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(6) THE BIODEGRADATION OF TNT IN ENHANCED SOIL AND COMPOST SYSTEMS.

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The ability of microorganisms to degrade TNT under a variety of conditions has been examined. A technique involving the degradation of TNT in soil which had been enhanced with additional nutrients was found to yield undesirable end products and to proceed at too slow a rate to be practical as a means of disposing of large quantities of TNT. A procedure using a composting technique was found to be acceptable in that reasonably large quantities (up to 10% dry weight) of TNT could be degraded in a reasonable time and no detectable undesirable end products

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resulted. The composting process was examined in bench scale experiments using standard analytical procedures and also carbon-14 tracer methodology.

FOREWORD

As a result of Executive Order 11507 of 4 February 1970 (superseded by Executive Order 11752 of 17 December 73), the US Army Armament Research and Development Command (ARRADCOM) (formerly Picatinny Arsenal) was directed to establish a program for the abatement of air, water, and solid waste pollution at Army Ammunition Plants.

Multi-task Project 54114 was initiated by the Special Technology Branch, Manufacturing Technology Division, Large Caliber Weapon Systems Laboratory, ARRADCOM (Dover site) as part of a concerted effort to meet the objectives of this directive.

This report reflects the efforts funded under Task 27, Project 54114, and is concerned with the abatement of solid waste pollution; specifically, with using biological soil and composting disposal techniques for waste TNT generated at the Army Ammunition Plants. This study was conducted by the Biological Sciences Branch of the Weapons Quality Engineering Center at the Naval Weapons Support Center, Crane, Indiana. The object of this study was to develop techniques to effect the biodegradation of TNT waste as a solid material. The problem of pink water or red water or TNT in aqueous solutions is not addressed by this study. As a corollary to this investigation, an attempt was made to determine the rate of TNT migration through soil by use of bench-scale lysimeters. This effort proved less than satisfactory; however, results of these experiments have been included as a reference to future investigators examining similar types of problems.

TABLE OF CONTENTS

	Page No.
Introduction	1
Approach	2
Landfill Simulation	2
Experiment 1	4
Experiment 2	5
Experiment 3	9
Migration Studies	20
Methods	20
Results	22
Conclusions	22
Compost Studies	23
Introductory Remarks	23
Bench-Scale Studies	24
^{14}C-TNT Compost Experiment	29
Conclusions	32
Soil Studies	32
Compost Studies	33
Recommendations	34
Performing Organizations Summary	34
ARRADCOM's Summary	35
References	36
Appendixes	
A Analysis Procedures	37
B Pilot Plant Design	61
Distribution List	73

Tables

1	Residual TNT in soil samples	6
2	Plate counts of bacteria on media with and without TNT	7
3	Composition of samples	8
4	Percent TNT in field plots	19
5	Composition of lysimeters	20
6	Lysimeter results	22
7	TNT degradation in composts	25
8	Effectiveness of various nitrogen sources in composting TNT	28
9	Compounds not detected as products of TNT composting	30

Figures

1	Some conversion products resulting from biological action on TNT	3
2	20% moisture glucose nutrient	10
3	40% moisture glucose nutrient	11
4	20% moisture beef extract peptone glucose nutrient	12
5	40% moisture beef extract peptone glucose nutrient	13
6	40% moisture beef extract peptone nutrient	14
7	20% moisture beef extract peptone nutrient	15
8	20% moisture glucose nutrient	16
9	40% moisture glucose nutrient	17
10	Lysimeter design	21

11 Degradation of TNT in bench-scale composts 26

12 Degradation of TNT in bench-scale composts 27

13 Recovery of ^{14}C activity from compost 31

INTRODUCTION

The disposal of large quantities of TNT in an environmentally acceptable manner poses serious difficulties. Previously used methods such as open burning are no longer acceptable due to the effects of particulates, NO_x, and other noxious products which result as air pollutants from this process. The practice of detonation of quantities of explosive suffers from similar shortcomings. Some methods of incineration are available which overcome these difficulties but suffer from extremely high capital and operating costs and the consumption of valuable fossil fuels. It was therefore determined that a biological approach to the disposal of solid TNT would be desirable, and the laboratory at NAVWPNSUPPCEN Crane undertook to develop suitable biodisposal techniques.

The development of biological methods for the disposal of TNT is not without its own problems. This laboratory and others have found through previous investigations involving the biodegradation of TNT in aqueous solutions that the usual degradation of TNT by microorganisms is incomplete. This results in the formation of undesirable end products of unknown toxicity and environmental effect. These substances are normally derivatives of TNT which are formed by the reduction of the nitro groups to various amine substitutions on the benzene ring. These products and the corresponding hydroxylamine derivatives can condense to form azo and azoxy compounds. Three of the most commonly found products are shown in Figure 1. Considering all the isomeric possibilities, the resultant number of TNT conversion products is quite large and makes analysis of the end products of TNT degradation difficult. The problem is further compounded due to the fact that the methyl substitution group may undergo oxidation to an alcohol, aldehyde, or carboxylic acid grouping. Fortunately most of these compounds are detectable using thin-layer chromatographic analytical procedures. While it is extremely difficult to identify the end products of TNT degradation in a biological system, it is normally possible to determine whether any products are present. Thus, the results of a particular experiment may show the presence of four conversion products derived from TNT, although it may not be possible to determine with certainty the identity of any of those products.

Rather than expend the time and effort required to develop analytical procedures and identification techniques for each of the possible TNT conversion products, the objective of this laboratory was to develop a system in which no conversion products would appear as end products. The inability to detect any of the commonly found conversion compounds

normally detectable by thin-layer, gas, or liquid chromatographic analysis was taken as presumptive evidence of either ring scission or complete incorporation of the TNT molecule into biomass. Either of these situations should result in the formation of environmentally acceptable products. The analysis procedures used in this study are summarized in Appendix A.

APPROACH

Upon the initiation of this study, it was decided that any procedure for disposing of large quantities of solid TNT waste should interface acceptably with existing techniques for the disposal of conventional solid wastes. Perhaps the most common method of solid waste disposal which utilizes biological processes (at least in part) is sanitary landfilling. It was therefore decided to design a series of experiments to simulate the conditions in a sanitary landfill situation. The first part of this study concerns itself with those experiments performed in a soil environment using indigenous microbial populations as the active biological agent.

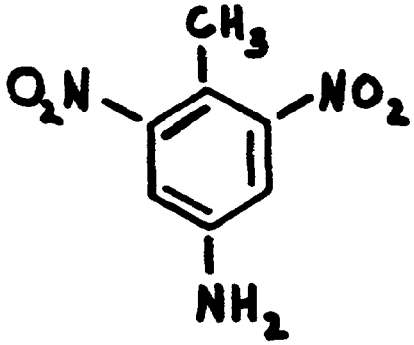
A less widely used but highly effective means of biologically treating solid waste is the composting process. A series of experiments was designed to examine the feasibility of treating TNT by this technique. The second part of this study involves bench-scale experiments in which TNT was composted with domestic refuse.

As a corollary to these experiments, attempts were made to measure the rate of migration of TNT through soil in bench-scale lysimeters. These experiments were deemed to be necessary since leaching of TNT might be a factor, especially if landfilling were chosen as the disposal method for solid TNT waste.

LANDFILL SIMULATION

In a landfill environment, soil, refuse, and TNT would be in close association. The microbial flora present in the soil would degrade the refuse and presumably the TNT at the same time. Previous experiments (Ref 1, 2) showed that bacteria would degrade TNT only in the presence of other nutrients.

In these experiments, soil, nutrient, and TNT were mixed together and incubated at a constant temperature. The moisture content of the samples was controlled at various levels for two reasons: The moisture



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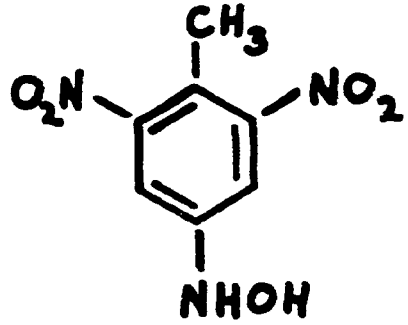

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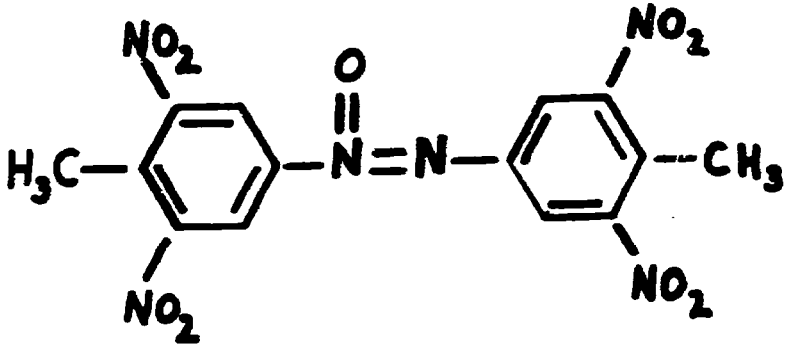

2, 2', 6, 6'-tetranitro-4,4'-azoxytoluene

Fig 1. Some conversion products resulting from biological action on TNT

level influences the type of organisms which would be likely to develop, and only the TNT which is in solution would be available to the organisms. Thus the moisture level would determine the amount of TNT available at any given time.

Various nutrients including laboratory chemicals and natural materials were used in the first experiment. Only laboratory chemicals were used in the second experiment because of a desire to have a more chemically defined nutrient source and one which was water soluble.

EXPERIMENT 1

Objective

The following study examined the ability of soil organisms to degrade TNT in the presence of various nutrients.

Procedure

A large sample of TNT-free soil was collected. The sample was thoroughly mixed and a small control portion held back. The remaining soil was blended with TNT until sampling revealed a homogeneous mixture. The resultant TNT concentration was 1.1% TNT weight/soil weight. This soil-TNT mixture was then divided into 10 lots. One lot was used as a control while various nutrients were blended evenly into the other nine lots. Each lot was divided into separate 50-gram samples. This was done to overcome errors due to using only a part of a given sample for analysis. The original homogeneity of a sample is soon lost during incubation, therefore an entire 50-gram sample was used for analysis. Each lot of 50-gram samples was further divided into four groups, each of which was maintained at a different moisture level. All samples were incubated at 30°C and 95% relative humidity.

Results

Preliminary results showed that the spectrodensitometeric method of analysis was satisfactory for measuring the TNT content of soil. However, during the course of the experiment, TNT conversion products appeared which interfered with this analysis. An improved, although somewhat more lengthy, procedure using thin-layer, gas, and liquid chromatography was developed that overcomes these difficulties. However, all results obtained during the early part of the experiment had to be discarded. Data are therefore available only for samples collected at 78 and 128 days incubation.

On the assumption that the nutrient source may have been exhausted during the incubation period thereby halting TNT degradation, additional nutrient equal to the original concentration was added to some samples at 100 days incubation. The residual TNT concentrations for all samples are given in Table 1.

The bacteria present in the samples collected at 128 days were counted to determine the effect of adding additional nutrient at 100 days. The objective was to see if TNT-tolerant organisms were benefited, or if the nutrient increased the proportion of non-TNT tolerant bacteria. If the latter case had proven correct, it would indicate that much of the additional nutrient was "wasted" on promoting the growth of organisms not able to degrade TNT. The procedure used was that developed by Klausmeier, et al (Ref 3).

The results shown in Table 2 demonstrate that TNT-tolerant organisms, i.e., those growing on media containing TNT, increased at least as dramatically as the total bacterial count. This indicates that the nutrient addition was effective in stimulating the growth of the proper organisms.

Conclusion

The experiment suggested that moisture content and nutrient level should be controlled to maximize the rate of TNT disappearance. Therefore, the experiment was repeated using a modified procedure.

EXPERIMENT 2

Objective

The purpose of this experiment was to determine the rate of TNT disappearance in soil systems, identify the end products, and examine the effect of the following parameters utilized as controlled variables:

1. Presence of nutrient in the soil
2. Type of nutrient present
3. Moisture level of the soil
4. Rate of nutrient replacement
5. Initial TNT content of the soil

Table 1

Residual TNT in soil samples[a]

Nutrient	% moisture	% TNT remaining after 78 days	% TNT remaining after 128 days	% TNT remaining after 128 days with nutrient replaced
None	7	0.71	0.88	
None	14	1.25	0.69	
None	21	1.13	0.83	
None	42	1.07	1.01	
1% YE[b]	7	0.90	0.39	0.42
1% YE	14	0.70	0.42	0.24
1% YE	21	0.59	0.39	0.33
1% YE	42	0.50	0.47	0.42
1% YE 1% Glucose	7	0.71	0.61	0.41
1% YE 1% Glucose	14	0.61	0.44	0.35
1% YE 1% Glucose	21	0.45	0.46	0.37
1% YE 1% Glucose	42	0.49	0.48	0.27
1% Glucose	7	0.87	0.70	0.41
1% Glucose	14	0.63	0.71	0.53
1% Glucose	21	0.70	0.39	0.54
1% Glucose	42	0.76	0.31	0.48
1% Glucose + 0.1% Fertilizer[c]	7	0.61	0.98	
1% Glucose + 0.1% Fertilizer	14	0.68	0.29	
1% Glucose + 0.1% Fertilizer	21	0.48	0.55	
1% Glucose + 0.1% Fertilizer	42	0.78	0.66	
0.1% Fertilizer	7	0.87	1.01	
0.1% Fertilizer	14	0.80	0.94	
0.1% Fertilizer	21	0.84	1.07	
0.1% Fertilizer	42	0.80	0.85	
1% Whey	7	0.69	0.58	0.49
1% Whey	14	0.65	0.52	0.52
1% Whey	21	0.61	0.46	0.22
1% Whey	42	0.51	0.47	0.28
3% Hay	7	0.84	0.57	
3% Hay	14	0.77	0.66	
3% Hay	21	0.69	0.47	
3% Hay	42	0.49	0.49	
3% Cardboard	7	0.72	1.02	
3% Cardboard	14	0.58	0.81	
3% Cardboard	21	0.71	0.67	
3% Cardboard	42	0.73	0.81	
1% Napthalene	7	0.85	1.12	
1% Napthalene	14	1.10	0.56	
1% Napthalene	21	1.03	0.55	
1% Napthalene	42	0.95	0.50	

[a] Initial TNT concentration was 1.1% in all cases

[b] Yeast Extract

[c] Commercial 12-12-12 chemical fertilizer

Table 2

Plate counts of bacteria on media with and without TNT

Nutrient	% moisture	Nutrient not replenished (Cells X 10^4 /gm) YEG	YEG+TNT	Nutrient replenished (Cells X 10^4 /gm) YEG	YEG+TNT
None	7	69			
None	14	43			
None	21	40			
None	42	24			
1% YE	7	23	23	3500	3600
1% YE	14	1.9	0.1	11	7
1% YE	21	4	2	140	NC*
1% YE	42	22	NC	670	430
1% YE 1% Glucose	7	22	22	420	420
1% YE 1% Glucose	14	58	57	470	430
1% YE 1% Glucose	21	220	170	2300	3600
1% YE 1% Glucose	42	340	460	4200	12000
1% Glucose	7	19	NC	580	490
1% Glucose	14	13	NC	160	120
1% Glucose	21	4	NC	NC	NC
1% Glucose	42	17	NC	40	10
1% Whey	7	15	3.1	3600	4000
1% Whey	14	170	190	1100	1100
1% Whey	21	200	190	2000	2700
1% Whey	42	650	420	11000	14000

*No count available

Procedure

A large soil sample was allowed to partially dry in air at room temperature. Care was taken not to overdry the sample and destroy the microflora. The soil was sieved and mixed in a rotating drum type blender to insure uniformity. The mixed soil was divided into two portions, A and B. Portion A was blended with crystalline TNT to yield a mixture of 5% TNT on a dry-soil weight basis. The soil/TNT mixture was divided into two portions, one of which was divided into 16 samples having a dry weight of 10 grams each. The remainder was blended with glucose to a 1% glucose concentration. The soil-TNT-glucose mixture was divided into 32 samples or 4 groups of 8 each. All of the samples were placed in individual containers.

Water was added to one group of eight soil/TNT samples and two groups of soil-TNT-glucose samples so that each sample contained 40% moisture. The remaining three groups of samples received 20% moisture.

Portion B of the soil was blended to 1% TNT concentration, and subdivided to yield 20 groups of 8 samples each. One group received no nutrient and served as a control. Other groups received either glucose, beef extract and peptone, or a mixture of both. Beef extract-peptone, which contains organic nitrogen, was used to check the effect of nitrogen sources on TNT degradation. Due to the difficulty of pulling a representative sample from a large pot of soil, groups of eight identical samples were used so that one entire sample could be pulled at each sampling period. Table 3 shows the composition of each group of tubes.

