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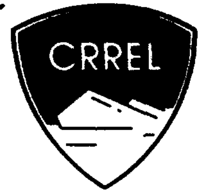

SPECIAL REPORT 94-5

Evaluation of Pre-extraction Analytical Holding Times for Tetryl in Soil

Thomas F. Jenkins

April 1994

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Abstract
A study was conducted to experimentally evaluate the maximum acceptable pre-extraction analytical holding times (MHTs) for tetryl in soil. Three soils fortified with tetryl at the low microgram-per-gram level were used in the study. Subsamples of each soil were extracted with acetonitrile in an ultrasonic bath after being held for 0, 1, 3 and 7 days at either room temperature (22°C), under refrigeration (2°C) or frozen (–15°C). Extracts were analyzed by RP-HPLC. Tetryl concentrations in soils stored at room temperature and under refrigeration declined rapidly over the 7-day study period and several transformation products accumulated. After 7 days of storage at 2°C, tetryl concentrations were reduced by 46, 97 and 99% in the three soils studied. When the soils were frozen, there were no statistically significant analyte losses over the 7-day study period (95% confidence level). On the basis of the results of these experiments, the recommended MHT for soils containing tetryl is 7 days if kept frozen. Longer holding times may be possible, but they were not investigated here. Refrigeration is inadequate to prevent significant transformation of tetryl in soil samples being held for analysis. A question regarding the ability to use analyte-fortified soil to mimic field-contaminated soils in holding time studies is raised.

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

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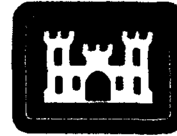
Special Report 94-5



US Army Corps of Engineers
Cold Regions Research & Engineering Laboratory

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Thomas F. Jenkins

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PREFACE

This report was prepared by Dr. Thomas F. Jenkins, Research Chemist, Geological Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding was provided by the U.S. Army Environmental Center (AEC) (formerly the U.S. Army Toxic and Hazardous Materials Agency), Aberdeen Proving Ground, Maryland, Martin H. Stutz, Project Monitor.

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Evaluation of Pre-extraction Analytical Holding Times for Tetryl in Soil

THOMAS F. JENKINS

INTRODUCTION

A serious environmental problem facing the U.S. military is the presence of soil contaminated with residues of munitions compounds at a large number of its installations. One of the most common problems comes from the manufacture, use, storage and demilitarization of high explosives. These residues are often composed of nitroaromatics and nitramines, along with their manufacturing impurities and environmental transformation products (Walsh et al. 1993). Since many of these compounds are relatively stable in the environment and quite mobile in the soil, they have become sources of groundwater pollution at military facilities (Pugh 1982, Spaulding and Fulton 1988).

Tetryl (2,4,6-trinitrophenylnitramine) can be classified as either a nitroaromatic or a nitramine. It was used by the U.S. Army as early as 1904 as a booster in a number of munitions formulations (Kayser et al. 1984). While the use of tetryl was discontinued in 1979, residues of tetryl have been identified at a number of military facilities in the United States (Keirn et al. 1981, Batzer et al. 1982, Walsh et al. 1993).

Laboratory methods have been developed to characterize sites potentially contaminated with nitroaromatic and nitramine explosives. Because explosives residues in contaminated soils were known to be composed of a variety of chemicals, often occurring together, and many of these chemicals are known to be thermally labile, most methods are based on High-Performance Liquid Chromatography (HPLC) (AOAC 1990, ASTM 1991, EPA 1992). While almost all the specifications in these methods were based on experimental results (Jenkins et al. 1989, Bauer et al. 1990), the Maximum pre-extraction Holding Time (MHT) of 7 days for soil and water samples in SW846 Method 8330 (EPA 1992) was, to our knowledge, based on best judgment and consistency with other methods for semivolatile organics. According to the ASTM (1986), MHT is defined as the "maximum period of time during which a properly preserved sample can be stored before such degradation of the constituent of interest occurs or change in sample matrix occurs that the systematic error exceeds the 99% confidence interval (not to exceed 15%) of the test about the mean concentration found at zero time." Holding time studies are often configured to experimentally assess stability, usually using analyte-fortified samples.

Recently, Maskarinec et al. (1991) estimated maximum pre-extraction holding times for several nitroaromatics and nitramines in soil and water samples. Similar studies were reported by Grant et al. (1993a,b) using a slightly different experimental protocol. Neither of these studies included tetryl, even though it is a target analyte of SW846 Method 8330, probably because it has been less frequently found in samples from military sites compared with other high explosives such as TNT (2,4,6-trinitrotoluene) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) (Walsh et al. 1993). In addition, preliminary experiments indicated that environmental transformation products of tetryl eluted at similar retention times and thus interfered with determination of other nitroaromatics and their transformation products. Thus, unlike some of the other analytes of interest in Method 8330, which could be studied together, tetryl had to be evaluated separately.

