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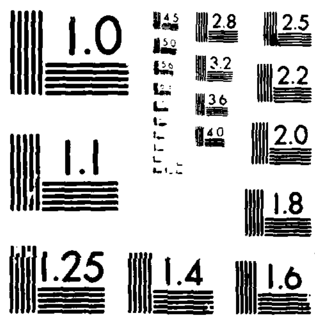

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Report No. CG-D-83-79
TASK No. 794153.4

LEVEL II

12

A STUDY OF RAPID BIODEGRADATION OF OILY WASTES THROUGH COMPOSTING

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October 1979

Final Report

Document is available to the public through the National Technical Information Service, Springfield, Virginia 22151

Prepared for

U.S. DEPARTMENT OF TRANSPORTATION
United States Coast Guard
Office of Research and Development
Washington, D.C. 20590

NOTICE

Technical Report Documentation Page

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
(19) CG-D-83-79	(18) 4526	

4. Title and Subtitle

(6) A Study of Rapid Biodegradation of Oily Wastes Through Composting

5. Report Date

(11) Oct [redacted] 79

6. Performing Organization Code

7. Author(s)

W. Taffel, E. Epstein (12) 57

8. Performing Organization Report No.

9. Performing Organization Name and Address

Energy Resources Co., Inc.
185 Alewife Brook Parkway
Cambridge, MA 02138

10. Work Unit No. (TRAIS)

794153.4

11. Contract or Grant No.

(15) DOT-CG-910121-A New

13. Type of Report and Period Covered

(9) Final Report,

12. Sponsoring Agency Name and Address

Commandant (G-FCP-2/TP64)
U. S. Coast Guard
Washington, DC 20593

14. Sponsoring Agency Code

15. Supplementary Notes

(10) William/Taffel Eliot/Epstein

16. Abstract

The potential for rapid biodegradation of oily wastes through composting was studied on a laboratory scale. Mixtures of crude and No. 6 oil with various bulking materials were analyzed for physical and chemical characteristics, and test composted in the bin composter developed by Energy Resources Co., Inc. During the several week composting periods, samples of the composting material were analyzed to quantify the population of hydrocarbon degrading microbes and to determine the degree of biodegradation achieved. Results of the study show that both crude and No. 6 oils were degraded, with a much greater observable breakdown of the No. 6 oil. This laboratory study suggests that composting may hold significant promise as a method of treating oily wastes on a large scale. Additional investigations to further clarify the nature of the process are recommended.

410 708

17. Key Words	18. Distribution Statement
Composting Oil wastes Petroleumlytic Biodegradation	Document is available to the U. S. public through the National Technical Information Service, Springfield, Virginia 22161.

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
		57	

Form DOT F 1700.7 (8-72) Reproduction of completed page authorized

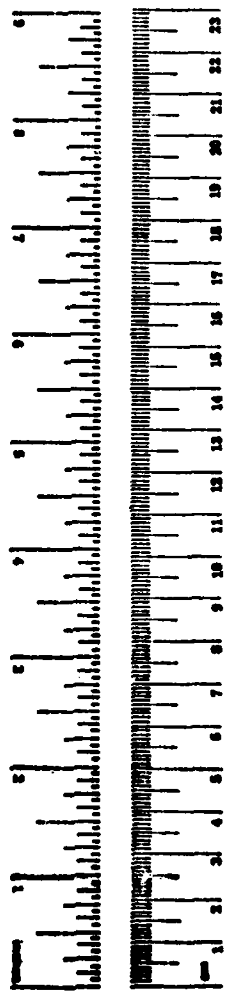
410708

METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

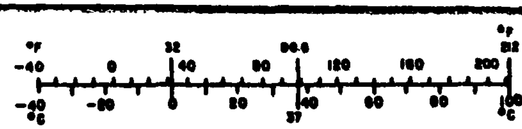
Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.



Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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INTRODUCTION

The objective of this laboratory study was to determine whether oily wastes could be biodegraded by composting. In recent years, the disposal of oily wastes produced during oil spill cleanup operations has become increasingly difficult and expensive. These materials - such as straw used to soak up oil from an oil slick - contain a high level of water, and thus require an inordinate amount of fuel for complete incineration. Landfilling the wastes is ceasing to be a viable option as landfill sites become more and more difficult to obtain, and requirements for environmental protection make safe landfills increasingly more expensive to build and operate.

Composting is the biological decomposition of organic materials into a semi-stable product. Naturally occuring microbes are used in a controlled environment to break down potentially toxic organic substances into non-toxic byproducts. The purpose of this project was to determine whether oily wastes could be biodegraded by composting. If the oily wastes could be composted, then one of several currently available composting technologies could be utilized for the conversion of the wastes into a non-toxic material, possibly with some commercial value.

The project was performed on a small scale in the laboratory, using the bin composter developed by ERCO. This device duplicates full scale composting conditions in the laboratory, and thus permits the conduct of composting experiments at a low cost. In this study, two oils - crude and No. 6 - were introduced into organic matrices, and composted. Periodic samples of the composting material were taken to monitor the biodegradation of the oils, and to quantify the microbes capable of degrading the oil.

The results obtained indicate that some biodegradation occurred with both oils. These results, while not conclusive, strongly suggest that full-scale composting might be a feasible option for the disposal of oily wastes.

The remainder of this report is comprised of five sections. Section One presents background information on the composting process, and the scientific basis for this project. Section Two describes the composting methodology followed during the study. Section Three details the chemical analytical procedures used, and presents the results obtained, while a discussion of the results and their significance is given in Section Four. Future research needs are discussed in Section Five.

SECTION ONE

COMPOSTING: BASIC CONCEPTS AND PRINCIPLES

1.1 Composting: Basic Concepts

Composting is the biological decomposition of organic materials into a semi-stable product. Organic matter is composed of various constitutents. Some of these (such as sugars and carbohydrates) are easily biodegraded, whereas others (waxes, lignins, cellulose) are more resistant to microbial decomposition. Normally, biological degradation is slow. However, by optimizing and manipulating the various parameters and insulating the mass, it is possible to greatly accelerate the process. Processes currently used in composting are conducted under moist, hot, aerobic conditions and are considerably more rapid than natural biological degradation.

Microbial decomposition of the organic compounds is carried out primarily by three groups—bacteria, fungi, and actinomycetes. Over 75 different species have been identified in various composting materials. During the composting process, changes in the microbial population occur as a result of temperature increases. Gray et al. (1971) identify four stages in the process—mesophilic (ambient to 40° C), thermophilic (45 to 64° C), cooling, and maturing. Although the greatest activity takes place in the 40 to 60° C range, Spohn (1970) reported that thermophilic fungi and actinomycetes were present at temperature exceeding 80° C.

The primary consideration in composting is that the waste material must be well aerated. Aerobic decomposition - occurring in the presence of oxygen - is much more rapid, and develops higher temperatures than anaerobic decomposition. Different composting systems use different methods to ensure sufficient aeration. The windrow system consist of long, low (3 to 4 feet) piles which are turned periodically. Convective air and frequently turning serve to maintain aerobic conditions.

Several mechanical systems, consisting of either a rotating drum, multistage tower silos, moving elevators, or other devices, have been used to mix and aerate for composting. Some of these systems are in use in Europe, primarily for composting or refuse or combined refuse and sludge.

The static-pile, forced aeration method, which was developed by the U.S. Department of Agriculture (USDA) at Beltsville, Maryland, in 1974, consists of a stationary compost pile constructed over an aeration system. Aerobic conditions are maintained by a suction system which draws air through the pile. This system offers the advantages of low capital investment and low energy costs, and is becoming widely accepted as an economic and effective method for large-scale composting of organic wastes. This research project was based on the principles of the forced aeration technique. The Beltsville process is discussed below.

