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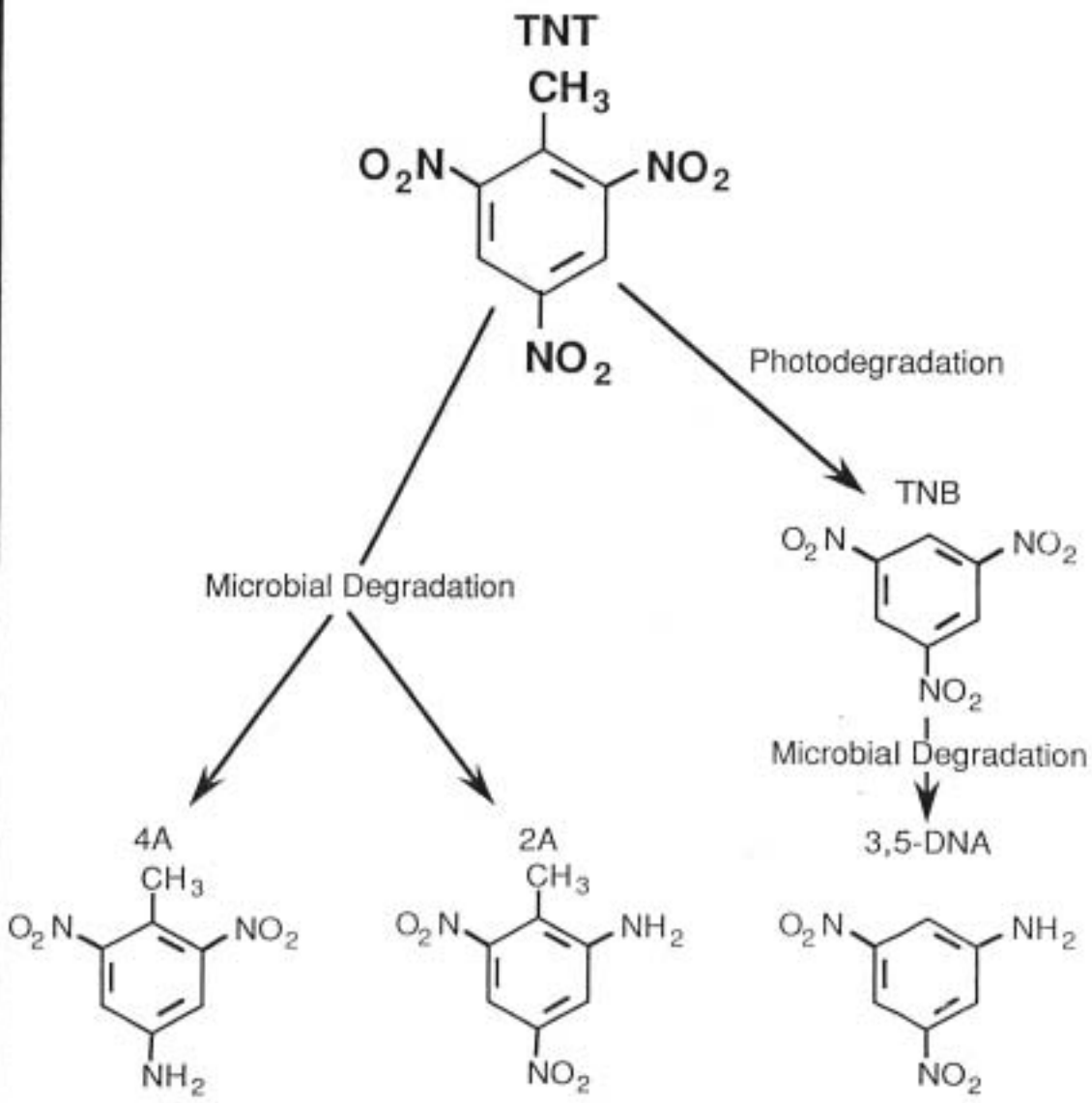
Evaluation of SW846 Method 8330 for Characterization of Sites Contaminated with Residues of High Explosives

Marianne E. Walsh, Thomas F. Jenkins, P. Stephen Schnitker, James W. Elwell and Martin H. Stutz

June 1993



Abstract

A large body of analytical results from CRREL and the Missouri River Division Laboratory was used to assess how well EPA SW846 Method 8330 satisfies the Army need for characterization of explosives-contaminated water and soil samples. About 97% of the explosives-contaminated soils contained TNT, RDX and/or 2,4-DNT, and these were the compounds found at highest concentrations. Environmental transformation products such as TNB, 2-amino- and 4-amino-DNT and 3,5-dinitroaniline (3,5-DNA) were also frequently observed. Explosives-contaminated water samples generally contained RDX, HMX and/or TNT. Transformation products commonly found included TNB, DNB, 2,4- and 2,6-DNT, 3,5-DNA and the two isomers of amino-DNT. Limitations of the primary and confirmatory RP-HPLC methods are discussed.

For conversion of SI metric units to U.S./British customary units of measurement consult *Standard Practice for Use of the International System of Units (SI)*, ASTM Standard E380-89a, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

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US Army Corps of Engineers
Cold Regions Research & Engineering Laboratory

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PREFACE

This report was prepared by Marianne E. Walsh, Research Physical Scientist, Applied Research Branch, Experimental Engineering Division, and Dr. Thomas F. Jenkins, Research Chemist, Geological Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory, by P. Stephen Schnitker and James W. Elwell, U.S. Army Corps of Engineers, Missouri River Division, and by Martin H. Stutz, U.S. Army Environmental Center.

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Evaluation of SW846 Method 8330 for Characterization of Sites Contaminated with Residues of High Explosives

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INTRODUCTION

An environmental problem of major concern to the U.S. Army is the presence of soil contaminated with residues of high explosives at military installations throughout the United States. This contamination has occurred over the greater part of this century by waste discharges from manufacturing of explosives and fabrication of finished munitions, and from residues produced during destruction of out-of-specification materiel, destruction of out-of-date bombs, rockets and ammunition, and utilization of munitions at Army training sites.

TNT (2,4,6-trinitrotoluene) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) are major ingredients in nearly every munition formulation (Table 1) and are used in the greatest quantities. Unlike many other organic chemicals, TNT and RDX are quite mobile in the soil. Thus residues of these chemicals in the soil can be a source of groundwater pollution both on Army installations and beyond installation boundaries (Kayser and Burlinson 1982, Pugh 1982, Rosenblatt 1986, Maskarinec et al. 1986, Spaulding and Fulton 1988). Recent studies have also demonstrated that bioaccumulation of transformation products of TNT (Palazzo and Leggett 1986, Harvey et al. 1990) and intact RDX (Harvey et al. 1991) can occur via plant uptake. Since the Army leases large areas of government land to private farmers at many installations across the United States and some of this land may be contaminated with explosives residues, the food chain may be contaminated as well. In addition, groundwater contaminated with these substances may have been used for crop irrigation on or near installation boundaries.

Several other organic chemical explosives have also been used in specific munition formulations, including 2,4-DNT (2,4-dinitrotoluene), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), m-NT (m-nitrotoluene), tetryl (methyl-2,4,6-trinitrophenyl nitramine), and TNB (1,3,5-trinitrobenzene) (Table 1). While some of these chemicals, such as tetryl, are no longer used in current munitions, residues from their manufacture and usage may remain.

In addition to chemicals intentionally added to explosives formulations, munition residues may contain chemicals that were impurities in production grade materiel or environmental transformation products of major or minor constituents. For example, military grade TNT contains a number of impurities including 2,4-DNT and other isomers of dinitrotoluene, 1,3-dinitrobenzene (DNB), and other isomers of trinitrotoluene, especially 2,4,5- and 2,3,4- (Leggett et al. 1977, U.S. Army 1984) (Table 2). In addition, TNT is subject to photodecomposition and microbial degradation from which a variety of transformation products have been identified in laboratory studies (Table 2). The major impurity in production grade RDX is HMX, which is present in concentrations as high as 12% (U.S. Army 1984). The major environmental transformation products of RDX have been less well characterized but they include the mononitroso-dinitro-, dinitrosomononitro- and trinitrosotriazines as well as several hydrazines, formaldehyde and methanol (Greene et al. 1985, McCormick et al. 1981, McCormick et al. 1984).

