SPECIAL REPORT 96-15

Assessment of Sampling Error Associated with Collection and Analysis of Soil Samples at Explosives-Contaminated Sites

Thomas F. Jenkins, Clarence L. Grant, Gurdarshan S. Brar,
Philip G. Thorne, Thomas A. Ranney and
Patricia W. Schumacher

September 1996

Abstract: This study is an assessment of short-range heterogeneity in contaminant concentrations within surface soils at explosives-contaminated sites. Intensive sampling was conducted over short distances. Discrete and composite samples were analyzed by both on-site colorimetric methods and standard laboratory protocols. Three locations were sampled at each of three installations and the results used to estimate the relative contributions of analytical error and sampling error to the total uncertainty. The major contaminant at seven of the nine sampling locations was TNT; results from the on-site colorimetric method were in excellent agreement with laboratory results using SW846 Method 8330. DNT and ammonium picrate were the contaminants present at the highest concentration in the other two locations. For four sampling locations, short-range concentration variations were modest and analyte distribution was sufficiently Gaussian to apply normal distribution statistics to fractionate the total error variances. For these four locations, analysis standard deviations were always much lower than the sampling standard deviations; total error was dominated by sampling error, whether characterization was done using on-site or laboratory analysis. The other five sampling locations had enormous short-range heterogeneity and sampling error overwhelmed analytical error. To improve the quality of site characterization data, emphasis should be placed on reducing sampling error by the use of composite sampling strategies. Characterization of explosives-contaminated sites using composite sampling, in-field sample homogenization, and on-site analysis is an efficient method of producing data that are accurate and precise, and also representative of the area.

How to get copies of CRREL technical publications:

Department of Defense personnel and contractors may order reports through the Defense Technical Information Center:

DTIC-BR SUITE 0944
8725 JOHN J KINGMAN RD
FT BELVOIR VA 22060-6218
Telephone 1 800 225 3842
E-mail help@dtic.mil
msorders@dtic.mil
WWW http://www.dtic.dla.mil/

All others may order reports through the National Technical Information Service:

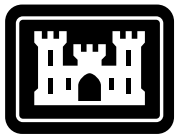
NTIS
5285 PORT ROYAL RD
SPRINGFIELD VA 22161
Telephone 1 703 487 4650
1 703 487 4639 (TDD for the hearing-impaired)
E-mail orders@ntis.fedworld.gov
WWW http://www.fedworld.gov/ntis/ntishome.html

A complete list of all CRREL technical publications is available from:

USACRREL (CECRL-TL)
72 LYME RD
HANOVER NH 03755-1290
Telephone 1 603 646 4338
E-mail techpubs@crrel.usace.army.mil

For information on all aspects of the Cold Regions Research and Engineering Laboratory, visit our World Wide Web site:
http://www.crrel.usace.army.mil

Special Report 96-15



US Army Corps of Engineers
Cold Regions Research & Engineering Laboratory

Assessment of Sampling Error Associated with Collection and Analysis of Soil Samples at Explosives-Contaminated Sites

Thomas F. Jenkins, Clarence L. Grant, Gurdarshan S. Brar, Philip G. Thorne, Thomas A. Ranney and Patricia W. Schumacher

September 1996

Prepared for
U.S. ARMY ENVIRONMENTAL CENTER
SFIM-AEC-ET-CR-96157

PREFACE

This report was prepared by Dr. Thomas F. Jenkins, Research Chemist, Dr. Gurdarshan S. Brar, Research Physical Scientist, Philip G. Thorne, Research Physical Scientist, and Patricia W. Schumacher, Physical Science Technician, Geological Sciences Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory, Dr. Clarence L. Grant, Professor Emeritus, University of New Hampshire, and Thomas A. Ranney, Science and Technology Corporation, Hanover, New Hampshire. Funding was provided by the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland, Martin H. Stutz, Project Monitor.

The authors gratefully acknowledge Alan D. Hewitt and Marianne E. Walsh, CRREL, for their technical review of this manuscript. In addition the authors acknowledge Clyde Murray, Bureau of Land Management, Carson City, Nevada; Douglas Peery, Quanterra Corporation, Knoxville, Tennessee; Sophie Hong, U.S. Army Engineer District, Sacramento, and Harry Craig, U.S. EPA Region 10, Portland, Oregon, for helping locate appropriate sites to conduct this field sampling study. Jane Mason, CRREL, is acknowledged for assistance in preparation of this report.

CONTENTS

ILLUSTRATIONS

Figure

TABLES

Assessment of Sampling Error Associated with Collection and Analysis of Soil Samples at Explosives-Contaminated Sites

THOMAS F. JENKINS, CLARENCE L. GRANT, GURDARSHAN S. BRAR,
PHILIP G. THORNE, THOMAS A. RANNEY AND PATRICIA W. SCHUMACHER

INTRODUCTION

Background

Determining the distribution of contaminants at hazardous waste sites is a fundamental problem facing site investigators. In general, distributions are very site-specific, depending on a number of variables, including how the site was contaminated, the physical and chemical properties of the contaminants involved, soil type, and the geology and hydrogeology of the site. Lacking distribution information, it is impossible to devise an optimal sampling strategy.

Accurate chemical characterization of a hazardous waste site requires a well-designed sampling plan. After defining the area of interest (target populations), which might be an entire site or several defined areas within a site, workers collect samples according to one of several possible schemes. In the absence of reliable historical information, it is difficult to choose among judgmental, random, systematic, stratified, or some combination of these sampling plans. Many references recommend a preliminary study before devising a sampling plan (Gilbert 1987, van Ee et al. 1990, Huesemann 1994, Keith et al. 1995, Williams 1996).

Until recently, most studies of hazardous waste sites have relied on shipping samples to off-site laboratories for analysis. Besides the high cost and potential for sample contamination or degradation of labile analytes, this arrangement does not lend itself to the timely decisions that are necessary in a step-wise plan. Recently, this problem has been addressed with the development and promotion of field analytical methods (Triegel 1988, Jenkins and Walsh 1992, EPA 1993, Triegel et al. 1994, Keith et al. 1995, Williams 1996, Barnard, in press). Inexpensive on-site analysis methods for the most common explosives in munitions-contaminated soils have been developed and are now in common use. These procedures appear to be sufficiently accurate and precise to enable their use in mapping locations of contamination and, if a sufficient number of samples are analyzed, in providing estimates of spatial contaminant heterogeneity. With these field methods, sequential modifications in sampling plans are feasible because data become available while sampling is in progress.

On-site analytical methods are sometimes criticized as having inadequate precision, accuracy and specificity. With respect to specificity, we agree that the QA/QC plan must include laboratory-based confirmatory measurements on selected samples. Similarly, accuracy should be verified against reference methods for an appropriate number of samples. The precision issue, however, is a different matter. Historically, the precision of methods used in hazardous waste characterization has received an inordinate amount of attention compared to sampling error. Contaminated soils are often extremely heterogeneous, which causes the major error source to be sampling and subsampling. No amount of improvement in analytical precision can significantly reduce total measurement error when the analytical error is a minor contributor to the total. Williams (1996) noted that the newly released U.S. EPA DQO guidelines focus on the uncertainty of a specific decision rather than the individual parameters that contribute to the overall uncertainty. This is an encouraging change.

A sampling plan can only be optimized after the process of obtaining representative samples has been adequately addressed. Numerous varia-

tions have been offered to describe the qualifications of representative samples (Gilbert 1987, Barcelona 1988, Smith et al. 1988, Barnard, in press). We are partial to the Gilbert definition, "A representative unit is one selected for measurement from the target population in such a way that it, in combination with other representative units, will give an accurate picture of the phenomenon being studied." According to Barnard, "Representativeness is a statistical concept that is a measure of how well a data set of sample measurements yields information concerning the population."

Explosives are solids at ambient temperature, dissolve slowly and sparingly in aqueous solution and have low vapor pressures. These properties limit modes of mobility compared to other contaminants such as fuels or solvents. Thus, the areas of high concentrations that serve as sources for contamination of ground water remain at or near the surface where deposited, unless the soils themselves are moved. Thus, characterizing the contamination distribution for explosives will often be possible using samples of near-surface soils.

In this study we focus on how to obtain representative samples from surface soils contaminated by munitions residues. Too often, local spatial heterogeneity is bypassed in favor of grab sampling on the theory that heterogeneity will be "averaged out" if sufficient samples are taken. While there is validity in this position, it hardly qualifies as cost-effective, especially when analysis cost often outpaces sample collection cost by orders of magnitude. In addition to our experience, several authors have reported large local spatial heterogeneity, often of the same magnitude as present on a much larger scale (see, for example, Parkin 1987, Sabbe and Marx 1987, van Ee et al. 1990, Starr et al. 1995). To address this problem, others have used or recommended composite sampling (Cameron et al. 1971, Schaeffer et al. 1980, Gilbert 1987, Garner et al. 1988, Paasivirta and Paukku 1989, Parrish et al. 1990, Huesemann 1994, Fabrizio et al. 1995). We decided to investigate the feasibility of this approach, coupled to both on-site analysis and conventional laboratory analysis.

Compositing is sometimes discouraged because it eliminates information regarding the variability of the individual samples composited. When applied to large areas, this limitation may represent a valid concern, especially when concentrations are near a regulatory limit. However, when used on localized areas in lieu of grab sampling, we believe it is an attractive option to improve representativeness of samples.

Objectives

The major objective of this work was to characterize the short-range heterogeneity of contaminants at explosives-contaminated sites. This was done by conducting field sampling and analysis studies at a number of explosives-contaminated sites that varied in explosives analytes present, mode of contamination, soil type and geohydrology. Statistical analyses of the results were conducted to determine the following:

1. Analytical error, which was estimated from the pooled variances from duplicate analyses of seven grab samples collected within a localized area. Short-range sampling error was estimated from the variance computed from the differences of mean values of the seven grab (soil) samples.

2. The degree to which some form of composite sampling could be used to reduce sampling error.

3. Whether inexpensive, colorimetric on-site analysis methods could be used to provide an accurate description of contaminant distribution and a reliable estimate of sampling error.

EXPERIMENTAL

Throughout this report the following terminology will be used: installation will refer to the government facility where sampling was conducted; sampling location will refer to any one of the nine areas (three at each installation) where sampling was conducted; and sample position (or sample number) will refer to the specific spatial position where a discrete sample was collected.

Sampling sites

Sampling studies were conducted at three installations. These are Monite, a BLM (Bureau of Land Management) installation near Sparks, Nevada; Hawthorne Army Ammunition Plant (AAP), Hawthorne, Nevada; and Volunteer AAP, Chattanooga, Tennessee (Fig. 1).

The Monite installation is a small former industrial area that has about 1.5 acres of land contaminated with TNT and DNT. The company that owned the site reportedly reclaimed explosives from out-of-date military munitions, but since that company declared bankruptcy and abandoned the site many years ago, the history of contamination

Figure 1. Sampling sites.

is largely unknown. Several years ago, children playing in the area found a barrel of DNT and the site subsequently has undergone preliminary site characterization. Based on the results of this characterization, C. Murray of BLM pointed out several potential sampling locations that had detectable explosives in the soil. Based on his suggestions, we conducted preliminary soil sampling and the samples were analyzed using the EnSys colorimetic on-site analysis method (EPA 1995b). The results of this initial sampling and analysis revealed three areas that had very different types of contamination. One had TNT concentrations in the thousands of µg/g (location 1), one had similar levels of DNT (location 2), and a third had low µg/g levels of TNT (location 3). These three locations were selected for intensive sampling and analysis.

The second installation we visited was Hawthorne AAP, which is located in west-central Nevada (Fig. 1). This facility was established in 1928 and was operated for many years as a load, assemble and pack facility for the Navy. In 1977 it was transferred to Army control. We visited a number of candidate sampling locations and selected three based on results of preliminary sampling and field analysis. The first sampling location was under a conveyer belt that took "empty" boxes and crates from the inside of a melt facility out for disposal. Red stains were visible on the soil surface apparently from residual TNT crystals released from these boxes. The major contaminant in this area was TNT with soil concentrations in the thousands of µg/g (location 4). The second sampling location at Hawthorne was at an open burning area. The area was free of vegetation and had concentrations of TNT in the hundreds of µg/g (location 5). The final location sampled at Hawthorne was a disposal lagoon where the surface soils were visually contaminated with intense yellow crystalline material that we believed to be ammonium picrate (location 6).

The third installation sampled was Volunteer AAP near Chattanooga, Tennessee (Fig. 1). This installation is a TNT and DNT production facility, although it has not actively produced these munitions compounds since 1977. Here again, we selected three sampling locations based on preliminary sampling and colorimetric on-site analysis. The first sampling location was at a loading area located adjacent to a TNT production building (location 7 and location 7R). This area was also contaminated from wash water from the facility and concentrations of TNT in the soil were in the thousands of µg/g. The second sampling location was within a drainage ditch that received spills of TNT production wastewater (location 8). Individual samples collected within the ditch had elevations that differed by only a maximum of 25 cm; however, TNT concentrations varied from 500–30,000 µg/g. The final sampling location at Volunteer was an area initially thought to be free of contamination, but upon sampling and on-site analysis, we found it to have TNT concentrations in the 4–40 µg/g range (location 9).

Soil sampling procedure

A common pattern was used for soil sampling at all nine locations. A plastic template was placed on the ground with the center at the selected sampling location and oriented as shown in Figure 2, with sample numbers 2 and 5 oriented north–south. Seven samples were collected in a wheel pattern with sample number 1 in the center. The radius of the wheel was 61 cm and samples arranged around the wheel were separated by 61 cm.

All seven soil samples were collected at the surface from 0 to 15 cm using a manual 5.0-cm stainless-steel hand auger. When vegetation was present, it was removed. Cores were transferred to plastic zip lock bags and taken to a processing area. At the Monite site, processing was conducted outdoors in the shade to minimize the possibility of photodegradation. At Hawthorne and Volunteer, soil processing was conducted in air-conditioned buildings.

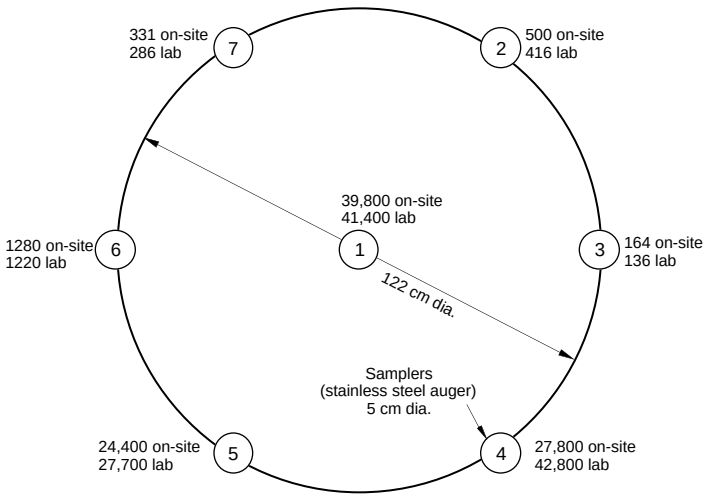


Figure 2. Sampling scheme (TNT concentrations shown are from sampling location 1).

On-site soil processing

Discrete samples

Soil samples from the Monite site and Hawthorne AAP were dry and mostly consisted of a mixture of sands and gravels. These samples were processed as follows. Soils were emptied from the zip lock bags into 23-cm-diameter aluminum pie pans. We dispersed the material by breaking up the large clumps with gloved hands and removing large rocks. The pans were covered with a second pie pan and the soil was swirled and shaken vigorously to disperse and homogenize the material, which was then coned and quartered. Approximately 5-g subsamples were removed from each quarter and combined to produce a sample of about 20-g for colorimetric on-site analysis. The bulk sample was remixed, coned and quartered again and a duplicate 20-g sample for field analysis was removed as described above. The sample was remixed a third time and another 20-g sample removed and placed in an amber 40-mL glass vial for subsequent laboratory analysis. The remaining sample was returned to its original zip lock bag and saved for preparation of a composite sample for that sampling location.

