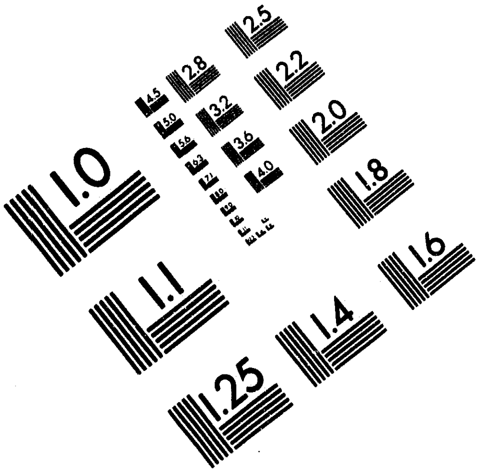

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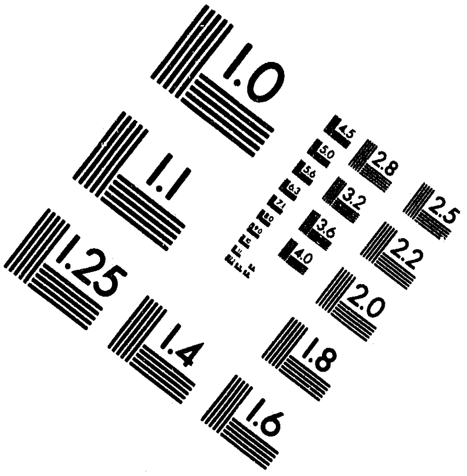

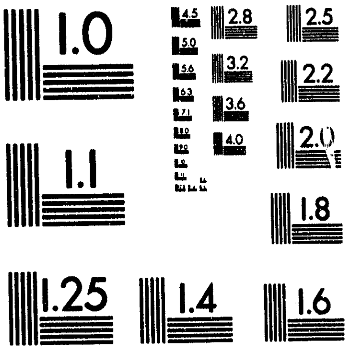

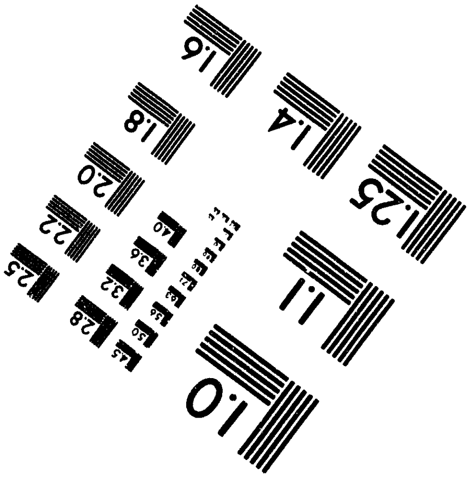

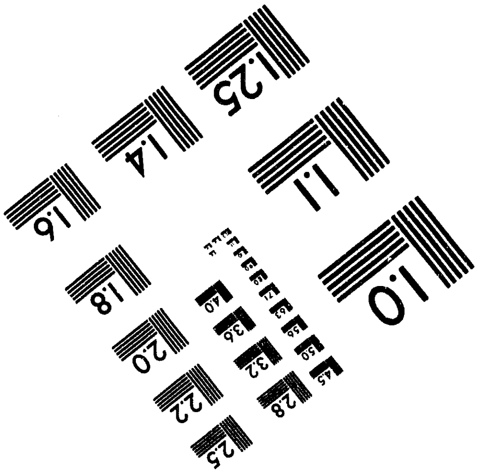

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Uptake of Explosives from Contaminated Soil by Existing Vegetation at the Joliet Army Ammunition Plant

by J.F. Schneider, N.A. Tomczyk, S.D. Zellmer, and W.L. Banwart*

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January 1994

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Acknowledgments

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Uptake of Explosives from Contaminated Soil by Existing Vegetation at the Joliet Army Ammunition Plant

by

J.F. Schneider, N.A. Tomczyk, S.D. Zellmer, and W.L. Banwart

Abstract

This study examines the uptake of explosives by existing vegetation growing in TNT-contaminated soils on Group 61 at the Joliet Army Ammunition Plant (JAAP). The soils in this group were contaminated more than 40 years ago. In this study, existing plant materials and soil from the root zone were sampled from 15 locations and analyzed to determine TNT uptake by plants under natural field conditions. Plant materials were separated by species if more than one species was present at a sampling location. Standard methods were used to determine concentrations of explosives, their derivatives, and metabolites in the soil samples. Plant materials were also analyzed. No explosives were detected in the aboveground portion of any plant sample. However, the results indicate that TNT, 2-amino DNT, and/or 4-amino DNT were found in some root samples of false boneset (*Kuhnia eupatorioides*), teasel (*Dipsacus sylvestris*), and bromegrass (*Bromus inermis*). It is possible that slight soil contamination remained on the roots, especially in the case of the very fine roots for species like bromegrass, where washing was difficult. The presence of 2-amino DNT and 4-amino DNT, which could be plant metabolites of TNT, increases the likelihood that explosives were taken up by plant roots, as opposed to their presence resulting from external soil contamination.

1 Introduction

1.1 Related Research

Limited information has been published on the uptake of explosives from contaminated soils by plants. Palazzo and Leggett (1986) investigated the uptake of 2,4,6-trinitrotoluene (TNT) by yellow nutsedge grown in hydroponic solutions. They discovered that the condition of plants (weight, height, length) was affected by the presence of TNT in the solution, but when the concentration was increased from 5 to 20 mg/L, they observed no significant difference in the effects. As the initial TNT concentration was increased, however, the metabolites 2-amino- and 4-aminodinitrotoluene (2-ADNT and 4-ADNT) also increased, with 4-ADNT produced more than three times as often as 2-ADNT in all parts of the plant except the leaves. Because no metabolites were detected in the solution, the authors believe that the plants were producing the metabolites. Folsom et al. (1988) and Pennington (1988) also studied TNT uptake by nutsedge from soils amended with TNT. Results of these studies show minimal uptake of TNT by the leafy portions of the plants.

Harvey et al. (1991) examined uptake of TNT by bush beans grown in hydroponic solutions containing 10 mg/L of TNT. Results of this study showed low concentrations of TNT (0.2 to 0.3 mg/kg) in leaf material but much higher concentrations of TNT (6.0 to 7.0 mg/kg) in root material. A study in hydroponics that used radio-labeled TNT (Harvey et al. 1990) showed uptake of TNT into the roots, with some radio-label deposition in stem and leaf tissue as well. Chromatographic results showed that aminodinitrotoluene isomers (2-ADNT and 4-ADNT) were found in root tissue, but investigators were unsure of their origin. Possible explanations for the isomers' presence were that the roots drew the isomers up from the solution or that the TNT was metabolized by either the root tissue or the microorganisms associated with the root tissue. Harvey et al. (1993) also showed uptake of tetryl by plants in a hydroponics study that used radio-labeled tetryl. The greater portion of tetryl was found in the root tissue, with less in the stems and still less in the leaves. The study also showed evidence of tetryl being metabolized to polar compounds.

Banwart et al. (1991) examined the uptake, in the greenhouse, of 1,3,5-trinitro-1,3,5-triazine (RDX) by corn, soybeans, sorghum, and wheat, from soils spiked with four levels of RDX. Results of their investigation showed that concentrations of RDX in plant materials increased as RDX levels in the soil increased. The investigation determined the uptake of explosives by plants grown in hydroponic solutions or grown in soils amended with explosives under greenhouse conditions. The potential for explosives entering the food chain through uptake by plants under field conditions has not been documented.