The toxicity of explosive chemicals has been studied extensively by the U.S. Army Biomedical Research and Development Laboratory (Fort Detrick, Maryland) and a summary of the results of these investigations has been

Table 1. Summary of explosive chemicals present in various military munitions (U.S. Army 1984, U.S. Army Materiel Command 1971).

		Explosives Present (%)				
Composition	*Use*	*TNT*	*RDX*	*HMX*	*DNT*	*Others*
Anatols	a,b	20–50				Ammonium nitrate
Comp A	c,d,e,f		91–98			
Comp B	b,e,f,j	40	55–60			
Comp C	k		88			
Comp C2	k	5	79		12	m-nitrotoluene, nitrocellulose
Comp C3	h,k	4	77		10	m-nitrotoluene, nitrocellulose, tetryl
Comp C4	g		91			
Cyclotol	b,e,f,i	25	75			
HBX–3	m	29	31			
H–6	m	30	45			
HTA–3	a,b	29		49		
Minol–2	a,l	40				Ammonium nitrate
Torpex	a,f,l	40	42			
DBX	l	40	21			Ammonium nitrate
PBX			0–95	0–95		Trinitrobenzene
Baratol	a	33				Barium nitrate
Baranal	a	35				Barium nitrate
Black powder	n,o					Potassium nitrate
Explosive D	a,b					Ammonium picrate
PTX–1	g,p	20	30			Tetryl
PTX–2	f,i		28–33	41–44		PETN
Comp CH6	d		98			
Ednatols	a,c,i	40–50				Ethylene dinitramine
LX–14				96		
Octols	a,b,f,i	25–35			70–75	
Pentolite	f,g,i	25–90				PETN
Picratol	h					Ammonium picrate
Tetrytols	i,k	65–80				Tetryl
Tritonal	a	80				
Amatex 20	c	40	40			Ammonium nitrate
HBX–1	m	40	38			

a Bombs
b High energy projectiles
c Projectile filler
d Boosters
e Grenades
f Shaped charges
g Demolition explosives
h Ammunition
i Bursting charges
j Fragmentation charge
k Formerly used demolition explosive
l Depth charges
m High energy charge
n Igniter powder
o Time fuses
p Land mines

published (Burrows et al. 1989). Based on these studies, the U.S. Environmental Protection Agency (EPA) and Oak Ridge National Laboratory have issued a series of Health Advisories and recommended drinking water criteria for several of these explosives (Table 3). Recommended maximum allowable concentrations range from 400 µg/L for HMX to 0.0068 µg/L for 2,6-dinitrotoluene (U.S. Environmental Protection Agency 1988a,b,c). No general recommendations have been issued for contaminant levels in soil. Instead soil levels have been evaluated on a site-by-site basis, depending on such factors as the proximity of the contaminated soil to locations of groundwater use (Dacre et al. 1980). For example, at Cornhusker Army Ammunition Plant, clean-up criteria of 5 µg/g for TNT, 10 µg/g for RDX and 15 µg/g for TNB (Rosenblatt 1986) were established.

A variety of analytical techniques have been examined for detecting and quantifying munition residues in environmental matrices. Since numerous compounds are potentially present, many with similar physical and chemical properties (Table 4), analytical methods have generally included a chromatographic separation. Methods have included thin layer chromatography (TLC) (Hoffsommer and McCullough 1968, Glover and Hoffsommer 1973, Twibell et al. 1984), gas chromatography (GC) with a variety of detectors (Hoffsommer

Table 2. Summary of major impurities and environmental transformation products associated with military grade TNT.

Compound	*Source*	*Reference*
2,4-dinitrotoluene	I	Leggett et al. (1977), U.S. Army (1984), Jenkins et al. (1989)
2,6-dinitrotoluene	I	U.S. Army Materiel Command (1971), Leggett et al. (1977), Jenkins et al. (1986)
1,3-dinitrobenzene	I	U.S. Army (1984), Jenkins et al. (1989)
2,4,5-trinitrotoluene	I	Leggett et al. (1977), U.S. Army (1984)
2,3,4-trinitrotoluene	I	Leggett et al. (1977), U.S. Army (1984)
2-amino-4,6-dinitrotoluene	M	Palazzo and Leggett (1986), Won et al. (1974), Jerger et al. (1976), Amerkhanova and Naumova (1978), Carpenter et al. (1978), Burlinson (1980), Greene et al. (1985), Spanggord et al. (1980, 1983), Naumova et al. (1982), Jenkins et al. (1989)
4-amino-2,6-dinitrotoluene	M	Palazzo and Leggett (1986), Won et al. (1974), Jerger et al. (1976), Parrish (1977), Amerkhanova and Naumova (1978), Carpenter et al. (1978), Osmon and Andrews (1978), Pereira et al. (1979), Burlinson (1980), Greene et al. (1985), Spanggord et al. (1980, 1983), Naumova et al. (1982), Jenkins et al. (1989)
Tetranitroazoxytoluene isomers	M	Won et al. (1974), Jerger et al. (1976), Parrish (1977), Spanggord et al. (1980)
2,4-diamino-6-nitrotoluene	M	Jerger et al. (1976), Carpenter et al. (1978), Spanggord et al. (1980)
2,6-diamino-4-nitrotoluene	M	Capenter et al. (1978), Spanggord et al. (1980)
2-hydroxylamino-4,6-dinitrotoluene	M	Jerger et al. (1976)
4-hydroxylamino-2,6-dinitrotoluene	M	Won et al. (1974), Jerger et al. (1976)
1,3,5-trinitrobenzene	I,P	U.S. Army (1984), Burlinson (1980), Kearney et al. (1983), Jenkins et al. (1989)
1,3,5-trinitrobenzaldehyde	I,P	U.S. Army (1984), Burlinson (1980), Spanggord et al. (1980), Karney et al. (1983), Jenkins et al. (1989)
1,3,5-trinitrobenzoic acid	I,P	U.S. Army (1984), Spanggord et al. (1980)
3,5-dinitroaniline	P,M	Burlinson (1980), Spanggord et al. (1983)
2-amino-4,6-dinitrobenzoic acid	P	Spanggord et al. (1983)
3,5-dinitrophenol	P	Kearney et al. (1983)
3,5-dinitrocatechol	P	Kearney et al. (1983)
3,5-dinitrohydroquinone	P	Kearney et al. (1983)
4,6-dinitroanthranil	P	Spanggord et al. (1980)
2,4,6-trinitrobenzonitrile	P	Spanggord et al. (1980)

* I - impurity in production grade TNT; M-microbial transformation product of TNT; P-photodegradation product of TNT.

Table 3. Drinking water criteria (µg/L) for munition-related chemicals.

Compound	*Criteria*	*Reference*
TNT	1.0*	EPA (1989)
RDX	2.0*	EPA 1988c)
HMX	400*	EPA (1988a)
2,4-DNT	0.17†	EPA (1980)
2,6-DNT	0.0068†	EPA (1980)
1,3,5-TNB	1.0*	Elmer (1987)

* Lifetime exposure cancer risk level 10^{-6}.
† Recommended criteria for cancer risk of 10^{-6}.

and Rosen 1972, Goerlitz and Law 1975, Jurinski et al. 1975, Pereira et al. 1979, Hashimoto et al. 1980, Douse 1981, Hoffsommer et al. 1981, Lafleur an Mills 1981, Douse 1983, Phillips et al. 1983, Weinberg and Hsu 1983, Belkin et al. 1985, Richard and Junk 1986, Rosencrance and Brueggemann 1986, Habel et al. 1991), high performance liquid chromatography (HPLC) Lafleur and Morriseau 1980, Bratin et al. 1981, Hoffsommer et al. 1981, Krull et al. 1981a, Krull et al. 1981b, Brueggemann 1983, 1986, Bongiovanni et al. 1984, Krull et al. 1984, Maskarinec et al. 1984, Cragin et al. 1985, Bauer et al. 1986, Jenkins et al. 1986, Rosen-

Table 4. Physical and chemical properties of nitroaromatics and nitramines.