Soils from Volunteer had a higher moisture content and were composed of a higher percentage of finer grained material than soils from either Monite or Hawthorne. This made field homogenization more difficult and time consuming. At Volunteer, soil samples were placed in zip lock bags and initially kneaded by hand to break up large clumps. They were then deposited in aluminum pie pans and further disaggregated by hand until approximately pea sized or smaller pieces were produced. For soil from sampling location 7, rocks greater than 0.5 cm were removed and weighed. Soils were then coned and quartered and further processed as described above.

Composite samples

For composite samples at the Monite site and Hawthorne AAP, the soil remaining after discrete samples were removed for each of the seven grab samples within a wheel was combined in a large aluminum roasting pan. While the portions used to make the composite were not individually weighed for Monite and Hawthorne, they were approximately equal in weight. The soil was homogenized by hand mixing. Clumps were reduced by hand crushing and the material was coned and quartered. Approximately 5-g samples were removed from each quarter and combined to produce a 20-g sample for field analysis. The soil was coned, quartered and sampled six more times to produce a total of seven replicates for field analysis. The soil was dispersed, coned and quartered one final time and a 50-g sample removed and placed in an amber glass bottle for subsequent laboratory analysis.

At Volunteer, a similar procedure was used except that equal weights of each individual sample (100 or 600 g each, depending on wheel location) were used to prepare composites. Otherwise samples were processed as above. A summary of the entire sampling design is shown in Figure 3.

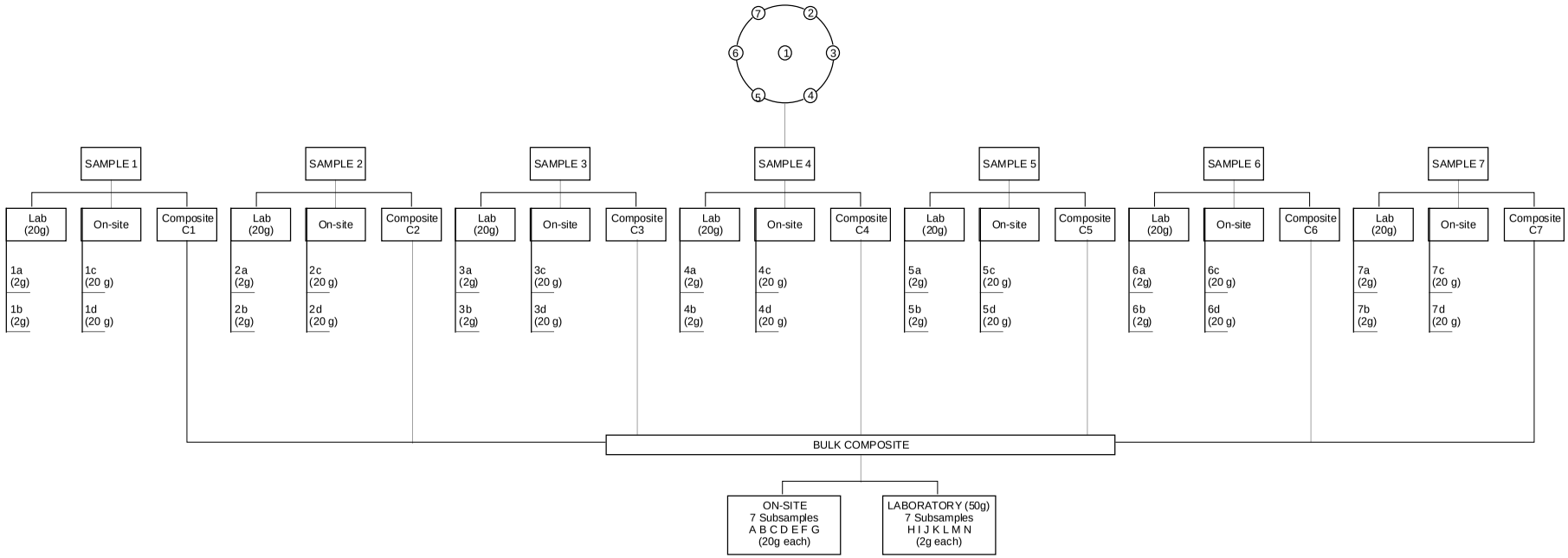


Figure 3. Soil sample preparation for analysis.

Colorimetric on-site analysis for TNT and 2,4-DNT

The 20-g soil samples at all three installations were extracted in 150-mL plastic extraction bottles by adding 100 mL of acetone, and shaking vigorously (Jenkins and Walsh 1992). Soil extracts from all locations were analyzed using the EnSys TNT method (EPA 1995b). The acetone contained 3% water to ensure that adequate water was present for the chemical reaction that produces color development. An extraction rate study was conducted on the soil from each site to determine the appropriate extraction time. For soils from the Monite site and Hawthorne AAP, a 3-minute extraction time was adequate. For samples from Volunteer AAP, the 3-minute extraction time was not adequate, so soils were extracted using 3 minutes of shaking, a 30-minute rest time, and a final 3-minute shaking period. After allowing the soil to settle for at least 15 minutes, we removed an aliquot of each extract using a Plastipak syringe and filtered it through a Millex SR membrane. Extracts were diluted as appropriate, such that absorbances after reaction with the EnSys reagent were less than 1.0.

For samples containing mainly TNT, the intensity of color of the extract prior to reaction with the EnSys reagent often indicated the TNT concentration and served as a rough guide for sample dilution. For extracts containing DNT, this was not true and the degree of dilution needed for each sample was obtained by on-site experimentation. Because soil concentration varied by such a large amount, with concentrations in excess of 100,000 µg/g, acetone extracts had to be diluted by ratios as high as 1:5000 to provide analyte concentrations in the linear range of the method (0–4 mg/L). In the field these dilutions were made using glass µL syringes and graduated cylinders. When this dilution process was assessed, relative standard deviations were always less than 3% (Jenkins et al. 1996).

For seven of the nine sampling locations, extracts became reddish when reacted with the EnSys reagent, meaning that TNT was likely present. For sampling location 2 at the Monite site, extracts became blue-purple when reacted with the EnSys reagent, showing that DNT was the likely contaminant rather than TNT. At sampling location 6, acetone extracts were fluorescent yellow, denoting the presence of ammonium picrate as the primary contaminant. Addition of the EnSys reagent to these yellowish solutions resulted in variable and unstable color changes.

Calibration for quantitation was achieved by reacting a known standard of TNT in acetone (containing 3% water) with the EnSys reagent for samples from locations 1, 3, 4, 5, 7, 7R, 8 and 9. Absorbance was measured at 540 nm with a battery operated spectrophotometer (Hach Model DR/2000). Likewise, a standard with a known concentration of DNT was used to calibrate soil extracts from sampling location 2 and absorbance was measured at 570 nm. Correction for background color in the extracts was obtained by measuring the absorbance of each extract prior to addition of the EnSys reagent, doubling the value, and subtracting it from the final absorbance after addition of the reagent. Doubling the initial absorbance prior to subtraction takes into account the increased absorbance caused by reaction of humic organics in the extract with base, as discussed elsewhere (Jenkins and Walsh 1992).

On-site analysis method for ammonium picrate

The on-site analysis method used for ammonium picrate was reported by Thorne and Jenkins (1995). We extracted 20-g subsamples of soil from sampling location 6 with 100 mL of acetone containing 3% (V/V) deionized water by manually shaking for 3 minutes. A 4-mL aliquot was removed and the absorbance measured at 400 nm. If the absorbance was above 1.0, the extract was diluted with deionized water until the absorbance was below 1.0. This dilution factor was used to calculate how much of the original acetone extract could be applied to a 3-mL SPE-ALUMINA-A (Supelco) cartridge.

The volumes used for analysis of the duplicate subsamples of the discrete samples and for composites were as follows: for discrete samples from positions 2, 3 and 7—20 mL; from positions 1 and 4—10 mL; from position 6—2 mL; from composites—1 mL; from position 5—0.4 mL. These quantities were diluted one-to-one with deionized water and added to the cartridges.

Picrate ions were retained on the alumina. Most interferences were removed by passage of a 5-mL aliquot of methanol followed by a 3-mL aliquot of acetone. Picric acid was eluted from the cartridges with 10 mL of acetone, which had been acidified with four drops of concentrated sulfuric acid. The initial absorbance at 400 nm was recorded and used as a background correction. After adding an

additional 5 mL of unacidified acetone, we diluted this solution with 5 mL of deionized water; a change from colorless or brownish- yellow to deeper yellow revealed the presence of picrate. The final absorbance at 400 nm was recorded. The corrected absorbance was converted to μg/g of picric acid on the basis of the response from calibration standards.

Soil processing for laboratory analysis

All soil samples were returned to the laboratory in coolers by overnight carrier. Upon receipt they were maintained at 4°C until processed. Samples were placed in plastic weigh boats, plant and other debris were removed, and they were air dried in the dark until a constant weight was achieved, usually within 48 hours or less. Weight loss upon drying was used to calculate percent moisture, which was then used to correct field-measured analyte concentrations to a dry weight basis for comparison with laboratory results. Stones were removed from dried samples, which were ground with a mortar and pestle to a fine powder. The weight of stones removed from each sample was recorded. Except for wheels 7 and 7R, the amount of stones removed prior to laboratory analysis did not significantly modify the soil from that analyzed in the field. For wheels 7 and 7R, the amount removed was large and this had an effect on the level of agreement of results from on-site and laboratory analyses, as will be discussed later.

Duplicate 2.00-g subsamples from each discrete soil sample and seven replicate 2.00-g subsamples from composites were weighed into 22-mL glass vials equipped with Teflon-lined caps. A 10.0-mL aliquot of acetonitrile was added to each vial, the contents were vortex mixed for 15 seconds, and the vials were placed in an ultrasonic bath that was maintained below 35°C with cooling water. Extractions were conducted for 18-hours. After extraction, the vials were cooled to room temperature and a 10.0-mL aliquot of aqueous $CaCl_2$ (about 3 g/L) was added. The vials were vortex mixed and allowed to stand for at least 15 minutes while the solids settled. A portion of the supernatant was removed using a Pasteur pipette and filtered through a Millex SR membrane (0.5 μm). The extracts were diluted, based on the results from on-site analysis, using 1:1 acetonitrile/reagent grade water. Processed extracts were maintained at 4°C in the dark until analyzed.

Laboratory analysis for TNT and other neutral nitroaromatics and nitramines

Reversed phase HPLC analysis was conducted as described in EPA SW846 Method 8330 (EPA 1995a). Primary analysis was conducted on a Supelco LC-18 column eluted with 1:1 methanol/water at 1.5 mL/min. Absorbance was recorded at 254 nm on a Spectra Physics Model 8490 variable wavelength detector and peaks were recorded on a Hewlett Packard 3396 Digital Integrator operated in the peak height mode. Selected samples were subjected to second column confirmation on a Supelco LC-CN column using either 35:65 methanol/water or 23:12:65 acetonitrile/methanol/water, depending on the specific analytes detected in the primary analysis (Jenkins and Golden 1993).

Laboratory analysis for ammonium picrate

Picrate was analyzed by RP-HPLC on a 25- × 4.6-cm (5-μm) LC-18 (Supelco) column. The picrate was eluted using 1.5 mL/min. of 60:40 0.05 M KH_2PO_4 (pH 3.5)/methanol and detected at 365 nm. Aliquots of the acetone extracts prepared for the field method were diluted in eluent before analysis. A minimum dilution of 1 to 4, extract to eluent, had to be used to obtain an acceptable peak shape for picrate. The estimated detection limit at this dilution was 0.1 μg/g.

Chemicals and reagents

All standards for TNT and DNT were prepared from Standard Analytical Reference Materials (SARMS) obtained from the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland. Standards of TNT and DNT in acetone were prepared using OmniSolv grade acetone from EM Science. Standards of ammonium picrate for field and laboratory procedures were prepared from military grade material obtained from Hawthorne AAP.

All acetone used in the field for soil extraction and glassware cleaning was hardware grade obtained locally at each site. Acetonitrile and methanol used in the laboratory for soil extraction and preparation of HPLC eluents were Baker, EM or Mallinckrodt HPLC grade. Water used in the field for cleaning, and for addition to extracts to ensure that an adequate water content was present for the color-forming reaction, was distilled water obtained from local food stores. Laboratory

reagent grade water used for preparation of HPLC eluents was obtained from a Millipore Milli-Q Type 1 reagent grade water system.

Statistical analyses

To see if there were significant concentration differences among sample positions at each sampling location, analytical results from both methods of analysis were subjected to one variable of classification, completely randomized Analysis of Variance (ANOVA) using CoStat version 1.03 software (CoHost Software, Inc.). For sampling locations 1, 2, 3, 6 and 8, where concentration variations were extremely large, variances were not homogeneous (standard deviations were proportional to concentrations, i.e., relative standard deviations [RSDs] were constant). In these instances, the concentrations were log-transformed prior to doing ANOVA. When the ANOVA demonstrated that there were significant differences among sample positions for a given sampling location, least significant differences (LSDs) were computed to identify specific differences.

For sampling locations 4, 5, 7, 7R and 9, concentration ranges were less extreme and variances approached homogeneity. In these cases variances were fractionated to yield estimates of the standard deviations for subsampling plus analysis (S_A) and for the field sampling (S_S). Henceforth, all references to analytical error should be understood to include contributions from mixing and subsampling, extraction, dilution, measurement and concentration computations, while sampling error refers to spatial heterogeneity at the sampling location. CoStat software was also used to compute means and standard deviations of duplicates, overall means of the seven duplicates, plus means and standard deviations of composites. Analytical precision of the seven duplicates for each sampling location and each analysis method was expressed as the average of the seven RSDs.

One-way ANOVA was also used to compare on-site vs. laboratory analyses of composites. A paired *t*-test and correlation analysis was used to compare on-site vs. laboratory analysis for sets of seven samples for a given sampling location. These tests were done with Sigma Stat (Jandel Scientific). In addition to the linear least squares model with intercept, correlations were also computed for the linear zero-intercept model on untransformed data. When intercepts are close to zero, the correlation coefficient for the zero-intercept model approaches the value for the model with intercept. As the intercept moves away from zero, the correlation coefficient (r) for the zero-intercept model will decrease relative to the value for the model with intercept, thereby giving an indication of the significance of the intercept.

For all on-site vs. laboratory comparisons, except location 6 (picrate), the sum of TNB, TNT and 2,4-DNT laboratory concentration estimates were compared to on-site measurements. The Janowsky ions produced for TNT and TNB both have wavelengths of maximum absorption around 540 nm and their molar absorptivities at that wavelength are nearly equal. (There is a peak with higher absorptivity at lower wavelength but high humic background makes measurement at this peak wavelength prone to interference.) In any case, the on-site TNT method will record the sum of TNT and TNB (Jenkins and Walsh 1992). The absorptivity of the Janowsky ion from 2,4-DNT is not maximum at 540 nm but it is significant. However, DNT reacts slower with the EnSys reagent than TNT and TNB, and the rate of color formation varies with water concentration in the extract. Since the contribution of DNT to the field TNT estimates will depend on analysis conditions, corrections are impractical, so we decided to use the total of these three analytes to represent laboratory concentrations.

One further aspect of the statistical analysis requires mention. It has already been noted that total absolute variances for the seven sample positions in some sampling locations were non-Gaussian. Furthermore, they were computed without regard to the presence of variable amounts of spatial correlation between positions. We observed that the spatial correlations were irregular in some cases, in contrast to a regular gradient such as the directional concentration change that one might find on the edge of a plume of highly mobile compounds. For example, see the pattern of TNT concentrations observed for sampling location 1 (Fig. 2). This spatial correlation undoubtedly introduces some bias in the variance estimates, but we believe that the magnitude of this effect is insufficient to significantly affect the conclusions.