Table 3

Composition of samples

Sample No.	TNT	% moisture	Nutrient	Nutrient replacement rate
1	1	20	None (Control)	0
2	1	40	None (Control)	0
3	1	20	Glucose	0
4	1	40	Glucose	0
5	1	20	Glucose	.25%/wk
6	1	40	Glucose	.25%/wk
7	1	20	Glucose	.75%/wk
8	1	40	Glucose	.75%/wk
9	1	20	Glucose & BEP	0
10	1	40	Glucose & BEP	0
11	1	20	Glucose & BEP	.25%/wk
12	1	40	Glucose & BEP	.25%/wk
13	1	20	Glucose & BEP	.75%/wk
14	1	40	Glucose & BEP	.75%/wk
15	1	20	Beef Extract Peptone (BEP)	0
16	1	40	Beef Extract Peptone (BEP)	0
17	1	20	Beef Extract Peptone (BEP)	.25%/wk
18	1	40	Beef Extract Peptone (BEP)	.25%/wk
19	1	20	Beef Extract Peptone (BEP)	.75%/wk
20	1	40	Beef Extract Peptone (BEP)	.75%/wk
21	5	20	None (Control)	0
22	5	40	None (Control)	0
23	5	20	Glucose	0
24	5	40	Glucose	0
25	5	20	Glucose	.25%/wk
26	5	40	Glucose	.25%/wk

When samples were taken, an entire container was removed from incubation, placed in a desiccator at room temperature to remove most of the moisture, then extracted with acetone. The extract was analyzed for TNT by gas and/or liquid chromatography. At times, the extract was examined by thin-layer chromatography for the presence of conversion products.

Results

The results of this experiment are shown graphically in Figures 2 through 9.

Conclusions

The results demonstrated graphically illustrate the following conclusions:

1. TNT is readily bioconverted by soil organisms.

2. The conversion rate is higher at 40% than at 20% moisture, probably a solubility effect.

3. The presence of other organic nutrients speeds conversion.

4. Organic nitrogen (BEP) is neither more nor less effective than glucose.

5. Periodic readdition of nutrient maximizes conversion rate.

6. The highest rate of readdition was most effective in these studies.

7. End products included 4-amino-dinitrotoluene after all of the TNT had disappeared, indicating that TNT was not completely mineralized in the soil system.

EXPERIMENT 3

Objective

As an extension of the bench-scale studies, experiments were conducted in outdoor plots of soil to determine the feasibility of degrading TNT in soil under ambient field conditions.

