Characterization of Air Emissions from Open Burning at the Radford Army Ammunition Plant

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Abstract

The Department of the Army (PD Joint Services, Picatinny Arsenal) commissioned NASA-Ames to fly their unmanned aerial vehicle (UAV), a hexacopter, into the plumes from open burning of propellant and manufacturing discards at the Radford Army Ammunition Plant while carrying a gas and particle sensor system designed and operated by the EPA Office of Research and Development (ORD). Over a 2-week period the NASA/ORD team sampled 33 plumes, determining emissions factors for particulate matter, metals, chloride, perchlorate, volatile organic compounds, chlorinated dioxins/furans, and nitrogen-based organics. Results show agreement with published emission factors and good reproducibility (e.g., 11% relative standard deviation for $PM_{2.5}$). The UAS/sampler presents a significant advance in emission characterization capabilities for open area sources, safely and effectively making measurements heretofore deemed too hazardous for personnel or beyond the reach of land-based samplers.

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List of Acronyms

CO	Carbon monoxide
CO_2	Carbon dioxide
Cr(VI)	Chromium VI
DOD	U.S. Department of Defense
DQI	Data Quality Indicator
EF	Emission Factor
EPA	U. S. Environmental Protection Agency
FOD	Foreign object debris
GC	Gas chromatography
GPS	Global positioning system
HCl	Hydrogen chloride
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	High-Performance Liquid Chromatography
IC	Ion chromatography
ICP	Inductively coupled plasma
LC	Liquid chromatography
LRGC	Low resolution gas chromatography
LRMS	Low resolution mass spectrometer
MCE	Mixed cellulose ester
MK-90	MK-90 rocket motors
NASA	National Aeronautics and Space Administration
NC	Nitrocellulose
NDIR	Non-dispersive infrared
NG	Nitroglycerine

NIST	National Institute for Standards and Technology
NO	Nitrogen oxide
NO_2	Nitrogen dioxide
NRE	New river energetics
OB/ OD	Open burning/Open detonation
OBG	Open burning ground
OD	Outer diameter
ORD	Office of Research and Development
$PM_{2.5}$	Particulate matter equal to and less than 2.5 µm
PUF	Polyurethane foam
QA	Quality Assurance
QAPP	Quality assurance project plan
RDX	Research Department Formula X, 1,3,5-Trinitroperhydro-1,3,5-triazine
RFAAP	Radford Army Ammunition Plant
RPD	Relative percent difference
SD	Secure digital
SDS	Safety Data Sheets
SIM	Selective ion monitoring
SRM	Standard reference material
SVOC	Semivolatile organic compounds
UAV	Unmanned aerial vehicle
UDRI	University of Dayton Research Institute
USB	Universal serial bus
VOCs	Volatile organic compounds
XRF	x-ray fluorescence spectrometry

1. Introduction

1.1 Brief

The Radford Army Ammunition Plant (RFAAP) conducts on-site disposal of a variety of hazardous energetic wastes via open burn pans located at the facility's open burning ground (OBG). Data on potential combustion emissions and their emission factors are available only from small laboratory and pilot scale simulations and their relevance to the RFAAP's scenario is uncertain. To resolve this issue, the RFAAP asked the U.S. Environmental Protection Agency's (EPA) Office of Research and Development (ORD) to perform direct sampling and quantification of the RFAAP's OBG emissions. ORD has considerable experience sampling emissions from open burning and open detonation (OB/OD) of military ordnance and static firing of rocket motors (for example, see Aurell et al. [1]). Since 2010, ORD has worked with the Department of Defense's (DoD's) Joint Munitions Command (and their predecessor, the Defense Ammunition Center), the Army Corps of Engineers, and the Defence Research and Development Canada -Valcartier to sample OB/OD emissions at three sites in the US and Canada. ORD has developed a suite of technologies for sampling an array of OB/OD emission constituents from both aerial and ground-based sampling platforms. These sampling methods have been developed over the last five years and include novel methods employing small sensors and samplers, necessitated by the challenge of sampling within a plume located several hundred feet in the open air. To transport ORD's emission sensors/samplers into the plumes, RFAAP entered into an Interagency Agreement with the National Aeronautics and Space Agency, Ames Research Center (NASA Ames) for them to pilot their hexacopter unmanned aerial vehicle (UAV).

1.2 Objective

The objective of this work was to characterize and quantify emissions from open burning of dry propellant burns (MK-90 rocket motors) and so-called "skid burns", which are a combination of process wastes from onsite production operations. This skid waste is generally a combination of energetic material, soil, gravel, and other foreign object debris (FOD). Skid burns are what the facility refers to as "assisted burns," where the materials are placed on wooden skids, and nested with dunnage and diesel fuel to promote burning. Quantification of the emissions includes determination of emission factors relating the amount of compound emitted to the amount present in the original material.

2 Materials and Methods

2.1 Test Site Location and Description

The sampling was conducted at the Radford Army Ammunition Plant (RFAAP) in the mountains of southwest Virginia, approximately five miles northeast of the city of Radford, Virginia.

RFAAP lies along the New River in the relatively narrow northeastern corner of the valley. Approximate GPS coordinates are 37.1925 N, 80.5233 W. Figure 2-1 shows an overview of the RFAAP burn pan site.

Figure 2-1. Overhead View of RFAAP Burn Pan Site.

2.2 Test Ordnance and Test Schedule

Two fuel sources were sampled: dry propellant burns (MK-90) and skid burns (two types). The test schedule is shown in Table 2-1. The composition of these fuel sources, particularly metals, is critical toward assessing the environmental fate of the constituents. Knowledge of the carbon content of the fuel is required for determination of emission factors, as explained in 2.5.1, below.

Table 2-1. Test schedule, amount of total pan load and amount of waste burned per test day.

Test Date	Fuel	Amount of burn pans	Amount of Total pan load lb (kg)	Amount of Total waste lb (kg)
09/27/2016	MK-90	5	3,000 (1,364)	3,000 (1,364)
09/28/2016	Skid waste: Type 1	3	3,254 (1,479)	1,620 (736)
09/29/2016	MK-90	5	3,000 (1,364)	3,000 (1,364)
09/30/2016	Skid waste: Type 2	2	1,589 (722)	500 (227)
10/03/2016	MK-90	5	3,000 (1,364)	3,000 (1,364)
10/04/2016	Skid waste: Type 1	3	3,254 (1,479)	1,620 (736)
10/05/2016	MK-90	5	3,000 (1,364)	3,000 (1,364)
10/06/2016	Skid waste: Type 2	2	1,589 (722)	500 (227)

2.2.1 MK-90

The test MK-90 composition was constant for all burn tests as shown in Table 2-2. Data were derived from two sources in order to complete the carbon composition. Safety Data Sheet (SDS) compositional data were used to supplement RFAAP laboratory analyzed composition data where components such as nitrocellulose were missing (see footnote "a" in Table 2-2). Each burn pan charge was comprised of 99% MK-90 and 1% NRE contaminated waste, by weight, as shown in Table 2-2.

Table 2-2. Constituents in each burn pan of "MK-90" burns.

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2.2.2 Skid Waste

Two different types of skid waste compositions were tested as shown in Figure 2-2. The main difference between the two skid waste types were the chlorine, lead, copper, and chrome fractions. Skid waste type 1 was designed to be a high chlorine burn and skid waste type 2 was a high metals burn. The majority of the carbon in the skid waste originated from the wood pallets (Table 2-3). Both skid waste types contained the same number of wood pallets, however, skid waste type 2 contained 26% more carbon than skid waste type 1 due to a higher mass fraction of pallets (less waste mass in type 2).

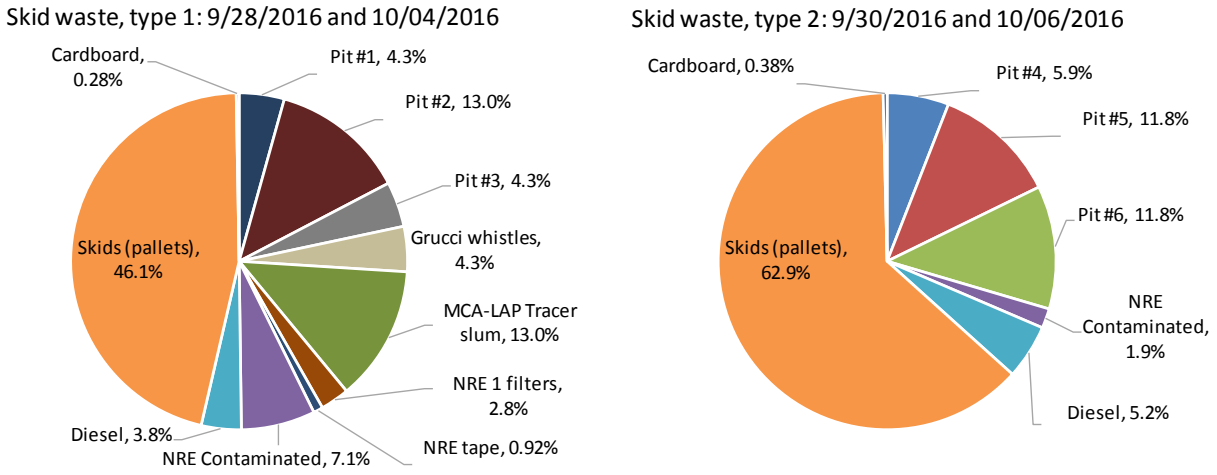

Figure 2-2. Composition of the two types of skid wastes tested, type 1 (left, total mass 3,254 lbs.) and type 2 (right, total mass 1,589 lbs.).

Table 2-3. Skid waste carbon and metal fraction.

Waste type/ Test Dates	Composition	Carbon Fraction of each component	Carbon fraction in burn pan

Waste type/ Test Dates	Composition	Carbon Fraction of each component	Carbon fraction in burn pan
Skid waste Type 1 09/28/2016 and 10/04/2016	Pallets 46%	0.502[a]	0.23
	Cardboard 0.28%	0.46[b]	0.0013
	Diesel 3.8%	0.86[b]	0.033
	Pit #1 4.3%	0.017[d]	0.00074
	Pit #2 13%	0.046[d]	0.0059
	Pit #3 4.3%	0.41[d]	0.0018
	Grucci whistles 4.3%	0.16[d]	0
	MCA-LAP Tracer slum 13%	0.0003[d]	0.000043
	NRE 1 filters 2.8%	0.013[d]	0.00035
	NRE tape 0.92%	0	0.00016
	NRE Contaminated 7.1%	0.046[d]	0.0032
	Total Carbon fraction		**0.28**
Skid waste Type 2 09/30/2016 and 10/06/2016	Pallets 63%	0.502[a]	0.32
	Cardboard 0.38%	0.46[b]	0.0017
	Diesel 5.2%	0.86[c]	0.045
	Pit #4 5.9%	0.052[d]	0.0031
	Pit #5 11.8%	0.038[d]	0.0045
	Pit #6 11.8%	0.056[d]	0.0066
	NRE Contaminated 1.9%	0.046[d]	0.00086
	Total Carbon Fraction		**0.38**

[a] [2]
[b] [3]
[c] Calculated using molecular formula $C_{12}H_{23}$ and density 0.832 kg/L.
[d] Analytical measured data from BAE.

2.3 Testing Procedures

2.3.1 Target Analytes and Collected Target Analytes

The target analytes are listed in Table 2-4. The full list of target VOCs are listed in Chapter 2.4.5. CO_2 and CO were successfully measured continuously through all burns. The total number of target analyte samples collected for each type of waste are shown in Table 2-5.

Table 2-4. Target Analytes.

Analyte	Instrument/Method	Frequency
CO_2	Non-dispersive infrared	Continuous
CO	Electrochemical cell	Continuous
$PM_{2.5}$[a]	Impactor, Teflon filter	Batch
Nitrocellulose	Glass fiber filter	Batch
Nitroaromatics	Glass fiber filter	Batch
PCDD/PCDF	Glass fiber filter and PUF[b]	Batch

Elements	Teflon filter from $PM_{2.5}$ batch filter	Batch
Cr(VI)	Bicarbonated-impregnated MCE[c] filter	Batch
HCl	Na_2CO_3 coated quartz filter	Batch
Perchlorate/chlorate	Quartz filter	Batch
VOCs	Carbotrap 300	Batch

[a]Fine particles in the ambient air with particles less than or equal to 2.5 μm in diameter.
[b] PUF – polyurethane foam plug.
[c] MCE – mixed cellulose ester.