1.2 Beltsville Method

The basic system for composting by the Beltsville method is shown in Figure 1.1. If the physical and chemical properties of the waste are such that it cannot be composted alone (e.g., moisture content too high, porosity too low, etc.) it is first mixed with a suitable bulking agent. It is important that the final moisture content be between 40 and 60 percent. The mixture is then piled over an aeration system. The entire pile

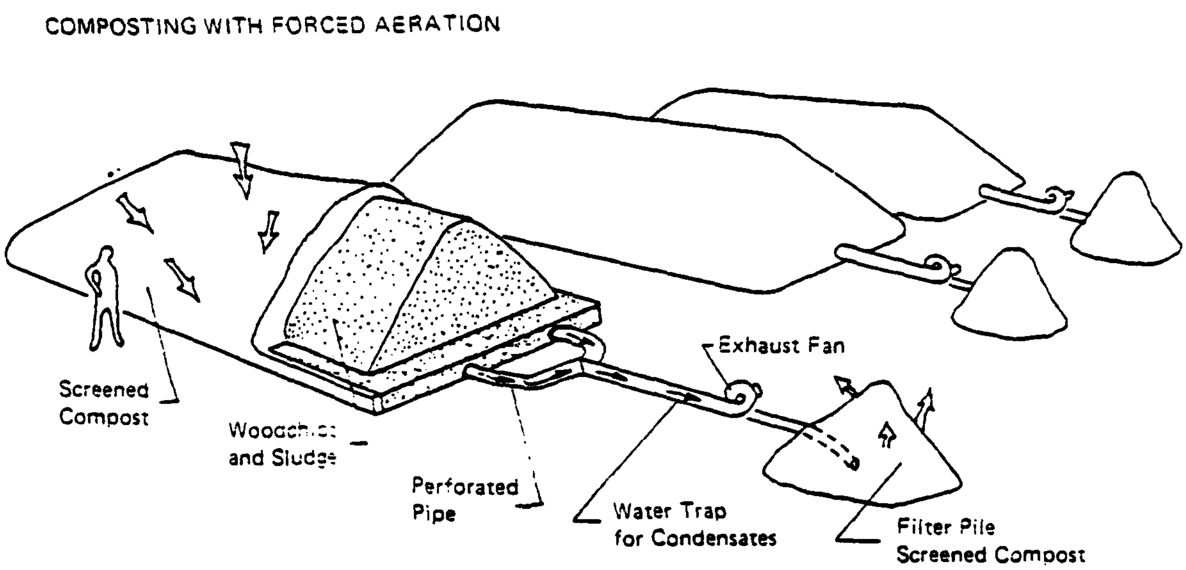

Figure 1-1: Three dimensional schematic diagram of the Beltsville Aerated Pile Method for composting sewage sludge.

is then covered with previously manufactured compost, or with additional bulking material. This material acts as an insulation blanket to retain heat and maintain high temperatures throughout the mass. The insulation also prevents odors from leaking into the environment.

Once the pile is constructed, air is withdrawn by means of a blower at a rate of about 500 cubic feet/minute, which provides oxygen levels between 5 and 15 percent. The use of a timer controls the rate of aeration.

Potentially odorous gases withdrawn from the pile are scrubbed through a small pile of compost or bulking material. Since the gases from the pile are hot, moisture will condense in the pipe. This condensate is removed by using a water trap.

The amount of time required for composting depends on the particular waste in question, and must be determined empirically. Composting of sewage sludge usually takes 21 days. Curing involves the stacking of the material for several weeks after composting to allow for futher stabilization. During the 21 days, only the most volatile organic components break down. Curing allows for further decomposition of the organic matter and the prevention of odors.

1.3 Process Parameters Affecting Composting

The bioconversion of wastes into compost is greatly affected by several key parameters. These influence the rate and extent of temperature rise which, in turn, affect pathogen survival. The six most important factors are:

1. Carbon/nitrogen ratio.

2. Aeration.

3. Volatile solids content of wastes.

4. Bulking material.

5. Bulk density.

6. pH of sludge.

Although several of these factors are interrelated, each will be discussed separately.

1.3.1 Carbon/Nitrogen (C/N) Ratio

Carbon is used by all living organisms as an energy source. Nitrogen is utilized as a building block in the production of proteins. Cells require more carbon than nitrogen. If excess carbon is present, however, rapid cell growth will cause a depletion of available nitrogen and a temporary slowdown in cellular growth. As cells begin to die, their stored nitrogen again becomes available to living cells and the system is brought back into balance. This restoration requires time to occur, and in a composting situation excess carbon results in heat loss and subsequent reduction in effectiveness of pathogen destruction.

It is therefore desirable to maintain the C/N ratio at a level that allows for optimum microbial growth. This has been shown to be between 26 and 31 units of carbon for every unit of nitrogen (Gottas, 1956; Poincelot, 1977). Carbon values greater than 31 tend to slow the process and result in low temperatures.

Low C/N ratios (<20) generally affect the compost product rather than the process. With low C/N ratios, ammonia is released and the nitrogen content of the compost is reduced. One of the major goals of composting is to produce an economical, useable product. Therefore, it is important to have the nitrogen content as high as possible.

1.3.2 Aeration

Higher temperatures are achieved under aerobic conditions than under anaerobic conditions. Over-aeration results in cooling of the compost piles while under-aeration results in low temperatures due to anaerobic conditions. Willson (1977) showed that 1200 cubic feet per hour (cfh) of air moving through a forced aeration pile developed temperatures in excess of 70° C for 15 days. An unaerated pile under the same conditions developed temperatures below 30° C. Over-aerating at a level of 3300 cfh provided high temperatures but resulted in rapid cooling. The result of these and other studies suggested that 12 to 14 cfh per dry ton of sludge provided on an intermittent basis results in oxygen levels from 5 to 15 percent throughout the pile.

1.3.3 Volatile Solids

Gray and Sherman (1959) reported increased CO_2 production (i.e., greater microbial respiration) with increased volatile solids. Presumably this results from more nutrients being available to support a larger microbial population. Increased respiration and microbial activity will result in higher temperatures.

1.3.4 Bulking Material

In composting, a bulking material may need to be mixed in with the waste to provide the necessary texture, structure, and porosity for aeration. The bulking material also lowers moisture content of the biomass to 50 to 60 percent, and provides an additional carbon source for micro-organisms to ensure rapid composting. Many of these factors help to create and maintain high temperatures during composting. A variety of materials (e.g., paper, refuse, straw, peanut hulls, bark, leaves and other agriculture residues) can be used as bulking materials.

1.3.5 Bulk Density

The bulk density of the waste, i.e., the weight per unit volume, influences the porosity and free air space necessary for aerobic composting. The correct combination of bulk density and moisture is necessary for proper composting. In most cases, this can be provided by adjusting the volume of bulking material.

1.3.6 pH

Compost pH is a dynamic phenomenon and, as composting proceeds, the pH of acid materials tends to shift upward toward neutrality while the pH of alkaline materials decreases. While microbial activities may be initially inhibited at these extreme pH values, it is unlikely that they would be suppressed for very long.

1.3.7 Curing

The term "curing" or "maturation" has been referred to as "further stabilization." It essentailly consists of stockpiling the compost for a period of time during which temperatures decrease and further decomposition of the organic matter occurs. The need for and extent of curing will depend on the original stability of the organic matter and the final degree of stabilization desired. Golueke (1973) has pointed out that stabilization is a highly relative term since "ultimate" stabilization would result in CO_2, H_2O, and residual mineral matter, which of course is not desirable.

1.4 Composting of Industrial Material

Historically, composting has been used to biodegrade and stabilize animal, human or municipal solid waste. Recently (Epstein et al., 1978) there has been considerable interest in a system which rapidly composts sewage sludge under aerobic thermophilic conditions. Presently there is very little data on the composting of industrial organic compounds. Rose and Mercer (1968) investigated the composting of insecticides in agricultural wastes. Continuous thermophilic composting rapidly decreased the concentration of the pesticides diazinon and parathion. In 10 days the diazinon concentration was reduced approximately 50 percent and in 42 days the initial concentration of 3.3 ppm was reduced to less than 0.002 ppm. The concentration of parathion was reduced by 50 percent in 12 days of composting. Degradation of pp-DDT was considerably slower. Fifty days of composting were required to reduce the level of DDT from 2.2 ppm to 0.8 ppm. It was interesting to note that DDD and DDE, which are normally produced by DDT degradation in soils, were not detected in the composted material. This aspect is extremely important since breakdown products such as DDD and DDE may be as environmentally undesirable as the parent compound.

Osmon and Andrews (1978) investigated the biodegradation of TNT, a nitro-amino-toluene compound, by composting. They were able to degrade large quantities (5 to 10 percent) of TNT in a relatively short time to zero or acceptable levels. No breakdown products or compounds of environmental concern were found.

As part of a sewage sludge composting project for the Boston Metropolitan District Commission (MDC), Energy Resources Co. Inc. (ERCO) investigated the effect of composting on the degradation of hydrocarbons in sewage sludge. Sludge extracts were fractionated into classes of compounds and a detailed analysis was performed on the aromatic fraction. The aromatic fraction was chosen for analysis because it would contain polynuclear aromatic hydrocarbons, many of which are known or suspected carcinogens.

