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Aerostat-based sampling of emissions from open burning and open detonation of military ordnance

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HIGHLIGHTS

- PM emission factors were higher for soil-covered vs surface detonations.
- Large amounts of soil were ejected during detonations and entrained into the plumes.
- Energetics in the detonation plumes were less than 0.0005% of original munitions.
- Al-containing AP propellants showed that 7–17% of Al partitioned to the emissions.

GRAPHICAL ABSTRACT



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Emissions from open detonation (OD), open burning (OB), and static firing (SF) of obsolete military munitions were collected using an aerostat-lofted sampling instrument maneuvered into the plumes with remotely controlled tether winches. PM_{2.5}, PM₁₀, metals, volatile organic compounds (VOCs), energetics, and polycyclic aromatic hydrocarbons (PAHs) were characterized from 121 trials of three different munitions (Composition B (hereafter, “Comp B”), V453, V548), 152 trials of five different propellants (M31A1E1, M26, SPCF, Arc 451, 452A), and 12 trials with static firing of ammonium perchlorate-containing Sparrow rocket motors. Sampling was conducted with operational charge sizes and under open area conditions to determine emission levels representative of actual disposal practices. The successful application of the tethered aerostat and sampling instruments demonstrated the ability to sample for and determine the first ever emission factors for static firing of rocket motors and buried and metal-cased OD, as well as the first measurements of PM_{2.5} for OB and for surface OD.

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1. Introduction

Open burning (OB) and open detonation (OD) are used to dispose of obsolete military munitions, and static firing (SF) is used to destroy obsolete rocket motors. In OB, the materials are placed in a steel pan and ignited. In SF, the rocket motor is placed either vertically, facing down, or held in place horizontally and fired. Explosives are destroyed at ground level (surface detonation) or buried under a soil cover. In the U.S., most demilitarization facilities use the buried detonation method because they are located near population centers and want to minimize blast noise, blast overpressure, and shrapnel travel distance.

In the U.S., OB, OD and static firing are regulated under environmental permits that use pollutant dispersion models and emission factors (EFs) to set limits on the quantities of the munitions and rocket motors that can be destroyed over a specified time period. The EFs used for these permits were derived through a series of OB and uncovered OD emission plume characterization studies conducted at Dugway Proving Ground, UT (DPG) between 1989 and 1995 [1,2] and at the Nevada Test Site, NV, between 1997 and 2000 [3,4] that attempted to simulate real-world OB and OD operations. Some of the EFs were derived by flying an instrumented aircraft through OB and OD plumes produced on an open test range, but most of the EFs were derived by sampling OB and OD plumes held in a detonation chamber (BangBox). However, these efforts did not credibly address EFs for buried detonations and static fire events, and there were no PM_{2.5} (particulate matter (PM) with an aerodynamic diameter less than or equal to 2.5 μm) EFs for OB events [5], leading the U.S. Department of Defense (DOD) to conclude that open test range experiments were needed to derive the missing EFs [6].

The difficulty of open atmosphere sampling [7] and questions regarding the representativeness of small-charge and enclosed conditions from BangBox tests [8] have prompted efforts to determine and further validate representative emission factors. These efforts must address the inherent difficulty of sampling OB/OD emission plumes: rapid dispersion, short event duration, heterogeneous emission concentrations, large plume lift, soil entrainment, and explosive safety restrictions. Improvements to the sampling methods and equipment for conducting open atmosphere emissions testing for OB/OD can help to develop and verify these emission factors as well as produce a larger set of high quality emission factors that address known data gaps.

Emissions of concern include PM_{2.5} and PM₁₀ (PM with an aerodynamic diameter less than or equal to 10 μm) metals, volatile organic compounds (VOCs), energetics, and polyaromatic hydrocarbons (PAHs). PM_{2.5} can cause decreased visibility in the form of haze and is also a criteria pollutant regulated by the U.S. EPA due to its adverse health effects. VOCs are comprised of many compounds, a number of which are on the U.S. EPA's list of hazardous air pollutants (HAPs) [9]. For example, benzene is a VOC that is toxic to humans, and toluene can form ground level ozone, a criteria pollutant tied to respiratory ailments. PAHs are a large group of compounds, 16 of which are prioritized by U.S. EPA since some of them have mutagenic and carcinogenic properties [10]. Energetics such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) include toxics and possible human carcinogens [11–13].

The objective of this effort was to: (1) determine the applicability of an open air sampling methodology [14] to the first ever determination of emission factors from open detonations of metal-encased munitions and static firing of rocket motors; (2) determine distinctions in emissions from different methods of OB and OD disposal; and (3) develop methods for aerial sampling and quantification of semi-volatile energetics. Specifically, emission factors

were derived for open pan burns of single-, double-, and triple-base propellants (comprised of nitrocellulose (NC), nitroglycerin (NG), and nitroguanidine (NQ) bases), open pan burns and static firing of perchlorate-based rocket propellants, open and buried detonations of bulk explosives, and buried detonations of metal-cased munitions. These munitions were selected for this testing based on their representativeness of the U.S. demilitarization stockpile, emission uncertainties, emission factor data quality issues, and uncertainties in the analyte-specific sampling methods. Sampling was performed using a lightweight, aerostat-lofted instrument/sampling apparatus maneuvered into the OB and OD plumes for continuous monitoring and batch sample collection.

2. Experimental method

Two three-week field campaigns for OB and OD of military munitions were conducted at the Tooele Army Depot, Utah, USA, March 2011 and June 2012, respectively.

2.1. Munitions

Air emissions from OD of three different munitions (Composition B hereafter, “Comp B”, V453, V548), and OB of five different propellants (M31A1E1, M26, SPCF, Arc 451, and 452A) were characterized. In addition, air emissions from static firing of a rocket motor (Sparrow, SRM) were also characterized. Two of the propellants (Arc 451, 452A) and the rocket motor were ammonium perchlorate (AP)-based, while the SPCF was a single-base (94% NC), M26 was a double-base (67% NC and 25% NG), and M31A1E1 was a triple-base (22% NC, 18% NG, and 55% NQ). The composition of the propellants, munitions, and detonation donor charges are shown in Table 1.

2.2. Aerostat sampling method

An aerostat-borne instrument package named the “Flyer” (Fig. 1) was used to sample emissions from soil-covered and uncovered ODs, OB in pans, and static firing of rocket motors (Fig. 2). This aerial sampling method has been described in detail elsewhere [14–17]. In summary, the method used a 4.3 m-diameter helium-filled aerostat to loft the Flyer instrument package. Two all-terrain vehicles (ATVs), each mounted with a remotely controlled electric winch with 305 m-long tethers, were used to anchor and maneuver the aerostat into the emission plume. The instrumented Flyer contains an onboard computer with a data acquisition and control program and wireless communication which enables viewing data in real time as well as controlling the sampling process from the ground. During one exceptionally windy test day which precluded safe aerostat operation, two Flyers were attached to a forklift approximately 2.5 m above ground level to sample emissions.

