan).

5.0 RESULTS

5.1 Ventilation Assessment

5.1.1 Velocity Measurements. The air velocity was measured at the firing line using the nine-point measurement approach (see Figure 2). On the first 2 days, the right side of the range (stalls 12-21) was not functioning (Figure 3A-B). On the third day, the full range was operational, and it remained functional on the remaining 3 days tested (Figure 3C-E). On these days, a pronounced dip at stall 11 appeared, and the variability on the right side of the range (stalls 12-21) appeared to be slightly less than the left. When the range was fully functional, the velocity averages appeared to be consistent in the same stall across different days (compare the shape of the plots in Figure 3C-F). However, the averages were inconsistent across different firing stalls, and error bars indicated a large amount of variability.

The overall average velocities were 54, 50, 81, 88, 89, and 82 fpm on days 1-6, respectively, which corresponds to Figure 3A-F. All values were above the minimum 50-fpm standard and within 20% of the ideal 75-fpm standard.

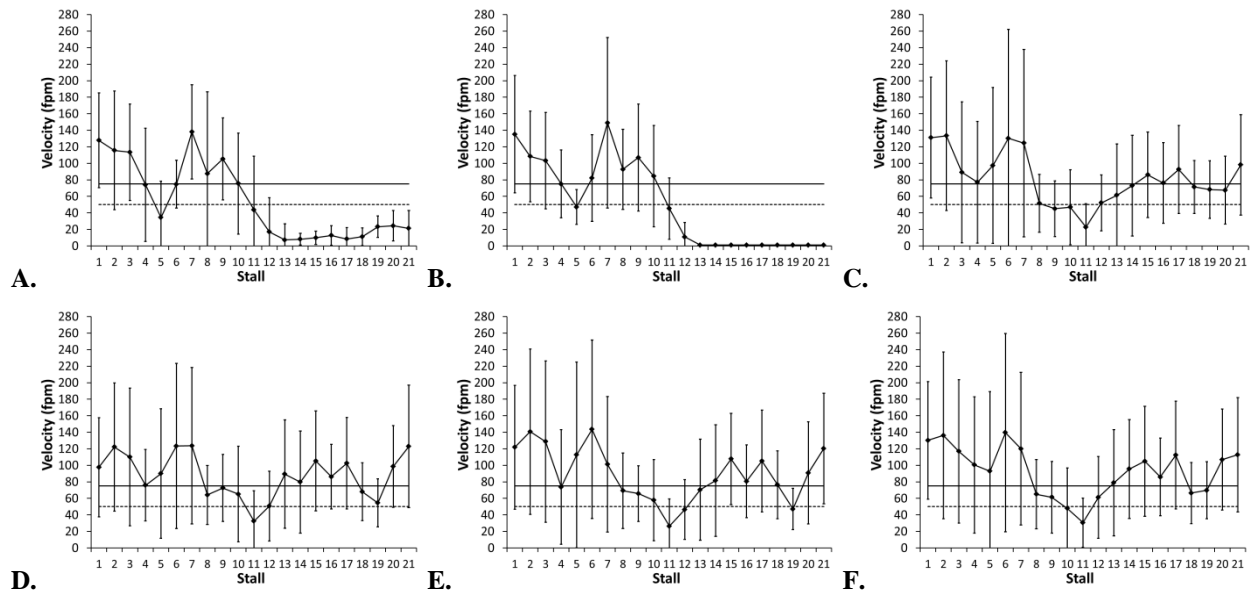


Figure 3. Average velocity at the firing line using the nine-point method. The dotted line indicates the minimum 50-fpm standard and the solid horizontal line indicates the ideal 75-fpm standard.

5.1.2 Smoke Tests. Smoke tests were used to provide a visualization of flow patterns on a day when the range was not fully functional compared to a day when the range was fully functional (Figure 4). Results indicate that the flow was stagnant or moving backwards in the stalls on the right side of the range (stalls 12-21) on the first day (Figure 4A). The flow was moving downrange in more of the stalls on the second day tested when the right side of the range (stalls 12-21) was functional (Figure 4B).

5.1.3 Range Pressure. Beyond meeting the air velocity and laminar flow standards, an additional requirement of the ventilation system is to maintain slight negative pressure (-0.003 ± 0.0015 inHg). This is to prevent firing emissions from infiltrating the building that houses the firing range [18]. We measured the barometric pressure in the range and in the building corridor outside the range on five different days (Table 3). Since the pressure sensor was only sensitive to the second decimal, we used smoke tests to confirm whether smoke generated within the range had a tendency to flow out of the range near the door. Results indicated that the range was at a slight positive pressure on all of the days tested.

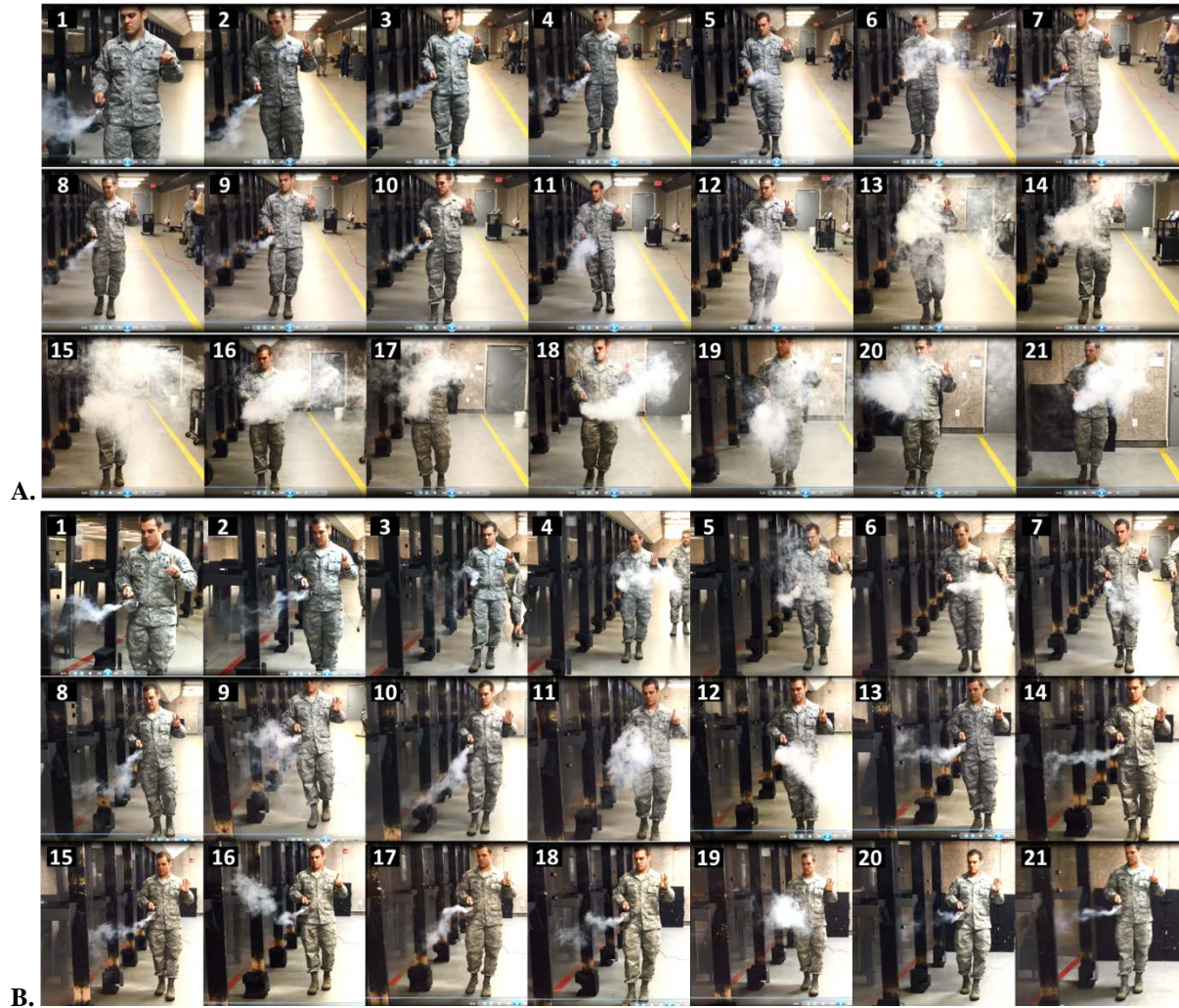


Figure 4. Images from smoke tests. A: Range not fully functional (see Figure 3A for velocity averages). B: Range fully functional (see Figure 3C for velocity averages). The firing stall number is located on the top left of each image. The location of the smoke tests was just upstream of the firing line. Downrange is to the left from the perspective of the reader.