While the fate of tetryl under environmental conditions is not completely understood, it is known that tetryl is subject to hydrolysis, photodegradation and biotransformation. Kayser et al. (1984) found that tetryl photolyses under ambient lighting conditions at least an order of magnitude faster than it hydrolyzes. The major phototransformation product detected was N-methylpicramide (N-methyl-2,4,6-

trinitroaniline). The products detected from hydrolysis in the dark were pH dependent. Under acidic conditions, the major organic hydrolysis products detected were picric acid (2,4,6-trinitrophenol) and N-methypicramide. Under basic conditions, the rate of reaction was faster and the major transformation products were methylnitramine and picrate ion.

Recently, Harvey et al. (1992) studied the biotransformation of tetryl in soil. They concluded that the transformation in soil was extremely rapid and that the primary transformation product was N-methylpicramide. Unfortunately, they chose to extract tetryl and its transformation products from soil using Soxhlet extraction prior to RP-HPLC analysis. Subsequent research has indicated that tetryl is not stable to this procedure (Jenkins and Walsh 1994) and their conclusions, relative to the instability of tetryl in the soil and the transformation products produced, are suspect.

OBJECTIVE

The major objective of this study is to estimate the MHT for tetryl in soil. This will be done by fortifying several different soils using an aqueous spiking solution and measuring the concentration of tetryl and any observable transformation products as a function of time.

EXPERIMENTAL

Chemicals

All standards and test solutions of tetryl were prepared from Standard Analytical Reference Materials (SARM) obtained from the U.S. Army Environmental Center (USAEC), Aberdeen Proving Ground, Maryland. The aqueous solution used for soil fortification was prepared in reagent grade water obtained from a Milli-Q Type I Reagent Grade Water System (Millipore Corp.). Methanol used in the preparation of HPLC eluent and acetonitrile used for soil extraction were HPLC grade from Alltech and Baker respectively. Eluent was prepared by combining equal volumes of methanol and water and vacuum filtering through a nylon membrane (0.45 µm) to degas and remove particulate matter.

Tetryl fortification solution

The soil fortification solution was prepared using water. The SARM for tetryl was placed in a brown glass jug, reagent grade water was added, and the contents were stirred at room temperature for a week. The solution was then filtered through 0.45-µm nylon membranes into a clean brown glass jug. No solvents, other than water, were used in the preparation of this solution.

The concentration of tetryl in the fortification solution was determined against standards prepared in acetonitrile (Jenkins et al. 1986, SW846 Method 8330) and diluted 1:1 with reagent grade water prior to analysis. The concentration of tetryl in this spiking solution was determined to be 30.6 mg/L.

Soils

Blank test soils were obtained locally from Vermont (Windsor), New Hampshire (Charlton) and New York (Fort Edwards). These soils were air dried, ground with a mortar and pestle and passed through a 30-mesh sieve (590 µm). Some physical and chemical properties of these soils are presented in Table 1. Replicate 5.0 ± 0.1-g subsamples of each blank soil were placed in individual 20-mL glass scintillation vials.

Table 1. Physical and chemical properties of test soils.

	Soil		
Property	*Fort Edwards clay*	*Windsor sandy loam*	*Charlton silty loam*
pH	8.4	6.2	6.0
TOC (%)*	0.5	1.1	1.8
Clay (%)	70	30	20
CEC (meq/100 g)**	>150	3.5	7.3

*Total organic carbon.
**Cation exchange capacity.

A field-contaminated soil containing tetryl and some of its transformation products was obtained from the Nebraska Ordnance Plant, Mead, Nebraska. The soil was air dried, ground with a mortar and pestle and mixed thoroughly.

Soil wetting and analyte spiking

Prior to the onset of the experiment, previously air dried test soils were rewetted. Because the texture and water holding capacity of the various soils differed, the volume of water added to each soil was varied such that, after spike additions were also made, there was no evidence of free-standing water. For the three initially blank soils, 0.20 mL of reagent grade water was added to the Windsor sandy loam and 1.00 mL was added to the Fort Edwards Clay and Charlton silty loam. After water addition, all soils were allowed to stand at room temperature in

the dark for 3 days to allow microbiological activity to reestablish (Maskarinec et al. 1991, Grant et al. 1993a).

