Characterization of Air Emissions from Open Burning and Open Detonation of Gun Propellants and Ammunition

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Abstract

Emissions from open burning (OB) and open detonation (OD) of military ordnance and static fires (SF) of rocket motors were sampled in fall, 2013 at the Dundurn Depot (Saskatchewan, Canada). Emission sampling was conducted with an aerostat-lofted instrument package termed the "Flyer" that was maneuvered into the downwind plumes. Forty-nine OB events, 94 OD events, and 16 SF on four propellants types (Triple base, 105 M1, 155 M4A2 white bag, and 155 M6 red bag), two smokes (HC grenade and red phosphorus), five explosive types (Trigran, C4, ANFO, ANFO+HC grenade, and ANFO+Flare), and two rocket motors types (CVR-7 and MK 58) resulted in emission factors for particulate matter (PM), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), volatile organic compounds (VOCs), chlorine species (HCl, chloride, chlorate, perchlorate), polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDDs/PCDFs) and PM-based metals. These data provide Canada and the United States with additional air emissions data to support health risk assessments and permitting for safe treatment of military ordnance by OB/OD/SF. In addition, the data will be used to conduct air dispersion modelling assessing the impact of treatment of various ordnance on the air quality, to support mandatory reporting requirements of the Canadian Environmental Protection Act (CEPA), the National Pollutant Release Inventory (NPRI), and to update the Canadian Ammunition Chemical Database.

Results showed that complete combustion (absence of CO) occurred during OB of triple base, 105 M1, and 155 M4A2 white bag propellant while 155 M6 red bag showed detectable levels of CO in the plume. The 155 M6 red bag plume showed only a slightly higher benzene emissions, 4.2 mg/kg net explosive quantity (NEQ) (4.2E-06 lb/lb net explosive weight, NEW), compared to 2.1, 0.93, and 0.029 mg/kg NEQ (2.1E-06, 9.3E-07, 2.9E-08 lb/lb NEW) for 155 M4A2 white bag, 105 M1, and triple base, respectively. The $PM_{2.5}$ emission factors were in the same range for the four propellant types 3.1-11 g/kg NEQ (3.1E-03 to 1.1E-02 lb/lb NEW) and continuous and simultaneous measurements of PM_1, $PM_{2.5}$, PM_{10}, and Total PM indicated that the predominant particle size was PM_1 or less. The Pb air emissions were less than 8% and 5% of the original 105 M1 and 155 M6 red bag composition, respectively.

The PM emissions from HC grenade and red phosphorus were approximately 200 and 100 times higher than from OB of propellant. The Zn, Cl, and K metal emissions from HC indicated that half of the metals in the grenade ended up in the plume. Burning of red phosphorus showed complete combustion while HC smoke showed poor combustion resulting detectable chlorinated VOC compounds such as vinyl chloride at 8.1 mg/kg NEQ (8.1E-06 lb/lb NEW). The highest VOC emission factor for HC was benzene with a level of 589 mg/kg NEQ (5.9E-04 lb/lb NEW) while red phosphorus levels were 39 mg/kg NEQ (3.9E-05 lb/lb NEW) which is approximately 10-1000 times higher than from OB of propellant. The HC grenades showed very high emissions of PCDD/PCDF (2,700 ng TEQ/kg NEQ) as well as chlorinated VOCs. Detonating HC with ANFO reduced the PCDD/PCDF emissions (1,400 ng TEQ/kg NEQ) by approximately 50%. Detonating HC with ANFO did not reduce the chlorinated VOCs emissions although it reduced the more common VOCs from combustion such as benzene, 1,3-butadiene, and styrene. However, benzene, 1,3-butadiene, and styrene emission factors were all higher than when only detonating ANFO. The first known emissions data for Cl species from open detonations show that 18% of the Cl is emitted as chlorides, with 7% as HCl. HC was disposed of by both stand-alone burning and detonating with ANFO.

Detonation with ANFO resulted in calculation of emission factors for Si, K, and Ca above levels possible from the ordnance composition, most certainly reflecting soil entrainment of these elements. However, Cl and Zn emissions were reduced when detonating HC with ANFO instead of burning.

Results from OD of explosives ranged from poor to complete combustion, as reflected by CO levels and modified combustion efficiencies ($\Delta CO_2/(\Delta CO + \Delta CO_2)$) of 0.706-0.993. Of the hydrocarbons, propene, acetonitrile, and benzene were the most predominant VOCs across all OD types. Detonating ANFO together with the HC smoke grenade or Flare resulted in 3-20 higher levels of benzene than from ANFO, Trigran, and C4. Time resolved PM data by size showed very similar PM_1, $PM_{2.5}$, and PM_4 mass traces within each ordnance type. PM_{10} and Total PM exhibit a slight time lag from the smaller particles, approximately 1-2 s, suggesting that the larger particles may be entrained soil that follows behind the initial ordnance-derived fine PM.

Static firing of CRV-7 and MK 58 rockets resulted in good combustion as indicated by the few detectable levels of VOCs as well as high modified combustion efficiencies. The $PM_{2.5}$ emissions from the CRV-7 rockets were twice those from MK 58 rockets at 34 g/kg NEQ (3.4E-02 lb/lb NEW) and 16 g/kg NEQ (1.6E-02 lb/lb NEW), respectively. HCl was found in the CRV-7 and MK 58 plumes at levels of 86 and 30 g/kg NEQ (8.6E-02 and 3.0E-02 lb/lb NEW), respectively. No perchlorate was detected but low levels of chlorate were found in the CRV-7 and MK 58 plumes. Of the total chloride amount in the original CRV-7 and MK 58 ordnance 34% and 14% was found in their respective plumes. Static firing of CRV-7 and MK 58 rockets resulted in detectable levels of PCDD/PCDF at 1.5 and 3.3 ng TEQ/kg NEQ respectively, similar to biomass combustion values.

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List of Acronyms

AD	Absolute difference
ANFO	Ammonium Nitrate Fuel Oil
ATV	All-terrain vehicle
CFAD	Canadian Forces Ammunition Depot
Cl	Chloride
CO	Carbon monoxide
CO_2	Carbon dioxide
DGLEPM	Director General Land Equipment Program Management
DND	Canadian Department of National Defence
DoD	U.S. Department of Defense
DP	Destruction point
DRDC-Valcartier	Defence Research and Development Canada -Valcartier
EF	Emission factor
EPA	U.S. Environmental Protection Agency
FID	Flame ionization detector
GC/LRMS	Gas chromatograph-low resolution mass spectrometer
GPS	Global positioning system
HRGC/HRMS	High resolution gas chromatography/high resolution mass spectrometry
ISSI Inc.	Integrated Systems Solution, Inc.
JMC	U.S Army Joint Munitions Command
LOD	Limit of detection
MIPR	Military Interdepartmental Purchase Requests
MOP	Method operating procedures
NA	Not analyzed
ND	Not detected
NDIR	Non-dispersive infrared
NEQ	Net Explosive Quantity

NEW	Net Explosive Weight
OB	Open burning
OD	Open detonation
ORD	Office of Research and Development, U.S. EPA
PCDD/PCDF	Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans
PCF	Photometric calibration factor
PM	Particulate matter
PM2.5	Particulate matter equal to or less than 2.5 µm
PM10	Particulate matter equal to or less than 10 µm
PUF	Polyurethane foam plug
PVC	Polyvinyl Chloride
QAPP	Quality Assurance Project Plan
RCRA	Resource Conservation and Recovery Act
SERDP	Strategic Environmental Research and Development Program
SF	Static Fire
STDV	Standard deviation
SVOC	Semi-Volatile Organic Compound
TEF	Toxic equivalent factor
TEQ	Toxic equivalent
TPM	Total Particulate Matter
UDRI	University of Dayton Research Institute
VOC	Volatile Organic Compound
WHO	World Health Organization

1. Introduction

1.1 Brief

The U.S. Department of Defense (DoD) has undertaken three emission sampling campaigns of open burning and open detonation (OB/OD) of military ordnance since 2010. The purpose of these sampling efforts has been to quantify emissions for Resource Conservation and Recovery Act (RCRA), Clean Air Act permits, and emission reporting, as well as to provide a representative data set for use in Human Health and Environmental Risk Assessments. The U.S Army Joint Munitions Command (JMC), Logistics Integration Directorate, Engineering and Demil Technology Office (formerly the U. S. Army Defense Ammunition Center, DAC), has been working in collaboration with their counterparts in the Canadian Department of National Defence (DND) specifically the Director General Land Equipment Program Management (DGLEPM) and the Defence Research and Development Canada -Valcartier (DRDC-Valartier) to assess environmental effects of Open Burning / Open Detonation (OB/OD) during ordinance treatment throughout these three sampling campaigns.

The U.S. EPA/ORD has undertaken these three campaigns of emission sampling during OB/OD operations with JMC at the Tooele Army Depot in Utah to provide emission factor data to the DoD Strategic Environmental Research and Development Program (SERDP). In this work, the U.S. EPA aerial sampling equipment named «The Flyer» has been used to capture gas and particles emitted from these treatment activities, an effort observed by members of the DND. The unique expertise and specialized equipment of the joint U.S. Army JMC/U.S. EPA team led to a cooperative effort with DND to study the air emissions from OB/OD of Canadian ordnance formulations in a demilitarization context. For the last few years, staff from DND DGLEPM and the DRDC-VALCARTIER-Val have been very active in assessing environmental and health impacts of OD/OB of ammunition and explosives. In order to better assess the impact OB/OD has on the environment, more specifically on the air quality, and to significantly expand the DND databases needed to address environmental compliance and potential health risks, a field sampling campaign was undertaken at the CFAD - Dundurn Depot test site in Saskatchewan, Canada. The air emission data collected will expand the U.S. DoD air emission factor database for OB/OD and Static Fire demilitarization processes and provide additional environmental data to support permitting and reporting requirements of these processes.

This report presents results of sampling conducted by JMC, DND, and EPA to support Canadian and United States military needs for air emission characterization from Open Burning, Open Detonation, and Static Fire of military ordnance at the CFAD - Dundurn Depot test site in Saskatchewan, Canada in fall, 2013. This work encompassed a three week sampling program from September 23th to October 11th, 2013 at Canadian Forces Ammunition Depot (CFAD) Dundurn, Saskatchewan, the Canadian national demolition site (Appendix C, Figures C-1 and C-2). At this site, OB/OD/Static Fire (SF) activities were performed during which time the emissions were sampled. The data derived from this work consists of emission factors that relate a particular analyte to the initial ordnance amount. For carbonaceous ordnance, this is typically

accomplished with the carbon balance method. These emission factor data can provide input for dispersion modeling, exposure concentrations, pollutant inventories, and regulatory installation and activity permits.

This work involved open burning of different types of propellants, static firing of rocket motors, and detonation of various munitions in order to study the emissions from these military activities in a demilitarization context. Aerial sampling equipment was used to capture gas and particles emitted from these test scenarios. This equipment had been used in three prior test campaigns with JMC and at JMC facilities in the U.S.

DND conducted the ammunition and explosive detonations, and burns, while JMC/EPA sampled the emissions with DND's support. The unique expertise and equipment of these teams enabled this effort to effectively and safely study the air emissions from open burning and open detonation (OB/OD) of Canadian ordnance formulations in a demilitarization context.

This research effort was comprised of participants from U.S. EPA/ORD, University of Dayton Research Institute (UDRI), ARCADIS US, Inc., U.S. Army JMC, ISSI, Inc., and the DND Canada. ORD, UDRI, and ISSI, Inc. were funded separately through individual Military Interdepartmental Purchase Requests (MIPRs). DND was the host site provided support in-kind, including test ordnance and site operations as well as fund for the major part of the project.

1.2 Objectives

The objectives for this effort are:

- Sample emissions for determination of emission factors
- Further develop/verify sampling methods for application to OB/OD

2 Materials and Methods

2.1 Test Materials

A total of eleven different ordnance types as well as two combinations of three ordnance types were sampled for air emissions during open detonation, open burning, and static firing.

2.1.1 Open Detonation

Three different test materials and two mixtures of test materials were investigated for emissions from open detonation (Table 2-1, Figure 2-1).

Table 2-1. Open detonation test materials and donor charge.

Ordnance	Amount* NEQ per Detonation	Relevant Composition	Carbon Fraction	Metal Fraction	Donor		
					Type	Amount	Composition
Trigran	36 kg	TNT, Aluminum	0.2962	Al – 0.20	C4 C3 –electric blasting cap Detonation cord	0.568 kg 1 cap, 4 or 8 m	RDX, DEHA
ANFO	50 kg	Ammonium Nitrate Fuel Oil	0.05		C4 C3 –electric blasting cap Detonation cord	0.284 kg 1 cap, 6 m	RDX, DEHA
C4	17 kg	RDX, DEHA	0.2034		C3 –electric blasting cap Detonation cord	1 cap, 4 m	
ANFO + Trip Flare	53 kg	Ammonium Nitrate Fuel Oil Sodium Nitrate, Magnesium, Polyvinyl acetate binder	0.0487	Mg – 0.026	C4 C3 – electric blasting cap Detonation cord	0.568 kg 1 cap, 6 m	RDX, DEHA
ANFO + HC grenade	56 kg	Ammonium Nitrate Fuel Oil, Potassium nitrate, Hexachloroethane, Zinc Oxide, Calcium silicide	0.0487	Cl – 0.041 Si – 0.012 Zn – 0.032 K – 0.0019 Ca – 0.0040	C4 C3 –electric blasting cap Detonation cord or No. 12 – non electric blasting cap Blast time Fuze M700	0.568 kg 1 cap, 6 m 1 cap, 0.76 m	RDX, DEHA

* Only ordnance, no donor. NEQ = Net Explosive Quantity. DEHA – Bis(2-ethylhexyl) adipate (plasticizer). RDX – Research Department Formula X (1,3,5-Trinitroperhydro-1,3,5-triazine). TNT – trinitrotoluene.

Figure 2-1. ANFO.

2.1.2 Open Burning

Four different types of propellants and two smoke grenades were investigated for air emissions, Table 2-2, Figure 2-2, and Figure 2-3.

Table 2-2. Open burning test materials and donor charge.

Ordnance	Amount NEQ per Burn	Relevant Composition*	Carbon Fraction	Metal Fraction	Donor Type
M1 – 105 mm	199.7 kg	Nitrocellulose, DNT, dibutyl pthahalate, diphenylamine potassium sulfate, lead	0.3236	Pb – 0.0162	Electric squib and match
M6 – Red bag, 155 mm	199.1 kg or 208.6 kg	Nitrocellulose, DNT, dibutyl phthalate, lead, potassium sulphate	0.3155	Pb – 0.0088	Electric squib and match
M1 – White bag, 155 mm	194.6 kg or 206.4 kg	Nitrocellulose, DNT, dibutyl phthalate diphenylamine, potassium sulfate	0.3236		Electric squib and match
Triple base – 76 mm Cougar	192 kg or 200 kg	Nitrocellulose, Nitroglycerin, Nitroguanidine, ethyl centralite, cryolite	0.1961	Al – 0.00039 Na – 0.00033	Electric squib and match
HC (C11) – Smoke grenade	0.3 kg	Potassium nitrate, Hexachloroethane, Zinc Oxide, Calcium silicide	0.038	Si – 0.112 Cl – 0.386 Zn – 0.301 K – 0.0174 Ca – 0.0375	None
Red phosphorus – Marine Marker	14.8 kg or 29.6 kg	Red phosphorus, Linseed oil, zinc oxide, magnesium, manganese dioxide	0.0385	Mg – 0.070 Mn – 0.215 Zn – 0.241 P – 0.510	C3 –electric blasting cap Detonation cord

* DNT – dinitrotoluene.

Figure 2-2. Propellant tested: A) M1, 105 mm, B) M1, 155 mm white bag, C) M6, 155 mm red bag, and D) Triple base.

Figure 2-3. HC smoke grenade.

2.1.3 Static Fires

Air emissions from static fires of 144 CRV-7 and 10 MK 58 rocket motors were collected (see Figure 2-4).

Table 2-3. Static Fire test materials and donor charge.

Ordnance	Amount NEQ per Static Fire	Relevant Composition	Carbon Fraction	Metal Fraction	Donor Type

CRV-7	49.56 kg	Ammonium perchlorate, hydroxyl-terminated polybutadiene, Fe_2O_3, $ZrSiO_4$	0.0874	Fe – 0.0035 Zr – 0.0025 Si – 0.0012 Cl – 0.263	None Electric tied into ignition boxes
MK 58	132.9 kg (n=1) or 398.7 kg (n=3)	Ammonium perchlorate, carboxyl-terminated polybutadiene, Aluminum	0.116	Cl – 0.241 Al – 0.060	Squib and matches

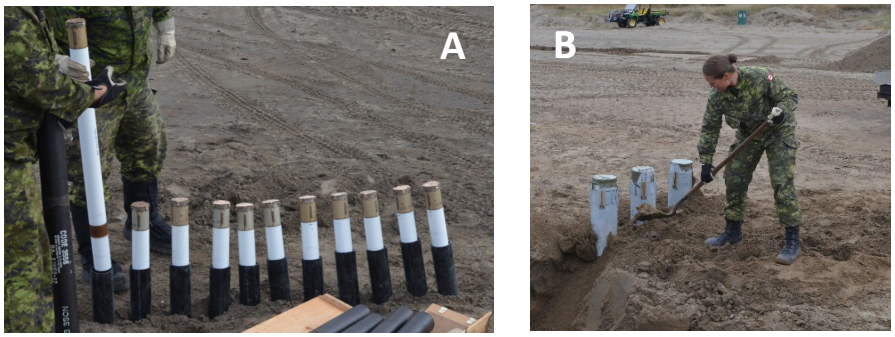


Figure 2-4. A) CRV-7 rocket motors and B) MK 58 rocket motors.