Table 2-5. Collected Target Analytes from MK-90 and Skid Waste.

Analyte	MK-90	Skid waste	Total
$PM_{2.5}$	5	2	7
Nitrocellulose	2	0	2
Nitroaromatics	4	0	4
PCDD/PCDF	0	4	4
Elements	5	2	7
Cr(VI)	5	3	8
HCl	0	6	6
Perchlorate/chlorate	0	6	6
VOCs	0	4	4

2.3.2 Unmanned Aerial Vehicle Based Sampling Method

Figure 2-3 shows the sampling instrumentation attached to the bottom of the UAV. This combined system was used for collecting air emissions from propellant plumes.

Figure 2-3. UAV-Based Sampling Method

2.3.2.1 Unmanned Aerial Vehicle – UAV

Aerial sampling was conducted by a UAV operated by NASA Ames. NASA used a DJI Matrice M600 UAV (Figure 2-4). It is a 6-rotor hexacopter with a 9.1 kg weight and a 15.1 kg maximum acceptable gross take-off weight. Its maximum loaded flight time was approximately 13.5 min whereupon the remaining battery charge was 40%. The UAV can be controlled automatically or by pilot-in-command modes and provides the operator a GPS display screen of location in real time with a 2.4 GHz telemetry system. The M600 has an inertial measurement unit and GPS with a return to base function at a preset charge threshold.

Figure 2-4. NASA's UAV.

2.3.2.2 Kolibri – Sampling System

EPA/ORD's sampling system called the "Kolibri" has been developed specifically for sample collection of plumes from open combustion sources. There are two configurations of the Kolibri primarily relating to the different sizes of the pumps needed for specific analytes. There are duplicate models of both Kolibris configurations for redundancy, referred to as "Oden" and "Balder" for the smaller unit and "Tor" and "Loke" for the larger unit (Figure 2-5). Because of payload limitations on the UAV, it was not possible to sample all of the target analytes with all of the pumps on a single platform. In addition, one pump has to be used for multiple analytes ($PM_{2.5}$ or Total PM, Nitrocellulose or Nitroaromatics) and these can only be sampled separately. Hence, the full suite of analytes could only be collected using both Kolibris with sampler variations on each one (Table 2-6). In addition, energetics and VOCs required composite samples comprised of emission sampling from plumes of multiple burns. Because each of these samples has to be collected separately with composite samples, the number of repeat samples was limited. The Kolibri is capable of plotting real time CO_2 and CO data, displaying sampling time and VOC sampling volume, while performing real time calculations to estimate the total amount of gaseous carbon sampled for the energetic sample.

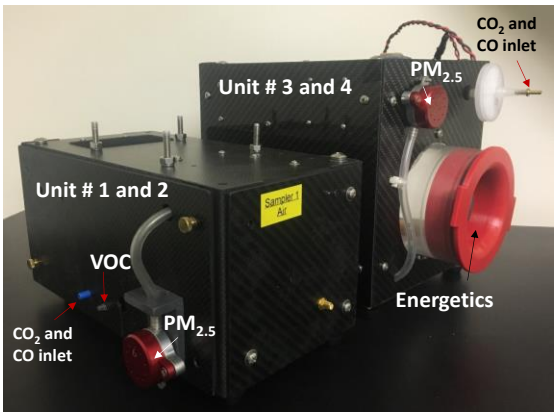

Figure 2-5. Kolibri Instrumentation, Oden and Balder in foreground and Tor and Loke in background.

225 *Table 2-6. Sampling Instrumentation used during each test day.*

Test Date	Ordnance	Kolibri Unit	Analytes Collected
09/27/2016	MK-90	Unit 4: Loke	Nitroaromatics/$PM_{2.5}$/Metals
09/29/2016	MK-90	Unit 4: Loke	Nitrocellulose/Cr(VI)
10/03/2016	MK-90	Unit 4: Loke	Nitroaromatics/Cr(VI)
10/05/2016	MK-90	Unit 4: Loke	Nitrocellulose/$PM_{2.5}$ /Metals
09/28/2016 10/04/2016	Skid waste	Unit 4: Loke	PCDD/PCDF/ HCl/Perchlorate/Chlorate
09/30/2016	Skid waste	Unit 2: Balder	VOCs/Cr(VI)
10/06/2016	Skid waste	Unit 1: Oden	VOCs/Cr(VI)
10/06/2016	Skid waste	Unit 1: Oden	VOCs/$PM_{2.5}$/Metals

2.4 Emission Sampling and Analytical Methods

2.4.1 CO_2

The system CO_2 sensor (DX62210/DX6220 OEM Model, RMT Ltd, Moscow, Russia) measured CO_2 concentration by means of non-dispersive infrared absorption (NDIR). The
230 DX62210/DX6220 CO_2 concentration was recorded on a standard secure digital (SD) card at a rate of one sample per second (1 Hz). The DX62210/DX6220 was calibrated for CO_2 and checked for drift on a daily basis in accordance with EPA Method 3A [4]. The gas cylinders used for calibration were certified by the suppliers and traceable to National Institute of Standards and Technology (NIST) standards. A precision dilution calibrator Serinus Cal 2000
235 (American ECOTECH L.C., Warren, RI, USA) was used to dilute the high-level span gases for acquiring the mid-point concentrations for the DX62210/DX6220 calibration curves. The daily CO_2 system drift for Unit 4 (Loke) varied from -4.6% to -0.4% of the full span and +1.0% for

Unit 2 (Balder), which is within the 5% acceptance limit of the sensor. Unit 1 (Oden) did not have a long enough warm up period before calibration therefore the drift of 7.9% was slightly outside acceptance limit, for this reason, the post-calibration curve was used for calculations as opposed to the pre-calibration curve.

2.4.2 CO

The CO sensor (e2V EC4-500-CO) was an electrochemical gas sensor (SGX Sensortech Ltd, High Wycombe, Buckinghamshire United Kingdom) which measured CO concentration by means of an electrochemical cell through CO oxidation and changing impedance. The sensor was calibrated for CO on a daily basis in accordance with U.S. EPA Method 3A[4]. The e2V CO concentration was recorded on a SD card at a rate of one sample per second (1 Hz). All gas cylinders used for calibration are certified by the suppliers and traceable to NIST standards. A precision dilution calibrator Serinus Cal 2000 (American ECOTECH L.C., Warren, RI, USA) was used to dilute the high-level span gases for acquiring the mid-point concentrations for the e2V EC4-500-CO calibration curves. The daily CO system drift for Unit 4 (Loke) varied from -8.4% to 2.8% and -1.2% for Unit 2 (Balder) and -4.5% for Unit 1 (Oden), which is within the 10% acceptance limit of the sensor.

2.4.3 PM and Elements

$PM_{2.5}$ was sampled with SKC impactors (761-203B) using 37 mm tared Teflon filter (obtained from Chester LabNet) with a pore size of 2.0 µm via a constant micro air pump (C120CNSN, Sensidyne, LP, St. Petersburg, FL, USA) of 10 L/min. Total PM was sampled using cassette with a 37 mm tared Teflon filter (Chester LabNet) with a constant air pump (C120CNSN, Sensidyne, LP, St. Petersburg, FL, USA). PM were measured gravimetrically following the procedures described in 40 CFR Part 50 [5]. The constant flow pump was calibrated daily with a Gilibrator Air Flow Calibration System (Sensidyne LP, St. Petersburg, FL, USA). The plume samples $PM_{2.5}$ concentrations were more than 100 times higher than the collected ambient air background sample.

Elements were determined by x-ray fluorescence spectrometry (XRF) analysis of the Teflon $PM_{2.5}$ and Total PM filters using EPA Compendium Method I0-3.3 [6]. The elements analyzed using XRF are stated in Table 2-7. Chester LabNet evaluated precision with a multi-element quality control standard (QS285) and accuracy using NIST standard reference materials (SRMs): SRM 1832, SRM 1833 and SRM 2783. The SRMs used for quality assurance/quality control (QA/QC) had a recovery of 91.9-108.6%, which is within the 80-120% acceptance criteria of the method. The plume samples' element concentrations were at least 4 times higher than the ambient air background concentration.

Table 2-7. Elements determined using XRF.

Elements			
Aluminum (Al)	Copper (Cu)	Molybdenum (Mo)	Strontium (Sr)
Antimony (Sb)*	Gallium (Ga)	Nickel (Ni)*	Sulfur (S)
Arsenic (As)*	Germanium (Ge)	Palladium (Pd)	Tin (Sn)
Barium (Ba)	Indium (In)	Phosphorus (P)	Titanium (Ti)
Bromine (Br)	Iron (Fe)	Potassium (K)	Vanadium (V)
Cadmium (Cd)*	Lanthanum (La)	Rubidium (Rb)	Yttrium (Y)
Calcium (Ca)	Lead (Pb)*	Selenium (Se)*	Zink (Zn)
Chlorine (Cl)	Magnesium (Mg)	Silicon (Si)	Zirconium (Zr)
Chromium (Cr)*	Manganese (Mn)*	Silver (Ag)	
Cobalt (Co)*	Mercury (Hg)*	Sodium (Na)	

* On U.S. EPA's list of hazardous air pollutants [7].

2.4.4 Chromium(VI)

Chromium(VI) (Cr(VI)) was sampled on a bicarbonate-impregnated "acid hardened" cellulose filter via a constant micro air pump (C120CNSN, Sensidyne, LP, St. Petersburg, FL, USA) of 10 L/min. Cr(VI) was determined using a proprietary method (ChesterLabNet, Tigard, OR) based on an EPA standard procedure [8]. The control sample had recoveries of 97.6 to 101.0% which is within the acceptance limits for the method 75-125%. No detectable levels of Cr(VI) were found in the ambient air background collected sample.

2.4.5 VOCs

VOCs was sampled using Carbotrap 300 stainless steel TD Tube (Supelco Inc., Bellefonte, PA, USA) via a constant micro air pump with an air flow rate of 0.185 L/min (3A120CNSN, Sensidyne, LP, St. Petersburg, FL, USA) in accordance with U.S. EPA Method TO-17 [9]. The Carbotrap 300 tubes were analyzed by ALS Simi Valley for VOCs by thermal desorption GC/MS according to U.S. EPA Method TO-17 [9]. The target VOCs analyzed from Carbopack 300 are stated in Table 2-8. The surrogate spikes used for the QA/QC had recoveries of 85-107% for all samples, which is within the accuracy of the method 70-140%. Eight (Trichlorofluoromethane, methylene chloride, carbon disulfide, trichloroethene, 1,1,2-trichloroethane, toluene, 1,2-dibromoethane, bromoform) of sixty-one VOCs had recoveries slightly outside the acceptance limits for the laboratory control sample. The other 53 VOCs had recoveries of 99-118%, which is within the acceptance limit of the method 52-135%. The VOC method blank showed all non-detectable levels of VOCs except for carbon disulfide. The VOC trip blank showed detectable levels of ethanol, acetonitrile, and acetone. The VOC plume sample levels were 2-14, 22-53, and 4-35 times higher for ethanol, acetonitrile, and acetone, respectively, than the trip blank and ambient background levels. The VOC plume samples were corrected for the trip blank concentrations as well as corrected for ambient air background

concentrations. The constant flow pump was calibrated daily with a Gilibrator Air Flow Calibration System (Sensidyne LP, St. Peterburg, FL, USA).