Figure 1.2 shows chromatograms for raw and composted sludge from the MDC's Deer Island treatment plant. Comparison of the two chromatograms shows that composting almost completely degraded the hydrocarbons. The single large peak in the composted sludge chromatogram has not yet been identified. Data from gas chromatography and mass spectrometry show that composting at Deer Island removed all but one of the resolved aromatic compounds, all of the resolved aliphatic components, and a sizable portion of the unresolved components from the raw sludge.

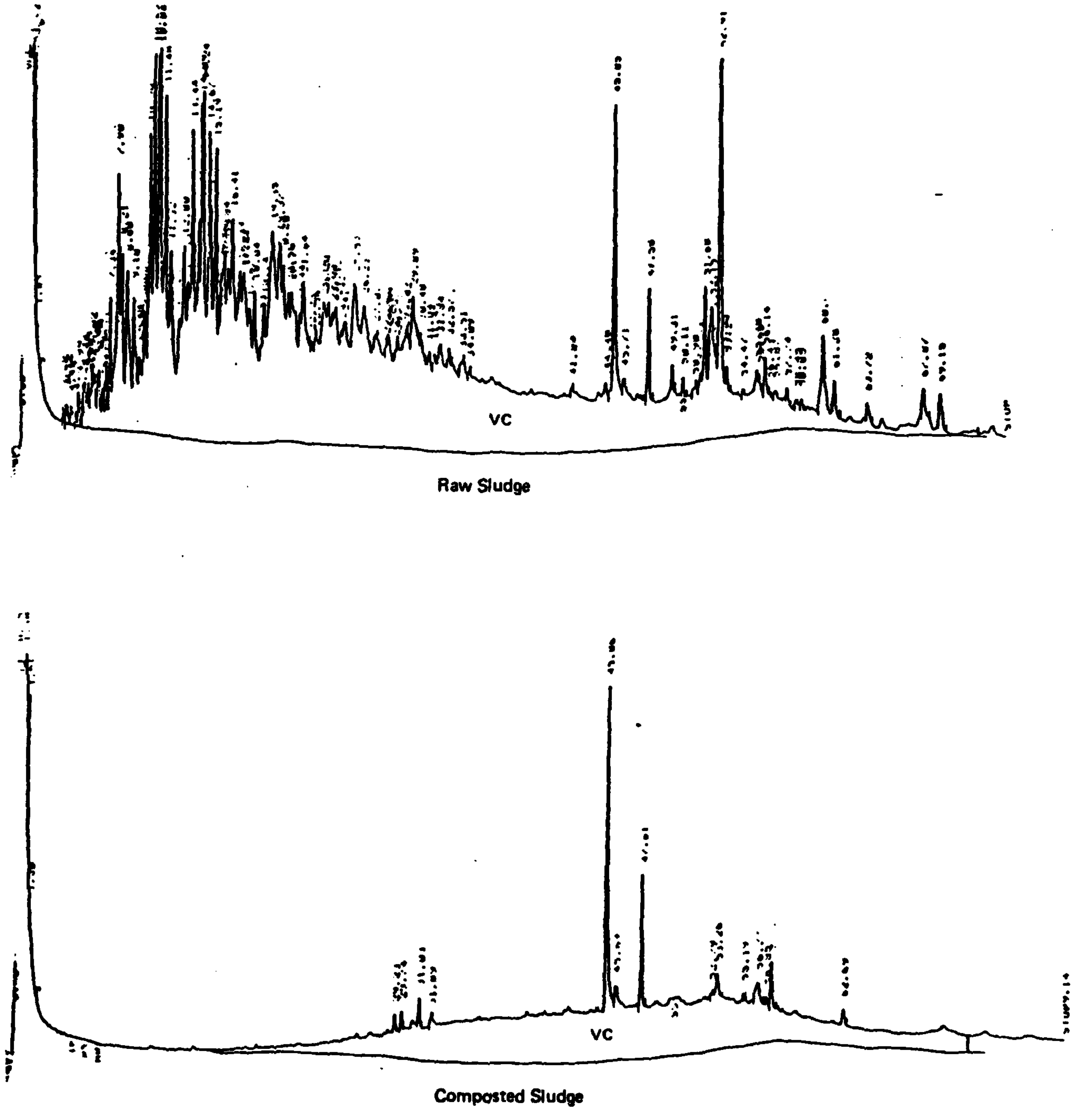

Figure 1.2: Gas Chromatographic Analysis of Organic Compounds Present in Raw Sewage Sludge Prior and After Composting.

This analysis represents only the aromatic fraction, one of the many classes of organic compounds contained in sludge. Further work is necessary to ascertain whether other classes of compounds could be biodegraded through composting. The data on the aromatic fraction indicated the potential of composting not only for stabilizing putrescible material but also for degrading or decomposing environmentally hazardous organics.

On the basis of these results, it was apparent that composting offered some potential for the rapid degradation of oils, and of oily wastes. This possibility had not yet been studied in depth, and a realistic evaluation of the potential could not be made. The project was designed to provide scientific data necessary to determine whether composting of oily wastes was feasible.

SECTION TWO

COMPOSTING METHODOLOGY

2.1 The Bin Composter

For the purposes of this study, the laboratory investigations were conducted using the bin composter designed by ERCO for simulation of full-scale composting conditions on a laboratory scale. A diagram of the device is shown in Figure 2-1.

For each experiment, the test mixture was placed into the bin, resting on the support screen shown in the diagram. Air was pulled down through the material by the pump, and exhausted into an odor scrubber composed of existing compost.

The copper coils in the bin provide for the addition or removal of heat by pumping water of a desired temperature through the system. For these experiments, the water system was not used, since the material was composted under natural conditions, and the addition of heat was not desired. Temperature and oxygen readings were taken by inserting probes from the top down to the sampling points of interest.

2.2 Preliminary Laboratory Characterizations

Prior to conducting the bin composting trials, mixtures of the two oils to be studied (crude and No. 6) were prepared and analyzed for a number of chemical and physical parameters. The data obtained in these analyses was then utilized in conducting the bin composting tests.