2.3. Instrumentation, sampling and analytical methods

The instrumentation on the Flyer was varied depending on the composition of the different munition types (Table 2; Fig. 1). Carbon dioxide (CO₂) was measured continuously for all munition trials and was subject to daily three-point calibrations for CO₂ according to U.S. EPA Method 3A [18]. Energetics (HMX, RDX, and TNT) and by-product compounds were analyzed from the PM collected on a large (20.3 cm × 25.4 cm) quartz filter from the OD tests, as past experience with energetic sampling at Dugway Proving Ground [19] suggested that the airborne energetic compounds were solely associated with the particles. This assumption enabled collection of a large sample using the Flyer's high surface area filter and its high volume pump (1200 Lmin⁻¹) in an effort to minimize or eliminate non-detects. Composite samples for nitrobenzene and nitrotoluene

Table 1
Composition of the munitions and propellant test materials.^a

	Casing material	Weight (%), without casing material							NEW (kg)	GWT (kg)
		RDX	TNT	HMX	C	AP	NC/NG/NQ	Other		
Comp B	None	60	39	–	25	–	–	–	27	27
V453	Thick-wall steel	45	29	–	22	–	–	Al:21	29	64
V548	Thick-wall steel	0.32	–	86	23	–	–	Pb:0.0235, PETN: Si:Ca:trace	16	39
Electric blasting cap	Cu	4.5	–	–	73	–	–	Pb: 0.92 Plastic: 83	0.02	0.03
Non-electric blasting cap	Fe	–	–	0.28	0.046	–	–	Al:0.070 Pb: 0.0006	0.86	0.91
Demolition charge	None	90	–	–	22	–	–	Dioctyl Sebacate: 5.3	0.566	0.571
M31A1E1	None	–	–	–	18	–	22/18/55	K: 0.56	–	–
M26	None	–	–	–	25	–	67/25/0	Ba: 0.39, K: 0.27	–	–
SPCF	None	–	–	–	26	–	94/0/0	Pb: 0.78, K: 0.45	–	–
Sparrow rocket motor	None	–	–	–	11	77	–	Al: 7.5, Cl:23, Mo 0.24, Fe: 0.22	60	60
452A	None	–	–	–	9.4	69	–	Al:19, Cl:20, Fe:0.7	24.5	24.5
Arc 451	None	–	–	–	9.7	69	–	Al:19, Cl:21	24.5	24.5

^a NC–Nitrocellulose, NG–nitroglycerin, NQ–nitroguanidine, AP–ammonium perchlorate, ARC–arcadene, NEW–net explosive weight, GWT–gross weight.

were collected from multiple pan burns of M31A1E1, M26, and SPCF propellants during OB, as well as static firing of rocket motors. Similarly, due to the short sampling duration of each OB and OD, multiple events were used to create single composite samples for PAHs, PM, metals, VOCs, and energetics samples. The nitrobenzene

and nitrotoluene were analyzed with the PAHs using a method described elsewhere [14]. The target metals for the OB of propellants and rocket motors were based on the munition composition.

During some detonation series (V453 and V548), the lighter payload allowed use of a DustTrak DRX Aerosol Monitor (model

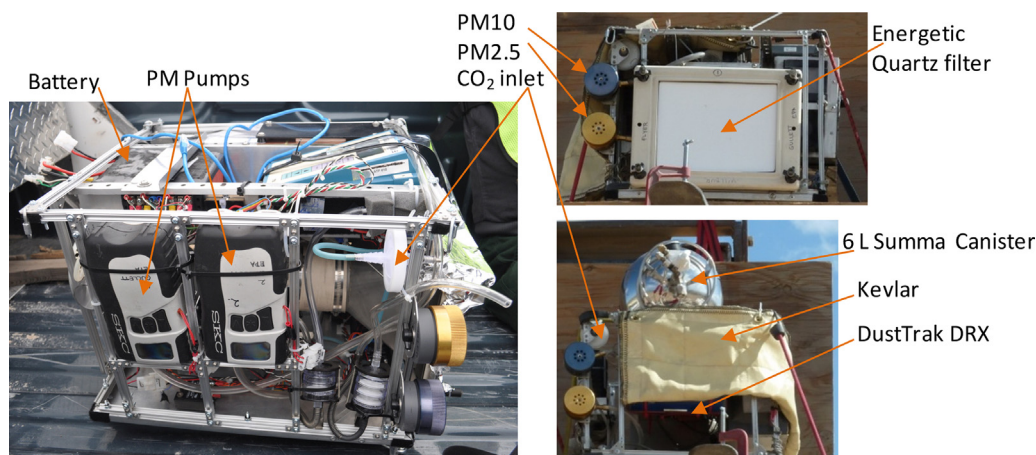


Fig. 1. Three views and configurations of the Flyer with computer and wireless transmission.



Fig. 2. Aerostat with Flyer (left) and aerostat attached to two ATVs (right).

Table 2

Analytes, instrumentation and sampling and analytical methods used for each of the ordnance studied.

Munition	Analytes	Instrument/sampling method	Mode	Sampling period/rate	Analyses
Comp B, V453, V548, 452A	PM _{2.5}	Impactor ^a , 47 mm Teflon filter (pore size 2.0 μm)	Batch	Constant 10 L min ^{-1b}	Gravimetric, method procedures in 40 CFR Part 50 [20]
All	PM ₁₀	Impactor ^a , 47 mm Teflon filter (pore size 2.0 μm)	Batch	Constant 10 L min ^{-1b}	Gravimetric, method procedures in 40 CFR Part 50 [20]
Comp B, V453, V548	Total PM		Batch	Constant 10 L min ^{-1b}	Gravimetric, method procedures in 40 CFR Part 50 [20]
V453, V548	PM ₁ , PM _{2.5} , PM ₄ , PM ₁₀ and total PM	DustTrak 8533 ^c	Continuous	Every second	Light-scattering laser photometer
Comp B, V453, V548	Energetics	Quartz filter	Batch	1200 L min ⁻¹	HPLC [21,22]
All	Metals	47 mm Teflon filter (pore size 2.0 μm)	Batch	Constant 10 L min ^{-1b}	ICP U.S. EPA Compendium Method IO-3.4. [23] or XRF U.S. EPA Compendium Method IO-3.3 [24]
M31A1E1, M26, SPCF, SRM	PAH, nitrobenzene, nitrotoluenes	Quartz filter-PUF/XAD/PUF modified U.S. EPA TO-13A [25]	Batch	650 L min ⁻¹	GC/LRMS U.S. EPA Method 8270D [26]
Comp B V548, 451, 452A	VOC	6 L SUMMA Canister/U.S. EPA Method TO-15 [27]	Batch	~15–30 s	GC/LRMS, U.S. EPA Method TO-15 [27]
M31A1E1, M26, SPCF, SRM	VOC	1 L SUMMA Canister/U.S. EPA Method TO-15 [27]	Batch	~15–30 s	GC/LRMS, U.S. EPA Method TO-15 [27]
Comp B V548, 451, 452A	CO, CO ₂	6 L SUMMA Canister/U.S. EPA Method TO-15 [27]	Batch	~15–30 s	GC, U.S. EPA Method 25C [28]
M31A1E1, M26, SPCF, SRM	CO, CO ₂	1 L SUMMA Canister/U.S. EPA Method TO-15 [27]	Batch	~15–30 s	GC, U.S. EPA Method 25C [28]
All	CO ₂	LI-COR-820 ^d	Continuous	Every second	Non-dispersive infrared (NDIR)
All	CO	RC01000F ^e	Semi-continuous ^g	Every second	Electrochemical oxidation of CO, range of 0–1000 ppm
All	Ambient pressure, elevation, and location	MTi-G ^f	Continuous	Every second	Global position system, attitude and heading reference system (AHRS), static pressure sensor

^a SKC Inc. USA.^b Leland Legacy pump, SKC Inc., USA.^c TSI Inc., USA.^d LI-COR Biosciences, USA.^e Transducer Technology Inc., USA.^f Xsens, Netherlands.^g Response time: 20–30 s.

number 8533) for continuous determination of PM concentration. Concurrently, an enclosed 37-mm pre-weighed filter cassette provides a simultaneous total PM gravimetric sample that was used to calculate a custom photometric calibration factor as per manufacturer recommendations.

