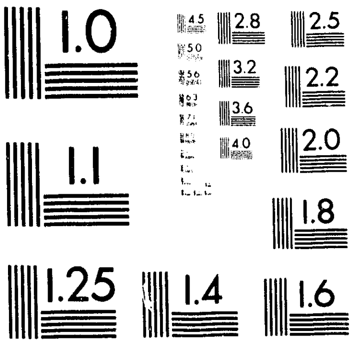
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THE ENVIRONMENTAL BEHAVIOR AND CHEMICAL FATE OF ENERGETIC COMPOUNDS (TNT, RDX, TETRYL) IN SOIL AND PLANT SYSTEMS [1]

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ABSTRACT

Munitions materiels can accumulate or cycle in terrestrial environs at production and manufacturing facilities and thus pose potential health and environmental concerns. To address questions related to food chain accumulation, the environmental behavior of energetic compounds (2,4,6-trinitrotoluene,TNT; hexahydro-1,3,5-trinitro-1,3,5-triazine, RDX; 2,4,6-trinitrophenylmethylnitramine, tetryl) was evaluated. Emphasis was placed on determining the potential for soil/plant transfer of munitions residues, translocation and distribution within the plant, the extent to which compounds were metabolized following accumulation, and the chemical nature and form of accumulated residues. Both TNT and tetryl undergo extensive chemical transformation in soil, forming aminodinitrotoluene isomers and N-methyl-2,4,6-trinitroaniline residues, respectively, along with a series of unknowns. After 60 days, only 30% of the amended TNT and 8% of the amended tetryl remained unchanged in the soil. In contrast, 78% of the soil-amended RDX remained unchanged after 60 days. The relative order of plant availability was RDX >> tetryl ≥ TNT, with the extent of plant uptake being dependent on both soil type (sand > silt >> organic soil) and plant species. After 60 days, plants grown in soils containing 10 ppm residues contained from 5 μg TNT /g to 600 μg RDX/g fresh wt. tissue. TNT and tetryl residues were primarily accumulated in roots (75%), while RDX was concentrated in leaves and seed. The principal transport form for TNT (root to shoot) was an acid labile conjugate of aminodinitrotoluene; RDX was transported unchanged. On accumulation in roots and leaves, highly polar and non-extractable TNT metabolites dominated, with the aminodinitrotoluene isomers accounting for less than 20% of the residues present. Only a few percent were present as the parent TNT. RDX was partitioned similarly to TNT, with 8 to 30% of the RDX appearing as polar metabolites, 20-50% as parent RDX, and the balance as non-extractable residues. Tetryl was metabolized to N-methyl-2,4,6-trinitroaniline and a variety of polar metabolites. The results obtained to date clearly indicate that munitions residues accumulate in plants, that significant chemical transformation occurs, and that risk assessment estimates must be implemented through the use of biomarkers or other modes of toxicity testing.

1.0 INTRODUCTION

The production and disposal of energetic compounds, including 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and 2,4,6-trinitrophenylmethylnitramine (tetryl) can lead to their dissemination within the environment and can impose unacceptable risk to humans and the environment. Thus, a need exists to understand the chemical fate and behavior of these compounds before environmental risk can be reliably estimated and remediation methods adopted. A

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substantial body of data describes the behavior of energetic compounds in soils, waters, and biota. Much of the data deals with the presence or absence of the parent compounds and their immediate decomposition products (see Cataldo et al. 1989). Neither mass balance nor elucidation of more polar transformation products has been approached systematically.

This document summarizes research performed to elucidate the behavior of TNT, RDX, and tetryl in soils and plants. Emphasis is placed on understanding the chemical transformations and rates of transformations in soils and soil/plant systems.

2.0 MATERIALS AND METHODS

Experimental designs, and chemical fractionation and analytical procedures have been described in several reports (Cataldo et al. 1989; Cataldo et al. 1990; Fellows et al. 1993). All studies employed radiolabeled compounds to enable elucidation of fractionation/partitioning patterns, analysis of polar and non-polar products, plant uptake, metabolism and partitioning, and mass balance determination.

3.0 RESULTS AND DISCUSSION

3.1 Soil Behavior and Fate of Energetic Compounds

Soils amended with 60 ppm of TNT, RDX, or tetryl were incubated for 60 days or until chemical equilibrium was attained based on analytical detection limits. Soils used included Burbank sandy loam (0.5% organic matter), Palouse silt loam (1.7% organic matter), and Cinebar clay loam (7.2% organic matter). Soils were incubated and sampled over time for analysis of Soxhlet extractables and non-extractables; extractables were analyzed for parent compounds and transformation products. Results are presented for Burbank and Cinebar soils only; behavior in Palouse soil was intermediate.