Analyte	Molecular weight	Melting point (°C)	Boiling point (°C)	Water solubility (mg/L)	Vapor pressure at 20°C (torr)	Log K_{ow}*	Henry's Law constant Hc (torr M^{-1})
TNT	227.13	80.1–81.6[1]	240 (explodes)[7]	130 @ 20°[11]	1.1×10^{-6}[13]	1.86[16]	0.18[15]
RDX	222.26	204.1[2]	(decomposes)	42 @ 20°[8]	4.1×10^{-9}[14]	0.86[16]	2×10^{-5}[15]
HMX	296.16	276–280[3]	(decomposes)	5.0 @ 25°[9]	3.3×10^{-14}[12]	0.061[16]	
TNB	213.11	122.5[4]	315[4]	278 @ 15°[4]	2.2×10^{-4}[15]	1.18[17]	1.5[14]
DNB	168.11	89.6[4]	(300–303)[4]	460 @ 15°[4]	3.9×10^{-3}[14]	1.49[17]	1.8[14]
Tetryl	287.14	129.5[5]	(decomposes)	80[10]	5.7×10^{-9}@25°[12]	1.65[16]	
2,4-DNT	182.15	70[6]	300 (decomposes)[7]	270 @ 22°[11]	2.2×10^{-4}@25°[12]	1.98[17]	3.4[14]
2,6-DNT	182.15	64–66[6]		206 @ 25°[12]	5.67×10^{-4}[12]	2.02[16]	18[14]
2-Am-4,6-DNT	197.17	176[18]		2800 @ 20°[18]	4×10^{-5}[18]	1.94[16]	3×10^{-3}[18]
4-Am-2,6-DNT	197.17	171[18]		2800 @ 20°[18]	2×10^{-5}[18]	1.91[16]	1×10^{-3}[18]

* Octanol/water partition coefficient.

Literature citations:

(1) EPA (1989)
(2) EPA (1988c)
(3) EPA (1988a)
(4) Wentsel et al (1979)
(5) Lindner (1989)
(6) Etnier (1987)
(7) Verschueren (1983)
(8) Sikka et al. (1978)
(9) Glover and Hoffsommer (1973)
(10) Urbanski (1964)
(11) EPA (1980)
(12) Burrows et al. 1989)
(13) Leggett (1977)
(14) Spanggord et al. (1980b)
(15) Spanggord et al. (1980a)
(16) Jenkins (1989)
(17) Hansch and Leo (1979)
(18) Layton et al. (1987)

crance and Brueggemann 1986, Voyksner and Yinon 1986, Yinon and Hwang 1986, Selavka et al. 1987, Jenkins et al. 1988, Jenkins et al. 1989, Bauer et al. 1990, Miyares and Jenkins 1990, 1991) and recently, supercritical fluid chromatography (SFC) (Griest et al. 1989, Douse 1988). The Army and the USEPA have selected a reversed-phase high-performance liquid chromatographic (RP-HPLC) procedure for routine analysis of soils and waters from potentially contaminated sites. This method has been issued in draft by the EPA Office of Solid Waste as Method 8330 (U.S. Environmental Protection Agency 1990). Based on an isocratic-HPLC separation and UV (ultraviolet) detection, it is capable of detecting and quantifying 14 individual nitroaromatics and nitramines (HMX, RDX, TNB, DNB, tetryl, NB, TNT, 2-amino-4,6-DNT, 4-amino-2,6-DNT, 2,6-DNT, 2,4-DNT, and the three isomers of NT). This method has been used extensively in our laboratories and in a number of commercial contractor laboratories conducting analyses for the Army. It has also been accepted by the Association of Official Analytical Chemists (1990a,b) and American Society for Testing and Materials (ASTM 1991) as the standard method of determining explosives residues in soil and water.

One objective of this report is to assess how well Method 8330 has satisfied the Army's analytical requirements for determining explosive residues in soil and water. This will be done by summarizing a large body of analytical results from CRREL and the Missouri River Division Laboratory (MRD) using several related RP-HPLC procedures for environmental samples from several Army installations throughout the United States. In addition, results of HPLC and GC/MS analysis of extracts of munition-contaminated soils will be discussed in relation to the detection of environmental transformation products that cannot be determined using Method 8330. Finally, observations from extensive experience with this technology will be provided and recommendations made for future changes and additions, including the possible utility of field screening methods, which could improve our ability to characterize soils and waters from these types of sites.

EXPERIMENTAL

Chemicals

Analytical standards of TNT, RDX, DNB, TNB, nitrobenzene (NB), HMX, tetryl, 2,4-DNT, 2,6-DNT, 2,4,6-trinitrophenol (picric acid) and 2,4,6-trinitrobenzaldehyde (TNBA) were Standard Analytical Reference Materials (SARM) from the U.S. Army Environmental Center. Standards of 2-amino-4,6-dinitrotoluene (2-Am-DNT), 4-amino-2,6-dinitrotoluene (4-Am-DNT), 2,4-diamino-6-nitrotoluene (2,4-DiAm-NT), and 2,6-diamino-4-nitrotoluene (2,6-DiAm-NT) were obtained from Natick Laboratories, Natick, Massachusetts. Standards of the remaining isomers of dinitrotoluene and trinitrotoluene were obtained from Picatinny Arsenal, Dover, New Jersey. Standards of 3-nitroaniline, 4-amino-2-nitrotoluene, 2-amino-4-nitrotoluene and 2,4,6-trinitrobenzoic acid were obtained from Chem Services Inc., West Chester, Pennsylvania. Standards of 3,5-dinitroaniline and 2,4-dinitrophenol were obtained from Aldrich and Kodak, respectively. The identity of all non-SARM standards was verified by GC/MS (Jenkins et al. 1973).

Soil and water samples were obtained from 46 present and past Defense Department installations in 29 states. Samples were shipped and handled under chain-of-custody and were maintained at 4°C in the dark until extracted (soils and low concentration waters) or analyzed (high concentration waters).

Methanol, acetone, acetonitrile and tetrahydrofuran (THF) used in preparation of the HPLC eluent and to extract samples were HPLC grade solvents from either Baker or Aldrich. Reagent grade water, used to prepare the eluent and to dilute soil and water extracts, was purified using a Milli-Q Type 1 Reagent-Grade Water System (Millipore Corp). The sodium chloride (NaCl) used in salting-out extractions and calcium chloride ($CaCl_2$) used for flocculation were Baker reagent-grade chemicals.

Soil extraction

Routine extraction of soils for RP-HPLC analysis was accomplished as described in Method 8330 (Jenkins et al. 1989, U.S. Environmental Protection Agency 1990). Soils were air dried to constant weight and ground with a mortar and pestle. Two-gram subsamples were extracted with 10 mL of acetonitrile for 18 hours in a sonic bath that was maintained at room temperature (< 30°C) with cooling water. The samples were then removed from the bath and allowed to stand for 30 minutes. A 5.00-mL aliquot was removed and mixed with 5.00 mL of 5-g/L aqueous calcium chloride ($CaCl_2$). The extracts were allowed to stand at least 15 minutes before filtering through a 0.5-µm Millex SR filter unit. Extracts were stored at 4°C in the dark until analyzed.

Soil samples to be analyzed by GC/MS were extracted in a sonic bath (< 30°C) for up to 18 hours with acetone. Extracts were preconcentrated under a stream of nitrogen gas at room temperature.

