



# Improving post-detonation energetics residues estimations for the Life Cycle Environmental Assessment process for munitions

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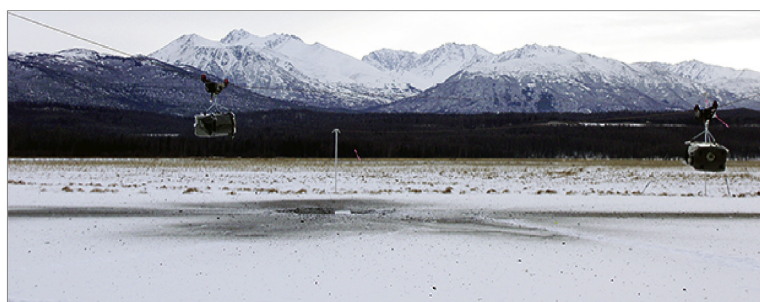
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## HIGHLIGHTS

- Life Cycle Environmental Assessments report no significant post-detonation residue.
- Field testing of munitions indicates gram quantities or more of detonation residues.
- Detonation tests were conducted to compare aerial residues with residues deposition.
- Aerial residues data account for <10% of total post-detonation energetics residues.
- Live-fire detonation residues deposition data is needed for accurate assessments.

## GRAPHICAL ABSTRACT



Air sampling instruments (Flyers) suspended above detonation residues on snow

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## ABSTRACT

The Life Cycle Environmental Assessment (LCEA) process for military munitions tracks possible environmental impacts incurred during all phases of the life of a munition. The greatest energetics-based emphasis in the current LCEA process is on manufacturing. A review of recent LCEAs indicates that energetics deposition on ranges from detonations and disposal during training is only peripherally examined through assessment of combustion products derived from closed-chamber testing or models. These assessments rarely report any measurable energetic residues. Field-testing of munitions for energetics residues deposition has demonstrated that over 30% of some energetic compounds remain after detonation, which conflicts with the LCEA findings. A study was conducted in the open environment to determine levels of energetics residue deposition and if combustion product results can be correlated with empirical deposition results. Energetics residues deposition, post-detonation combustion products, and fine aerosolized energetics particles following open-air detonation of blocks of Composition C4 (510 g RDX/block) were quantified. The deposited residues amounted to 3.6 mg of energetic per block of C4, or less than 0.001% of the original energetics. Aerial emissions of energetics were about 7% of the amount of deposited energetics. This research indicates that aerial combustion products analysis can provide a valuable supplement to energetics deposition data in the LCEA process but is insufficient alone

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to account for total residual energetics. This study demonstrates a need for the environmental testing of munitions to quantify energetics residues from live-fire training.

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Considering Energetics Residues in the Life Cycle Environmental Assessment Process for Munitions.

## 1. Introduction

Munitions developed in the United States must go through a process known as the life cycle environmental assessment (LCEA) as part of the certification process for use. The LCEA process is detailed in DoD Instruction (DoDI) 5000.02 and includes a section on environment, safety, and occupational health (ESOH) (US DoD, 2015). Section 16 of Enclosure 3 of DoDI 5000.02 states that “The Program Manager will integrate ESOH risk management into the overall systems engineering process for all engineering activities throughout the system’s life cycle” to manage, reduce, or eliminate ESOH risks associated with the materiel under development. Regulatory impetus is derived from the National Environmental Policy Act (NEPA) of 1969 (as amended) (US Executive Office, 1969). The NEPA requires analyses to determine whether a Finding of No Significant Impact (FONSI) or a Notice of Intent (NOI) to file an Environmental Impact Statement (EIS) is to be assigned to the item being examined. The resulting document is known as the Life-Cycle Environmental Assessment. In addition, Executive Order 12144—Environmental Effects Abroad of Major Federal Actions further strengthens the guidance as set forth in the NEPA act of 1969 (US Executive Office, 1979). Reportage of results occurs through a Programmatic ESOH evaluation (PESHE) that documents “data generated by ESOH analyses conducted in support of program execution.” The PESHE includes “identification of ESOH risks and their status; and, identification of hazardous materials, wastes, and pollutants (discharges/emissions/noise) associated with the system and its support as well as the plans for minimization and/or safe disposal.”

