



## Field observations of the persistence of Comp B explosives residues in a salt marsh impact area

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### ABSTRACT

Field observations of weathering Comp B (RDX/TNT 60/40) residue were made on a live-fire training range over four years. The Comp B residue was formed by low-order detonations of 120-mm mortar projectiles. Physical changes were the disaggregation of initially solid chunks into masses of smaller diameter pieces and formation of red phototransformation products that washed off with rain or tidal flooding. Disaggregation increased the surface area of the residue, thereby increasing the potential for dissolution. The bulk of the mass of Comp B was in the craters, but solid chunks were scattered asymmetrically up to 30 m away.

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### 1. Introduction

The accumulation and persistence of energetic compounds resulting from the live-fire of howitzers, mortars, and other weapons must be understood to ensure long-term sustainable use of military training lands. High explosive ordnance detonations normally leave very little energetic residue in the impact area (Hewitt et al., 2005; Walsh, 2007). Occasionally, a malfunction will produce either unexploded or partially (low order) detonated ordnance that will serve as a source for surface water and groundwater contamination with energetic compounds. Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is the energetic compound of greatest concern due to its prevalent use by the military in training and in disposal of unexploded ordnance. Once dissolved, it has physical properties that are conducive to migration to groundwater; these include low sorption to soil and low biodegradation rates in aerobic conditions. RDX has been detected in the groundwater at military installations in the United States (Clausen et al., 2004) and Canada (Bordeleau et al., 2008a,b; Martel et al., 2009).

Several laboratory studies have been conducted to estimate the mass transfer rate from discrete solid high explosive particles to soil pore water. These studies were done to define the source term

for modeling the mass transfer from the solid phase to an aqueous phase solution that is a rate-limiting factor for fate and transport processes. Models of the dissolution of explosives must mathematically represent natural phenomena to which the high explosives solids are exposed under field conditions. Lynch et al. (2002a) found that for military grade 2,4,6-trinitrotoluene (TNT), RDX and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), dissolution rates approximately doubled for every 10 °C increase in temperature between 10 and 30 °C and the rate of dissolution was greatest for TNT. Dissolution rates for the explosives compounds in formulations such as Comp B (60/40 RDX/TNT) and Octol (70/30/ HMX/TNT) were generally lower than for the individual compounds (Lynch et al., 2002b), which in turn changed their predicted persistence (Lynch et al., 2003). Phelan et al. (2003) noted that the RDX concentrations in the aqueous effluent from laboratory porous media columns were near the maximum water solubility for RDX at 5, 23 and 38 °C, and they concluded that rainfall will result in rapid mass transfer of RDX to pore water. Lever et al. (2005) measured the dissolution of individual, field-collected Comp B particles in a laboratory drip experiment designed to mimic rainfall. The Comp B particles were from actual detonations. They found that the slow dissolution of RDX limits the dissolution of TNT once the surface TNT dissolved from the Comp B particles. They developed two models based on solubility, diffusivity and density, that provided good agreement with laboratory experimental data. The models predict that a 1 mg Comp B particle

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would dissolve after 170 rainfall days. Webb et al. (2006) studied the mass transfer of TNT and RDX from undetonated military-grade Comp B and from low-order detonation debris to pore water in soil columns packed with glass beads and found that the total surface area of energetic material particles strongly affects the effluent concentrations of RDX and TNT. Columns with small Comp B particle diameters produced higher effluent concentrations than columns with the same mass of high explosive, but five times greater Comp B particle diameters. Dontosava et al. (2006) compared the dissolution and transport of pure TNT and RDX to TNT and RDX combined in Comp B under saturated soil column conditions. They concluded that dissolution was the controlling transport process; dissolution depended on the physical properties of the solid phase Comp B.

Laboratory studies provide valuable insights into dissolution kinetics, but additional information from field studies is needed to either validate the laboratory findings or suggest other factors that need to be considered. We had the opportunity to observe Comp B residues on a live-fire training range over several years. The objective of this paper is to document observations of the distribution, appearance, and persistence of Comp B residues from live-fire training under actual field conditions to provide data for source zone definition in modeling and for the design of sampling schemes to characterize source zones.