3.1.1 TNT

Figure 1 shows the time course of TNT fate in soil. In the low-organic-matter (OM) Burbank soil, the non-extractable fraction increases proportionally to the decrease in extractable TNT residues. Analysis of the extractable fraction shows parent TNT levels decrease to below 3% of the amended levels in 10 days. The behavior of TNT in the high-OM Cinebar soil is similar to that in Burbank, except that more sequestration occurs, extractables decline more rapidly, and levels of TNT after 60 days are higher. Chemical analysis of the extractable fraction indicates that TNT is rapidly converted to aminodinitrotoluene (AMDNT) isomers, and a range of unidentified more polar compounds. Mass balance based on radiocarbon for these studies was >90%.

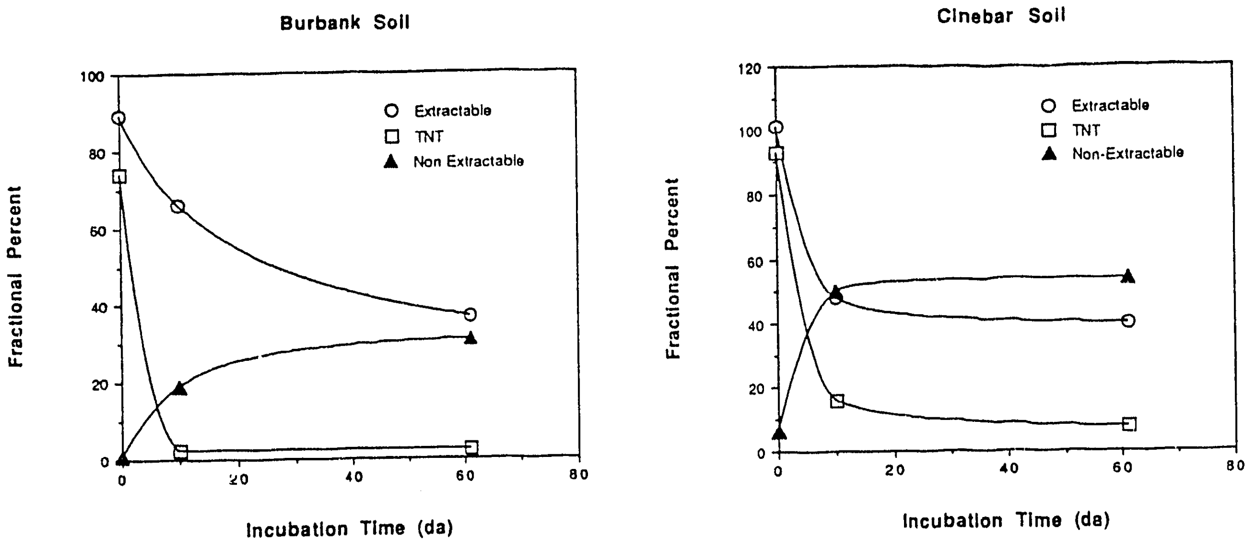

Figure 1. Time Course of TNT Behavior in Soil.

3.1.2 RDX

The time course for RDX in soil is provided in Figure 2. RDX amended to both low- and high-OM soils remains >95% extractable, and remains unchanged as parent RDX. The non-extractable fraction appears to come to equilibrium within 60 days, with <2% being non-extractable. No significant transformation products were observed for RDX. Mass balance based on radiocarbon for these studies was >90%.

3.1.3 Tetryl

Figure 3 shows the time course of tetryl fate in soil. In the low-OM Burbank soil, the non-extractable fraction increases proportionally to the decrease in extractable tetryl residues. Analysis of the extractable fraction shows parent tetryl levels to decrease to below 1% of the amended levels after 20 days. The behavior of tetryl in the high-OM Cinebar soil is similar to that in Burbank, except that slightly less sequestration occurs (50 versus 60%), and extractables decline less rapidly; tetryl is just detectable after 60 days. Chemical analysis of the extractable fraction indicates that tetryl is rapidly converted to N-methyl-2,4,6-trinitroaniline and a dinitroaminophenylmethylnitramine isomer, and several unidentified more polar compounds hypothesized to be reduction products of the initial transformation products. Mass balance based on radiocarbon for these studies was >80%.