The LCEA process evaluates possible contamination generated during the use of munitions in training, disposal, demilitarization, and war. For this paper, we focused on detonations of munitions on training ranges, considering only high-order detonations from properly functioning munitions. We did not consider improperly functioning munitions (low-order, partial-detonations, and duds) as those types of events are extremely variable. For the determination of high-order detonation residues, combustion model predictions or actual sampling results are used. For the latter, testing typically occurs in enclosed blast chambers where post-detonation combustion products are measured. Energetics residues deposition is estimated based on the analysis of the combustion products collected by gas-collection samplers, gas sensors, and instrumentation. Samples are analyzed for over 250 analytes, including explosive compounds (Krupacs, 2004). However, the extent of deposition on the walls, shot to shot carryover, and ground residue of the target analytes remains uncertain. Five LCEAs were reviewed for this paper, four from the US (Krupacs, 2004, 2014; Antreassian et al., 1992; Boyce, 2009) and one from Sweden (Hägval et al., 2004). Two of the five estimates relied on the sampling of combustion gasses, while the remaining three modeled the combustion products rather than rely on blast chamber data (Krupacs, 2004, 2014; Boyce, 2009; Hägval et al., 2004). Only one of the five LCEAs reviewed (PAX-21 high-explosive mortar rounds) also examined post detonation residues. None of the LCEAs reported

significant environmental impacts from detonations.

Field-testing of the PAX-21 mortar rounds was undertaken as part of the Strategic Environmental Research and Development Program (SERDP) project ER-2219 to determine if measurable detonation residues were deposited following training with these rounds (SERDP Project ER-2219, 2016). Seven PAX-21 60-mm mortar rounds were drawn from inventory and command detonated in the open environment in 2012. Results indicated that, on average, 14 g of perchlorate ( $\text{ClO}_4$ ) residue resulted from high-order detonations, 15% of the original perchlorate mass (Walsh et al., 2013). A subsequent re-evaluation of residues data from the original 60-mm PAX-21 mortar round LCEA revealed a similar mass of perchlorate (13 g) resulting from the detonation of two rounds during the enclosed chamber tests (Krupacs, 2004). An addendum was issued by Picatinny Arsenal shortly after the release of these findings, reclassifying the rounds because of “the residual risk of perchlorate contamination” (Boyce, 2012).

Field deposition residues data differ significantly from the impact findings of current LCEAs. Past LCEA data and model results indicate less than 0.01 mg energetics residues following detonation, whether for 60-mm or 155-mm munitions, with over 99.99% of all energetics consumed (Krupacs, 2004, 2014; Antreassian et al., 1992; Boyce, 2009; Hägval et al., 2004). Field data indicate much higher mass deposition, up to tens of grams in some cases, with consumption rates of less than 60% in one case (Walsh et al., 2013, 2011, 2014). A more definitive analysis of air emission detonation combustion products with residues deposition data was needed to determine if the LCEA process adequately estimates energetics residues from detonations or if modifications to the process should be considered. To do this, we detonated a series of Composition C4 demolitions blocks in the field and compared residues estimates derived from gaseous emissions with residues deposited on the ground surrounding the detonation.

## 2. Materials and methods

Tests analyzing airborne residues and combustion products to residues deposited on a snow surface were conducted in Anchorage, Alaska, in February 2015. The test location was the Eagle River Flats impact area (ERF) on Joint Base Elmendorf Richardson (JBER)—Richardson Training Area. At the time of the tests, the Flats were covered with ice that varied in thickness up to 60 cm. There was 2–5 cm of snow cover at the test site. Meteorological conditions for testing were as follows: Mean temperature  $-1^\circ\text{C}$ , no precipitation, overcast sky, and winds variable 0–4 m/s, averaging 2 m/s. Wind direction was erratic, unusual for the site. Testing was conducted with blocks of Composition C4 explosive (C4) consisting of 510 g of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) (up to 10% Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) as a manufacturing byproduct) and 57 g of plasticizer. For the test, a total of five co-located detonations of two blocks of C4 each were executed over a 2 h period. Gaseous emissions and suspended particles were sampled during and immediately after the detonations. Surface residues were sampled upon completion of the five detonations. All results are based on estimates derived from the gas and residues accumulation from all five detonations.