Table 3. Pressure Measurements in the Range and Building

Measurement	Date				
	8/21	8/24	8/28	8/31	11/3
Range Pressure (inHg)	30.24	30.10	30.29	30.22	30.27
Building Pressure (inHg)	30.23	30.09	30.29	30.22	30.23
Pressure Differential (data)	+	+	neutral	neutral	+
Pressure Differential (smoke)	+	+	+	+	+

5.2 Exposure Assessment

5.2.1 Personal Sampling. Particle counts were measured in RT in the breathing zone of firing range instructors using a PUFP during two M9 and two M4 training exercises (Figure 5). Peaks in particle concentration corresponding to firing events were of 1-5 orders of magnitude above background and lasted on the order of seconds. The peak heights were slightly lower during the M9 training exercise (Figure 5A-B) compared to the M4 training exercise (Figure 5C-D). The maximum peak height was about 14% lower during the M9 compared to the M4 training exercises.

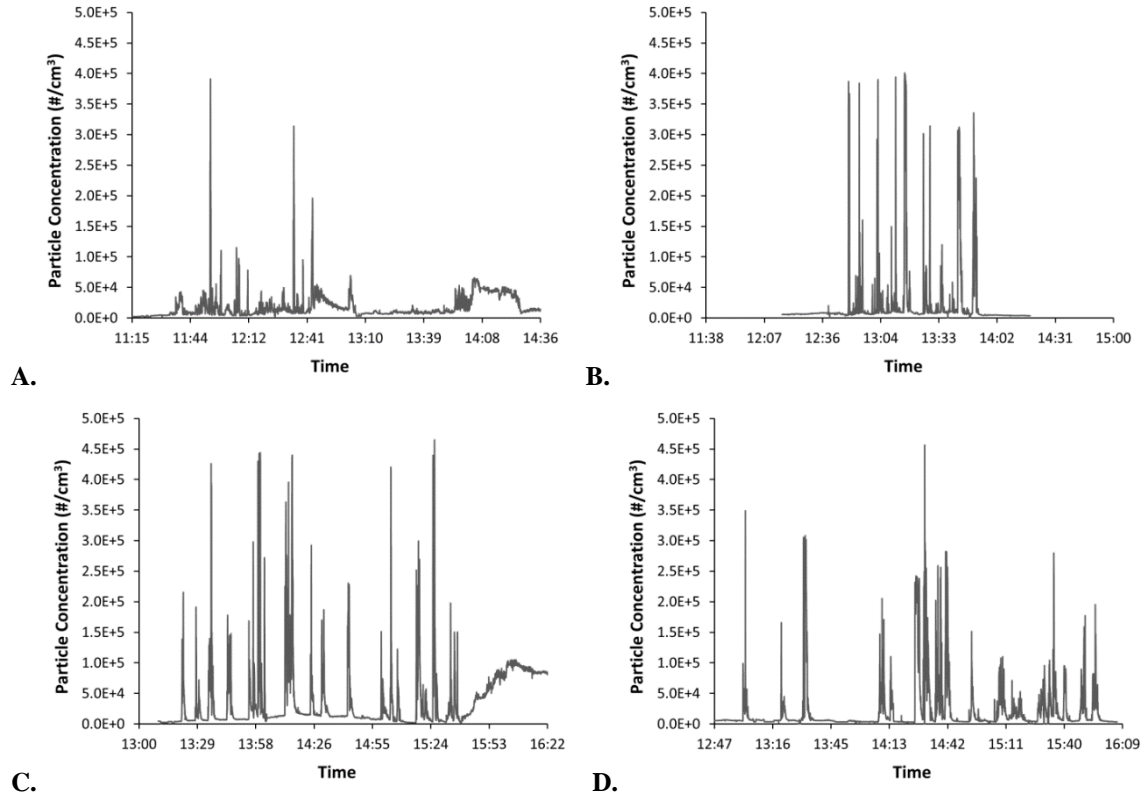


Figure 5. Particle number concentration in the breathing zone of firing range instructors. A-B: M9 training exercises. C-D: M4 training exercises.

The mass of PM was measured in personal and area samples during the same training exercises. Copper, zinc, bismuth, and lead were measured, but only copper and zinc were detected (Table 4). The mass for copper was always about an order of magnitude higher than zinc. Copper was detected during one of the two M9 training exercises and both M4 training exercises. Even the highest 8-hour TWA value for copper was <1% of the copper dust OEL and about 5% of the copper fume OEL. The cumulative number of ultrafine particles for the duration of each exercise was about twice as high for M4 compared to M9 exercises (Table 4). The 8-hour TWA for particle number also tended to be greater for M4 compared to M9 exercises.

Table 4. Particulate Matter Mass Based Measurement Data

Measurement	M9				M4			
	13 Students Task Duration 162 min		13 Students Task Duration 72 min		12 Students Task Duration 146 min		10 Students Task Duration 192 min	
	<i>Task</i>							
Particle count (#/cm ³)	1.8 × 10 ⁸	1.8 × 10 ⁸	1.3 × 10 ⁸	1.3 × 10 ⁸	2.6 × 10 ⁸	2.6 × 10 ⁸	2.5 × 10 ⁸	2.5 × 10 ⁸
Element	Copper	Zinc	Copper	Zinc	Copper	Zinc	Copper	Zinc
Area mass (mg/m ³)	0.001 ± 0.0002	<0.001	<0.002	<0.002	0.002 ± 0.001	<0.00	0.011 ± 0.0001	0.001 ± 0.0001
Personal-1 mass (mg/m ³)	0.002	<0.001	<0.002	<0.002	0.016	0.002	0.013	0.001
Personal-2 mass (mg/m ³)	<0.001	<0.001	<0.002	<0.002	0.008	<0.001	0.011	0.001
	<i>8-h TWA</i>							
Particle count (#/cm ³)	6.2 × 10 ⁷	6.2 × 10 ⁷	2.0 × 10 ⁷	2.0 × 10 ⁷	7.9 × 10 ⁷	7.9 × 10 ⁷	9.9 × 10 ⁷	9.9 × 10 ⁷
Element	Copper	Zinc	Copper	Zinc	Copper	Zinc	Copper	Zinc
Area mass (mg/m ³)	0.001 ± .00001	<0.0003	<0.0003	<0.0003	0.001 ± 0.0003	<0.0003	0.005 ± 0.0001	0.001 ± 0.0001
Personal-1 mass (mg/m ³)	0.001	<0.0003	<0.0003	<0.0003	0.005	0.001	0.005	0.001
Personal-2 mass (mg/m ³)	<0.0003	<0.0003	<0.0003	<0.0003	0.002	<0.0003	0.005	0.001

Note: The bold numbers indicate values that were above the lower limit of detection.

5.2.2 Area Sampling – Background PM. Background PM concentration was averaged for the first 5 minutes on each morning of firing range exercises (Table 5). The values ranged from 6,700 to 11,700 #/cm³.

