H-26-05
W-25-30

LANDFARM AIR EMISSIONS

API PUBLICATION NO. 4500
HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
MARCH 1989

American Petroleum Institute
1220 L Street, Northwest
Washington, DC 20005

LANDFARM AIR EMISSIONS

Prepared for the American Petroleum Institute
1220 L Street, NW
Washington, DC 20005

Prepared under contract by:
Woodward-Clyde Consultants
500 12th Street, Suite 100
Oakland, CA 94607-4014

March 1989

FOREWORD

API PUBLICATIONS NECESSARILY ADDRESS PROBLEMS OF A GENERAL NATURE. WITH RESPECT TO PARTICULAR CIRCUMSTANCES, LOCAL, STATE, AND FEDERAL LAWS AND REGULATIONS SHOULD BE REVIEWED.

API IS NOT UNDERTAKING TO MEET DUTIES OF EMPLOYERS, MANUFACTURERS, OR SUPPLIERS TO WARN AND PROPERLY TRAIN AND EQUIP THEIR EMPLOYEES, AND OTHERS EXPOSED, CONCERNING HEALTH AND SAFETY RISKS AND PRECAUTIONS, NOR UNDERTAKING THEIR OBLIGATIONS UNDER LOCAL, STATE, OR FEDERAL LAWS.

NOTHING CONTAINED IN ANY API PUBLICATION IS TO BE CONSTRUED AS GRANTING ANY RIGHT, BY IMPLICATION OR OTHERWISE, FOR THE MANUFACTURE, SALE, OR USE OF ANY METHOD, APPARATUS, OR PRODUCT COVERED BY LETTERS PATENT. NEITHER SHOULD ANYTHING CONTAINED IN THE PUBLICATION BE CONSTRUED AS INSURING ANYONE AGAINST LIABILITY FOR INFRINGEMENT OF LETTERS PATENT.

.90397B-TOC CON-1

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (concluded)

LIST OF TABLES

LIST OF TABLES

LIST OF FIGURES

EXECUTIVE SUMMARY

INTRODUCTION

Hazardous waste land treatment (HWLT), or landfarming, is a waste management technology involving the controlled application of liquid, solid, and semisolid sludges to the upper zone of a soil system. The process, which is widely employed throughout the petroleum industry, is designed to assimilate waste into the soil and thereby degrade, transform, and/or immobilize hazardous chemical constituents. Research published to date has demonstrated that properly designed and operated landfarms are an effective and economical means of managing oily hazardous wastes generated by petroleum refineries.

With the passage of the Hazardous and Solid Waste Amendments of 1984, there has been increased scientific and regulatory interest in assessing the potential for atmospheric release of volatile hazardous constituents from refinery HWLT units. This report presents and discusses the results of a field investigation of volatile hydrocarbon emissions from an operating HWLT facility at a major West Coast petroleum refinery. The study was conducted over an 18-day period during September 1987 and involved the collection of oily waste, soil, and air samples to ascertain the environmental fate of oil and specific organic constituents applied to a 96,000 ft^2 landfarm test plot. In addition to field monitoring activities, the project involved the fabrication and testing of two devices to capture emissions from the landfarm surface. These were an Isolation Flux Chamber (IFC), which has been used in similar studies previously sponsored by the Environmental Protection Agency (EPA), and an experimental Wind Tunnel Device (WTD). Emissions predictions were also made using

theoretical models developed by Thibodeaux and Hwang (1982) and by EPA (1987a).

OBJECTIVES

The major objectives of this research were as follows:

(1) Evaluate the experimental WTD and determine if it offers any advantages over the IFC for measurement of landfarm emissions.

(2) Using the IFC and WTD, obtain direct measurements of emission rates for total non-methane hydrocarbons (TNMHC) and specific volatile constituents in refinery wastes. The waste constituents of interest were:

2-Methylpentane
3-Methylpentane
n-Hexane
Benzene
Toluene
Ethylbenzene
Total Xylenes
Phenol
Naphthalene

(3) Compare measured emissions to model predictions.

(4) Assess the relative importance of biodegradation and volatilization as fate pathways for volatile organic compounds in a refinery landfarm.

(5) Make a preliminary assessment of ambient hydrocarbon levels around a refinery landfarm during waste application and tilling.

WASTE

The liquid waste applied to the test plot during this study consisted of a mixture of dissolved air flotation (DAF) sludge (EPA Waste No. K048), API separator sludge (EPA Waste No. K051), slop oil emulsion solids (EPA No. K049), and nonleaded tank sludges. On a mass basis, the applied waste contained 25.0 weight percent oil, 4.4 weight percent solids, and 70.6 weight percent water. Benzene, toluene, and total xylenes concentrations were 47 mg/kg, 300 mg/kg, and 520 mg/kg, respectively. Comparisons with data reported elsewhere in the literature showed that the oily waste used in this experiment contained levels of volatile constituents which were representative of sludges across the refining industry that are typically managed in HWLT facilities.

The waste was applied to the surface of the test plot as a liquid and immediately mixed into the soil by an agricultural disc attached to the back of the sludge applicator. The oil loading was 0.42 lb/ft^3 of soil, also representative of refinery HWLT operations according to data reported by API (1983).

METHOD COMPARISON

With regard to the two emissions collection devices, it was determined that the WTD, as configured for this study, offers no advantage over the IFC for field measurements of organics volatilization from soil surfaces. Comparative TNMHC emissions data showed that results obtained with the WTD were more variable and of consistently greater magnitude than mass flux rates determined with the IFC at the same sampling locations. It is believed that these differences were due primarily to the much larger air flow rate passed through the WTD and the inability of the field analytical procedures used on this project to accurately quantify small TNMHC concentration changes (often less than 0.5 ppmv as hexane)

obtained across the WTD. In addition, the WTD proved to be an unwieldy and inefficient instrument under field conditions. Recommendations are made for improvements to the WTD design should this device be used again for measurement of low-level hydrocarbon emissions from a refinery landfarm.

TNMHC EMISSIONS

Emissions for both TNMHC and specific volatile constituents followed the same general pattern. Mass flux rates increased significantly from very low background levels when waste was first applied by surface spreading followed by immediate tilling. Average daily emissions then declined with time. Volatilization increased again with tilling of the test plot and then declined as before.

Instantaneous flux rates measured at individual sampling points were quite sensitive to variations in the temperature of the surface soil throughout the day. Emissions during the night were substantially lower than those measured during daylight hours.

MODELING

Under the conditions of this experiment, CHEMDAT6, the EPA land treatment air emissions model, was found to be a reasonably accurate predictor of observed volatilization rates for specific waste constituents immediately after sludge application and tilling. However, it overpredicted observed emissions at longer time intervals and thus tended to overestimate the cumulative mass of volatiles emitted to the atmosphere during the experiment. Inclusion of biodegradation coefficients provided with the CHEMDAT6 land treatment model had little effect on predicted emission rates over the short duration of this study. The Thibodeaux-Hwang model seriously overestimated emissions during all phases of the experiment.

ENVIRONMENTAL FATE OF HAZARDOUS CONSTITUENTS

Constituent concentrations in the applied waste were compared with cumulative mass emissions (determined with the IFC) and residual soil levels 10 days after waste application. These data are summarized on Table ES-1. Volatilization and biodegradation/experimental error each accounted for 30-40 percent of the aliphatic hydrocarbons (n-hexane, 2-methylpentane, and 3-methylpentane) placed on the test plot. Mass emissions of monoaromatics (benzene, toluene, total xylenes, and ethylbenzene) were 8-17 percent of the applied wasteload, with biodegradation/experimental error accounting for 35-60 percent. Naphthalene was apparently neither degraded nor volatilized during the experiment. The environmental fate of phenol in the landfarm could not be determined because none was detected in samples of the applied waste.

It should be noted that the cumulative mass emissions estimates presented on Table ES-1 are conservatively high. Constant flux rates from the soil surface were assumed for the time between field measurements, which were generally made only during daylight hours. Actual emissions after sunset were probably much lower. This conservatism suggests that biodegradation/experimental error may be a more important environmental fate process for organic constituents in landfarmed oily refinery wastes than indicated by the data on Table ES-1.

AMBIENT AIR MEASUREMENTS

Ambient air samples collected on two occasions showed only trace (1-2 ppbv) concentrations of several volatile constituents downwind of the test plot, and then only on the day of sludge application. Otherwise, ambient air at the test site was determined to be free of the organics of interest to this project (all concentrations <1.0 ppbv) at points upwind and downwind of the operating landfarm. Of perhaps greater significance, no detectable organic constituents were found in ambient air samples

Table ES-1. API LANDFARM STUDY - ENVIRONMENTAL FATE OF ORGANIC CONSTITUENTS APPLIED TO TEST PLOT

Compound	Applied To Test Plot (kg)	Cumulative Emissions[1] (kg)	Cumulative Emissions[1] Pct. of Applied	Remaining in Soil[2] (kg)	Remaining in Soil[2] Pct. of Applied	Biodegraded/ Experimental Error[1] (kg)	Biodegraded/ Experimental Error[1] Pct. of Applied
2-Methylpentane	9.648	3.694	38.3	2.875	29.8	3.079	31.9
3-Methylpentane	5.548	2.132	38.4	1.894	34.1	1.522	27.4
n-Hexane	9.045	2.787	30.8	2.686	29.7	3.572	39.5
Benzene	2.834	0.480	16.9	0.654	23.1	1.700	60.0
Toluene	18.090	1.789	9.9	5.509	30.5	10.792	59.7
Ethylbenzene	4.462	0.339	7.6	2.600	58.3	1.523	34.1
Xylenes (Total)	31.356	1.544	4.9	19.110	60.9	10.702	34.1
Naphthalene	2.231	0	0.0	3.684	165.1	0.0	0.0

1. During 10 days between waste application and end of experiment.

2. Assumes 10 in plow depth, soil density = 1.52 and test plot = 96,000 ft^2. See Table 3-8 for soil constituent concentrations at conclusion of test (September 24, 1987).

collected in the breathing zone of workers within the boundaries of the test plot on the day of sludge application and on the day of first tilling. However, it should be noted that this was only a preliminary ambient sampling exercise which should be supported by data from a more extensive monitoring network.

1.0 BACKGROUND

Hazardous waste land treatment (HWLT), or landfarming, is a waste management technology involving the controlled application of liquid, solid, and semisolid sludges to the upper zone (usually the top foot) of a dedicated soil system. The process is designed to assimilate waste into the soil to degrade, transform, and/or immobilize hazardous chemical constituents. A number of physical, chemical, and microbiological processes act in concert to achieve the goal of simultaneous waste treatment and disposal in a manner which protects public health and the environment.

To date, engineering research and design studies of industrial land treatment facilities have generally emphasized two major topics. First, field and laboratory research has been conducted to evaluate and enhance the biodegradation rate of oil and hazardous organic substances in landfarms. A second area of active research has investigated the in-soil fate and mobility of waste constituents during land treatment operations, with particular emphasis on ensuring protection of groundwater resources against the leaching of waste materials through the soil column.

Over the last several years, there has also been growing scientific and regulatory interest in assessing emissions of volatile waste constituents to the atmosphere during and after waste application at HWLT units. Based on preliminary modeling studies, it has been suggested that a significant fraction of the total hydrocarbons applied to a refinery landfarm could be emitted to the air (EPA 1986b). Since 1984, the Environmental Protection Agency (EPA) has sponsored at least a dozen projects addressing the issue

of air emissions from land treatment facilities. These studies have included laboratory investigations, evaluations of emissions monitoring protocols, field monitoring programs, and efforts to develop predictive mathematical models of landfarm air emission release rates.

As a major operator of HWLT facilities in the United States, the petroleum industry has also been concerned with many of the same technical issues. The research reported here was initiated by the American Petroleum Institute (API) to gain further insight into the significance of air emissions from petroleum refinery land treatment units. Woodward-Clyde Consultants (WCC) was retained to measure hydrocarbon releases before and after waste application to an operating landfarm. Off-site analytical support was provided by Rocky Mountain Analytical Laboratory (RMAL) under separate contract to API. The resulting emissions data, along with residual concentrations of applied waste constituents in the soil column, were used to assess the environmental fate of a selected group of hydrocarbons in a HWLT facility.

1.1 HWLT PRACTICES IN THE PETROLEUM REFINING INDUSTRY

A number of excellent review articles are available which discuss HWLT practices in the petroleum refining industry. The discussion presented in the following paragraphs has been taken largely from Grove (1978), Weldon (1979), Knowlton and Rucker (1978), API (1983, undated), Ryan et al. (1986), and Martin, Sims, and Matthews (1986). The reader is referred to these references for further detailed information.

In the United States, EPA has estimated that approximately 100 HWLT units are in operation in the petroleum industry, primarily in the refining sector (Ryan et al. 1986). As of 1983, the most recent survey data available, about one-third of all U.S. refineries operated full-scale or pilot-scale land treatment facilities in widely dispersed geographical areas. In addition, 26 of 38 Canadian refineries and at least 10 European

refineries were also known to have landfarms (API 1983). While the number of operating HWLT units in U.S. refineries has certainly decreased in recent years, the practice is still widespread across the industry. Compared to other accepted waste disposal technologies, land treatment is considered to be an effective yet low cost alternative for management of refinery sludges (API undated).

Landfarming practices vary widely across the industry. However, all land treatment facilities take advantage of the well-known ability of soil bacteria to metabolize petroleum hydrocarbons (Bossert et al. 1984; Raymond et al. 1976). Both listed hazardous wastes (API separator bottoms, dissolved air flotation sludge, slop oil emulsion solids, and leaded tank bottoms) and non-listed wastes (biological sludges, filter clays, non-leaded tank bottoms, alkylation sludges, oil spill debris, etc.) may be disposed in refinery HWLT units. The applied sludges may be liquids or dewatered solids. Soil characteristics vary from site to site, as do waste loading rates and frequency of application. Management practices generally include tilling to aerate the soil, application of fertilizers to supply necessary inorganic nutrients (nitrogen, phosphorous, and potassium), and, in arid climates, irrigation to maintain soil moisture. Some facilities also add lime to maintain soil pH within the range necessary to sustain optimum biodegradation rates.

In addition to oil, refinery sludges contain a number of constituents identified as hazardous by EPA at 40 CFR 261. Grouped in terms of broad chemical classes, these include monoaromatic hydrocarbons, polynuclear aromatic hydrocarbons, phenolic compounds, cyanide, sulfide, and heavy metals. Available information indicates that all these constituents are degraded and/or effectively immobilized in refinery landfarms (API 1984, 1987) and that properly designed and operated facilities do not pose a significant threat to groundwater resources. The existing data base on air emissions from refinery land treatment operations is summarized below in Section 1.2.

The Resource Conservation and Recovery Act (RCRA) authorizes EPA to develop and enforce regulations governing hazardous waste management. Existing EPA regulations require all owners/operators of HWLT facilities to obtain a final RCRA permit under 40 CFR 270, complete a land treatment demonstration, meet certain design specifications, and conduct groundwater and unsaturated zone monitoring.

The Hazardous and Solid Waste Amendments of 1984 (HSWA) contain an additional provision which directly affects operation of refinery HWLT facilities. This is the restriction on future land disposal of hazardous wastes. As stated in Section 1002(b)(7) of HSWA, Congress found that some land disposal practices pose substantial risk and that "land disposal . . . should be the least favored method for managing hazardous wastes." Although landfills and surface impoundments were the primary motivation behind this finding, Section 3004(k) also defines land treatment as "land disposal." Under Section 3004(g), EPA must prohibit continued land disposal of listed wastes, including certain refinery wastes, according to a set schedule. HSWA requires that listed refinery wastes be banned from land disposal unless EPA is satisfied "that there will be no migration of hazardous constituents from the disposal unit . . . as long as the waste remains hazardous" [Section 3004(g)(5)].