1.2 Group 61 Field Investigation

This study examines the uptake of explosives by existing vegetation growing in TNT-contaminated soils on Group 61 at the Joliet Army Ammunition Plant (JAAP). JAAP is a government-owned, contractor-operated U.S. Army industrial facility encompassing 23,544 acres of prime agricultural land in Will County, approximately 17 mi south of Joliet, Illinois. Group 61 is located in the north-central portion of the Load-Assemble-Package (LAP) area of JAAP, covers approximately 80 acres, and was constructed in 1941 as part of the installation (Figure 1). Group 61 facilities were originally used for crystallizing ammonium nitrate, but they were extensively modified in 1945 to reclaim TNT from high-explosive shells. The reclamation operation involved the removal and recycling of explosives and a shell washout operation. Process water (pink water) from the washout operation was collected in a large sump. Overflow from the sump was disposed of by infiltration and evaporation in a 4-acre ridge-and-furrow area (Figure 2).

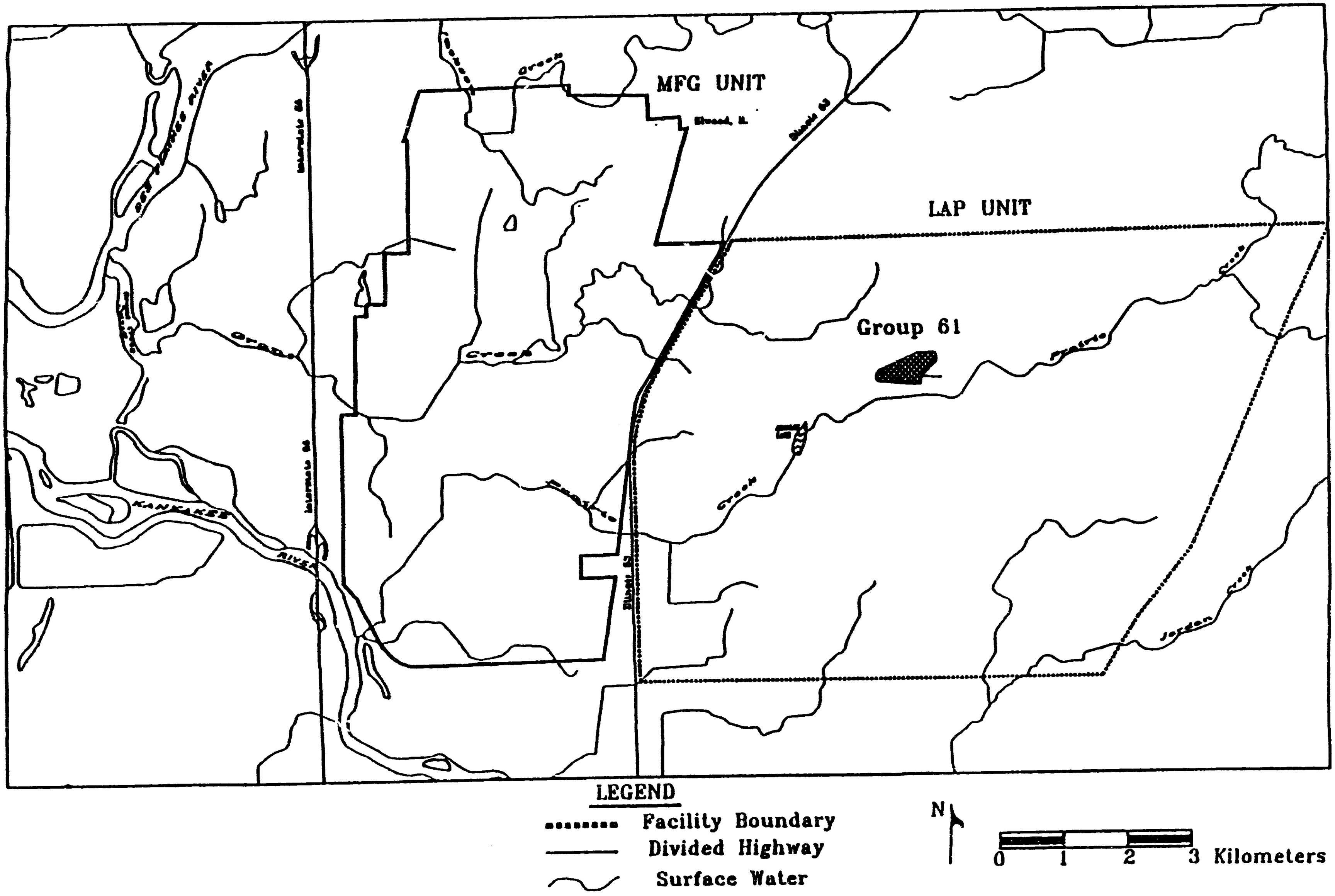

FIGURE 1 Location of Group 61 at the Joliet Army Ammunition Plant

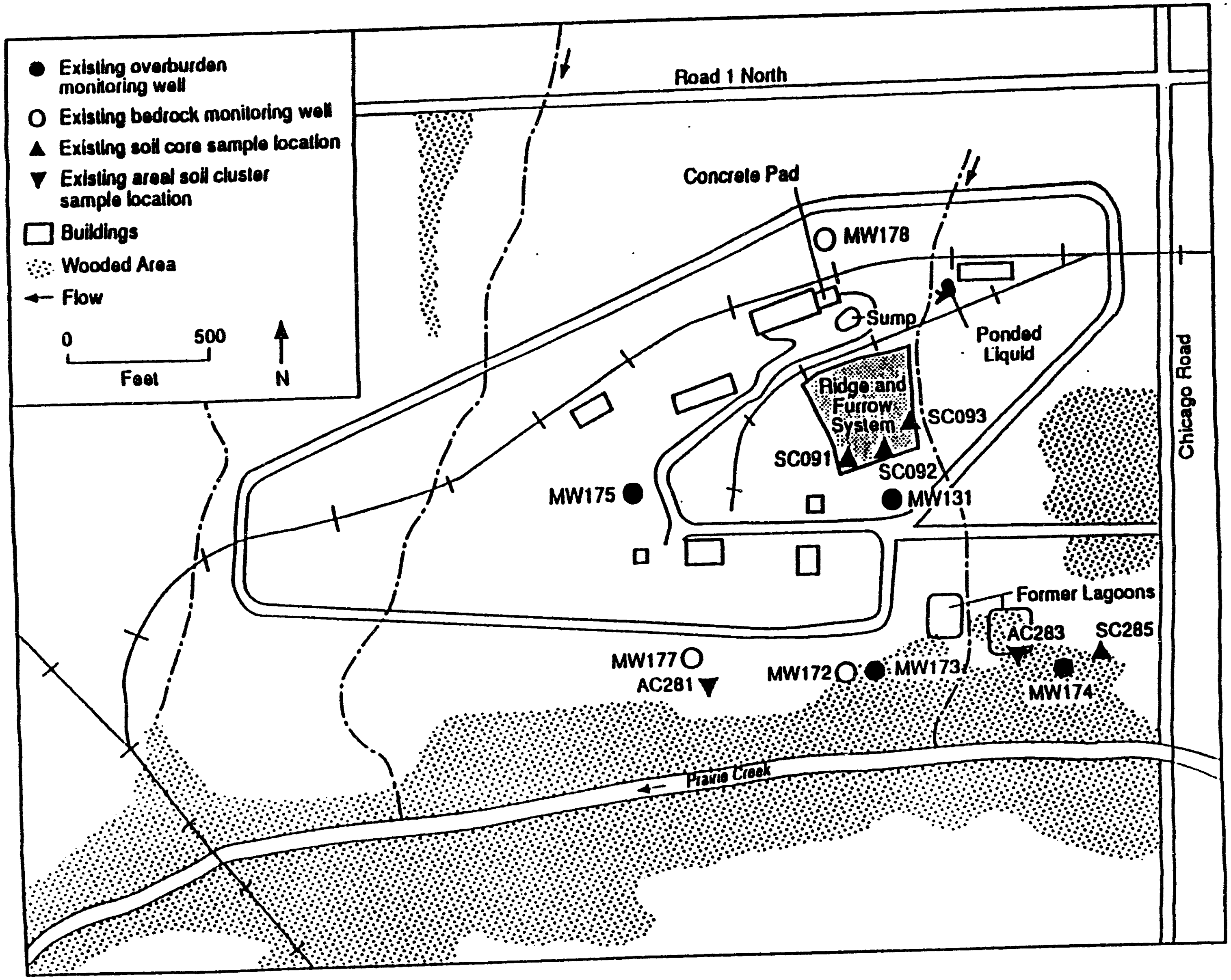

FIGURE 2 Previous Sample Locations at Group 61 (Source: Adapted from Ritchie et al. 1991)