Water samples

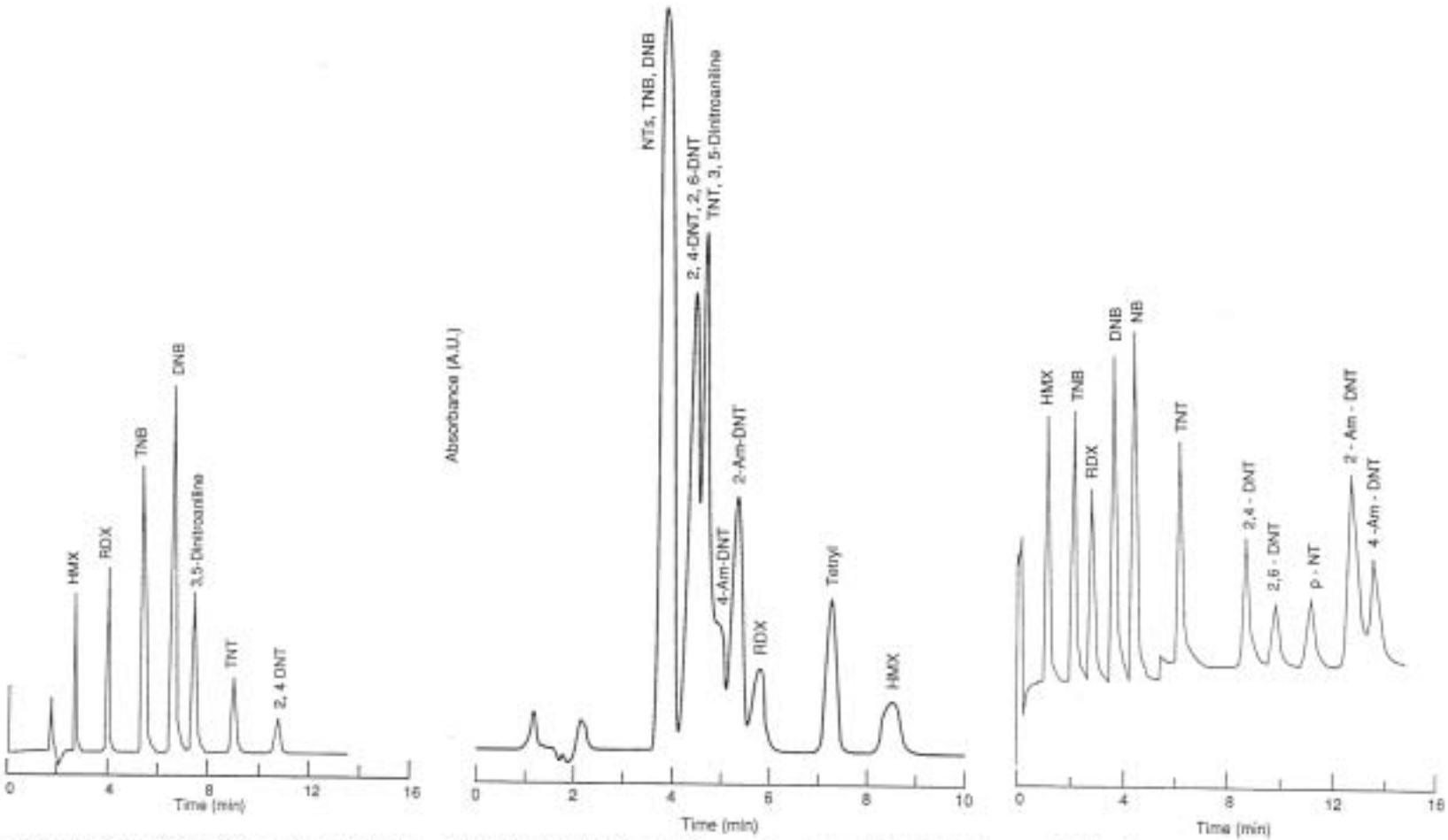
Water samples to be analyzed by RP-HPLC were processed by two different protocols. For high-concentration analysis, samples were diluted 1:1 with methanol and filtered through a 0.5-µm Millex SR filter. For low-concentration analysis, samples were preconcentrated using either of two salting-out solvent extraction procedures. In the first method (Miyares and Jenkins 1990), a 400-mL aliquot was placed in a 500-mL separatory funnel and 130 g of NaCl was added. The funnel was shaken vigorously to completely dissolve the salt and 100 mL of acetonitrile was added. The funnel was shaken for 5 minutes and then allowed to stand undisturbed for 30 minutes to allow phase separation. The upper acetonitrile-rich layer (about 23 mL) was collected and the volume reduced to 1.0 mL using a Kuderna-Danish microconcentrator. This concentrated extract was diluted with 3.0 mL of reagent water prior to RP-HPLC analysis.

In the second method (Jenkins and Miyares 1991, Miyares and Jenkins 1991, Jenkins et al. 1992), a 251.3-g portion of reagent grade NaCl was added to a 1-L volumetric flask. A 770-mL sample of water was measured with a 1-L graduated cylinder and added to the flask. A stir bar was added and the contents stirred at maximum speed (1500 rpm) until the salt was completely dissolved. A 164-mL aliquot of acetonitrile was added while the solution was being stirred for 15 minutes. The stirrer was turned off and the phases allowed to separate for 10 minutes. The acetonitrile phase (about 8 mL) was removed and 10 mL of fresh acetonitrile added. The flask was stirred for another 15 min followed by 10 min for phase separation. The acetonitrile was removed and combined with the initial extract. The extract was placed in a 100-mL volumetric flask and 84 mL of salt water (325 g NaCl per 1000 mL of water) was added. A stir bar was placed in the flask and the contents stirred for 15 min. After allowing the phases to separate for 10 min. the acetonitrile phase was carefully removed using a Pasteur pipette and placed in a 10-mL graduated cylinder. An additional 1.0-mL aliquot of acetonitrile was then added to the volumetric flask and the contents stirred for 15 minutes. Again the phases were allowed to separate for 10 minutes and the resulting acetonitrile phase was added to the 10-mL graduated cylinder. The resulting extract, about 5–6 mL, was then diluted 1:1 with reagent grade water prior to analysis and the preconcentration factor was based on the measured volume.

RP-HPLC analysis

Analyses of all soil extracts and most of the water samples were conducted on a 25-cm × 4.6-mm (5 µm) LC-18 (Supelco) column (Fig. 1a). A mobile phase composed of 1:1 (v/v) methanol/water was used at a flow rate of 1.5 mL/min. A 100-µL aliquot of sample was injected using a sample loop injector, and a 254-nm UV detector was used for peak quantitation. When peaks were detected at retention times corresponding to the analytes of interest (Table 5), the samples were reanalyzed using the same mobile phase and flow rate on a 25-cm × 4.6-mm (5-µm) LC-CN (Supelco) column for analyte confirmation (Fig. 1b).

Some of the water extracts, prepared using salting-out solvent extraction with acetonitrile, were analyzed at CRREL on either a 3.3-cm or a 7.5-cm × 4.6-mm (3-µm) LC-8 column (Supelco). A mobile phase composed of 70.7:27.8:1.5 (v/v/v) water/methanol/THF was used at a flow rate of 2.0 mL/min (Fig. 1c, Table 5).



a. LC-18 column (25 cm × 4.6 mm × 5 µm) eluted with 1.5 mL/min of 1:1 methanol–water.

b. LC-CN column (25 cm × 4.6 mm × 5 µm) eluted with 1.5 mL/min of 1:1 methanol–water.

c. LC-8 column (7.5 × 4.6 mm × 3 µm) eluted with 2 mL/min of 8:1.5 water–methanol–THF.

Figure 1. Chromatograms obtained by HPLC separation on LC-18, LC-CN and LC-8.

Table 5. Retention times (min.) for analytes of interest for various RP-HPLC separations.