On August 17, 1988, EPA promulgated final regulations which restrict land disposal of listed refinery wastes effective August 8, 1990 (53 Fed Reg. 31187-31222). These restrictions apply to many of the sludges currently disposed in refinery HWLT units. Continued land treatment after the effective date is prohibited unless the wastes are first processed to meet certain technical standards. Limits on organics in treatment residuals are based on solvent extraction and/or fluidized bed incineration of listed hazardous refinery wastes. Standards for heavy metals reflect performance data for chemical fixation of treatment residuals. Individual facilities may be granted an exemption from the land disposal prohibition

pursuant to a "no migration" petition approved by EPA under 40 CFR 268.6. The Agency has recently released technical guidance to implement the petition process. It is anticipated that volatiles emissions will be an important aspect of the required "no migration" demonstration for refinery HWLT units.

1.2 PREVIOUS INVESTIGATIONS OF REFINERY HWLT AIR EMISSIONS

1.2.1 Laboratory Studies

One of the earliest laboratory investigations of atmospheric emissions from refinery HWLT operations was reported by Minear et al. (1981). This work, which was jointly funded by API and EPA, was intended to characterize oily refinery wastes and examine the effects of a number of parameters on the rate and mass of fugitive hydrocarbon emissions from land treatment facilities shortly after waste application. The variables that were studied included sludge type (API separator bottoms or tank bottoms), sludge volatility, soil moisture content, wind speed, relative humidity, air temperature, soil temperature, sludge loading on soil, and sludge application technique (surface or subsurface). All the studies were conducted in an enclosed landfarm simulator containing 0.3 ft^3 (approximately 1 ft square and 4 in deep) of soil from an operating refinery HWLT facility. Air was passed over the enclosed soil surface at a rate of 1-3 mi/hr and the total non-methane hydrocarbon (TNMHC) content of the off-gas was monitored.

When oily sludges were applied to the landfarm simulator, TNMHC emissions showed an initial sharp increase, usually reaching a maximum value within 2 min. This was followed by an equally rapid decline, such that emissions 6 min after waste was applied were on the order of 10 percent of the maximum values. TNMHC volatilization then followed a slow approach to background values.

Important factors affecting TNMHC emission rates and mass emissions included sludge volatility (as measured by a sludge stripping test developed for this study), sludge loading, and soil moisture. Tilling of the soil was found to increase emissions, and subsurface application of waste resulted in decreased TNMHC volatilization.

The second phase of the work initiated by Minear et al. (1981) was reported by EPA (1984a). Using the same landfarm simulator, this follow-up study was performed to provide a more comprehensive characterization of oily refinery sludges and HWLT soils and to evaluate the effect of operating and process variables on TNMHC emissions over periods up to 6-8 hr. Nine refinery sludges (including API separator sludge, dissolved air flotation sludge, slop oil emulsion solids, and leaded tank bottoms as well as a variety of non-listed refinery wastes) and eight landfarm soils were collected and characterized. Air passing over the sludge/soil mixture was maintained at a constant speed of 3 mi/hr. Over 40 successful simulation test runs were completed and reported. In addition to TNMHC measurements, samples of landfarm simulator off-gas from several tests were collected in stainless steel canisters for analysis of specific volatile constituents.

Data reported by EPA (1984a) show that the level of TNMHC emissions was influenced primarily by sludge volatility, sludge loading to the soil, and atmospheric humidity. In contrast to results from the first phase of the study (Minear et al. 1981), moisture content of the soil was not found to be a significant variable affecting TNMHC emissions.

Changes in TNMHC emissions with time followed the same general pattern observed by Minear et al. (1981). TNMHC concentrations in the off-gas from the landfarm simulator rose to a peak value immediately after sludge application, then declined in an approximately exponential manner. Peak TNMHC concentrations, cumulative mass emissions, and the rate of emissions decline were all apparently related to oily waste volatility, as measured by the same sludge stripping test used by Minear et al. (1981). EPA

(1984a) also found that tilling of sludge-amended soils resulted in a TNMHC emissions increase. The peak concentrations attained after tilling also declined exponentially.

Cumulative mass emissions for specific volatile constituents were not determined. However, EPA (1984a) did show that measured flux rates shortly after waste application to the landfarm simulator were within a factor of two to ten of predictions obtained using a mathematical model for HWLT emissions developed by Thibodeaux and Hwang (1982). Compounds for which predictions were made included benzene, toluene, xylene isomers, and naphthalene.

Laboratory studies conducted at Utah State University evaluated emission flux rates of seven volatile constituents during simulated land treatment of oily refinery wastes (EPA 1986d). Compounds of concern included benzene, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, and naphthalene. Two soil types and two listed refinery wastes, API separator bottoms and slop oil emulsion solids, were tested. Emissions were collected using a laboratory-scale isolation flux chamber (IFC), sorbed on Tenax tubes, and analyzed by gas chromatography using a flame ionization detector.

The primary objective of the Utah State University laboratory studies (EPA 1986d) was to evaluate the predictive model developed by Thibodeaux and Hwang (1982). When wastes were applied to the soil surface, measured flux rates for each of the compounds evaluated were a linear function of the inverse square root of time since sludge application, indicating the validity of a modeling approach assuming primarily diffusion-controlled vapor movement within the soil column. The model of Thibodeaux and Hwang (1982) was not a good emissions predictor for subsurface waste applications, however.

The laboratory data also showed that subsurface application of wastes to a simulated landfarm operation resulted in a one to four order of magnitude decrease in flux rates for volatile constituents compared to surface sludge applications (EPA 1986d). It was also concluded that interactions between volatiles and soil organic matter may be of some importance in suppressing emissions when subsurface waste application techniques are used at HWLT facilities.

In 1987, Radian Corporation reported the results of an assessment of air emissions from a laboratory land treatment facility (EPA 1987e). The objective of this work was to measure TNMHC and compound-specific emissions during simulated HWLT activities over extended time periods (minimum of 31 days). Experiments were conducted in covered boxes with a soil surface area of approximately 3 ft^2 and a tilled depth of 8 in. A gas collection system directed air over the laboratory land treatment plots at a constant flow rate (approximately 3 mi/hr), temperature, and humidity. Emissions were analyzed in the off-gas. Sludges tested included API separator bottoms and dissolved air flotation sludge. Soils for the laboratory land treatment units came from two active refinery HWLT facilities.

TNMHC emissions were measured on a semi-continuous basis and showed the same general trends with time observed in other laboratory studies discussed above. Emission rates were highest during and within a few hours after sludge application to the soil surface and at the first tilling one day after sludge was applied. After a period of four to eight hours, TNMHC emissions diminished to a relatively low level and then gradually decreased to background levels. Tillings during the test runs caused temporary increases in TNMHC emissions. Cumulative TNMHC mass emissions during each month-long test represented 4.0-7.6 weight percent of the oil applied to the simulated landfarms (EPA 1987e).

Emissions of individual volatile compounds were profiled during sludge application and tilling. The relative proportions of alkanes and aromatics

in the off-gas were found to vary with each sludge type tested. From data for one of the test runs, emissions flux rates of 21 compounds (primarily alkanes and monoaromatic hydrocarbons) were calculated and correlated with the inverse square root of time since the soil was last disturbed by sludge application or tilling. Statistically significant linear relationships were obtained, again confirming the validity of a modeling approach for HWLT emissions based on diffusion-controlled vapor movement in the soil column (EPA 1987e).

1.2.2 Field Investigations

The Utah State University landfarm studies (EPA 1986d) also evaluated air emissions at six locations within a full-scale HWLT facility operating at a Midwestern refinery. Oily wastes, applied as a liquid to the soil surface, were a mixture of API separator bottoms and dissolved air flotation sludge. The landfarm was tilled twice during the experiment, approximately one day and seven days after sludge application.

Emissions of the same seven volatile constituents evaluated in the laboratory were measured using an IFC. Tenax traps were used to capture volatile constituents in the IFC off-gas. The traps were analyzed by gas chromatography using a flame ionization detector.

The emissions pattern with time for individual volatile constituents was the same as that observed in earlier laboratory studies for TNMHC. Emission spikes were produced during waste application and tilling for all compounds assessed, followed by subsequent emissions declines.

Furthermore, the field emissions rate data for all compounds investigated followed a linear relationship of flux versus the inverse square root of time since waste application or tilling. This finding lends further support to the air emissions modeling approach suggested by Thibodeaux and Hwang (1982). However, the Utah State University researchers also observed significant spatial variability across the test

plot, suggesting it is not appropriate to make general emissions estimates for an entire landfarm based on only a small number of IFC samplers. In particular, it was determined that sludge loadings, soil temperature, and soil air-filled porosity, all of which are important variables when correlating predicted and measured flux rates, were highly variable across the test site and that this variance should be considered when applying the model of Thibodeaux and Hwang (1982).

EPA (1987c) also reported the results of a five-week field study to measure TNMHC and specific compound emissions from an operating HWLT facility at a major West Coast refinery. Mixed oily wastes were applied to the soil surface. The effect of soil tilling and subsurface injection of waste on atmospheric emissions was also monitored.

Measurements were made using an IFC. Samples of IFC off-gas were collected in syringes and analyzed on-site using a dedicated gas chromatograph equipped with a flame ionization detector. Air samples for speciation of volatile organics were collected in stainless steel canisters and shipped to a remote laboratory for analysis by gas chromatography using a flame ionization detector and cryogenic preconcentration techniques.

TNMHC emissions were observed to rise immediately after sludge application or tilling and then decline with time in an approximately exponential manner. Measured TNMHC emissions were found to be related to the ambient air temperature above the soil surface. As a result, a significant diurnal effect was observed, with TNMHC emission rates determined before dawn to be only 25-50 percent of comparable measurements made during daylight hours (EPA 1987c). Over the entire experiment, it was estimated that 30-35 percent of the applied TNMHC was volatilized.

Subsurface waste application was not found to reduce TNMHC emissions in the EPA (1987c) field study. However, the authors noted that it would be difficult to generalize from this particular experiment to other sites,

because the test plot was tilled immediately after the waste was injected. Different results may have been obtained for the case of subsurface waste application if more time had elapsed prior to the first tilling.

The 12 specific compounds evaluated (both aliphatic and aromatic hydrocarbons) behaved in the same manner as TNMHC. Emission rates rose after sludge application, decreased with time, increased after tilling, and showed diurnal fluctuations. Depending on the specific compound of interest, it was estimated that 17-94 percent of the mass originally applied to the test plot was emitted to the atmosphere during the five weeks of testing (EPA 1987c). On a percentage basis, emissions of applied aliphatic hydrocarbons were generally greater than those for aromatic hydrocarbons.

Measured emissions were compared to predictions obtained using the model of Thibodeaux and Hwang (1982). The model was found to predict mean emission rates that were generally higher than those observed, but which agreed with the field data within an order of magnitude (EPA 1987c).

1.3 RESEARCH OBJECTIVES

With the above information as background, the study described in this report was initiated by API to achieve the following five objectives:

(1) Evaluate a proposed Wind-Tunnel Device (WTD) and determine if this procedure offers any advantage over EPA's IFC for measurement of landfarm air emissions.

(2) Obtain direct measurements of emission rates for TNMHC and specific volatile constituents present in refinery wastes using the IFC and WTD. The constituents of interest were:

n-Hexane
Benzene
Toluene
Ethylbenzene
Total Xylenes
Phenol
Naphthalene

(3) Compare emissions measured at a landfarm using the IFC and WTD with estimates from the CHEMDAT6 land treatment model (EPA 1987a) and the Thibodeaux-Hwang model (Thibodeaux and Hwang 1982).

(4) Obtain preliminary measurements of ambient hydrocarbon levels around a refinery landfarm during waste application and tilling.

(5) Assess the relative importance of biodegradation and volatilization as environmental fate processes for volatile organic compounds in a refinery landfarm.

2.0
METHODS AND MATERIALS

2.1 EQUIPMENT CONSTRUCTION

Prior to the field activities described in Section 2.3, WCC fabricated and tested two WTDs and one IFC for the direct measurement of landfarm air emissions. These devices were designed and constructed according to API's specifications at the WCC laboratory in Pleasant Hill, California. The following sections provide details regarding equipment construction and subsequent validation.

2.1.1 WTD

Figure 2-1 shows a schematic diagram of the WTD. This device was designed to pass purified air at a velocity approaching typical ground-level conditions (1-2 mph) over an enclosed portion of the landfarm surface. Air samples were taken upstream and downstream of the exposed soil. Hydrocarbon emission rates were determined from the difference between upwind and downwind concentrations, the measured air velocity, and the known landfarm surface area. Each of the major sections of the WTD is described below.

2.1.1.1 Blower. The blower was an electrically-driven Dayton fan (Model 4C754) capable of delivering air at up to 200 cfm. Fan speed was controlled with an industrial-quality 500 watt light dimmer. Power to the blower was supplied via extension cords connected to diesel-fired electric generators positioned at various locations outside the test plot.

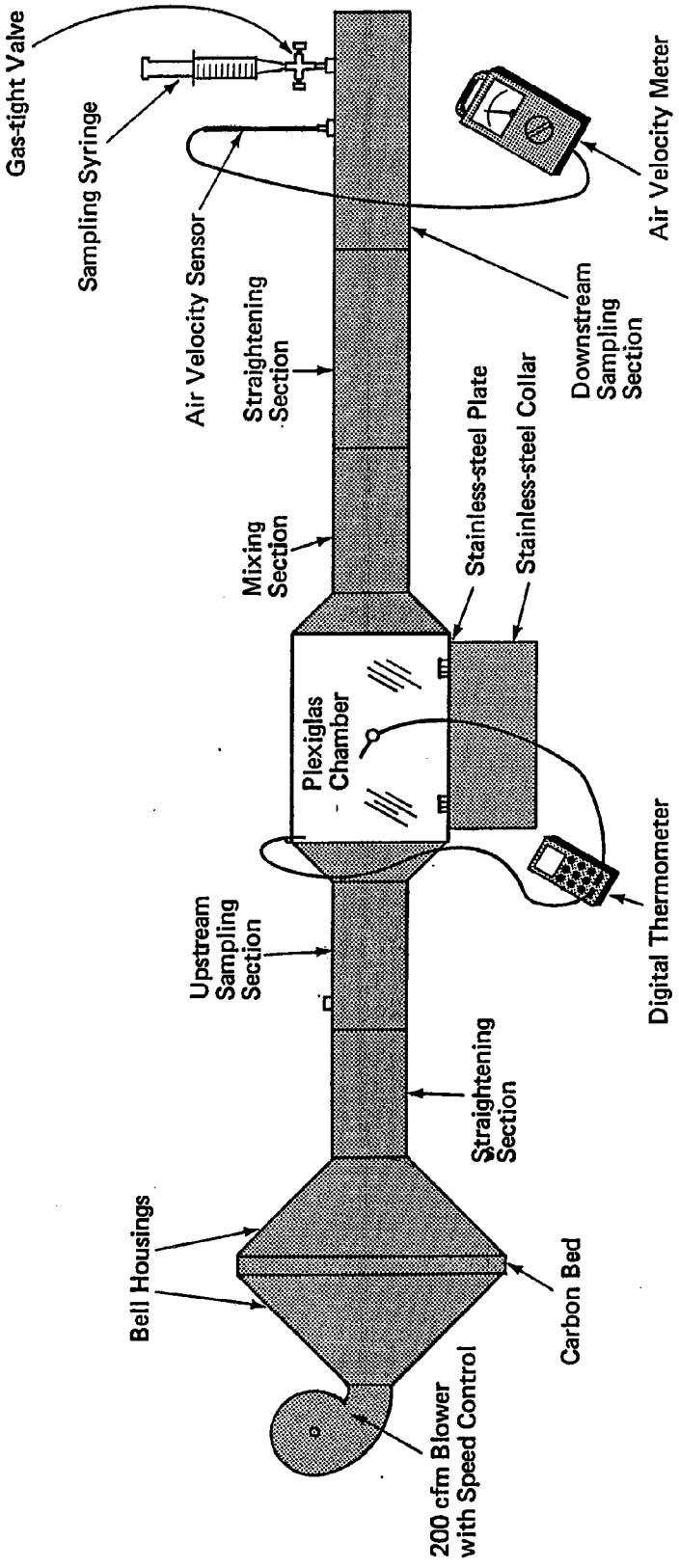


Figure 2-1. SCHEMATIC DIAGRAM OF WIND TUNNEL DEVICE (WTD)

2.1.1.2 Carbon Filter Section. The carbon filter section consisted of a bell housing (to reduce air velocity), a carbon filter, and an identical bell housing downstream of the filter. The carbon filter, supplied by Charcoal Filtration Media Co., measured 18 in x 18 in x 1.125 in (see Figure 2-2), with the carbon bed depth sized to remove background hydrocarbons (butane and above) from the inlet air at an assumed concentration of 20 ppm for up to 240 hr.