2.2 Test Site Description

The test site for the campaign was the Canadian Forces Ammunition Depot (CFAD) - Dundurn, located in Saskatchewan, Canada (Appendix C). CFAD - Dundurn is a remote site, approximately 55 km southeast of Saskatoon, a town of about 250,000 people. CFAD - Dundurn has been the site of numerous military efforts, including a bombing range and a bivouac area during World War II for soldiers prior to being sent overseas. Today CFAD Dundurn is used as an ammunition depot and training range.

The test area for the OB/OD/SF activities consists of a destruction area, bunker, and storage sheds as depicted in Figure 2-5. The rectangular test field is approximately 170 m x 90 m in size and consists of an earthen field in which considerable small debris objects from previous treatment efforts are present.

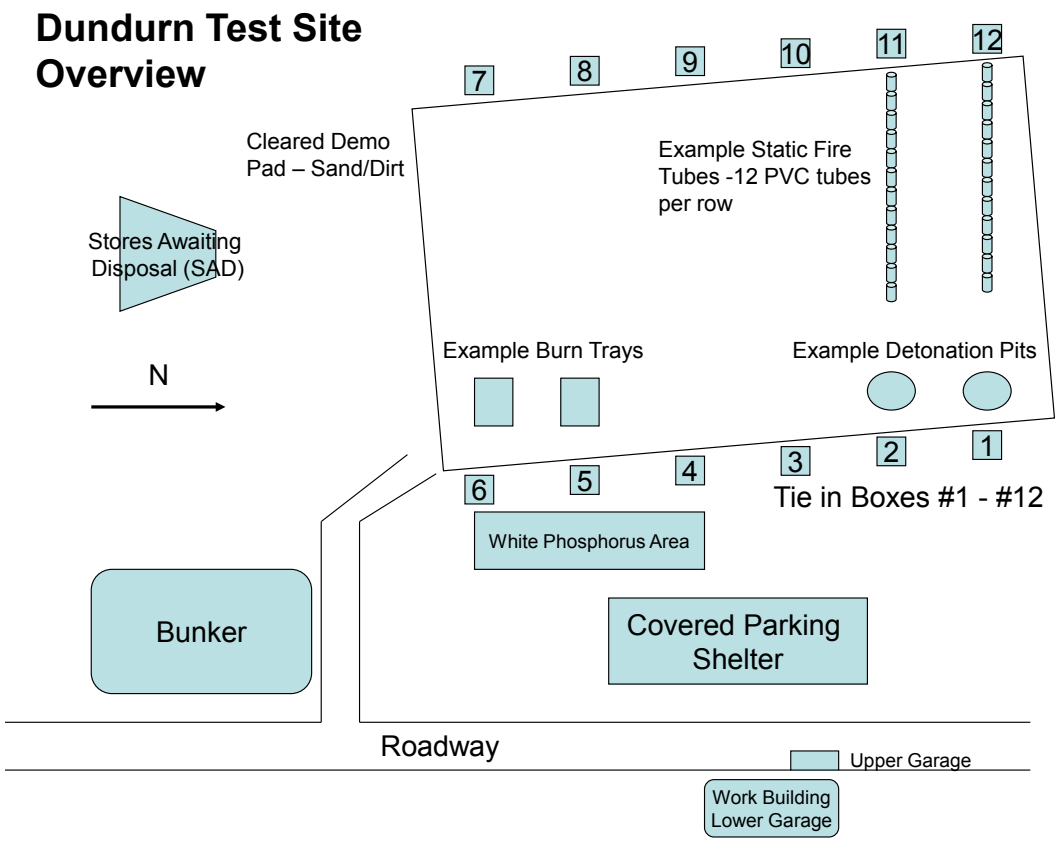


Figure 2-5. CFAD - Dundurn test site overview.

2.2.1 Detonations

For the detonations, earthen pits were dug with a front end loader, such that each pit was approximately 3m × 10m × 1.8 m deep. The detonation area consisted of twelve detonation pits in a rectangular configuration as shown in Appendix F, Figures F1-F3, F9, and F12-F18. Each pit had a maximum of 100 kg NEQ (220 lbs NEQ) per detonation. The ordnance was placed in the 1.8 m deep pit and covered with 1.8 m of available soil from the site, Figure 2-6. This soil cover was described as high grade sand. The soil contained numerous shrapnel components as the site is an active demilitarization site. Up to 14 detonations were accomplished each day.

Figure 2-6. Covered ordnance (ANFO).

2.2.2 Open Burns

The four propellants listed in Table 2-1 were placed in four burn trays separated by 25 m in a square pattern, Figure 2-2. The specific burn tray layouts for each of the propellants are shown in Appendix F Figures F-4 to F-6 and F-10 to F-11. The burn trays nominally process a maximum of 200 kg net explosive quantity (NEQ) per burn tray; 3-4 series of four burn trays was accomplished each day.

The HC grenades were tested outside the “Work building” (Figure 2-5 and Appendix F Figure F-21). The sampling equipment was placed on wooden boxes for this ground-based smoke sampling, Figure 2-7. The HC grenade was place on a shovel and maneuvered to position the downwind plume towards the Flyer by a soldier equipped wearing a respirator.

The red phosphorus burns were located inside the “White phosphorus area” (Figure 2-5). The Flyer was pre-positioned outside and downwind of the White phosphorus area on a couple of wooden pallets, Figure 2-7. The DP layout and approximate location of the ground based flyer are shown in Appendix F Figures F-19 and F-20.

Figure 2-7. Ground based sampling for HC smoke grenade (left), and Red phosphorus (right)

2.2.3 Static Firing

Static firing of CRV-7 rocket motors was accomplished by lowering the rocket motors face down into polyvinyl chloride pipes embedded vertically in the ground. Four sets of twelve rocket motors were fired (48), comprising a series, with a total of three series per day. The twelve firing tubes located together comprised a single destruction point (DP), and all twelve rockets in a single DP were fired simultaneously, Figure 2-4. The DP layout and approximate location of the aerostat projected onto the ground are shown in Appendix F Figure F-7.

The MK 58 rocket motors (three sets of three rocket motors and one single rocket motor, totaling 10) were placed vertically into a hole in the ground with the nose pointing down and the tail sticking out of the ground approximately 0.15-0.20 m. The DP layout and approximate location of the aerostat projected onto the ground are shown in Appendix F Figure F-8.

2.3 Testing Procedures

2.3.1 Methods Introduction

The aerostat-lofted instrument platform (the "Flyer", see Figure 2-8) was developed for sample collection of plumes from open area sources such as prescribed burning. The Flyer is a remotely controlled sampling system, including an on-board computer, control software, and wireless transmitters which allow sampling to be controlled from the ground. Sampling is also controlled using "triggers" and software to operate multiple on/off valves. Interchangeable sampling instruments allow for continuous CO_2, CO, temperature, global positioning, and PM measurements as well as batch sampling of volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), PM_{10} and $PM_{2.5}$, Cl species, and PM-borne metals. The on-board computer and wireless data transfer also allows the ground crew to monitor CO_2 concentration, battery life, and pressure drop across a filter in real time. Monitoring these data remotely allows maximization of flight time and optimization of sample collection by avoiding problems such as premature battery change-outs or battery depletion and signaling the need for changing plugged filters. All sensor data and flow rates are logged to the on-board computer. In addition, the Flyer has a global positioning system (GPS) on board to pinpoint position and altitude. Specific information on the instruments, their operation, calibration, and performance are covered in the associated Quality Assurance Project Plans (QAPPs) (**Appendix A**).

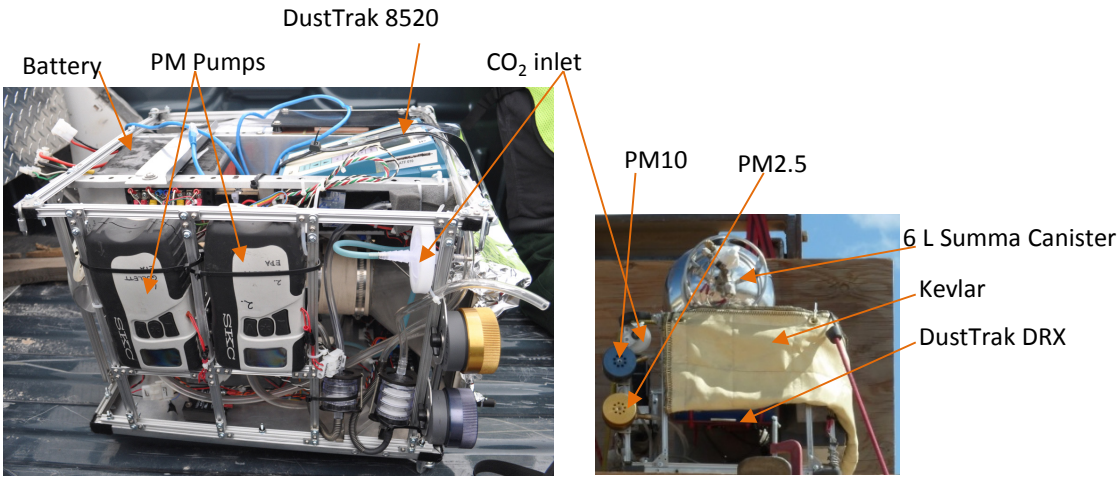


Figure 2-8. Flyer sampling instrument

To quantify the designated target analytes, the Flyer was comprised of the instruments indicated in Table 2-4. Samples from multiple detonations or burns within several minutes were often consolidated into a single sample in an effort to exceed the method detection limits for trace target compounds. Since the target compounds are present at different concentrations, different measurements will exceed their method detection limit with different amounts of sampling. At least one sample per ordnance type (typically comprised of three series of burns or detonations per day) was collected, as indicated in Attachment B: Test Schedule. The makeup of each series, including the number of DPs and the number of items/load per DP, is also indicated. The most limiting analyte on the Cl-containing ordnance was anticipated to be polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF), where composite samples were made to limit the possibility of congener non-detects. Determination of the number of samples per composite is based on the operators' experience relating to the amount of carbon sampled for similar events that achieved acceptable detection levels. This requirement was assessed in the field by monitoring the cumulative carbon collection. Previous work suggests that 10 - 20 g of carbon collected as CO_2 are considered minimally acceptable for detection of PCDD/PCDF. For VOCs, the SUMMA canisters were programmed to open at high CO_2 concentrations (ca. 450-600 ppm, determined by field observation of CO_2 levels and ordnance type), conditions indicative of the sampler being in the concentrated part of the plume and therefore likely to see elevated VOC concentrations.

Table 2-4. Target analytes and sampling instrumentation.

Measurement	Device/Method	Targets
CO_2	Li-COR 820 NDIR	CO_2
$PM_{2.5}$	SKC filter impactor, Teflon filter	PM mass and metals via XRF
PM_{10}	SKC filter impactor, Teflon filter	PM mass and metals via XRF
Total PM	Teflon filter	PM mass and metals via XRF
VOC	SUMMA canister	CO, CO_2, CH_4, VOCs
SVOC	PUF/filter	PCDD/PCDF
Chlorides	SKC filter cassette, sodium carbonate treated cellulose filter	HCl
PM	DustTrak 8520	$PM_{2.5}$
PM	DustTrak DRX	PM_1, $PM_{2.5}$, PM_4, PM_{10}, Total PM
Temperature	Thermistor	Ambient temperature
Location/altitude	Global position system (GPS)	

The total amount of collected samples for each target compound and ordnance type is presented in Table 2-5 below. Further delineation of the number of samples per relay is covered in Appendix D

Table 2-5. Collected samples for each target analyte and ordnance type.

Ordnance Type	Summa Canisters VOCs	$PM_{2.5}$	PM_{10}	TPM	DustTrak 8520	DustTrak DRX	Metals XRF	HCl	Perchlorate / Chlorate	PCDD / PCDF*
OD										
Trigran	4	3	6	2	0	1	11	0	0	0
ANFO	4	3	5	2	0	1	10	0	0	0
C4	2	1	3	0	0	1	4	0	0	0
ANFO+HC	1	1	1	1	0	0	3	1	0	1
ANFO+Flare	1	1	1	1	0	0	3	0	0	0
OB										
105, M1	5	2	2	2	0	1	6	0	0	0
155, M6 red bag	1	2	2	2	1	1	6	0	0	0
155 M4A2, White bag	3	1	1	1	0	1	3	0	0	0
Triple base	3	1	1	1	0	1	3	0	0	0
HC	3	3	3	3	0	0	9	3	0	1
Red phosphorus	3	2	2	2	0	0	6	0	0	0
Static Fire										
CRV-7	1	1	1	1	1	0	3	1	1	1
M58	1	1	1	1	1	0	3	1	1	1
Background	2	1	1	1	1	0	3	1	1	1
Total	**34**	**23**	**30**	**20**	**4**	**7**	**73**	**7**	**3**	**5**

*These are composite samples consisting of one day's worth of tests on each of the ordnance types indicated. TPM = Total PM.

2.3.2 Trial Observations

Prior to commencement of the test matrix and actual emission sampling, trial burns and detonations were conducted to familiarize the samplers and observers with testing procedures, plume behavior, and rock and shrapnel behavior. Trial tests were conducted to observe the ordnance behavior before sampling commenced. OD trials included three ordnance types and OB trials included four propellants. These observations allowed pre-positioning of the aerostat sampler to maximize sample collection while minimizing the risk of shrapnel or heat damage to the aerostat and Flyer.

2.3.3 Aerostat-Based Emission Sampling

The aerial sampling method uses two all-terrain vehicles (ATVs), each with a remotely-controlled electric winch for 305 m tethers, to anchor and maneuver a helium-filled aerostat (Figure 2-9)

under which is attached the Flyer. A Kingfisher (K16N, Aerial Products Inc., USA) 4.9 × 3.9 m-diameter helium aerostat lofted the 21 kg Flyer. Flyer operating/sampling procedures were as described in Aurell et al. [1, 2] and Kim et al. [3]. In short, the aerostat and Flyer were positioned downwind of the detonation/burn sites at an altitude expected to intersect with the plume's path. The two ATVs were positioned to allow maximum flexibility in maneuvering the aerostat/Flyer across the plume paths from the multiple detonation sites/burn pans. Transmissions from the bunker (Figure 2-10) to the radio-controlled winches adjusted the lateral positioning and height of the aerostat between and during detonations/burns in an effort to maximize the likelihood of plume intersection. The distance from the bunker to the Flyer was about 250 m – 350 m, depending on the location of the aerostat. After initiating detonations and burns, the Flyer was repositioned for optimal intersection of the visible plume by controlling the electric tether winches. These adjustments were aided by real time images from two cameras, one from atop the bunker and the other placed in an orthogonal position in the field.

Figure 2-9. Aerostat with the Flyer instrument sampling package.

Figure 2-10. Personnel and control bunker with top-mounted camera (left). View of orthogonally-located transmitting camera in the field (right).

2.3.4 Ground-Based Emission Sampling

Ground-based sampling was conducted for smoke canisters and during periods of high winds. By design, smoke canister emissions stayed on the ground and were sampled by the stationary Flyer (See Figure 2-7). Handling the aerostat during periods of high winds (>29-32 mph) is impractical. In addition, high winds tend to bend the plume down to the ground where they are more easily captured by ground-based instruments. The Flyer was mounted atop a platform support in the bed of an ATV or atop a wooden platform.

Due to high winds the first two days (September 24 and 26) detonations of Trigran were sampled from the ground. The Flyer was placed on one ATV and positioned downwind of the DPs. Emissions from HC and red phosphorus were also sampled from the ground-based Flyer as their smoke plumes remained close to the ground.

2.3.5 Background Emission Samples

Background samples were taken during non-test days. The Flyer was placed atop a platform to sample for an extended period of time. Background emission sampling was conducted during two separate rainy days which precluded field activities. The Flyer sampler was located in the parking area outside the work building, covered by wood pallets as shown in Appendix F, Figures F-22 and F-23. PM and metals were both sampled for 5:51 h:min, HCl for 3:25 h:min, PCDD/PCDF for 9:50 h:min; and two VOCs for SUMMA canister openings of 5 sec and 52 sec.

2.4 Emission Sampling and Analytical Methods

2.4.1 CO_2

CO_2 was continuously measured using a non-dispersive infrared (NDIR) instrument (LI-COR 820 model, LI-COR Biosciences, USA). This unit is configured with a 14 cm optical bench, giving it an analytical range of 0-20,000 ppm with an accuracy specification of less than 3% of reading. The LI-820 calibration range was set to 0- 4,500 ppm, the LICOR was calibrated in accordance with U.S. EPA Method 3A [4] with 3 point zero & calibration drift test. A particulate filter precedes the optical lens. The LI-COR 820 CO_2 concentration was recorded every second on the onboard computer using the FlyerDAQ program, a LabView generated data acquisition and control program. The LI-820 was calibrated for CO_2 according to U.S. EPA Method 3A [4] at the EPA laboratory prior to shipping the equipment to Canada. The post-field CO_2 drift of the LI-820 was checked at the EPA Laboratory after the equipment returned from Canada. In-field calibration checks were not possible due to receipt of the wrong regulators. Nonetheless, the post drift tests showed that the system drift for each of the calibration concentrations were below the

less than ±5% acceptance criteria as stated by the U.S. EPA Method 3A [4]. The calibration and drift data are shown in Appendix G.