The three initially blank soils were fortified by carefully adding 1.00 mL of aqueous tetryl spiking solution to each test vial. Except for the soils designated for 30-minute exposure and those to be stored frozen, the spiked soils were immediately placed in the dark at the appropriate storage temperature. The 30-minute samples and the samples to be frozen were permitted to stand for 30 minutes at room temperature in the dark after fortification to allow time for tetryl to interact with the soils prior to either extraction or freezing.

Soil holding time test parameters

A summary of the test parameters used for the soil holding time study is presented in Table 2. For the fortified soils, three storage conditions were examined, room temperature (22 ± 2°C), refrigerator storage (2 ± 2°C) and freezer storage (–15 ± 2°C), all in the dark. Portions stored under these conditions were extracted after 1, 3 and 7 days of storage and the tetryl concentration determined. Because of expected variability among subsamples, triplicate portions were analyzed for each storage temperature for each storage time.

Table 2. Experimental factors for soil holding time study.

	Fortified soils	
Factors	*No. of levels*	*Levels*
Analytes	1	Tetryl
Soils	3	Fort Edwards, Charlton, Windsor
Storage temp. (°C)	3	–15, 2, 22
Storage time	4	30 min, 1 day, 3 days, 7 days
Replicates	3	a,b,c

Soil extraction for RP-HPLC analysis

For extraction, the vials containing the soil were allowed to warm to room temperature and 9.00 mL of acetonitrile was added. The vials were vortex mixed for 1 minute and placed in a sonic bath for 18 hours. The temperature of the bath was maintained at less than 25°C with cooling water. The vials were then removed from the bath and allowed to stand undisturbed for 30 minutes. A 10.00-mL aliquot of aqueous $CaCl_2$ (5 g/L) was then added and the soil particles were allowed to flocculate for 30 minutes before a 5-mL aliquot of the supernatant was filtered through a 0.5-µm Millex SR filter.

This extraction procedure was based on the method developed by Jenkins et al. (1989) (SW846 Method 8330) with two differences. First, the soils were not air dried prior to extraction, because it was judged that the time required to dry the soil in the vials at room temperature could result in analyte loss and confound the effect of the holding time temperatures. Second, a 5-g portion of soil was used for the fortified samples, instead of the usual sample size of 2 g, to conform to the test protocol used earlier for TNT, TNB, 2,4-DNT, RDX and HMX (Grant et al. 1993a).

RP-HPLC analysis

All soil extracts were analyzed by Reversed-Phase High Performance Liquid Chromatography (RP-HPLC) on a modular system composed of a Spectra-Physics Model SP8800 ternary HPLC pump, a Spectra-Physics Spectra 100 UV variable wavelength detector set at 254 nm (cell path 1 cm), a Dynatech Model LC 241 auto sampler equipped with a Rheodyne Model 7125 Sample Loop Injector, Hewlett Packard 3393A digital integrator and a Linear strip chart recorder.

All extracts were analyzed on a 25-cm × 4.6-mm (5 µm) LC-18 column (Supelco) eluted with 1:1 methanol–water (v/v) at 1.5 mL/min (Jenkins et al. 1989). Samples were introduced by overfilling a 100-µL sampling loop.

Soil extraction for GC–MS analysis

A 2.0-g portion of the field-contaminated soil from the Nebraska Ordnance Works was extracted with 10.0 mL of acetonitrile as specified above (Jenkins et al. 1989). A 2.0-mL aliquot of the extract was filtered through a Millex-SR filter into a glass scintillation vial and the acetonitrile was allowed to evaporate to about 0.5 mL in a fume hood. A 2.0-µL aliquot was analyzed by GC–MS as described below.

GC-MS analysis

GC–MS analysis was conducted on an HP5992 MSD (mass selective detector). The sample was introduced into the MSD through a Hewlett-Packard 5890 Series 2 gas chromatograph operated in the splitless mode. An HP-5 (cross-linked 5% phenyl methyl silicone, 25-m × 0.20-mm × 0.33-µm film thickness) column was maintained at 75°C for 2 minutes and then the oven was temperature programmed at 20°C/min to 240°C and held for 10 minutes.