Table 2-8. VOCs analyzed from Carbotrap 300

VOCs		
1,1,1-Trichloroethane*	2-Hexanone	Ethanol
1,1,2,2-Tetrachloroethane*	2-Propanol (Isopropyl Alcohol)	Ethylbenzene*
1,1,2-Trichloroethane*	4-Methyl-2-pentanone	Hexachlorobutadiene*
1,1-Dichloroethane	Acetone	m,p-Xylenes*
1,1-Dichloroethene	Acetonitrile*	Methyl tert-Butyl Ether
1,2,4-Trichlorobenzene*	Benzene*	Methylene Chloride*
1,2,4-Trimethylbenzene	Bromodichloromethane	Naphthalene*
1,2-Dibromo-3-chloropropane	Bromoform*	n-Heptane
1,2-Dibromoethane	Carbon Disulfide*	n-Hexane
1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114)	Carbon Tetrachloride*	n-Octane
1,2-Dichlorobenzene	Chlorobenzene*	o-Xylene*
1,2-Dichloroethane	Chloroethane	Styrene*
1,2-Dichloropropane	Chloroform*	Tetrachloroethene
1,3,5-Trimethylbenzene	Chloromethane*	Tetrahydrofuran (THF)
1,3-Butadiene*	cis-1,2-Dichloroethene	Toluene*
1,3-Dichlorobenzene	cis-1,3-Dichloropropene*	trans-1,2-Dichloroethene
1,4-Dichlorobenzene*	Cumene*	trans-1,3-Dichloropropene*
1,4-Dioxane	Cyclohexane	Trichloroethene
2,2,4-Trimethylpentane* (Isooctane)	Dibromochloromethane	Trichlorofluoromethane
2-Butanone (MEK)*	Dichlorodifluoromethane (CFC 12)	Trichlorotrifluoroethane
		Vinyl Chloride*

* On U.S. EPA's list of hazardous air pollutants [7].

2.4.6 Energetics

Nitroaromatics/Nitrocellulose were sampled using two 15 cm glass fiber filters (Fisher Scientific) with a nominal rate of 500 L/min. Energetics were sampled using a low voltage MINIjammer brushless blower (AMTEK, USA). The flow rate was measured by a 0-622 Pa Model 265 pressure differential transducer (Setra, USA) across a Herschel Standard Venturi tube (EPA in-house made). The Venturi tube is specially designed to meet the desired sampling rate for the target compound. The voltage equivalent to this pressure differential is recorded on the onboard Teensy USB microcontroller board, which was calibrated with a Roots meter (Model 5M, Dresser Measurement, USA) in the U.S. EPA metrology laboratory before sampling effort.

The energetics samples were analyzed by an outside laboratory using analytical methods U.S. EPA Method 8330b [10] for nitroaromatics and the nitrocellulose by U.S EPA Method 353.2 [11] which is a nitrate-nitrite colorimetric method. The surrogate spikes used for the

nitroaromatics QA/QC had recoveries of 99.9-104% for all samples, which is within the accuracy of the method 70-130%. The laboratory control spike recoveries for nitroaromatics were between 99.5% and 100%, which is within the accuracy of the method 70-150%. The laboratory control spike recovery for nitrocellulose was 108%, which is within the accuracy of the method 40-120%. Nitroaromatics and nitrocellulose were not detected in the ambient air background sample.

2.4.7 HCl, Perchlorate, and Chlorate

HCl was sample using an alkali-impregnated filter following a solid perchlorate and chloride filter (ISO Method 21438-2) [12]. The sampling was conducted at a flow rate of 2 L/min using a constant micro air pump (C120CNSN, Sensidyne, LP, St. Petersburg, FL, USA). The constant flow pump was calibrated daily with a Gilibrator Air Flow Calibration System (Sensidyne LP, St. Petersburg, FL, USA). Perchlorate salts were captured as a solid on the filter, which assumes no perchloric acid formation [13]. Samples were analyzed at ALS, NY. The alkali-impregnated filter was analyzed for HCl by ion chromatography methods specified in U.S. EPA Method 26 [14]. The laboratory control spike recovery for perchlorate and chlorate was 100% and 115%, respectively which is within the accuracy of the methods 40-120%. The laboratory control spike recovery for chloride was 107%, which is within the acceptance limit of the method 90-110%. Chlorate, perchlorate, or HCl were not detected in the ambient air background sample.

2.4.8 PCDD/PCDF

PCDD/PCDF were sampled as for energetics (see 2.4.6) but with the addition of a polyurethane foam plug (PUF) following the glass fiber filter. PCDD/PCDF samples were cleaned up and analyzed using an isotope dilution method based on U.S. EPA Method 23 [15]. Concentrations were determined using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) with a Hewlett-Packard gas chromatograph 6890 Series coupled to a Micromass Premier mass spectrometer (Waters Corp., Milford, MA, USA). U.S. EPA Method 8290 [16] was used for analysis of tetra- through octa-CDDs/Fs. The laboratory control spike recoveries were within the acceptable 40-130% range for Tetra to Hexa PCDD/PCDF and 25-130% for Hepta to Octa PCDD/PCDF for most of the congeners. The HpCDF recovery was slightly outside the acceptance criteria for three of the four samples (13-23%), PentaCDD was outside the acceptance criteria in two of the four samples (155% and 178%). The collected plume samples had 10-250 and 700- >10,000 times higher levels of Total and TEQ PCDDs/PCDFs, respectively, than the collected ambient background sample.

The 2005 World Health Organization (WHO) toxic equivalent factors (TEFs) [17] were used to determine the PCDD/PCDF toxic equivalent (TEQ) emission factors (see Chapter 2.5.2 for calculations). Some of the seventeen TEF-weighted PCDD/PCDF congeners were undetected. The congeners that were not detected (ND) were considered as zero mass for the reported text calculations, however Appendix B shows both ND = 0 and ND = limit of detection mass value.

2.5 Calculations

2.5.1 Converting from mass/mass Carbon to mass/mass initial source

The emission ratio of each analyte/species of interest was calculated from the ratio of background-corrected pollutant concentrations to background-corrected carbon dioxide (CO_2) and carbon monoxide (CO) concentrations. Emissions factors were calculated using these emissions ratios following the carbon balance method [18], and presented as mass pollutant per mass of charge weight. For the two skid waste types, the charge weight was expressed both as 1) the total initial weight of the waste plus the supplemental pallet and diesel fuel ("mass pollutant/mass initial source") as well as 2) the weight of the RFAAP waste alone ("mass pollutant/mass waste"). For the MK-90s the charge weight was the total mass of initial MK-90 source material in the pan, resulting in emission factors expressed as "mass pollutant/mass initial source" which is the same meaning as "mass pollutant/mass waste" since no supplemental fuels were added to the waste, Equations 2-1 to 2-4. Emission factors determined here are compared with the emission factors used in the RFAAP Human Health Risk Assessment document, specifically Table 2-13 [citation?].

$$EF_i = f_c \times \frac{Anlyte_i}{\sum C_j} \qquad \textit{Equation 2-1}$$

where:

- EF_i = Emission factor of target analyte i in terms of mass pollutant per mass initial source
- fc = mass fraction of carbon in the initial source
- $Analyte_i$ = the mass emission ratio of species i,
- ΣC_j = the background corrected mass concentration of carbon in major carbon emissions species j (carbon calculated from ΔCO_2 and ΔCO).

$$EF_{Waste} = EF_i \times \frac{IW}{IW+SF} \qquad \textit{Equation 2-2}$$

where:

- EF_{Waste} = Emission factor of target analyte i in terms of mass pollutant per mass waste
- IW = Initial weight of waste
- SF = Supplement fuel (pallet, cardboard, and diesel)
- IW/(IW+SF) = 2.01 and 3.18 for skid waste type 1 and 2, respectively

The majority of the carbon emissions were emitted as CO_2 and CO. With this assumption, CO_2 and CO are the only carbon-containing compounds that were required to be measured.

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 (Table 2-9). 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.

395

Table 2-9. The 2005 World Health Organization PCDD/PCDF Toxic Equivalent Factors for mammals/humans.[17]

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 Data Variability

400 Standard deviation, as well as the relative standard deviation (RSD), were used for showing the measure of dispersion of three or more data values, see Equations 2-5 and 2-6. RSD indicates how precise the data is, for example a RSD of 50% indicates that the data is more spread out than a RSD of 20%.

$$Standard\ Deviation = \sqrt{\frac{\sum(x-\bar{x})^2}{(n-1)}} \qquad \textit{Equation 2-5}$$

405 where:

x = each sample value, $\bar{x}$ = mean value of samples, n = number of samples

$$RSD\ (\%) = 100 \times \frac{Standard\ Deviation}{Sample\ Average} \qquad \textit{Equation 2-6}$$

410 The relative percent difference (RPD) was used as a quality indicator when only two data values (duplicate samples) were obtained, Equation 2-7. RPD indicates how precise the data is, for example a RPD of 20% indicates that the data is more precise than a RPD of 50%.

$$RPD\ (\%) = 100 \times \frac{x-y}{(\frac{x+y}{2})} \qquad \textit{Equation 2-7}$$

where:

x = sample number one, y = sample number two

3 Results and Discussion

3.1 PM

The $PM_{2.5}$ emissions are reported in Table 3-1. $PM_{2.5}$ emissions were higher from the MK-90 than from the skid waste (Table 3-1). The MK-90 $PM_{2.5}$ emission factor (15.5 g/kg initial source) is similar to those from static firing of CRV-7 (16 g/kg initial source) and MK-58 (34 g/kg initial source) rocket motors [19] and lower than static firing of Sparrow rocket motors (120 g/kg initial source) [1]. The HHRA document lists no PM emission factors, precluding comparison of these site-sampled values.

Table 3-1. $PM_{2.5}$ emission factors in g/kg initial source and lb/lb initial source.

		$PM_{2.5}$	
		MK-90	**Skid Waste - Type 2**
	Unit	**n[a] = 5**	**n[a] = 2**
Average	g/kg initial source	15.5	2.3
Stand. Dev.[b]	g/kg initial source	1.73	N/A[e]
RSD[c]	%	11	N/A[e]
RPD[d]	%	N/A[e]	9.8
Average	lb/lb initial source	0.0155	0.0023
Stand. Dev.[b]	lb/lb initial source	0.0017	N/A[e]
Average	g/kg waste	15.5	7.3
Average	lb/lb waste	0.0155	0.0073

[a] Number of samples collected.
[b] Stand. Dev. – standard deviation, calculated only if $n \geq 3$.
[c] RSD – relative standard deviation, calculated only if $n \geq 3$.
[d] RPD – relative percent difference, calculated only if $n = 2$.
[e] N/A – not applicable.

3.2 Elements/Metals

3.2.1 Elements/Metals

Sixteen metals/elements were detected above instrument limits for one or both of the ordnance sources (Table 3-2). Lead (Pb) and copper (Cu) had the highest emission factors from the MK-90 burns of all the metals analyzed, 0.0102 and 0.00307 lb/lb initial source, respectively (Tables 3-2 to 3-4). Pb, chloride (Cl), potassium (K), Cu, and zinc (Zn) had the highest element emission factors for the "high metal" skid waste. The average standard deviation for the MK-90 metal/element emission factors was 29%. The average relative percent difference for the skid waste emission factors (only two samples were taken) was 55%. These relatively low values validate the precision of the sampling method, particularly given the small number (less than

five) of samples. All element values from the XRF analyses for each collected sample are shown in Appendix A.

Table 3-2. Element emission factors in $PM_{2.5}$ fraction in mg/kg initial source and mg/kg waste.[a]

Element	MK-90				Skid waste – Type 2			
	n[b]	Average	Stand. Dev.[c]	RSD[d]	n[b]	Average	Average	RPD[e]
		mg/kg initial source		%		mg/kg initial source	mg/kg waste	%
Pb	5	10,186	1,103	11	2	678.9	2,158	40
Cu	5	3,073	380	12	2	17.4	55.4	92
Cl	5	30	24	80	2	80.4	255.5	24
Ca	5	28	5.8	20	2	2.17	6.91	20
K	5	25	5.2	20	2	43.4	138.0	1.9
As	4	21	5.3	25	2	1.45	4.62	62
Fe	5	16	3.3	21	2	0.53	1.70	129
Br	5	15	2.5	17	2	1.53	4.86	45
Ge	5	11	2.7	24	2	0.66	2.09	57
Y	5	11	2.8	26	2	0.80	2.53	46
Rb	5	8	1.6	20	2	0.81	2.57	41
Ba	4	6.4	0.42	6.6	2	0.24	0.75	36
Al	3	7.3[f]	5.9	80	0	ND[g]	ND[g]	N/A[h]
Cd	5	2.0	1.2	59	1	0.19	0.62	N/A[h]
Cr	4	1.4	0.21	15	1	0.038[f]	0.12[f]	N/A[h]
Zn	5	ND[g]	N/A[h]	N/A[h]	2	7.6	24.1	121

[a] Element concentrations were 22 times higher than the ambient air levels except for Cr which was four times higher than the ambient levels. All element values from XRF analyses are presented in Appendix A.
[b] Number of samples collected with detectable levels.
[c] Stand. Dev. – standard deviation, calculated only if $n \geq 3$
[d] RSD – relative standard deviation, calculated only if $n \geq 3$.
[e] RPD – relative percent difference, calculated only if $n = 2$.
[f] Results less than three times the uncertainty level of the analyses.
[g] ND – not detected.
[h] N/A – not applicable.