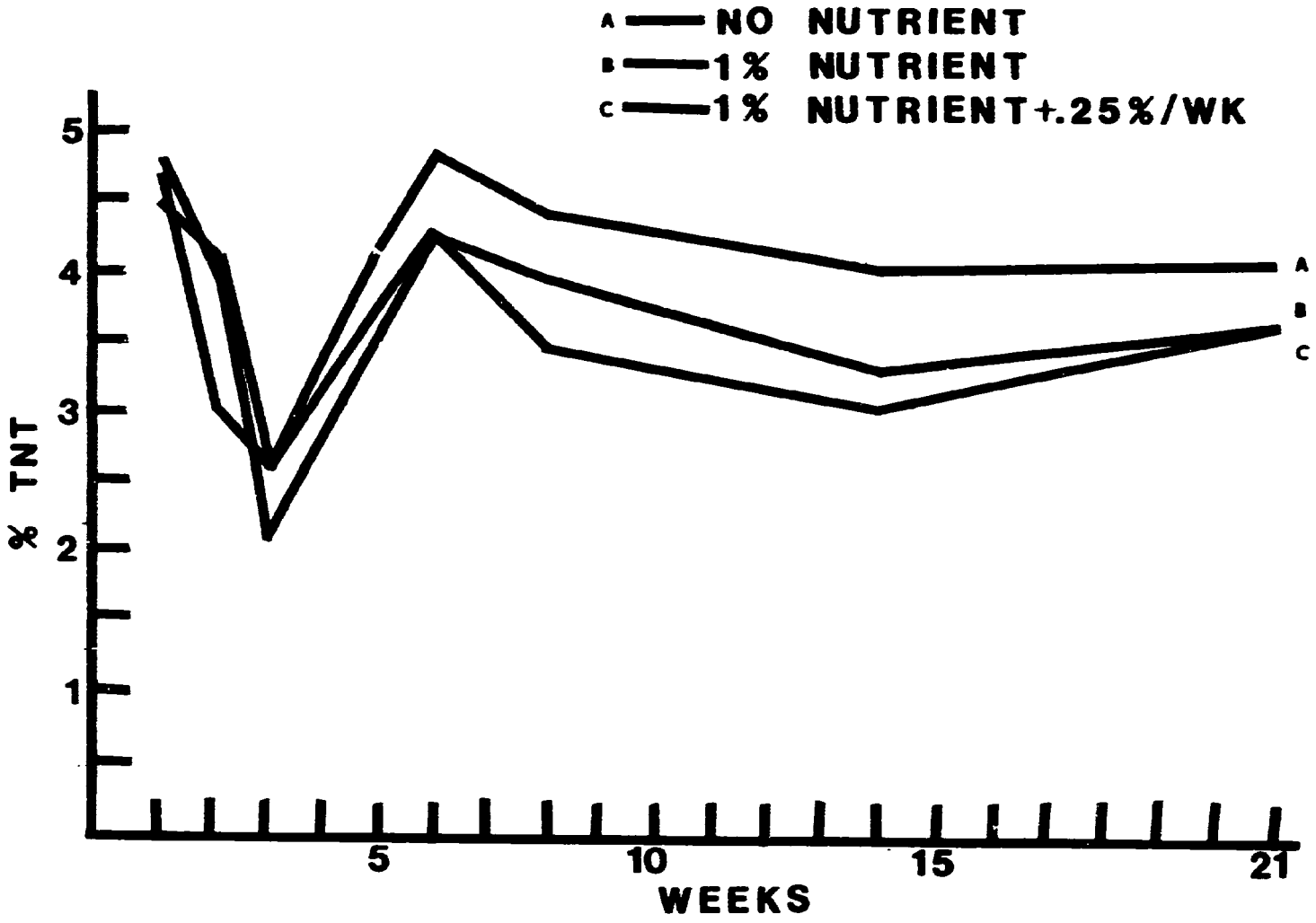

Fig 2 20% moisture glucose nutrient

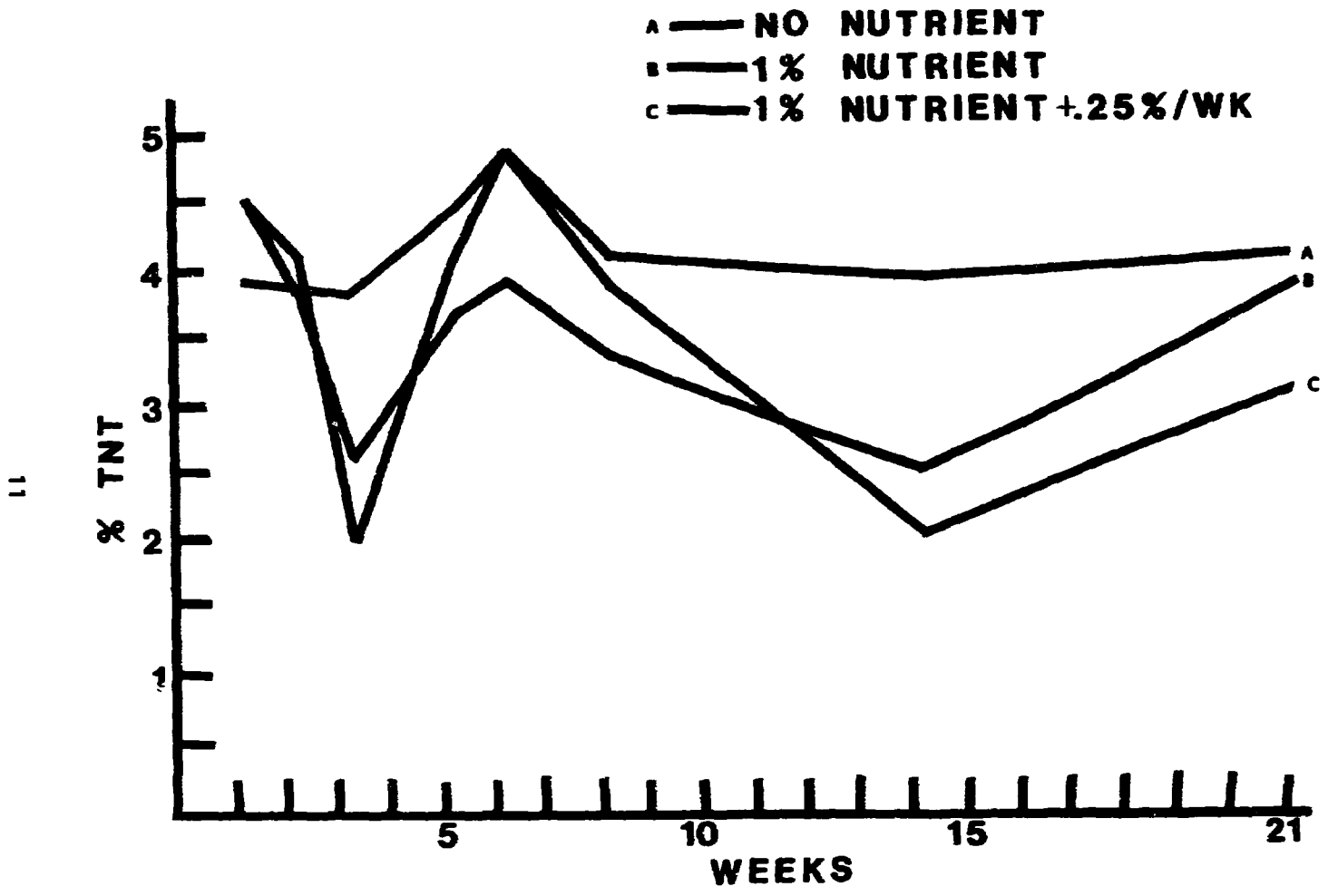

Fig 3 40% moisture glucose nutrient

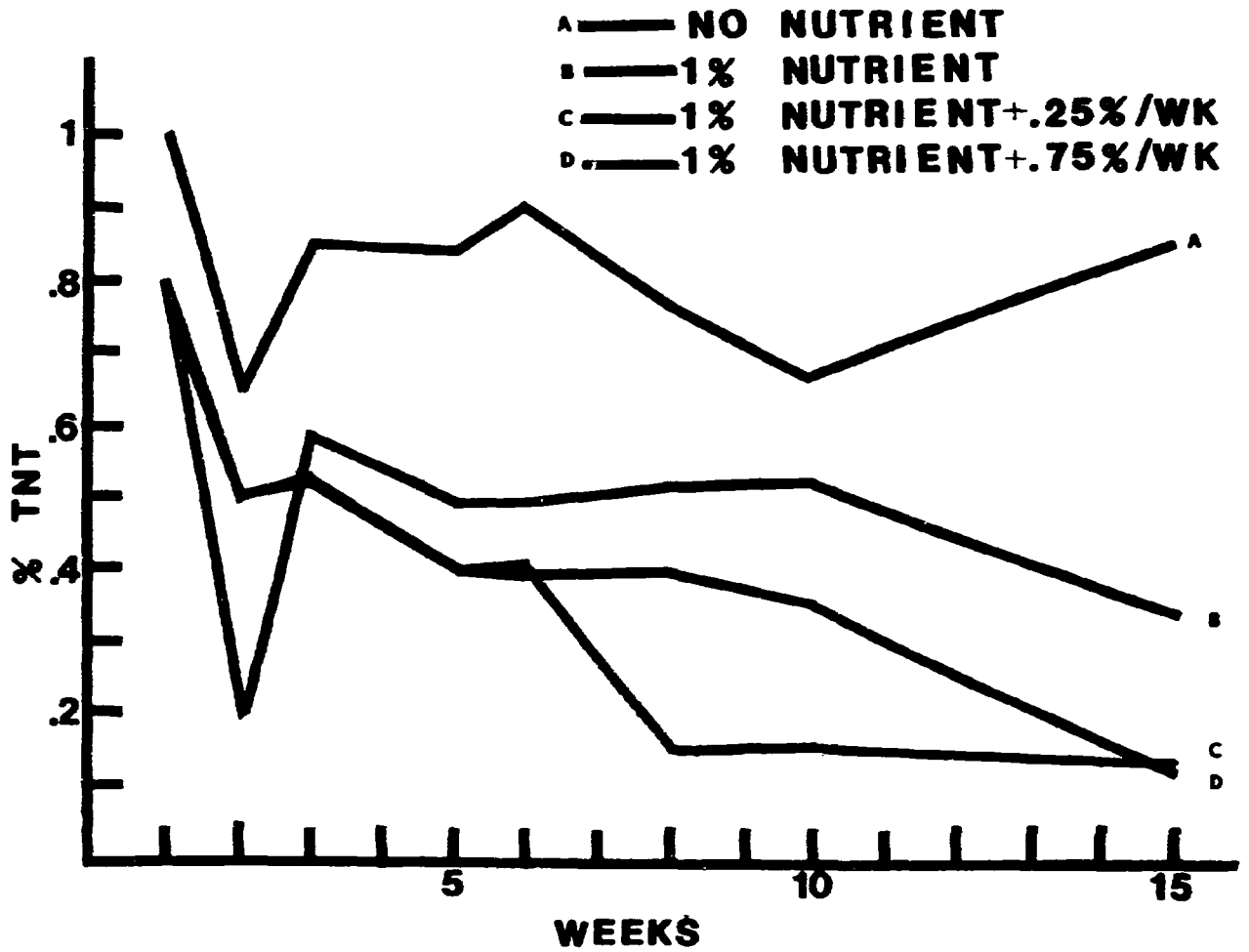

Fig 4 20% moisture beef extract peptone glucose nutrient

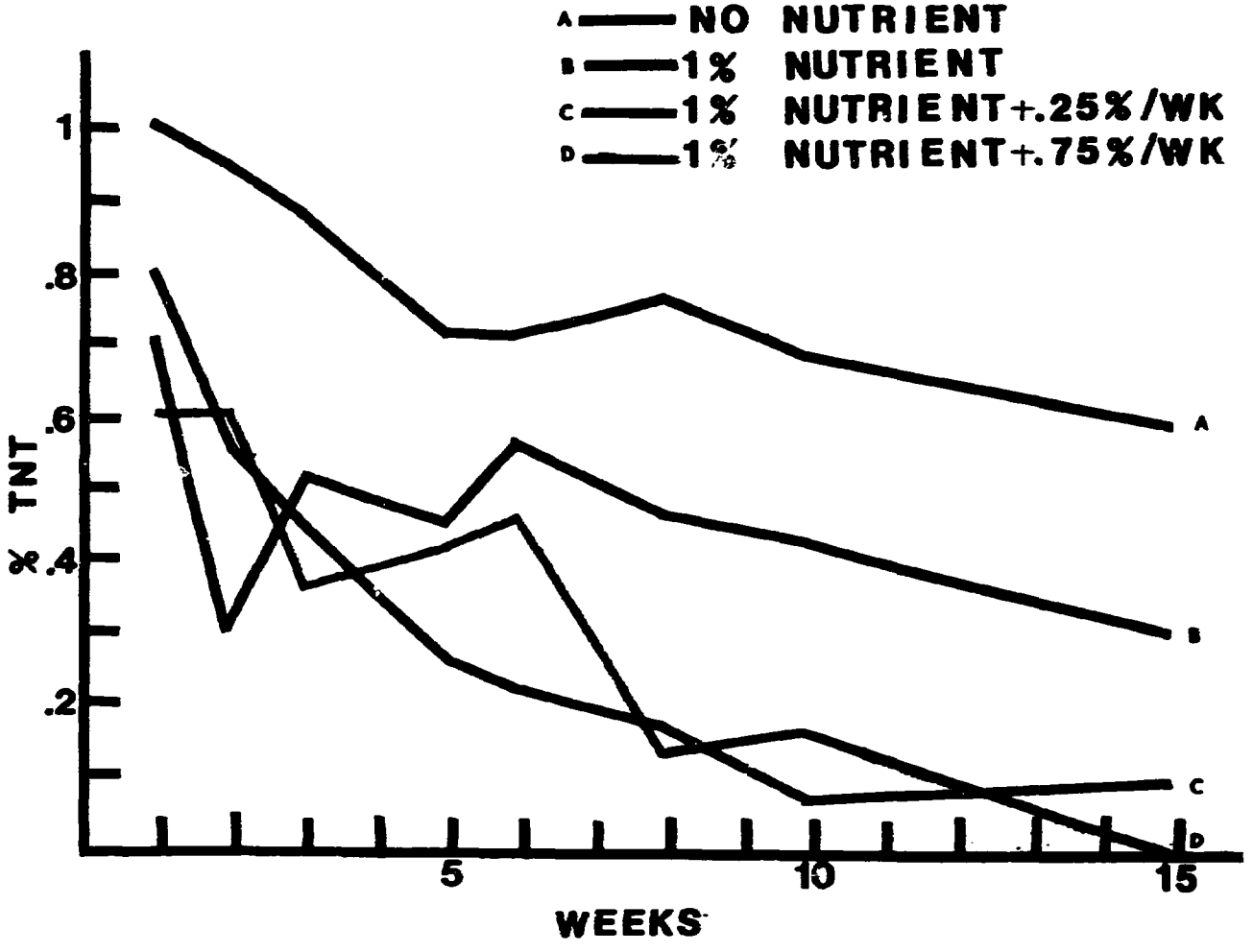

Fig 5 40% moisture beef extract peptone glucose nutrient

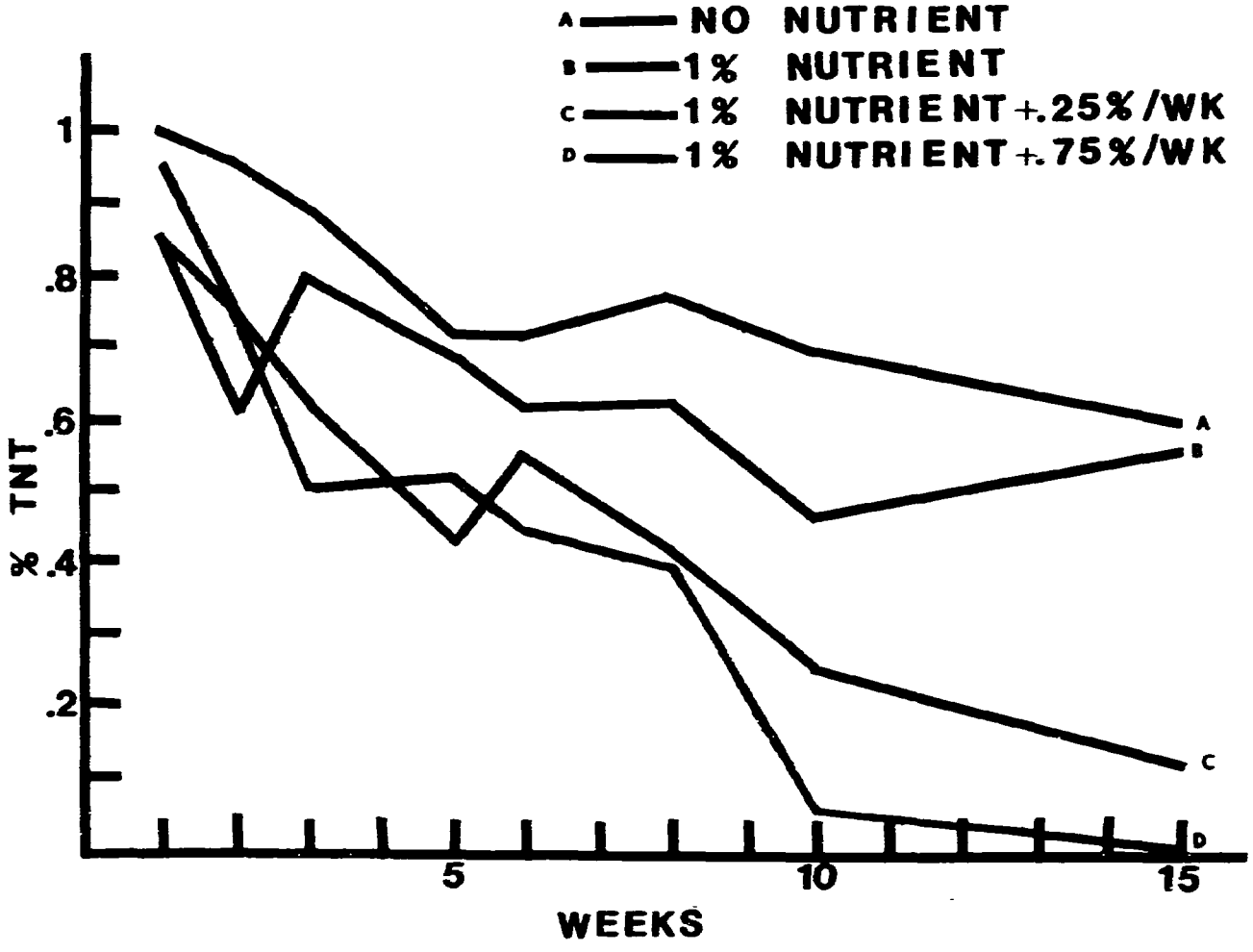

Fig 6 40% moisture beef extract peptone nutrient

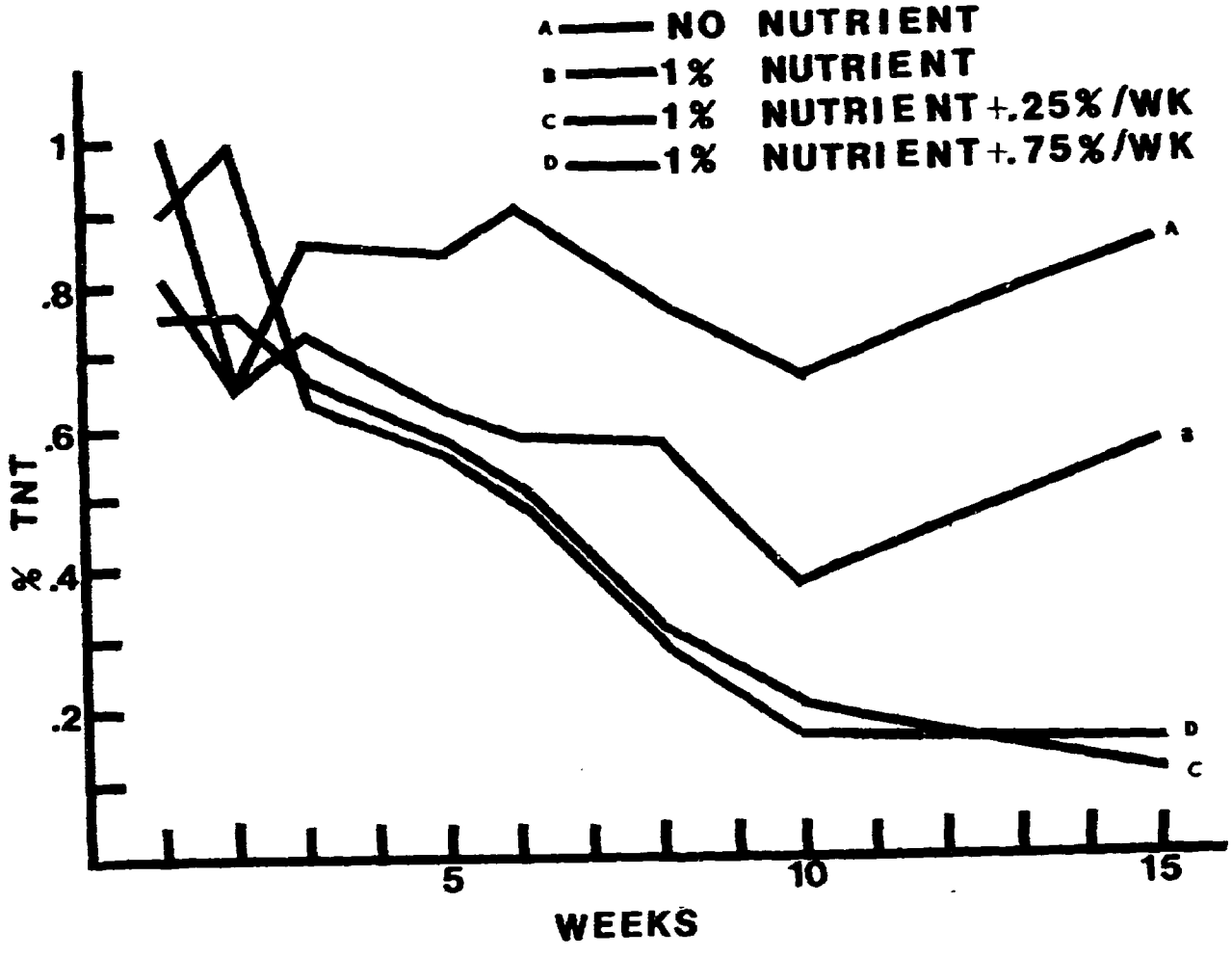

Fig 7 20% moisture beef extract peptone nutrient

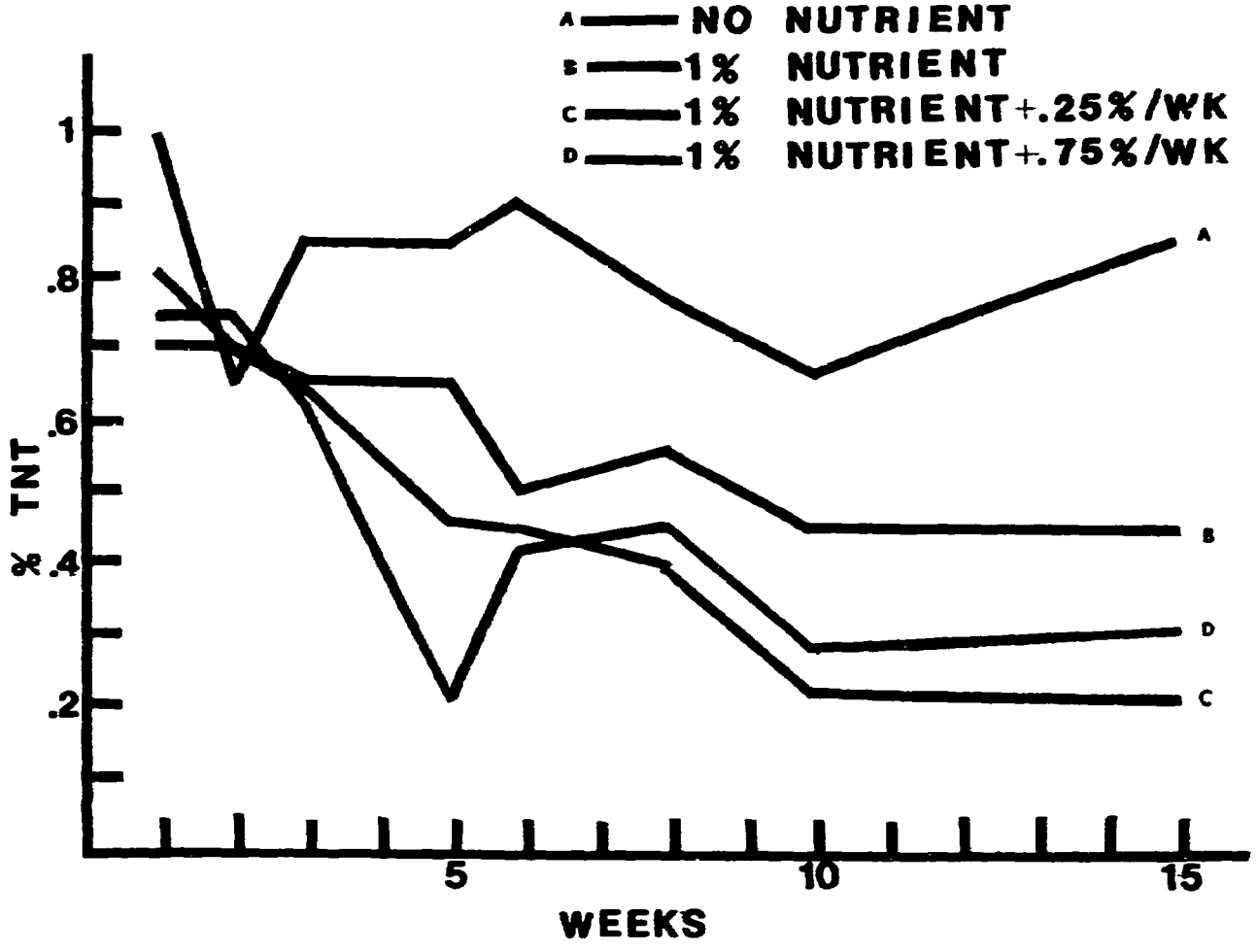

Fig 8 20% moisture glucose nutrient

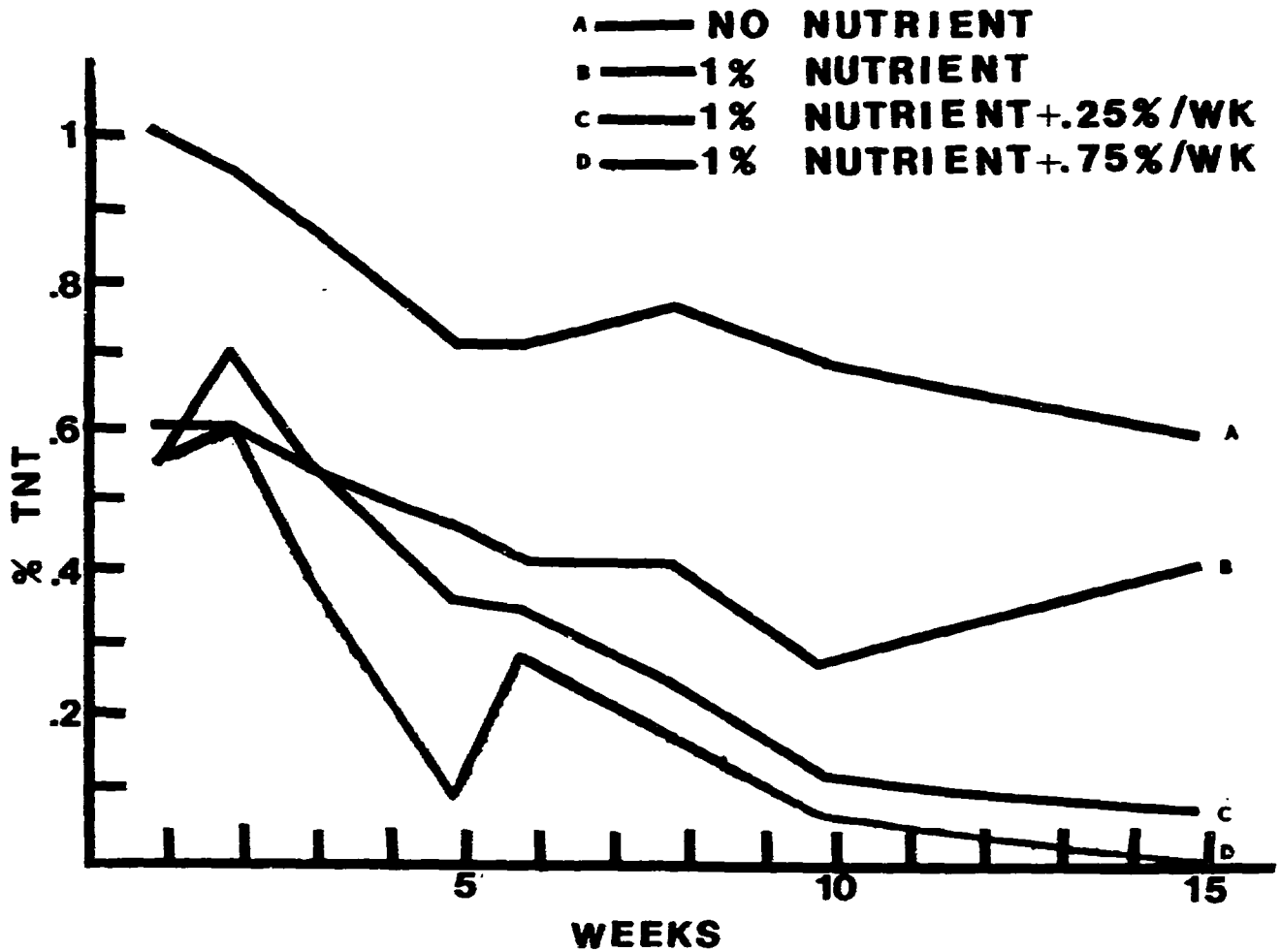

Fig 9 40% moisture glucose nutrient

Procedure

Twelve plots, each approximately 3 x .6 m (10 ft by 2 ft), were delineated. Each plot was tilled with a rotary type garden tiller into a reasonable state of tilth to a depth of about 15.2 cm (6 in.). Each plot then received 3 kilograms of TNT in ground crystalline form. The TNT was scattered over the surface of each plot and mixed with the soil by repeated passes with the garden tiller. Several samples were taken from each plot, combined, and assayed for TNT content. Plots then received various nutrients (listed below) and were mixed by tilling. According to the schedule some plots were tilled once each week to maintain mixing and aeration while other plots were left untilled for comparison.

