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Estimating Energetic Residue Loading on Military Artillery Ranges

Large Decision Units

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Alan D. Hewitt, Thomas F. Jenkins, Charles A. Ramsey, Kevin L. Bjella, Thomas A. Ranney, and Nancy M. Perron March 2005

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ABSTRACT

Sampling experiments were conducted at three artillery/mortar impact ranges at Fort Hood, Texas; 29 Palms, California; and Fort Carson, Colorado, and at a mortar firing point at Fort Carson. The objective of these investigations was to assess the use of multi-increment sampling as a means of estimating the concentrations and mass loading of energetic compounds in surface soils for decision units ranging in size from 100 to 10,000 m². In some cases, chunks of pure explosives were observed on the surface within the areas being sampled. These chunks were presumably present due to the partial (low-order) detonation of some type of munition during past training exercises, or from blowing in place of unexploded ordnance.

Characterization was conducted using 49- to 100-increment surface samples that were collected using a systematic sampling design where individual increments were collected at equally spaced distances across the area. This was accomplished by dividing the area of concern into 49 to 100 equally sized subareas and collecting an increment from each sub-area to build the sample. The mass of multi-increment samples collected generally ranged from 1 to 2 kilograms. Replicate samples were collected to assess the reproducibility, i.e., sampling error.

Average concentration estimates for the studied areas were used to estimate the mass loading for the energetic substances that were detected. The energetic compounds detected were generally RDX, HMX, and TNT for impact areas where the residue deposition appeared to be mostly from Composition-B-filled rounds. Sometimes the environmental transformation products of TNT, namely 2ADNT, 4ADNT, and TNB, were also detected. For the firing point area, only NG and 2,4DNT were detected.

Overall, this sampling strategy was adequate to characterize a decision unit as large as $10,000 \text{ m}^2$ at a heavily used firing point. Compositional and distributional sources of error confounded efforts to consistently achieve a comparable level of uncertainty for these larger decision units on artillery and mortar impact ranges. Nevertheless, the collection of replicate multi-increment samples enhances the reliability of this sampling strategy and yields information on the extent and type of heterogeneity present.

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PREFACE

This report was prepared by Alan D. Hewitt, Dr. Thomas F. Jenkins, and Kevin L. Bjella, Environmental Sciences Branch, U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research and Development Laboratory (CRREL), Hanover, New Hampshire; Charles A. Ramsey, Envirostat, Fort Collins, Colorado; Thomas A. Ranney, Science and Technology Corporation, Hanover, New Hampshire; and Nancy M. Perron, Snow and Ice Branch, ERDC-CRREL.

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The Commander and Executive Director of the Engineer Research and Development Center is COL James R. Rowan, EN. The Director is Dr. James R. Houston.

Estimating Energetic Residue Loading on Military Artillery Ranges: Large Decision Units

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1 INTRODUCTION

Over the past several years a number of studies have been conducted in the United States and Canada with a goal of understanding whether the deposition of residues of energetic compounds presents a major environmental problem at military firing ranges. For the purposes of this discussion, we will limit the meaning of energetic compounds to those chemicals used by the military as propellants or secondary explosives because they constitute the largest mass of chemicals of this type used by the military. A major aspect of the work has been to determine the identities and to estimate the concentrations of these energetic substances at the various types of military training ranges. These training ranges vary tremendously in size from an acre or less for a hand grenade range to many square miles for artillery and bombing ranges. They also differ because of the variety of munition items used.

To date, most of the studies that have been conducted have taken place at ranges used by either the United States or Canadian Army. Much less information is available about residues at ranges controlled by the other military services. Army ranges include artillery and mortar ranges, antitank rocket ranges, multipurpose range complexes used for tank firing, hand grenade ranges, rifle grenade ranges, demolition ranges of various types, and portions of Army ranges that have been used by the Air Force or Navy for bombing practice (Houston 2002). Some ranges use high-explosive-filled munitions while others use simulated (or inert) munitions. Portions of the ranges are used for firing the munition whereas other portions of the range are used as impact areas where detonations occur. These two areas are generally distinct at Army ranges, so the types of energetic substances found at firing points are generally different from those found at impact areas.

For the Army, the high explosives used in the greatest amounts are TNT (2,4,6-trinitrotoluene), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine). The energetic substances used in the largest amounts for gun and rocket propellants include NC (nitrocellulose), NG (nitroglycerin), 2,4DNT (2,4-dinitrotoluene), and NQ (nitroguanidine). With the exception of NC and NQ, which are not typically determined, these compounds are the ones detected at the greatest concentration. Additional compounds that often are detected are impurities or environmental transformation products of TNT, such as 1,3,5-TNB (1,3,5-trinitrobenzene, 2ADNT (2-amino-4,6-dinitrotoluene), and 4ADNT (4-amino-2,6-dinitrotoluene). These high explosives are sometimes used alone-for example, some 155-mm howitzer rounds contain only TNT-or they may be used in various compositions such as Octol, which is composed of HMX and TNT, and Composition B, which is composed of RDX and TNT. Propellants are generally based on nitrocellulose combined with 2,4DNT in single base propellants, NG is used in double-base propellants, and NG and NQ are used in triple-base propellants.

Several papers have described the uncertainty associated with the collection of representative samples at areas where residues of energetic compounds have been distributed on the ground surface (Jenkins et al. 1997, 1999, 2001, 2004a, 2004b, 2005; Pennington et al. 2002, 2003; Thiboutot et al. 1998, 2003; Walsh et al. 2001, 2004, 2005). There are a number of different types of Department of Defense (DoD) training ranges where various types of munitions are used.

The energetic residues in impact areas and at firing points differ substantially in the specific chemicals present, their concentrations, and typical pattern of distribution. For example, at artillery and mortar range impact areas, the major residues are either TNT or Composition B (60% military-grade RDX and 39% TNT) (Pennington et al. 2002, 2003, 2004), while either or both NG and 2,4DNT can be found in surface soils at the firing point (Jenkins et al. 2001, Walsh et al. 2004).

The dispersion of propellant residues at a firing point occurs within tens of meters from the nozzle of the gun (Jenkins et al. 2001). Moreover, because the residue particles (i.e., NC-based fibers) tend to be typically less than 3 mm long and 0.3 mm in diameter and the same general area is used repeatedly, their distribution becomes fairly uniform at heavily used positions (Walsh et al. 2005). At artillery and mortar impact ranges, the major source of energetic residues is from munitions that failed to function properly. For instance, munitions that low-order (partially detonate) upon impact deposit orders of magnitude more residue than rounds that detonate as designed (Hewitt et al. 2003). Also, rounds that initially fail to detonate (duds) can be ruptured by nearby detonations. Duds are some-

times destroyed using a demolition charge. These blow-in-place operations deposit greater amounts of residue than rounds that detonate as designed. When these instances occur, the residues are distributed randomly as particles of pure explosive with a variable range of sizes, masses, and shapes (Taylor et al. 2004). This results in a heterogeneous distribution both in the environment and in the subsequent samples collected for characterization. Because these residue-laden surface soils potentially serve as the major source for off-site migration, it is of utmost importance for fate and transport modeling to correctly estimate the mass of residues to allow facility managers to implement sound range sustainment practices.

In studies conducted at the Canadian Forces Base-Valcartier (CFB-Valcartier), Donnelly Training Area (Delta Junction, Alaska), Canadian Forces Base-Gagetown (CFB-Gagetown), and Fort Polk (Louisiana), various sampling protocols were evaluated with regard to their ability to provide samples representative of the mean concentrations for an area of concern (Jenkins et al. 2004a, 2004b, 2005; Thiboutot et al. 2004; Walsh et al. 2005). Both discrete and multiincrement samples were collected within 10-m × 10-m areas and larger areas at both firing points and in the impact zone of anti-armor and artillery/mortar training ranges. The largest problem that had to be overcome was compositional and distributional heterogeneity. Compositional heterogeneity is due to the fact that not all of the particles that make up the population within the decision unit have the same concentration of target analytes. This heterogeneity is at a maximum when a portion of the target analytes is present as discrete particles. The error due to compositional heterogeneity is called the fundamental error and is inversely related to the sample mass. Distributional heterogeneity is due to the fact that contaminant particles are scattered across the site unevenly, sometimes with a systematic component as well as a short-range random component. The error associated with distributional heterogeneity is inversely related to the number of individual increments used to build the sample. This type of error is at a maximum when a single discrete sample is used to estimate the mean for a decision unit.

These potential sources of uncertainty compromise the ability to use statistical estimators based upon normal distributions. From these studies it was evident that basing estimates of the mass loading for various energetic compounds on a limited set of discrete samples, multi-increment samples built from only a few increments, or inadequately processed samples will result in very unreliable estimates. Another finding was that discrete samples generally underestimate the average concentrations for an area (Jenkins et al. 2004a, 2004b, 2005), whereas multi-increment samples, built from 30 or more increments, provide concentration estimates that were much more reproducible. The distribution of values from replicate multi-increment (30 or greater) was also much more normally distributed, therefore allowing for the computation of uncertainty estimates associated with means (Jenkins et al. 2004b, 2005).

Two studies (Thiboutot et al. 2004 and Walsh et al. 2005) have explored the use of multi-increment samples to obtain a mean surface energetic residue concentration for larger decision units (areas greater than 500 m²). In these studies, the entire area of concern was treated as a single unit, with further stratification to consider the potential influence of vegetation or other topographical features. For example, the collection of a single multi-increment sample was used to characterize the energetic residue loading over an entire firing position and around a cluster of targets within an impact area. In both instances the multi-increment samples were found to provide adequate estimates of mean concentrations based on sample replication and alternative sampling designs. These initial tests were encouraging and additional work to assess the approach of using multi-increment samples to provide concentration estimates over large areas needs to be further validated. An additional benefit of multiincrement samples is that they reduce the number of samples that will need to be collected, processed, and analyzed to establish the mass loading of energetic residues on various sections of military training ranges.

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2 OBJECTIVES

The major objective of this work was to evaluate the use of multi-increment samples to characterize areas of artillery and mortar range firing points and impact areas that are larger than we have previously addressed. A judgmental approach will be used to select areas where it is anticipated that detonation of military munitions could result in the accumulation of energetic residues on the surface. Previous studies have established that munitions that do not function properly produce low-order detonations that can lead to the dispersal of residue chunks and heavily influence surface soil concentrations over areas of unspecified size (Jenkins et al. 2001; Pennington et al. 2001, 2002, 2003, 2004). These particles of explosive residues reside on soils, grasses, mosses, leaves, etc., all of which are variables that contribute to compositional heterogeneity. Within impact areas, there are locations in which residue concentrations appear to be dominated by individual events, i.e., where a low-order detonation or a ruptured round has resulted in localized clustering of residue particles that result in soil concentrations that exceed 100 mg/kg. These we refer to as "hot spots," a form of distributional heterogeneity. To enhance our chances of capturing energetic residues, locations where detonations have occurred over a long period of time, often decades, were selected for investigation. From these data, initial estimates of the masses of various energetic compounds in the soil will be computed. These source estimates can be used in models to assess the potential of off-site migration of energetic compounds.

3 SOIL SAMPLE COLLECTION AND ANALYSIS

Sample increments were obtained with either small stainless steel scoops or specially designed coring tools (Walsh 2004). Sampling tools were cleaned between sampling locations by rinsing with water followed by acetone, then wiping dry with a clean paper towel. If visible chunk explosive residue was observed on the surface, it was avoided during the sampling activity, i.e., not included in the sample. This precaution is necessary to avoid special shipping requirements that are needed when samples contain enough energetic residue for the incidental propagation of a detonation (AEC 1994). Sample increments were either individually placed into 4-oz wide-mouth jars or combined within specially cleaned plastic bags for storage and shipment.