Data analysis

The mean and standard deviation for each set of triplicate measurements were calculated. Using the

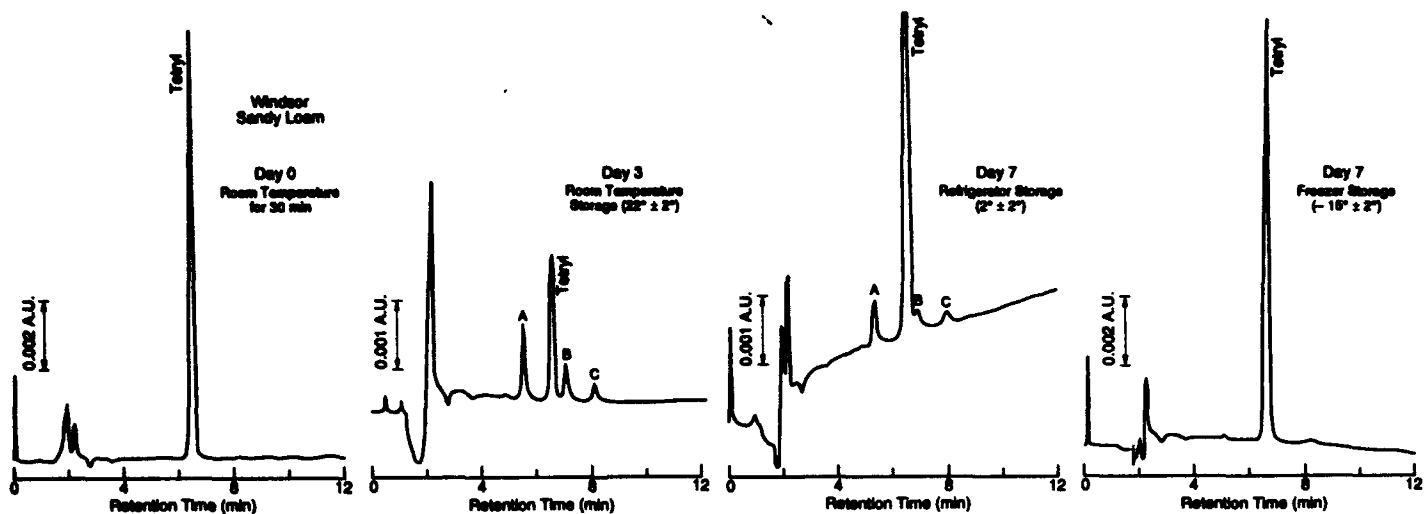

Figure 1. RP-HPLC chromatograms for extracts of tetryl-fortified Windsor sandy loam soil.

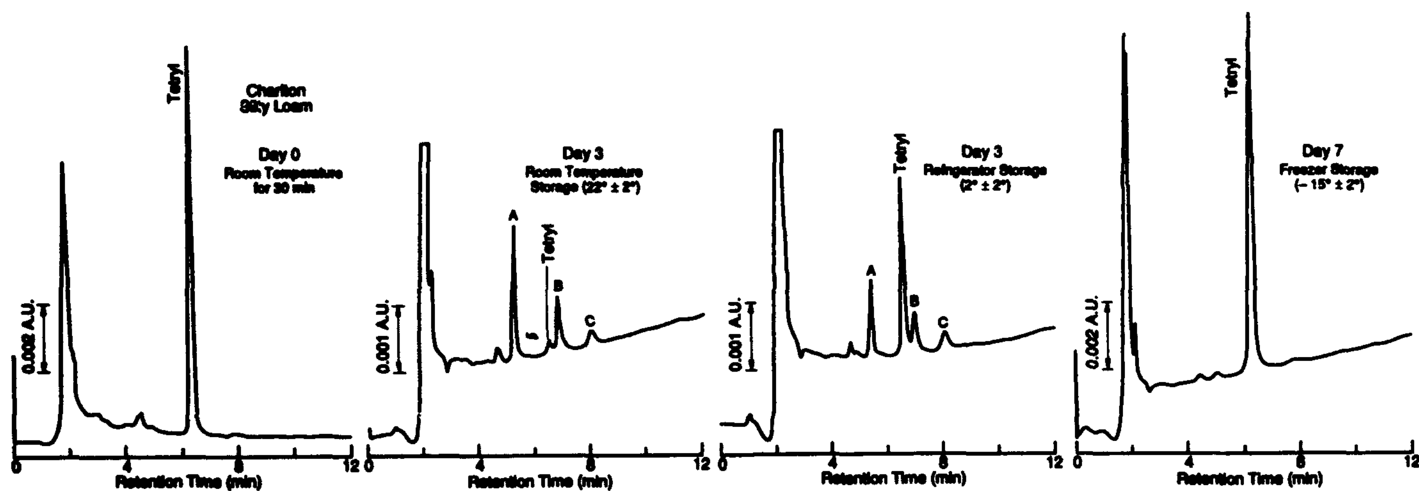

Figure 2. RP-HPLC chromatograms for extracts of tetryl-fortified Charlton silty loam soil.