Table 3-3. Metal emission factors in $PM_{2.5}$ fraction in lb/lb initial source and lb/lb waste.[a]

Element	MK-90				Skid waste - Type 2			
	n[b]	Average	Stand. Dev.[c]	RSD[d]	n[b]	Average	Average	RPD[e]
	lb/lb initial source			%		lb/lb initial source	lb/lb waste	%
Pb	5	1.02E-02	1.10E-03	11	2	6.79E-04	2.16E-03	40
Cu	5	3.07E-03	3.80E-04	12	2	1.74E-05	5.54E-05	92
Cl	5	2.97E-05	2.37E-05	80	2	8.04E-05	2.56E-04	24
Ca	5	2.84E-05	5.80E-06	20	2	2.17E-05	6.91E-06	20
K	5	2.53E-05	5.17E-06	20	2	4.34E-05	1.38E-04	1.9
As	4	2.08E-05	5.29E-06	25	2	1.45E-06	4.62E-06	62
Fe	5	1.60E-05	3.32E-06	21	2	5.34E-07	1.70E-06	129
Br	5	1.47E-05	2.49E-06	17	2	1.53E-06	4.86E-06	45
Ge	5	1.11E-05	2.71E-06	24	2	6.59E-07	2.09E-06	57
Rb	5	8.41E-06	1.64E-06	20	2	8.08E-07	2.57E-06	41
Y	5	1.07E-05	2.78E-06	26	2	7.95E-07	2.53E-06	46
Ba	4	6.36E-06	4.19E-07	6.6	2	2.37E-07	7.53E-07	36
Al	3	7.32E-06[f]	5.89E-06	80	0	ND[g] (6.11E-05)	ND[g]	N/A[h]
Cd	5	1.99E-06	1.18E-06	59	1	1.94E-07	6.18E-07	N/A[h]
Cr	4	1.40E-06	2.06E-07	15	1	3.79E-08[f]	1.21E-07[f]	N/A[h]
Zn	0	ND[g] (4.73E-07)	N/A[h]	N/A[h]	2	7.58E-06	2.41E-05	121

[a] Elements levels were 22 times higher than the ambient air levels except for Cr which was four times higher than the ambient levels. All element values from XRF analyses are presented in Appendix A
[b] Number of samples collected with detectable levels.
[c] Stand. Dev. – standard deviation, calculated only if n ≥ 3
[d] RSD – relative standard deviation, calculated only if n ≥ 3.
[e] RPD – relative percent difference, calculated only if n = 2.
[f] Results less than three times the uncertainty level of the analyses.
[g] ND – not detected, method detection limit within parentheses.
[h] N/A – not applicable.

The sampled emission factors were compared with the assumed emission factors used in the RFAAP EFs listed in the HHRA (Table 3-4) [reference]. Of the twelve metals that overlapped for the MK-90s, seven sampled emission factors were lower than the RFAAP EFs and four emission factors were higher than the RFAAP EF (As, Cd, Pb, and Ag). One metal, Hg, was reported as ND so its ratio (<2.2) is not clearly greater or less than unity. For the twelve metals from the skid waste burns, emission factors for ten metals were less than estimated in the HHRA. Two metals, As and Pb, were above unity.

Table 3-4. Comparison of EFs derived in this project with EFs used by RFAAP's HHRA.

Element	MK-90			Skid waste		
	EF	RFAAP EF	Ratio	EF	RFAAP EF	Ratio
	lb/lb initial source		EF/RFAAP EF	lb/lb waste		EF/RFAAP EF
Al	7.32E-06[a]	1.00E-02	0.00073	ND[b] (<6.11E-05)	5.36E-02	<0.0011
Sb	2.32E-06[a]	5.62E-06	0.41	ND[b] (<2.14E-07)	5.62E-06	<0.038
As	2.08E-05	5.54E-07	37.5	4.62E-06	5.54E-07	8.3
Ba	6.36E-06	8.80E-07	0.072	7.53E-07	8.80E-05	0.0086
Cd	1.99E-06	1.32E-05	1.5	6.18E-07	1.32E-06	0.47
Cr	1.40E-06	1.20E-05	0.12	1.21E-07[f]	1.20E-05	0.010
Pb	1.02E-02	2.06E-03	5.0	2.16E-03	2.06E-03	1.1
Hg	ND[b] (<1.65E-06)	7.38E-07	<2.2	ND[b] (<1.65E-07)	7.38E-07	<0.22
Ni	ND[b] (<3.32E-07)	1.98E-05	<0.017	8.19E-09[a]	1.98E-05	0.00041
Se	9.38E-07[a]	1.56E-06	0.60	ND[b] (<6.68E-08)	1.56E-06	<0.043
Ag	1.27E-06[a]	2.12E-07	6.0	2.06E-07[a]	2.12E-07	0.97
Zn	ND[b] (<4.73E-07)	7.55E-05	<0.0063	2.41E-05	7.55E-05	0.32

[a] Results less than three times the uncertainty level of the analyses.
[b] ND – not detected, detection limit within parentheses.

3.2.2 Chromium(VI)

The Cr(VI) emission factors are reported in Table 3-5. Analysis of the $PM_{2.5}$ solids showed that the percentage of Cr(VI) to total Cr in the emissions was 28% and 14% for the MK-90 and skid waste, respectively. Table 3-4 indicates that the total Cr emission factor from sampling was less than used in the HHRA for both MK-90 (12% of the HHRA emission factor) and skid waste (1% of the HHRA emission factor).

Table 3-5. Cr(VI) emission factors.

		Cr(VI)	
		MK 90	Skid Waste -Type 2
	Unit	n[a] = 5	n[a] = 1
Average	mg/kg initial source	0.39	0.0053
Stand. Dev.[b]	mg/kg initial source	0.13	N/A[d]
RSD[c]	%	34	N/A[d]
Average	lb/lb initial source	3.95E-07	5.31E-09
Stand. Dev.[b]	lb/lb initial source	1.34E-07	N/A[d]
Average	mg/kg waste	0.39	0.017
Average	lb/lb waste	3.95E-07	1.69E-08

[a] Number of samples collected with detectable levels. [b] Stand. Dev. – standard deviation,
[c] RSD – relative standard deviation, calculated only if $n \geq 3$. [d] N/A – not applicable.

Cr(VI) was detected in all five MK-90 samples collected but only in one of the three samples collected from the skid waste type 2 (Table 3-2). The collection time for the three Cr(VI) skid waste samples was approximately the same but the amount of carbon collected was approximately two times higher in the detected sample than the two with no detectable levels. This simply indicates a greater plume sampling efficiency (collection of oxidized carbon) during the one detectable sample.

3.3 HCl, chlorate, and perchlorate

No chlorate or perchlorate compounds were detected in any of the six samples collected from skid waste type 1 which was the "high Cl" waste (Table 3-6). The HCl emissions (0.000229 lb/lb initial source) from the skid waste were over 100 times lower than those emitted from static firing (versus open burning) of MK-58 (0.030 lb/lb initial source) and CRV-7 rocket motors (0.086 lb/lb initial source) [19]. Three of the six collected HCl samples were under the method reporting limit (no detectable levels of chloride).

Table 3-6. HCl, chlorate, and perchlorate emission factors from skid waste type 1.

		Skid Waste -Type 1		
	Unit	**HCl** $n^a = 3$	**Chlorate** $n^a = 0$	**Perchlorate** $n^a = 0$
Average	mg/kg initial source	229	ND (0.054)[b]	ND (0.054)[b]
Stand. Dev.[d]	mg/kg initial source	135	N/A[c]	N/A[c]
RSD[e]	%	59	N/A[c]	N/A[c]
Average	mg/kg waste	459	ND (0.11)[b]	ND (0.11)[b]
Stand. Dev.[d]	mg/kg waste	272	N/A[c]	N/A[c]
Average	lb/lb initial source	2.29E-04	ND (5.40E-08)[b]	ND (5.40E-08)[b]
Stand. Dev.[d]	lb/lb initial source	1.35E-04	N/A[c]	N/A[c]
Average	lb/lb waste	4.59E-04	ND (1.08E-07)[b]	ND (1.08E-07)[b]
Stand. Dev.[d]	lb/lb waste	2.72E-04	N/A[c]	N/A[c]
Average	% into air from initial source[f]	8.4	N/A[c]	N/A[c]
Stand. Dev.[d]	% into air from initial source[f]	5.0	N/A[c]	N/A[c]
Average	% into air from waste[f]	26.8	N/A[c]	N/A[c]
Stand. Dev.[d]	% into air from waste[f]	15.9	N/A[c]	N/A[c]

[a] Number of samples collected with detectable levels.
[b] ND – not detected, detection limit within parentheses.
[c] N/A – not applicable.
[d] Stand. Dev. – standard deviation.
[e] RSD – relative standard deviation.
[f] percent of Cl in skid waste going into air as HCl.

3.4 PCDD/PCDF

The PCDD/PCDF emission factor from the Type 1, high Cl skid waste (1.77±1.59 ng TEQ/kg waste) was in the same range as emission factors from prescribed forest burns (1.55±1.65 ng TEQ/kg biomass [20]) and much lower than from open burning of municipal solid waste (1,765±1,474 ng TEQ/kg waste [21]). The sampled emission factor was less than 0.1% of the value used in the HHRA. Values are shown in Table 3-7 and Figure 3-1. Emission factors for each homologue group and each TEF-weighted congener are shown in Appendix B, Tables B-1 to B-6. The MK-90s were not sampled for PCDD/PCDF.

Table 3-7. PCDD/PCDF results.

	Skid waste – Type 1					
	Unit	**Average**	**Stand. Dev.**	**RSD**	**EF RFAAP**	**Ratio EF/EF RFAAP**
PCDD Total	ng/kg initial source	13.2	8.6	66%	NV[b]	
PCDF Total	ng/kg initial source	33.4	37.5	112%	NV[b]	
PCDD/PCDF Total	ng/kg initial source	46.6	41.1	88%	NV[b]	
PCDD TEQ[a]	ng TEQ/kg initial source	0.10	0.15	158%	NV[b]	
PCDF TEQ[a]	ng TEQ/kg initial source	0.79	0.71	90%	NV[b]	
PCDD/PCDF TEQ SUM[a]	ng TEQ/kg initial source	0.88	0.79	90%	NV[b]	
PCDD Total	ng/kg waste	26.5	17.4	66%	105.7	0.25
PCDF Total	ng/kg waste	67.1	75.3	112%	105000	0.00064
PCDD/PCDF Total	ng/kg waste	93.6	82.6	88%	105000	0.00089
PCDD TEQ[a]	ng TEQ/kg waste	0.19	0.30	158%	17.8	0.0107
PCDF TEQ[a]	ng TEQ/kg waste	1.58	1.43	90%	9940	0.00016
PCDD/PCDF TEQ SUM[a]	ng TEQ/kg waste	1.77	1.59	90%	9950	0.00018

[a] Not detected congeners set to zero. Appendix B shows data with not detected congeners set to the limit of detection. [b] NV = no value.