2.1.1.3 Straightening Sections. The upstream and downstream straightening sections each consisted of a 24 in length of 8 in diameter stove pipe. The stove pipe was tightly packed with 2 in diameter plastic tubes which served as flow straighteners.

2.1.1.4 Sampling Sections. The upstream and downstream sampling sections were each 24 in lengths of 8 in diameter stove pipe with several small holes punched for sample ports and insertion of instrument probes. The sampling ports consisted of Swagelock fittings coupled with approximately 6 in of 0.25 in O.D. Teflon tubing. One end of the tubing was inserted into the approximate center of the flowing air stream in each sampling section. A syringe needle was inserted snugly into the other end. The needle was coupled to a gas-tight syringe for collection of gas samples for TNMHC analysis (see Section 2.3.2.5 for additional details on gas sampling from the WTD). The downstream sampling section also contained a port for insertion of a hot wire anemometer (for air velocity measurements) and a thermocouple (for quantification of exhaust air temperature).

2.1.1.5 Emissions Collection Section. The emissions collection section consisted of an inlet bell housing, a flow director, a plexiglass chamber, and a second bell housing section. The bell housings simply connected the emissions collection section to the rest of the tunnel. The flow director aimed the air stream down to the soil surface. The plexiglass chamber covered the soil surface to be sampled and had the necessary ports to allow air and soil temperature measurements to be taken. The chamber dimensions were 10 in x 10 in x 20 in, for a total volume of 2000 in^3.

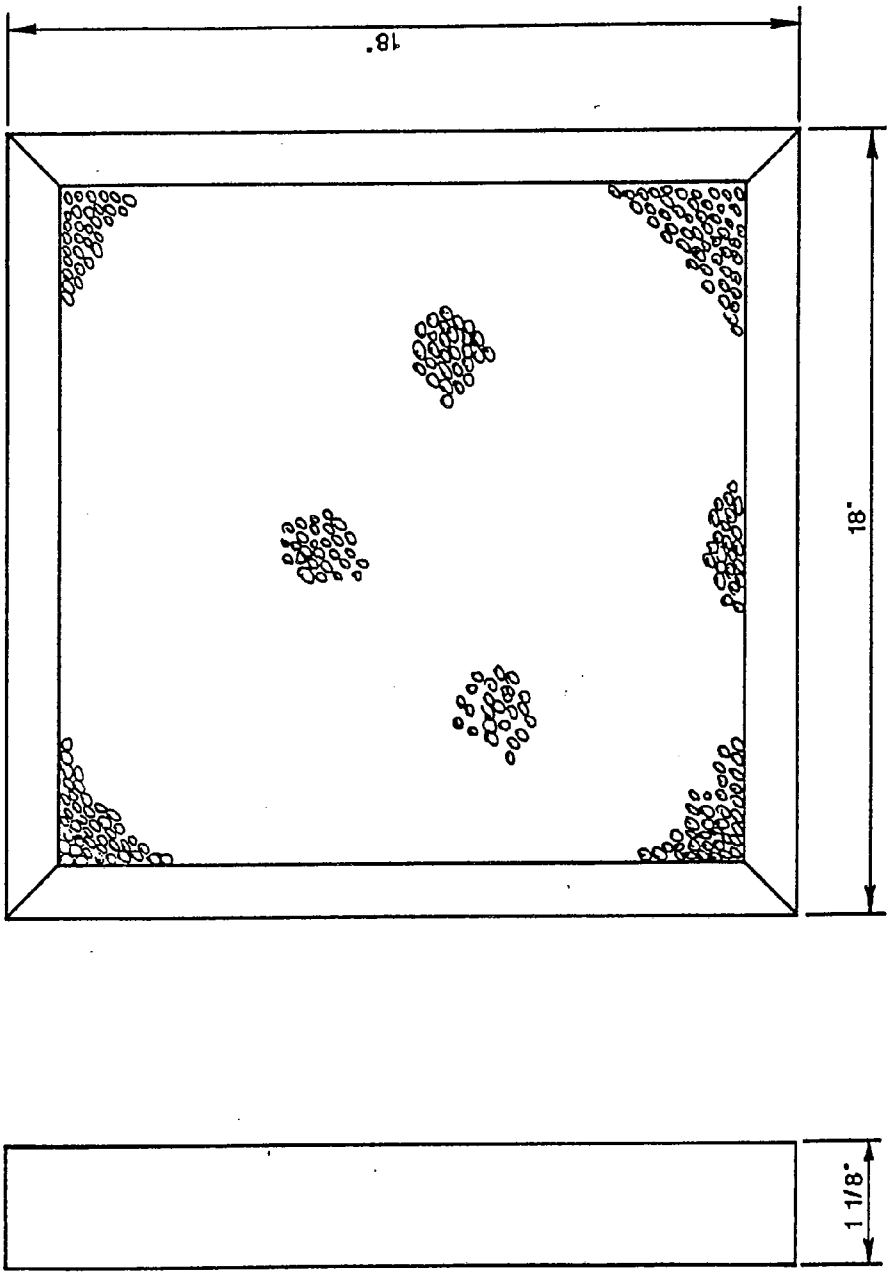


Figure 2-2. WIND TUNNEL DEVICE: CARBON FILTER

2.1.1.6 Sampling Collar. The sampling collars were rectangular stainless steel boxes, open on the top and bottom and inserted into the soil at approximately 20 fixed locations across the test plot. As shown in Figure 2-3, each collar was designed to capture emissions from a defined surface area of 200 in^2. The plexiglass chamber of the WTD fit snugly over the collar and was secured in place with stainless steel bolts. The same collars were also used for the IFC (see Section 2.1.2). During the course of sampling, the emissions collection devices (WTD and IFC) were carried from collar to collar according to a fixed sequence (see Sections 2.3.2.5 and 2.3.2.6).

2.1.1.7 Mixing Section. The air stream was exhausted from the plexiglass chamber into a mixing section prior to collection of the downstream sample. The mixing section was a 24 in length of 8 in diameter stove pipe with curved vanes which caused turbulent air flow and generated a homogenous mixture. Figure 2-4 shows details of the mixing section.

Before going to the field, a series of calibration runs was performed in the laboratory to test the air velocity measurement equipment and the WTD air speed control system. The carbon filter was removed and a standard gas mixture containing isobutylene was introduced through a mass flow controller at the blower inlet. Air speed in the WTD was set using the anemometer in the downstream sampling port. Downstream isobutylene concentrations in the diluted gas were measured using a portable photoionization detector (PID) inserted into the sampling port. Gas flow and WTD air flow were changed during each run. The laboratory calibration results, shown on Table 2-1, indicate that the WTD was able to quantitatively recover a spiked standard material under laboratory conditions.

This experiment was repeated in the field under slightly different conditions at the conclusion of the experiment. A cylinder containing a

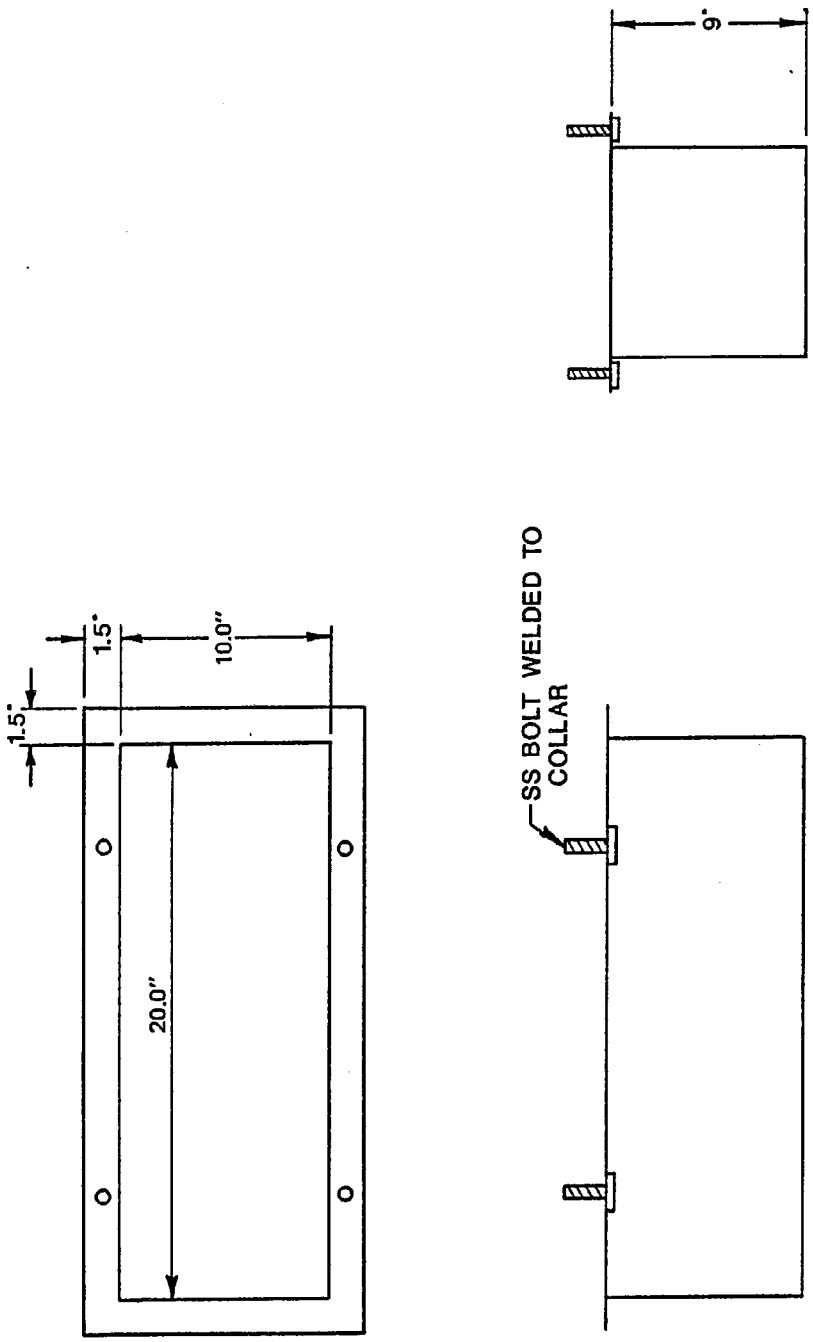
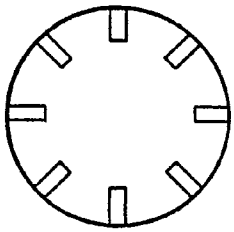
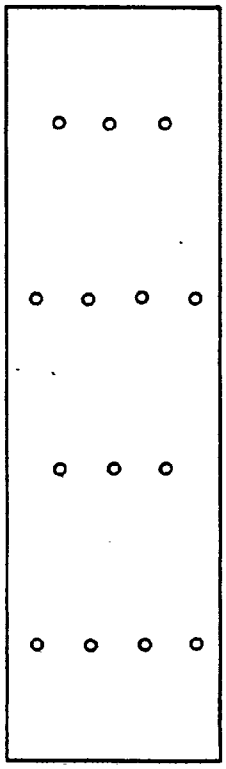


Figure 2-3. STAINLESS STEEL SAMPLING COLLAR FOR IFC AND WTD





8" STOVE PIPE, 24" LONG WITH TABS POP RIVETED IN SIDE

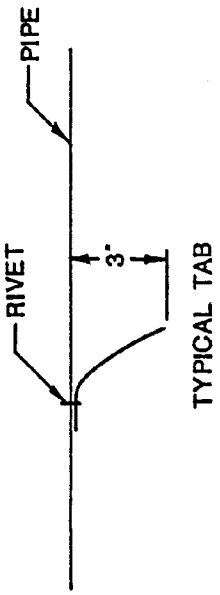


Figure 2-4. WIND TUNNEL DEVICE: MIXING SECTION

Table 2-1. LABORATORY CALIBRATION OF WTD

Run	Expected Downstream Isobutylene Concentration (ppmv)	Measured Downstream Isobutylene Concentration (ppmv)	Percent Recovery
1	100	97	97.0
2	200	205	102.5
3	400	410	102.5
4	1000	985	98.5

standard 3000 parts per million by volume (ppmv) isobutylene mixture in zero air (equivalent to 2000 ppmv hexane) was metered into the upstream sampling port through a rotameter. The flow rate of the standard gas was varied while the air flow rate through the tunnel was held constant at 157 ft^3/min (4450 L/min). Downstream gas samples were collected in syringes (see Section 2.3.2.5) and analyzed for total hydrocarbons using a flame ionization detector (FID), as described in Section 2.4.3.1. Upstream gas samples were collected prior to the experiment to determine background hydrocarbon levels.

Results of the field validation experiment are given in Table 2-2. These data reveal two limitations to the WTD under the field conditions of this study. First, the WTD measures emissions by calculating the difference between upstream and downstream hydrocarbon concentrations. Inherent analytical errors thus become significant when the concentration differences are on the same order as the measurements themselves. This issue is described in greater detail in Section 3.3, which discusses the WTD emissions data.

Second, the analytical limit of detection for the field hydrocarbon measurements has been estimated to be in the range of 0.05-0.1 ppmv (as hexane). Analytical uncertainty is an important consideration when reviewing data, such as those on Table 2-2, which are at or near the limit of detection. Moreover, the reasonably consistent isobutylene recovery reported on Table 2-2 (generally 200-250 percent) may be evidence of a systematic error in the field calibration curve that could bias reported values at low hydrocarbon concentrations (on the order of 1.0 ppmv).

2.1.2 IFC

A schematic of the complete IFC assembly is shown in Figure 2-5. Figure 2-6 presents construction details for the flux chamber dome.

