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DETERMINATION OF VOLATILE HYDROCARBON EMISSIONS FROM LAND TREATMENT OF PETROLEUM OILY SLUDGES

The University of Oklahoma PH.D. 1984

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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

DETERMINATION OF VOLATILE HYDROCARBON EMISSIONS FROM LAND TREATMENT OF PETROLEUM OILY SLUDGES

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

By

AZAR HABIBAFSHAR

Norman, Oklahoma

1984

DETERMINATION OF VOLATILE HYDROCARBON

EMISSIONS FROM LAND TREATMENT OF

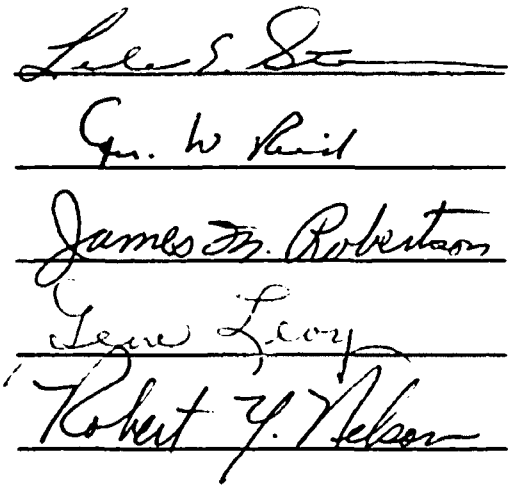
PETROLEUM OILY SLUDGES

A DISSERTATION

APPROVED FOR THE DEPARTMENT OF CIVIL ENGINEERING

AND ENVIRONMENTAL SCIENCE

By



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ABSTRACT

This study was designed to assess the atmospheric emissions from land treatment of petroleum oily sludges. Sampling, analytical techniques and instrumentation developed during the first year of the project were perfected and evaluated for monitoring, collection and analysis of volatile hydrocarbons being emitted to the atmosphere. The areas of investigations included 1) determining the rate of emission and concentration of total volatiles; 2) the quantification and identification of some pollutants being emitted to the atmosphere, 3) developing a statistical model to evaluate the effects of sludge loading rate, soil temperature, soil moisture content and relative humidity on the rate of emission.

Experimental soil-disposal tests were conducted in the laboratory in a controlled environment and on the field plots. Approximately 4792 kg sludge was spread on the six experimental plots in the field over a six-month test period during which 4.7% of this sludge was lost to the atmosphere by volatilization. This was equivalent to 6.5 percent of the total oil applied. Fourteen different hydrocarbons were identified and quantified by gas

chromatographic analysis.

Regression analysis was made on the data and statistically valid relationships were found between the rate of emission and the loading rate, soil temperature, soil moisture content, relative humidity and time since application of sludge.

TABLE OF CONTENTS

Table of Contents continued

LIST OF TABLES

List of Tables continued

List of Tables continued

LIST OF FIGURES

List of Figures continued

List of Figures continued

List of Figures continued

DETERMINATION OF VOLATILE HYDROCARBON EMISSIONS FROM LAND TREATMENT OF PETROLEUM OILY SLUDGES

CHAPTER I

INTRODUCTION

This study was designed to assess the atmospheric emissions from land treatment of petroleum oily sludges. Since petroleum refineries are targeted as one of the top ten industrial waste generators, a large percentage of refineries are converting to economical land treatment systems with little or no previous experience concerning resulting adverse environmental impacts. In 1973 9% of the refinery sludges was disposed of by land treatment; an increase to 34% was projected for 1983.[1]

When oil is applied to soil, losses occur through volatilization, downward migration and biodegradation. A high percentage of the volatilization takes place during and immediately after application and tilling; after a few days it approaches a baseline level and decreases at a very slow rate for several months. Losses through volatilization and migration are undesirable, while

losses through biodegradation, the primary mode of organic decomposition, are desirable. It is preferable, therefore, to maximize the decomposition process and minimize the rate of volatilization and migration to avoid adverse environmental impacts. It is also important to determine if any designated pollutants are released into the environment, and if so, in what concentration.

An extensive review of literature has been conducted. In general, information exists concerning biodegradation and downward migration of oily sludges in soil. Despite recent and intense interest in the release of organic chemicals to the atmosphere, the literature available on the measurement of volatile emissions from land treatment operations is very limited.

The objectives of this study were 1) to determine the rate and magnitude of fugitive hydrocarbon emissions from land treatment of refinery sludges, 2) to identify the relative effects of such parameters as sludge loading rate, temperature, soil moisture content and relative humidity on the magnitude of hydrocarbon emissions, 3) to identify and quantify individual compounds being emitted to the atmosphere, and 4) to develop a statistical model to project the total volatile emission rate based on the above mentioned variables.

Research techniques were developed to achieve the

objectives of this study. Laboratory and field measurements were taken. A hydrocarbon analyzer (TLV Sniffer) was used to monitor total volatile concentration. In addition, to identify and quantify each individual compound, air samples were collected on adsorbent tubes packed with Tenax-GC and silica gel. The samples were subjected to gas chromatography/mass spectrometry (GC/MS) and gas chromatographic (GC) analysis using a flame ionization detector (FID). A multiple regression model was used to analyze the collected data.

This study was part of a land treatment project funded as a cooperative agreement between the University of Oklahoma and the Robert S. Kerr Research Laboratory at Ada, Oklahoma. The project established the identity and concentration of volatile compounds and examined the effects of a number of parameters on the mass and rate of fugitive compound emissions from land treatment of refinery oily sludges.

Background Information

This study was a part of land treatment research project which was directed at optimizing the land treatment for petroleum refinery sludge, establishing appropriate monitoring techniques and determining the environmental impact of adding waste constituents to soil. The scope of this land treatment research project is

summarized as follows:[1]

A 10 acre land treatment site for the project was established at the University of Oklahoma on the north side of Norman. Extensive testing of the surface soils indicated that the zone of incorporation was very uniform across the site and suitable for statistical evaluation.

A total of 32 test plots and 8 control plots were established on the selected research site to carry out necessary studies for the project. The dimensions of each plot were 9 ft. by 20 ft. (2.7 m by 6.1 m). Buffer zones between each plot prevented interference between plots loaded at different rates.

The residue used in this study was typical API separator sludge. The sludge was transported from the refinery and stored in two tanks. An onsite storage capacity of 12,000 gallons (55,000 L) was provided for the refinery sludge. A three horsepower, slow speed (70 rpm), turbine mixer was used to blend the waste and destratify the water and oil layers which developed after the waste had been stored in the tanks. The sludge was applied in such a way to produce a uniform application to the soil surface.

Oil is the major organic constituent of the sludge which undergoes volatilization and biological decomposition. Therefore, the waste residues applied to the research site were analyzed for oil content. The oil con-

tent of the waste varied from a minimum of 19% to a maximum of 80% on a weight basis.

Four different loading rates and four different frequencies were examined to accomplish the proposed objectives of the project. Table 1 shows the loading rates and application frequencies. Figure 1 shows the randomized allocation of plot treatments.

Table 1 Application Frequencies and Loading Rates

Level	Application Frequency No. Application/year	Selected Loading Rate (% oil in soil--dry wt. basis)
1	1	3
2	2	6
3	6	10
4	12	13

The loading rate parameter is defined as mg of oil per kg of soil spread per acre per year to the zone of incorporation (plow zone) of each plot in the land treatment site. The plow zone is the vertical extent of distribution of the oil into the soil as a result of application and subsequent mixing. In this study the depth of the plow zone was 12 inches.

The application frequency is defined as the number of applications of sludge made to achieve the desired

1 LR=13% FR=6	6 LR=13% FR=6	11 LR=6% FR=6	16 LR=6% FR=1	21 LR=13% FR=1	26 LR=13% FR=12	31 LR=3% FR=1	36 LR=13% FR=2
2 LR=13% FR=12	7 LR=6% FR=6	12 C	17 LR=3% FR=1	22 LR=10% FR=1	27 C	32 LR=6% FR=12	37 C
3 C	8 LR=13% FR=1	13 LR=10% FR=12	18 LR=3% FR=12	23 LR=13% FR=2	28 LR=10% FR=2	33 C	38 LR=3% FR=2
4 LR=3% FR=6	9 LR=6% FR=12	14 LR=3% FR=6	19 C	24 LR=3% FR=2	29 LR=10% FR=2	34 LR=10% FR=12	39 C
5 LR=10% FR=6	10 LR=6% FR=2	15 LR=6% FR=2	20 LR=10% FR=6	25 LR=3% FR=12	30 LR=6% FR=1	35 LR=10% FR=1	40 C

LEGEND: Plot Numbers are located in the upper left hand corner of plot squares
FR = Loading Frequency
LR = Equivalent Annual Loading Rate for Plot as %
C = Control Plot

Figure 1 Randomized allocation of plot treatment

annual loading rate.

Prior to sludge application each plot was tilled. The sludge was transferred from storage tanks to a two-hundred gallon fiberglass tank equipped with positive displacement pumps. The pumping system had a maximum capacity of 10 gpm. This pumping system was connected to a spray manifold by a flexible high pressure hose. The manifold system consisted of six spray nozzles, piping and a control valve. Before sludge application, the manifold flow rate was calibrated. Sludge application was accomplished by making a sufficient number of timed passes over the plot until the desired volume of sludge was applied. After application was completed, the plots were tilled to mix the oily sludge into the zone of incorporation (12 inches) and to provide oxygen for microorganisms. Tilling was accomplished by a sixty-inch (152 cm) rototiller connected to a twenty-two horse-power tractor. The application frequency was primarily determined by antecedent soil and climatic conditions.

The continental climate of the county is characterized by hot summers and relatively short mild winters. However, several severe cold spells occur each winter accompanied by strong northerly winds. Minimum temperatures of 10 to 15 degrees Fahrenheit and maximum temperature of 105 degrees are common.

The mean annual precipitation is 33.31 inches, but

it has ranged from 19.19 to 56.64 inches. The wettest months are May, June, April, and October; and the driest are February, January, and December. Table 2 presents average temperature and precipitation data.

Table 2 Climatogical Data of Norman[1]

Month	Mean Temperature °F	Mean Precipitation (in.)
December	40.7	1.61
January	38.0	1.40
February	41.5	1.18
March	51.7	2.49
April	60.8	3.47
May	68.9	5.20
June	77.6	3.90
July	81.5	2.53
August	82.0	2.74
September	74.7	3.21
October	62.7	3.34
November	50.7	2.24
Year	60.9	33.31

Literature Review

Many papers dealing primarily with the land treatment of petroleum sludges were reviewed. There is a paucity of data on the volatile organic emissions from land treatment operations. Most papers discussed the following topics:

1. Construction and operation of a land treatment facility.
2. Microbial degradation of hydrocarbons during

land treatment of refinery sludges.

3. The effect of oily waste on water quality and soil characteristics.
4. The effect of land treatment of petroleum sludges on vegetation.
5. Land treatment technology, environmental effects and economics.

Three sources, however, contained information about volatile organic emissions from land treatment facilities.

Minear et al.[2] conducted a study to assess the atmospheric emissions from the land treatment of refinery sludges. This study was jointly funded by the American Petroleum Institute and the U.S. Environmental Protection Agency (EPA). These researchers developed a small laboratory unit to simulate land treatment operations. The effects of certain variables on emission rates such as sludge type, sludge volatility, soil moisture content, wind speed, relative humidity, air temperature, soil temperature, sludge loading rate and the method of sludge application were studied. The authors found that sludge volatility, sludge loading rate, application method and soil moisture content were important parameters affecting emission rates.

API separator and tank bottom sludges were used in this study. Sludge and soil samples were subjected to physical and chemical tests. These tests are shown in

Tables 3 and 4.

Table 3 Physical Tests Run on the Oily Sludges

1. Total solids
2. Total volatile solids
3. Total suspended solids
4. Total volatile suspended solids
5. Weight loss on heating
6. Centrifugation

Table 4 Chemical Tests Run on the Sludge and Soil Samples

Tests	Methods
1. Oil and grease content of sludges	Extraction with freon and infra-red adsorption
2. Volatile organics on soils and sludges	Gas chromatography Mass spectrometry (GC/MS)
3. Volatile organics on soil	High temperature (GC/MS)

Table 5 presents the physical characteristics of land treatment sludges. The results of centrifugation of sludge samples are also given in Table 6. Chemical composition of sludge and soil samples are presented in Table 7.

The authors used a stripping test to obtain a quantitative measure of relative volatility of three different sludge samples. It was reported that there was a marked difference in the volatility of sludge samples.

Table 5 Physical Characteristics of Land Treatment Sludges[2]

Sludge sample**	Oil* and grease by IR (mg/l)	Oil* and grease by gravimetric (mg/l)	Total solids (mg/l)	Total volatile solids mg/l	(%)	Total suspended solids (mg/l)	Total volatile suspended solids mg/l	(%)
T-A		159,600	82,200	66,700	81			
T-B						93,400	32,400	35
T-C	80,500	110,000				790,000	94,000	12
T-D	38,400	66,000				410,000	100,000	25
SJ-A		82,500	74,400	54,200	73			
SJ-B						12,500	4,300	35
SJ-C	142,000	150,000				21,000	16,000	76
SJ-D	177,000	340,000				11,000	6,000	55
SI-A		726,800	196,200	153,600	78			
SI-B						1,100	1,070	97
SI-C	598,000	800,000				2,900	2,700	93
SI-D	619,000	820,000				2,000	1,900	94
Average Values								
T Avg	59,500	111,900	82,200	66,700	81	431,000	75,500	18
SJ Avg	159,500	191,000	74,400	54,200	73	14,800	8,800	59
SI Avg	608,500	782,000	196,200	153,600	78	2,000	1,890	95

*Reference oil contained 37.5% isooctane, 37.5% hexadecane, and 25.0% benzene.

**SI = Tank bottoms
SJ = API separator sludge
T = API separator sludge

Table 6 Results of Centrifugation of Sludge Samples[2]

Sample*	Centrifugation time (min)	Solids (Vol %)	Water (Vol %)	Oil (Vol %)
T-A	15	40	50	10
T-B	15	40	50	10
S3-A	15	15	79	6
S3-B	15	15	79	6
S1-A	15	6	0	94
S1-B	15	6	0	94

*S1 = Tank bottoms
S3 = API separator sludge
T = API separator sludge

Table 7 Chemical Composition of Sludge and Soil Samples[2]

RT(min)	Compound (M/E)	Concentration, PPM* API separator sludge S3	Tank bottoms S1	API separator sludge T	S Soil	T Soil
9.2	Benzene (78)	1,400	1,800	N.D.	0.0085	0.55
15.2	Toluene (92)	5,600	9,300	0.02	0.0075	0.50
18.1	Ethylbenzene (106)	4,300	5,200	0.46	0.0065	1.8
20.5	M,P-Xylene (106)	15,000	23,000	1.2	0.012	5.5
21.2	O,Xylene (106)	32,000	42,000	0.55	0.016	5.0
23.2	Saturated Hydrocarbon (85)	24,000	4,000	5.0	N.D.	6.5
26.2	Indane (118)	28,000	34,000	9.2	N.D.	1.6
25.4	C_3-Benzene (120)	160,000	220,000	7.9	N.D.	12.0
24.0	Dimethylpentene (98)	1,900	2,200	5.0	N.D.	5.0
24.8	Saturated Hydrocarbon (57)	5,200	6,200	6.6	N.D.	13.0
	TOTAL	277,400	347,700	35.9		

*Compounds with retention times up to 21 minutes were quantitated based on actual response factors and compounds with retention times above 21 minutes were quantitated with a response factor of 1.

Sludge S_1 was the most volatile and sludge T the least. Table 8 presents the stripping test results.

A land treatment simulation apparatus was designed in the Minear et al.[2] study. This design consisted of a detachable soil box with a soil surface area of one square foot and the mixing chamber containing probes, the plenum and the blower system. The air velocity across the soil was regulated by the holes in the plenum. Monitoring equipment for this study was Kurtz (hot wire) air velocity meter, a soil test MC 300B analyzer to measure soil moisture and temperature, and a TLV Sniffer to monitor hydrocarbon concentration in the air leaving the soil chamber. Air temperature and relative humidity were monitored in the exit duct. A space heater was used to heat incoming air, while a buried heater (one inch below the soil surface) was used to vary the soil temperature.

The waste was spread by a spreader bar in less than a minute. The spreader bar consisted of a one gallon jug attached to a piece of teflon tubing leading to a 12 inch piece of 1/2 inch plexiglass tube. A number of 1/8 inch holes along one surface of the plexiglass tube allowed spreading of the sludge. A small, four-tined garden hoe was used to till the soil.

A parametric matrix of experimental conditions shown in Table 9 was considered in this study. This matrix was based primarily on a linear design. Each parameter was

Table 8 Stripping Test Results[2]

Stripping time, minutes	Hydrocarbon concentration, ppmw/µl		
	Sludge T*	Sludge S3*	Sludge S1*
0	91	1900	6100
4	15	140	310
8	8.2	72	150
12	5.2	39	170
16	3.7	27	150
20	3.0	21	140
24	2.4	16	-
28	1.9	13	120
32	1.6	10	110
36	1.4	8.9	100
40	1.2	7.6	100
44	1.0	6.5	96
48	.91	5.8	92
52	.80	5.0	87
56	.69	4.7	84
60	.63	4.5	80
64	.62	4.0	74
68	.56	3.6	76
72	.54	2.8	71
76	.44	2.6	70
Bag sample, 0-36 minutes	17	23	140
Sample size, µl	20	5	1

* S1 = Tank bottoms
S3 = API separator sludge
T = API separator sludge

Table 9 Matrix of Experimental Conditions for Land Treatment Simulation Runs[2]

Run No.	Waste Material**	Waste Loading (lb/ft²)***	Soil Type	Soil Moisture (wt%)	Soil/Air Temperature (°F/°F)	Air Velocity (mph)	Relative Humidity (%)	Spreading Mechanism	Remarks
1	Hexane	1.0	None	NA	NA/100	3	Amb*	Pour	
2	Hexane	1.0	S	10.7	120/100	3	Amb*	Surface	
3	Gasoline	1.0	None	NA	NA/100	3	Amb*	Pour	
4	Gasoline	1.0	S	10.7	120/100	3	Amb*	Surface	
5	S1	2.5	None	NA	NA/100	3	Amb*	Pour	
6	S1	2.5	S	10.7	120/100	3	Amb*	Surface	Base case
7	S1	2.5	S	10.7	120/100	3	Amb*	Surface	Repeat of base case
8	S1	2.5	S	10.7	120/100	1	Amb*	Surface	
9	S1	2.5	S	10.7	100/80	3	40	Surface	
10	S1	1.0	S	10.7	120/100	3	Amb*	Surface	
11	S1	1.0	S	10.7	120/100	3	Amb*	Surface	Repeat of Run 10
12	S1	2.5	T	4.7	120/100	3	Amb*	Surface	
13	S1	2.5	S	20.7	120/100	3	Amb*	Surface	
14	S1	2.5	S	10.7	120/100	3	75	Surface	
15	T	2.5	S	10.7	120/100	3	Amb*	Surface	
16	S1	2.5	S	10.7	120/100	3	Amb*	Surface	
17	S1	4.0	S	10.7	120/100	3	Amb*	Surface	
18	S1	0.5	S	10.7	120/100	3	Amb*	Surface	
19	S1	2.5	S	10.7	120/100	3	Amb*	Surface	Heat sludge to 140°F
20	S3	1.0	S	10.7	120/100	3	Amb*	Surface	
21	S3	2.5	S	10.7	120/100	3	Amb*	Surface	
22	S3	4.0	S	10.7	120/100	3	Amb*	Surface	
23	S3	1.0	T	4.7	120/100	3	Amb*	Surface	
24	S3	4.0	T	4.7	120/100	3	Amb*	Surface	
25	S3	2.5+	S	10.7	120/100	3	Amb*	Surface	Spike sludge with 0.5 lb of gas
26	S3	2.5+	S	10.7	120/100	3	Amb*	Surface	Spike sludge with 1.5 lb of gas
27	S3	2.5+	S	10.7	120/100	3	Amb*	Surface	Spike sludge with 1.5 lb of H_2O
28	S1	2.5	S	10.7	120/100	3	Amb*	Sub-surface	Till soil after spreading
29	S1	2.5	S	10.7	120/100	3	Amb*	Sub-surface	Use deeper injection

*Amb = ambient humidity was typically 50% at room temperature but measured <<30% at 100°F.

**Sludge S1 = Tank Bottoms
Sludge S3 = API Separator Sludge
Sludge T = API Separator Sludge

***Loading of 2.5 lb/ft² is equivalent to approximately 300 barrels/acre.

varied from base conditions (run number 6 in Table 9) to a higher or lower value.

The authors reported that the hydrocarbon concentration in the air had a very sharp rise during or shortly after sludge applications. The maximum hydrocarbon concentration remained for less than five minutes. In most of the tests, the hydrocarbon concentration decreased to a comparatively low level in about 30-36 minutes from the time of spreading. Monitoring continued until the concentration dropped to the baseline level. Figure 2 shows a concentration time plot for the hydrocarbon concentration leaving the soil chamber.

Table 10 presents the results of the air monitoring for the 29 test runs. The maximum hydrocarbon concentration and the integrated area in six minutes and thirty minutes from spreading are given for each test. The total integrated area for thirty minutes after spreading was used as an indicator of relative emission rates and quantities. The effect of variables on emissions was also measured and compared at thirty minutes after spreading.

In order to get quantitative results from the land treatment simulation experiments, Minear and his coworkers calibrated the TLV Sniffer disc integrator using a Mettler P4400 balance. They measured the weight loss of hexane and sludge due to vaporization as a function of

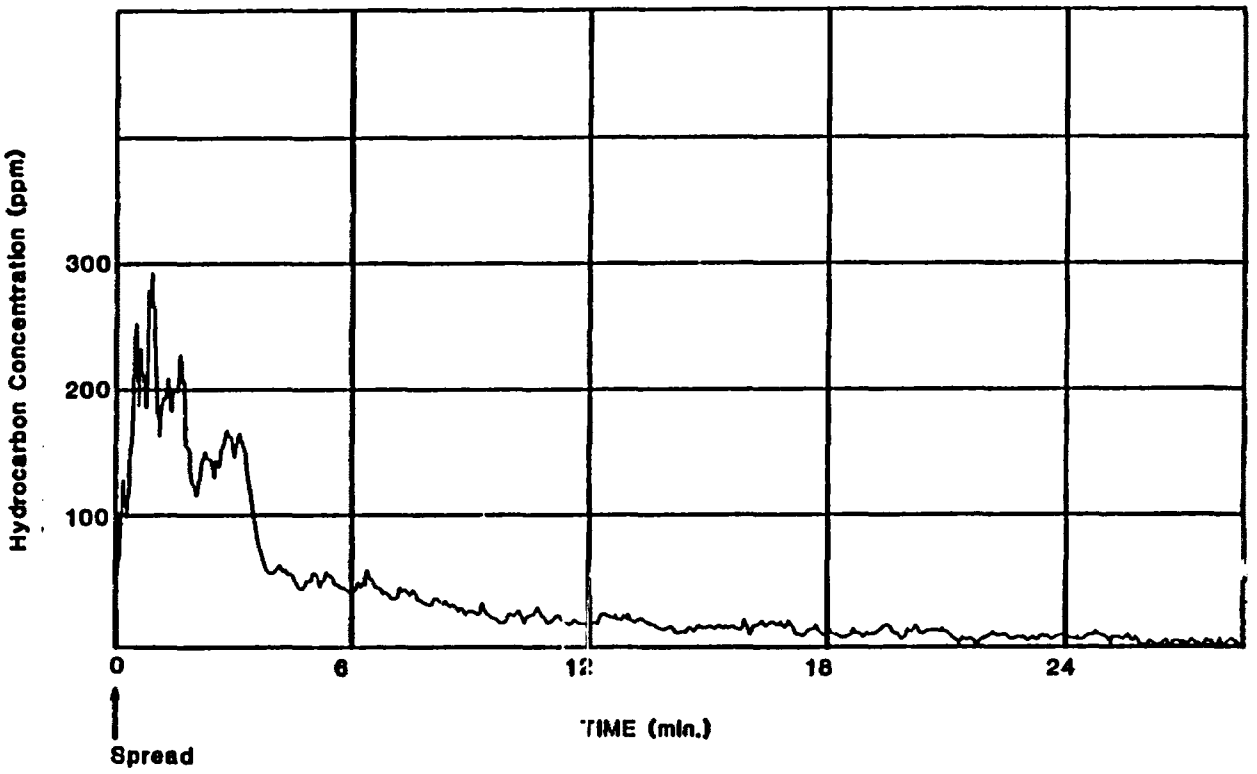


Figure 2 Typical chart trace from THC monitor[2]

Table 10 Results of Simulation Runs[2]

Run No.	Variable[1]	Maximum hydrocarbon concentration (ppm)	Integrated area in 6 Min.	Integrated area in 30 min.	Remarks
1	Pure hexane (false bottom)	>10,000	2,460	7,980	Total area at dryness was 8580
2	Pure hexane	>10,000	3,900	5,500	
3	Gasoline (false bottom)	> 5,000	690	1,810	Total area at zero hydrocarbon
4	Gasoline	>10,000	1,750	2,470	concentration was 2400
5	S1 (false bottom)	400	43	342	
6	Base case	215	21	78	
7	Base case (repeat)	200	22	62	
8	Air velocity decreased to 1 mph	310	57	231	
9	Air/soil temperature decreased	260	23	53	
10	Loading decreased	325	49	143	
11	Loading decrensed (repeat of 10)	200	31	136	
12	Soil T used	485	86	230	
13	Moisture in soil increased	> 500	85	263	
14	Moisture in air increased	> 500	68	116	
15	Waste T used	35	1	1	
16	Base Case in a deeper box	350	27	71	
17	Loading increased	425	33	81	
18	Loading decreased drastically	250	31	61	
19	Waste heated before spreading	350	45	74	
20	Waste S3 at low loading	23	4	10	
21	Waste S3 used	15	1.5	5	
22	Waste S3 at high loading	25	4	16	
23	Waste S1 low load on T soil	17	2	5	
24	Waste S3 high load on T soil	34	4	17	
25	Waste S3 with low gas spike	7,000	480	760	
26	Waste S3 with high gas spike	>10,000	760	1,360	
27	Waste S3 cut with water	25	5	8	
28	Sub-surface injection	300	17	114	
28A	Tilling of 28	375	29	68	Tilled 80 min. after spreading
29	Sub-surface deep injection	0	0	0	
29A		225	15	15	Tilled 4 days after spreading
29B		50	1	1	Tilled 6 days after spreading

[1]Variable changes from the base case conditions of Runs 6 and 7. All other variables remained as in Runs 6 and 7.

time. They also monitored the integrated area under the TLV Sniffer recorder curve as a function of time. From these results, they estimated a calibration factor to relate the integrated area to the weight loss for other experimental runs. Table 11 presents the weight loss of hydrocarbons for each of the simulation runs.

From the results it was concluded that from .45 to 3.2 percent of the total S1 (tank bottom) sludge (the most volatile sludge) applied was lost in 30 minutes. Approximately .07 to .22 percent of total weight of S3 sludge was emitted in 30 minutes. Sludge T, the least volatile sludge, emitted the least hydrocarbons.

In further tests of volatility effect, the authors reported that addition of gasoline to the sludge increased the emission rate; however, the addition of water had no effect on the emission rate.

The effects of variable loading were examined. The results are presented in Figure 3. Sludge S1 at loading rate of 1 lb/ft^2 had a higher emission rate than sludge S3. According to the authors, this may have been because of varying amounts of water in the two sludges: The first sludge contained insignificant amounts of water, while the second sludge was composed almost entirely of water.

From the results of the two subsurface injection experiments, the authors concluded that emission can be minimized by subsurface injection and a reasonable wait-

Table 11 Estimated Emissions from Sludge Applied to Soil in Land Treatment Simulation Tests[2]

Run/Sludge	Area 30	Grams volatilized*	Weight Sludge applied, g	% Total Sludge volatilized	Weight Oil applied**	% volatilized	Weight Oil applied, g#	% Oil volatilized
6/S1	78	7.9	1135	0.70	1067	.74	999	.79
7/S1	62	6.3	1135	0.56	1067	.59	999	.63
9/S1	53	5.4	1135	0.48	1067	0.51	999	0.54
10/S1	143	14.5	454	3.2	427	3.4	400	3.6
11/S1	136	13.8	454	3.0	427	3.2	400	3.5
12/S1	230	23.3	1135	2.1	1067	2.2	999	2.3
13/S1	263	26.7	1135	2.4	1067	2.5	999	2.7
14/S1	116	11.8	1135	1.0	1067	1.1	999	1.2
15/T	1	0.10	1135	0.009	114	0.88	110	0.90
16/S1	71	7.2	1135	0.63	1067	.67	999	.72
17/S1	81	8.2	1816	0.45	1707	.48	1590	.52
18/S1	61	6.2	227	2.7	213	2.9	200	3.1
19/S1	74	7.5	1135	0.66	1067	.70	999	.75
20/S3	10	1.0	454	0.22	27.2	3.7	91	1.1
21/S3	5	0.51	1135	0.045	68.1	0.75	227	0.22
22/S3	16	1.6	1816	0.088	109	1.5	363	.44
23/S3	5	.51	454	.11	27.2	1.9	91	.56
24/S3	12	1.2	1816	0.066	109	1.1	363	.33
27/S3	8	.81	1135	0.071	68.1	1.2	227	.36

* Based on Figure D response factor.
** Based on % oil data of Table 4.
# Based on gravimetric oil and grease data of Table 5.
*** S1 = Tank bottoms
S3 = API separator sludge
T = API separator sludge

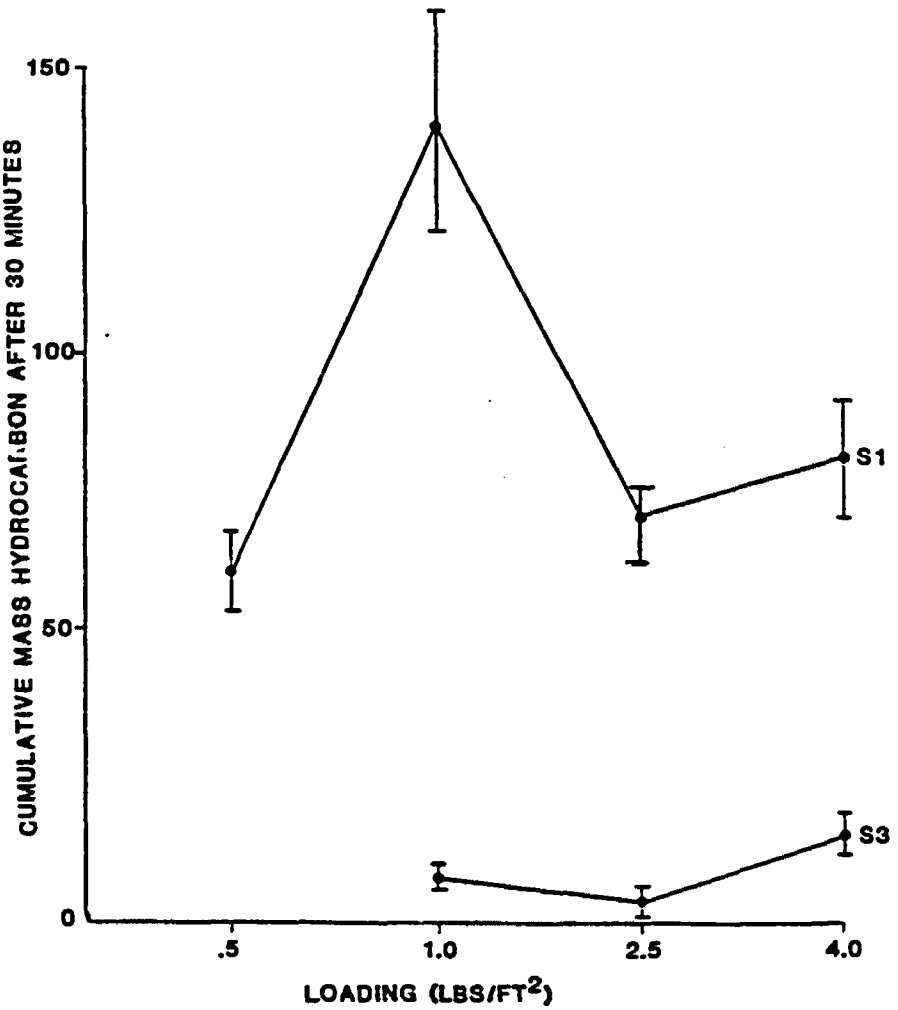


Figure 3. Effect of loading on emissions from simulated land treatment[2]

ing period before tilling. Figure 4 shows the effect of resting time before tilling on emissions after subsurface injection.

The effect of many variables on the relative magnitude of emissions from land treatment simulation is shown in Figure 5. In all runs, the researchers used sludge S1 (storage tank bottom) and a consistent loading of 2.5 lbs per square foot. The moisture content of the soil was 10.7 percent by weight in all runs except one which was 20.7 percent. There was a larger increase in the amount of volatile hydrocarbon emission with higher moisture content. It was reported that the wetter soil might have been less permeable to the liquids in the sludge.

According to the authors, heating of sludge before application had no effect on emission rate. Air velocity also had no effect on the quantity of hydrocarbon emitted.

Francke and Clark (1978)[3] conducted land farming experiments at Oak Ridge National Laboratory to evaluate a biological assimilatory process for disposal of waste oil and machine coolant. They applied oil and fertilizer to a 0.088 acre plot, tilled to a depth of 6 inches and cultivated regularly for 4 months. Average oil application rate was 1.15 gallons per cubic foot of soil. Decomposition rate of oily waste was reported 1.5 lb per cubic foot of soil per month; decomposition rate of

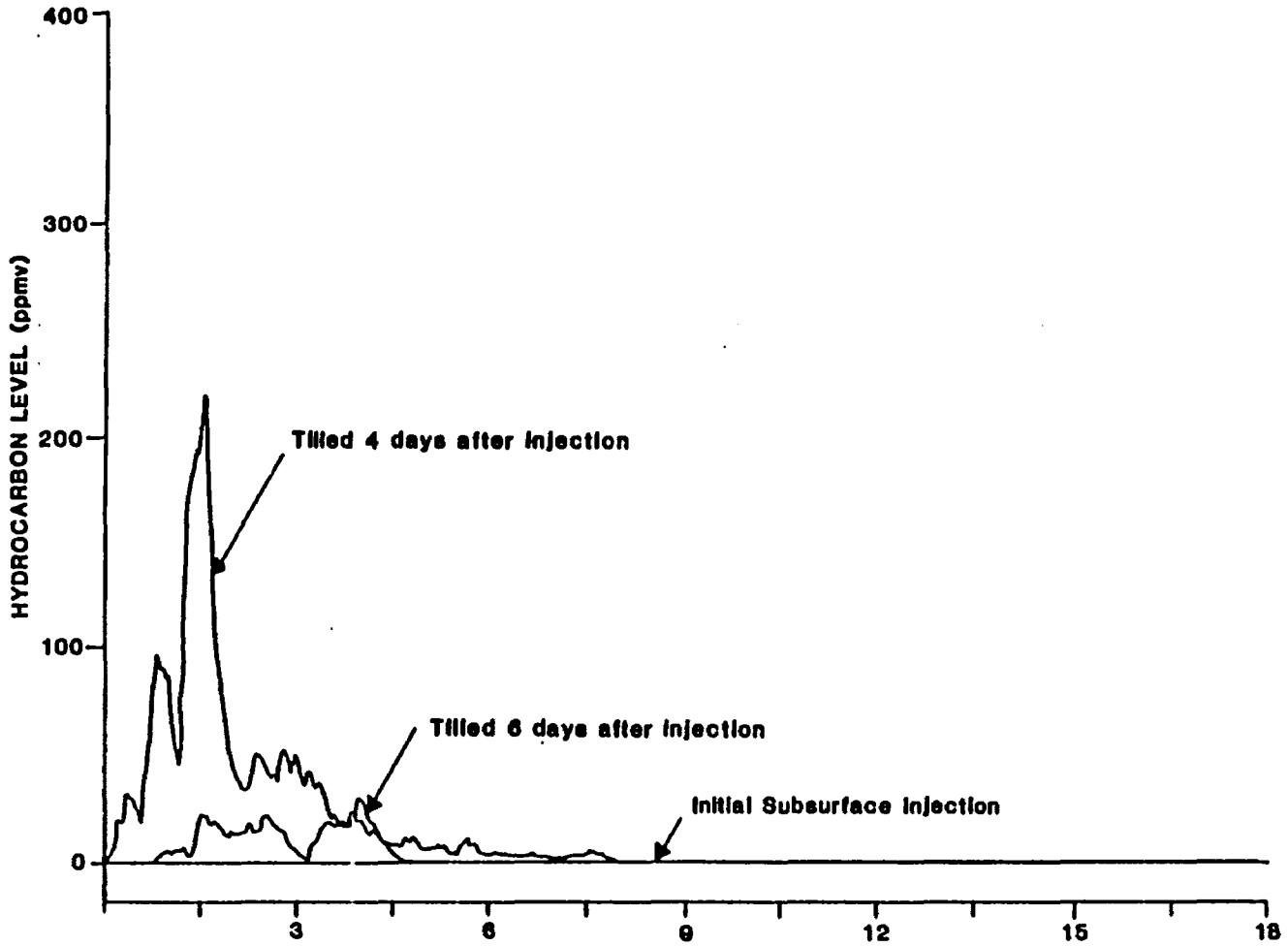


Figure 4 Effect of resting time before tilling on emissions after subsurface injection [2]

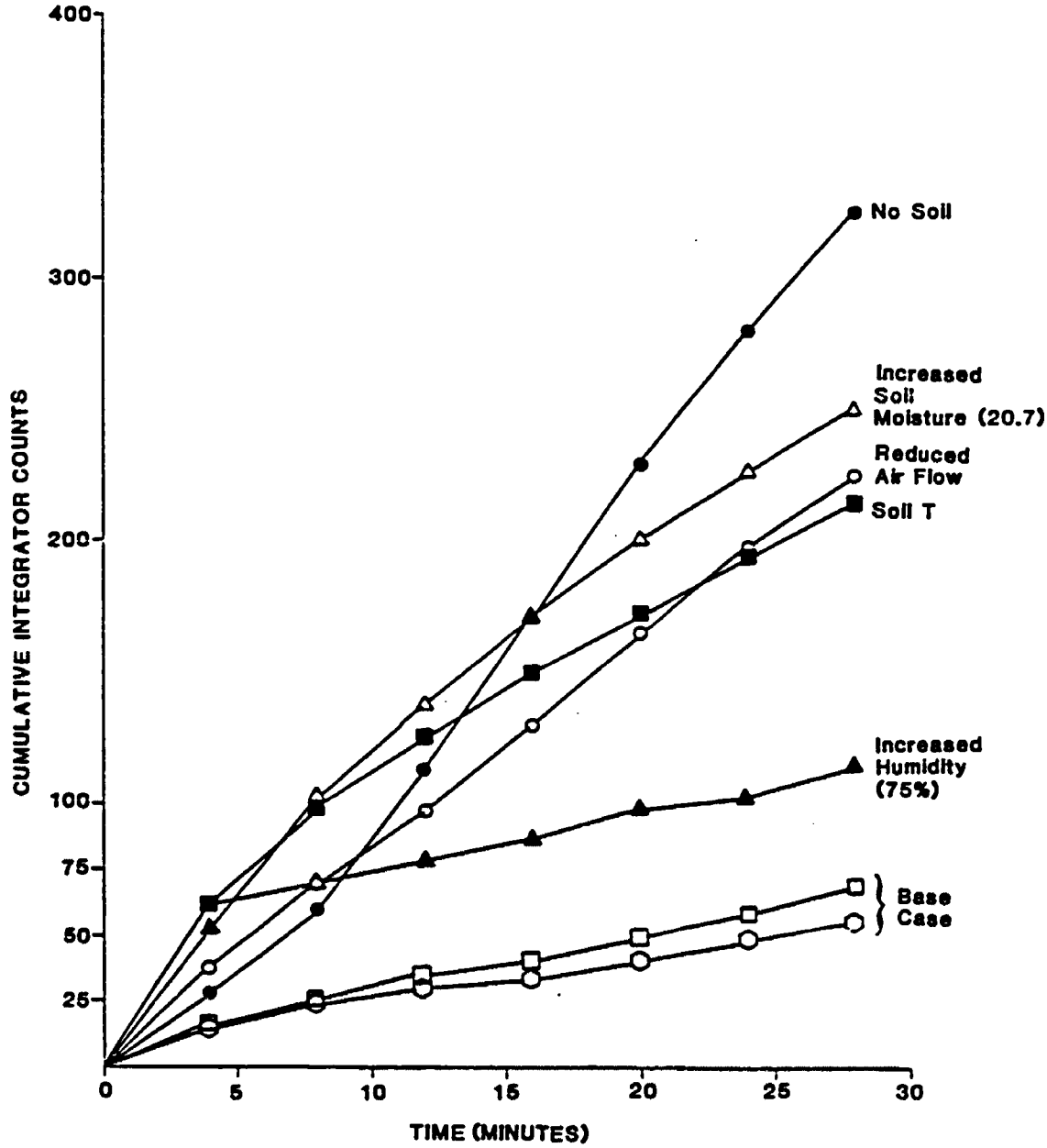


Figure 5 Effect of Soil Moisture, Humidity and Air Flow on Emissions

coolant was reported 4.45 lb/ft^3/month.