2.4.2 PM Samplers

$PM_{2.5}$ and PM_{10} were sampled with SKC impactors using 47 mm tared Teflon filters with a pore size of 2.0 µm via a Leland Legacy sample pump (SKC Inc., USA) with a constant airflow of 10 L/min. PM was measured gravimetrically following the procedures described in 40 CFR Part 50 [5]. Particles larger than 10 µm in the PM_{10} impactor (or larger than 2.5 µm in the $PM_{2.5}$ impactor) were collected on an oiled 37 mm impaction disc. The particulate matter collected on the Teflon filters were used to determine metal concentrations through analysis by energy dispersive x-ray fluorescence spectrometry (ED-XRF) according to U.S. EPA Compendium Method IO-3.3 [6]. The Leland Legacy Sample pump was calibrated with a Gilibrator Air Flow Calibration System (Sensidyne LP, USA).

Three methods were used to collect $PM_{2.5}$ and PM_{10} in order to discern the best way to accurately sample particle-size-specific weight gain and avoid spurious results observed in previous sampling campaigns in Tooele, Utah in 2012. These results showed the unexpected presence of large particles in the fine PM sampler, believed to be due to the presence of high concentrations of soil particles ejected during detonations. The SKC impactors were designed as ambient samplers for low particle loadings. During use with OD events, the impactors were sometimes prone to capture large particles due to the sand and soil ejected by the blast or entrained by the plume. These large particles, not anticipated during ambient operation, transferred to the filter and increased the apparent weight gain, affecting the PM determination. The three trial methods consisted of the SKC impactor with 1) a rain cover attached, 2) a field-fabricated pre-impaction plate, and 3) no cover. Each method was paired in tandem with another method for comparison purposes.

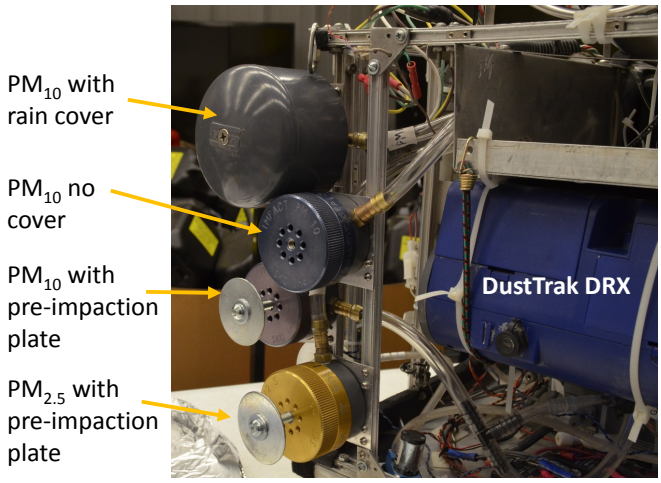


Figure 2-11. Three different PM sampling methods.

The TSI DustTrak DRX Model 8533 or DustTrak 8520 were used to measure time-resolved particle size distributions, as the payload limitations on the Flyer allowed. The DustTrak DRX measures light scattering by aerosols as they intercept a laser diode and has the capability of simultaneous real time measurement (every second) of PM_1, $PM_{2.5}$, Respirable (PM_4), PM_{10} and Total PM (up to 15 µm). The aerosol concentration range for the DustTrak DRX is 0.001-150 mg/m^3 with a resolution of ±0.1% of reading. The flow accuracy is ±5% of internal flow controlled. Concurrently, an enclosed, 37-mm pre-weighed filter cassette provides a simultaneous Total PM gravimetric sample for calibration. The total flow rate is 3 L/min where 1/3 of the flow rate is used for the continuous measurements and 2/3 is used for the gravimetric sample. The enclosed gravimetric sample is used to conduct a custom photometric calibration factor (PCF) for the Total PM. The DustTrak DRX is factory calibrated to the respirable fraction (PM_4), with a PCF value of 1.00. A custom PCF are conducted as per manufacturer's recommendations for $PM_{2.5}$ and PM_{10} using the simultaneously sampled $PM_{2.5}$ and PM_{10} by filter impactor concentrations (averaged continuous $PM_{2.5}$ (or PM_{10}) concentration divided by $PM_{2.5}$ (or PM_{10}) by filter mass concentration). This factor is applied to scale the real time data. A zero calibration was performed before each day using a zero filter which comes with the DustTrak DRX. Similarly, a daily flow calibration was performed with a Gilibrator flowmeter, following procedures in Operation and Service Manual Model 8533/8534 (P/N 6001898, Revision F, January 2011). The DustTrak inlet was cleaned after each day with a cotton swab.

The DustTrak 8520 is also a light-scattering laser photometer which measures mass fraction of PM_1, $PM_{2.5}$, or PM_{10} (depending on the chosen impactor plate and nozzle size, for this project $PM_{2.5}$ impactor plate was used) every second. The measurement range for DustTrak 8520 is 0.001-100 mg/m^3. The zero stability is ±0.001 mg/m^3 over 24 hours. The DustTrak 8520 is factory calibrated to the respirable fraction, with a PCF value of 1.00. A custom PCF are conducted as per manufacturer's recommendations for $PM_{2.5}$ using the simultaneously sampled $PM_{2.5}$ by filter impactor concentrations (averaged continuous $PM_{2.5}$ concentration divided by $PM_{2.5}$ by filter

mass concentration). This factor is applied to scale the real time data. A zero calibration was performed before each day using a zero filter which comes with the DustTrak 8520 and a flow calibration was performed before each day with a flowmeter that comes with the DustTrak 8520, following procedures in Operation and Service Manual Model 8520 (1980198, Revision S, June 2010).

2.4.3 Metals on PM

The PM collected on the 47 mm Teflon filters was also used to determine concentrations of target metals. X-ray fluorescence (XRF) protocol IO-3.3 [6] was used to determine concentration of most elements between Na and Pb. The $PM_{2.5}$, PM_{10} and Total PM filters were analyzed for the ten target metals (Pb, Hf, Zr, Al, K, Fe, Mg, Mn, Na and Ca) as well as twenty-nine other metals by X-ray fluorescence (XRF) according to EPA Compendium Method IO-3.3 (USEPA 1999b). The standard reference materials used for the QA/QC had a recovery of 93.1-104.4%, which is within the accuracy of the method 90-100%.

2.4.4 VOCs

Volatile organic compounds were sampled via U.S. EPA Method TO-15 [7]. Sampling for VOCs was accomplished using laboratory-supplied 6 L SUMMA Canisters. Each SUMMA was equipped with a manual valve, metal filter (frit), pressure gauge, pressure transducer, and an electronic solenoid valve. The SUMMA canisters were analyzed by ALS Environmental (California, USA). The frit filter's pore size determines the SUMMA's sampling rate. Pre-sampling tests showed canister fill times of 179, 113, and 60 seconds for a 6 L SUMMA with a 0.5, 7, and 15 µm frit filter, respectively. This range of sampling durations is meant to sample multiple short, 10-20 sec peak concentration plumes to provide a composite sample. Shorter sampling periods risk representativeness and the longer sampling periods risk sample dilution and detectability.

The SUMMA valves were checked for leakage before sample collection by ensuring that the pressure gauge was not showing decreased pressure with time. The SUMMA was attached on the bottom of the Flyer and had its electronic solenoid valve controlled by the Flyer data acquisition (FlyerDAQ) program. The pressure transducer and electronic solenoid valve was connected to the Flyer and the manual valve was opened. The electronic solenoid valve sampling system is opened and closed based on CO_2 concentration set points using the FlyerDAQ program. When the LI-820 measures elevated levels of CO_2, the Flyer DAQ enables the solid state relay, opening the SUMMA's solenoid valve to start sampling at the chosen frit filter sampling rate. The pressure transducer provided information on the status of the SUMMA (i.e., empty, filling, or full) to the FlyerDAQ interface. The solenoid valve was closed and sampling was stopped when CO_2 readings returned to ambient levels. Following the end of sampling, the manual valve was closed, the SUMMA dismounted from the Flyer, the solenoid valve removed, and the canister was returned to its shipping container. SUMMA canisters were shipped to and from the field in boxes as per (ALS Environmental) instructions. SUMMA canisters were shipped overnight for morning delivery to the contract laboratory.

The VOCs were analyzed by CAS Laboratories (Simi Valley, CA) using U.S. EPA Method TO-15 [7] using full scan mode gas chromatograph-low resolution mass spectrometer (GC/LRMS). The SUMMA Canisters were also analyzed for CO_2, CO, and CH_4 by a GC/ flame ionization detector (FID) according to modified U.S. EPA Method 25C [8].

2.4.5 Chloride samples

Cl species were sampled using a cassette with an alkali-impregnated ($NaCO_3$), mixed cellulose ester (mCE) membrane filter in accordance with ISO 21438-2 Method [9] followed by a second mCE $NaCO_3$ coated filter. The first $NaCO_3$ coated mCE filter was preceded by an uncoated mCE filter for sampling of chloride, perchlorate, and chlorate. The Cl sample cassette is shown in Figure 2-12. HCl gas is expected to pass through the chloride, perchlorate, chlorate filter and be adsorbed onto the first filter coated with $NaCO_3$. The second $NaCO_3$ coated filter is used as a backup filter to sample any HCl that is not absorbed onto the first coated filter. These coated filters are available in a closed-face cassette from SKC (SKC Inc., USA). Any hydrochloric acid transiently collected on the initial filter is expected to rapidly evaporate and be collected along with the gaseous HCl [10]. This filter was analyzed for HCl by ion chromatography using U.S. EPA Method 300.0 [11]. The limit of detection for this method is 4 µg/filter (ALS, New York, USA).

Perchlorate was sampled using a modification of the method discussed in Lamm et al. [12]. In this method, perchlorate salts are captured as a solid on a cassette filter and analyzed by ion chromatography. Cassette filter samples were dissolved in a 10-mL aliquot of 30 mM sodium hydroxide prior to measurement of perchlorate concentration using U.S. EPA Method 6850 [13]. The detection limit for perchlorate is cited as 0.004 µg/filter by ALS New York (USA).

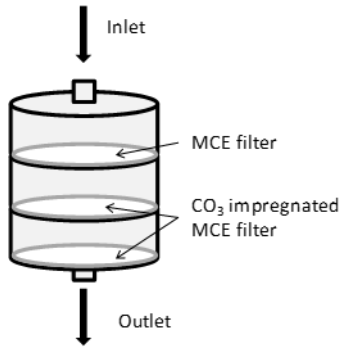


Figure 2-12. Sampling cassette cartridge for HCl, perchlorate, and chlorate.

2.4.6 PCDD/PCDF

SVOCs were sampled using a low voltage Windjammer brushless direct current blower (AMETEK Inc., USA). The blower was triggered by the CO_2 concentration set points (5 ppm above ambient background level) using the flyerDAQ program or started from the ground by the operator via wireless control (30 seconds prior to the plume hitting the sampler. The flow rate was measured

by a 0-622 Pa pressure differential transducer (Setra, Model 265, USA) across a Herschel Standard Venturi tube. The Venturi tube was specially designed (diameter labeled = 0.900 in) to meet the desired sampling rate (0.85 m^3/min) for the target compound. The Venturi tube was mounted on the outlet of the Windjammer blower. The voltage equivalent to this pressure differential was recorded on the onboard computer using the FlyerDAQ program, which was calibrated with a Roots meter (Model 5M, Dresser Measurement, USA) in the U.S. EPA metrology laboratory before sampling effort. A temperature thermistor was measuring the air temperature exiting the venturi.

PCDD/PCDF was sampled via modified U.S. EPA Method TO-9A [14] using a polyurethane foam plug (PUF) sorbent preceded by a quartz microfibre filter (20.3×25.4 cm) with a nominal sampling rate of 0.85 m^3/min (Windjammer). The PUF was cleaned before use by solvent extraction with dichloromethane and dried with flowing helium to minimize contamination of the media with the target analytes and remove unreacted monomer from the sorbent. The PUF sorbent was mounted in a glass cartridge (TISH Scientific, USA) and inserted in a cartridge holder mounted on the Windjammer blower. The quartz microfiber filter was mounted before the PUF sorbent cartridge. The Flyer had battery capacity for about one hour of PCDD/PCDF sampling. The samples was extracted and cleaned up according to U.S. EPA Method 23 [15] and analyzed using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Field blank was collected and analyzed. The PUF had the ends sealed with new aluminum foil and was refrigerated after collection and prior to extraction.

Analysis of tetra- through octa-CDDs/CDFs was performed according to modified U.S. EPA Method 23 [15]. Identification and quantification of the PCDD/PCDF congeners made use of a mixture of standards containing tetra- to octa-CDD/CDF native and 13C-labeled congeners designed as per modified U.S. EPA Method 23 [15]. The PCDD/PCDF calibration solutions were prepared in house and contained native PCDD/PCDF congeners at concentration from 0.25 to 40 ng/mL.

The 2005 World Health Organization (WHO) toxic equivalent factors (TEFs) [16] were used to determine the PCDD/PCDF toxic equivalent (TEQ) emission factors (see Chapter 2.5.2 for calculations). Not all TEF-weighted PCDD/PCDF congeners were detected in all samples. The congeners that were not detected (ND) were set to zero in the text although Appendix D, Tables D-9 to D-13 show the PCDD/PCDF values both at ND = 0 and ND = limit of detection (LOD).

2.5 Calculations

2.5.1 Converting from mass/mass of Carbon to mass/mass of Net Explosive Quantity

The emission factor for each species was calculated from the ratio of background-corrected pollutant concentrations to background-corrected carbon concentration as calculated from CO_2 measurements. Emissions factors were calculated using these concentrations and the fraction of carbon (C) in the ordnance, following the carbon balance method as in Ref. [17].

$$EF_i = f_c \times \frac{Analyte_{ij}}{C_j}$$ Eq.1

$$EF_i = \frac{f_c}{f_i} \times \frac{Analyte_{ij}}{C_j}$$ Eq.2

where:

EF_i = Emission Factor for target analyte i (g/g Net explosive quantity (NEQ) eq.1 or g Metal/g Metal in ordnance (eq. 2)).

f_c = mass fraction of carbon in the ordnance

f_i = mass fraction of analyte *i* in the ordnance

$Analyte_{ij}$ = background-corrected concentration (g $analyte_i/m^3$) of the target analyte i collected from the volume element j of the plume.

C_j = background-corrected concentration of carbon (g C/m^3) collected from volume element j of the plume (carbon calculated from CO_2 from CEM or for VOC CO_2, CO and CH_4 from the SUMMA canister)

The majority of the carbon emissions were *a priori* assumed to be emitted as carbon dioxide making carbon dioxide the only carbon-containing compound that is required to be measured at each measurement location. This assumption was based on the expected completeness of oxidation reactions for which the ordnance was designed. Limited testing of C4 detonations have shown that CO is less than 10% of the CO2 measured[18].

Field data were transferred from the data loggers to external hard drives via a laptop computer with a USB port. Electronic data and pictures were posted in the folder L:\Lab\NRML_Aurell\Canada September 2013 on the EPA network scientific drive upon return from the field or as they were generated or received.

2.5.2 PCDD/PCDF Toxic Equivalent Calculations

PCDDs and PCDFs include 75 and 135 congeners, respectively. Of these 210 congeners 17 are toxic and have been assigned toxic equivalency factor (TEF) values [16] (Table 2-6). The TEQ value is obtained by multiplying the concentration of a PCDD/PCDF congener by its TEF-value and summing the result for all 17 toxic congeners.

Table 2-6. The 2005 World Health Organization PCDD/PCDF Toxic Equivalent Factors for mammals/humans [16].

PCDDs	TEF	PCDFs	TEF
2,3,7,8 - TCDD	1	2,3,7,8 - TCDF	0.1
1,2,3,7,8 - PeCDD	1	1,2,3,7,8 - PeCDF	0.03
1,2,3,4,7,8 - HxCDD	0.1	2,3,4,7,8 - PeCDF	0.3
1,2,3,6,7,8 - HxCDD	0.1	1,2,3,4,7,8 - HxCDF	0.1
1,2,3,7,8,9 - HxCDD	0.1	1,2,3,6,7,8 - HxCDF	0.1
1,2,3,4,6,7,8 - HpCDD	0.01	1,2,3,7,8,9 - HxCDF	0.1
1,2,3,4,6,7,8,9 - OCDD	0.0003	2,3,4,6,7,8 - HxCDF	0.1
		1,2,3,4,6,7,8 - HpCDF	0.01
		1,2,3,4,7,8,9 - HpCDF	0.01
		1,2,3,4,6,7,8,9 - OCDF	0.0003

2.5.3 Modified Combustion Efficiency

The modified combustion efficiency (MCE) (Eq. 3) was calculated using the SUMMA Canister CO_2 and CO concentrations. The MCE is a measure of combustion behavior or how well the fuel is being burned where MCE=1.0 is complete combustion. The MCE can be categorized in MCE ≥ 0.95 indicating flaming conditions (good combustion) and MCE < 0.90 indicating smoldering conditions (poor combustion).

$$MCE = \frac{\Delta CO_2}{\Delta CO_2 + \Delta CO} \qquad \text{Eq. 3}$$

3 Results and Discussion

3.1 Detonations

Five ordnance types (Table 2-1) were detonated for emission sampling:

- Trigran
- C4
- Ammonium Nitrate Fuel Oil (ANFO)

- Trip Flare with ANFO
- Smoke Grenade HC (C11) with ANFO

3.1.1 PM

Six to sixteen filter-based PM measurements were made for each of Total PM, PM_{10}, and $PM_{2.5}$ on the open detonations. Emission factors for each PM sample collected are presented in Appendix D, Table D-3. Table 3-1 shows PM emission factors generally in the 100 to 2,000 g/kg NEQ range, the upper end clearly reflecting ejection and entrainment of the cover soil. A substantial fraction of the PM mass shows up in the $PM_{2.5}$ size. C4 and Trigran have larger emission factors than the ANFO (Figure 3-2). Due to the minimal number of trials and the limitation of only two PM samplers per flight, most of the samples were not repeated. Four PM_{10} samples were done in duplicate, resulting in three values of AD/2 about half of the average and one at less than 3% of the average.