## 2. Materials and methods

The source of the Comp B residues were two live-fire training events with 120-mm HE M933 point detonating mortar projectiles. The impact area was an estuarine salt marsh on Cook Inlet in Alaska. The Comp B residue that we monitored was scattered on a periodically inundated mudflat that is ice-covered from November until April each year. The sediments on the mudflat are glacially derived silts and clays that are saturated much of the year.

The first event was in February 2005 when a total of 160 projectiles were fired from 120-mm mortars, of which eight projectiles (5%) did not detonate and four projectiles (2.5%) produced low-order detonations. The dud and low-order detonation rates for this ordnance are reported to be 4.7% and 0.1% (Stewart et al., 2006). In May 2005, we located a crater, (LO#1 in Fig. 1), that contained an incompletely fragmented projectile with Comp B adhered to the remains of the projectile and discrete particles of Comp B within and around the crater (Fig. 2). We mapped the distribution of Comp B chunks outside the crater. Then we collected them to obtain an estimate of the mass of macroscopic Comp B scattered outside the crater. To determine Comp B concentrations within the sediment, we collected two sets of 100 discrete core samples at 10-cm intervals covering a 1-m<sup>2</sup> areas; one set was from the crater and the other was around one chunk of Comp B that landed 16.3 m from the crater.

Another live-fire exercise in March 2006 with 120-mm projectiles produced additional low-order detonations near LO#1. We mapped the distribution of macroscopic Comp B residues around two more low-order detonation craters, designated at LO#2 and LO#3 (Fig. 1). At each site, we photographed 14 discrete deposits of Comp B residue in May and August of 2006. The location of each deposit was marked with a flag, and the universal transverse mercator (UTM) coordinates obtained using a Trimble GPS Pathfinder Pro XR system. Additional photographs of those points with visible residue remaining were obtained in May and August of 2007 and 2008 and in May and July 2009. We did not touch the residues; we monitored them in situ. During this time, the site was not impacted by live-fire training events.

We also measured the explosives concentrations in the sediment under two Comp B chunks in August 2006. One set of depth samples was collected using a hammer corer and the second set

was collected by digging a pit next the Comp B chunk and sampling from the wall of the pit.

Sediment samples were air-dried. Each individual sample was extracted with acetonitrile on a platform shaker for 18 h. The volume in milliliters of acetonitrile was twice the mass of each dried sample in grams.

Concentrations of RDX, TNT, and HMX were determined by high-performance liquid-chromatography (HPLC). Prior to injection, a 1.00-mL aliquot of each acetonitrile extract was mixed with 3.00 mL of Milli-Q (reagent-grade) water and filtered through a Millex-FH (Millipore, PTFE, 0.45  $\mu$ m) filter unit. Determinations were made on a modular system from Thermo Electron Corporation composed of a Finnigan SpectraSYSTEM Model P4000 pump, a Finnigan SpectraSYSTEM UV2000 dual wavelength UV/VS absorbance detector set at 254 nm (cell path 1 cm), and a Finnigan SpectraSYSTEM AS300 autosampler. Samples were introduced with a 100- $\mu$ L sample loop. Separations were achieved on a 15-cm  $\times$  3.9-mm (4- $\mu$ m) NovaPak C8 column (Waters Chromatography Division, Milford, Massachusetts) at 28 °C and eluted with 1.4 mL min<sup>-1</sup> of 15:85 isopropanol/water (v/v). Calibration standards were prepared from the analytical reference material 8095 Calibration Mix A (HMX, RDX, TNT, 2,4-DNT, 2,6-DNT, 1,3-DNB, 1,3,5-TNB, 2-Am-4,6-DNT, 4-Am-2,6-DNT, and tetra) obtained from Restek Corporation (Bellefonte, Pennsylvania). Extracts that had concentrations greater than 20 mg L<sup>-1</sup> were diluted with acetonitrile prior to mixing with water and HPLC analysis. Detection limits for this method are estimated to be 0.04  $\mu$ g g<sup>-1</sup>.