Two sampling methods were used to estimate the detonation

residues. Multi-increment (MI) sampling was used for the residues deposited on the snow surface (Walsh et al., 2012). Samples of gaseous carbon and energetics within the detonation plume were collected aurally (Aurell et al., 2015). The MI sampling method enables a direct estimate of RDX/HMX residues mass. The aerial gas and energetics particle samples are used to estimate energetics in the air. The suspended particle data can also be used to estimate particles of mass median diameter 2.5  $\mu\text{m}$  and 10  $\mu\text{m}$  in the air, important from a human health perspective (USEPA, 1987).

### 2.1. Energetics deposition residues mass

For MI deposition sampling, quintuplicate independent multi-increment sampling ( $n = 5$ ,  $i \approx 90$  increments) was conducted following completion of the five test detonations (Figs. 1 and 2). Samples were obtained from the snow surface with 10-cm polytetrafluoroethylene (PTFE)-lined square scoops to a depth of 2 cm within the visually demarcated deposition area surrounding the detonation point. For quality assurance (QA), triplicate MI samples were taken from 0–3 m and 3–6 m annuli outside the demarcated deposition area. Sampling, field QA, and initial sample processing followed the protocol established by Walsh et al., 2012. Final sample processing and the analyses for the RDX and HMX followed EPA Method 8330B and 8095 (USEPA, 2006; USEPA, 2007).

### 2.2. Aerial energetics residues mass

Aerial energetic residues and carbon-based gases were collected aboard two suspended instrumentation modules located  $\approx 20$  m downwind of the detonation point and 2 m above ground level (Fig. 2). The instrumentation within the two gas/particle samplers, termed the “Flyers”, is listed in Table 1.

The energetic particles collected on quartz filters by the Flyers were analyzed using gas chromatography (GC- $\mu\text{ECD}$ ). Each Flyer contained a  $203 \times 254$  mm quartz microfiber filter through which 1200 L/min of air was pulled for the determination of residual energetics using methods described in a previous publication (Aurell et al., 2015). Upon completion of the sampling test, each filter, which contained an unknown mass of particles of various composition, was placed in a wide-mouth 500-mL jar. Acetonitrile was added to each jar in 10-mL aliquots until the filters were immersed in solvent. A total of 50 mL of solvent were needed to immerse the filters. The jars containing the filters and solvent were



Fig. 2. Flyer airborne sampling instrument.

placed on a platform shaker and processed at 175 rpm for 18 h. The acetonitrile filter extracts were drawn through Millipore Millex-FH (PTFE 0.45  $\mu\text{m}$ ) filter units and transferred to autosampler vials that were then placed into an Agilent 7693 Series autosampler tray. A 1- $\mu\text{L}$  aliquot of each extract was directly injected into the Agilent 7890A purged packed inlet port (250  $^{\circ}\text{C}$ ) containing a deactivated Restek Uniliner (Catalog #20964). The primary determinations were conducted on a 6-m  $\times$  0.53-mm-ID RTX<sup>®</sup>-TNT fused-silica column that had a 1.5- $\mu\text{m}$ -thick film of a proprietary Crossbond phase. The GC oven was temperature-programmed as follows: 100  $^{\circ}\text{C}$  for 2 min followed by a 10  $^{\circ}\text{C}/\text{min}$  ramp up to 250  $^{\circ}\text{C}$ . The carrier gas was hydrogen at 1.4 psi inlet pressure. The micro electron capture device ( $\mu\text{ECD}$ ) detector temperature was 290  $^{\circ}\text{C}$ . The makeup gas was nitrogen at 45 mL/min.

Extracts were also analyzed using an RTX<sup>®</sup> TNT2 confirmation column on an HP6890A GC equipped with a splitless injector. The injection port liner was a deactivated Restek Uniliner (Catalog #20336). Column dimensions were 6-m  $\times$  0.53-mm-ID with a 1.5- $\mu\text{m}$  film thickness. The GC oven was temperature-programmed as follows: 130  $^{\circ}\text{C}$  for 1 min, followed by a 10  $^{\circ}\text{C}/\text{min}$  ramp to 160  $^{\circ}\text{C}$  and a 30  $^{\circ}\text{C}/\text{min}$  ramp to 270  $^{\circ}\text{C}$ . The carrier gas was hydrogen at 1.6-psi inlet pressure. The  $\mu\text{ECD}$  temperature was 275  $^{\circ}\text{C}$  and the



a. Ground view, taken during tests.

b. Aerial view. Samplers are collecting their second

replicate sample. Note the demarcated 0–3 m annuli.