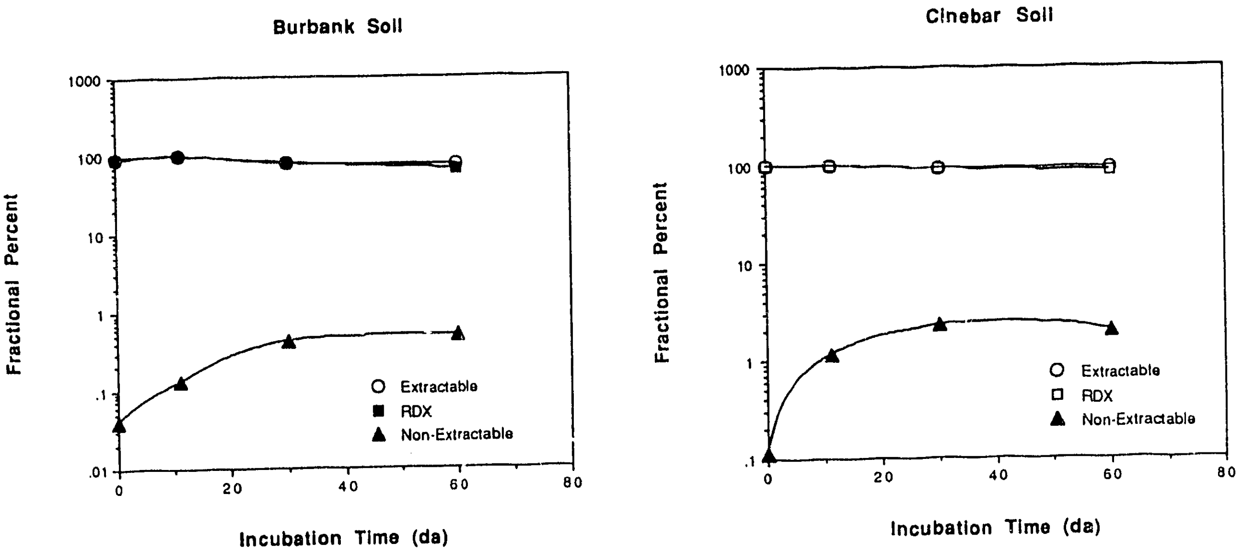

Figure 2. Time Course of RDX Behavior in Soil.

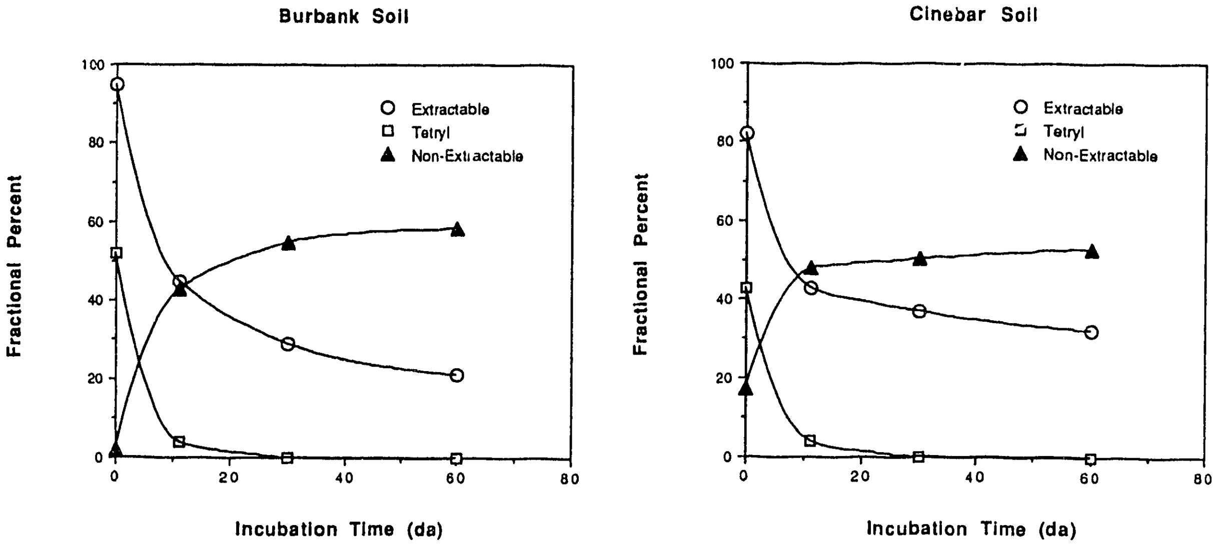

Figure 3. Time Course of Tetryl Behavior in Soil.

