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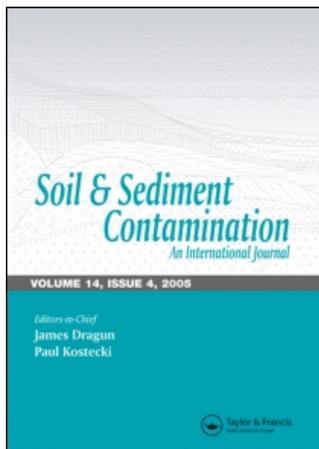
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Subsampling Variance for 2,4-DNT in Firing Point Soils

M. E. WALSH,¹ C. A. RAMSEY,² S. TAYLOR,¹ A. D. HEWITT,¹
K. BJELLA,¹ AND C. M. COLLINS¹

¹U.S. Army Engineer Research and Development Center, Cold Regions
Research and Engineering Laboratory, Hanover, NH, USA

²Envirostat, Inc., Fort Collins, CO, USA

At 105-mm howitzer firing points, 2,4-DNT is detectable in the surface soils, but field sampling and laboratory subsampling uncertainty can be large during quantitation. The 2,4-DNT is in particulate form, within fibers or slivers of the nitrocellulose-based propellant. The slender fibers range up to 7.5 mm in length with masses of several 100 µg. Size fractionation of a firing point soil revealed that most of the 2,4-DNT was in the 0.595- to 2.00-mm size range, although the bulk of the soil was less than 0.6 mm prior to grinding. Machine grinding for five minutes was needed to pulverize the propellant fibers sufficiently so that estimates of 2,4-DNT were reproducible in replicate analytical subsamples. To determine 2,4-DNT, we have adopted the practice of grinding firing point soils for five one-minute intervals, with time for heat dissipation between grinds, prior to obtaining individual or replicate 10-g subsamples.

Keywords propellant, training ranges, sampling

Introduction

Soil concentration of a potential contaminant is used to assess risk to human health and the environment and is the basis for decisions about the need for remedial action (U.S. EPA, 1996). Soil concentration is estimated by the collection and analysis of soil samples. Each soil sample, typically a few hundred grams, is assumed to represent the tons of soil within a decision or exposure area. The actual determination of soil concentration is made from an analytical subsample, which is typically less than 10 g. The potential for measurement errors by selecting non-representative samples and subsamples is high for particulate materials such as soils (Nocerino *et al.*, 2005), and is extreme when the potential contaminant is also particulate. Overestimation or underestimation of the soil concentration will result in incorrect decisions about the need for remedial action; therefore appropriate sampling and subsampling procedures must be used.

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Address correspondence to M.E. Walsh, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, 72 Lyme Road, Hanover, NH 03755, USA. E-mail: Marianne.E.Walsh@erdc.usace.army.mil

We have investigated proper sampling and subsampling procedures for energetic residues on military training ranges in an effort to support sustainable range management (Jenkins *et al.*, 2006). Energetic residues are particulates (Taylor *et al.*, 2004), and the uncertainty associated with both field sampling and laboratory subsampling of soils from training ranges can be very large (i.e., concentration estimates in field and/or laboratory replicates ranging over a factor of ten). The problem of unacceptably high laboratory subsampling variance for soils containing high explosives residues has been solved by grinding the soil with a ring mill, thereby reducing its particle size. A grind time of 60 s is generally sufficient to obtain relative standard deviations of less than 10% for replicate analyses (Walsh *et al.*, 2002; Hewitt *et al.*, 2005). However, similar sample processing procedures are not adequate for soils containing propellant residue (Walsh *et al.*, 2003, 2004, 2005).

The focus of this paper is the laboratory experiments designed to clarify the source of subsampling uncertainty for firing point surface soils and the procedures developed to reduce laboratory subsampling variance. The soil at several 105-mm howitzer firing points at the Donnelly Training Area (DTA), Alaska, was sampled to determine the concentrations of 2,4-dinitrotoluene (2,4-DNT), a potential human carcinogen (ATSDR, 1998) that makes up $10 \pm 2\%$ of the M1 propellant used. [M1 propellant is mostly ($85 \pm 2\%$) nitrocellulose, with $5 \pm 1\%$ dibutylphthalate added as a plasticizer and 1% diphenylamine added as a stabilizer (Department of Defense, 1973)]. 2,4-DNT was easily detectable in most of the surface soil samples from each of the firing points, and concentrations were typically in the low part-per-million range (Walsh *et al.*, 2001, 2004). However, estimates of 2,4-DNT concentrations from replicate multi-increment and discrete samples from the same location in the field showed that sampling error can be large. We hypothesized that most of the 2,4-DNT was associated with fibers of the nitrocellulose-based propellant that were heterogeneously dispersed on the ground surface. These polymeric fibers could contribute to unacceptably high laboratory subsampling error (e.g., relative standard deviations greater than 50%), even in samples that had been sieved and ground on a ring mill for 60 s. To develop improved subsampling procedures, we performed a series of experiments involving splitting, grinding, and size fractionation of soils from a firing point and examined propellant residue collected following a live-fire training exercise.