Plot	Nutrients
1	3 kg of dried whey, untilled
2	1 kg dried sewage sludge, 1 kg shredded newspaper, 0.5 kg dried lawn clippings, tilled
3	1 kg dried lawn clippings, tilled
4	control, no nutrient, tilled
5	control, no nutrient, untilled
6	3 kg dried whey, tilled
7	3 kg chopped newspaper, tilled
8	3 kg dried sewage sludge, tilled
9	1 kg dried sewage sludge, 1 kg shredded newspaper, 0.5 kg dried lawn clippings, tilled
10	3 kg dried sewage sludge, tilled
11	1 kg dried lawn clippings, tilled
12	3 kg dried whey, tilled

Results

Table 4 shows the results of composite samples taken at intervals and assayed for TNT. Samples represent only the surface, i.e., upper 15.2 cm (6 inches) of soil which is tilled.

Table 4

Percent TNT in field plots

Plot No.	Week of test			
	0	4	6	10
1	.78	.70	.41	.42
2	1.32	.34	.53	.29
3	.92	.70	.77	.29
4	.78	.74	.84	.53
5	.98	1.21	.57	.49
6	.81	.69	.52	.25
7	.86	.49	.36	.17
8	.93	.50	.58	.33
9	.96	.47	.69	.33
10	.97	.58	.48	.52
11	.68	.56	.56	.25
12	1.02	.81	.56	.33

The above data illustrate the difficulty involved in collecting absolutely uniform samples from an experiment of this kind. Obviously plot 4 did not generate more TNT between weeks 4 and 6. The data should not, therefore, be considered as absolute representative values for the amount of TNT in each plot, but rather as trends.

Analyses by thin-layer chromatography showed undesirable conversion products to be present in most samples. Unfortunately this experiment was terminated due to lack of funds prior to completion. Unfinished work included the analysis of deeper soil layers beneath the plots to determine the amount of leaching of TNT from this system.

Conclusions

The behavior of TNT in a field situation appears to parallel that of TNT in bench-scale soil experiments. Disappearance of the explosive is largely due to conversion to other products and not degradation.

MIGRATION STUDIES

Methods

In an attempt to measure the rate of TNT migration through soil, a series of bench-scale lysimeters were constructed (Fig 10). As shown in the diagram, soil was packed into each lysimeter to a depth of 18 cm (7 in.). A 2.5 cm (1 in.) deep section in the center of each lysimeter was excised and mixed with TNT and, if appropriate, nutrient. A clay, sand, and loam soil was used in various of the units to compare migration rate in different soil types.

The lysimeters were watered on a regular schedule in a manner which simulated rainfall. In some cases additives were used in the "rain." Table 5 gives the composition of the soil-nutrient-rainfall for each lysimeter.

Table 5

Composition of lysimeters

Unit No.	Soil type	Nutrient	CM/WK rainfall	Additives to rainfall
1	Clay	None	1.5	None
2	Clay	YEG[a]	1.5	None
3	Sand	None	1.5	None
4	Sand	YEG	1.5	None
5	Loam	None	1.5	None
6	Loam	YEG	1.5	None
7	Loam	YEG	1.5	YEG
8	Loam	YEG	3.0	YEG
9	Loam	None	3.0	None
10	Loam	Whey	1.5	Whey
11	Loam	YEG	1.5	YEG, MS[b]
12	Loam	None	1.5	YEG

[a] YEG = Yeast extract and glucose

[b] MS = An inorganic solution of phosphorus and nitrogen salts

The rainfall was collected after it percolated through each lysimeter and was analyzed by gas and thin-layer chromatography for TNT and any conversion products present. The idea was to determine the time interval required for TNT to appear in the effluent and thus calculate a migration rate.

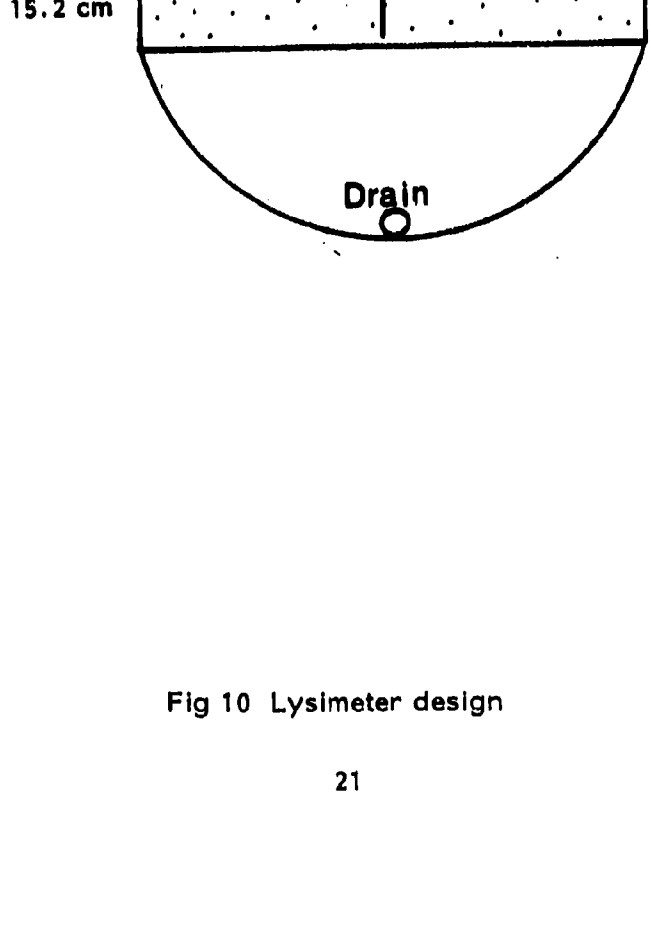

Fig 10 Lysimeter design

Results

The results of this experiment are shown in Table 6.

Table 6

Lysimeter results

Lysimeter No.	TNT breakthrough (WKS)
1	6
2	10
3	19
4	25
5	29
6	27
8	29
11	30

None of the other lysimeters (7, 9, 10 and 12) showed significant TNT in the effluent through 50 weeks testing.

The results, therefore, show only that TNT moved fastest through clay (probably due to microchannels), slower through sand, and slowest through loam soil. The presence of nutrient also slowed TNT migration and reduced its concentration in the effluent, although conversion products were evident in such cases.

As an extension of these studies, samples of TNT weighing 0.5 kg placed in holes 20 cm (7.9 in.) deep in the field were used to measure migration under outdoor conditions. However, after more than 40 weeks exposure, TNT in measurable quantities had failed to migrate more then 7.6 cm (3 in.) from the samples. These results suggest that TNT is not as mobile in soil as might have been expected.

Conclusions

The bench-scale lysimeter technique proved to be an unsatisfactory method for measuring TNT migration. The field studies were limited in scope but indicate a slow rate of TNT migration through the clay soil present at the field sites used.

COMPOST STUDIES

Introductory Remarks

Composting, a technique familiar to most gardeners, is essentially a process of controlled biological degradation. The starting materials, which may be virtually any degradable organic substance, are converted through the action of microorganisms into a substance which has deteriorated to the point that further degradation proceeds at a much slower rate. The product, compost, is then said to be stable. The characteristics of a finished compost are those of a somewhat fluffy loam-like material, dark in color, and possessing excellent moisture-absorbing capacity.

In order to optimize the composting process, it is necessary to shred or grind the initial materials into reasonably small particles. It is also necessary to maintain the proper levels of moisture and aeration. The balance of certain nutrient elements in the composting material is also important. The ratio of carbon to nitrogen is especially important. When these factors are properly controlled, the growth of certain microorganisms (called thermophiles) is enhanced. During growth, these organisms liberate heat as evidenced by the fact that the temperature in a properly maintained compost may reach as high as 70°C. Since the rate of chemical reactions increases with temperature, it is not surprising that thermophiles are among the fastest growing microorganisms. Composting is, therefore, one of the most rapid biodeterioration processes known. It is perhaps due to the combination of heat and biological action that the composting process is effective as a means of degrading TNT where other biological degradation techniques are not. It is also possible that the effectiveness of composting is due to unique properties of thermophilic microorganisms. In any event, composting is the only biological method for the disposal of TNT in quantity which has been demonstrated to be effective.

Furthermore, composting as a step prior to landfilling has been shown to be a valuable and effective solid-waste management technique in that the life of the sanitary landfill is increased by 50% or more and the problems associated with exudates from landfill operations are eliminated or drastically reduced. The composting of TNT, and possibly other explosives, would therefore not only eliminate pollution problems associated with the disposal of explosives but would also assist in the growing problem of solid waste management.

In order to produce an active compost, the following elements must be present:

1. A source of available carbon

2. A source of available nitrogen

3. Moisture

4. Oxygen

5. Various minerals (i.e., phosphorus, potassium, magnesium, etc.)

6. Thermophilic microorganisms

The proper organisms and minerals (required in small amounts) are normally present in most organic refuse materials. Phosphorus is an exception in some cases. The first four elements must be considered as the variables which affect compost performance. Further, the balance of these factors is critical in insuring optimal composting. If the ratio of carbon to nitrogen is too high, the organisms grow too slowly due to nitrogen starvation. If the carbon/nitrogen ratio is too low, the microbes produce ammonia from excess nitrogen and the pH becomes intolerable for further growth. Too little moisture prevents microbial growth, but too much moisture results in the establishment of anaerobic conditions which retard the rate of degradation and produce foul odors.

Bench-Scale Studies

Methods

In our studies a variety of types of starting materials were examined: paper, garbage, cardboard, leaves, grass clippings, potatoes, straw, wheat flour, sucrose, and commercial horse feed as carbon sources. Grass clippings, garbage, manure, sewage sludge, commercial fertilizer and chemicals such as sodium nitrate were used as nitrogen sources.

These materials were chopped or ground to various degrees of fineness, mixed in various proportions, moistened to varying degrees, and manipulated in several different ways until reasonably standard methods of preparing suitable composts were established. Experiments which examined the effects of adding TNT to these otherwise functional compost systems were then performed.

Results

Results from composting experiments are very encouraging. A wide variety of starting materials have been used successfully and TNT degradation proceeds rather rapidly. Successful composts have been initiated with TNT comprising as much as 10% of the dry weight of the original material.

The graphs in Figures 11 and 12 show the decreasing concentration of TNT with time for four different compost assays. All curves appear asymptotic with the rate of the TNT'S disappearance, decreasing as the TNT concentration approaches zero. The asymptotic nature of the curves is probably due to the concentration effect and to the fact that biological activity is much greater in the compost during the first 20 days than thereafter.

Table 7 shows the effectiveness of four identical composts in degrading concentrations of TNT ranging from 1% to 10% on a dry-weight basis.

Table 7

TNT degradation in composts

Days	(% TNT in compost)			
0	1.0	5.0	5.0	10.0
2	0.9	4.3		
4	0.4	3.0		
6			2.8	7.0
7	0.4	3.3		
9			3.1	5.5
11	0.2	2.5		
13			1.6	3.7
17			1.4	3.8
18	0.13	2.2		
32	0.05	1.0		
38			0.8	2.0
46	0.01	0.5		
52			0.7	1.2
53	0.01	0.4		

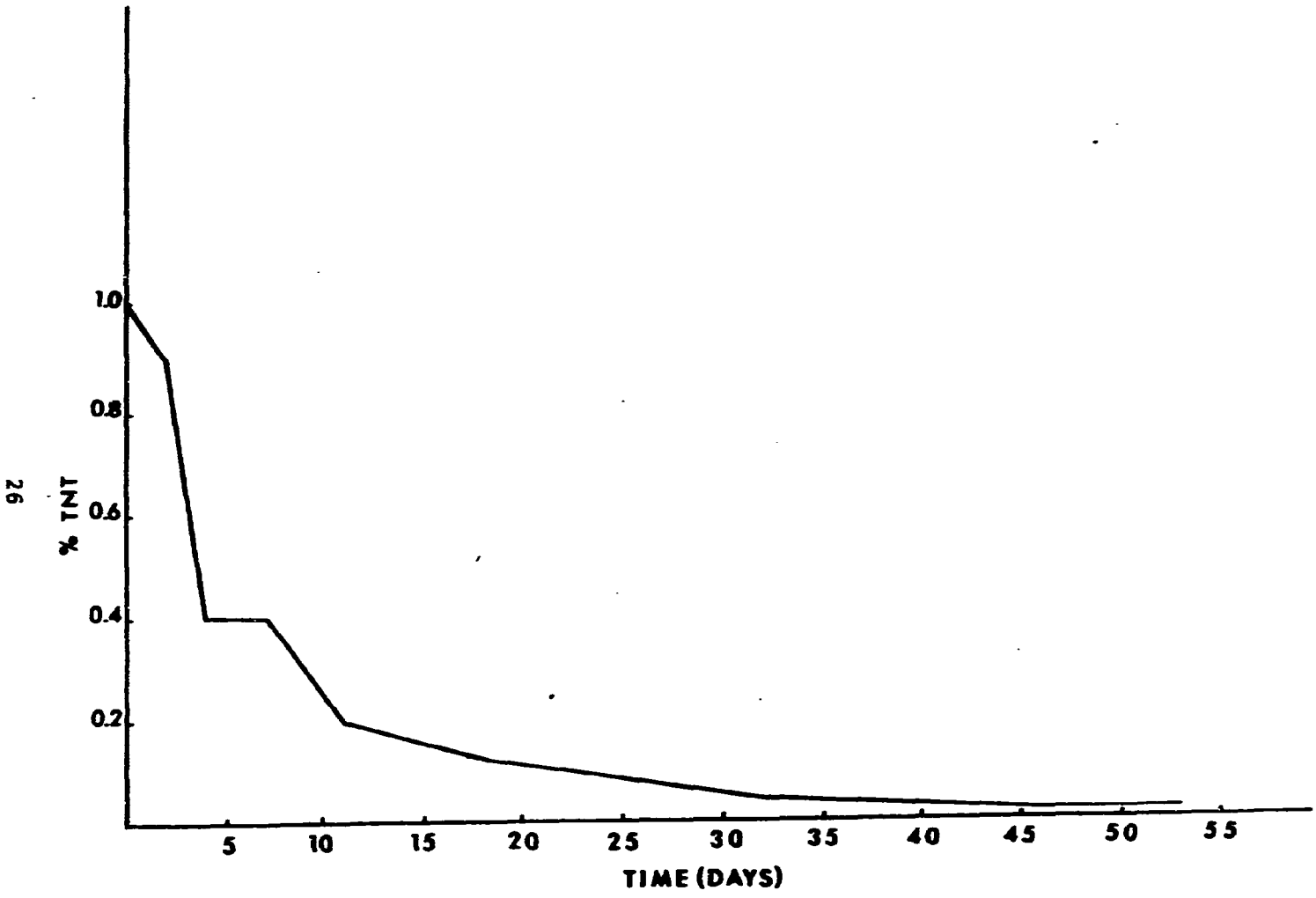

Fig 11 Degradation of TNT in bench-scale composts

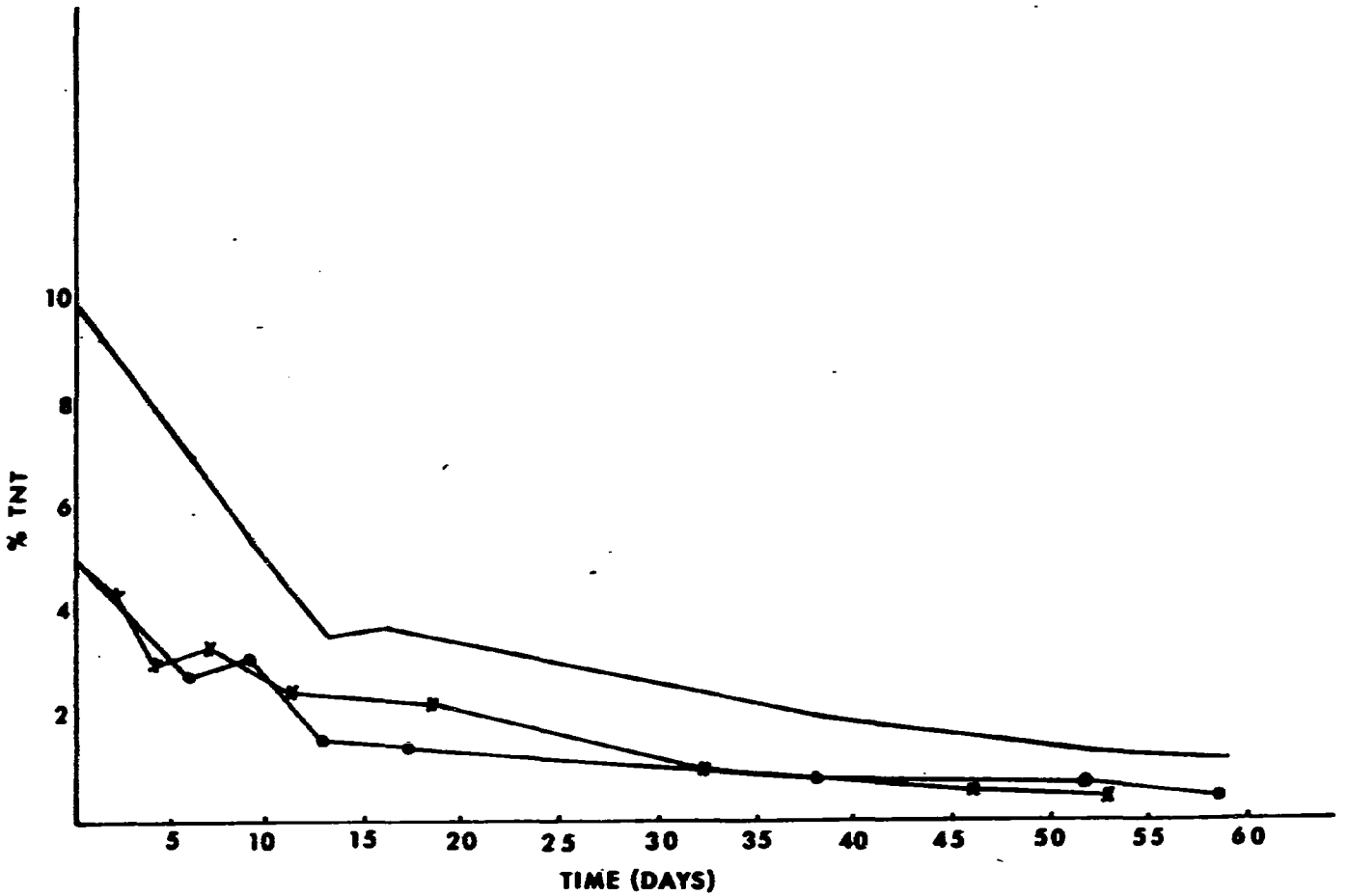

Fig 12 Degradation of TNT in bench-scale composts

In another experiment the feasibility of using the $NaNO_3$ solution resulting from a pyrotechnic washout procedure as a nitrogen source was examined. These results are given in Table 8.