Analyte	LC-18 1:1 methanol/water	LC-CN 1:1 methanol/water	LC-CN†† 35:65 methanol/water	LC-8 70.7:27.8:1.5 water/methanol/THF
HMX	2.6	8.4	9.6	1.6
RDX	3.8	6.2	7.0	3.0
TNB	5.1	4.1	4.7	2.5
DNB	6.0	4.2	5.0	3.7
TETRYL	6.7	7.4	9.6	8.1
NB	7.2	3.8		4.2
TNT	8.4	5.0	5.9	5.6
4-Am-DNT	8.7	5.1		11.5
2-Am-DNT	9.0	5.6	7.4	10.8
2,6-DNT	9.5	4.6		8.5
2,4-DNT	9.6	4.9	6.2	7.6
2-NT	11.5	4.4		9.6
4-NT	12.5	4.4		9.8
3-NT	13.5	4.5		10.2
3,5-DNA	6.7	5.0		6.0
2-Am-4-NT	5.5	3.8		4.6
4-Am-2-NT	5.1	3.7		4.9
3-Am-NB	3.9			2.0
2,6-Di-Am-NT	2.4	3.7		1.4
2,4-Di-Am-NT	3.2	4.2		2.8

GC/MS analysis

GC/MS analyses were obtained on a Hewlett-Packard 5970 Mass Selective Detector using electron impact ionization at 70 eV. Samples were introduced through a Hewlett-Packard 5890 Series 2 gas chromatograph. An HP-5 cross-linked 5% phenylmethylsilicone column (25-m × 0.20-mm × 0.33-µm film thickness) was temperature programmed from 75° to 240° C at 20°/min after an initial hold time of two minutes. Splitless injections were used with a linear velocity of 30 cm/sec of helium carrier gas. Injection port and transfer line temperatures were 250° and 280°C, respectively.

Field screening tests for munitions

In addition to analysis by RP-HPLC, some soils were analyzed using field-screening procedures designed to detect RDX and TNT. Details of these colorimetric procedures are given elsewhere (Jenkins and Walsh 1992), but a brief description follows.

For each soil sample, a 20-g subsample of undried soil was extracted with 100 mL of acetone by manually shaking for three minutes. The extract was filtered and an aliquot removed for the TNT test. TNT was detected by the addition of a strong base (KOH), which results in the production of the red-colored Janowsky anion. Absorbance was measured at 540 nm using a Hach DR/2000 battery-operated spectrophotometer. Other nitroaromatics were also detected and gave various colors: TNB (red), DNB (purple), 2,4-DNT (blue), 2,6-DNT (purple), and tetryl (orange).

For the RDX test an aliquot of the filtered acetone extract was passed through an ion-exchange resin to remove nitrate and nitrite. The extract was acidified and mixed with zinc dust, thereby forming nitrous acid that was then detected using a Griess color-forming reaction. A pink solution indicates the presence of RDX. The absorbance was measured at 507 nm. Other nitramines (such as HMX) and nitrate esters (such as nitroglycerine and PETN) also give a pink color with this procedure.

The absorbances measured for both these procedures were converted to analyte concentrations in terms of µg/g based on the response from calibration standards.

RESULTS

Analytes detected in soil extracts using Method 8330

Using Method 8330, CRREL detected explosives residues in 175 out of 433 soil samples from 31 sites, and MRD detected these analytes in 144 out of 722 soil samples from 21 sites. For the combined data set, 28% of the samples analyzed were found to be contaminated with one or more explosives residues (Table 6). Of these positive samples, 97% contained TNT, RDX and/or 2,4-DNT. The analytes found in highest concentration varied with the type of site from which the samples were collected.

For soil samples collected at sites such as arsenals, depots, and ammunition plants, the analyte TNT was

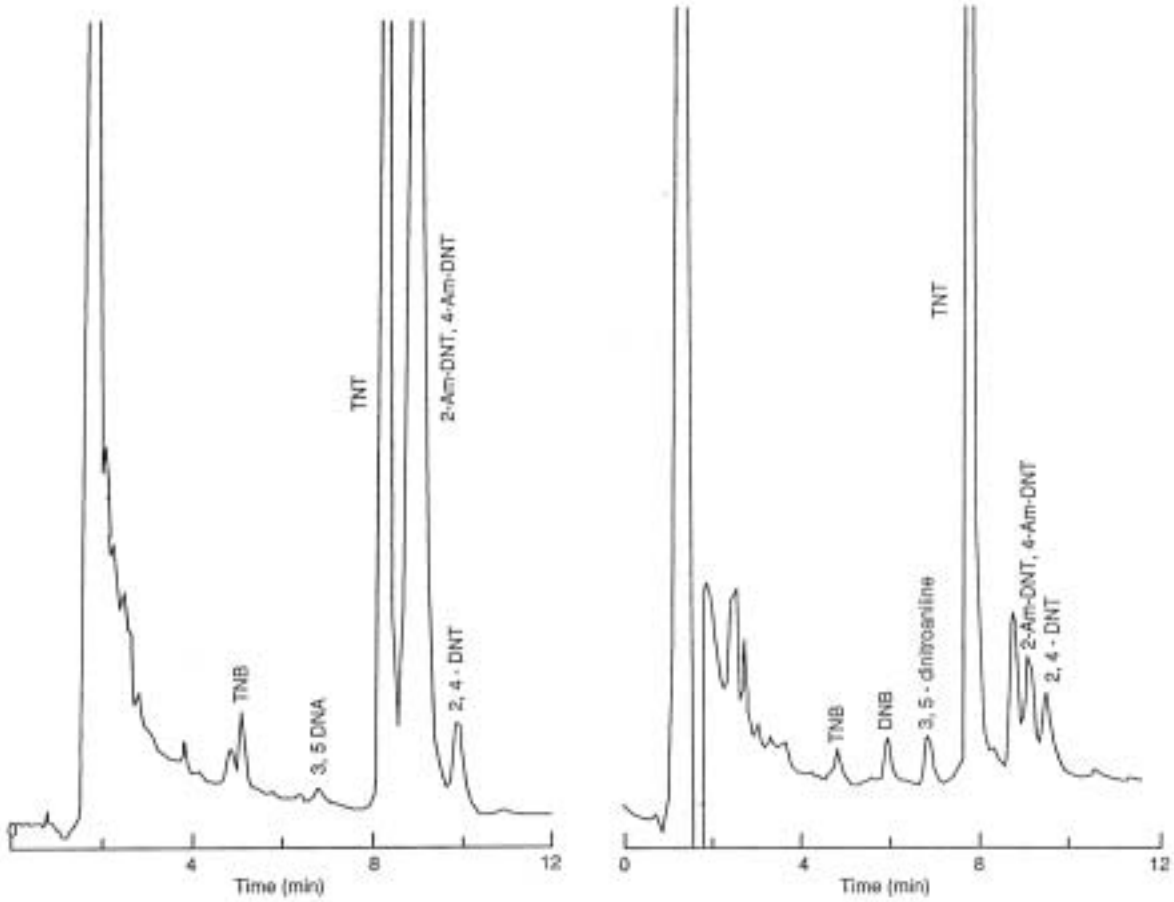


Figure 2. Chromatograms obtained from TNT contaminated with soil and water, showing commonly occurring co-contaminants, TNB, 2,4–DNT and the isomers of amino–DNT.

found most frequently (195 out of 243 positive samples or 80%) and at the highest concentrations (i.e., up to parts per hundred) (Tables 6, 7, Fig. 2a). Of these TNT-contaminated soils, 54% also were contaminated with TNB, a phototransformation product of TNT. DNB and 2,4-DNT, manufacturing byproducts of TNT, were present at detectable levels in 26% and 32%, respectively, of these samples, and 2-Am-DNT, a biotransformation product of TNT, was reported in 22% of these samples (although detection of this analyte was limited due to availability of standards). Conversely, over 94% of all detections of TNB, DNB, the isomers of DNT, and the isomers of amino-DNT were in samples contaminated with TNT. RDX was detected in 60% of the samples containing TNT. It is the main ingredient in several explosive compositions (Table 1) , frequently with TNT. Samples contaminated with TNT and/or RDX accounted for 94% of all these samples collected from arsenals, depots, and ammunition plants with detectable explosives residues.

Of those samples contaminated with RDX, 37% also had HMX, generally at a lower concentration than RDX. HMX is an impurity in munitions-grade RDX, as well as an ingredient in several explosives compositions (Table 1) . Tetryl was infrequently found, perhaps because it is no longer used as a military explosive due to its instability. The instability can also contribute to loss during sample preparation (Jenkins et al. 1989). NB and the isomers of NT were never found in any samples.