Table 3-1 showed that the use of the rain cover during soil-covered OD resulted in significantly lower filter loadings of particles. While this method precluded the large, loose particles observed in previous testing in Tooele, Utah, Figure 3-1 shows that its impactor plate (in this example, PM_{10}) is almost devoid of any visible particles, suggesting that the cover created a low bias of the results (see Figure 3-3). This is borne out by the very low emission factors in Table 3-1 as compared to the “regular” and “plate” results.

Comparison of four pairs of the regular and plate methods of PM sampling shows mixed results. For one detonation each of Trigran and C4, there’s no significant distinction. In one ANFO detonation (regular and plate), $PM_{2.5}$ and PM_{10} emission factors are about 2-3 times higher with the regular impactor than with the plate impactor. It’s not clear if this distinction, which is for both $PM_{2.5}$ and PM_{10} from this single sampling event, is due to differences in the method or due to a whole-plume sampling bias (for example, separation of particles from detonation CO_2). More testing is necessary to discern any distinction.

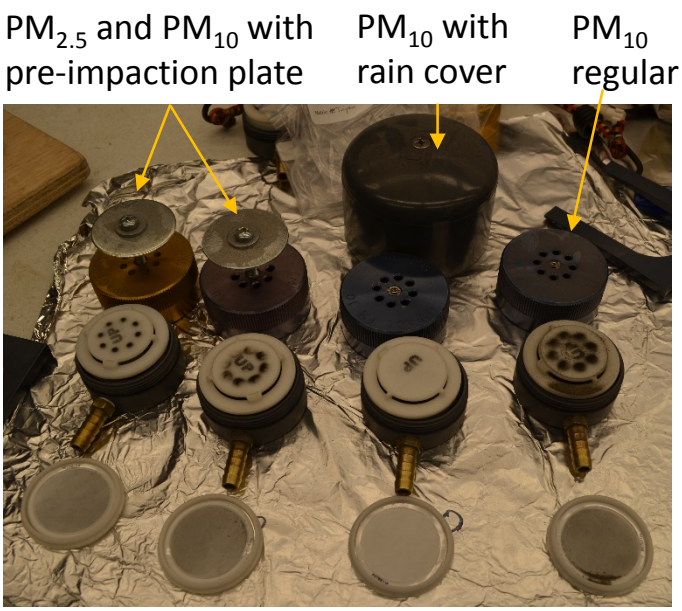


Figure 3-1. Three different PM sampling approaches.

Table 3-1. PM emission factors from open detonation, g/kg NEQ.*

	$PM_{2.5}$		PM_{10}			Total PM	
Ordnance Type	**No. of samples**	**Average**	**No. of samples**	**Average**	**AD/2**	**No. of samples**	**Average**
Trigran, ground$ rain cover	1	249	1	306		1	1598
Trigran, regular	NS		2	1150	582.2	1	878
Trigran, plate	1	705	1	1322		NS	
Trigran, rain cover	1	84	2	123	112	NS	
C4, regular	NS		1	2840		NS	
C4, plate	1	958	1	2598		NS	
C4, rain cover	NS		1	30		NS	
ANFO, regular	1	92	2	204	5.9	1	161
ANFO, plate	1	283	1	559		NS	
ANFO, rain cover	1	11	2	128	108	1	83
ANFO+HC	1	155	1	337		1	265
ANFO+Flare	1	150	1	155		1	396

* For lb/lb NEW divide the EF in g/kg NEQ with 1000. $ Ground sampling during a windy day.

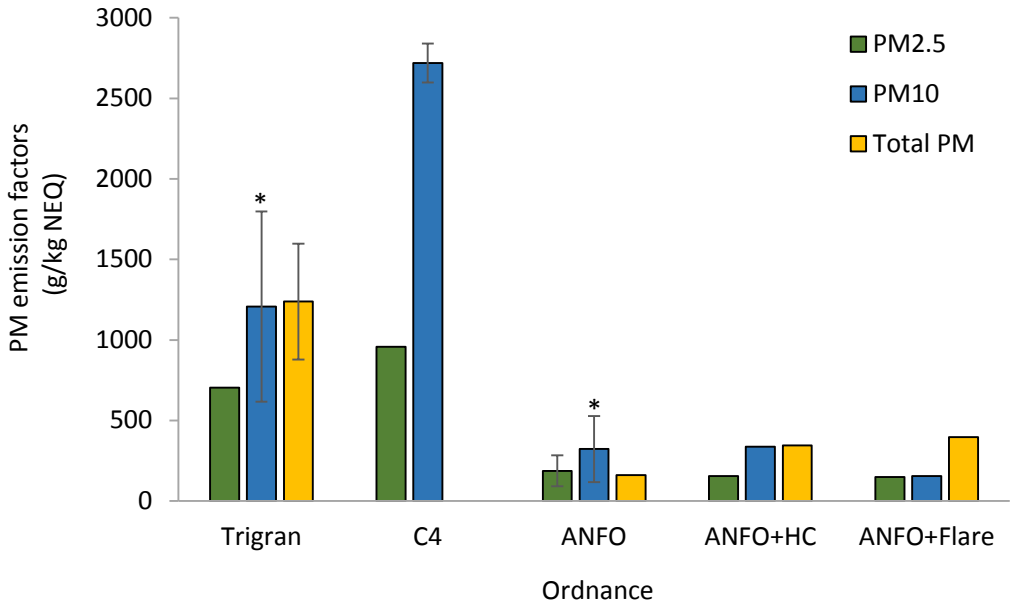


Figure 3-2. PM emission factors from open detonation including sampling approaches "regular" (no cover) and with "pre-impaction plate". Error bars denoted 1 STDV (*) or AD/2.

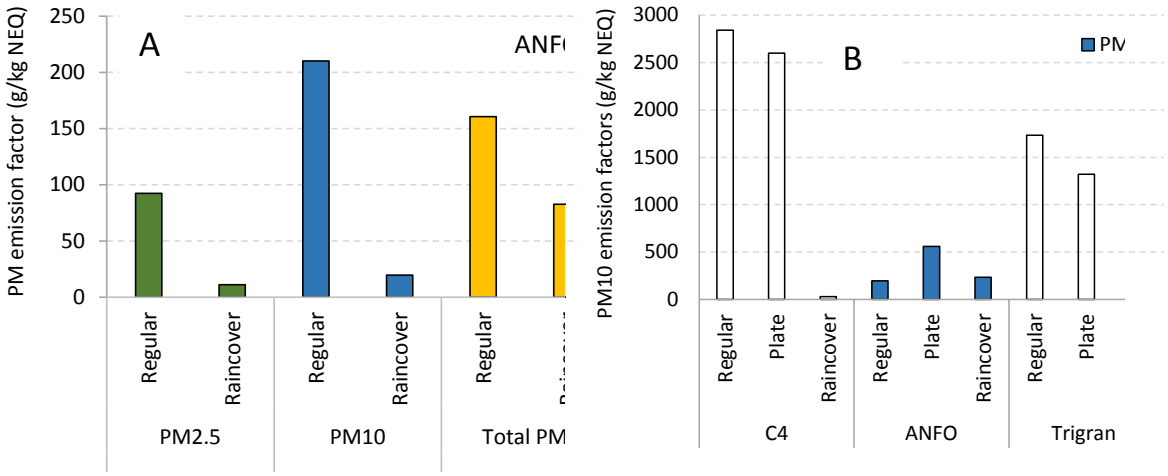


Figure 3-3. PM emission factors using different sampling approaches. A) $PM_{2.5}$, PM_{10}, and Total PM regular sampled simultaneously and $PM_{2.5}$, PM_{10}, and Total PM raincover sampled simultaneously. B) Regular, plate, and rain cover sampled simultaneously for each ordnance.

Time resolved PM data by size were recorded by the DustTrak for all ODs of the Trigran, C4, and ANFO. Figure 3-4 shows representative PM traces for these three ordnance types. The left hand column graphs show the $PM_{2.5}$ and CO_2 traces for a series of detonations. The graphs in the right hand column take one of those detonations and elongate the time scale to show the time-variant particle size distribution. The CO_2 traces correspond to the PM traces, indicating that

that the PM are clearly associated with the combustion products. The data show very similar PM_1, $PM_{2.5}$, and PM_4 mass traces within each ordnance type (Figure 3-5), with peak concentrations ranging from about 200 to 300 mg/m^3, during the 12-15 s period in which the plume passes the aerostat/Flyer. PM_{10} and Total PM exhibit a slight time lag from the smaller particles, approximately 1-2 s, suggesting that the larger particles are entrained soil that follows behind the initial ordnance-derived finer PM. Two of these three illustrated peaks also appear to be bimodal for all particle sizes, suggesting an initial particle wave from the ordnance detonation followed by a secondary wave from entrained particles.

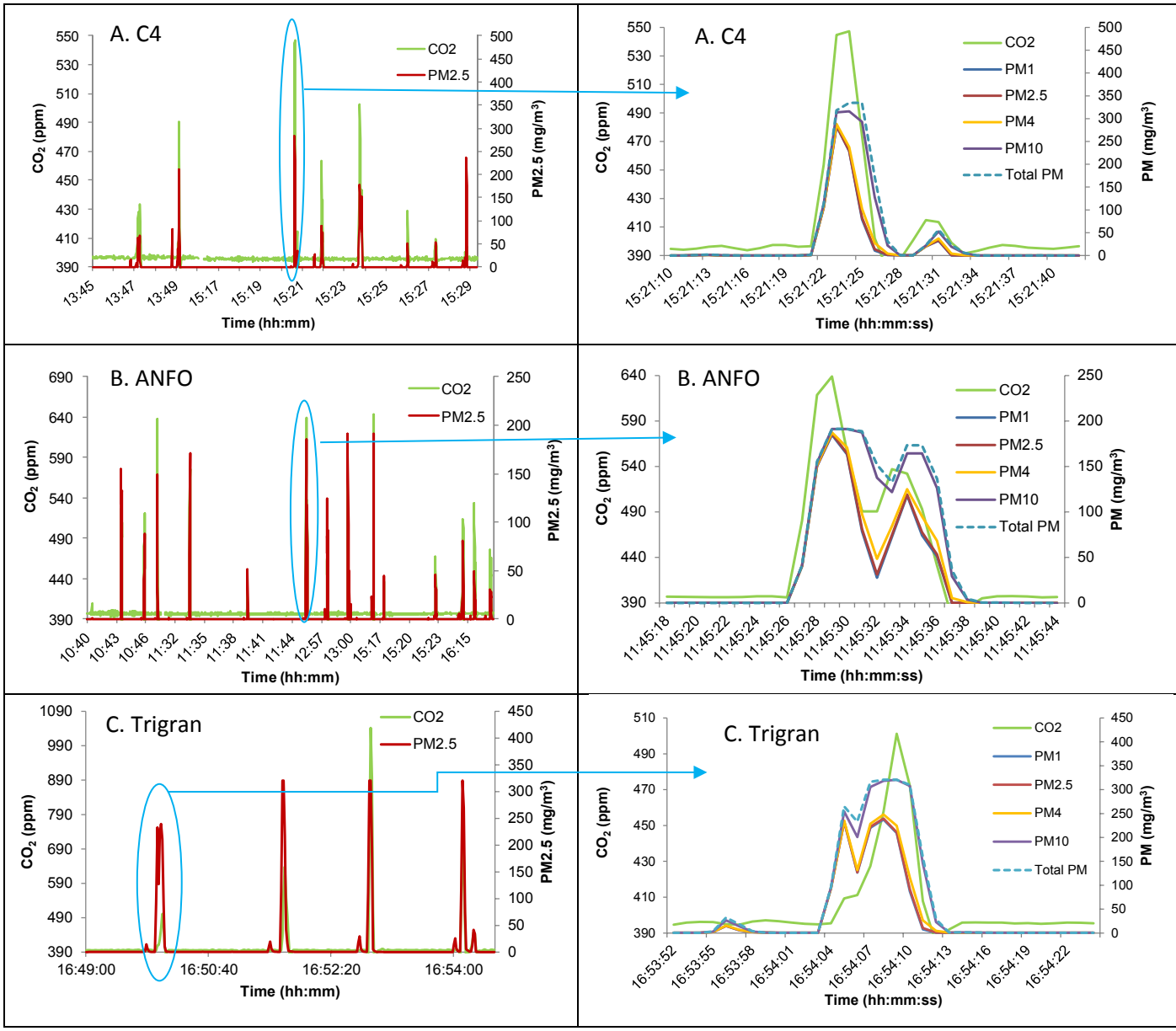


Figure 3-4. Continuous emission measurements of CO_2 and PM from representative events of open detonation of A) C4, B) ANFO, and C) Trigran.

Table 3-2. PM emission factors from DustTrak.

Ordnance	Amount of Detonations		PM_1 g/kg NEQ	$PM_{2.5}$ g/kg NEQ	PM_4 g/kg NEQ	PM_{10} g/kg NEQ	TPM g/kg NEQ
Trigran	17	Average	NS	170	NS	NS	NS
		STDV	NS	173	NS	NS	NS
C4	8	Average	1574	1596	1717	2516	2762
		STDV	2362	2370	2468	3229	3407
C4*	7	Average	741	760	846	1379	1563
		STDV	181	181	190	321	352
ANFO	19	Average	119	120	128	170	186
		STDV	101	102	102	118	129

* Without last detonation (very low CO_2 concentration). TPM = Total PM.

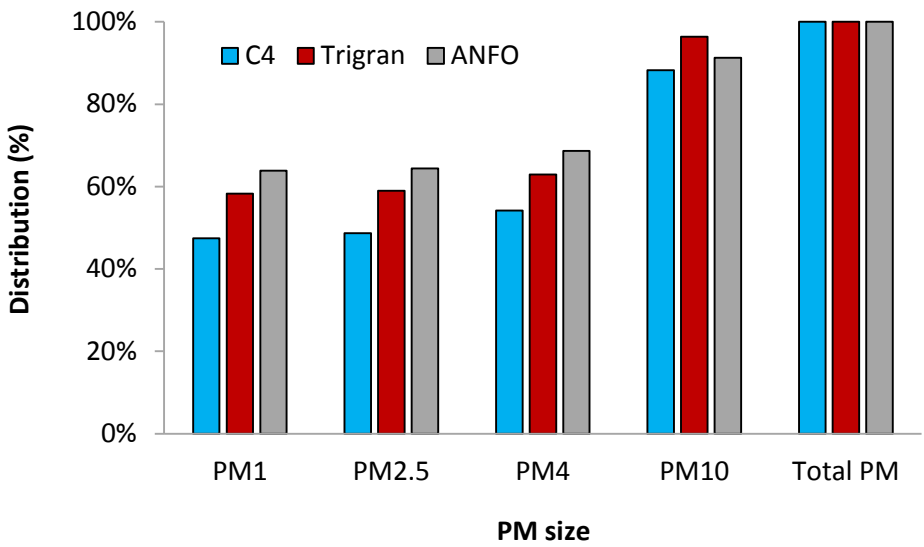


Figure 3-5. PM size distribution from open detonation of C4, Trigran, and ANFO. The PM_{10} and Total PM channels were saturated for Trigran.

3.1.2 Metals

Metals were analyzed from the Teflon filters on the PM impactors. The Si, K, and Ca emission factors for $PM_{2.5}$ (Table 3-3), PM_{10} (Table 3-4), and Total PM (Table 3-5) from HC+ANFO exceeded the possible amount from the ordnance itself suggesting that most of the metals originate from the soil. The Si, K, and Ca emission factors from HC+ANFO also exceeded the emission factors for open burning of HC (Table 3-12, Table 3-13, Table 3-14, and Figure 3-7)

emphasizing that most of these metals originated from the soil. Due to the limited number of samples, only a single repeat is available (Trigran, PM_{10}, regular configuration) indicating about a 50% absolute difference between the two values.

Table 3-3. Metal emission factors from $PM_{2.5}$ fraction. Blank data indicate the absence of the metal in the ordnance composition.

Ordnance Type	Configuration	Number of Samples	Mg g/kg Mg	Al g/kg Al	Si g/kg Si	Cl g/kg Cl	K g/kg K	Ca g/kg Ca	Zn g/kg Zn
Trigran	Ground, rain cover	1		23					
Trigran	Plate	1		147					
Trigran	Rain cover	1		30					
ANFO + HC	Regular	1			2828	14	1418	477	6.9
ANFO + Flare	Regular	1	28						

Table 3-4. Metal emission factors from PM_{10} fraction. Blank data indicate the absence of the metal in the ordnance composition.