RESULTS AND DISCUSSION

Monite site

Sampling location 1

Results for the on-site analysis and laboratory analyses for sampling location 1 are presented in

Table 1a. TNT was the major analyte present, with concentrations varying from sample to sample over $2\frac{1}{2}$ orders of magnitude. Acetone extracts for field analysis were highly colored even before reaction with the EnSys reagent. Extracts for samples 2, 3 and 7 were yellow, extracts from sample 6 and the composites were orange, and extracts of samples 1, 4 and 5 were dark brick red. These colors are caused by the presence of phototransformation products of TNT in these surface soils. The intensity of color before reaction with the EnSys reagent correlated very well with the TNT concentrations obtained by the colorimetric on-site method. Reaction of the acetone extracts with the EnSys reagent resulted in the development of red solutions, indicative of the presence of TNT. Substantial dilutions (as high as 1:2000) were required to obtain absorbances in the linear range of 0.0–1.0 absorbance units at 540 nm after reaction with the EnSys reagent.

Duplicate field analyses for a given soil at sampling location 1 were in excellent agreement (mean RSD was 3.9%), pointing out that field sample homogenization was adequate. Duplicate laboratory analyses varied to a greater extent than field analyses (mean RSD was 11.1%), probably because of the smaller sample size used for lab analysis (2 vs. 20 g).

Since TNT concentrations varied by such a large amount from sample to sample, the data were not normally distributed and absolute variances were not homogeneous. Since relative standard deviations were similar, this indicates that standard deviations were proportional to concentration.

Table 1. Results from sampling location 1, Monite site.

a. Analytical results.

Sample	*TNT on-site analysis (μg/g)*	*Laboratory analysis (μg/g)*			
		TNB	*TNT*	*2,4-DNT*	*Total*
Discrete samples					
1a	42,700	107	37,500	70	37,700
1b	36,900	104	45,000	—	45,100
2a	492	30	390	—	420
2b	507	30	382	—	412
3a	174	12	113	20	145
3b	154	11	116	—	127
4a	28,000	97	44,400	—	44,500
4b	27,600	—	41,200	—	41,200
5a	24,400	—	33,000	—	33,000
5b	24,400	—	22,400	—	22,400
6a	1,240	42	1,170	—	1,210
6b	1,310	33	1,200	—	1,230
7a	327	23	305	—	328
7b	334	17	227	—	244
mean	13,500				16,300
Composites					
C1	12,900	—	11,800	—	11,800
C2	12,900	—	13,400	—	13,400
C3	13,300	—	13,600	—	13,600
C4	14,200	—	15,200	—	15,200
C5	13,000	—	13,900	—	13,900
C6	13,200	—	15,000	—	15,000
C7	12,500	—	16,100	—	16,100
mean	13,100				14,100
std. dev.	532				1,420

Table 1 (cont'd). Results from sampling location 1, Monite site.

b. Statistical analysis of TNT concentrations (μg/g) for discrete and composite samples.

Discrete samples

	On-site analysis		*Laboratory total*	
Sample	*Mean*	*Mean of logs*	*Mean*	*Mean of logs*
1	39,800	4.599**a**†	41,400	4.615**a**
2	500	2.699**e**	416	2.619**e**
3	164	2.214**g**	136	2.132**g**
4	27,800	4.444**b**	42,800	4.632**a**
5	24,400	4.387**c**	27,700	4.434**c**
6	1,280	3.105**d**	1,220	3.087**d**
7	331	2.519**f**	286	2.452**f**

† Numbers designated with the same letter are not significantly different at the 95% confidence level.

ANOVA for log on-site analyses

F ratio = 233***
Error MS = 0.0005547
Least sign. diff. = 0.056

ANOVA for log lab analyses

F ratio = 613***
Error MS = 0.00396
Least sign. diff. = 0.149

Linear correlation analysis for on-site analysis vs. lab analysis
*(*r *= correlation coefficient)*

	Slope	*Intercept*	r
untransformed, non-zero intercept	0.805	359.1	0.973
untransformed, zero intercept	0.815	0	0.973
log-transformed data	0.926	0.251	0.999

Results of paired t*-tests for on-site vs. lab results*

Means of seven discrete samples, t = 1.35 (NS)
Means of log values for seven discrete samples, t = 0.07 (NS)

Composite samples

	On-site analysis	*Laboratory total*
n	*7*	*7*
mean value	13,100	14,100
standard deviation	532	1,420
RSD	4.06%	10.1%

ANOVA comparing on-site and lab analyses

F ratio = 3.05 (NS at 95% level)

* Significant at the 95% level
** Significant at the 99% level
*** Significant at the 99.9% level
NS Not significant at the 95% level

Thus, to perform analysis of variance (ANOVA), we transformed data by taking the logarithm of individual values (Table 1b). This was done for both the field and laboratory results and an ANOVA was conducted on both sets of log-transformed data (Table 1b). For the on-site analyses, the *F* ratio was 233, indicting that a significant difference was detected among the seven discrete samples at greater than the 99.9% confidence level. Results of a least significant difference test (LSD) showed that all seven discrete samples were significantly different from each other at the 95% confidence level. Similar results were obtained when ANOVA was done on the laboratory results (Table 1b). An *F* ratio of 613 was found, which was significant at greater than the 99.9% level, and the least significant difference test indicated that all samples were statistically different from

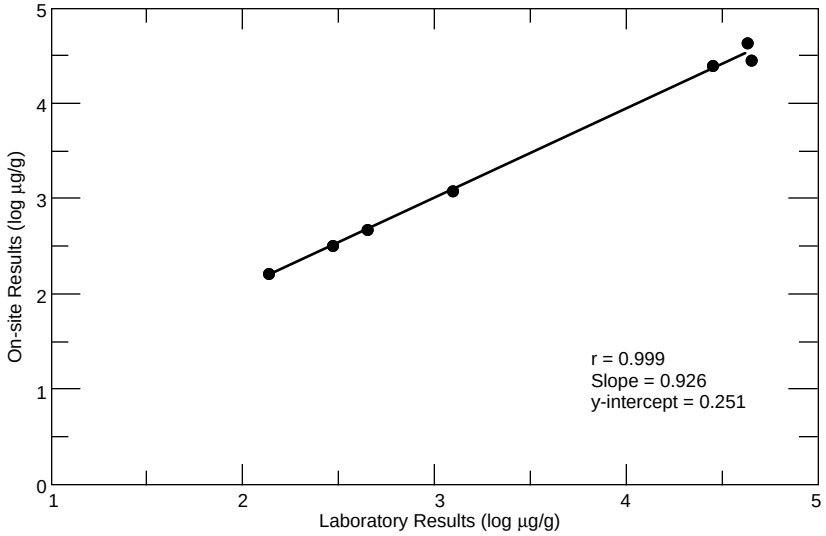


Figure 4. Log-transformed TNT concentrations from sampling location 1—linear model with intercept.

one another, except samples 1 and 4. Thus, for sampling location 1, very similar conclusions were reached regarding the nature of the analyte distribution using either the results of on-site analyses or results of laboratory analyses.

Because the mean concentrations and absolute analytical variances for various samples from site 1 differ so drastically, it is not possible to directly compare the uncertainties introduced by sampling with those from analysis by partitioning variances of untransformed data using normal distribution statistics. ANOVA of the log-transformed data indicates that even the log concentrations from various samples differ significantly from one another, using analytical error as the yardstick.

A simple way to compare sampling and analytical uncertainties is to compare the ratios of extreme mean concentrations obtained for the seven samples with those for duplicate analyses from the same location. For location 1, the ratio of highest mean concentration to lowest mean concentration was 243 for the field analyses and 304 for the laboratory analyses. The highest ratios for duplicates were 1.16 for the field analyses and 1.47 for the laboratory analyses. Thus, for this location, sampling error contributes many times more uncertainty than analytical error for either field or laboratory analysis.

Results for the field and laboratory analyses of these discrete samples were compared in two ways. Linear correlation analysis was conducted using the untransformed data with and without intercept, and for the log-transformed values with intercept (Table 1b). Correlation coefficients were 0.973, 0.973 and 0.999 for untransformed data with and without intercept and the log-transformed data respectively. The correlation coefficient for the zero intercept model is identical to that for the model with non-zero intercept, and we interpret this to mean that the intercept is not significantly different from zero and that the accuracy of the field method vs. the lab method can be estimated from the slope of the best fit linear least squares line (81.5%). The excellent correlation for the log-transformed data, as shown in Figure 4, demonstrates the equivalency of the results for the two methods over several orders of magnitude of concentration.

Paired *t*-tests were also conducted on the seven mean values and the log-transformed mean data for the two methods of analysis (Table 1b). The *t*-value for the untransformed data was 1.35 and that for the log-transformed data was 0.07, neither significant at the 95% confidence level. We must acknowledge that comparison of the untransformed results is not truly legitimate because the concentration distribution is non-Gaussian. Results of the paired *t*-tests agree with those from correlation analysis, i.e., the laboratory and on-site results compare very favorably.

Results of the analyses of the composite samples at sampling location 1 were also quite interesting. The mean and standard deviation of the seven on-site analyses for the composite was 13,100 ± 532 µg/g in comparison to the mean of the

seven discrete samples, which was 13,500 µg/g (Table 1b). Clearly, analysis of the composite provides a good estimate of the mean concentration for the area sampled. For the laboratory analyses, the mean and standard deviation of the seven composites was 14,100 ± 1420 µg/g, while the mean of the results for the seven discrete samples was 16,300 µg/g. These results do not agree as well as those for the on-site analyses, but they appear to be quite adequate when compared to the wide range of concentrations found for the discrete samples. ANOVA was conducted to compare the laboratory and on-site analysis results for the composite samples (Table 1b). The *F* ratio of 3.05 says that the results of the laboratory and on-site analyses for this sampling location were not significantly different at the 95% confidence level. This is true even with the good precision (RSDs of 4.1 and 10.1% for field and laboratory) obtained for the analyses of these composite samples. Thus, for this location, a good indication of the degree of contamination could be obtained using a combination of composite sampling and colorimetric on-site analysis.

Sampling location 2

Results for laboratory and on-site analyses of soils from sampling location 2 are presented in Table 2a. Soil samples from location 2 had an aroma of shoe polish, pointing to the presence of mononitrotoluenes, often present in conjunction with high concentrations of DNT. Acetone ex-

Table 2. Results from sampling location 2, Monite site.

a. Analytical results.

Sample	DNT on-site analysis (µg/g)	Laboratory analysis (µg/g)			
		TNB	TNT	2,4-DNT	Total
Discrete samples					
1a	31,700	—	2,370	113,000	115,000
1b	42,100	—	2,800	131,000	134,000
2a	8,290	—	1,900	5,820	7,720
2b	6,130	—	2,330	7,670	10,000
3a	29,300	—	5,260	47,000	52,300
3b	17,700	—	3,750	32,000	35,800
4a	24,400	—	4,700	29,500	34,200
4b	16,500	—	5,000	31,100	36,100
5a	9,610	—	334	10,600	10,900
5b	6,640	—	386	10,500	10,900
6a	14,500	—	383	16,700	17,100
6b	11,800	—	421	15,900	16,300
7a	3,070	—	481	3,450	3,930
7b	3,910	—	432	3,120	3,550
mean	16,100				34,900
Composites					
C1	27,100	—	1,840	28,900	30,700
C2	23,500	—	2,060	31,600	33,700
C3	28,500	—	2,210	35,100	37,300
C4	23,400	—	2,020	31,300	33,300
C5	19,300	—	2,140	32,000	34,100
C6	23,200	—	2,120	33,200	35,300
C7	21,500	—	1,650	28,900	30,600
mean	23,800				33,600
std. dev.	3,140				2,390

Table 2 (cont'd).

b. Statistical analysis of DNT concentrations (μg/g) for discrete and composite samples.

Discrete samples

	On-site analysis		*Laboratory total*	
Sample	*Mean*	*Mean of logs*	*Mean*	*Mean of logs*
1	36,950	4.563**a**†	125,000	5.094**a**
2	7,210	3.853**c**	8,860	3.944**d**
3	23,500	4.358**ab**	44,000	4.636**b**
4	20,450	4.302**ab**	35,200	4.546**b**
5	8,125	3.903**c**	10,900	4.038**d**
6	13,150	4.117**bc**	16,700	4.223**c**
7	3,490	3.540**d**	3,740	3.572**e**

† Numbers designated with the same letter are not significantly different at the 95% confidence level.

ANOVA for log on-site analyses

F ratio = 22.3***
Error MS = 0.01098
Least sign. diff. = 0.248

ANOVA for log lab analyses

F ratio = 153***
Error MS = 0.00333
Least sign. diff. = 0.136

Linear correlation analysis for on-site analysis vs. lab analysis
(r = *correlation coefficient)*

	Slope	*Intercept*	r
untransformed, non-zero intercept	0.262	6983	0.949
untransformed, zero intercept	0.350	0	0.817
log-transformed data	0.684	1.155	0.988

Results of paired t*-tests for on-site vs. lab results*

Means of seven discrete samples, t = 1.58 (NS)
Means of log values for seven discrete samples, t = 3.12*

Composite samples

	On-site analysis	*Laboratory total*
n	*7*	*7*
mean value	23,800	33,600
standard deviation	3,140	2,390
RSD	13.2%	7.1%

ANOVA comparing on-site and lab analyses
F ratio = 43.0***

* Significant at the 95% level
** Significant at the 99% level
*** Significant at the 99.9% level
NS Not significant at the 95% level

tracts for location 2 were yellowish and, unlike location 1, the intensity of the color did not correlate with the results of colorimetric on-site analysis. Addition of the EnSys reagent to extracts of soils from this sampling location caused the development of an intense blue-purple color, also indicative of the presence of DNT as the major contaminant. Concentrations of DNT were estimated using absorbance measurements at 570 nm as recommended by Jenkins and Walsh (1991). On-site analysis results showed that DNT concentrations in the soil varied by over an order of magnitude, ranging from about 3000 to 30,000 μg/g. Laboratory analyses showed the presence of TNT at concentrations ranging from approximately 300–5000 μg/g. These amounts were included in the totals for lab results.

Agreement of duplicates for field analyses at location 2 was poorer than at location 1, with a mean RSD of 23.0%. A mean RSD of 10.0% was

found for the duplicate laboratory analyses, a value very similar to that obtained for location 1. The poorer agreement for field duplicates may be in part attributable to incomplete field homogenization, but may also be ascribable to the on-site method for DNT not being as reproducible as it is for TNT (Jenkins and Walsh 1991). In fact, EnSys does not even market their reagent for on-site analysis of DNT.

As discussed for location 1, mean concentrations and analytical variances differed significantly for samples at location 2. Thus, data did not appear to be normally distributed and were log-transformed. ANOVA and LSD tests were conducted with the log-transformed data (Table 2b). Even with the large analytical error for the field results, a significant difference was found among samples using ANOVA (F ratio = 22.3) at greater than the 99.9% confidence level, and many discrete samples at location 2 were significantly different from one another according to LSD analysis. A significant difference among samples was also detected for the laboratory analyses (F ratio = 153) at greater than the 99.9% level, with more differences detected among individuals using LSD analysis. If we use the same simple approach for comparing the uncertainties introduced by sampling error and analytical error that we used for location 1, ratios of highest to lowest means for individual samples were 10.6 for on-site analyses and 33.4 for lab analyses. The maximum differences in duplicates ratios were 1.48 and 1.46 for field and lab analyses respectively. Thus, here again, sampling error dominates over analytical error with both methods.

To compare the field and laboratory results, we again used both correlation analysis and a paired t-test (Table 2b). Correlation analysis of the log-transformed results revealed a strong relationship between the two methods (r = 0.988) but a slope of 0.684 was found for these log values, indicating a significant low bias for the field DNT results (Fig. 5). The paired t-test confirmed this bias with a value of 3.12, which is significant at the 95% level. Part of this bias is accounted for by the laboratory total including TNT that is not fully accounted for in the on-site analysis when using measurements at 570 nm.