3.2 Plant Accumulation and Chemical Fate

Plant availability was performed in hydroponic systems to allow analysis of munitions residues in contact with absorbing roots and to establish extraction and short-term partitioning patterns. Soil studies were employed to establish long-term uptake and distribution patterns and the extent to which munitions residues were metabolized.

3.2.1 Availability of Parent Residues and Transformation Products

Comparisons were made of the chemical transformations occurring in hydroponic culture solutions maintained over time with and without light, aeration, and plant roots. While transformation occurred with TNT and tetryl in the presence of light and/or aeration, transformations were dramatic and rapid when plant roots were present. TNT was rapidly converted to AMDNT isomers, and both species were accumulated by plant roots. Tetryl was rapidly converted to N-methyl-2,4,6-trinitroaniline and possibly dinitroaminophenylmethylnitramine isomer in the presence of plant roots, and depletion of radiolabel from the uptake solution indicated plant availability of tetryl and its transformation products. The rapid formation of TNT and tetryl transformation products in the presence of plant roots, like the soil transformations, indicates a surface catalytic process. RDX underwent no significant transformations in solution culture. These results indicate that plant-based transformations associated with subsequent soil-based plant uptake studies will be complicated by plant absorption of both parent compounds and their soil transformation products.

3.2.2 Plant Availability and Distribution of Munitions Residues from Soil

Several plant species (wheat, blando brome, and bush bean) were planted in soils varying in physicochemical properties and amended with 10 ppm TNT, RDX, or tetryl, and after 60 days of growth the plants were analyzed for total uptake, tissue distribution, and transformations.

Tables 1 and 2 describe the behavior of TNT. In bush bean and wheat, the major repository for accumulated TNT residues was the root, with substantially less being transported to the shoot tissues. Only in Burbank-grown blando brome do the shoot concentrations deviate from this trend. In bush bean, stem concentrations were generally higher than those in leaves, indicating that the evapotranspiration stream transport form was sequestered prior to completing transit to the leaves. Concentrations of TNT-derived residues in seed and pod tissue were minimal, reflecting the lack of mobility of the residues.

In all cases, total uptake of TNT by each of the three plant species follows a distinct pattern with soil type, Burbank > Palouse > Cinebar. Correlation analysis indicates that uptake in these systems was inversely related to levels of soil organic matter.

Table 1. Uptake and Distribution in Bush Bean Grown for 60 Days on Soils Amended with 10 ppm TNT.

Soil	Leaf	Stem	Pod	Seed	Root
	(μg TNT Equivalents/g Fresh Weight)				
Cinebar	0.3	0.9	0.1	0.1	4.8
Palouse	6.8	9.1	0.7	0.6	35.4
Burbank	8.9	23.9	0.6	0.5	104.0

Table 2. Uptake and Distribution in Wheat and Blando Brome Grown for 60 Days on Soils Amended with 10 ppm TNT. [1]

Plant/Soil	Leaf	Root
	(μg TNT Equivalents/g Fresh Weight)	
Wheat		
Cinebar	0.6	4.9
Palouse	9.2	40.9
Burbank	54.0	217.0
Bland Brome		
Cinebar	0.8	2.5
Palouse	9.5	19.9
Burbank	65.3	59.4

[1] Seeds not present

Tables 3 and 4 provide uptake and distribution data for tetryl. As with TNT, the root was the major repository of accumulated tetryl residues. In bush bean, shoot distributions are similar to those for TNT, except that pod and seed tissues had detectable residues. In the grass species (wheat and blando brome), shoot accumulation levels were higher than those observed for TNT, and tetryl was accumulated into the seed head. This suggests that tetryl residues are more mobile than those of TNT.

The effect of soil organic matter is consistent with that observed for TNT, with plant accumulation of tetryl being inversely proportional to soil OM.

Tables 5 and 6 provide uptake and distribution data for RDX. Unlike TNT and tetryl, RDX was accumulated to a much higher degree and was much more plant mobile. In vegetative plants, total uptake and tissue concentration was once again inversely proportional to soil OM. Leaves

Table 3. Uptake and Distribution in Bush Bean Grown for 60 Days on Soils Amended with 10 ppm Tetryl.