Table 8

Effectiveness of various nitrogen sources in composting TNT

	Nitrogen source		
	$NaNO_3$	Protein	Manure
Days incubation	(% TNT in compost)		
0	5.0	5.0	5.0
2	3.8	3.0	4.6
4	3.6	2.3	4.1
14	3.0	1.6	3.9
22	3.0	0.56	3.6
35	3.04	0.75	2.23
44	2.40	0.29	2.88
66	2.48	0.46	1.42
85	0.90	0.11	0.80
105	1.25	0.06	0.92
119	1.42	0.11	0.91

These results indicate that although pyro-wash solution may not be an optimal nitrogen source, it was effective enough to warrant further investigation in larger scale experiments.

The most encouraging aspect of the composting studies is the failure of any conversion products to appear as end products. For example, a recent compost initially contained 5% TNT. Maximum temperature of 46.5°C was attained on the eighth day of composting. At 31 days, analysis by gas chromatography showed 0.48% TNT remaining, and analysis by thin-layer chromatography showed no nitroaromatic residue other than TNT. This suggests that TNT is being mineralized by the compost organisms.

Conclusions

Almost any biodegradable organic materials will produce a workable compost. The more readily degradable the waste, the faster composting will proceed. The activity of a compost is also optimized when the following conditions are met:

1. The carbon/nitrogen ratio = 30: 1

2. The moisture content is 40% to 60%

3. Oxygen level is maintained high

4. Compost is mixed frequently

5. Materials are ground or shredded prior to composting

Results suggest that relatively large quantities of TNT may be disposed of quickly by composting a material containing 5% or more TNT. As the concentration approaches 1% and the disappearance curve begins to level off, this compost could be mixed with fresh material and recomposted as a second stage to maintain a high rate of degradation throughout the process of reducing TNT concentration to essentially zero or to acceptable levels. This two-stage process could be examined more effectively in large scale experiments and has not been attempted in bench-scale studies.

It is emphasized again that TNT does not yield the undesirable end products in composting experiments that it does in soil experiments. In an attempt to identify the end products, a micro-compost was set up using ^{14}C-labeled TNT.

^{14}C-TNT Compost Experiment

Objective

The purpose of this experiment was to identify the end products of TNT composting.

Methods

A compost was prepared from grass clippings, NH_4Cl, KH_2PO_4, and 10 mg of uniformly labeled ^{14}C-TNT having an activity of 2.25 cpm/mg. The total weight of the compost was 1 gram. The compost was placed in an incubator at 55°C. Air was passed through the sample continuously and efferent air was passed through NaOH traps to collect CO_2. The CO_2 was converted to $BaCO_3$ and counted by liquid scintillation. The sample was incubated 105 days. This prolonged incubation was necessary because of the lower level of biological activity present as compared to some larger composts.

The compost analysis was initiated by soaking the compost in a 5% solution of sodium pyrophosphate. This separated some microbial cells from the compost solids. The cell suspension was centrifuged and the cells washed. The compost solids were extracted with benzene and acetone, then extracted with 0.45N acetic acid. The compost solids were treated with cellulase enzyme to break linkages and release any strongly absorbed material. All aqueous extracts and solutions were extracted with benzene and acetone. The activity of each fraction was determined and TLC analysis was performed on each extract.

The flow chart (Fig 13) outlines the experimental treatment and results.

Results

Of the 68.44% of total activity recovered in aqueous fractions, only 0.085% was extractable from aqueous materials using benzene and acetone. These results show that these products are not any of the conversion compounds such as those often found in TNT biodegradation systems. The products are highly polar, water soluble, and not yet identified. Consultation with other laboratories working with TNT failed to yield any clue as to the identity of these materials. While it is not possible to state what these compounds are, Table 9 lists compounds which may be excluded from consideration.

Table 9

Compounds not detected as products of TNT composting

2,5-dinitrotoluene
3,5-dinitrotoluene
2,4-dinitrotoluene
2,4,6-trinitroethylbenzene
2,6-dinitrotoluene
2,4,6-trinitrobenzaldehyde
2,4,6-trinitrobenzyl alchol
2,4,6-trinitrobenzoic acid
2,4,6-trinotrophenol
4-amino-2,6-dinitrotoluene
2,4-diamino-6-nitrotoluene
4-hydroxylamino-2,6-dinitrotoluene
2,2',6,6'-tetranitro-4,4' azoxytoluene
4,4',6,6'-tetranitro-2,2' azoxytoluene
all isomers of dinitrophenols

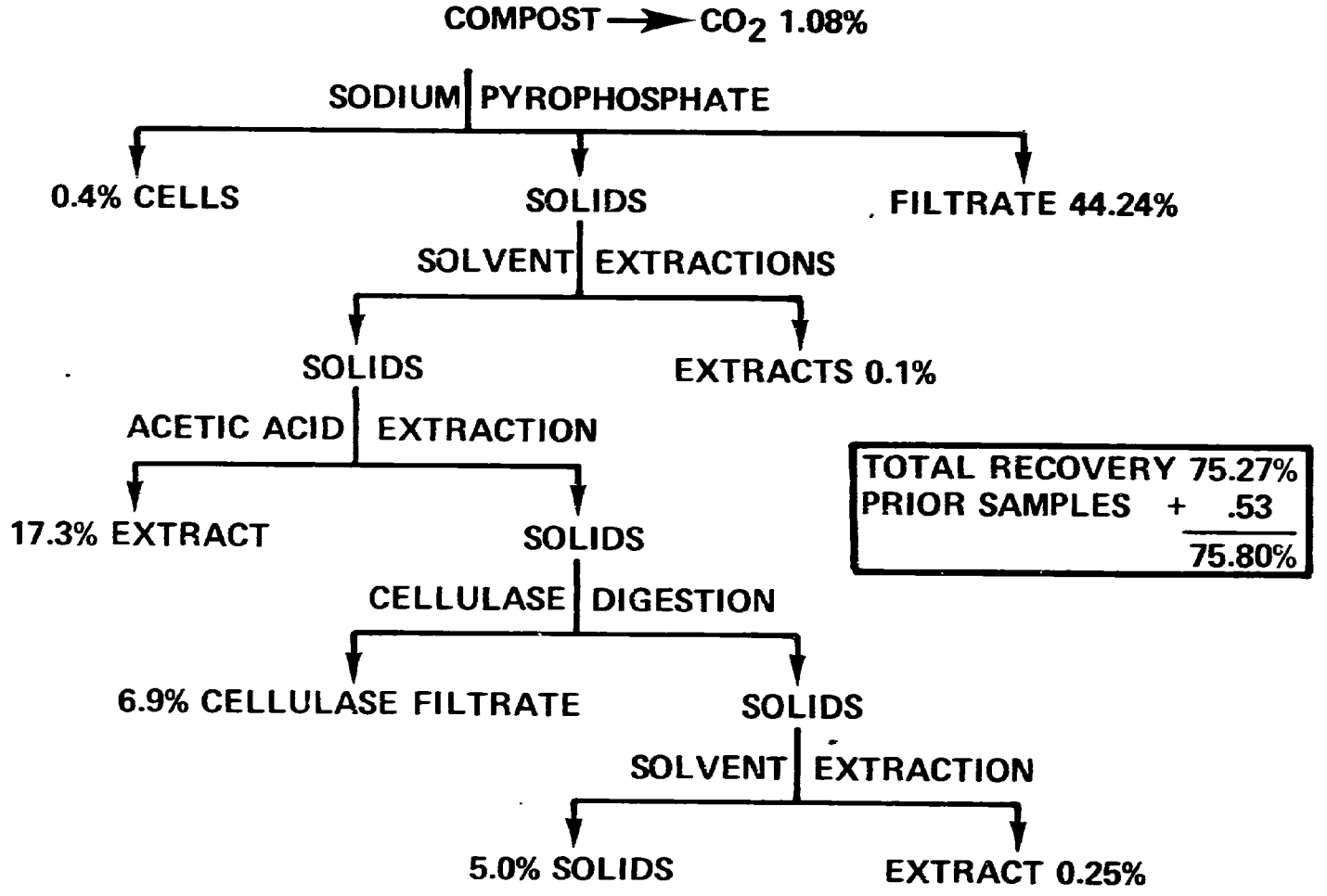

Figure 13. Recovery of ^{14}C activity from compost

Nearly 25% of the activity was not recovered in this experiment. A small portion of this might be accounted for by losses during sample handling. Another small fraction might be lost through the inability of counting equipment to detect extremely minute activity in some fractions. These factors probably do not account for more than a small portion of the non-recovered activity. It seems likely that the bulk of the loss was due to the escape of volatile materials through the forced air stream during incubation. These compounds would have to be of such a nature that they would not be absorbed in the NaOH traps.

Conclusions

Only a slight amount of TNT was recovered from the composted material (i.e., approximately 0.3 ppm). No indication of known conversion products was obtained by TLC analysis. A very small percentage of the TNT was converted to cellular material and CO_2. The bulk of the material was converted to non-solvent-extractable, water-soluble materials of unknown identity. These materials may represent the contents of dead ruptured cells or any number of possible compounds, but in the opinion of this laboratory and that of other investigators working on similar problems, they are not aromatic nitrobodies of environmental consequence.

CONCLUSIONS

Soil Studies

1. Microorganisms exist in most if not all natural environments which are capable of affecting molecular rearrangements of the TNT molecule. This may range from complete mineralization of TNT to CO_2, water, and nitrogen to relatively insignificant modifications in the structure of substitution groups resulting in the production of a number of conversion products of unknown environmental and toxicological properties.

2. Evidence gathered in this study indicates that, in a soil environment under the conditions of this study, the soil microflora tend to rearrange the TNT molecule with production of various conversion products in significant quantities.

3. In no case was the manipulation of such factors as soil moisture, concentration and types of nutrient, and degree of soil aeration effective in causing the organisms to completely degrade TNT.

4. It is concluded that complete degradation of TNT, if it occurred at all, proceeded at too slow a rate for this technique to be considered as a feasible method for the disposal of large quantities of solid TNT waste.

5. Due to the difficulties encountered with microchannels and voids, the experiments designed to measure the rate of migration of TNT through soil did not give meaningful results but did give an indication that TNT probably migrates quite slowly through soil when in a natural outdoor environment.

Compost Studies

1. Results of composting experiments indicate that the action of microorganisms present in composting may take the same or similar initial pathways in attacking the TNT molecule as do the soil organisms, but that the organisms in compost carry the degradation process to completion. This may merely reflect a higher rate of degradation in the compost system or it may result from differences in the inherent capabilities of the thermophilic compost organisms to degrade the TNT-molecule.

2. The conversion products commonly isolated from soil experiments were not present as end products of TNT degradation in the composting system, even though there is a possibility of their existence for a very short life span during the composting period.

3. The degradation of TNT by composting with other organic materials results in the formation of no compounds which are of environmental consequence and should be a viable method for large scale biodegradation of waste TNT.

4. Almost any organic biodegradable material will serve as starting material for producing an effective compost.

5. The temperature reached within the compost is an accurate measure of the biological activity occuring within the compost materials, and the rate of TNT degradation is directly related to the biological activity occuring within the compost and, thus, can be monitored indirectly by monitoring the temperature of the compost.

6. The activity of a TNT-containing compost is optimized when the following conditions are met:

a. The carbon/nitrogen ratio = 30:1.
(Organic nitrogen in the form of proteins and similar compounds are a more effective source of nitrogen than inorganic nitrogen sources such as sodium nitrate.)

b. The moisture content is 40% to 60%.

c. Materials are ground or shredded prior to composting.

d. The compost is mixed frequently in order to maintain a high oxygen level and to promote an infusion of outer undegraded material into the active interior of the compost mass.

RECOMMENDATIONS

Performing Organization's Summary

As a result of this study the following recommendations are submitted for consideration.

1. The concept of disposing of TNT in a soil environment through techniques similar to landfilling should be abandoned. The method should, however, be considered as a possibility for the decontamination of soil in areas where explosives have accumulated due to various ordnance production and loading or disposal operations.

2. Bench-scale composting studies should be initiated to examine the application of the composting technique to the biological disposal of other compounds of military significance. A variety of explosive and propellant compounds may be expected to be amenable to this process.

3. As an extension of the bench-scale studies described in this report, a pilot plant should be constructed to determine the feasibility of disposing of TNT by the composting method on a large scale. It is suggested that domestic or industrial refuse be used as the matrix for TNT composting. The facility should be constructed at a military installation where TNT is available and should be operated by personnel who are competent in the areas of biological degradation of materials and are especially familiar with the concepts and applications of composting technology. A suggested design of such a pilot facility is included in Appendix B.

ARRADCOM's Summary

Of the two TNT disposal methods described in this report, soil disposal and composting, only the latter will be considered for the large scale abatement of TNT wastes. This is because bench-scale studies have shown that the soil disposal route proceeds only very slowly via an anaerobic biotransformation which may possibly yield harmful aromatic TNT derivatives.

Composting appears to provide a low energy, effective, ecologically acceptable disposal technique for TNT. The resulting solid product will result in an acceptable landfill. Additional benefits include a method which is efficient and non-polluting and which requires only compostable waste materials to function. In a plant-sized operation where the only energy requirement is for shredding and mixing operations and delivery of compostable waste materials, the operating costs should be low. It may also be possible to recover some of the heat generated from the composting to heat the buildings and water used in showers, etc.

Since the quantity (10% maximum) of TNT that may be composted at any given time is a function of the amount of compostable refuse generated and available at an Army Ammunition Plant, a definite consideration must be given as to the average quantity of compostable material available at the plant including possible seasonal variations which would cause fluctuations in the supply. For each metric ton (2,205 lb) of waste TNT, a minimum of 9 metric tons (19,845 lb) of compostable plant refuse is required to effect proper decomposition. For example at ARRADCOM, Dover, NJ approximately 122.5 metric tons of general refuse is generated monthly, most of which is compostable. The ARRADCOM sewage treatment plant generates approximately 26.7 metric tons of sludge a month (based on a current employment of 5,000+ employees) which can be used as the nitrogen source for the composting operation. Based on the amount of refuse and sewage sludge available at the Dover site, a maximum of approximately 14 metric tons of waste TNT could be disposed of by the composting process each month.