Table 2-2. FIELD VALIDATION OF WTD

Run	Flow Rate of Standard Gas (L/min)	Measured Upstream Hydrocarbon Concentration (ppmv as hexane)	Measured Downstream Hydrocarbon Concentration (ppmv as hexane)	Measured Change Across WTD (ppmv as hexane)	Expected Change Across WTD (ppmv as hexane)	Percent Recovery
1	0.730	0.20	0.97	0.77	0.33	233.3
2	0.275	0.20	0.56	0.36	0.12	300.0
3	1.480	0.20	1.60	1.40	0.67	208.9
4	1.980	0.20	2.69	2.49	0.89	279.6
5	1.480	0.20	1.80	1.60	0.67	237.8

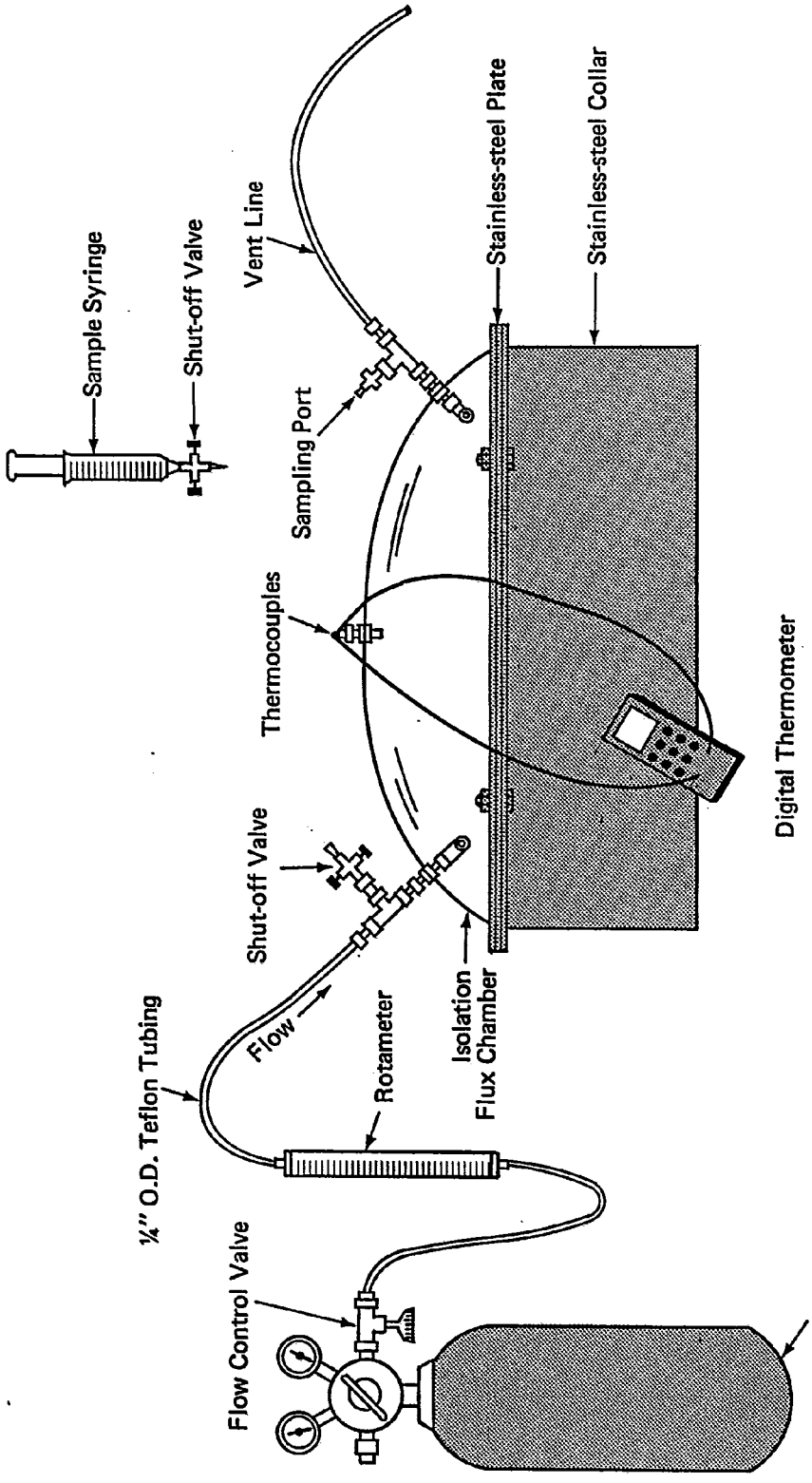


Figure 2-5. SCHEMATIC DIAGRAM OF ISOLATION FLUX CHAMBER(IFC)

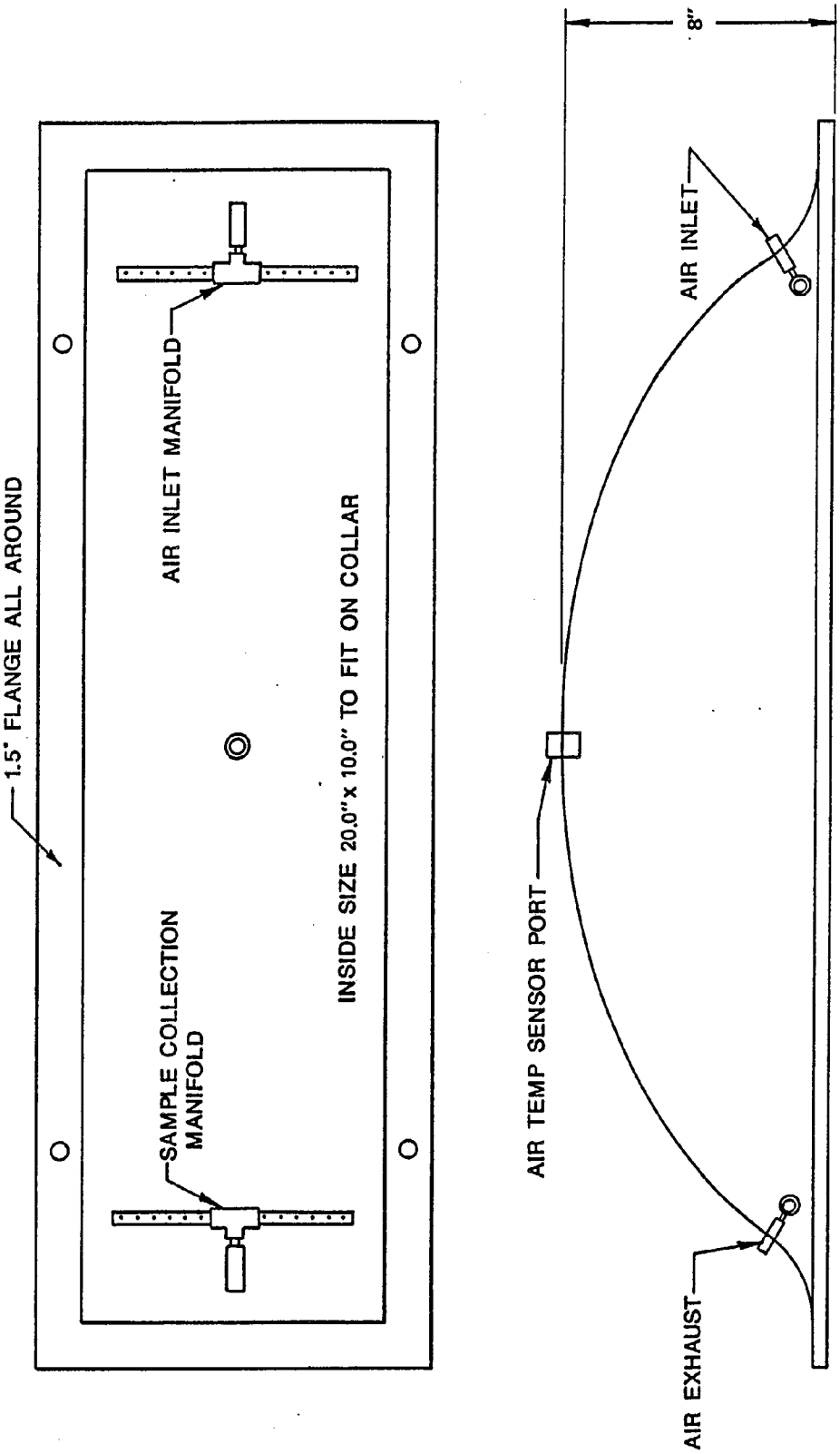


Figure 2-6. CONSTRUCTION DETAILS FOR ISOLATION FLUX CHAMBER DOME

The IFC provided a straightforward means of measuring hydrocarbon emissions from the landfarm surface. Volatile compounds emitted from a defined surface area were trapped within the enclosure. Contaminant-free air was added to the chamber at a controlled rate. Once equilibrium was established, samples of exit air were collected and analyzed for the species of interest. The emission rate was then determined from the following equation, which is based on a steady-state material balance around the IFC:

$$E_i = \frac{(C_i)(Q)(MW_i)(60)}{(A)(24.15)(1000)}$$

where

E_i = emission rate for compound i ($mg/m^2/hr$)
C_i = concentration of compound i measured in IFC exhaust gas (ppmv)
Q = purge gas flow rate (L/min)
MW_i = molecular weight of compound i ($\mu g/\mu mol$)
60 = conversion factor (60 min/hr)
A = enclosed landfarm surface (0.13 m^2 or 200 in^2)
24.15 = volume (L) of 1 mole of an ideal gas at 70°F
1000 = conversion factor (1000 $\mu g/mg$)

Note that all parameters in the above equation are either physical constants or direct measurements.

The IFC used for this project was constructed to generally meet EPA specifications (EPA 1986c). The major difference from the EPA design was a rectangular shape to accommodate the same collars used for the WTD. Stainless steel gas manifolds (0.25 in O.D. tubing with drilled holes) were placed on the inlet and exhaust lines to minimize short-circuiting of sweep air in the IFC.

Prior to shipping equipment to the field, the IFC was calibrated by placing the dome over a stainless steel plate and purging with a standard mixture of 15.0 ppmv isobutylene in zero air. The flow rate of the purge gas was 6.86 L/min. Exhaust air samples were analyzed using a portable PID and showed stable readings of 15.2 ppmv isobutylene (101.3 percent recovery) after approximately 5 min. This result compares favorably to recoveries for volatile petroleum hydrocarbons of 88.7-124 percent reported by EPA (1986c) and Eklund, Balfour, and Schmidt (1985).

As a second quality control check, the flow of isobutylene was shut off and replaced with contaminant-free air at 2.0 L/min. Exhaust air samples were periodically monitored using the portable PID. Results are shown on Figure 2-7. As expected, the isobutylene decay curve approximated a declining exponential function. Residence time (τ) in the IFC was calculated as 3.7 min at a sweep air flow rate of 2.0 L/min. Figure 2-7 also shows that the experimental decay curve was very close to the theoretical decay curve for a completely mixed volume with τ = 3.7 min, thus indicating that there was no appreciable short-circuiting of sweep air in the IFC.

A final check on the IFC was completed at the end of the field program. A known volume (10.0 mL) of 3000 ppmv isobutylene standard (equivalent to 0.828 µmol hydrocarbon as hexane) was injected into the IFC. The sweep air was started at 1.86 L/min and exhaust gas samples were taken periodically in syringes for analysis of total hydrocarbon content. The data were plotted and the resulting decay curve was integrated numerically to determine the total mass of hydrocarbon recovered. This experiment was repeated twice.

Measured hydrocarbon spike recoveries for the IFC in the field were 35.1 to 202.5 percent, considerably poorer than the results from the laboratory presented above. However, it is believed that these poor recoveries reflect the limitations of the FID procedure used in the field

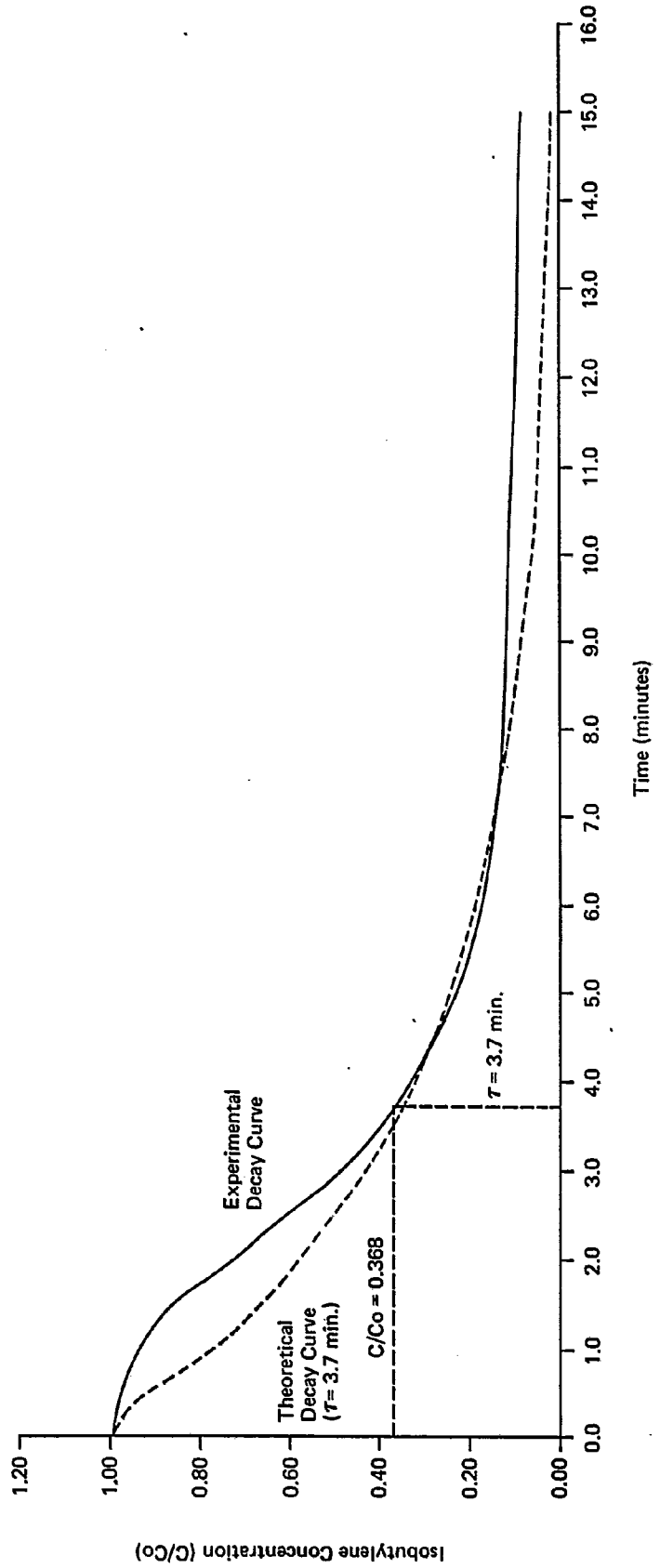


Figure 2-7. DECAY CURVE FOR ISOBUTYLENE IN ISOLATION FLUX CHAMBER

laboratory to quantify total hydrocarbons. TNMHC levels in the exhaust gas were generally well below 5 ppmv. At these low concentrations, the IFC system was operating outside the lower bound of its practical quantification range (5.4-540,000 μg-C/m^2/sec) as reported by Eklund, Balfour, and Schmidt (1985).

2.2 SITE DESCRIPTION

Field activities for this project were conducted during the period September 8-25, 1987 in a test plot located within an active HWLT facility at a major West Coast refinery. The refinery has been in operation since the early part of this century and currently has a rated capacity of 405,000 bbl of crude oil per day. Major products include motor gasoline, aviation gasoline, jet fuel, diesel fuel, asphalt, fuel oil, liquefied petroleum gas, kerosene, petroleum coke, sulfur, lubricants, and petrochemicals (including benzene, cumene, hydrocarbon solvents, and polymers).

The landfarm, which began operations during the 1970s, is located within the refinery boundaries. It includes approximately 22 acres of cultivated surface area along with a tank to store liquid wastes prior to application. Only those oily wastes generated within the refinery itself are applied to the land treatment area, including the following:

- Dissolved air flotation (DAF) sludge--EPA Waste No. K048
- API separator sludge--EPA Waste No. K051
- Nonleaded tank sludges
- Slop oil emulsion solids--EPA Waste No. K049 (nonleaded)
- Oily dirt from spill cleanup operations (intermittent)

Note that oily dirt and nonleaded tank sludges are not hazardous wastes under current RCRA regulations.

The average rate of sludge generation at the refinery is 42,000 bbl/yr, exclusive of oily dirt. Maximum sludge generation is estimated at 93,000 bbl/yr. Based on the average composition of the various liquid sludges, it is estimated that landfarm oil loadings are approximately 7500 lb oil/acre/month. Assuming a 10 in zone of incorporation, this is equivalent to 0.2 lb oil/ft of incorporation zone/month, well within the range of loadings considered typical for the refining industry (API 1983).