Two Explosive Ordnance Disposal (EOD) sites were sampled. At both sites 2,4-DNT was detected in all samples with detectable analytes (Table 6). The 2,4-DNT was present at much higher concentrations than TNT, the reverse of what is found at other types of sites. The source of this contamination was probably the improper demolition of excess propellant (i.e., it was detonated, not burned). In fact, whole propellant grains were found scattered about each EOD area. GC/MS analysis of acetonitrile extracts of soil samples and propellant grains confirmed the presence of diphenylamine

Table 6. Frequency of detection of explosives residues in soil using Method 8330.

	a. All samples collected			*b. Samples collected from Army ammunition plants, arsenals and depots*			*c. Samples collected from ordnance disposal (EOD) sites*		
	CRREL	*MRD*	*Total*	*CRREL*	*MRD*	*Total*	*CRREL*	*MRD*	*Total*
Installations	31	21	46	29	20	44	2	1	2
Samples analyzed	433	722	1,155	210	653	863	223	69	292
Samples with detectable explosives	175	144	319	108	135	243	67	9	76
Analytes detected									
HMX	31	6	37	29	6	35	2	0	2
RDX	49	38	87	48	38	86	1	0	1
1,3,5-TNB	57	51	108	57	51	108	0	0	0
1,3-DNB	27	26	53	27	26	53	0	0	0
Tetryl	9	19	28	9	19	28	0	0	0
NB	0	0	0	0	0	0	0	0	0
TNT	106	103	209	92	103	195	14	0	14
4-Am-DNT	17	4	21	7	4	11	10	0	10
2-Am-DNT	39	15	54	29	15	44	10	0	10
2,6-DNT	22	1*	23	0	1*	1	22	0	22
2,4-DNT	111	32	143	44	23	67	67	9	76
2-NT	0	0	0	0	0	0	0	0	0
4-NT	0	0	0	0	0	0	0	0	0
3-NT	0	0	0	0	0		0	0	0
TNT and/or RDX	103	126	229	103	126	229			

* Didn't differentiate 2,4- and 2,6-DNT.

Table 7. Concentration ranges observed for various analytes in soil and water.

	CRREL		*MRD*		*Median conc for combined data sets*	
Analyte	*Soil (µg/g)*	*Water (µg/L)*	*Soil (µg/g)*	*Water (µg/L)*	*Soil (µg/g)*	*Water (µg/L)*
HMX	*t* – 5700	0.13–673	0.13–365	2.45*	3.7	76
RDX	*t* – 13,900	0.02–1400	0.19–105	0.1–162	3.6	3.0
TNB	0.3–550	1.0–46	0.08–1790	0.10–36.1	5.0	1.5
DNB	0.2–4 5	0.15–1.4	0.11–61	0.06– 8.7	0.66	0.78
Tetryl	*t* – 1260	0.18–0.4	0.36–171	0.07–11.6	3.0	0.92
TNT	*t* – 102,000	0.07–981	0.13–31,000	0.08–125	5.5	3.5
2–AmDNT	*t* – 37	0.02–218	0.32–373	0.86–216	0.62	11.2
4–AmDNT	*t* – 3.9	0.06–217	0.15–10.6	1.09–2.58	0.27	4.6
2,4–DNT	*t* – 84	0.05–4.6	0.22–318	0.12–6.74	0.65	1.2
2,6–DNT	0.08–4.5	0.02–29	1.23*	1.5*	0.53	0.10

* Only one sample where analyte detected.

t–Analyte detected but concentration below reporting limit.

and dibutylphthalate, which along with nitrocellulose (U. S. Army 1984) are the ingredients of M1 propellant.

During the course of these analyses, we found that most analytes could be confirmed using the cyano (LC-CN) confirmation column eluted with 1.5 mL/min 1:1 methanol/water as specified in Method 8330. HMX and RDX, which elute several minutes before TNT on the analytical column (LC-18), elute after TNT on the confirmation separation (Table 5). This dramatic shift in retention makes the confirmation of nitramines certain. However, confirmation of DNT is difficult in many cases. The isomers of DNT elute close to TNT on the confirmation separation, and since they are often present at much lower concentrations than TNT, their confirmation may be ambiguous. However, some improvement in the resolution of 2,4-DNT and TNT can be achieved using a slower flow rate (1.2 mL/min) and a weaker eluent (35:65 methanol:water) (Table 5). Additionally, this flow rate and eluent greatly improves the separation of 2-Am-DNT and TNT.

Another problem associated with the confirmatory separation for some samples is the presence of many more peaks in the confirmation chromatogram than in the analytical chromatogram. The cyano function on the LC-CN confirmation column is less retentive for aromatic compounds than the hydrocarbon-based phase of

the LC-18 analytical column. Since the confirmation column is less retentive, it is more prone to interference from non-target analytes that have long retention times on the LC-18.

Transformation products detected in soil extracts

As evidenced by the presence of TNB and the isomers of amino-DNT in the soils contaminated by TNT, explosives residues in soil may be transformed by photochemical and microbiological processes. While the transformation pathways of some explosives have been studied in cell cultures, composting systems and water, little research has been conducted to define what by-products are present in soil. Potential transformation products of TNT are numerous (Table 2). Of the compounds listed in Table 2, only TNB and the isomers of amino-DNT have been reported by previous investigators (Layton et al. 1987).

For an initial study of TNT transformation products present in soil, 11 soils that had been analyzed by Method 8330 were selected to represent a range of TNT concentrations (1 µg/g to 14 mg/g). The soils came from the following locations: Weldon Spring (Missouri), Hawthorne (Nevada), Hastings East (Nebraska), Sangamon (Illinois), Raritan (New Jersey) and VIGO (Indiana). Subsamples (20 g) were extracted with 100 mL of acetone by manually shaking for 3 min and equilibrating in an ultrasonic bath at 20°C for 14 hr. A subsample (10 mL) of each extract was filtered through a Millex SR filter unit and a 1-µL aliquot was analyzed by GC/MS as described in the *Experimental* section. Then the 10-mL subsample was placed under a gentle stream of nitrogen until the volume was approximately 0.5 mL and another 1-µL aliquot was analyzed by GC/MS.

The most commonly found transformation products were 2-Am-DNT and 4-Am-DNT, the microbiological reduction products of TNT (Table 8). TNB, a photodecomposition product of TNT, was identified in 5 of the 11 soils. Other transformation products identified in 4 of the 11 soils were trinitrobenzaldehyde (TNBA) and 3,5-dinitroaniline (DNA). TNBA, like TNB, is a photodecomposition product of TNT, and converts to TNB by decarbonylation (Burlinson 1980). We have detected TNBA using Method 8330, but TNBA slowly converts to TNB in acetonitrile (Jenkins et al. 1989). Because of this instability, the TNB concentration estimated using Method 8330 is the sum of the TNB and TNBA initially present (Jenkins et al. 1989). Because 3,5-DNA is a microbiological reduction product of TNB, its formation from TNB in soil would be consistent with the formation of 2-Am-DNT and 4-Am-DNT from TNT in soil. Its presence in soil was further investigated by HPLC.

The retention time on the LC-18 column for 3,5-DNA is the same as that for tetryl (i.e., 6.9 min) (Fig. 1). However, tetryl and 3,5-DNA are well separated on the LC-CN column with retention times of 7.4 and 5.0 min, respectively (Table 5). When we were developing Method 8330 and examining chromatograms of explosives-contaminated soils, we frequently observed a peak corresponding to the retention time for tetryl on the LC-18,

Table 8. Compounds found by GC/MS analysis of acetone extracts of 11 soils from various Army installations.

Analyte	*Number of times detected*
2,4,6-TNT	11
2,3,6-TNT	1
2,4,5-TNT	1
2-Am-4,6-DNT	8
4-Am-2,6-DNT	6
TNB	5
Dinitroaniline (3,5-DNA)	4
Trinitrobenzylaldehyde (TNBA)	4
2,4-DNT	7
2,6-DNT	6
Dinitrophenol	1
DNB	2
Trinitrophenol	1
Dinitronaphthalene	1

Table 9. Detections of 3,5-dinitroaniline (3,5-DNA) by Method 8330.