Studies using carbon-14 tracer methodology STLC have shown that, by using the composting technique, no TNT or TNT derivatives remain in the compost after the biodegradation is complete. Because nearly 25% of the radioactivity from the TNT was not recovered in these experiments, ARRADCOM is concerned with the possibility that harmful organic biotransformation products are being volatilized and possibly released into the atmosphere. Before any larger scale compost pilot studies are initiated, experimental data will be obtained to determine if airborne TNT or TNT

derivatives are released during the composting operation. Experimental work to confirm this has been initiated by ARRADCOM at the NWSC in Crane, Indiana.

The Special Technology Branch of Manufacturing Technology Division, LCWSL, ARRADCOM, concurs with the recommendations of the Naval Weapons Center, Crane, Indiana on the following points:

1. Initiation of bench scale work to study the application of the composting technique for the biological disposal of other military-unique propellants and explosives, e.g., RDX and HMX.

2. Large pilot-scale composting of TNT should be implemented after demonstrating that the release of TNT or harmful TNT derivatives from the composting operation is either nonexistent or insignificant.

REFERENCES

1. *Explosives and the Environment,* Technical Report No. QEEL/C 73-217, Naval Weapons Support Center, Crane, Indiana, 6 June 1973.

2. J. L. Osmon and R. E. Klausmeier, *The Microbial Degradation of Explosives.* Developments in Industrial Microbiology. 14, 247, 1973.

3. R. E. Klausmeier, J. L. Osmon, and D. R. Walls, *The Effect of Trinitrotoluene on Microorganisms.* Developments in Industrial Microbiology, 15, 309, 1974.

APPENDIX A
ANALYSIS PROCEDURES

TABLE OF CONTENTS

	Page No.
Drying of Samples	41
Extraction of Soil Samples	41
Compost Extraction Procedure	41
Weapons Quality Engineering Center (WQEC) Standard Test Method QTM-LC1	42
Introduction	42
Sample Preparation	42
Liquid Chromatographic Analysis	43
Calculation	43
WQEC Standard Test Method QTM-GC1	44
Introduction	44
Samples	44
Procedure	45
Vapor Phase Chromatographic Analysis	45
Results and Discussion	46
Water Analysis	47
WQEC Standard Test Method QTM-GC2	48
Introduction	48
Sample Preparation	48
GC Analysis	48
Calculation of %TNT	49
WQEC Standard Test Method QTM-GC3	49
Introduction	49
Sample Preparation	50
Gas Chromatographic Analysis	50
Calculation of %TNT	50
TLC Analysis for TNT and TNT Metabolites from Soil Samples	50

WQEC Standard Test Method QTM-TLC2 52

Introduction 52
Separation Procedure 53

WQEC Standard Test Method QTM-TLC4 57

Introduction 57
Sample Preparation (benzene solubles) 57
Sample Analysis (benzene solubles) 58
Photography 58
Sample Preparation (acetone solubles) 59
Sample Analysis (acetone solubles) 59
Concentration Determination 60

References 60

Table

1A Retention times and peak height responses for a mixture of TNT, RDX, tetryl, and 1,2-dinitrobenzene 46

Figures

1A TLC separation of TNT and derivatives using Chandler's solvent system No. 1 54

2A TLC separation of TNT and derivatives using Chandler's solvent system No. 2 55

3A TLC separation of TNT and derivatives using Chandler's solvent system No. 1 56

DRYING OF SAMPLES

Samples of soil or compost as collected normally contain a high moisture content. When these samples are extracted while wet, the water prolongs the time necessary to evaporate the extract to dryness. Samples are therefore normally dried prior to extraction. This is accomplished by placing the sample in a chamber or oven which allows free circulation of air. The temperature should not exceed 50°C since some of the TNT and related compounds are volatile at fairly low temperatures. It is not necessary to obtain a state of absolute dryness but is sufficient if the sample is dried to a constant weight at that temperature. Further drying may be accomplished by desiccation at room temperature if desired.

A duplicate sample may be dried at high temperatures to an absolutely dry state to determine the moisture content, if this is required, for purposes of calculation of explosives concentration. This is practical only if the explosive concentration is not a significant portion of the total sample weight. Otherwise, desiccation of the duplicate sample is required.

EXTRACTION OF SOIL SAMPLES

A dry sample of known weight is placed in a scintered glass crucible. The solvent (acetone or benzene) is added to the sample and stirred until a slurry results. The solvent is then filtered off by vacuum. This procedure is repeated three times. The residual soil compacted in the crucible is then thoroughly rinsed with the solvent while maintaining suction through the system. The solvent extract is collected and the soil sample discarded. The choice of a solvent is dependent upon the specific analysis to be performed.

COMPOST EXTRACTION PROCEDURE

A 20-gram sample of compost is dried at 43°C for two to three days. To determine if the compost material is completely dry, a portion should be weighed immediately upon sampling and weighed on several consecutive days during the drying procedure. When the weight remains static, there is no appreciable moisture remaining in the sample.

Five grams of the dried sample is extracted with benzene. It is mixed in a scintered glass crucible with 20 ml of benzene and the benzene is filtered off into an acid-washed beaker (all glassware should be acid washed) utilizing an aspirator or vacuum pump. (All work should be done

in a vented hood.) This procedure is repeated two more times. The extracted compost is then rinsed twice with two 20-ml aliquots of benzene which are collected in the same beaker. The beaker contents are then evaporated to dryness. The concentrated material is analyzed by gas chromatography and thin-layer chromatography for the presence of TNT and conversion products.

Some TNT conversion products are more efficiently extracted using acetone. Unfortunately, so are many chlorophyll and carotenoid pigments derived from herbacious material which may be present in the compost. These pigments severely interfere with TLC analysis. The more commonly occurring TNT conversion products are benzene extractable. Acetone extraction need only be resorted to in such instances where benzene extraction has proved negative and the determination of the possible presence of conversion products is absolutely necessary.

WEAPONS QUALITY ENGINEERING CENTER (WQEC) STANDARD TEST METHOD QTM-LC1

Liquid Chromatographic Analysis of TNT and RDX in Soil and Water

Range: 0.5 to 5 ppm

Precision: 2 - 5%

Instrument: Model 2 Liquid Chromatograph

Introduction

This method was developed for explosive analysis for the Date Base Program.

The method is used in conjunction with method QTM-GC2 and QTM-GC3 for explosive analysis.

Sample Preparation

The evaporate residue from 150-ml acetone extraction of a 50-gram soil sample is transferred quantitatively to a 100-ml volumetric flask with benzene. The flask is filled to the mark with benzene.

A 10-ml aliquot of benzene solution is transferred to a second 100-ml volumetric flask and diluted to the mark with benzene.

A 1-ml aliquot of the second 100-ml volumetric flask is evaporated to dryness at room temperature.

The residue is quantitatively transferred to a 100-ml volumetric flask with a small amount of acetone and diluted to the mark with water.

Water samples are filtered through a 0.45-nanometer filter before liquid chromatograph analysis.

Liquid Chromatographic Analysis

A 1-ml aliquot of the aqueous solution is injected on the liquid chromatograph.

Liquid Chromatograph parameters:

Column:	Sephadex G-10 39 cm long x 6 mm I. D.
Column Temperature:	Ambient
Mobile Phase:	Distilled Water
Flow Rate:	60 ml/hr
Sensitivity:	0.04 absorbance units full scale
Detector:	UV, 254 nanometers
Chart Speed:	5.1 cm/hour (2 inches/hour)

Calculation

$$\% \text{ Explosive} = \frac{(\text{Intercept} + (\text{peak area} \times \text{slope})) \times (\text{Dil factor}) \times 100}{\text{Sample wt.}}$$

WQEC STANDARD TEST METHOD QTM -GC1

Electron Capture Gas Chromatographic Method for TNT and RDX

Range: 0.05% to 0.05 ppm

Precision: 5%

Instrument: Gas Chromatograph with nickel-63 detector

Introduction

The following method is recommended by the Navy Industrial Environmental Health Center, 3333 Vine Street, Cincinnati, Ohio 45220. It is the method for quantitative analysis of NIEHC certification samples.

This method has been modified slightly for use at NAVWPNSUPPCEN Crane. See method QTM-GC2 for setup using Beckman GC-5 with electrical ionization electron capture detector.

For many years obsolete munitions have been disposed of by dumping in deep water. In 1963, the United States Navy initiated a program in which obsolete Maritime Administration hulks were used. These old liberty ships were loaded with munitions and scuttled at sea (Ref 1A). Because of the possibility of pollution of sea water near these areas, sites were selected and sea water samples near these sites were analyzed for the presence of explosive contaminants.

Since TNT (2,4,6-trinitrotoluene), RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), and tetryl (methyl-2,4,6-trinitrophenylnitramine) were the most common and abundant types of explosives dumped, methods were developed using these compounds as standards. This report describes the methods employed for the analyses of TNT, RDX, and tetryl in the part-per-billion to part-per-trillion range (1×10^{-9} to 1×10^{-12} g/ml), and the results obtained.

Samples

Sea water samples were collected from two locations, one in the Atlantic Ocean and one in the Pacific. Sea water samples were collected in both Niskin and Nansen bottles and stored in 1.5-pt Mason jars for the first area and in 200-ml all-glass pyrex bottles for the second area. However,

it should be immediately pointed out that storage of sea water samples in Mason jars is definitely not advised because material extracted from rubber or plastic components during storage contaminate the samples. This aspect is covered more completely in the results and discussion section. Analyses were performed within two weeks after the samples were taken.

Procedure

Approximately 100 ml of the sea water sample was poured into a clean, dry 200-ml separatory flask, and 5.00 microliters (μℓ) of an internal standard (8.12×10^{10} g/μℓ of 1,2-dinitrobenzene in acetone) was added by means of a #701, 10 μℓ Hamilton syringe. Forty to fifty ml of benzene (MCB, specially purified for work with electron capture detectors) were then added to the separatory flask, the flask stoppered, and the contents shaken vigorously for 2 to 3 min and allowed to stand 5 to 10 min for layer separation. The bottom layer (extracted sea water) was discarded while the benzene extract was poured through the top of the separatory flask into a clean, dry, 100-ml round-bottom flask containing a small, clean boiling chip. The benzene was then completely removed under reduced pressure with a water aspirator and a flask temperature maintained between 30° and 35°C. To the dry flask was added 0.20 to 0.25 ml of pure benzene. The benzene was swirled lightly on the sides of the flask and allowed to drain into a small pool on the bottom.

Vapor Phase Chromatographic Analysis

In all work connected with the nickel-63 electron capture detector, extreme caution must be exercised to avoid contamination (Ref 2A) and over-loading of this very sensitive detector. As little as one microgram of TNT will desensitize the detector.

An 8.0 to 9.0 μℓ portion of this benzene solution containing the extract was injected into an F&M model 5754A research gas chromatograph, equipped with a model 5763A electron capture nickel-63 detector and pulser kit together with a model 7128A Mosely dual-channel recorder. One to two μℓ of pure benzene solvent was used as a "back flush" for all standards injected. "Back flush" was accomplished by drawing approximately 2 μℓ of pure benzene into a 10 μℓ syringe, followed by about 0.2 μℓ of benzene extract.

Samples were chromatographed on a 10.1 cm x .6 cm (4 in. x 1/4 in.) glass column packed with 2.92% Dexsil 300 GC (polycarboranesiloxane

stationary phase with an average molecular weight of 18,000 to 20,000) on Chromosorb WAWDMCS 80/100 mesh; isothermally, 165°C; injection per temperature, 200°C; nickel-63 detector temperature, 295°C; carrier gas, Ar/CH_4: 95/5, v/v; flow rate, 217 ml/min; pulse interval, 150 usec; chart speed, 2.54 cm (1 in./min); attenuation, 40. Chromatograms of the benzene sea water samples were compared with standard chromatograms containing known concentrations of TNT, RDX, and tetryl with 1,2-dinitrobenzene as internal standard.

Results and Discussion

Table 1A shows typical retention times and peak height responses for the vapor phase chromatographic separation of a standard mixture of TNT, RDX, and tetryl with 1,2-dinitrobenzene as internal standard. Calculation of the concentrations for TNT, RDX, and tetryl that may be

Table 1A

Retention times and peak height responses for a mixture of TNT, RDX, tetryl, and 1,2-dinitrobenzene

Component of mixture	Concentration 10^{-12} g/μℓ	Peak height response mm (a)	Retention time min (b)
1,2-dinitro-benzene (c)	4.06	24.8	1.10
TNT	10.3	27.5	2.55
RDX	31.9	18.5	6.70
Tetryl	140	24.5	15.9

(a) 8 to 9 μℓ injection at attenuation, 40.
(b) Measured from solvent pressure peak.
(c) Internal standard.

present in the concentrated benzene extract of the sea water sample may be made by normalizing standard and sample peak heights for TNT, RDX, and tetryl with internal standard peak heights. Since the same aliquot of internal standard is put into both the standard mixture and the sea water sample, an expression for the concentration of TNT in sea water is given by:

$g_{TNT/ml} = [(^{V}std)/(^{V}sea\ sample)][(^{h}IS\ std)/(^{h}ISx)][(^{h}TNTx)/(^{h}TNT\ std)]$ $(^{C}TNT\ std)$ where V represents the volume for the vapor phase chromatographic standard (1.00 ml benzene), and the sea sample (100 ml); h, the chromatographic peak height maximum for the internal standard (IS), in both standard (std) and benzene extract (x), and also the peak heights of TNT in standard and sample extract; and C, the concentration of TNT in the chromatographic standard, expressed in grams per milliliter. Similar expressions involving (^{C}RDX) std or $(^{C}tetryl)$ std may be used to calculate the concentrations of RDX and tetryl in sea water.

This procedure works well only in those cases where there are no interfering peaks with the 1,2-dinitrobenzene, internal standard. Sea samples stored in all-glass bottles with glass stoppers gave relatively clean vapor-phase chromatograms with 4 to 5 peaks on the average. None of these peaks interfered with the peak for 1,2-dinitrobenzene, or peaks that would correspond to TNT, RDX, or tetryl. On the other hand, the benzene extracts of sea water samples stored in glass Mason jars with screw caps containing rubber seals and plastic liners gave chromatograms containing anywhere from 10 to 15 peaks, some of which interfered with 1,2-dinitrobenzene. Presumably, various plasticizers from the rubber seals and plastic liners were leached out by the sea water (Ref 3A). All-glass containers are obviously preferred.

The efficiency of the combined extraction and evaporation procedure for the determination of TNT, RDX, or tetryl in sea water at levels of 103, 320, and 1,400 parts per trillion (10^{12} g/ml sea water), respectively, has been found experimentally to be 70% $\pm$ 10%. Efficiency was not determined at other concentrations. Similar (70% efficiency) results were obtained when the internal standard was added after the extraction and concentration procedure. The limits of vapor phase chromatographic detection for TNT, RDX, and tetryl by the present method are estimated to be in the order of 2, 5, and 20, parts per trillion, respectively.

Water Analysis

We were not able to observe any peaks on the chromatographic traces corresponding to TNT, RDX, and tetryl in any of the samples taken in either the Pacific or Atlantic Ocean areas. By intentional, low-level introduction of TNT, RDX, and tetryl into sea water which was analyzed, we have estimated these materials may be detected at levels of 2, 5, and 20 parts per trillion, respectively. If explosives were present in the sea water samples, they must be at concentrations below those stated above.

WQEC STANDARD TEST METHOD QTM-GC2

Gas Chromatographic Analysis of TNT in Soil and Water

Range: 0.05 ppm to 0.05%

Precision: 5%

Instrument: Beckman GC-5

Introduction

This method is a modification of method QTM-GC1.

The method is applicable to the Beckman GC-5.

Sample Preparation

The evaporate residue from 150-ml acetone extraction of a 50-g soil sample is transferred quantitatively to a 100-ml volumetric flask with benzene. The flask is filled to the mark with benzene.

A 10-ml aliquot of the benzene solution is transferred to a second 100-ml volumetric flask and diluted to the mark with benzene.

GC Analysis

A 10 µl aliquot from the second flask is spotted on a chromar 500 TLC sheet (20 x 20 cm) and developed with benzene to a height of 15 cm.

The TLC sheet is dryed and examined under a 254-nm UV lamp. The TNT spot is marked and cut from the TLC sheet with a 1.9-cm (3/4 inch) dia cork borer.

The circle of TLC sheet containing TNT is placed in 20 ml of benzene which contains the internal standard 1,2-dinitrobenzene (0.1 ppm).

A 5 µl aliquot of the solution is injected into the Beckman GC-5A with electron capture detector.