The results from the analysis of the composite samples further confirmed the analytical bias detected for the discrete samples. A ratio of the mean concentration for the on-site results divided by the lab results was 0.71. ANOVA was conducted to compare the on-site and lab results and an F ratio of 43.0 was found, which was significant at the 99.9% level (Table 2b).

The mean and standard deviation of the seven composites analyzed by the field method were 23,800 ± 3140 µg/g, which compared to a mean of the seven discrete samples of 16,100. For the laboratory results, the mean and standard deviation for the seven composites were 33,600 ± 2390 µg/g vs. a mean of the seven discrete samples of 34,800 µg/g. Compositing again appears to provide a reliable estimate of the mean analyte concentration for the laboratory results. We initially thought

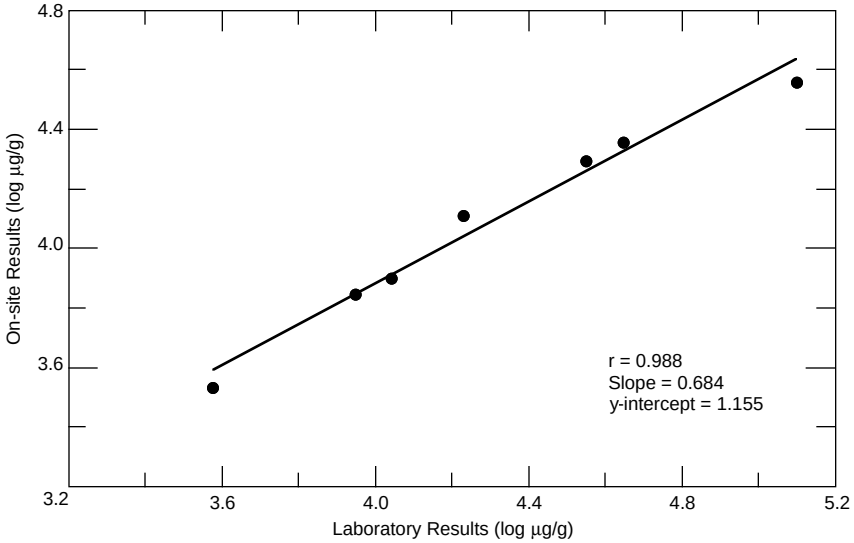


Figure 5. Log-transformed DNT concentrations from sampling location 2—linear model with intercept.

that the difference between means for the discrete samples and composites observed for the field results may be attributable to our using only roughly equal weights of individual samples when preparing the composites here. However, this should also have affected the laboratory results and clearly this was not the case.

Sampling location 3

On-site analytical results for sampling location 3 are presented in Table 3a. At this location six of the seven samples had very low levels of TNT (2–5 µg/g), but the seventh location had a much higher TNT concentration (> 80 µg/g). Because TNT concentrations were low, the acetone extracts used for on-site analysis were run without dilution. Extracts had a straw-yellow color that resulted in a significant background absorbance at 540 nm. Reaction with the EnSys reagent for these samples resulted in a pink or orangish solution, denoting the presence of low levels of TNT. Only the extract from sample 7 needed to be diluted to maintain the absorbance in the linear range after reaction with the EnSys reagent.

Duplicate analyses for samples at this location appeared to be quite acceptable, with mean RSDs of 16.7% for the on-site analyses, meaning that field homogenization was adequate. Laboratory analyses for samples from this location were consistently lower than corresponding field analyses. This was also true for the composite samples and it shows a positive bias for the field TNT method for these soils.

ANOVA and LSD tests were conducted for field and lab data both with and without logarithmic transformation (Table 3b). We obtained *F* ratios of 64.6 for on-site and 911 for the lab that were significant at greater than the 99.9% confidence level,

Table 3. Results from sampling location 3, Monite site.

a. Analytical results.

Sample	*TNT on-site analysis (µg/g)*	*Laboratory analysis (µg/g)*			
		TNB	*TNT*	*2,4-DNT*	*Total*
Discrete samples					
1a	4.6	0.03	4.1	1.0	5.1
1b	3.6	0.02	3.3	1.0	4.3
2a	1.7	—	0.2	1.5	1.7
2b	2.9	—	0.3	1.5	1.8
3a	3.1	0.12	0.8	1.1	2.0
3b	3.6	0.14	0.7	1.0	1.8
4a	4.1	—	0.6	0.8	1.4
4b	4.4	0.03	0.6	0.8	1.4
5a	5.3	—	0.4	0.5	0.9
5b	5.1	—	0.3	0.5	0.8
6a	4.6	—	0.1	0.6	0.7
6b	4.4	—	0.3	0.5	0.8
7a	149	0.04	75.4	0.7	76.1
7b	81.8	0.04	80.2	0.6	80.8
mean	19.8				12.9
Composites					
C1	10.9	—	3.6	1.1	4.7
C2	13.0	—	2.4	1.1	**3.5**
C3	**11**.2	0.04	2.5	1.0	3.5
C4	13.3	—	2.6	1.2	3.8
C5	14.2	—	3.0	1.1	4.1
C6	12.4	—	4.1	1.2	5.3
C7	13.5	—	3.1	1.1	4.2
mean	12.6				4.2
std. dev.	1.22				0.66

Table 3 (cont'd). Results from sampling location 3, Monite site.

b. Statistical analysis of TNT concentrations (μg/g) for discrete and composite samples.

Discrete samples

	On-site analysis		*Laboratory total*	
Sample	*Mean*	*Mean of logs*	*Mean*	*Mean of logs*
1	4.1**b**†	0.610**b**	4.7**b**	0.670**b**
2	2.3**b**	0.346**b**	1.8**b**	0.243**c**
3	3.4**b**	0.524**b**	1.9**b**	0.278**c**
4	4.3**b**	0.628**b**	1.4**b**	0.146**d**
5	5.2**b**	0.716**b**	0.9**b**	–0.072**e**
6	4.5**b**	0.653**b**	0.8**b**	–0.126**e**
7	115**a**	2.043**a**	78.5**a**	1.894**a**

†Numbers designated with the same letter are not significantly different at the 95% confidence level.

ANOVA for log on-site analyses

F ratio = 64.6***
Error MS = 0.00991
Least sign. diff. = 0.235

ANOVA for log lab analyses

F ratio = 911***
Error MS = 0.00106
Least sign. diff. = 0.077

Linear correlation analysis for on-site analysis vs. lab analysis
(r = *correlation coefficient)*

	Slope	*Intercept*	r
untransformed, non-zero intercept	1.447	1.23	0.999
untransformed, zero intercept	1.464	0	0.998
log-transformed data	0.715	0.479	0.879

Results of paired t*-tests for on-site vs. lab results*

Means of seven discrete samples, t = 1.40 (NS)
Means of log values for seven discrete samples, t = 2.87*

Composite samples

	On-site analysis	*Laboratory total*
n	7	7
mean value	12.6	4.16
standard deviation	1.22	0.66
RSD	9.66%	15.9%

ANOVA comparing on-site and lab analyses
F ratio = 264***

* Significant at the 95% level
** Significant at the 99% level
*** Significant at the 99.9% level
NS Not significant at the 95% level

indicating differences among samples. LSD tests confirmed the difference between sample 7 and the other six. Analysis of the log-transformed lab data showed some differences among other samples as well.

Comparison of the on-site and lab results using both correlation analysis and a paired *t*-test yielded somewhat contradictory results owing to the very large effect of one extremely high concentration sample (Table 3b). The positive bias of the field method for soils at this location was unambiguously confirmed by the composite analyses (mean 12.6 μg/g for field and 4.16 μg/g for lab). This bias may be caused by the presence of unspecified environmental transformation products of TNT, which were not determined using the RP-HPLC conditions specified in Method 8330, but which react with the EnSys reagent to form a colored Janowsky complex.

The results for this sampling location show the value of both compositing and on-site analysis for site characterization at explosives-contami-

nated areas. If this location was characterized with a single grab sample, the hot spot at sample 7 would most likely be missed. The availability of an inexpensive on-site test would increase the likelihood that investigators would detect this hot spot and delineate its dimensions, thereby allowing its cleanup with minimal inclusion of soils with concentrations below action levels.

Hawthorne AAP

Sampling location 4

Analytical results for sampling location 4 at Hawthorne AAP are presented in Table 4a. Acetone extracts at this location turned reddish upon reaction with the EnSys reagent, indicating that TNT was likely to be the major contaminant present. Laboratory analysis confirmed TNT being present at concentrations ranging from less than 100 to over 6000 µg/g.

Precision estimates from duplicate on-site analyses for sampling location 4 were approximately equivalent to corresponding laboratory analyses (mean RSD for field was 12.5 vs. 13.5% for lab), suggesting that on-site methods of homogenization were adequate for this soil.

Mean concentrations for individual samples at location 4 differed substantially, but much less so than those obtained for locations 1–3. For this reason, ANOVA was first conducted with untransformed data. The *F* ratios obtained were 166 and 133 for field and lab data, respectively (Table 4b), which were statistically significant at greater than the 99.9% level. Although log-transformed data were also analyzed and ANOVA gave similar results, the variances for untransformed

Table 4. Results from sampling location 4, Hawthorne AAP site.

a. Analytical results.

	TNT on-site analysis	*Laboratory analysis (µg/g)*			
Sample	*(µg/g)*	*TNB*	*TNT*	*2,4-DNT*	*Total*
Discrete samples					
1a	6180	68.2	6580	13.8	6660
1b	5570	63.3	5810	8.2	5880
2a	2900	18.8	3490	—	3510
2b	3320	48.2	3980	—	4030
3a	1270	50.8	1340	—	1390
3b	1060	47.6	1050	—	1100
4a	578	92.2	492	21.6	606
4b	549	79.1	472	15.7	567
5a	63.1	18.3	126	—	144
5b	107	—	72.5	—	72.5
6a	1740	44.0	2010	—	2050
6b	1920	50.3	1910	11.9	1970
7a	1090	50.3	1140	—	1190
7b	1270	36.4	1070	—	1110
mean	1970				2160
Composites					
C1	1680	35.7	1510	7.1	1550
C2	1810	42.8	1660	6.9	1710
C3	1480	40.8	2170	—	2210
C4	1930	52.1	2300	—	2350
C5	2010	62.1	2180	25.9	2270
C6	1690	44.6	1890	—	1930
C7	1680	—	1930	21.6	1950
mean	1760				2000
std. dev.	178				298

Table 4 (cont'd). Results from sampling location 4, Hawthorne AAP site.

b. Statistical analysis of TNT concentrations (μg/g) for discrete and composite samples.

Discrete samples

	On-site analysis		*Laboratory total*	
Sample	*Mean*	*Mean of logs*	*Mean*	*Mean of logs*
1	5880**a**†	3.769**a**	6270**a**	3.797**a**
2	3110**b**	3.492**b**	3770**b**	3.575**b**
3	1170**d**	3.065**c**	1240**d**	3.092**c**
4	563**e**	2.727**d**	587**de**	2.768**d**
5	85.1**e**	1.915**e**	108**e**	2.009**e**
6	1830**c**	3.262**c**	2010**c**	3.304**c**
7	1180**d**	3.071**c**	1150**d**	3.060**c**

† Numbers designated with the same letter are not significantly different at the 95% confidence level.

ANOVA for on-site and lab analyses

	Untransformed	
	On-site	*Lab*
F ratios	166***	133***
Error MS	47,163	70,287
Least sign. diff.	514	627
Analysis s	217	265
Sampling s	1,971	2,154
(s = standard deviation)		

Linear correlation analysis for on-site analysis vs. lab analysis
(r = *correlation coefficient)*

	Slope	*Intercept*	r
untransformed, non-zero intercept	0.912	–1.846	0.997
untransformed, zero intercept	0.911	0	0.997
log-transformed data	1.020	–0.110	0.999

Results of paired t*-tests for on-site vs. lab results*

Means of seven discrete samples, t = 2.07 (NS)

Composite samples

	On-site analysis	*Laboratory total*
n	7	7
mean value	1760	2000
standard deviation	178	298
RSD	10.1%	14.9%

ANOVA comparing on-site and lab analyses
F ratio = 3.44 (NS)

* Significant at the 95% level
** Significant at the 99% level
*** Significant at the 99.9% level
NS Not significant at the 95% level

results were sufficiently homogeneous to make transformation unnecessary. LSD tests for both on-site and lab results showed that six of the seven samples were significantly different from one another. Partitioning the variances into analytical error and sampling error gave analysis standard deviations of 217 and 265 for the field and lab methods, respectively (Table 4b), and estimates for the sampling standard deviation of 1971 and 2154 from the field and lab data. Thus, even for this sampling location, where the analyte distribution was the least heterogeneous of the four locations discussed thus far, sampling error was eight to nine times greater than analytical error, regardless of whether analysis was conducted on-site or in the lab.

The results from on-site and lab analysis were linearly correlated, and a slope of the best fit regression line of 0.912 was obtained with an r of 0.997 (Table 4b). The relationship with zero intercept was slope = 0.911 and r = 0.997, indicating that the accuracy of the field test vs. the lab test was 91.1%. A paired t-test of the on-site and lab results said that they were not significantly different (Table 4b). ANOVA comparing on-site and lab methods for the composite analyses produced an F ratio of 3.44, which is not significant at the 95% level. Overall, the on-site TNT method provided very reliable results for sampling location 4.

Analysis of composite samples provided mean and standard deviation concentrations of 1760±178 and 2000±298 μg/g for on-site and lab methods respectively. Mean values from the seven discrete samples were 1970 and 2160 μg/g respectively. Here, again, analysis of composites provides acceptably reliable results with both methods. Overall, the results for sampling location 4 confirm the value of the on-site test in providing rapid, reliable results for areas with concentrations varying over orders of magnitude.

Sampling location 5

Analytical results for sampling location 5 are presented in Table 5a. Reaction of acetone extracts with the EnSys reagent produced pink to reddish solutions, again pointing to TNT as the likely major contaminant. Laboratory analysis confirmed that TNT was the contaminant present at the highest concentration for all except sample 5. In sample 5, the TNT con-

centration was very low (less than 2 µg/g) and TNB was the compound present at the highest concentration (about 10 µg/g). TNB reacts to the EnSys reagent identically as does TNT with similar absorptivity and is not distinguishable from TNT using on-site colorimetric analysis. In addition to TNB, 2,4-DNT was also present in these samples at significant concentrations, but considerably lower than TNT, and it also reacts with the EnSys reagent and contributes to the absorbance at 540 nm. The TNT concentrations estimated from the screening test for this location (about 12 to almost 400 µg/g) agree reasonably well with the concentrations of total nitroaromatics (sum of TNT, TNB and 2,4-DNT) obtained from laboratory analysis.

Duplicate on-site and laboratory analyses for soils from location 5 agree very well with mean RSDs of 3.3 and 4.9%, respectively, indicating that field homogenization was excellent and the precision of the on-site test is equivalent to that of the lab method under these circumstances.

ANOVA was conducted on the data from discrete sample analysis, both with and without log-transformation, but as with location 4, transformation was unnecessary (Table 5b). The *F* ratios for field and lab results were 1061 and 282, respectively, meaning that discrete samples from location 5 were significantly different from one another at greater than the 99.9% confidence level. LSD tests showed that all seven samples were significantly different from one another. Partitioning the variances into analytical and sampling components gave estimates for analytical standard deviation of 5.3 and 11.0 µg/g for the on-site and lab methods, respectively, while estimates

Table 5. Results from sampling location 5, Hawthorne AAP site.

a. Analytical results.