Figure 1. Area at Fort Hood, Texas, where 100-m × 100-m grid was established.

Sample collection at Fort Hood, Texas, 26–31 March 2004

We investigated a number of potential sampling areas on an artillery/mortar impact range at Fort Hood and selected a location that was heavily cratered. This location had a tank target in one corner of the area, and our initial inspection failed to detect any low-order detonations that would tend to dominate surface residues (Fig. 1). A 100-m \times 100-m decision unit was established with a global

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positioning system (Appendix A for GPS positions); two EOD technicians inventoried the craters, dividing them into three classifications: old, new, and fresh. A crater was classified as "old" if it was covered by grasses and shrubs, "new" if there was partial coverage with grasses, and "fresh" if it was devoid of all vegetation. A total of 673 craters was identified within this 100-m \times 100-m area: 488 were classified as old, 130 as new, and 55 as fresh.

Surface unexploded ordnance were also inventoried in this area. Seven 155-mm high-explosive rounds were found on the surface; none appeared to be breached. One 2.75-inch rocket warhead was found that had the fuse broken off from the remainder of rocket assembly. This warhead was filled with what appeared to be Composition B from colorimetric tests using an EXPRAY kit (Plexus, Inc.). No residue was observed on the ground surface in the vicinity of the warhead. One 90-mm high-explosive plastic (HEP) round that appeared to be cracked was found. Fins from both 81-mm and 120-mm mortars were also observed within the area, but they were not counted and were not unearthed to determine whether the warheads were intact.

Initially the 100-m by 100-m area was subdivided into 100 10-m × 10-m subareas by placing flags at 10-m intervals around the perimeter of the area. Using a systematic sampling design, six replicate multi-increment samples for this entire 100-m × 100-m area were obtained by combining a soil plug from each of these 10-m by 10-m sub-areas (Fig. 2). Every sample increment used to build these samples was obtained using a 28-mm-diameter coring tool adjusted to sample the top 2.5 cm (Fig. 3). The location within each sub-area where plugs were collected was established by rolling a pair of differently colored dice, to establish the northing and easting positions for each multi-increment sample. These northing and easting positions were maintained for a given sample in each of the 100 subareas. This is sometimes referred to as a systematic random design because we are using a systematic sampling strategy with a random starting point.

The 100-m × 100-m grid also was divided into 20-m × 20-m sub-areas and discrete core samples were collected at the corners of each sub-area grid (36 total) (Fig. 2). A 4.5-cm-diameter coring tool was used to collect discrete samples at the same depth as the multi-increment samples (0–2.5 cm) (Fig. 4).

While sampling the 100-m \times 100-m area, a chunk of explosives residue was discovered and tentatively identified as Composition B using an EXPRAY Kit (Fig. 5). Further investigation led to the discovery of several more chunks, the locations of which formed an elliptical pattern around a shallow crater where the first chunk was found. A 10-m \times 10-m decision unit was established that encompassed these chunks of pure explosive, and a second 10-m \times 10-m decision



unit was randomly established in an area where no chunk material was observed, i.e., a control grid (Fig. 2).

Figure 2. Diagram of 100-m \times 100-m grid at Fort Hood, Texas, divided into 100 10-m \times 10-m subgrids. Sample numbers for discrete samples where target energetic compounds were detected are shown with a dot locating their position within the grid.

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Figure 3. Coring tool (28-mm diameter) used to collect increments for composite samples at Fort Hood, Texas.



Figure 4. Coring tool (4.5-cm) used to collect discrete samples at Fort Hood, Texas.



Figure 5. Chunks of Composition B and TNT and the colors generated for each using the EXPRAY field detection kit.

Two 25-increment samples were collected with the 4.5-cm-diameter coring tool systematically in these decision units by dividing the area into $2\text{-m} \times 2\text{-m}$ cells and collecting an increment within each cell at a northing and easting position determined using dice. Soil profile samples also were collected using a scoop near some pieces of Composition B at depths of 0-2 cm, 2-6 cm, 6-9 cm, 9-12 cm, and 12-16 cm in the potential "hot spot" area and, likewise, at depths of 0-1 cm, 1-3 cm, 3-8 cm, 10-12 cm, 2-15 cm, and 16-18 cm, in the $10\text{-m} \times 10\text{-m}$ area where no chunk material was observed.

Lastly, samples were collected around the tank target to determine whether there was any correlation between residue concentrations and distance from the target. A segmented circular grid was laid out based on the major compass headings, around the tank target as shown in Figure 6. A 4.5-cm-diameter coring tool was used to randomly collect 10 increments of surface soil (0–2.5 cm) from each designated segment, to build a sample. A total of 16 multi-increment samples was collected at distances of 0–2, 2–5, 5–10, and 10–20 m from the tank target. Discrete samples were also collected with this coring tool along the major compass headings at intervals 2, 5, 10, and 20 m.





Sampling at 29 Palms, California, 4-5 May 2004

Soil sampling was conducted at the U.S. Marine Corps Base at 29 Palms, California, at three areas in the Emerson Lake and Quackenbush impact ranges on 4–5 May 2004. Because of a heavy training schedule at the base, we were given access to these ranges for only a day and a half. Unlike most Army ranges, the impact ranges at 29 Palms are subject to firing from artillery, mortars, tanks, small arms, and Marine air assets. Troops also maneuver through these ranges and hence there is an ongoing effort to maintain a surface clear of unexploded ordnance (UXO). The soils at 29 Palms were composed of sands and small pebbles with very little vegetation. All sampling was conducted using stainless steel scoops because the soil was not sufficiently cohesive to use core samplers. With the exception of areas where soil profiles were sampled, sample increments were collected from the top 1.5 cm.



Figure 7. Area at the Emerson Lake Range at 29 Palms, California, where a 100-m × 100-m sampling grid was established.

On 4 May we entered the Emerson Lake impact range along a cleared access road and sampled in a canyon where two target tanks were positioned at the base of the hill (Appendix B for GPS positions). The canyon floor and lower slopes were covered with fine-textured sand with very little vegetation. There also was a sand-covered road that led to a narrow pass to the opposite side of the hill (Fig. 7). The steep slopes and tops of the hills were covered with large rocks. The tank targets were positioned to the right and left side of this road and were about 150 m from each other in the level portion of the canyon (Fig. 8). Upon approaching the tank on the right side of the road, several small (< 1-cm-diameter) chunks of what appeared to be explosives residues were observed on the surface. Several of these chunks were tested using an EXPRAY kit and the presence of both a nitro-aromatic and a nitramine/nitrate ester was qualitatively identified. Subsequent laboratory analysis at CRREL confirmed the proper concentration ratio of RDX/TNT for Composition B.

Further investigation indicated that there were hundreds of individual small pieces of this explosive material on the surface in this area and in another area (Fig. 9). These pieces of energetic residues were readily identified by their reddish brown color and a small reddish halo surrounding the particles (Fig. 10). We believe that this halo is a result of photodegradation of TNT, forming a reddishcolored transformation product that is rinsed from the particle by rainfall and subsequently redeposited around the perimeter of the particle by evaporation.



Figure 8. Diagram of 100-m × 100-m sampling grid established at the Emerson Lake Range at 29 Palms, California.



Figure 9. Small pieces of explosive observed on the surface of the soil at the Emerson Lake Range at 29 Palms, California.



Figure 10. Small chunk of explosive showing halo of color that develops as these chunks weather, found at the Emerson Lake Range, 29 Palms, California.

Both a 100-m \times 100-m and a 10-m \times 10-m area were established as decision units at the Emerson Lake site. The 10-m \times 10-m decision unit was located in the area where the greatest density of chunks was observed (Fig. 8); the perimeter was marked by placing pin flags at 2-m intervals. This 10-m \times 10-m area was sampled using three different strategies. Three replicate 25-increment samples were collected using a simple random collection strategy within the boundaries of the 10-m \times 10-m area (29P-13 to 29P-15). Three replicate 25-increment samples were collected using a systematic method to ensure that increments were collected at equal spacings across the entire surface area (29P-10 to 29P-12). Three discrete samples also were collected from randomly chosen positions. A set of profile samples from the surface to a depth of 12 cm (29P-1 through 29P-6) were collected below a 2.0-g chunk of what subsequently was determined to be Composition B. As noted previously, visible chunks of explosive residues were intentionally excluded from all samples.

The 100-m \times 100-m sampling area was established in the basin of the canyon between the two target tanks (Fig. 8) that encompassed the 10-m \times 10-m decision unit discussed above. This large decision unit was positioned closer to the tank on the right side because bees were observed in close proximity to the other target. After locating the four corners using a global position system (GPS), orange pin flags were set at 10-m intervals along the north and south edges of the grid. Six approximately 100-increment samples (29P-20 through 29P-25) were collected systematically by obtaining a surface soil increment approximately every 10 m while walking in the middle of the 10 rows between the flags along opposite sides of the grid. Two such multi-increment samples were collected by each of three different samplers. During this sampling activity, several additional chunks of energetic residues were observed throughout the 100-m \times 100-m decision unit.

On May 5th we sampled on the Quackenbush training area near two different targets. No visible pieces of energetic residues were found during an initial survey of the area adjacent to the first target vehicle we investigated (Fig. 11). Flags were positioned to delineate a 30-m radius around this target (2800 m²). Three 50-increment surface soil samples were collected using a systematic sampling strategy, moving back and forth from the perimeter to the target while moving around the circle. During this sampling activity a chunk (2 to 3 mm in diameter) of energetic residue was found next to the target, but careful scrutiny of the area did not reveal any additional pieces of explosive within the sampled area. The chunk was tested with the EXPRAY kit; a nitroaromatic and nitramine/nitrate esters were qualitatively identified. Although no laboratory analysis was conducted, we believe this material was Composition B.



Figure 11. Target at the Quackenbush Range at 29 Palms, California, where a circular sampling grid 30 m in diameter was established.

The second target sampled was some 200 m northwest from the first. Visual inspection of the area around this target revealed the presence of numerous chunks of energetic residues ranging in size from 2 mm in diameter to pieces larger than the size of a baseball. Over 150 chunks were flagged in an attempt to delineate the area covered with visible energetic residue. We estimated that 5 to 10 kg of energetic residue chunks were present on the surface. All of the residue chunks tested in the field with the EXPRAY kit gave a response similar to what has been previously stated. While driving between the two targets, a large unexploded bomb (500 lbs) was observed. Moreover, around the first target and between the two targets, several craters that appeared to be formed by the detonation of a munition of this size were also observed. Because of these observations, one possible explanation for the large amount of energetic chunk residue present in this area was the partial detonation of a bomb. A low-order detonation may have occurred either upon impact or when an attempt was made by EOD personnel to blow a dud in place. It also was noted that the chunks of explosives residue in this area had less rounded edges, the interior was a light grey color, and the interior surfaces sparkled in the sunlight. Subsequently it was determined that there were aluminum flakes present.

A 100-m \times 100-m decision unit was established using the target as the southeast corner (Fig. 12). Within this large grid a 10-m \times 10-m grid was positioned in a location where 30 to 40 small (< 3-cm) visible chunks of energetic residue were observed (Appendix C for GPS positions). As before, flags were positioned at the corners and at 10-m intervals along two opposite sides of the larger area, and at 2-m intervals around the smaller area. Using only the systematic sampling strategies described for the samples collected at the first Emerson Lake Range, six 100-increment surface soil samples were collected (29P-35 through 29P-40) within this 100-m \times 100-m area, and triplicate 25-increment samples were obtained within the 10-m \times 10-m area (29P-29 to 29P-31). A set of depth-profile samples also were collected as deep as 8 cm below a 7.5-g chunk of explosive that was located within the smaller area (29P-32 to 29P-34).