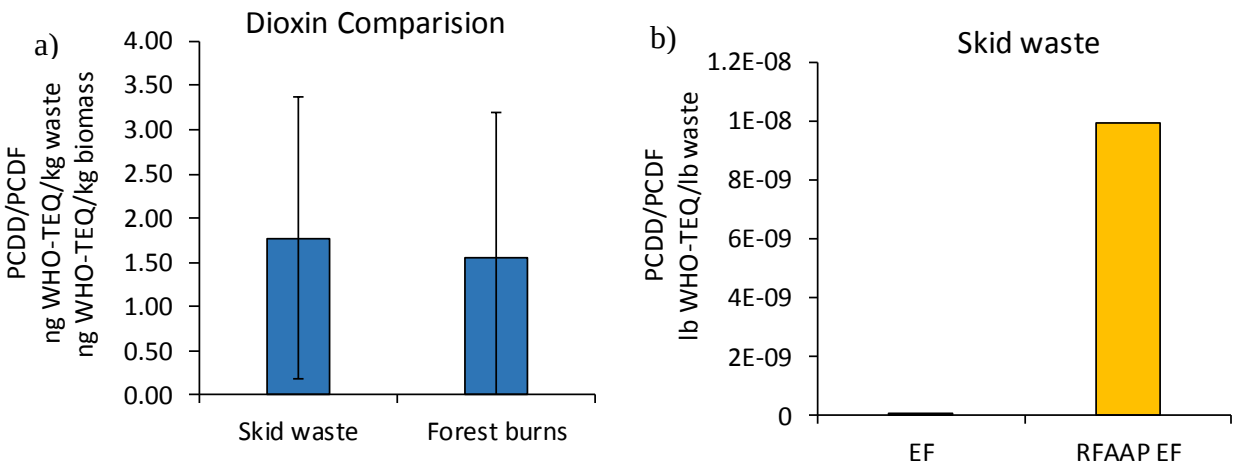

Figure 3-1. Comparison of PCDD/PCDF (Dioxin) emission factors from a) skid waste and forest burns [20], and b) emission factor derived from this study (EF) and emission factor used today by RFAAP (RFAAP EF).

3.5 VOCs

VOC sampling was prioritized only for the type 2 skid waste due to project time limitations. All VOCs analyzed are presented in Tables 3-8 to 3-11. Toluene (3.26E-4 lb/lb waste), benzene (3.11-04 lb/lb waste), naphthalene (1.45E-04 lb/lb waste), methylene chloride (1.26E-04 lb/lb waste), styrene (5.07E-05 lb/lb waste), and xylenes (5.73E-05 lb/lb waste) were the most abundant VOCs emitted from skid waste type 2, all on EPA's list of hazardous air pollutants [7]. These emission values compare to emissions from static fire of rocket motors: toluene 4.5E-04 lb/lb waste, naphthalene 9.2E-06 lb/lb waste, and xylenes 1.2E-03 lb/lb waste [1]. Of the 26 compounds common between sampled and detectable VOC emissions at Radford and the HHRA, 25 of the VOCs were less than the HHRA emission factor (Table 3-8). Only chloromethane was found at RFAAP to be higher (2.3 times) the HHRA emission factor.

Table 3-8. VOC Emission Factors in lb/lb waste from skid waste type 2.

Compound	n[a]	Average[b]	Stand. Dev.[c]	RSD[d]	RPD[e]	Reference	Ratio
		lb/lb waste		%	%	lb/lb waste	EF/ RFAAP EF
1,1,1-Trichloroethane[f]	0	ND (8.04E-08)				1.00E-04	
1,1,2,2-Tetrachloroethane[f]	0	ND (9.38E-08)				1.04E-04	
1,1,2-Trichloroethane[f]	1	1.11E-06				1.15E-04	0.010
1,1-Dichloroethane	0	ND (3.95E-08)				2.92E-05	
1,1-Dichloroethene	0	ND (1.14E-07)				4.94E-05	

Compound	n[a]	Average[b] lb/lb waste	Stand. Dev.[c]	RSD[d] %	RPD[e] %	Reference lb/lb waste	Ratio EF/ RFAAP EF
1,2,4-Trichlorobenzene[f]	0	ND (2.75E-07)				3.28E-06	<0.084
1,2,4-Trimethylbenzene	4	2.72E-05	1.53E-05	56		5.09E-04	0.053
1,2-Dibromo-3-chloropropane	0	ND (1.41E-07)					
1,2-Dibromoethane	0	ND (6.57E-08)					
1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114)	3	1.46E-07	1.51E-07	103			
1,2-Dichlorobenzene	0	ND (1.14E-07)				3.28E-06	<0.035
1,2-Dichloroethane	1	1.01E-07				4.31E-05	0.002
1,2-Dichloropropane	1	1.34E-06				4.31E-05	0.031
1,3,5-Trimethylbenzene	4	7.28E-06	4.13E-06	57		4.31E-05	0.169
1,3-Butadiene[f]	4	1.97E-05	5.32E-06	27		4.35E-05	0.453
1,3-Dichlorobenzene	1	1.14E-07				NV[g]	
1,4-Dichlorobenzene	1	1.73E-07				3.28E-06	0.053
1,4-Dioxane	2	6.93E-07			71	NV[g]	
2,2,4-Trimethylpentane (Isooctane)	4	7.21E-07	7.11E-07	99		NV[g]	
2-Butanone (MEK)	4	1.02E-05	6.02E-06	59		NV[g]	
2-Hexanone	1	6.43E-06				NV[g]	
2-Propanol (Isopropyl Alcohol)	1	3.95E-06				NV[g]	
4-Methyl-2-pentanone	4	1.47E-06	1.60E-06	109		NV[g]	
Acetone	4	4.47E-05	2.70E-05	35		7.44E-04	0.060
Acetonitrile[f]	4	2.69E-05	1.58E-05	56		NV[g]	
Benzene[f]	4	3.11E-04	1.85E-04	59		9.69E-04	0.321
Bromodichloromethane	0	ND (6.37E-08)				9.69E-04	
Bromoform	0	ND (9.38E-08)				NV[g]	
Carbon Disulfide[f]	1	1.07E-06				3.25E-06	0.329
Carbon Tetrachloride[f]	4	1.09E-06	1.15E-06	106		3.25E-06	0.335
Chlorobenzene[f]	1	1.71E-06				3.25E-06	0.526
Chloroethane	3	2.35E-06	1.68E-06	71		3.25E-06	0.723
Chloroform[f]	3	2.23E-07	1.55E-07	70		3.25E-06	0.069
Chloromethane[f]	4	7.58E-06	6.64E-06	88		3.25E-06	2.332
cis-1,2-Dichloroethene	0	ND (6.23E-08)				NV[g]	
cis-1,3-Dichloropropene[f]	0	ND (7.37E-08)				NV[g]	
Cumene[f]	4	3.75E-06	2.41E-06	64		NV[g]	
Cyclohexane	1	8.71E-06				2.67E-05	0.326
Dibromochloromethane	0	ND (4.56E-08)				NV[g]	
Dichlorodifluoromethane (CFC 12)	3	6.72E-06	5.64E-06	84		NV[g]	
Ethanol	4	1.06E-05	7.98E-06	80		NV[g]	
Ethylbenzene[f]	4	2.08E-05	1.00E-05	48		4.53E-05	0.459

Compound	n[a]	Average[b] lb/lb waste	Stand. Dev.[c]	RSD[d] %	RPD[e] %	Reference lb/lb waste	Ratio EF/ RFAAP EF
Hexachlorobutadiene[f]	0	ND (2.01E-07)		N/A		NV[g]	
m,p-Xylenes[f]	4	4.11E-05	1.91E-05	46		NV[g]	
Methyl tert-Butyl Ether	0	ND (4.69E-08)				NV[g]	
Methylene Chloride[f]	4	1.26E-04	2.37E-04	189		1.17E-03	0.108
Naphthalene[f]	4	1.45E-04	8.23E-05	57		7.87E-04	0.184
n-Heptane	4	4.70E-06	1.85E-06	39		NV[g]	
n-Hexane	4	1.63E-05	2.94E-05	180		2.56E-05	0.637
n-Octane	4	1.56E-05	6.08E-06	39		NV[g]	
o-Xylene[f]	4	1.61E-05	8.53E-06	53		NV[g]	
Styrene[f]	4	5.07E-05	3.15E-05	62		5.56E-05	0.912
Tetrachloroethene	2	6.11E-07			185	NV[g]	
Tetrahydrofuran (THF)	3	7.30E-07	2.04E-07	28		NV[g]	
Toluene[f]	4	3.26E-04	4.10E-04	126		4.75E-04	0.686
trans-1,2-Dichloroethene	0	ND (8.04E-08)				NV[g]	
trans-1,3-Dichloropropene	0	ND (7.37E-08)				NV[g]	
Trichloroethene	1	2.81E-07				6.59E-05	0.004
Trichlorofluoromethane	4	2.48E-06	1.91E-06	77		NV[g]	
Trichlorotrifluoroethane	4	1.00E-06	1.11E-06	111		NV[g]	
Vinyl Chloride[f]	0	ND (9.38E-08)				9.28E-05	
Xylenes	4	5.73E-05	2.75E-05	48		4.52E-04	0.127

[a] Number of samples with detectable levels out of 4 samples.

[b] ND – not detected. Detection limit within parentheses.

[c] Stand. Dev. – standard deviation, calculated only if $n \geq 3$.

[d] RSD – relative standard deviation, calculated only if $n \geq 3$.

[e] RPD – relative percent difference, calculated only if $n = 2$.

[f] On U.S. EPA's list of hazardous air pollutants [7]

[g] NV = no value.

Table 3-9. VOC Emission Factors in mg/kg waste from skid waste type 2.

Compound	n[a]	Average[b] mg/kg waste	Stand. Dev.[c]	RSD[d] %	RPD[e] %
1,1,1-Trichloroethane[f]	0	ND (0.080)			
1,1,2,2-Tetrachloroethane[f]	0	ND (0.094)			
1,1,2-Trichloroethane[f]	1	1.11			
1,1-Dichloroethane	0	ND (0.040)			
1,1-Dichloroethene	0	ND (0.11)			
1,2,4-Trichlorobenzene[f]	0	ND (0.28)			
1,2,4-Trimethylbenzene	4	27.17	15.31	56	
1,2-Dibromo-3-chloropropane	0	ND (0.14)			
1,2-Dibromoethane	0	ND (0.066)			
1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114)	3	0.15	0.15	103	
1,2-Dichlorobenzene	0	ND (0.11)			
1,2-Dichloroethane	1	0.1			
1,2-Dichloropropane	1	1.34			
1,3,5-Trimethylbenzene	4	7.28	4.13	57	
1,3-Butadiene[f]	4	19.67	5.32	27	
1,3-Dichlorobenzene	1	0.11			
1,4-Dichlorobenzene	1	0.17			
1,4-Dioxane	2	0.69			71
2,2,4-Trimethylpentane (Isooctane)	4	0.72	0.71	99	
2-Butanone (MEK)	4	10.24	6.02	59	
2-Hexanone	1	6.43			
2-Propanol (Isopropyl Alcohol)	1	3.95			
4-Methyl-2-pentanone	4	1.47	1.6	109	
Acetone	4	44.7	26.95	60	
Acetonitrile[f]	4	26.9	15.8	59	
Benzene[f]	4	310.88	184.78	59	
Bromodichloromethane	0	ND (0.064)			
Bromoform	0	ND (0.094)			
Carbon Disulfide[f]	0	1.07			
Carbon Tetrachloride[f]	4	1.09	1.15	106	
Chlorobenzene[f]	1	1.71			
Chloroethane	3	2.35	1.68	71	
Chloroform[f]	3	0.22	0.16	70	
Chloromethane[f]	4	7.58	6.64	88	
cis-1,2-Dichloroethene	0	ND (0.062)			
cis-1,3-Dichloropropene[f]	0	ND (0.074)			
Cumene[f]	4	3.75	2.41	64	
Cyclohexane	1	8.71			
Dibromochloromethane	0	ND (0.046)			

Compound	n[a]	Average[b] mg/kg waste	Stand. Dev.[c]	RSD[d] %	RPD[e] %
Dichlorodifluoromethane (CFC 12)	3	6.72	5.64	84	
Ethanol	4	10.63	7.98	75	
Ethylbenzene[f]	4	20.81	10.04	48	
Hexachlorobutadiene[f]	0	ND (0.20)			
m,p-Xylenes[f]	4	41.14	19.07	46	
Methyl tert-Butyl Ether	0	ND (0.047)			
Methylene Chloride[f]	4	125.62	237.46	189	
Naphthalene[f]	4	144.54	82.32	57	
n-Heptane	4	4.7	1.85	39	
n-Hexane	4	16.35	29.36	180	
n-Octane	4	15.62	6.08	39	
o-Xylene[f]	4	16.12	8.53	53	
Styrene[f]	4	50.71	31.49	62	
Tetrachloroethene	2	0.61			185
Tetrahydrofuran (THF)	3	0.73	0.2	28	
Toluene[f]	4	326.46	409.87	126	
trans-1,2-Dichloroethene	0	ND (0.080)			
trans-1,3-Dichloropropene	0	ND (0.074)			
Trichloroethene	1	0.28			
Trichlorofluoromethane	4	2.48	1.91	77	
Trichlorotrifluoroethane	4	1	1.11	111	
Vinyl Chloride[f]	0	ND (0.094)			

[a] Number of samples with detectable levels out of 4 samples.