Fig. 1. Sampling the detonation surface residues. a Ground view, taken during tests. b. Aerial view. Samplers are collecting their second replicate sample. Note the demarcated 0–3 m annuli.



**Table 1**  
Flyer measurements/devices.

Measurement	Device	Range	Accuracy	Notes
CO <sub>2</sub>	LI-820 NDIR <sup>a</sup>	0–3000 ppm	<3% of reading	Non-Dispersive Infra-Red
CO	E2V EC4-500-CO <sup>b</sup>	1–500 ppm	±5% of range	Electrochemical gas sensor
Energetics	Quartz microfiber filter <sup>c</sup>	>0.0001 mg		Airborne RDX particles
Temperature	Type T Thermistor	–100°/350 °C	±1.1 °C	Ambient temperature

<sup>a</sup> LI-COR Biosciences, Inc (USA).<sup>b</sup> SGX Sensortech (UK).<sup>c</sup> Analyzed on an HP6890 Gas Chromatography – micro Electron Capture Detector (GC-μECD), Hewlett-Packard, Inc. (USA).

makeup gas was nitrogen at 60 mL/min.

To correlate the mass of RDX recovered from the quartz filters to the total mass of RDX residue from the detonation, the Carbon Balance Method was used. In this method, the emission factor, or the mass of sampled RDX on the intake filters per mass of co-sampled C (as CO<sub>2</sub> + CO, corrected for background levels), was multiplied by the total mass of carbon in the explosive to estimate the total amount of RDX that is emitted during the detonation. Sensors on the Flyers monitored CO<sub>2</sub> concentration using a non-dispersive infrared (NDIR) instrument at a sampling rate of 1 sample/s. The CO<sub>2</sub> concentration was recorded in real time on a LabVIEW<sup>®</sup>-based computer program on the Flyer. The CO concentrations were measured using an electrochemical gas sensor that measures concentration by means of an electrochemical oxidation reaction. Calibration for both sensors occurred daily and followed EPA Method 3A (USEPA, 2012).

The emission ratio of each species of interest was calculated from the ratio of background-corrected target compound concentrations to background-corrected carbon dioxide concentrations. Emissions factors were calculated using these emissions ratios following the carbon balance method (Eq. (1)) (Burling et al., 2010):

$$EF_i = f_c \frac{M_i}{\sum_j C_j} \quad (1)$$

where EF<sub>i</sub> is the emission factor of species *i* (RDX) in terms of grams effluent per kilogram of fuel (C4 explosive), *f<sub>c</sub>* is the fraction of carbon in the C4 fuel, *M<sub>i</sub>* is the mass of species *i* sampled, and  $\sum_j C_j$  is the background-corrected mass of co-sampled carbon in the major gaseous carbon species *j*. For this test, the target compound, RDX in particulate form, was co-sampled with CO and CO<sub>2</sub>, the oxidation products that make up the vast majority of the gaseous carbon compounds. When the ratio of the sampled RDX mass to the sampled carbon mass is multiplied by the carbon fraction in the C4 fuel composition, 0.20, and multiplied by the total C4 mass, the total amount of the RDX released during detonation can be estimated.

### 3. Results

#### 3.1. Energetics deposition

Data for the detonation residues samples collected from the snow surface following the test were consistent. The demarcated deposition area size was 1600 m<sup>2</sup> and the areas sampled outside the demarcated area (ODAs) were 700 m<sup>2</sup> (0–3 m) and 730 m<sup>2</sup> (3–6 m). The mean and median mass for RDX in the deposition area was 35 mg (Table 2). The mean and median mass for HMX in the deposition area was 1.2 and 0.99 mg, respectively. Mean and median detonation efficiency for the C4 blocks was 99.9993%. No energetics residues were detected in the ODA annuli or in the background sample taken prior to testing. The mean energetics deposition per block of C4 was 3.6 mg, or 0.0007% of the original

**Table 2**  
Residues mass estimates and calculated efficiency of C4 detonations.

Sample Rep	HMX Mass Est. (mg)	RDX Mass Est. (mg)	Detonation Efficiency
1	0.95	35	99.9993%
2	0.89	27	99.9994%
3	0.99	34	99.9993%
4	1.5	43	99.9991%
5	1.5	36	99.9993%
Means	1.2	35	99.9993%
%RSD	26%	16%	0.0001%
(Per block C4)	0.12	3.5	99.9993%

mass of RDX.