Sampling at Fort Carson, Colorado

On May 19, 2004, we sampled a mortar firing point at Fort Carson. This firing point was located within a fenced area that was approximately 130 m wide and 150 m long and was sparsely vegetated. We selected a 100-m \times 100-m area to serve as the decision unit for this firing point, the boundaries of which were located about 5 m in front of an observation tower, 15 m from the fence on the east and west sides, and about 40 m from a ditch where a 40-mm rifle grenade (UXO) was laying on the surface. Flags were positioned at 14.3-m intervals around the perimeter of the area, effectively dividing the area into 7 \times 7 or 49 sub-areas (Fig. 13). Within this 100-m \times 100-m grid, four replicate 49-increment samples were collected from the surface to a 2.5-cm depth using small stainless steel scoops. Samples were collected systematically, one increment from each sub-area from predetermined northing and easting positions as established by two dice (GPS position in Appendix D).

On 22 May 2004, sampling was conducted in a heavily cratered area on an artillery impact range at Fort Carson. This was the most heavily impacted area that we encountered during the investigation at Fort Carson and the number of craters appeared to be similar to the area we studied at Fort Hood. A 100-m × 100-m area was established in an area centered among four target tanks (Fig. 14). The boundary of this decision unit was only about 10 m from the targets located to the southwest and northeast (Fig. 15). A flag was placed every 10 m around the outer perimeter of the designated area to effectively delineate 100 10-m × 10m sub-areas. Six systematically collected 100-increment samples (labeled FC-47 through FC-52) were collected (GPS positions in Appendix D) in an identical manner as described for the same size decision unit sampled at Fort Hood (Fig. 15). All samples at Fort Carson were collected with small stainless steel scoops from the top 2.5 cm of soil. During and after this sampling event, the field team looked carefully at the ground surface in an attempt to locate pieces of pure explosive. Only one 2-mm-sized piece of what appeared to be TNT (EXPRAY kit) was found, even after an exhaustive search.



Figure 12. Diagram of 100-m × 100-m sampling grid established at the Quackenbush Range, 29 Palms, California.



Figure 13. Diagram of 100-m × 100-m sampling grid established at a fencedin mortar firing point at Fort Carson, Colorado.



Figure 14. Impact area at Fort Carson, Colorado, where a 100-m × 100-m sampling grid was established.

Soil sample analysis

Soil samples from all of these field activities were overnight-shipped to the Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, New Hampshire. Discrete samples were air-dried at room temperature in the 4-oz amber containers, weighed, passed through a #10 (2-mm) sieve to remove oversize material, the sieved portion weighed, and the samples then returned to the 4-oz containers. The entire sieved portions of the discrete samples were extracted as follows.

A volume of acetonitrile in mL, approximately double the mass of the sample in grams, was added to each 4-oz jar unless the sample was too large (> 60 g). For those cases, the sample was transferred to an 8-oz jar and acetonitrile was added. All jars were capped and placed on a tabletop shaker at 150 rpm overnight (18 hours). The samples were removed from the shaker and allowed to settle for at least an hour. An aliquot of each extract was filtered through a 0.45- μ m Millex FH filter, placed in a 7-mL amber glass vial, and stored in a refrigerator until analyzed.





Multi-increment soil samples were placed on sheets of aluminum foil to airdry. Dried samples were weighed and sieved though a #10 sieve. The material that passed the sieve was weighed and ground in a Lab TechEssa LM2 (LabTech Essa Pty. Ltd., Bassendean, WA, Australia) puck mill grinder. Two different procedures were used. For samples from impact areas thought to contain mainly residues of high explosives, the sample was ground once for 60 seconds. For samples from firing point areas thought to contain mainly propellant residues, each sample was ground five times for 60 seconds with a 20-second rest period between each grind. This procedure was necessary to obtain adequate reproducibility among subsamples from soils containing propellant residues (Walsh et al. 2005).

After grinding, multi-increment samples were mixed thoroughly, spread to form a 1-cm-thick layer, and a subsample was obtained by collecting at least 30 increments randomly from the ground material for a mass of about 10 g. For every tenth sample from an impact range, two additional subsamples were collected in an identical manner to enable an assessment of subsampling uncertainty. Because the grinding procedure for samples from firing points had been recently developed, triplicate laboratory subsamples were collected from each firing point multi-increment sample. Each 10-g subsample was extracted with 20 mL of acetonitrile in an ultrasonic bath overnight at room temperature. After sonication, samples were allowed to settle for at least an hour. An aliquot was removed, filtered, and placed in a 7-mL amber vial for storage in a refrigerator.

Commercial sand was used as a laboratory processing blank. For discrete samples, 50 g of the commercial sand was placed in a jar, air-dried, and extracted with each batch (approximately 20 samples). For the multi-increment samples, approximately 500 g of this blank soil was air-dried, ground, subsampled, and extracted with each batch of field samples. A standard soil obtained from the U.S. Army Environmental Center was used for preparation of the laboratory control sample matrix. This soil was spiked with a suite of target analytes anticipated to be present in the field samples.

Prior to analysis, pre-screening of every soil extract was performed utilizing the EXPRAY kit to establish the presence of high concentrations of energetic residues. The screening was performed following the general guidelines provided with the kits. Sample extracts showing a faint intensity color generally required a tenfold dilution, medium intensity required a hundredfold dilution, and bright intensity required a thousandfold dilution (Bjella 2005).

Following the pre-screening step, all of the extracts were analyzed using the general procedures of SW 846 Method 8330 (EPA 1994). An aliquot of each sample was diluted 1 to 4 with reagent-grade water. Analysis was conducted on a modular RP-HPLC system from Thermo Finnigan composed of a Spectra-SYSTEM Model P1000 isocratic pump, a SpectraSYSTEM UV2000 dual wavelength UV/VS absorbance detector set at 210 and 254 nm (cell path 1 cm), and a SpectraSYSTEM AS300 auto sampler. Samples were introduced with a 100- μ L sampling loop. Separations were made on a 15-cm × 3.9-mm (4- μ m) NovaPak C-8 column (Waters Chromatography Division, Milford, Massachusetts) main-

tained at 28° C and eluted with 15:85 isopropanol/water (v/v) at 1.4 mL/min. Concentrations were estimated from peak heights compared to commercial multianalyte standards (Restek). Estimates of detection limits for the target analytes for this method are given in Table 1.

Table 1. Estimates of explosives detection limits for soil.									
Analyte	Soil (mg kg ⁻¹)								
	RP-HPLC	GC-ECD							
HMX	0.026	0.026							
RDX	0.034	0.003							
1,3,5-TNB	0.016	0.003							
TNT	0.016	0.001							
2,6DNT	0.019	0.001							
2,4DNT	0.028	0.001							
2ADNT	0.038	0.002							
4ADNT	0.032	0.002							
NG	0.02	0.02							
3,5-DNA	Co-elutes with NB	0.002							
1,3-DNB	0.1	0.001							
TETRYL	0.6	0.02							
PETN	0.5	0.016							

To confirm the presence of analytes, a second analysis was conducted on a subset of sample extracts, including all those with low concentrations of energetic compounds, by GC-ECD following the general procedure outlined in SW846 Method 8095 (EPA 1998). These analyses were conducted on an HP 6890 Gas Chromatograph equipped with a micro ECD detector. Direct injection of 1 µL of soil extract was made into a purged packed inlet port (250°C) equipped with a deactivated Restek Uniliner. Primary separation was conducted on a 6-m- \times 0.53-mm-ID fused-silica column, with a 1.5-µm film thickness of 5%-(phenyl)-methylsiloxane (Rtx-5 from Restek, Bellefonte, Pennsylvania). The GC oven was temperature-programmed as follows: 100°C for 2 min, 10°C/min ramp to 280°C. The carrier gas was hydrogen at 10 mL/min (linear velocity approximately 90 cm/sec). The ECD detector temperature was 310°C and the makeup gas was nitrogen flowing at 45 mL/min. If a peak was observed in the retention window for a specific signature compound, the extract was reanalyzed on a confirmation column, 6-m- \times 0.53-mm-ID having a 1.5-µm film thickness of a proprietary polymer (Rtx-TNT-2 from Restek).

The GC oven was temperature-programmed as follows: 130°C for 1 min, 10°C /min ramp to 280°C. The carrier gas was helium at 20 mL/min (linear velocity approximately 180 cm/sec) and the nitrogen makeup gas was flowing at 60 mL/min. Inlet and detector temperature were the same as above. Multi-analyte standards were purchased from Restek and the instrument was calibrated over five concentrations. Estimates of the detection limits for the GC-ECD method are given in Table 1.

4 RESULTS

Quality control

For quality assurance purposes, laboratory-processing samples (blanks), spiked laboratory control samples (LCS), and replicate subsamples were analyzed along with soil samples. Results for the LCS are presented in Tables 2 and 3 for HPLC and GC-ECD analysis, respectively.

from Fort Hood, 29 Palms, and Fort Carson.													
Sample type		Soil concentration (mg/kg)											
Fort Hood samples	нмх	TNB	RDX	TNT	2,4DNT	2ADNT	4ADNT	2,6DNT					
Mean (n=16)	0.991		0.906	1.00	1.02	1.00	0.978						
mean % recovery	99.1		90.6	99.9	102	100	97.8						
29 Palms samples	нмх	TNB	RDX	TNT	2,4DNT	2ADNT	4ADNT	2,6DNT					
Mean (n=2)	0.114	0.081	0.113	0.105	0.102	0.095	0.088						
mean % recovery	114	80.7	113	105	102	94.7	87.7						
Fort Carson samples	нмх	TNB	RDX	TNT	2,4DNT	2ADNT	4ADNT	2,6DNT					
Mean (n=3)	0.969	0.962	0.881	0.939	1.03	0.979	0.967	0.971					
mean % recovery	96.9	96.2	88.1	93.9	103	97.9	96.7	97.1					

Table 2. RP-HPLC QA results for spiked samples analyzed with batches of soil samples

Of the laboratory blank samples processed with the Fort Hood samples and analyzed by HPLC, TNT was detected twice. GC-ECD analysis confirmed only the TNT found in Blank #9. No other target analyte was detected. Blanks #7 and #9 were processed and analyzed with a batch of samples that had been collected next to rounds that had undergone low-order detonations, and, therefore these samples frequently had very high TNT concentrations. The TNT found in Blank #9 probably was due to equipment carryover, whereas the TNT in Blank #7 probably was due to instrumental carryover during the HPLC analysis run. Because of this incident, the protocol used for subsequent field sampling activities and analyses specified that samples collected in the vicinity of chunk residues be physically separated from all other samples from collection through determination. Samples collected next to rounds that have low-ordered and have

visibly covered the surrounding surface with chunks of energetic residue typically have analyte concentrations in excess of 1,000 ppm, which is about five orders of magnitude greater than our detection limits. Both the samples from 29 Palms and Fort Carson were processed after adopting this policy. The only energetic residue detected for these two ranges in a processing blank was HMX in one sample processed with the Fort Carson samples.

Sample type	Soil concentration (mg/kg)								
Fort Hood samples	нмх	TNB	RDX	TNT	2,4DNT	2ADNT	4ADNT		
Mean (n=4)	1.08	0.965	0.890	0.875	0.988	1.01	0.975		
mean % recovery	108	96.5	89.0	87.5 98.8		101	97.5		
29 Palms samples	нмх	TNB	RDX	TNT	2,4DNT	2ADNT	4ADNT		
Mean (n=2)	0.099	0.105	0.098	0.108	0.103	0.092	0.101		
mean % recovery	99.0	105	98.2	108	103	91.5	101		
Fort Carson samples	нмх	TNB	RDX	TNT	2,4DNT	2ADNT	4ADNT		
Mean (n=3)	0.986	0.968	0.958	1.01	0.976	0.963	0.968		
mean % recovery	98.6	96.8	95.8	101	97.6	96.3	96.8		

Table 3. GC-ECD QA results for spiked samples analyzed with soil samples from Fort Hood, 29 Palms, and Fort Carson.