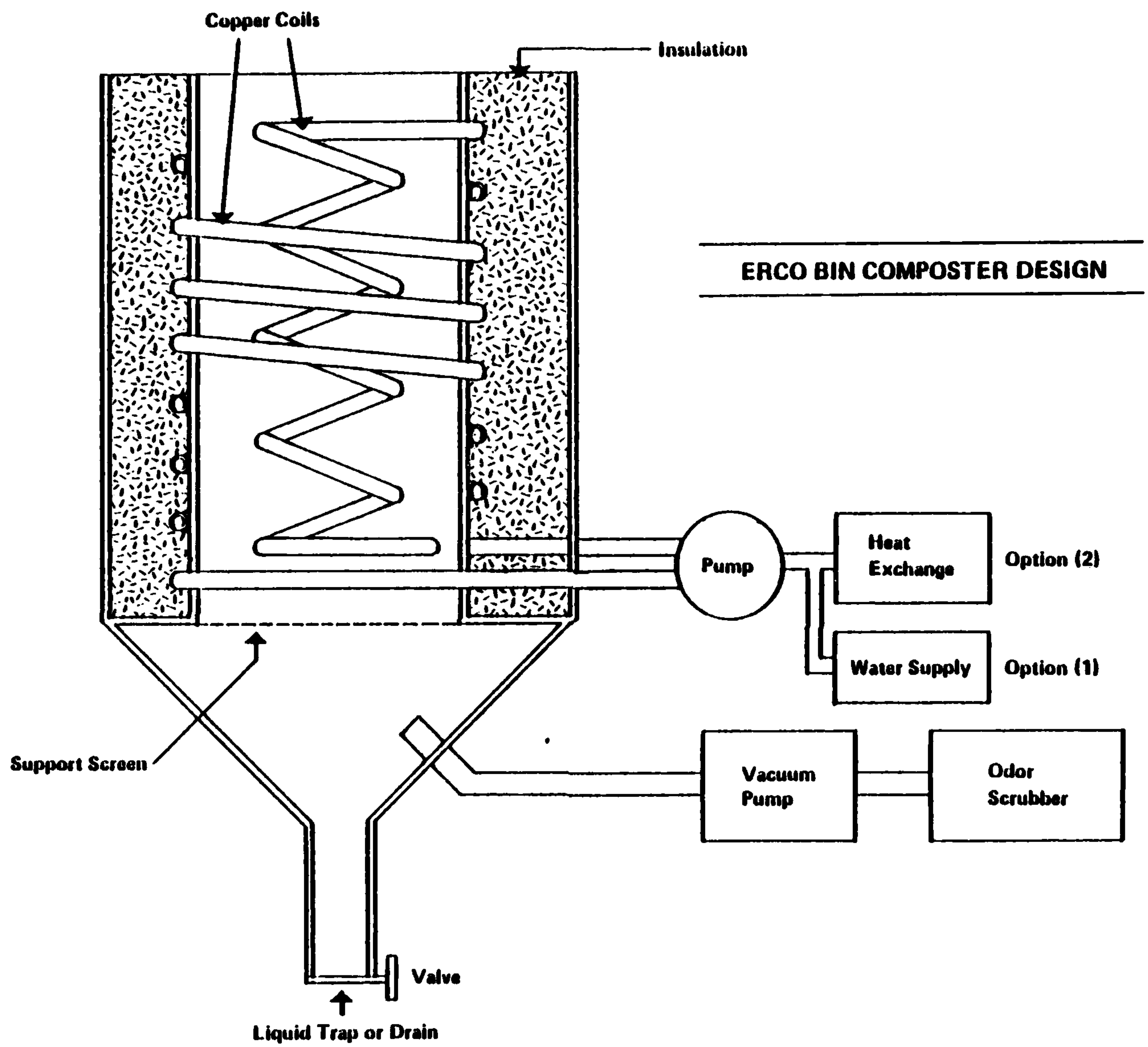

Figure 2–1. The Bin Composter.

Samples of straw were soaked in crude oil and in No. 6 fuel oil for approximately 30 minutes. The straw was removed from the oil and drained. The analyses performed on the samples, and the results obtained, are listed in Table 2-1.

Both mixtures of oil and straw were too dry for optimum composting. For optimal degradation, the moisture content of the material to be composted should be between 50 and 60 percent, as opposed to the values of 23.5 and 13.1 percent observed here. Also, the nitrogen content of the mixes was low. The ideal C:N ratio for composting is 26 to 31, versus the values of 214 and 197 seen here.

Hence, it was decided that both water and a nitrogen source should be added to the mixtures for the bin composting tests. This was accomplished by soaking the material in a water solution of urea as described below.

2.3 Bin Composting Trials

According to the original plan, one bin composting test was to be performed on a mixture of each of two types of oil and straw. However, the first test with the crude oil proved unsuccessful, and several different approaches were tried before successful composting was achieved. The method that finally proved successful on the crude oil was then applied to the No. 6 oil, and worked on that mixture on the first attempt. Five bin tests were conducted in all -- four on mixtures using crude oil, and one on a mix with No. 6 oil. The procedures used, the composition of the mixture, and the results of each test are described below.

TABLE 2-1

PHYSICO-CHEMICAL PARAMETERS OF TEST OIL:STRAW MIXES

Parameter	Straw:Crude Mix	Straw:No. 6 Mix
Specific Gravity	0.64	0.68
Total Carbon	77.0%	72.8%
Total Nitrogen	0.36%	0.37%
C:N Ratio	214	197
Wet Weight	0.40 lb	0.35 lb
Dry Weight	0.31 lb	0.30 lb
Ash Weight	0.23 lb	0.19 lb
% Moisture	23.5%	13.1%
% Volatiles	19.0%	32.6%

2.3.1 Bin Trial 1 - Crude Oil and Straw

2.3.1.1 Procedure

Unshredded straw was weighed and then soaked in the crude oil for 5 to 15 minutes. It was then removed from the oil, drained, weighed, and placed in a 9.1 percent urea solution for 5 to 15 minutes. It was then drained and weighed again and placed in the bin to compost. The final composition of the mix is shown in Table 2-2. The total nitrogen content of the mixture was 1 percent.

2.3.1.2 Results

This mixture was tested in the bin composter for 6 days. During this time no composting at all was observed. Temperatures in the bin never rose above ambient, as can be seen from Table 2-3.

Microbiological studies showed that there were organisms present in the mix. Bacteria were living in all phases of the medium -- the oil, water, the oil-water interface, etc. Bacteria were isolated which were capable of deriving nutrients from the oil fumes alone. Nevertheless, all microbial activity was occurring at ambient temperatures and not in the thermophilic as was desired. The failure to achieve proper composting may be attributable to one of several possibilities -- too little nitrogen, too much oil, or too little surface area in the mixture. These possibilities were addressed in Bin Trial 2.

TABLE 2-2

BIN TRIAL 1 - MIX COMPOSITION

Element	Weight (lb)	Percent of Total Mix
Straw	6.23	24.2
Crude Oil	13.74	53.5
9.1% urea solution	5.73	22.3
Total	25.70	100.0

TABLE 2-3

BIN TRIAL 1 - RESULTS (°C)

Composting Day	Bin Temperature	Ambient Temperature
1	7	13
4	15	
5	16	23
6	17	20

2.3.2 Bin Trial 2 -- Crude Oil and Straw

2.3.2.1 Procedure

For this trial, the straw was shredded prior to use in the bin in order to provide greater surface area and thus to enhance the potential for composting. The straw was then soaked first in a urea solution (12.2 percent urea) to ensure penetration of the urea into the straw. The urea content of this second solution was 12.2 percent, as compared to 9.1 percent in Trial 1. Then the wet straw was drained and soaked in crude oil. It was then drained again and placed in the bin. The composition of the mixture is shown in Table 2-4. Additional characteristics of the mixture are listed in Table 2-5.

2.3.2.2 Results

Again no increase in temperature was observed in this trial. The temperatures observed are shown in Table 2-6. A strong ammonia smell was produced by the material in the bin, indicating the presence of a viable microbiological community in the medium, but also suggesting that too much nitrogen had been added to the mix. It was also apparent that the addition of a material containing a bacterial population known to be capable of composting was desirable. This was accomplished in Trial 3.

TABLE 2-4

BIN TRIAL 2 - MIX COMPOSITION

Element	Weight (lb)	Percent of Total Mix
Shredded Straw	10.79	18.9
Crude Oil	4.89	8.6
12.2% Urea Solution	41.26	72.5
Total	56.94	100.0

TABLE 2-5

BIN TRIAL 2 - MIX CHARACTERISTICS

Parameter	Value
Nitrogen Content	4.2%
Carbon Content	14.3%
C:N Ratio	3.35%
Percent Volatiles	31.1%

TABLE 2-6

BIN TRIAL 2 - RESULTS (°C)

Composting Day	Bin Temperature	Ambient Temperature
1	18	21
2	17	20
3	19	19
4	15	20
5	21	21
6	14	16
7	14	18
8	19	19
9	20	19

2.3.3 Bin Trial 3 -- Crude Oil and Straw and Stable Wastes

2.3.3.1 Procedure

The Trial 3 mixture was prepared by mixing the material from Trial 2 with an equal volume of stable wastes containing horse manure, straw, and wood shavings. It was thought that this would provide a healthy dose of seed organisms which might then accelerate the degradation process. The composition of the Trial 3 mix is shown in Table 2-7. The mixture contained 4.4 percent oil, by weight.

2.3.3.2 Results

The temperature in the bin during Trial 3 was observed to rise from a low of 15°C to a high of 35°C within several days. However, temperatures never achieved the thermophilic range and so the trial was ended on the seventh day. The temperature data obtained from Trial 3 are shown in Table 2-8.

An ammonia smell was produced during this trial also, again indicating that the mix contained too much nitrogen. Both the Trial 2 mixture and stable wastes were high in nitrogen, resulting in an excessive nitrogen content in the final mix. The excess nitrogen, on conversion to ammonia, was most likely damping the composting process by inhibiting the growth of microorganisms. However, the fact that a temperature increase was observed was encouraging and suggested that a similar mix with a lower nitrogen content might compost properly. This approach was tested in Trial 4.

TABLE 2-7

BIN TRIAL 3 - MIX COMPOSITION

Element	Weight (lb)	Percent of Total Mix
Trial 2 Mixture	26.35	45.3
Stable Wastes	31.05	54.01
Total	57.40	100.0

TABLE 2-8

BIN TRIAL 3 - RESULTS (°C)

Composting Day	Bin Temperature	Ambient Temperature
1	27	20
2	24	26
3	30	25
4	35	24
5	18	23
6	30	25
7	34	21

2.3.4 Bin Trial 4 -- Crude Oil and Straw and Stable Wastes

2.3.4.1 Procedure

The Trial 4 was prepared by mixing shredded straw, crude oil, and stable wastes simultaneously. The composition of the mixture is presented in Table 2-9. The straw and stable wastes were mixed in a 1:1 ratio by volume.