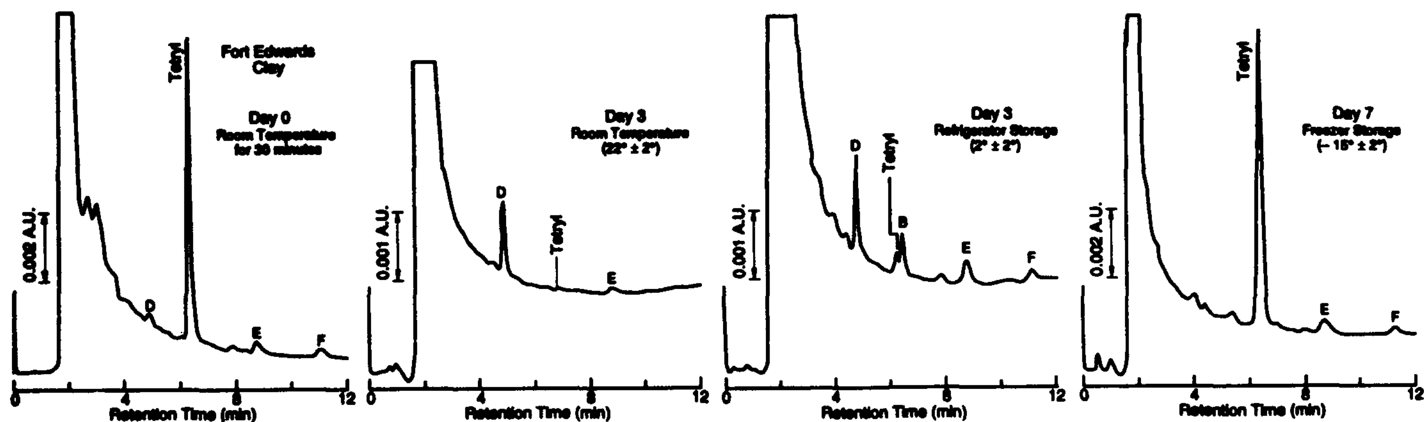

Figure 3. RP-HPLC chromatograms for extracts of tetryl-fortified Fort Edwards clay.

30-minute values as initial concentrations, we determined percent recoveries for each period.

RESULTS AND DISCUSSION

Concentration of tetryl vs. refrigerator holding time

Chromatograms from several of the soil extracts for various holding times and storage temperatures are presented in Figure 1 for Windsor sandy loam. A large reduction in the concentration of tetryl can be seen after only 3 days at room temperature, and three apparent transformation products (labeled A, B and C) are also evident. After 7 days under refrigeration, the tetryl concentration is reduced by about 46% (Table 3) and the same transformation products are seen.

Chromatograms for the extracts of the Charlton silty loam are shown in Figure 2. Loss of tetryl is much faster than that for the Windsor soil, both at room temperature and under refrigeration. The same three transformation products observed in the extracts of the Windsor soil are again evident. After 7 days under refrigeration, the initial concentration of tetryl is reduced by 97%.

Figure 3 presents chromatograms of the extracts of Fort Edwards clay. Peaks labeled as D, E and F are impurities present in unfortified Fort Edwards clay. The rate of degradation of tetryl in this soil is even faster than that found for the Charlton, resulting in over 99% loss of tetryl after 7 days of refrigeration. The relative amounts of the various transformation products observed for this soil appear to be different from those observed for the Windsor and Charlton soils. One of the reasons for the different behavior of this soil is its pH, which is 8.4 compared to 6.2 for Windsor and 6.0 for Charlton (Table 1). As discussed above, Kayser et al. (1984) observed that hydrolysis products were different at acidic and basic pH and that hydrolysis proceeds much faster under basic conditions. Perhaps the very rapid loss of tetryl for the Fort Edwards clay is partially attributable to hydrolysis rather than biodegradation. The lower initial concentration of tetryl for this soil, relative to Windsor and Charlton, may be a reflection of rapid hydrolysis during the 30-minute period where tetryl was allowed to interact with the soil before initial extraction.

Table 3. Concentration (µg/g) of tetryl as a function of holding time for three test soils.