[b] ND – not detected. Detection limit within parentheses.

[c] Stand. Dev. – standard deviation, calculated only if $n \geq 3$.

[d] RSD – relative standard deviation, calculated only if $n \geq 3$.

[e] RPD – relative percent difference, calculated only if $n = 2$.

[f] On U.S. EPA's list of hazardous air pollutants [7]

Table 3-10. VOC Emission Factors in lb/lb initial source from skid waste type 2.

Compound	n[a]	Average[b] lb/lb initial source	Stand. Dev.[c]	RSD[d] %	RPD[e] %
1,1,1-Trichloroethane[f]	0	ND (2.53E-08)			
1,1,2,2-Tetrachloroethane[f]	0	ND (2.95E-08)			
1,1,2-Trichloroethane[f]	1	3.48E-07			
1,1-Dichloroethane	0	ND (1.24E-08)			
1,1-Dichloroethene	0	ND (3.58E-08)			
1,2,4-Trichlorobenzene[f]	0	ND (8.64E-08)			
1,2,4-Trimethylbenzene	4	8.55E-06	4.82E-06	56	

Compound	n[a]	Average[b] lb/lb initial source	Stand. Dev.[c]	RSD[d] %	RPD[e] %
1,2-Dibromo-3-chloropropane	0	ND (4.43E-08)			
1,2-Dibromoethane	0	ND (2.07E-08)			
1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114)	3	4.60E-08	4.74E-08	103	
1,2-Dichlorobenzene	0	ND (3.58E-08)			
1,2-Dichloroethane	1	3.16E-08			
1,2-Dichloropropane	1	4.22E-07			
1,3,5-Trimethylbenzene	4	2.29E-06	1.30E-06	57	
1,3-Butadiene[f]	4	6.19E-06	1.67E-06	27	
1,3-Dichlorobenzene	1	3.58E-08			
1,4-Dichlorobenzene	1	5.45E-08			
1,4-Dioxane	2	2.18E-07			71
2,2,4-Trimethylpentane (Isooctane)	4	2.27E-07	2.24E-07	99	
2-Butanone (MEK)	4	3.22E-06	1.89E-06	59	
2-Hexanone	1	2.02E-06			
2-Propanol (Isopropyl Alcohol)	1	1.24E-06			
4-Methyl-2-pentanone	4	4.64E-07	5.04E-07	109	
Acetone	4	1.78E-05	6.16E-06	35	
Acetonitrile[f]	4	1.10E-05	6.20E-06	56	
Benzene[f]	4	9.78E-05	5.81E-05	59	
Bromodichloromethane	0	ND (2.00E-08)			
Bromoform	0	ND (2.95E-08)			
Carbon Disulfide[f]	1	3.37E-07			
Carbon Tetrachloride[f]	4	3.43E-07	3.63E-07	106	
Chlorobenzene[f]	1	5.37E-07			
Chloroethane	3	7.40E-07	5.28E-07	71	
Chloroform[f]	3	7.02E-08	4.89E-08	70	
Chloromethane[f]	4	2.38E-06	2.09E-06	88	
cis-1,2-Dichloroethene	0	ND (1.96E-08)			
cis-1,3-Dichloropropene[f]	0	ND (2.32E-08)			
Cumene[f]	4	1.18E-06	7.58E-07	64	
Cyclohexane	1	2.74E-06			
Dibromochloromethane	0	ND (1.43E-08)			
Dichlorodifluoromethane (CFC 12)	3	2.11E-06	1.77E-06	84	
Ethanol	4	3.56E-06	2.85E-06	80	
Ethylbenzene[f]	4	6.55E-06	3.16E-06	48	
Hexachlorobutadiene[f]	0	ND (6.32E-08)			
m,p-Xylenes[f]	4	1.29E-05	6.00E-06	46	
Methyl tert-Butyl Ether	0	ND (1.48E-08)			
Methylene Chloride[f]	4	3.95E-05	7.47E-05	189	
Naphthalene[f]	4	4.55E-05	2.59E-05	57	

Compound	n[a]	Average[b]	Stand. Dev.[c]	RSD[d]	RPD[e]
		lb/lb initial source		%	%
n-Heptane	4	1.48E-06	5.81E-07	39	
n-Hexane	4	5.14E-06	9.24E-06	180	
n-Octane	4	4.92E-06	1.91E-06	39	
o-Xylene[f]	4	5.07E-06	2.68E-06	53	
Styrene[f]	4	1.60E-05	9.91E-06	62	
Tetrachloroethene	2	1.92E-07			
Tetrahydrofuran (THF)	3	2.30E-07	6.41E-08	28	
Toluene[f]	4	1.03E-04	1.29E-04	126	
trans-1,2-Dichloroethene	0	ND (2.53E-08)			
trans-1,3-Dichloropropene	0	ND (2.32E-08)			
Trichloroethene	1	8.85E-08			
Trichlorofluoromethane	4	7.80E-07	6.02E-07	77	
Trichlorotrifluoroethane	4	3.15E-07	3.50E-07	111	
Vinyl Chloride[f]	0	ND (2.95E-08)			

[a] Number of samples with detectable levels out of 4 samples.
[b] ND – not detected. Detection limit within parentheses.
[c] Stand. Dev. – standard deviation, calculated only if $n \geq 3$.
595 [d] RSD – relative standard deviation, calculated only if $n \geq 3$.
[e] RPD – relative percent difference, calculated only if $n = 2$.
[f] On U.S. EPA's list of hazardous air pollutants [7].

Table 3-11. VOC Emission Factors in mg/kg initial source.

Compound	n[a]	Average[b]	Stand. Dev.[c]	RSD[d]	RPD[e]
		mg/kg initial source		%	%
1,1,1-Trichloroethane[f]	0	ND (0.025)			
1,1,2,2-Tetrachloroethane[f]	0	ND (0.030)			
1,1,2-Trichloroethane[f]	1	0.35			
1,1-Dichloroethane	0	ND (0.012)			
1,1-Dichloroethene	0	ND (0.036)			
1,2,4-Trichlorobenzene[f]	0	ND (0.086)			
1,2,4-Trimethylbenzene	4	8.55	4.82	56	
1,2-Dibromo-3-chloropropane	0	ND (0.044)			
1,2-Dibromoethane	0	ND (0.021)			
1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114)	3	0.046	0.047	103	
1,2-Dichlorobenzene	0	ND (0.036)			
1,2-Dichloroethane	1	0.03			
1,2-Dichloropropane	1	0.42			
1,3,5-Trimethylbenzene	4	2.29	1.3	57	
1,3-Butadiene[f]	4	6.19	1.67	27	
1,3-Dichlorobenzene	1	0.04			

Compound	n[a]	Average[b] mg/kg initial source	Stand. Dev.[c]	RSD[d] %	RPD[e] %
1,4-Dichlorobenzene	1	0.05			
1,4-Dioxane	2	0.22			71
2,2,4-Trimethylpentane (Isooctane)	4	0.23	0.22	99	
2-Butanone (MEK)	4	3.22	1.89	59	
2-Hexanone	1	2.02			
2-Propanol (Isopropyl Alcohol)	1	1.24			
4-Methyl-2-pentanone	4	0.46	0.5	109	
Acetone	4	14.06	8.48	60	
Acetonitrile[f]	4	8.46	4.97	59	
Benzene[f]	4	97.8	58.13	59	
Bromodichloromethane	0	ND (0.020)			
Bromoform	0	ND (0.030)			
Carbon Disulfide[f]	0	ND (0.17)			
Carbon Tetrachloride[f]	4	0.34	0.36	106	
Chlorobenzene[f]	1	0.54			
Chloroethane	3	0.74	0.53	71	
Chloroform[f]	3	0.07	0.05	70	
Chloromethane[f]	4	2.38	2.09	88	
cis-1,2-Dichloroethene	0	ND (0.020)			
cis-1,3-Dichloropropene[f]	0	ND (0.023)			
Cumene[f]	4	1.18	0.76	64	
Cyclohexane	1	2.74			
Dibromochloromethane	0	ND (0.014)			
Dichlorodifluoromethane (CFC 12)	3	2.11	1.77	84	
Ethanol	4	3.34	2.51	75	
Ethylbenzene[f]	4	6.55	3.16	48	
Hexachlorobutadiene[f]	0	ND (0.063)			
m,p-Xylenes[f]	4	12.94	6	46	
Methyl tert-Butyl Ether	0	ND (0.015)			
Methylene Chloride[f]	4	39.52	74.71	189	
Naphthalene[f]	4	45.47	25.9	57	
n-Heptane	4	1.48	0.58	39	
n-Hexane	4	5.14	9.24	180	
n-Octane	4	4.92	1.91	39	
o-Xylene[f]	4	5.07	2.68	53	
Styrene[f]	4	15.95	9.91	62	
Tetrachloroethene	2	0.19			185
Tetrahydrofuran (THF)	3	0.23	0.06	28	
Toluene[f]	4	102.71	128.94	126	
trans-1,2-Dichloroethene	0	ND (0.025)			

Compound	n[a]	Average[b]	Stand. Dev.[c]	RSD[d]	RPD[e]
		mg/kg initial source		%	%
trans-1,3-Dichloropropene	0	ND (0.023)			
Trichloroethene	1	0.09			
Trichlorofluoromethane	4	0.78	0.6	77	
Trichlorotrifluoroethane	4	0.32	0.35	111	
Vinyl Chloride[f]	0	ND (0.030)			

[a] Number of samples with detectable levels out of 4 samples.
[b] ND – not detected. Detection limit within parentheses.
[c] Stand. Dev. – standard deviation, calculated only if $n \geq 3$.
[d] RSD – relative standard deviation, calculated only if $n \geq 3$.
[e] RPD – relative percent difference, calculated only if $n = 2$.
[f] On U.S. EPA's list of hazardous air pollutants [7].

3.6 Energetics

None of the energetics and nitroaromatic compounds for the MK-90 rocket motors exceeded the analytical method detection limit (Table 3-12). Energetics were not sampled for the skid waste due to time limitations. The ratio of the method detection limit (for the sampled emission factor) to that of the HHRA emission factor resulted in eight overlapping compounds to be less than 1.1.

Table 3-12. Energetics based on method detection limit.