With the omission of NG, Tables 2 and 3 present the LCS results for those energetic compounds that were observed in the soil samples. That includes HMX, TNB, RDX, TNT, 2,4-DNT, 2,6-DNT, 2ADNT, and 4ADNT. We neglected to include NG in the LCS for these samples; however, it has been previously included in our LCS in the same matrix, and good recoveries (> 95 to < 105%) were obtained (e.g., Thiboutot et al. 2004). The performance of the analytical methods was very good for eight of the nine compounds that were detected. The mean spike recovery results for the LCS ranged from 87.5% to 108%.

With the exception of the firing point samples at Fort Carson, multiincrement samples were randomly selected and triplicate laboratory subsamples were taken to evaluate the sample processing and subsampling methodology employed. All of the firing point multi-increment samples had triplicate subsamples analyzed to evaluate a newly adopted grinding protocol. Eight samples from Fort Hood were analyzed in triplicate (Table 4). The mean and percent relative standard deviation were calculated for all samples when all three determinations were above analytical detection limits. When one or two of the three values were below the detection limit, a value half the detection limit was used to estimate the mean only. Almost all of the concentrations determined for these eight samples were less than 1 mg/kg. The only exception was RDX in sample H-73, where the mean value was 1.69 mg/kg with a RSD of 4.6%. Even for samples with lower concentrations, only two of 16 had RSD estimates greater than 10%, indicating that the samples had been properly mixed and subsampled. The highest RSD obtained was only 18.7% and that was for a sample with a mean concentration of RDX of 0.125 mg/Kg (Table 4).

	Table 4. R	esults for re	eplicated s	amples fr	om Fort H	ood.	
Sample #			Sc	oil concent	ration (mg/	kg)	
Lab replicates		нмх	RDX	TNT	2ADNT	4ADNT	2,4DNT
H-36a		0.044	0.118	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-36b		0.040	0.128	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-36c		0.042	0.104	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
	H-36AVE*	0.042	0.117	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
	% RSD	4.8	10.3				
H-39a		0.038	0.116	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-39b		0.036	0.152	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-39c	_	0.032	0.108	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
	H-39ave	0.035	0.125	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
	% RSD	8.65	18.7				
H-73a		0.542	1.76	0.232	0.118	0.100	<d< td=""></d<>
H-73b		0.536	1.71	0.214	0.124	0.118	<d< td=""></d<>
H-73c		0.536	1.61	0.212	0.142	0.116	<d< td=""></d<>
	H-73ave	0.538	1.69	0.219	0.128	0.111	<d< td=""></d<>
	% RSD	0.644	4.64	5.02	9.76	8.86	
H-59a		0.0128 [†]	0.0396	<d< td=""><td>0.0090</td><td>0.0092</td><td>0.0370</td></d<>	0.0090	0.0092	0.0370
H-59b		0.0138	0.0430	0.0042	0.0098	0.0098	0.0358
H-59c		0.0114	0.0368	<d< td=""><td>0.0086</td><td>0.0088</td><td>0.0346</td></d<>	0.0086	0.0088	0.0346
	H-59ave	0.013	0.0398	0.0021	0.0091	0.0093	0.0358
	% RSD	13.5	7.80		6.69	5.43	3.35
H-61a		<d< td=""><td><d< td=""><td>0.0206</td><td>0.0038</td><td>0.0044</td><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td>0.0206</td><td>0.0038</td><td>0.0044</td><td><d< td=""></d<></td></d<>	0.0206	0.0038	0.0044	<d< td=""></d<>
H-61b		<d< td=""><td><d< td=""><td>0.0148</td><td>0.0042</td><td>0.0044</td><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td>0.0148</td><td>0.0042</td><td>0.0044</td><td><d< td=""></d<></td></d<>	0.0148	0.0042	0.0044	<d< td=""></d<>
H-61c		<d< td=""><td><d< td=""><td><d< td=""><td>0.0036</td><td>0.0038</td><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>0.0036</td><td>0.0038</td><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td>0.0036</td><td>0.0038</td><td><d< td=""></d<></td></d<>	0.0036	0.0038	<d< td=""></d<>
	H-61ave	<d< td=""><td><d< td=""><td>0.0121</td><td>0.0039</td><td>0.0042</td><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td>0.0121</td><td>0.0039</td><td>0.0042</td><td><d< td=""></d<></td></d<>	0.0121	0.0039	0.0042	<d< td=""></d<>
	% RSD				7.9	8.2	A DOUGH OF BUILD A
H-64a		<d< td=""><td>0.0062</td><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	0.0062	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-64b		<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-64c		<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>

Table 4 (cont'd).											
Sample #		Soil concentration (mg/kg)									
Lab replicates		нмх	RDX	TNT	2ADNT	4ADNT	2,4DNT				
	H-64ave	<d< td=""><td>0.0027</td><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	0.0027	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>				
	% RSD										
H-67a		<d< td=""><td>0.0072</td><td>0.0072</td><td>0.0042</td><td>0.0042</td><td>0.0028</td></d<>	0.0072	0.0072	0.0042	0.0042	0.0028				
H-67b		<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>				
H-67c		<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>				
	H-67ave	<d< td=""><td>0.0034</td><td>0.0027</td><td>0.0027</td><td>0.0027</td><td>0.0016</td></d<>	0.0034	0.0027	0.0027	0.0027	0.0016				
	% RSD										
H-70a		<d< td=""><td><d< td=""><td>0.026</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>0.026</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	0.026	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>				
H-70b		<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>				
H-70c		<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>				
	H-70ave	<d< td=""><td><d< td=""><td>0.0093</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>0.0093</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	0.0093	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>				
	% RSD					v					

When a value was less than the detection limit, a value of half the detection was used to compute the mean.

¹ Shaded values were obtained by GC-ECD; unshaded by HPLC.

Similar results were obtained for the 29 Palms and Fort Carson multiincrement samples (Tables 5 and 6). The majority of RSDs were below 10%, except for 2,4-DNT in samples from the firing point at Fort Carson. These four multi-increment samples of the firing point were ground for five consecutive one-minute intervals. The mean concentrations of NG in these samples ranged from 9.5 to 13.7 mg/kg, about two orders of magnitude higher than those for 2,4DNT. The RSDs for NG ranged from 2.53% to 7.29%, while those for 2,4DNT ranged from 19.3% to 40.1%. This suggests that the subsampling precision is dependent on analyte concentration.

In subsequent sections of the report, when individual samples are discussed or used in computations, the mean values will be used when triplicate subsamples were analyzed as part of our quality assurance program.

Fort Hood, Impact Range

Results from the six 100-increment samples (H-34 through H-39) representing the entire $100\text{-m} \times 100\text{-m}$ area are presented in Table 7. Only energetic compounds detected above method detection limits (Table 1) are reported in the tables and discussed in the text. RDX and HMX were detected in all six of the multi-increment samples with values ranging from 0.117 to 3.68 mg/kg, and 0.035 to 0.632 mg/kg, respectively (Table 7). TNT was detected in three samples with values ranging from 0.222 to 0.806 mg/kg, but TNT was below the detection limit of the HPLC method (0.016 mg/kg) in the other three samples.

Table 5. Results for replicated samples from 29 Palms.										
Sample #			S	oil conce	entration (mg/kg)				
Lab replicates	cates HMX RDX TNT TNB 2ADNT 1a 0.190 0.678 0.150 <d< td=""> <d< td=""></d<></d<>									
29P-21a		0.190	0.678	0.150	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
29P-21b		0.142	0.678	0.150	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
29P-21c		0.168	0.738	0.138	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
	29P-21ave	0.167	0.698	0.146						
	% RSD	14.4	4.96	4.75						
29P-40a		1.37	9.72	1.56	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
29P-40b		1.36	9.34	1.43	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
29P-40c		1.29	9.14	1.35	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
	29P-40ave	1.34	9.40	1.44	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
	% RSD	3.19	3.13	7.39						
29P-29a		1.49	12.8	4.78	0.064	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
29P-29b		1.44	12.5	4.86	0.058	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
29P-29c		1.48	13.0	4.80	0.058	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
	29P-29ave	1.47	12.8	4.81	0.060	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
	% RSD	1.68	2.31	0.86	5.77					

The mean ratios for HMX/RDX and TNT/RDX are 0.222 and 0.314, respectively, which are consistent with the source being weathered Composition B (Jenkins et al. 2004b). For fresh military-grade Composition B, we expect an HMX/RDX ratio of about 0.12 and a TNT/RDX ratio of about 0.73. Since the solubility of these three compounds is in the order TNT > RDX > HMX, an increased ratio of HMX/RDX and a decreased ratio of TNT/RDX indicates that the Composition B has weathered by dissolution. Composition B is the main charge for 81-mm mortars, 2.75-inch rockets, and some 155-mm howitzer rounds, and its presence is consistent with the UXO observed on the surface in this area. We need to be cautious with conclusions based on these ratios, however, because munitions with a main charge of TNT were certainly fired onto this range, and perhaps others, such as Octol (HMX/TNT), as well.

Table 6. Results for replicated samples from Fort Carson.												
Sample# Soil concentration (mg/kg)												
Lab replicates		TNB	TNT	3,5DNA	NG	2,4DNT	2,6DNT	2ADNT	4ADNT			
FC-1a		<d< td=""><td><d< td=""><td><d< td=""><td>9.46</td><td>0.060</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>9.46</td><td>0.060</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>9.46</td><td>0.060</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	9.46	0.060	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
FC-1b		<d< td=""><td><d< td=""><td><d< td=""><td>10.9</td><td>0.076</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>10.9</td><td>0.076</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>10.9</td><td>0.076</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	10.9	0.076	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
FC-1c		<d< td=""><td><d< td=""><td><d< td=""><td>10.0</td><td>0.038</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>10.0</td><td>0.038</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>10.0</td><td>0.038</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	10.0	0.038	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
	FC-1ave				10.1	0.058						
	% RSD				7.29	32.9	-					
FC-2a		<d< td=""><td><d< td=""><td><d< td=""><td>14.3</td><td>0.204</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>14.3</td><td>0.204</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>14.3</td><td>0.204</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	14.3	0.204	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
FC-2b		<d< td=""><td><d< td=""><td><d< td=""><td>12.9</td><td>0.390</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>12.9</td><td>0.390</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>12.9</td><td>0.390</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	12.9	0.390	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
FC-2c		<d< td=""><td><d< td=""><td><d< td=""><td>13.7</td><td>0.206</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>13.7</td><td>0.206</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>13.7</td><td>0.206</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	13.7	0.206	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
	FC-2ave				13.6	0.267						
	% RSD				4.95	40.1						
FC-3a	5	<d< td=""><td><d< td=""><td><d< td=""><td>13.0</td><td>0.054</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>13.0</td><td>0.054</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>13.0</td><td>0.054</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	13.0	0.054	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
FC-3b		<d< td=""><td><d< td=""><td><d< td=""><td>13.5</td><td>0.068</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>13.5</td><td>0.068</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>13.5</td><td>0.068</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	13.5	0.068	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
FC-3c		<d< td=""><td><d< td=""><td><d< td=""><td>13.7</td><td>0.080</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>13.7</td><td>0.080</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>13.7</td><td>0.080</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	13.7	0.080	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
	FC-3ave				13.4	0.067						
	% RSD				2.53	19.3						
FC-4a		<d< td=""><td><d< td=""><td><d< td=""><td>8.92</td><td>0.088</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>8.92</td><td>0.088</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>8.92</td><td>0.088</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	8.92	0.088	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
FC-4b		<d< td=""><td><d< td=""><td><d< td=""><td>9.64</td><td>0.044</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>9.64</td><td>0.044</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>9.64</td><td>0.044</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	9.64	0.044	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
FC-4c		<d< td=""><td><d< td=""><td><d< td=""><td>9.94</td><td>0.064</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>9.94</td><td>0.064</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>9.94</td><td>0.064</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	9.94	0.064	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
	FC-4ave				9.50	0.065						
	% RSD				5.52	33.7						
FC-26a		<d< td=""><td>0.118</td><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td>0.1</td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	0.118	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td>0.1</td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td>0.1</td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td>0.1</td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>0.1</td></d<></td></d<>	<d< td=""><td>0.1</td></d<>	0.1			
FC-26b		<d< td=""><td>0.090</td><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	0.090	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
FC-26c		<d< td=""><td>0.090</td><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	0.090	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>			
	FC-26ave		0.099									
	% RSD		16.3									
FC-28a		0.148	21.2	0.104	<d< td=""><td>0.048</td><td><d< td=""><td>1.58</td><td>1.64</td></d<></td></d<>	0.048	<d< td=""><td>1.58</td><td>1.64</td></d<>	1.58	1.64			
FC-28b		0.148	22.8	0.102	<d< td=""><td>0.038</td><td><d< td=""><td>1.64</td><td>1.73</td></d<></td></d<>	0.038	<d< td=""><td>1.64</td><td>1.73</td></d<>	1.64	1.73			
FC-28c		0.144	22.8	0.106	<d< td=""><td>0.042</td><td><d< td=""><td>1.64</td><td>1.77</td></d<></td></d<>	0.042	<d< td=""><td>1.64</td><td>1.77</td></d<>	1.64	1.77			
	FC-28ave	0.147	22.3	0.104		0.043		1.62	1.71			
	% RSD	1.57	4.15	1.92		11.80		2.06	3.91			