Holding time (days)	Storage temperature (°C) 22 ± 2	2 ± 2	−15 ± 2
	Windsor Sandy Loam		
0	5.48 ± 0.74	5.48 ± 0.74	5.48 ± 0.74
1	3.16 ± 0.13	3.92 ± 0.70	5.00 ± 0.13
3	1.63 ± 0.72	4.15 ± 0.09	4.44 ± 0.78
7	0.66 ± 0.42	2.94 ± 1.01	5.10 ± 0.87
	Charlton Silty Loam		
0	5.58 ± 0.04	5.58 ± 0.04	5.58 ± 0.04
1	0.30 ± 0.12	2.82 ± 0.10	4.07 ± 0.05
3	0.04 ± 0.01	0.91 ± 0.10	4.47 ± 0.12
7	0.04 ± 0.00	0.17 ± 0.02	5.00 ± 0.16
	Fort Edwards Clay		
0	4.43 ± 0.29	4.43 ± 0.29	4.43 ± 0.29
1	0.03 ± 0.02	0.17 ± 0.04	3.75 ± 0.11
3	0.00	0.06 ± 0.01	3.43 ± 0.05
7	0.00	0.04 ± 0.01	4.05 ± 0.06

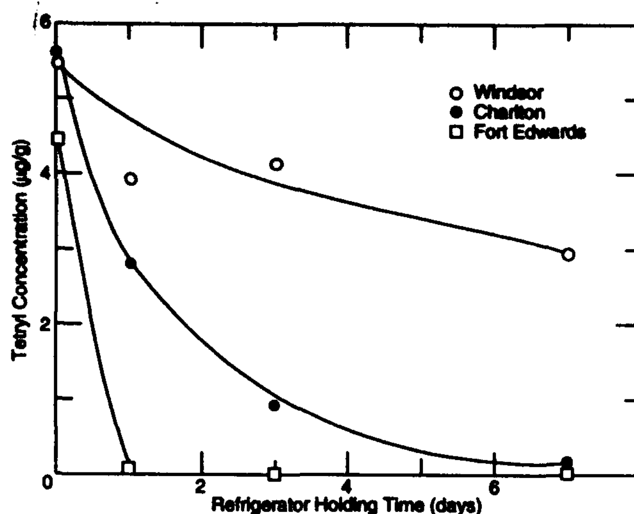

Figure 4. Tetryl concentration as a function of holding time for samples stored under refrigeration.

Plots of the concentration of tetryl for the three soils vs. refrigerator holding time are shown in Figure 4. Clearly, tetryl is not stabilized adequately using refrigerator storage for the current 7-day holding time.

Effect of freezing

Storage by freezing improves the stability of tetryl substantially. Figure 5 shows the concentration of tetryl as a function of freezer holding time for the three soils studied. Linear regression analysis of the mean tetryl concentration vs. holding time for the three soils results in a slope of −0.021 and an intercept of 4.624. The slope, however, was not statistically different from zero at the 95% confidence level,

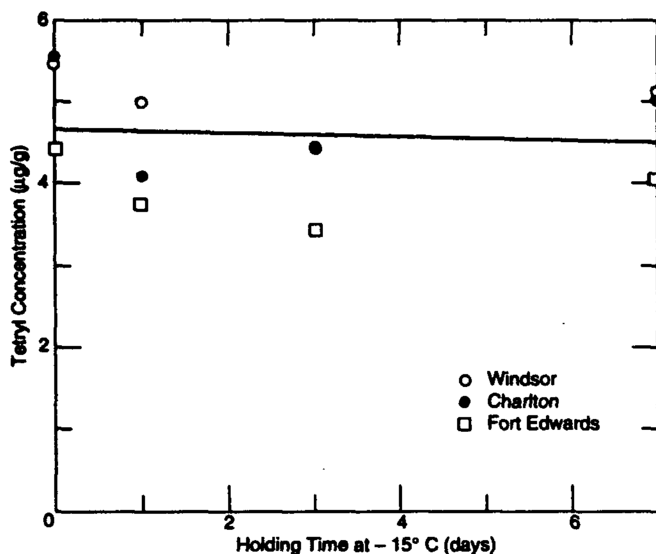

Figure 5. Tetryl concentration as a function of holding time for samples stored frozen at –15°C.

indicating that there was no statistically significant loss of tetryl for freezer storage at –15°C over the 7-day study period. In addition, no accumulations of transformation products A, B or C were observed after 7 days of frozen storage. Longer storage periods were not tested, but future work should assess the possibility of longer-term storage.