The use of an additional dedicated particle size sampler and pump for total PM was deemed weight-prohibitive for the aerostat. To accommodate this constraint, the PM₁₀ samplers were modified to include the addition of a total PM filter measurement on the impactor plate of the cartridge. The total PM measurements consisted of the weight gain on a 37-mm polycarbonate filter disk pre-sprayed with Apiezon grease (1:20 mix of Apiezon grease and hexane) to minimize particle bounce and the downstream PM₁₀ filter.

2.4. Testing and sampling procedure

2.4.1. Open detonation

The detonation site consisted of a gravel/sand area surrounded by three ~7 m high berms in a U-shape to partially shelter on-site facilities (Fig. 3). Charge sizes were varied as in Table 3. Up to four series of four detonation tests were conducted each day. The metal encased munitions (V453 and V548) were detonated with 0.9 and 1.8 m (3 and 6 ft) of soil cover (Fig. 3) by being placed in

approximately 0.9 m holes and covered to ground level or 0.9 m above ground level with local soil. Bulk Comp B, which is comprised of some of the same energetics as the encased V543 munitions, was detonated at ground level (surface) and under 0.9 and 1.8 m of cover soil to characterize the emissions from unencased munitions.

Detonation plumes were sampled by downwind pre-positioning of the aerostat/Flyer at a height of 30–70 m above ground level and a distance of 100 m from the detonation site, and then repositioning after the detonation based on plume direction (Fig. 4A). Pre- and post-detonation positioning of the aerostat into the plume was accomplished by both the pilot and an observer, both in radio communication and orthogonal to each other. Movement of the aerostat/Flyer after the detonation was accomplished with line-of-sight, radio-controlled tether winches mounted on two ATVs. These winches were controlled simultaneously by the aerostat pilot. Open detonation test matrix and analytes are shown in Table 3.

2.4.2. Open burning and static firing

The propellants were placed in four reusable metal burn pans (1.5 m × 3 m × 0.4 m deep) situated on a concrete pad (~20 m × 25 m) (Fig. 3). The aerostat/Flyer was pre-positioned downwind or in some cases straight above the propellant burn site with the aid of wind socks (Fig. 4B and C). The propellant



Fig. 3. Detonation site (left), concrete burn pad with four reusable burn pans (right), and covered munitions detonations (bottom).

burns were ignited sequentially when winds blew in towards the pre-positioned aerostat/Flyer. When necessary, the aerostat/Flyer was maneuvered into the plume by reeling the tethers in or out, as guided by visual observations. The pans were brush-cleaned, allowed to cool, and reloaded after each burn series.

Static firing of Sparrow rocket motors (61 kg net explosive weight, NEW) was conducted by lowering four rockets, nose down, into underground silos, then igniting sequentially, approximately 15 s apart. The aerostat was pre-positioned downwind inside the safety zone (Fig. 4C). Personnel were evacuated to an observation bunker approximately 0.5 km distance from the rocket motors.

Upwind personnel were in radio contact to guide the position of the aerostat with respect to the plume. The open burning test matrix and target analytes are shown in Table 4.

2.5. Soil

Five soil scoops taken from a 1 m² area and combined to comprise a single sample, were gathered during the OD test series: one sample prior to all of the detonations, one sample of the soil fill staging area, and one sample after the last detonation. The purpose of these limited soil sampling efforts was a preliminary test of

Table 3
Open detonation test matrix and analytes.

Test Item	Total Number of Det'ns	Total Charge NEW (kg)	Soil Cover (m)	PM & Metal Samples by Filter		PM by light scattering DustTrack (# det'ns)	Energetics Sample	CO, CO ₂ , VOCs by Canister	CO ₂ by CEM
				Total PM/PM ₁₀ + Metals	PM _{2.5} + Metals				
Comp B	20	136	0	2	2	No	1	0	Yes
Comp B	15	136	0.90	4	4	No	4	1	Yes
Comp B	16	136	1.8	2	2	No	2	0	Yes
V453	12	88	0.90	3	3	Yes (4)	1	2	Yes
V453	12	88	1.8	3	3	No	3	0	Yes
V453	8	29	1.8			No			Yes
V548	22	48	0.90	2	2	No	3	0	Yes
V548 ^a	16	48	0.90	6	6	Yes (10)	2	1	Yes

^a Ground based air measurements due to high winds.