Table 5. Average Background Particle Concentration on Different Days

Day	Particle Concentration (#/cm ³)
M9-1	8,100 ± 150
M4-1	6,700 ± 240
M9-2	9,200 ± 930
M4-2	11,700 ± 460

Background PM concentration was plotted throughout the morning during a day when there were no firing exercises (Figure 6). The values varied throughout the day and ranged from 2,700 to 18,200 #/cm³.

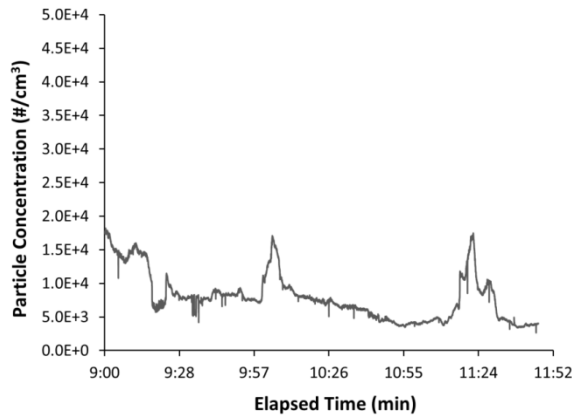


Figure 6. Background PM concentration over time. Data were collected over the course of a morning during a day with no firing exercises.

Particle number concentration was measured simultaneously to air velocity measurements in firing stalls before firing exercises (Figure 7). There was a general trend of higher particle concentrations on the left side of the range (stalls 1-10) where the average air velocity was higher compared to the right side of the range (stalls 12-21).

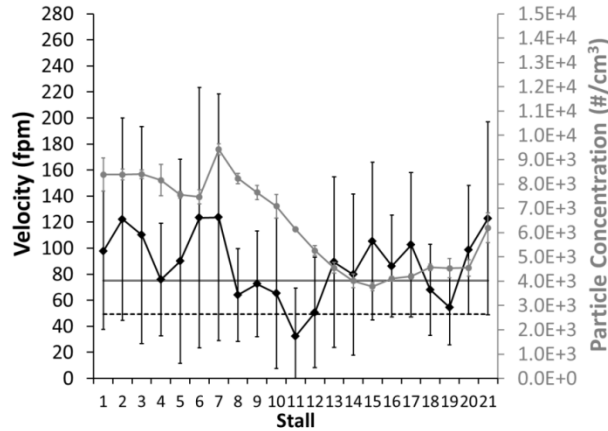


Figure 7. Average air velocity and particle concentration at the firing line in individual stalls.

We further characterized background PM for morphology using TEM (Figure 8). We observed two common particle types, including an amorphous soot-like particle and a porous particle (Figure 8A-B). Moisture was released from the porous particles when they were exposed to the electron beam (Figure 8C). A similar phenomenon has been observed previously for hydrated salt particles [25].

EDS elucidated the composition of these two common morphologies (Figure 9). The amorphous soot-like particle was carbonaceous with traces of silicon (Figure 9A). The porous particle was composed primarily of potassium with traces of silicon, phosphorous, sulfur, copper, and zinc (Figure 9B).

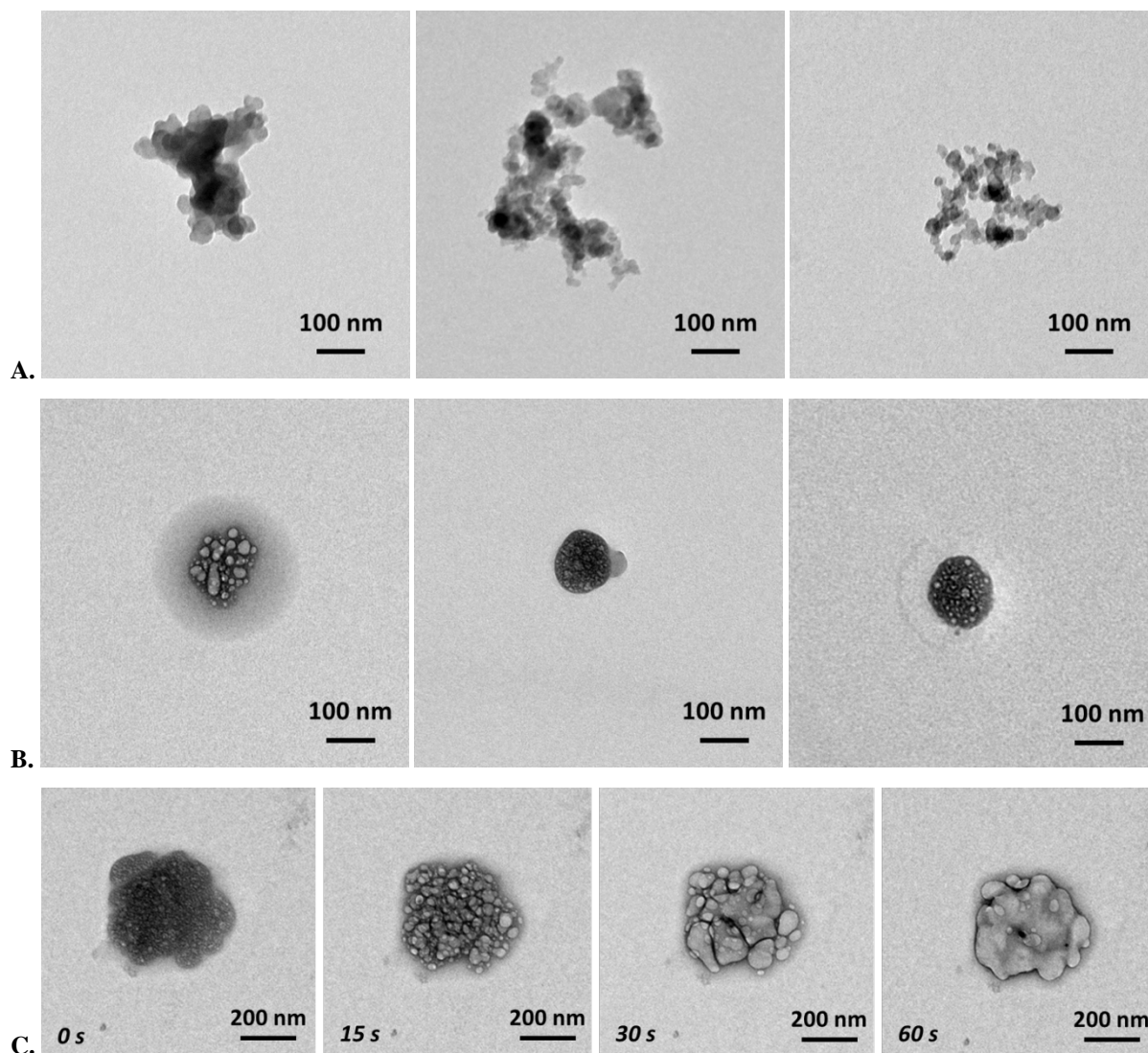


Figure 8. Morphology of PM in background air. A: Amorphous carbonaceous particles. B: Porous particles. C: Porous particle imaged over time.