Transformation products of tetryl

Harvey et al. (1992) investigated the environmental transformation of tetryl in soils and concluded that the major microbiological pathway resulted in the production of N-methylpicramide. Our recent experiments indicate that their results probably were an artifact of the Soxhlet extraction procedure they used (Jenkins and Walsh 1994). Identification of transformation products of tetryl by GC–MS is complicated by the instability of the nitramine nitro group to GC–MS analysis (Tamiri and Zitrin 1986). For tetryl itself, a loss of NO_2, apparently caused by thermolysis in the injector, results in the formation of N-methylpicramide (Fig. 6). Walsh and Jenkins (1992) identified three compounds when acetonitrile extracts of tetryl-contaminated soils were analyzed by GC–MS: N-methylpicramide, 4-amino-2,6-dinitro-N-methylaniline and 2,4,6-trinitroaniline (Fig. 7). A major portion of the N-methylpicramide found was probably created by degradation of tetryl in the injection port of the GC–MS. Likewise, 4-amino-2,6-N-methylaniline could have resulted from loss of NO_2 from the nitramine NO_2 portion of 4-amino-N-methyl-N,2,6-trinitroaniline in the injector (Fig. 8). Microbiological reduction of tetryl to 4-amino-N-methyl-N,2,6-trinitroaniline is consistent with the production of 2-amino-2,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene from 2,4,6-trinitrotoluene (McCormick et al. 1976) and 3,5-dinitroaniline from 1,3,5-trinitrobenzene (Walsh et al. 1993). A standard of 4-amino-N-methyl-N,2,6-trinitroaniline was not available, but either unknown A or B in the chromatograms shown in Figures 1–3 may be ascribable to this compound. On the basis of the retention times of the transformation products of TNB and TNT relative to the unaltered compounds (Walsh et al. 1993), peak B is most likely due to this component.

Peak C in Figures 1–3 appears to be caused by N-methylpicramide. This peak, along with peak A, was also observed by RP-HPLC in the extract of a tetryl-contaminated soil from Mead Nebraska (Fig. 9). Thus, it appears that N-methylpicramide is an environmental transformation product of tetryl as reported by Harvey et al. (1992); however, it does not appear to be the major one, and it could be attributable to hydrolysis rather than microbiological degradation (Kayser et al. 1984).

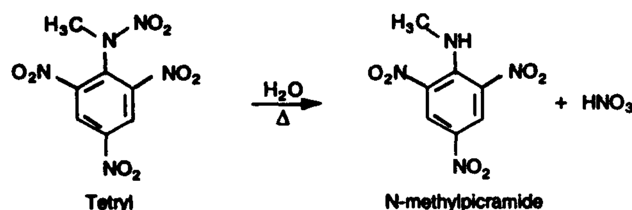

Figure 6. Hydrolysis of tetryl to N-methylpicramide during GC–MS analysis (after Tamiri and Zitrin 1986).

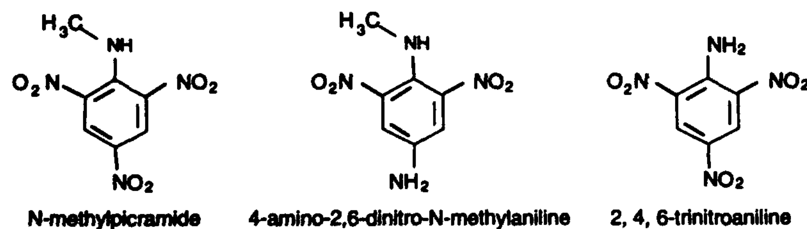

Figure 7. Chemical structures for compounds identified by GC–MS analysis of extract of field-contaminated soil containing tetryl.

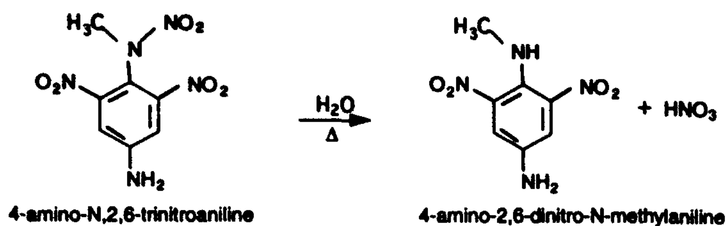

Figure 8. Possible decomposition reaction occurring during GC–MS analysis of extract of field-contaminated soil containing tetryl.