In the years following the closure of Group 61 facilities, erosion partially leveled the ridges and filled the furrows of the ridge-and-furrow area. Furrows on 7-ft centers are still evident, varying from 0 to 8 in. deep, depending on the degree of erosion. Plant cover, consisting of smooth bromegrass, other grasses, and forbs, has developed on the eastern portion of the site. Vegetative cover has developed on the ridges, but the presence of TNT in some areas of the furrow surface soil is evident by a reddish color and a lack of vegetation. The surface soil of the western portion of the site is rocky and has the appearance of subsoil or glacial till. Vegetative cover in this portion of the site is sparse and consists mainly of forbs. The lack of plant cover in this portion of the ridge-and-furrow area may result from high concentrations of TNT in the soil, low soil fertility, or poor physical condition of the soil. The soil in Group 61 was contaminated with TNT more than 40 years ago. In this study, existing plant materials and soil from the root zone were sampled and analyzed to determine TNT uptake by plants under natural field conditions.

2 Experimental Procedure

Fifteen sampling locations were selected within the ridge-and-furrow area at Group 61 at JAAP (Figure 3). Sampling locations were divided into three groups, with five locations in each group, representing high, intermediate, and low levels of soil TNT contamination. (The level of contamination has been determined by previous studies; see Appendix A, adapted from Dames & Moore 1991.) Soil samples were taken to confirm the level of contamination (Appendix B). Soil from the root zone and existing vegetative materials were collected from each location. Plant materials were separated by species if more than one species was present at a sampling location (see Table 1). Standard U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) methods were used to determine concentrations of explosives, their derivatives, and metabolites in the soil samples (see Appendix C). All analyses were performed by Wayne Banwart (University of Illinois at Champaign-Urbana), who is USATHAMA-certified.[1] Plant materials were analyzed to determine concentrations of explosives, their derivatives, and metabolites by using the methods described below. Additional soil samples were collected from random locations in the ridge-and-furrow area to characterize the toxicity of the soil by means of the U.S. Environmental Protection Agency (EPA) toxic characteristic leaching procedure (TCLP).

At each selected sampling location, vegetation was clipped to about 1 in. above the soil surface. Care was taken to prevent contact of the plant material with the soil and not to include plant materials that had been in direct contact with the soil in the plant samples. Plant materials were separated by species during collection. Roots were analyzed separately from the above-ground portions of the plants. Previous studies have shown that rinsing with distilled water removes surface TNT contamination from plant material. Root samples were washed with a mechanical elutriator in an attempt to remove any surface TNT contamination.

USATHAMA-approved high-pressure liquid chromatographic (HPLC) methods were employed to determine concentrations of explosives and their derivatives in soil at each sampling location. A method developed by Banwart and Hassett (1990), involving extraction, cleanup, and HPLC with ultraviolet detection, was used to analyze plant materials. The following procedure was used to determine presence of and concentrations of TNT in plant material:

1. Plant samples are dried at 26°C. One-half gram of ground plant sample (60 mesh) is weighed into a 25-mL Corvex tube equipped with a Teflon-lined screw cap.

2. Ten milliliters of dichloromethane is added to each tube. The tubes are placed in a water bath with cooling water and sonicated for 12 to 15 h.

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[1] Wynne, D.J., Technical Support Division, U.S. Army Environmental Center, Aberdeen, Md., personal communication to W.L. Banwart, March 5, 1993.

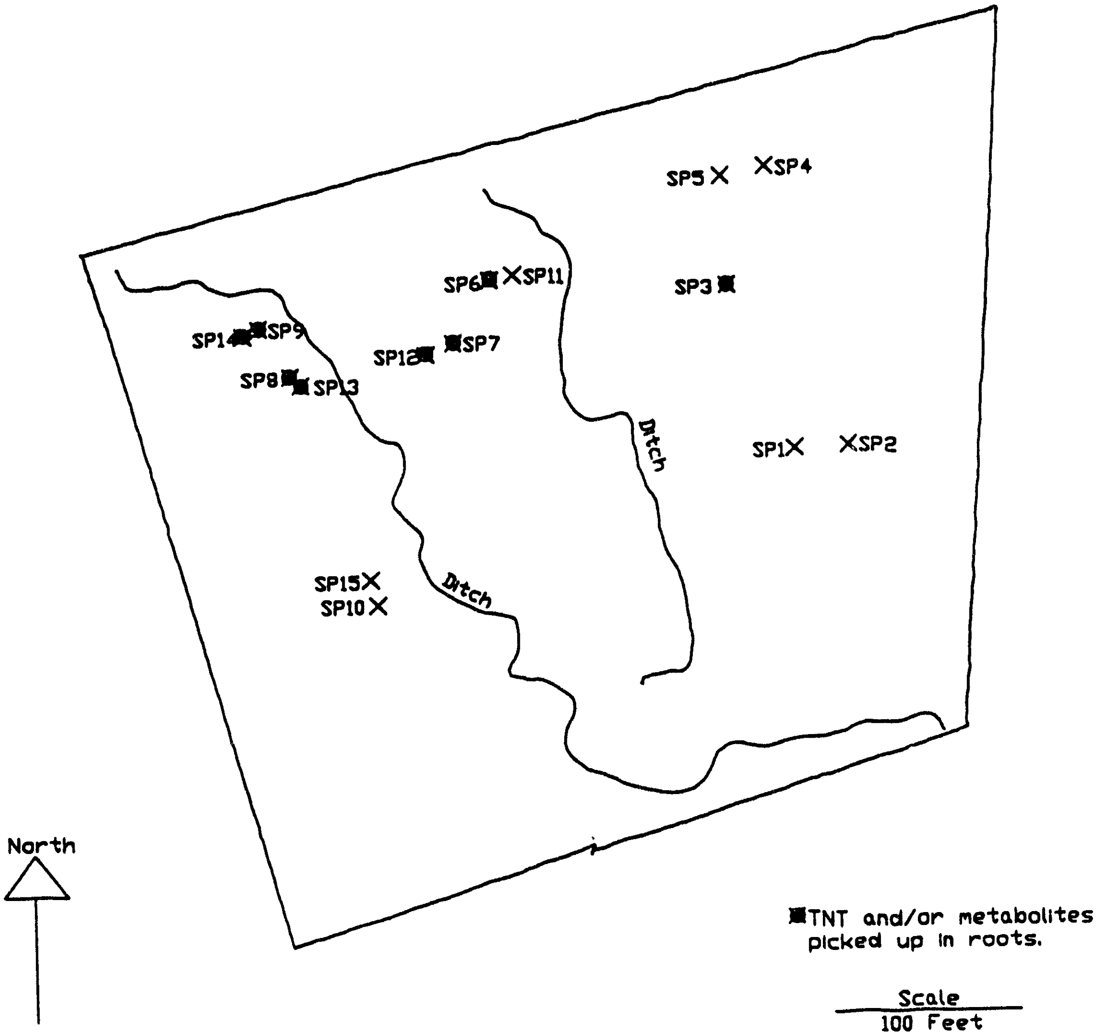

FIGURE 3 TNT Sample Locations at the Joliet Army Ammunition Plant, Group 61 — Ridge and Furrow Area

3. A 2.5-mL aliquot of dichloromethane extract is removed, placed in a glass scintillation vial, and evaporated to dryness by air.

4. Five milliliters of 15% hexane in dichloromethane is added on the surface of a Florisil solid-phase extraction cartridge to equilibrate the cartridge.

5. The residue of sample from Step 3 is dissolved in 1 mL of 15% hexane in dichloromethane and added on the surface of the cartridge.

6. Three milliliters of 15% hexane in dichloromethane is eluted through the Florisil cartridge to wash out the less polar compounds.

TABLE 1 Results of Explosives Analysis[a]

Location	Plant		Soil TNT	Plant Top			Root		
	Common Name	Botanical Name		TNT	4-ADNT	2-ADNT	TNT	4-ADNT	2-ADNT
SP1	Bromegrass	*Bromus inermis*	BDL[b]	BDL	BDL	BDL	BDL	BDL	BDL
SP1	Milkweed	*Asclepias syriaca*	BDL	BDL	BDL	BDL	BDL	BDL	BDL
SP2	Bromegrass	*Bromus inermis*	BDL	BDL	BDL	BDL	BDL	BDL	BDL
SP2	Teasel	*Dipsacus sylvestris*	BDL	BDL	BDL	BDL	BDL	BDL	BDL
SP3	False Boneset	*Kuhnia eupatorioides*	1.00	BDL	BDL	BDL	0.13	BDL	0.93
SP3	Milkweed	*Asclepias syriaca*	1.00	BDL	BDL	BDL	0.60	BDL	BDL
SP3	Bromegrass	*Bromus inermis*	1.00	BDL	BDL	BDL	4.50	BDL	BDL
SP4	Vervain	*Verbena hastata*	1.50	BDL	BDL	BDL	BDL	BDL	BDL
SP4	Bromegrass	*Bromus inermis*	1.50	BDL	BDL	BDL	BDL	BDL	BDL
SP5	Ground Cherry	*Physalis heterophylla*	1.60	BDL	BDL	BDL	BDL	BDL	BDL
SP5	Bromegrass	*Bromus inermis*	1.60	BDL	BDL	BDL	BDL	BDL	BDL
SP6	Teasel	*Dipsacus sylvestris*	6,260	BDL	BDL	BDL	0.15	2.12	1.15
SP6	Bromegrass	*Bromus inermis*	6,260	BDL	BDL	BDL	2.33	4.29	4.43
SP7	Teasel	*Dipsacus sylvestris*	492	BDL	BDL	BDL	BDL	0.57	BDL
SP7	Bromegrass	*Bromus inermis*	492	BDL	BDL	BDL	BDL	0.63	BDL
SP8	Milkweed	*Asclepias syriaca*	278	BDL	BDL	BDL	BDL	BDL	BDL
SP8	Bromegrass	*Bromus inermis*	278	BDL	BDL	BDL	0.29	0.88	1.28
SP9	Bromegrass	*Bromus inermis*	5,840	BDL	BDL	BDL	5.85	5.71	7.71
SP9	Alfalfa	*Medicago sativa*	5,840	BDL	BDL	BDL	NT	NT	NT
SP10	Chicory	*Cichorium intybus*	3,360	BDL	BDL	BDL	BDL	BDL	BDL
SP10	Queen Anne's Lace	*Daucus carota*	3,360	BDL	BDL	BDL	BDL	BDL	BDL
SP11	Bromegrass	*Bromus inermis*	3,410	BDL	BDL	BDL	BDL	BDL	BDL
SP12	Teasel	*Dipsacus sylvestris*	39,350	BDL	BDL	BDL	BDL	BDL	BDL
SP12	Bromegrass	*Bromus inermis*	39,350	BDL	BDL	BDL	3.85	3.72	4.35
SP13	Alfalfa	*Medicago sativa*	5,340	BDL	BDL	BDL	BDL	BDL	BDL
SP13	Bromegrass	*Bromus inermis*	5,340	BDL	BDL	BDL	0.86	2.74	3.20
SP14	Milkweed	*Asclepias syriaca*	3,350	BDL	BDL	BDL	BDL	BDL	BDL
SP14	Chicory	*Cichorium intybus*	3,350	BDL	BDL	BDL	BDL	BDL	BDL
SP14	Bromegrass	*Bromus inermis*	3,350	BDL	BDL	BDL	BDL	1.55	1.13
SP14	Alfalfa	*Medicago sativa*	3,350	BDL	BDL	BDL	BDL	BDL	BDL
SP15	Chicory	*Cichorium intybus*	202	BDL	BDL	BDL	BDL	BDL	BDL
SP15	Queen Anne's Lace	*Daucus carota*	202	BDL	BDL	BDL	BDL	BDL	BDL
		DETECTION LIMIT		0.08	0.20	0.20	0.08	0.20	0.20

[a] All units mg/kg (ppm).

[b] BDL = Below Detection Limit.

7. Five milliliters of 12% ethyl acetate in dichloromethane is added to elute the explosive compounds.

8. The collected fraction is evaporated to dryness, and the residue is dissolved in 1 mL of acetonitrile. One milliliter of HPLC-grade water is added, and the sample mixture is filtered through a Nalgene 0.2-µm filter. The sample is then analyzed by HPLC.

These analyses were performed in a USATHAMA-certified laboratory at the University of Illinois at Urbana, Illinois. Spiked samples were run to check the validity of the procedure. On plant tops, spike recovery averaged 89% for TNT, 60% for 4-ADNT, and 90% for 2-ADNT. For roots, the spike recovery averaged 66% for TNT, 48% for 4-ADNT, and 84% for 2-ADNT.

Four soil samples for TCLP analyses were collected from each quadrant of Group 61 (Figure 4). Samples were placed in precleaned glass bottles, sealed, and delivered to a commercial laboratory (Heritage Laboratories, Inc.) for TCLP analysis by means of EPA method SW846-1311. Results from the TCLP analyses were used to characterize the toxicity of the soil from the ridge-and-furrow area.

Table 2 contains the analytical results of the TCLP samples taken in the ridge-and-furrow area of Group 61. No targeted TCLP compounds were detected in the samples. For the purposes of this study, the results indicate that the soil in Group 61 cannot be classified as a toxic waste.

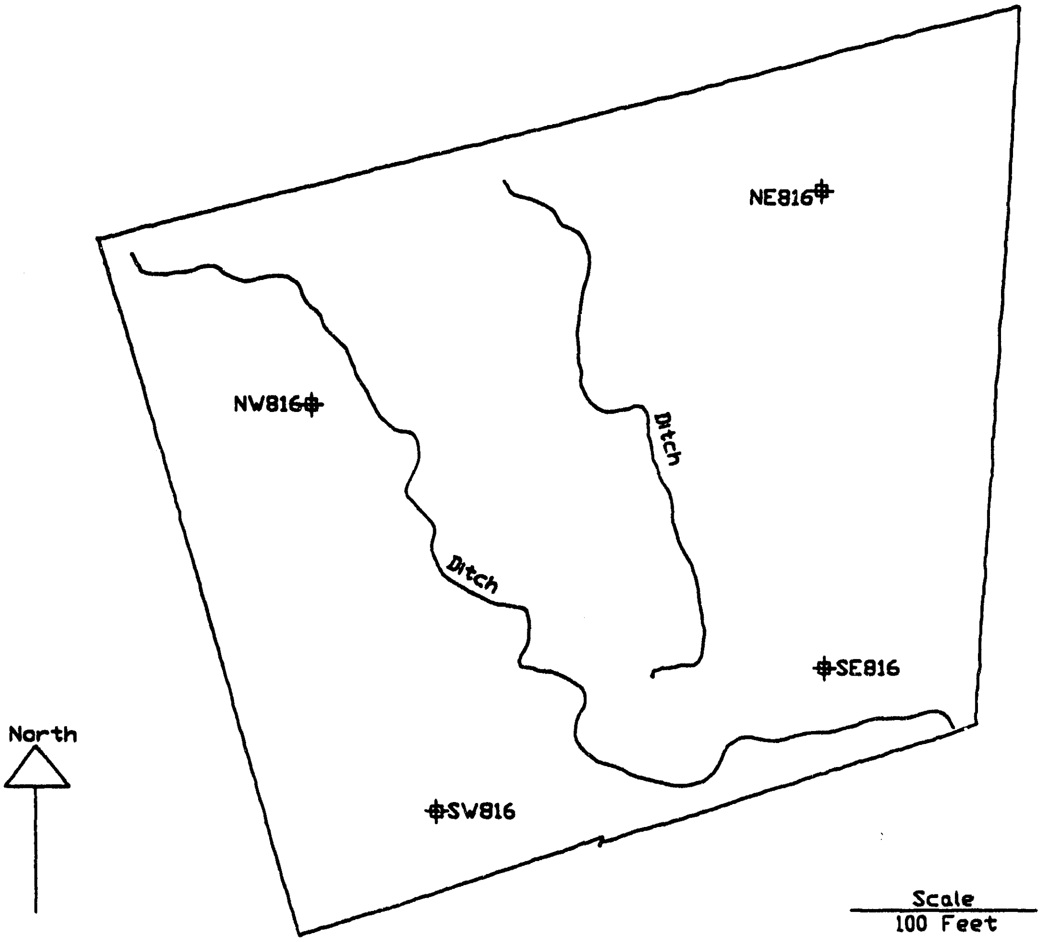

FIGURE 4 TCLP Sample Locations at the Joliet Army Ammunition Plant, Group 61 — Ridge and Furrow Area

TABLE 2 TCLP Results[a]

Analyte	Sample				Detection Limits
	NM	NE	SW	SE	
Barium	3.4	1	0.56	0.98	0.02
Cadmium	BDL[b]	BDL	BDL	BDL	0.04
Chromium	BDL	BDL	BDL	BDL	0.05
Lead	BDL	BDL	BDL	BDL	0.25
Silver	BDL	BDL	BDL	BDL	0.05
Arsenic	BDL	BDL	BDL	BDL	0.01
Selenium	BDL	BDL	BDL	BDL	0.01
Mercury	BDL	BDL	BDL	BDL	0.005
1,4-Dichlorobenzene	BDL	BDL	BDL	BDL	0.05
2,4-Dinitrotoluene	BDL	BDL	BDL	BDL	0.05
Hexachlorobenzene	BDL	BDL	BDL	BDL	0.05
Hexachlorobutadiene	BDL	BDL	BDL	BDL	0.05
Hexachloroethane	BDL	BDL	BDL	BDL	0.05
Nitrobenzene	BDL	BDL	BDL	BDL	0.05
Pyridine	BDL	BDL	BDL	BDL	0.25
2-Methyl Phenol	BDL	BDL	BDL	BDL	0.13
3-Methyl Phenol	BDL	BDL	BDL	BDL	0.13
4-Methyl Phenol	BDL	BDL	BDL	BDL	0.13
Pentachlorophenol	BDL	BDL	BDL	BDL	0.25
2,4,5-Trichlorophenol	BDL	BDL	BDL	BDL	0.13
2,4,6-Trichlorophenol	BDL	BDL	BDL	BDL	0.13
Benzene	BDL	BDL	BDL	BDL	0.05
Carbon Tetrachloride	BDL	BDL	BDL	BDL	0.05
Chlorobenzene	BDL	BDL	BDL	BDL	0.05
Chloroform	BDL	BDL	BDL	BDL	0.05
1,2-Dichloroethane	BDL	BDL	BDL	BDL	0.05
1,1-Dichloroethylene	BDL	BDL	BDL	BDL	0.05
Methyl Ethyl Ketone	BDL	BDL	BDL	BDL	0.1
Tetrachloroethylene	BDL	BDL	BDL	BDL	0.05
Trichloroethylene	BDL	BDL	BDL	BDL	0.05
Vinyl Chloride	BDL	BDL	BDL	BDL	0.1
Lindane	BDL	BDL	BDL	BDL	
Heptachlor	BDL	BDL	BDL	BDL	
Heptachlor Epoxide	BDL	BDL	BDL	BDL	
Endrin	BDL	BDL	BDL	BDL	
Methoxychlor	BDL	BDL	BDL	BDL	
Chlordane	BDL	BDL	BDL	BDL	

[a] All units mg/kg (ppm).

[b] BDL = Below Detection Limit.

3 Results and Conclusions

Table 1 (page 8) contains the analytical results for the soil and plant material sampled in 15 locations in the ridge-and-furrow area. Locations SP1 to SP5 were areas of low contamination (less than 5 mg/kg). Locations SP6 to SP15 were areas of intermediate to high levels of TNT contamination. For all areas, only one sample (SP8 milkweed) gave an indication of TNT in the aboveground portion of the plant, and that was below the detection limit of 0.08 mg/kg. Therefore, no detection of TNT or the amino compounds was confirmed in any of the plant parts above the ground. Some chromatograms contained peaks that represent unidentified organic compounds extracted from plants, but retention times did not match those for TNT or the amino derivatives. Figure 5 is a chromatogram of a standard mix of explosives.

The results indicate that TNT, 2-ADNT, and/or 4-ADNT were found in some root samples of false boneset *(Kuhnia eupatorioides)*, teasel *(Dipsacus sylvestris)*, and bromegrass *(Bromus inermis)*. Visual observation of the root samples showed that the mechanical elutriator appeared to have removed all of the potential contaminants from the soils. However, it is possible that some slight soil contamination remained, especially in the case of the very fine roots for species like bromegrass, for which washing was more difficult. The presence of 2-ADNT and 4-ADNT, which could be plant metabolites of TNT, increases the likelihood that explosives were taken up by plant roots, as opposed to their presence resulting from external soil contamination.

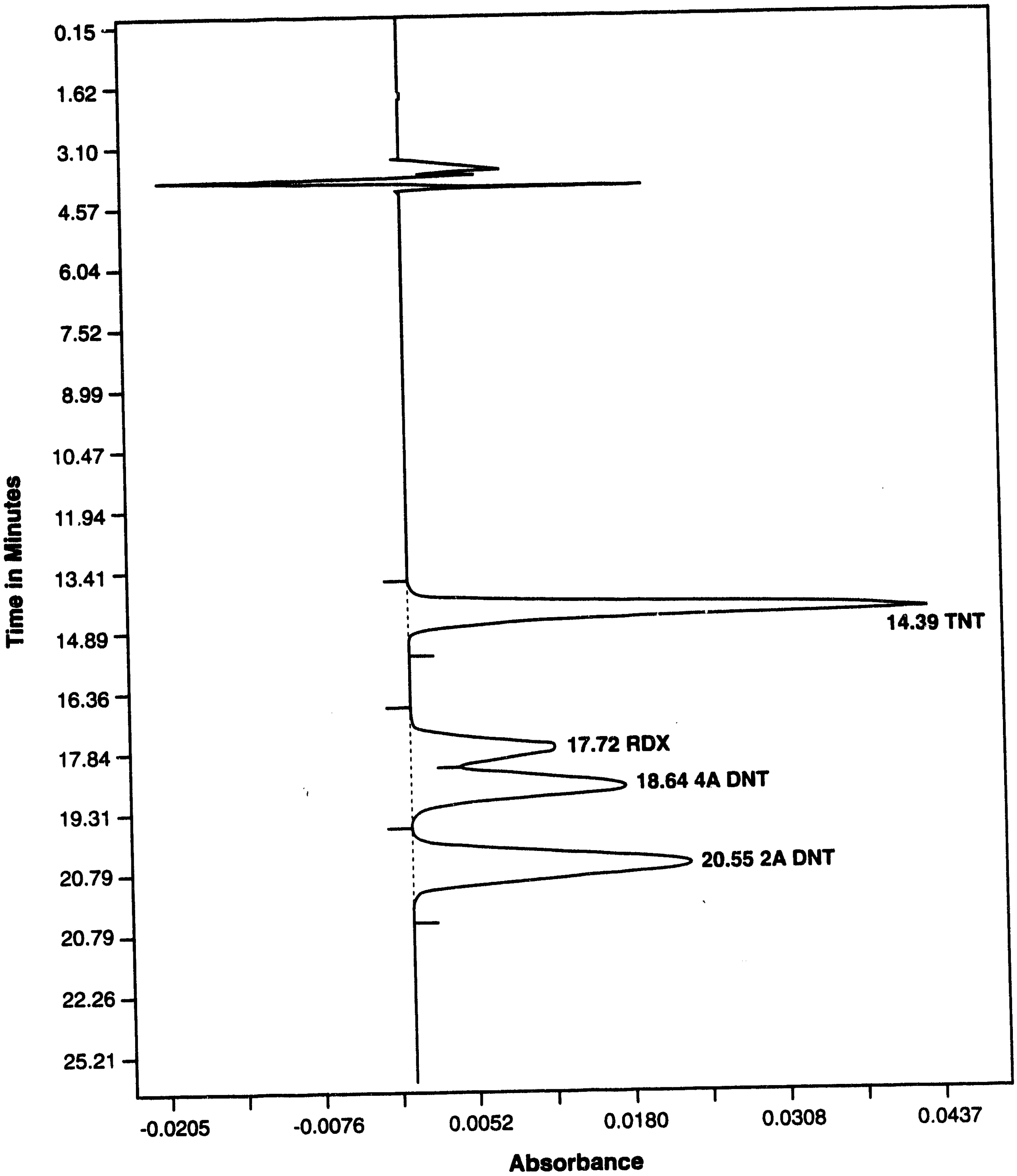

FIGURE 5 Chromatogram of Standard Explosives Mix

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Appendix A:

Analytical Chemistry Data from Previous Sampling Events at Group 61*

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* Adapted from Dames & Moore 1991. (Samples SC091, SC092, and SC093 are from the ridge-and-furrow area.)

Chemical Analysis Results from Group 61

Sample Location	Date	Sample Depth (cm) or Aquifer	Units	2,4,6-TNT	2,6-DNT	2,4-DNT	2NT	1,3,5-TNB	1,3-DNB	TETRYL	NNDMA	RDX	HMX
SC091	5/27/81	0	mg/kg	14,400.00 +	BDL	BDL	BDL	235.00 +	-	-	-	-	-
	5/27/81	15	mg/kg	25.00 +	BDL	BDL	BDL	10.20 +	-	-	-	-	-
	5/27/81	30	mg/kg	5.42 +	BDL	BDL	BDL	BDL	-	-	-	-	-
SC092	5/26/81	0	mg/kg	20.30 +	BDL	BDL	BDL	BDL	-	-	-	-	-
	5/26/81	18	mg/kg	3.14 +	BDL	BDL	BDL	BDL	-	-	-	-	-
	5/26/81	43	mg/kg	20.00 +	BDL	BDL	BDL	BDL	-	-	-	-	-
SC093	5/26/81	0	mg/kg	14,500.00 +	BDL	12.70 +	10.4	182.00 +	-	-	-	-	-
	5/26/81	18	mg/kg	6.27 +	BDL	BDL	BDL	28.90 +	-	-	-	-	-
	5/26/81	49	mg/kg	430.00 +	BDL	BDL	BDL	54.10 +	-	-	-	-	-
AC281	11/2/82	0	mg/kg	BDL	BDL	BDL	BDL	BDL	-	-	-	-	-
AC283	11/2/82	0	mg/kg	BDL	BDL	BDL	BDL	BDL	-	-	-	-	-
SC285	11/2/82	0	mg/kg	BDL	BDL	BDL	BDL	BDL	-	-	-	-	-
	11/2/82	30	mg/kg	BDL	BDL	BDL	BDL	BDL	-	-	-	-	-
	11/2/82	61	mg/kg	BDL	BDL	BDL	BDL	BDL	-	-	-	-	-
MW131	6/10/81	U	mg/kg	2,250.00 +	3.40 +	0.98 +	BDL	973.00 +	-	-	-	-	-
	6/24/82 R	U	mg/kg	744.00 +	1.80	0.70 +	1.90 +	725.00 +	-	-	-	-	-
	11/15/85	U	mg/kg	2,150.00 +	4.14 +	2.01 +	-	1,610.00 +	5.00 +	58.60 +	-	BDL	-
	4/22/84	U	mg/kg	576.00 +	8.54 +	BDL	-	755.00 +	BDL	21.7	-	BDL	-
MW172	3/9/83	D	mg/kg	40.80 +	BDL	BDL	BDL	9.20 +	-	-	-	-	-
	10/30/85	D	mg/kg	16.20 +	BDL	BDL	-	3.06 +	BDL	BDL	-	14.20 +	-
	4/14/86	D	mg/kg	12.90 +	BDL	BDL	-	3.84 +	BDL	BDL	-	7.22	-
MW173	3/9/83	U	mg/kg	50.30 +	BDL	BDL	BDL	6.87 +	-	-	-	-	-
	10/31/85	U	mg/kg	105.00 +	BDL	BDL	-	14.00 +	BDL	BDL	-	56.50 +	-
	4/14/86	U	mg/kg	11.00 +	BDL	BDL	-	2.09 +	BDL	BDL	-	8	-
MW174	3/10/83	U	mg/kg	BDL	BDL	BDL	BDL	BDL	-	-	-	-	-
	10/31/85	U	mg/kg	BDL	BDL	BDL	-	BDL	BDL	BDL	-	BDL	-
	4/14/86	U	mg/kg	BDL	BDL	BDL	-	BDL	BDL	BDL	-	BDL	-
MW175	4/14/86	U	mg/kg	BDL	BDL	BDL	-	BDL	BDL	BDL	-	BDL	-
MW177	3/9/83	U	mg/kg	0.31	BDL	BDL	BDL	BDL	-	-	-	-	-
	10/30/85	U	mg/kg	BDL	BDL	BDL	-	BDL	BDL	BDL	-	BDL	-
	4/14/86	U	mg/kg	BDL	BDL	BDL	-	BDL	BDL	BDL	-	BDL	-
MW178	3/9/83	U	mg/kg	0.38	BDL	BDL	BDL	BDL	-	-	-	-	-
	11/6/85	U	mg/kg	BDL	BDL	BDL	-	BDL	BDL	BDL	-	BDL	-
	4/14/86	U	mg/kg	BDL	BDL	BDL	-	BDL	BDL	BDL	-	BDL	-

Appendix B:

Summary of Analysis for Explosives from Previous Sampling Events at Group 61

SUMMARY OF ANALYSIS FOR EXPLOSIVES

SAMPLES RECEIVED FROM JOLIET AAP

METHOD OF ANALYSIS: EPA METHOD 8330: ACN EXTRACTION

LOCATION	SAMPLE NUMBER	DATE REC'D	DATE EXTR	DATE ANALYZED	DATE CONFIRMED	ANAL	HMX	TNB	RDX	DNB	NB	TNT	24DNT	26DNT	pNT	2ADNT	4ADNT
SOIL SAMPLES FROM JOLIET AAP																	
CLS100W*4-MS	A-1		12/18/91	12/21/91	12/22/91	PHM	<D	177	31.6	1.80	<D	29800	13.2	<D	<D	<D	<D
CLS100W*4-MS	A-2		12/18/91	12/21/91	12/22/91	PHM	<D	171	28.2	2.70	<D	31100	13.6	<D	<D	<D	<D
CLS100W*4-MS	B-1		12/18/91	12/21/91	12/22/91	PHM	<D	179	29.5	2.60	<D	27000	10.4	<D	<D	<D	<D
CLS100W*4-MS	B-2		12/18/91	12/21/91	12/22/91	PHM	<D	162	33.4	1.90	<D	23600	9.80	<D	<D	<D	<D
SOIL BLANK			12/18/91	12/21/91	12/22/91	PHM	<D	<D	<D	<D	<D	<D	<D	<D	<D	<D	<D
SPIKED SOIL	A		12/18/91	12/21/91	12/22/91	PHM	4.47	0.57	0.90	0.92		0.73	0.99			0.76	
	B		12/18/91	12/21/91	12/22/91	PHM	4.12	0.55	0.76	0.86		0.73	0.99			0.75	
KNOWN CONC							5.00	1.00	1.00	1.00		1.01	1.00			0.70	
CERTIFIED REPORTING LIMITS (ug/g)							2.20	0.24	1.00	0.12	0.11	0.24	0.07	0.16	0.25	0.11	0.2est

CONCENTRATION IN SOIL SAMPLES (ug/g)

t = TRACE LEVELS DETECTED BUT CONCENTRATION IS BELOW THE CRL

Appendix C:

Documentation of Analytical Method (LW-22) for Explosives Analysis

DOCUMENTATION OF ANALYTICAL METHOD (LW-22)

FOR EXPLOSIVES ANALYSIS

I. Summary

A. Analytes

Chemical Name	Abbreviation
1. hexahydro - 1,3,5 - trinitro - 1,3,5 - triazine	(RDX)
2. 1,3,5 - trinitrobenzene	(135TNB)
3. 2,4,6 - trinitrotoluene	(246TNT)
4. 2,6 - dinitrotoluene	(26DNT)
5. 2,4 - dinitrotoluene	(24DNT)

B. Matrix

The matrix is soil.

C. General Method for Explosives Analysis in Soils

Soil is extracted with acetonitrile. The extractant is combined with an aqueous $CaCl_2$ solution and filtered. The filtered extract is analyzed by UV detection on reverse phase HPLC. Analyte concentrations in the soil are then calculated.

II. Application

A. Tested Concentration Range (soil matrix)

Analyte	Conc. range in a soil matrix
RDX	1.0 µg/g to 100 µg/g soil
135TNB	0.5 µg/g to 50 µg/g soil
246TNT	1.0 µg/g to 100 µg/g soil
26DNT	1.0 µg/g to 100 µg/g soil
24DNT	1.0 µg/g to 100 µg/g soil

B. Sensitivity

Analyte	
RDX	90.0 Height Units for 50 ng = 1.80 H.U./ng
135TNB	83.0 Height Units for 50 ng = 1.66 H.U./ng
246TNT	112.0 Height Units for 50 ng = 2.24 H.U./ng
26DNT	69.7 Height Units for 50 ng = 1.39 H.U./ng
24DNT	133.3 Height Units for 50 ng = 2.67 H.U./ng

C. AEC Certified Reporting Limit (μg/g)

RDX	0.269
TNB	0.228
26 DNT	0.569
24 DNT	0.222
TNT	0.337

(See attached letter)

D. Interferences

If tetryl is present in environmental samples it may interfere with TNT analysis [Jenkins, Leggett, Grant, and Bauer, 1986]. However, it is not anticipated that tetryl will be present in high enough concentrations to create a problem.

E. Analysis Rate

We estimate that 40 samples can be analyzed in an 8 hour day. The instrument in the laboratory is fully automated with an autosampler and data storage such that we have the capability of running analysis much longer than eight hours per day if necessary or desirable.

F. Safety Information

246TNT and RDX may be hazardous if absorbed through the skin or inhaled with particulate matter. 26DNT and 24DNT are considered to be toxic and 135TNB is considered to be a carcinogen. Care is taken to avoid skin contact with the compounds and to avoid inhalation of any particulate matter.

III. Apparatus and Chemicals

A. Glassware and Hardware

Gilson/Rainin pipetman #F1000
Gilson/Rainin pipetman #P200
Gilson/Rainin pipetman #P2000
Volac 1-10 mL high precision dispenser #MD049IX
25 mL Corex glass screw top test tubes #8446
20 mL screw top scintillation vials - Research Products Int'l Crop.
100 to 2000 mL glass graduated cylinders - Pyrex, Exax
0.1 to 10 mL glass pipettes - Corning, Kimax, Exax
10 to 100 mL glass volumetric flasks - Kimax, Pyrex

5 to 200 μL Eppendorf pipettes
Kimwipes wipers
50 to 2000 mL Erlenmeyer flasks - Kimax, Pyrex
20 to 2000 mL glass beakers - Kimax, Pyrex
various size plastic squeeze bottles
Amber glass jars, screw top
Sartorius balance #1601A, max 110 g
Mettler PE 3600 balance

B. Instrumentation

1. HPLC System

Beckman Analog Interface Module 406
Beckman Scanning Detector Module 167
Beckman model 110 - A Pump
Micromeritics Autoinjector Model 725
AST 286 Premium Computer
System Gold Chromatography Software

2. Sonic Probe

Sonics and Materials Inc.
Vibra Cell Sonic Probe Model VC250

3. Vortex

Curtin Matheson Scientific Inc.
Super Mixer Catalog Number 215-434

4. HPLC Parameters

Flow Rate	1.5 mL/min
Mobile Phase	58% methanol, 42% water
Length of Run	10 min
Sample Loop	50 μL
Peak Width	0.25
Threshold	0.000150
Wavelength	254 nm

C. Analytes

1. Chemical Properties

Analyte	mp (°C)	bp (°C)	density (g/mL)	CAS - #
RDX	205	-	1.82	121-82-4
135TNB	121	315	1.4775	25377-32-6
246TNT	80	240	1.6540	118-96-7
26DNT	66	-	1.2833	606-20-2
24DNT	71	300	1.3207	121-14-2

2. Retention Times and Windows

Compound	Retention Time (min)	Window (min)
RDX	3.17	0.32
135TNB	4.16	0.42
246TNT	5.92	0.59
26DNT	6.54	0.65
24DNT	6.80	0.68

Note: Retention times may vary slightly as columns age or with slight variation in mobile phase solvent mixing.

D. Reagents and SARMs

1. HPLC grade Acetonitrile from Fisher Labs (99.9%)
2. HPLC grade Methanol from Fisher Labs (99.9%)
3. HPLC grade Water from Millipore System (approx. 18 megaohm/cm)
4. All analytes prepared from Standard Analytical Reference Materials (SARMs) came from the Picattiny Arsenal.

IV. Calibration

A. Preparation of Standards

1. Concentrated Stock Solutions

An individual stock solution was prepared for each analyte by the following method. The target reporting limit (TRL) for RDX, 246TNT, 24DNT, and 26DNT is 1 µg/g soil and for 135TNB it is 0.5 µg/g soil. The soil is extracted at a 10:1 ratio. Therefore, the concentration of explosive in the extract comparable to the TRL limit is 0.1 mg/L for RDX, 246TNT, 24DNT, and 26DNT, and 0.05 mg/L for 135TNB. An amount of analyte is weighed out so that the final stock solution has a concentration of 1000 * TRL (if the TRL is 0.1 mg/L, then the stock solution is actually 100 mg/L; if the TRL is 0.5 mg/L, then the stock solution concentration is 50 mg/L). The exact weights and volumes of the analyte and solution are listed on the next page.

SARMs STOCK SOLUTIONS

Compound	Weight (mg)	Volume (mL)	Conc. (mg/L)
RDX	25.0	250	100.0
135TNB	12.5	250	50.0
246TNT	25.0	250	100.0
26DNT	25.0	250	100.0
24DNT	25.0	250	100.0

The solvent is HPLC grade acetonitrile (ACN). The SARMs stock solutions are made in 250 mL volumetric flasks and are stored in the dark (wrapped flask in aluminum foil) in the freezer (about -10° C). They are checked periodically and are expected to have a shelf life of approximately 6 months.

2. Working Stock Solutions

A working stock solution (Working Stock I) was prepared with a concentration of approximately 10 mg/L of RDX, 246TNT, 26DNT, and 24DNT; 5 mg/L 135TNB. Working Stock I was prepared by adding 10.00 mL of each of the five stock solutions to a 100 mL volumetric flask with a volumetric pipet, diluting to volume with HPLC grade methanol, and thoroughly mixing. These working stock solutions were stored in the freezer and have a shelf life of 2 weeks. The preparation is shown in tabular form below.

WORKING STOCK I

Analyte	Conc. in Stock (mg/L)	Dilution	Concentration (mg/L)
RDX	100	1:10	10
135TNB	50	1:10	5
246TNT	100	1:10	10
26DNT	100	1:10	10
24DNT	100	1:10	10

3. Daily Calibration Standards

The daily calibration standards are made by diluting an appropriate volume of the working stock solution. For example, if a daily standard of approximately 1.0 mg/L is desired, then 0.50 mL of working stock I (measured out with a glass pipet) is diluted to 5.00 mL with 4.50 mL methanol. The shelf life for the daily standards is one day. Preparation of each of the daily standards is shown below.

DAILY CALIBRATION STANDARDS

Tgt[1] Con. (µg/L)	Soln[2] Used	Volume Added Soln	Dil. Soln.	Total	Actual Concentration RDX	135-TNB	246-TNT	26-DNT	24-DNT
		------ mL		------	----------------		µg/L	----------------	
0	ACN	0	5.00	5.00	0	0	0	0	0
100	1000 std.	0.50	4.50	5.00	100	50	100	100	100
200	2000 std.	0.50	4.50	5.00	200	100	200	100	200
500	5000 std.	0.50	4.50	5.00	500	250	500	500	500
1000	W.S.I	0.50	4.50	5.00	1000	500	1000	1000	1000
2000	W.S.I	1.00	4.00	5.00	2000	1000	2000	1000	2000
5000	W.S.I	2.00	2.00	4.00	5000	2500	5000	5000	5000
10000	W.S.I	5.00	0.00	5.00	10000	5000	10000	10000	10000

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[1] The numbers in this column are target concentrations for the standard calibration curve. Target concentrations of 135TNB are one half the values shown in this column. The actual concentrations are calculated from the standard weights and are shown in the right hand columns.

[2] W.S. I refers to Working stock I as given previously. The dilution solution was methanol.

B. Instrument Calibration

Standards are analyzed with a Beckman System Gold HPLC System. The system is capable of automatic tuning including lamp calibration and autozeroing of baseline. The system automatically sets the baseline at the base of each peak and calculates the peak area and height. Detector output which produces each chromatogram is stored on computer disk. A hard copy of each chromatogram is also printed out. At the conclusion of the analysis, the resulting chromatograms are studied and peak quantification parameters are optimized such that baseline placement is accurate and consistent for all samples.

V. Preparation of Spike Solutions

A. Concentrated Spike Stock Solutions

An individual spike stock solution is prepared for each of the analytes. An amount of analyte was weighed out so that the final concentration of the solution was 1600 mg/L for most analytes. For example, approximately 40 mg of 246TNT was weighed out and dissolved in 25 mL of HPLC grade ACN in a volumetric flask. These solutions were stored in the dark (wrapped in aluminum foil) in the freezer (about -10° C). The shelf life for these solutions is expected to be approximately 6 months.

CONCENTRATED SPIKE STOCK SOLUTIONS

Analyte	Weight (mg)	Volume ACN (ml)	Actual Conc. (mg/L)
RDX	40.0	25	1600
135TNB	20.0	25	800
246TNT	40.0	25	1600
26DNT	40.0	25	1600
24DNT	40.0	25	1600

B. Working Spike Stock Solutions

The working spike stock solutions contain all of the analytes of interest. Working spike stock I, used for the high level spike, was prepared by mixing equal volumes of each of the five spike stock solutions together. Thus, the final concentration of the Working Spike Stock Solution I is approximately 320 mg/L for RDX, 246TNT, 2,6DNT, 24DNT; 160 mg/L for 135TNB. This solution was stored in the freezer and has a shelf life of 2 weeks. An appropriate volume of this working spike solution was added to the soil for spiking studies. The actual values follow.

WORKING SPIKE STOCK I

Analyte	Stock Conc. (mg/L)	Dilution of Conc. Spike Soln.	Final Conc. in Working Spike Stock I (mg/L)
RDX	1600	1:5	320
135TNB	800	1:5	160
246TNT	1600	1:5	320
26DNT	1600	1:5	320
24DNT	1600	1:5	320

Working Spike Stock Solution II, used for the low level spike, was prepared by mixing 5ml of each of the five Spike Stock Solutions together and diluting this mixture to 100 ml. Thus the final concentration of Working Spike Stock Solution II is approximately 80 mg/L for RDX, 246TNT, 2,6DNT, 24DNT; 40 mg/L for 135TNB.

WORKING SPIKE STOCK II

Analyte	Stock Conc. (mg/L)	Dilution of Conc. Spike Soln.	Final Conc. in Working Spike Stock I (mg/L)
RDX	1600	1:20	80
135TNB	800	1:20	40
246TNT	1600	1:20	80
26DNT	1600	1:20	80
24DNT	1600	1:20	80

C. Soil Spiking Solutions

Soils were spiked using the working spike stock solutions shown above. The amounts of the various spike stock solutions and the dilutions used are given in the table below.

Level	Spike Soln.	Volume (uL)	Soil (g)	Concentration Soil Basis (ug/g)				
				RDX	135-TNB	246-TNT	26-DNT	24-DNT
Blank	--	0	0.0	0.0	0.0	0.0	0.0	0.0
L	WSSII	25	2.0	1.0	0.5	1.0	1.0	1.0
M	WSSII	250	2.0	10.0	5.0	10.0	10.0	10.0
H	WSSI	500	2.0	80.0	40.0	80.0	80.0	80.0

[1] If expressed on a solution concentration assuming a 1:10 soil to extracting solution the values would be 1/10 of those shown in this table. After spiking, soil was allowed to equilibrate for 1 hour. Extraction followed using the method described in Section VII A.

VI. SAMPLE HANDLING STORAGE

A. Sampling Procedure

Detailed sampling procedure is described in the Project QA Program. Field sampling involves coring with a hydraulic probe and separating the corings into the desired depth samples. All sampling equipment is cleaned with a high pressure, hot water cleaner between samples. Immediately after processing in the field samples are placed in a cooler with blue ice and transported to the laboratory.

B. Containers

Soil samples are placed in amber glass bottles that have been cleaned according to the protocol outlined in the USATHAMA QA Program. Bottle cleaning includes wash and scrub with detergent, rinse with distilled water, rinse with acetone, rinse with methylene chloride, rinse with hexane, air-drying, heat to 200° C , cooling and caping with clean caps with Teflon liners. Bottle caps are also washed with detergent and rinsed with distilled water and dried at 40° C. The Teflon liners are washed with detergent, rinsed with distilled water, rinsed with acetone, rinsed with hexane, air dried, heated for 2 hours, allowed to cool and then placed in the lid and used to cap clean bottles.

C. Storage Conditions

As described samples are processed in the field and placed immediately in a cooler with blue ice. Samples are then be transported to the laboratory as soon as feasible (within 48 hours) and stored in a freezer in the laboratory until extracted. Samples are in the field and in the laboratory to maintain sample integrity.

D. Holding Time Limits

All soil samples are extracted within 7 days of sampling and will be analyzed for explosives within 40 days of sampling. Both samples and extracts are stored in a freezer until extracted and analyzed.

VII. Procedure

A. Separations

The general method for explosives analysis in soils we are using is a modification of the procedure proposed by Jenkins (personal communication). The modified procedure can be outlined as follows:

1. 2.00 g of soil and 20.0 mL of acetonitrile are placed in a 2.5 cm x 20 cm glass screw-cap test tube.

2. Soil is dispersed with a vortex mixer for approximately 1 min.

3. Tubes are placed in a water bath at 22°C and sonicated for 18 hrs.

4. A 10.0 mL aliquot is combined with 10.0 mL of a 2.0 g/L aqueous $CaCl_2$ solution. The mixture is shaken and left standing for 15 min.

5. An aliquot of the supernatant is filtered through a 0.2 um nylon filter.

6. 50 μL of the filtered extract is injected into an HPLC with C-18 reverse phase guard and separating columns. The separating column is an Ultrasphere ODS 5 μ column. Column lengths were 4.5 and 25.0 cm for the guard and separating columns, respectively. The mobile

phase consists of 58/42 (v/v) methanol/water and has a flow rate of 1.5 mL/min. Compounds are detected at 254 nm. Peak heights are used to quantify explosive levels in the extracts.

B. Chemical reactions

None

VIII. References

Jenkins, T.F., D.C. Leggett, C.L. Grant and C.F. Bauer. 1986. Reversed-phase high-performance liquid chromatographic determination of nitroorganics in munitions waste water. Analytical Chemistry 58: 170-175.

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