Installation	*Concentration (µg/g) TNT*	*TNB*	*3,5-DNA*
Savanna Army Depot	0.12	< d	<d
Savanna Army Depot	1.5	0.16	0.12
Savanna Army Depot	3.14	19.8	0.35
Savanna Army Depot	3.68	2.04	0.1
Savanna Army Depot	4.07	1.6	0.07
Savanna Army Depot	13.1	9.44	0.14
Savanna Army Depot	17	0.46	0.14
Savanna Army Depot	40.6	12.9	0.24
Savanna Army Depot	69100	52.4	6.8
Nebraska Ord. Plant	< d	13.5	0.311
Nebraska Ord. Plant.	4	0.94	< d
Nebraska Ord. Plant.	0.12	< d	< d
Nebraska Ord. Plant.	2809	14.5	14.4
Nebraska Ord. Plant.	81	74.1	0.51
Nebraska Ord. Plant.	0.12	2.72	0.075
Nebraska Ord. Plant.	2.17	73.9	1.45
Nebraska Ord. Plant.	0.33	0.12	1.65
Nebraska Ord. Plant.	20350	42.5	2.77
Nebraska Ord. Plant.	259	0.86	< d
Nebraska Ord. Plant.	6.82	0.12	0.059
Detections	19	18	16
Total Occurrence (%)	95%	90%	80%
Occurrence with TNT (%)	100%	95%	84%
Occurrence with TNB(%)	94%	100%	89%
Low Conc. (µg/g)	0.12	0.12	0.059
High Conc. (µg/g)	69100	74.1	14.4
Median Conc.(µg/g)	4.07	6.08	0.28

< d–Less than detection limit.

but no tetryl was present on the LC-CN. Often 3,5-DNA cannot be confirmed on the LC-CN since it co-elutes with TNT. To see if 3,5-DNA is a commonly occurring transformation product, 20 soils with either TNT or TNB contaminants, but no tetryl, were analyzed using the parameters specified in 8330. An additional calibration standard was prepared to allow determination of 3,5-DNA. For the 18 samples with TNB, 16 also had peaks corresponding to 3,5-DNA (Table 9).

The formation of 3,5-DNA was observed in three soils spiked in the laboratory with aqueous solutions of TNB and held at either room temperature for 3 days or refrigerated for 2 weeks (Grant et al. 1993). Similarly, the two expected microbiological transformation products of 2,4-DNT, 2-amino-4-nitrotoluene and 4-amino-2-nitrotoluene were observed under these conditions.

Test of improved RP-HPLC separation for soils

As specified in Method 8330, a 25-cm × 4.6-mm × 5-µm octadecyldimethylsilyl (LC-18) column is eluted with 1.5 mL/min of 1/1 v/v methanol-water. This column and eluent combination provides baseline resolution of the most commonly found analytes in explosives-contaminated soils (i.e., HMX, RDX, TNB, DNB, TNT, DNT, and 2-Am-DNT). The column is rugged, maintaining resolution after the analysis of hundreds of samples. It does not, however, resolve the isomers 2,4-DNT and 2,6-DNT, nor the isomers 2-Am-4,6-DNT and 4-Am-2,6-DNT. Thus, in general, only one of the two pairs of isomers was identified and quantified for a given sample depending on which was present in higher concentration. Because the isomers of Am-DNT elute close to TNT, they will not be detected at low concentrations in the presence of high concentrations of TNT. Also, 3.5-dinitroaniline co-elutes with tetryl.

The separation scheme described for water analyses (Miyares and Jenkins 1990) was tested for soil analyses. Acetonitrile extracts of 16 soil samples with TNT concentrations ranging from 0.1 to 69100 µg/g (as determined using Method 8330) were diluted 1:3 with water prior to filtration and injection onto a 7.5-cm × 4.6-mm × 3-µm octyldimethylsilyl (LC-8) column eluted with 2 mL/min of 70.7/27.8/1.5 (V/V/V) water-methanol-THF.

Use of this separation scheme improved the detection capability for the isomers of Am-DNT and DNT. For example, 2-Am-DNT was detected in 16 out of 16 samples (Table 10) using the LC-8 column, and 11 out of the same samples using the LC-18 column. Of the five samples where 2-Am-DNT was not detected on the C-18 column, all had concentrations of TNT high enough to mask the significantly smaller amounts of the amino-DNTs. The LC-8 separation also improves the detection of 2,6-DNT. This analyte was found in 11 out of 16 samples using the LC-8 separation, but it was not detected in any samples using the LC-18 separation where it is not resolved from 2,4-DNT. In most cases, the concentration of 2,4-DNT reported for the LC-18 separation is actually the sum of 2,4-DNT and 2,6-DNT. In the two cases where 2,4-DNT was detected on the LC-8 and not the LC-18, the samples had been diluted by a factor of 10 prior to analysis on the LC-18. This dilution was made based on the deep orange color of the acetonitrile extracts of these soils that generally indi-

Table 10. Isomers of DNT and Am-DNT detected using using LC-18 and LC-8 columns.

	Concentration (µg/g)									
	TNT		2-Am-DNT		4-Am-DNT		2,6-DNT		2,4-DNT	
Installation	C-18	C-8	C-18	C-8	C-18	C-8	C-18	C-8	C-18	C-8
Savanna	0.12	0.117	0.33	0.22	< d	0.27	< d	<d	0.06	0.05
Nebraska	0.33	0.5	0.33	0.36	0.25	0.36	< d	<d	0.2	0.225
Savanna	1.5	1.25	0.78	0.44	< d	0.51	< d	<d	< d	< d
Nebraska	4	3.05	1.99	1.9	1.6	2.4	< d	<d	< d	< d
Savanna	3.14	3.47	0.28	0.09	< d	0.11	< d	0.08	0.28	0.02
Nebraska	2.17	3.65	0.25	0.35	< d	<d	< d	0.17	3.27	3.05
Savanna	3.68	3.66	< d	0.09	< d	0.09	< d	0.06	0.15	0.02
Savanna	4.07	4.12	< d	0.14	< d	0.19	< d	0.07	0.05	0.03
Nebraska	6.82	5.45	8.03	7.35	< d	4.5	< d	0.08	0.25	0.25
Savanna	13.1	12.9	< d	0.2	< d	0.13	< d	0.13	0.35	0.014
Savanna	17	15.7	7.99	5.4	< d	7.2	< d	0.1	0.65	0.58
Savanna	40.6	41.2	< d	0.38	< d	0.42	< d	0.31	< d	0.27
Nebraska	81	78.2	0.05	0.14	< d	0.92	< d	0.14	3.03	1.34
Nebraska	259	187.5	6.67	6.15	< d	8.35	< d	0.09	< d	0.5
Nebraska	2809	2910	2.7	8.3	< d	8.3	< d	< d	2.66	3.15
Savanna	69100	45800	< d	65.2	< d	70	< d	4.3	14.5	17
Detections	16	16	11	16	2	15	0	11	12	14
Occurrence (%)			69%	100%	13%	94%	0%	69%	75%	88%
Median	5.45	4.79	0.78	0.37	0.93	0.51		0.10	0.32	0.26

cates high concentrations of TNT. Without this dilution, 2,4-DNT most likely would have been detected. Thus, the LC-8 separation improves the determination of the individual concentrations of the isomers of DNT, but does not improve the ability to detect the presence of DNT.

The LC-8 separation has some drawbacks. First, the column has not proven to be rugged when used for long periods of time. Additionally, the separation is very sensitive to the eluent composition (i.e., small changes in the THF concentration result in significant changes in the separation of analytes). Also, in many samples, an unidentified compound co-elutes with TNB; the peak for this compound is observed in the chromatograms from blank soils as well as contaminated soils. For routine analysis, the LC-18 separation has proven to be reliable in that it resolves the analytes most likely to be present in munition-contaminated soils. The eluent is easy to prepare and the separation has been consistent from column to column. Therefore, we do not recommend a change to the LC-8 separation for routine analysis. If the objectives of a particular study require the resolution of isomers of DNT and Am-DNT, the LC-8 separation could be used for samples where explosives residues are detected by the LC-18 separation.