Soil within the land treatment area is classified as a dune sand. Since the facility is located in a semi-arid climate, the landfarm must be watered periodically to maintain optimum conditions for hydrocarbon biodegradation. Operating guidelines at the plant call for a soil moisture of 7-12 percent (dry weight basis) and an oil content of 5-15 percent (dry weight basis). Soil is generally kept at a pH 7-8, although a range of pH 6-9 is considered acceptable under some circumstances.

Liquid wastes are applied to the landfarm using a specially designed vacuum truck fitted with an apparatus which cuts furrows and either injects waste into the soil or applies it directly to the surface. The vacuum truck pulls a double-row agricultural disc which immediately covers the furrows and mixes the waste into the soil to a depth of about 10 in. The disc is used to till the soil between waste applications, a function that can also be accomplished with a tractor-pulled rotary tiller that is available at the site. The vacuum truck is fitted with a device which irrigates the plot by spraying water across the landfarm surface, where it can either be mixed into the soil or allowed to percolate.

Routine maintenance activities at the landfarm include tilling, irrigation, and addition of inorganic nutrients (nitrogen and phosphorus). During July 1987, a major maintenance project was conducted which involved adjustment of the surface slope of the landfarm. This included scraping the top foot of soil from the landfarm (the zone of incorporation), adding soil to achieve the desired grade, and replacing the

top soil. As a result of these activities, soil from the zone of incorporation was placed in a pile and not watered or tilled for a period of approximately one week. Normal maintenance activities were then resumed and one application of DAF sludge was made to the affected area of the landfarm prior to the experimental work described in this report.

The WCC experiments were conducted in a rectangular test plot established within the active HWLT facility. Dimensions of the test area were 400 ft x 240 ft, giving an overall surface area of 96,000 ft^2. The plot was then subdivided into 80 ft x 80 ft square blocks, with stations for soil, WTD, and IFC sampling subsequently located near the block centers. This sampling grid is shown on Figure 2-10.

As noted in Section 2.3.3, the actual sampling points were not located exactly at the block centers, but at random locations within a 10 ft radius of those points. The WCC field team used tables of random coordinates uniformly distributed around the block centers to identify sampling locations. This sampling scheme was chosen to provide representative coverage of the test plot given WCC's expectation of significant spatial heterogeneity in the soil/waste mixture both on a short scale (due to furrows resulting from waste application) and on a broad scale (due to possible uneven waste applications across the plot).

2.3 FIELD PROGRAM

The WCC field team was at the test site for a total of 19 days. Major activities accomplished during this period included collection of a preliminary sludge sample (day 1), equipment set-up and calibration (days 1-3), two rounds of background soil and emissions measurements (days 4-6), 10 rounds of soil and air sampling after sludge application (days 7-17), and equipment demobilization (days 18-19). The study schedule is summarized on Table 2-3.

Table 2-3. OVERALL STUDY SCHEDULE

Sampling Round	Calendar Day	Events
	September 8	Collect preliminary sludge sample; prepare equipment
	9	Prepare equipment
	10	Training on use of gas canisters
1	11-12	Pre-application sampling
2	13	Pre-application sampling
3	14	Sludge application
4	15	
5	16	
6	17	
7	18	Till and irrigate field
8	19	
	20	Off day
9	21	
10	22	
11	23	
12	24	Till and irrigate field
	25	Demobilize
	26	Demobilize

2.3.1 Sludge Application and Tilling

Approximately one week prior to the scheduled sludge application date (September 14, 1987), the refinery ceased all inputs of oily wastes and water to the sludge storage tank adjacent to the test plot. The sludge was allowed to settle by gravity. Free water was drawn from the tank bottom into the vacuum truck and applied to the landfarm outside the WCC test plot. The tank was then mixed via its internal mechanical mixer and also by repeated backflushing from the vacuum truck.

A single sludge sample was collected by WCC on September 8, 1987, and shipped via overnight air freight to RMAL for preliminary screening analyses. The purpose of these tests was to ensure that the test sludge contained representative levels of oil and volatile aromatics prior to starting the experiment. The screening analyses characterized the sludge as follows:

Approximate analysis:

Oil	19 weight percent
Solids	4 weight percent
Water	77 weight percent

Constituent analysis:

Benzene	13 mg/kg
Toluene	100 mg/kg
Total xylenes	179 mg/kg
Ethylbenzene	15 mg/kg

These results indicated that the test sludge met the pre-study criterion established by API of at least 15 weight percent oil but was approximately an order of magnitude below specified levels for the volatile constituents benzene (300 mg/kg) and toluene (1000 mg/kg). After

discussing these results with API staff, it was decided that the volatile constituent levels, while lower than desired, were within ranges previously observed for refinery sludges. WCC was therefore directed by API to proceed with the test as planned.

The sludge holding tank was allowed to sit quiescently during the period September 8-14, 1987. On the morning of September 14, additional free-phase water (approximately 350 bbl) was taken from the tank bottom and transported to landfarm areas outside the WCC test plot. The tank was then mixed for approximately 2 hours. After this period, the mixers were turned off. Dark oily sludge was then drawn from the tank and applied to the landfarm surface. The waste was immediately mixed into the soil by the agricultural disc attached to the back of the sludge applicator. Based on the measured change in tank levels, a total of 387 bbl of oily sludge was determined to have been applied to the test plot.

Eight batches of sludge (approximately 50 bbl each) were drawn from the storage tank by the vacuum truck. Initial applications were to the northeast corner of the plot, with the truck moving in an east-west direction to eventually reach the southwest corner. While sludge was drawn from the tank, it was noted that each batch became progressively darker, thicker, and more viscous. Thus, the thicker sludge was generally placed on the south side of the test plot. Moreover, the east and west ends of the test plot also received heavier sludge applications where the vacuum truck slowed to make turns.

The complete sludge application took approximately 2 hours. As the vacuum truck was finished in one portion of the test plot, the WCC field team began to locate sampling collars and to measure hydrocarbon emissions using the IFC and the WTD. Initial emissions measurements (as described in Section 2.3.2.5 and Section 2.3.2.6) were started in the northeast corner of the plot 1 hour after the first batch of sludge was applied.

The WCC work plan called for the test plot to be tilled and irrigated twice during the experiment. This was accomplished on September 18 and 24, 1987, as part of the refinery's routine landfarm maintenance program. Prior to each tilling, WCC removed the sampling collars from the plot to allow heavy-equipment access. Refinery staff watered and mixed the surface soils using the vacuum truck and attached disc. The soil was subsequently rototilled. WCC then replaced the sampling collars and resumed emissions measurements. On both occasions, initial emissions measurements began within 1 hour of the time tilling started.

2.3.2 Sampling and Data Collection

For those volatile organic waste constituents applied to the test plot (both TNMHC and individual volatile compounds), the major objective of this experiment was to estimate the proportion emitted to the atmosphere, the proportion remaining as a residue in the soil, and the proportion biodegraded. These proportions changed with time and probably varied spatially across the landfarm. To meet the goals of the study, the temporal variations were of great interest, whereas the spatial variations were of little concern. For this reason, the sampling program was designed to resolve temporal differences while averaging out spatial variability. Where possible, samples were composited in the field prior to shipment to off-site laboratories. Otherwise, results were averaged for those parameters requiring analysis of individual samples collected at discrete points (e.g., field measurements of TNMHC emissions using the IFC and WTD).

The basic data gathering and sampling efforts for this project were as follows:

- Meteorological measurements
- Waste sampling
- Soil sampling - chemical parameters
- Soil sampling - microbial analyses
- Emissions sampling - WTD

- Emissions sampling - IFC
- Ambient air sampling (individual organic constituents only)

Each of these sampling programs is described below.

2.3.2.1 Meteorological Measurements. Meteorological data were recorded throughout the experiment because weather conditions are thought to influence volatilization and biodegradation of organic constituents during landfarm operations. Weather information monitored during the study included ambient air temperature, wind direction, wind speed, barometric pressure, relative humidity, and precipitation. These data, obtained from a National Weather Service station located less than 5 miles from the refinery, are summarized on Table 2-4.

Weather conditions were generally consistent throughout the study. The small amount of precipitation (0.08 in) on September 23, 1987 did not appear to affect results.

2.3.2.2 Waste Sampling. Two 8 oz bottles were used to collect samples from the fill pipe of the vacuum truck as each batch of waste was applied to the test plot on September 14, 1987. These were placed in an iced cooler. At the end of the day, the sludge samples were composited by mixing the contents of each bottle in a bucket placed in an ice bath. The composited sludge was then poured into four clean 32 oz wide-mouth glass bottles with Teflon-lined lids for measurement of oil, water, and solids (OSW) content, boiling point curve of the recovered oil, and density of recovered oil. Four clean 40 mL vials with Teflon-lined septa were also filled for analysis of individual volatile sludge constituents. The bottles were labeled, placed in a cooler at 4°C, and shipped by overnight air courier to RMAL.

2.3.2.3 Soil Sampling - Chemical Parameters. Soil samples were collected from Stations 1-15 (see Figure 2-8) according to the schedule given on

Table 2-4. METEOROLOGICAL DATA[a] RECORDED DURING STUDY

Round	Date	Hours Sampled	Temperature (°F) High	Low	Relative Humidity (%)	Wind Speed[b] (mi/hr)	Wind Direction (deg)	Precipitation	Comments
1	9/11/87	1515-1745	72	69	69-79	8-9	250-260	None	
	9/12/87	0845-1915	70	67	66-76	9-10	110-130	None	overcast, some sunshine 1430-1700 hrs
2	9/13/87	0930-2200	71	65	66-78	5-10	230-260	None	
3	9/14/87	1345-2215	72	65	68-90	8-13	250-260	None	
4	9/15/87	1015-1930	74	68	64-87	8-10	230-270	None	
5	9/16/87	1645-2400	70	65	76-88	6-9	250	None	
6	9/17/87	1245-2145	72	66	54-84	9-12	250-270	None	
7	9/18/87	1145-2130	70	65	71-90	8-10	240-250	None	
8	9/19/87	0915-1900	71	67	73-79	6-13	200-260	None	
9	9/21/87	1000-1945	80	69	52-87	4-9	240-330	None	
10	9/22/87	1000-1915	82	75	45-72	6-17	010-250	None	
11	9/23/87	1115-1815	77	71	72-87.3	10-12	240-250	0.08 in.	precipitation occurred before 1100 hours
12	9/24/87	815-1600	76	67	71-94	6-12	100-260	None	

[a] Source: National Weather Service.

[b] Measured at 30 ft above ground level.

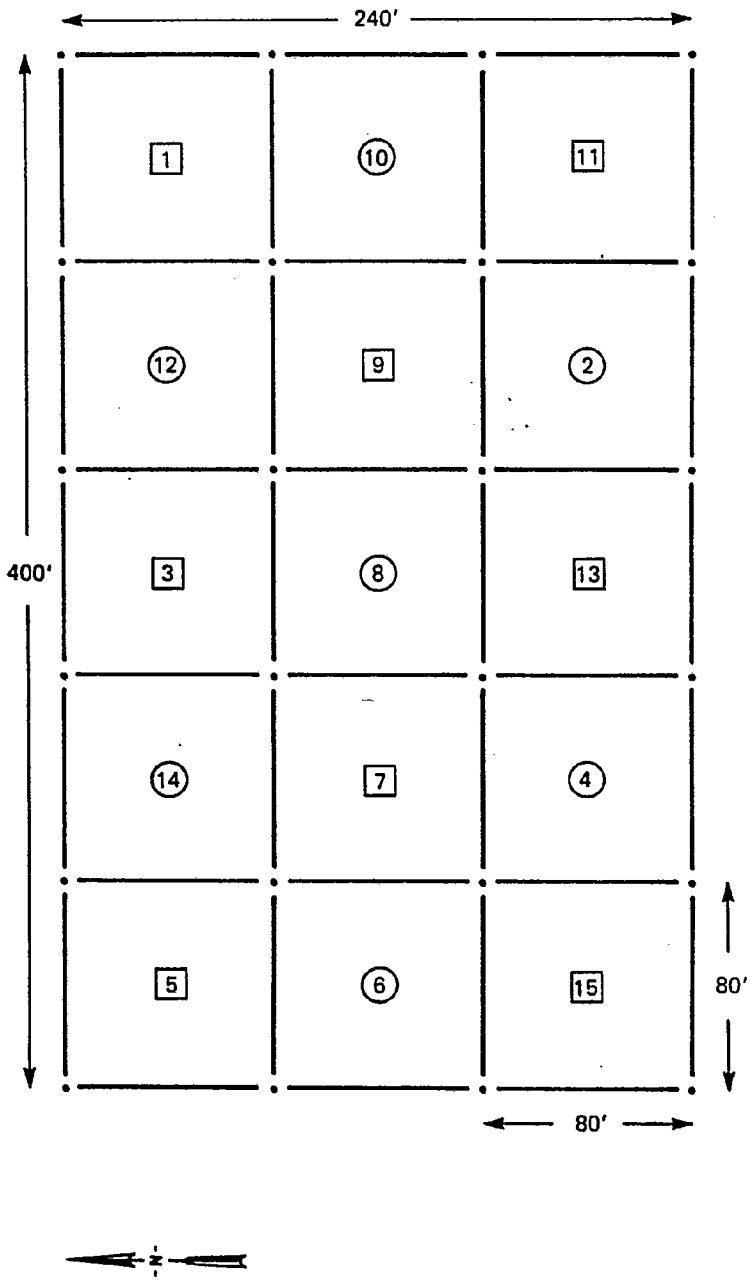


Figure 2-8. STATION NUMBERS AND LOCATIONS WITHIN TEST PLOT

Table 2-5. Using a hand auger, samples were taken to a depth of 3-5 in at two locations within a 10 ft radius of the center of each block in the test plot. Exact sampling points were determined from a set of random coordinates provided to the WCC field team. The samples were transferred from the auger to clean 32 oz wide-mouth glass bottles with Teflon-lined lids. When sampling was completed, the soils were mixed to form one composite. The composited soil was then placed in four clean 16 oz glass jars with Teflon-lined lids for measurement of OSW and nutrients/ inorganics. Four clean 40 mL vials with Teflon-lined septa were also filled with the soil composite for analysis of volatile constituents. All bottles were labeled, placed in a cooler at 4°C, and shipped by overnight air courier to RMAL.

2.3.2.4 Soil Sampling - Microbial Analyses. Soil samples were collected for microbial enumeration prior to sludge application (Round 2) and also two days following sludge application (Round 5). Surface soil was scooped directly into the sample bottle (sterilized 8 oz wide-mouth glass jar with Teflon-lined lid) from four points near the approximate center of the test plot. The soil sample was labeled, placed on ice, and shipped by overnight air courier to San Diego State University.

2.3.2.5 Emissions Sampling - WTD. Emissions sampling using the WTD comprised a major portion of the test program. As shown on Table 2-6, the WTD was used on every sampling round. TNMHC emissions were determined at each sampling location by collection of discrete samples. Gas samples for speciation of volatile organics were collected in a single stainless steel canister that composited emissions from across the test plot.