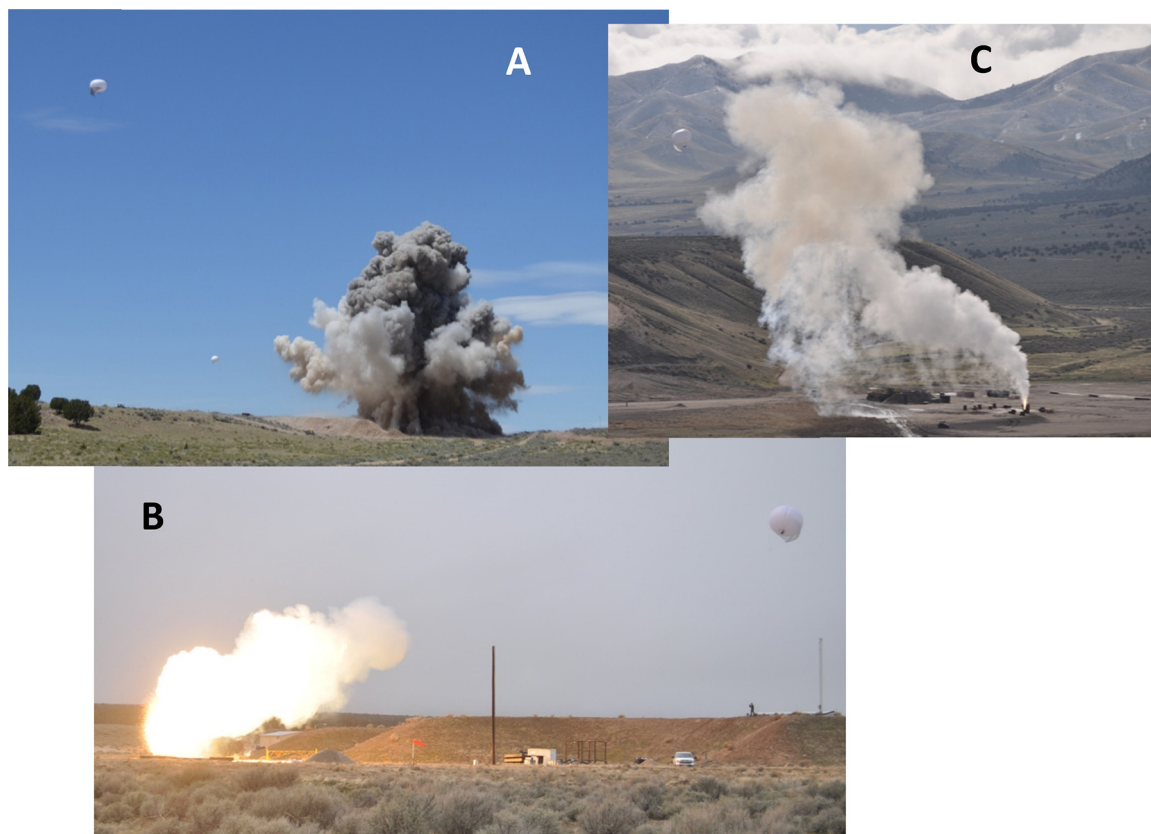


Fig. 4. Aerostat sampling of open detonation (A), open burning (B) and static firing (C).

whether metals and energetics collected from the plume emissions could be related to the existing soil content or to constituents of the munition itself. For example, the first test munition, Comp B, had no metals in its composition, so the only metals present in the emission samples should be those from the surrounding soil. Other munition types were comprised of metals unique to their formulation and not found in natural soil. Comparison of the soil composition with that of the plume sample would provide a preliminary assessment of whether the emission constituents were derived from the munition or the soil and would inform future efforts as to the efficacy of soil sampling to distinguish soil contributions.

2.6. Calculations

The carbon mass balance method (see, for example [29]) was used to calculate emission factors. In this method, the ratio of the sampled target pollutant concentration to the total sampled carbon from the detonation or burn, the latter represented by the increase in CO_2 concentration from ambient levels, ΔCO_2 , was

related back to the initial munition weight using the carbon concentration/carbon fraction in the original munition and the assumption of 100% oxidation of the carbon. The CO_2 concentration was determined using a continuous emission monitor (CEM) or, when using data from a SUMMA canister, both ΔCO_2 and ΔCO . In all emission factors, the background concentration of the target pollutant, determined from Flyer-based instruments, was subtracted from the measured amount. Emission factor calculations are shown in Appendix A.

3. Results and discussion

The Flyer successfully sampled emissions from 67% of the 121 open detonations from different munitions types and burial depths, 94% of the 152 open burns from different propellant types, and 92% of the 12 rocket motors (Table 5), as determined by the number of times that ΔCO_2 exceeded 5 ppm. Unsuccessful sampling was due to unanticipated plume paths, primarily due to wind shifts, and dilution of the plume with ambient air.

Table 4
Open burn test matrix and analytes.

Test item	Total number of burns	Charge size NEW (kg)	PM and metal samples by filter		CO, CO ₂ , VOCs by Canister	PAH	CO ₂ by CEM
			PM ₁₀ + metals	PM _{2.5} + metals			
SPCF	46	96	2	2	3	2	Yes
M26	52	146–151	2	2	5	1	Yes
M31A1E1	41	84–180	3	3	4	2	Yes
Arc 451	9	24–49	1	1	1	0	Yes
452A	4	24–49	1	0	1	0	Yes
AP Sparrow rocket motor	12	60	1	0	1	1	Yes

Table 5
Sampling success.

Ordnance	Buried depth (m)	No. of detonations/burns	No. of successful samples ^d	Successful samples (%)	Avg. plume sampling time (s)	Average ΔCO_2 (ppm)
Comp B ^a	Surface	20	15	75	13	21
Comp B ^b	Surface	16	15	94	13	21
Comp B	0.9	15	13	87	20	19
Comp B	1.8	16	8	50	8	27
V453	0.9	12	9	75	33	9
V453	1.8	20	12	60	19	5
V548	0.9	22	14	64	9	6
V548 ^c	0.9	16	10	63	18	12
M31AE1	NA	41	40	98	24	494
M26	NA	52	47	90	19	505
SPCF	NA	46	43	93	23	421
AP Sparrow Rocket Motor	NA	12	11	92	7	104
Arc AP 451	NA	9	9	100	62	88
AP 452	NA	4	4	100	64	71

^a With the first four trial detonations.

^b Without first four trial detonations.

^c Ground based sampling during high winds.

^d Number of times that ΔCO_2 exceeded 5 ppm.

3.1. Open detonation

3.1.1. PM and metals

Multiple detonations resulted in two to twelve composite PM_{10} , $\text{PM}_{2.5}$, and total PM filter samples for the seven munition type/soil cover depth scenarios. In all, 93 PM samples were collected (Fig. 5). $\text{PM}_{2.5}$ emission factors for the OD scenarios ranged from 0.42 to 13 $\text{g PM}_{2.5} \text{ g}^{-1} \text{ NEW}$ (RSD = 57%) with an average of 9.7 $\text{g PM}_{2.5} \text{ g}^{-1} \text{ NEW}$ (Table 6). The values greater than unity indicate that the majority of the $\text{PM}_{2.5}$ in the plume is derived from entrained and ejected soil rather than from particles originating from the munitions. PM_{10} emission factors range from 0.29 to 445 $\text{g PM}_{10} \text{ g}^{-1} \text{ NEW}$ with a six-trial average of 237 $\text{g PM}_{10} \text{ g}^{-1} \text{ NEW}$ (RSD = 142%). The PM_{10} emission factor for the surface detonation of Comp B, $0.29 \pm 0.13 \text{ g PM}_{10} \text{ g}^{-1} \text{ NEW}$, was quite similar to that reported for surface detonation of TNT, $0.13 \pm 0.07 \text{ g PM}_{10} \text{ g}^{-1} \text{ NEW}$ [14]. Total PM from the PM_{10} sampler ranged from 0.43 $\text{g PM total g}^{-1} \text{ NEW}$ for Comp B on the surface to 476 $\text{g PM total g}^{-1} \text{ NEW}$ for V453 with 1.8 m of soil cover. The higher PM values for soil-covered versus surface detonations are clearly due to the large amounts of soil ejected during the detonation and entrained into the plume. The higher PM_{10} versus $\text{PM}_{2.5}$ values are also likely due to the presence of relatively large sand/dirt particles characteristic of the surrounding soils. The magnitude of the relative standard deviation values between detonations reflects the extreme variation in plume appearance and, hence, particle density, underscoring a

need to sample multiple plumes to arrive at a robust PM emission factor. As for depth of soil cover, no conclusive distinction can be made between PM emission values for detonation at 0.9 and 1.8 m of cover, for both Comp B and V453. In addition, no conclusions can be made regarding the efficacy of surface versus soil-covered detonations of cased munitions, as no tests of the former were done.