	TNT on-site analysis	*Laboratory analysis (µg/g)*			
Sample	*(µg/g)*	*TNB*	*TNT*	*2,4-DNT*	*Total*
Discrete samples					
1a	127	33.5	63.8	27.7	125
1b	125	32.8	48.2	27.3	108
2a	116	52.8	214	2.6	269
2b	103	52.8	210	10.6	273
3a	379	57.0	286	14.7	358
3b	366	61.7	312	17.7	391
4a	59.1	14.6	37.6	1.9	54.1
4b	56.0	15.5	34.0	1.8	51.3
5a	12.4	10.0	1.9	1.0	12.9
5b	13.3	10.7	1.7	—	12.4
6a	170	17.2	222	12.2	251
6b	173	16.8	207	11.7	236
7a	240	40.4	53.4	15.4	109
7b	245	37.6	48.4	14.4	100
mean	156				168
Composites					
C1	129	32.1	145	11.4	189
C2	137	32.1	144	9.2	185
C3	116	32.4	150	11.2	194
C4	138	34.1	163	10.8	208
C5	139	34.5	149	10.9	194
C6	147	33.7	142	11.5	187
C7	170	33.5	152	11.8	197
mean	139				193
std. dev.	16.6				7.72

Table 5 (cont'd). Results from sampling location 5, Hawthorne AAP site.

b. Statistical analysis of TNT concentrations (μg/g) for discrete and composite.

Discrete samples

	On-site analysis		*Laboratory total*	
Sample	*Mean*	*Mean of logs*	*Mean*	*Mean of logs*
1	126**d**†	2.101**d**	117**d**	2.065**d**
2	110**e**	2.039**e**	271**b**	2.433**b**
3	373**a**	2.571**a**	375**a**	2.573**a**
4	57.6**f**	1.760**f**	52.7**e**	1.722**e**
5	12.9**g**	1.109**g**	12.7**f**	1.102**f**
6	172**c**	2.234**c**	244**c**	2.387**c**
7	243**b**	2.385**b**	105**d**	2.019**d**

† Numbers designated with the same letter are not significantly different at the 95% confidence level.

ANOVA for on-site and lab analyses

	Untransformed	
	On-site	*Lab*
F ratios	1061***	282***
Error MS	27.601	122.00
Least sign. diff.	12.4	26.1
Analysis s	5.3	11.0
Sampling s	121	131
(s = standard deviation)		

Linear correlation analysis for on-site analysis vs. lab analysis
(r = *correlation coefficient)*

	Slope	*Intercept*	r
untransformed, non-zero intercept	0.688	40.63	0.745
untransformed, zero intercept	0.847	0	0.714
log-transformed data	0.848	0.296	0.894

Results of paired t*-tests for on-site vs. lab results*

Means of seven discrete samples, $t = 0.35$ (NS)

Composite samples

	On-site analysis	*Laboratory total*
n	7	7
mean value	139	193
standard deviation	16.6	7.72
RSD	12.0%	4.0%

ANOVA comparing on-site and lab analyses
F ratio = 60.8***

* Significant at the 95% level
** Significant at the 99% level
*** Significant at the 99.9% level
NS Not significant at the 95% level

for sampling standard deviations were 121 and 131 μg/g. Thus, here again, sampling error overwhelms analytical error by over an order of magnitude.

Linear correlation analyses for the field and lab results were conducted in the same manner as described for samples from other sampling locations (Table 5b). The best fit linear regression is shown in Figure 6. The slope for the best fit line with intercept was 0.688, which was considerably lower than the slope for the best fit line with zero intercept (slope = 0.847). Nevertheless, a paired *t*-test of field vs. lab results indicated that results for the two methods were not significantly different at the 95% confidence level. As can be seen in Figure 6, the two highly divergent samples from the fitted model are on opposite sides, which is to say that the large random error tends to mask the systematic difference. However, ANOVA comparing field and lab data for the composite samples yielded an *F* ratio of 60.8, which was significant at the 99.9% confidence level. The ratio of field (139 μg/g) to laboratory (193 μg/g) results is 0.72, which is in excellent agreement with the slope (0.688) of the linear least squares model (Fig. 6) and confirms the presence of bias. Overall, the relationship between the field and lab methods for location 5 is poorer than those found for other sampling locations. Thus, while the accuracy of the field method for soils at location 5 is not optimal compared with what we have described previously, it is still acceptable in light of the large degree of concentration heterogeneity.

Sampling location 6

Acetone extracts for soils at sampling location 6 were bright fluorescent-yellow, an indication that the major contaminant was probably ammonium picrate. Laboratory results confirmed that ammonium picrate was the contaminant present at highest concentration, with TNT and other nitroaromatics present at lower concentrations (Table 6a). Reaction of these acetone extracts with the EnSys TNT reagent produced very erratic results; the test was probably not functioning properly in the presence of ammonium picrate. Subsequent laboratory experiments confirmed that ammonium picrate interferes with the on-site TNT analysis test.

Table 6. Results from sampling location 6, Hawthorne AAP site.

a. Analytical results.

Sample	Picrate on-site analysis (µg/g)	Laboratory analysis (µg/g) DNB	TNT	2,4-DNT	Picrate
Discrete samples					
1a	23	0.44	0.67	2.28	7.5
1b	33	0.48	0.66	1.73	4.0
2a	5.6	0.22	0.39	0.29	<0.1
2b	8.4	0.20	0.42	0.17	<0.1
3a	6.2	1.07	0.38	1.54	0.7
3b	5.9	1.05	0.37	1.52	0.7
4a	82	2.09	0.16	0.24	80.7
4b	79	1.66	0.14	0.39	93.4
5a	4000	8.92	0.47	1.49	4260
5b	4400	9.46	0.48	1.49	4340
6a	1700	3.05	0.49	1.49	1700
6b	1800	2.90	0.11	0.28	2110
7a	12	0.56	0.41	1.40	1.4
7b	14	0.61	0.41	1.45	1.7
mean	869				899
Composites					
C1	930	2.10	0.38	0.36	925
C2	940	2.15	0.48	0.48	981
C3	1000	2.37	0.38	0.41	1050
C4	1000	2.32	0.42	0.42	1100
C5	1000	2.52	0.38	0.43	1140
C6	980	2.13	0.38	0.41	980
C7	940	2.11	0.41	0.43	888
mean	970				1010
std. dev.	32.1				91.7

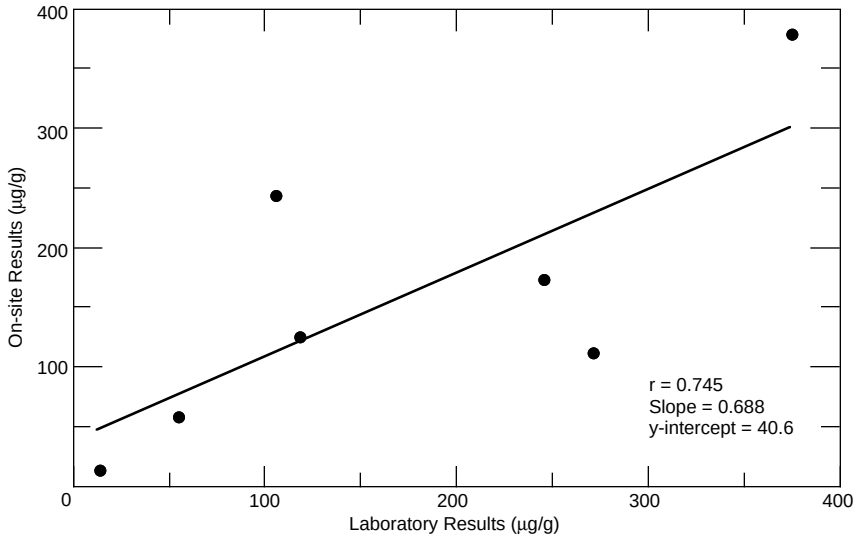


Figure 6. Untransformed TNT concentrations from sampling location 5—linear model with intercept.

Table 6 (cont'd). Results from sampling location 6, Hawthorne AAP site.

b. Statistical analysis of ammonium picrate concentrations (μg/g) for discrete and composite samples.

Discrete samples

	On-site analysis		*Laboratory total*	
Sample	*Mean*	*Mean of logs*	*Mean*	*Mean of logs*
1	28	1.447**d**†	5.8	0.763**d**
2	7.0	0.845**f**	<0.1	< –0.1**f**
3	6.1	0.785**f**	0.7	–0.155**f**
4	81	1.909**c**	87.1	1.940**c**
5	4200	3.623**a**	4300	3.634**a**
6	1750	3.243**b**	1900	3.279**b**
7	13	1.114**e**	1.6	0.204**e**

† Numbers designated with the same letter are not significantly different at the 95% confidence level.

ANOVA for log on-site analyses

F ratio = 589***
Error MS = 0.00451
Least sign. diff. = 0.159

ANOVA for log lab analyses

F ratio = 923***
Error MS = 0.00675
Least sign. diff. = 0.194

*Linear correlation analysis for on-site analysis vs. lab analysis (*r *= correlation coefficient)*

	Slope	*Intercept*	r
untransformed, non-zero intercept	0.968	–1.74	0.999
untransformed, zero intercept	0.967	0	0.999
log-transformed data	0.634	1.07	0.971

Results of paired t*-tests for on-site vs. lab results*

Means of seven discrete samples, t = 1.19(NS)
Means of log values for seven discrete samples, t = 2.34(NS)

Composite samples

	On-site analysis	*Laboratory total*
n	7	7
mean value	970	1010
standard deviation	32.1	91.7
RSD	3.31%	9.10%

ANOVA comparing on-site and lab analyses

F ratio = 1.14(NS)

* Significant at the 95% level
** Significant at the 99% level
*** Significant at the 99.9% level
NS Not significant at the 95% level

We were not equipped to conduct ammonium picrate screening in the field. However, an on-site method has been developed for ammonium picrate (Thorne and Jenkins 1995) and samples were extracted in the laboratory with acetone and the extracts subjected to the screening procedure as described in the *Experimental* section. Results of the field analysis procedure and the lab (HPLC) method, also conducted with these same acetone extracts, were consistent and demonstrated that the ammonium picrate concentrations varied from below detection limits to over 4000 μg/g for soils at sampling location 6 (Table 6a).

We found, using the on-site method, that duplicate analyses on samples homogenized in the field had a mean RSD of 11.6%, and, using the HPLC method, a mean RSD of 11.9%. Unlike all other comparisons, aliquots of the same extract were used in these tests. Therefore, the two procedures appear to have approximately equal precision. Field homogenization was clearly adequate for site characterization. ANOVA, using log-trans-

formed data from both the screening and HPLC determinations for the discrete samples, indicated that samples were significantly different at greater than the 99.9% confidence level. LSD tests showed that the discrete samples were nearly all significantly different from one another (Table 6b).

Means and standard deviations from composite analyses were 970 ± 32 and 1010 ± 91 µg/g for the screening and HPLC methods, respectively, which were not significantly different at the 95% level. The mean values from the seven discrete analyses were 869 and 901 µg/g for the screening and HPLC methods respectively.

Correlation of screening results with those from HPLC resulted in an *r* of 0.999 and a slope of 0.968 using a model with an intercept and the untransformed data (Table 6b). The model with zero intercept likewise gave a slope of 0.967 and an *r* value of 0.999, indicating that the intercept in the above model is not significantly different from zero. Nevertheless, at very low levels (<10 µg/g), there does appear to be a small positive bias for the screening method and this is reflected by the lower slope and correlation coefficient for the log-transformed model. At present we have not been able to identify the source of this bias. This bias was not detected using a paired *t*-test for the results from the seven discrete samples, which meant that results from the two methods were not significantly different at the 95% confidence level. Similarly, there was no significant bias in the means of the two methods applied to the composite samples where the concentrations were about 1000 µg/g.

Clearly, composite sampling and screening analysis provides an inexpensive, precise approach for estimating site contamination levels for ammonium picrate at this sampling location.

Volunteer AAP

Sampling locations 7 and 7R

Analytical results for sampling location 7, and a duplicate set of samples from location 7, labeled 7R, are presented in Tables 7a and 7c respectively. Location 7R was offset from location 7 by 15 cm, so like-numbered samples from location 7 and 7R are all located 15 cm apart. Acetone extracts for these soils were dark brick-red, implying that analyte concentrations were probably quite high. When extracts were diluted (4.0 µL to 20 mL) and reacted with EnSys reagent, a reddish color resulted, indicating that TNT was probably the major analyte present; this was later confirmed by laboratory analysis. Concentrations of TNT ranged from about 55,000 to 112,000 µg/g for location 7 and from about 40,000 to 119,000 µg/g for location 7R.

Samples from both locations 7 and 7R contained a high percentage of stones compared with samples from any other location. In the field, 15–59% of the soil weight was removed during homogenization for location 7 and 20–40% was excluded for location 7R. RSDs for field analyses were 13.3 and 4.9% for 7 and 7R, respectively, indicating that the resulting material was fairly homogeneous.

When these samples were further processed in the laboratory, a large percentage of the remaining material proved to be smaller stones, which we removed before laboratory analysis. The material excluded in the laboratory ranged from 51–64% for location 7 and 47–67% for location 7R. This was in addition to the material already excluded during field homogenization. Samples of the segregated stones were extracted and analyzed in the same manner as the soil and the results for the stones segregated from sample 4 for both locations 7 and 7R are presented in Table 7e. TNT concentrations obtained for the stones ranged from 6025 to 8150 µg/g, while the corresponding soil for these samples had TNT concentrations over 100,000 µg/g. Because the small stones had much lower concentrations of TNT than the soil, their exclusion from the material originally analyzed in the field using the colorimetric method, prior to laboratory analysis, is the major factor accounting for the higher concentrations observed in the laboratory analyses.

A problem was encountered in the field that affects the screening results presented for sample location 7 (but not 7R). The automatic pipette used to dispense the proper volume of extracting solvent malfunctioned at location 7 and the problem was not discovered until the on-site analyses had been completed. This problem resulted in varying amounts of acetone being used for extraction from sample to sample rather than the 100 mL specified. Probably the differences were not large, but there is additional uncertainty in the results because of this problem. The mean RSD for the field analyses for location 7R was 4.9%, compared to 13.3% for location 7. Laboratory results were unaffected by this problem and nearly identical mean RSDs were found for locations 7 and 7R (6.0 and 5.1% respectively).

ANOVA was conducted on the mean concentrations from the seven samples for both loca-

Table 7. Results from sampling location 7, Volunteer AAP site.

a. Analytical results.

Sample	TNT on-site analysis (µg/g)	Laboratory analysis (µg/g) TNB	TNT	2,4-DNT	Total
Discrete samples					
1a	101,000	—	114,000	—	114,000
1b	129,000	—	109,000	—	109,000
2a	28,600	—	55,700	—	55,700
2b	27,300	—	54,700	—	54,700
3a	53,600	—	74,300	—	74,300
3b	49,700	—	71,000	—	71,000
4a	90,100	—	106,000	—	106,000
4b	130,000	—	102,000	—	102,000
5a	90,100	—	101,000	—	101,000
5b	95,700	—	101,000	—	101,000
6a	104,000	—	101,000	—	101,000
6b	65,300	—	101,000	—	101,000
7a	116,000	—	65,200	—	65,200
7b	108,000	—	93,000	—	93,000
mean	84,900				89,300
Composites					
C1	56,400	—	105,000	—	105,000
C2	58,600	—	95,700	—	95,700
C3	54,300	—	126,000	—	126,000
C4	60,600	—	105,000	—	105,000
C5	54,600	—	104,000	—	104,000
C6	59,700	—	105,000	—	105,000
C7	54,900	—	108,000	—	108,000
mean	57,000				107,000
std. dev.	2,600				9,230

tions 7 and 7R (Tables 7b and 7d). Since concentrations differed by only a factor of 5 for individual samples, ANOVA was conducted on untransformed data. *F* ratios for field analyses were 7.8 and 47.8 for locations 7 and 7R, which were significant at the 99% level and greater than the 99.9% level respectively. Corresponding *F* ratios from the lab results were 14.3 and 39.0, significant at 99% and greater than the 99.9% levels. These ratios show that significant differences existed among individual samples for both 7 and 7R. Samples 1, 4, 5 and 6 were not significantly different from each other using the lab results for both 7 and 7R according to LSD tests. Likewise, samples 3 and 7 were not significantly different from each other, while sample 2 was significantly different from the other six samples for both 7 and 7R. The fact that these two sets of independent results give an identical picture of the analyte distribution on the site gives us added confidence that the results are not random, but are depicting an accurate representation of concentration distributions.