Ordnance Type		Number of Samples	Mg g/kg Mg	Al g/kg Al	Si g/kg Si	Cl g/kg Cl	K g/kg K	Ca g/kg Ca	Zn g/kg Zn
Trigran	Ground, rain cover	1		62					
Trigran	Regular	2		272±135*					
Trigran	Plate	1		341					
Trigran	Rain cover	1		72					
ANFO + HC	Regular	1			6028	48	2962	1003	15
ANFO + Flare	Regular	1	25						

* Absolute difference divided by 2 (AD/2).

Table 3-5. Metal emission factors from Total PM. Blank data indicate the absence of the metal in the ordnance composition.

Ordnance Type		Number of Samples	Mg g/kg Mg	Al g/kg Al	Si g/kg Si	Cl g/kg Cl	K g/kg K	Ca g/kg Ca	Zn g/kg Z
Trigran	Ground, rain cover	1		390					
Trigran	Regular	1		337					
ANFO + HC	Regular	1			5564	39	3139	1227	37
ANFO + Flare	Regular	1	64						

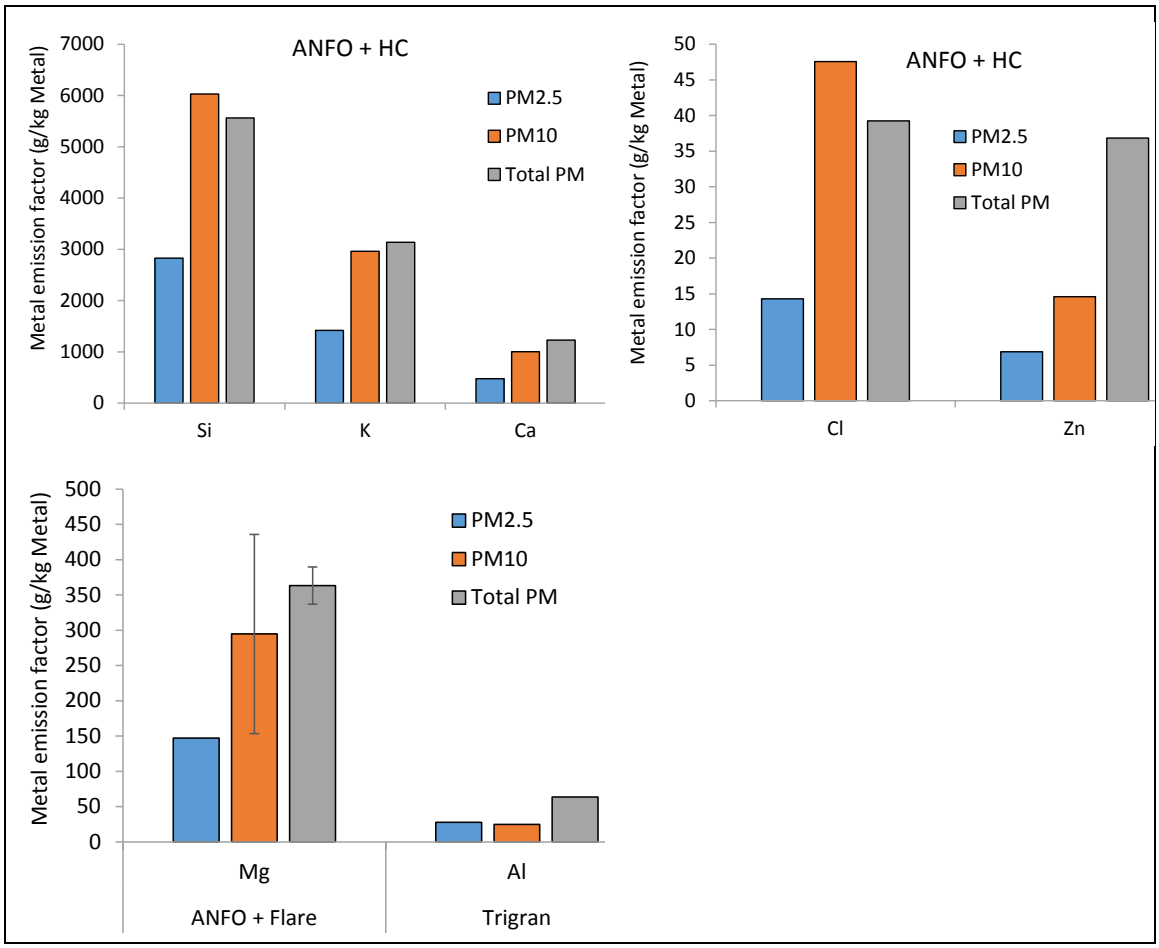


Figure 3-6. Metal emission factor from open detonation of ANFO+HC, Trigran, and ANFO+Flare.

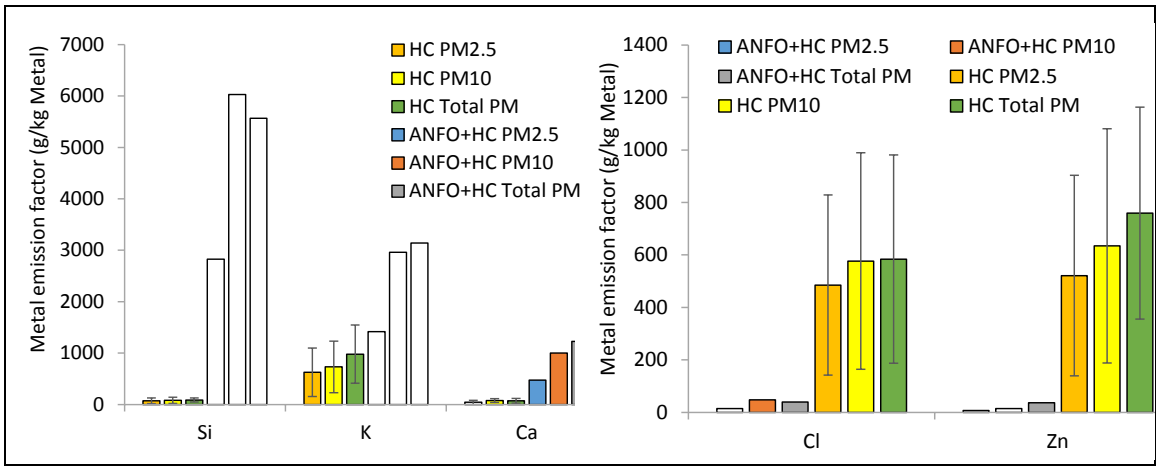


Figure 3-7. Metal emission factor comparison between open detonation of ANFO+HC and open burning of HC.

3.1.3 Chlorides

Emission factors for OD of HC ordnance, a Cl-containing explosive, are shown in Table 3-6. These results are derived from only a single sample. The cassette method indicates that 18% of the Cl in the original composition is emitted, with 7.1% of it as HCl. A comparison of the cassette and XRF analysis of the filters for chloride determination shows reasonable agreement, Table 3-7. These two methods have resulted in the first known Cl emissions data derived from open detonation sources. Additional sampling would assist in determining the precision of the method of sampling.

Table 3-6. Chloride emission factors from open detonation, cassette method (single sample).

Ordnance	Chloride g/kg NEQ	HCl g/kg NEQ	Chloride g/kg Cl	HCl g/kg Cl	Total Cl g/g Cl
HC+ANFO	2.4	2.9	58	71	0.18

Table 3-7. Comparison between Chloride sampling methods (single sample).

Ordnance	Cassette Chloride g/kg Cl	XRF Chloride g/kg Cl
HC+ANFO	58	39

3.1.4 VOCs

SUMMA canister analyses for VOCs from ODs are reported in Table 3-8. Standard deviations (STDVs) are reported for results with more than two values and half absolute difference (AD/2) is reported for data with two values. Overall, the relative standard deviation (STDV/average) from the repeat analyses are small, indicating good precision of the results. Of the hydrocarbons, propene, acetonitrile, and benzene are the most predominant across all OD types. Acrolein, an inhalable air toxic, has a notable concentration during Trigran detonation. Acetonitrile is the most dominant VOC observed, at 399 mg/kg NEQ for C4 detonation. Detonating HC with ANFO yielded in many chlorinated VOCs such as tetrachloroethene (576 mg/kg NEQ), carbon tetrachloride (106 mg/kg NEQ), trichloroethene (37 mg/kg NEQ), and vinylchloride (8.6 mg/kg NEQ).

The $\Delta CO/\Delta CO_2$ volumetric values range from 0 to 46%, indicating a significant amount of incomplete combustion. On a mass basis average 67% of the carbon emitted during sampling of the C4 detonation was emitted as CO_2. Combustion efficiency also appears to be shown by VOC concentrations of propene, acetonitrile, benzene, and toluene, where concentrations rise in parallel with those of CO and CH_4.

Table 3-8. VOC emission factors from Open Detonation. Detection limits are found in Appendix D.[#]

Compound	ANFO		Trigran		C4		ANFO+HC	ANFO+Flare
	Average	STDV	Average	STDV	Average	AD/2		
	mg/kg NEQ		mg/kg NEQ		mg/kg NEQ		mg/kg NEQ	mg/kg NEQ
Propene	14	5.4	27	7.3	40	3.5	39	136
Dichlorodifluoromethane (CFC 12)	ND		ND		ND		ND	ND
Chloromethane	ND		1.2		ND		4.8	ND
1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114)	ND		ND		ND		ND	ND
Vinyl Chloride	ND		ND		ND		8.6	ND
1,3-Butadiene	0.76	0.24	4.6	1.3	4.1	0.42	17	17
Bromomethane	ND		ND		ND		ND	ND
Chloroethane	ND		ND		ND		2.0	2.0
Ethanol	1.0		1.1		3.4	0.018	ND	ND
Acetonitrile	10	5.5	80	24	399	15	34	75
Acrolein	1.0	0.58	14	5.9	2.9		8.7	4.3
Acetone	0.68		ND		ND		1.4	ND
Trichlorofluoromethane	ND		ND		ND		ND	ND
2-Propanol (Isopropyl Alcohol)	1.3		10		6.7		ND	ND
Acrylonitrile	1.9	1.1	18	5.4	5.9	0.25	4.9	ND
1,1-Dichloroethene	ND		ND		ND		17	ND
Methylene Chloride	ND		ND		ND		13	ND
3-Chloro-1-propene (Allyl Chloride)	ND		ND		ND		ND	ND
Trichlorotrifluoroethane	ND		ND		ND		ND	ND
Carbon Disulfide	ND		ND		6.7		ND	10
trans-1,2-Dichloroethene	ND		ND		ND		1.3	ND
1,1-Dichloroethane	ND		ND		ND		0.92	ND
Methyl tert-Butyl Ether	ND		ND		ND		ND	ND
Vinyl Acetate	ND		4.5		ND		4.9	8.4
2-Butanone (MEK)	ND		14	8.3*	2.8		ND	ND
cis-1,2-Dichloroethene	ND		ND		ND		1.5	ND
Ethyl Acetate	2.1		ND		ND		3.5	ND
n-Hexane	ND		ND		ND		ND	ND
Chloroform	ND		ND		ND		46	ND
Tetrahydrofuran (THF)	ND		ND		ND		1.5	ND
1,2-Dichloroethane	ND		ND		ND		ND	ND
1,1,1-Trichloroethane	ND		ND		ND		1.2	ND

Benzene	12	5.8	19	4.8	39	9.1	236	144
Carbon Tetrachloride	ND		ND		ND		106	ND
Cyclohexane	ND		13		ND		ND	ND
1,2-Dichloropropane	ND		ND		ND		ND	ND
Bromodichloromethane	ND		ND		ND		ND	ND
Trichloroethene	ND		ND		ND		37	ND
1,4-Dioxane	ND		ND		2.7		ND	ND
Methyl Methacrylate	ND		ND		ND		ND	ND
n-Heptane	ND		1.7	1.0*	ND		ND	ND
cis-1,3-Dichloropropene	ND		ND		ND		ND	ND
4-Methyl-2-pentanone	ND		ND		ND		ND	ND
trans-1,3-Dichloropropene	ND		ND		ND		ND	ND
1,1,2-Trichloroethane	ND		ND		ND		ND	ND
Toluene	1.8	0.86	17	0.59*	6.8		ND	ND
2-Hexanone	ND		5.0	3.8*	2.6		ND	2.0
Dibromochloromethane	ND		ND		ND		ND	ND
1,2-Dibromoethane	ND		ND		ND		ND	ND
n-Butyl Acetate	ND		ND		ND		ND	ND
n-Octane	0.48	0.27	2.4	0.54*	ND		ND	ND
Tetrachloroethene	ND		ND		ND		576	4.7
Chlorobenzene	ND		ND		ND		5.2	ND
Ethylbenzene	0.12	0.051*	6.9	0.03*	ND		4.0	6.2
m,p-Xylenes	ND		16	7.2*	ND		ND	ND
Bromoform	ND		ND		ND		ND	ND
Styrene	0.90	0.24	2.6	0.83	2.0	0.47	12	15
o-Xylene	ND		6.9		ND		ND	ND
n-Nonane	0.86	0.66	2.4		ND		ND	ND
1,1,2,2-Tetrachloroethane	ND		ND		ND		ND	ND
Cumene	ND		ND		ND		ND	ND
alpha-Pinene	ND		9.1		ND		ND	ND
n-Propylbenzene	0.27		4.0		ND		ND	ND
4-Ethyltoluene	0.25	0.069*	5.9		ND		ND	ND
1,3,5-Trimethylbenzene	0.28	0.10*	5.9		ND		ND	ND
1,2,4-Trimethylbenzene	ND		6.9		ND		ND	ND
Benzyl Chloride	ND		ND		ND		0.63	ND
1,3-Dichlorobenzene	ND		ND		ND		1.5	ND
1,4-Dichlorobenzene	ND		ND		ND		0.69	ND
1,2-Dichlorobenzene	ND		ND		ND		1.0	ND
d-Limonene	ND		3.5		1.6		ND	ND
1,2-Dibromo-3-chloropropane	ND		ND		ND		ND	ND

1,2,4-Trichlorobenzene	ND		ND		ND		1.6	ND
Naphthalene	1.9	0.90	ND		ND		26	36
Hexachlorobutadiene	ND		ND		ND		4.9	ND
g/kg NEQ								
Carbon Monoxide	1.7	0.38*	63	6.1	132	7.8	7.9	19
Methane	0.63	0.18	0.92	0.13*	15	1.3	1.9	3.7
Carbon Dioxide	180	2.0	987	12	498	16	161	138
Modified Combustion Efficiency	0.993	0.0089	0.909	0.009	0.706	0.019	0.928	0.821

* half absolute difference (AD/2). # Boldface compounds are on the U.S. EPA hazardous air pollution list [19], detection limits can be found in Appendix D

3.1.5 PCDD/PCDF

The Cl-containing, HC + ANFO ordnance was sampled for PCDD/PCDF emissions. Table 3-9 indicates the concentration distribution of the 2,3,7,8-Cl-substituted toxic congeners for HC + ANFO during OD. Virtually all of the congeners formed are PCDFs, commonly found for surface catalyzed reactions. Most of the toxicity emanates from the 2,3,4,7,8-PeCDF, as is common for most combustion sources. The weight-based PCDD/PCDF emission factor is extremely high in comparison to other fuel sources. Assuming rough equivalence of the denominator mass units, these emission factors are about 500-1,000 times those from biomass burning and about 10 times that of open waste burning. Detonation of the HC + ANFO resulted in PCDD/PCDF (in TEQ) emissions equivalent to those from prescribed burning of 2 ha of forest biomass (emission factor from Aurell & Gullett [20]; biomass density from Ottmar [21]).

Table 3-9. PCDD/PCDF TEQ and PCDD/PCDF Total emission factors from open detonation of HC + ANFO.

Isomer.	Open Detonation HC+ANFO ng TEQ/kg NEQ ND=0		Homologue	Open Detonation HC+ANFO ng/kg NEQ
2,3,7,8 - TCDD	ND		TeCDD Total	ND
1,2,3,7,8 - PeCDD	ND		PeCDD Total	ND
1,2,3,4,7,8 - HxCDD	0.99		HxCDD Total	61
1,2,3,6,7,8 - HxCDD	1.4		HpCDD Total	202
1,2,3,7,8,9 - HxCDD	0.82		OCDD	378
1,2,3,4,6,7,8 - HpCDD	1.0			
1,2,3,4,6,7,8,9 - OCDD	0.11			
2,3,7,8 - TCDF	44		TeCDF Total	27,224
1,2,3,7,8 - PeCDF	28		PeCDF Total	18,618
2,3,4,7,8 - PeCDF	430		HxCDF Total	19,963
1,2,3,4,7,8 - HxCDF	238		HpCDF Total	21,503
1,2,3,6,7,8 - HxCDF	187		OCDF	13,819
1,2,3,7,8,9 - HxCDF	105			
2,3,4,6,7,8 - HxCDF	241			
1,2,3,4,6,7,8 - HpCDF	96			
1,2,3,4,7,8,9 - HpCDF	30			
1,2,3,4,6,7,8,9 - OCDF	4.1			
PCDD TEQ Total	4.3		PCDD Total	640
PCDF TEQ Total	1,403		PCDF Total	101,127
PCDD/PCDF TEQ Total	1,407		PCDD/PCDF Total	101,767

3.2 Open Burns

Open burning tests were conducted on four propellants listed in Table 2-2. Photos of each of these as well as smoke grenade are shown in Figure 3-8 below.