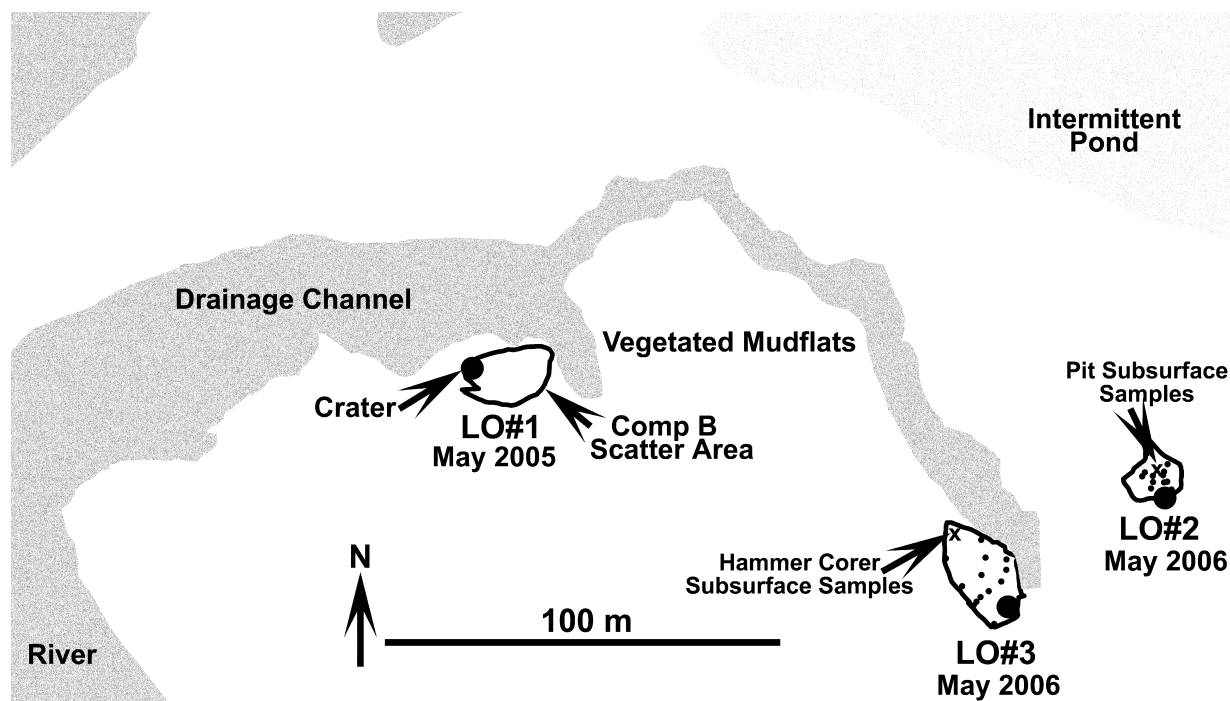
## 3. Results

The crater of LO#1 contained the tail assembly and part the projectile body with Comp B adhered to the metal. There were also large pieces of metal and discrete pieces of Comp B within the crater (Fig. 2). The surface of the Comp B was stained a reddish-orange. The chunks appeared to be friable and were easily broken apart to reveal the underlying Comp B that was beige, the typical color of Comp B. Eighteen discrete deposition points of solid Comp B were found over a 247-m<sup>2</sup> area, mostly between 13.3 and 18.3 m east of the crater. Each point had a chunk that was 2–4 cm in its longest dimension and most deposits had smaller (centimeter to less than 1 mm) pieces of Comp B (Fig. 3). The total mass of the centimeter-size Comp B chunks found outside of the crater was 120 g, which is 4% of the 2.99 kg Comp B explosive load.

The craters from the March 2006 live-fire event (LO#2 and LO#3) were similar to LO#1 in that they each contained the tail assembly and a portion of the projectile body. The physical form of the Comp B residues that were deposited around the craters varied from red stains on the surface of the sediment to clusters of millimeter-sized particles to individual Comp B chunks up to 3 cm long.