Energetics	MK-90 mg/kg initial source	MK-90 lb/lb initial source	RFAAP EF lb/lb initial source	Ratio EF/RFAAP EF
Nitrocellulose (n=2)	< 51	< 5.1E-05	NV[a]	
1,3,5-Trinitrobenzene[b]	< 1.1	< 1.1E-06	2.28E-05	<0.048
1,3-Dinitrobenzene	< 1.1	< 1.1E-06	8.19E-06	<0.13
2,4,6-Trinitrotoluene	< 1.1	< 1.1E-06	3.48E-05	<0.032
2,4-Dinitrotoluene	< 1.1	< 1.1E-06	1.05E-04	<0.010
2,6-Dinitrotoluene	< 1.1	< 1.1E-06	9.81E-07	<1.1
2-Amino-4,6-Dinitrotoluene	< 1.1	< 1.1E-06	NV[a]	
2-Nitrotoluene	< 1.1	< 1.1E-06	NV[a]	
3,5-DNA	< 1.1	< 1.1E-06	NV[a]	
3-Nitrotoluene	< 1.1	< 1.1E-06	NV[a]	
4-Amino-2,6-Dinitrotoluene	< 1.1	< 1.1E-06	NV[a]	
4-Nitrotoluene	< 1.1	< 1.1E-06	NV[a]	
HMX	< 1.1	< 1.1E-06	2.16E-05	<0.051
Nitrobenzene	< 1.1	< 1.1E-06	3.28E-06	<0.34
Nitroglycerin	< 1.1	< 1.1E-06	3.07E-06	<0.36
PETN	< 2.7	< 2.7E-06	NV[a]	
RDX	< 1.1	< 1.1E-06	NV[a]	
Tetryl	< 1.1	< 1.1E-06	NV[a]	

[a] NV = no value.

[b]Four samples for all energetics except nitrocellulose.

4 Conclusions

Aerial sampling methods for emission quantification of demilitarization efforts have only been comprehensively in use since their first deployment in 2010. The logistical challenges experienced in these earlier efforts and recent developments in UAV and sensor technology prompted EPA's Office of Research and Development to create a new system applicable for sampling open demilitarization plumes. Working with pilots and a hexacopter from NASA Ames, EPA/ORD demonstrated the first comprehensive test of a UAV-borne emission sampler at RFAAP's open burning grounds. Plume sampling of open burns of MK-90 rocket motors and skid waste was successfully accomplished with the UAV/Kolibri system based on the number of plumes sampled (100%), the repeatability of the emission factors, and the comparability of the emission factors with previous aerial sampling methods.

Emissions were sampled for PM, elements including metals, particularly Cr(VI), VOCs, dioxins, and nitroaromatics. $PM_{2.5}$ emission factors for MK-90s were within the range of three other previously-documented sources. The majority of the metal emission factors, 17 of 24, were lower than those emission factors used in the HHRA. Cr(VI) emissions were 28% and 14% of the total Cr emitted from the burns of the MK-90 and skid waste, respectively. Emission factors

were compared with other recently sampled, aerial emission data and found to be consistent or, in some cases (for example, HCl) found to be considerably lower. Chlorate and perchlorate emission were below detection limits. Dioxin emissions were less than 0.1% of the emission factor found in the HHRA for skid waste and were similar to those values typically reported from prescribed forest or biomass burns. Residual energetics and nitroaromatics for the MK-90s were below the detection limit. Of the 26 compounds in common between detectable VOC emissions from Radford's skid waste and the listed HHRA emission factors, 25 of the VOCs were less than the HHRA emission factor.

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Appendices

Appendix A: Element emission factors

Table A-1. Elements analyzed for each sample collected in mg/kg initial source.[a]

		MK90	MK90	MK90	MK90	MK90	Skid waste	Skid waste
	Date	09/27/16	09/27/16	10/05/16	10/05/16	10/05/16	10/06/16	10/06/16
Element	Unit	Burn 1	Burn 2,3	Burn 1	Burn 2	Burn 3	Burn 1	Burn 1
Na	mg/kg initial source	8.58E+02	9.24E+02	1.06E+03	1.05E+03	6.66E+02	2.77E+01	4.32E+01
Na Unc.	mg/kg initial source	1.16E+02	1.37E+02	1.62E+02	1.68E+02	1.32E+02	1.40E+01	1.61E+01
Mg	mg/kg initial source	1.40E+02	1.66E+02	1.96E+02	1.86E+02	1.25E+02	1.91E+00	2.92E+00
Mg Unc.	mg/kg initial source	1.99E+01	2.56E+01	2.89E+01	3.03E+01	2.45E+01	1.29E+00	1.43E+00
Al	mg/kg initial source	1.54E+00	ND	ND	1.33E+01	7.11E+00	ND	ND
Al Unc.	mg/kg initial source	4.13E+00	5.50E+00	6.43E+00	6.72E+00	5.62E+00	6.11E-01	6.50E-01
Si	mg/kg initial source	1.56E+02	1.22E+02	1.66E+02	1.72E+02	1.39E+02	1.90E+01	2.27E+01
Si Unc.	mg/kg initial source	1.02E+01	9.31E+00	1.18E+01	1.21E+01	9.87E+00	1.33E+00	1.52E+00
P	mg/kg initial source	3.82E+00	2.20E+00	4.06E+00	5.93E+00	5.20E+00	4.30E-01	7.16E-01
P Unc.	mg/kg initial source	1.85E+00	2.30E+00	2.89E+00	2.96E+00	2.39E+00	2.41E-01	2.80E-01
S	mg/kg initial source	ND	ND	ND	ND	ND	ND	ND
S Unc.	mg/kg initial source	1.72E+02	1.49E+02	3.99E+01	1.93E+02	3.06E+01	1.76E+00	2.40E+00
Cl	mg/kg initial source	4.38E+01	6.31E+01	8.86E+00	2.46E+01	7.98E+00	7.08E+01	9.00E+01
Cl Unc.	mg/kg initial source	6.64E+00	9.41E+00	6.73E+00	7.07E+00	5.74E+00	3.70E+00	4.69E+00
K	mg/kg initial source	3.34E+01	2.58E+01	2.00E+01	2.58E+01	2.18E+01	4.30E+01	4.38E+01
K Unc.	mg/kg initial source	2.37E+00	2.70E+00	1.83E+00	2.13E+00	1.75E+00	2.23E+00	2.28E+00
Ca	mg/kg initial source	3.74E+01	2.19E+01	2.82E+01	2.96E+01	2.51E+01	2.39E+00	1.96E+00
Ca Unc.	mg/kg initial source	2.42E+00	2.20E+00	2.13E+00	2.13E+00	1.79E+00	2.21E-01	2.22E-01
Ti	mg/kg initial source	1.89E+00	ND	1.61E+00	9.88E-01	1.82E+00	2.48E-01	1.24E-01
Ti Unc.	mg/kg initial source	4.37E-01	6.97E-01	4.64E-01	4.72E-01	4.02E-01	5.34E-02	5.73E-02
V	mg/kg initial source	ND	1.99E-01	3.25E-01	2.36E-01	ND	3.34E-02	ND
V Unc.	mg/kg initial source	4.37E-01	4.98E-01	3.83E-01	4.72E-01	3.32E-01	3.34E-02	4.10E-02
Cr	mg/kg initial source	1.27E+00	4.98E-01	1.47E+00	1.66E+00	1.20E+00	2.67E-02	4.92E-02
Cr Unc.	mg/kg initial source	3.06E-01	5.97E-01	3.25E-01	3.93E-01	2.82E-01	4.01E-02	4.10E-02
Mn	mg/kg initial source	5.25E-01	ND	ND	1.57E-01	ND	ND	ND
Mn Unc.	mg/kg initial source	5.25E-01	9.96E-01	4.10E-01	5.16E-01	3.55E-01	5.34E-02	7.37E-02
Fe	mg/kg initial source	1.62E+01	1.44E+01	1.53E+01	2.15E+01	1.27E+01	8.79E-01	1.89E-01
Fe Unc.	mg/kg initial source	1.14E+00	1.41E+00	9.80E-01	1.34E+00	8.25E-01	9.43E-02	7.37E-02
Co	mg/kg initial source	ND	ND	ND	ND	ND	ND	ND
Co Unc.	mg/kg initial source	3.94E-01	5.97E-01	3.25E-01	3.93E-01	3.08E-01	3.34E-02	4.10E-02

Element	Unit	Date	MK90 09/27/16 Burn 1	MK90 09/27/16 Burn 2,3	MK90 10/05/16 Burn 1	MK90 10/05/16 Burn 2	MK90 10/05/16 Burn 3	Skid waste 10/06/16 Burn 1	Skid waste 10/06/16 Burn 1
Ni	mg/kg initial source		ND	ND	ND	ND	ND	ND	8.19E-03
Ni Unc.	mg/kg initial source		4.37E-01	6.97E-01	3.56E-01	4.32E-01	3.32E-01	3.34E-02	3.28E-02
Cu	mg/kg initial source		2.99E+03	2.55E+03	3.40E+03	3.48E+03	2.95E+03	2.54E+01	9.44E+00
Cu Unc.	mg/kg initial source		1.50E+02	1.27E+02	1.70E+02	1.74E+02	1.47E+02	1.28E+00	4.85E-01
Zn	mg/kg initial source		ND	ND	ND	ND	ND	3.00E+00	1.22E+01
Zn Unc.	mg/kg initial source		5.25E-01	7.97E-01	5.46E-01	6.34E-01	4.73E-01	1.68E-01	6.26E-01
Ga	mg/kg initial source		9.71E+00	5.30E+00	2.70E+00	3.79E+00	ND	ND	ND
Ga Unc.	mg/kg initial source		2.86E+00	3.30E+00	3.05E+00	3.12E+00	2.55E+00	1.94E-01	2.55E-01
Ge	mg/kg initial source		1.08E+01	6.81E+00	1.29E+01	1.12E+01	1.39E+01	4.70E-01	8.48E-01
Ge Unc.	mg/kg initial source		1.14E+00	1.19E+00	1.28E+00	1.30E+00	1.16E+00	6.68E-02	9.83E-02
As	mg/kg initial source		1.35E+01	2.20E+00	2.09E+01	2.27E+01	2.61E+01	1.01E+00	1.90E+00
As Unc.	mg/kg initial source		6.16E+00	6.81E+00	6.95E+00	7.11E+00	5.95E+00	4.09E-01	5.77E-01
Se	mg/kg initial source		ND	ND	ND	1.26E+00	6.14E-01	ND	ND
Se Unc.	mg/kg initial source		1.10E+00	1.19E+00	1.20E+00	1.22E+00	1.02E+00	6.68E-02	9.01E-02
Br	mg/kg initial source		1.49E+01	1.05E+01	1.69E+01	1.61E+01	1.53E+01	1.19E+00	1.87E+00
Br Unc.	mg/kg initial source		1.06E+00	9.96E-01	1.20E+00	1.18E+00	1.06E+00	8.01E-02	1.24E-01
Rb	mg/kg initial source		7.34E+00	8.40E+00	1.02E+01	9.84E+00	6.28E+00	6.44E-01	9.72E-01
Rb Unc	mg/kg initial source		8.80E-01	8.96E-01	1.01E+00	1.03E+00	8.02E-01	6.01E-02	8.19E-02
Sr	mg/kg initial source		1.54E+00	2.00E+00	ND	9.88E-01	2.17E+00	2.67E-02	ND
Sr Unc.	mg/kg initial source		6.18E-01	7.97E-01	7.36E-01	7.13E-01	5.67E-01	4.01E-02	5.73E-02
Y	mg/kg initial source		1.44E+01	7.41E+00	1.26E+01	9.76E+00	9.31E+00	6.11E-01	9.80E-01
Y Unc.	mg/kg initial source		1.80E+00	1.71E+00	1.94E+00	1.90E+00	1.61E+00	1.01E-01	1.48E-01
Zr	mg/kg initial source		ND	ND	ND	ND	ND	ND	ND
Zr Unc.	mg/kg initial source		7.05E-01	9.96E-01	7.63E-01	8.31E-01	6.61E-01	5.34E-02	6.55E-02
Mo	mg/kg initial source		1.14E+00	6.97E-01	5.42E-02	1.34E+00	1.06E+00	3.34E-02	ND
Mo Unc.	mg/kg initial source		7.05E-01	1.19E+00	7.36E-01	8.31E-01	6.37E-01	6.68E-02	8.19E-02
Pd	mg/kg initial source		2.15E+00	9.96E-02	1.36E-01	ND	1.91E+00	8.76E-02	ND
Pd Unc.	mg/kg initial source		1.36E+00	2.50E+00	1.12E+00	1.34E+00	9.46E-01	1.54E-01	1.98E-01
Ag	mg/kg initial source		1.27E+00	ND	ND	ND	ND	ND	2.06E-01
Ag Unc.	mg/kg initial source		1.32E+00	2.50E+00	1.06E+00	1.34E+00	9.22E-01	1.54E-01	1.89E-01
Cd	mg/kg initial source		1.23E+00	3.10E+00	3.27E+00	1.82E+00	5.43E-01	1.94E-01	ND
Cd Unc.	mg/kg initial source		1.32E+00	2.50E+00	1.12E+00	1.34E+00	9.46E-01	1.48E-01	1.89E-01