Emissions measurements were made at stainless steel sampling collars placed across the test plot. Collar locations were determined in the following manner. The first 15 collars were located using a table of random coordinates within 10 ft of the center of each of the blocks in the test plot (see Figure 2-8). In addition, five "twin" collars were placed

Table 2-5. SAMPLING SCHEDULE FOR SOILS

Round	OSW & Nutrients[d] Sample Type[a]	OSW & Nutrients[d] No. Sent to Lab	TNMHC and Organic Constituents Sample Type[b]	TNMHC and Organic Constituents No. Sent to Lab	Microbial Sample Type[c]	Microbial No. Sent to Lab
1	Composite	4	Composite	4		
2					Grab	1
3	Composite	4	Composite	4		
4	Composite	4	Composite	4		
5	Composite	4	Composite	4	Grab	1
6	Composite	4	Composite	4		
7	Composite	4	Composite	4		
8	Composite	4	Composite	4		
9	Composite	4	Composite	4		
10	Composite	4	Composite	4		
11						
12	Composite	4	Composite	4		
Totals	--	40	--	40	--	2

[a] Composite sample collected from around Stations No. 1-15; placed in 16 oz glass jars

[b] Composite sample collected from around Stations No. 1-15; placed in 7 oz VOA bottles

[c] Grab sample collected directly in wide-mouth 8 oz jars

[d] Nutrients were determined on sample from Round No. 1 only. OSW was determined on all samples

Table 2-6. SAMPLING SCHEDULE FOR WTD

	TNMHC				Canisters			Temperature			
Round	WTD Upstream	WTD Downstream	Blank WTD Downstream	Dup. WTD Downstream	WTD Upstream	WTD Downstream	WTD Downstream Dup.	Air Inside	Air Outside	Soil Inside	Soil Outside
1	4	20	1	2	1*	1*		20	20	20	20
2	20	20	3	4				20	20	20	20
3	20	20	3	4	1*	1*		20	20	20	20
4	20	20	4	4	1*	1*	1*	20	20	20	20
5	20	20	4	4	1*	1*		20	20	20	20
6	20	20	5	4	1*	1*		20	20	20	20
7	20	20	3	4	1*	1*		20	20	20	20
8	20	20	3	4	1*	1*	1*	20	20	20	20
9	20	20	4	4	1*	1*		20	20	20	20
10	20	20	4	4	1*	1*		20	20	20	20
11	15	15	3	3				15	15	15	15
12	15	15	2	3	1*	1*		15	15	15	15
Totals	214	230	37	44	10	10	2	230	230	230	230

* Single sample composited at Stations No. 1-15.

to the north of Collars 1, 5, 8, 11, and 15 and were numbered, in respective order, Collars 16, 17, 18, 19, and 20. The purpose of these "twin" collars was to assess short-scale spatial variability in landfarm emissions.

Sampling collar locations were initially established prior to measurement of background emissions (Round 1 and Round 2). After sludge application and after each tilling, new collar locations were determined in the same manner as before. However, for each collar placement, a different set of random coordinates was used to locate individual collars with respect to the block centers.

On each day that emissions were measured, the two WTDs were moved simultaneously from station to station across the test site. The first 15 stations were usually sampled in numerical succession, starting on Round 1 with Collars 1 and 11. On alternate days, sampling would begin with Collars 10 and 20 and proceed in reverse numerical order. "Twin" collars were sampled one after the other, thus breaking the numerical sequence established at the beginning of each sampling round. The purpose of varying the sequence of WTD sampling was to partially randomize the measurements and thus reduce the possibility of correlations in the data base between the time of day samples were collected and any emissions "hot spots" that may have existed in the test plot. A complete round of WTD sampling took about 8 hours once the field team had developed a routine.

Emissions sampling at each station was accomplished as follows. With the WTD positioned on a collar, the blower was started and air velocity was adjusted to 450 ft/min at the exhaust (equivalent to 2.6 mph through the sampling chamber). The WTD was maintained at this rate for a minimum of 15 min to establish steady-state conditions. During this time, air, surface soil, and subsurface soil temperature measurements were made both inside and outside the chamber. After the equilibration period, gas samples were drawn from both the upstream and downstream sampling ports with 50 mL glass

syringes for on-site TNMHC analyses. The syringes were flushed at least three times with sample gas before the sample was slowly drawn. Filled syringes were shielded from direct sunlight and delivered as quickly as possible (< 60 min) to the field trailer for analysis. After analyses had been completed, used syringes were thoroughly flushed with ultrapure air and returned to the field team.

In addition to the 20 sampling stations noted above, 2 to 4 stations were randomly selected every day for replicate downstream measurements. A table of random permutations of the first 20 integers was used to select the replicate stations. Except for the first day, at least three blank measurements were also made for every round. Blanks were established by placing a stainless steel plate over the sampling collar to isolate the soil surface from the WTD.

As shown on Table 2-6, composite samples of WTD gas were also collected for off-site analysis of individual hydrocarbon compounds during 10 sampling rounds. Upstream and downstream gas was sampled at Collars 1-15 in evacuated 6.0 L stainless steel canisters with electropolished interiors. The canisters were supplied by RMAL. Before shipment to the field site, each canister was cleaned and evacuated at the RMAL facilities. Canister pressure was also recorded. Upon receipt in the field, canister pressure was measured again to determine if leakage had occurred in transit. (No leakage was found for the canisters used in this project.)

On the day of sampling, each canister was fitted with a vacuum flow regulator (VFR) upstream of the inlet valve. The VFRs were calibrated daily to determine the time needed to collect 200 mL of gas at ambient pressure. When taken into the field, the VFR/canister apparatus was connected via 0.25 in O.D. Teflon tubing and a Swagelock fitting to a WTD sampling port. The canister valve was opened slightly and filled with sample gas for the prescribed time period as determined by calibration of

the VFR. After sample collection was complete, the canister valve was closed and the canister/VFR apparatus was disconnected from the WTD. This procedure was repeated at each station to produce a single set of composite upstream and downstream canister samples for each round. Two duplicate downstream gas canisters were also collected during the course of the study, as noted on Table 2-6.

After sample collection, the residual vacuum in each canister was determined and recorded. The canisters were labeled, packed in the original shipping containers, and shipped at ambient temperature via air freight to RMAL.

2.3.2.6 Emissions Sampling - IFC. Emissions sampling and analysis using the IFC was also conducted daily for comparison to the WTD. The IFC sampling schedule is shown on Table 2-7.

IFC emissions measurements were made at the same fixed sampling collars used for the WTD. However, only one IFC was used during the field program and samples were taken only at the eight odd-numbered stations noted on Figure 2-8. No IFC measurements were made at the "twin" collars.

Once the IFC was placed on a sampling collar, purge air was started at a rate of 1.86 L/min. Air flow rate was monitored with a rotameter positioned between the air supply cylinder and the IFC inlet. Care was taken not to shield the IFC from direct sunlight. The IFC was maintained in position with the purge air flowing for a minimum of 20 min (equivalent to approximately five IFC residence times) to ensure equilibrium conditions. Minimum equilibration time for an IFC has been established by EPA (1986c) as four residence times. After reaching steady state, samples for on-site TNMHC analysis were drawn from the IFC exhaust line into 25 mL glass syringes using the same techniques described previously for the WTD. Just before sample collection, the temperature of air, surface soil, and subsurface soil was also measured both inside and outside the IFC.

Table 2-7. SAMPLING SCHEDULE FOR IFC

	TNMHC			Canisters			Temperature			
Round	IFC	IFC Dup.	IFC Blank	IFC	IFC Dup.	Field Blank	Air Inside	Air Outside	Soil Inside	Soil Outside
1	8	2	2	1*			8	8	8	8
2	8	2	2				8	8	8	8
3	8	2	2	1*			8	8	8	8
4	8	2	2	1*			8	8	8	8
5	8	2	2	1*	1*		8	8	8	8
6	8	1	2	1*			8	8	8	8
7	8	2	2	1*			8	8	8	8
8	8	2	2	1*			8	8	8	8
9	8	2	2	1*	1*		8	8	8	8
10	8	2	2	1*			8	8	8	8
11	8	2	2				8	8	8	8
12	8	1	2	1*		1	8	8	8	8
Totals	96	22	24	10	2	1	96	96	96	96

* Single sample composited at Stations No. 1, 3, 5, 7, 9, 11, 13, and 15.

In addition to the eight sampling locations, one or two collars were selected every day for replicate TNMHC measurements. Two blank measurements were also made during each round by isolating the IFC from the exposed surface soil with a stainless steel plate. Collars for blank and replicate measurements were selected using a table of random permutations of the first 20 integers, as described above.

Integrated gas canister samples were also collected from the IFC during 10 of the 12 sampling rounds to determine emission rates of specific volatile compounds. Duplicate canister samples were taken twice over the course of the experiment. Canister sampling, labeling, and shipping procedures for the IFC were identical to those used for the WTD.

2.3.2.7 Ambient Air Sampling. Ambient air samples were collected for analysis of volatile organic constituents on September 14, 1987 (day of sludge application) and on September 18, 1987 (day of first tilling). These occasions were chosen for ambient sampling as they were assumed to represent worst-case conditions for organics emissions during landfarm operations.

On both days, ambient air samples were collected in evacuated stainless steel canisters from points upwind and downwind of the test plot. The sampling points were on dikes surrounding the landfarm approximately 10 ft above the soil surface. For each sample, the canister inlet valve was opened and air was drawn in until there was no residual vacuum. During sampling, the canister inlets were pointed to the north, perpendicular to the prevailing wind.

Ambient air sampling was also done within the test plot itself. In order to obtain a representative composite, the canister was fitted with a VFR and WCC personnel collected approximately 200 mL of air at each of the 15 stations noted on Figure 2-8. Samples were taken in the breathing zone

(about 5 ft above ground level) with the canister intake pointed to the north.

Canister labeling and shipping procedures for the ambient samples were identical to those used for the WTD.

2.4 ANALYTICAL METHODS

2.4.1 Waste

2.4.1.1 Percent Oil, Solids, and Water. OSW content of the waste samples was determined by RMAL using the Modified Oven Drying Technique (MODT) developed by Chevron Research Company. A copy of this procedure is in Appendix A.

2.4.1.2 Boiling Point Curve of Recovered Oil. Non-volatile oil recovered during the MODT analysis was submitted to Hauser Chemical Research, Inc., Boulder, Colorado, for simulated distillation by ASTM Method D28-87.

2.4.1.3 Density of Recovered Oil. The density of non-volatile oil recovered during the MODT analysis was also determined by Hauser using ASTM Method D70-76.

2.4.1.4 TNMHC. The volatile TNMHC content of the waste samples was measured at RMAL by headspace analysis using a modification to EPA Method 3810 (EPA 1986g). Approximately 2.0 g of waste was placed in a sealed vial and equilibrated at 45°C for 55 min in a Perkin-Elmer HS-101 Headspace Sampler. Each sample was pressurized for 30 sec and, with an injection time of 0.08 min, was injected into a heated transfer line. This gaseous sample was cryogenically trapped in liquid argon and then quickly released to an FID using water at 85-95°C and a heater attached to the trap. Each vial was sampled multiple times, producing decreasing area counts. TNMHC concentrations were then quantified as hexane using Perkin-Elmer software for multiple headspace extraction quantitation. The reference standard for

this analysis was an empty vial spiked with 1.0 mL of hexane and analyzed in the same manner as the waste samples. Further details on the theory of headspace analysis are provided by Kolb and Pospisil (1977) and by Ettre, Kolb, and Hurt (1983).

2.4.1.5 Volatile Organics. RMAL determined volatile organics in the waste by purge and trap GC/MS according to EPA Method 8240 (EPA 1986g). The method was modified to accommodate the analyte list specified for this project.

During the course of the initial data review, it became apparent that the waste:methanol ratio specified by Method 8240 (4.0 g waste:10.0 mL methanol) did not provide for efficient extraction of organic constituents from the oily waste matrix. This problem was evident for both aliphatic and aromatic hydrocarbons at the observed waste concentrations (50-350 mg/kg). A smaller extraction ratio (1.0 g waste:20.0 mL methanol) was found to give better analytical results for purposes of this project. This issue is discussed in more detail in Section 3.1.

2.4.2 Soil

2.4.2.1 Percent Oil, Solids, and Water. OSW in soils was determined by RMAL using the MODT procedure.

2.4.2.2 TNMHC. RMAL measured volatile TNMHC in soil samples by headspace analysis with FID quantification as described in Section 2.4.1.4. All TNMHC results were quantified as hexane.

2.4.2.3 Volatile Organics. RMAL determined volatile organics in soils using Method 8240 modified to accommodate the target analyte list for this project.

2.4.2.4 Nutrients/Inorganics. RMAL analyzed soil pH, conductance, nitrate/nitrite, ammonia, and total Kjeldahl nitrogen using procedures

recommended in EPA's technical guidance for conducting hazardous waste land treatment demonstrations required under 40 CFR 264 (EPA 1986a).

2.4.2.5 Microbial Enumeration. Enumeration of soil bacteria was done at San Diego State University, San Diego, California. The analytical method involved acridine orange staining of bacteria followed by visual counts under an epifluorescent microscope. Appendix B provides procedural details and results for the soil bacterial counts.

2.4.3 Air

2.4.3.1 TNMHC. Syringe samples collected from the IFC and WTD were analyzed for TNMHC content in an on-site laboratory operated under subcontract by Environmental Analytical Service, San Luis Obispo, California. Draft Method TO12 (EPA 1984e) was used for these determinations, with modifications. A copy of Method TO12 is included in this report as Appendix C.

In summary, the method as applied in the field involved direct injection of 10-50 mL of gas sample from a syringe onto a trap of glass beads cooled with liquid argon. This cryogenic trap simultaneously concentrated TNMHC compounds while separating and passing methane, oxygen, nitrogen, etc. The trap was subsequently heated with water at approximately 90°C to desorb the organics, which were flushed by helium directly into an FID operated without a GC column. The FID response was integrated automatically and translated into mass units (μmol carbon) via equations derived from instrument response to gas standards (propane, isobutylene, and mixed volatile hydrocarbons) analyzed throughout the project. The volatile organic carbon concentration was calculated as the mass of carbon detected divided by the volume of gas sample injected. This result was further divided by six so that all TNMHC emissions data were reported as ppmv hexane.

The response of the FID to hydrocarbon gas standards is shown on Figures 2-9 through 2-11. (TNMHC calibration data for the entire project are provided in spreadsheet format as Appendix F.) Instrument response curves were determined by linear regression of integrated FID peak area (dependent variable) against the known mass of organic carbon injected (independent variable). The three curves developed for this project explained between 96.02 percent (Figure 2-10) and 99.33 percent (Figure 2-11) of the observed variance in instrument response. The slopes of the regression equations were all highly significant ($p \leq 0.0001$). None of the regressions was forced through the origin. However, in all cases, the intercepts were not significantly different from zero ($p \leq 0.1$).

Separate high and low range curves were prepared because the slope of the FID response was not constant as the mass of organic carbon injected was increased. The low range curve given in Figure 2-9 shows instrument response to 0.000-0.025 µmol carbon for all days except September 14, 1987. The high range curve (Figure 2-10) plots FID response to 0.00-0.40 µmol carbon over the same time period. Gas flow rates to the FID were altered on September 14, 1987, resulting in a single calibration curve which applies to that day only (Figure 2-11).