GC parameters:

Column 3% Dexsil 300 GC on 100/120 Supelcort

Column Temp 165°C

Inlet Temp 170°C

Detector Line Temp 200°C

Detector 250°C

Polarizing Voltage Setting 500

He Flow Column 100cc/min

Discharge He Flow 130cc/min

CO_2 Flow 2-3cc/min

Calculation of %TNT

$$\text{Concentration} = \frac{\text{pk hgt Int Std in Std}}{\text{pk hgt Int Std in Sample}} \times \frac{\text{pk hgt TNT in Sample}}{\text{pk hgt TNT in STD}} \times \frac{\text{TNT}}{\text{Conc Std}}$$

$$\%\text{TNT} = \frac{\text{Concentration} \times 100}{\text{Sample Wt}}$$

WQEC STANDARD TEST METHOD QTM-GC3

Gas Chromatographic Analysis of TNT in Soil

Range: 0.05% to 5%

Precision: 5%

Instrument: Beckman GC-2A

Introduction

This method is used in place of method QTM-GC2 when TNT concentrations are 0.05% or greater.

Sample Preparation

The evaporated residue from 150-ml acetone extraction of a 50-gram or 10-gram soil sample is transferred quantitatively to a screw cap bottle with exactly 10 ml of benzene.

Gas Chromatographic Analysis

A 20 µl aliquot of the benzene solution is injected into the Beckman GC-2A using a thermal conductivity detector.

Gas Chromatograph Parameters:

Column	3% Dexsil 300 GS on 100/120 supelcoport
Column Temp	190°C
Helium Pressure	140 kPa (20 psig)
Attenuation	X1

Calculation of %TNT

$$\text{Concentration} = \frac{\text{pk hgt TNT peak of sample}}{\text{pk hgt TNT peak of standard}} \times \text{concentratin of TNT standard}$$

TLC ANALYSIS FOR TNT AND TNT METABOLITES FROM SOIL SAMPLES

In preparation for thin-layer chromatography all glassware should be chromic-acid washed and acetone rinsed to avoid the possibility of TNT contamination. All solvents used should be reagent grade or better.

A dry soil sample of known weight is divided into two equal parts. One part is extracted with benzene (1:10 ratio of soil to benzene); the other part is extracted with acetone (same ratio). Each recovered solvent portion is evaporated to dryness. The extracted soil is discarded.

The benzene residue is then dissolved in 2 ml of benzene and transferred to a 5-ml test tube. The acetone residue is treated accordingly with acetone. An air purge or dry nitrogen purge is used to evaporate the solvents to dryness. After the evaporation procedure, a 50 µl (microliter)

portion of benzene is allowed to run down the test tube containing the benzene residue. The procedure is repeated for the acetone residue, using acetone. A 20 µℓ aliquot of the benzene sample is spotted onto a Quantum Industries LQDF silica gel thin-layer chromatography plate. An equivalent aliquot of the acetone sample is spotted onto another plate. Each plate should also be spotted with samples of standard TNT solutions of various concentrations for semi-quantitative determinations as well as qualitative comparisons.

Glass tanks equipped with filter paper (to maintain a saturated environment) and heavy glass lids are used for development. Hoffsommer's solvent is used for the development of plates containing non-polar components. Chandler's No. 2 solvent system is used to develop polar components.

Hoffsommer's solvent system contains the following:

50 parts benzene

40 parts hexane

10 parts pentane

10 parts acetone

When the tank containing the Hoffsommer's is considered to have a well saturated environment, the plate spotted with the benzene extract is introduced. The chromatogram is developed 3/4 way up the plate. The solvent front is duly marked and the plate is examined under UV light (253 nm) and the R_f value of each spot is determined. The plate is then sprayed with a 1:6 solution of ethylenediamine (EDA) and dimethylsulfoxide. The R_f value and color of each component spot is determined and compared with standard TNT control spots. Both UV analysis as well as color analysis are used since certain spots are frequently only discernible in one system and not the other.

The plate spotted with the acetone sample is developed in the Chandler No. 2 system. It contains the following:

50 parts penzene

30 parts ethyl ether

20 parts ethanol

0.25 parts concentrated NH_4OH to prevent tailing

The above procedure is repeated for the development and determination of these spots and the R_f value of their components as compared with the standards.

WQEC STANDARD TEST METHOD QTM-TLC2

Qualitative Analysis of TNT Decomposition Products by Thin-Layer Chromatography in Explosives and Explosive Exudates

Range: Not Determined

Precision: NA

Instrument: Thin-Layer Chromatography

Introduction

This is a modification of a method published by Dr. C. D. Chandler, Journal of Chromatography, Vol 64 (1972) pages 123-128 and a method published by Dr. J. C. Hoffsommer, Journal of Chromatography, Vol 51 (1970) pages 243-251).

The TLC separation is used to determine if TNT decomposition products are present in a sample. Other methods are used for confirmation and quantitative analysis.

The silica gel TLC plates with starch binder are not now commercially available but silica gel with gypsum binder seems to give similar separation. The Quantum Industries TLC plates LQDF and Q4F give satisfactory separations.

A spray reagent consisting of 1 part ethylenediamine (EDA) and 5 parts dimethylsulfoxide (DMSO) is substituted for EDA because EDA tends to clog the sprayer.

Dr. Chandler's solvent system No. 1 is used for non-polar separations:

50 parts benzene

45 parts cyclohexane

5 parts ethylacetate

The "non-polar" solvent system developed by Dr. Hoffsommer has been substituted for the system described by Dr. Chandler.

Hoffsommer's solvent:

50 parts benzene

40 parts hexane

10 parts pentane

10 parts acetone

Separation Procedure

Two solvent systems are generally employed, viz (1) Hoffsommer Solvent, and (2) a more polar system, 50:30:20 benzene-ethyletherethanol (Chandler Solvent No. 2).

If tailing is a problem for acid components, a 0.25 portion of a concentrated ammonium hydroxide may be added to Chandler Solvent No. 2. Care must be taken not to use excess ammonium hydroxide; too much can change the order of elution.

A 25-microliter aliquot was placed about 1 inch from the bottom of the plate and developed in a chromatographic tank containing the desired solvent mixture.

After development the plate was allowed to dry for visualization with UV light and subsequent spraying with EDA:DMSO.

Another useful spray reagent was a 10% aqueous solution of tetraethylammonium hydroxide (TEAH). This reagent is not as sensitive as EDA:DMSO, but gives differences in color. A separate sample is needed for spraying.

COLOR	LOCATION	COMPOUND
Colorless		mono-nitrotoluene's
Yellow		2,5-dinitrotoluene
Red		2,4,6-trinitroethylbenzene
Blue		2,4,6-trinitro-m-xylene
Dark red		2,4,6-trinitrotoluene
Blue		3,5-dinitrotoluene
Red		Trinitrobenzene
Blue		2,6-dinitrotoluene
Blue		2,4-dinitrotoluene
Orange		2,3,6-trinitrotoluene
Red		2,3,5-trinitrotoluene
Tan		2,4,6-trinitrotoluene
Yellow		2,3-dinitrotoluene
Yellow		3,4-dinitrotoluene
Purple		m-dinitrobenzene
Pink		∝-nitrato-2,4,6-trinitrotoluene
Pink		2,4,6-trinitrobenzaldehyde
Yellow		3,4,5-trinitrotoluene
Yellow		2,3,4-trinitrotoluene
Red-brown		2,4,6-trinitrobenzyl alcohol
Dark		Residue

Fig 1A TLC separation of TNT and derivatives using Chandler's solvent system No. 1

Color produced with ethylenediamine spray reagent and starch-bound silica gel support are shown in Figure 1A.

COLOR	LOCATION	COMPOUND
Dark red Yellow		Non-polar compounds Separations in Figure 1 TNT, DNT, etc
Black		Unknown
Red		2'-hydroxy-3,3',5,5'-tetranitroazoxybenzene
Blue		monocarboxy-3,3',5,5'-tetranitroazoxybenzene
Yellow		2,4,6-trinitro-m-cresol
Yellow-orange		2,6-dinitro-p-cresol
Yellow		Picric acid
Yellow		4,6-dinitro-o-cresol
Red-brown		3-hydroxy-4,6-dinitrobenzoic acid
Yellow		Unknown
Red		2,4,6-trinitrobenzoic acid
Yellow		3,4-dinitrobenzoic acid
Yellow		Unknown
Blue		2,2'-dicarboxy-3,3',5,5'-tetranitroazoxybenzene
Yellow		Unknown
Blue		2,4-dinitrobenzoic acid
Yellow		Unknown

Fig 2A TLC separation of TNT and derivatives using Chandler's solvent system No. 2

Color produced with ethylenediamine spray reagent and starch-bound silica gel support are shown in Figure 2A.

COLOR	LOCATION	COMPOUND
Yellow	o	Mono-nitrotoluene
Dark red	◯	2,4,6-trinitrotoluene
Red	◯	Trinitrobenzene
Blue	o	2,6-dinitrotoluene
Blue	o	2,4-dinitrotoluene
Tan	◯	2,4,5-trinitrotoluene
Yellow	o	3,4-dinitrotoluene
Pink	◯	∝-nitrato-2,4,6-trinitrotoluene
Pink	o	2,4,6-trinitrobenzaldehyde
Yellow	◯	2,3,4-trinitrotoluene
Red-brown	◯	2,4,6-trinitrobenzyl alcohol
	●	Origin

Fig 3A TLC separation of TNT and derivatives using Chandler's solvent system No. 1

Color produced with ethylenediamine spray reagent and starch-bound silica gel are shown in Figure 3A. The same compounds were shown in Figure 1A.

WQEC STANDARD TEST METHOD QTM-TLC4

Thin-Layer Chromatography Method for TNT and TNT Metabolites
in Lysimeter Effluents

Range: Not determined

Precision: Semi-quantitative

Instrument: Silica Gel Thin-Layer Plates

Introduction

The method has been developed for determining the concentrations of 2,4,6-trinitrotoluene (TNT) and the presence of TNT metabolites which are eluted from soil during percolation studies conducted by the Biological Sciences Branch.

Since the identity of metabolites has not been completely established, their relative concentrations are estimated by comparison to TNT standards.

All glassware is chromic-acid washed and rinsed with acetone to avoid TNT contamination.

All solvents are reagent grade or better.

Sample Preparation (benzene solubles)

Approximately 100 ml of lysimeter effluent is collected and filtered through a 0.2-micrometer filter unit.

The particulate matter is discarded.

A 50-ml aliquot of the filtrate is extracted with 50 ml of benzene (spectrophotometric or pesticide analysis grade). The benzene is decanted and evaporated to dryness. The water is saved for later extraction.

The benzene residue is dissolved in 2 ml of benzene and transferred to a 5-ml centrifuge tube.

A jet of dry nitrogen is used to evaporate the benzene to dryness.

A 50-microliter (μℓ) portion of benzene is allowed to run down the sides of the centrifuge tube to redissolve the residue.

A 20 μℓ aliquot of the solution is spotted on a Quantum Industries LQDF silica thin-layer chromatography (TLC) plate in the middle of the spot application zone.

Sample Analysis (benzene solubles)

A glass tank equipped with Whatman #1 filter paper saturation pads is used for plate development.

The tank is cleaned after a day's use.

Hoffsommer's solvent system (Ref 1A) is used for separation of weakly polar components:

50 parts benzene

40 parts hexane

10 parts pentane

10 parts acetone

The TLC is developed 3/4 of the way up the plate.

The plate is sprayed with 1:5 ethylenediamine (EDA)/dimethylsulfoxide (DMSO).

Photography

The plate is dated and given a code number prior to photographing.

Camera Setup:

Polaroid MP-3 Camera System

3-foot focal length (.915-meter focal length)

11 or 16 f stop

2 color balance lights at 3400K

Total wattage 1300

Indirectly lighted with umbrellas

Type L Kodak 4" x 5" film

Sample Preparation (acetone solubles)

Calcium chloride dihydrate (23.3 grams) is dissolved in the water sample after benzene extraction. The calcium chloride prevents acetone from being miscible in the water (Ref 2A).

The solution is extracted with 50 ml of acetone (spectrophotometric or pesticide analysis grade) to remove polar metabolites. The acetone is decanted and evaporated to dryness. The water is discarded.

The acetone residue is dissolved in 2 ml of acetone and transferred to a 5-ml centrifuge tube.

A jet of dry nitrogen is used to evaporate the acetone to dryness.

A 50 µℓ portion of acetone is allowed to run down the sides of the centrifuge tube to dissolve the residue.

A 20 µℓ aliquot of the solution is spotted on a LQDF TLC plate.

Sample Analysis (acetone solubles)

A glass tank equipped with saturation pads is used for plate development.

Chandler's solvent system #2 (Ref 3) is used for separation of polar components:

50 parts benzene

30 parts ethyl ether

20 parts ethanol

The TLC is developed 3/4 of the way up the plate.

The plate is sprayed with 1:5, EDA/DMSO to develop color.

The plate is photographed as described above.

Concentration Determination

TNT standards of 0.5, 1, 2, 5 and 10 micrograms are spotted on an LQDF plate and developed as described previously.

The color intensity of the TNT spot is compared to TNT standards to estimate the concentration.

If the TNT spot intensity is greater than the 10 micrograms TNT standard, the sample is diluted and chromatographed again.

The metabolite concentrations are not reported.

References

1. J. C. Hoffsommer, J. of Chromatog, 51, (1970) pages 243-251

2. C.E. Matovich, G.D. Christian, Anal Chem, 46 #1 (1974) pages 102-106

3. C.D. Chandler, J.A. Kohlbeck & W.T. Bolleter, J of Chromatog, 64 (1972) pages 123-128

APPENDIX B

Pilot Plant Design

DESIGN CONSIDERATIONS

The operation of a composting facility on a large scale involves the following six operations:

1. Collection of the refuse. Since domestically generated refuse is proposed as the organic matrix within which TNT will be composted, the collection of the refuse should pose no problems. Existing procedures should be adequate. The only modifications necessary being that the refuse as collected be delivered to the composting facility rather than the currently used solid waste disposal area.

2. Preparation of the refuse. Preparation of the refuse entails the separation of those items which are noncompostable or which have significant salvage value from the organic material which is to be composted. This compostable material must then be reduced to a particle size which will encourage the rapid degradation of the material by microorganisma.

3. The preparation of TNT. It has been found that TNT will degrade much faster if the particle size is reduced to that of a powdery or granular material rather than the flakes or chunks of TNT normally encountered.

4. Mixing. The ground refuse, pulverized TNT, and water must be properly mixed in the appropriate amounts to insure a uniform homogeneous material and to provide optimal conditions for the growth of microorganisms.

5. Composting. This is the heart of the process. During this stage the microbial flora prolifereates and degrades both the organic refuse and the TNT.

6. Control of pollutants. Since under certain conditions some amount of undesirable products may be generated by the composting process and released to the environment, it is desirable that these be collected and treated at the site of the composting operation.

There are basically three methods of composting currently in use. The first involves the arranging of the material to be composted into long piles called windrows and periodically turning or mixing these windrows to both aerate and mix the composting materials. This process may take place in an open environment or an enclosed structure dependent upon

the size of the operation envisioned and the costs involved in constructing a suitable enclosure. The second composting technique is termed digestion. In this process the composting takes place in an enclosed container which provides for the control of both temperature and aeration of the composting materials and also incorporates a suitable device to effect the continuous mixing of the composting materials. The third method employed is essentially the combination of the first two in which digestion is used as a first step to initiate and accelerate the composting process which is then allowed to run to completion in windrows. This last is probably the most effective of the composting techniques currently available and is the most desirable design for the pilot composting operation envisioned in this report. However, the inclusion of the digestor would approximately double the cost of the proposed pilot TNT composting facility. Therefore, the system described in this report is an open windrow arrangement with provisions made to collect any runoff and leachate from the composting operation and treat this material by readdition to the compost windrows.

The facility described in this section will handle up to 30 tons of refuse per day. If TNT is added to the system at a concentration of 10%, the capacity of the pilot facility to dispose of solid TNT wastes is shown to be 3 tons of TNT per day. It is suggested, however, that this figure be used as a target capacity and that the operation of the facility be initiated at a lower rate and gradually built up to the capacity of the facility as operating problems are worked out.