Table 7 shows the EF of selected metals in the OD plume samples. Metal concentrations in the soil (mass target compound/mass soil, data not shown) were compared to those from the Flyer's plume PM samples to discern the contribution of the soil from the munition to the PM sample composition. Major soil elements showing enrichment (EF > 1) in the plume samples included Al, K, and Na while Ca and Fe showed depletion; minor elements suggesting enrichment included Zr, Hf, and Pb, while Mn showed depletion. A metal enrichment/depletion phenomenon in the plume PM samples may be due to a number of factors including (1) metals from the munition, (2) a non-uniform distribution of metals by soil particle size, accompanied by a particle size bias in the plume sample (larger particles are less likely to be captured), and (3) selective post-explosive deposition of metals on small, high surface area particles. Consideration of Zr and Hf highlights these factors.

One munition, V453, contains Zr and Hf, metals not typically found in the soil, allowing for a possible distinction between soil and munition contributions to the PM. The V453 Total PM emission factors for Zr and Hf (g g^{-1} metal expressed as a %) for the 0.9 and 1.8 m soil-covered detonations ranged between 0.42% and

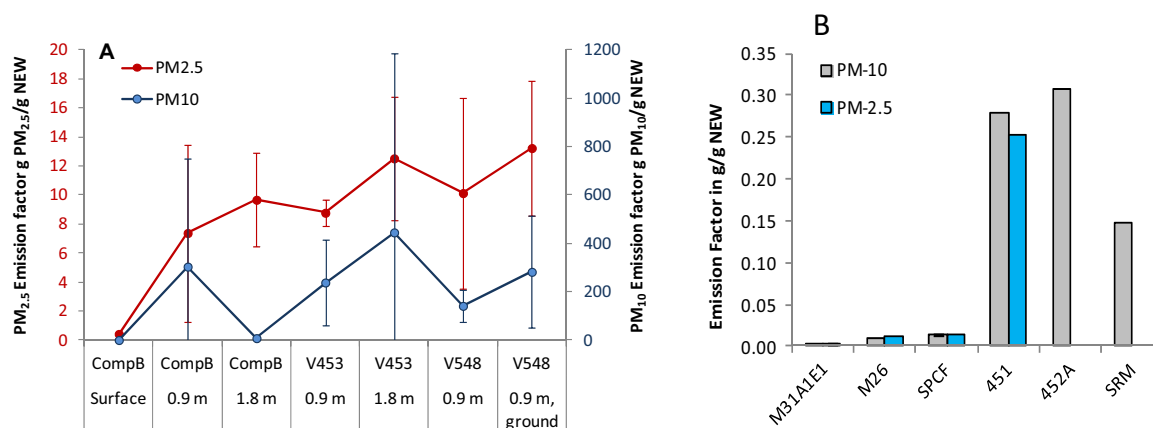


Fig. 5. PM_{10} and $\text{PM}_{2.5}$ emission factors from OD of munitions (A), OB of propellant and rocket motor, SRM (B). Error bars denote one standard deviation (Comp B–0.9 m, V453, V458–0.9 m ground, M31AE1) or range of data (Comp B–surface and 1.8 m, V458–0.9 m, M26 and SPCF).

Table 6Emission factor from open detonation of three munitions and buried depth.^a

Pollutant	Comp B surface	Comp B 0.9 m	Comp B 1.8 m	V453 0.9 m	V453 1.8 m	V548 0.9 m	V548 0.9 m, ground based sampling
PM ₁₀ (g g ⁻¹ NEW)	0.29	304	8.0	238	445	141	282
PM _{2.5} (g g ⁻¹ NEW)	0.42	7.4	9.7	8.8	13	10	13
HMX-Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (g g ⁻¹ C)	5.0E-07	2.6E-06 ± 2.9E-06	1.9E-06 ± 1.1E-06 ^b	5.8E-06	4.7E-06	3.6E-04 ± 3.5E-04 ^b	1.1E-04
HMX-Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (g g ⁻¹ HMX)	DNA	DNA	DNA	DNA	DNA	9.6E-05 ± 4.6E-05 ^b	3.0E-05
RDX-Hexahydro-1,3,5-trinitro-1,3,5-triazine (g g ⁻¹ C)	2.6E-06	7.9E-06 ± 1.1E-06	4.6E-06 ± 2.8E-06 ^b	5.6E-06	5.2E-06	ND	1.1E-06
RDX-Hexahydro-1,3,5-trinitro-1,3,5-triazine (g g ⁻¹ RDX)	1.1E-06	3.3E-06 ± 4.5E-06	1.9E-06 ± 1.2E-06 ^b	2.8E-06	2.5E-06	ND	7.5E-05
TNT-2,4,6-Trinitrotoluene (g g ⁻¹ C)	2.6E-06	8.4E-06 ± 8.1E-06 ^b	1.7E-06 ± 1.3E-06 ^b	ND	ND	ND	ND
TNT-2,4,6-Trinitrotoluene (g g ⁻¹ TNT)	1.7E-06	5.4E-06 ± 5.2E-06 ^b	1.1E-06 ± 8.7E-07 ^b	ND	ND	DNA	DNA
PETN-Pentaerythritol tetranitrate (g g ⁻¹ C)	2.6E-07	5.5E-07 ± 2.3E-08	ND	5.8E-06	ND	ND	4.7E-06
PETN-Pentaerythritol tetranitrate (g g ⁻¹ PETN)	DNA	DNA	DNA	DNA	DNA	ND	0.22
Tetryl-methyl-2,4,6-trinitrophenylnitramine (g g ⁻¹ C)	ND	ND	ND	ND	ND	ND	ND
1,3,5-Trinitrobenzene (g g ⁻¹ C)	ND	ND	ND	ND	ND	ND	ND
1,3-Dinitrobenzene (g g ⁻¹ C)	ND	ND	ND	ND	ND	ND	ND
4-Amino-2,6-dinitrotoluene (g g ⁻¹ C)	ND	ND	ND	ND	ND	ND	ND
2-Amino-4,6-dinitrotoluene (g g ⁻¹ C)	1.0E-07	6.5E-07 ± 6.8E-07	5.3E-07 ± 4.7E-08 ^b	3.0E-06	2.1E-06 ± 1.6E-07	1.3E-06	ND
2,4-Dinitrotoluene (g g ⁻¹ C)	1.0E-06	1.1E-05 ± 4.2E-06	8.9E-06 ± 6.9E-07 ^b	ND	ND	ND	ND
2,6-Dinitrotoluene (g g ⁻¹ C)	ND	ND	ND	ND	ND	ND	ND
3,5-Dinitroaniline (g g ⁻¹ C)	ND	ND	ND	2.4E-06	2.5E-06	ND	ND
Benzene (g g ⁻¹ C)	NS	3.5E-04	NS	1.2E-03 ± 2.2E-04 ^b	NS	NS	2.0E-03
Toluene (g g ⁻¹ C)	NS	1.5E-04	NS	6.7E-04 ± 4.9E-04 ^b	NS	NS	8.1E-04
Ethylbenzene (g g ⁻¹ C)	NS	ND	NS	8.1E-04 ± 6.1E-05 ^b	NS	NS	5.8E-05
Sum xylene (g g ⁻¹ C)	NS	7.0E-05	NS	2.5E-04	NS	NS	ND
1,2,4-Trimethylbenzene (g g ⁻¹ C)	NS	3.7E-05	NS	4.5E-05	NS	NS	ND
ΔCO ₂ (ppm) from SUMMA Canister	NS	90	NS	15 ± 5 ^b	NS	NS	20 ^c
ΔCO (ppm) from SUMMA Canister	NS	100	NS	13 ± 3 ^b	NS	NS	11

^a FS—Failure during sampling. Metals emission factors from PM_{2.5} within brackets. ND—not detected. NS—not sampled. DNA—does not apply. Error equals 1 STDV. RDX values 1-6 times higher than detection limit (DL), benzene values 13-67 times higher than DL, metal values 1-20 times higher than DL.