2.3.4.2 Results

Successful composting was achieved in Trial 4. A good temperature rise was observed with temperatures peaking at 56°C within 2 to 3 days of initiation of the test. The temperature then declined gradually, stabilizing in the low 30°C after the tenth day of composting. The temperature data obtained are listed in Table 2-10 and are shown graphically in Figure 2-2. Samples were taken during this trial for microbiological and hydrocarbon analyses as indicated in Table 2-10. It is clear from the temperature data that proper conditions for composting of the oily straw were achieved in Trial 4. Results of the laboratory analyses are discussed below.

2.3.5 Bin Trial 5 -- No. 6 Oil and Straw and Stable Wastes

2.3.5.1 Procedure

Bin Trial 5 was conducted using the same method as Trial 4, however, No. 6 fuel oil was used in this case. Again, the shredded straw was mixed with No. 6 oil and stable

TABLE 2-9

BIN TRIAL 4 - MIX COMPOSITION

Element	Weight (lb)	Percent of Total Mix
Shredded Straw	6.70	11.9
Crude Oil	4.35	7.7
Stable Wastes	45.20	80.4
Total	56.25	100.0

TABLE 2-10

BIN TRIAL 4 - RESULTS (°C)

Composting Day	Bin Temp	Ambient Temp	Samples Taken Hydrocarbon	Samples Taken Microbiology
1	35	20	*	*
2	48	22		
3	56	20		
4	49	17		
5	50	16		
6	48	18	*	
7	47	22		
8				
9	42	24		
10	38	23		
11	34	22		
12				
13				
14				
15	32	23		
16	30	22		
17	30	20		
18	29	21		
19	30	22		
20	32	23		
21	34	25		
22	35	27	*	*

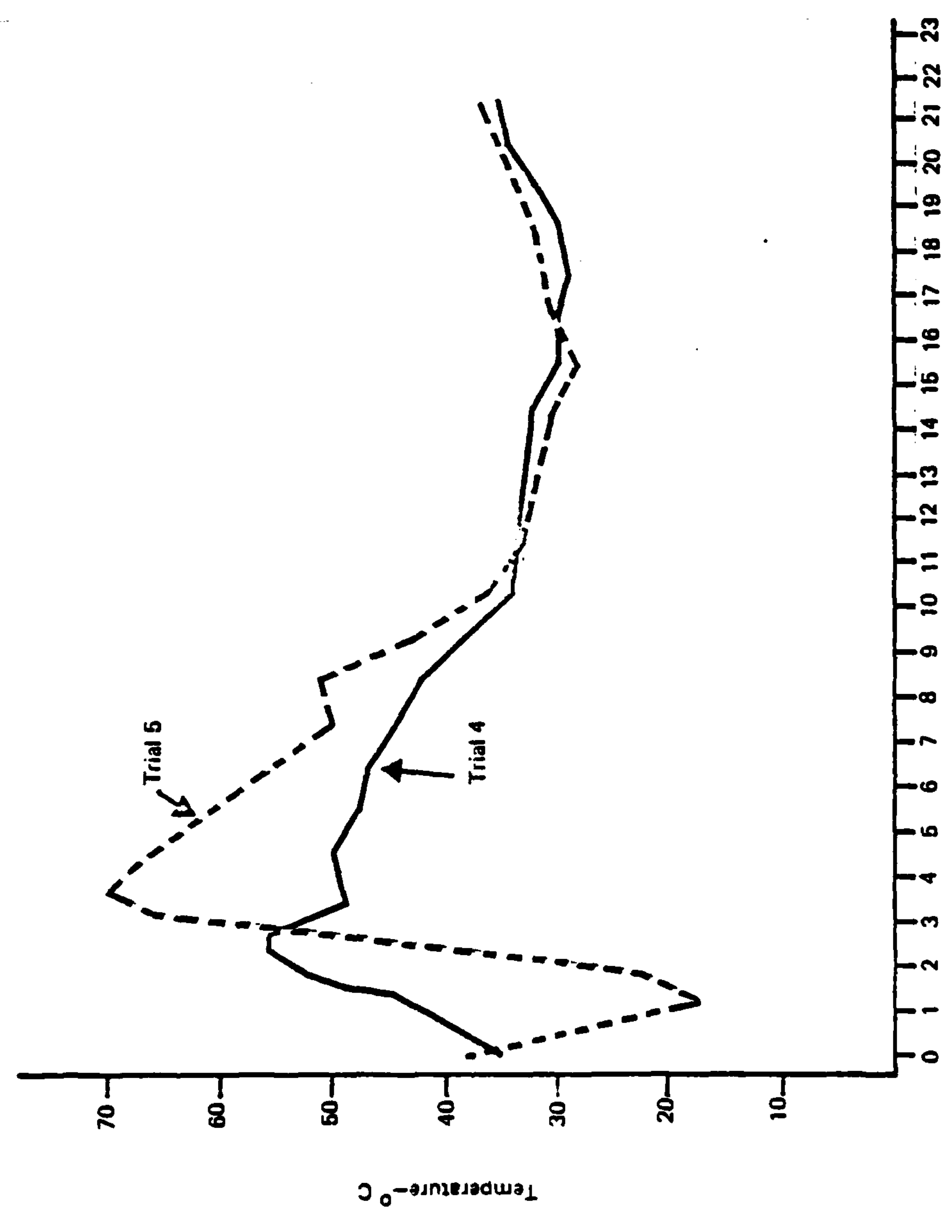

Figure 2–2 Time–Temperature Relationships Coast Guard–Oil Wastes. Bin Trials 4 & 5.

wastes, with the straw and stable wastes being mixed in a 1:1 ratio by volume. The mix composition is shown in Table 2-11.

2.3.5.2 Results

Proper composting was again achieved in Trial 5. Initially (in the first day) the temperature was observed to drop dramatically from 38°C to 17°C. This was thought to be due to overaeration with cool air, so the aeration system was shut off. The temperature recovered rapidly, reaching 70°C in the first week, and then gradually falling to the mesophilic range (30°C to 35°C) after about 10 days. This pattern is similar to that observed in Trial 4. The temperature data for Trial 5 is listed in Table 2-12 and shown graphically in Figure 2-2. Samples were taken for microbiological and hydrocarbon analyses as shown in Table 2-12. Results of the analyses are discussed in Section Three.

TABLE 2-11

BIN TRIAL 5 - MIX COMPOSITION

Element	Weight (lb)	Percent of Total Mix
Shredded Straw	7.60	13.2
No. 6 Fuel Oil	4.79	8.4
Stable Wastes	45.00	78.4
Total	57.39	100.0

TABLE 2-12

BIN TRIAL 5 - RESULTS (°C)

Composting Day	Bin Temperature	Ambient Temperature	Samples Taken Hydrocarbon	Microbiology
1	38	28	*	*
2	17	20		
3	41	24		
4	70	22		
5	67	27		*
6				
7	55	30		
8	50	27	*	
9	51	21		
10	42	22		
11	36	23		
12	33	26		
13				
14				
15	30	22	*	
16	28	25		
17	30	22		
18				
19	32	28		
20				
21				
22	36	27		
23				
24				
25	32	22	*	*

SECTION THREE

LABORATORY ANALYSES

3.1 Hydrocarbon Analyses

3.1.1 Sampling Analysis Procedure

At predetermined times, samples of the composted material were collected from several locations within the compost bin. The samples were placed in solvent rinsed glass jars and stored at -10°C awaiting analysis.

The compost material was analyzed for petroleum hydrocarbons by a combination of extraction, fractionation and gas chromatography techniques. The samples from a given sampling time were thawed and combined and a 25g aliquot removed by a coning and quartering technique. The sample was placed in a 200 ml glass centrifuge tube and shaken with 100 ml of a solvent mixture (90 percent dichloromethane, 10 percent methyl alcohol) to extract the petroleum hydrocarbons.

The solvent extract was dried over sodium sulfate and concentrated by rotary evaporation. An aliquot of the solvent extract was evaporated on a taped aluminum pan and weighed on a Cahn electrobalance to yield a total lipid weight. A second aliquot was taken and fractioned by silica gel/alumina column chromatography in f_1, saturated hydrocarbon and f_2, aromatic hydrocarbon fraction. An aliquot of the fractions were weighed using the technique described above. A second aliquot of the fractions was analyzed by high resolution gas chromatography using 30m SE-30 columns installed in a Hewlett-Packard 5840A gas chromatograph with a spitless injection port and a flame ionization detector.