DESIGN DETAILS

The diagrams, Figures 1B, 2B, and 3B, illustrate the layout of the proposed pilot compost facility as presently envisioned. Figure 1B is an overview of the entire operation. Item 1 represents a trailer which will be used as office space, lunch and locker facilities, restroom facilities, and will house a small laboratory for onsite determinations of such parameters as moisture content, temperature, and pH of the compost pile. Item 2 is the receiving area where trucks will unload the refuse prior to being processed. Item 3 represents the building which will house the process operation. Within this building the refuse will be sorted, ground, mixed with TNT and raised to the proper moisture content for efficient composting. The composting itself will take place on a concrete or asphalt pad, Item 4. The refuse mixed with TNT will be formed into windrows (long piles approximately 1.8 x 1.2 meters (6 feet wide by 4 feet) tall and as long as is convenient). The windrows will be arranged such that turning can be accomplished by means of a specialized piece of mobilized equipment called a

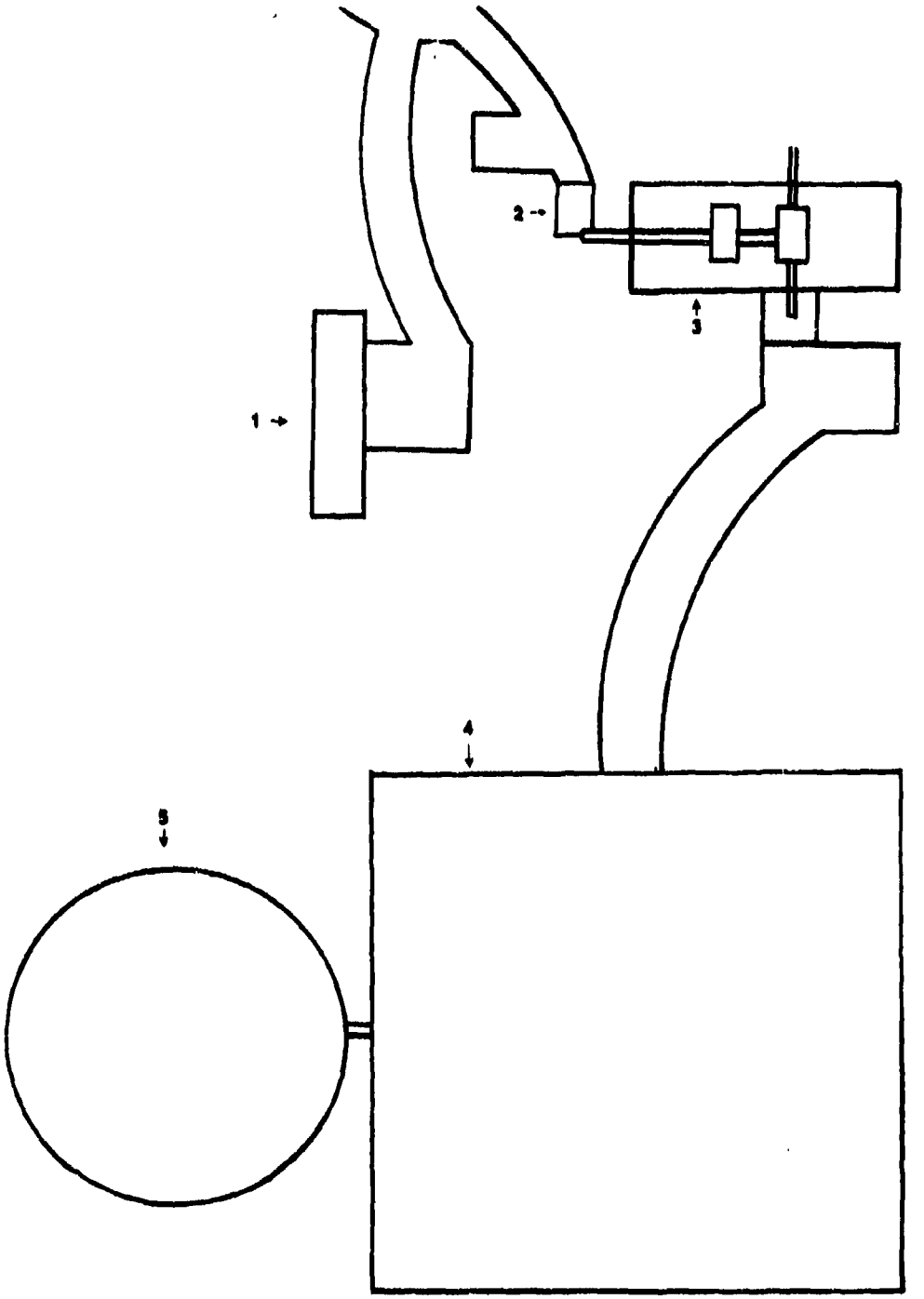

Fig 1B Overview

compost turner which is described later in this proposal. The pad will be graded so that all runoff water from rainfall will be directed toward a holding lagoon, Item 5. Rainfall can be expected to leach some amount of TNT from the windrows especially the newer or younger windrows and, therefore, collection and treatment of the runoff water from this area is necessary. Since normally a compost windrow loses moisture due to the temperature developed within the windrow and becomes excessively dry, it is necessary from time to time not only to turn the windrow or mix the windrow in order to improve aeration but also to add water. This will be accomplished by recirculating water from the treatment lagoon to the windrows by means of a recirculating pump. This will serve not only to maintain moisture levels within the windrows, but also to provide a means of treating the explosive pollutants present in the waters of the treatment lagoon. Figure 2B is a more detailed view of the process area. Item 1, again, is the trailer which houses the facilities previously mentioned. Item 2 is a concrete or asphalt pad which serves as a receiving area. This is the spot at which refuse will be offloaded from incoming trucks. The refuse will undergo a preliminary sorting at this stage and items that are too bulky or that might cause damage to equipment or are obviously noncompostable will be segregated out at this point and routed to other disposal facilities. Item 3 is an apron conveyor. This is a steel belt conveyor which is recessed 1.2 meters (4 feet) below ground level. Refuse to be processed will be pushed onto this conveyor which will move the material up and into the processing building. Item 4 is an inclined belt conveyor which will serve to move the material to the hammermill for grinding. This belt is inclined at an angle of approximately 15°. Item 5 represents the two picking stations. Personnel will be located on raised platforms to effect a final inspection and segregation of the refuse prior to its introduction in the hammermill. Objects which are not compostable or have salvage value will be segregated out during this final inspection. Item 6 represents the hammermill which shreds the refuse to a particle size of approximately 2.54 cm (1 inch) or less. Item 8 is another belt conveyor which serves to move the material from the hammermill to the following stages in the process. Item 7 is a magnetic separator. This device will pick out ferrous metal objects and deposit them in a refuse bin. Item 9 is a magnetic pulley which serves as the terminal of the belt conveyor, Item 8. The magnetic pulley serves as an assurance that no ferrous metal objects will be introduced into the mixing stage of the process. Item 11 is a continuous feed paddle-type mixer. This device will thoroughly mix the ground refuse with TNT and water yielding a homogeneous product which had the proper moisture content for optimal composting. Item 10 is a belt conveyor which serves to move the material from the mixer to the outside of the process building to the collection area, Item 15.

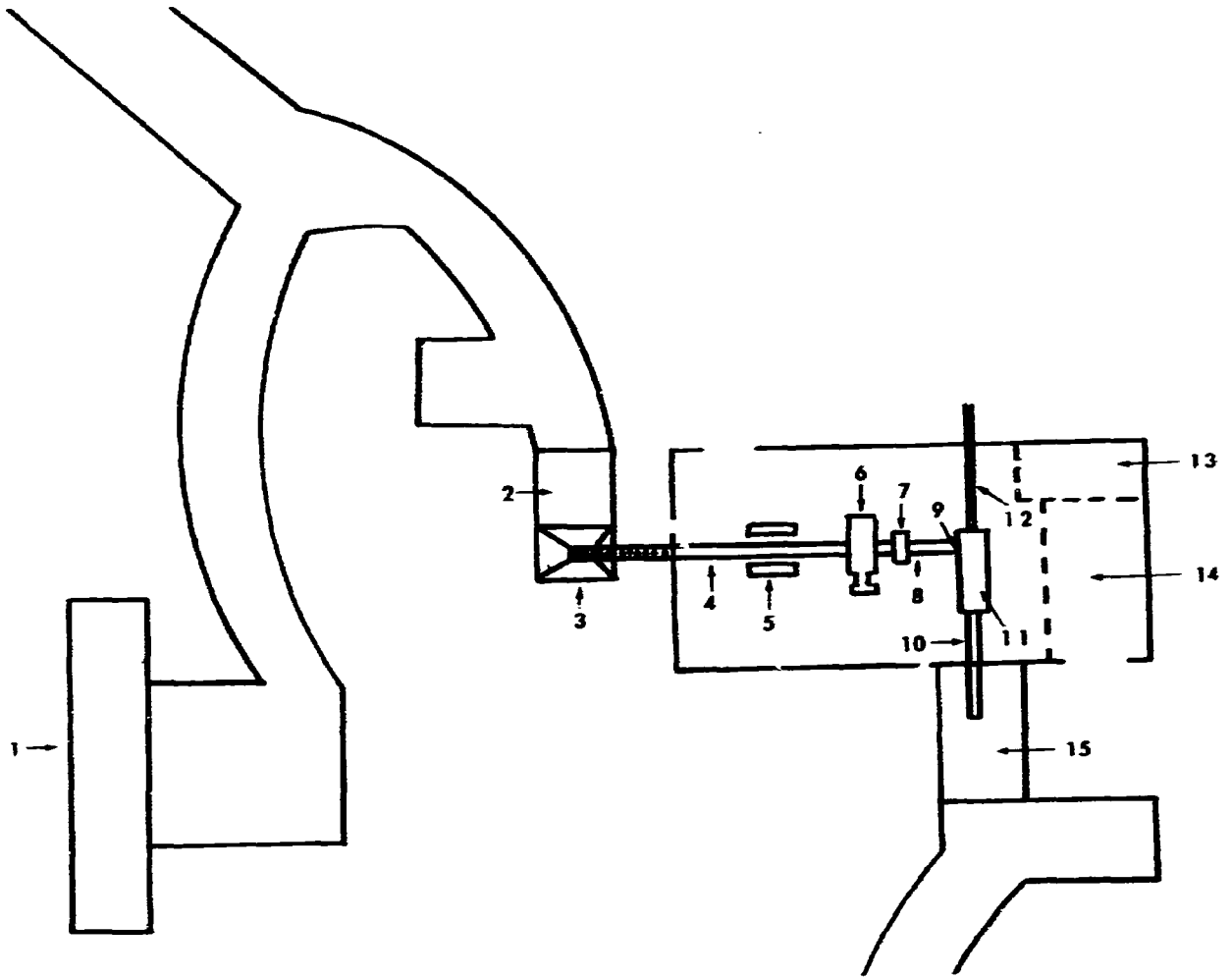

Fig 2B Process area

Item 12 is an incoming belt conveyor which will move the TNT to the paddle mixer. In order to effect degradagion of the TNT, the explosive must first be ground to a reasonably fine powder. A suitable device for effecting this size reduction from standard flake TNT has not been decided upon. Therefore the conveyor, Item 12, is shown as originating somewhere outside the process building; however, no attempt has been made to illustrate the facilities at the origin of this conveyor. The possibilities under consideration for a facility to effect the size reduction of flake TNT will be discussed later. Item 13 represents a storage area for tools and maintenance equipment and supplies. Item 14 is the garage area where the compost turner will be parked when not in use. The dashed lines on the figure indicate that partitions for these areas may or may not be desired. Depending upon the availability of a suitable vehicle, the processed refuse may be directly loaded onto a truck at point 15 or may be allowed to collect in a pile to be loaded onto a truck for conveyance to the composting pad at a more convenient time. Figure 3B is a side view of the process operation to help visualize the arrangement and orientation of some of the various pieces of equipment: Item 1, apron conveyor; Item 2, belt conveyor; Item 3, picking station; Item 4, hammermill; Item 5, magnetic separator; Item 6, belt conveyor; Item 7, magnetic pulley; Item 8, incoming belt conveyor which carries ground TNT; Item 9, paddle mixer; and Item 10, belt conveyor which moves the processed waste outside the processing building.

If funding were adequate, the addition of a digestor at point 15 in Figure 2B would be of significant benefit. This modification should be considered in the design of subsequent facilities if results of the pilot facility are satisfactory.

The selection of a process to effect the grinding of TNT to a suitable particle size was dominated by consideration of safety factors. The grinding process will be controlled remotely. Therefore, consideration is being given to locating this operation in an existing facility at another location somewhat removed from the compost processing area. In this event the conveyor belt, Item 12, Figure 2B, would originate at a feed hopper used to store an amount of already ground TNT sufficient for one day's operation. Among the devices being considered for the grinding operation are a knife mill, similar to the Wiley mill used to grind TNT samples for laboratory analysis, and a corning mill which is a type of roll crusher formerly used to pulverize black powder in commercial production operations. The decision as to which system will ultimately be selected is primarily dependent on safety considerations; however, cost and availability will have an influence on this decision.

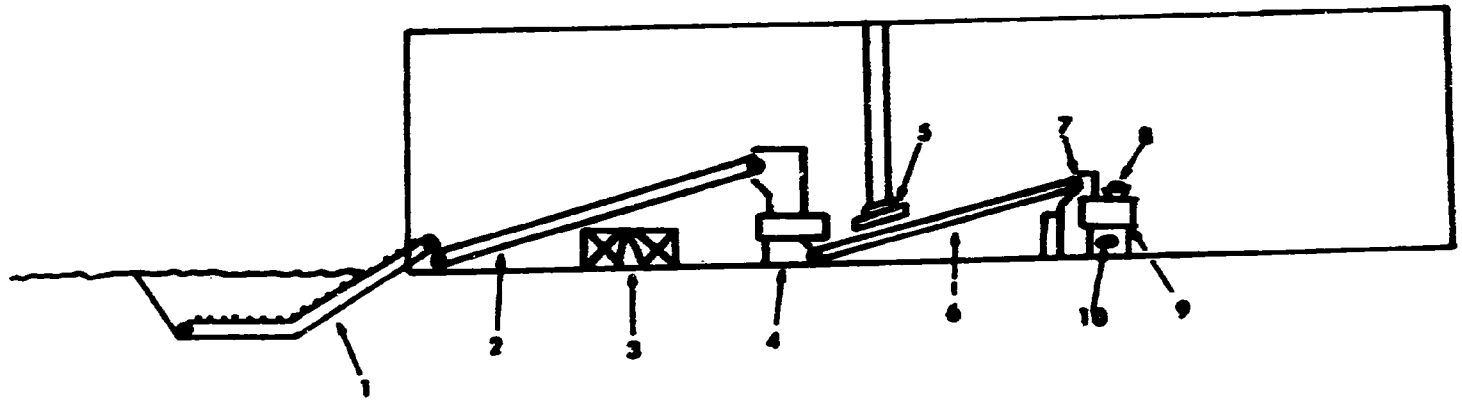

Fig 3B Elevation of process area

The compost turner under consideration is a specially modified forced feed loader. The vehicle is selfpropelled and is equipped with special collector scrapers which serve to move the windrow on to an elevated conveyor which deposits the composting materials to the rear of the vehicle as it moves along the windrow. Alternative types of equipment are available although at a considerably higher cost.

CONSTRUCTION COSTS

The following table gives an estimate of costs of purchase, installation, and construction of this facility based on informal contacts with several suppliers of this type of equipment.

FIG	ITEM	DESCRIPTION	PRICE
1	1	Trailer	$ 7,000
1	3	Building 13.2 x 27.4 meters (40' x 90')	56,750
1	3	Receiving hopper	11,500
2	3	Apron conveyor 1.2 x 15.2 meters (4' x 50')	45,000
2	4	Belt conveyor 1.2 x 16.8 meters (4' x 55')	16,000
2	5	Picking station	5,000
2	6	Hammermill 149.2 kilowatts (200 hp)	43,000
2	7	Magnetic separator	5,500
2	8	Belt conveyor .6 x 15.2 meters (2' x 50')	7,500
2	11	Paddle mixer	20,000
2	10	Belt conveyor .6 x 6.1 meters (2' x 20')	3,500
2	9	Magnetic pulley	2,000
1	4	Compost pad (61.0 x 61.0 meters (200' x 200')	42,000
		Lagoon and site preparation	45,000
		Compost turner	35,000
		Recirculating pump	8,000
		Front end loader	15,000
		TOTAL	$367,750

Note: Prices listed include installation

It should be noted that no cost estimates are available for the TNT grinding portion of the process. These costs will be influenced by the type of process used and the availability of an existing building to house the operation. A reasonable estimate would be $56,000 - $80,000. It is emphasized that the prices listed do not represent firm quotes but are merely estimates based on prices for similar equipment.

The foregoing diagrams and discussion are not necessarily final. Slight modifications may be necessary as further information becomes available; however, major processes and cost elements are not expected to change significantly.

OPERATING COSTS

The cost of operating the proposed pilot facility for the first year has been identified and is estimated in the following breakdown.

PERSONNEL

FUNCTION	NUMBER		COST
Plant manager/technician	1		$ 40,250
Technician	1		33,000
Operator	4		137,000
Chemist	1/2		25,000
Microbiologist/program manager	1/2		22,500
		Subtotal	$257,750
Repair and maintenance			5,000
Utilities			51,000
		TOTAL	$313,750

The operation of this facility would be considerably cheaper if it were operated as a line facility not concerned with the manipulation of experimental variables. The cost trade-offs resulting from more efficient treatment of solid wastes and extended life of sanitary landfill facilities have also been omitted.

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