They also conducted laboratory tests to determine the hydrocarbon evaporation rate from the test plots. Total evaporative losses from actual test plots over the 53 day test period were calculated to be about 8.4 gallons, equivalent to less than .1 percent of the total oil applied.

Laboratory tests were also conducted to determine the evaporation rate from the machine coolant. Estimated losses during the 78 day test period were 29-37 gallons, less than .6 percent of the total oil applied. The author reported that the primary evaporative constituents were those identified with oils and coolants.

Volatile Organic Compound (VOC) emissions from a land treatment operation of petroleum sludge were studied by the Suntech group (undated)[4]. API separator sludge containing about 5 weight percent oil, and centrifuge sludge containing about 8 weight percent oil were land-treated.

Centrifuge sludge was spread and tilled and volatile organics were measured during a 13 day period. Volatile organic compound emissions averaged about 530 pounds of hexane equivalent per acre, or approximately 41 pounds per acre per day. Total emissions were reported to be about two weight percent of the oil applied.

Spreading of API separator sludge resulted in VOC

emissions of 1960 pounds of hexane equivalent per acre, or 76 pounds per acre per day which represented about 11 weight percent of the oil spread. Tilling after spreading increased VOC emissions to 2103 pounds per acre, or about 14 weight percent of the oil spread.

It was reported that tilling and high temperature increased the emission rates from both types of sludges. Tilling, however, was not a factor over an extended period, although it initially increased emissions.

Stearn and his co-worker[5] conducted a literature review relating to oily waste decomposition, volatilization, migration through soils and interaction with environment when oily waste was disposed on land.. Four case studies were performed to determine if the method was practical and environmentally acceptable.

Stearn et al.[5] indicated that the degree of oil loss by volatilization is related to the vapor pressure of hydrocarbons, soil porosity, tortuosity and surface absorption characteristics of the soil. Hydrocarbons with high vapor pressures, such as propane, evaporate before outward migration or biological oxidation occurs in soils. However, lower vapor pressure hydrocarbons such as heavy oils, residual fuel oils, grease, solid paraffins and high molecular weight asphaltenes migrate or biologically oxidize before evaporation. Using information from the literature, the authors estimated

that for highly volatile hydrocarbon deposited in a soil to a concentration of 0.1 g/cm^3, it would require approximately one month for all oil in the top 1.8 inch layer to evaporate. Further, for a heavier fuel oil, it was estimated that for a contamination zone depth of 9.8 inches, approximately 6% of the oil would evaporate in two years. The range of time constants relevant to biological oxidation of oil is estimated between two and twenty months. Therefore, the oil evaporation rate is insignificant as compared to the biological oxidation rate.

The authors reported that the relative amounts of evaporated versus biologically oxidized oil can be affected by the disposal methods employed. For any hydrocarbon having a vapor pressure less than 100 mm of Hg, the ratio of evaporation to biological oxidation can be minimized by maximizing the depth of plowed zone as long as the soil is not completely saturated with water. Although this procedure will decrease the biological degradation rate, it will decrease the evaporation rate even more.

Chamber techniques to measure the gas transfer across the soil-atmosphere interface have received considerable emphasis the past few years[6]. Matthias et al.[7] described a chamber technique for field measurement of emissions of nitrous oxide from soil. The researchers

placed an insulated cylindrical metal chamber (diameter 88 cm; height 17 cm) over the soil surface for 20 minutes and collected air samples in 1 liter evacuated glass bottles fitted with glass stopcock in 5 minute intervals. A rotary valve pump was used to evacuate each sample bottle to a gage pressure of <0.1 mm Hg. A windbreak was used to minimize wind-induced movement.

The air samples then were analyzed for nitrous oxide (N_2O) within 24 hours by a gas chromatographic procedure. The rate of nitrous oxide emission was calculated from the increase in the concentration of N_2O in the air within the chamber.

The effects of wind break, insulation, air pressure fluctuation and mixing air within the chamber were studied. The authors reported that the concentration of nitrous oxide in air within the chamber increased linearly with time on calm days; however, it did not increase linearly with time on windy days. The effect of insulation showed that the temperature perturbation of air within the insulated metal chamber was very small compared with the perturbation observed within the metal and plexiglass chambers. Since temperature has a very significant effect on the rate of microbial activity and the resulting nitrous oxide emission from the soil, extensive tests showed that the above described chamber would not significantly affect the soil temperature.

The authors used an electric fan to mix the air within the chamber. The repeated tests revealed that there was no significant difference between results obtained with and without using a fan.

Studies by Kimball and Lemon[8,9] have shown that air-pressure fluctuations caused by turbulent movement of air over the soil surface may affect gaseous mass flow within the soil. However, Matthias and his co-workers[7] reported that air-pressure fluctuation induced by withdrawing and reinjecting air over the soil did not significantly affect the rates of N_2O emission at various sites using the chamber technique. According to the authors, the chamber technique has the important advantages of not significantly disturbing the structure or the environment of the soil under study.

CHAPTER II

EXPERIMENTAL DESIGN AND METHODOLOGY

General Description

The first quarter of this project was devoted to developing methodology for reliably sampling and accurately analyzing volatile compounds being emitted to the atmosphere from land treatment of petroleum sludge and to procuring supplies and equipment for the planned field and laboratory studies.

Two separate studies were performed to accomplish the objectives of this research:

1. Study 1: Effects of four loading rates having a frequency of application of six/year on hydrocarbon emissions from land treatment of refinery oily sludge.
2. Study 2: Laboratory experiments to evaluate hydrocarbon emissions and to identify the influence of different sludge loading rates and temperatures on the rate of hydrocarbon emissions.

Other parameters including soil moisture content,

relative humidity and sludge volatility were also measured and their relative effects were identified.

Simulation Equipment

A simple method for the measurement of the rate of emission of volatile hydrocarbon resulting from the land treatment operation of petroleum oily sludge was designed and constructed. Flexibility, simplicity, reliability, portability and durability were features sought in the design of the monitoring and collecting system. Figures 6 and 7 depict the simulation apparatus. Figure 8 shows the physical arrangement of the apparatus in the field.

This design incorporated an insulated, rectangular, open bottom chamber fabricated from aluminum with a length of 16.25 inches, a width of 5.75 inches and a height of 11.5 inches. It was insulated with 1.5 inches of styrofoam. The bottom of the chamber circumscribed an area of 0.78 square feet. The following accessories were provided:

1. A small variable speed AC fan was installed on the top of the chamber to mix the air within the chamber.
2. Two dial thermometers were inserted through ports to record air and soil temperature inside the chamber.
3. A dew point hygrometer was used to measure va-

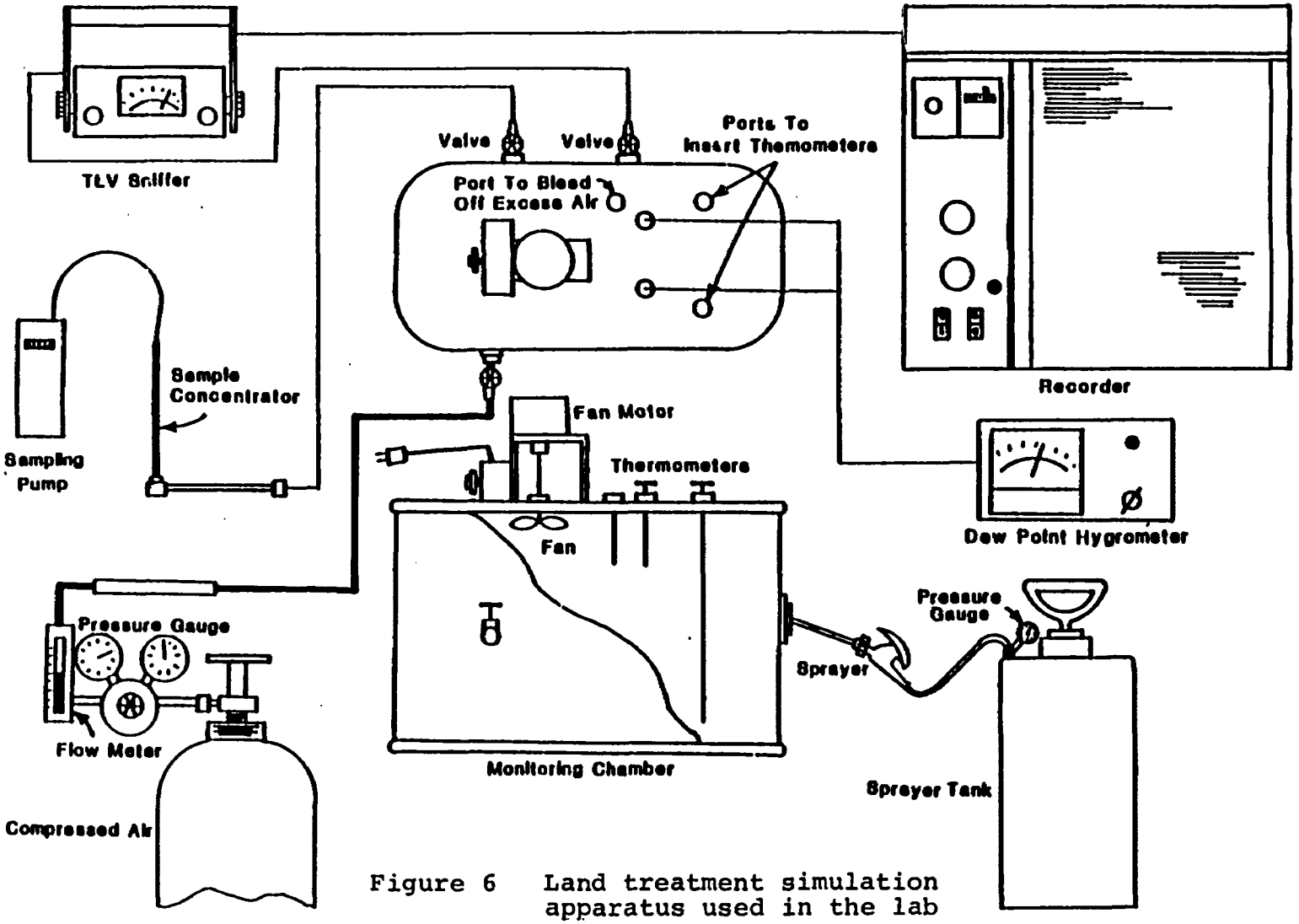


Figure 6 Land treatment simulation apparatus used in the lab

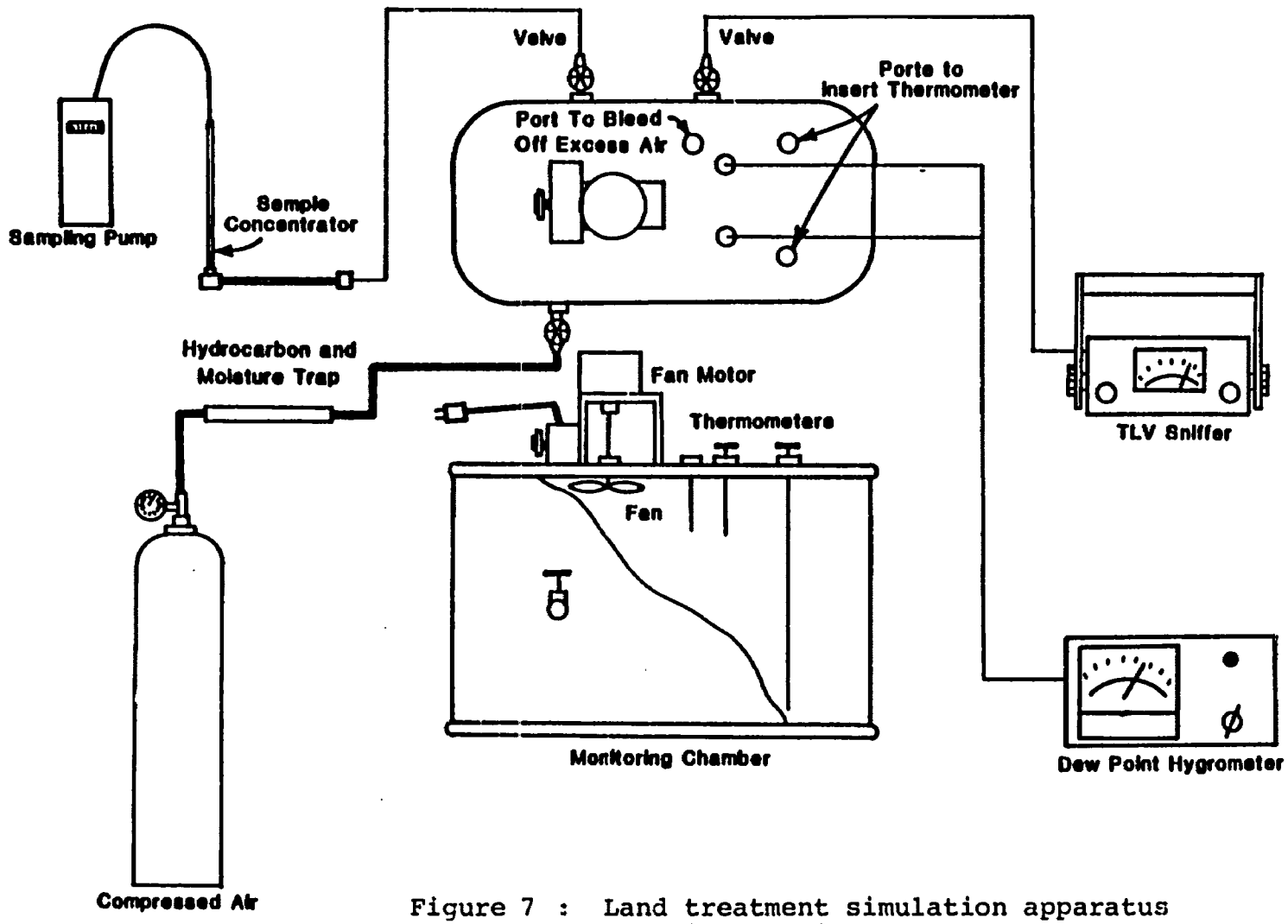


Figure 7 : Land treatment simulation apparatus used in the field

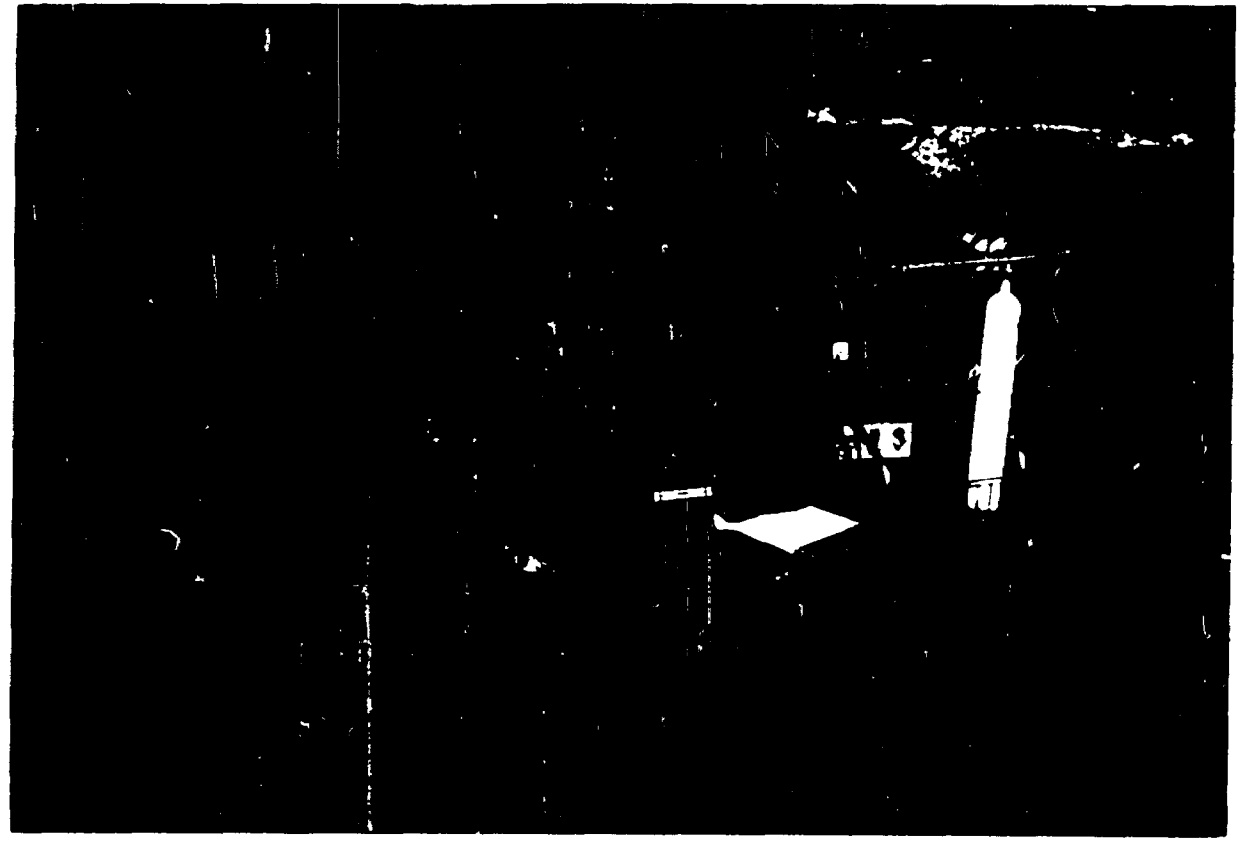


Figure 8 Monitoring apparatus used in the field.

por pressure and relative humidity inside the chamber.

4. A port through which breathing quality compressed air was provided to transport pollutants from the sampling chamber to the hydrocarbon detector and columns packed with appropriate adsorbents. Air flow rate was controlled with a regulator equipped with a flow meter.
5. Ports were provided on the opposite side of the chamber from the inlet port, to monitor total volatile hydrocarbon by TLV Sniffer and to concentrate volatile compounds on an appropriate adsorbent material.
6. A sprayer consisting of a two-gallon, polished stainless steel tank, with removable syphon tube, hose adaptor and discharge units was attached to a fan pattern nozzle inside the chamber, to distribute the sludge evenly over the soil surface.
7. The inside of the chamber was coated with epoxy paint to eliminate contamination from the aluminum.
8. To insure a good seal between the chamber and the soil surface, an aluminum band 1½ inches in depth was extended from the bottom edge of the box and embedded in the soil.

Table 12 presents the equipment chosen for monitoring.

Table 12 Monitoring Equipment for Land Farming Simulation Equipment

1. Bacharach TLV Sniffer with a total range of 0-10,000 PPMV. The instrument was calibrated with hexane.	To measure total volatile compound concentration
2. Potentiometric Recorder	To record hydrocarbon concentration with time
3. Dew Point Hydrometer	To measure relative humidity inside the box
4. Electric fan	To mix air inside the box
5. Dial thermometers	To measure soil and air temperature
6. Speedy Moisture Tester (Soil Test, Inc.)	To determine the moisture content of soil
7. MDA Accuhaler 808, personal sampling pump	To draw the air into the adsorbent cartridge
8. Adsorbent cartridge	To concentrate volatiles
9. Regulator equipped with flow meter	To compensate down stream pressure changes and control air flow through the box.
10. Compressed air cylinder	To provide a hydrocarbon free air supply

Experimental Procedures

Testing the Simulation Equipment in the Laboratory

Initially the simulation equipment was tested in the laboratory. The effects of tilling, mixing the air with-

in the chamber, air flow rate, and sampling frequency were determined.

Primarily to identify each volatile compound, air samples were concentrated in traps packed with Tenax-GC and silica gel. These samples were analyzed by use of the Gas Chromatograph (GC), Mass Spectrometer (MS) system in the Kerr Research Laboratory at Ada, Oklahoma. A total of ten hydrocarbons were identified. The hydrocarbons include saturated aliphatic and alicyclic compounds. Identification of these compounds helped in the selecting of standards for the GC use.

The following conclusions were obtained during initial testing:

1. The selected monitoring equipment was adequate.
2. Tilling caused high emissions.
3. An air flow rate of 3-4.5 l/min through the chamber was adequate for accurate sampling.
4. Operating the fan at high speed resulted in complete mixing of the contents in the head space of the chamber.
5. The monitoring and sampling were essential before, during and immediately after application, after tilling, at two hour intervals throughout the first day of application, daily for the next two days after application, weekly for the next three weeks and monthly thereafter.

Preparation of Equipment for Sampling

The TLV Sniffer, for monitoring total volatile hydrocarbons, was calibrated with hexane; calibration was checked with known concentrations of hexane before and after each run.

MDA Accuhaler 808 personal sampling pump, for collecting volatiles in adsorbent tubes, was also calibrated before and after sampling using a soap bubble flow meter. Flow rate through the trap was 30 and 31 ml/min.

The hygrometer probes were dried in a 60-80°C (140-180°F) oven for about ½ hour to remove excess moisture before using.

Field Sampling Protocol and Procedure

After the measurement methodology was developed and equipment was tested and calibrated in the laboratory, field studies were conducted at the research site.

Four loading rates were studied which provided a range that included all possible loading rates. The selected loading rates were 3%, 6%, 10%, and 13% of oil in soil on dry weight basis. The selected loading frequency was six times per year. Therefore, six of the forty experimental plots were selected (plots #1, 6, 3, 7, 4, 5,) for this study. Plot #1 is a replicate of plot #6. A control plot (#3), to which no sludge was applied, was

included. The locations of these plots are shown in Figure 1.

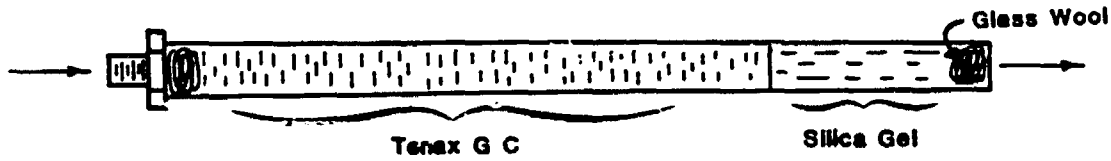
The procedure for using the chamber involved placing it over the plot and inserting it into the soil to a depth of 1.5 inches. Meanwhile, the air control valve was opened to maintain the desired air flow rate and the head-space fan was turned on. The dew point hygrometer was turned on at least 10 minutes before sampling for probes to equilibrate. The hygrometer probes were then inserted into the chamber through two sealable ports on the top surface of the chamber.

Soil and air temperatures were determined by dial thermometers (range -40, +160°F). The temperature of the air within the chamber was measured at 2.5 inches above ground level. The temperature of air outside the chamber was also measured at the same height. The temperatures of soil inside and outside the chamber were measured at a depth of 2 inches below ground level. Samples were taken using the TLV Sniffer and solid sorbent tubes.

The Sniffer was allowed to run for at least 10 minutes prior to sampling. It was then zeroed with ambient air prior to sampling. The Sniffer probe was connected to the brass valve in one side of the chamber via quick connect (Figures 6 and 7). The total volatile hydrocarbon concentration in the air leaving the chamber was then monitored with the Sniffer until equilibrium concen-

tration was reached. This usually took 15 minutes.Samples were collected according to the predetermined sampling schedule. The sampling schedule was adjusted to take into consideration abnormalities in the field. The resulting sampling schedule was determined by the concentration vs time curve which was the product of many experiments.

To determine the identity and relative quantity of organic pollutants, sampling was also performed by drawing exiting air through a 1/4 inch (outside diameter) stainless steel trap packed with 3 inches of Tenax-GC (60/80) and 1 inch of silica gel (100/200). Figure 9 shows the sampling cartridge.



Dimensions: $4\frac{2}{5}$ in. by .25in. O.D. Stainless Steel Tube

Figure 9 Sample Concentrator

Tenax-GC is a porous polymer that is based on 2,6,-diphenyl-p-phenylene oxide. It is a typical sorbent for collecting volatile compounds at room temperature [10].

However, many of the lighter organic compounds are not adequately retained at room temperature by Tenax-GC[11]. By using the cryogenic method, in addition to increasing the efficiency of collecting low molecular weight hydrocarbons (C_2-C_6)[10,11,12,13,14] the oxidation or polymerization of constituents is minimized[10]. Nevertheless, cryogenic trapping was dismissed due to difficulty of using this system in the field.

Pellizzari[15,16] developed an analytical technique to determine the collection efficiency of many sorbents, including Tenax-GC, during the concentration of hazardous vapors from a moving air stream. He reported that Tenax-GC was > 90% efficient in trapping hazardous vapors.

The addition of a small amount of silica gel in front of Tenax-GC served to protect the Tenax-GC from the moisture without altering the efficiency and to trap organic compounds that were not trapped by Tenax-GC.

It was reported that organic compounds with a minimum of three carbon atoms would be trapped on silica gel. Silica gel exhibits a great selectivity among atmospheric gaseous and vaporous constituents. It readily adsorbs compounds with hydroxyl groups and with many of the more common hologenated hydrocarbons[17,18]. Silica gel adsorbs water more than any other substance; therefore, under conditions of high humidity, the efficiency of adsorbing

other compounds is much reduced[17,19,20].

To prepare the traps, the tubing was first cleaned using a soap solution and then distilled water, and was subsequently rinsed with methanol and oven dried. A glass wool plug was inserted, and the sorbents were added, followed by slight tapping and another glass wool plug to hold the sorbent material.

After trap preparation and before sampling, a clean trap was analyzed as a blank by GC-FID. Analyses of two traps indicated some quantities of methylene chloride. Investigation revealed that the methylene chloride was a contaminant from the laboratory used for oil content analysis. Subsequently, traps were prepared in a lab free of contamination. The traps were transferred to and from the field in the ice chest at a temperature of 4-10°C.

To start sampling, a quick connect was used to connect the trap through a stainless steel valve to the chamber. The use of quick connect facilitated sampling and storage operations. All fittings used were stainless steel. A dual tandem cartridge arrangement was used to check for breakthrough periodically. Volatiles were collected using MDA Accuhaler 808 personal sampling pump.

The length of time of sampling varied depending on the concentration of the volatiles: after application, with high concentration of volatiles, 5 minutes; after tilling, with moderate concentration, 10 minutes; and be-

fore application and tilling, 20 minutes. The collected samples, sealed and labeled in the field, were refrigerated and analyzed in the laboratory within a week. Samples were taken before and immediately after application, before and after tilling, as well as every other week until the next application.

During the period from July 13 through November 17, 1982, regular applications and samplings were made except during two weeks of rains and strong winds. From November through April, application was not made because of inclement weather and exceptionally wet soil.

Laboratory Study

Field measurements of volatile hydrocarbons were complemented by conducting limited exploratory measurements in the laboratory in the controlled temperature and humidity of the environmental chamber. Volatilization rates of the waste were studied at three different temperatures. In addition, for each temperature range, the application rate was varied. In these tests the soil moisture content and relative humidity were held constant. Other tests with varying soil moisture content and relative humidity were also conducted at fixed temperatures and loading rates. The purpose of this study was to determine the effects of soil temperature, loading rate, soil moisture content and relative humidity on the

rate of emission of volatiles. Table 13 presents the experimental conditions for laboratory study.

Another important variable was volatility of sludge. In order for this variable to be relatively constant for all experimental runs, the sludge was used from only one batch, originated from API separator, brought from the field and stored in a closed container. However, prior to each application, the volatility of the sludge was determined to detect any changes in volatility.

Samples of soil were obtained from control plots in the field and placed in rectangular wooden boxes (13x12x10 inches) to a depth of 8 inches. For each temperature range, three boxes of soil, for application of three different amounts of sludge, were placed in the environmental chamber. A fourth box was also included as a control. After placing soil boxes in the environmental chamber, the desired air temperature was set. The chamber was then placed over the soil. The monitoring chamber used in the laboratory had a sprayer; therefore, monitoring and sampling were accomplished during spraying too. The operating procedure was the same as for the field plots.

The appropriate volume of sludge was predetermined and poured into the sprayer tank. The tank was pressurized by pumping to a certain pressure (max. 30 psi). When all of the desired test conditions were stabilized,

Table 13 Experimental Conditions for Laboratory Study

Run. No.	Loading Rate (% oil in soil-dry wt.)	Soil Temp. °F	Soil Mois. Cont. (wt %)	Relative Humidity (%)	Air Flow Thru the Box (l/min)
1	3	35	12	52	3.5
2	6	35	12	52	3.5
3	10	35	12	52	3.5
4	3	60	12	52	3.5
5	6	60	12	52	3.5
6	10	60	12	52	3.5
7	3	85	12	52	3.5
8	6	85	12	52	3.5
9	10	85	12	52	3.5
10	6	60	23	52	3.5
11	10	60	23	52	3.5
12	6	60	12	75	3.5
13	10	60	12	75	3.5

the background hydrocarbon concentration was recorded; the sludge was then applied evenly over the surface. During the application and for one hour afterward, the atmosphere of head space was continuously monitored. Prior to and after each run, using the zero adjustment of the TLV Sniffer, chart recorder readings were obtained to verify recorder-to-analyzer linearity. After the sludge was applied and volatiles were monitored, a small garden hoe was used to till the soil under the chamber to a depth of 8 inches to ensure even mixing.

Each series of experiments was performed over a seven day period. Sampling and monitoring took place before and during application, immediately after application, before and immediately after tilling, at two hour intervals throughout the first day of application and daily for the next two days of application. Three and five days after application, the soil and sludge mixture was tilled. Samples were then taken prior, immediately after and two hours after tilling. On days four, six, and seven volatiles were also monitored. In all, 18 samples were taken with TLV Sniffer in each run. Because of limited hours for GC work, only 10 samples were taken using adsorbent tubes for each temperature and loading rate range.

Analytical Procedure

Air Sample Analysis. The collected samples were analyzed in the laboratory within a week by Hewlett-Packard (HP) Model 7675 purge and trap system and HP Model 5880A Gas Chromatograph (GC) equipped with Flame Ionization Detector (FID). A 1/8" stainless steel column, packed with carbopack B/1% SP-1000 was used to separate the hydrocarbon compounds thermally desorbed from the sampling cartridge. Recovery of trapped vapors was accomplished using thermal desorption which allowed for direct introduction of the total sample into the GC column. Limited Gas Chromatography-Mass Spectrometry (GC-MS) analysis was also performed in the Ada Laboratory for quality control.

The identity of volatile compounds was based on retention times of standard compounds and confirmed from subsequent GC analyses. Relative concentrations of compounds were determined using the Internal Standard Calibration Method (ISTD). Absolute quantities could not be given, since it was not known for all samples whether breakthrough had occurred from the sorbent trap. First, 1,4-dichlorobutane was used as an internal standard. However, with the last batch of sludge one compound co-eluted with 1,4-dichlorobutane, and they could not be separated by changing temperature programming nor even by using a capillary column. Therefore, after trying many

compounds, methylene chloride was chosen to be used as an internal standard.

Since petroleum sludge contains a complex mixture of organic compounds, chromatographic separation of such compounds was a difficult task. Three different GC columns, including 60/80 carbopack C/.2% carbowax 1500, 10% SP-2100 on 100/120 suplecoport and 60/80 carbopack B/1% SP-1000, were examined at different conditions. It was found that 60/80 carbopack B/1% SP-1000 gave the best resolution. Nevertheless, peaks frequently overlapped, and it was difficult to identify and quantify all the unknown compounds. Thus, it was essential to reduce the number of organic compounds to be quantified. Of the volatile hydrocarbons identified, only fourteen were quantified. Table 14 presents these target compounds along with their retention time.

A calibration mixture of the fourteen compounds which were quantified (Table 14) was prepared every week. The purge and trap and GC were tested every day before the analysis of samples. The clean trap was then easily changed to the sample trap in the purge and trap system. A leak test was performed to confirm that all fittings were tight. Internal standard was first purged into the sample trap in a known concentration. Nitrogen gas was used as a purge gas. Purge flow was maintained at 50 ml/min for 10 minutes. Trapped volatiles were then

Table 14 Pollutants Identified and Quantified in Air Samples Along with Their Retention Time

Chromatographic Peak Number	Compound	Retention Time (min)
*1	Propanol	8.71
2	Methylene Chloride (IS)	9.30
*3	2-Propanone	9.56
4	Cyclopentane	13.47
*5	2-Butanone	18.05
6	Pentane	19.58
7	Cyclohexane	21.06
8	Methylcyclopentane	22.36
9	Benzene	26.84
10	Methylcyclohexane	29.84
*11	2,4-Dimethylpentane	31.46
12	Hexane	32.95
13	3-Methylhexane	35.58
14	1,4-Dichlorobutane (IS)	37.23
15	2,3,4-Trimethylpentane	38.995
16	2,5-Dimethylhexane	42.76
17	3-Methylheptane	44.65
18	2,2,5-Trimethylhexane	46.67
19	1,4-Dimethylbenzene	57.12
*20	2-Pentanone	
*21	Cyclohexanol	
*22	Ethylcyclopentane	
*23	2-Methyl-1-Pentanol	
*24	1,1-Dimethylcyclopentane	
*25	Cis-1,2-Dimethylcyclopentane	

* These hydrocarbons were only identified, not quantified

thermally desorbed at 250°C and backflushed to the GC column. Optimum results were achieved by temperature programming from 45°C to 200°C at 4°C/min with initial and final isothermal periods of 2 and 20 minutes, respectively. Carrier gas (nitrogen), hydrogen and air flow rates were 30, 30, 450 ml/min, respectively. Flow rates were checked by a bubble tube flow meter every day before analysis began. The injector port and detector temperatures were 250°C. Analysis time was approximately 60 minutes. Table 15 summarizes the GC conditions for the analysis of hydrocarbon components. At the end of each analysis, the column was cooled back to 45°C for the next analysis.

A small amount of carry-over (less than five percent) of the heavier compounds was observed from the concentrator when a blank was run immediately after the concentrated sample. Thus, in order to have a clean trap for the next sampling, a blank was run on the same trap immediately after each analysis.

Stripping Test. A simple laboratory test was devised to measure the extent of hydrocarbon emissions to be expected from the land treatment of a given sludge. The basic idea of this test was to purge an inert gas (hydrocarbon-free air) through a small sludge sample and to sweep all volatile hydrocarbons out of the sample.

For the stripping test, a 25 ml impinger, compressed

Table 15 Purge & Trap and Chromatographic Conditions for the Analysis of Hydrocarbon Components

1.	Purge & Trap Conditions:	
	Prepurge Time	3 minutes
	Nitrogen Purge Flow	50 ml/min
	Purge Time	10 minutes
	Desorb Temperature	250°C
	Desorb Time	10 minutes
	Auxiliarly Temperature	200°C
	Vent Time	10 minutes
2.	GC Conditions:	
	Nitrogen Flow (carrier gas)	30 ml/min
	Air Flow	450 ml/min
	Hydrogen Flow	30 ml/min
	Detector Temperature	250°C
	Injector Port Temperature	250°C
	Oven Temperature	45°C Initial, to 200°C at 4°C/min
	Chart Speed	.5 in/min
	Attenuation	8

air and TLV Sniffer were used. Figure 10 depicts a diagram of stripping test set up.

The experimental procedure involved the following steps:

1. The empty impinger tube was first weighed.
2. The tube was filled with 15 ml of sludge sample and weighed.
3. The stripping apparatus was set up.
4. The flow rate of air (purge gas) through the sludge sample was adjusted to 2 l/min in all stripping runs.
5. The hydrocarbon concentration in the stripping air was monitored with TLV Sniffer at 5 minute intervals for two hours, a constant time in all stripping tests.
6. The compressed air and TLV Sniffer were removed or disconnected from the impinger tube at 5-minute intervals and the impinger tube containing sludge was weighed.
7. The percentage volatile loss was calculated from the difference in sludge weight.
8. The data collected allowed for evaluation of the weight loss rate and a determination of the relationship between concentration (reading taken with TLV Sniffer) and weight volatilized.