For selected samples, the f_2 was analyzed by combined gas chromatograph/mass spectrometry on a Hewlett Packard 5985 GC/MS system. This technique identifies and measures the concentrations of aromatic hydrocarbons present in the fraction.

3.1.2 Hydrocarbon Analysis Results

Observations of petroleum spilled in the marine environment have shown that different chemical classes of compounds degrade at different rates. Generally N-alkanes are degraded faster than branched alkanes which are degraded faster than cyclic alkanes and aromatic hydrocarbons. The progress of degradation can be monitored by either measuring the absolute change in concentration of individual components or by measuring the relative abundance of each class of the compounds in the hydrocarbon fraction. The latter approach is useful for measuring degradation in early stages of weathering or where inhomogeneities of sampling hinder absolute quantitation.

In these composting experiments, the material comprising the piles is suspected to be inhomogeneous, due to the large size of the bulking material relative to the size of sample ash to be analyzed. Therefore, the latter technique for monitoring the progress of the degradation is relied on.

3.1.2.1 Bin Trial 4 -- Crude Oil and Straw and Stable Wastes

In this trial, degradation had not proceeded very far after two weeks. The absolute concentrations of the n-alkanes with carbon numbers greater than N-C20 remain fairly constant. Some loss of the lower molecular weight n-alkanes is noticed; however, this could possibly be attributed to evaporation.

There is some evidence for early degradation of the oil in the n-alkane/isoprenoid (branched alkane) ratio. The ratio decreased from 2.98 in the original oil mixture to 1.46 in the final compost sample (see Table 3-1). However, the greater abundance of n-alkanes relative to branched alkanes (ratio ≥ 1.0) indicates that degradation did not proceed very far. On a total oil basis, only a few percent of the oil has degraded.

3.1.2.2 Bin Trial 5 -- No. 6 Oil and Straw and Stable Wastes

In this trial, degradation of the oil has proceeded to a greater extent. Apparent inhomogeneities in the compost pile cause the absolute concentrations of hydrocarbons to fluctuate widely. Therefore, the relative concentrations of individual compounds and compound classes are monitored to measure the progress of the degradation. The n-alkane/isoprenoid ratio decreases from 1.96 in the original oil to 0.44 in the compost sample collected after 24 days. The n-alkanes are greatly depleted and are now less abundant than the branched alkanes (ratio <1.0). Degradation of the branched alkanes would proceed next. (see Table 3-2)

Figures 3-1 and 3-2 show the dramatic changes during Trial 5 in aliphatic hydrocarbons as a result of composting. Figure 3-1 represents the neat oil prior to composting whereas Figure 3-2 shows the composted oil after 24 days.

A plot of the relative concentrations of prominant aromatic hydrocarbons in the original oil and the day 24 compost (Figure 3-3) shows the aromatic assemblages in each sample to be quite similar. The primary difference is the deletion of some of the substituted naphthalenes in the compost sample. Preferential depletion of certain aromatics would be expected if appreciable degradation of the aromatics had occurred.

TABLE 3-1

BIN TRIAL 4 - HYDROCARBON DEGRADATION

Sample	N-C17/Pristane* Ratio	N-C18/Phytane* Ratio	Alkanes/Isoprenoids* Ratio
Crude Oil	2.60	3.54	2.86
Mixture:			
Day 1	2.66 (+2.3%)	5.58 (+57.6%)	2.98 (+4.2%)
Day 6	1.32 (-49.2%) (-50.4%)	3.09 (-12.7%) (-44.6%)	1.54 (-46.1%) (-48.3%)
Day 22	1.29 (-50.4%) (-51.5%)	2.20 (-37.8%) (-60.5%)	1.46 (-48.9%) (-51.0%)

*For each number given, the first precentage in parentheses represents the increase or decrease from the crude oil value. The second percentage in parentheses represents the decrease from the value in the Day 1 mixture. For example, the Day 22 n-C17/pristane ratio of 1.29 is a 50.4% decrease from the crude oil value of 2.60, and a 51.5% decrease from the Day 1 value of 2.66.

TABLE 3-2

BIN TRIAL 5 - HYDROCARBON DEGRADATION

Sample	N-C17/Pristane* Ratio	N-C18/Phytane* Ratio	Alkanes/Isoprenoids* Ratio
No. 6 Oil	1.76	1.44	1.97
Mixture:			
Day 0	1.81 (+2.8%)	1.46 (+1.4%)	1.96 (-0.5%)
Day 7	0.90 (-48.9%)	0.84 (-41.7%)	1.03 (-47.7%)
	(-50.3%)	(-42.5%)	(-47.4%)
Day 24	0.43 (-75.6%)	0.33 (-77.0%)	0.44 (-77.7%)
	(-76.2%)	(-77.4%)	(-77.5%)

*For each number given, the first percentage in parenthesis represents the increase or decrease from the crude oil value. The second parenthesis represents the decrease from the value in the Day 0 mixture. For example, the Day 24 n-C17/pristane ratio of 0.43 is a 75.6% decrease from the crude oil value of 1.76, and a 76.2% decrease from the Day 0 value of 1.81.

CG 20/21 f1

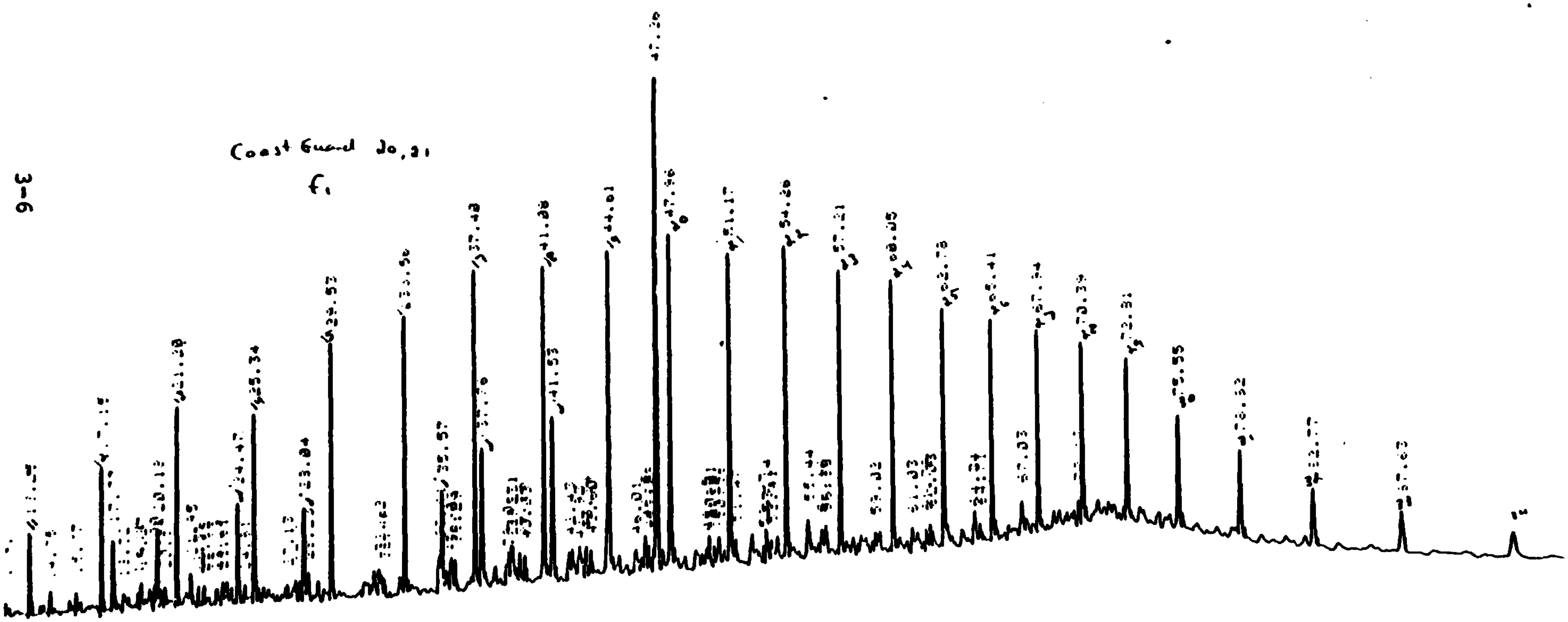

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Figure 3-1. GC of aliphatic hydrocarbons of no 6 oil prior to composting.