Figure 3-8. Open burning of four propellant types and HC smoke grenade.

3.2.1 PM

PM data for all six ordnance types in Table 2-2 based on filter collection methods are shown in Table 3-10, below. While minimal replicates were conducted, none of the deviations exceeded 50% of the value, indicating reasonably good precision.

Red Phosphorous smoke had much higher PM emission factors (about 100 times) than the other propellants and smoke grenades. HC grenades showed higher emission factors than possible (> 1 kg/kg NEQ, Table 3-10), most certainly due to acid moisture found on the HC particulate filter by the analytical laboratory (Appendix M).

All values for PM_1, $PM_{2.5}$, PM_{10}, and Total PM are similar indicating that the predominant particle size is PM_1 or less. Consistent with this finding, the CEM DustTrak data for the smokes (non-obscurant propellants) reveals that most of the PM are in the size of PM_1 (Figure 3-10). In contrast to OD, OB is conducted in raised pans so it's not anticipated that soil ejection or entrainment from the surrounding surface affects the particle size distribution. The peak concentrations for these particles appears to range from 15 to 100 mg/m^3 and are closely associated with CO_2 peaks, as expected. As with OD results, some evidence for a bimodal temporal distribution is indicated, with a time lag of about 5 s.

Table 3-10. PM emission factors in g/kg NEQ from open burning.

	Number of	$PM_{2.5}$			PM_{10}			Total PM		
Ordnance Type	**Samples**	**Average**	**STDV**	**AD/2**	**Average**	**STDV**	**AD/2**	**Average**	**STDV**	**AD/2**
M1, 105	2	5.8		0.89	5.2		1.5	4.7		0.68
M6, 155, Red bag	2	11		2.0	9.6		0.75	17		8.3
M4A2, 155, White bag	1	6.8			7.3			8.5		
Triple base	1	3.1			3.7			5.3		
HC*	3	1,276	1,009		1,568	988		1,327	852	
Red phosphorus	2	566		16	582		19	516		23

* Acid moisture was found on all filters collected from the HC smoke grenade. The laboratory report (Appendix M) states that there might be volatile matter on these HC filters.

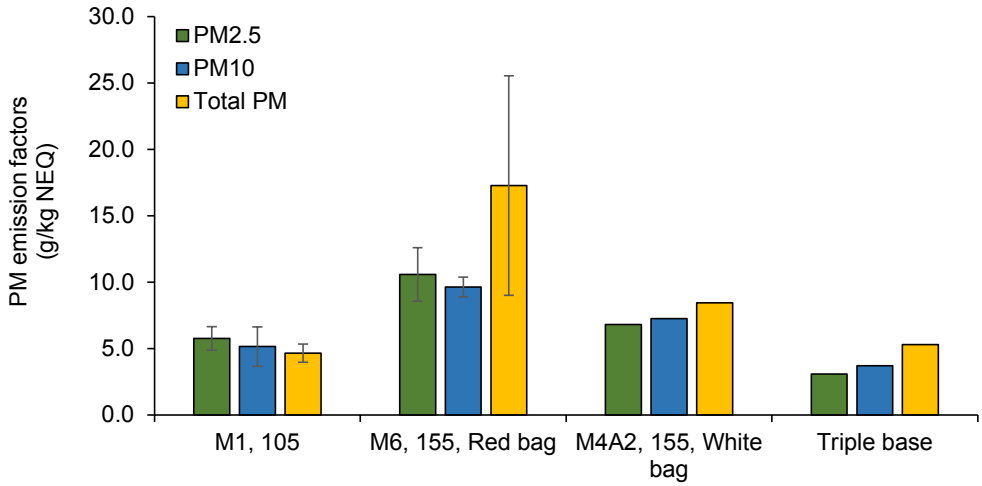
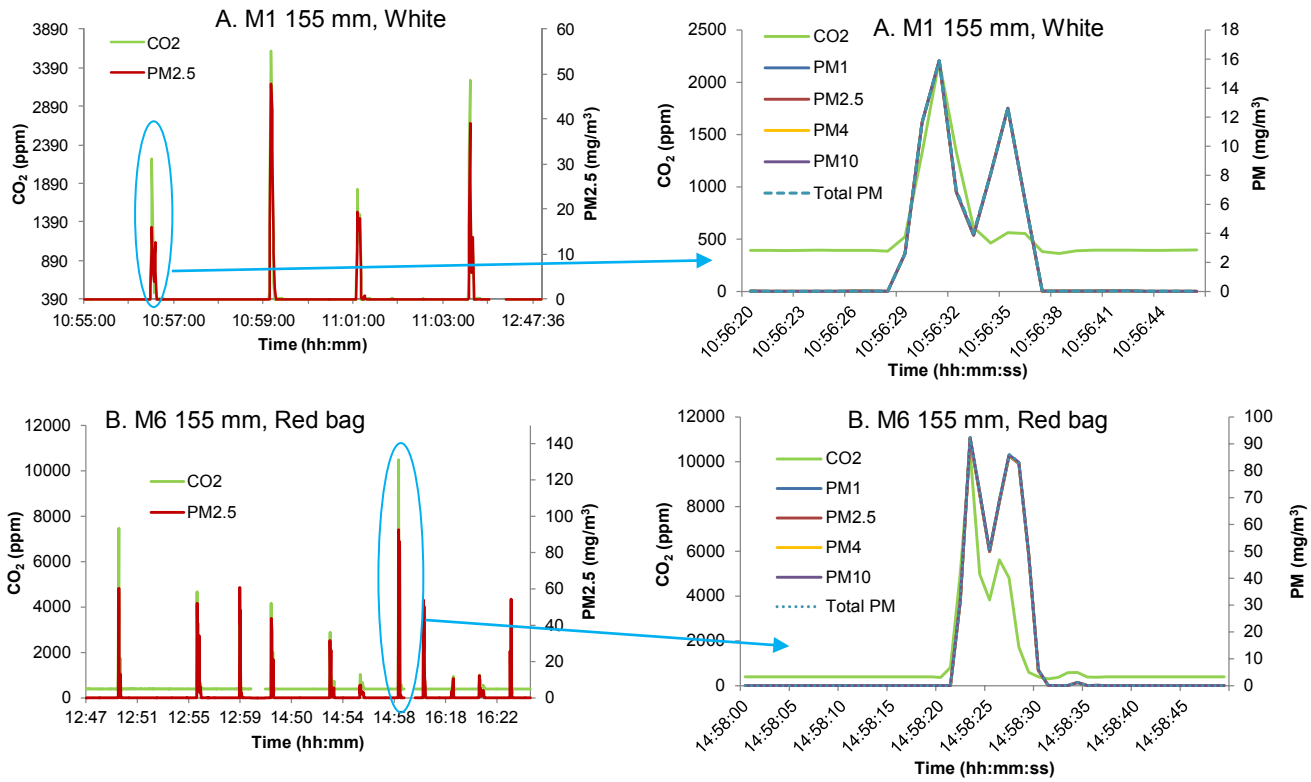


Figure 3-9. PM emission factors from open burning of propellant. Error bars denoted absolute difference divided by two.



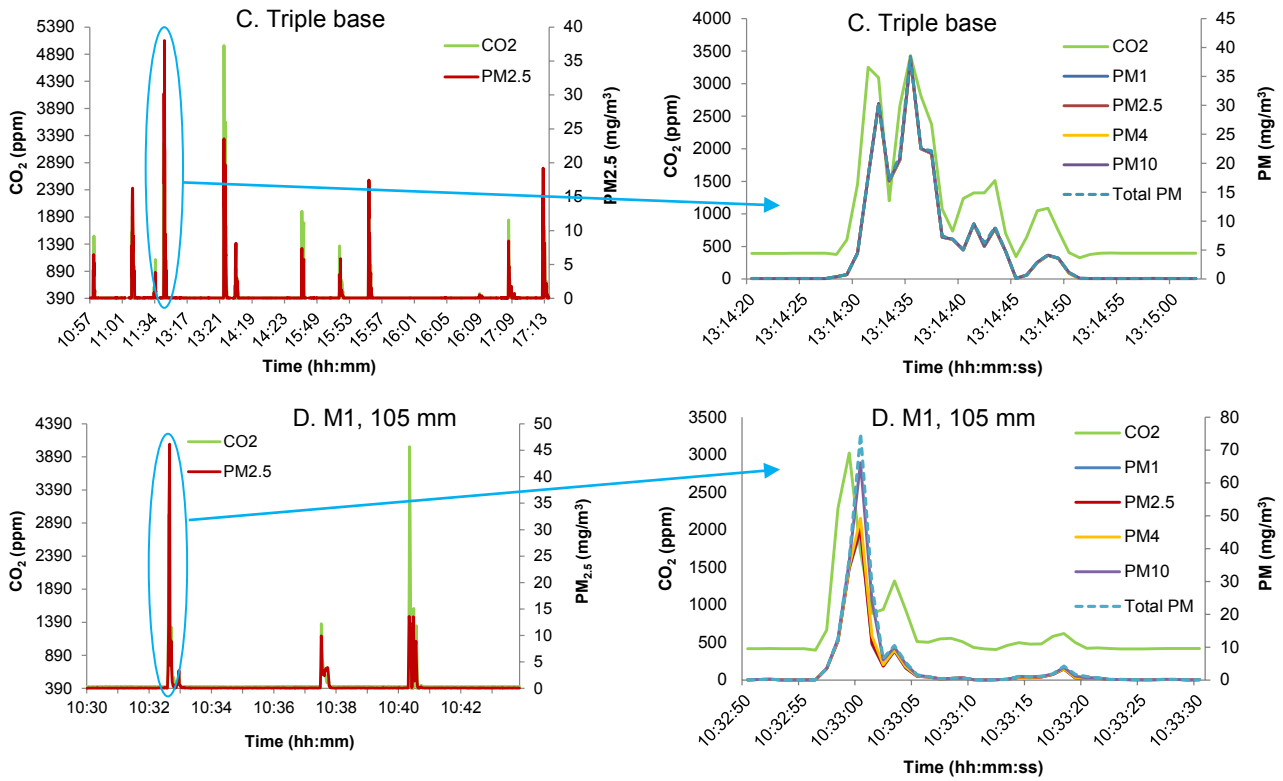


Figure 3-10. Continuous PM and CO_2 emission sampling of A) 155 mm, White bag, B) M6, 155 mm red bag, C) Triple base, and D) M1, 105 mm propellant.

Table 3-11. PM CEM DustTrak emission factors for OB.

Ordnance	Amount of Burns		PM_1	$PM_{2.5}$	PM_4	PM_{10}	TPM
			g/kg NEQ				
M1, 105 mm	3	Average	7.58	7.78 [6.6*]	8.03	9.13	9.72
		STDV	2.3	2.4 [4.0*]	2.5	3.4	3.8
M6, 155 mm Red bag	11	Average	10.4	10.4	10.4	10.5	10.6
		STDV	2.2	2.2	2.2	2.2	2.3
M1, 155 mm, White bag	8	Average	10.3	10.3	10.4	10.4	10.5
		STDV	1.1	1.1	1.1	1.1	1.3
Triple base	12	Average	2.95	2.96	2.96	2.98	3.00
		STDV	0.78	0.78	0.78	0.78	0.79

* Average and STDV of ten burns using DustTrak 8520 (09-27-2013) and DustTrak DRX (09-28-2013). DustTrak correction factor employed. TPM = Total PM.

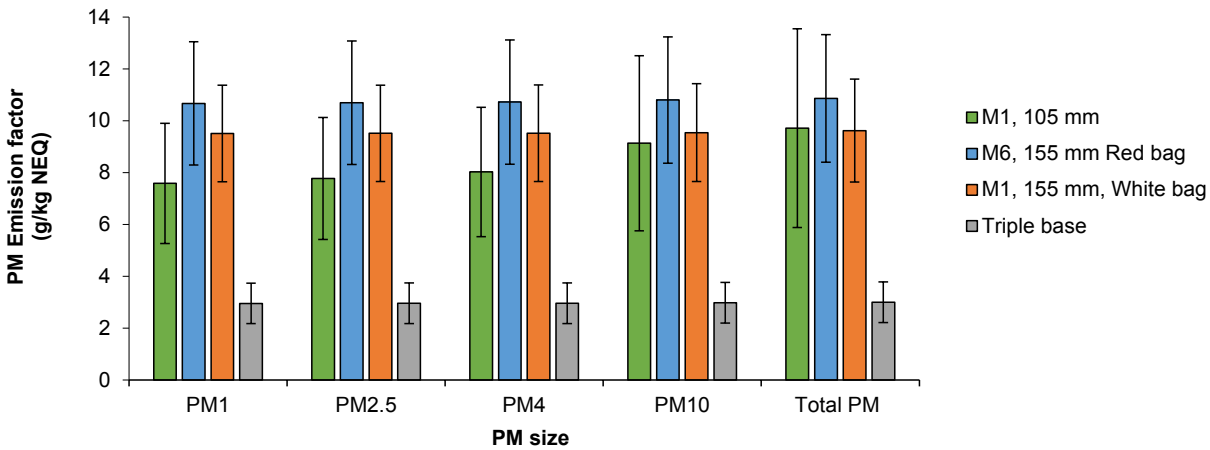


Figure 3-11. PM emission factor and PM size distribution derived from PM CEM DustTraks.

3.2.2 Metals

Metals were analyzed from the Teflon filters on the PM impactors. For $PM_{2.5}$ (Table 3-12), Pb emissions were less than 8% and 5% of the composition for M1 and M6, respectively. The HC smoke revealed emissions of Zn, Cl, and K that average half of their starting composition, indicating that half of the metal ends up in the plume. These emission factors increase slightly from $PM_{2.5}$ to PM_{10} to Total PM (Table 3-12, Table 3-13, and Table 3-14, respectively) indicating that metals are more common in the larger particles. These data are also presented graphically in Figure 3-12.

Table 3-12. Metal emission factors in g/kg Metal from $PM_{2.5}$ fraction. Blank data indicate the absence of the metal in the ordnance composition.

Ordnance Type	Number of Samples	$PM_{2.5}$ Pb g/kg Pb	Al g/kg Al	Na g/kg Na	Mg g/kg Mg	P g/kg P	Mn g/kg Mn	Zn g/kg Zn	Si g/kg Si	Cl g/kg Cl	K g/kg K	Ca g/kg Ca
M1, 105	2	49										
	AD/2	4.4										
M6, 155, Red bag	2	79										
	AD/2	16										
M4A2, 155, White bag	1											
Triple base	1		ND	810								
HC	3							485	72	521	626	45
	STDV							344	56	382	471	35
Red phosphorus	2				61	107	3.0	108				
	AD/2				26	42	2.7	40				

Table 3-13. Metal emission factors from PM_{10} fraction. Blank data indicate the absence of the metal in the ordnance composition.

Ordnance Type	Number of Samples	PM_{10} Pb g/kg Pb	Al g/kg Al	Na g/kg Na	Mg g/kg Mg	P g/kg P	Mn g/kg Mn	Zn g/kg Zn	Si g/kg Si	Cl g/kg Cl	K g/kg K	Ca g/kg Ca
M1, 105	2	41.1										
	AD/2	0.41										
M6, 155, Red bag	2	65										
	AD/2	10										
M4A2, 155, White bag	1											
Triple base	1		ND	718								
HC	3							577	80	634	731	77
	STDV							413	61	447	503	35
Red phosphorus	2				93	146	1.5	141				
	AD/2				8	5	0.91	10				

Table 3-14. Metal emission factors in g/kg Metal from Total PM fraction. Blank data indicate the absence of the metal in the ordnance composition.