At LO#2 in May 2006 (2 months after the live-fire event), 81 discrete deposits of Comp B were scattered over 146-m<sup>2</sup>, and all the visible residues were stained dark red. Fourteen Comp B deposits were photographed. These included 10 chunks of Comp B (Fig. 4a), two disaggregated deposits of solid residues, and two red stains with no solid residue visible. By August 2006 (5 months after the live-fire event), after a series of flooding tides and 18 cm of rainfall, the red stain was gone from all the deposits and the remaining residues were orange-yellow (Fig. 4b).<sup>1</sup> Five of the original 10 chunks were intact, four were either broken, roughened or flaking, and one was actually a piece of metal surrounded by a stain from Comp B. Two points had deposits of several small particles,

<sup>1</sup> For interpretation of color in Fig. 4, the reader is referred to the web version of this article.



**Fig. 1.** Map showing relative locations of three low-order detonation events on an estuarine salt marsh impact area. The solid circles correspond to the impact craters and the solid outlines delineate the boundaries of the scatter of solid Comp B chunks. The dots at LO#2 and LO#3 are the locations of discrete points with Comp B residue that were monitored between May 2006 and July 2009.

and no residues were visible at the two remaining points that were originally red surface stains. In May and August of 2007 (14 and 17 months after the live-fire event) solid Comp B residue was visible at only seven of the 14 original photo points. Each point with visible residue remaining originally had Comp B pieces that were at least 2 cm in one dimension. All pieces were dark red in May and appeared friable and were disaggregating (Fig. 4c). In August 2007, one deposit had a plant (*Triglochin palustris*) growing through the disaggregating Comp B residue (Fig. 4d). In 2008 and 2009 (up to 40 months after the live-fire event), visible solid residue was still present at the seven disaggregated masses. The residue shown in Fig. 4e–h was typical.

At LO#3 in May 2006 (2 months after the live-fire event), 133 discrete points with Comp B were found over 378-m<sup>2</sup> scatter area. In contrast to LO#1 and LO#2, the residue at this site was predominately disaggregating deposits of Comp B, rather than intact chunks. Fourteen points were photographed, of which seven had chunks, six were disaggregating deposits of Comp B and one was a red stain on the surface sediment. This low-order detonation was in close proximity to a drainage channel and may have experienced more frequent inundation than the other two locations. In May 2007 (14 months after the live-fire event), solid Comp B residue was visible at only six of the 14 photo points and all the residues were in the form of small, crumbled particles. By August 2008 (29 months), only four deposits were visible. In July 2009 (40 months), solids remained at only one deposit.

Surface samples of the sediment in contact with solid Comp B residues were collected in 2005 at LO#1 to determine the magnitudes and the distributional heterogeneity of RDX, TNT and HMX concentrations. The residues in the sediment would include both the dissolved aqueous phase and the solid phase composed of particles that were not readily visible.

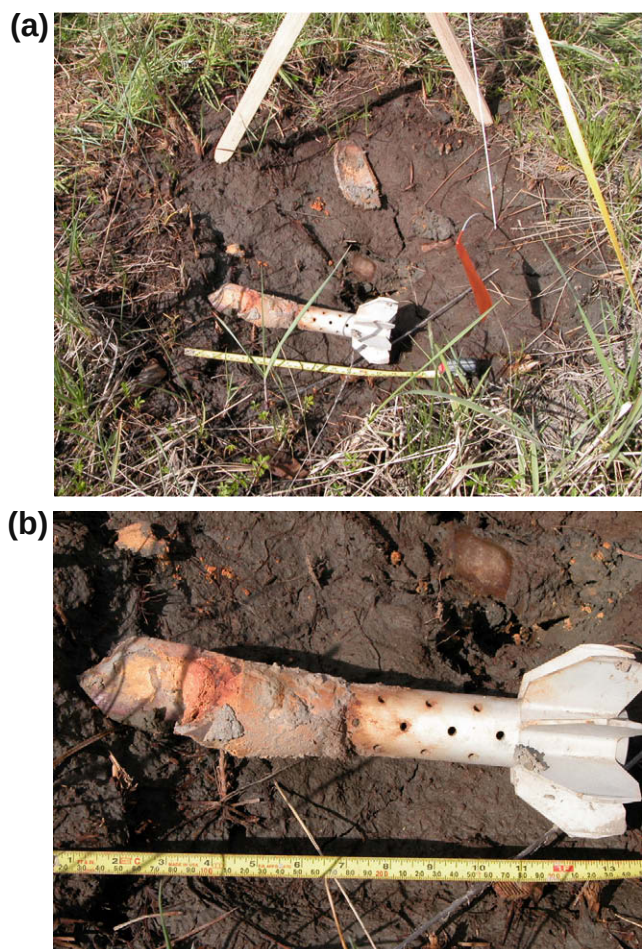
After the visible pieces of Comp B were collected at LO#1 in May 2005, a set of 100 core samples were collected at 10 cm intervals from a 1-m × 1-m area centered on one of the deposits. The corer diameter was 2.6 cm and the core depth was 2.5 cm. Each core was