		Soil co	oncentration	(mg/kg)	Ra	tio
Sample #		НМХ	RDX	TNT	HMX/RDX	TNT/RDX
H-34		0.048	0.204	<d< td=""><td>0.235</td><td></td></d<>	0.235	
H-35		0.632	3.68	0.806	0.172	0.219
H-36ave*		0.042	0.117	<d< td=""><td>0.360</td><td></td></d<>	0.360	
H-37		0.402	2.70	0.762	0.149	0.282
H-38		0.068	0.504	0.222	0.135	0.440
H-39ave*		0.035	0.125	<d< td=""><td>0.282</td><td></td></d<>	0.282	
	Max	0.632	3.68	0.806		
	Min	0.035	0.117	0.008 [†]		
	Mean	0.205	1.22	0.302 [†]	0.222	0.314**
	Median	0.058	0.354	0.115 [†]		
	Std dev	0.253	1.56	0.382 [†]		
	% RSD	124	128	109		
* The reporte	ed values are	the mean of th	ree laborator	/ subsamples.		

Table 7. Results for 100-increment composite samples from 100-m × 100-m grid at Fort Hood impact area from HPLC analysis.

[†] One half the detection limit used for <d.

** Only for ratios with values.

Considering that we counted over 600 craters in this area, it was interesting that the mean concentrations of energetic substances for all six multi-increment samples are below 1.5 ppm (mg/kg). Because the means and medians for this data set (Table 7) do not agree, and the % RSDs are greater than 100%, the underlying distribution of concentrations does not appear to be Gaussian. Nevertheless, the computed mean is the most appropriate descriptor to estimate the mass of these energetic compounds in this 100-m × 100-m area, because pure Composition B explosive was observed to be present. Thus the influence of high values should not be diminished. Using the means for HMX, RDX, and TNT, respectively, we estimate the masses of residues in this decision unit to be 87, 518, and 128 grams for a 2.5-cm depth, using a soil density of 1.7 g/cm³.

Several small (> 0.2-cm to < 2-cm) chunks of Composition B were found with a total measured mass of 16.5 g (Fig. 16). Overall, the mass of explosive estimated to be present in the top 2.5 cm of soil for this sampling area (733 g) is about 44 times the amount of pure explosive that we observed on the surface (excluding that in the 2.75-inch warhead). In a similar study in a 10-m × 10-m area at Fort Polk, we found about three times as much mass of explosive residue in the soil than was present as chunk explosive on the surface (Jenkins et al. 2004b). Both Fort Hood and Fort Polk are in temperate climates (Houston et al. 2001), and apparently most of the energetic residues in the areas sampled in these artillery impact ranges exist in a size category that typically is used for soil, i.e., < 2 mm, and cannot be detected by visual inspection.



Figure 16. Field scale measuring the mass of a chunk of explosive found at Fort Hood, Texas.

The 1 to 2 kg of RDX, HMX, and TNT in the warhead we observed within this $100\text{-m} \times 100\text{-m}$ area is equivalent to or three times the mass we estimated to be present in and on the soil. This indicates that periodic range maintenance to remove these ruptured rounds can have a major effect on the sources of energetic compounds on these ranges. However, the rate at which that material would leach from this round is unknown.

Within this 100-m × 100-m area, we also collected a set of 36 discrete samples as described previously. Results for these samples are presented in Table 8. Of the 36 samples, HMX, RDX, 2ADNT, and 4ADNT were detected in eight, seven, two, and two samples, respectively. In most cases, more than one energetic compound was present in a discrete sample; therefore, overall only nine of the 36 discrete samples contained energetic residues detectable by HPLC analysis. The inability to detect the presence of energetic compounds in three quarters of the discrete samples illustrates the hit-or-miss nature of using this sampling strategy when the analytes of concern are heterogeneously distributed particles. In comparison, RDX and HMX were detected in all six composite samples and TNT was found in three.

Table 8. Discrete samples	collected	in	100-m	×	100-m	grid	at	Fort	Hood,
and analyzed by HPLC.									

-				
		Soil concentration (mg/kg) by HPI	_C	
Sample #	HMX	RDX	2ADNT	4ADNT
H-99	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-100	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-101	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-102	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-103	0.073	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-104	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-105	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-106	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-107	<d< td=""><td>0.056</td><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	0.056	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-108	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-109	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-110	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-111	0.738	0.745	0.122	0.080
H-112	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-113	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-114	0.031	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-115	0.050	0.056	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-116	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-117	0.038	0.055	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-118	0.038	0.081	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-119	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-120	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-121	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-122	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-123	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-124	0.605	3.75	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-125	0.224	0.451	0.078	0.031
H-126	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-127	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-128	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-129	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-130	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-131	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>

	Soil concentration (mg/kg) by HPLC									
Sample #	НМХ	RDX	2ADNT	4ADNT						
H-132	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>						
H-133	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>						
H-134	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>						
Max	0.738	3.750	0.122	0.080						
Min	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>						
Mean*	0.060	0.158	0.024	0.018						

Table 8 (cont'd). Discrete samples collected in 100-m × 100-m grid at Fort

The highest RDX and HMX concentrations established for a discrete sample were similar to maximum values established for the 100-increment samples (Tables 7 and 8). For example, the highest RDX values for the discrete samples and multi-increment samples were 3.75 and 3.68 mg/kg, respectively. The location of this discrete sample with the high RDX concentration (H-124) did not correspond to the area where residues were observed on the surface or which was near a broken-open round. The mean values for HMX and RDX for these 36 discrete samples were, respectively, 0.060 and 0.158 mg/kg, when values of onehalf the detection limit were used to represent the non-detects in Table 8.

Moreover, the 36 discrete samples collectively comprise a total sample mass comparable to each of the 100-increment samples. A comparison between these two sampling strategies for establishing the mean concentrations of RDX and HMX within this decision unit shows that the discrete samples resulted in much lower estimates and completely missed the presence of TNT. Since the sampling strategies acquired similar masses, the higher mean concentrations, and intermittent detection of TNT may also be a function of number of increments. This potential variable should be further investigated, since the comparison in this study is unbalanced i.e., 100-increment samples vs. 36 discrete samples.

Another consideration is that analysis costs typically are greater than sample collection and preparation. Therefore, an additional benefit from composite sampling is that it is more economical. Overall, these findings are consistent with a comprehensive study of sampling a $10\text{-m} \times 10\text{-m}$ decision unit within an artillery and mortar impact range (Jenkins et al. 2004b, 2005) and reaffirms that discrete samples tend to underestimate the mean or increases the possibility that analytes of interest will be completely missed when the analytes are heterogeneously distributed particles and the objective is to obtain an estimate of the average concentration.

The RDX and HMX estimates for the six 100-increment samples were not normally distributed. The results for multi-increment samples for a recent study at Fort Polk indicated that the non-normal distribution of energetic residue concentrations was due, at least in part, to the presence of a hot spot, (Jenkins et al. 2004b). This is an example of distributional heterogeneity. From visual observations made as these multi-increment samples were collected at Fort Hood, it was determined that there was one area where small chunks of Composition B were present on the surface that could be indicative of a hot spot. Chunks of explosive were not observed across the remainder of the sampling area. The results indicate that not only was pure Composition B present on the surface, but that RDX concentrations in surface soil were as high as 13.5 mg/kg for a 25-increment sample collected in this area. This RDX concentration is approximately 11 times larger than the computed mean for the six samples from this 100-m × 100-m area. Inclusion of a single soil increment with an RDX concentration of 13.5 mg/kg into one of the 100-increment samples would increase its concentration by only about 1%. To have a large influence on the 100-increment sample, an increment from this sub-area would have to have had an RDX concentration at least 10 times higher than 13.5 mg/kg. The range of discrete RDX values established in the Jenkins et al. 2004b study extended over five orders of magnitude, with the maximum concentrations two orders of magnitude higher than the mean. Therefore, it is very possible that an increment from this Fort Hood area had an RDX concentration that was 10 times or perhaps higher than 13.5 mg/kg. Thus the large differences found among the six 100-increment samples could be due to the variability in analyte concentrations among the increments from this hot spot area.

Results for the two $10\text{-m} \times 10\text{-m}$ areas established within the $100\text{-m} \times 100\text{-m}$ area are presented in Table 9. The systematically collected multi-increment samples from the area where chunk explosives were observed on the surface had much higher concentrations of energetic compounds (13.5 and 1.69 mg/kg for RDX) compared with the similarly collected multi-increment samples from the area where no visual explosive was observed (0.025 and 0.032 mg/kg for RDX). Thus, within this 100-m \times 100-m area, we have significant distributional heterogeneity (Table 7). The poor agreement between the replicate multi-increment samples from the 10-m \times 10-m area with residue on the surface and the 100-m \times 100-m area shows that the sampling strategy failed to adequately address the compositional and distribution heterogeneity at this site. However, because we used a systematic sampling pattern in both cases, the variability is anticipated to be lower than if a totally random sampling pattern was used. A larger variation in concentrations would be anticipated for a random sampling strategy because

	Soil concentration (mg/kg)									
Sample #	нмх	RDX	TNT	2ADNT	4ADNT					
	10-m x 10-m	n area with chun	k material prese	ent						
H-72	2.06	13.5	0.626	0.248	0.202					
H-73ave	0.538	1.69	0.219	0.128	0.111					
mean	1.30	7.61	0.423	0.188	0.157					
10-	-m x 10-m area w	ithout observab	le chunk materi	al present						
H-160	0.012*	0.025	<d< td=""><td>0.010</td><td>0.010</td></d<>	0.010	0.010					
H-161	0.018	0.032	<d< td=""><td>0.011</td><td>0.011</td></d<>	0.011	0.011					
mean	0.015	0.029	<d< td=""><td>0.011</td><td>0.011</td></d<>	0.011	0.011					

areas with higher concentrations could be either missed entirely or oversampled relative to the total decision unit.