#### 3.2. Aerial energetics

The average Flyer sampling time after the five detonations was 21.5 s, resulting in a cumulative sampling volume of 4.05 m<sup>3</sup>. The residues collected on the filters from the Flyers were extracted and analyzed using two different columns on the GC-μECD. For the primary column, the estimated masses on the filters were 0.25 μg and 0.14 μg RDX for Flyers 1 and 2. Results from the secondary column are quite close, at 0.20 and 0.13 μg. No RDX was detected on the filter of one of the Flyers that was operated prior to the tests to obtain background analyte levels.

The emission factors for the two Flyers (column averages) were 0.60 and 0.36 mg RDX/kg C4. In terms of RDX recovered, this translates to 0.65 and 0.40 mg RDX/kg RDX (Table 3). For the 5.1 kg of RDX used for the five detonations of two blocks each, a total mass of between 3.3 mg and 2.0 mg of RDX is estimated to have been entrained in the aerial plume following detonation, or 0.00005% of the original RDX.

### 4. Discussion

The surface sampling method provides a combined RDX/HMX residue estimate of 3.6 mg/block (6.3 mg/kg) of C4. Aerial residues captured on the Flyers' quartz filters and extrapolated to the full charge mass using the emission factor average 0.24 mg RDX/block of C4 (Tables 3 and 4), or about 6.6% of the residue deposition mass. The approximate order of magnitude difference between the results of the surface residue sampling and air emissions sampling is contrary to the current LCEA method, which relies on combustion product modeling to predict residues. The deposition and emission

**Table 3**  
Results for aerial energetics study.

Flyer	RDX EF (mg/kg C4)	RDX EF (mg/kg RDX)	RDX EF (mg/block C4)
#1	0.60	0.65	0.30
#2	0.36	0.40	0.18
Means	0.48	0.53	0.24

**Table 4**

Comparison of estimated energetics residues (per block of C4).

Method	RDX + HMX (mg)	Emission Factor (mg/mg) <sup>b</sup>	Detonation Efficiency
Surface Sampling	3.6	$7.1 \times 10^{-6}$	99.9993%
Aerial Energetics			
Flyer #1	0.30 <sup>a</sup>		
Flyer #2	0.18 <sup>a</sup>		
Averaged	0.24 <sup>a</sup>	$4.7 \times 10^{-7}$	99.99995%
Combined Total	3.8	$7.5 \times 10^{-6}$	99.9992%

<sup>a</sup> RDX only; HMX was below the detection limits of the instrumentation.<sup>b</sup> mg residues per mg pre-detonation energetics.

methods measure different aspects of the detonation residues and are additive, representing the total energetic release to the environment.

The replicate data ( $n = 5$ ) for the surface deposition samples are consistent, and the ODA samples were below the detection limits (BDL) for both analytes. The mean and median values for RDX are the same, indicative of non-skewed data. The standard deviation for the RDX data is 5.8 mg, with a relative standard deviation (RSD) of 16%. For HMX, the mean and median are similar, 1.2 mg vs. 0.99 mg, with a standard deviation of 0.31 mg and an RSD of 26%. Concentrations of RDX in the Flyer filter samples were quite low, requiring the use of the more sensitive GC analytical instrument rather than the more accurate liquid chromatography (LC) instrument. HMX was not detected with either instrument. The detection limit for RDX in soils for the GC- $\mu$ ECD system used for these analyses is 3  $\mu$ g/L, very close to the analytical results, resulting in a less-accurate estimate. The high-performance LC instrument, which returns more precise analyses, could not be used because its detection limit for RDX is 20  $\mu$ g/L. RSDs for data near the detection limits of analytical instrumentation tend to be higher as accuracy falls off at the instrument's limits.

Surface samples are typically taken below previously sampled locations to determine if residues extend beneath the 2.5-cm depth of the snow surface samples. However, the snow was not deep enough during these tests to conduct that quality assurance (QA) procedure. Most sample increments penetrated the full depth of the surface snow. Replicate sampling and sampling outside the demarcated area were conducted to ensure sampling integrity, and typical lab QA procedures such as filter blanks, SPE blanks, running triplicates of the aqueous and solid phase portions, and matrix spikes. The data for the LCEA test correspond well to previous data on single-block detonations of C4 explosive (Walsh et al., 2011). The mean RDX deposition from 11 prior single-block detonations was 19 mg. The higher residues mass for the single block tests was expected, as lower-mass detonations tend to be less efficient.