Field screening method for explosives residues in soil

Since the distribution of contamination at hazardous wastes sites is nonuniform, the more samples analyzed, the better the zones of contamination will be delineated. However, laboratory analyses are expensive, which sometimes limits the number of samples taken, and turnaround times can be weeks to months, reducing the efficiency of a site investigation. The ability to rapidly analyze samples on-site is a cost-effective alternative to laboratory analyses of every sample collected, especially when we consider that 72% of the samples we analyzed resulted in below-detection results (analytical zeros). To meet this need, we developed field screening procedures to detect RDX and TNT in soil.

Since almost all (94%) the soil samples with explosives detectable with Method 8330 contained TNT and/or RDX, testing soils for these two compounds would be an efficient way to screen for explosives-residue contamination. Of the contaminated soils that did not have TNT and/or RDX, all had tetryl, TNB, DNB, or 2,4-DNT, all of which are detectable by the field screening procedure described in the *Experimental* section.

Since the development and initial field testing of these procedures (Jenkins and Walsh 1992), the methods have been used by private contractors doing site assessments at Department of Defense installations. At Seneca Army Depot, 163 soils were tested for TNT using the field-screening approach. Of these, 18 gave positive results. When 15 of these positives were analyzed using Method 8330, nine had measurable levels of TNT, two had 2,4-DNT and two had TNB. Only two samples proved to be false positives. Of the samples giving negative results using the field screen method, 56 were analyzed by Method 8330, and all proved to be blank, indicating the procedure does not produce large numbers of false negatives. At Savanna Army Depot, nine samples were analyzed using the field screen procedures and Method 8330. RDX was not detected in any of these soils by either procedure. TNT was detected in eight samples using the field screening procedure, and the estimated concentration correlated well with the sum of TNT and TNB concentrations obtained using Method 8330 (Fig. 3).

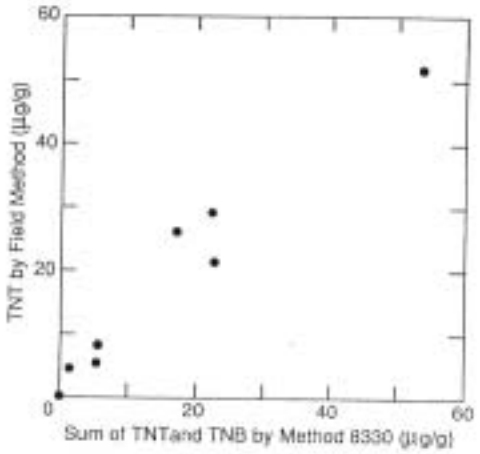


Figure 3. Correlation of estimates of TNT concentration obtained by the field method with those obtained by Method 8330 ($y = 1.03x + 0.39$, $R^2 = 0.98$).

The field screening procedures will produce quantitative estimates of TNT and RDX concentrations for many soils; however, they were not designed to replace laboratory analyses. While acetone is an excellent solvent for both TNT and RDX, extraction kinetics will be slow in some soils, specifically heavy, dense clays where diffusion is a rate-limiting step. Thus for these soils, the field protocol using only 3 minutes of manual shaking will result in lower results than for the laboratory method where an 18-hour extraction in an ultrasonic bath is specified.

Analytes found in water

Of the 812 water samples analyzed using Method 8330 by CRREL and MRD, 14% were found to be contaminated with explosives residues. Like the soils we analyzed, the principal contaminants were TNT and RDX (Tables 4, 11). Of the water samples with de-

Table 11. Explosives residues detected in water samples analyzed using Method 8330.

	CRREL	MRD	Total	
Installations	25	12	32	
Samples analyzed	462	350	812	
Samples with detectable explosives	57	57	114	
	No. of samples contaminated			
Analytes detected				% detections
HMX	15	1	16	14%
RDX	37	33	70	61%
1,3,5-TNB	16	16	32	28%
1,3-DNB	4	11	15	13%
Tetryl	2	13	15	13%
NB	2*	0	2	2%
TNT	34	30	64	56%
4-Am-DNT	15	2	17	15%
2-Am-DNT	13	13	26	23%
2,6-DNT	9	1†	10	9%
2,4-DNT	12	12	24	21%
2-NT	0	0	0	0%
4-NT	0	0	0	0%
3-NT	0	0	0	0%
TNT and/or RDX	54	53	107	94%

* Detected below reporting limit.
† Didn't differentiate 2,4- and 2,6-DNT.

tectable explosives, 61% contained RDX. This rate of detection was greater than that observed for soils, where RDX was found in 27% of the soils with detectable explosives. While both RDX and TNT can migrate through soil, RDX is less readily sorbed by soil than TNT (Table 4), and leaches at a higher rate (Kayser and Burlinson 1982). For example, when Spalding and Fulton (1988) investigated groundwater contamination from munition residues at Cornhusker Army Ammunition Plant, they found that the TNT plume was 0.8 km long while the plume for RDX was 6.5 km long, although TNT manufacture was initiated a decade before the manufacture of RDX. Since RDX migrates through soil more rapidly than TNT, it is more likely to be detected in monitoring wells farthest from the source of the contamination.

Of the water samples that were contaminated with RDX, 23% were also contaminated with HMX. All detections of HMX were in samples contaminated with RDX. Of the analytes determined by Method 8330, HMX is the least readily sorbed and will migrate the fastest through soil.

The TNT manufacturing by-products and transformation products observed in soils were also observed in water samples, and the rates of detection were similar. These analytes and rates of detection in TNT contaminated water samples were TNB(38%), DNB(16%), 2,6-DNT(14%), 2,4-DNT(36%), 4-Am-DNT (17%) and 2-Am-DNT (30%).

Throughout these water analyses, 3,5-dinitroaniline was not reported because it was not considered an analyte of interest. After 3,5-dinitroaniline was identified by GC/MS in extracts from soils, we began to analyze for it and find it in water samples (Fig. 2b).

CONCLUSIONS AND RECOMMENDATIONS

Method 8330 is intended for the analysis of explosives residues in soil and water. This RP-HPLC procedure was designed for routine analysis, and it uses laboratory equipment and supplies that are customarily available in analytical laboratories.

Of the analytes determined by Method 8330, TNT and RDX are the most commonly found in munition-contaminated soil and water. The environmental transformation products TNB and the isomers of Am-DNT, as well as the manufacturing by-products DNB and the isomers of DNT, are also frequently found. Neither the potential manufacturing by-product NB nor the isomers of nitrotoluene were detected above reporting limits in any of the 1155 soil or 812 water samples we analyzed. However, 3,5-dinitroaniline, a microbiological reduction product of TNB, was detected in soils and waters, and we recommend that this analyte be added to Method 8330. The inclusion of NB and the isomers of nitrotoluene as target analytes, however, appears to be unnecessary and leads to difficulties during calibration, because NB can interfere with tetryl and the inclusion of the nitrotoluenes requires unnecessarily lengthy run times.

The chromatographic separation specified in Method 8330 is adequate for the routine analysis of munition-contaminated soils. The isocratic elution of the octadecyldimethylsilyl (LC-18) column does not resolve isomers of some of the analytes, but is adequate for standard analysis of soil extracts. Confirmation of analytes using the cyano (LC-CN) column is satisfactory for the confirmation of TNT and of the nitramines, HMX and RDX. However, large concentrations of TNT interfere with the confirmation of DNT and 3,5-dinitroaniline. Since DNT is often found at concentrations that are orders of magnitude lower than TNT and the isomers of DNT have lower drinking water criteria than TNT, another scheme should be found to allow for their confirmation.

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13. ABSTRACT (*Maximum 200 words*)

A large body of analytical results from CRREL and the Missouri River Division Laboratory was used to assess how well EPA SW846 Method 8330 satisfies the Army need for characterization of explosives-contaminated water and soil samples. About 97% of the explosives-contaminated soils contained TNT, RDX and/or 2,4-DNT, and these were the compounds found at highest concentrations. Environmental transformation products such as TNB, 2-amino- and 4-amino-DNT and 3,5-dinitroaniline (3,5-DNA) were also frequently observed. Explosives-contaminated water samples generally contained RDX, HMX and/or TNT. Transformation products commonly found included TNB, DNB, 2,4- and 2,6-DNT, 3,5-DNA and the two isomers of amino-DNT. Limitations of the primary and confirmatory RP-HPLC methods are discussed.

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