Ordnance Type	Number of Samples	Total PM Pb g/kg Pb	Al g/kg Al	Na g/kg Na	Mg g/kg Mg	P g/kg P	Mn g/kg Mn	Zn g/kg Zn	Si g/kg Si	Cl g/kg Cl	K g/kg K	Ca g/kg Ca
M1, 105	2	60										
	AD/2	1.7										
M6, 155, Red bag	2	97										
	AD/2	17										
M4A2, 155, White bag	1											
Triple base	1		0.63	805								
HC	3							584	88	759	980	72
	STDV							397	41	404	565	46
Red phosphorus	2				65	98	2.2	114				
	AD/2				34	34	1.4	40				

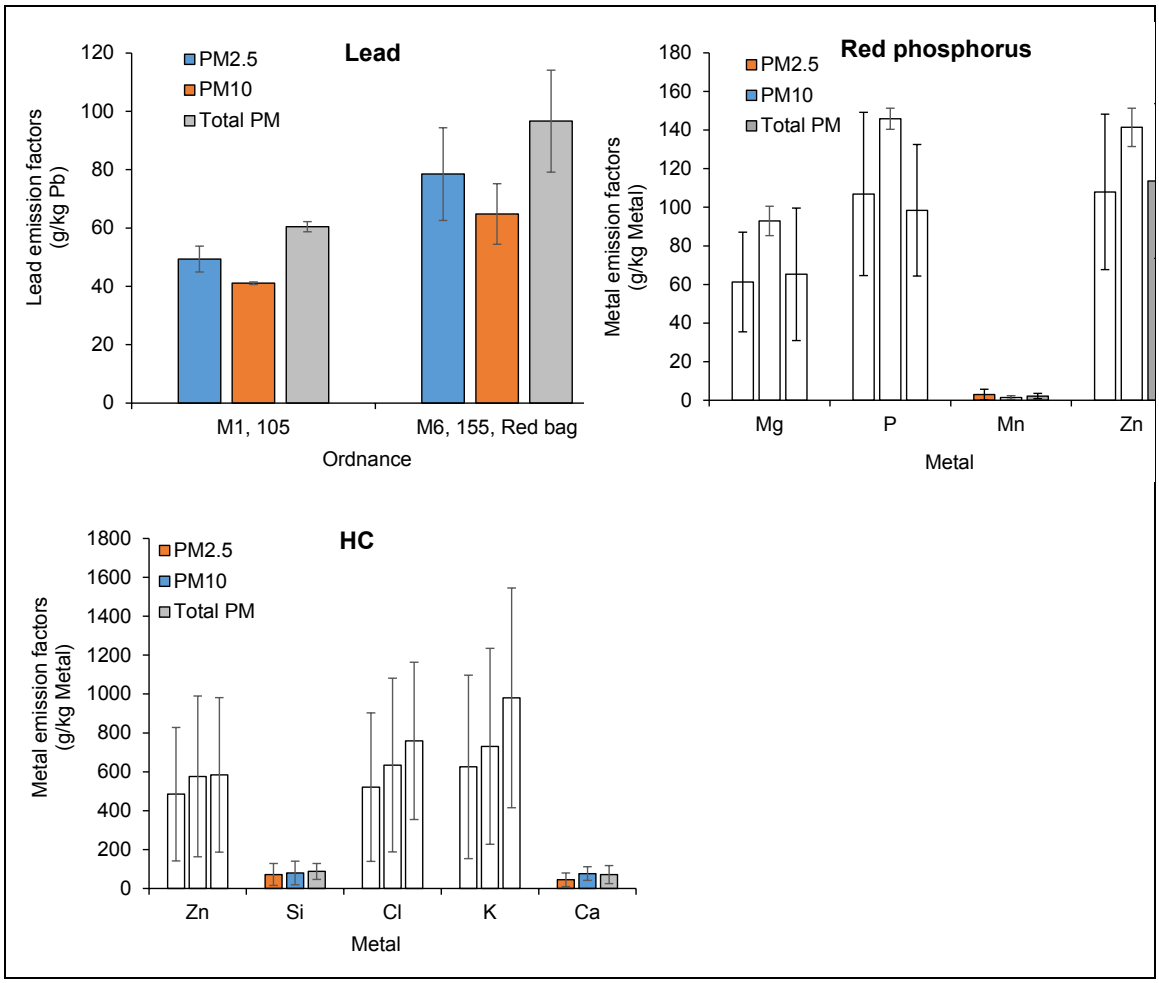


Figure 3-12. Metal emission factors in g/kg metal for M1, M6, Red Phosphorous, and HC.

3.2.3 Chlorides

Three trials of HC, a chlorine-containing ordnance, were sampled for Cl species in the emissions (Table 3-15) using the cassette method. The third run of HC was high in chlorides and HCl compared to the other two. Its Total Cl, 1.77 g/g Cl, exceeded unity, indicating the cumulative error in the sampling and analytical method. The high chloride value from the cassette study is supported by an XRF analysis on the contemporaneously-sampled, yet distinct, Total PM filter (Table 3-16). This finding tends to suggest a high degree of variability in the HC smoke emissions.

Table 3-15. Chloride emission factors from open burning of HC.

Ordnance	Chloride g/kg NEQ	HCl g/kg NEQ	Chloride g/kg Cl	HCl g/kg Cl	Total Cl g/g Cl
HC	79	57	206	147	0.35
HC	131	83	339	215	0.55
HC	398	294	1029	760	1.77

Average	203	144	525	374	0.89
STDV	171	130	442	336	0.77

Table 3-16. Comparison of two different chloride methods.

Ordnance	Cassette Chloride g/kg Cl	XRF Chloride g/kg Cl
HC	206	258
HC	339	474
HC	1029	1045
Average	525	592
STDV	442	407

3.2.4 VOCs

Nineteen VOC SUMMA canister samples were taken on the six propellants and smokes in Table 2-2. Over 40 VOC compounds were analyzed and reported in Table 3-17 with those compounds on the hazardous air pollutant list [19] in bold. The highest total VOCs observed are from the HC grenade and its highest compound was benzene at 589 mg/kg NEQ (STDV = 164). These OB propellant emission factors were approximately ten times lower than those for the propellant types found in previous testing in Tooele, Utah [2].

Table 3-17. VOC and C species emission factors from open burning.

Compound#	HC grenade		Red phosphorus		Triple base		155 M4A2 White bag		105 M1		155 M6 Red bag
	Average	STDV	Average	STDV	Average	STDV	Average	STDV	Average	STDV	
	mg/kg NEQ		mg/kg NEQ		mg/kg NEQ		mg/kg NEQ		mg/kg NEQ		mg/kg NEQ
Propene	47	23	114	190	ND		0.48	0.15	0.31	0.40	1.8
Chloromethane	79	24	0.021		ND		ND		ND		ND
Vinyl Chloride	8.1	3.0	ND		ND		ND		ND		ND
1,3-Butadiene	31	10	19	30	ND		ND		ND		ND
Ethanol	ND		ND		ND		ND		ND		1.7
Acetonitrile	80	23	4.6	7.1	0.16	0.025	3.5	2.9	2.4	2.5	3.2
Acrolein	17	4.9	10	13	0.50		0.67	0.20*	0.26		0.53
Acetone	ND		0.39		ND		ND		0.62	0.19*	ND

Trichlorofluoromethane	ND		ND		ND		ND		ND		0.48
Acrylonitrile	15	4.1	4.3	3.5*	0.11	0.0018*	4.6	1.1	9.5	8.2	2.9
Methylene Chloride	6.7	9.0	ND		ND		0.41		ND		ND
3-Chloro-1-propene (Allyl Chloride)	2.9	1.1	ND		ND		ND		ND		ND
Carbon Disulfide	24	15	ND		0.39		0.66	0.99	1.0		0.048
1,1-Dichloroethane	1.7		ND		ND		ND		ND		ND
Vinyl Acetate	ND		1.3	0.21*	ND		ND		ND		ND
2-Butanone (MEK)	0.84	0.28*	1.5		ND		ND		0.66	0.18*	ND
Ethyl Acetate	ND		ND		ND		ND		ND		6.0
Chloroform	17		ND		ND		ND		ND		ND
Benzene	589	164	39	57	0.029	0.00062*	2.1	0.47	0.93	0.51	4.2
Carbon Tetrachloride	35	34*	ND		ND		ND		ND		ND
Trichloroethene	10		ND		ND		ND		ND		ND
1,1,2-Trichloroethane	ND		ND		ND		ND		ND		ND
Toluene	94		1.8	1.1*	ND		ND		ND		5.3
2-Hexanone	ND		ND		ND		ND		0.50	0.21*	ND
n-Octane	ND		ND		ND		0.47		0.38	0.19	ND
Tetrachloroethene	79	110	ND		ND		ND		ND		ND
Chlorobenzene	30	11	ND		ND		ND		ND		ND
Ethylbenzene	1.6	0.18	ND		ND		ND		0.52	0.21*	0.34
m,p-Xylenes	8.4		ND		ND		ND		1.7	0.46*	ND
Styrene	22	4.9	2.7	3.8	ND		0.51	0.047*	0.95	0.26*	0.98
o-Xylene	0.52	0.42	ND		ND		ND		0.39	0.069*	ND
n-Nonane	ND		ND		ND		0.36	0.052*	0.31	0.027	1.5
n-Propylbenzene	ND		ND		ND		ND		0.31	0.036*	ND
4-Ethyltoluene	ND		ND		ND		ND		0.43	0.076*	ND
1,3,5-Trimethylbenzene	1.2	0.29*	ND		ND		ND		0.41	0.090*	ND
1,2,4-Trimethylbenzene	ND		ND		ND		ND		ND		ND
Benzyl Chloride	8.3	2.9	ND		ND		ND		ND		ND
1,3-Dichlorobenzene	2.4		ND		ND		ND		ND		ND
1,4-Dichlorobenzene	1.2		ND		ND		ND		ND		ND
1,2-Dichlorobenzene	1.4		ND		ND		ND		ND		ND
d-Limonene	ND		1.4	1.6	ND		0.36		ND		ND
1,2,4-Trichlorobenzene	1.5		ND		ND		ND		ND		ND
Naphthalene	71	14	2.4	3.3	ND		ND		0.38		ND
Hexachlorobutadiene	4.0		ND		ND		ND		ND		ND
g/kg NEQ											
Carbon Monoxide	41	11	ND		ND		3.8	2.0*	ND		18
Methane	1.4	0.31	ND		ND		ND		ND		ND

Carbon Dioxide	71	18			1183	4.6		1130
MCE	0.525	0.132			0.997	0.0039		0.976

* Absolute difference divided by two. # Boldface compounds are on the U.S. EPA hazardous air pollution list [19]. MCE = modified combustion efficiency.

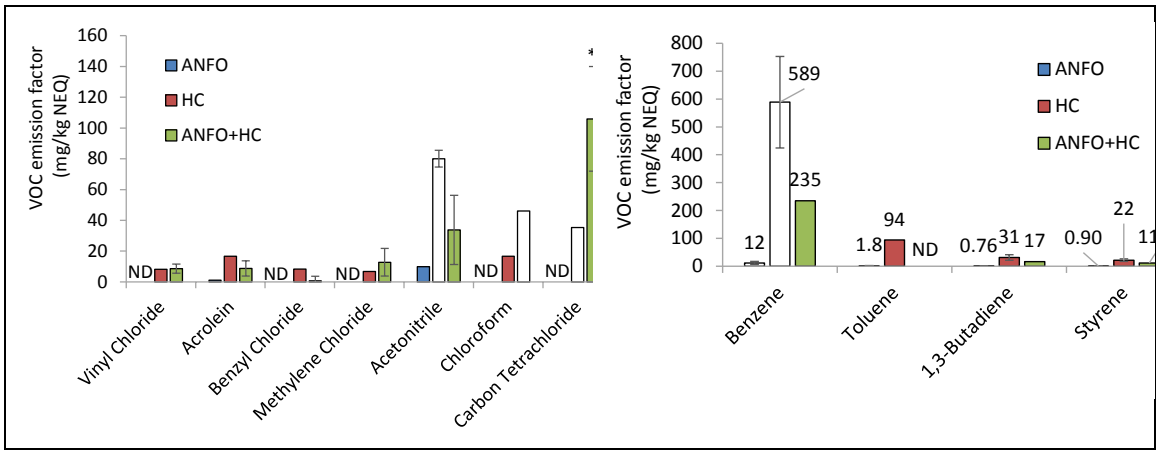


Figure 3-13. Comparison of VOC emission factors for open detonation of ANFO, ANFO+HC and open burning of HC.

3.2.5 PCDD/PCDF

The Cl-containing HC smoke grenades were sampled for PCDD/PCDF. A single sample showed 2,700 ng TEQ/kg NEQ (Table 3-18). On an assumed weight equivalency basis (kg NEQ = kg material), this value is at least 1,000 times that of typical biomass burns and about 10-20 times that for opening burning of residential waste. Additional testing would confirm this extremely high value.

Table 3-18. PCDD/PCDF TEQ and PCDD/PCDF Total emission factors from open burning of HC.

Isomer.	**Open Burning HC ng TEQ/kg NEQ ND=0**		**Homologue**	**Open Burning HC ng/kg NEQ**

2,3,7,8 - TCDD	ND		TeCDD Total	2,102
1,2,3,7,8 - PeCDD	41		PeCDD Total	498
1,2,3,4,7,8 - HxCDD	3.2		HxCDD Total	583
1,2,3,6,7,8 - HxCDD	3.6		HpCDD Total	245
1,2,3,7,8,9 - HxCDD	4.9		OCDD	177
1,2,3,4,6,7,8 - HpCDD	1.1			
1,2,3,4,6,7,8,9 - OCDD	0.053			
2,3,7,8 - TCDF	42		TeCDF Total	34,625
1,2,3,7,8 - PeCDF	53		PeCDF Total	30,322
2,3,4,7,8 - PeCDF	378		HxCDF Total	43,654
1,2,3,4,7,8 - HxCDF	524		HpCDF Total	68,982
1,2,3,6,7,8 - HxCDF	434		OCDF	139,075
1,2,3,7,8,9 - HxCDF	351			
2,3,4,6,7,8 - HxCDF	383			
1,2,3,4,6,7,8 - HpCDF	330			
1,2,3,4,7,8,9 - HpCDF	122			
1,2,3,4,6,7,8,9 - OCDF	42			
PCDD TEQ Total	54		PCDD Total	3,605
PCDF TEQ Total	2,660		PCDF Total	316,657
PCDD/PCDF TEQ Total	2,714		PCDD/PCDF Total	320,262

3.3 Static Firing

Two rocket types were used for static firing emission tests: the MK58 and the CRV-7 (Figure 3-14).

Figure 3-14. Photos of static firing of CRV-7 (ground view, left) and MK 58 (aerial view, right).

3.3.1 PM

Single test results (Table 3-19) from $PM_{2.5}$ filters show that the MK 58 has about twice the particle emissions as the CRV-7 ($PM_{2.5}$ = 34 g/kg NEQ versus $PM_{2.5}$ = 16 g/kg NEQ, respectively). Previous same-method results (Tooele 2011) for static firing of an ammonium perchlorate-containing Sparrow rocket motor resulted in a single PM_{10} result of 150 g/kg NEW [3]. There is little distinction between the emission factors for $PM_{2.5}$, PM_{10}, and Total PM, suggesting the majority of the particle mass is made up of particle diameters 2.5 µm or less (see Figure 3-15).

Table 3-19. PM emission factors (g/kg NEQ) from static fire.

Rocket Motor	Number of Samples	$PM_{2.5}$	PM_{10}	Total PM
CRV-7	1	16	17	16
MK 58	1	34	53	39

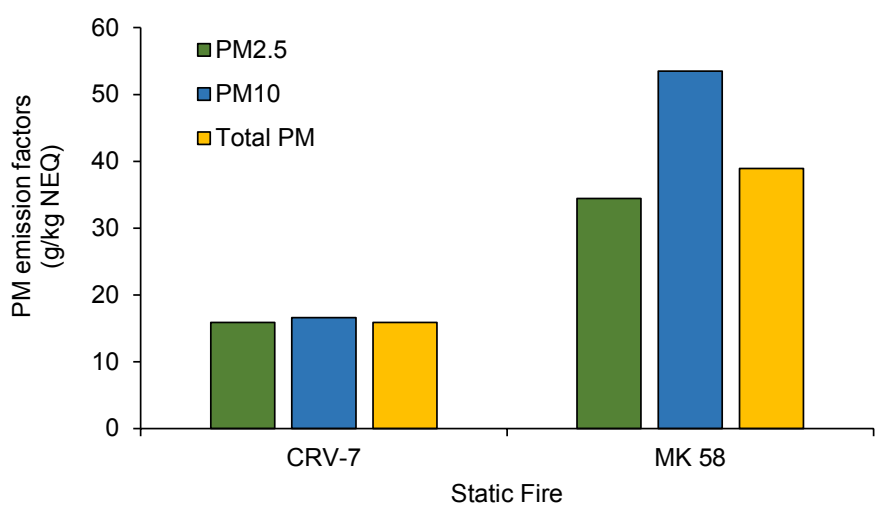


Figure 3-15. PM emission factors from static firing of CRV-7 and MK 58 rocket motors. Single samples.

Continuous PM data (Figure 3-16) show higher particle concentrations for the MK 58 than the CRV-7, consistent with the emission factor data. Calculation of the emission factors from these DustTrak data (Table 3-20) show excellent agreement with the filter based methods (Table 3-19), differing only about 10%.

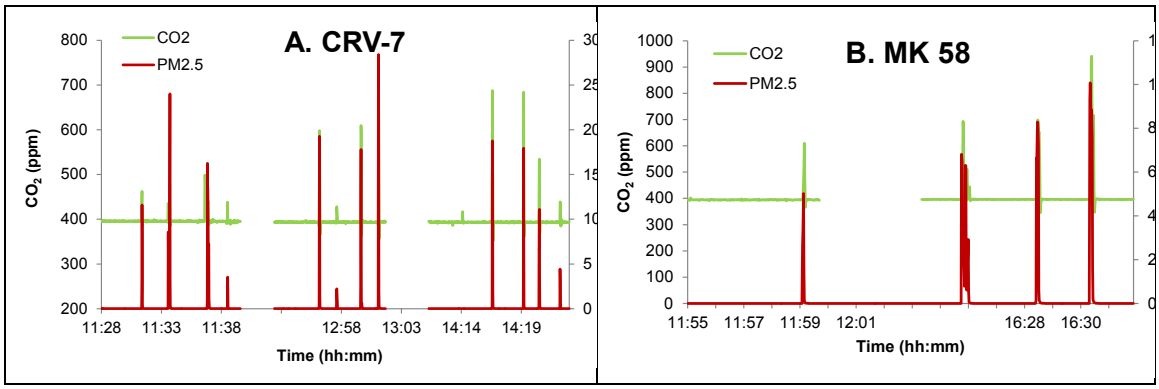


Figure 3-16. Continuous emission measurements of CO_2 and $PM_{2.5}$ from static firing of A) CRV-7 (three series of four DPs, each DP containing 12 rockets) and B) MK 58 (one single rocket followed by three series of three rockets each).