The regression equations shown on Figures 2-9 through 2-11 were rearranged to compute the TNMHC content of gas samples collected from the IFC and WTD:

- For FID area $\leq$ 2,460,000 (except September 14, 1987):

  $$\mu\text{mol carbon} = (3.7386 \times 10^{-9})\ (\text{area}) + 0.000217$$

- For FID area > 2,460,000 (except September 14, 1987):

  $$\mu\text{mol carbon} = (5.236 \times 10^{-9})\ (\text{area}) - 0.00346$$

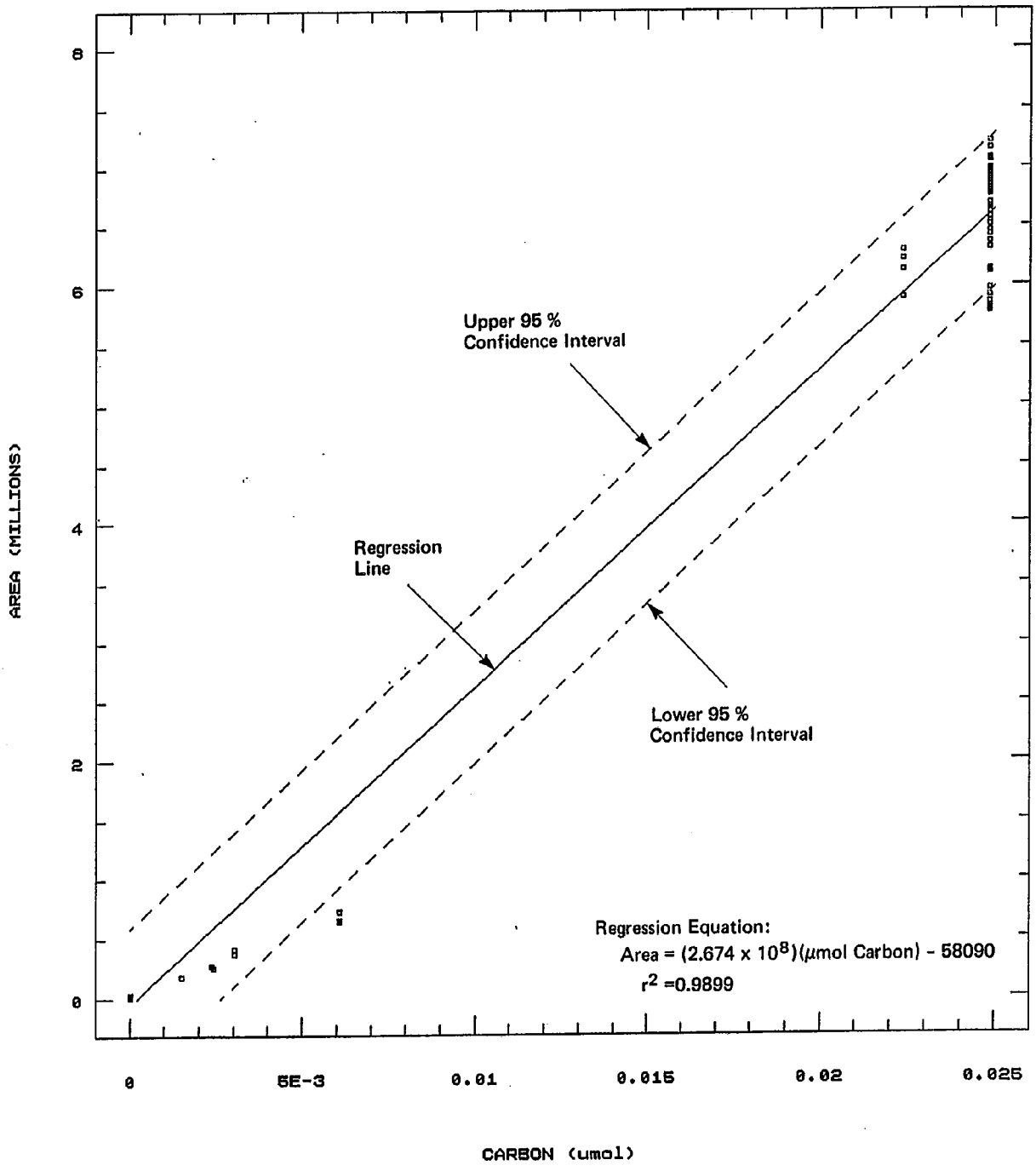


Figure 2-9. LOW RANGE CALIBRATION CURVE FOR TNMHC ANALYSES

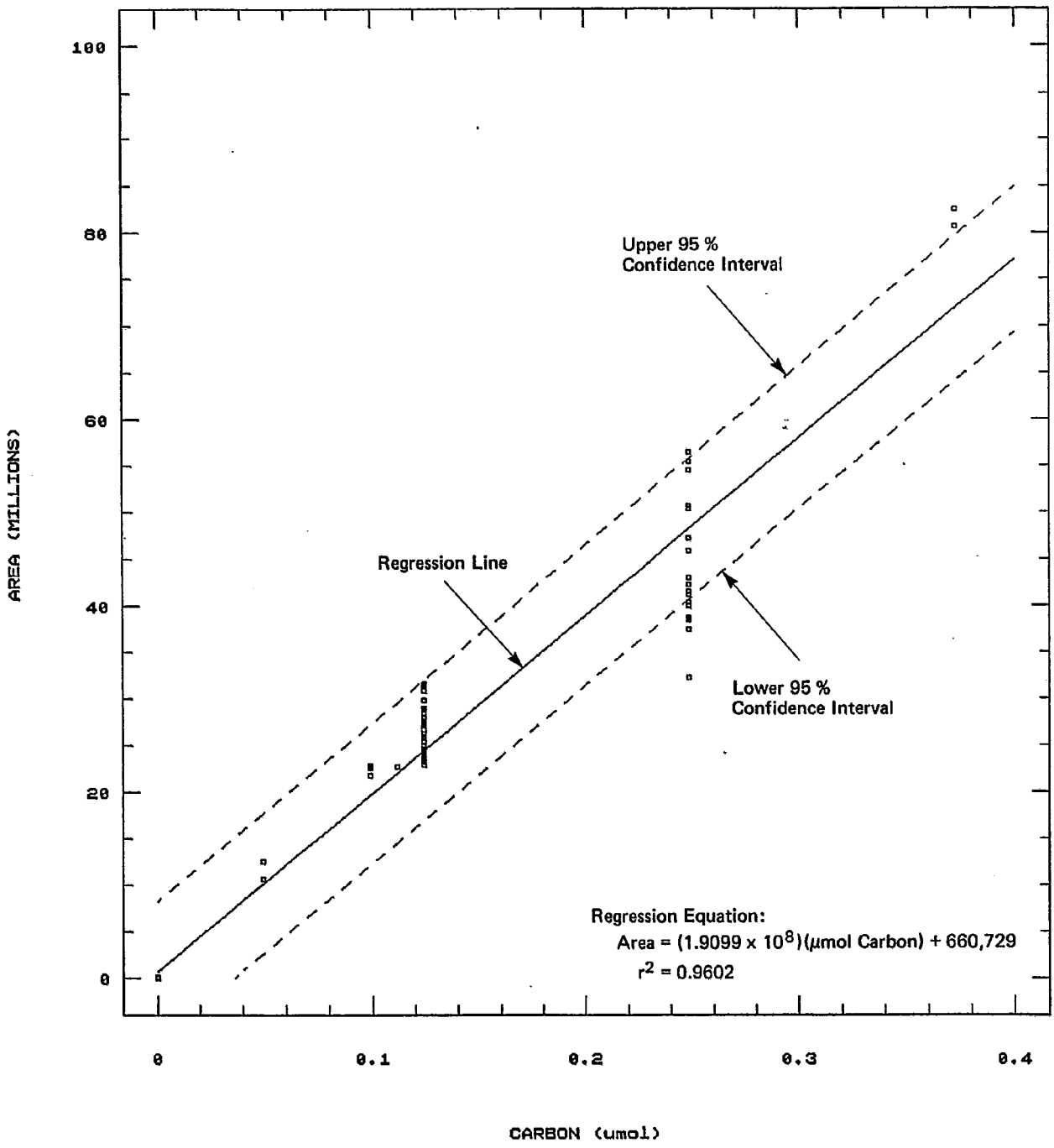


Figure 2-10. HIGH RANGE CALIBRATION CURVE FOR TNMHC ANALYSES

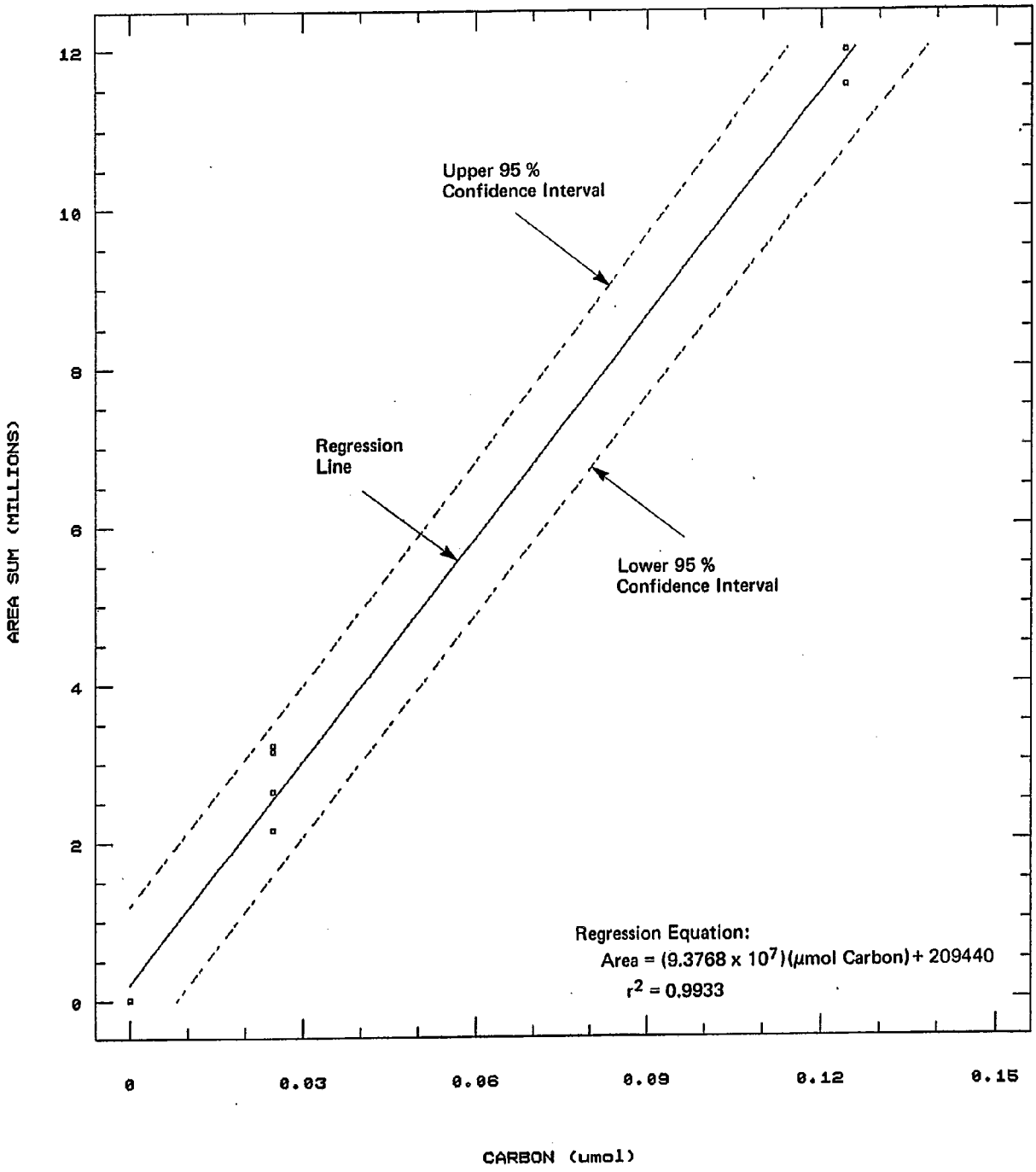


Figure 2-11. CALIBRATION CURVE FOR TNMHC ANALYSES
(September 14, 1987 only)

- For data from September 14, 1987 only:

$$\mu mol\ carbon = (1.066 \times 10^{-8})\ (area) - 0.0022$$

The transition between the low and high range calibration curves (FID area = 2,460,000) was the point of intersection between these two lines.

2.4.3.2 Volatile Organics. Gas samples collected in canisters were analyzed at RMAL. The canisters were pressurized to approximately 30 psig and then discharged through a cryogenic trap to a "capture" canister. After the sample had been transferred through this system, pressure readings were made to determine the amount of sample taken. The trap was desorbed into a GC/MS system and analyzed using a modification of EPA Method 8240.

Gas calibration standards were analyzed in the same manner as the samples. Multipoint calibration curves were prepared for each compound of interest from 100 ppbv to 3000 ppbv to demonstrate system linearity. Quantification of identified compounds was performed using this external standard.

2.5 QUALITY ASSURANCE/QUALITY CONTROL

Quality assurance/quality control (QA/QC) procedures for this project included pre-study evaluation of the WTD and IFC, development of a detailed work plan for use by the field team, documentation of field and laboratory activities, use of approved EPA or ASTM methods where available, and daily analysis of standards, blanks, matrix spikes, and replicates as appropriate for each method. The following sections discuss several QA/QC issues in more detail.

2.5.1 Chain-of-Custody Procedures

All samples shipped to off-site laboratories were done so under strict chain-of-custody procedures. Copies of the chain-of-custody documentation are maintained in the WCC project files and are available upon request.

2.5.2 RMAL QC Report

The QC report provided by RMAL is provided as Appendix D. Quality control activities included the analysis of standard soil samples for nutrients/inorganics and comparison to laboratory control limits, matrix duplicates for volatile TNMHC in soil, matrix spikes and duplicates for volatile organic constituents in soil, and matrix duplicates for volatile organics in the gas canister samples.

2.5.3 Sample Holding Times

At the time this work was done, none of the procedures used for analysis of soils and sludges specified allowed sample holding times. The MODT and trace organics analyses were completed within 6 weeks of sample collection. The sludge samples were re-analyzed for organic constituents 10 months after sample collection with no apparent loss of constituents. Volatile TNMHC determinations were made about 10-12 weeks after samples were taken in the field. Bacterial counts on the soils were completed within 2 weeks of sample receipt at San Diego State University. All soil and sludge samples were kept under refrigeration prior to analysis.

Gas samples for TNMHC determination were analyzed in the field within 1-2 hours of collection. The gas canister samples were analyzed at RMAL in January 1988, approximately 4 months after collection. Other studies have demonstrated that volatile aromatic and aliphatic hydrocarbons at concentrations on the order of 1-2100 ppbv are stable in gas canisters for periods from 2 weeks up to 4 years (Oliver and Pleil 1986; Dayton et al. 1987; Rhoderick and Zielinski 1988). It should be noted, however, that long-term studies (> 30 days) have only evaluated analyte stability in moisture-free air. In the presence of water vapor and other trace

environmental contaminants such as O_3, NO, and NO_2 (which would be expected in gas samples collected during this study), Oliver and Pleil (1986) have determined that aromatic hydrocarbons stored in stainless steel canisters for 30 days at approximately 0.5-1.0 ppbv will degrade at a rate on the order of 0.1 percent per day. Extrapolated to the holding times at RMAL, these results imply a 10-15 percent negative bias in volatile constituent data obtained during this study.

3.0
RESULTS AND DISCUSSION

3.1 WASTE CHARACTERIZATION

Laboratory reports for the waste samples are given in Appendix E and summarized on Table 3-1. Included are results for OSW, TNMHC, and individual volatile constituents. The report from Hauser Chemical Research characterizing the oil fraction recovered during MODT analysis is also provided in Appendix E.

As noted in Section 2.4.1.5, RMAL and WCC conducted an initial review of these data and concluded that results originally reported for individual trace organics were biased low. It was hypothesized that the waste:methanol ratio specified by EPA Method 8240 (and used for the waste analyses performed during October 1987) did not efficiently extract volatile organic constituents from the oily waste matrix. To test this suspicion, RMAL repeated the analyses on retained waste samples in July 1988, approximately 10 months after the samples were originally collected.

Results of these experiments, also shown on Table 3-1, led to two conclusions. First, good agreement (within 20 percent) was obtained between the original and repeat analyses of RMAL Sample 64548-021, suggesting little deterioration of the waste sample when maintained under refrigeration for up to 10 months. Second, reducing the waste:methanol ratio resulted in substantially greater recovery of organic constituents. This confirmed the hypothesis that the extractant in the original (October 1987) analyses had been saturated due to the low solubility of hydrocarbons (particularly aliphatics) in methanol.