analyzed individually. Concentrations ranged from less than 0.04 mg kg<sup>-1</sup> to 5630, 3100 and 870 mg kg<sup>-1</sup> for RDX, TNT, and HMX, respectively. The maximum concentrations for all three analytes were from the core taken under the large chunk of Comp B that was removed prior to sampling. Concentrations were one to two orders of magnitude lower in cores taken from the neighboring 10 cm × 10 cm cells. The sum of the masses of high explosives extracted from the 100 cores was 0.12 g of RDX, 0.06 g of TNT and 0.02 mg of HMX for a total mass of 0.2 g. Eighty percent of the total high explosives mass in the sediment samples was from the one core taken directly under the deposit of Comp B.

A similar set of core samples were collected from a 1-m × 1-m area centered on the crater of LO#1. The tail assembly with associated Comp B filler and visible solid Comp B pieces were removed prior to sampling. A 4.75 cm diameter corer was used to collect 100 discrete increments at 10-cm intervals to a depth of 3 cm. Core volume was 53 cm<sup>3</sup>. Concentrations within this 1-m × 1-m area were 205–25 400 mg kg<sup>-1</sup> for RDX, 20–14 700 mg kg<sup>-1</sup> for TNT and 32–3600 mg kg<sup>-1</sup> for HMX. Collectively, 18 g of RDX, 7.1 g of TNT and 2.5 g of HMX were extracted from the 100 discrete cores that represented 18% of the 1-m<sup>2</sup> area. The sediment was saturated with water at the time of sampling. The total volume of pore water for these 100 core samples was about 2 L. If the pore water was saturated with RDX and TNT, approximately 80 mg of RDX and 200 mg of TNT would be in the dissolved phase in the 100 core samples. Given that several grams of RDX and TNT were recovered, the bulk of the energetics were in the solid phase.

Subsurface samples were collected in August 2006 to determine if dissolved Comp B residues were migrating down into the underlying sediments 5 months after the live-fire event. The first depth samples were obtained under a deposit of Comp B at LO#3. This location was not one of the photopoints described above, so the residue was scraped off the surface of the sediment and weighed. The mass was 2.8 g. An AMS (American Falls, ID) hammer corer that was 4.6 cm in diameter was used to obtain a core from 0 to 16 cm and a second core from 16 to 32 cm. The core was divided





**Fig. 2.** Crater and incompletely fragmented 120-mm mortar projectile with Comp B at LO#1: (a) crater and (b) close-up of the partially detonated ordnance with Comp B.



**Fig. 3.** One of the 18 deposits of Comp B found outside the crater of LO#1.

into approximately 2 cm intervals. Almost all the mass (92, 98, and 90%, for RDX, TNT and, HMX respectively) was in the top

2 cm (Table 1) where milligram quantities were detected. Given that the sparse aqueous solubility of each analyte, much of the mass was solid phase in the surface sediment. Energetic residues were detectable along the entire 32-cm long core. As the corer passed through the zone with the highest concentrations of analytes, some of the residues detected in the subsurface sediment may have been pushed down from the surface.

A second set of depth samples was obtained under another deposit of Comp B using a different method to minimize cross-contamination between the surface and subsurface. A pit was dug adjacent to the mass of Comp B. Starting from the base of the pit at 40 cm depth, the mud on the wall of the pit was scraped away, then sediment increments were obtained from under the mass of Comp B. The sampling depth intervals were 5 cm for the bottom 30 cm and 2 cm for the top 10 cm. Like the hammer profile, most of the mass of the energetics was in the top few centimeters (Table 2). Unlike the hammer profile, the energetics were generally not detectable below 20 cm.