Linear correlation analysis was conducted on the results from lab and field analyses for 7 and 7R (Tables 7b and 7d); however, the introduction of bias by excluding stones prior to lab analysis makes these results only of marginal interest. In fact, paired *t*-tests for field vs. lab data from the two locations give contradictory conclusions, but the composite samples from both locations clearly demonstrate the expected bias. Thus, the results for this location do not offer a valid comparison of the accuracy of the field method and the lab method. Nevertheless, the field method and the lab analyses provide very similar pictures of analyte distributions.

Table 7 (cont'd). Results from sampling location 7, Volunteer AAP site.

b. Statistical analysis of TNT concentrations (μg/g) for discrete and composite samples.

Discrete samples

	On-site analysis		*Laboratory total*	
Sample	*Mean*	*Mean of logs*	*Mean*	*Mean of logs*
1	115,000**a**†	5.058**a**	112,000**a**	5.047**a**
2	28,000**b**	4.447**c**	55,200**d**	4.742**d**
3	51,700**ab**	4.713**b**	72,700**cd**	4.861**c**
4	110,000**a**	5.034**a**	104,000**ab**	5.017**ab**
5	92,900**a**	4.968**a**	101,000**ab**	5.004**ab**
6	84,800**a**	4.917**a**	101,000**ab**	5.004**ab**
7	112,000**a**	5.048**a**	79,100**bc**	4.891**bc**

† Numbers designated with the same letter are not significantly different at the 95% confidence level.

ANOVA for on-site and lab analyses

	Untransformed	
	On-site	*Lab*
F ratios	7.80**	14.3**
Error MS	285,585,544	58,980,714
Least sign. diff.	39,960	18,160
Analysis s	16,900	7,680
Sampling s	31,200	19,800
(s = standard deviation)		

Linear correlation analysis for on-site analysis vs. lab analysis
(r = *correlation coefficient)*

	Slope	*Intercept*	*r*
untransformed, non-zero intercept	1.319	–32,833	0.815
untransformed, zero intercept	0.967	0	0.784

Results of paired t*-tests for on-site vs. lab results*

Means of seven discrete samples, $t = 0.56$ (NS)

Composite samples

	On-site analysis	*Laboratory total*
n	7	7
mean value	57,000	107000
standard deviation	2600	9230
RSD	4.56%	8.63%

ANOVA comparing on-site and lab analyses

F ratio = 190***

* Significant at the 95% level
** Significant at the 99% level
*** Significant at the 99.9% level
NS Not significant at the 95% level

The results from analysis of composite samples from locations 7 and 7R are particularly interesting (Tables 7b and 7d). Since the two sampling locations were only 15 cm apart, either set of samples could be used to characterize the site. If composite sampling is a useful approach, results from analysis of the two composites should produce similar results. In fact, nearly identical estimates of concentration were obtained by both the laboratory and on-site analyses: 57,000 μg/g vs. 55,200 μg/g for the field and 107,000 μg/g for both from the lab.

Table 7 (cont'd). Results from sampling location 7, Volunteer AAP site.

c. Analytical results for sampling location 7R.

Sample	TNT on-site analysis (µg/g)	Laboratory analysis (µg/g) TNB	TNT	2,4-DNT	Total
Discrete samples					
1a	81,200	—	98,000	—	98,000
1b	82,800	—	119,000	—	119,000
2a	21,600	—	42,600	—	42,600
2b	21,900	—	37,900	—	37,900
3a	36,600	—	76,000	—	76,000
3b	40,700	—	67,200	—	67,200
4a	77,600	—	120,000	—	120,000
4b	74,800	—	119,000	—	119,000
5a	72,200	—	100,000	—	100,000
5b	70,400	—	103,000	—	103,000
6a	69,100	—	99,500	—	99,500
6b	87,400	—	100,000	—	100,000
7a	35,000	—	66,400	—	66,400
7b	33,200	—	68,600	—	68,600
mean	57,500				86,900
Composites					
C1	63,200	—	117,000	—	117,000
C2	58,200	—	94,300	—	94,300
C3	58,100	—	111,000	—	111,000
C4	49,800	—	107,000	—	107,000
C5	51,500	—	101,000	—	101,000
C6	46,400	—	112,000	—	112,000
C7	56,600	—	105,000	—	105,000
mean	55,200				107,000
std. dev.	5,800				7,520

Sampling location 8

The analytical data for sampling location 8 are presented in Table 8a. Acetone extracts of these soils varied in color intensity, indicating that the concentrations of contaminants were quite variable from sample to sample. After appropriate dilution (ranging from 1:50 to 1:5000), reaction with EnSys reagent produced reddish solutions, showing that TNT was the probable contaminant. Laboratory analysis confirmed the presence of TNT with concentrations ranging from about 500 to almost 30,000 µg/g.

The mean RSD for duplicate field analyses of the discrete samples from location 8 was 19.7%, which was higher than for any of the other TNT sites. In contrast, the mean RSD for the lab data was 4.5%. Very similar RSDs were obtained from the replicate analyses of the composite samples (17.9% for field analyses and 4.3% for lab analyses). No specific explanation can be offered for the unusually poor precision of the field measurements.

Because concentrations for the seven samples at location 8 were clearly not normally distributed, log-transformed data were subjected to ANOVA (Table 8b). *F* ratios were 71.2 for the field results and 1553 for the lab results, denoting significant differences among samples at greater than the 99.9% confidence level. LSD calculations for both the field and lab data indicated that most individual samples were significantly different from one another.

Correlation analysis was conducted on the field and lab data for both the untransformed and log-transformed data. The best fit linear regression line for the untransformed data had a slope of

Table 7 (cont'd).

d. Statistical analysis of TNT concentrations (μg/g) for discrete and composite samples from sampling location 7R.

Discrete samples

	On-site analysis		*Laboratory total*	
Sample	*Mean*	*Mean of logs*	*Mean*	*Mean of logs*
1	82,000a†	4.914a	109,000a	5.034a
2	21,700c	4.337c	40,300c	4.604c
3	38,700b	4.587b	71,600b	4.854b
4	76,200a	4.882a	119,000a	5.076a
5	71,300a	4.853a	101,000a	5.006a
6	78,200a	4.890a	100,000a	5.000a
7	34,100b	4.533b	67,500b	4.829b

† Numbers designated with the same letter are not significantly different at the 95% confidence level.

ANOVA for on-site and lab analyses

	Untransformed	
	On-site	*Lab*
F ratios	47.8***	39.0***
Error MS	26,175,779	39,933,637
Least sign. diff.	12,097	14,943
Analysis s	5,120	6,320
Sampling s	24,700	27,560

(s = standard deviation)

Linear correlation analysis for on-site analysis vs. lab analysis
*(*r *= correlation coefficient)*

	Slope	*Intercept*	r
untransformed, non-zero intercept	0.860	–17,291	0.960
untransformed, zero intercept	0.677	0	0.936

Results of paired t*-tests for on-site vs. lab results*

Means of seven discrete samples, t = 9.55***

Composite samples

	On-site analysis	*Laboratory total*
n	7	7
mean value	55,200	107,000
standard deviation	5,840	7,520
RSD	10.6%	7.05%

ANOVA comparing on-site and lab analyses
F ratio = 209***

* Significant at the 95% level
** Significant at the 99% level
*** Significant at the 99.9% level
NS Not significant at the 95% level

e. Analytical results for stones separated from soils from sampling locations 7 and 7R during laboratory homogenization.

		Stones		*Soil*	
Sample location	*Discrete sample no.*	*Weight (g)*	*TNT concentration (μg/g)*	*Weight (g)*	*TNT concentration (μg/g)*
7	4	9.44	6,025	8.93	106,000
			8,150		102,000
7R	4	10.70	7,125	10.10	120,000
			6,500		119,000

Table 8. Results from sampling location 8, Volunteer AAP site.

a. Analytical results.

Sample	TNT on-site analysis (μg/g)	Laboratory analysis (μg/g) TNB	TNT	2,4-DNT	Total
Discrete samples					
1a	4,760	24.6	3,180	30.5	3,240
1b	3,160	53.1	3,250	21.7	3,320
2a	24,300	53.7	30,300	46.4	30,400
2b	37,300	53.1	28,200	36.4	28,300
3a	22,100	33.7	21,000	94.0	21,100
3b	24,300	48.8	21,400	123.0	21,600
4a	1,340	11.9	844	13.1	869
4b	2,320	12.5	801	17.7	831
5a	578	5.9	534	—	540
5b	582	6.1	506	2.9	515
6a	6,100	22.8	6,170	12.3	6,210
6b	7,460	18.1	5,210	11.4	5,240
7a	1,980	8.8	1,340	—	1,350
7b	2,650	10.5	1,230	18.7	1,260
mean	9,920				8,900
Composites					
C1	9,690	26.6	9,970	30.8	10,000
C2	11,300	25.7	8,930	31.7	8,990
C3	12,700	31.4	9,880	38.7	9,950
C4	9,100	28.6	10,000	31.4	10,100
C5	15,000	26.2	9,440	—	9,470
C6	10,200	27.6	9,500	19.4	9,550
C7	11,000	26.9	9,260	26.0	9,310
mean	11,300				9,620
std. dev.	2,020				409

1.038 and an r of 0.999, indicating a very strong relationship for the data (Table 8b). Similarly, a slope of 1.070 and an r of 0.998 were found for the best fit linear relationship with zero intercept. A paired t-test for the untransformed data showed a statistically significant t value of 4.71. A significant t value of 2.60 was also found for the paired t-test with the log-transformed data. For all seven samples, the field result was somewhat higher than the lab result and this consistent pattern caused the paired t-test to show a significant difference. Despite this small bias, the lab and field data for the discrete samples at location 8 both did quite well in portraying the levels of contamination for individual samples.

Results from replicate analyses of the composites failed to show that field results were significantly larger than lab results at the 95% level (Table 8b), because of the unusually large variance for the field results. The means and standard deviations of the seven composites were 11,300±2020 and 9620±409 μg/g for the field and lab data, respectively, compared with the means of the discrete samples of 9940 μg/g from the field results and 8900 μg/g from the lab results. Thus, results from the composite analysis provide an acceptably accurate estimate of the average concentrations on site.

Sampling location 9

The field and laboratory analyses for sampling location 9 are presented in Table 9a. Acetone extracts from these soils were light yellow, implying that, if analytes were present, they were in low concentration. When undiluted extracts were reacted with EnSys reagent, pink to reddish solu-

Table 8 (cont'd).

b. Statistical analysis of TNT concentrations (μg/g) for discrete and composite samples.

Discrete samples

	On-site analysis		*Laboratory total*	
Sample	*Mean*	*Mean of logs*	*Mean*	*Mean of logs*
1	3,960	3.589**bc**†	3,280	3.516**d**
2	30,800	4.479**a**	29,300	4.467**a**
3	23,200	4.365**a**	21,300	4.329**b**
4	1,830	3.246**d**	850	2.929**f**
5	580	2.763**e**	527	2.722**g**
6	6,780	3.829**b**	5,720	3.756**c**
7	2,320	3.365**cd**	1,300	3.115**e**

† Numbers designated with the same letter are not significantly different at the 95% confidence level.

ANOVA for log on-site analyses

F ratio = 71.2***
Error MS = 0.01060
Least sign. diff. = 0.244

ANOVA for log lab analyses

F ratio = 1553***
Error MS = 0.00059
Least sign. diff. = 0. 057

*Linear correlation analysis for on-site analysis vs. lab analysis (*r = *correlation coefficient)*

	Slope	*Intercept*	r
untransformed, non-zero intercept	1.038	686	0.999
untransformed, zero intercept	1.070	0	0.999
log-transformed data	0.991	0.062	0.960

Results of paired t*-tests for on-site vs. lab results*

Means of seven discrete samples, $t = 4.71$**
Means of log values for seven discrete samples, $t = 2.60$*

Composite samples

	On-site analysis	*Laboratory total*
n	7	7
mean value	11,300	9,620
standard deviation	2,020	409
RSD	17.9%	4.3%

ANOVA comparing on-site and lab analyses

F ratio = 4.54 (NS)

* Significant at the 95% level
** Significant at the 99% level
*** Significant at the 99.9% level
NS Not significant at the 95% level

tions were produced, indicative of the probable presence of TNT. This site was located in an area that was thought to be free of contamination by personnel at Volunteer AAP. Laboratory analyses confirmed the presence of TNT in these soils at concentrations ranging from 7 to 40 μg/g.

Analytical precision for both the field and lab analyses for samples from location 9 was excellent. The mean RSD for the field analyses was 4.1% for the discrete samples and the RSD from replicate analysis of the composite was 9.0%. Likewise, the mean RSD for lab analysis of the discrete samples was 5.0% and the RSD from replicate analysis of the composite was 2.8%.

Like sampling locations 4, 5 and 7, results from location 9 appeared to be sufficiently normally distributed to conduct ANOVA without log-transformation. When this was done, *F* ratios of 217 and 321 were obtained for field and lab results, respectively, indicating highly significant differences among discrete samples (Table 9b). LSD tests showed that nearly all of the discrete samples

Table 9. Results from sampling location 9, Volunteer AAP site.

a. Analytical results.

Sample	TNT on-site analysis (µg/g)	Laboratory analysis (µg/g) TNB	TNT	2,4-DNT	Total
Discrete samples					
1a	4.3	—	5.7	0.6	6.3
1b	4.1	—	4.9	0.5	5.4
2a	6.1	—	5.3	1.7	7.0
2b	5.9	—	5.5	0.9	6.4
3a	17.6	—	17.5	2.5	20.0
3b	19.9	—	16.1	2.0	18.1
4a	10.5	—	5.5	1.5	7.0
4b	10.7	—	5.2	1.4	6.6
5a	33.0	—	30.8	3.7	34.5
5b	35.8	—	29.6	3.5	33.1
6a	13.9	—	10.7	1.5	12.2
6b	14.4	—	10.4	1.3	11.7
7a	7.8	—	5.5	0.9	6.4
7b	7.3	—	5.4	0.9	6.3
mean	13.7				16.0
Composites					
C1	15.1	—	10.4	1.4	11.8
C2	15.9	—	10.1	1.4	11.5
C3	16.5	—	10.7	1.4	12.1
C4	17.6	—	10.1	1.3	11.4
C5	19.4	—	10.3	1.4	11.7
C6	15.1	—	10.7	1.4	12.1
C7	16.6	—	10.9	1.4	12.3
mean	16.6				14.9
std. dev.	1.52				0.33

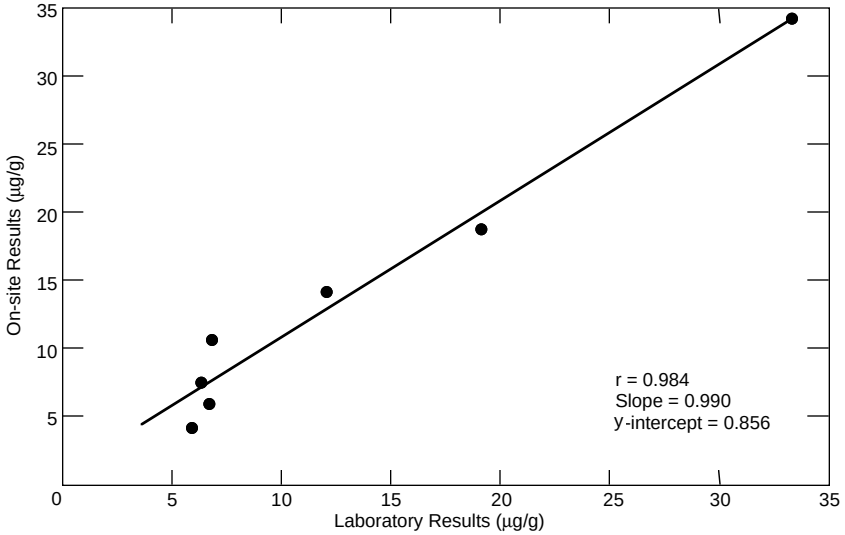


Figure 7. Untransformed TNT concentrations from sampling location 9—linear model with intercept.