^b Range of data.

^c CO₂ from the simultaneous CEM data—SUMMA CO₂ was below ambient background level.

Table 7
Metal emission factors from open detonation in $g\ g^{-1}$ metal.^a

		PM _{2.5} ($g\ g^{-1}$ metal)							Total PM ($g\ g^{-1}$ metal) ^b					
		Al	Hf	Zr	Fe	Mn	Pb	Cr	Al	Hf	Zr	Fe	Mn	Pb
V453 0.9 m	Avg	1.9	0.0027	0.0049	0.087	0.25	DNA	0.20	1.8	0.012	0.010	0.27	0.82	DNA
	N	3	1	3	3	3	DNA	3	3	1	3	3	3	DNA
	SD	1.4	DNA	0.0017	0.026	0.072	DNA	0.045	0.31	DNA	0.0025	0.072	0.23	DNA
		PM ₁₀ ($g\ g^{-1}$ metal)												
		Al	Hf	Zr	Fe	Mn	Pb	Cr	Al	Hf	Zr	Fe	Mn	Pb
V453 0.9 m	Avg		0.92	0.012	0.0042	0.089	0.25	DNA	0.22	0.012	0.57	1.7	DNA	0.22
	N		3	1	3	3	3	3	3	2	3	3	3	3
	SD		0.39	DNA	0.0013	0.017	0.049	DNA	0.072	0.20	0.54	DNA	0.23	DNA
		PM _{2.5} ($g\ g^{-1}$ metal)							Total PM ($g\ g^{-1}$ metal)					
		Al	Hf	Zr	Fe	Mn	Pb	Cr	Al	Hf	Zr	Fe	Mn	Pb
V453 1.8 m	Avg	1.8	0.093	0.0084	0.20	0.46	DNA	0.48	3.7	0.22	0.012	0.57	1.7	DNA
	N	3	2	3	3	3	DNA	3	3	2	3	3	3	DNA
	SD	1.1	0.036 ^c	0.0040	0.12	0.26	DNA	0.21	1.3	0.15 ^c	0.0072	0.20	0.54	DNA
		PM ₁₀ ($g\ g^{-1}$ metal)												
		Al	Hf	Zr	Fe	Mn	Pb	Cr	Al	Hf	Zr	Fe	Mn	Pb
V453 1.8 m	Avg		1.2	0.22	0.0078	0.25	0.60	DNA	0.22	0.012	0.57	1.7	DNA	0.22
	N		3	2	3	3	3	3	3	2	3	3	3	3
	SD		0.50	0.15 ^c	0.0024	0.076	0.14	DNA	0.072	0.20	0.54	DNA	0.23	DNA
		PM _{2.5} ($g\ g^{-1}$ metal)							Total PM ($g\ g^{-1}$ metal)					
		Al	Hf	Zr	Fe	Mn	Pb	Cr	Al	Hf	Zr	Fe	Mn	Pb
V548 0.9 m	Avg	6.9	DNA	DNA	0.11	0.44	1.5	0.22	45	DNA	DNA	1.4	5.6	13
	N	8	DNA	DNA	8	8	8	8	8	DNA	DNA	8	8	8
	SD	5.3	DNA	DNA	0.077	0.35	1.2	0.26	37	DNA	DNA	1.3	5.1	5.8
		PM ₁₀ ($g\ g^{-1}$ metal)												
		Al	Hf	Zr	Fe	Mn	Pb	Cr	Al	Hf	Zr	Fe	Mn	Pb
V548 0.9 m	Avg		1.1	DNA	DNA	0.20	0.84	2.8	0.20	0.84	2.8	0.42	0.42	0.42
	N		8	DNA	DNA	8	8	8	8	8	8	8	8	8
	SD		0.57	DNA	DNA	0.10	0.45	1.4	0.10	0.45	1.4	0.31	0.31	0.31

^aDNA = Does not apply; metal is not in munition composition. N = number of samples. SD = standard deviation.
^bTotal PM results from PM₁₀ impactor.
^cAbsolute difference divided by two.

22%, which shows that only a small fraction of these metals become airborne.

3.1.2. Energetics and by-products

The background soil sample, taken prior to detonations, showed trace amounts of TNT (Fig. 6), likely reflecting the considerable amount of prior TNT testing that had been done on this test site. In addition, since the initial soil cover was comprised of large numbers of rocks that caused safety and equipment hazards upon detonation, the cover material was replaced with fine local sand after

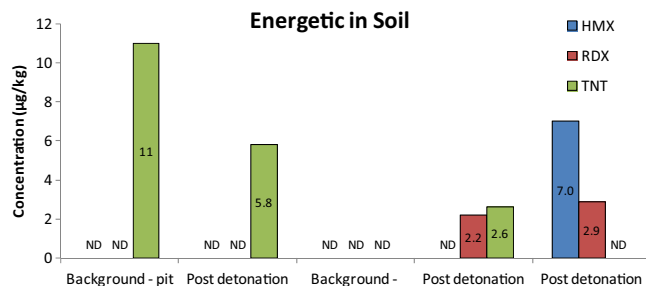


Fig. 6. HMX, RDX, and TNT concentration in soil, pre- and post-detonation.

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the Comp B detonation test series and prior to the onset of V453 detonations. This fine sand showed no detectable energetic levels.

Energetics emission factors are shown in Table 6 and Fig. 7. Results are normalized by mass of energetics in the ordnance and

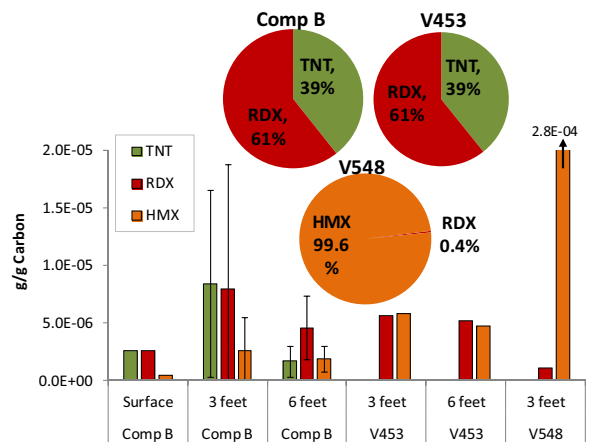


Fig. 7. Energetics in air samples from different munitions and burial depths; tests shown in chronological order. Error bars denote one standard deviation (Comp B—0.9 m, V548—0.9 m) or range of data (Comp B—1.8 m, V453—1.8 m).