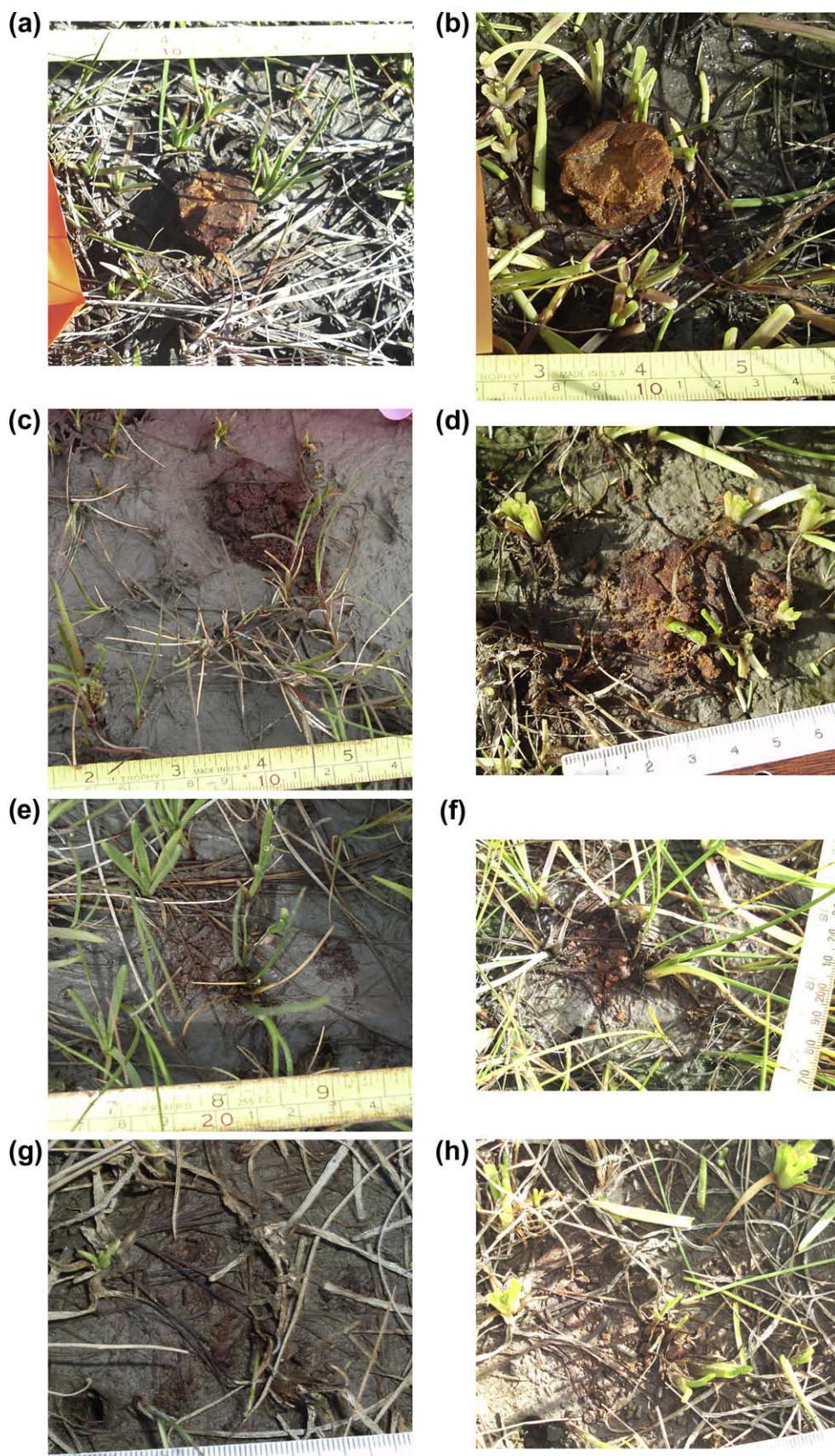
#### 4. Discussion

This paper documents actual field observations of the persistence of Comp B residues on a military training range. Military training ranges are found in a wide variety of environments, from deserts to forests to prairie to wetlands (Doe et al., 1999). The setting for this case study was a salt marsh mudflat subjected to periodic tidal flooding, seasonal freezing and thawing, precipitation in the form of rain and snow, exposure to long hours of sunlight in the summer, and bioperturbations by plants and animals. These factors contributed to the physical and chemical transformations of the solid Comp B residues. The persistence of the Comp B chunks in the salt marsh environment is much less than would be predicted by dissolution of Comp B chunks by rainfall in an upland environment. Based on laboratory experiments with simulated rainfall at  $0.55 \text{ cm h}^{-1}$ , Lever et al. (2005) predicted that a 0.1 g (equivalent to a sphere with a diameter of 0.5 mm) particle of Comp B would dissolve in 600 rainfall days. Particles of this size that we observed in May 2006 were gone by August 2006; during this time, there were 15 rainfall days with a total of 18 cm of precipitation.

The principal morphological changes in the solid Comp B residue were the formation of dark red surface staining that washed off with rain or tidal flooding and the disaggregation of solid chunks into loose masses of crumbled pieces. The disaggregation dramatically increases the surface area of the residue and needs to be incorporated into dissolution models. The formation of dark red staining on the surface of Comp B has been documented previously and is due to the phototransformation of TNT (Fedoroff et al., 1960). Although the phototransformation of TNT in aqueous solutions has been studied extensively, the compound(s) responsible for the red stain on the solid has not been identified. If the phototransformation products on the solid are more soluble than TNT, then their formation could be a significant factor that also needs to be included in dissolution models. Because the phototransformation of TNT in aqueous solution produces a complex mixture of highly polar nitroaromatic compounds (Spangford et al., 1983; Godejohann et al., 1998), it is reasonable to assume that the phototransformation products on the solid are also polar.

The distribution of the Comp B residue that we describe has implications for source zone definition in modeling and for the design of sampling schemes to characterize source zones. The pattern of the residue from each low-order detonation that we examined had the following characteristics: the bulk of the residue was in the crater, which was less than 1 m in diameter (Fig. 2); chunks (up to 4 cm in their longest dimension) of Comp B were scattered 20–30 m asymmetrically from the crater (Fig. 1); the concentra-





**Fig. 4.** Images documenting the changes in one chunk of Comp B at LO#2 over 4 years. Date of image (time since live-fire event): (a) 24 May 2006 (2 months); (b) 23 August 2006 (5 months); (c) 22 May 2007 (14 months); (d) 24 August 2007 (17 months); (e) 4 June 2008 (27 months); (f) 25 August 2008 (29 months); (g) 14 May 2009 (38 months); (h) 18 July 2009 (40 months).

**Table 1**

Concentrations of RDX, TNT, and HMX in sediment obtained with a hammer corer after removal of a 2.8-g Comp B chunk.