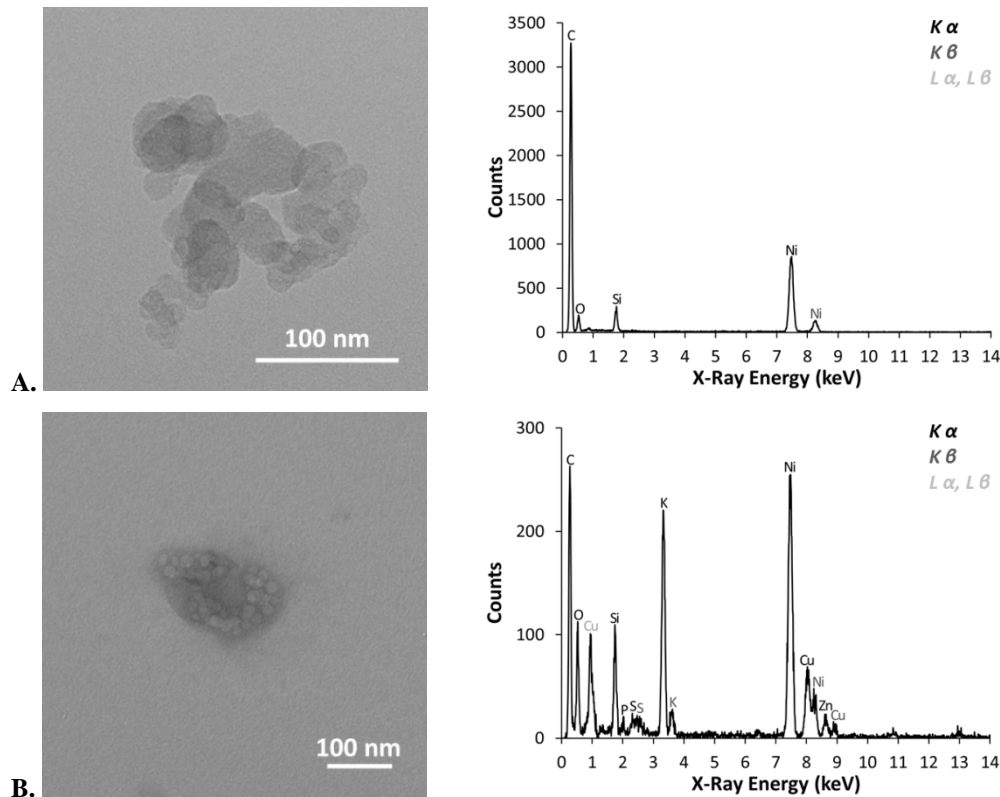


Figure 9. Morphology and composition of PM in background air. A. Amorphous carbonaceous particle. Elements identified include carbon (C), oxygen (O), and silicon (Si). B. Porous mineral-rich particle. Elements identified include carbon (C), oxygen (O), silicon (Si), phosphorous (P), sulfur (S), potassium (K), copper (Cu), and zinc (Zn).

5.2.3 Area Samples – Firing Byproducts. The median ultrafine particle size was measured in area samples during two M9 and two M4 training exercises using an instrument capable of measuring particles from about 10-420 nm in diameter (Figure 10). There was no consistent trend in median particle size with peaks in particle number concentration during the M9 exercise (Figure 10A-B). However, there was a pronounced dip in median particle size with peaks in particle number concentration during the M4 exercises (Figure 10C-D). During M4 exercises, the median particle size reduced to about 20 nm.

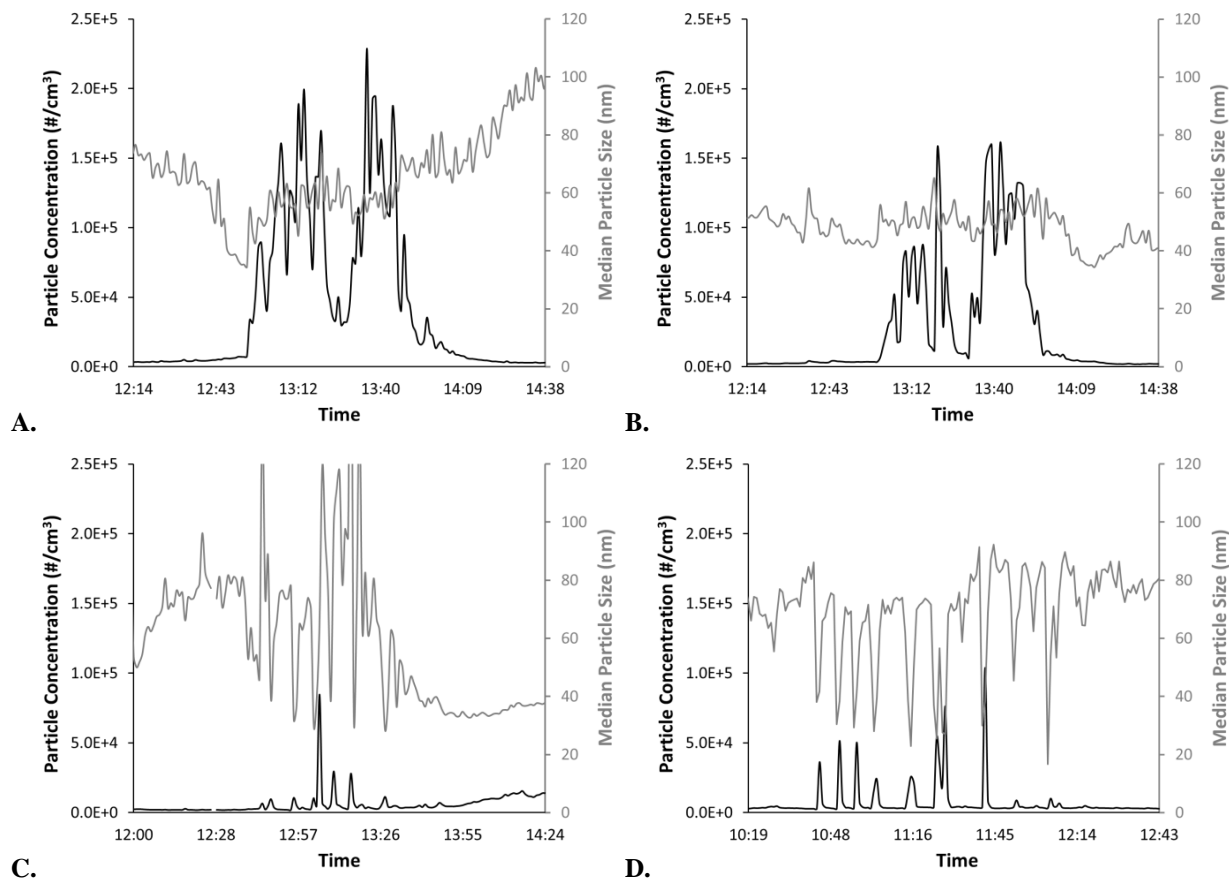


Figure 10. Particle size distribution measured in the area sample. A-B: M9 training exercises. C-D: M4 training exercises.

We further characterized PM emitted during firing exercises for morphology using TEM (Figure 11). PM emitted during both M9 and M4 firing appeared as complexes with both high- and low-density regions. In some cases, there appeared to be very small sub-10 nm high-density particles embedded in the less dense matrix (Figure 11 A-B,F). However, the general morphology was unique for the M9 compared to the M4. The particles emitted during M9 firing were highly irregular (Figure 11A-C). The particles emitted during M4 firing appeared to contain one or more dense ultrafine spherical particles surrounded by a low-density matrix (Figure 11D-F).