Table 8Emission factor from open burning of five propellants and one rocket motor.^a

Pollutant	M31A1E1	M26	SPCF	Arc 451	452A	Sparrow Rocket Motor
PM ₁₀ (g g ⁻¹ NEW)	4.0E-03 ± 5.0E-04 ^b	1.1E-02 ± 1.0E-04 ^c	1.4E-02 ± 3.8E-04 ^c	2.8E-01	3.1E-01	1.2E-01
PM _{2.5} (g g ⁻¹ NEW)	3.6E-03 ± 4.0E-04 ^b	1.1E-02 ± 6.3E-04 ^c	1.5E-02 ± 1.1E-04 ^c	2.5E-01	NS	NS
K (g g ⁻¹ K)	1.6E-01 ± 2.1E-02 ^b [1.5E-01 ± 2.0E-01 ^b]	6.5E-01 ± 1.1E-02 ^c [6.5E-01 ± 1.0E-02 ^c]	5.3E-01 ± 2.3E-02 ^c [5.3E-01 ± 1.9E-02 ^c]	NA	NA	NA
Ba (g g ⁻¹ Ba)	NA	6.6E-01 ± 3.9E-03 ^c [6.3E-01 ± 2.4E-03 ^c]	NA	NA	NA	NA
Pb (g g ⁻¹ Pb)	NA	NA	7.9E-01 ± 2.0E-02 ^c [7.8E-01 ± 1.9E-02 ^c]	NA	NA	NA
Al (g g ⁻¹ Al)	NA	NA	NA	7.2E-02 [6.8E-02]	1.0E-01	1.7E-01
Fe (g g ⁻¹ Fe)	NA	NA	NA	NA	1.1E-01	2.2E-00
Mo (g g ⁻¹ Mo)	NA	NA	NA	NA	NA	2.2E-00
Nitrobenzene (g g ⁻¹ C)	4.0E-06 ± 1.5E-06 ^c	1.4E-07	ND	NS	NS	ND
Nitrotoluenes (g g ⁻¹ C)	2.1E-07	ND	ND	NS	NS	ND
Naphthalene (g g ⁻¹ C)	6.7E-06 ± 2.1E-07 ^c	1.2E-07	1.0E-07 ± 2.7E-08 ^c	NS	NS	8.4E-07
Acenaphthylene (g g ⁻¹ C)	2.1E-07 ± 5.0E-08 ^c	2.9E-08	2.1E-08 ± 2.0E-08 ^c	NS	NS	5.3E-08
Acenaphthene (g g ⁻¹ C)	1.2E-07 ± 2.9E-08 ^c	8.5E-09	9.3E-09 ± 2.7E-09 ^c	NS	NS	ND
Fluorene (g g ⁻¹ C)	5.9E-07 ± 1.1E-08 ^c	3.3E-08	3.1E-08 ± 1.4E-08 ^c	NS	NS	1.6E-07
Phenanthrene (g g ⁻¹ C)	6.1E-07 ± 2.8E-07 ^c	6.2E-08	1.0E-07 ± 4.9E-08 ^c	NS	NS	5.5E-07
Anthracene (g g ⁻¹ C)	4.8E-08 ± 2.5E-08 ^c	3.8E-09	7.4E-09 ± 5.2E-09 ^c	NS	NS	5.7E-08
Fluoranthene (g g ⁻¹ C)	8.2E-08 ± 4.9E-08 ^c	1.7E-08	2.0E-08 ± 8.5E-09 ^c	NS	NS	1.9E-07
Pyrene (g g ⁻¹ C)	6.4E-08 ± 3.9E-08 ^c	1.2E-08	1.6E-08 ± 7.0E-09 ^c	NS	NS	ND
Chrysene (g g ⁻¹ C)	ND	ND	9.3E-09	NS	NS	ND
Benzene (g g ⁻¹ C)	1.1E-05 ± 1.2E-05 ^b	1.1E-05 ± 5.5E-06 ^b	ND	ND	ND	ND
Toluene (g g ⁻¹ C)	2.3E-04 ± 2.3E-04 ^b	6.7E-06 ± 1.2E-05 ^b	4.2E-06 ± 1.6E-06 ^c	BBL	BBL	4.1E-05
Ethylbenzene (g g ⁻¹ C)	2.2E-05 ± 1.7E-05 ^b	9.8E-06	8.7E-06	ND	ND	ND
Sum Xylene (g g ⁻¹ C)	1.3E-04 ± 9.4E-05 ^b	2.5E-05 ± 2.5E-05 ^b	4.1E-05 ± 3.3E-06 ^c	ND	ND	1.1E-04
1,2,4-Trimethylbenzene (g g ⁻¹ C)	3.4E-05 ± 2.2E-05 ^b	1.4E-05 ± 1.2E-05 ^b	4.3E-05 ± 6.4E-05 ^b	ND	ND	5.6E-05
ΔCO ₂ (ppm) from SUMMA Canister	403 ± 195 ^b	678 ± 757 ^b	427 ± 243 ^b	80	30	20
ΔCO (ppm) from SUMMA Canister	ND	ND	ND	ND	ND	ND

^a Metals emission factors from PM_{2.5} within brackets. ND—Not detected. BBL—Below background levels. NS—Not sampled. NA—Not analyzed. Naphthalene values 25 to >3000 times higher than detection limit (DL), Benzene values 2–8 times higher than DL, Metal values >100 times higher than DL, PM_{2.5} values >215 times higher than DL.

^b 1 STDV.

^c Range of data.

per mass of C, the latter expression to account for energetics that are sampled but not in the original ordnance. Comp B detonations showed detectable levels of RDX, TNT, and HMX despite the apparent lack of the latter in the formulation. However, RDX has been reported to contain minor amounts (4 to 15% by weight) of HMX [1]. The detonation cord used in all of the tests consisted of 80% HMX, so both of these sources may have contributed HMX. A single sample from Comp B surface detonation plumes shows residual RDX and TNT both to be less than 2 ppm as a mass ratio with the original energetics (data derived from Fig. 7). A similar value for HMX is approximated, as the composition of HMX is uncertain.

V453 plumes ($n=2$) showed no TNT emissions despite a 39% TNT composition, suggesting that all of its TNT is quantitatively combusted. Similarly, the background sand fill provided no TNT contributions to the plume sample as it was found free of energetics (Fig. 6) prior to the OD 453 testing. Assuming that the TNT in Comp B also combusts quantitatively, these observations suggest that the TNT observed from Comp B emissions may have been due solely to entrainment of TNT found in the background pit soil. V453 similarly shows that the plume contains only approximately 2 ppm of RDX in mass per initial RDX mass. As with Comp B, comparable levels of HMX are recorded despite the absence of known levels of HMX in the original composition.