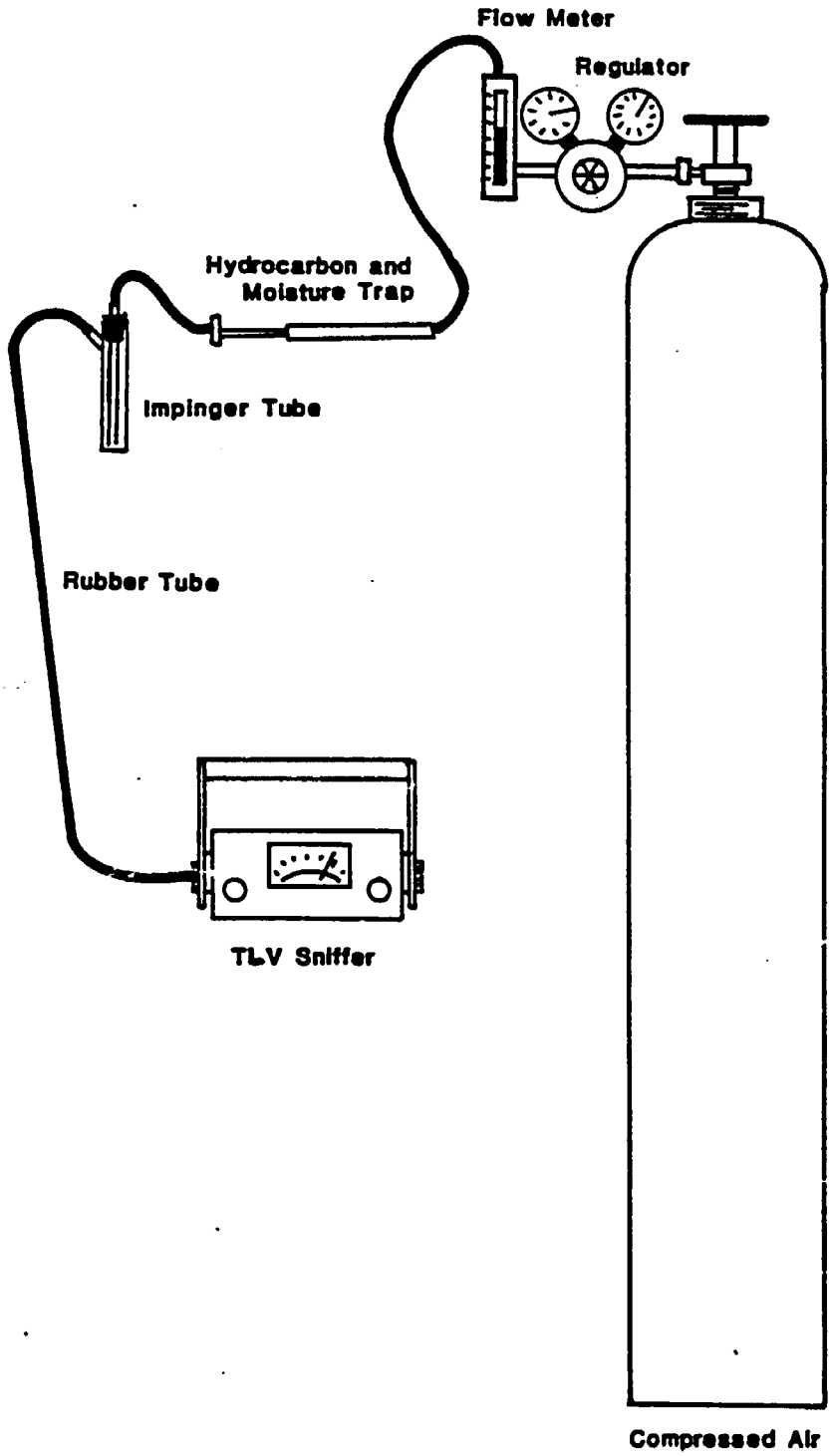


Figure 10: Stripping test setup

Oil Content and Moisture Content Analysis. The oil content and moisture content of the oily sludge added to the soil and of soil from the aerobic tilled zone before and after sludge application were analyzed.

The modified Soxhlet extraction method was used to extract oil from sludge and soil-sludge mixture. Methylene chloride was used as a solvent. Details of extraction procedures have already been published[21].

The moisture content of the soil-sludge mixture was determined simultaneously with the oil content analysis. Later on, a Speedy Moisture Tester was purchased and used to determine the moisture content of the plow zone in the field and in the laboratory.

Quality Control and Quality Assurance

The following on going quality assurance and quality control were conducted:

1. The TLV Sniffer was calibrated every two months. The calibration was checked with known concentrations of hexane prior to and after each sampling.
2. The sampling pump was calibrated before and after sampling, using a bubble flow meter.
3. Two forms were prepared. Table 16 illustrates the sampling protocol that was followed for each field sample and Table 17 shows the form

to record analytical conditions and results for each sample.

4. Upon return from a sampling trip, each sample code and the results obtained from TLV Sniffer and other monitoring equipment were entered into a sample log book. This log was updated as samples proceeded through work up and analysis.
5. Vials for standards, glassware etc., were cleaned with soap and water, rinsed with distilled/deionized water and methanol, and heated to 450-500°C to insure the removal of all traces of organic compounds.
6. After the preparation of a set of sampling cartridges, one cartridge was checked for background prior to the cartridge's commitment to field sampling.
7. All sampling cartridges were transferred to and from the field in an ice chest at a temperature of 4-10°C.
8. If two cartridges were used in series to check for breakthrough, they were separated and sealed individually immediately after sampling to avoid errors arising from diffusion which might have occurred later.
9. The collected samples were analyzed within a week.

10. To insure the accuracy and precision of the data acquired, instrument and chromatographic performance were monitored as follows:

    (a) The linearity of the gas chromatograph was verified once a week. Three different concentrations of working calibration standards were used to obtain instrument response with thirteen compounds. When sample concentration versus instrument response was plotted, the result fell along a straight line.

    (b) A strict step-sequence of analysis was followed. At the start of each working day, the analysis cycle began with the blank (using organic-free water), the multi-component working standard and three samples. Each sample was followed by a blank. This way, the purge and trap and GC column performances were monitored every day. Running the blank also indicated that the syringe, needle and all lines from the purge and trap through the injection port and the FID were free of contaminants.

11. Each sample run by GC was logged into a notebook, detailing analysis conditions, compounds

found and where the data were archived.

12. Periodically, air samples were analyzed by GC-MS in the Ada Laboratory.

Table 16 Sampling Protocol

Project #	Pump #
Date	Start Time
Plot #	Stop Time
L. R.	Operator
P. F.	Sampling:
Adsorbent Tube #	Sniffer ( ) Adsorbent Tube ( )

Sampling	Conc.	Air Flow	Soil Temp (F°)		Air Temp. (F°)		Ambiant		Dew Point		Relative	Sampling
Time	(22M)	Through the Box	Inside Box	Outside Box	Inside Box	Outside Box	Temp (C°)	Vapor Pressure	Temp (C°)	Vapor Pressure	Humidity	Flow Rate

Table 17 Form to Record Analytical Conditions and Results for Each Sample

Cartridge #
Sampling Rate
Air flow through the box
Time: Start
Stop

Operation Performed						
Time	Date	GC Conditions and Column Used	Standards	Compounds Name	Compounds Conc.	Remark

CHAPTER III

RESULTS AND DISCUSSIONS

The atmospheric emissions from land treatment of petroleum sludge was assessed in this study. This chapter presents results and analyses made on the data. The first section is a summary of the sniffer data for laboratory and field experiments. The second section presents the results of statistical analyses. The third section shows the significance of results from the stand point of pollution. The fourth section shows the results and interpretation of the gas chromatography data.

Discussion of TLV Sniffer Data

Stripping Tests

Stripping tests were carried out to measure volatility of the sludge and to estimate weight loss of individual sludge components due to volatilization from land treatment operations. The procedures have been described in Chapter II.

Hydrocarbon concentrations in the stripping gas were monitored every five minutes and weight loss of sludge was measured every ten minutes during at least a two-hour

test run. Because of differences in volatility of the different batches of sludge, a stripping test was conducted each time the application was made. The volatility of these sludges was calculated and presented in Table A-1, Appendix A. Table 18 presents the stripping test results for the last batch of sludge which was also used for laboratory experiments. In this test the air was purged into the sludge sample at 2.02 l/min. These data were used to construct curves of cumulative calculated TLV Sniffer responses as a function of sludge weight loss (Figures 11 and 12). These curves can be used to relate the emission rate to the weight loss for other experimental tests using the same kind of sludge.

As might be expected, the rates of emission and weight loss are time-dependent. For example, the initial weight loss rate was 278.4 mg/10 min. and declines to about 3.9 mg/10 min. within 110 minutes. During the same period the volatile losses measured by the Sniffer was 22.76 mg/min. initially and dropped to .14 mg/min. after 100 minutes. The percentage of weight loss during a 110 minute test period for the last batch of sludge was calculated to be 8.50.

In view of the results obtained, the author decided to conduct an experiment with clear water under the same conditions as the sludge sample to estimate water loss. During the test period, the water loss was insignificant

Table 18 Stripping Test Results*

Stripping Time (min.)	Reading from sniffer Direct (ppm)	Reading from sniffer Calculated (mg/min.)	Area Count	Mass of Volatiles (mg)	Cumulative Mass (mg)	Wt** Loss (mg)	Cumulative Wt. Loss (mg)
<1	3200	22.76					
5	2000	14.23					
10	1500	10.67	37	148	148	278.4	278.4
15	1200	8.54					
20	1000	7.11	20.5	82	230	169.3	447.7
25	900	6.40					
30	600	4.27	14.5	58	288	154.8	602.5
40	380	2.40	9.0	36	324	87.3	689.8
45	310	2.21					
50	300	2.13	5.5	22	346	85.3	775.1
55	230	1.63					
60	190	1.35	4.0	16	362	65.0	840.1
65	140	.99					
70	110	.78	3.0	12	374	61.7	901.8
80	80	.57	1.9	7.6	381.6	36.7	938.5
90	30	.21	1.0	4.0	385.6	8.3	946.8
100	20	.14	.7	2.5	388.1	4.5	951.3
110			.2	.1	388.1	3.9	955.2

* Air flow through the sludge = 2.02 1/min.

** Initial wt. of sludge = 11045.3 gr.

% wt. loss of sludge = 8.5

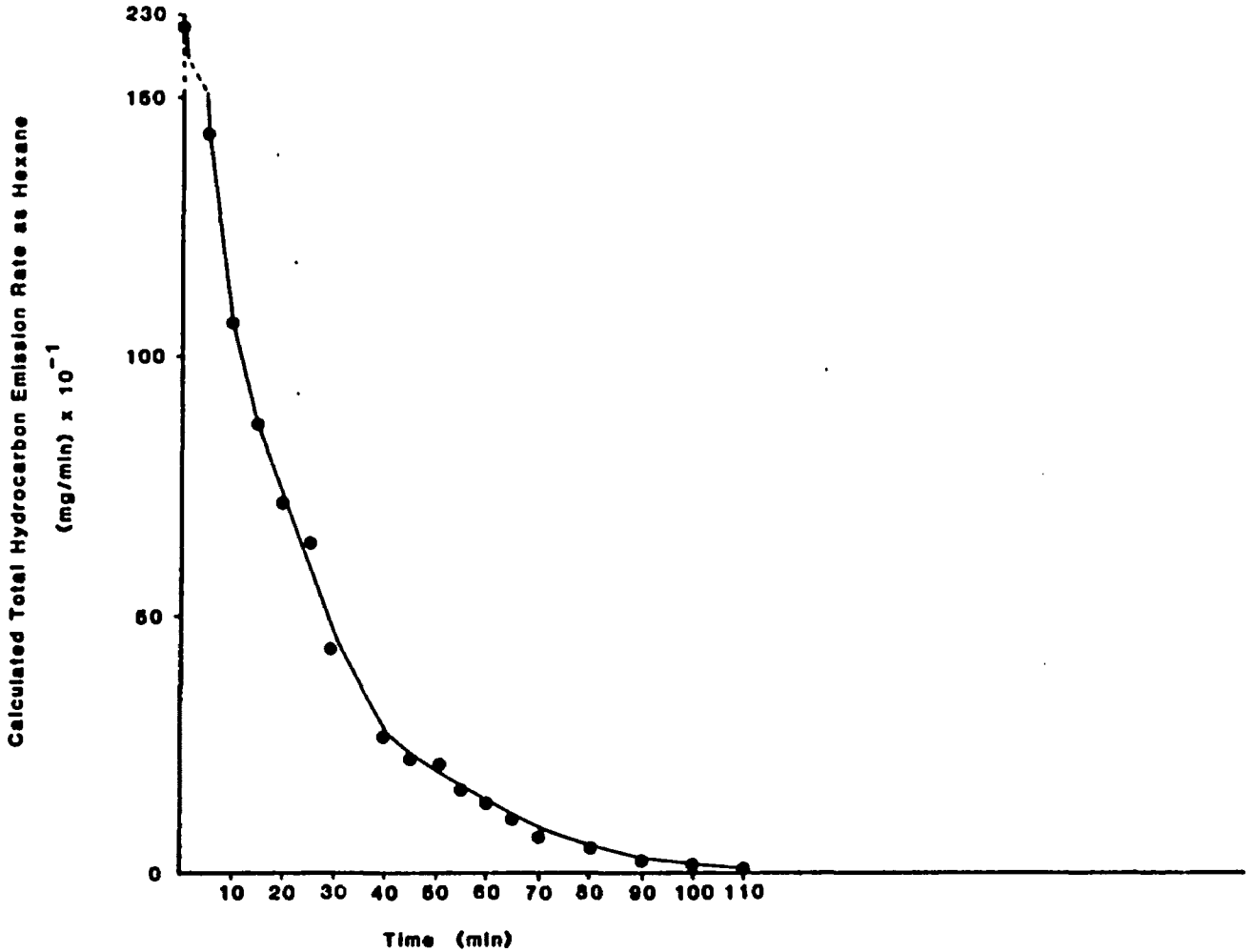


Figure 11 Calculated Total Volatile Emission of Sludge Sample vs Time

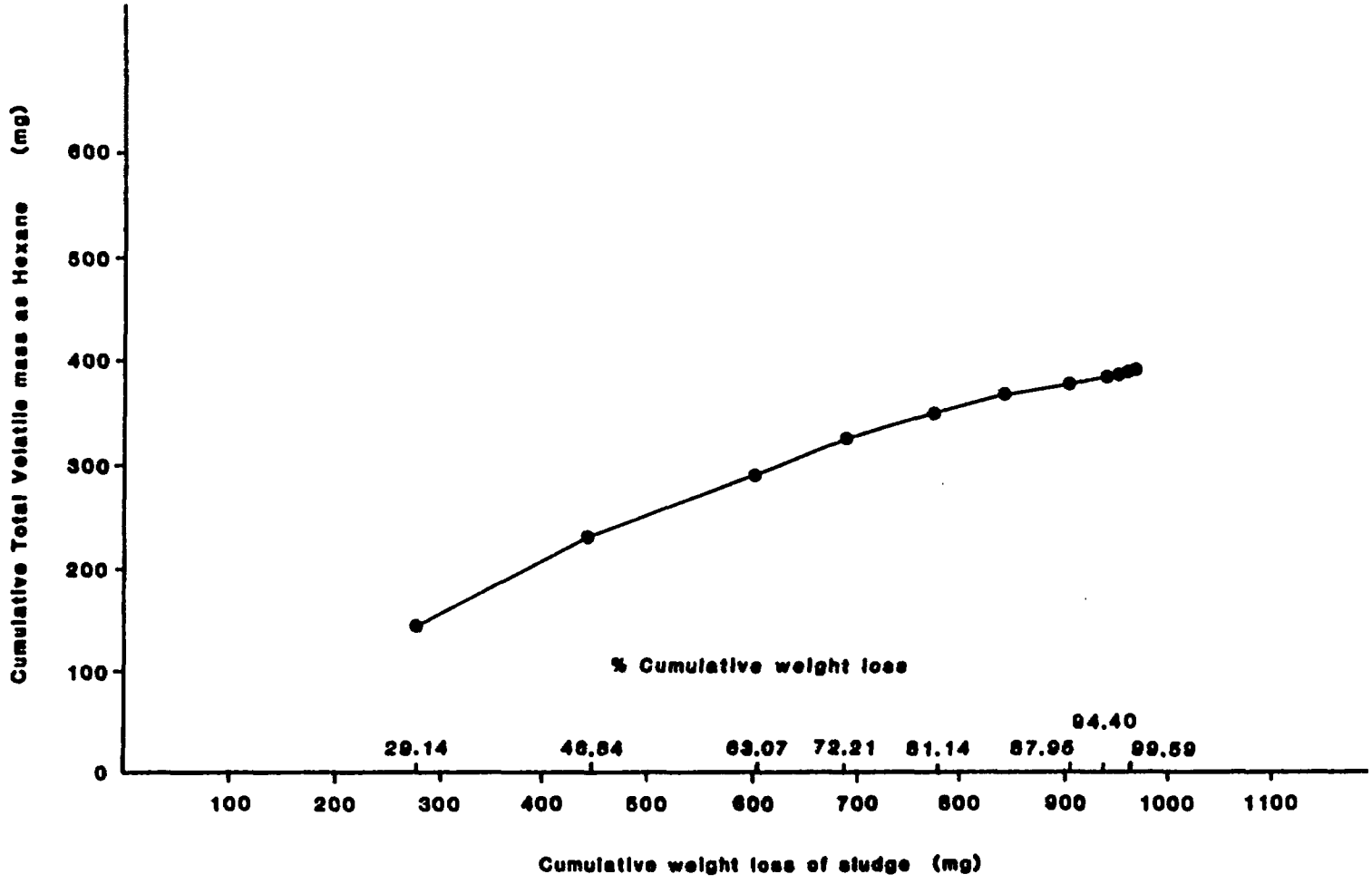


Figure 12 Relationship Between Cumulative Total Volatile Mass and Sludge Weight Loss

(X.12%) compared to the volatile loss.

Total Volatile Emission

Throughout the sampling and testing period, the laboratory and field analytical results were transferred to a master log. The data were then stored on a tape in an IBM computer system. Preparation of the raw data into usable form involved converting ppm reading from sniffer to g/hr of total volatile emission rate. Tables A-1 and A-2 in Appendix A present calculated concentrations of total volatile hydrocarbon for field and laboratory experiments. From these data, calculated concentration-time plots, such as those shown in Figures 13 and 14, were generated. (To differentiate between points in all time concentration curves in this section the starting times of application were off-set by sufficient time intervals to give a distinct separation between the three curves.). The patterns observed in these figures are typical of all loading rates and all temperature ranges, although the emission rates at any point in time vary with different loading rates and environmental conditions.

These figures show that in the laboratory a very sharp rise in the hydrocarbon concentration in the air appeared immediately after sludge application began. The maximum hydrocarbon concentration was reached during the

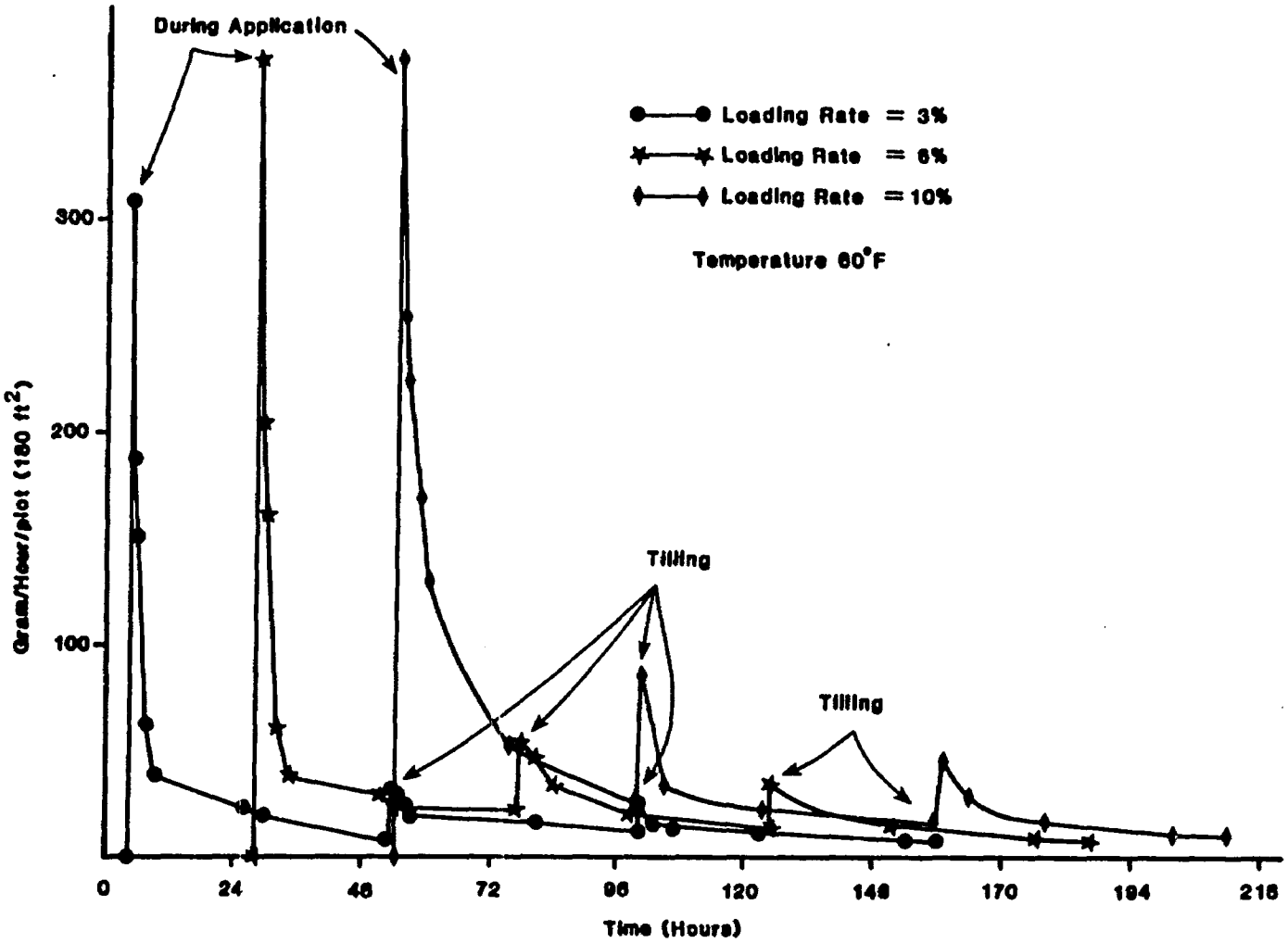


Figure 13 The Effect of Loading Rate and Tilling Frequency on Emission in Laboratory Experiments at 60°F

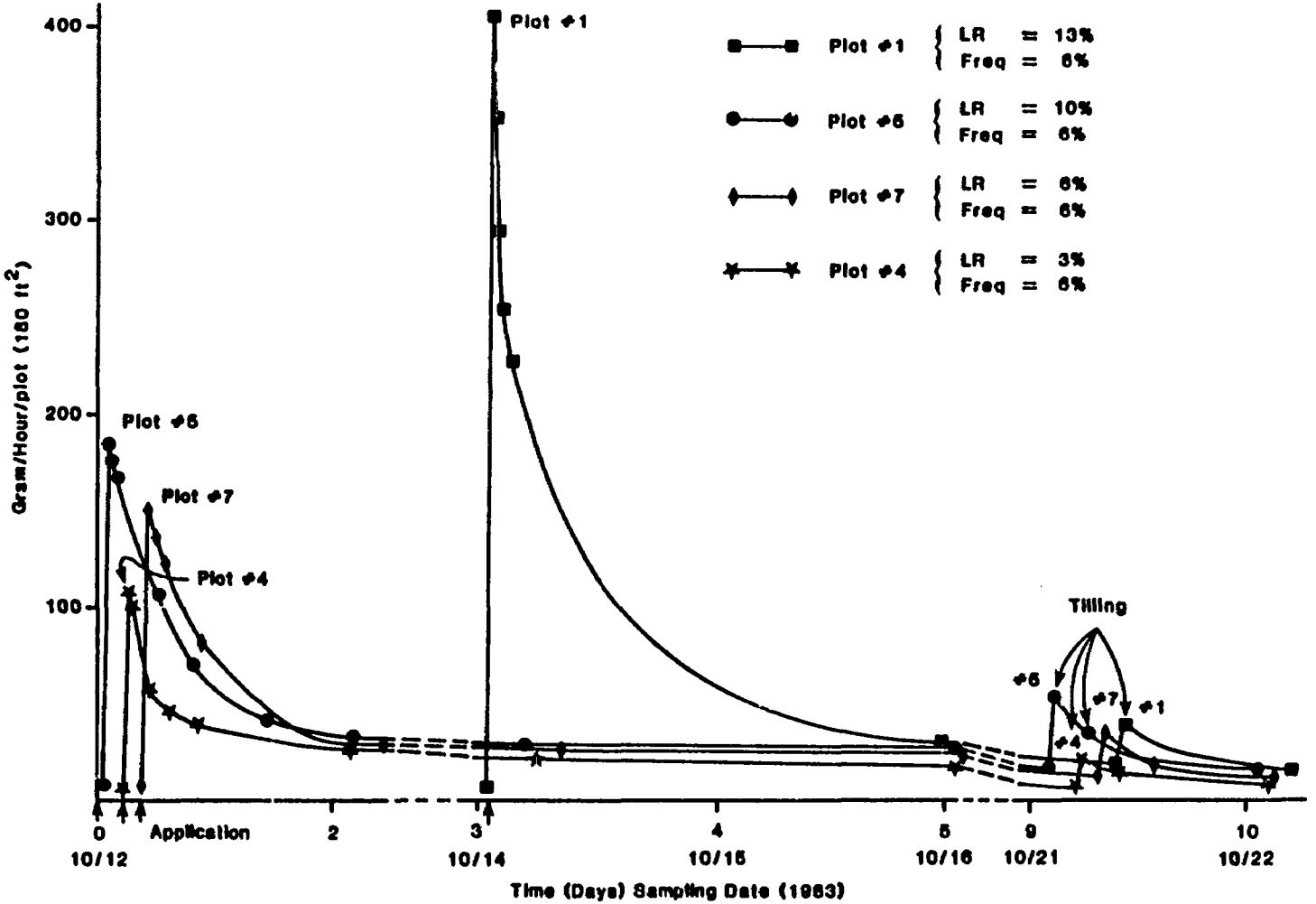


Figure 14 The Effect of Loading Rate and Tilling on Total Hydrocarbon Loss in Field Studies

application or very shortly thereafter. However, an abrupt decline from the maximum concentration and a gradual approach to a lower concentration followed. These results are similar to the results achieved by Minear et al.[2].

In the field, because of losses which occurred during application and elapse of time after applying the sludge and placing the chamber over the soil, a gradual rise in the hydrocarbon concentration was noted for equilibrating the sampling chamber (Figure 14).

The hydrocarbon concentration in most tests dropped to less than 50 percent of its maximum value within two hours after application. Therefore, it was evident that comparisons of the concentrations for the first two hours and for the first day would give a quick estimation of the relative hydrocarbon emission losses. Figures 15 and 16 show the maximum concentration and rate of decrease in emission in the first two hours from application at three different temperatures and loading rates.

The areas under the time-concentration curves were determined at two hours, one day and seven days from application for field and laboratory data, as well as from application to application for field data only. The areas were determined by planimetry. From these areas the losses were calculated for each loading rate. Table 19 gives the summarized data by plot number and loading rate

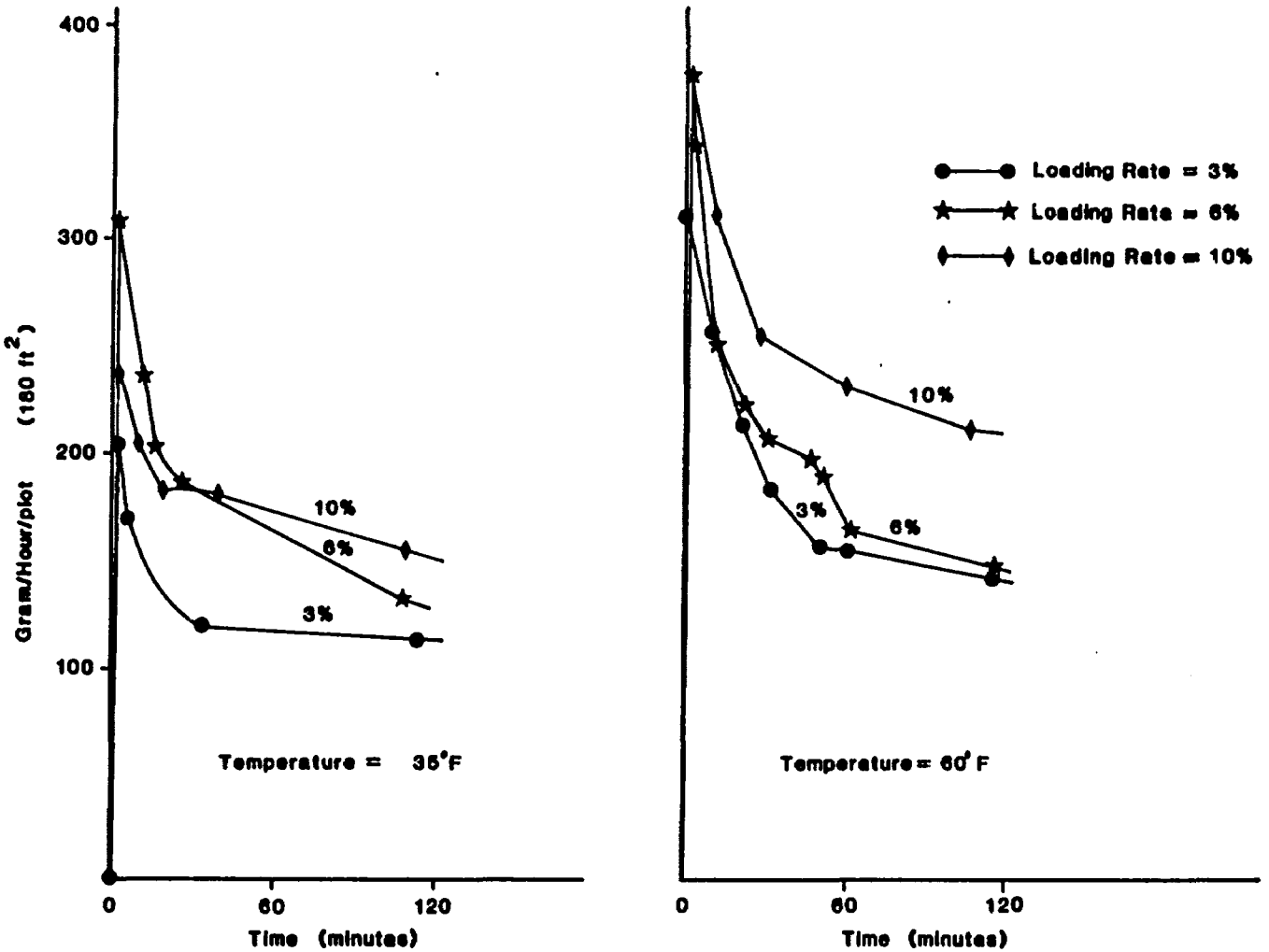


Figure 15 Rate of Emission of Volatiles in First Two Hours After Application of Temperature 35°F and 60°F

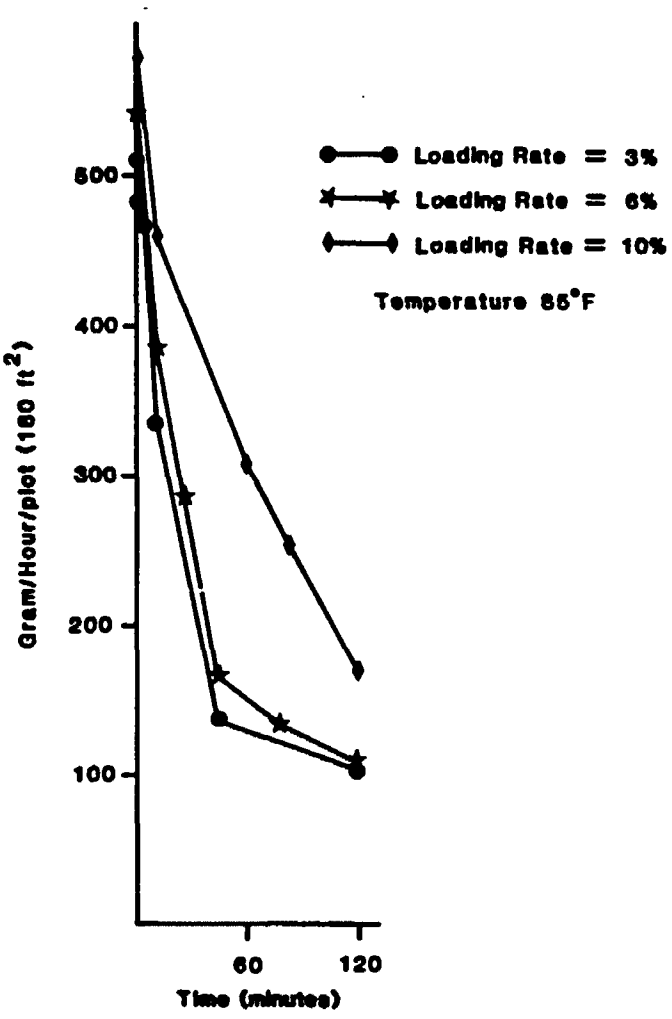


Figure 16 Rate of Emission of Volatiles in First Two Hours After Application at Temperature 85°F

Table 19 Total Volatile Loss from Field Data

Date of Appl.	Plot No.	Nominal Loading Rate	Appl. No.	Sludge Applied (kg)	Oil Applied (kg)	Volatility of Sludge (%)	Total Loss in-2 hr. (kg)	Total Loss in-1 d (kg)	Total Loss in 7 d (kg)	Total Loss Since Appl. (kg)	Total No. of Days Since Appl.
07/19/82	1	13	1	230.3	195.755	-	.220	.923	3.073	8.173	29
08/17/82	1	13	2	230.3	195.755	8.0	.070	.320	2.090	6.990	24
09/10/82	1	13	3	230.3	195.755	7.8	.053	.620	2.800	11.250	34
10/14/82	1	13	4	262.2	157.320	13.6	.530	2.550	6.050	9.790	18
11/02/82	1	13	5	262.2	157.320	12.5	.903	3.990	8.700	11.700	15
11/17/82	1	13	6	206.53	163.158	9.1	.130	.630	2.130	4.530	33**
Subtotal				1421.83	1065.063		1.906	9.033	24.843	52.433	153
07/13/82	4	3	1	45.31	38.513	-	.070	.390	1.910	5.849	31
08/13/82	4	3	2	45.31	38.513	8.4	.063	.386	1.452	4.992	41
09/23/82	4	3	3	60.49	36.294	14.0	.340	2.020	6.280	8.340	19
10/12/82	4	3	4	45.31	27.186	13.8	.100	.860	3.230	4.010	20
11/02/82	4	3	5	60.49	36.294	12.5	.260	1.610	3.910	5.220	15
11/17/82	4	3	6	47.67	37.659	9.1	.056	.400	1.400	3.800	33**
Subtotal				304.58	214.459		.889	5.666	18.182	32.211	159
07/13/82	5	10	1	150.58	127.993	-	.150	.720	2.660	7.240	30
08/12/82	5	10	2	150.58	127.993	8.5	.090	.600	2.200	8.390	42
09/23/82	5	10	3	201.67	121.002	14.0	.810	3.100	8.150	13.123	19
10/12/82	5	10	4	201.67	121.002	13.8	.320	1.360	5.260	11.260	20
11/02/82	5	10	5	262.67	157.320	12.5	.330	1.820	5.370	8.290	15
11/17/82	5	10	6	158.86	125.499	9.1	.130	.650	1.850	4.250	33**
Subtotal				1125.56	780.809		1.830	8.250	25.490	52.533	159

(continued)

Table 19 Total Volatile Loss from Field Plots (continued)

Date of Appl.	Plot No.	Nominal Loading Rate	Appl. No.	Sludge Applied (kg)	Oil Applied (kg)	Volatility of Sludge (%)	Total Loss in-2 hr. (kg)	Total Loss in-1 d (kg)	Total Loss in 7 d (kg)	Total Loss Since Appl. (kg)	Total No. of Days Since Appl.
07/20/82	6	13	1	230.30	195.755	-	.203	1.013	3.163	8.263	28
08/17/82	6	13	2	230.30	195.755	8.0	.070	.310	2.100	6.950	24
09/10/82	6	13	3	230.30	195.755	7.8	.053	.620	2.800	11.250	34
10/14/82	6	13	4	262.20	157.320	13.6	.500	2.510	6.040	9.780	18
11/02/82	6	13	5	262.20	157.320	12.5	.903	3.990	8.700	11.600	15
11/17/82	6	13	6	206.53	163.158	9.1	.130	.630	2.130	4.520	33**
Subtotal				1421.83	1065.063		1.859	9.073	24.933	52.343	152
07/20/82	7	6	1	90.62	77.027	-	.110	.680	2.490	6.800	28
08/17/82	7	6	2	90.62	77.027	8.0	.045	.280	1.700	5.530	37
09/23/82	7	6	3	121.01	72.606	14.0	.560	3.310	6.930	11.110	19
10/12/82	7	6	4	121.01	72.606	13.8	.130	1.000	3.550	10.210	35
11/17/82	7	6	5	95.33	75.310	9.1	.093	.510	1.610	4.010	33**
Subtotal				518.59	374.576		.938	5.780	16.280	37.660	152
TOTAL				4792.39	3499.97		7.422	37.802	109.728	227.200	775
% Total sludge volatilized:							.154	.788	2.289	4.740	
% Total oil volatilized:							.212	1.080	3.135	6.491	

* Application number
** No. of days from 11/17/82 to 12/20/82
d = days

for all the samples collected from the field plots. This table can be used to obtain an estimate of volatile loss at various time intervals and of an expected range in various sludge loading rates. Included in the table are the date of application of sludge, percent volatility of sludge, the amount of sludge and equivalent oil applied each time that produced the calculated losses at different times and total number of days between two applications.

During a six-month test period in the field (July 13 - December 20, 1983) total volatile losses for each plot individually and for all five plots combined were also calculated. The volatile loss is given in kilograms/16.72 m^2 (180 ft^2) of plot area.

The results indicate that of the 4792 kg (10,560 lb) of sludge applied to plots 1,4,5,6 and 7, during the six months, 4.7 percent was lost through volatilization to the atmosphere. This is equivalent to 6.5 percent of the total oil applied. Based on the total sludge applied, the total percentages of losses in two hours, one day and seven days from application were estimated at 0.16, 0.78 and 2.29, respectively. The percentage of loss was estimated on the basis of total sludge and total oil applied and is given in Table 19. Since the loss rate decreases with time, the percentage of loss in about six months was only twice the percentage found in seven days.

Table 20 Percent of Total Loss from Different Loading Rates at Different Times from Application

Plot #	% Loading Rate	Total # of days *	Total Loss kg	% of Total Loss in two hours	one day	seven days
4	3	159	32.211	2.75	17.59	56.44
7	6	152	37.660	2.49	15.34	43.22
5	10	159	52.553	3.48	15.69	48.50
1	13	153	52.433	3.63	17.22	47.38
6	13	152	52.343	3.55	17.33	47.63

* Total # of days that total losses were calculated for each plot starting from first application (7/13/1982-7/20/82) to the last sampling date (12/20/82).