Element	Unit	Date	MK90 09/27/16 Burn 1	MK90 09/27/16 Burn 2,3	MK90 10/05/16 Burn 1	MK90 10/05/16 Burn 2	MK90 10/05/16 Burn 3	Skid waste 10/06/16 Burn 1	Skid waste 10/06/16 Burn 1
In	mg/kg initial source		2.37E+00	1.71E+00	2.10E+00	1.97E-01	1.98E+00	ND	1.64E-02
In Unc.	mg/kg initial source		1.36E+00	2.70E+00	1.15E+00	1.46E+00	9.69E-01	1.61E-01	2.06E-01
Sn	mg/kg initial source		ND	7.97E-01	7.71E+00	1.66E+00	2.82E-01	8.01E-02	ND
Sn Unc.	mg/kg initial source		1.58E+00	3.30E+00	1.36E+00	1.66E+00	1.11E+00	2.01E-01	2.47E-01
Sb	mg/kg initial source		ND	ND	3.27E+00	ND	1.37E+00	ND	ND
Sb Unc.	mg/kg initial source		1.67E+00	3.50E+00	1.36E+00	1.74E+00	1.18E+00	2.14E-01	2.63E-01
Ba	mg/kg initial source		5.84E+00	8.96E-01	6.68E+00	6.72E+00	6.19E+00	1.94E-01	2.80E-01
Ba Unc.	mg/kg initial source		1.41E+00	2.30E+00	1.55E+00	1.66E+00	1.32E+00	1.48E-01	1.73E-01
La	mg/kg initial source		3.87E+00	1.31E+00	5.53E+00	6.16E+00	4.37E+00	2.00E-02	1.57E-01
La Unc.	mg/kg initial source		9.68E-01	1.31E+00	1.04E+00	1.15E+00	8.72E-01	9.43E-02	1.16E-01
Hg	mg/kg initial source		ND	ND	ND	ND	ND	ND	ND
Hg Unc.	mg/kg initial source		1.80E+00	2.00E+00	2.04E+00	2.01E+00	1.65E+00	1.21E-01	1.65E-01
Pb	mg/kg initial source		1.00E+04	8.77E+03	1.15E+04	1.11E+04	9.57E+03	5.42E+02	8.16E+02
Pb Unc.	mg/kg initial source		5.02E+02	4.39E+02	5.74E+02	5.55E+02	4.79E+02	2.71E+01	4.08E+01

[a] Yellow box with red text = less than three times the uncertainty level. ND = not detected. Unc. = Uncertainty level

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Appendix B: PCDD/PCDF emission factors

Table B-1. PCDD/PCDF total emission factors from skid waste.

Homologue	n[a]	Skid Waste -Type 1 Average ng/kg initial source	Stand. Dev.[b]	RSD[b] %	RPD[c] %
TeCDD Total	0	ND[d]			
PeCDD Total	1	0.14			
HxCDD Total	3	1.25	1.33	107	
HpCDD Total	4	3.71	2.07	56	
OCDD	4	8.49	5.32	63	
TeCDF Total	4	25.51	30.19	118	
PeCDF Total	3	8.51	7.30	86	
HxCDF Total	2	0.85			70
HpCDF Total	2	1.26			64
OCDF	4	0.45	0.17	37	
PCDD Total		13.17	8.66	66	
PCDF Total		33.41	37.48	112	
PCDD/PCDF Total		46.58	41.13	88	

[a] Number of samples with detectable levels. [b] Stand. Dev. = standard deviation, RSD = relative standard deviation calculated when n = 3 or more. [c] RPD = relative percent difference, calculated when n=2. [d] ND = not detected.

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Table B-2. PCDD/PCDF TEQ emission factors from skid waste, ND = 0.

Homologue	n[a]	Skid Waste -Type 1 Average ND=0 ng TEQ/kg initial source	Stand. Dev.[b]	RSD[b] %	RPD[c] %
2,3,7,8 - TCDD	0	ND			
1,2,3,7,8 - PeCDD	1	0.208			
1,2,3,4,7,8 - HxCDD	0	ND			
1,2,3,6,7,8 - HxCDD	1	0.037			
1,2,3,7,8,9 - HxCDD	1	0.025			
1,2,3,4,6,7,8 - HpCDD	4	0.025	0.015	60	
1,2,3,4,6,7,8,9 - OCDD	4	0.0025	0.0016	64	
2,3,7,8 - TCDF	4	0.371	0.389	105	
1,2,3,7,8 - PeCDF	2	0.045			31
2,3,4,7,8 - PeCDF	3	0.503	0.285	57	
1,2,3,4,7,8 - HxCDF	2	0.024			64
1,2,3,6,7,8 - HxCDF	1	0.017			
1,2,3,7,8,9 - HxCDF	0	ND			
2,3,4,6,7,8 - HxCDF	0	ND			
1,2,3,4,6,7,8 - HpCDF	0	ND			
1,2,3,4,7,8,9 - HpCDF	0	ND			
1,2,3,4,6,7,8,9 - OCDF	3	0.000145	0.000046	31	
PCDD TEQ Total		0.10	0.15	158	
PCDF TEQ Total		0.79	0.71	90	
PCDD/PCDF TEQ Total		0.88	0.79	90	

[a] Number of samples with detectable levels. [b] Stand. Dev. = standard deviation, RSD = relative standard deviation calculated when n = 3 or more. [c] RPD = relative percent difference, calculated when n=2. [d] ND = not detected.

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780 Table B-3. PCDD/PCDF TEQ emission factors from skid waste, ND = LOD.

Homologue	Skid Waste -Type 1		
	Average ND=LOD[b] ng TEQ/kg initial source	Stand. Dev.[a]	RSD[a] %
2,3,7,8 - TCDD	0.141	0.0591	42
1,2,3,7,8 - PeCDD	0.152	0.0393	26
1,2,3,4,7,8 - HxCDD	0.010	0.00119	12
1,2,3,6,7,8 - HxCDD	0.019	0.0124	65
1,2,3,7,8,9 - HxCDD	0.014	0.00709	49
1,2,3,4,6,7,8 - HpCDD	0.025	0.0152	60
1,2,3,4,6,7,8,9 - OCDD	0.0025	0.00163	64
2,3,7,8 - TCDF	0.371	0.389	105
1,2,3,7,8 - PeCDF	0.025	0.0244	98
2,3,4,7,8 - PeCDF	0.390	0.324	83
1,2,3,4,7,8 - HxCDF	0.017	0.0105	61
1,2,3,6,7,8 - HxCDF	0.013	0.00232	17
1,2,3,7,8,9 - HxCDF	0.014	0.000949	7.0
2,3,4,6,7,8 - HxCDF	0.012	0.000806	6.6
1,2,3,4,6,7,8 - HpCDF	0.0022	0.00132	61
1,2,3,4,7,8,9 - HpCDF	0.0026	0.00158	61
1,2,3,4,6,7,8,9 - OCDF	0.00014	0.000037	26
PCDD TEQ Total	0.36	0.10	27
PCDF TEQ Total	0.85	0.69	81
PCDD/PCDF TEQ Total	1.21	0.69	57

[a] Stand. Dev. = standard deviation, RSD = relative standard deviation. [b] ND = not detected, LOD = limit of detection.

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Table B-4. PCDD/PCDF total emission factors from skid waste.

Homologue	n[a]	Skid Waste -Type 1 Average ng/kg waste	Stand. Dev.[b]	RSD[b] %	RPD[c] %
TeCDD Total	0	ND[d]			
PeCDD Total	1	0.28			
HxCDD Total	3	2.51	2.68	107	
HpCDD Total	4	7.45	4.17	56	
OCDD	4	17.06	10.68	63	
TeCDF Total	4	51.25	60.63	118	
PeCDF Total	3	17.10	14.67	86	
HxCDF Total	2	1.71			70
HpCDF Total	2	2.53			64
OCDF	4	0.91	0.34	37	
PCDD Total		26.5	17.4	66	
PCDF Total		67.1	75.3	112	
PCDD/PCDF Total		93.6	82.6	88	

[a] Number of samples with detectable levels. [b] Stand. Dev. = standard deviation, RSD = relative standard deviation calculated when n = 3 or more. [c] RPD = relative percent difference, calculated when n=2. [d] ND = not detected.

Table B-5. PCDD/PCDF TEQ emission factors from skid waste, ND = 0.

Homologue	n[a]	Skid Waste -Type 1 Average ND=0 ng TEQ/kg waste	Stand. Dev.[b]	RSD[b] %	RPD[c] %
2,3,7,8 - TCDD	0	ND			
1,2,3,7,8 - PeCDD	1	0.417			
1,2,3,4,7,8 - HxCDD	0	ND			
1,2,3,6,7,8 - HxCDD	1	0.075			
1,2,3,7,8,9 - HxCDD	1	0.050			
1,2,3,4,6,7,8 - HpCDD	4	0.051	0.030	60	
1,2,3,4,6,7,8,9 - OCDD	4	0.005	0.003	64	
2,3,7,8 - TCDF	4	0.745	0.781	105	
1,2,3,7,8 - PeCDF	2	0.091			31
2,3,4,7,8 - PeCDF	3	1.011	0.572	57	
1,2,3,4,7,8 - HxCDF	2	0.049			64
1,2,3,6,7,8 - HxCDF	1	0.033			
1,2,3,7,8,9 - HxCDF	0	ND			
2,3,4,6,7,8 - HxCDF	0	ND			
1,2,3,4,6,7,8 - HpCDF	0	ND			
1,2,3,4,7,8,9 - HpCDF	0	ND			
1,2,3,4,6,7,8,9 - OCDF	3	0.000291	0.000091	31	
PCDD TEQ Total		0.19	0.30	158	
PCDF TEQ Total		1.58	1.43	90	
PCDD/PCDF TEQ Total		1.77	1.59	90	

[a] Number of samples with detectable levels. [b] Stand. Dev. = standard deviation, RSD = relative standard deviation calculated when n = 3 or more. [c] RPD = relative percent difference, calculated when n=2. [d] ND = not detected.

Table B-6. PCDD/PCDF TEQ emission factors from skid waste, ND = LOD.

Homologue	Skid Waste -Type 1 Average ND=LOD[b] ng TEQ/kg waste	Stand. Dev.[a]	RSD[a] %
2,3,7,8 - TCDD	0.283	0.119	42
1,2,3,7,8 - PeCDD	0.306	0.079	26
1,2,3,4,7,8 - HxCDD	0.020	0.0024	12
1,2,3,6,7,8 - HxCDD	0.038	0.025	65
1,2,3,7,8,9 - HxCDD	0.029	0.014	49
1,2,3,4,6,7,8 - HpCDD	0.051	0.030	60
1,2,3,4,6,7,8,9 - OCDD	0.0051	0.0033	64
2,3,7,8 - TCDF	0.745	0.781	105
1,2,3,7,8 - PeCDF	0.050	0.049	98
2,3,4,7,8 - PeCDF	0.784	0.651	83
1,2,3,4,7,8 - HxCDF	0.034	0.021	61
1,2,3,6,7,8 - HxCDF	0.027	0.0047	17
1,2,3,7,8,9 - HxCDF	0.027	0.0019	7.0
2,3,4,6,7,8 - HxCDF	0.024	0.0016	6.6
1,2,3,4,6,7,8 - HpCDF	0.0043	0.0026	61
1,2,3,4,7,8,9 - HpCDF	0.0052	0.0032	61
1,2,3,4,6,7,8,9 - OCDF	0.00029	0.000075	26
PCDD TEQ Total	0.73	0.20	27
PCDF TEQ Total	1.70	1.38	81
PCDD/PCDF TEQ Total	2.43	1.38	57

[a] Stand. Dev. = standard deviation, RSD = relative standard deviation. [b] ND = not detected, LOD = limit of detection.