Soil	Leaf	Stem	Pod	Seed	Root
	(µg Tetryl Equivalents/g Fresh Weight)				
Cinebar	1.4	2.4	0.4	0.5	26.2
Palouse	3.0	4.5	0.4	0.5	65.3
Burbank	9.5	9.1	0.7	1.0	126.6

Table 4. Uptake and Distribution in Wheat and Blando Brome Grown for 60 Days on Soils Amended with 10 ppm Tetryl.

Plant/Soil	Leaf	Root	Seed
	(µg Tetryl Equivalents/g Fresh Weight)		
Wheat			
Cinebar	2.4	8.9	0.3
Palouse	10.7	47.3	not present
Burbank	29.0	59.2	0.3
Bland Brome			
Cinebar	2.6	5.2	0.4
Palouse	14.6	31.2	1.8
Burbank	34.4	78.2	3.0

Table 5. Uptake and Distribution in Bush Bean Grown for 60 Days on Soils Amended with 10 ppm RDX.

Soil	Leaf	Stem	Pod	Seed	Root
	(µg RDX Equivalents/g Fresh Weight)				
Cinebar	22.4	19.4	10.5	39.5	8.1
Palouse	119.4	98.1	33.4	300.8	49.1
Burbank	216.7	186.9	44.5	602.6	75.0

Table 6. Uptake and Distribution in Wheat and Blando Brome Grown for 60 Days on Soils Amended with 10 ppm RDX.

Plant/Soil	Leaf	Root	Seed
	(µg RDX Equivalents/g Fresh Weight)		
Wheat			
Cinebar	75.7	17.9	not present
Palouse	422.7	45.1	not present
Burbank	549.9	40.1	not present
Bland Brome			
Cinebar	43.8	40.0	7.6
Palouse	454.4	257.9	21.8
Burbank	564.5	317.1	27.9

and stems were the major repository for RDX in both the dicot and monocots. At maturity when seeds are formed, they become by far the major sites of accumulation based on concentration. Seed accumulation was consistently noted in those plants sampled post-anthesis.

3.2.3 Chemical Fate and Transformations Following Plant Uptake

Assuming that both TNT and its AMDNT isomers formed in soil are plant available, analysis of tissue residues should provide information as to the biotic fate of the material. In roots and leaves, a small amount of TNT-derived radioactivity was associated with TNT (1-2%) and AMDNT isomers (<20%), and the balance was associated with either highly polar metabolites or insoluble tissue residues. Analysis of the xylem transport fluid showed the root-to-shoot transport form to be an acid labile organic conjugate of AMDNT.

The chemical fate of tetryl was similar to that of TNT. Less than 1% of the tissue activity was parent tetryl, 40-50% was present as highly polar metabolites, and 40-50% was associated with insoluble residues. The principal transformation products were those found in soils, namely, N-methyl-2,4,6-trinitroaniline and dinitroaminophenylmethylnitramine. Insufficient activity was associated with the xylem fluid for analysis of transport forms.

The fate of RDX in plant tissues was substantially different from that of TNT and tetryl. In storage tissues (i.e., roots and stems), only 20% of the activity present was as parent RDX, while in leaves and seed tissues >50% was as RDX. This suggests that RDX itself is the mobile plant form. The balance of the activity accumulated was as either unidentified polar metabolites (30-50%) or associated with insoluble plant fractions.

4.0 Summary and Conclusions

The overall soil and plant behaviors of TNT and tetryl were similar, but varied greatly from RDX. In soils, TNT and tetryl were transformed rapidly, whereas RDX remained substantially unchanged. Approximately 50% of the soil TNT and tetryl was irreversibly bound up in soil compartments, while only about 1% of RDX was bound.

Plants appear able to accumulate not only the parent munitions compounds, but the identified transformation products. Once accumulated, TNT is rapidly converted to AMDNT and other unidentified polar compounds and to insoluble residues. Tetryl behavior is very similar, with the principal transformation products being N-methyl-2,4,6-trinitroaniline and dinitroaminophenylmethylnitramine isomer and their reduction products. The fate of RDX is different in that a significant fraction of accumulated radioactivity is associated with the parent compound (20-50%), and 8-30% occurs as unidentified polar residues and the balance as non-extractable residues.

The overall uptake rate of munitions residues and their extensive chemical transformation indicate that, particularly in the case of RDX, *in situ* bioremediation using higher plants is feasible.

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