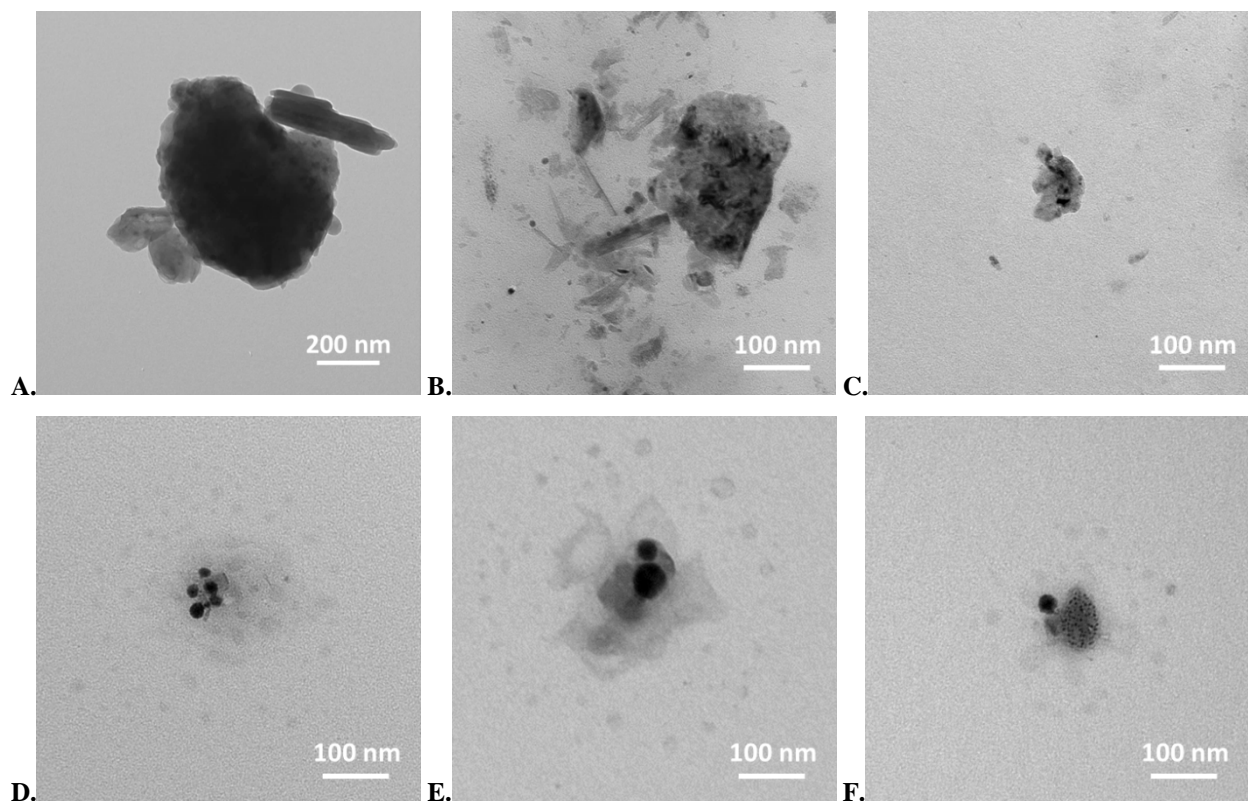


Figure 11. Morphology of PM emitted during firing of the M9 pistol (A-C) or M4 rifle (D-F).

Additional characterization was completed using TEM-EDS. Elements found in particles emitted during M9 firing included aluminum, sulfur, calcium, iron, copper, and lead (Figure 12). Three regions were characterized for one of the samples (Figure 12B). Lead was found to be present in the densest region, but not in the less dense regions that were characterized. Aluminum was the dominant metal in the less dense regions. Iron was primarily present near the edge of the composite.

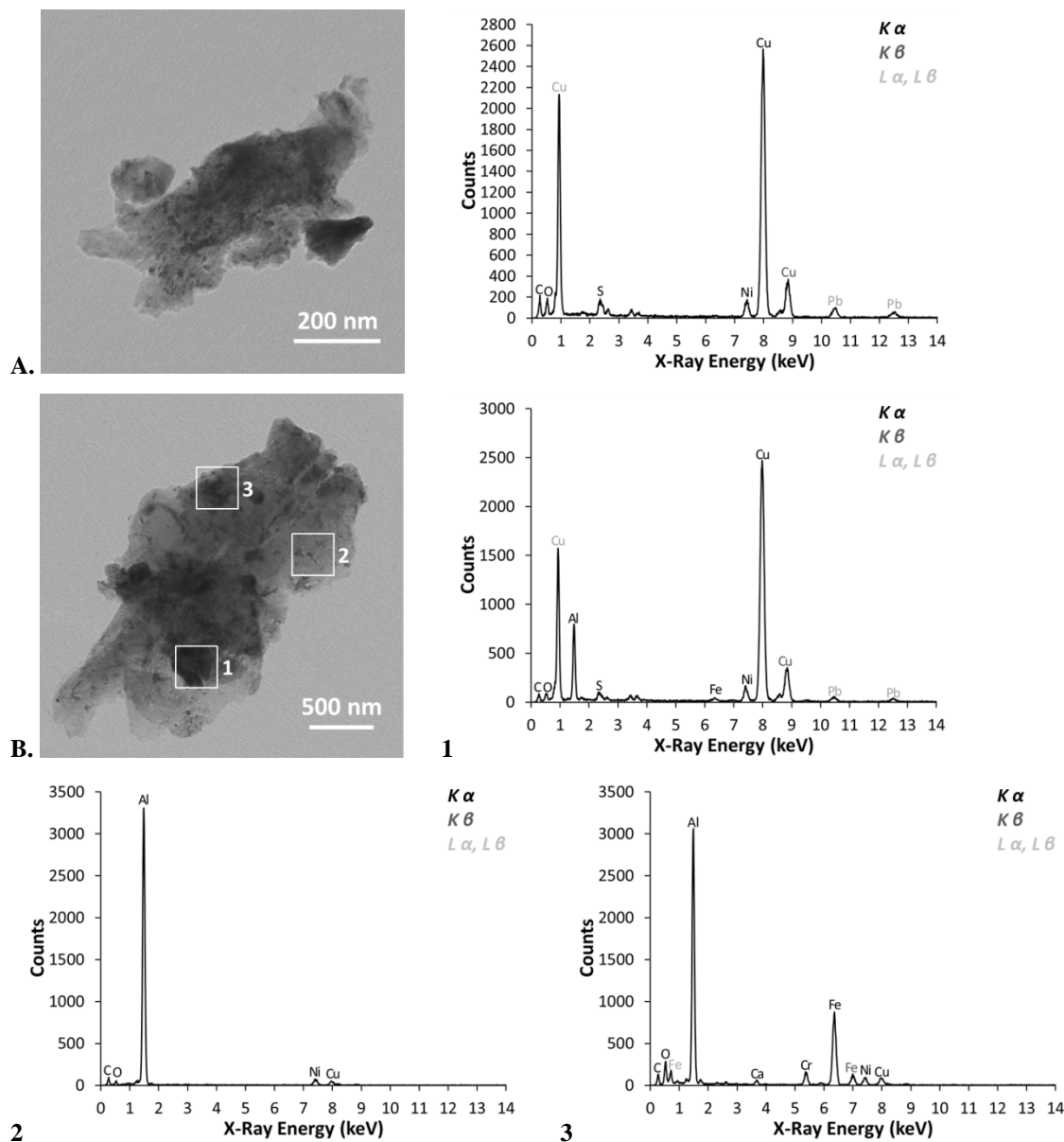


Figure 12. Morphology and composition of PM emitted during M9 firing. Elements identified include carbon (C), oxygen (O), aluminum (Al), sulfur (S), calcium (Ca), iron (Fe), copper (Cu), and lead (Pb).

Key elements found in particles emitted during M4 firing included silicon, sulfur, potassium, copper, zinc, and bismuth (Figure 13). Sodium was found in two out of the three samples. By focusing EDS analysis on the different portions of the particles emitted during M4 firing, there is evidence that the dense spherical nanoparticle is composed primarily of bismuth, while copper is found in the region containing smaller sub-10 nm particles (Figure 13C).