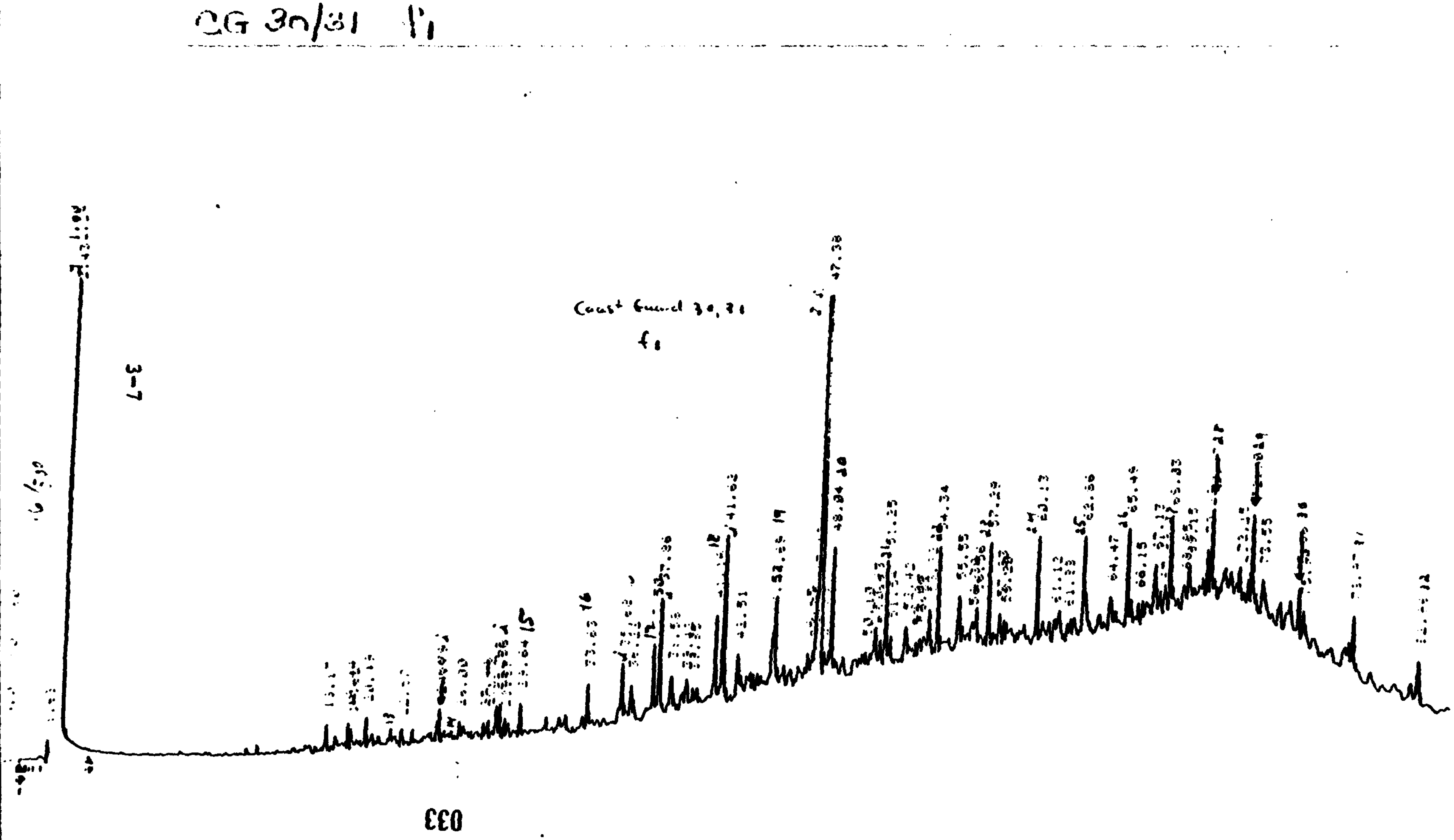

Figure 3-2. GC of aliphatic hydrocarbons of no. 6 oil after 24 days of composting.

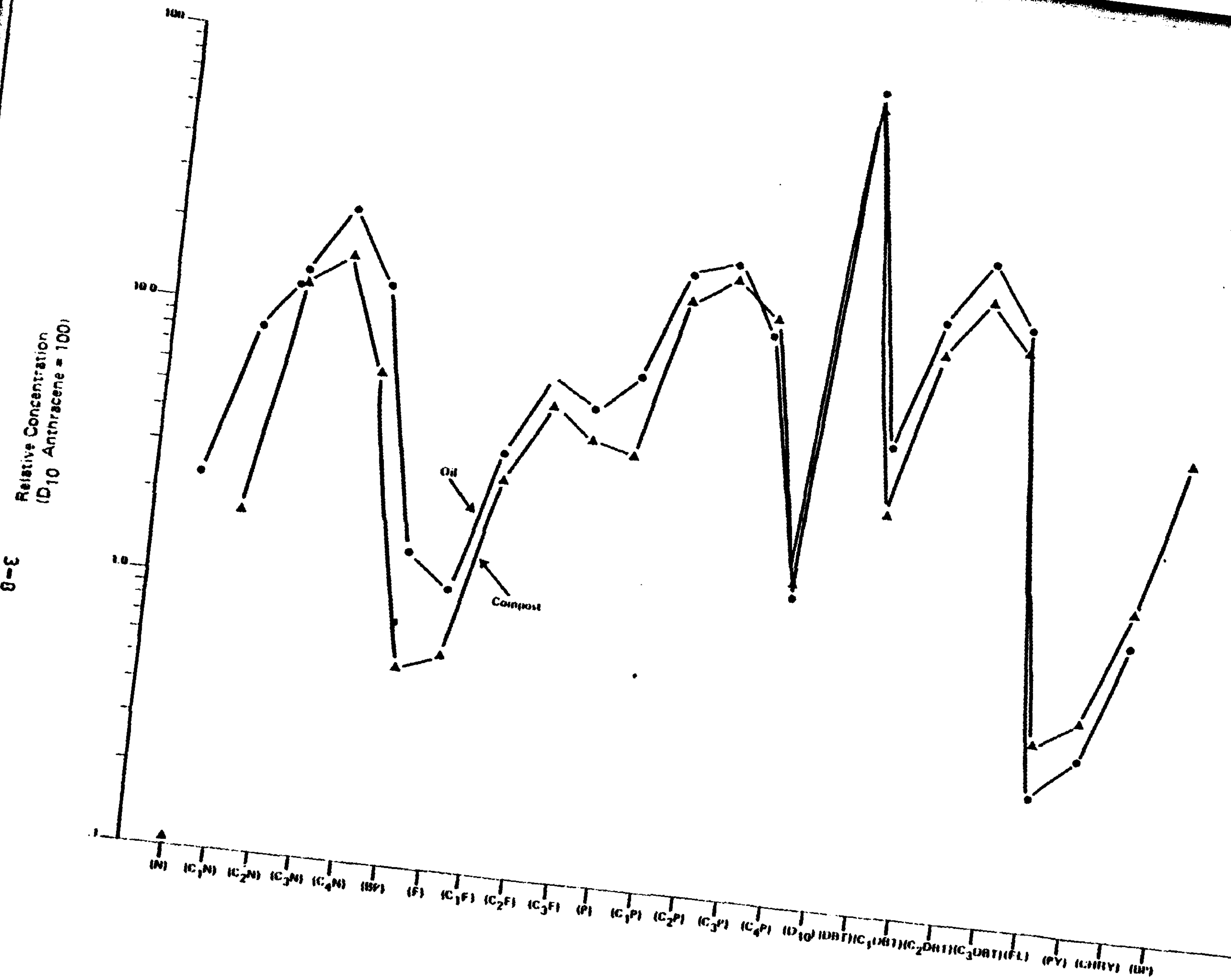

Figure 3-3. Relative Aromatic Hydrocarbon Composition of Oil and Composted Oil, Trial 5.

3.2 Microbiological Analyses

Samples were taken from the bins during Trials 4 and 5 and processed to quantify the population of petroleumlytic bacteria in the mixture at the various sampling times. Samples were taken at the times indicated in Tables 2-10 and 2-12. Methods of analysis and the results obtained are discussed in this section.