| Depth (cm) | Mass of sediment (g) | RDX       |                              | TNT       |                              | HMX       |                              |
|------------|----------------------|-----------|------------------------------|-----------|------------------------------|-----------|------------------------------|
|            |                      | Mass (mg) | Conc. (mg kg <sup>-1</sup> ) | Mass (mg) | Conc. (mg kg <sup>-1</sup> ) | Mass (mg) | Conc. (mg kg <sup>-1</sup> ) |
| 0–2        | 52.4                 | 35.3      | 670                          | 19        | 360                          | 4.14      | 79                           |
| 2–4        | 43.5                 | 0.73      | 17                           | 0.087     | 2.0                          | 0.10      | 2.3                          |
| 4–6        | 37.5                 | 0.58      | 15                           | 0.098     | 2.6                          | 0.083     | 2.2                          |
| 6–8        | 30.7                 | 0.077     | 2.5                          | 0.006     | 0.2                          | 0.014     | 0.44                         |
| 8–10       | 32.9                 | 0.15      | 4.6                          | 0.029     | 0.88                         | 0.023     | 0.70                         |
| 10–12      | 24.8                 | 0.27      | 11                           | 0.042     | 1.7                          | 0.047     | 1.9                          |
| 12–14      | 25.3                 | 0.076     | 3.0                          | 0.030     | 1.2                          | 0.012     | 0.46                         |
| 14–16      | 15.8                 | 0.079     | 5.0                          | 0.005     | 0.3                          | 0.014     | 0.87                         |
| 16–18      | 30.9                 | 0.40      | 13                           | 0.003     | 0.1                          | 0.062     | 2.0                          |
| 18–20      | 34.7                 | 0.14      | 4.1                          | 0.003     | 0.09                         | 0.022     | 0.62                         |
| 20–22      | 45.6                 | 0.16      | 3.4                          | 0.009     | 0.2                          | 0.020     | 0.44                         |
| 22–24      | 44.3                 | 0.058     | 1.3                          | 0.001     | 0.02                         | 0.007     | 0.16                         |
| 24–26      | 55.9                 | 0.089     | 1.6                          | 0.004     | 0.07                         | 0.015     | 0.27                         |
| 26–28      | 39.7                 | 0.064     | 1.6                          | 0.002     | 0.05                         | 0.007     | 0.17                         |
| 28–30      | 39.2                 | 0.078     | 2.0                          | 0.010     | 0.26                         | 0.015     | 0.39                         |
| 30–32      | 35.9                 | 0.21      | 5.9                          | 0.017     | 0.46                         | 0.031     | 0.85                         |
| Sum        |                      | 38.5      |                              | 19.4      |                              | 4.6       |                              |