Analytical results for the discrete and multi-increment samples collected around the tank target at Fort Hood are presented in Table 10. Of the 16 discrete samples collected at distances from 2 to 20 meters from the target, energetic compounds were detected in just two: TNT in one sample and NG in another. RDX and HMX were not detected in any of these samples analyzed by HPLC. Of the 16 multi-increment samples collected around the tank target (Table 10), three samples were lost during the field sampling exercise. Concentrations of energetic substances within the 13 multi-increment samples that were analyzed were generally near the detection limits of the GC-ECD method. The highest concentration obtained was 0.138 mg/kg for RDX in a sample that was collected from a region 10 to 20 m west of the tank target. There appears to be no correlation of concentration with sampling position with regard to the target for these samples, which agrees with what was found for samples near an artillery target at Fort Polk (Jenkins et al. 2004b) and elsewhere (Jenkins et al. 2001, Pennington et al. 2002).

Results from the two profile samples are shown in Table 11. For the samples collected in a crater within the 10-m × 10-m area where chunk residue was found on the surface (H-263.5 to H-267), HMX and RDX were detectable to a depth of 16 cm below surface. Consistent with all previous profiles collected under chunks of residue, the concentrations declined with depth (Jenkins et al. 2001; Pennington et al. 2001, 2002, 2003). For example, where the chunks were observed on the surface, the concentrations of HMX and RDX went from 0.951 and 2.21 mg/kg, respectively, at the surface to approximately an order of magnitude lower in concentration, i.e., 0.102 and 0.218 mg/kg, respectively, at a depth

of 12–16 cm. TNT, NG, 2ADNT, and 4ADNT were detected in the surface sample only from 0 to 2 cm, and not in any subsurface samples. The combined concentrations of 2ADNT and 4ADNT at the surface were greater than the TNT concentration. Profile samples from a crater with no visual evidence of explosive present (H-268 to H-273) overall had much lower concentrations of energetic compounds, but showed the same general trends as described above for the other profile. These trends in the profile samples, combined with the larger mass of energetic materials in the soil fraction (< 2 mm), and the HMX/RDX and TNT/ RDX ratios observed at this site, indicate that weathering mechanisms have greatly influenced the distribution of energetic residues.

Emerson Lake Range, 29 Palms, Impact Range

Results for the six multi-increment samples collected in the $100\text{-m} \times 100\text{-m}$ area chosen at the Emerson Lake Range are presented in Table 12. RDX, TNT, and HMX were detected in all six samples. No other energetic compounds were detected in any of the six samples, not even 2ADNT and 4ADNT, which are almost always detected when TNT is present at concentrations in this range. It may be that the very arid nature of this site limits the rate of formation of these environmental transformation products. Possibly 2ADNT and 4ADNT would have been detected at low concentration if the samples with relatively high TNT concentrations had been subjected to GC-ECD analysis, but the high concentration difficulties.

Concentrations in this set of six multi-increment samples ranged from 0.288 to 6.48 mg/kg for RDX (range factor of 22.5), 0.096 to 0.776 mg/kg for HMX (factor of 8.1), and 0.006 to 4.00 mg/kg for TNT (factor of 667) (Table 12). The concentrations for these replicates are likely not normally distributed, probably because of the presence of hundreds of various sized particles of pure explosive on the surface, i.e., a visible source of compositional heterogeneity. Similar to the decision units sampled at Fort Hood, the multi-increment systematic sampling strategy failed to adequately address compositional heterogeneity, and perhaps distributional heterogeneity, too. Even if we had not visually detected the presence of this chunk material, the large range found among replicate multi-increment samples could be used to infer the presence of compositional variability and/or hot spot(s) of high concentration within the boundaries of the grid, i.e., distributional variability.

Table 10.	Fort Hood discrete	and com	posite so	il sample	s collecte	ed around	l tank tarç	get.
				Soil con	centration	(mg/kg)		
Sample #	Location	HMX	RDX	TNT	NG	2,4DNT	2ADNT	4ADNT
	Discrete soil sam	oles collec	ted at vari	ous distar	ices from t	ank target		
H-40	2m-S	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-41	5m-S	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-42	10m-S	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-43	20m-S	<d< td=""><td><d< td=""><td>0.175</td><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>0.175</td><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	0.175	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-44	2m-W	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-45	5m-W	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-46	10m-W	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-47	20m-W	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-48	2m-N	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-49	5m-N	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-50	10m-N	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-51	20m-N	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-52	2m-E	<d< td=""><td><d< td=""><td><d< td=""><td>0.028</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>0.028</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>0.028</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	0.028	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-53	5m-E	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-54	10m-E	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-55	20m-E	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>

Composite soil samples (10 increments) collected in areas at various distances and directions from tank target

H-56	SE-SW, 0-2m	0.010*	0.016	0.006	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-57	SE-SW, 2–5m	<d< td=""><td>0.008</td><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	0.008	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-58	SE-SW,5-10m	samp	le lost					
H-59ave	SE-SW, 10-20m	0.013	0.0400	0.002	<d< td=""><td>0.036</td><td>0.009</td><td>0.009</td></d<>	0.036	0.009	0.009
H-60	SW-NW, 0-2m	samp	le lost					
H-61ave	SW-NW, 2-5m	<d< td=""><td><d< td=""><td>0.012</td><td><d< td=""><td><d< td=""><td>0.004</td><td>0.004</td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>0.012</td><td><d< td=""><td><d< td=""><td>0.004</td><td>0.004</td></d<></td></d<></td></d<>	0.012	<d< td=""><td><d< td=""><td>0.004</td><td>0.004</td></d<></td></d<>	<d< td=""><td>0.004</td><td>0.004</td></d<>	0.004	0.004
H-62	SW-NW, 5-10m	samp	le lost					
H-63	SW-NW, 10-20m	0.092	0.138	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-64ave	NW-NE, 0-2m	<d< td=""><td>0.003</td><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	0.003	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-65	NW-NE, 2-5m	<d< td=""><td>0.010</td><td>0.059</td><td><d< td=""><td><d< td=""><td>0.040</td><td>0.040</td></d<></td></d<></td></d<>	0.010	0.059	<d< td=""><td><d< td=""><td>0.040</td><td>0.040</td></d<></td></d<>	<d< td=""><td>0.040</td><td>0.040</td></d<>	0.040	0.040
H-66	NW-NE, 5-10m	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-67ave	NW-NE, 10-20m	<d< td=""><td>0.003</td><td>0.003</td><td><d< td=""><td>0.002</td><td>0.003</td><td>0.003</td></d<></td></d<>	0.003	0.003	<d< td=""><td>0.002</td><td>0.003</td><td>0.003</td></d<>	0.002	0.003	0.003
H-68	NE-SE, 0-2m	<d< td=""><td>0.013</td><td>0.008</td><td><d< td=""><td><d< td=""><td>0.007</td><td>0.004</td></d<></td></d<></td></d<>	0.013	0.008	<d< td=""><td><d< td=""><td>0.007</td><td>0.004</td></d<></td></d<>	<d< td=""><td>0.007</td><td>0.004</td></d<>	0.007	0.004
H-69	NE-SE, 2–5m	<d< td=""><td>0.007</td><td>0.007</td><td><d< td=""><td><d< td=""><td>0.007</td><td>0.004</td></d<></td></d<></td></d<>	0.007	0.007	<d< td=""><td><d< td=""><td>0.007</td><td>0.004</td></d<></td></d<>	<d< td=""><td>0.007</td><td>0.004</td></d<>	0.007	0.004

Estimating Energetic Residue Loading

		Tal	ble 10 (co	ont'd).					
Soil concentration (mg/kg)									
Sample #	Location	нмх	RDX	TNT	NG	2,4DNT	2ADNT	4ADNT	
		oil comple	e (10) incre	montel col	lloctod in	31036			
	at various	oil sample distances	s (10 incre s and dired	ements) col	tank tar	areas get			
H-70ave	At various	oil sample distances <d< td=""><td>s (10 incre s and dired <d< td=""><td>ctions from 0.009</td><td>tank tar</td><td>areas get <d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	s (10 incre s and dired <d< td=""><td>ctions from 0.009</td><td>tank tar</td><td>areas get <d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	ctions from 0.009	tank tar	areas get <d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>	

Table	11. Depth profile samp	oles collec	ted in are	a around	tank targe	et at Fort H	lood.
			Sc	oil concent	ration (mg	/kg)	
Sample #	Depth	HMX	RDX	TNT	NG	2ADNT	4ADNT
D	epth samples in 10-m ×	10-m grid v	vhere no su	urface expl	osives wer	e observed	
H-268	0–1cm	0.070*	0.135	<d< td=""><td><d< td=""><td>0.054</td><td>0.055</td></d<></td></d<>	<d< td=""><td>0.054</td><td>0.055</td></d<>	0.054	0.055
H-269	1–3cm	0.047	0.085	<d< td=""><td><d< td=""><td>0.048</td><td>0.045</td></d<></td></d<>	<d< td=""><td>0.048</td><td>0.045</td></d<>	0.048	0.045
H-270	3–8cm	0.021	0.070	<d< td=""><td><d< td=""><td>0.032</td><td>0.029</td></d<></td></d<>	<d< td=""><td>0.032</td><td>0.029</td></d<>	0.032	0.029
H-271	10–12cm	0.014	0.101	<d< td=""><td><d< td=""><td>0.022</td><td>0.021</td></d<></td></d<>	<d< td=""><td>0.022</td><td>0.021</td></d<>	0.022	0.021
H-272	12-15cm	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-273	16–18cm	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
Depth s	samples in 10-m × 10-m	grid where	chunk exp	losives we	re observe	d on the su	rface.
H-263.5	0-2cm	0.951	2.21	0.064	0.030	0.235	0.215
H-264	2-6cm	0.395	3.71	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-265	6–9cm	0.117	0.331	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-266	9–12cm	0.131	0.252	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
H-267	12–16cm	0.102	0.218	<d< td=""><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
* Shaded va	alues were determined by	GC-ECD; u	nshaded va	lues were d	etermined I	by HPLC.	

Results for all samples from the 10-m × 10-m area where 40 to 50 chunks of Composition B were observed are presented in Table 13. Within this area, samples were collected in triplicate using three different strategies: simple random discrete samples (29P-13 to 29P-15), simple random 25-increment samples (29P-10 to 29P-12), and systematically collected 25-increment samples (29P-7 to 29P-9). In terms of reproducibility, the results for the systematically collected 25-increment samples have much lower sampling % RSD than the other two approaches. Using RDX as an example, the RSD for the systematic multiincrement samples was 9.69%, 55.2 % for the multi-increment random samples, and 50.8% for the discrete samples. These results agree with what was predicted from a recent study at an artillery impact area at Fort Polk, Louisiana (Jenkins et al. 2004b). These mean and median values for these data also agree with earlier results that demonstrate that results for discrete samples are generally lower than those for multi-increment samples collected in the same area (Jenkins et al. 2004a, 2004b). Using the mean values for the systematically collected multi-increment samples, estimates of the masses of HMX, RDX, and TNT within this 10-m \times 10-m area are 0.344, 0.87, and 0.041 g, respectively. Within this area there was estimated to be between 10 and 20 g of chunk energetic residues on the surface.