The emission factors for the aerial residues are based on gas analyses and the RDX residues recovered from the quartz microfiber filter. The emission factor values are similar to previous studies with explosives. The RDX emission factor for Comp B (60% RDX, 40% TNT) surface detonations conducted on sand at the Tooele Army Depot in Utah (USA) was 1.1 mg/kg RDX (Aurell et al., 2015) versus the 0.53 mg/kg RDX reported here (Table 3). This difference may have been due to site-specific differences in temperature profiles resulting in less dispersion in Alaska. The determination of the emission factor is based on assumptions similar to those of the residue method, such as representative sampling and homogeneous mixing or density of residues and combustion products. Energetic emission factors from the two Flyer samplers had a relative percent difference (RPD) of 24%. The extent to which the JBER climate affected the upward and downwind aerial dispersion of emissions and the relevance of these findings to other climate and ordnance-type scenarios remain to be tested.

The surface sampling method provided a direct correlation of sample to mass, the ability to do replicate sampling for each event, the ability to do statistical analyses on the data, and ability to measure the area of deposition, important for determining areas requiring cleanup in a remediation environment. Surface sampling is easy to set up and conduct and can be done on any type of dry surface but needs to be done on a snow surface to obtain the resolution needed for very low analyte concentrations, such as we saw with these tests. Replicate samples and sampling the ODAs are important checks on the data. One possible downside is that sample processing exposes the residues to liquid water (melted snow), which may be a problem in cases such as when base hydrolysis of an energetic compound may occur.

The advantages of the aerial estimation of energetics mass are the ability to estimate residues from larger detonations and that the method works equally well no matter the test surface. Characterization of the energetics residues is more complete because the airborne residues that are not typically captured with the surface sampling method can be quantified and added to surface residues estimates. Both methods work best at low wind velocities, preferably below 3 m/s, although the Flyer system has operated at wind speeds up to 9 m/s.

We have shown that air emissions from surface detonations consist of a comparatively minor proportion of the total detonation residues mass and should not be solely relied upon to estimate uncombusted energetic residues. The aerial sampling method can provide additional useful detonation characterization data, such as gross suspended particle size and mass, and can provide essential data when a more complete mass balance estimate is required. This test was the first time air emissions and ground deposition residues have been measured for the same series of detonations and demonstrates that only a fraction of the energetics residues mass is airborne and may drift out of the demarcated deposition areas.

## 5. Conclusions

A previous LCEA conducted on a recently certified munition found no explosives residues based on post-detonation sampling of gaseous emissions. Residues recovered from the enclosed chamber where the assessment was conducted showed evidence of gram quantities of energetics, and follow-on field-testing for detonation residues confirmed the presence of 14 g of energetics per round. A study comparing energetics residues derived from the detonation of Composition C4 demolitions blocks was conducted on snow-covered ice on the ERF impact range in Alaska to compare estimates of airborne residues to surface-based residues mass estimates. Ground deposition of post-detonation residues were sampled in replicate and analyzed to obtain an estimate for RDX deposition per block of C4. Two instrumentation modules containing CO and CO<sub>2</sub> sensors and particle impingement filters were suspended 2 m above the ground surface 20 m from the detonation point. Aerial energetics mass was estimated using carbon-balance-

based emissions factors based on the gaseous carbon sensed by the instruments and the RDX recovered from the sensor intake filters. The mean residues estimate for the surface sample replicates was 3.6 mg RDX/HMX per C4 block. The mean airborne residues estimate from the suspended samplers was 0.24 mg RDX per C4 block. We have shown that air emissions are a comparatively minor component of total energetics residues mass, amounting to only 6.6% of the estimated ground deposition residues and 6.3% of total estimated residues for these tests. Similar differences in estimated residues quantities are anticipated for other munitions. Air emission sampling and combustion product modeling should not be solely relied upon to estimate energetic residues. We recommend surface sampling as the most feasible method to quantify post-detonation residues and the inclusion of airborne particle mass estimates when a more complete mass balance estimate is required. Analysis of gaseous emissions based on the carbon balance method described in this paper can be a valuable complement to the surface deposition method, providing particle size information that will affect human health, quantifying the mass of energetics not normally recovered during surface sampling, and providing an indication of small-particle entrainment in the air column that is not captured by the surface sampling method.

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