**Table 2**

Concentrations of RDX, TNT, and HMX in sediment from a pit adjacent to a disaggregating Comp B chunk.

| Depth (cm) | Mass of sediment (g) | RDX       |                              | TNT       |                              | HMX       |                              |
|------------|----------------------|-----------|------------------------------|-----------|------------------------------|-----------|------------------------------|
|            |                      | Mass (mg) | Conc. (mg kg <sup>-1</sup> ) | Mass (mg) | Conc. (mg kg <sup>-1</sup> ) | Mass (mg) | Conc. (mg kg <sup>-1</sup> ) |
| 0–2        | 66.5                 | 88.3      | 1300                         | 35.8      | 540                          | 11.0      | 170                          |
| 2–4        | 64.0                 | 20.4      | 320                          | 11.7      | 180                          | 2.37      | 37                           |
| 4–6        | 71.7                 | 1.18      | 17                           | 0.14      | 1.9                          | 0.20      | 2.4                          |
| 6–8        | 85.8                 | 0.66      | 7.7                          | <0.004    | <0.04                        | 0.14      | 1.6                          |
| 8–10       | 56.7                 | 0.29      | 5.2                          | 0.01      | 0.18                         | 0.06      | 1.1                          |
| 10–15      | 194                  | 0.28      | 1.4                          | <0.008    | <0.04                        | 0.08      | 0.41                         |
| 15–20      | 267                  | 0.91      | 3.4                          | 0.12      | 0.45                         | 0.18      | 0.68                         |
| 20–25      | 328                  | <0.01     | <0.04                        | <0.01     | <0.04                        | <0.01     | <0.04                        |
| 25–30      | 280                  | <0.01     | <0.04                        | <0.01     | <0.04                        | <0.01     | <0.04                        |
| 30–35      | 292                  | <0.01     | <0.04                        | <0.01     | <0.04                        | <0.01     | <0.04                        |
| 35–40      | 328                  | 0.02      | 0.050                        | <0.01     | <0.04                        | <0.01     | <0.04                        |
| Sum        |                      | 112       |                              | 48        |                              | 14        |                              |

tions of energetics in sediment core samples that excluded visible solid Comp B residue were consistently high within the crater, but varied by orders of magnitude; the sediment concentrations of energetics under a Comp B chunk away from the crater was high, but decreased by orders of magnitude in samples taken within 20 cm distant both horizontally and vertically. These observations indicate that the distributional heterogeneity is extreme and that source zone characterization by sampling must be carefully planned.

In summary, field observations of residue from three low-order detonations indicate that disaggregation of chunks of Comp B with weathering is a major factor that contributed to enhanced dissolution kinetics of the residue. Additionally, the phototransformation products on the surface of Comp B residues needs to be examined to determine their identity and solubility. The bulk of the residue was within the surface few centimeters where concentrations varied considerably over very short distances. Shallow monitoring wells or unsaturated zone lysimeters, where appropriate, are needed to evaluate movement of RDX, TNT, and HMX to groundwater.

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