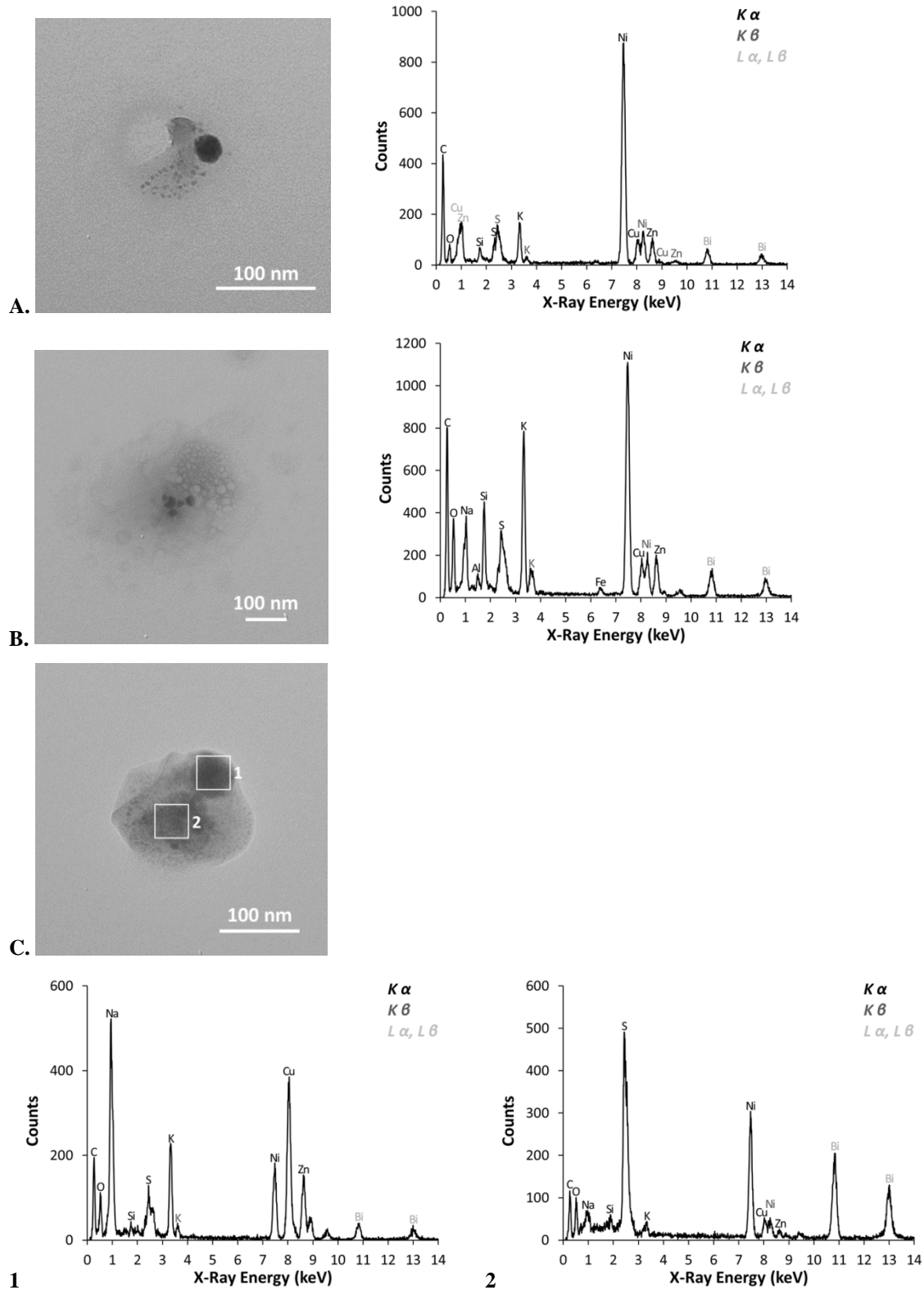


Figure 13. Morphology and composition of PM emitted during M4 firing. Elements identified include carbon (C), oxygen (O), sodium (Na), aluminum (Al), silicon (Si), sulfur (S), potassium (K), copper (Cu), zinc (Zn), and bismuth (Bi).

5.2.4 Surface Dust. During firing, a yellow dust accumulated on the floor of the range about 10 feet downrange from the firing line (Figure 14A). We characterized this dust for composition and morphology (Figure 14B-C). The dust was 100-600 μm in diameter. There were smaller particles closer to 1 μm in diameter on the surface of the large dust particles (Figure 14C). The dust contained <1% metals, and the primary metal found was copper.

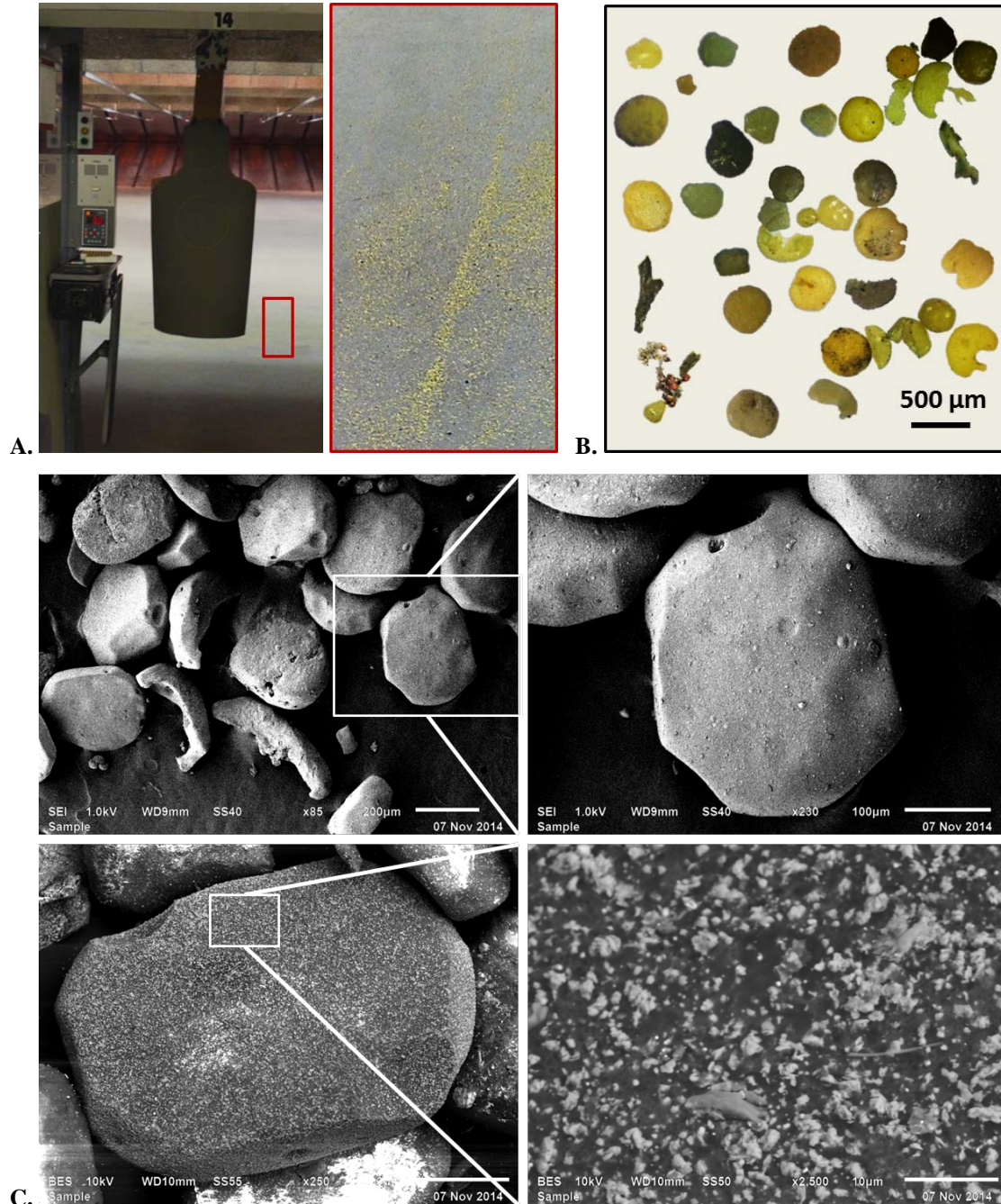


Figure 14. Surface dust accumulated on the floor of the range during firing, about 10 feet downrange from the firing line. A: Picture of the dust. B: Light micrograph of the dust particles. C: Electron micrographs of the dust particles.