Methods

Field Soil Sample Collection Methods

The laboratory processing experiments were performed on multi-increment samples (composed of more than one soil aliquot) of surface soil collected from Firing Point (FP) Mark, a sparsely vegetated firing point where glacial till is covered with a veneer of loess. The field samples were collected from either 1-m \times 1-m, 10-m \times 10-m, or 90-m \times 120-m areas as part of a study of field sampling uncertainty of 2,4-DNT in the surface 2.5 cm of soil (Walsh *et al.*, 2005). All samples were collected with AMS (American Falls, ID) #3 sampling scoops.

General Laboratory Procedures

All soil samples were air-dried by spreading them on polyethylene-covered trays on shelves in a well-ventilated windowless laboratory. Lights were turned off unless needed to prevent potential photodegradation. The air-dried samples were sieved through a #10

mesh (2-mm) sieve and the less-than-2-mm fraction used for determinations of analyte concentrations.

Most of the samples were ground on a ring mill. The model was a LabTech Essa (Belmont, Western Australia) LM-2 equipped with a B800 bowl. The bowl nominally holds 800 g (but current practice is to grind no more than 500 g).

If manual subsampling was performed, the general procedure was to spread the sample over a flat surface, and a 10.0-g subsample formed from several small increments taken from random locations. Instead of manual subsampling, some soil samples were divided using a LabTech Essa Rotary Sample Divider Model RSD5 and the mass of the splits depended on the total mass of the sample.

Either acetone or acetonitrile was used to extract the analytes from the samples. Samples were agitated using a sonic bath or shaker table. Extraction time was 18 hours.

After subsamples were removed from large multi-increment samples, the analyte in the remaining sample was determined using "whole sample extraction." We used acetone for these large-volume extractions because it is less toxic and much less expensive than acetonitrile. It is an excellent solvent for the analyte of interest (2,4-DNT), and it does not cause substantial analytical problems using the HPLC separation described below. For the whole sample extraction procedure, the soil sample was weighed and transferred to a large polyethylene carboy. The volume of acetone added was based on the mass of the sample; 2 L of acetone were used for each kilogram of sample. The carboy was capped and the sample shaken vigorously, then allowed to stand. The sample was shaken vigorously again a few hours later and again the following morning. Then the sample was allowed to stand while the solids settled.

Aliquots of the acetone and acetonitrile extracts were filtered through Millex-FH (Millipore, PTFE, 0.45 μm) filter units into 7-mL Teflon-capped vials. Prior to HPLC analysis, 1.00 mL of filtered extract was mixed with 3.00 mL MilliQ Water. The HPLC separations were achieved on a 15-cm by 3.9-mm (4- μm) Nova Pak C₈ (Waters Millipore) column eluted with 1.4 mL/min 15:85 isopropanol:water at 28°C and on a 25-cm by 4.6-mm (5- μm) Supelco LC-CN column eluted with 1.2-mL/min 65:14:21 water:methanol:acetonitrile. Detection was by UV at 254 nm. The analytical precision for the HPLC-UV method was estimated to be 3% relative standard deviation for 2,4-DNT in soils spiked in duplicate at 7.8 $\mu\text{g/g}$ on four separate days (Jenkins and Walsh, 1987).

Laboratory Processing and Subsampling Experiments Using Firing Point Soil

We performed a variety of experiments to understand why laboratory subsampling error is higher for machine-ground soils with propellant residue compared to machine-ground soils with high explosives residues (Walsh *et al.*, 2002). These experiments included use of a rotary divider (otherwise known as a sectorial splitter or spinning riffler) to obtain subsamples, use of increased subsample size (up to 900 g), extension of grinding time up to five minutes using a ring mill, sieve analysis to determine the size fraction associated with residues of 2,4-DNT before and after grinding, and examination of fibers of propellant residue produced during a winter live-fire exercise. Details of each of the experiments are described with the corresponding results below. Some of the multi-increment samples were used for subsampling experiments; however, for all multi-increment samples, all of the soil that was less than 2 mm was extracted and the concentrations reported are based on the total soil mass and total 2,4-DNT mass determined for each sample.

Effect of Grinding on Subsampling Variance of Spiked Ottawa Sand Samples

Based on past experience of poor subsampling precision of firing point samples, we hypothesized that the 2,4-DNT was associated with nitrocellulose fibers that did not grind sufficiently in a ring mill within 60 seconds. To test this hypothesis we spiked two 500-g portions of Ottawa sand. One portion was spiked with a fiber of M1 Propellant and the other with crystalline grains of Standard Analytical Reference Material (SARM) 2,4-DNT. Each spiked sample was ground on the ring mill for 60 s and twelve 10-g subsamples taken for analysis. Then the remainder of the sample was further ground for another four continuous minutes and twelve 10-g subsamples taken for analysis.

Propellant Residue Morphology Studies

Propellant residue was collected from trays placed in front of and beside the muzzle of a M119A1 105-mm howitzer during a winter live-fire exercise on a snow-covered firing point. Five projectiles (DODIC C445) were fired from the howitzer. Fibrous propellant residue was visible on the snow surface (Walsh *et al.*, 2004) and on the trays. Fibers from the tray that was 3 m in front of the muzzle were examined under a light microscope and photographed. Image software was used to calculate major and minor axes. To estimate the mass of 2,4-DNT in individual fibers, a subset of 10 fibers was selected. Selected fibers were weighed and then placed in individual vials. A 1.00-mL aliquot of acetonitrile was added to extract the 2,4-DNT from the fibers.

Results

Subsampling Variance Following Rotary Division of an Unground Soil Sample

Our first subsampling experiment was to see if we could split a large sample and use only a portion for further processing. Of the methods available for dividing a large particulate sample (i.e., cone-and-quartering, fractional shoveling, chute riffing, spinning riffing), the spinning riffle sample divider is recognized as the least likely to discriminate with respect to size, density, or other particle characteristics (Cross, 2000; Gerlach *et al.*, 2002). We used a Labtech Essa Rotary Sample Divider (Model RSD5) to divide a 200-increment sample from FP Mark. The divider is composed of a hopper, vibratory feeder, and a rotating turntable containing 12 receiving sectorial buckets. When we split the 10.95 kg sample into 12 subsamples, the relative standard deviation for the subsample masses was 2.7%. Each approximately 900-g subsample was extracted with acetone, and we determined the 2,4-DNT concentrations. The concentrations ranged from 0.50 to 1.28 $\mu\text{g/g}$, the mean was 0.76 $\mu\text{g/g}$, and the relative standard deviation was 28%. These results demonstrate that even under ideal laboratory conditions, reduction in sample volume by splitting or subsampling unground soils is a major source of uncertainty in the determination of 2,4-DNT.

Effect of Grinding Using a Ring Mill on the Variance of Mean 2,4-DNT Concentrations

Multi-increment samples from FP Mark were used to study why 60 s of grinding on a ring mill was not sufficient to reduce the subsampling error associated with 2,4-DNT propellant residue.

We used ten-increment samples collected from individual 1-m \times 1-m areas to measure subsampling error associated with 2,4-DNT before and after machine grinding. The

Table 1

Estimates of 2,4-DNT concentrations in duplicate 10-g subsamples of multi-increment samples from FP Mark before (A and B) and after (C and D) grinding for 60 s, then extraction of the remaining sample

Lab ID	2,4-DNT Concentration ($\mu\text{g/g}$)				
	Before Grinding		After Grinding		Remaining Sample
	A	B	C	D	
FP121	3.52	1.57	0.56	1.37	0.99
FP123	4.95	0.33	1.16	1.10	0.79
FP124	0.59	0.08	0.10	0.91	0.47*
FP125	5.70	0.10	0.08	0.48	0.68 [†]
FP126	0.07	4.90	0.28	0.25	1.64
FP129	1.54	0.34	0.95	1.51	1.09
FP130	0.73	0.23	1.63	0.11	1.4*
FP131	1.56	3.34	1.49	2.12	1.2
FP132	0.56	0.38	0.93	0.33	0.75
FP133	0.07	0.86	1.06	0.10	1.05 [†]
FP135	0.01	0.03	2.54	7.06	0.87
FP137	0.04	0.02	1.71	0.43	0.73
FP138	0.01	0.01	0.01	0.01	0.33
FP139	0.02	2.76	0.32	0.80	0.81 [†]
FP140	0.02	0.10	0.44	0.41	0.95

*Rotary division (Table 2).

[†]Further grinding (Table 3).

less-than-2-mm fraction for 14 of the samples was spread on a flat surface and duplicate 10-g subsamples formed by manually taking at least 30 small increments of soil. Then the rest of the sample was ground for 60 s on a LabTech Essa LM-2 Ring Mill, and another set of 10-g subsamples manually collected. Table 1 shows the results of duplicate 10-g subsamples taken before and after grinding and the 2,4-DNT concentration found by whole sample extraction in the remaining sample. Without question, the subsampling variance was unacceptably high before and after grinding for 60 s. We used a rotary divider to subsample two samples (FP124 and FP130) to see if machine division using a rotary divider and larger subsamples (~60 g) would improve precision. The data suggest some improvement in precision (Table 2), but subsampling error remained unacceptably high.

We hypothesized that the 2,4-DNT was associated with fibers of nitrocellulose-based propellant and that longer grinding times may be necessary to reduce the fiber size sufficiently for precise subsampling. However, longer grind times generate heat that could result in analyte loss. We performed a series of experiments to study the effect of grinding times on 2,4-DNT propellant residues.

First, we ground three samples (FP125, FP133 and FP139) that had extremely poor subsampling precision (Table 1) for an additional two 2-minute intervals and manually obtained triplicate 10-g subsamples from each sample after each grind. Then we extracted the remaining soils. The lowest relative standard deviation (RSD %) was for FP125 after an additional two minutes of grinding (Table 3); however, the mean 2,4-DNT concentration

Table 2

Estimates of 2,4-DNT in four of twelve splits obtained using a rotary division of two ground (60 s) multi-increment samples from FP Mark. The remaining eight splits for each sample were combined and 2,4-DNT concentration determined without subsampling

<i>FP124</i>			<i>FP130</i>		
Split	Mass (g)	2,4-DNT ($\mu\text{g/g}$)	Split	Mass (g)	2,4-DNT ($\mu\text{g/g}$)
5	62.5	0.35	4	58.6	1.1
6	66.0	0.41	5	57.9	0.61
10	47.0	0.66	7	62.6	2.34
11	58.6	0.20	12	54.7	1.26
	mean	0.41		mean	1.33
	s	0.19		s	0.73
	RSD (%)	47%		RSD (%)	55%
Split	Mass (g)	2,4-DNT ($\mu\text{g/g}$)	Split	Mass (g)	2,4-DNT ($\mu\text{g/g}$)
All Remaining Splits	450	0.51	All Remaining Splits	503	1.43

Table 3

Estimates of 2,4-DNT in manually collected 10-g subsamples of multi-increment samples from FP Mark after grinding for two 2-minute intervals. Triplicate 10-g subsamples were taken for analysis after each grind cycle, then 2,4-DNT concentrations were determined in the remainder of each sample without further subsampling

Replicate (10 g)	2,4-DNT Concentration ($\mu\text{g/g}$)		
	FP125	FP133	FP139
Plus 2 minutes grinding			
1	0.29	1.51	0.61
2	0.29	1.02	0.10
3	0.30	1.15	0.26
mean	0.29	1.23	0.32
s	0.0058	0.25	0.26
RSD (%)	2.0%	21%	81%
Plus 2 more minutes grinding			
1	0.65	0.99	0.55
2	0.63	1.06	0.73
3	0.52	0.87	0.83
mean	0.60	0.97	0.70
s	0.070	0.096	0.14
RSD (%)	12%	10%	20%
Remaining Sample			
2,4-DNT ($\mu\text{g/g}$)	0.70	1.05	0.81
Mass of Sample (g)	642	697	692

doubled for the triplicate 10-g subsamples after an additional 2 min of grinding (total of 5 min) and was similar to the concentration for the remaining 642 g of the sample. These results imply that at least one propellant fiber was not adequately ground after 3 min of grinding. The additional grinding reduced the subsampling variance for the other two samples (FP133 and FP139) (Table 3).

To further explore the effect of grind time on subsampling variance, we divided one 30-increment sample (FP150) from a 10-m \times 10-m area into three splits using the rotary divider. One split was ground for 1 min, the second for three continuous minutes, and the third for five continuous minutes. Each ground sample was then divided into 12 subsamples using the rotary divider. The subsamples were approximately 60 g each. The means (relative standard deviations) were 0.68 (61%), 0.61 (29%), and 1.1 (13%) for the 1-, 3-, and 5-min grind times, respectively. Thus, one min is an inadequate grind time and extended grinding for 5 min reduced the subsampling variance. However, the subsampling error was greater than the error associated with ground soils containing crystalline high explosives residues, which is typically less than 5% RSD.

To further test our hypothesis that the 2,4-DNT in the firing point soils is more resistant to the effects of grinding because it is associated with propellant fibers, we added a fragment of an M1 propellant grain (12 mg) to 500 g of Ottawa sand and ground the sand for 60 s, manually obtained twelve 10-g subsamples, and ground the remainder of the sand for an additional four continuous minutes. Likewise, we added four crystals (totaling less than 1 mg) of 2,4-DNT (Standard Analytical Reference Material [SARM]) to another 500 g of Ottawa sand and processed the sand in the same way. The one-minute grind resulted in relative standard deviations of 53% and 1.7% for the propellant fiber and the SARM samples, respectively, thereby supporting our hypothesis. The 5-min grind time reduced the subsampling variance for the propellant fiber sample to 6.5% and had an insignificant effect on the variance for the SARM sample. However, the estimate of the mean of 2,4-DNT was reduced significantly by extended grinding of the SARM-spiked soil (1.74 $\mu\text{g/g}$ after one min and 1.15 $\mu\text{g/g}$ after five min), but not in the M1 propellant-spiked soil (2.05 $\mu\text{g/g}$ after one min and 2.27 $\mu\text{g/g}$ after five min). 2,4-DNT has a relatively high vapor pressure, and the loss from the SARM soil may have been due to heat generation and thermal desorption. Even though the 2,4-DNT that is within a nitrocellulose matrix may be less susceptible to loss by vaporization if the sample is heated, we have adopted the practice of grinding firing point soils for five 60-s intervals with sufficient time between grind cycles to prevent the sample from significant warming.

Size Fractionation of Machine Ground Soils

We performed a series of studies to understand which soil size fraction was associated with the 2,4-DNT before and after grinding of firing point soils.

Three 30-increment samples from the 10-m \times 10-m area at FP Mark (FP142, FP144, and FP149) were divided into three size fractions by passing each sample through #10 (2-mm mesh) and #30 (0.595-mm mesh) sieves. Then each size fraction was extracted with acetone and 2,4-DNT determined. 2,4-DNT was not found in the greater-than-2-mm fraction. For the remaining two fractions, the larger mass of soil was in the less-than-0.595 mm fraction, but the largest mass of 2,4-DNT was in the greater-than-0.595-mm intermediate fraction (Table 4).

To determine the effect of machine grinding on the distribution of 2,4-DNT between the size fractions, we divided one of the 30-increment samples from the 10-m \times 10-m grid of FP Mark (FP145) into 12 splits using the rotary divider, randomly chose five splits, and

Table 4
2,4-DNT in three size fractions of unground 30-increment samples from 10-m × 10-m grid at FP Mark (FP142, FP144 FP149)

Size Fraction	Soil Mass (kg)	2,4-DNT Mass (mg)	2,4-DNT ($\mu\text{g/g}$)
FP142			
>2 mm	1.87	<0.02	<0.01
>0.595 mm and <2 mm	0.80	1.51	1.9
<0.595 mm	1.61	0.68	0.42
FP144			
>2 mm	1.26	<0.01	<0.01
>0.595 mm and <2 mm	0.50	1.65	3.3
<0.595 mm	1.16	0.60	0.51
FP149			
>2 mm	1.6	<0.02	<0.01
>0.595 mm and <2 mm	0.61	0.78	1.3
<0.595 mm	1.47	0.50	0.34

ground each for 1, 2, 3, 4, or 5 minutes in the ring mill. Each ground split was fractionated by size and the unground splits were extracted whole without subsampling. We found that the ring mill grinder performed according to specifications (i.e., 95% of sample ground to less than 0.075 mm in three min) (Table 5a); however, after three min of grinding, over half of the 2,4-DNT mass was still greater than 0.075 mm. After 5 min of grinding, 99.5% of the sample mass was less than 0.075 mm, whereas 65% of the 2,4-DNT mass was less than 0.075 mm (Table 5b). These results demonstrate why one minute of grinding was inadequate and why five minutes of grinding reduces the subsampling variance, but not to the extent achievable for crystalline contaminants.

Propellant Residue Morphology

Multi-perforated propellant grains (Figure 1), such as those used to fire 105-mm projectiles, are designed to burn progressively. The burning surface area increases with time until most of the propellant between perforations is consumed, leaving slivers of degressively burning propellant (Department of the Army, 1969). Unconsumed slivers may be ejected from the howitzer and are the fibers that we observed on the snow surface and collection trays.

A total of 201 fibers was recovered from the collection tray that was placed 3 m in front of the muzzle. The average major axis was 2.3 mm (range of 0.41 to 7.54 mm) and the average minor axis was 0.34 mm (range of 0.11 to 1.12 mm). Most of the fibers were a green color, similar to that of an unburned propellant grain (Figure 2a).

Ten fibers were randomly selected and weighed between 8 and 565 μg . 2,4-DNT was detectable in each of the fibers. 2,6-DNT was detectable in all but the fiber with the lowest mass, which also appeared to be burned. The total mass of the DNT isomers increased linearly as a function of the fiber mass (Figure 2b).

Discussion

We performed a series of experiments to evaluate the compositional and distributional heterogeneity associated with propellant residues. Starting with the hypothesis that 2,4-DNT is coupled with propellant fibers, proper laboratory subsampling of firing point soils

Table 5

Size fractionation of five machine-ground splits of a 30-increment sample (FP145) from the 10-m × 10-m area at FP Mark. Grind time was 1 to 5 minutes. 2,4-DNT was determined in the remaining seven splits without grinding or subsampling.

(a) Soil and 2,4-DNT masses in size fractions

Size Fraction*	Size Fraction Mass (g)	2,4-DNT Mass (μg)	2,4 DNT Soil Concentration ($\mu\text{g/g}$)
Split 1: 1 minute grind			
>0.595 mm to <1 mm	0		
>0.177 mm to <0.595 mm	10.7	191	18.0
>0.125 mm to <0.177 mm	18.4	10	0.55
>0.075 mm to <0.125 mm	35.8	8.9	0.25
<0.075 mm	134	21	0.15
Total	199	231	1.2 (mean for split)
Split 5: 2 minute grind			
>0.595 mm to <1mm	0.020		
>0.177 mm to <0.59 5mm	2.14	311	145
>0.125 mm to <0.177	2.18	64	30
>0.075 mm to <0.125 mm	17.0	56	3.3
<0.075 mm	193	178	0.92
Total	214	610	2.9 (mean for split)
Split 6: 3 minute grind			
>0.595 mm to <1 mm	0.020		
>0.177 mm to <0.595 mm	0.220	56.3	256
>0.125 mm to <0.177	0.440	69.0	157
>0.075 mm to <0.125 mm	5.75	49.3	8.57
<0.075 mm	205	134	0.651
Total	212	308	1.5 (mean for split)
Split 8: 4 minute grind			
>0.595 mm to <1 mm	0.230	0.10	0.54
>0.177 mm to <0.595 mm	0.570	7.4	13
>0.125 mm to <0.177	0.180	20	110
>0.075mm to <0.125 mm	1.19	18	15
<0.075 mm	202	60	0.30
Total	204	106	0.52 (mean for split)
Split 9: 5 minute grind			
>0.595 mm to <1mm	0		
>0.177 mm to <0.595 mm	0.600	3.9	6.48
>0.125 mm to <0.177	0.070	9.8	140
>0.075 mm to <0.125 mm	0.810	23	28.1
<0.075 mm	200	68	0.342
Total	201	105	0.52 (mean for split)
Whole sample extractions			
Split 2	203	276	1.36
Split 3	209	199	0.95
Split 4	193	102	0.53
Split 7	198	234	1.18
Split 10	201	59.6	0.30
Split 11	204	144	0.71
Split 12	198	61.2	0.31

*Sieves: #10 (2 mm), #18 (1 mm), #30 (0.595 mm), #80 (0.177 mm), #120 (0.125 mm), and #200 (0.075 mm). All ground soils passed through the #18 sieve.

Table 5b
Percent of total soil and 2,4-DNT mass that is less than 0.075 mm as a function of grinding time

Grind Time (minutes)	Soil Mass <0.075 mm (% of total)	2,4-DNT Mass <0.075 mm (% of total)
1	67.3	9.1
2	90.2	29
3	96.7	44
4	99.0	57
5	99.5	65

requires that each subsample has adequate mass to contain the same proportion of fibers as the field sample. For example, if the field sample contains one fiber in each 20 grams of soil, collection of only two grams of soil for extraction will not represent the proportion of fibers in the field sample. In this case most of the samples will show a very low concentration of 2,4-DNT and some of the subsamples will show a higher concentration of 2,4-DNT than actually exists in the field sample. Also, the subsample must be formed by taking an adequate number of increments to overcome any segregation of the fibers within the field sample. The best method available is a rotary divider that forms subsamples with hundreds of random increments. When we used a rotary divider to split an 11-kg sample into 12 900-g subsamples, the range of 2,4-DNT concentrations was 0.50 to 1.28 $\mu\text{g/g}$, the mean was 0.76, and the relative standard deviation was 28%. The fact that 900-g soil subsamples failed to

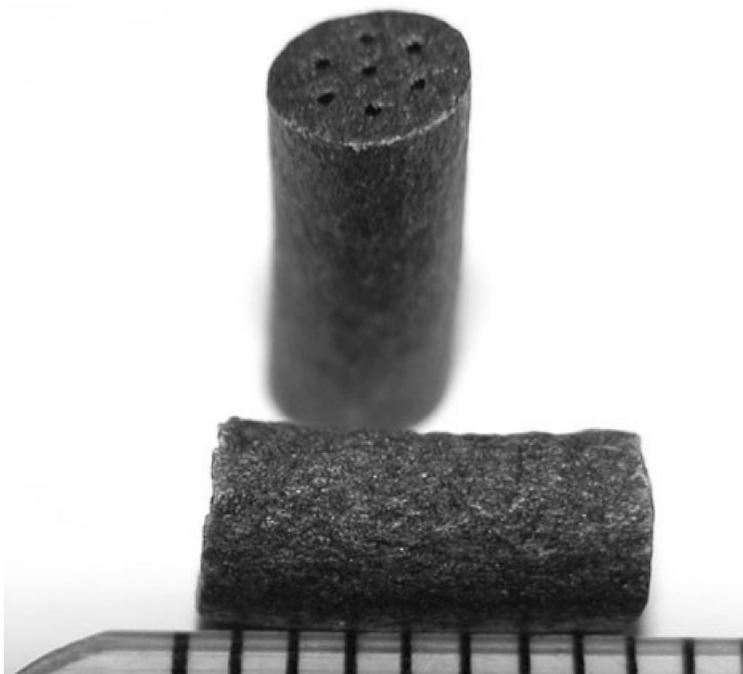
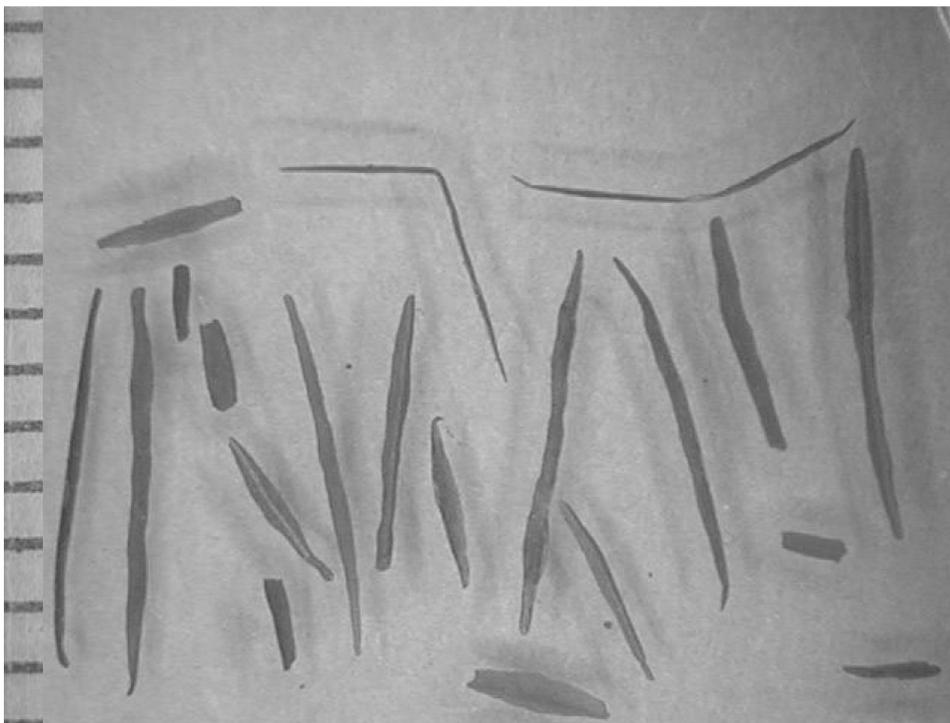
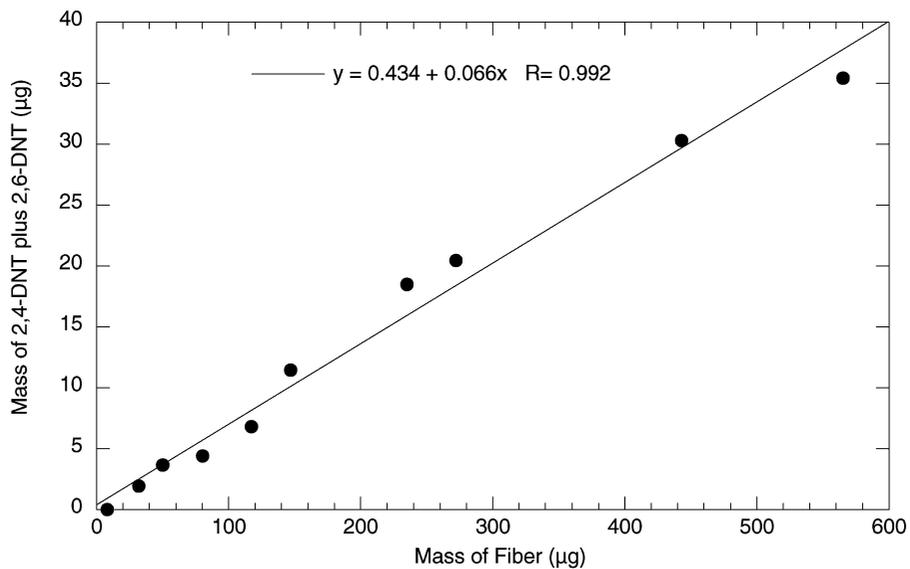


Figure 1. M1 multi-perforated propellant grain. The scale gradations are millimeters.



(a)



(b)

Figure 2. Fibrous propellant residue that contains 2,4-DNT. (a) A subset of fibers or slivers deposited on a collection tray located 3 m from a 105-mm howitzer muzzle. The gradations of scale on the left are millimeters. (b) Mass of DNT isomers as a function of fiber mass in 10 randomly selected fibers.

reproducibly represent fibers in the 11-kg field sample indicates that subsample masses that are typically taken for analysis (tens of grams at most) cannot represent the field sample with any degree of confidence. Either the entire field sample needs to be extracted for analysis or some form of laboratory processing is needed to improve the precision and accuracy of subsampling.

We focused most of our laboratory processing on comminution to diminish the fiber particle sizes and increase the number of fiber particle fragments in our field samples, which should reduce the subsample mass required to represent the field sample. The protocol that we developed for soils contaminated with high explosives (e.g., grinding for 60 s using a ring mill) did not reduce the subsampling variability for propellant-contaminated soils. Grinding for a longer period of time, up to five minutes, did reduce the subsampling variability for field-contaminated soils and a soil spiked with a piece of propellant, but not always to the extent of that obtained after 2,4-DNT was added as crystalline material to clean sand and the sample ground.

Sieve analyses to fractionate field-contaminated samples demonstrated that the size fraction between 0.595 mm and 2 mm contained most of the 2,4-DNT mass. Sieve analysis of ground field-contaminated soils showed that 96.7% of the soil mass was less than 0.075 mm after grinding for three minutes, but only 65% of the DNT mass was less than 0.075 mm after five minutes of grinding. The propellant fibers are much more difficult to comminute than the soil particles and crystalline energetics, thus requiring longer grind times.

Two issues concerning grinding time need to be emphasized. First, a low relative standard deviation does not necessarily indicate that all the propellant fibers are pulverized sufficiently. In one of our experiments, three minutes of grinding resulted in a relative standard deviation of only 2.0% for triplicate subsamples (Table 3), but the estimate of the mean doubled after an additional two minutes of grinding of the same sample, indicating that some fibers were not pulverized. Secondly, heat generation due to friction between the puck, soil, and bowl is undesirable for analytes that may thermally desorb or degrade. Our current practice for propellant-contaminated soils is to grind for five 60-s cycles with at least 60-s rest between grinding cycles. This procedure is used for all soils from locations that potentially have nitrocellulose-based propellant residues, including firing points for small arms, light antitank rockets, and mortars, and for propellant burning and demolition areas. Soils from these locations have NG (nitroglycerin) if double-base propellants have been used (Jenkins *et al.*, 2006) and this sample processing procedure has been found to be appropriate for the determination of NG (Hewitt *et al.*, 2005). Propellant formulations contain several other semi-volatile chemicals, including dibutylphthalate, diphenylamine, and ethyl centralite, and we have no reason to believe that this sample processing procedure would negatively affect these chemicals. We would expect a reduction in subsampling variance similar to that observed for 2,4-DNT and NG.

The soils used for these laboratory studies were from a sparsely vegetated firing point. We have also studied soils from vegetated firing points and found that the surface vegetation contains propellant residue; therefore, it should not be discarded. Whether it is included as part of a soil sample or analyzed separately depends on the objectives of the site investigation. We have found that five 60-s grind cycles in the ring mill sufficiently pulverizes vegetated samples, provided the vegetation is thoroughly air-dried. In most cases, the mass of the air-dried vegetation accounts for less than 10%, and frequently less than 1%, of the sample.

Conclusions

2,4-DNT in soils from firing points is in a particulate form that resists comminution. Evidence suggests that the 2,4-DNT remains in the nitrocellulose matrix of single-base

propellants as discrete fibers distributed on the soil surface. Size fractionation of a firing point soil showed that the bulk of the soil was less than 0.595 mm, but that most of the analyte of interest, 2,4-DNT, was found in the 0.595- to 2-mm size range. These results are consistent with the sizes of fibers or slivers of unconsumed propellant collected during a live-fire training exercise. Machine grinding of soils using a ring mill for 5 minutes was required to move 65% of the 2,4-DNT to the size fraction containing 99.5% of the soil (<0.075 mm). These results support the hypothesis that the 2,4-DNT remains in a nitrocellulose matrix when it is deposited at a firing point. Isolation and further characterization of propellant residue fibers may allow us to apply sampling theory (Pitard, 1993) to confirm appropriate sampling procedures. Further studies are also needed to define the environmental fate and the human and ecological risk associated with 2,4-DNT in propellant residue.

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