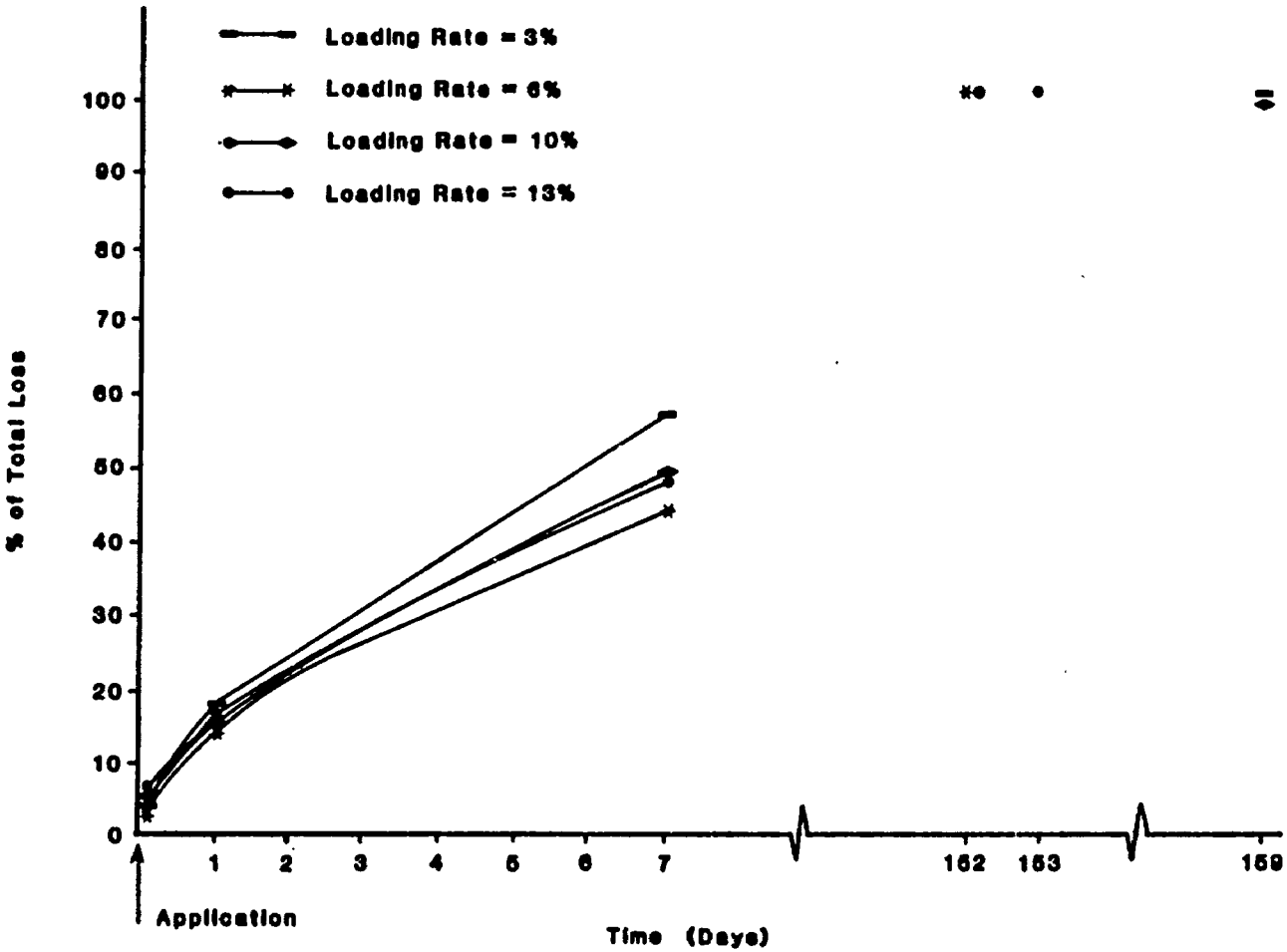


Figure 17 Percent Volatile Loss at Different Loading Rates vs Time

The percentages of total loss in two hours, one day and seven days from application were also calculated on the basis of total loss. The results are presented in Table 20. Figure 17, generated from Table 20 also shows the percentage of total loss as a function of time for different loading rates. One important result from the review of Table 20 and Figure 17 was the fact that approximately 50 percent of total volatiles was lost in seven days after application from each plot. Therefore, the seven-day period chosen for laboratory experiments was an adequate time period to use in comparing the effects of variables on emission.

From Table 19 it is evident that the higher loading rates result in higher volatile losses, assuming all other conditions were constant. However, losses from plot 5 were higher than the expected value for two reasons. First, there was a misapplication on 11/2/82 of 262 kg (13% loading rate) instead of 206 kg (10% loading rate). The second reason was that on 9/23/82 application to plot 5 was made from a new batch of sludge with high volatility (14%), while on 9/10/82 old sludge with low volatility (7.8%) was applied to plots 1 and 6. These facts have resulted in about 4-5 kg more volatile loss from plot 5 than expected. Occurrences of this kind compound the problems of predicting volatile losses. The range of total volatile loss was from a low of 3.80 kg

to a high of 13.12 kg. Plots 1 and 6 are duplicates. The results from Table 19 for plots 1 and 6 show the reproducibility of the procedure.

The arithmatic means and standard deviation of total loss for each plot separately and all five plots together are presented in Table 21. It should be noted that statistical variations in the mean of the total amount of sludge applied and the mean of total volatile losses follow the same pattern as that mentioned earlier.

Another important discovery (refer to Table 19) was the variation of volatile losses within each loading rate from one application to another. This variation could be explained primarily on the basis of volatility of different batches of sludges. It was found that volatility of the sludge was a very important factor in determining emission rates. For this reason a stripping test was developed in an attempt to provide a quantitative measure of relative volatility which could be related to emission rates. The method was described in Chapter II, and the results of one stripping test were presented previously in this section. Besides volatility, environmental conditions such as soil temperature, soil moisture content and relative humidity were partially responsible for these variations.

Monitoring of volatiles in the field was continued on 4/19, 5/9 and 6/19, 1983. The last application on the

Table 21 Mean and Standard Deviation of Total Amount of Sludge Applied and Total Volatile Loss

Effective Date (1982)	Plot #	Nominal Loading Rate	Weight Sludge Applied, kg (six appl.)	Mean/ APP	Std. Dev.	Weight Oil Applied	Total Volatile Loss/kg	Mean/ APP	Std. Dev.
7/13-12/20	4	3	305	50	8.0	214	32.2	5.37	1.65
7/20-12/20	7	6	519	104	15.9	375	37.7	7.53	3.04
7/13-12/20	5	10	1126	188	43.7	781	52.6	8.76	3.11
7/19-12/20	6	13	1422	237	21.6	1065	52.4	8.74	2.73
7/20-12/20	6	13	1422	237	21.6	1065	52.5	8.75	2.73
Totals			4794	163		3500	227.4	7.84	

APP = Application

plots was on 11/17/82. On 5/9 and 6/19, 1983 a higher rate of emission was observed (Table A-1, Appendix A) than on 12/20/82. This could be due to higher soil moisture content and elevated temperatures in May-June 1983.

As previously discussed, the laboratory experiments were conducted in controlled environmental conditions to investigate the effects of loading rate and temperature on the rate of emissions of volatiles. The procedures and conditions for conducting these experiments were discussed in the previous chapter. Since it was difficult to evaluate statistically the effects of relative humidity and soil moisture content from field data, because of insufficient data for those two parameters, two separate studies, one with high soil moisture content (23%) and the other with high relative humidity (75%), were performed in the laboratory. The soil temperatures for both tests were held constant at 60°F. One loading rate (6%) was tested with high soil moisture content, while two different loading rates (6% and 10%) were studied with high relative humidity.

The calculated rates of emissions for laboratory experiments are presented in Table A-2, Appendix A. From these data using the same methodology as for data in Table 19, the data in Table 22 were generated. Based on these data, the effects of loading rate, soil temperature, relative humidity, soil mositure content and tilling

Table 22 Total Volatile Loss from Laboratory Experiments

Date of Appl.	Loading Rate (%)	Soil Temp. (°F)	Soil Moist. Content (%)	Relative Humidity (%)	No. of Tilling	Amt.* Sludge Applied (kg)	Amt.** Oil Applied (kg)	Total Loss in 2-hr. (kg)	Total Loss in 1-d (kg)	Total Loss in 7-d (kg)	Max Emission Rate g/hour
3/31/83	3	35	12	52	2	41.746	26.30	0.243	.90	2.35	204.762
5/16/83	3	60	12	52	2	41.746	26.30	0.335	1.10	2.50	307.144
6/1/83	3	85	12	52	2	41.746	26.30	0.350	1.30	4.15	511.906
4/4/83	6	35	12	52	2	82.040	51.68	0.330	1.00	2.75	307.143
5/17/83	6	60	12	52	2	82.040	51.68	0.367	1.40	3.90	375.397
6/1/83	6	85	12	52	2	82.040	51.68	0.388	1.90	5.60	546.033
4/1/83	10	35	12	52	2	133.960	84.39	0.433	1.15	3.15	238.889
5/24/83	10	60	12	52	2	133.960	84.39	0.473	2.65	5.60	375.397
6/3/83	10	85	12	52	2	133.960	84.39	0.622	2.90	7.00	580.160
6/10/83	6	60	23	52	2	82.04	51.68	0.550	2.40	7.60	511.906
7/5/83	6	60	12	75	2	82.04	51.68	0.300	.80	2.30	341.270
7/5/83	10	60	12	75	2	133.96	84.39	0.400	1.50	3.50	341.270

* Volatility of sludge was 8.5% and density of sludge was .90 g/ml
** Amount of oil based on the 63% oil in sludge determined by Extraction Method

on emissions were determined.

The Effect of Loading Rate on Emissions.

Three different loading rates (3%, 6% and 10%) were examined in the laboratory at three temperature ranges. The results from laboratory experiments confirmed the field results; i.e., higher mass emission was achieved at higher loading rates. The relationship between emission rates and different loading rates of sludge is shown in Figures 13, 18 and 19. From these figures and data in Table 22, it can be seen that highest emission rate was achieved at 10% loading rate for all temperature ranges.

The Effect of Soil Temperature on Emissions.

As would be expected, the volatilization rate was strongly affected by temperature changes. The higher the temperature, the higher was the vapor pressures of volatile compounds, and the greater was the amount of volatiles emitted. Figures 20-22 illustrate the effect of three temperatures (35°F, 60°F, 85°F) at three different loading rates on the rate of emission of volatiles. A trend can be observed for each temperature within one loading rate. Temperature, in addition to its effect on vapor pressure, may also affect such factors as desorption, diffusion to the surface and rates of water loss - all factors that can contribute to the overall rate of loss of volatiles from a soil system. Total seven day loss as a function of variable temperatures and loading

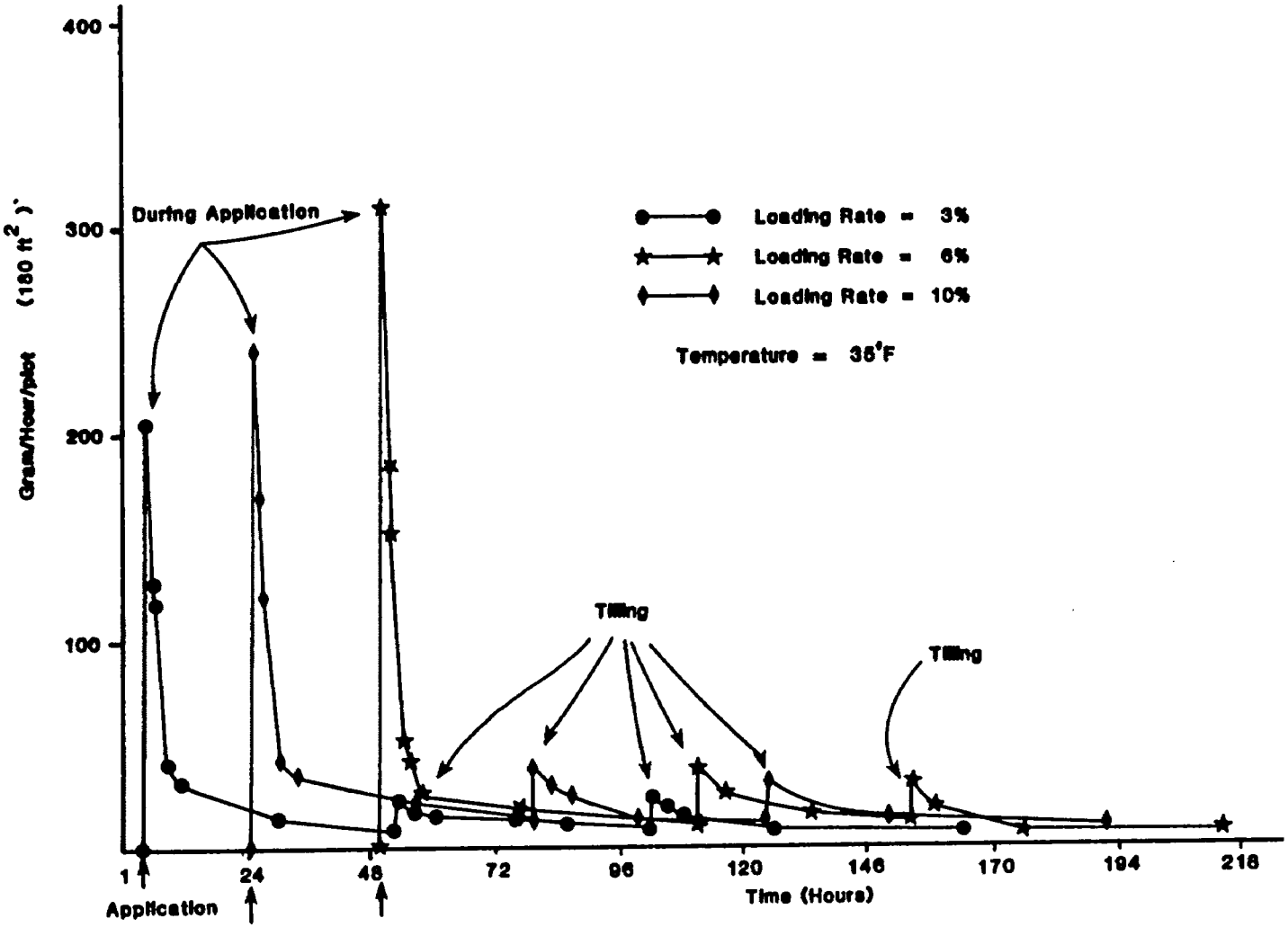


Figure 18 The Effect of Loading Rate and Tilling Frequency on Emission in Laboratory Experiments at 35°F

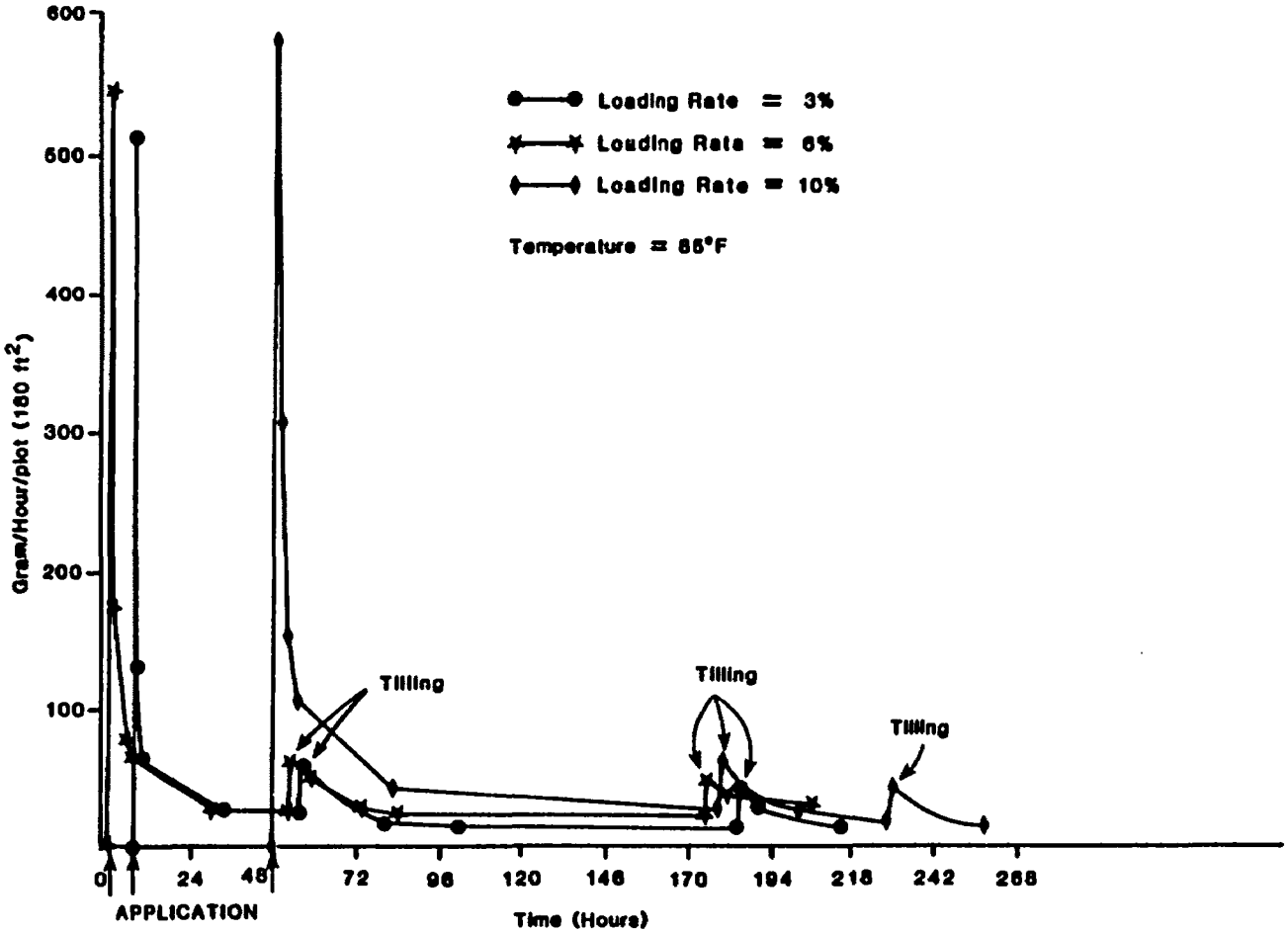


Figure 19 The Effect of Loading Rate and Tilling Frequency on Emission in Laboratory Experiments at 85°F

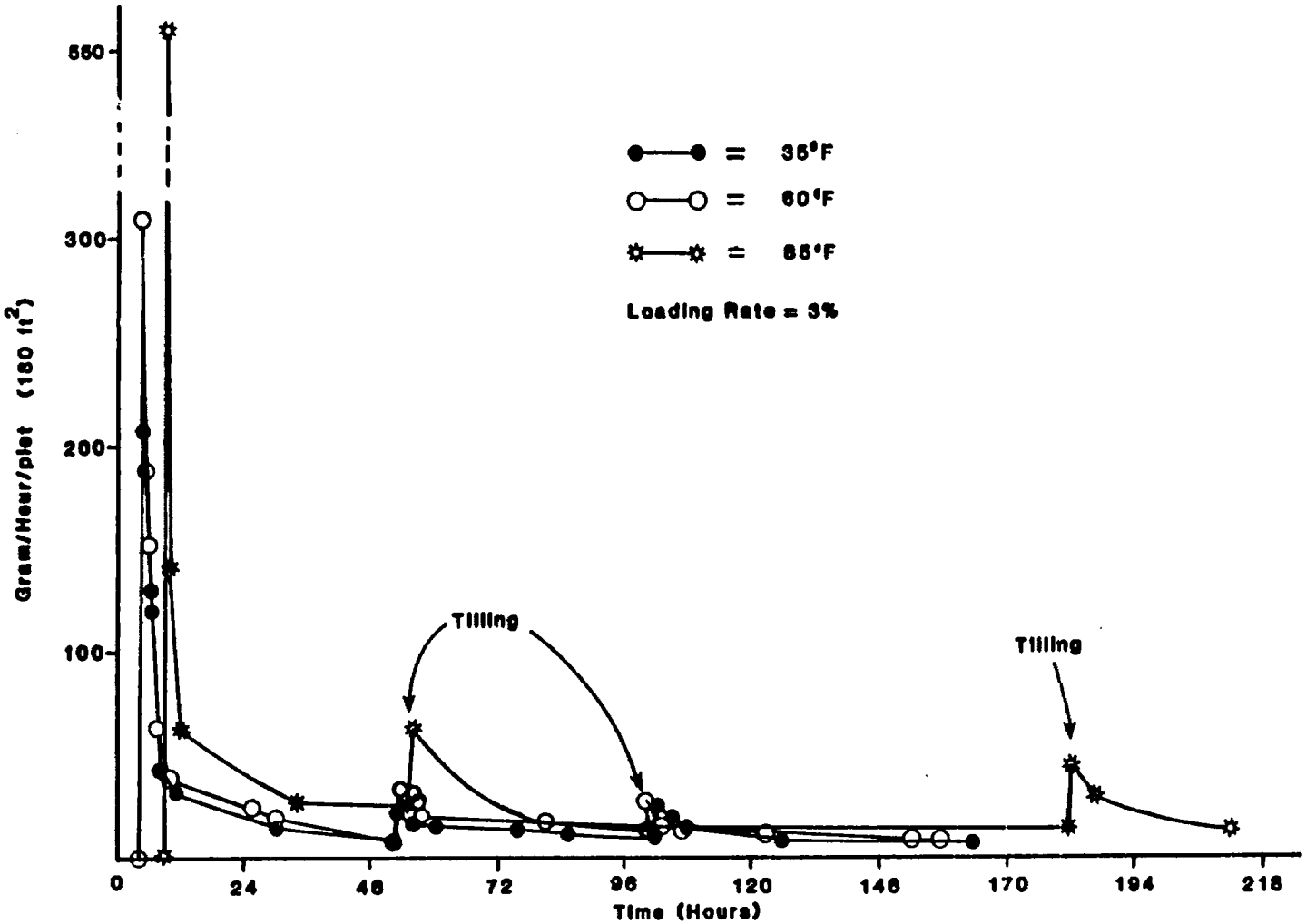


Figure 20 The Effect of Temperature on Emission at 3% Loading Rate

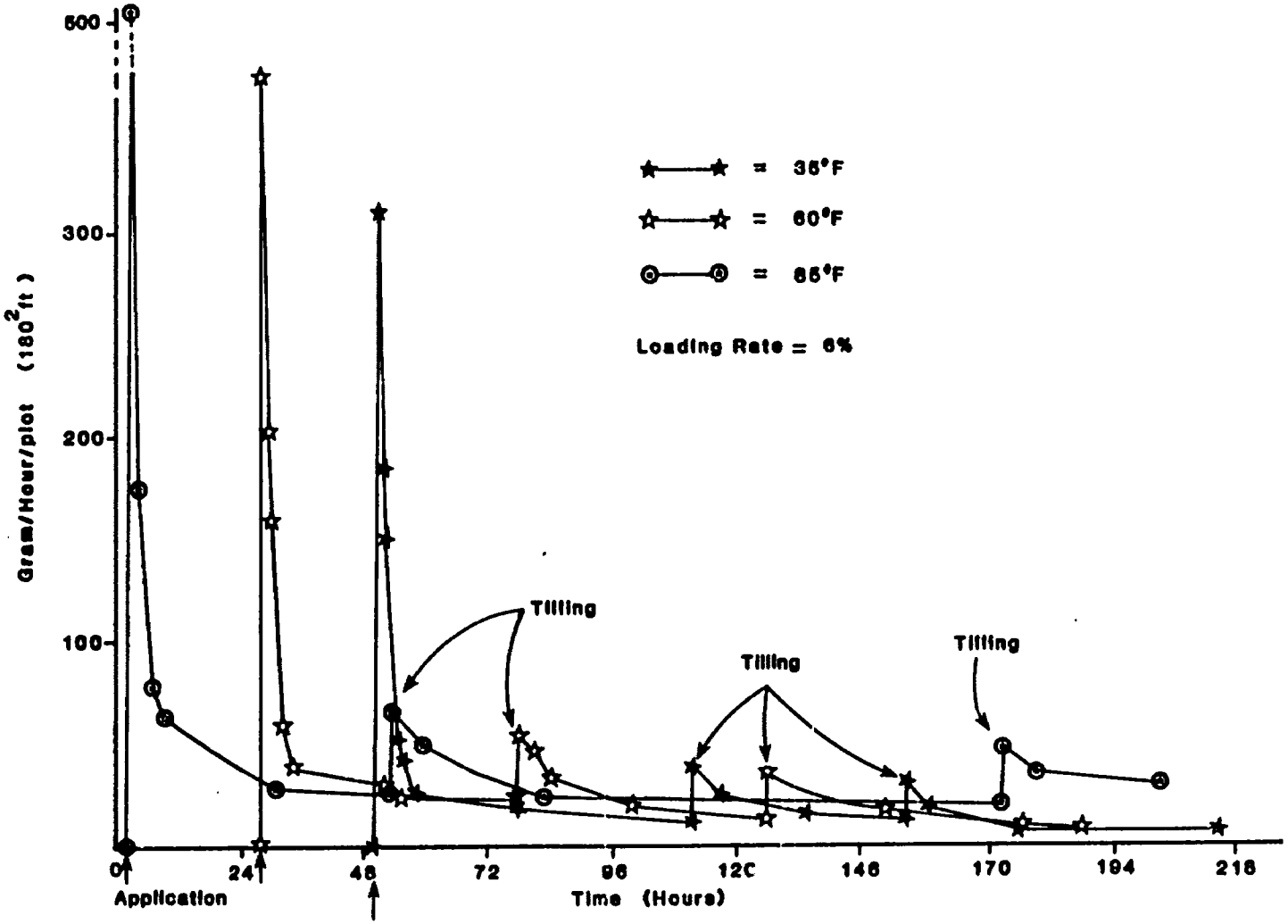


Figure 21 The Effect of Temperature on Emission at 6% Loading Rate

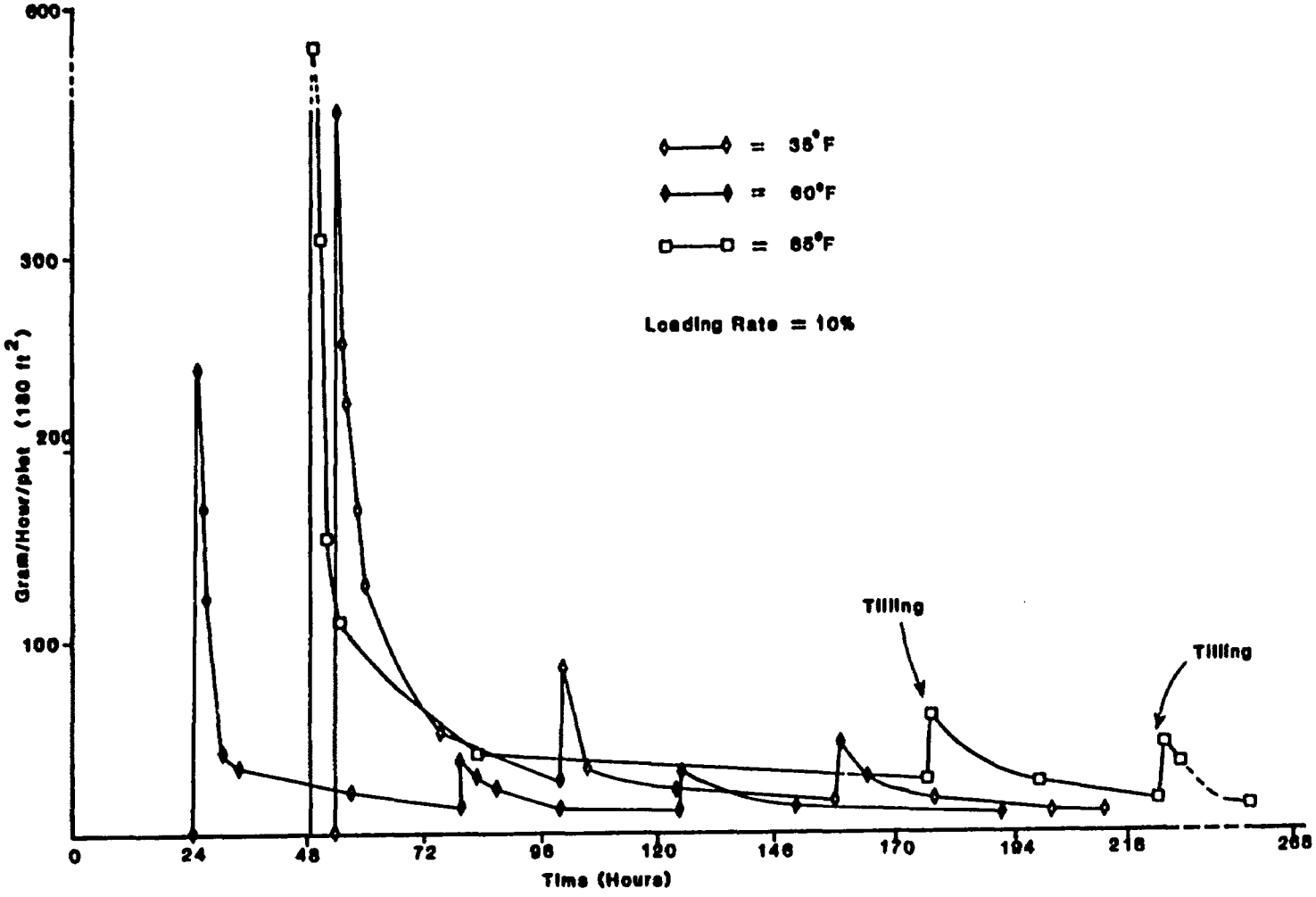


Figure 22 The Effect of Temperature on Emission at 10% Loading Rate

rates is shown in Figure 23.

The Effect of Relative Humidity on Emissions.

In all except two experiments, the relative humidity was maintained at 52 percent. Two experiments, one with 6 percent and the other with 10 percent loading rate, were made at 75 percent relative humidity. Soil temperature in these two studies was held at 60°F. The results of these experiments are given in Table A-2, Appendix A and Figure 24. As shown in Figure 24 there were slight differences in volatilization immediately after sludge application with increased relative humidity. However, later there was a marked decrease in the rate of emission. This is because of the fact that the initial rate of volatile loss of compounds from soil is primarily a function of the concentration of the volatiles at the surface. Once this initial reservoir is depleted, further loss depends on the rate at which additional chemicals diffuse through the soil column to the surface. Reduction of the humidity means that there is moisture loss from the surface of soil column, and this results in the movement of water to the surface of the soil column which may enhance the rate of migration to the surface; they are then lost by volatilization. Under saturated conditions diffussion will occur at a slow rate through the saturated soil column, and under unsaturated conditions compounds will volatilize from the soil-oil

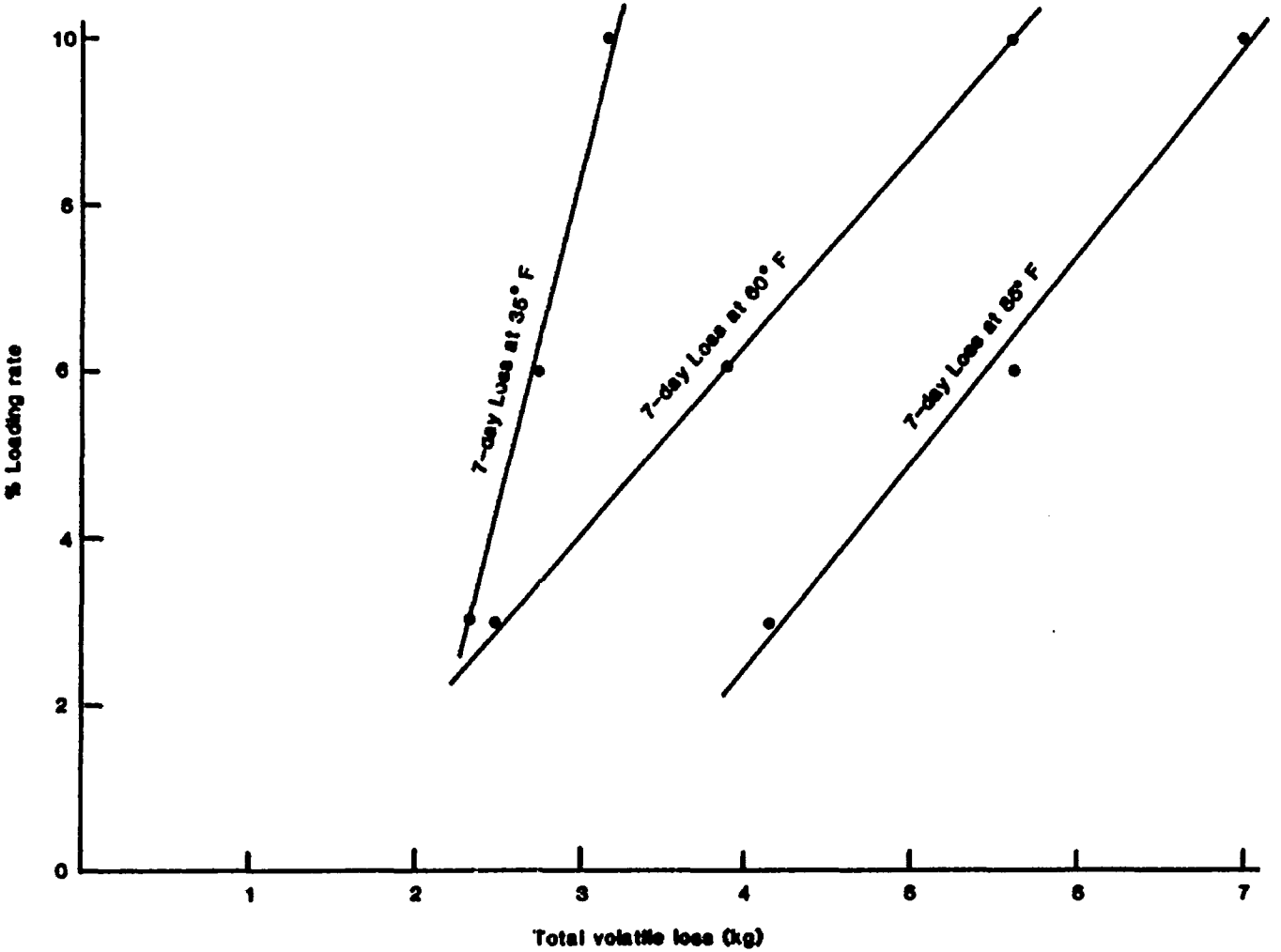


Figure 23 Total 7-Day Loss as a Function of Variable Temperatures and Loading Rates

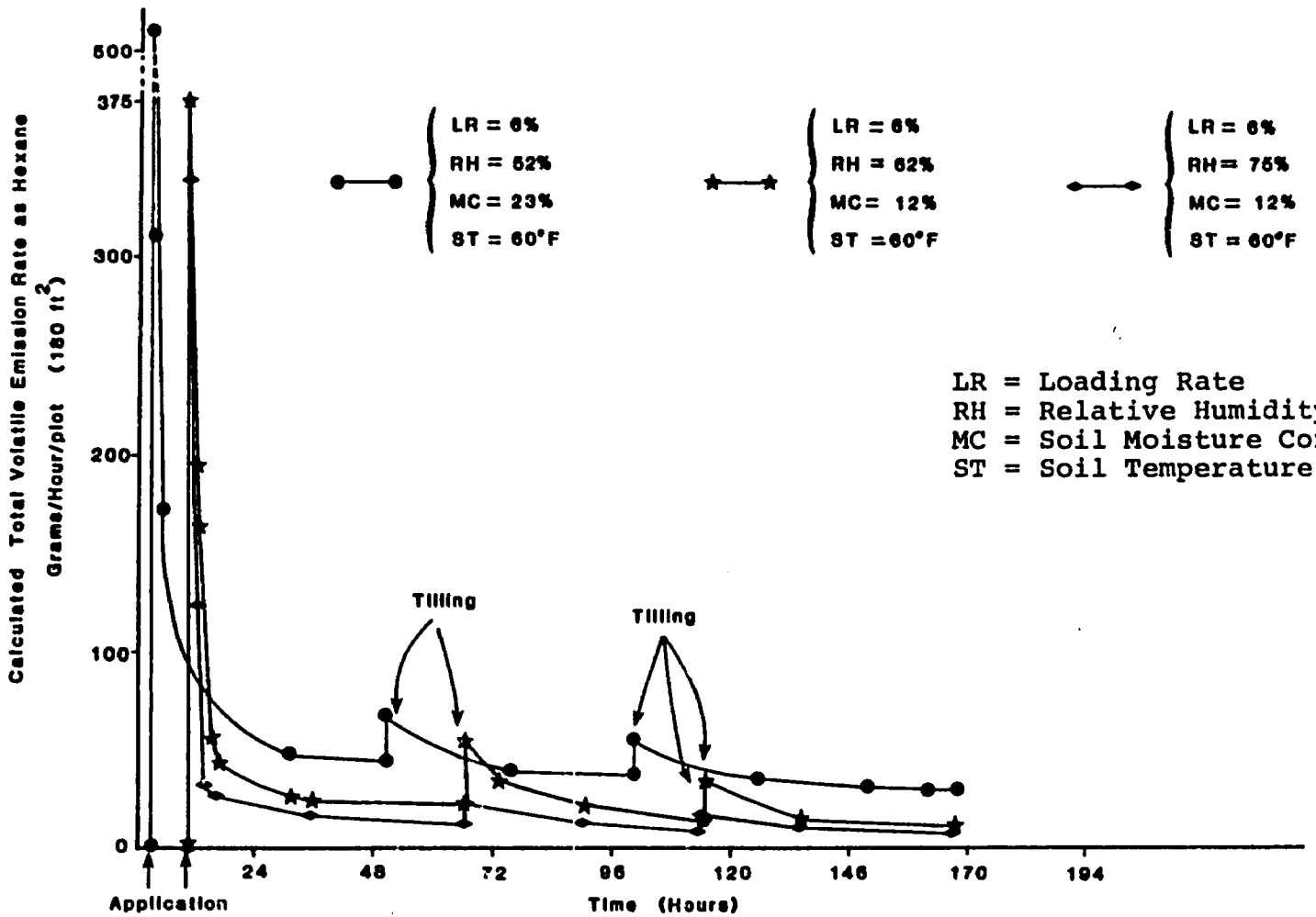


Figure 24 The Effect of Increased Relative Humidity and Moisture Content on Emission

surface and then diffuse as a gas through the soil atmosphere.

The Effect of Soil Moisture Content on Emissions.

All tests but one were run at 12 percent soil moisture content. One test was made at approximately 23 percent by weight soil moisture content. The loading rate and temperature were 6 percent and 60°F, respectively. As shown in Figure 24 and by the data in Table 22, soil moisture content appeared to have a pronounced effect on the emission rate and mass loss. These data (Table 22) suggest that as water content increases from 12 percent to 23 percent, the mass loss over a seven day period increased from 3.90 to 7.60 kg. The author hypothesizes that this increase was due to water saturation of the soil particle surfaces, thereby rendering the surfaces unavailable for the compounds. The wetter soil surface was much less permeable to the liquids in the sludge than dry surface.

The Effect of Tilling on the Rate of Emissions.

In the field the plots were tilled to ensure aerobic conditions for soil microorganisms and to enhance the biodegradation rate. To evaluate tilling effect on emission, in the laboratory the soil and sludge mixture was tilled two times, first on day three and then on day five after application. It was found that tilling initially increased the amount of volatilization for short periods

of time, but it was expected that release rate after an extended period of time was less with tilling than without tilling. The concentration after tilling was observed to be at least two times greater than before tilling. It was also observed that the increase in volatilization due to the first tilling was greater than that due to the second tilling. The effect of tilling is illustrated clearly in Figures 12, 13, 17-22 and 24.

Statistical Analysis of Data and Development of Model.

Data was analyzed for the purpose of constructing a 'model'. This model was to relate emission rate mathematically to variables such as soil temperature, soil moisture content, relative humidity and sludge loading rate.

The Statistical Analysis System (SAS) computer package was used to determine the significance of each variable. Within that package the multiple linear regression model was used to process the data. By this procedure, the parameters of the model were estimated on the basis of least-squares regression. For any multiple linear model, least-squares minimizes the residual sum of squares and provides an unbiased, linear estimate with minimum variance of parameters[22].

After the model was constructed by estimating the parameters of the regression line, the parameters were tested to make sure that they were significantly differ-

ent from zero[23]. The t-test was used to determine the significance of each of the coefficients. F-test was also used to determine the significance of the entire regression equation through the analysis of variance.

The backward elimination method and the coefficient of multiple correlation (R^2) were also used to select the best set of independent variables in the model by utilizing the following variables: loading rate, soil temperature, soil moisture content, relative humidity and time since application. In the backward elimination method the deletion of an independent variable is based on the result of an overall and partial F-test. The R^2 value is also calculated in each step and compared to each other. Finally, residual analyses were performed to provide information as to whether or not the suggested model meets the basic assumption of the regression technique[23].

An attempt was made to analyze field data and develop an appropriate model from these data. Nevertheless, while several sets of regression trials were made, the results were unacceptable. The effects of relative humidity and soil moisture content could not be evaluated and an appropriate model including all variables could not be developed. Therefore, regression analysis was made only on laboratory data.

Besides the previously mentioned variables, an attempt was made to include in the model such variables

as time since application, inverse of time (1/t) and several combinations of these variables. However, only loading rate, soil temperature, soil moisture content, relative humidity and time since application were found to affect significantly the emission rate. The others were screened out by utilizing backward elimination method, F-test and t-test.

The form of equation used in this study is as follows:

$$Y = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_5 X_5 + e$$

where:

Y = emission rate [g/hr],

β_o = intercept of X on Y axis [g/hr],

X_1 = percent loading rate [%],

X_2 = soil temperature [°F],

X_3 = soil moisture content [%],

X_4 = relative humidity [%],

X_5 = time since application [hr]

β_i = (i=1-4) regression coefficients which weigh the independent variables as their importance [(g/hr - %) or (g/hr - °F) or (g/hr - hr)]

e = residual term [g/hr].

Higher order models were also attempted, but no better results were found.

The model was first used in one step using the time from starting of application until the end of the test. The model found had an F-ratio of 17.51, and t-test

showed the coefficients of all independent variables except relative humidity to be significantly different from zero. Nevertheless, the coefficient of determination (R^2) was .44.

In an attempt to increase the value of the coefficient of determination (R^2), including all five variables in the model and fulfilling the basic assumption of the regression analysis, analyses were made in two steps:

1. when time <10 hours in which rapid decline of emission was observed.
2. when time >10 hours in which slow decline of emission was noted.

After several trials utilizing the new approach, the following two models were found to be the best of several:

Model I

Time <10 hours,

$$Y = 76.594 + 9.985X_1 + .769\ X_2 + 8.828\ X_3 - 2.025X_4 - 20.645\ X_5$$

$$R^2 = .830 \qquad F = 27.49$$

Model II

Time >10 hours,

$$Y = .184 + .931\ X_1 + .268\ X_2 + 1.879\ X_3 - .371\ X_4 - .084\ X_5$$

$$R^2 = .766 \qquad F = 49.83$$

Table B-1, in Appendix B, presents the detailed informa-

tion for both models.

Both models I and II are found to be significant from a statistical standpoint. Coefficient of determination (R^2) and F-ratios, are high and standard error of estimate in either model is low. Further, the signs of all regression coefficients in both models are correct. Also, the individual t-test for the regression coefficients (Table B-1, Appendix B) show a high degree of significance for the variables in the model. Negative signs for time since application and relative humidity show that these variables inversely affect the rate of emission of volatiles.

To check the validity of the basic assumption of the regression line, (linearity of the regression function, the constancy of the error variance, and the independency and normality of the error terms), residual analysis was made. This analysis did not show any reason to assume that there is violation of the basic assumption. Thus, these models were chosen for predictive purposes.

To correlate field data with laboratory data using models developed from laboratory data, two-hour, one-day, and seven-day losses were calculated utilizing average field conditions, i.e., soil temperature, relative humidity and soil moisture content at three different loading rates (3%, 6%, 10%).

The average loss from field plots for each loading

rate was also calculated from actual data reported on Table 19. Table 23 compares the losses of volatiles from actual field plots with data generated using predictive models.

Using linear regression, it was found that there was high correlation between the field results and the results obtained from predictive models. Figure 25 shows this relationship. Table 24 represents predicted laboratory data, predicted field data and actual field data.

Based on the above information, it was concluded that positive correlation exists between laboratory and field tests, and the predictive models developed from laboratory data can be used to estimate actual field losses.

Significance of Results from Standpoint of Air Pollution

The land treatment of petroleum sludge is a potential source of air pollution. To check the significance, the results are compared to National Air Quality Standards (CFR, Nov. 25, 1972). The primary and secondary standards for hydrocarbon for a 3-hour average in time was set 160 $\mu g/m^3$ in 1971 which was changed to 240 $\mu g/m^3$ in 1979.

To obtain pollution concentration on the land treatment area, the "box model"[24] was used. In this model the equilibrium concentration, C_e at a point s distant from

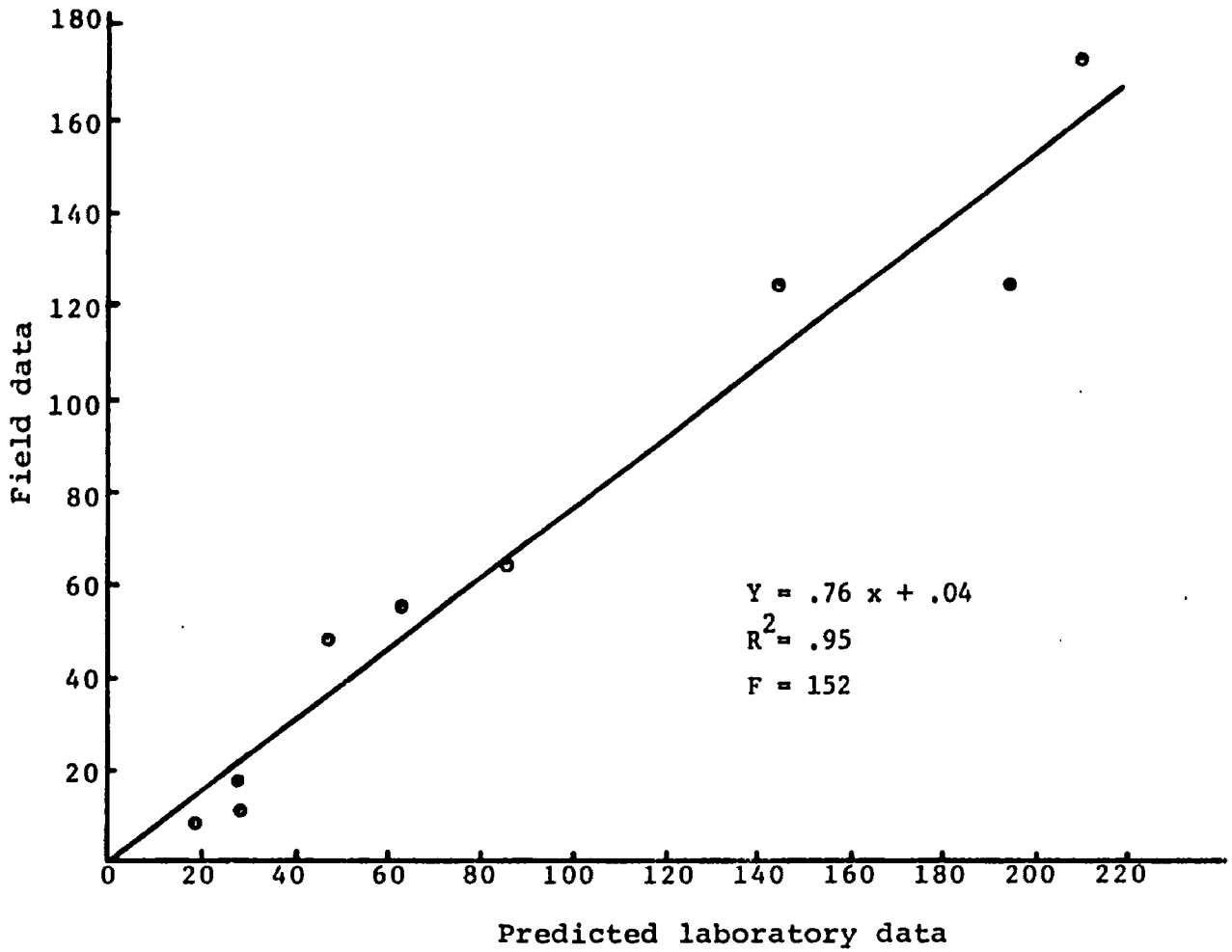


Figure 25 Relationship between field data and data obtained from predictive models.

Table 23 Total Volatile Losses from Field Plots and Predictive Models

Time Since Application	% Loading Rate					
	3		6		10	
	Loss (g/m^2)		Loss (g/m^2)		Loss (g/m^2)	
	Model	Field	Model	Field	Model	Field
1 hour*	18	8.86	27	11.2	29	18.23
1 day-*2 hour	48.5	47.6	63	57.90	86	63.99
7 day- 1 day	145	124.74	195	125.58	211.5	171.82

Table 24 Predicted Laboratory, Predicted Field and Actual Field Data

Time Since Application	% Loading Rate								
	3			6			10		
	Loss (g/m^2)			Loss (g/m^2)			Loss (g/m^2)		
	Predicted Lab	Predicted Field	Actual Field	Predicted Field	Predicted Field	Actual Field	Predicted Field	Predicted Field	Actual Field
2 hour*	18	13.72	8.86	27	20.56	11.2	29	22.08	18.23
1 day-*2 hour	48.5	36.22	47.6	63	47.92	57.90	86	65.4	63.99
7 day- 1 day	145	110.24	124.74	195	148.24	125.58	211.5	160.78	171.82

* First 2 hour loss was subtracted from 1 day loss and first day loss was subtracted from 7 day loss.

the upwind edge of the land treatment area is:

$$C_e = \frac{ys}{uz}$$

where:

y = rate of emission per unit time per unit area ($g/hr/m^2$) determined from statistical models developed in this study

s = length of the box, lies in the direction of the mean wind

u = average annual wind velocity in Oklahoma City

z = height of the box (average mixing height in Oklahoma City)

For the purpose of this study the following assumptions were made:

A total land treatment area of 10 acres was assumed

$s = \sqrt{4046.868} = 63.615$ m, (area was assumed to be square)

u = 13 miles/hour = 6.69 meters/sec in Oklahoma City

z_1 = 400 m, mean annual morning mixing height in Oklahoma City

z_2 = 1350 m, mean annual afternoon mixing height in Oklahoma City

Furthermore, the following average and extreme of the observed field conditions with 6% loading rate were used to determine the rate of emission from statistical models developed in this study:

Average Field Conditions		Extreme Field Conditions
soil moisture content	= 15%	27.4%

soil temperature	=	77°F	91°F
relative humidity	=	65%	54%
time since application	=	1.5 hrs	1.5 hrs
volatility of sludge	=	8.5%	8.5%

It is also assumed that oil was applied to only one acre each day over a 10 day period before sequence was repeated. Statistical Model I was used to calculate the emission rate from the last acre, 1.5 hours after application, and Model II was used to determine the emission rate from nine single previous applications for the other nine acres. The correlation model from Figure 25 ($Y = .76x + .04$) was then used to convert laboratory predicted rate to the field predicted rate of emission. The equilibrium concentration was calculated on the 10th day for each acre using Box model. The mean annual morning mixing height was used in this calculation. Table 25 presents the rate of emission and equilibrium concentration of hydrocarbons after sludge application from each single acre using average and extreme field conditions.

Assuming that pollutants were completely mixed over a 10 acre site, the equilibrium concentration above the total land treatment area was estimated 107.18 $\mu g/m^3$ at average field conditions and 234.22 $\mu g/m^3$ at extreme field conditions which is lower than Ambient Air Quality Standard (240 $\mu g/m^3$).

Assuming loading rate of 10%, and using extreme

Table 25 Rate of Emission and Equilibrium Concentration of Hydrocarbons after Sludge Application

Days After Appl.	Acre No.	Y = Rate of Emission Avg. Field Cond. ($g/hr/m^2$)	C_e = Equilibrium Concentration ($\mu g/m^3$)	Y = Rate of Emission Ext. Field Cond. ($\mu g/m^3$)
.0625 = 1.5 hr	10	7.56	49.92	14.04
1	9	1.32	8.72	2.74
2	8	1.28	8.45	2.65
3	7	1.14	7.53	2.56
4	6	1.04	6.87	2.47
5	5	0.96	6.34	2.38
6	4	0.87	5.75	2.29
7	3	0.78	5.15	2.20
8	2	0.69	4.56	2.12
9	1	0.59	3.89	2.02
		Total	107.18	234.22

field conditions, the equilibrium concentration was estimated 255.91 $\mu g/m^3$ which is sightly above the standard level.

Therefore, based on the above information, land treatment of petroleum sludge does not cause air pollution problems. If the process is operated properly, there is no need for a buffer zone unless the sludge is highly volatile (>8.5%), temperature and soil moisture content are high or loading rate is greater than 10%. Under these conditions it is preferable to apply (against the wind-ward direction) in the afternoon when mixing height is higher than in the morning.

Analysis of Gas Chromatographic Data

As previously discussed in Chapter 2, the air samples collected over sludge-laden plots were analyzed by gas chromatography (GC) using a flame ionization detector. Because of GC malfunctioning while conducting field studies, most of the samples collected from the field plots and some of the data were discarded. However, later, after the GC problems were resolved, many samples were taken from laboratory experiments and analyzed at appropriate times.

Of the volatile hydrocarbons identified, only fourteen were quantified. These target compounds along with their vapor pressures at 35°F, 60°F and 85°F and their

Table 26 Boiling Points and Vapor Pressures of Measured Compounds

Compound Name	Boiling Point °F	Vapor Pressure mm/Hg		
		35°F	60°F	85°F
Pentane	36.1	199.52	334.96	562.34
Cyclopentane	49.2	112.20	199.53	398.10
Hexane	69	47.32	94.41	177.82
Methylcyclopentane	72	47.32	94.41	177.82
Benzene	80.1	28.11	63.10	117.48
2,4-Dimethylpentane	80.5	31.62	63.10	117.48
Cyclohexane	80.7	26.61	53.09	112.20
3-Methylhexane	91.85	17.78	35.48	70.79
Methylcyclohexane	100.9	12.59	26.61	50.11
2,5-Dimethylhexane	109	6.68	14.96	31.62
2,3,4-Trimethylpentane	113.467	6.68	14.96	31.62
3-Methylheptane	118.925	4.47	10.59	23.71
2,2,5-Trimethylhexane	124.084	4.47	10.00	19.95
1,4-Dimethylbenzene	138.351	1.496	3.98	10.00

boiling points are presented in Table 26 according to increasing boiling points or decreasing vapor pressures. Besides these compounds, other compounds such as propanol, 2-propanone, 2-butanone, 2-pentanone, cyclohexanol, ethylcyclopentane, 2-methyl-1-pentanol and 1,1-Dimethylcyclopentan, were identified by GC-MS in the RSKERL laboratory, in Ada, Oklahoma.

Tables C-1 through C-9 in Appendix C summarize data on all of the pollutants measured during the nine laboratory studies. The data in these tables are grouped according to three different temperatures and three different loading rates. In addition, Table C-10 presents data from field experiments.

Much of the information in Tables C-1 through C-10 is self-explanatory, so only salient observations will be made here.

The above mentioned tables provide information on emission rates at different times following sludge application at three temperatures and three loading rates. They also show emission rates due to the tilling. Included in the tables are total emission rates of the fourteen compounds at each time with the corresponding total volatile emission rates measured as hexane. In addition, the percentage ratio of the fourteen hydrocarbons from GC analyses to the total volatile hydrocarbons measured at the same time with TLV Sniffer

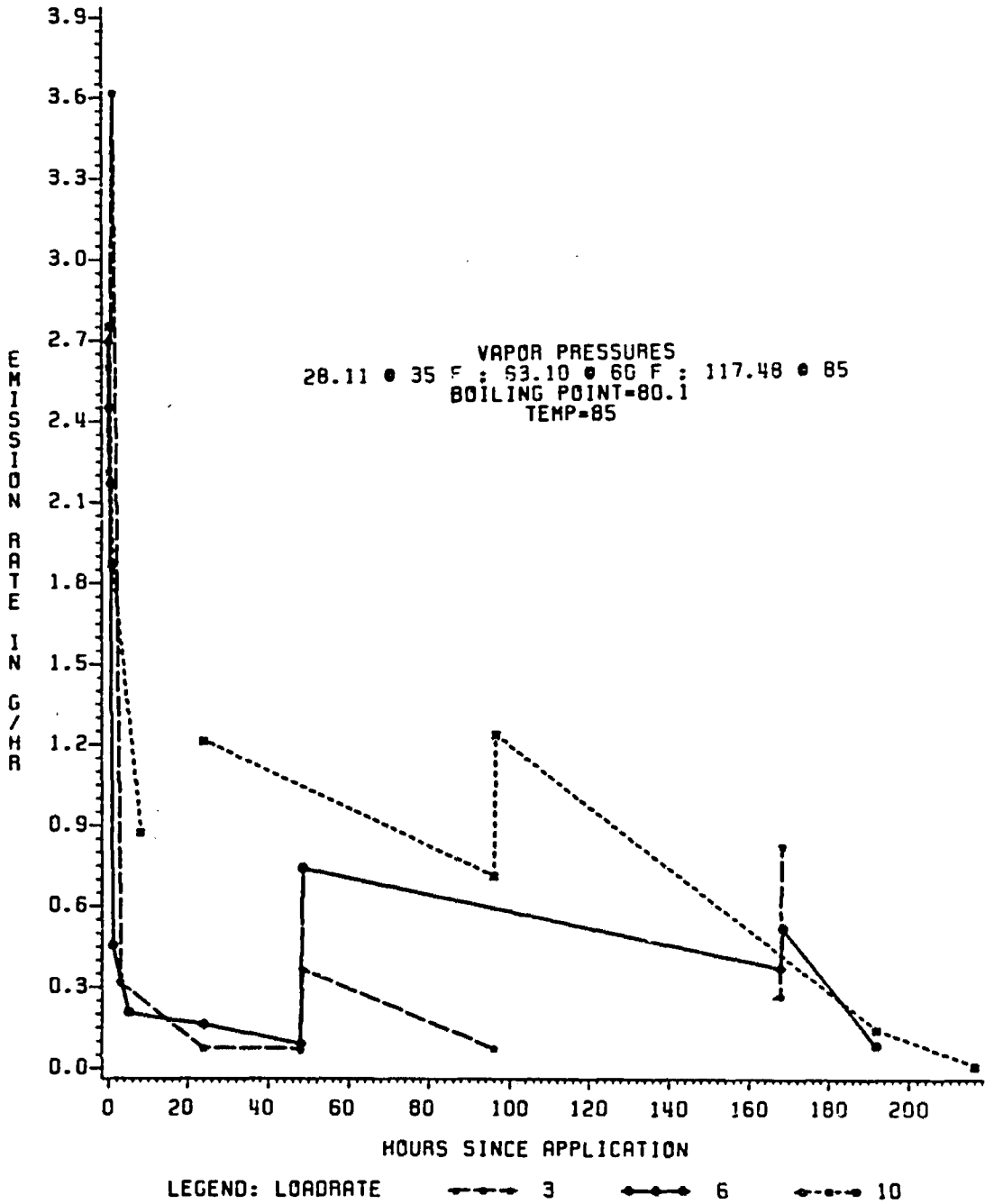


Figure 26 Time Relation of Emission Rate and Loading Rate-Benzene

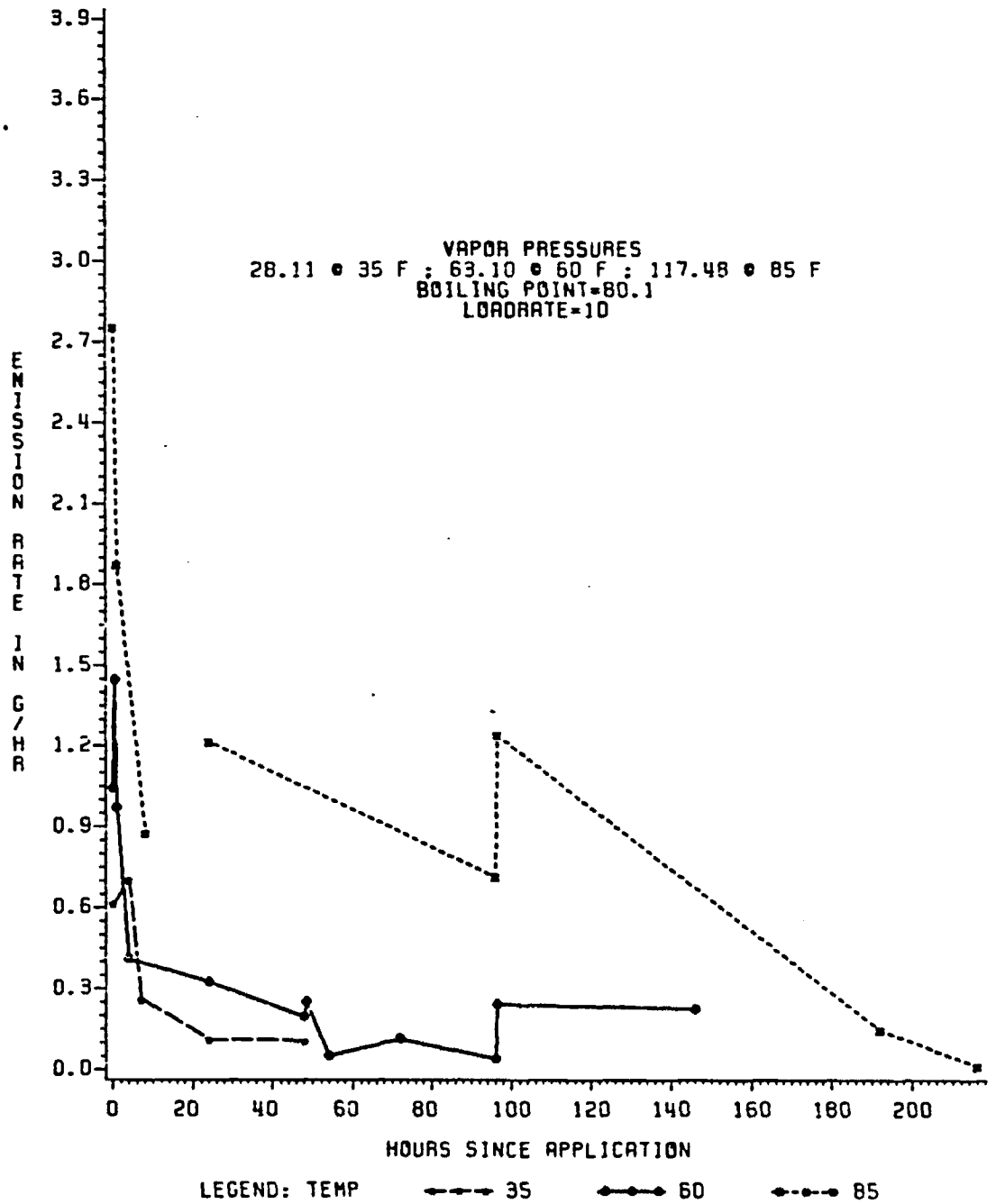


Figure 27 Time Relation of Emission Rate and Temperature-Benzene

is presented.

Figure 26 shows the time relationship between emission and loading rate at 85°F for benzene, and Figure 27 demonstrates the relationship of emission rates and temperature at 10% loading rate for benzene. Also Figures C-1 through C-16 in Appendix C illustrate the time-concentration curves for other compounds.

As it is clear from these figures, the rate of emission of each hydrocarbon increased with increasing temperature and loading rate. For exact emission rates see Tables C-1 through C-9.

Tables C-1 through C-10, show that compounds having low boiling points and high vapor pressures, such as pentane, cyclopentane, methylcyclopentane and hexane, had lower emission rates than high boiling point and low vapor pressure compounds. This was related to the fact that high vapor pressure hydrocarbons had already been vaporized during transportation and storage of sludge. Analysis of air samples taken above the sludge sample confirmed this idea.

The higher emission rates were found among the hydrocarbons with boiling point ranges from 70 to 119°C. Among these hydrocarbons 2,3,4-Trimethylpentane, with a boiling point of 113.467°C, had the highest rate. The next highest rates pertained to 2,4-Dimethylpentane and 3-Methylheptane, respectively.

It was observed that the emission rates of all hydrocarbons decreased with time. In some cases, the opposite trends were seen (cyclopentane and pentane); the emission rate was low immediately after application, and it increased for 10 to 60 minutes, and decreased, thereafter, and then followed the pattern of other compounds.

It was further found that, in general, the hydrocarbons identified immediately after sludge application were also identified several months later, but their relative emission rates were much lower.

It is clear from Tables C-1 through C-9 and corresponding figures that tilling increased the release rate of each compound. Figures 28 and 29 show before- and after-tilling concentrations of each compound. Air samples which produced these chromatograms were taken from plot 4 on April 1983, which had received sludge on November 17, 1982.

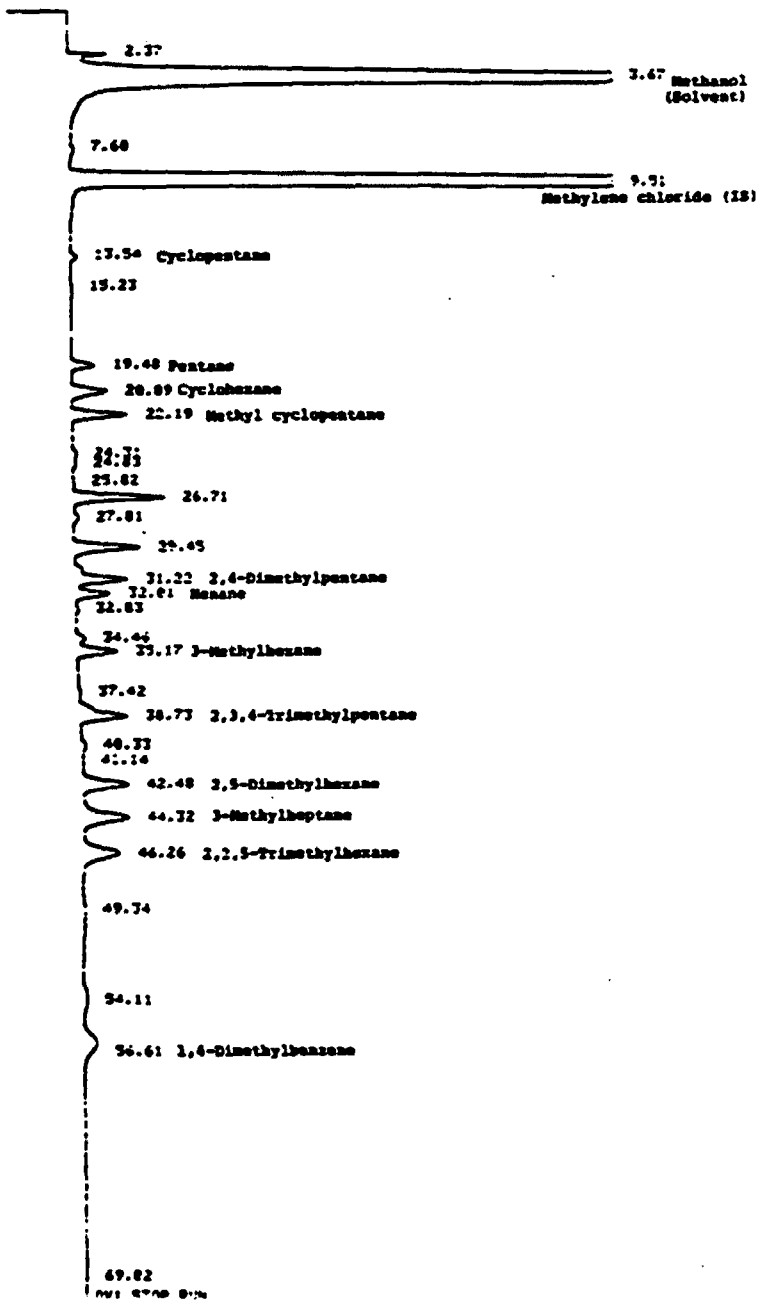


Figure 28 Chromatogram of Air Sample Taken from Plot 4 (before tilling)

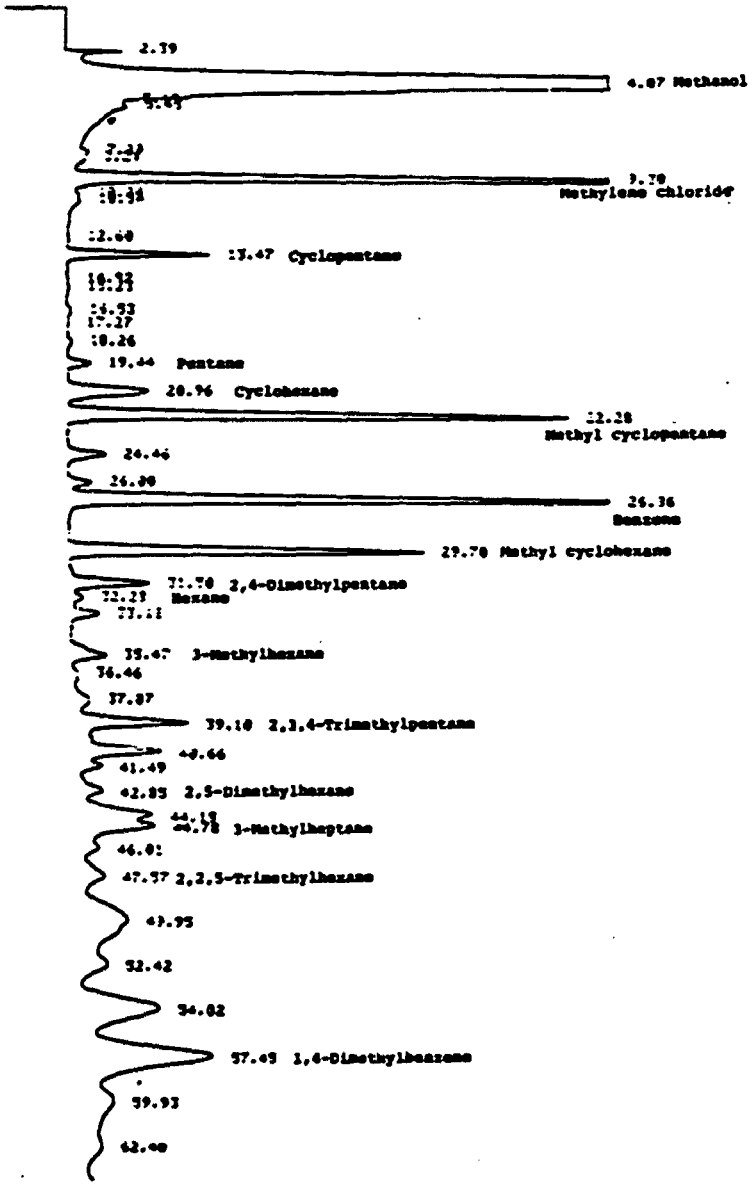


Figure 29 Chromatogram of Air Sample Taken from Plot 4 (after tilling)

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

Land application of petroleum residues is not new; however, there is a paucity of data on volatile organic emission to the atmosphere. The overall objective of this exploratory investigation was to develop an economically feasible method to determine the rate and magnitude of volatile hydrocarbon emissions from land treatment of petroleum residues. The effects of several parameters such as sludge loading rate, soil temperature, soil moisture content and relative humidity on emission rates were evaluated.

Experiments were conducted in the field and laboratory. The emission of volatiles was evaluated using two methods. Total volatiles were monitored with a TLV Sniffer. Individual hydrocarbons were identified and quantified by concentrating air over the plots on adsorbent tubes and analyzing them by gas chromatography (GC) using flame ionization detector and by gas chromatography mass spectrometery (GC-MS).

A multiple regression analysis was used to develop a

predictor model for estimating the rate of emission of volatiles being emitted to the atmosphere. Soil temperature, soil moisture content and sludge loading rate were found to have positive effects on emission while relative humidity and time had negative effects.

The results and conclusions of this study provide information which can be used for evaluation and development of land treatment operation of petroleum sludges.

CONCLUSIONS

As a result of this investigation the following conclusions are drawn:

1. The land treatment of petroleum sludge does not present air pollution problems if it is operated properly.
2. The volatility of sludge is the most important parameter in evaluating the emission rates from land treatment of petroleum sludges. If the volatility of sludge is too high, it may be necessary to strip the volatiles in a controlled system prior to application.
3. The stripping tests used in this study measure the volatility of sludge and estimates weight loss of individual sludge components due to volatilization from land treatment operations.
4. The emission rates from land treatment of sludge are

affected by soil moisture content. High moisture content increases the volatile emissions. Therefore, soil moisture content must be high enough to achieve optimum conditions for microbial degradation of oily wastes yet as low as possible to minimize the emissions of volatiles to the atmosphere.

5. Sludge loading rate and soil temperature were identified as being statistically important to the emissions of volatiles to the atmosphere. The higher the loading rate and temperature, the higher was the emission rate.
6. Relative humidity and time since application both have inverse relationship with the emission rate.
7. Tilling increased the rate of volatilization drastically. The ratio of volatilization to biological oxidation can be minimized by maximizing the depth of plowed zone as long as the soil is not completely saturated with water. This will result in lower biodegradation rates but will decrease the volatilization rate even more. Subsurface injection and subsurface tilling are also other alternatives which can minimize the emission rate.
8. Positive correlation between laboratory and field tests was achieved.
9. Analyses of air samples using purge and trap and gas

chromatography permitted the identification and quantification of fourteen individual hydrocarbons. All compounds decreased in concentration with time. The higher concentrations were found among the hydrocarbons with boiling point ranges from 70 to 119°C. The highest concentration was 2,3,4-Trimethylpentane

10. Two statistical models were developed to relate emission rate to the previously mentioned variables: first, when time since application was less than 10 hours and there was a rapid decline of emission; second, when time since application was greater than 10 hours and there was slow and almost constant decline in the volatile loss.
11. The results indicate that from 518.59 kg sludge applied to plot 7 (loading rate - 6%), the total percentages of losses of sludge in two hours, one day, seven days, and 152 days from application were estimated at .18, 1.11, 3.14 and 7.26, respectively.

RECOMMENDATIONS

Based on the results of this study, the following recommendations are made:

1. The effect of soil moisture content, relative humidity and sludge volatility should be further evaluated. Tests should be conducted in the laboratory in controlled environmental conditions.

2. Research is needed to evaluate the effect of soil porosity and adsorption characteristics of the soil on the rate of emission.
3. An unacceptably high fraction of volatile hydrocarbons remains unidentified and unquantified. Additional research efforts, especially with capillary columns and GC-MS, should be conducted to overcome this problem.
4. Specific hydrocarbon species are toxic; further investigation of the evaporation losses and identification of these compounds are recommended to insure that no obnoxious or toxic substances enter the environment.
5. Research is also needed in the area of control measurements.
6. A substantial area for future work involves continuing the laboratory studies that are investigating the validation and verification of the procedure used in this study.

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APPENDIX A

Emission Rates Data for Field and Laboratory Experiments

Table A-1 Calculated Emission Rates of Total Volatile Hydrocarbons for Field Experiments

Date of Sampling	Plot No.	Nominal Loading Rate (%)	Sampling Status	Rate of Emis.* (g/hr)	Vola. of Slud. (%)	Soil Mois. Cont. (%)	Soil Temp. (°F)	Rela. Humid. (%)
07/19/82	1	13	AT	7.90	.	.	90	57
07/19/82	1	13	AA1	118.47	.	.	91	54
07/19/82	1	13	IAT,AA	98.89	.	27.4	91	54
07/20/82	1	13	BETA	24.57	.	.	90	57
07/21/82	1	13	BETA	14.50	.	.	85	58
08/02/82	1	13	BETA	11.70	.	.	92	58
08/17/82	1	13	BT	7.90	.	.	87	66
08/17/82	1	13	AT	13.16	.	.	87	66
08/17/82	1	13	AA2	39.89	8	.	86	65
08/17/82	1	13	5AA	21.45	.	24.9	87	66
08/17/82	1	13	IAT,AA	19.50	.	24.9	91	76
08/17/82	1	13	2CAT,AA	19.50	.	24.9	91	76
08/26/82	1	13	BETA	12.43	.	20.5	87	35
08/31/82	1	13	BETA	11.70	.	20.0	84	38
09/01/82	1	13	AT	19.25	.	18.1	93	20
09/02/82	1	13	9CAT	16.33	.	17.5	91	21
09/09/82	1	13	12CAT	15.68	.	15.4	91	48
09/10/82	1	13	BETA	11.70	.	.	76	49
09/10/82	1	13	AA3	35.10	8	.	76	56
09/10/82	1	13	IAT,AA	40.22	.	.	84	85
09/11/82	1	13	BETA	19.83	.	.	86	62
09/21/82	1	13	BETA	13.16	.	.	87	61
10/07/82	1	13	BT	10.81	.	.	85	40
10/07/82	1	13	AT	17.55	.	.	90	45
10/14/82	1	13	BETA	11.70	.	.	84	60
10/14/82	1	13	BETA	18.65	.	.	84	61
10/14/82	1	13	AA4	409.52	14	.	84	62
10/14/82	1	13	IAT,AA	190.14	.	29.7	83	73
10/15/82	1	13	BETA	57.51	.	.	80	65
10/17/82	1	13	BETA	25.26	.	.	79	66
10/21/82	1	13	BT	16.09	.	23.1	75	55
10/21/82	1	13	AT	39.49	.	24.0	76	71
10/26/82	1	13	BETA	11.70	.	21.0	72	31
11/02/82	1	13	BT	11.70	.	.	69	35
11/02/82	1	13	AT,BA	38.66	.	.	68	38
11/02/82	1	13	AA5	367.69	13	.	69	77
11/02/82	1	13	IAT,AA	402.51	.	.	77	85
11/02/82	1	13	2HA,AT	325.15	.	.	77	85
11/02/82	1	13	4HA,AT	255.26	.	.	77	84
11/02/82	1	13	6HA,AT	199.28	.	.	77	84
11/03/82	1	13	BETA	65.01	.	.	75	80
11/05/82	1	13	BETA	29.25	.	.	68	61
11/09/82	1	13	BETA	26.33	.	.	65	58
11/17/82	1	13	BT	10.82	.	28.8	50	60
11/17/82	1	13	AT	15.15	.	28.8	55	84
11/17/82	1	13	AA6	72.57	9	.	55	84
11/17/82	1	13	3CAT,AA	62.77	.	.	50	85
11/17/82	1	13	4HAAA,A	35.11	.	.	50	82
11/18/82	1	13	24HA,AA	15.13	.	.	51	70
11/24/82	1	13	BETA	5.85	.	.	44	50
12/20/82	1	13	BETA	3.21	.	.	41	43
07/20/82	6	13	BA	7.90	.	.	90	56
07/20/82	6	13	AA1	112.60	.	.	90	56
07/20/82	6	13	AT,AA	98.87	.	.	90	56
07/21/82	6	13	BETA	24.57	.	.	81	55
07/25/82	6	13	BETA	11.90	.	.	82	50
08/26/82	6	13	BETA	5.12	.	17.3	91	36
08/19/82	6	13	BETA	5.12	.	17.2	105	36
08/10/82	6	13	BETA	5.12	.	17.0	105	63

(continued)

Table A-1 Calculated Emission Rates of Total Volatile Hydrocarbons for Field Experiments (continued)

Date of Sampling	Plot No.	Nominal Loading Rate (%)	Sampling Status*	Rate of Emis. (g/hr)	Vola. of Slud. (%)	Soil Mois. Cont. (%)	Soil Temp. (°F)	Rela. Humid. (%)
08/10/82	6	13	BETA	11.70	.	18.4	106	68
08/17/82	6	13	BETA	11.70	.	.	87	65
08/17/82	6	13	AA2	35.89	8	.	89	72
08/17/82	6	13	1.5HRAT	21.45	.	23.9	89	71
08/26/82	6	13	BETA	6.82	.	20.5	92	39
08/31/82	6	13	BETA	6.82	.	19.0	89	31
09/01/82	6	13	.5HR AT	18.28	.	18.1	94	31
09/02/82	6	13	1.5HR A	15.67	.	17.7	94	31
09/09/82	6	13	BETA	6.65	.	.	88	52
09/09/82	6	13	1.5 AT	17.55	.	.	88	53
09/10/82	6	13	AA3	35.10	8	.	82	60
09/10/82	6	13	IAT,AA	40.22	.	.	82	60
09/11/82	6	13	BETA	19.83	.	.	86	61
09/21/82	6	13	BETA	13.16	.	.	87	62
10/07/82	6	13	BETA	10.24	.	.	88	45
10/07/82	6	13	IAT,BA	13.16	.	.	88	52
10/14/82	6	13	BETA	9.51	.	.	80	35
10/14/82	6	13	IAT,BA	13.16	.	.	81	37
10/14/82	6	13	AA4	398.90	.	.	80	81
10/14/82	6	13	IAT,AA	116.99	14	22.4	80	81
10/15/82	6	13	BETA	45.67	.	22.1	80	81
10/17/82	6	13	BETA	24.82	.	.	69	60
10/21/82	6	13	BETA	14.62	.	.	66	58
10/21/82	6	13	BA,AT	39.48	.	.	65	58
10/26/82	6	13	BT	11.70	.	.	70	59
11/02/82	6	13	BA	10.23	.	.	65	60
11/02/82	6	13	AT	34.59	.	.	65	62
11/02/82	6	13	IAA,BT	387.83	13	.	69	77
11/02/82	6	13	IAT,AA	401.30	.	.	69	85
11/03/82	6	13	BETA	64.58	.	.	59	75
11/05/82	6	13	BETA	29.95	.	.	62	78
11/09/82	6	13	BT	23.40	.	.	69	80
11/17/82	6	13	BT	11.70	.	28.5	50	60
11/17/82	6	13	AT,BA	13.65	.	28.5	53	65
11/17/82	6	13	AA	69.90	.	.	52	86
11/17/82	6	13	IAT,AA	54.59	9	.	50	86
11/24/82	6	13	BT	5.85	.	.	44	50
12/20/82	6	13	BT	3.90	.	.	40	49
07/13/82	5	10	BA	4.39	.	.	95	60
07/13/82	5	10	AT,BA	11.70	.	.	95	60
07/13/82	5	10	AA	98.51	.	.	95	62
08/06/82	5	10	BT,BA	5.85	.	.	104	23
08/10/82	5	10	BT,BA	4.39	.	.	96	62
08/10/82	5	10	IAT,BA	11.70	.	18.7	97	68
08/12/82	5	10	BT,BA	5.12	.	.	97	63
08/12/82	5	10	IAA	66.55	9	.	102	64
08/12/82	5	10	IAT,AA	38.39	.	20.1	102	54
08/26/82	5	10	BT	7.80	.	.	95	39
08/31/82	5	10	BT	5.85	.	.	97	38
09/01/82	5	10	IAT,BA	23.16	.	.	96	45
09/12/82	5	10	IAT	17.55	.	.	83	67
09/09/82	5	10	BT	5.85	.	.	60	38
09/09/82	5	10	IAT,BA	14.63	.	10.5	89	72
09/23/82	5	10	BT,BA	5.85	.	15.7	63	40
09/23/82	5	10	IAT,BA	12.40	.	.	59	41
09/23/82	5	10	IAA,BT	394.80	14	.	72	60
09/23/82	5	10	IAT,AA	453.40	.	.	74	67
09/23/82	5	10	2HR AA	268.12	.	.	74	65
09/23/82	5	10	4HR AA	179.40	.	.	74	65

(continued)

Table A-1 Calculated Emission Rates of Total Volatile Hydrocarbons for Field Experiments (continued)

Date of Sampling	Plot No.	Nominal Loading Rate (%)	Sampling* Status	Rate of Emis. (g/hr)	Vola. of Slud. (%)	Soil Mois. Cont. (%)	Soil Temp. (°F)	Rela. Humid. (%)
09/24/82	5	10	BETA	61.24	.	.	70	.
09/26/82	5	10	BETA	31.17	.	.	75	58
10/07/82	5	10	BT	17.55	.	.	84	56
10/07/82	5	10	IAT,BA	61.43	.	16.2	91	58
10/12/82	5	10	BT,BA	11.70	.	.	90	59
10/12/82	5	10	IAT,AA	175.51	13	.	91	62
10/21/82	5	10	BT,BA	16.09	.	.	73	37
10/21/82	5	10	IAT,BA	51.19	.	.	73	61
10/26/82	5	10	BT,BA	16.95	.	.	64	39
11/02/82	5	10	BT,BA	16.09	.	.	66	45
11/02/82	5	10	AT,BA	23.84	.	.	67	46
11/02/82	5	10	SAA,BT	248.64	13	.	67	79
11/02/82	5	10	6OAT	162.35	.	.	75	56
11/02/82	5	10	2HA AT	107.12	.	.	75	64
11/02/82	5	10	4HA AT	71.29	.	.	76	64
11/03/82	5	10	BETA	45.21	.	.	78	70
11/05/82	5	10	BETA	27.89	.	.	73	71
11/09/82	5	10	BT,BA	16.09	.	.	69	65
11/09/82	5	10	IAT,BA	24.13	.	.	69	68
11/17/82	5	10	BT	10.01	.	.	64	68
11/17/82	5	10	AT,BA	32.99	.	.	64	88
11/17/82	5	10	IAT,AA	101.74	12	.	64	92
11/17/82	5	10	2HA AA	63.21	.	.	65	85
11/17/82	5	10	4HA AA	41.24	.	.	65	85
11/18/82	5	10	BETA	14.98	.	.	53	72
11/24/82	5	10	BT,BA	6.83	.	.	49	43
12/20/82	5	10	BT,BA	3.90	.	.	51	31
07/20/82	7	6	BT,BA	3.22	.	.	73	44
07/20/82	7	6	IAA,BT	60.24	.	.	89	37
07/20/82	7	6	IAT,AA	53.24	.	.	88	40
08/05/82	7	6	BT,BA	5.85	.	.	107	25
08/06/82	7	6	BT,BA	5.85	.	.	98	24
08/10/82	7	6	BT,BA	3.90	.	.	96	58
08/10/82	7	6	3OAT,BA	7.80	.	20.7	97	60
08/17/82	7	6	BT,BA	3.90	.	.	80	50
08/17/82	7	6	AT,BA	7.80	.	.	80	50
08/17/82	7	6	AA	27.30	8	.	82	54
08/17/82	7	6	IAT,AA	18.53	.	18.4	85	74
08/26/82	7	6	BT,BA	5.85	.	.	87	33
09/31/82	7	6	BT,BA	5.85	.	.	89	31
09/01/82	7	6	AT,BA	23.40	.	.	90	26
09/02/82	7	6	3OAT,BA	17.55	.	.	86	51
09/09/82	7	6	18OAT	13.16	.	6.9	85	58
09/23/82	7	6	BA	5.85	.	.	72	51
09/23/82	7	6	AA	350.09	14	.	72	51
09/23/82	7	6	IAA,AT	385.95	.	.	72	51
10/07/82	7	6	BA	11.85	.	.	82	56
10/07/82	7	6	IAT,BA	17.55	.	14.3	82	58
10/12/82	7	6	BT,BA	5.85	.	.	73	58
10/12/82	7	6	IAT,AA	1170.07	14	.	74	59
10/21/82	7	6	BT,BA	11.70	.	.	62	36
10/21/82	7	6	AT,BA	36.56	.	.	63	63
10/26/82	7	6	BT,BA	7.31	.	.	62	37
11/02/82	7	6	BT,BA	4.33	.	.	59	37
11/09/82	7	6	BT,BA	4.33	.	.	69	39
11/17/82	7	6	BT,BA	4.33	.	15.7	52	89
11/17/82	7	6	AT,BA	15.15	.	15.7	47	86
11/17/82	7	6	AA,BT	67.10	9	.	50	93
11/17/82	7	6	6OAT,AA	29.14	.	.	50	83

(continued)

Table A-1 Calculated Emission Rates of Total Volatile Hydrocarbons for Field Experiments (continued)

Date of Sampling	Plot No.	Nominal Loading Rate (%)	Sampling* Status	Rate of Emis. (g/hr)	Vola. of Slud. (%)	Soil Mois. Cont. (%)	Soil Temp. (°F)	Rela. Humid. (%)
11/24/82	7	6	BT,BA	5.85	.	.	[illegible]	[illegible]
12/20/82	7	6	BT,BA	2.93	.	.	[illegible]	[illegible]
07/13/82	4	3	BT,BA	3.22	.	.	[illegible]	[illegible]
07/13/82	4	3	AA	35.57	.	.	[illegible]	[illegible]
07/13/82	4	3	IAT	24.57	.	.	[illegible]	[illegible]
08/09/82	4	3	BT,BA	5.85	.	.	[illegible]	[illegible]
08/10/82	4	3	AT,BA	14.62	.	27.0	[illegible]	[illegible]
08/13/82	4	3	AA,BT	42.90	8	.	[illegible]	[illegible]
08/13/82	4	3	AT,AA	30.22	.	17.0	[illegible]	[illegible]
08/25/82	4	3	BT,BA	2.92	.	.	[illegible]	[illegible]
08/31/82	4	3	BT,BA	2.92	.	.	[illegible]	[illegible]
09/09/82	4	3	BT,BA	2.92	.	.	[illegible]	[illegible]
09/09/82	4	3	20AT,BA	14.62	.	6.3	[illegible]	[illegible]
09/23/82	4	3	BT,BA	3.80	.	13.4	[illegible]	[illegible]
09/23/82	4	3	AT,BA	12.64	.	13.9	[illegible]	[illegible]
09/23/82	4	3	AT,AA	190.11	14	.	[illegible]	[illegible]
10/07/82	4	3	BT,BA	5.85	.	.	[illegible]	[illegible]
10/07/82	4	3	AT,BA	16.09	.	11.5	[illegible]	[illegible]
10/12/82	4	3	BT,BA	4.39	14	.	[illegible]	[illegible]
10/12/82	4	3	60AA	116.99	14	.	[illegible]	[illegible]
10/12/82	4	3	AT,AA	51.18	14	.	[illegible]	[illegible]
10/21/82	4	3	AT,BA	21.20	14	.	[illegible]	[illegible]
10/22/82	4	3	BT,BA	13.16	14	.	[illegible]	[illegible]
10/26/82	4	3	BT,BA	4.39	14	.	[illegible]	[illegible]
11/02/82	4	3	BT,BA	4.39	14	.	[illegible]	[illegible]
11/02/82	4	3	AT,BA	12.64	14	.	[illegible]	[illegible]
11/02/82	4	3	15AA,BT	233.98	13	.	[illegible]	[illegible]
11/02/82	4	3	35AT,AA	145.09	13	.	[illegible]	[illegible]
11/09/82	4	3	BT,BA	8.66	13	.	[illegible]	[illegible]
11/09/82	4	3	AT,BA	15.15	13	.	[illegible]	[illegible]
11/17/82	4	3	BT,BA	5.85	13	.	[illegible]	[illegible]
11/17/82	4	3	AT,BA	12.99	13	13.3	[illegible]	[illegible]
11/17/82	4	3	AT,AA	32.48	9	.	[illegible]	[illegible]
11/24/82	4	3	BT,BA	5.85	9	.	[illegible]	[illegible]
12/20/82	4	3	BT,BA	2.93	9	.	52	29

* AT = After Tilling, AA = After Application, IAT = Immediately After Tilling, BT = Before Tilling, BETA = Between Two Application, BA = Before Application, 20 AT = 20 Min. After Tilling, 90 AT = 90 Min. After Tilling, 2 HR AA = 2 Hours After Application

Table A-2 Calculated Emission Rates of Total Volatile Hydrocarbons for Laboratory Experiments

Date of Sampling	Time Since Appl. (hr.)	Loading Rate (%)	Rate of Emission (g/hr)	Soil Temp. (°F)	Rela. Humid. (%)	Soil Mois. Cont. (%)	Vola. of Slud. (%)
06/01/83	0.033	3	511.906	85	52	12	8.5
06/01/83	0.066	3	477.779	85	52	12	8.5
06/01/83	0.083	3	392.461	85	52	12	8.5
06/01/83	0.166	3	341.270	85	52	12	8.5
06/01/83	0.750	3	136.508	85	52	12	8.5
06/01/83	3.000	3	59.722	85	52	12	8.5
06/02/83	24.000	3	25.595	85	52	12	8.5
06/03/83	48.000	3	23.595	85	52	12	8.5
06/03/83	48.500	3	58.015	85	52	12	8.5
06/04/83	72.000	3	13.650	85	52	12	8.5
06/05/83	96.000	3	12.790	85	52	12	8.5
06/08/83	168.000	3	12.790	85	52	12	8.5
06/08/83	168.500	3	42.558	85	52	12	8.5
06/09/83	192.000	3	14.620	85	52	12	8.5
06/01/83	0.033	6	546.033	85	52	12	8.5
06/01/83	0.066	6	546.033	85	52	12	8.5
06/01/83	0.166	6	392.460	85	52	12	8.5
06/01/83	0.416	6	238.889	85	52	12	8.5
06/01/83	0.750	6	170.638	85	52	12	8.5
06/01/83	1.330	6	136.508	85	52	12	8.5
06/01/83	3.500	6	76.785	85	52	12	8.5
06/01/83	4.250	6	68.254	85	52	12	8.5
06/02/83	24.000	6	28.154	85	52	12	8.5
06/03/83	48.000	6	25.595	85	52	12	8.5
06/03/83	48.500	6	63.135	85	52	12	8.5
06/04/83	72.000	6	23.876	85	52	12	8.5
06/08/83	168.000	6	21.938	85	52	12	8.5
06/09/83	168.500	6	46.815	85	52	12	8.5
06/09/83	192.000	6	30.710	85	52	12	8.5
06/03/83	0.033	10	590.150	85	52	12	8.5
06/03/83	0.066	10	580.150	85	52	12	8.5
06/03/83	0.166	10	460.715	85	52	12	8.5
06/03/83	1.000	10	307.143	85	52	12	8.5
06/03/83	1.500	10	255.953	85	52	12	8.5
06/03/83	3.000	10	153.570	85	52	12	8.5
06/03/83	6.500	10	110.913	85	52	12	8.5
06/04/83	24.000	10	42.657	85	52	12	8.5
06/08/83	120.000	10	28.030	85	52	12	8.5
06/08/83	120.500	10	69.722	85	52	12	8.5
06/09/83	144.000	10	24.161	85	52	12	8.5
06/10/83	168.000	10	14.626	85	52	12	8.5
06/10/83	168.500	10	43.721	85	52	12	8.5
06/10/83	172.000	10	32.215	85	52	12	8.5
06/11/83	192.000	10	15.720	85	52	12	8.5
05/16/83	0.033	3	307.144	60	52	12	8.5
05/16/83	0.066	3	307.144	60	52	12	8.5
05/16/83	0.166	3	255.953	60	52	12	8.5
05/16/83	0.350	3	213.294	60	52	12	8.5
05/16/83	0.500	3	187.698	60	52	12	8.5
05/16/83	0.666	3	170.635	60	52	12	8.5
05/16/83	0.933	3	153.571	60	52	12	8.5
05/16/83	1.000	3	153.571	60	52	12	8.5
05/16/83	3.000	3	61.428	60	52	12	8.5
05/16/83	5.000	3	37.539	60	52	12	8.5
05/17/83	24.000	3	18.769	60	52	12	8.5
05/18/83	48.000	3	5.215	60	52	12	8.5
05/18/83	48.500	3	32.428	60	52	12	8.5
05/18/83	72.000	3	30.718	60	52	12	8.5
05/19/83	96.000	3	15.357	60	52	12	8.5

(continued)

Table A-2 Calculated Emission Rates of Total Volatile Hydrocarbons for Laboratory Experiments (continued)

Date of Sampling	Time Since Appl. (hr.)	Loading Rate (%)	Rate of Emission (g/hr)	Soil Temp. (°F)	Rela. Humid. (%)	Soil Mois. Cont. (%)	Vola. of Slud. (%)
05/20/83	96.000	3	10.238	60	52	12	8.5
05/20/83	96.500	3	23.889	60	52	12	8.5
05/20/83	98.000	3	14.504	60	52	12	8.5
05/20/83	101.000	3	14.504	60	52	12	8.5
05/21/83	120.500	3	10.238	60	52	12	8.5
05/22/83	144.000	3	7.676	60	52	12	8.5
05/17/83	0.033	6	375.397	60	52	12	8.5
05/17/83	0.066	6	341.270	60	52	12	8.5
05/17/83	0.166	6	255.953	60	52	12	8.5
05/17/83	0.333	6	221.826	60	52	12	8.5
05/17/83	0.500	6	204.762	60	52	12	8.5
05/17/83	0.750	6	196.230	60	52	12	8.5
05/17/83	0.833	6	187.698	60	52	12	8.5
05/17/83	1.000	6	162.103	60	52	12	8.5
05/17/83	4.000	6	59.722	60	52	12	8.5
05/17/83	6.000	6	37.500	60	52	12	8.5
05/18/83	22.000	6	25.595	60	52	12	8.5
05/18/83	24.000	6	20.476	60	52	12	8.5
05/19/83	48.000	6	20.475	60	52	12	8.5
05/19/83	48.500	6	54.603	60	52	12	8.5
05/19/83	49.010	6	51.190	60	52	12	8.5
05/19/83	53.000	6	34.127	60	52	12	8.5
05/20/83	72.000	6	20.476	60	52	12	8.5
05/21/83	96.000	6	11.944	60	52	12	8.5
05/21/83	96.500	6	32.420	60	52	12	8.5
05/22/83	120.000	6	13.650	60	52	12	8.5
05/23/83	144.000	6	8.531	60	52	12	8.5
05/24/83	0.033	10	375.394	60	52	12	8.5
05/24/83	0.166	10	307.143	60	52	12	8.5
05/24/83	0.333	10	273.016	60	52	12	8.5
05/24/83	0.500	10	255.953	60	52	12	8.5
05/24/83	0.750	10	238.889	60	52	12	8.5
05/24/83	1.000	10	230.357	60	52	12	8.5
05/24/83	1.750	10	213.294	60	52	12	8.5
05/24/83	4.000	10	170.635	60	52	12	8.5
05/24/83	5.000	10	133.095	60	52	12	8.5
05/25/83	21.000	10	29.008	60	52	12	8.5
05/25/83	24.000	10	27.813	60	52	12	8.5
05/25/83	48.000	10	26.448	60	52	12	8.5
05/26/83	46.500	10	88.730	60	52	12	8.5
05/26/83	49.010	10	81.904	60	52	12	8.5
05/26/83	54.000	10	30.714	60	52	12	8.5
05/27/83	72.000	10	23.868	60	52	12	8.5
05/28/83	96.000	10	11.944	60	52	12	8.5
05/28/83	96.500	10	47.777	60	52	12	8.5
05/29/83	120.500	10	13.650	60	52	12	8.5
05/30/83	144.000	10	11.091	60	52	12	8.5
03/31/83	0.033	3	204.762	35	52	12	8.5
03/31/83	0.083	3	170.635	35	52	12	8.5
03/31/83	1.000	3	127.976	35	52	12	8.5
03/31/83	2.000	3	119.444	35	52	12	8.5
03/31/83	4.000	3	40.952	35	52	12	8.5
03/31/83	6.000	3	32.761	35	52	12	8.5
03/31/83	8.000	3	29.008	35	52	12	8.5
04/01/83	24.000	3	13.650	35	52	12	8.5
04/02/83	48.000	3	5.972	35	52	12	8.5
04/03/83	72.000	3	22.182	35	52	12	8.5
04/03/83	73.000	3	13.650	35	52	12	8.5
04/03/83	74.000	3	11.944	35	52	12	8.5

(continued)

Table A-2 Calculated Emission Rates of Total Volatile Hydrocarbons for Laboratory Experiments (continued)

Date of Sampling	Time Since Appl. (hr.)	Loading Rate (%)	Rate of Emission (g/hr)	Soil Temp. (°F)	Rela. Humid. (%)	Soil Mois. Cont. (%)	Vola. of Slud. (%)
04/03/83	78.000	3	11.944	35	52	12	8.5
04/04/83	96.000	3	8.531	35	52	12	8.5
04/04/83	96.500	3	20.476	35	52	12	8.5
04/04/83	99.000	3	15.357	35	52	12	8.5
04/04/83	101.000	3	11.944	35	52	12	8.5
04/05/83	120.000	3	8.531	35	52	12	8.5
04/06/83	144.000	3	5.972	35	52	12	8.5
04/04/83	0.083	6	307.143	35	52	12	8.5
04/04/83	0.166	6	238.889	35	52	12	8.5
04/04/83	0.500	6	187.698	35	52	12	8.5
04/04/83	0.750	6	153.571	35	52	12	8.5
04/04/83	2.000	6	136.508	35	52	12	8.5
04/04/83	4.000	6	54.603	35	52	12	8.5
04/04/83	6.000	6	42.658	35	52	12	8.5
04/04/83	8.000	6	23.688	35	52	12	8.5
04/05/83	24.000	6	17.063	35	52	12	8.5
04/06/83	48.000	6	10.238	35	52	12	8.5
04/06/83	48.500	6	35.833	35	52	12	8.5
04/07/83	72.000	6	12.797	35	52	12	8.5
04/08/83	96.000	6	10.238	35	52	12	8.5
04/08/83	96.500	6	34.127	35	52	12	8.5
04/09/83	120.000	6	6.825	35	52	12	8.5
04/10/83	144.000	6	5.119	35	52	12	8.5
04/01/83	0.083	10	238.889	35	52	12	8.5
04/01/83	0.083	10	204.762	35	52	12	8.5
04/01/83	0.500	10	170.635	35	52	12	8.5
04/01/83	1.000	10	127.979	35	52	12	8.5
04/01/83	5.000	10	40.952	35	52	12	8.5
04/01/83	8.000	10	34.127	35	52	12	8.5
04/02/83	24.000	10	22.182	35	52	12	8.5
04/03/83	48.000	10	11.944	35	52	12	8.5
04/03/83	48.500	10	39.246	35	52	12	8.5
04/04/83	72.000	10	13.650	35	52	12	8.5
04/05/83	96.000	10	11.944	35	52	12	8.5
04/05/83	96.500	10	35.833	35	52	12	8.5
04/06/83	120.000	10	10.238	35	52	12	8.5
04/07/83	144.000	10	8.531	35	52	12	8.5
06/10/83	0.083	6	511.905	60	52	23	8.5
06/10/83	0.166	6	477.778	60	52	23	8.5
06/10/83	0.166	6	375.397	60	52	23	8.5
06/10/83	0.250	6	307.143	60	52	23	8.5
06/10/83	1.000	6	280.082	60	52	23	8.5
06/10/83	2.000	6	240.550	60	52	23	8.5
06/10/83	4.000	6	204.762	60	52	23	8.5
06/10/83	6.000	6	127.979	60	52	23	8.5
06/10/83	24.000	6	54.603	60	52	23	8.5
06/12/83	48.000	6	40.952	60	52	23	8.5
06/12/83	48.500	6	64.841	60	52	23	8.5
06/13/83	72.000	6	37.539	60	52	23	8.5
06/14/83	96.000	6	34.127	60	52	23	8.5
06/14/83	96.500	6	50.337	60	52	23	8.5
06/15/83	120.000	6	34.127	60	52	23	8.5
06/16/83	144.000	6	30.714	60	52	23	8.5
07/05/83	0.083	6	341.270	60	75	12	8.5
07/05/83	0.083	6	290.080	60	75	12	8.5
07/05/83	0.166	6	204.762	60	75	12	8.5
07/05/83	0.333	6	170.635	60	75	12	8.5
07/05/83	1.000	6	123.550	60	75	12	8.5
07/05/83	3.000	6	30.714	60	75	12	8.5

(continued)

Table A-2 Calculated Emission Rates of Total Volatile Hydrocarbons for Laboratory Experiments (continued)

Date of Sampling	Time Since Appl. (hr.)	Loading Rate (%)	Rate of Emission (g/hr)	Soil Temp. (°F)	Rela. Humid. (%)	Soil Mois. Cont. (%)	Vola. of Slud. (%)
07/05/83	6.000	6	27.330	60	75	[illegible]	6.5
07/06/83	24.000	6	15.350	60	75	[illegible]	6.5
07/07/83	48.000	6	10.230	60	75	[illegible]	6.5
07/07/83	48.500	6	19.620	60	75	[illegible]	6.5
07/08/83	72.000	6	10.230	60	75	[illegible]	6.5
07/09/83	96.000	6	6.820	60	75	[illegible]	6.5
07/09/83	96.500	6	14.500	60	75	[illegible]	6.5
07/10/83	120.000	6	8.530	60	75	[illegible]	6.5
07/11/83	148.000	6	5.110	60	75	[illegible]	6.5
07/05/83	0.033	10	341.270	60	75	[illegible]	6.5
07/05/83	0.166	10	238.880	60	75	[illegible]	6.5
07/05/83	0.333	10	204.760	60	75	[illegible]	6.5
07/05/83	0.500	10	195.230	60	75	[illegible]	6.5
07/05/83	1.000	10	153.570	60	75	12	6.5
07/05/83	4.000	10	93.940	60	75	[illegible]	6.5
07/05/83	6.000	10	75.780	60	75	[illegible]	6.5
07/05/83	24.000	10	18.760	60	75	[illegible]	6.5
07/07/83	48.000	10	14.500	60	75	[illegible]	6.5
07/07/83	48.500	10	23.880	60	75	[illegible]	6.5
07/08/83	72.000	10	15.350	60	75	12	6.5
07/09/83	96.000	10	10.230	60	75	12	6.5
07/09/83	96.500	10	20.470	60	75	12	6.5
07/10/83	120.000	10	11.940	60	75	12	6.5
07/11/83	148.000	10	8.530	60	75	12	6.5

* Soil and sludge mixture was tilled.

APPENDIX B

The Total Volatile Emission Models for Laboratory Data

Table B-1 The Total Volatile Emission Models for Laboratory Data

1. Model 1 Time <10 hours
Dependent Variable: Emission Rate

R^2 = .83 , F Value = 27.49

Independent Variables	Estimate	T for Ho: Independent Variables = 0	Probability |t| Cal.>|t|tab.*	Standard Error of Estimate
Intercept	76.594	1.48	.1508	51.849
Soil Temperature	.769	1.77	.0874	.434
Moisture Content	8.828	5.08	.0001	1.737
Time Since Application	-20.645	-7.35	.0001	2.810
Loading Rate	9.985	4.31	.0002	2.316
Relative Humidity	-2.025	-2.81	.0090	.721

2. Model 2 Time <10 hours
Dependent Variable: Emission Rate

R^2 = .76 , F Value = 49.83

Intercept	.184	.04	.9716	5.163
Soil Temperature	.268	8.18	.0001	.032
Moisture Control	1.879	9.67	.0001	.194
Time Since Application	-.084	-7.15	.0001	.011
Loading Rate	.931	4.51	.0001	.206
Relative Humidity	-.371	-5.26	.0001	.070

* Ho is rejected if the probability |t| cal.> |t| tab. >95%.

APPENDIX C

Emission Rates of Measured Hydrocarbons At Different Temperatures and Sludge Loading Rates

Table C-1 Emission Rates of Measured Hydrocarbons by Gas Chromatography
Temp = 85, Loading Rate = 3%

TIME SINCE APPL. (HOURS)	.033	.166	1.0	3	24	48	48.5*	96	168	168.5*
COMPOUND NAME	GRAMS / HOUR / 180 SQ.FT. (PLOT AREA)									
1. PENTANE	0.416	0.397	0.29	0.018	0.003	0.006	0.007	0.005	0.012	0.021
2. CYCLOPENTANE	0.916	0.935	0.959	0.47	0.107	0.105	0.361	0.56	0.53	0.865
3. HEXANE	6.878	4.508	1.194	0.313	0.204	0.027	0.033	0.019	0.018	0.025
4. METHYL CYCLOPENTANE	3.594	2.26	3.16	0.27	0.036	0.073	0.252	0.051	0.201	0.672
5. BENZENE	2.6	2.212	3.615	0.314	0.074	0.069	0.364	0.073	0.269	0.824
6. 2,4-DIMETHYLPENTANE	16.7	12.811	4.544	1.707	0.153	0.159	0.288	0.055	0.047	0.067
7. CYCLOHEXANE	4.272	2.828	1.272	0.262	0.023	0.016	0.077	0.069	0.05	0.119
8. 3-METHYLHEXANE	8.839	7.963	2.311	0.764	0.248	0.206	0.291	0.074	0.107	0.54
9. METHYLCYCLOHEXANE	7.252	4.746	4.759	1.465	0.398	0.21	0.316	0.088	0.036	0.417
10. 2,5-DIMETHYLHEXANE	7.871	6.511	2.984	0.967	0.682	0.427	0.794	0.274	0.124	0.349
11. 2,3,4-TRIMETHYLPENTANE	33.018	26.696	10.255	3.527	1.382	0.728	1.012	0.394	0.234	0.471
12. 3-METHYLHEPTANE	7.218	3.972	2.345	0.856	0.426	0.386	1.632	0.388	0.246	0.988
13. 2,2,5-TRIMETHYLHEXANE	4.687	4.279	3.259	1.284	0.714	0.672	1.479	0.587	0.419	0.529
14. 1,4-DIMETHYLBENZENE	5.326	5.203	3.642	1.546	1.374	1.295	2.472	0.996	0.988	1.458
SUM OF 14 COMPOUNDS	109.587	85.321	44.589	13.763	5.824	4.379	9.368	3.636	3.281	7.345
TOTAL VOLAT. AS HEXANE	477.779	341.270	136.508	59.722	25.595	23.095	58.016	12.790	12.793	42.658
% 14 COMP/TOTAL VOLAT	22.94	25.00	32.66	23.05	22.75	18.96	16.15	28.43	25.65	17.22

* SOIL AND SLUDGE MIXTURE WAS TILLED

Table C-2 Emission Rates of Measured Hydrocarbons by Gas Chromatography
Temp. = 85, Loading Rate = 6%

TIME SINCE APPL. (HOURS)	.033	.166	.50	1	5	24	48	48.5*	168	168.5*	192
COMPOUND NAME	GRAMS / HOUR / 180 SQ.FT. (PLOT AREA)										
1. PENTANE	0.382	0.342	0.336	0.0167	.	.	.	0.022	0.0405	0.095	0.006
2. CYCLOPENTANE	0.402	0.46	0.11	0.078	0.04	0.058	0.021	1.34	0.945	0.946	0.172
3. HEXANE	8.848	7.419	2.19	1.006	0.314	0.1836	0.018	0.08	0.017	0.113	0.02
4. METHYL CYCLOPENTANE	4.42	3.66	3.304	0.524	0.168	0.135	0.1021	0.598	0.26	0.382	0.048
5. BENZENE	2.694	2.45	2.168	0.453	0.204	0.161	0.09	0.742	0.372	0.52	0.084
6. 2,4-DIMETHYLPENTANE	20.156	20.085	11.906	4.97	1.86	0.197	0.104	0.194	0.038	0.052	0.046
7. CYCLOHEXANE	5.388	4.708	2.098	0.793	0.21	0.086	0.051	0.098	0.068	0.193	0.02
8. 3-METHYLHEXANE	10.002	9.711	3.685	2.496	1.074	0.3939	0.479	0.268	0.042	0.083	0.04
9. METHYLCYCLOHEXANE	8.254	6.773	6.147	1.249	0.514	0.128	0.074	0.698	0.0375	0.047	0.028
10. 2,5-DIMETHYLHEXANE	9.988	9.345	4.207	3.195	1.448	0.264	0.198	0.666	0.091	0.095	0.81
11. 2,3,4-TRIMETHYLPENTANE	34.968	33.365	16.009	11.836	3.554	1.438	0.324	1.114	0.15	0.45	0.18
12. 3-METHYLHEPTANE	8.104	8.676	4.609	4.287	1.65	0.376	0.169	0.594	0.331	1.082	0.324
13. 2,2,5-TRIMETHYLHEXANE	4.49	4.304	2.318	2.247	1.19	0.387	0.23	0.95	0.245	0.646	0.466
14. 1,4-DIMETHYLBENZENE	4.08	4.718	4.555	4.062	2.624	1.341	0.552	2.516	0.433	1.928	0.582
SUM OF 14 COMPOUNDS	122.176	116.016	63.642	37.212	14.850	5.144	2.412	9.880	3.070	6.632	2.826
TOTAL VOLAT. AS HEXANE	548.000	394.480	235.889	135.508	64.284	28.154	25.598	63.135	21.938	46.415	30.710
% 14 COMP/TOTAL VOLAT	22.29	29.41	26.98	27.46	23.10	18.29	9.42	15.65	13.99	14.29	9.20

*SOIL AND SLUDGE MIXTURE WAS TILLED

Table C-3 Emission Rates of Measured Hydrocarbons by Gas Chromatography
Temp. = 85, Loading Rate = 10%

TIME SINCE APPL. (HOURS)	.166	1.0	8.0	24	96	96.5*	192	216
COMPOUND NAME	GRAMS / HOUR / 180 SQ.FT. (PLOT AREA)							
1. PENTANE	0.294	0.166	0.006	0.03	0.026	0.036	0.022	0.032
2. CYCLOPENTANE	0.404	1.069	0.639	0.577	0.423	1.293	0.22	.
3. HEXANE	8.198	2.855	0.88	0.07	0.079	0.084	0.064	0.028
4. METHYL CYCLOPENTANE	3.88	2.355	0.756	0.844	0.44	0.816	0.074	.
5. BENZENE	2.75	1.87	0.872	1.212	0.711	1.236	0.144	0.01
6. 2,4-DIMETHYLPENTANE	21.58	9.817	3.104	0.736	0.196	0.3	0.084	0.054
7. CYCLOHEXANE	3.136	2.885	0.123	0.192	0.096	0.109	0.032	0.008
8. 3-METHYLHEXANE	11.658	5.229	1.98	0.404	0.139	0.182	0.3	0.212
9. METHYLCYCLOHEXANE	9.33	3.164	1.426	1.034	0.521	0.614	0.074	0.008
10. 2,5-DIMETHYLHEXANE	13.284	5.689	2.126	0.774	0.22	0.964	0.816	0.224
11. 2,3,4-TRIMETHYLPENTANE	46.726	22.71	7.144	2.146	0.591	1.286	0.504	0.274
12. 3-METHYLHEPTANE	9.642	5.496	3.028	0.902	0.492	0.919	1.426	0.758
13. 2,2,5-TRIMETHYLHEXANE	7.77	3.694	2.05	0.82	0.521	1.306	1.024	0.532
14. 1,4-DIMETHYLBENZENE	8.536	5.854	4.502	1.092	0.827	2.187	1.56	1.19
SUM OF 14 COMPOUNDS	147.288	72.853	28.636	10.833	5.282	11.332	6.344	3.330
TOTAL VOLAT. AS HEXANE	460.715	307.143	110.913	42.658	28.030	59.722	24.161	14.625
% 14 COMP/TOTALVOL	31.97	23.72	25.82	25.40	18.84	18.97	26.26	22.77

* SOIL AND SLUDGE MIXTURE WAS TILLED

Table C-4 Emission Rates of Measured Hydrocarbons by Gas Chromatography
Temp. = 60, Loading Rate = 3%

TIME SINCE APPL. (HOURS)	.033	1.0	3.0	24	48	48.5*	72	96	96.5*	99	168
COMPOUND NAME	GRAMS / HOUR / 100 SQ. FT. (PLOT AREA)										
1. PENTANE	0.026	0.089	0.0082	0.005	0.003	0.039	0.0051	0.004	0.032	0.007	0.002
2. CYCLOPENTANE	0.082	0.356	0.102	0.104	0.06	0.032	0.057	0.2	0.43	0.298	0.058
3. HEXANE	3.766	0.657	0.436	0.007	0.006	0.28	0.019	0.008	0.036	0.008	0.001
4. METHYL CYCLOPENTANE	2.782	1.624	0.314	0.3	0.048	0.246	0.172	0.148	0.326	0.126	0.018
5. BENZENE	1.248	1.11	0.388	0.328	0.074	0.378	0.102	0.093	0.43	0.127	0.025
6. 2,4-DIMETHYLPENTANE	2.476	2.082	1.702	0.069	0.057	0.068	0.048	0.025	0.062	0.02	0.004
7. CYCLOHEXANE	1.088	1.228	0.332	0.06	0.015	0.268	0.022	0.008	0.014	0.022	0.006
8. 3-METHYLHEXANE	7.68	2.516	0.882	0.092	0.057	0.312	0.156	0.058	0.156	0.066	0.017
9. METHYLCYCLOHEXANE	5.002	4.098	0.608	0.4	0.066	0.252	0.148	0.1	0.464	0.152	0.024
10. 2,5-DIMETHYLHEXANE	3.202	2.642	0.94	0.152	0.102	0.592	0.262	0.06	0.2	0.434	0.138
11. 2,3,4-TRIMETHYLPENTANE	9.992	9.404	3.852	0.612	0.21	1.108	0.507	0.121	0.268	0.126	0.018
12. 3-METHYLHEPTANE	1.536	1.208	0.856	0.762	0.128	0.756	0.414	0.142	0.488	0.149	0.141
13. 2,2,5-TRIMETHYLHEXANE	3.596	1.818	0.758	.	0.105	0.708	0.315	0.122	0.368	0.167	0.094
14. 1,4-DIMETHYLBENZENE	3.68	2.187	0.806	0.4652	0.309	1.52	1.293	0.32	0.598	0.472	0.116
TOTAL VOLAT. AS HEXANE	46.156	31.108	11.984	3.356	1.240	6.559	3.520	1.409	3.872	2.174	0.662
READING FROM SNIFFER	307.144	153.571	61.428	18.769	5.210	32.420	15.357	10.238	23.838	14.504	7.678
% 14 COMP/TOTAL VOLAT	15.03	20.26	19.51	17.88	23.80	20.23	22.92	13.76	16.24	14.99	8.62

* SOIL AND SLUDGE MIXTURE WAS TILLED

Table C-5 Emission Rates of Measured Hydrocarbons by Gas Chromatography
Temp. = 60, Loading Rate = 6%

TIME SINCE APPL. (HOURS)	.033	6.0	24	48	48.5*	72	96	96.5*	120	146
COMPOUND NAME	GRAMS / HOUR / 180 SQ. FT. (PLOT AREA)									
1. PENTANE	0.313	0.024	0.0041	0.007	0.022	0.016	0.004	0.01	0.006	.
2. CYCLOPENTANE	0.304	0.294	0.109	0.085	0.24	0.125	0.189	0.286	0.182	0.004
3. HEXANE	5.872	0.428	0.037	0.018	0.298	0.078	0.023	0.05	0.065	.
4. METHYL CYCLOPENTANE	4.722	0.36	0.171	0.085	0.122	0.094	0.077	0.086	0.054	0.001
5. BENZENE	2.842	0.32	0.297	0.194	0.294	0.109	0.104	0.204	0.072	0.003
6. 2,4-DIMETHYLPENTANE	13.132	2.02	0.349	0.236	0.596	0.22	0.074	0.184	0.076	0.091
7. CYCLOHEXANE	1.892	0.342	0.137	0.026	0.235	0.086	0.014	0.024	0.014	0.004
8. 3-METHYLHEXANE	7.198	0.965	0.359	0.104	0.309	0.169	0.072	0.117	0.104	0.052
9. METHYLCYCLOHEXANE	6.791	0.564	0.485	0.139	0.253	0.131	0.099	0.136	0.088	0.043
10. 2,5-DIMETHYLHEXANE	5.696	0.599	0.292	0.213	0.601	0.225	0.112	0.251	0.12	0.125
11. 2,3,4-TRIMETHYLPENTANE	26.65	3.33	0.729	0.632	1.897	0.628	0.186	0.521	0.086	0.125
12. 3-METHYLHEPTANE	3.098	0.788	0.48	0.333	0.73	0.436	0.12	0.41	0.208	0.239
13. 2,2,5-TRIMETHYLHEXANE	4.314	1.318	.	0.226	0.761	0.456	0.248	0.428	0.11	.
14. 1,4-DIMETHYLBENZENE	3.738	1.372	0.539	0.427	1.168	0.544	0.29	0.655	0.36	0.33
SUM OF 14 COMPOUNDS	86.562	12.724	3.988	2.725	7.526	3.317	1.612	3.362	1.545	1.017
TOTAL VOLAT. AS HEXANE	341.270	37.510	20.476	20.376	54.603	20.476	11.944	32.420	13.650	8.531
% 14 COMP/TOTAL VOLAT	25.36	33.92	19.48	13.37	13.78	16.20	13.50	10.37	11.32	11.92

* SOIL AND SLUDGE MIXTURE WAS TILLED

Table C-6 Emission Rates of Measured Hydrocarbons by Gas Chromatography Temp. = 60, Loading Rate = 10%

TIME SINCE APPL. (HOURS)	.033	.50	1.0	4	24	48	48.5*	54	72	96	96.5*	146
COMPOUND NAME	GRAMS / HOUR / 100 SQ.FT. (PLOT AREA)											
1. PENTANE	0.252	0.126	0.098	0.01	0.006	0.002	0.029	0.006	0.017	0.007	0.02	0.025
2. CYCLOPENTANE	0.296	0.189	0.308	0.286	0.251	0.205	0.316	0.139	0.11	0.325	0.362	0.277
3. HEXANE	6.09	3.384	2.281	2.431	0.12	0.041	1.28	0.098	0.072	0.064	0.264	0.012
4. METHYL CYCLOPENTANE	6.648	1.538	1.144	0.37	0.161	0.096	0.32	0.242	0.095	0.016	0.172	0.207
5. BENZENE	1.042	1.445	0.971	0.41	0.324	0.196	0.25	0.05	0.113	0.041	0.242	0.224
6. 2,4-DIMETHYLPENTANE	15.47	9.886	4.938	3.055	0.6	0.271	2.202	0.328	0.281	0.208	0.587	0.099
7. CYCLOHEXANE	4.014	2.036	1.644	0.535	0.393	0.035	0.248	0.142	.	0.033	0.05	0.037
8. 3-METHYLHEXANE	7.388	4.945	2.925	1.536	0.628	0.143	0.867	0.194	0.141	0.102	0.36	0.115
9. METHYLCYCLOHEXANE	6.955	2.67	2.101	0.039	0.57	0.142	0.26	0.092	0.066	0.049	0.201	0.246
10. 2,5-DIMETHYLHEXANE	6.204	4.727	2.037	1.773	0.385	0.194	1.345	0.702	0.262	0.209	0.699	0.188
11. 2,3,4-TRIMETHYLPENTANE	28.99	19.45	7.644	7.227	1.375	0.69	4.7	1.094	0.613	0.603	1.933	0.396
12. 3-METHYLHEPTANE	5.164	4.581	2.914	2.039	0.508	0.227	1.557	0.741	0.364	0.304	0.942	0.388
13. 2,2,5-TRIMETHYLHEXANE	4.606	2.335	1.304	1.272	0.704	0.369	0.98	0.78	0.348	0.251	0.625	0.496
14. 1,4-DIMETHYLBENZENE	4.667	4.141	2.86	2.263	0.883	0.548	1.565	0.834	0.517	0.99	1.215	0.616
SUM OF 14 COMPOUNDS	97.786	61.450	33.167	24.046	6.908	3.159	15.919	5.442	2.999	3.202	7.752	3.216
TOTAL VOLAT. AS HEXANE	307.143	304.016	203.000	170.635	27.813	26.448	88.730	30.774	23.868	11.841	44.000	13.650
% 14 COMP/TOTAL VOLAT	31.84	20.21	16.34	14.09	24.84	11.94	17.94	17.68	12.56	27.04	17.62	23.56

* SOIL AND SLUDGE MIXTURE WAS TILLED

Table C-7 Emission Rates of Measured Hydrocarbons by Gas Chromatography
Temp. = 35, Loading Rate = 3%

TIME SINCE APPL. (HOURS)	2.0	6.0	48	48.5*
COMPOUND NAME	GRAMS / HOUR / 180 SQ.FT. (PLOT AREA)			
1. PENTANE	0.111	0.035	0.034	0.073
2. CYCLOPENTANE	0.122	0.198	0.068	0.116
3. HEXANE	0.386	0.183	0.009	0.011
4. METHYL CYCLOPENTANE	.	0.198	0.034	0.147
5. BENZENE	0.478	0.172	0.083	0.132
6. 2,4-DIMETHYLPENTANE	.	.	.	0.173
7. CYCLOHEXANE	.	.	0.029	.
8. 3-METHYLHEXANE	0.617	0.164	0.056	0.152
9. METHYLCYCLOHEXANE	0.608	0.252	0.114	0.167
10. 2,5-DIMETHYLHEXANE	0.792	0.191	0.094	0.186
11. 2,3,4-TRIMETHYLPENTANE	3.383	0.69	0.216	0.259
12. 3-METHYLHEPTANE	0.786	0.266	0.13	0.26
13. 2,2,5-TRIMETHYLHEXANE	2.398	1.609	0.1	0.214
14. 1,4-DIMETHYLBENZENE	1.287	0.573	0.192	0.38
SUM OF 14 COMPOUNDS	11.048	4.531	1.159	2.270
TOTAL VOLAT. AS HEXANE	119.000	32.761	5.972	22.182
% 14 COMP/TOTAL VOLAT	9.28	13.83	19.41	10.23

* SOIL AND SLUDGE MIXTURE WAS TILLED

Table C-8 Emission Rates of Measured Hydrocarbons by Gas Chromatography
Temp. = 35, Loading Rate = 6%

TIME SINCE APPL. (HOURS)	.50	96	146
COMPOUND NAME	GRAMS / HOUR / 180 SQ.FT. (PLOT AREA)		
1. PENTANE	0.236	0.085	0.039
2. CYCLOPENTANE	0.463	0.167	0.163
3. HEXANE	1.499	0.091	0.007
4. METHYL CYCLOPENTANE	1.058	0.125	0.16
5. BENZENE	1.592	0.216	0.164
6. 2,4-DIMETHYLPENTANE	5.302	0.206	0.047
7. CYCLOHEXANE	1.347	0.04	0.048
8. 3-METHYLHEXANE	3.623	0.113	0.033
9. METHYLCYCLOHEXANE	3.53	0.218	0.217
10. 2,5-DIMETHYLHEXANE	2.1	0.167	0.49
11. 2,3,4-TRIMETHYLPENTANE	8.648	0.501	0.094
12. 3-METHYLHEPTANE	2.903	0.229	0.08
13. 2,2,5-TRIMETHYLHEXANE	2.243	0.166	0.071
14. 1,4-DIMETHYLBENZENE	2.022	0.355	0.149
SUM OF 14 COMPOUNDS	36.566	2.679	1.762
TOTAL VOLAT. AS HEXANE	187.698	10.238	5.119
% 14 COMP/TOTAL VOLAT	19.48	26.17	34.42

* SOIL AND SLUDGE MIXTURE WAS TILLED

Table C-9 Emission Rates of Measured Hydrocarbons by Gas Chromatography
Temp. = 35, Loading Rate = 10%

TIME SINCE APPL. (HOURS)	.033	4.0	7.0	24	48
COMPOUND NAME	GRAMS / HOUR / 180 SQ.FT. (PLOT AREA)				
1. PENTANE	0.134	0.177	0.056	0.073	0.065
2. CYCLOPENTANE	0.581	0.397	0.126	0.09	0.122
3. HEXANE	1.723	0.171	0.122	0.042	0.07
4. METHYL CYCLOPENTANE	.	0.198	0.116	0.092	0.07
5. BENZENE	0.61	0.699	0.255	0.108	0.102
6. 2,4-DIMETHYLPENTANE	.	0.722	0.581	0.333	0.245
7. CYCLOHEXANE	.	0.235	0.147	0.059	0.022
8. 3-METHYLHEXANE	4.742	0.381	0.282	0.134	0.122
9. METHYLCYCLOHEXANE	3.803	0.861	0.398	0.263	0.263
10. 2,5-DIMETHYLHEXANE	2.573	0.466	0.274	0.258	0.248
11. 2,3,4-TRIMETHYLPENTANE	8.759	1.123	0.93	0.509	0.433
12. 3-METHYLHEPTANE	3.005	0.465	0.292	0.283	0.311
13. 2,2,5-TRIMETHYLHEXANE	3.305	0.509	0.253	0.273	0.243
14. 1,4-DIMETHYLBENZENE	2.988	0.958	0.53	0.518	0.504
SUM OF 14 COMPOUNDS	32.223	7.362	4.361	3.035	2.818
TOTAL VOLAT. AS HEXANE	204.000	40.952	34.127	22.182	11.944
% 14 COMP/TOTAL VOLAT.	15.80	17.98	12.78	13.68	23.59

* SOIL AND SLUDGE MIXTURE WAS TILLED

Table C-10 Emission Rates of Measured Hydrocarbons
Gas Chromatographic Field Data

	Plot # 4								
	8/10/82	8/13/82		10/7/82		10/12/82	11/24/82	5/9/83	
	AT	AA	AT,AA	BT	AT	AT,AA	BT	BT	AT
Pentane	1.30	+	+	.721	6.010	.109		.026	.028
Cyclopentane	+	+	+	1.242	6.24	.790	+	.012	.204
Hexane	+	+	+	+	+	+	+	.054	.095
Methylcyclopentane	+	+	+	+	.702	.159	.802	.061	.567
Benzene	3.521	2.748	1.460	1.264	2.296	1.900	.730	.087	.569
2,4-Dimethylpentane	.060	.093	1.617	.148	.108	2.229	.150	.079	.105
Cyclohexane	.139	+	+	.392	1.377	.650	2.100	.048	.139
3-Methylhexane	.076	.513	1.729	.447	+	13.559	.447	.068	.123
Methylcyclohexane	.108	.783	1.868	.579	.835	8.920	.598	.128	.627
2,5-Dimethylhexane	.089	.674	2.319	.544	.689	6.806	.662	.132	.240
2,3,4-Trimethylpentane	.118	1.524	2.293	1.235	1.480	26.090	.882	.122	.181
3-Methylheptane	.223	2.213	2.500	.521	1.739	7.770	1.000	.156	.231
2,2,5-Trimethylhexane	.119	2.907	+	.438	.902	12.104	.802	.161	.163
1,4-Dimethylbenzene	.274	5.773	2.462	1.423	1.448	12.480	2.481	.096	.658

(continued)

Table C-10 Emission Rates of Measured Hydrocarbons
Gas Chromatographic Field Data (continued)

	Plot # 5						
	10/7/82	10/12/82		11/24/82	12/02/82	5/9/83	
	BT	AA	AT,AA	BA	BT	BT	AT
Pentane	+	+	+	.032	.029	+	.044
Cyclopentane	+	+	+	.114	.113	+	.218
Hexane	+	+	+	.044	.034	+	.023
Methylcyclopentane	+	+	+	.316	.277	.145	.570
Benzene	+	2.879	2.345	2.071	1.534	.323	.707
2,4-Dimethylpentane	+	.195	.210	.343	.212	.044	.190
Cyclohexane	.073	+	+	.144	.140	.040	.123
3-Methylhexane	.076	.955	1.041	.187	.128	.034	.134
Methylcyclohexane	.061	.831	1.169	1.118	1.090	.258	.679
2,5-Dimethylhexane	+	.866	1.657	.186	.104	.077	.223
2,3,4-Trimethylpentane	.112	3.486	3.040	.288	.174	.066	.165
3-Methylheptane	.657	11.970	12.597	.309	.131	.094	.425
2,2,5-Trimethylhexane	.183	+	+	.208	.117	+	.181
1,4-Dimethylbenzene	.557	20.770	16.610	.878	.408	.190	.660

(continued)

Table C-10 Emission Rates of Measured Hydrocarbons
Gas Chromatographic Field Data (continued)

	Plot # 7 5/9/83		Plot # 1 6/9/83
	IAT	30 min. AT	AT
Pentane	.004	.065	.044
Cyclopentane	.041	.280	.285
Hexane	.034	.023	.035
Methylcyclopentane	.282	.522	.597
Benzene	.289	.508	.611
2,4-Dimethylpentane	.100	.088	.177
Cyclohexane	.094	.129	.134
3-Methylhexane	.203	.125	.153
Methylcyclohexane	.289	.616	.732
2,5-Dimethylhexane	.073	.110	.197
2,3,4-Trimethylpentane	.193	.211	.310
3-Methylheptane	.110	.110	.343
2,2,5-Trimethylhexane	.075	.065	.238
1,4-Dimethylbenzene	.423	.472	.782

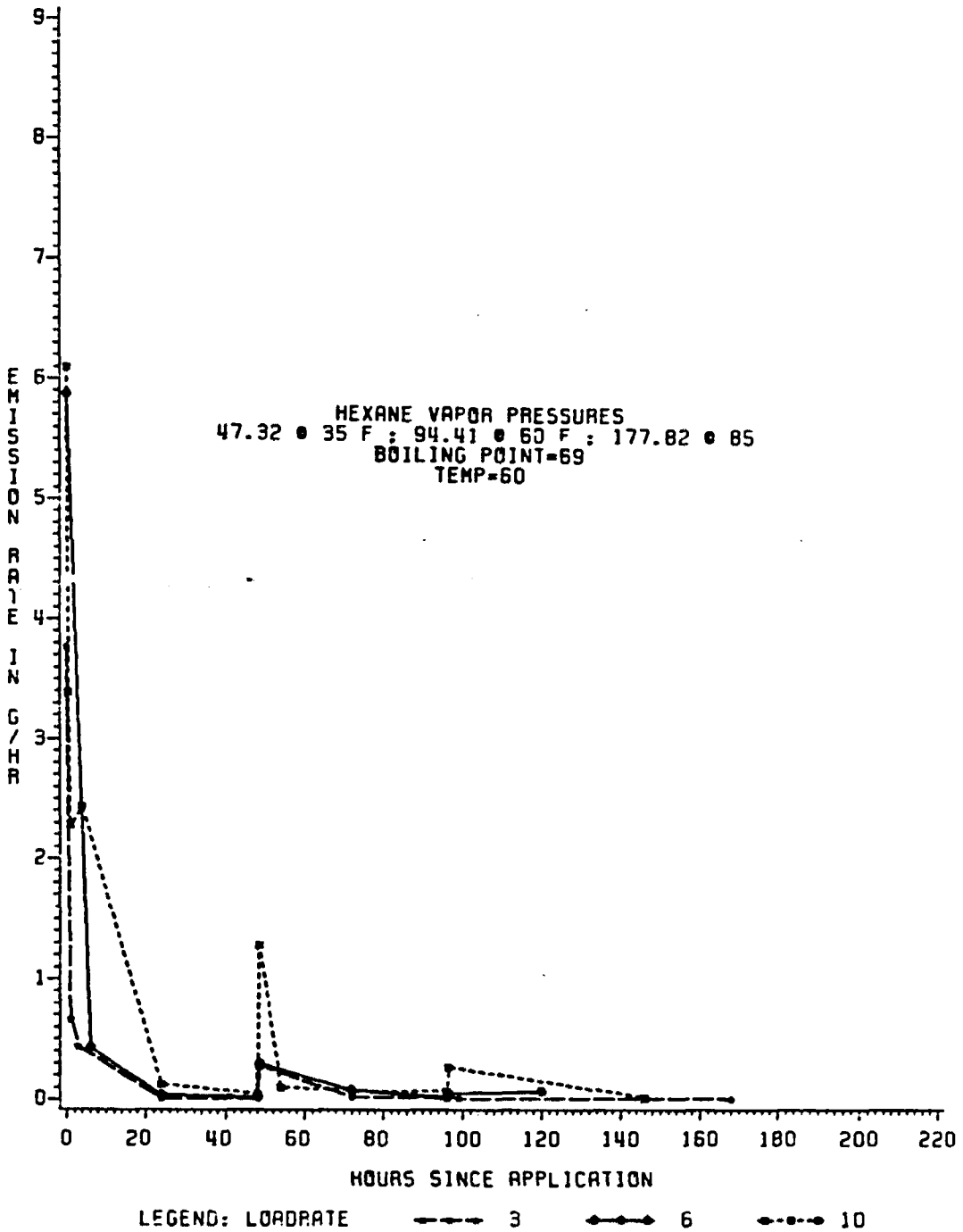

Figure C-1 Time Relation of Emission Rate and Loading Rate-Hexane, Temp. = 60°F

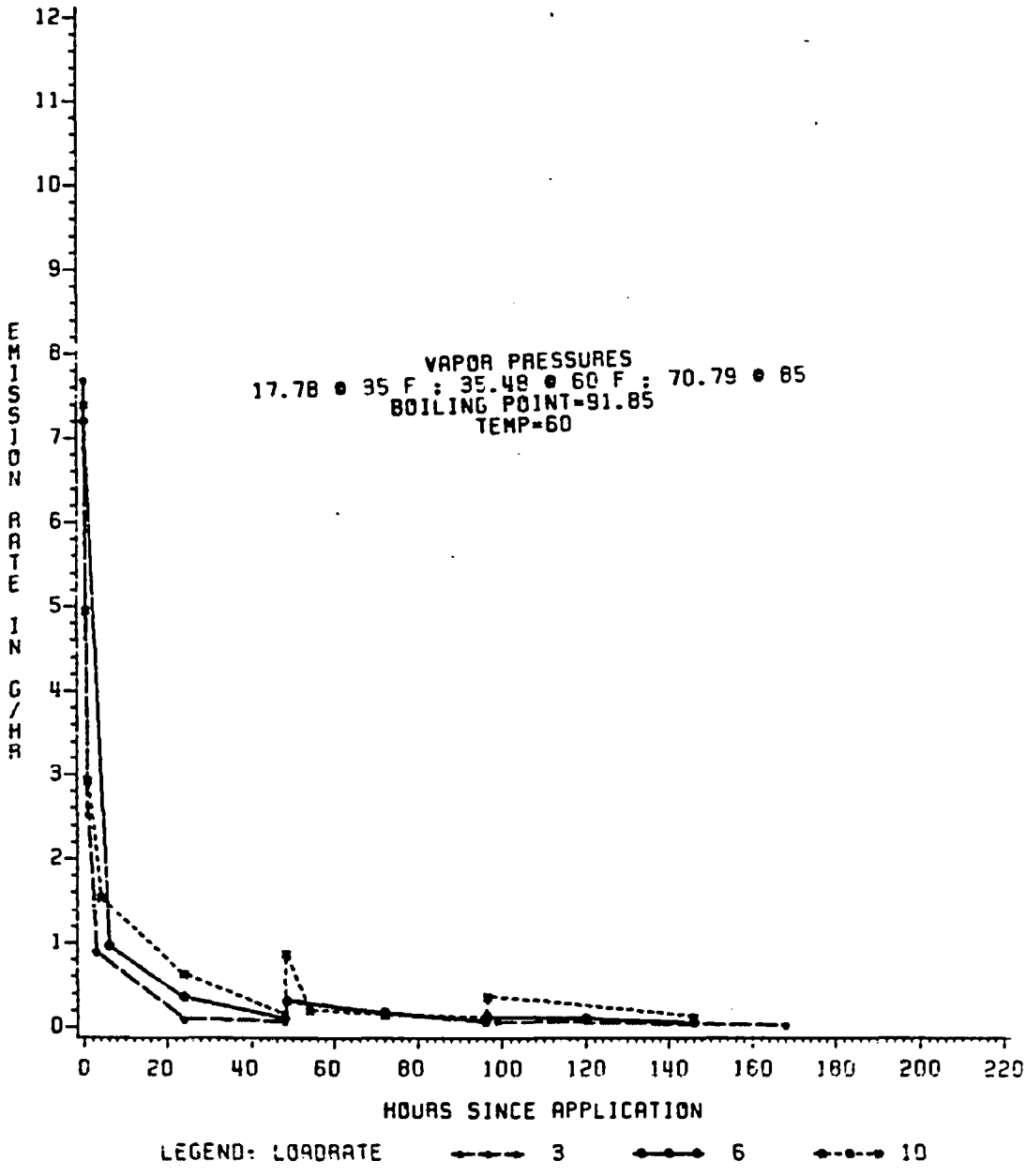

Figure C-2 Time Relation of Emission Rate and Loading Rate-3-Methylhexane, Temp. = 60°F

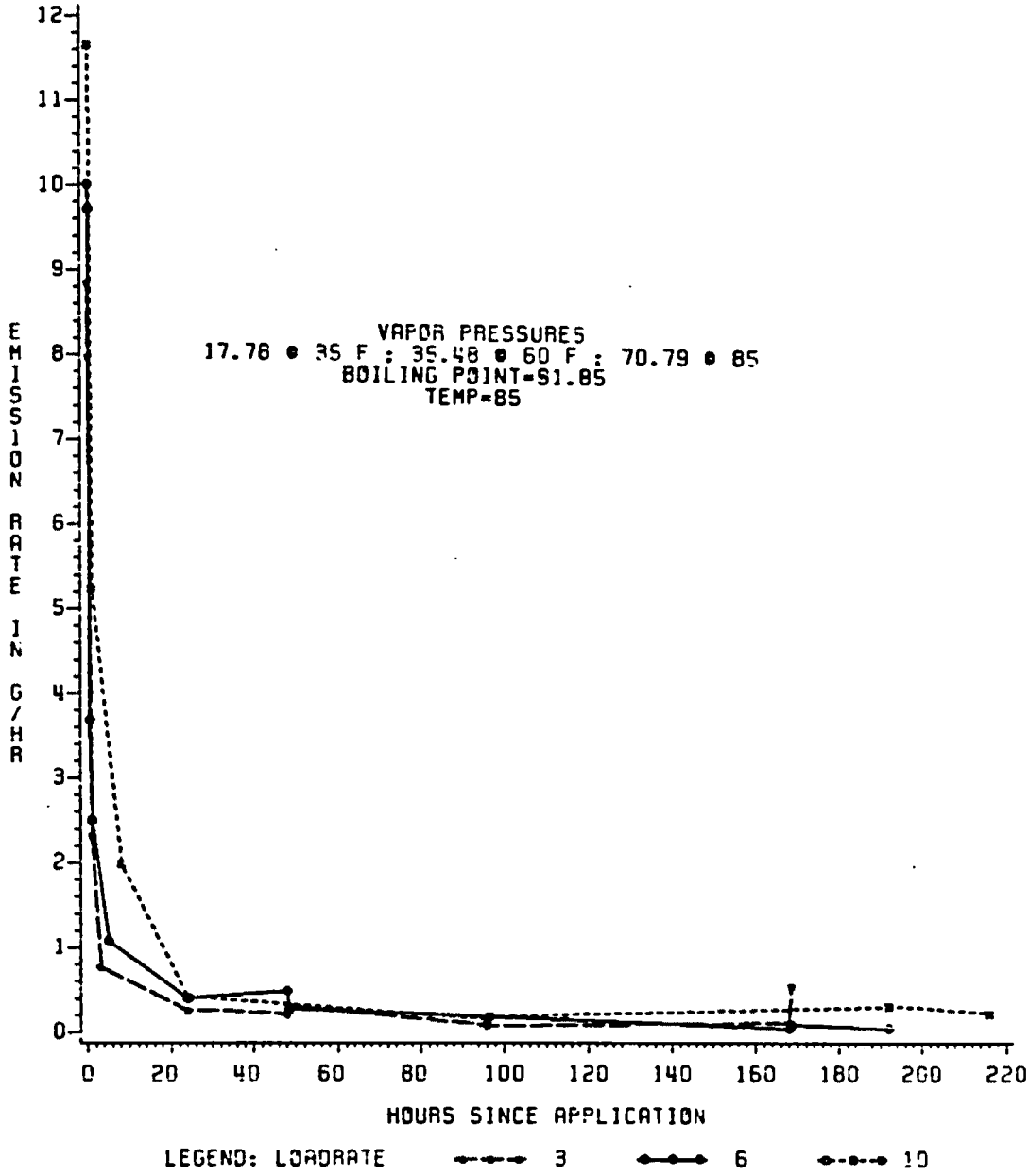

Figure C-3 Time Relation of Emission Rate and Loading Rate-3-Methylhexane, Temp. = 85°F

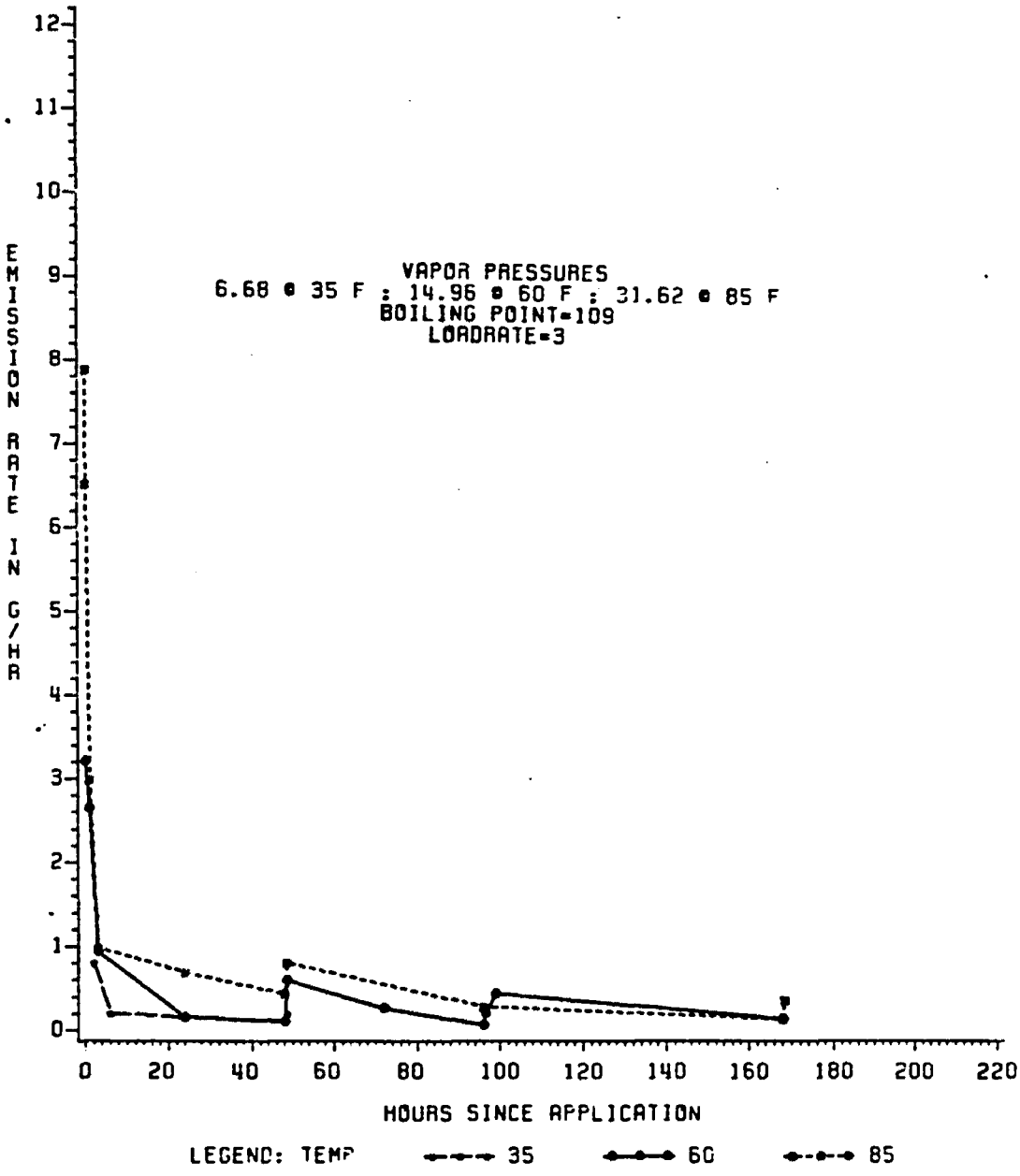

Figure C-4 Time Relation of Emission Rate and Temperature-2,5-Dimethylhexane, Loading Rate = 3%

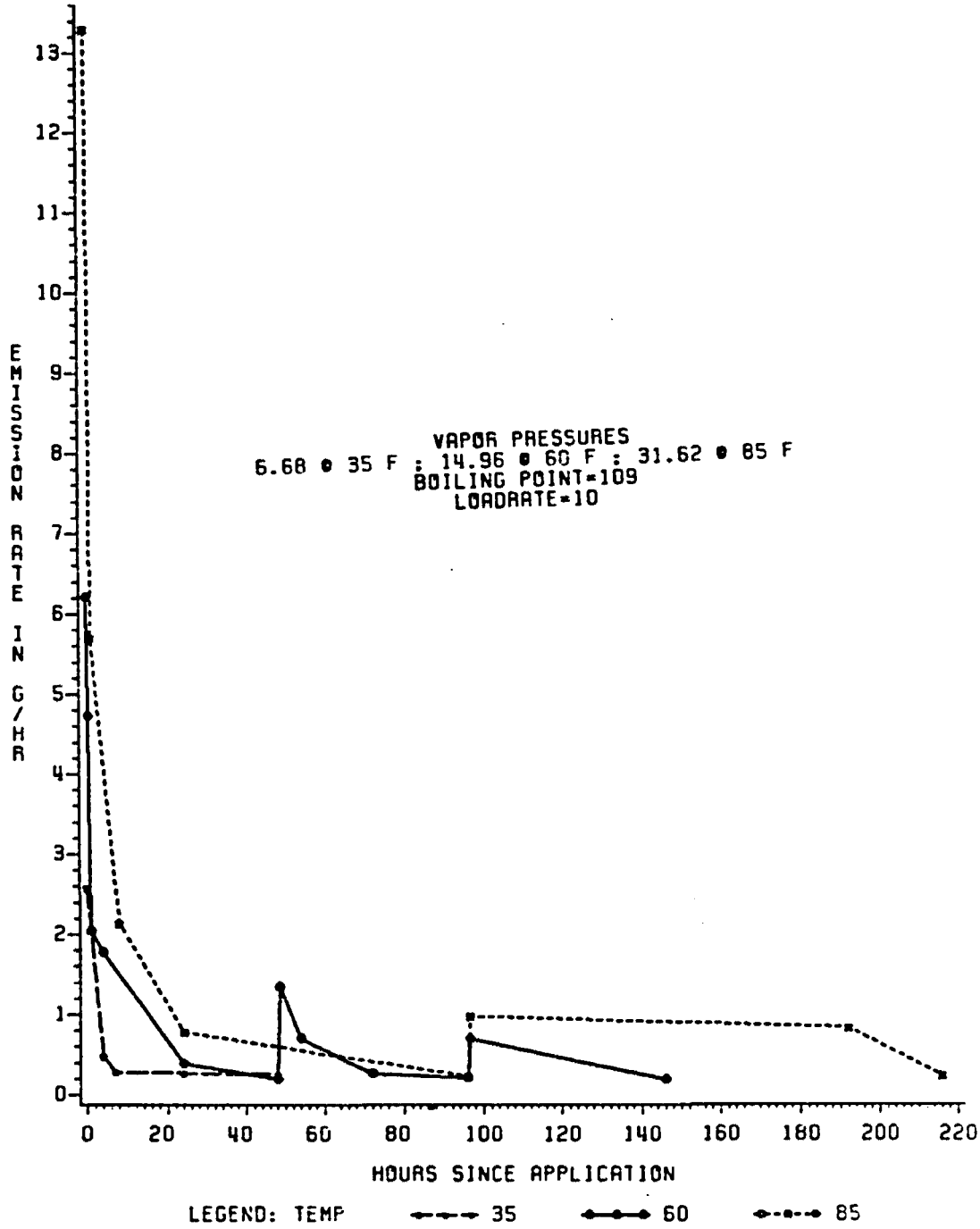

Figure C-5 Time Relation of Emission Rate and Temperature-2,5-Dimethylhexane, Loading Rate = 10%

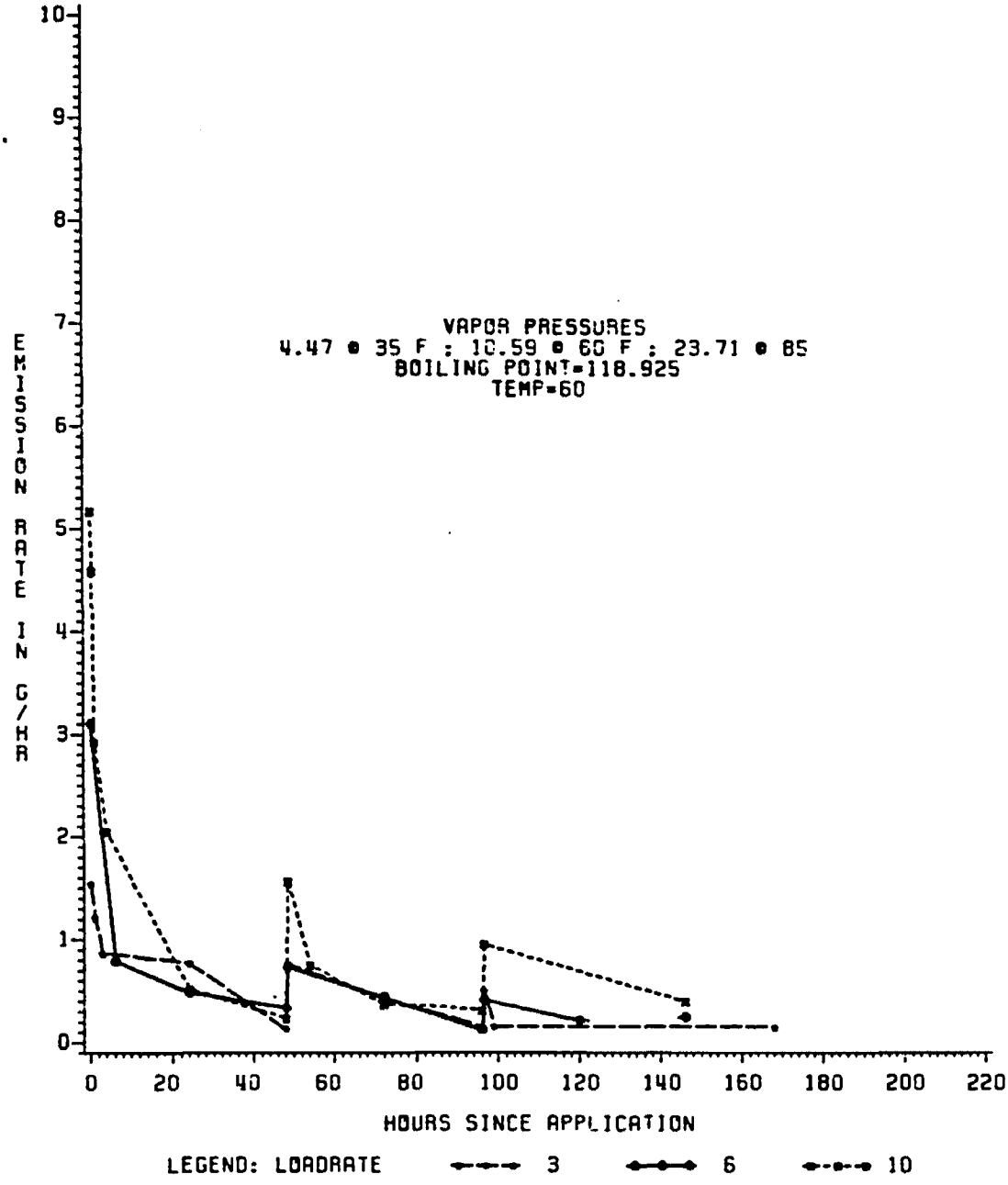

Figure C-6 Time Relation of Emission Rate and Loading Rate-3-Methylheptane, Temp. = 60°F

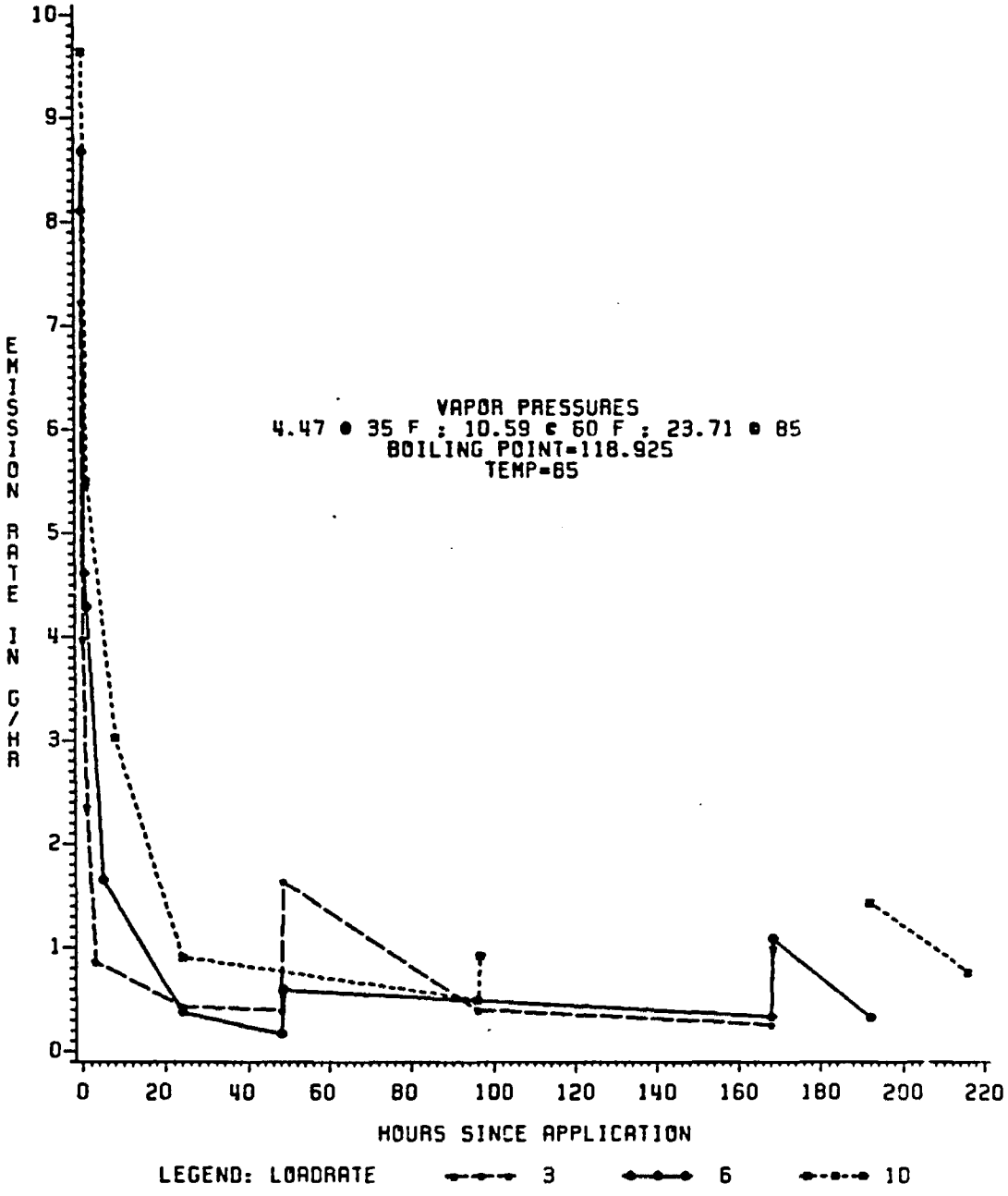

Figure C-7 Time Relation of Emission Rate and Loading Rate-3-Methylheptane, Temp. = 85°F

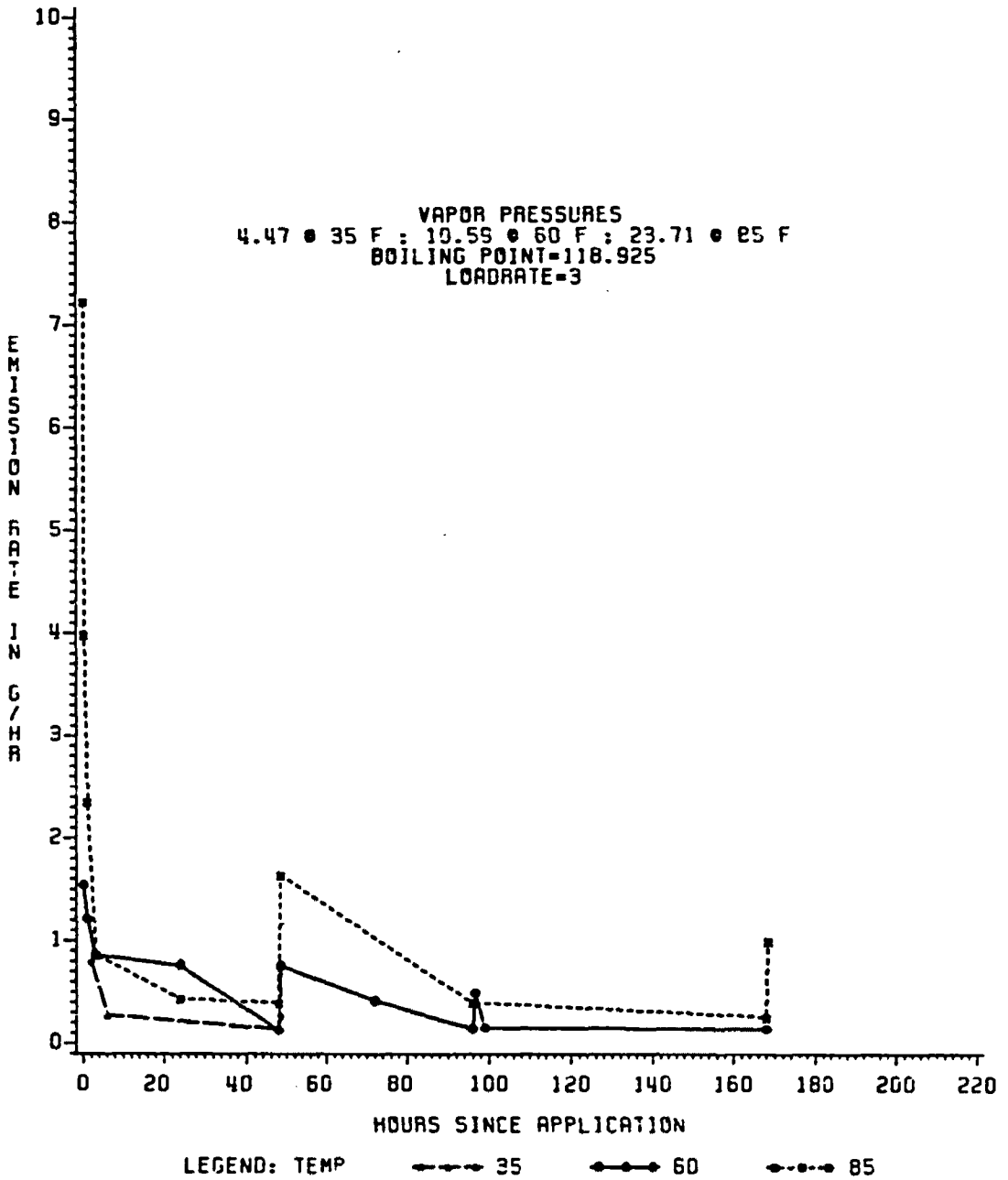

Figure C-8 Time Relation of Emission Rate and Temperature-3-Methylheptane, Loading Rate = 3%

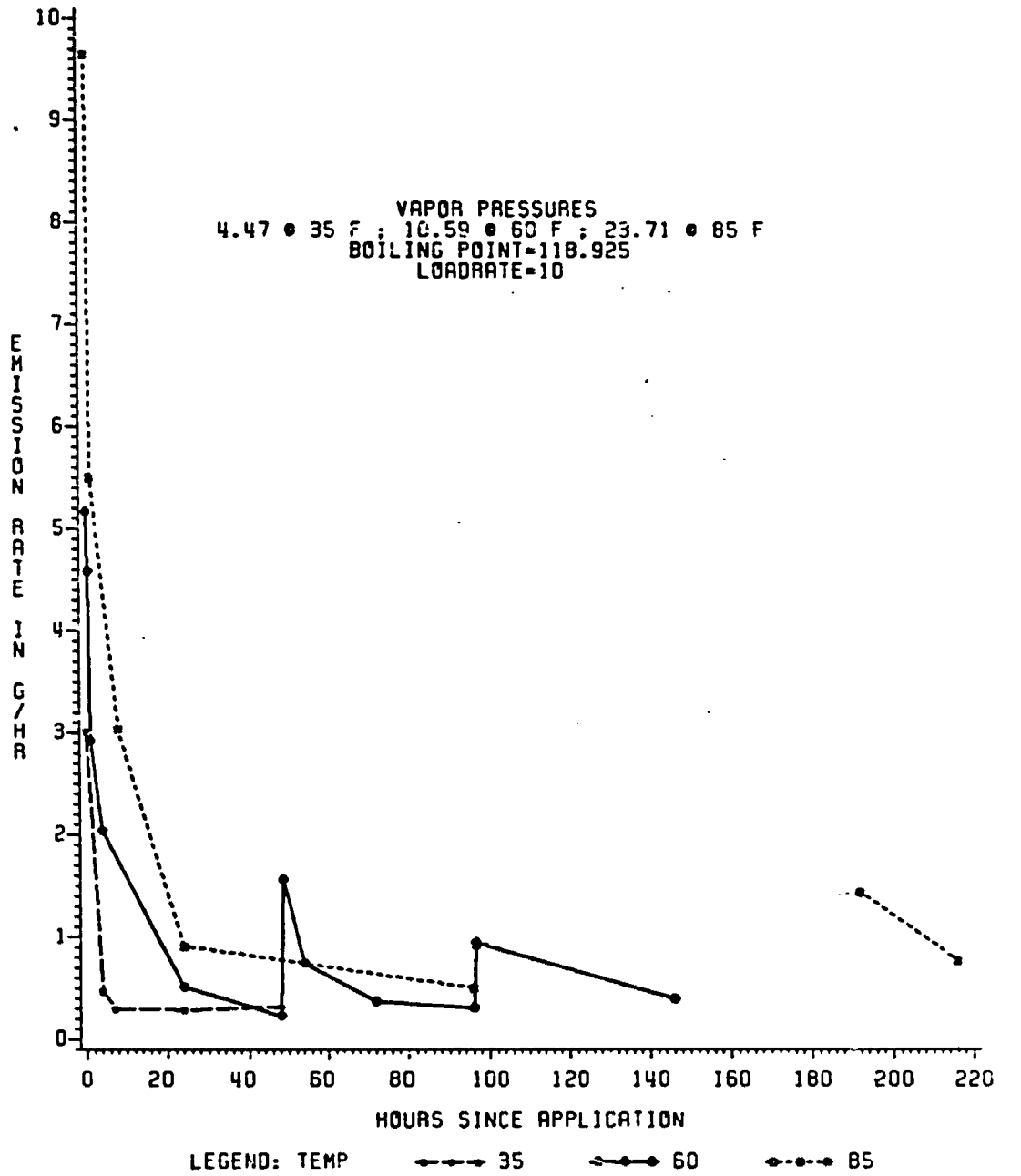

Figure C-9 Time Relation of Emission Rate and Temperature-3-Methylheptane, Loading Rate = 10%

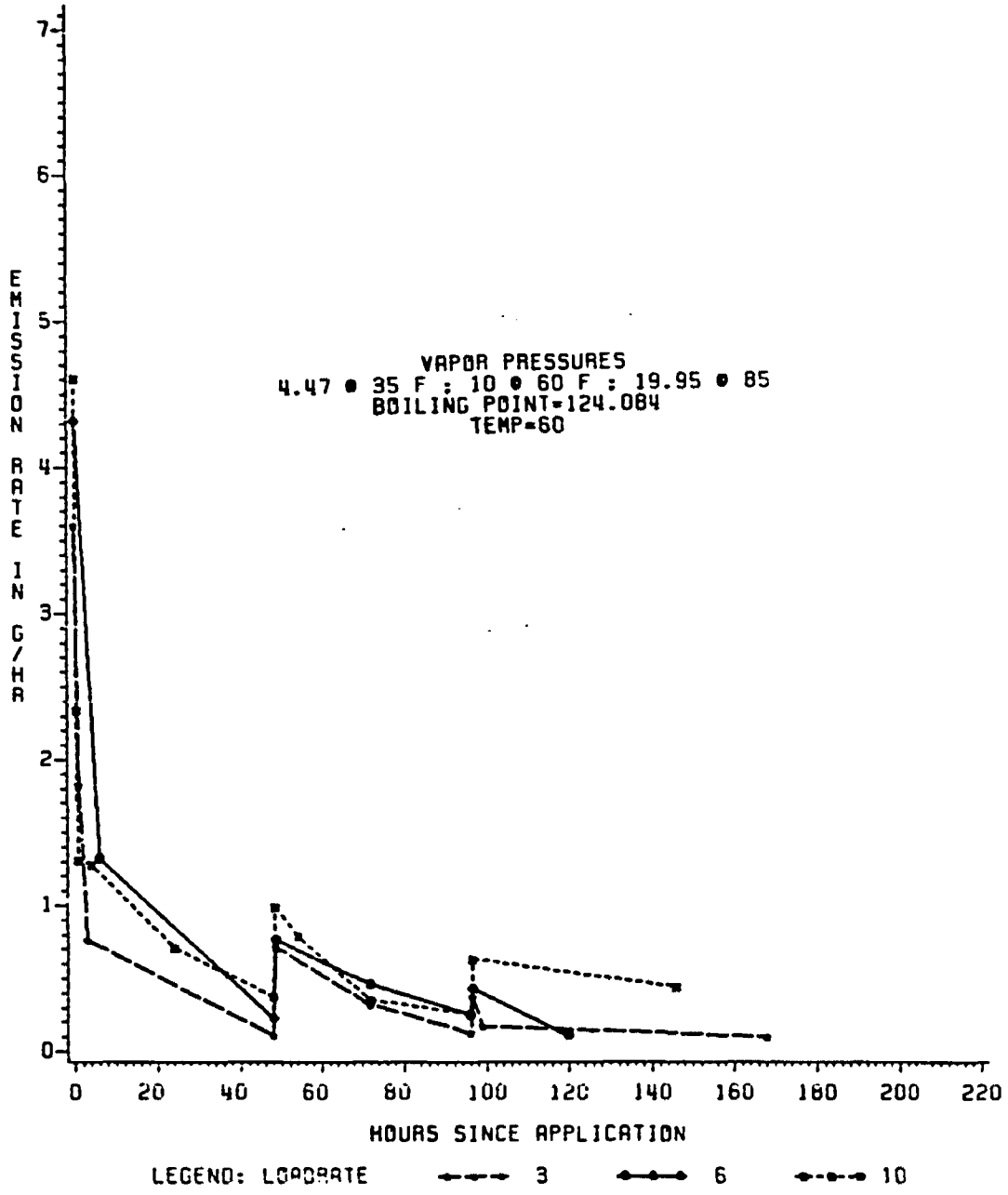

Figure C-10 Time Relation of Emission Rate and Loading Rate-2,2,5-Trimethylhexane, Temp. = 60°F

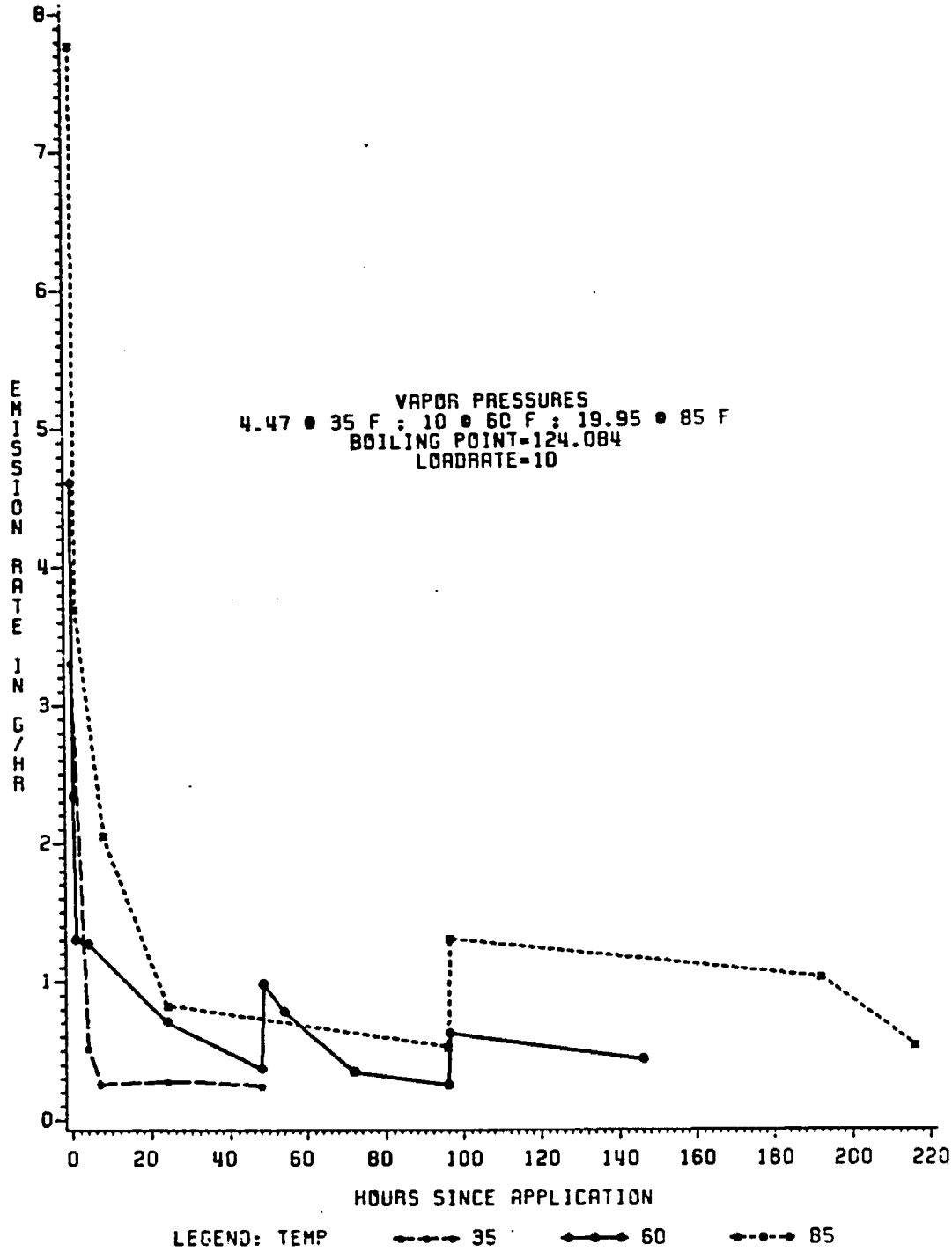

Figure C-11 Time Relation of Emission Rate and Temperature-2,2,5-Trimethylhexane, Loading Rate = 10%

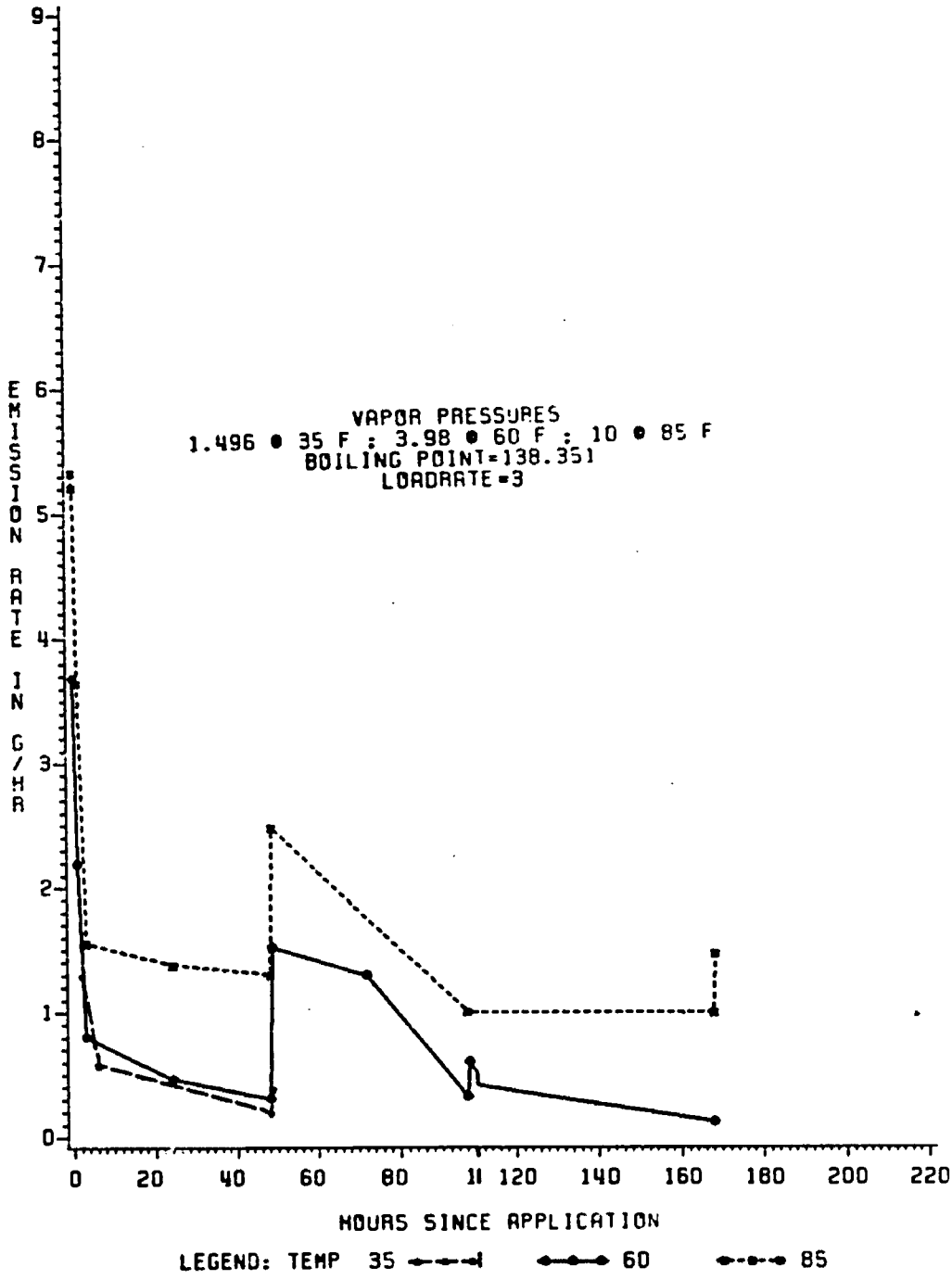

Figure C-12 Time Relation of Emission Rate and Temperature-1,4-Dimethylbenzene, Loading Rate = 3%

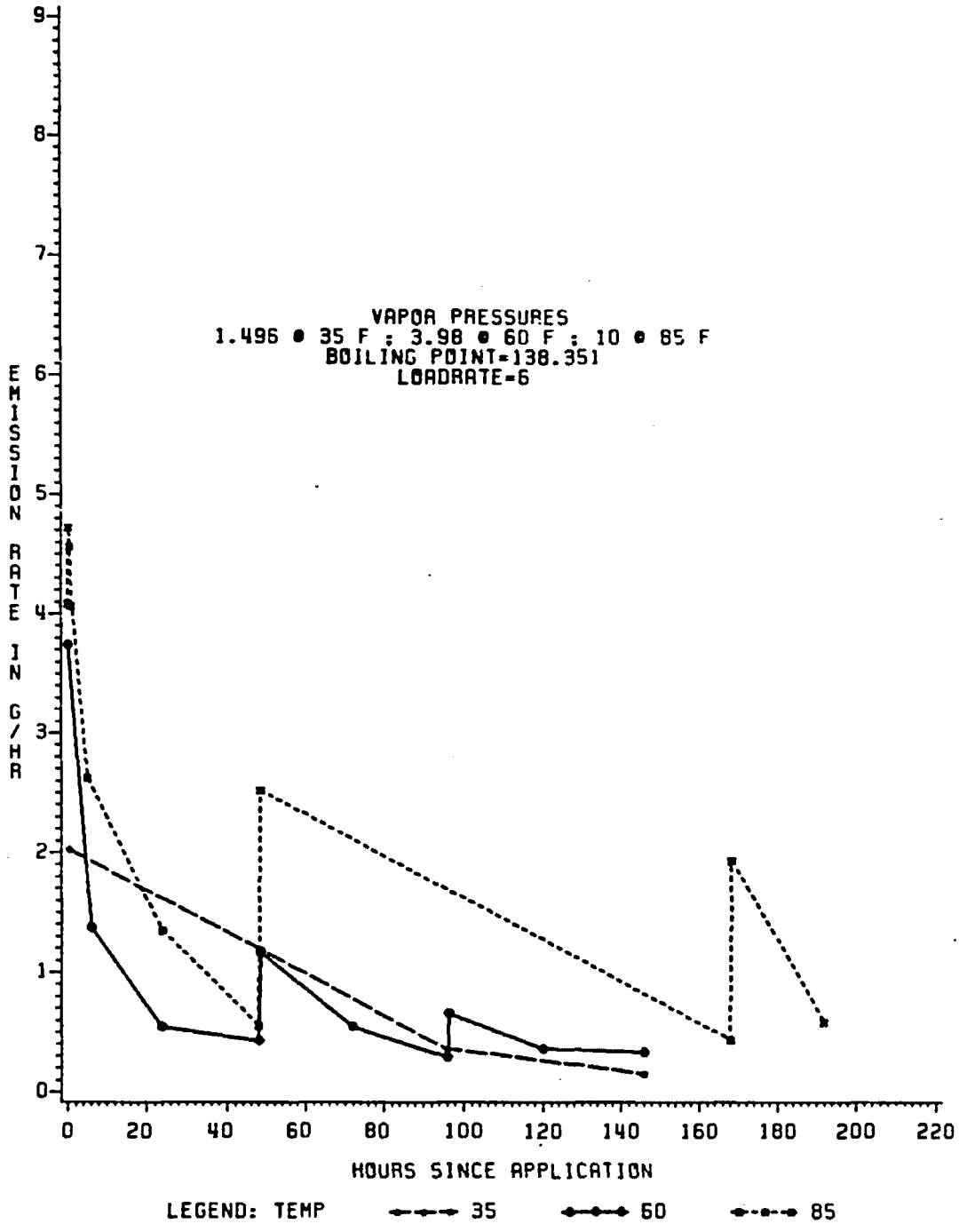

Figure C-13 Time Relation of Emission Rate and Temperature-1,4-Dimethylbenzene, Loading Rate = 6%

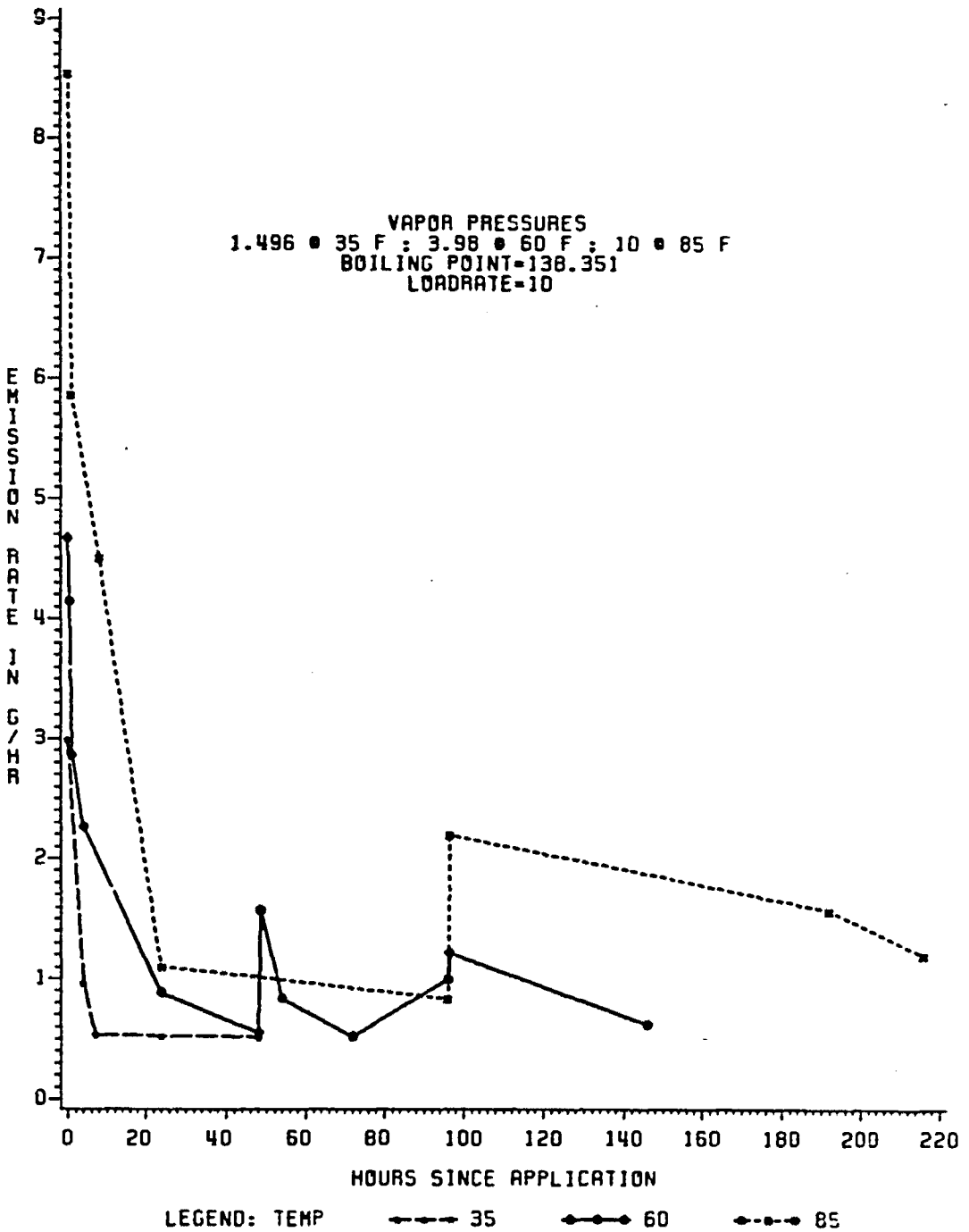

Figure C-14 Time Relation of Emission Rate and Temperature-1,4-Dimethylbenzene, Loading Rate = 10%

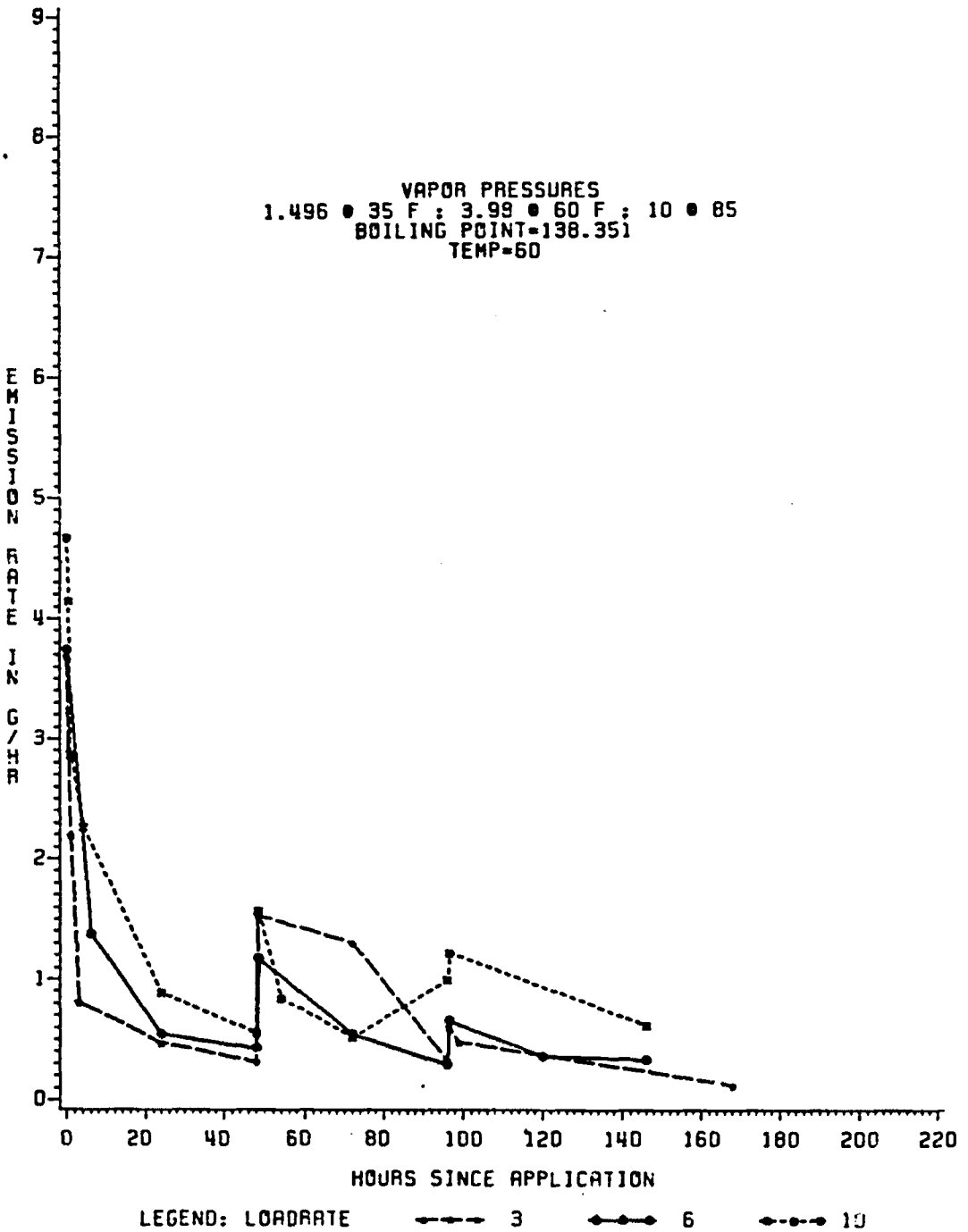

Figure C-15 Time Relation of Emission Rate and Loading Rate-1,4-Dimethylbenzene, Temp. = 60°F

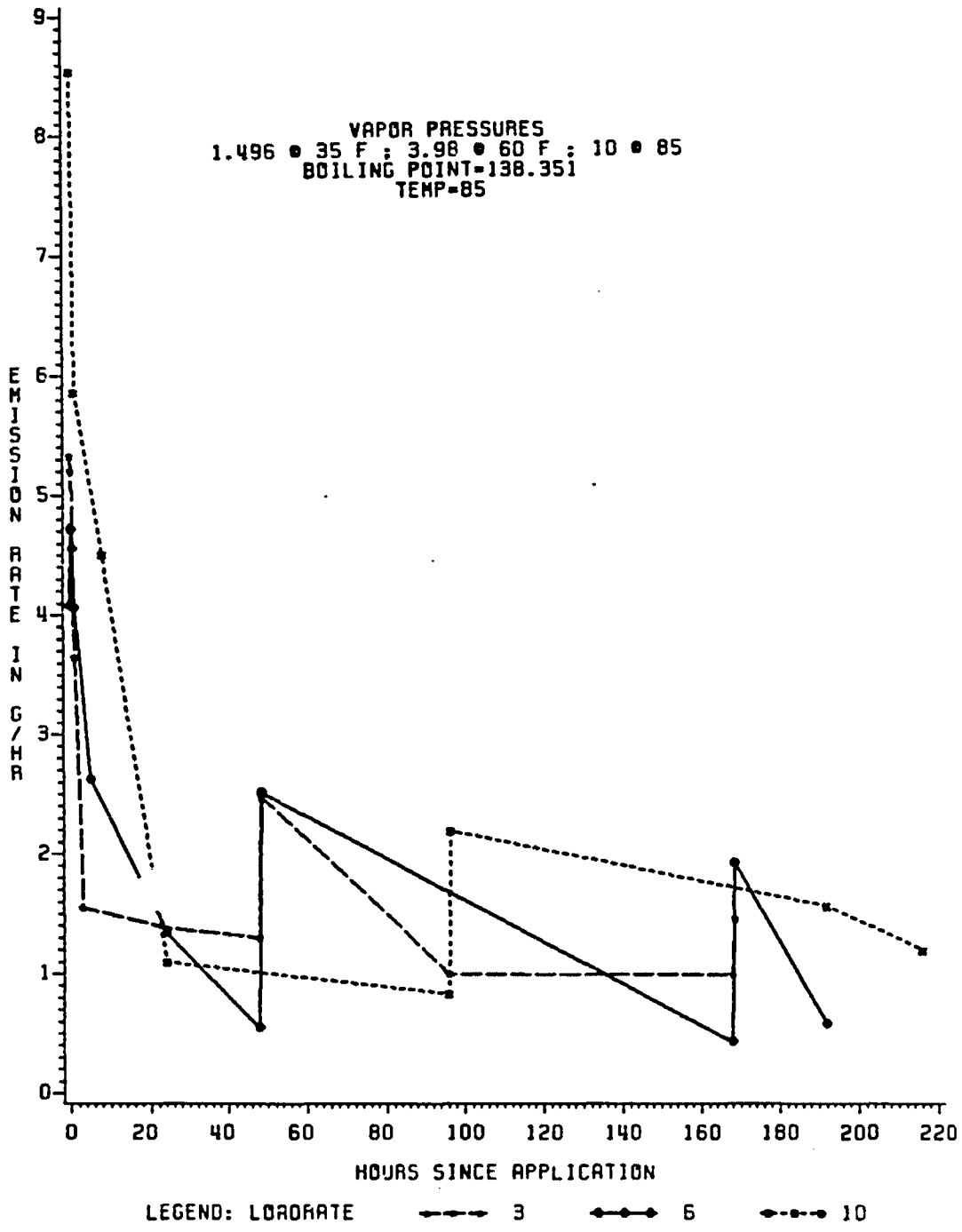

Figure C-16 Time Relation of Emission Rate and Loading Rate-1,4-Dimethylbenzene, Temp. = 85°F