Table 9 (cont'd).

b. Statistical analysis of TNT concentrations (μg/g) for discrete and composite samples.

Discrete samples

	On-site analysis		*Laboratory total*	
Sample	*Mean*	*Mean of logs*	*Mean*	*Mean of logs*
1	4.2**f**†	0.625**g**	7.2**d**	0.854**d**
2	6.0**ef**	0.779**f**	7.6**d**	0.879**d**
3	18.7**b**	1.271**b**	24.3**b**	1.385**b**
4	10.6**d**	1.024**d**	8.8**d**	0.945**d**
5	34.4**a**	1.536**a**	40.5**a**	1.607**a**
6	14.1**c**	1.151**c**	14.7**c**	1.167**c**
7	7.6**e**	0.879**e**	8.7**d**	0.940**d**

† Numbers designated with the same letter are not significantly different at the 95% confidence level.

ANOVA for on-site and lab analyses

	Untransformed	
	On-site	*Lab*
F ratios	217***	321***
Error MS	0.9974	95,854
Least sign. diff.	2.36	2.32
Analysis s	1.0	1.0
Sampling s	10.4	12.4
(s = standard deviation)		

Linear correlation analysis for on-site analysis vs. lab analysis
*(*r *= correlation coefficient)*

	Slope	*Intercept*	r
untransformed, non-zero intercept	0.990	0.856	0.984
untransformed, zero intercept	1.032	0	0.982
log-transformed data	1.000	0.019	0.939

Results of paired t*-tests for on-site vs. lab results*
Means of seven discrete samples, $t = 2.17$ (NS)

Composite samples

	On-site analysis	*Laboratory total*
n	7	7
mean value	16.6	14.9
standard deviation	1.52	0.33
RSD	9.0%	2.8%

ANOVA comparing on-site and lab analyses
F ratio = 8.43*

* Significant at the 95% level
** Significant at the 99% level
*** Significant at the 99.9% level
NS Not significant at the 95% level

were significantly different from one another. When variances were fractionated into analytical and sampling error, a standard deviation for analysis of 1.0 μg/g was obtained for both the field and laboratory methods. Sampling error estimated from the field analysis data was 10.4 μg/g and from the lab data it was 12.4 μg/g, showing that sampling error again dominated the total error at this sampling location (Table 9b).

Correlation analysis with the field and lab data from location 9 gave a best fit linear relationship with a slope 0.990, a *y*-intercept of 0.856, and an *r* of 0.984 (Table 9b, Fig. 7). The best fit zero intercept model had a slope of 1.032 and an *r* of 0.982, suggesting that the intercept was probably not significant. Results of a paired *t*-test indicated that the results of the two methods were not significantly different at the 95% confidence level.

However, the analytical precision was so good that a significant difference was detected in the replicate analyses of the composite, even though the mean concentrations of the field and lab results were 16.6 and 14.9 µg/g respectively. The excellent agreement of on-site and lab results for sampling location 9 is particularly encouraging because the range of concentration encountered is quite low (4–40 µg/g) and yet the two methods provided very comparable results.

SUMMARY OF RESULTS

The results of this study provide information on several topics critical to efficient and appropriate characterization of explosives-contaminated sites. The first compares the capabilities of colorimetric on-site analysis for TNT, DNT and ammonium picrate in soil to laboratory analysis by HPLC. Secondly, this study directly compares analytical and sampling error, thereby allowing development of strategies for improving data quality. Third, the results provide some guidance on sampling strategies for collecting representative samples, despite the enormous heterogeneity present at these sites.

To assess the overall performance of the TNT colorimetric on-site analysis method across the soils from the three installations, the numerical on-site analysis results for sampling locations 1, 3, 4, 5, 8 and 9 were correlated with the corresponding laboratory results. Data for sampling locations 2, 6 and 7 were not used in this correlation. Results from sampling location 2 were eliminated because the major analyte present was DNT rather than TNT and the relationship between the two methods is different. Similarly, contamination at location 6 was largely ammonium picrate. Results from location 7 were not used because the major portion of the soils at this location were stones, and about 50% by weight of each sample processed in the field was eliminated prior to laboratory analysis, thereby introducing a large bias between methods.

Correlations of the results from the six locations are presented in Figures 8 and 9. The results for the means of duplicates for the seven discrete samples at each of the six sampling locations show a very strong correlation between the on-site and laboratory results (r = 0.979), with a slope of the best fit linear regression line of 0.867 (Fig. 8). Because this plot includes concentration data, in which the numerical values cover about five orders of magnitude, it is difficult to see the correlation for low-concentration data in Figure 8. Thus, we plotted the on-site vs. lab data on a log-log basis as well so that the characteristics of the relationship can be seen equivalently at different absolute concentrations (Fig. 9). Clearly, the log-log plot shows that the linear relationship between on-site and lab results is very strong for lab values above a log value of about 0.6 (concentration about 4 µg/g). Data below this value are all from sampling location 3, and it is not clear whether the poor correlation for these low-concentration

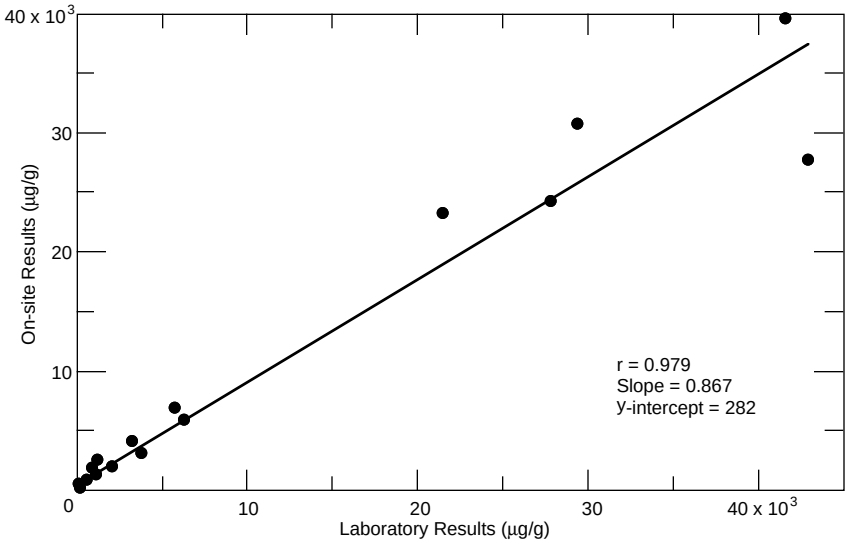


Figure 8. Untransformed TNT concentrations from sampling locations 1, 3, 4, 5, 8, 9—linear model with intercept.

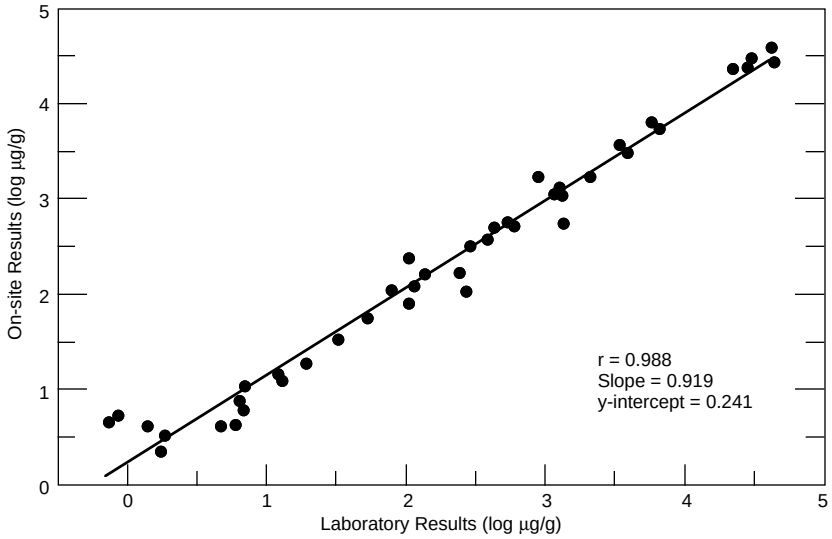


Figure 9. Log-transformed TNT concentrations from sampling locations 1, 3, 4, 5, 8, 9—linear model with intercept.

samples is specific to location 3 or is simply due to inaccuracy of the method at very low concentrations.

Figure 10 presents the results of a correlation of on-site vs. lab results for the composites for these same six sampling locations. For the composites, each point represents a mean of seven on-site and seven lab determinations. The on-site and lab data were even more strongly correlated for the composites (r = 0.989) and the slope of the best fit linear relationship was 0.999. In both cases the correlation coefficients for the best fit linear relationships with zero intercept were equal to those with non-zero intercept, which we interpret to mean that the y-intercepts were not significantly different from zero and that the slope (of the zero intercept line) can be considered an overall measure of the accuracy of the field method relative to the lab method. Using this interpretation and the computed slopes from the zero intercept models, we found the accuracy across these six sampling locations at three different installations, with concentrations varying from near the detection limit of 1 µg/g to over 40,000 µg/g, to be

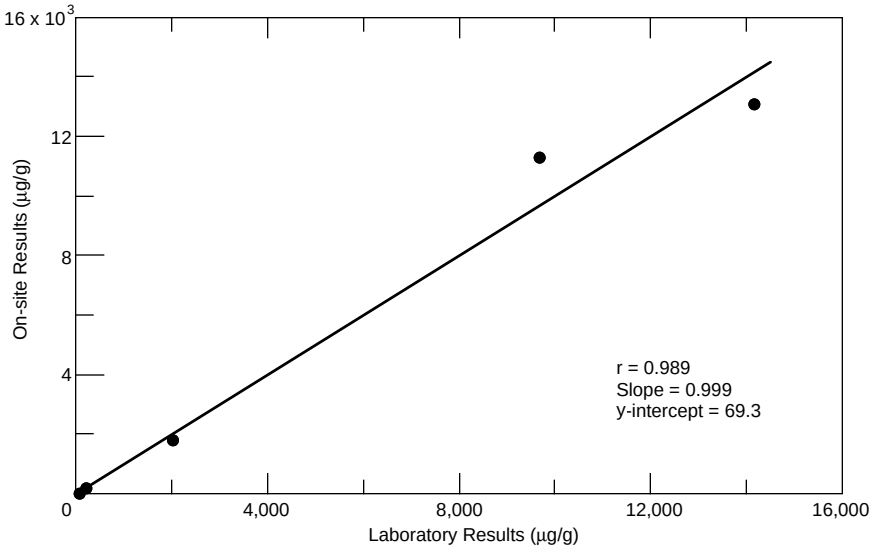


Figure 10. Untransformed TNT concentrations for composites from sampling locations 1, 3, 4, 5, 8, 9—linear model with intercept.

Table 10. Fractionation of total error into analytical and sampling components.

	Standard deviation				Ratio	
	Analytical		Sampling		Sampling/analytical	
Sampling location	On-site	Lab	On-site	Lab	On-site	Lab
Hawthorne location 4	217	265	1,970	2,150	9.1	8.1
Hawthorne location 5	5.3	11.0	121	131	22.8	11.9
Volunteer location 7	—*	7,680	—*	19,800	—*	2.6
Volunteer location 7R	5,120	6,320	24,700	27,600	6.1	4.4
Volunteer location 9	1.0	1.0	10.4	12.4	10.4	12.4

* Data unavailable.

either 87.6% for the discrete samples or 100.5% for the composites. Clearly, use of the TNT colorimetric method, with this degree of accuracy, is justified with nearly any conceivable data quality objective, but particularly where we have direct evidence of the short range heterogeneity present in soils concentrations at these locations.

On-site results for 2,4-DNT were only available for sampling location 2 at the Monite site. These results correlate well with laboratory analyses (Fig. 5) but the accuracy is not nearly as good as that for TNT. Results are adequate for mapping analyte distributions, selecting samples for more quantitative laboratory analysis and locating areas of high concentration. On-site results may not be adequate for making decisions in the field about concentrations necessary for action levels.

The data obtained for the ammonium picrate on-site method for sampling location 6 at Hawthorne AAP are the first validation results for the method developed by Thorne and Jenkins (1995). These results were very encouraging and it appears that this method may be as accurate, relative to the lab method, as the on-site TNT method.

The data from this study can also be used to put in perspective the uncertainty introduced in results by analysis vs. that from sampling. In doing so we must keep in mind that the goal of site characterization is to provide data that can be used to make decisions on whether the degree of contamination for a given area warrants a cleanup action. Although random grab sampling is appealing cost-wise, it may be totally inadequate for decisions about remedial procedures. To provide data that can satisfy this need with a high level of confidence, total error associated with site characterization must be understood and reduced to acceptable levels. Little or no information has been available where the components of error have been quantified for soil characterization at explosives-contaminated sites.

For some of the nine sampling locations studied here, analyte distribution exhibited such extremes that use of classical normal distribution statistics to fractionate the error was not possible. For locations 4, 5, 7, 7R and 9, however, we were able to fractionate the total error variances because concentration variations were modest (Table 10). For these four locations, standard deviations attributable to analysis were always much lower than the corresponding standard deviations from sampling and, hence, total error was dominated by sampling error. This was true whether characterization was done using field analysis or laboratory analysis. For the other sampling locations, sampling error was even greater and so overwhelmed analytical error that this type of fractionation would only be possible using asymmetric (logarithmic) limits. Clearly, if we want to significantly improve the quality of site characterization data, the major effort should be placed on reducing sampling error. Single grab samples are totally inadequate.

To reduce sampling error, samples analyzed must be more representative of average concentrations within the area that the sample is supposed to represent than is possible using discrete grab samples. For the data here, if we assume that the mean analyte concentration of the seven samples taken from this circle with 122 cm diameter is the "true" concentration, we can assess the difficulty in achieving representativeness by looking at the ratio of highest to lowest values in the group of seven mean determinations. These ratios are presented in Table 11 under the heading of local heterogeneity. These values range from 3.8 to 243 for the on-site TNT method and 3.0 to 315 for the lab method. Much larger grids than

Table 11. Comparison of measures of analytical precision, accuracy and discrete sample representativeness.

	Precision				*Accuracy*	*Local heterogeneity*	
			Largest concentration ratio of duplicates		*Slope of 0-intercept model*	*Ratio of highest mean concentration vs. lowest for discrete samples*	
Sample location	*RSD of duplicates*						
	On-site	*Lab*	*On-site*	*Lab*	*On-site vs. lab*	*On-site*	*Lab*
1	3.9	11.1	1.157	1.473	0.815	243	315
2 (DNT)	23.0	10.0	1.655	1.461	0.350	10.6	33.4
3	16.7	6.5	1.822	1.186	1.464	50.0	98.1
4	12.5	13.5	1.696	1.986	0.911	69.0	58.1
5	3.3	4.9	1.126	1.157	0.847	28.9	29.5
6 (Picrate)	11.6	11.9	1.500	1.875	0.967	688	43,000
7R	4.9	5.1	1.265	1.214	0.677	3.8	3.0
8	19.7	4.5	1.731	1.185	1.070	53.1	55.6
9	4.1	5.1	1.131	1.167	1.032	8.2	5.7
Mean (TNT only)	9.3	7.2	1.418	1.338	0.974	65.1	80.7

Table 12. Comparison of results for discrete and composite soil analysis.