6.0 DISCUSSION

AF small arms firing ranges have been experiencing ongoing exposure issues since the introduction of LFF ammunition about 15 years ago. The common theme is that instructors report symptoms of respiratory irritation, but exposure assessments do not find exposures to exceed OELs. Our primary objective was to evaluate ventilation and exposure assessment methods used in AF firing ranges and identify key gaps. We used both standard and state-of-the-art technologies to assess ventilation, monitor the accumulation of byproducts in the breathing zone of instructors, and characterize properties of firing byproducts.

First, we assessed the ventilation conditions. We took velocity measurements at nine points in each of the firing stalls, according to ventilation assessment guidance [18]. Velocity averages were within 20% of the ideal 75-fpm standard. Further, velocity averages were relatively consistent over the course of several days. Based on this information, the range may pass a regular inspection. However, when we plotted velocity averages for individual stalls, it became evident that the flow is highly variable within and among stalls (Figure 3). The standard also requires that airflow is laminar, i.e., moves evenly downrange from the firing line. The variable flow indicates that the laminar condition does not hold at the firing range investigated. Smoke tests confirmed our conclusion and identified points of stagnant, turbulent, and backwards flow (Figure 4).

The results of the ventilation assessments support the conclusion that the flow was not laminar in the closed firing range under investigation. It is important to note that this thorough assessment took over an hour of focused efforts to complete on each day. Our results highlight that an incomplete approach may provide the illusion that range ventilation conditions are acceptable. The majority of the time required to complete a ventilation assessment was consumed by velocity measurements. The smoke test took only 5-10 minutes to complete and provided similar information as velocity measurements. The main drawback is that the results are qualitative and may be difficult to document. These findings indicate that new approaches are required for evaluating and documenting the condition of firing range ventilation systems.

An additional feature of the ventilation system is that it should maintain a slight negative pressure in the range [18]. This is important to prevent firing byproducts from infiltrating the building enclosing the firing range. Negative pressure is achieved by pulling air from the range near the bullet trap at a slightly higher rate than pushing air into the range. A combination of measurements using a barometric pressure sensor and smoke tests indicated that the range was at positive pressure on all of the days tested (Table 3). Firing byproducts not removed by the ventilation system may infiltrate the building. At the firing range investigated, doors to offices and classrooms are located in the same corridor as the doors to the firing range. This is unacceptable, as individuals not working on the range may be unknowingly exposed to firing byproducts.

The comprehensive ventilation assessment conducted in this study suggests that the closed firing range under investigation should not have been operating on the days tested. Regardless, it is often the case that an OEL must be exceeded for resources to be allocated toward maintaining the ventilation system in a facility. Based on current knowledge, the primary inhalation exposure concern during firing of LFF ammunition is copper dust. However, past exposure assessments in a broad selection of ranges firing LFF ammunition have not often found copper OELs to be exceeded. One explanation is that the firing byproducts are dominated by PM in the ultrafine size range, which do not contribute to the mass-based measurement. Therefore,

we measured both copper mass and ultrafine particle counts in the breathing zone of instructors. It is important to note that analysis for copper in samples collected during firing exercises can take anywhere from a one to several weeks, while the ultrafine particle counts can be collected in RT.

Copper mass and particle counts were measured in the breathing zone of range instructors during two M9 and two M4 training exercises. Particle counts exhibited sharp peaks, which corresponded to firing events (Figure 5). The maximum peak in particle counts was about 14% higher during M4 compared to M9 training exercises, and the cumulative number of ultrafine particles for the duration of the exercise was twice as high during M4 compared to M9 training exercises (Table 4). Copper was detected more often in samples collected during M4 exercises, but never exceeded 1% of the copper dust OEL (Table 4). The values well below the copper dust OEL are consistent with previous exposure assessments in AF ranges firing LFF ammunition [1-3,21,22]. The direct correlation between ultrafine particle counts and copper mass in samples collected during M4 exercises supports the fact that ultrafine particle counts may be a great RT indicator of exposure.

Background PM concentration varied across different days and over the course of a single day (Table 5, Figure 6). However, the values were 1.4-2.6% of the maximum peak height, so we do not suspect that this will affect the conclusions. There were two distinct morphologies in background samples, including a carbonaceous soot particle and a porous particle composed of potassium, silica, phosphorus, sulfur, copper, and zinc (Figures 8 and 9). Carbonaceous soot could be drawn into the range from outside air contaminated with combustion byproducts. The presence of copper and zinc in background particles indicates that a portion of firing byproducts is sustained in the range well beyond firing training exercises.

Area sampling was completed for comprehensive analysis of firing byproducts beyond what was characterized in the breathing zone. The size distribution characterization of PM did not elucidate a consistent correlation between median particle size and particle count peaks during the M9 exercise, but there was a pronounced dip in median particle size correlated with particle count peaks during the M4 exercises (Figure 10). During M4 exercises, the median particle size reduced to about 20 nm, which is consistent with literature where PM byproducts were characterized during small arms firing of LFF ammunition by the Swedish military [26]. The median particle size in the breathing zone of the instructor may be even smaller than that found in the area samples due to the difference in the distance from the actual firing events.

TEM-EDS analysis revealed that PM generated by both the M9 and M4 are complex composites. The high concentration of ultrafine particles in close proximity after a firing event leads to a high probability that nucleated particles and vapors interact with each other. There were distinct differences in the morphology of PM generated during firing of the M9 pistol compared to the M4 rifle (Figures 11-13). The exact mechanism is not well understood, as the composition of the ammunition for each weapon is identical. Differences include the size of the rounds and length of the barrels. The longer barrel length of the M4 leads to a greater amount of friction against the projectile, which leads to higher temperatures. Therefore, we speculate that the greater amount of friction and higher temperatures could be correlated with the smaller PM sizes.

During observation of training exercises, a yellow dust accumulated on the range floor (Figure 14). We discovered that this dust is removed from the range floor every couple of weeks using a broom. Characterization of this dust is close to 100 μm in size, but smaller particles

closer to 1 μm were packed on the surface of the dust. A service contractor with appropriate expertise should be hired to clean this dust using a HEPA vacuum or wet mop.

7.0 CONCLUSION

Based on the findings of this research, the most important recommendation for mitigating instructor exposure to firing byproducts is for immediate characterization of AF firing range ventilation systems using both velocity measurements and smoke tests. Firing exercises should not ensue if individual velocity measurements are inconsistent at different heights and across stalls or smoke tests indicate instances of backwards, stagnant, or turbulent flow. The recommendation to improve engineering controls has already been made in previous reports investigating instructor exposure to byproducts from firing LFF ammunition in AF firing ranges [1,2]. However, there is little evidence that this recommendation has been transitioned to action.

The fact that little action has been taken to repair AF firing range ventilation systems may result from the fact that exposure assessments do not often find firing byproducts to exceed OELs, specifically copper dust. The results here showed that PM emitted during firing LFF ammunition is primarily in the ultrafine size range. Therefore, averaged mass-based measurement of copper dust is not likely a great indicator for exposure. Further, the PM emitted during firing was composed of a complex mixture, which suggests that the OEL developed for copper dust is not relevant to this specific case. The findings here suggest that the use of wearable ultrafine particle counters for RT exposure assessment is a promising avenue to consider. However, more research is required to determine safe levels of exposure to ultrafine particles. Additionally, since we routinely observe ultrafine particle concentrations above the upper measurement limit of the water-based particle counters used in this study (200,000 $\#/\text{cm}^3$), additional work is required to develop dilutors, increase the upper limit of the particle counters, or explore alternative ultrafine particle measurement technologies.