The energetics emissions from V548 had an HMX emission factor approximately fifty times higher than the other munitions studied; the presence of HMX could be expected since 86% of V548 contains HMX (Fig. 7). Based on ratios with measured carbon in the emissions and the munition, $0.007\% \pm 0.006$ of the total amount of HMX (in NEW) in V548 was found in the air samples. The significantly larger HMX concentration from V548 and the relatively high post-detonation soil concentration of HMX suggest that the soil-covered detonation of V548 results in proportionately higher unexploded energetics than the other munition.

The limited number of samples and the range of data show no convincing distinction between energetics emission factors for surface and soil-covered Comp B detonations nor between 0.9 and 1.8 m burial depths of V453.

3.1.3. VOCs

A limited number of SUMMA canister samples for VOCs were collected, each sample representing a composite from multiple plumes (Table 6). VOCs detected from the SUMMA canister included the common combustion products benzene, toluene, ethylbenzene, and xylene (BTEX) as well as other compounds. The BTEX compounds for the three munitions types, each covered with 0.9 m of soil, had emission factors in the $10E-3$ to $10E-4$ $g\ g^{-1}\ C$ range. Good agreement was noted for the benzene emission factors for Comp B ($3.5E-04$ $g\ g^{-1}\ C$) (buried 0.9 m) (Table 6), which is in the range of earlier reported emission factors of surface-detonated TNT ($7.3E-04$ $g\ g^{-1}\ C$ [14] and $2.6E-04$ $g\ g^{-1}\ C$ [19]) and Comp B from BangBox tests of $1.0E-05$ $g/g\ C$ [1].

CO and CO₂ from the canisters were also sampled; surprisingly, CO was detected at levels near those of the CO₂ concentrations, implying an incomplete carbon oxidation (Table 6). However, these results are based on a limited number of samples ($n=3$) and should be verified by additional testing.

3.2. Open burning of propellants and static firing of rockets

3.2.1. PM and metals

The PM₁₀ and PM_{2.5} emission factors for M31A1E1, M26, and SPCF propellants were very similar, as was the coefficient of variance and relative percent difference for each propellant's trials (1.4–12%) (Fig. 5), suggesting that the majority of the mass was less than 2.5 μm in size. The AP-based, aluminum-containing propellants (Arc 451, 452A and SRM) had PM₁₀ emission factors

substantially (9–77 times higher) larger than the non-AP-based propellants (Fig. 5 and Table 8). The AP-based propellant PM₁₀ emission factors are also similar (factor of 1.5–4 lower) to those derived from aluminized AP propellant from BangBox tests [1], but higher (factor of 20) than non-aluminized AP BangBox propellant tests. Comparison of the open pan burns of Arc 451 and 452A show higher PM₁₀ emission factors (about 2 times) than the single trial with static firing of the Sparrow rocket motors (SRMs), suggesting that the method of treatment influences the emissions. Metal emission data are shown in Table 8. The Pb emission factor for SPCF indicates that approximately 80% of the Pb found in the propellants is accounted for in the emission measurements. For the Sparrow rockets, Arc 451, and 452A, the Al measurements show that only 17%, 7.2%, and 10% of the Al, respectively, was accounted for in the emissions, consistent with literature data showing a 7% Al recovery from Al-AP propellant [1]. Values less than 100% suggest that the metals unaccounted for in the emissions remain as ash in the pan or are present in larger particles that did not reach the lofted sampler in the plume.

3.2.2. PAH

Ten of the 16 “EPA PAHs” plus nitrobenzene and nitrotoluenes were detected (Table 8). The naphthalene emission factor for the triple-base propellant (M31A1E1) was approximately 30 times higher than the single- and double-base propellants (SPCF and M26). The single- and double-base propellant emission factors (SPCF and M26) were similar (factor of 0.3–4.7) to the previously derived emission factors from open atmosphere testing [19]. The naphthalene emission factor for the sparrow rocket motor ($8.9E-08$ $g\ g^{-1}\ \text{NEW}$) was 7–20 times lower than emission factors derived from an open atmosphere tested manufacturing propellant residue (AP propellant) ($1.5E-06$ and $5.4E-07$ $g\ g^{-1}\ \text{NEW}$ [19]) and BangBox test of AP propellant ($1.4E-06$ $g\ g^{-1}\ \text{NEW}$ [30]). The double-base propellant (M26) emission factor was five times lower than BangBox test of double-base propellant [30] while the emission factor for M31A1E1 was considerably higher ($1.2E-06$ $g\ g^{-1}\ \text{NEW}$) compared to a BangBox-derived emission factor ($6.1E-10$ $g\ g^{-1}\ \text{NEW}$) [31].

3.2.3. VOCs

Detectable VOC levels were observed from the limited number of single-, double- and triple-base propellants that SUMMA canisters sampled while the AP-based samples were either non-detect or below background levels, indicating more complete combustion. The benzene emission factor was $1.1E-05$ $g\ g^{-1}\ C$ for triple-base (M31A1E1) and $1.1E-05$ $g\ g^{-1}\ C$ for double-base (M26) propellants, which is in the same range as from previous triple and double-base propellant burn tests from BangBox ($2.8E-06$ and $4.8E-06$ $g\ g^{-1}\ C$ [30,31]).

The ΔCO_2 values in each of the AP propellant SUMMA canisters were low compared to the non-AP propellants, 20–90 and 400–680 ppm, respectively. No CO was detected in any of the SUMMA canisters. These results are consistent with expectations as the AP propellant has a lower carbon fraction (~ 0.10) than the single- to triple-base propellants (0.18–0.29).

4. Conclusion

An aerostat-lofted instrument and sampling apparatus was successfully deployed into the plumes from open burning and open detonation of military munitions. Emissions were successfully collected from OB of five propellant types (M31A1E1, M26, SPCF, Arc 451, 452A), static firing of Sparrow rocket motors, and OD of three munitions (Comp B, V453, V548) with varied soil cover depth. In many cases, these data represent the first emission factors of their

type available or are the first measurements taken under representative conditions of open air detonations/burning.

PM emission factors are significantly higher for soil-covered versus surface detonations due to the large amounts of soil ejected during the detonation and entrained into the plume. The $PM_{10}/PM_{2.5}$ ratio for covered detonations is approximately 30/1; for open detonation of Comp B, the ratio is about 1/1, reflecting the large amount of surface soil particles ejected and entrained during soil-covered detonations.

Limited data on metals unambiguously originating from the detonating munitions showed between 0.3% and 22% of the metal transferred to the air emissions with the majority of the data indicating approximately 1% transferral or less.

Energetics data, often limited to single samples, show that energetics in the detonation plumes were less than 0.0005% of the original munitions. Limited data on the volatile BTEX combustion byproducts from detonations showed their individual emissions to be typically less than 0.05% by mass of the munition.

The PM_{10} and $PM_{2.5}$ emission factors for OB of non-AP-based propellants were similar and less than 2% of the propellant mass; single samples from AP-based propellants resulted in PM_{10} emission factors that were about 10–20 times higher, 15–30% of the propellant weight. For Al-containing AP propellants, limited trials showed 7–17% of the Al partitioned to the emissions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2014.10.029>

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