Installation	*Sampling location*	*Major analyte*	*On-site or lab*	*Discrete samples mean ± SD**	*Composite samples mean ± SD*
Monite	1	TNT	O	13,500 ± 16,800	13,100 ± 532
			L	16,300 ± 20,200	14,100 ± 1,420
Monite	2	DNT	O	16,100 ± 11,700	23,800 ± 3,140
			L	34,800 ± 42,200	33,600 ± 2,390
Monite	3	TNT	O	19.8 ± 42.0	12.6 ± 1.2
			L	12.9 ± 29.0	4.16 ± 0.7
Hawthorne	4	TNT	O	1,970 ± 1,980	1,750 ± 178
			L	2,160 ± 2,160	2,000 ± 298
Hawthorne	5	TNT	O	156 ± 121	139 ± 16.6
			L	168 ± 131	193 ± 7.7
Hawthorne	6	Ammonium Picrate	O	869 ± 1,600	970 ± 32
			L	901 ± 1,660	1,010 ± 92
Volunteer	7	TNT	O	84,900 ± 33,400	57,000 ± 2,600
			L	89,100 ± 20,500	107,000 ± 9,230
Volunteer	7R	TNT	O	57,500 ± 25,000	54,800 ± 5,840
			L	86,900 ± 27,900	107,000 ± 7,520
Volunteer	8	TNT	O	9,920 ± 12,000	11,300 ± 2,020
			L	8,910 ± 11,600	9,620 ± 409
Volunteer	9	TNT	O	13.7 ± 10.4	16.6 ± 1.5
			L	13.0 ± 10.3	11.8 ± 0.3

* The discrete sample standard deviations for locations 1, 2, 3, 6 and 8 are all larger than their corresponding means because the results from these locations are not normally distributed. These results may be log-normally distributed, in which case the data should be transformed.

the areas we sampled are typically used for site characterization and this would only serve to further increase uncertainties from sampling.

Analysis of composite samples, however, gave results that were good estimates of the mean of the seven discrete samples, with a low standard deviation (Table 12). It is also useful to note that standard deviations for the on-site analysis of all of the composite samples are low relative to mean concentration (low RSDs), indicating that in-field homogenization procedures used were adequate. Thus, the number of analyses of the composite

required to produce data with a high degree of confidence is low. Characterization using a combination of composite sampling, adequate in-field sample homogenization and on-site colorimetric analysis, is an efficient method of producing data that are not only accurate and precise, but are also representative of the area.

APPLICATION OF RESULTS

The results presented here have several unifying themes that can be applied in designing future investigations of munitions-contaminated sites. First, it is clear that there was extreme heterogeneity at all sampling locations. A single sample from any of the 122-cm-diameter circles could differ by orders of magnitude from the mean concentration of the small area sampled. Relative standard deviations (RSDs) for the seven discrete samples were often greater than 100%.

A second consistent finding was that composite samples of the seven discrete samples could be reliably homogenized and subsampled in the field. This also opens the possibility of compositing discrete samples representing a larger area if concentration variations suggest that this approach would be desirable. Most important, it permits field processing without elaborate apparatus.

Another major finding was that the specificity and accuracy of the TNT on-site method was quite adequate. The two locations where TNT was not the major contaminant were readily identified and the seven locations where TNT appeared to be the primary contaminant were confirmed by the reference HPLC method. The on-site concentration estimates agreed very well with laboratory estimates, except for location 7, where major bias was introduced by removing small stones during the grinding operation. For the other six TNT locations, the agreement shown in Figures 9 and 10 was excellent. Admittedly, there were small but statistically significant differences in concentration estimates at some locations, but their magnitude was insufficient to impart meaningful differences in conclusions. Of course, each site should include some reference laboratory analyses to validate the on-site analyses.

For location 2, where DNT was the major contaminant, there was a rather large bias between on-site and laboratory results. This was not unexpected since the on-site DNT method is not as reliable as the TNT method. On-site and laboratory results for ammonium picrate at location 6 were generally in good agreement but more results from other sites are needed.

Perhaps the most surprising finding was the consistency of the overall precision of results for TNT. For the seven locations where TNT was the primary contaminant, average RSDs for duplicate subsamples using the on-site method with the discrete samples ranged from 3.9 to 19.7%, with a mean value of 9.3%. Comparable laboratory results yielded RSDs from 4.6 to 13.5% with a mean value of 7.2%. Replicate analyses of composites produced RSDs ranging from 4.1 to 17.9% (pooled = 10.6%) for on-site results and 2.8 to 15.9% (pooled = 9.6%) for laboratory analyses. The estimates are approximately equal for composites despite the extra mixing step, probably because the wide concentration variations of discrete samples required large differences in dilutions and the ten-times larger sample size used in the on-site analysis. Nonetheless, the consistency of the pooled estimates is both surprising and reassuring. We believe that it is fair to claim that subsampling and analysis (S_A) typically yields RSDs of about 10% for both field and laboratory methods and that extremes of 5 to 20% are to be expected. Compared to the RSDs for sampling, these precision estimates represent very acceptable levels.

Compositing is an effective way to reduce intersample variance caused by the heterogeneous distribution of contaminants. The total variance for the formation and analysis of composites can be expressed as

$$C_T^2 = \frac{C_S^2}{n} + \frac{C_A^2}{k}$$

where C_T = total percent relative standard deviation
C_S = percent relative standard deviations of sampling
C_A = percent relative standard deviations of analysis
n = number of discrete samples formed into a composite
k = number of replicate analyses done on the composite.

In Table 13 we show values of C_T for various combinations of C_S, C_A, n and k. The values chosen for C_S and C_A are typical of those found here for field or laboratory analyses of TNT. There would be nothing to prevent using larger values of n, but there is no benefit in using larger values

Table 13. Dependence of total percent relative standard deviation (C_T) on compositing and analysis schemes using various assumed values for sampling and analysis standard deviations.

Number of samples composited (n)	*Number of replicate analyses* (k)	*Percent relative standard deviations*			*Cost of procedure ($)*	
		Sampling (C_S)	*Analysis* (C_A)	*Total* (C_T)	*On-site*	*Lab*
1	1	50	10	51.0	81	337
4	1	50	10	26.9	86	342
7	1	50	10	21.4	90	347
7	2	50	10	20.2	166	680
1	1	100	10	100.5	81	337
4	1	100	10	51.0	86	342
7	1	100	10	39.1	90	347
7	2	100	10	38.5	166	680
1	1	150	10	150	81	337
7	1	150	10	57.6	90	347
7	2	150	10	57.1	166	680
1	1	100	5	100	81	337
7	1	100	5	38.1	90	347
7	2	100	5	38.0	166	680
1	1	50	20	53.9	81	337
7	1	50	20	27.5	90	347
7	2	50	20	23.6	166	680
7	1	100	20	42.8	90	347
7	2	100	20	40.4	166	680

of k given the relationship of C_S to C_A. If desired, plots of C_T vs. n could be formed for various values of C_S, C_A and k. We should also remember that the values of C_T are for a single composite. Uncertainty in a mean of several composites would be reduced by $1/\sqrt{N}$ where N is the number of composites averaged.

Table 13 very obviously shows that improved reliability of concentration estimates can only be realized by reducing the magnitude of C_S relative to C_A. On-site analysis is just as reliable as laboratory analysis for TNT in surface soils, and the analysis step doesn't contribute much error anyway. When we look at the cost estimates (Table 13) for on-site vs. laboratory analysis and combine that with the fast turnaround of on-site analysis, the advantages of field analysis are clear. In arriving at the cost of on-site analyses, all materials and their disposal were included along with capital equipment costs and labor. An allowance was also made for 10% of the samples to be sent for laboratory analysis. Clearly, the cost of compositing is relatively small compared to the benefits. Unless C_S is much lower than found for the sites studied so far, there is no justification for performing replicate analyses of composites.

The approach to a new site should involve a preliminary field survey to obtain information on the magnitude of both short- and long-range heterogeneity. From these results, a flexible sampling plan would evolve with the understanding that it was subject to modifications (if necessary) as results accumulate. It is our intention to conduct one or more such studies (demonstration projects) as the next phase of this research.

LITERATURE CITED

Barcelona, M.J. (1988) Overview of the sampling process. In *Principles of Environmental Sampling* (L.H. Keith, Ed.). Washington, D.C.: American Chemical Society, p. 1–23.

Barnard, T.E. (In press) Extending the concept of data quality objectives to account for total sample variance. In *Principles of Environmental Sampling*, 2nd Edition (L.H. Keith, Ed.). Washington, D.C.: American Chemical Society.

Cameron, D.R., M. Nyborg, J.A. Toogood and D.H. Laverty (1971) Accuracy of field sampling for soil tests. *Canadian Journal of Soil Science*, **51**: 165–175.

EPA (1995a) Nitroaromatics and nitramines by HPLC. Second Update SW846 Method 8330.

EPA (1995b) Soil screening for trinitrotoluene (TNT), SW846 Method 8515. Third Update (Draft) January 1995.

Fabrizio, M.C., A.M. Frank and J.F. Savino (1995) Procedures for formation of composite samples from segmented populations. *Environmental Science Technology*, **29**: 1137–1144.

Garner, F.C., M.A. Stapanian and L.R. Williams (1988) Composite sampling for environmental monitoring. In *Principles of Environmental Sampling* (L.H. Keith, Ed.). Washington, D.C.: American Chemical Society, p. 363–374.

Gilbert, R.O. (1987) *Statistical Methods for Environmental Pollution Monitoring*, 1st Edition. New York: Van Nostrand Reinhold Co.

Huesemann, M.H. (1994) Guidelines for the development of effective statistical soil sampling strategies for environmental applications. In *Hydrocarbon Contaminated Soils and Groundwater* (E.J. Calabrese and P.T. Kostecki, Ed.), Vol. 4, Chap. 4. Amherst, Massachusetts: Association for the Environmental Health of Soils, p. 47–96.

Jenkins, T.F. and S.M. Golden (1993) Development of an improved confirmation separation suitable for use with SW846 Method 8330. USA Cold Regions Research and Engineering Laboratory, Special Report 93-14.

Jenkins, T.F. and M.E. Walsh (1991) Field Screening Method for 2,4-Dinitrotoluene in Soil. USA Cold Regions Research and Engineering Laboratory, Special Report 91-17.

Jenkins, T.F. and M.E. Walsh (1992) Development of field screening methods for TNT, 2,4-DNT, and RDX in soil. *Talanta*, **39**: 419–428.

Jenkins, T.F., P.W. Schumacher, J.G. Mason and P.G. Thorne (1996) On-site analysis for high concentrations of explosives in soil: Extraction kinetics and dilution procedures. USA Cold Regions Research and Engineering Laboratory, Special Report 96-10.

Keith, L.H., G.L. Patton, D.L. Lewis, P.G. Edwards and M.A. Re (1995) A new calculation tool for estimating numbers of samples. In *Proceedings of the Eleventh Annual Waste Testing and Quality Assurance Symposium, July 23–28, Washington D.C.*, p. 550–564,

Paasivirta, J. and R. Paukku (1989) Use of composited samples to optimize the monitoring of environmental toxins. *Chemosphere*, **19**: 1551–1562.

Parkin, T.B. (1987) Soil microsites as a source of denitrification variability. *Soil Science Society of America Journal*, **51**: 1194–1199.

Parrish, R.S., G.O. Ware, C.N. Smith and P.A. Banks (1990) Composite sampling techniques for determining pesticide concentrations. In *Proceedings of the 1990 Kansas State University Conference on Applied Statistics in Agriculture* (G.A. Milliken and J.R. Schwenke, Eds.). Manhattan, Kansas: Department of Statistics, Kansas State University, p. 21–32.

Sabbe, W.E. and D.B. Marx (1987) Soil sampling: Spatial and temporal variability. In *Soil Testing: Sampling, Correlation, Calibration, and Interpretation* (J.R. Brown, Ed.). SSSA Special Publication, no. 21. Madison, Wisconsin: SSSA, p. 1–14.

Schaeffer, D.J., H.W. Kerster and K.G. Janardan (1980) Grab versus composite sampling: A primer for the manager and engineer. *Environmental Management*, **4**: 157–163.

Smith, F., S. Kulkarni, L.E. Myers and M.J. Messner (1988) Evaluating and presenting quality assurance sampling data. In *Principles of Environmental Sampling* (L.H. Keith, Ed.). Washington, D.C.: American Chemical Society, p. 157–168.

Starr, J.L., T.B. Parkin and J.J. Meisinger (1995) Influence of sample size on chemical and physical soil measurements. *Soil Science Society of America Journal*, **59**: 713–719.

Thorne, P.G. and T.F. Jenkins (1995) Development of a field method for quantifying ammonium picrate and picric acid in soil and water. USA Cold Regions Research and Engineering Laboratory, Special Report 95-20.

Triegel, E.K. (1988) Sampling variability in soils and solid wastes. In *Principles of Environmental Sampling* (L.H. Keith, Ed.). Washington, D.C.: American Chemical Society, p. 385–394.

Triegel, E.K., L. Guo and S. Ward (1994) Cost-effective sampling approaches. Presented at *American Chemical Society Symposium of Principles of Environmental Sampling, 16 March 1994, San Diego, California*.

van Ee, J.J., L.J. Blume and T.H. Starks (1990) A rationale for the assessment of errors in the sampling of soils. Las Vegas, Nevada: Environmental Monitoring Systems Laboratory, EPA/600/4-90/013.

Williams, L.R. (1996) Criteria-based approach for solicitation and selection of field-measurement technologies. *American Environmental Laboratory*, **8**(2): 36–37.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	August 1996	

4. TITLE AND SUBTITLE

Assessment of Sampling Error Associated with Collection and Analysis of Soil Samples at Explosives-Contaminated Sites

5. FUNDING NUMBERS

6. AUTHORS

Thomas F. Jenkins, Clarence L. Grant, Gurdarshan S. Brar,
Philip G. Thorne, Thomas A. Ranney and Patricia W. Schumacher

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Cold Regions Research and Engineering Laboratory
72 Lyme Road
Hanover, New Hampshire 03755-1290

8. PERFORMING ORGANIZATION REPORT NUMBER

Special Report 96-15

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Environmental Center
Aberdeen Proving Ground, Maryland 21010-5401

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

SFIM-AEC-ET-CR-96157

11. SUPPLEMENTARY NOTES

For conversion of SI units to non-SI units of measurement consult ASTM Standard E380-93, *Standard Practice for Use of the International System of Units,* published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

Available from NTIS, Springfield, Virginia 22161

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

This study is an assessment of short-range heterogeneity in contaminant concentrations within surface soils at explosives-contaminated sites. Intensive sampling was conducted over short distances. Discrete and composite samples were analyzed by both on-site colorimetric methods and standard laboratory protocols. Three locations were sampled at each of three installations and the results used to estimate the relative contributions of analytical error and sampling error to the total uncertainty. The major contaminant at seven of the nine sampling locations was TNT; results from the on-site colorimetric method were in excellent agreement with laboratory results using SW846 Method 8330. DNT and ammonium picrate were the contaminants present at the highest concentration in the other two locations. For four sampling locations, short-range concentration variations were modest and analyte distribution was sufficiently Gaussian to apply normal distribution statistics to fractionate the total error variances. For these four locations, analysis standard deviations were always much lower than the sampling standard deviations; total error was dominated by sampling error, whether characterization was done using on-site or laboratory analysis. The other five sampling locations had enormous short-range heterogeneity and sampling error overwhelmed analytical error. To improve the quality of site characterization data, emphasis should be placed on reducing sampling error by the use of composite sampling strategies. Characterization of explosives-contaminated sites using composite sampling, in-field sample homogenization, and on-site analysis is an efficient method of producing data that are accurate and precise, and also representative of the area.

14. SUBJECT TERMS

Ammonium picrate	DNT	Heterogeneity	Soil
Analytical error	Explosives	On-site analysis	TNT
Colorimetric methods	Field screening	Sampling error	

15. NUMBER OF PAGES 47

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL