

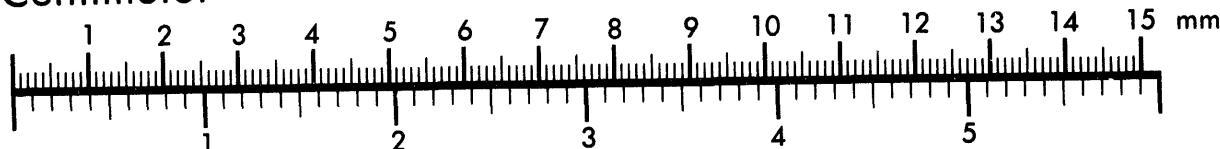


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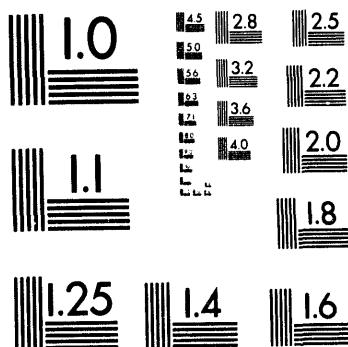
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**Uptake of Explosives from Contaminated Soil
by Vegetation at the
Joliet Army Ammunition Plant**

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UPTAKE OF EXPLOSIVES FROM CONTAMINATED SOIL BY VEGETATION AT THE JOLIET ARMY AMMUNITION PLANT

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ABSTRACT

This study examines the uptake of explosives by vegetation growing on soils contaminated by 2,4,6-trinitrotoluene (TNT) in Group 61 at the Joliet Army Ammunition Plant (JAAP). Plant materials and soil from the root zone were sampled and analyzed to determine TNT uptake under natural field conditions. Standard USATHAMA methods were used to determine concentrations of explosives, their derivatives, and metabolites in the soil samples. No explosives were detected in the aboveground portion of any plant sample. However, results indicate that TNT, 2-aminodinitrotoluene (2-ADNT), and/or 4-ADNT were present in some root samples. The presence of 2-ADNT and 4-ADNT increases the likelihood that explosives were taken up by plant roots, as opposed to their presence resulting from external soil contamination.

INTRODUCTION

Related Research

Although the uptake of explosives by vegetation is a potential pathway for human exposure, limited information has been published on the uptake of explosives from contaminated soils by plants. Palazzo and Leggett investigated the uptake of 2,4,6-trinitrotoluene (TNT) by



yellow nutsedge grown in hydroponic solutions.¹ 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.² and Pennington³ 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. examined uptake of TNT by bush beans grown in hydroponic solutions containing 10 mg/L of TNT.⁴ 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 showed uptake of TNT into the roots, with some radio-label deposition in stem and leaf tissue as well.⁵ Chromatographic results showed that aminodinitrotoluene isomers (2-ADNT and 4-ADNT) were present 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. also showed uptake of tetryl by plants in a hydroponics study that used radio-labeled tetryl.⁶ 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. 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.⁷ 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.

Group 61 Field Investigation

This study examines the uptake of explosives by existing vegetation growing in TNT-contaminated soils in 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).

The TNT-contaminated soil in Group 61 is "aged" contaminated soil, inasmuch as it was contaminated more than 40 years ago. 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



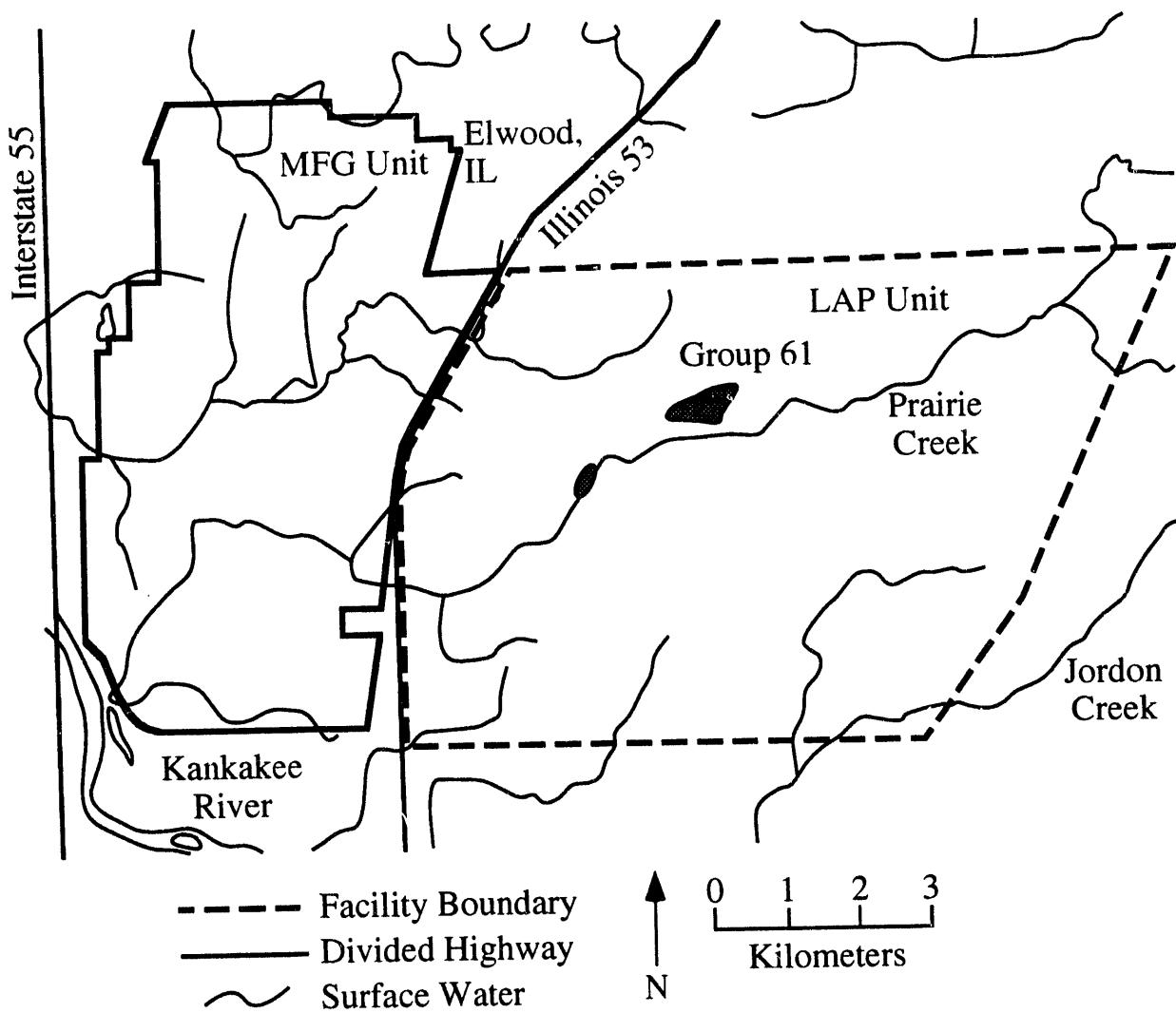


FIGURE 1 Location of Group 61 at the Joliet Army Ammunition Plant

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.

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 evidenced 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.



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. A crop study is also under way at JAAP to determine TNT uptake by agricultural crops. A forage crop and a grain crop have been planted in contaminated soil that has been amended with organic matter. Soil and plant material will be periodically sampled to determine the fate of explosive contaminants. The crop study is expected to be completed in the fall of 1994, after the crops are harvested.

EXPERIMENTAL PROCEDURE

Fifteen sampling locations were selected within the ridge-and-furrow area of Group 61 at JAAP (Figure 2). 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 had been determined by previous studies.) Soil samples were taken to confirm the

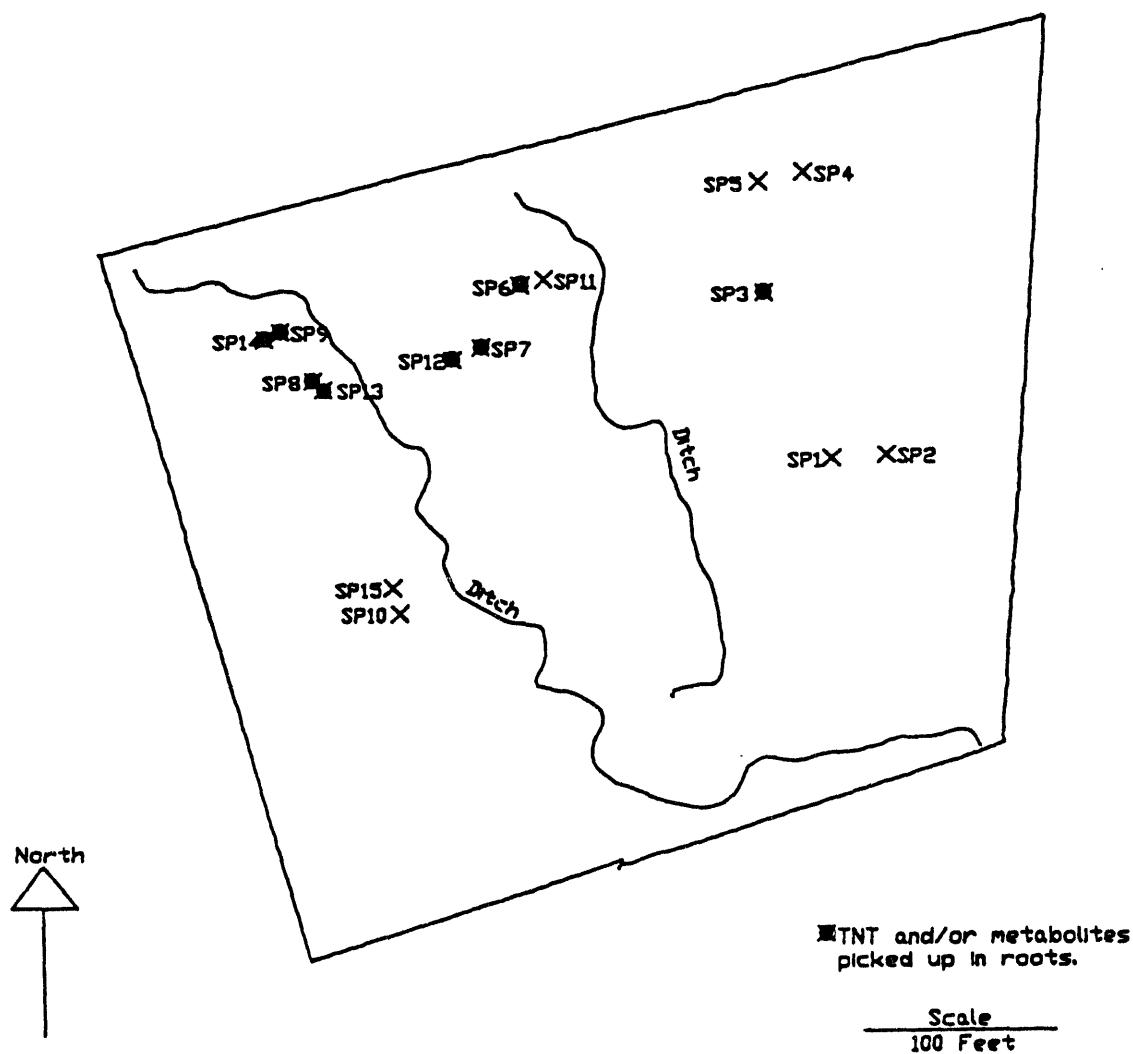


FIGURE 2 TNT Sample Locations at the Joliet Army Ammunition Plant, Group 61 —
Ridge-and-Furrow Area



level of contamination. 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. 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.

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 to exclude from the samples plant materials that had been in direct contact with the soil. 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, involving extraction, cleanup, and HPLC with ultraviolet detection, was used to analyze plant materials.⁹

These analyses were performed in a USATHAMA-certified laboratory at the University of Illinois at Urbana, Illinois.¹⁰ 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, spike recovery averaged 66% for TNT, 48% for 4-ADNT, and 84% for 2-ADNT.

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). No targeted TCLP compounds were detected in the samples.

CONCLUSIONS

Table 1 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 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 tops. 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.

The results indicate that TNT, 2-ADNT, and/or 4-ADNT were present 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





TABLE 1
Results of Explosives Analysis^a

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

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.

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REFERENCES

1. Palazzo, A.J., and D.C. Leggett, 1986, *Effect and Disposition of TNT in a Terrestrial Plant*, Journal of Environmental Quality, 15:49
2. Folsom, B.L. Jr., et al., 1988, *Effects of Soil pH and Treatment Level on Persistence and Plant Uptake of 2,4,6-Trinitrotoluene, 1988 Final Report*, EL-88-22, Environmental Laboratory, Waterways Experiment Station, U.S. Army Corps of Engineers, Vicksburg, Miss.
3. Pennington, J.C., 1988, *Soil Sorption and Plant Uptake of 2,4,6-Trinitrotoluene, Final Report*, EL-88-12, Environmental Laboratory, Waterways Experiment Station, U.S. Army Corps of Engineers, Vicksburg, Miss.
4. Harvey, S.D., et al., 1991, *Fate of the Explosive Hexahydro-1,3,5-Trinitro-1,3,5-Triazine (Rdx) in Soil and Bioaccumulation in Bush Bean Hydroponic Plants*, Environmental Toxicology and Chemistry, 10:845-855.
5. Harvey, S.D., et al., 1990, *Analysis of 2,4,6-Trinitrotoluene and Its Transformation Products in Soils and Plant Tissues by High-Performance Liquid Chromatography*, Journal of Chromatography, 518:361-374.
6. Harvey, S.D., et al., 1993, *Analysis of the Explosive 2,4,6-Trinitrophenylmethylnitramine (tetryl) in Bush Bean Plants*, Journal of Chromatography, 630:167-177.
7. Banwart, W.L., et al., 1991, *Plant Uptake of RDX from Spiked Soils*, in *Agronomy Abstracts*, American Society of Agronomy, Madison, Wis., p. 35.
8. Ritchie, E.S., et al., 1991, *Phase 1 Remedial Investigation/ Feasibility Study, Load-Assemble-Package (LAP) Area, Joliet Army Ammunition Plant, Joliet, Illinois*, prepared by Dames & Moore, Bethesda, Md., for U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Md., March.



9. Banwart, W.L., and J.J. Hassett, 1990, *Effects of Soil Amendments on Plant Tolerance and Extractable TNT from TNT Contaminated Soils*. in Agronomy Abstracts, American Society of Agronomy, Madison, Wis., p. 33.
10. U.S. Army Toxic and Hazardous Materials Agency, 1990, *Quality Assurance Program*, USATHAMA PAM 11-41, Aberdeen Proving Ground, Md.



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