3.2.1 Methods - Petroleumlytic Bacteria MPN

The procedure used for the enumeration of petroleumlytic bacteria in the samples was a modification of that described by Breuil et al. (in press). Five gram samples of the oil/straw mixtures were shredded, and weighed accurately. They were then transferred to 100 ml dilution water (Makula and Finnerty, 1969), homogenized for 1 minute using a Waring blender, and permitted to settle for 5 minutes. One ml portions were drawn and diluted in a five tube, five dilution series (Standard Methods 14th edition). The dilution tubes contained the Makula and Finnerty salts solution. After dilutions were completed, 0.1 ml of the appropriate oil, filter sterilized, was added to each tube. Tubes were incubated for four weeks in the dark at room temperature. Tubes showing indication of oil emulsification and bacterial growth were streaked onto hydrocarbon agar and incubated for one week in the dark at room temperature. Plates with abundant bacterial growth along streak lines were scored as positive. MPN (most probable number) indices were then computed and corrected for dilution from the original sample.

3.2.2 Results

The results obtained in the microbiological analyses are presented in Table 3-3 below:

TABLE 3-3

PETROLEUMLYTIC BACTERIA IN COMPOST SAMPLES
(MPN/g wet wt)

SAMPLE TIME	TRIAL 4 (MPN/g)	TRIAL 5 (MPN/g)
Start	5.1×10^3	$>4.8 \times 10^4$
Middle		$>4.8 \times 10^4$
End	3.1×10^2	$>4.8 \times 10^4$

It can readily be seen that the concentrations of petroleum degrading bacteria in the Trial 5 samples far exceed those in the Trial 4 samples. This may be due to the difference in the two oils, indicating that No. 6 oil (Trial 5) is more readily biodegraded than crude oil, and possibly also that there are more organisms capable of degrading No. 6 oil than crude oil degraders.

The initial titer of hydrocarbon (petroleum) degrading bacteria was much higher than expected in Trial 5. Accordingly, population dynamics were not resolved. The petroleumlytic population exceeded 4.8×10^4 cells/g (wet wt) in the material throughout this composting effort. This population undoubtedly played a significant role in effecting the mineralization of petroleum constituents during the composting, as shown by the results of the hydrocarbon analyses discussed above. The population should be examined more intensively.

Petroleum degraders should be isolated, and characterized, and interorganism relationships should be examined in order to optimize the degradation process.

SECTION FOUR

DISCUSSION OF RESULTS AND IMPLICATIONS OF RESEARCH

The objective of this study, as stated in the proposal, was to determine if oily wastes could be rapidly degraded by composting. It was decided that the most economical and effective manner to determine if decomposition would occur was by utilizing a bin composter to simulate field conditions. The bin composter tests were designed to utilize enough oily waste material to initiate a thermophilic composting process and allow it to continue for a finite period of time and then conclude the test. There was no attempt made to maintain thermophilic temperatures for a long period of time and carry the decomposition to its conclusion.

The results of the hydrocarbon analyses indicate that there was some degradation of the oils in the compost mixtures attributable to composting. The microbiological results confirm this assessment of enhanced petroleum breakdown by showing substantial populations of hydrocarbon degrading organisms in the material. The results obtained in both of these areas, however, are only preliminary. This study was designed to determine whether there was a potential application of composting in the treatment of oil spill cleanup wastes, and not to provide extensive data on the physical, chemical and microbiological parameters of the process. The study succeeded in demonstrating that composting can produce some enhancement of petroleum degradation. It is now recommended that further studies be undertaken to more clearly characterize the composting process as applied to oily materials, and to determine whether the "total" rapid degradation of the oils can be achieved by composting. The recommended studies are discussed in Section Five.

SECTION FIVE

FUTURE RESEARCH

The results of these studies clearly indicate that composting does, in fact, accelerate the biodegradation of crude and No. 6 oils, and thereby suggest that there may be some potential for the use of composting in the disposal of oily wastes. Due to the limited scope of the studies, however, such aspects of the problem as optimum mixtures, maximum degradation rates achievable, and characterization of the petroleum degrading population of micro-organisms were not fully investigated. In order to maximize the potential for successful composting of oily wastes, these aspects should be further studied.

We recommend the adoption of a two pronged program of research into the areas of continued interest. First, each oil spill and cleanup presents an opportunity for research. The oily wastes collected can be test composted on a large scale according to the Beltsville method as discussed in Section I. In each spill instance, this would not only provide the opportunity for research on a large scale, but could also simultaneously provide an option for the disposal of the wastes. ERCO is currently discussing the possibility of such a program with officials in New Hampshire regarding a recent spill in that state.

Second, a systematic program of experimental scientific research should be conducted to determine the parameters governing the rate and effectiveness of the biodegradation of oils by composting. Mixtures of different concentrations of oil and straw or other bulking agent would be prepared, and composted on a full scale, with monitoring of temperatures, oxygen, microbial populations, and petroleum degradation. A set of experiments should be performed, obtaining operational data for a variety of mixes of oil and bulking agents so that the mixture providing the optimum results in terms of speed and completeness of degradation could be identified. The rate of biodegradation should be measured as a function of oil concentration, time, and temperature.

It is important that the experiments be oriented toward the actual waste materials generated during oil spill cleanup operations. For this reason, a study should be made of the characteristics of these wastes. This information should be obtained both from personnel involved in cleanup operations and from performing chemical analyses on samples of wastes from different spills.

The research programs outlined above would be of great value in providing additional data needed for a complete understanding of the degradation of oil by composting. On the basis of the results obtained in laboratory studies, we recommend that full scale field tests now be conducted.

Once the scientific and engineering parameters governing the process of composting oily wastes have been characterized, it will be necessary to develop plans for implementation of composting on a full scale, and to evaluate the costs of composting. On the basis of data obtained thus far, it is not yet clear whether or not the addition of a bulking agent or other supplement will be necessary. This will have an impact on the design and cost of the composting system used. If the material can be composted by itself, then it need only be piled over an aeration system of perforated pipe and aerated according to the method discussed in Section I. If some additional material must be added, it could be mixed in using one of several approaches, ranging from using the front end loader to using a tractor drawn rototiller.

These issues, as well as others pertaining to actual operation and cost of a full scale oily waste composting facility, cannot be answered at the present time. The studies outlined above will provide the information necessary for the clarification of these aspects.

SECTION SIX

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APPENDIX

GLOSSARY OF TERMS

Aliphatic hydrocarbons: saturated organic compounds containing only carbon and hydrogen - a fraction of oils

Alkanes: saturated hydrocarbon compounds with carbon atoms in a straight chain.

Aromatic hydrocarbons: organic compounds containing carbon and hydrogen in at least one aromatic ring.

Beltsville method: a method of composting developed by the USDA in Beltsville, Maryland. This method, using static piles and forced aeration, is discussed in Section 1.2.

Bin composter: a mechanical device, developed by ERCO, that simulates full scale forced aeration composting on a laboratory scale. See Section 2.1.

Biodegradation: the breakdown and decomposition of materials by biological processes, in particular by digestion by organisms.

Bulking agent: a supplemental material that is mixed with the waste to be composted. The bulking agent provides the necessary texture, structure, and porosity for aeration. See Section 1.3.4.

Carbon/nitrogen (C/N) ratio: the ratio of available carbon to available nitrogen in a given material. The optimum C/N ratio for composting is between 26 and 31. See Section 1.3.1.

Composting: the biological decomposition of organic materials into a semi-stable end product. In generally, composting refers to aerobic (oxygen using) processes.

Coning and quartering: a statistically valid procedure for randomly subsampling a sample of dry material to yield subsamples representative of the original substance sampled.

Forced aeration: a method of composting whereby oxygenation of the composting material is achieved by blowing or drawing air through the pore space of the material.

Isoprenoids: a series of branched alkane hydrocarbons with methyl groups branching every 5 carbon atoms.

Mesophilic: refers to micro-organisms that preferentially live in the temperature range from ambient to about 40°C.

Microbial analyses: Laboratory analyses to characterize the populations of microbes (bacteria, fungi, actinomycetes, etc) in a particular substance (in this case compost). The analyses in this study served to quantify the petroleumlytic bacteria in the composting mixtures.

MPN (Most probable number): the "most probable number" of bacteria cells per gram of material analyzed. The MPN is based on a statistical laboratory approach to quantifying bacteria. The method uses a series of replicates at several different dilutions to generate an estimate of cells/gram.

Petroleumlytic: capable of digesting petroleum and petroleum compounds. In this instance, the term applies to those micro-organisms that can utilize petroleum hydrocarbons as a food source.

Thermophilic: refers to micro-organisms that preferentially live in the temperature range from about 45 to 64°C.

Volatile solids: the proportion of a material that is volatilized at a temperature of 400°C.

Windrow: a long, low pile. This term is often used to describe the method of composting where long, low piles of the waste are built, and turned periodically for aeration.