8.0 REFERENCES

1. Methner MM, Gibbons J, Niemeier T. Evaluation of instructor and range officer exposure to emissions from copper-based frangible ammunition at a military firing range. Cincinnati (OH): National Institute for Occupational Safety and Health; 2013. Health Hazard Evaluation Report 2012-0091-3187. [Accessed 1 Jun 2014]. Available from <https://www.cdc.gov/niosh/hhe/reports/pdfs/2012-0091-3187.pdf>.
2. Moran MP, Ott DK. Lead free frangible ammunition exposure at United States Air Force small arms firing ranges, 2005 – 2007. Brooks City-Base (TX): Air Force Institute for Operational Health; 2008. Report No. IOH-RS-BR-TR-2008-0002.
3. Cameron EJ. Comparative analysis of airborne chemical exposure to Air Force small arms range instructors [Thesis]. Wright-Patterson AFB, (OH): Air Force Institute of Technology; 2006. AFIT/GES/ENV/06M-01.
4. Brook RD, Rajagopalan S, Pope CA 3rd, Brook JR, Bhatnagar A, et al. Particulate matter air pollution and cardiovascular disease: an update to the scientific statement from the American Heart Association. *Circulation*. 2010; 121(21):2331-2378.
5. Donaldson K, Li XY, MacNee W. Ultrafine (nanometre) particle mediated lung injury. *J Aerosol Sci*. 1998; 29(5-6):553-560.

6. Donaldson K, Brown D, Clouter A, Duffin R, MacNee W, et al. The pulmonary toxicology of ultrafine particles. *J Aerosol Med.* 2002; 15(2):213-220.
7. Donaldson K, Borm PJ, Oberdörster G, Pinkerton KE, Stone V, Tran CL. Concordance between *in vitro* and *in vivo* dosimetry in the proinflammatory effects of low-toxicity low-solubility particles: the key role of the proximal alveolar region. *Inhal Toxicol.* 2008; 20(1):53-62.
8. Duffin R, Tran L, Brown D, Stone V, Donaldson K. Proinflammogenic effects of low-toxicity and metal nanoparticles *in vivo* and *in vitro*: highlighting the role of particle surface area and surface reactivity. *Inhal Toxicol.* 2007; 19(10):849-856.
9. Höhr D, Steinfartz Y, Schins RP, Knaapen AM, Martra G, et al. The surface area rather than the surface coating determines the acute inflammatory response after instillation of fine and ultrafine TiO₂ in the rat. *Int J Hyg Environ Health.* 2002; 205(3):239-244.
10. Li N, Sioutas C, Cho A, Schmitz D, Misra C, et al. Ultrafine particulate pollutants induce oxidative stress and mitochondrial damage. *Environ Health Perspect.* 2003; 111(4):455-460.
11. Oberdörster G. Pulmonary effects of inhaled ultrafine particles. *Int Arch Occup Environ Health.* 2001; 74(1):1-8.
12. Oberdörster G, Oberdörster E, Oberdörster J. Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles. *Environ Health Perspect.* 2005; 113(7):823-839.
13. Sager TM, Kommineni C, Castranova V. Pulmonary response to intratracheal instillation of ultrafine versus fine titanium dioxide: role of particle surface area. *Part Fibre Toxicol.* 2008; 5:17.
14. Sager TM, Castranova V. Surface area of particle administered versus mass in determining the pulmonary toxicity of ultrafine and fine carbon black: comparison to ultrafine titanium dioxide. *Part Fibre Toxicol.* 2009; 6:15.
15. Elder A, Gelein R, Silva V, Feikert T, Opanashuk L, et al. Translocation of inhaled ultrafine manganese oxide particles to the central nervous system. *Environ Health Perspect.* 2006; 114(8):1172-1178.
16. Nemmar A, Hoet PH, Vanquickenborne B, Dinsdale D, Thomeer M, et al. Passage of inhaled particles into blood circulation in humans. *Circulation.* 2002; 105(4):411-414.
17. Oberdörster G, Sharp Z, Atudorei V, Elder A, Gelein R, et al. Translocation of inhaled ultrafine particles to the brain. *Inhal Toxicol.* 2004; 16(6-7):437-445.
18. Navy Environmental Health Center. Indoor firing ranges industrial hygiene technical guide. Portsmouth (VA): Navy Environmental Health Center; 2002. Technical Manual NEHC-TM6290.99-10 Rev. 1. [Accessed 1 Feb 2018]. Available from <http://www.med.navy.mil/sites/nmcphc/Documents/policy-and-instruction/ih-indoor-firing-ranges-technical-guide.pdf>.
19. National Institute for Occupational Safety and Health. NIOSH pocket guide to chemical hazards. Cincinnati (OH): National Institute for Occupational Safety and Health; 2007. [Accessed 29 Feb 2016]. Available from <http://www.cdc.gov/niosh/npg/>.
20. Karta Technologies, Inc. Lead-free small arms ammunition study. Brooks AFB (TX): Air Force Institute for Environment, Safety, and Occupational Health Risk Analysis; 1999. Report No. IERA-RS-BR-SR-2000-0001. [Accessed 22 Jul 2014]. Available from <http://www.dtic.mil/dtic/tr/fulltext/u2/a379771.pdf>.
21. Culp KW. Acoustical evaluation and air sampling in a semi-enclosed firing range during use of frangible lead-free bullets, Randolph AFB, TX. Brooks AFB (TX): Air Force Institute for Environment, Safety, and Occupational Health Risk Analysis; 2001. Consultative Letter IERA-RS-BR-CL-2001-0013. [Available to those with access].

22. Culp KW. Hazardous materials exposure assessment and acoustical evaluation in an enclosed firing range during use of frangible lead-free bullets, building 980, Columbus AFB MS. Brooks AFB (TX): Air Force Institute for Environment, Safety, and Occupational Health Risk Analysis; 2001. Consultative Letter IERA-RS-BR-CL-2001-0017. [Available to those with access].
23. Air Force Civil Engineer Support Agency. Engineering technical letter (ETL) 11-18: small arms range design and construction. Washington (DC): Department of the Air Force; 2011. [Accessed 1 Jun 2014]. Available from https://www.wbdg.org/FFC/AF/AFETL/etl_11_18.pdf.
24. Deslattes RD, Kessler EG, Indelicato P, de Billy L, Lindroth, E, Anton J. X-ray transition energies: new approach to a comprehensive evaluation. *Rev Mod Phys.* 2003; 75(1):35-99.
25. Wise ME, Biskos G, Martin ST, Russell LM, Buseck PR. Phase transitions of single salt particles studied using a transmission electron microscope with an environmental cell. *Aerosol Sci Technol.* 2014; 39(9):849-856.
26. Wingfors H, Svensson K, Hägglund L, Hedenstierna S, Magnusson R. Emission factors for gases and particle-bound substances produced by firing lead-free small-caliber ammunition. *J Occup Environ Hyg.* 2014; 11(5):282-291.

LIST OF ABBREVIATIONS AND ACRONYMS

#/cm³	particle number per cubic meter
ACGIH	American Conference of Governmental Industrial Hygienists
AF	Air Force
AFB	Air Force Base
EDS	energy-dispersive X-ray spectroscopy
ESP	electrostatic precipitator
fpm	feet per minute
ICP-MS	inductively coupled plasma mass spectrometry
LFF	lead free frangible
NIOSH	National Institute for Occupational Safety and Health
OEL	occupational exposure limit
OSHA	Occupational Safety and Health Administration
PEL	permissible exposure limit
PM	particulate matter
PUFP	portable ultrafine particle counter
REL	recommended exposure limit
RT	real time
SMPS	scanning mobility particle sizer
TEM	transmission electron microscopy
TLV	threshold limit value
TWA	time-weighted average