	Soil	concentra by HPLC	ation (mg analysis	Ratio	Ratio	
Sample #		HMX	RDX	TNT	HMX/RDX	TNT/RDX
29P-20		0.096	0.288	0.006*	0.333	0.021
29P21ave		0.167	0.698	0.146	0.239	0.209
29P-22		0.136	0.904	0.170	0.150	0.188
29P-23		0.286	1.96	0.968	0.146	0.493
29P-24		0.286	1.64	0.934	0.175	0.571
29P-25		0.776	6.48	4.00	0.120	0.617
	Max	0.776	6.48	4.00		
	Min	0.096	0.288	0.006		
	Mean	0.291	1.99	1.04		
	Median	0.226	1.27	0.552		

It is surprising that mean and median concentrations for the $100\text{-m} \times 100\text{-m}$ grid are higher than for the $10\text{-m} \times 10\text{-m}$ grid where the highest numbers of small chunks of explosive were observed. However, chunk explosive was observed on the surface at several locations within this $100\text{-m} \times 100\text{-m}$ grid. Chunk explosive also was observed beneath the surface, i.e., presumably buried by blowing sand. Estimates of the mass of HMX, RDX, and TNT were made using the mean for this $100\text{-m} \times 100\text{-m}$ area and were 123, 846, and 442 g, respectively.

			So	il concenti	ration (mg	/kg)	
Sample #	Sample information	HMX	TNB	RDX	TNT	2ADNT	4ADN1
	Profile samples collec	ted under a	a 2.0-g ch	unk of Cor	nposition	в	
29P-1	0–1 cm	93.8	3.82	825	537	0.106	0.053
29P-2	1–3 cm	9.40	1.79	58.8	41.7	0.065	0.044
29P-3	3–6 cm	0.758	0.649	3.10	2.59	0.102	0.078
29P-4	6–8 cm	0.037	<d< td=""><td>0.281</td><td>0.158</td><td>0.039</td><td>0.043</td></d<>	0.281	0.158	0.039	0.043
29P-5	ed under a 2.0 93.8 9 6-8 cm 8-10 cm		0.240	0.078	0.051	0.055	
29P-6	10–12 cm	0.030	<d< td=""><td>0.192</td><td>0.055</td><td>0.032</td><td>0.030</td></d<>	0.192	0.055	0.032	0.030
	Composite samples of 25	increments	s collecter	d by syste	matic app	roach	
29P-7	rep 1	0.136	<d*< td=""><td>0.340</td><td>0.024</td><td><d< td=""><td><d< td=""></d<></td></d<></td></d*<>	0.340	0.024	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
29P-8	rep 2	0.138	<d< td=""><td>0.308</td><td>0.012</td><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	0.308	0.012	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
29P-9	rep 3	0.130	<d< td=""><td>0.374</td><td>0.012</td><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	0.374	0.012	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
	Max	0.138		0.374	0.024		
	Min	0.130		0.308	0.012		
	Median	0.136		0.340	0.012		
	Mean	0.135		0.341	0.016		
	Std dev	0.0042		0.0330	0.0069		
	% RSD	3.09		9.69	43.3		
	Composite samples of 2	5 incremen	ts collect	ed by rand	lom appro	ach	
29P-10	rep 1	0.096	<d< td=""><td>0.246</td><td>0.014</td><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	0.246	0.014	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
29P-11	rep 2	0.164	<d< td=""><td>0.448</td><td>0.012</td><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	0.448	0.012	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
29P-12	rep 3	0.166	<d< td=""><td>0.784</td><td>0.122</td><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	0.784	0.122	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
	Max	0.166		0.784	0.122		
	Min	0.096		0.246	0.012		
	Median	0.164		0.448	0.014		
	Mean	0.142		0.493	0.049		
	Std dev	0.0398		0.2718	0.0629		
	% RSD	28.1		55.2	128		
	Discrete sa	mples usin	ig random	approach	i		
29P-13	rep 1	0.054	<d< td=""><td>0.058</td><td>0.006</td><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	0.058	0.006	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
29P-14	rep 2	0.086	<d< td=""><td>0.169</td><td>0.008</td><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	0.169	0.008	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
29P-15	rep 3	0.042	<d< td=""><td>0.187</td><td>0.010</td><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	0.187	0.010	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>

Table 13. Results from samples collected in 10-m × 10-m grid containing small chunks of

		/kg)					
Sample #	Sample information	HMX	TNB	RDX	TNT	2ADNT	4ADNT
	Max	0.086		0.187	0.010		
	Min	0.042		0.058	0.006		
	Median	0.054		0.169	0.008		
	Mean	0.060		0.138	0.008		
	Std dev	0.0225		0.0699	0.0022		
÷	% RSD	37.2		50.8	26.8		

Table 13 (cont'd). Results from samples collected in 10-m × 10-m grid containing small

In the profile samples collected under the 2.0-g piece of Composition B (Sample 29P-1 to 29P-6), RDX, HMX, TNT, and TNB were detected. In the top cm, concentrations of RDX, HMX, and TNT were, respectively, 825, 93.8, and 537 mg/kg. The concentrations of RDX, HMX, and TNT are reduced by about an order of magnitude in the sample collected from the 1- to 3-cm depth compared to the 0-1 cm layer. At the deepest depth sampled (10-12 cm), RDX, HMX, and TNT were still measurable. Detectable concentrations of 2ADNT and 4ADNT were present only at the surface; combined, they were less than 1% of the concentration of TNT. Therefore, even directly below this chunk of pure explosive, only very small amounts of the energetic compounds leach deep into the profile, a likely consequence of the minimal precipitation that occurs within the desert environment of 29 Palms.

Quackenbush Range, 29 Palms, Impact Range

Results for the first target area sampled at the Quackenbush Range at 29 Palms are presented in Table 14. These results are for 50-increment samples collected systematically within the circle of radius 30 m around the target (surface area was about 2800 m²). As with samples from the Emerson Lake Range, only RDX, HMX, and TNT were detected in these samples. While there were only three replicates taken here, the range of concentrations for a given analyte is much smaller than found at either the Fort Hood Range or the 100-m × 100-m grid at the Emerson Lake Range. For example, the range for RDX is 1.32 to 4.76, a factor of 3.6, whereas the same ratio for the other two ranges was 31.5 and 22.5, respectively. The smaller range among replicates could be due to the absence of a hot spot of high concentration within this area. In contrast to the other ranges, only one small piece of explosive residue was found, even after an exhaustive search of the area. All of the areas sampled at this installation were

	Soil conce	entration (mg/kg) k	Ratio	Ratio		
Sam	ple #	HMX	RDX	TNT	HMX/RDX	TNT/RDX	
29P-26		0.250	1.32	0.258	0.189	0.195	
29P-27		0.912	4.76	1.13	0.192	0.238	
29P-28		0.640	2.16	0.536	0.296	0.248	
	Max	0.912	4.76	1.13			
	Min	0.250	1.32	0.258			
	Mean	0.601	2.75	0.642			
	Median	0.640	2.16	0.536			
	Std dev	0.333	1.79	0.447			
	% RSD	52.0	83.0	83.3			

completely denuded of vegetation, so the ability to visually detect the presence of small pieces of solid explosive on the surface was at a maximum.

Table 14. 50-increment composite samples collected systematically within

Results for the second area sampled at the Quackenbush Range are presented in Table 15. Six systematically collected 100-increment samples were collected in this 100-m × 100-m area. As usual, only RDX, HMX, and TNT were observed by HPLC. The agreement among the six replicate samples was excellent, with sampling RSDs of 37.0% for RDX, 36.8% for HMX, and 34.2% for TNT. We used the mean concentrations as the best estimate of the average concentration in this area. From these data and a soil density of 1.7 g/cm³, we estimate that the mass of residues present in this 100-m × 100-m area in the top 1.5 cm of soil was 1.4 kg for RDX, 0.31 kg for TNT, and 0.21 kg for HMX. This is a much larger estimate of the mass of residue in a given volume of soil than obtained for a similarly sized grid at Fort Hood and is consistent with our observations of about 5 to 10 kg of chunk pure explosive being present throughout this area. Clearly, the mass of energetic residues in this large area was dominated by that associated with the large chunks found on the surface. This, coupled with the findings from the Emerson Lake range, indicates that in arid climates, energetic residues are more likely to persist as particles larger than what is typically considered to be classified as soil for a longer period than in more temperate climates.

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		Conce	ntration (by HPLC			
Sample #		нмх	RDX	TNT	HMX/R DX	TNT/RD X
29P-35		0.496	4.30	0.622	0.115	0.145
29P-36		0.760	3.88	1.33	0.196	0.342
29P-37		1.06	6.62	1.65	0.160	0.250
29P-38		0.698	4.50	0.790	0.155	0.176
29P-39		0.662	5.04	1.51	0.131	0.300
29P-40ave		1.34	9.40	1.44		
	Max	1.34	9.40	1.65		
	Min	0.496	3.88	0.622		
	Mean	0.835	5.62	1.22		
	Median	0.729	4.77	1.39		
	Std dev	0.307	2.08	0.419		
	% RSD	36.8	37.0	34.2		

Table 15. 100-increment composite samples collected near second target at Quackenbush Range, 29 Palms.

Within a $10\text{-m} \times 10\text{-m}$ subgrid of this grid, the agreement among the three 25-increment replicate samples was also good, particularly for RDX, HMX, and TNB, where the RSDs were less than 24% (Table 16). The concentrations in this $10\text{-m} \times 10\text{-m}$ area were also about two times higher than found for the entire $100\text{-m} \times 100\text{-m}$ area. Estimates of the mass of residues in the top 1.5 cm of soil in this $10\text{-m} \times 10\text{-m}$ sub-grid using the same assumptions made above are 34 g for RDX, 11 g for TNT, and 4.0 g for HMX. For both of the decision units sampled at this location, the systematic collection of multi-increment samples of approximately 1-kg mass appears to have addressed the compositional and distributional heterogeneity.

Analytical results from soil profile samples are also shown in Table 16, and as found elsewhere, the highest concentrations by far are located in the top centimeter of soil. Concentrations of RDX, HMX, and TNT were still easily detectable in the 4- to 8-cm sample, but were approximately an order of magnitude lower than found in the surface. Likewise, the surface concentrations of 2ADNT and 4ADNT were less than 1% of the TNT concentration. The rapid decrease in concentration with depth, the limited degradation of TNT in the profile samples, and the greater mass of residues in the larger-than-2-mm particle size fraction indicate that influence of weathering mechanisms is not as large a factor at 29 Palms as is seen at Fort Hood.

		Soil concentration (mg/kg) by HPLC							
Sample #		HMX	TNB	RDX	TNT	2ADNT	4ADNT		
29P-29ave		1.47	0.060	12.8	4.81	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>		
29P-30		1.87	0.062	16.7	6.62	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>		
29P-31		1.29	0.040	10.4	1.64	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>		
	Max	1.87	0.062	16.7	6.62	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>		
	Min	1.29	0.040	10.4	1.64	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>		
	Median	1.47	0.060	12.8	4.81	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>		
	Mean	1.55	0.054	13.3	4.36	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>		
	Std dev	0.299	0.012	3.19	2.52	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>		
	% RSD	19.3	22.5	24.0	57.9	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>		
Profile s	amples collected unde	r a 7.5-g c	hunk of Co	ompositio	n B inside	grid area			
29P-32	0–1 cm	12.7	0.460	89.7	73.8	0.133	0.125		
29P-33	1–4 cm	0.715	<d< td=""><td>3.63</td><td>0.133</td><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	3.63	0.133	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>		
29P-34	4–8 cm	0.628	<d< td=""><td>5.57</td><td>0.439</td><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	5.57	0.439	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>		

Table 16. 25-increment composite samples from 10-m × 10-m grid divided into 2-m × 2-m subgrids at Quackenbush, 29 Palms.

Fort Carson, Colorado, Firing Point

The results for four 49-increment surface soils samples from the mortar firing point area at Fort Carson are shown in Table 17. The mean concentration for NG in this area was 11.7 mg/kg with an RSD of 18.5%, based on the replicate multi-increment samples. Thus the systematic collection of 49 increments (i.e., 2-kg mass) appears to be adequate to obtain reproducible subsamples. These findings are consistent with those reported by Walsh et al. (2005) for a heavily used firing point that also was sparsely vegetated and extensively sampled.