Table 3-20. $PM_{2.5}$ emission factors derived from DustTrak.

Rocket Motor	Amount of Burns		$PM_{2.5}$ g/kg NEQ
CRV-7	12	Average	18
		STDV	8.0
MK 58	4	Average	38
		STDV	9.0

3.3.2 Metals

One set of PM samples from each rocket motor were analyzed for metals/elements within the original ordnance. The Al emission factor ($PM_{2.5}$ 151 g/kg Al) for the MK 58 indicates that about 15% of the Al in the rocket composition was emitted (Table 3-21). The Fe, Zr, and Si for the CRV-7 rocket have notable emission levels, also. These values are complicated by the potential entrainment of metal-containing soil into the rocket plume for all particle sizes. All of the metals increased somewhat in emission factor with larger particle sizes, possibly indicating that the metals showed some preferential association with the larger particles. The Total PM emission factor for Si showed higher emission factor than possible (1.1 kg/kg Si, or 110%) which is likely

due to entrainment of soil. The emission factors for Cl appeared relatively constant across all particle sizes.

The Al emission factor for an ammonium perchlorate-containing Sparrow rocket motor (Tooele, 2011) was 170 g/kg Al for PM_{10} [3], which is about half of the MK 58 emission factor in the PM_{10} fraction (310 g/kg Al) but very similar to the $PM_{2.5}$ fraction (151 g/kg Al). It is possible that the differences in test methods from the Tooele study (rocket motors were placed in a silo below a concrete pad) and this study (rocket motors stood upright in loose soil) could be a reason for the emission factor differences but the single sampling event makes this a tenuous hypothesis.

Table 3-21. Metal/element emission factors in g/kg element in the ordnance composition. Blank data indicate the absence of the metal in the ordnance composition.

PM size	Metal	Number of Samples	CRV-7	MK 58
$PM_{2.5}$	Al	1		151
	Cl	1	1.9	0.45
	Fe	1	261	
	Zr	1	105	
	Si	1	417	
PM_{10}	Al	1		310
	Cl	1	2.0	0.66
	Fe	1	278	
	Zr	1	281	
	Si	1	608	
Total PM	Al	1		587
	Cl	1	2.5	1.3
	Fe	1	313	
	Zr	1	833	
	Si	1	1141	

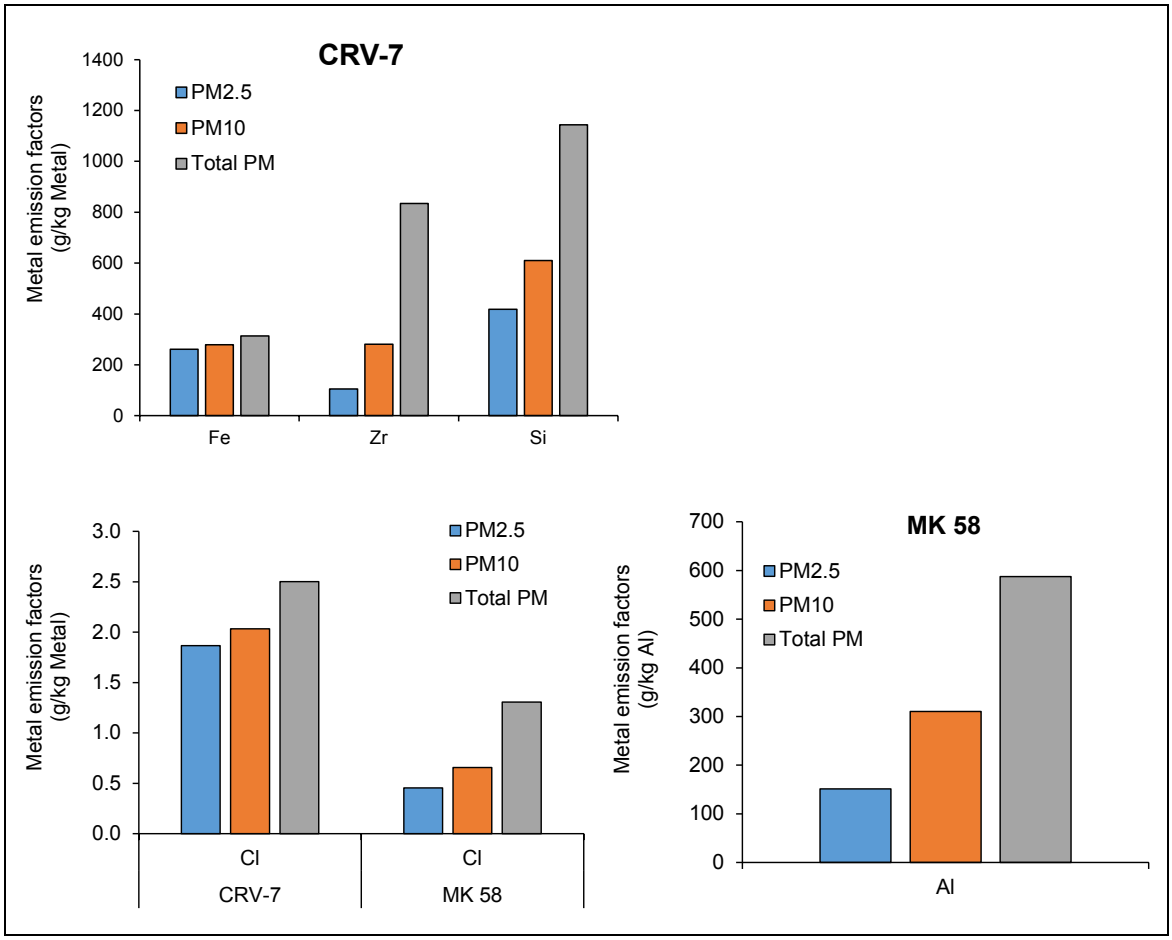


Figure 3-17. Metal emission factors in g/kg Metal from static fires of CRV-7 and MK58.

3.3.3 Chlorides

Cl species results using the alkali-impregnated filter method are reported in Table 3-22. Data from only single tests show similar chloride and chlorate emission factors but higher HCl for CRV-7 (329 g/kg Cl) than the MK 58 (124 g/kg Cl). A single sample from static firing of Sparrow

rocket motors (Tooele, 2011) showed a comparable HCl emission factor, 150 g/kg Cl. No perchlorate compounds were detected in any of these tests. A comparison of the Cl methods is shown in Table 3-23. The XRF method results in a 10-fold lower emission factor for chloride than does the cassette method. The single sample from each method limits explanations; this could be related to the difference in the proximity of each method to its detection limit – a factor of 20 for the XRF method but only a factor of 2 for the cassette method.

Table 3-22. Chlorides emission factors from Static Fire.

Ordnance	Chloride g/kg NEQ	Perchlorate g/kg NEQ	Chlorate g/kg NEQ	HCl g/kg NEQ	Chloride g/kg Cl	Perchlorate g/kg Cl	Chlorate g/kg Cl	HCl g/kg Cl	Total Cl g/g Cl
CRV-7	5.7	ND	0.011	86	22	ND	0.042	329	0.34
MK 58	5.4	ND	0.011	30	22	ND	0.047	124	0.14

Table 3-23. Comparison of Cassette and XRF methods of Cl species measurement.

Ordnance	Cassette Chloride g/kg Cl	XRF Chloride g/kg Cl
CRV-7	22	2.5
MK 58	22	1.3

3.3.4 VOCs

A single VOC sample was derived from each of the CRV-7 and MK 58 rockets; results are shown in Table 3-24. Few detectable compounds were noted, especially for the CRV-7 rockets.

Table 3-24. VOC emission factors from Static Fire.*

Compound	CRV-7 mg/kg NEQ	MK 58 mg/kg NEQ
Vinyl Acetate	ND	1.7
Chloroform	ND	0.46
2-Hexanone	ND	0.57
n-Octane	0.63	ND
n-Nonane	ND	0.50

n-Propylbenzene	ND	0.64
4-Ethyltoluene	ND	1.0
1,3,5-Trimethylbenzene	ND	0.93
1,2,4-Trimethylbenzene	ND	ND
d-Limonene	ND	0.23
g/kg		
Carbon Monoxide	3.5	ND
Methane	ND	1.4
Carbon Dioxide	315	420
Modified combustion efficiency	0.983	0.991

* Boldface compounds are on the U.S. EPA hazardous air pollution list [19]. MCE = modified combustion efficiency.

3.3.5 PCDD/PCDF

PCDD/PCDF emission factors for the static firing of CRV-7 and MK 58 rockets are shown in Table 3-25. Emission factors for both rockets are similar to emission factors observed for biomass burns, 1-3 ng TEQ/kg. These emission factors are placed in perspective with other test ordnance factors in this effort through Figure 3-18.

Table 3-25. PCDD/PCDF TEQ and PCDD/PCDF Total emission factors from static firing of rocket motors.

	Static Fire				**Static Fire**	
Isomer.	**CRV-7 ng TEQ/kg NEQ ND=0**	**MK 58 ng TEQ/kg NEQ ND=0**		**Homologue**	**CRV-7 ng/kg NEQ**	**MK 58 ng/kg NEQ**
2,3,7,8 - TCDD	0.47	0.63		TeCDD Total	5.1	10
1,2,3,7,8 - PeCDD	ND	ND		PeCDD Total	ND	ND
1,2,3,4,7,8 - HxCDD	ND	ND		HxCDD Total	ND	3.2
1,2,3,6,7,8 - HxCDD	ND	0.063		HpCDD Total	ND	2.5
1,2,3,7,8,9 - HxCDD	ND	0.13		OCDD	5.5	5.0
1,2,3,4,6,7,8 - HpCDD	ND	0.025				
1,2,3,4,6,7,8,9 - OCDD	0.0017	0.0015				
2,3,7,8 - TCDF	ND	ND		TeCDF Total	19	63
1,2,3,7,8 - PeCDF	ND	0.076		PeCDF Total	1.8	27
2,3,4,7,8 - PeCDF	ND	0.95		HxCDF Total	19	27
1,2,3,4,7,8 - HxCDF	0.29	0.32		HpCDF Total	23	34
1,2,3,6,7,8 - HxCDF	0.29	0.32		OCDF	8.1	21
1,2,3,7,8,9 - HxCDF	0.00	0.19				
2,3,4,6,7,8 - HxCDF	0.29	0.38				

1,2,3,4,6,7,8 - HpCDF	0.13	0.14				
1,2,3,4,7,8,9 - HpCDF	0.038	0.057				
1,2,3,4,6,7,8,9 - OCDF	0.0021	0.0063				
PCDD TEQ Total	0.48	0.85		PCDD Total	11	21
PCDF TEQ Total	1.0	2.4		PCDF Total	71	171
PCDD/PCDF TEQ Total	1.5	3.3		PCDD/PCDF Total	82	192

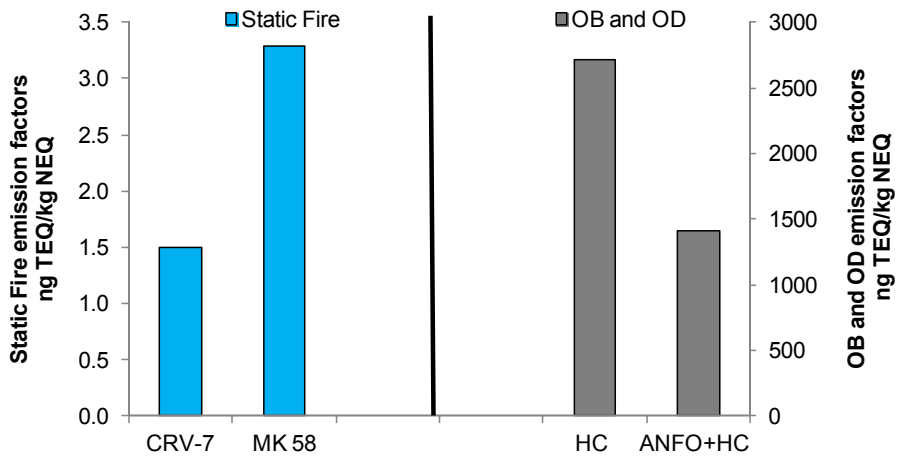


Figure 3-18. PCDD/PCDF TEQ emission factors from OB, OD, and SF.

4 Conclusions

Emission sampling was conducted with an aerostat-lofted instrument package termed the "Flyer" that was maneuvered into the downwind plumes. Forty-nine OB events, 94 OD events, and 16 SF on four propellants types (Triple base, 105 M1, 155 M4A2 white bag, and 155 M6 red bag), two smokes (HC grenade and red phosphorus), five explosive types (Trigran, C4, ANFO, ANFO+HC grenade, and ANFO+Flare), and two rocket motors types (CVR-7 and MK 58) resulted variously in emission factors for particulate matter (PM), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), volatile organic compounds (VOCs), chlorine species (HCl, chloride, chlorate, perchlorate), polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDDs/PCDFs) and PM-based metals. Additional testing would confirm the emission factors, which were derived from a limited number of replicates.

Results showed that complete combustion (lack of detectable CO) occurred during OB of triple base propellants, 105 M1 and 155 M4A2 white bag propellant, while 155 M6 red bag showed detectable levels of CO in the plume. The CO in the 155 M6 red bag plume showed a slight increase of benzene emission: 4.2 mg/kg net explosive quantity (NEQ) (4.2E-06 lb/lb net explosive weight, NEW) compared to 2.1, 0.93, and 0.029 mg/kg NEQ (2.1E-06, 9.3E-07, 2.9E-08 lb/lb NEW) for 155 M4A2 white bag, 105 M1, and triple base, respectively. The $PM_{2.5}$ emission factors were similar for the four propellant types 3.1-11 g/kg NEQ (3.1E-03 to 1.1E-02 lb/lb NEW). Continuous and simultaneous measurements of PM_1, $PM_{2.5}$, PM_{10}, and Total PM indicated that the predominant particle size was PM_1 or less. The Pb air emissions were less than 8% and 5% of the original composition for 105 M1 and 155 M6 red bag, respectively.

As designed, PM emissions from the HC grenade and red phosphorus smokes were approximately 200 and 100 times higher, respectfully, than from OB of propellant. The Zn, Cl, and K metal emissions from HC indicated that half of those metals in the grenade end up in the plume. Burning of red phosphorus showed near complete combustion of CO to CO_2 while HC smoke showed poor combustion, resulting in many detectable chlorinated VOC compounds such as vinyl chloride 8.1 mg/kg NEQ (8.1E-06 lb/lb NEW). The highest VOC emission factor for HC was benzene with a level of 589 mg/kg NEQ (5.9E-04 lb/lb NEW). Benzene for red phosphorus was lower, at 39 mg/kg NEQ (3.9E-05 lb/lb NEW), but both values were substantially higher than benzene from OB of propellant. The HC grenades showed very high emissions of PCDD/PCDF (2,700 ng TEQ/NEQ) as well as chlorinated VOCs. Detonating HC smoke with ANFO reduced the PCDD/PCDF emissions (1,400 ng TEQ/kg NEQ) by approximately 50%. Detonating HC with ANFO did not reduce the chlorinated VOCs emissions although it reduced the more common VOCs from combustion such as benzene, 1,3-butadiene, and styrene. The combined detonation of HC and ANFO did result in increases of benzene, 1,3-butadiene, and styrene than from detonations of ANFO alone. Similarly, detonation of HC with ANFO resulted in concentrations of metals such as Si, K, and Ca to levels above those attributable only to the ordnance, indicating soil entrainment into the plume. The first known emissions data for Cl species from open detonations show that 18% of the Cl is emitted as chlorides, with 7% as HCl.

Results showed that OD of explosives ranged from poor to complete combustion (modified combustion efficiencies of 0.706-0.993). Of the hydrocarbons, propene, acetonitrile, and benzene were the most predominant VOCs across all OD types. Detonating ANFO with HC smoke grenades or Flares resulted in 3-20 higher levels of benzene than from ANFO, Trigran, and C4. Time resolved PM data by size showed very similar PM_1, $PM_{2.5}$, and PM_4 mass traces within each ordnance type. PM_{10} and Total PM exhibit a slight time lag from the smaller particles, approximately 1-2 s, suggesting that the larger particles are entrained soil that lag behind the initial ordnance-derived finer PM.

Static firing of CRV-7 and MK 58 resulted in good combustion as was indicated by the few detectable VOCs as well as high modified combustion efficiency. The $PM_{2.5}$ emissions from MK 58 were twice those from the CRV-7 rockets, 34 g/kg NEQ (3.4E-02 lb/lb NEW) and 16 g/kg NEQ (1.6E-02 lb/lb NEW), respectively. HCl was found in the CRV-7 and MK 58 plumes at levels of 86

and 30 g/kg NEQ (8.6E-02 and 3.0E-02 lb/lb NEW), respectively. No perchlorate was detected but low levels of chlorate were found in the CRV-7 and MK 58 plumes. Of the total chloride amount in the CRV-7 and MK 58 ordnance, 34% and 14% was found in their respective plumes. Static Fires of CRV-7 and MK 58 resulted in detectable levels of PCDD/PCDF at 1.5 and 3.3 ng TEQ/kg NEQ, respectively.

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