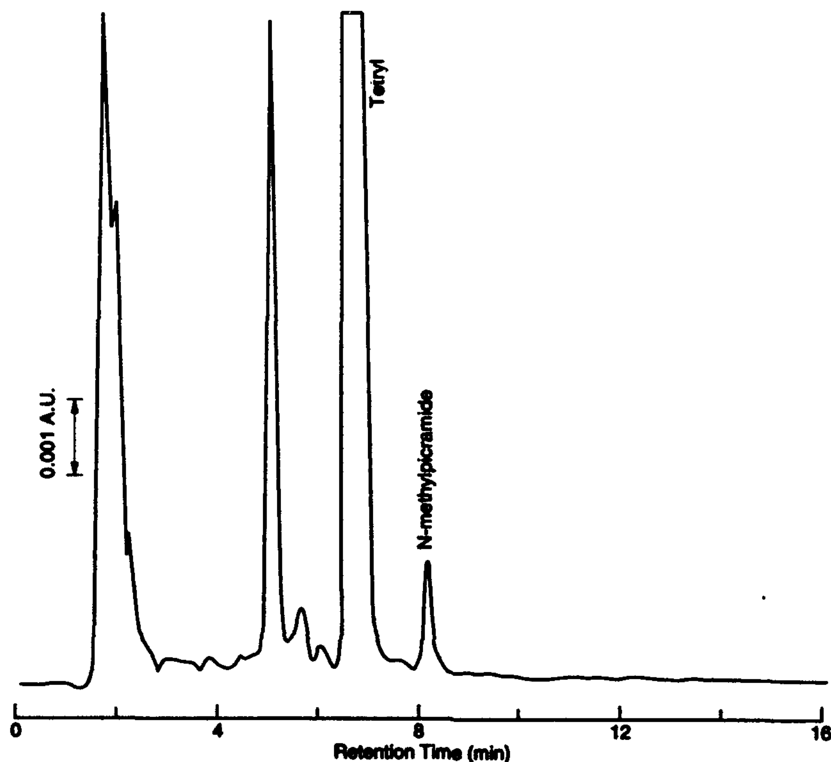

Figure 9. RP-HPLC chromatogram of extract from field-contaminated soil containing tetryl.

CONCLUDING REMARKS

Results from this study indicate that refrigeration is inadequate as a means of stabilizing tetryl in tetryl-fortified soils. After only 7 days of storage at 2°C, losses of tetryl ranged from 46–99%. Losses were reduced or eliminated when the fortified soils were frozen at –15°C. Since longer holding times were not tested, a MHT of 7 days is recommended when the soil is maintained frozen.

Several transformation products were observed as tetryl concentrations declined. Two of these are thought to be 4-amino-N-methyl-N,2,6-trinitroaniline and N-methylpicramide. Because tetryl is subject to hydrolysis as well as biotransformation, the mechanisms of transformation are very uncertain.

The above study was conducted using tetryl-fortified soils. This assumes that tetryl that is fortified into a soil behaves in a similar manner to tetryl that has been in contact with soils for years under field conditions. Elsewhere, Grant et al. (1993a) observed a large difference in nitroaromatics' (TNT, TNB and 2,4-DNT) stability between fortified and field contaminated soils. Analysis of tetryl-contaminated soils conducted years after contamination reveals large concentrations of intact tetryl. Whether this increased stability, relative to fortified soils, is from the difference in concentration of tetryl present, the difference in microorganisms present or their activity, or some other factor is uncertain. Additional research is urgently needed to determine if holding time studies, like the one discussed above, adequately mimic field-contaminated soil. If not, the results may be meaningless.

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13. ABSTRACT (*Maximum 200 words*)

A study was conducted to experimentally evaluate the maximum acceptable pre-extraction analytical holding times (MHTs) for tetryl in soil. Three soils fortified with tetryl at the low microgram-per-gram level were used in the study. Subsamples of each soil were extracted with acetonitrile in an ultrasonic bath after being held for 0, 1, 3 and 7 days at either room temperature (22°C), under refrigeration (2°C) or frozen (–15°C). Extracts were analyzed by RP-HPLC. Tetryl concentrations in soils stored at room temperature and under refrigeration declined rapidly over the 7-day study period and several transformation products accumulated. After 7 days of storage at 2°C, tetryl concentrations were reduced by 46, 97 and 99% in the three soils studied. When the soils were frozen, there were no statistically significant analyte losses over the 7-day study period (95% confidence level). On the basis of the results of these experiments, the recommended MHT for soils containing tetryl is 7 days if kept frozen. Longer holding times may be possible, but they were not investigated here. Refrigeration is inadequate to prevent significant transformation of tetryl in soil samples being held for analysis. A question regarding the ability to use analyte-fortified soil to mimic field-contaminated soils in holding time studies is raised.

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