The concentrations of 2,4DNT in these samples were about a factor of 100 lower than NG. The mean was 0.114 mg/kg; however, one field sample replicate had a value that was about four times the other three concentrations causing the RSD to be 88.9%, considerably larger than for NG. We anticipate that this variability can be attributed mostly to compositional heterogeneity, since propellant residues are believed to distribute more uniformly than the energetic materials associated with the main charge of munitions (Jenkins et al. 2004a). The mass of NG and 2,4DNT in this 100-m \times 100-m \times 2.5-cm volume of soil is estimated to be 5 kg and 0.048 kg, respectively.

		Soil con	centration (mg/kg)
Sample		NG	2,4DNT
FC-1ave		10.1	0.058
FC-2ave		13.6	0.267
FC-3ave		13.4	0.067
FC-4ave		9.50	0.065
	Max	13.6	0.267
	Min	9.50	0.058
	Mean	11.7	0.114
	Median	11.8	0.066
	Std dev	2.15	0.102
	% RSD	18.5	88.9

Table 17. Results for analysis of composite soil samples from a firing

Fort Carson, Colorado, Impact Range

One set of six multi-increment soil samples from a 100-m × 100-m grid was collected from the artillery range at Fort Carson (Table 18). Only TNT and its two major environmental transformation products (2ADNT and 4ADNT) were detected in these samples. The concentrations detected for all three energetic compounds were very low: maximum values obtained for TNT, 2ADNT, and 4ADNT were 0.009, 0.018, and 0.029 mg/kg, respectively. The absence of RDX and HMX indicates that the residues of TNT and its transformation products originated from military-grade TNT and not Composition B. Of the residues remaining, less than 25% were still present as the parent compound TNT, indicating that residue deposition in this area was not recent. We estimated that there was 1.7 g of TNT, 5.1 g of 2ADNT, and 7.7 g of 4ADNT residing in this area when these samples were collected. Overall, the results for these samples from the Fort Carson impact area show that significant residues of energetic compounds are not always present in heavily cratered areas in close proximity to the targets.

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Table	18.	100-increment	composite	surface	soil	samples	from	100-m	>
100-m	grid	d in the impact a	area at Fort	Carson.					

		Concentr	% of total		
Sample #		TNT	2ADNT	4ADNT	energetic remaining as TNT*
FC-47		0.003	0.014	0.021	6.84
FC-48		0.002	0.013	0.020	6.63
FC-49		0.005	0.018	0.029	10.3
FC-50		<d< td=""><td>0.007</td><td>0.011</td><td></td></d<>	0.007	0.011	
FC-51		0.003	0.008	0.011	13.4
FC-52		0.009	0.010	0.016	24.9
	Max	0.009	0.018	0.029	
	Min	<d< td=""><td>0.007</td><td>0.011</td><td></td></d<>	0.007	0.011	
	Median	0.003	0.011	0.018	
	Mean	0.004	0.012	0.018	
	Std dev	0.003	0.004	0.007	
	% RSD	61.5	37.1	37.7	
* Calculated	as 100 times	the TNT conce	entration divided	by the sum of T	NT, 2ADNT,

and 4ADNT.

Shaded values were taken from GC-ECD analysis.

5 SUMMARY AND CONCLUSIONS

This report is our first attempt to characterize areas as large as $100 \text{-m} \times 100 \text{-m}$ m at artillery/mortar impact ranges using a multi-increment sampling strategy to obtain one or two kilogram samples. Numerous chunks of energetic residues were present on the surface at several of the locations selected for sampling. Even though these chunks were intentionally avoided during the collection process, the ability to obtain a mean concentration for the energetic residues in the surface soils of a large decision unit with an acceptable degree of uncertainty was confounded by the extent of heterogeneity. The comparison of randomly and systematically multi-increment replicate samples collected within 10-m × 10-m decision units, presented here and elsewhere, (Jenkins et al. 2004b, 2005), suggests that perhaps the greatest portion of the total uncertainty for the larger decision unit is due to the presence of areas of high concentrations of particles in and on the soil, i.e., distributional heterogeneity. This, however, does not preclude compositional heterogeneity from adding to the uncertainty, i.e., the mass of the samples was inadequate to provide a reliable estimate of the concentration of energetic material in the soil within the 100-m × 100-m area. It has been suggested that, to reduce the uncertainty in the multi-increment samples in decision units of this large size in artillery/mortar impact ranges, a tenfold increase in the number of increments (mass) should be evaluated. To process these much larger samples, there are a couple possible alternatives: whole sample extraction (Hewitt and Walsh 2004, Walsh et al. 2005) and solvent slurry mixing (Radtke et al. 2002, Thiboutot et al. 2003), and particle size reduction (Walsh et al. 2004). However, since this has not been demonstrated, and may prove to be too cumbersome, we currently recommend the use of a systematic multi-increment sampling strategy with replication. Based on these findings and others, the systematic collection of multi-increment sample establishes the most appropriate mean concentration for estimating the mass of energetic compounds in a decision unit (Jenkins et al. 2004a, 2004b, 2005).

The collection of multi-increment samples at a sparsely vegetated firing point was shown to be adequate for estimating the mean concentration over a $100\text{-m} \times 100\text{-m}$ area or larger in this study and elsewhere (Walsh et al. 2005). An explanation for this phenomenon is that the distribution and amount of propellant residue particles present at these firing points were adequately represented in the sample mass collected. Propellant residues are thought be less than 3 mm in size and typically are more uniformly dispersed as compared to residues from the partial detonation of munitions, and the same general area is used repeatedly. Although not yet published, recent sampling activities at Canadian Forces Base,

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using the systematic approach to collecting replicate multi-increment samples, was shown to be adequate for estimating the mean analyte concentrations over large areas at three separate firing point locations.

Table 19 is a summary of the surface loading estimates we calculated with data from larger-scale areas at Fort Hood, 29 Palms, and Fort Carson. Once the mass has been estimated, it can be used in models to predict off-site migration of these compounds, either by leaching and interception with a groundwater aquifer, or in surface runoff. It also provides these estimates on the mg/m² basis to allow comparisons among decision units, energetic residues, and to support the implementation of efforts to clean up munitions that have undergone low-order (partial) detonations by emphasizing the magnitude of these potential source terms (e.g., the opened HE-filled 2.75 in war at Fort Hood). Contrarily, when samples were collected in heavily cratered areas and near targets that were absent of visible energetic residues, the concentrations of energetic compounds were generally in the low-to-sub-mg/m² range. This finding is consistent with the view that when munitions function as designed, there is little buildup of energetic residues (Hewitt et al. 2003).

Because multi-increment samples are large (a kilogram or greater) and the portion used for analysis small (we recommend 10 g), it is important to process these samples in a manner that allows reproducible subsampling. The results in this study indicate that excellent reproducibility is obtainable if samples are machine-ground with a puck mill grinder and the subsample prepared by randomly selecting 30 increments of ground soil to build a 10-g subsample.

Table 19. Summary of surface loading estimates for energetic residues at Fort Hood, 29 Palms, and Fort Carson.													
	Turne of	Size of	Denth	Chunks		RDX			TNT			нмх	
Installation	area	area (m ²)	(cm)	present (yes/no)	Average conc.	Mass (g) per area		Average conc.	Mass (g) per area		Average conc.	Mass (g) per area	
Fort Hood					(mg/kg)*	sampled	mg/m²	(mg/kg)	sampled	mg/m ²	(mg/kg)	sampled	mg/m ²
Target area	Impact range	10,000	2.5	Yes	1.22	518	51.8	0.111	47	4.7	0.205	87	8.7
Target area	Impact range	100	2.5	Yes	7.61	32	320	0.423	1.8	18	1.30	5.5	55
Target area	Impact range	100	2.5	No	0.029	0.12	1.2	<d< td=""><td><d< td=""><td><d< td=""><td>0.015</td><td>0.063</td><td>0.63</td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>0.015</td><td>0.063</td><td>0.63</td></d<></td></d<>	<d< td=""><td>0.015</td><td>0.063</td><td>0.63</td></d<>	0.015	0.063	0.63
29 Palms													
Emerson Lake	Impact range	10,000	1.5	Yes	1.99	507	50.7	1.04	265	26.5	0.291	74	7.4
Emerson Lake	Impact range	100	1.5	Yes	0.341	0.87	8.7	0.016	0.041	0.41	0.135	0.344	3.44
Quackenbush 1	Impact range	2,800	1.5	No	2.75	327	117	0.642	76	27.1	0.601	71	16.5
Quackenbush 2	Impact range	10,000	1.5	Yes	5.62	1,400	140	1.22	312	31.2	0.835	210	21
Quackenbush 2	Impact range	100	1.5	Yes	13.3	34	340	4.36	11	110	1.55	4	40
Fort Carson	Impact range	10,000	2.5	No	<d< td=""><td><d< td=""><td><d< td=""><td>0.004</td><td>1.7</td><td>0.17</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td><d< td=""><td>0.004</td><td>1.7</td><td>0.17</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<></td></d<>	<d< td=""><td>0.004</td><td>1.7</td><td>0.17</td><td><d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<></td></d<>	0.004	1.7	0.17	<d< td=""><td><d< td=""><td><d< td=""></d<></td></d<></td></d<>	<d< td=""><td><d< td=""></d<></td></d<>	<d< td=""></d<>
					NG		2,4DNT						
				Average conc. (mg/kg)	Mass (g)	mg/m²	Average conc. (mg/kg)	Mass (g)	mg/m²				
Fort Carson	Mortar firing point	10,000	2.5	No	11.7	5,000	500	0.114	48	4.8			

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14. ABSTRACT Sampling experiments were conducted at three a mortar firing point at Fort Carson. The objec concentrations and mass loading of energetic of pure explosives were observed on the surface detonation of some type of munition during pase 49- to 100-increment surface samples that were distances across the area. This was accomplish each sub-area to build the sample. The mass of to assess the reproducibility, i.e., sampling er energetic substances that were detected. The deposition appeared to be mostly from Com 4ADNT, and TNB, were also detected. For the characterize a decision unit as large as 10,000 consistently achieve a comparable level of unor replicate multi-increment samples enhances the 5. SUBJECT TERMS 2,4-DNT	e artillery/mortar impact ctive of these investigat compounds in surface so ce within the areas bein st training exercises, or f e collected using a syste hed by dividing the area frunti-increment sample ror. Average concentrat energetic compounds d position-B-filled rounds he firing point area, onl 0 m ² at a heavily used fi certainty for these larger te reliability of this samp Firing ranges	ranges at Fort Hood, Te fons was to assess the u ils for decision units rar g sampled. These chur rom blowing in place of matic sampling design of concern into 49 to 1 is collected generally ra- ion estimates for the st etected were generally . Sometimes the enviro y NG and 2,4DNT wer ring point. Compositio decision units on artille- bling strategy and yields	exas; 29 Palms, 6 se of multi-incre ging in size from ks were presum unexploded ord where individual 00 equally sized nged from 1 to 2 udied areas wer RDX, HMX, a numental transfor e detected. Ove nal and distributery and mortar in information on	California; and Fort Carson, Colorado, and at ement sampling as a means of estimating the n 100 to 10,000 m ² . In some cases, chunks of nably present due to the partial (low-order) nance. Characterization was conducted using increments were collected at equally spaced I sub-areas and collecting an increment from kilograms. Replicate samples were collected e used to estimate the mass loading for the nd TNT for impact areas where the residue symmation products of TNT, namely 2ADNT, rall, this sampling strategy was adequate to tional sources of error confounded efforts to mpact ranges. Nevertheless, the collection of the extent and type of heterogeneity present.
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