Table 3-1. API LANDFARM STUDY - CHARACTERIZATION OF APPLIED WASTE

	Original Analyses			Repeat Analyses			
RMAL Sample ID:	64548-013[1]	64548-014[1]					
	64548-021[2,3]	64548-022[2,3]		64548-021[2]	64548-021[2]	64548-021[2]	
Analysis Dates:	10-8-87[1]	10-9-87[1]					
	10-27-87[2]	10-29-87[2]		7-88[2]	7-88[2]	7-88[2]	
	12-1-87[3]	12-1-87[3]					
gm waste:mL methanol[2]	4:8	4:8		4:8	1:10	1:20	
Parameter, mg/kg	Replicate 1	Replicate 2	Average				Final Estimated Value
Water	659,000	752,000	706,000	NA	NA	NA	706,000
Oil	275,000	224,000	250,000	NA	NA	NA	250,000
Solids	66,000	24,000	44,000	NA	NA	NA	44,000
TNMHC (as hexane)	29,000	16,000	23,000	NA	NA	NA	23,000
2-Methylpentane	14	15	15	18	120	160	160
3-Methylpentane	10	11	11	12	71	92	92
n-Hexane	13	12	13	16	110	150	150
Benzene	27	31	29	20	39	47	47
Toluene	110	150	130	99	250	300	300
Ethylbenzene	25	31	28	19	62	74	74
Xylenes (Total)	160	200	180	130	430	520	520
Naphthalene	31	42	37	NA	NA	NA	37
Phenol	ND[4]	ND	ND	NA	NA	NA	ND

1 Analysis of OSW by MODT
2 Analysis of organic constituents by EPA Method 8240
3 Analysis of TNMHC by modified EPA Method 3810
ND = Not Detected
NA = Not Analyzed

Based on these data, WCC elected to use the results from the July 1988 analysis of RMAL Sample 64548-021 (1 g waste:20 mL methanol) as the best available characterization of volatile constituent levels in the waste applied to the test plot. This is shown in the right-hand column of Table 3-1. It is also noteworthy from this table that volatile TNMHC (as measured by headspace analysis at 55°C) constituted about 9.2 percent of the total oil content of the waste. Further, the nine volatile constituents of concern to this project only accounted for 4.8 percent of the TNMHC and less than 0.5 percent of the total oil applied to the test plot.

A review of available information on petroleum refinery wastes was conducted to compare the constituent levels shown on Table 3-1 with data reported for the industry as a whole. Results of this review are shown on Table 3-2. From this comparison, it was concluded that the oily waste used in this experiment contained oil and volatile constituents at concentrations representative of sludges across the refining industry that are typically managed in HWLT facilities.

Finally, the waste characterization data were used to compute mass loadings of various constituents to the test plot. Results of these calculations are given on Table 3-3.

3.2 TNMHC EMISSIONS - IFC

Figure 3-1 plots daily average TNMHC emission rates measured using the IFC throughout the experiment. Results are plotted against both the time of day that measurements were made and against the time since initial waste application. The complete IFC data base is given as Appendix G.

Several broad trends are apparent in Figure 3-1. From the low background values measured over the first two sampling rounds (average

Table 3-2. CONSTITUENT CONCENTRATIONS REPORTED FOR PETROLEUM REFINERY WASTES TYPICALLY APPLIED TO HAZARDOUS WASTE LAND TREATMENT UNITS

Reference	This Study	API 1984	API 1984	API 1984	API 1984	API 1984	API 1984	API 1987	EPA 1984a	EPA 1984a	EPA 1984a	EPA 1984a	EPA 1984a	EPA 1984a	EPA 1984a	EPA 1984a	Radian 1986	Radian 1986	Chevron 1987	Chevron 1987	EPA 1987a	EPA 1987a
Waste Type	Mixed Oily Wastes	API Separator Bottoms	Tank Bottoms	DAF Sludge	DAF Sludge	API Separator Bottoms	DAF Sludge	Mixed Oily Wastes	Mixed Oily Wastes	Mixed Oily Wastes	Mixed Oily Wastes	Mixed Oily Wastes	Mixed Oily Wastes	Mixed Oily Wastes	Mixed Oily Wastes	Mixed Oily Wastes	API Separator Bottoms	Tank Bottoms	API Separator Bottoms	Tank Bottoms	DAF Sludge	API Separator Bottoms
Water ($)	71	73	37	88	NR	NR	NR	66.6	25	40	65	70	—	—	80	5	50-79	0	71-79.6	76.7	70	65
Oil ($)	25	8	60	7	NR	NR	NR	18.9	62.5	35	20	25	—	—	12.5	10	6-10	94	6.75-8.8	20.7	21	30
Solids ($)	4	19	3	5	NR	NR	NR	14.5	12.5	25	15	5	100	100	7.5	85	15-40	6	13-22	2.7	9	5.5
2-Methylpentane, mg/kg	160	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	60	NR
3-Methylpentane, mg/kg	92	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
n-Hexane, mg/kg	150	NR	NR	NR	NR	130	81-800	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	10	NR
Benzene, mg/kg	47	NR	NR	NR	102	230	28-170	74	540	32	18	5	14	20	160	38	ND-1400	1800	134-255	224	27	NR
Toluene, mg/kg	300	NR	NR	NR	1700	1200	510-2800	390	1700	58	98	14	ND	ND	150	36	0.02-5600	9300	61-94	2808	410	NR
Ethylbenzene, mg/kg	74	NR	NR	NR	NR	330	12-740	130	NR	NR	NR	NR	NR	NR	NR	NR	0.46-4300	5200	35-92	231	400	NR
Xylenes (total) mg/kg	520	NR	NR	NR	NR	3300	2500-6300	770	1030	86	160	46	35	520	57	ND	1.8-47,000	65,000	NR	NR	2000	NR
Naphthalene, mg/kg	37	NR	NR	NR	ND	ND	620-2100	270	230	34	350	64	ND	50	500	ND	NR	NR	NR	NR	34	NR
Phenol, mg/kg	ND	NR	NR	NR	1.3	0.19	0.64-2.1	12	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	<2	NR

NR = Not reported
ND = Not detected

Table 3-3. MASS OF WASTE CONSTITUENTS APPLIED TO TEST PLOT

Parameter (mg/kg)	Estimated Waste Concentration[1] (mg/kg)	Applied to Test Plot[2] (kg)
Water	706,000	42,600
Oil	250,000	15,100
Solids	44,000	2,700
TNMHC (as hexane)	23,000	1,400
2-Methylpentane	160	9.648
3-Methylpentane	92	5.548
n-Hexane	150	9.045
Benzene	47	2.834
Toluene	300	18.090
Ethylbenzene	74	4.462
Xylenes, Total	300	31.356
Naphthalene	74	2.231
Phenol	ND[3]	NA[4]

1 See Table 3-1
2 Based on 387 bbl of waste applied to test plot with an average density of 0.98 kg/L. Total applied waste was 60,300 kg.
3 ND = Not detected
4 NA = Not applicable

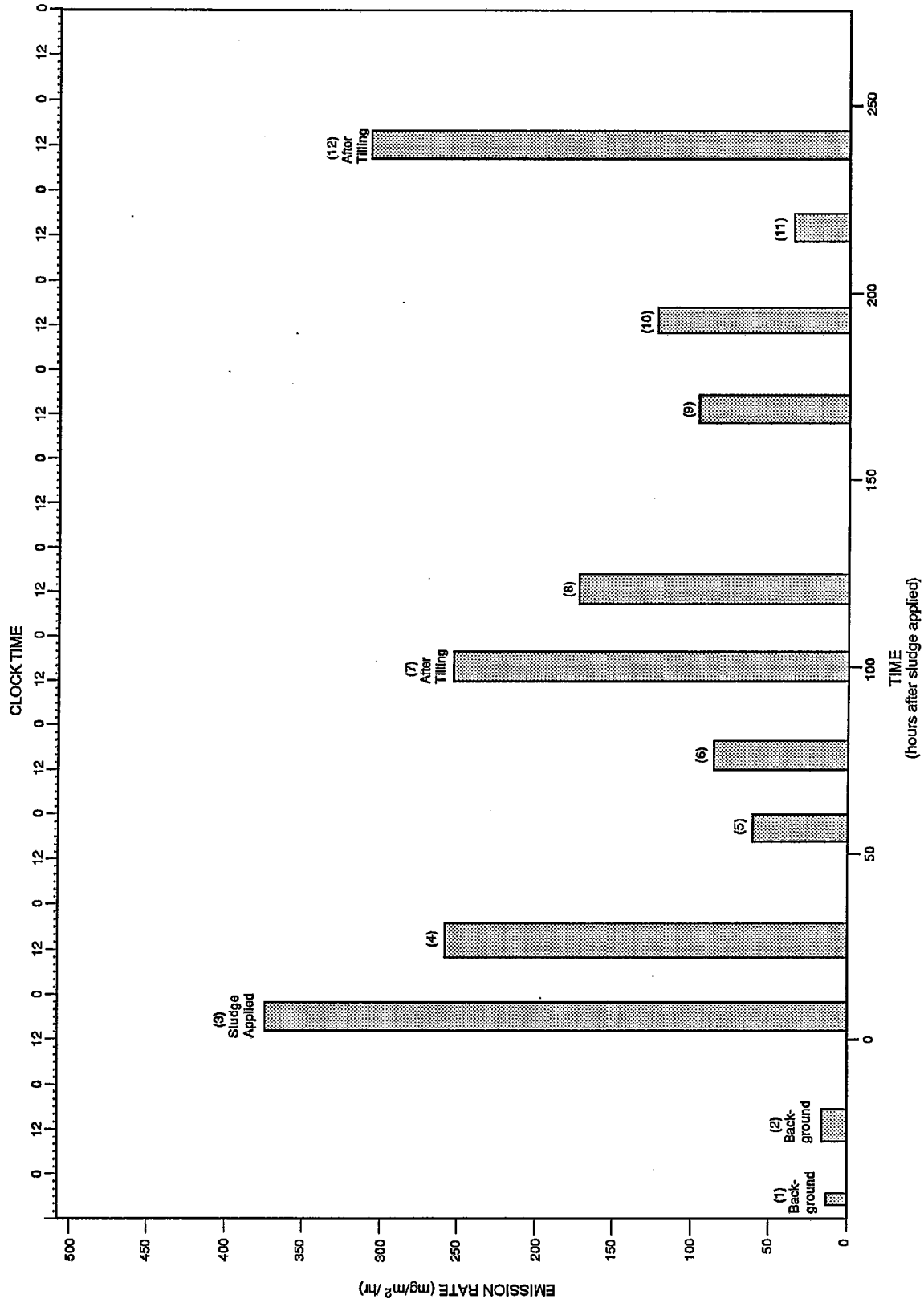


Figure 3-1. AVERAGE TNMHC EMISSION RATE: ISOLATION FLUX CHAMBER

Note: Number in parentheses above each bar indicates sampling round.

emissions of approximately 15.4 mg TNMHC/m^2/hr), TNMHC emissions rose significantly (to an average of 375 mg TNMHC/m^2/hr) upon application of waste to the test plot on September 14, 1987 (Round 3). Emissions then declined with time until rising again with the first tilling event (Round 7 - September 18, 1987), declined again after tilling, and increased once more following the second tilling event on September 24, 1987 (Round 12).

The effect of temperature on TNMHC volatilization is shown by the data from Round 5. These results, collected between 4:00 p.m. and midnight as the surface soil was cooling, are lower than would be expected given the trend in daytime measurements from the preceding and following rounds. It is also noteworthy that the final two stations (13 and 15) of Round 3 were sampled several hours after sunset. These locations showed TNMHC emissions approaching background levels even though fresh oily waste had been applied to the test plot earlier that afternoon. A thorough investigation of landfarm emissions during the night was outside the scope of this study. However, the data in Appendix G do suggest that volatilization of hydrocarbons from landfarms after dark, when surface soil temperatures are decreasing, may be substantially less than the average emissions rates reported on Table 3-1.

A casual review of the data in Appendix G also reveals significant within-round variability in the IFC measurements. Of course, a certain amount of variability is inherent in any study involving chemical measurements, reflecting sampling and analytical uncertainty as well as spatial heterogeneity within the test plot. Analytical uncertainties may be quantified by analysis of system blanks as well as field and laboratory replicates. The effect of spatial heterogeneity can be isolated by randomizing the order of sample collection and placement of sampling collars within the test plot.

Other components of variability may be related to assignable causes. The data in Appendix G suggest that one particularly important explanation

for the within-round variance of the IFC measurements may be changes in surface soil temperatures throughout the sampling day. In general, TNMHC emissions appeared to rise during the late morning, peak from noon to about 4:00 p.m., and then decline through the late afternoon and early evening. This trend was not uniform, however, and results for any individual round can be confounded by the other causes of variance discussed above.

To investigate the importance of the various sources of variability, WCC modeled the individual TNMHC emissions measurements reported in Appendix G using a linear least-squares multiple regression technique. These regressions were performed by NCSS (Number Cruncher Statistical Software), Version 5.0. Several potential models were investigated, including both purely empirical equations as well as models based to some extent on the physical principles believed to govern volatile emissions from HWLT facilities. Models were compared on the basis of overall r^2 values (fraction of variance in observed data explained).

The two models for the IFC data listed in Table 3-4 achieved the highest r^2 values among those evaluated. These equations use the inverse square roots of time since waste application ($t_a^{-\frac{1}{2}}$) and time since most recent tilling ($t_t^{-\frac{1}{2}}$) as emissions predictors. This functional form is consistent with predictive modeling equations based on physical phenomena developed by Thibodeaux and Hwang (1982) and EPA (1987a). The second model also incorporates IFC surface soil temperature (in °C) to explain emissions variations.

Table 3-4 lists a number of model inputs and outputs, including the following:

- Number of data points, which includes field duplicates but excludes field blanks and emissions data obtained before waste application.

Table 3-4. SUMMARY OF LINEAR MODELS FIT TO TNMHC EMISSIONS DATA OBTAINED BY IFC

Model	Number of Data Points	Linear Variable	Mean Value	Std Dev.	Simple Correlation	Partial Correlation	Parameter Estimate	r^2
1	98							0.4341
		$t_a^{-1/2}$	0.145	0.145	0.5369	0.3715	504.671	
		$t_t^{-1/2}$	0.262	0.265	0.5441	0.3819	283.524	
		Intercept	---	---	---	---	32.017	
		TNMHC Emission Rate	179.499	184.332	---	---	---	
2	98							0.4795
		(Temp) $(t_a^{-1/2})$	4.042	4.363	0.5610	0.3294	15.444	
		(Temp) $(t_t^{-1/2})$	7.254	7.022	0.6091	0.4059	11.826	
		Intercept	---	---	---	---	31.282	
		TNMHC Emission Rate	179.499	184.332	---	---	---	

- Names of linear predictor variables used in the regressions. The transformed variables were $t_t^{-\frac{1}{2}}$ (hours$^{-\frac{1}{2}}$), $t_a^{-\frac{1}{2}}$ (hours$^{-\frac{1}{2}}$), IFC surface soil temperature (°C) multiplied by $t_t^{-\frac{1}{2}}$, and IFC surface soil temperature (°C) multiplied by $t_a^{-\frac{1}{2}}$. Note that the $t_t^{-\frac{1}{2}}$ term includes the discing of the soil immediately after waste application as a tilling event.

- Name of the response variable, which was the TNMHC emission rate. The units of both the regression intercept and the response were mg TNMHC/m^2/hr.

- The mean and standard deviation of each of the predictor and response variables.

- The correlation coefficient between each predictor variable individually and the TNMHC emission rate (simple correlation).

- The correlation coefficient between each predictor variable and the TNMHC emission rate after the effect of the other predictor was removed (partial correlation).

- The estimated regression parameter for each variable.

- Overall unadjusted r^2 for each model, which is the percentage of the total variance in the experimental emissions data that can be explained by the linear multiple regression equation.

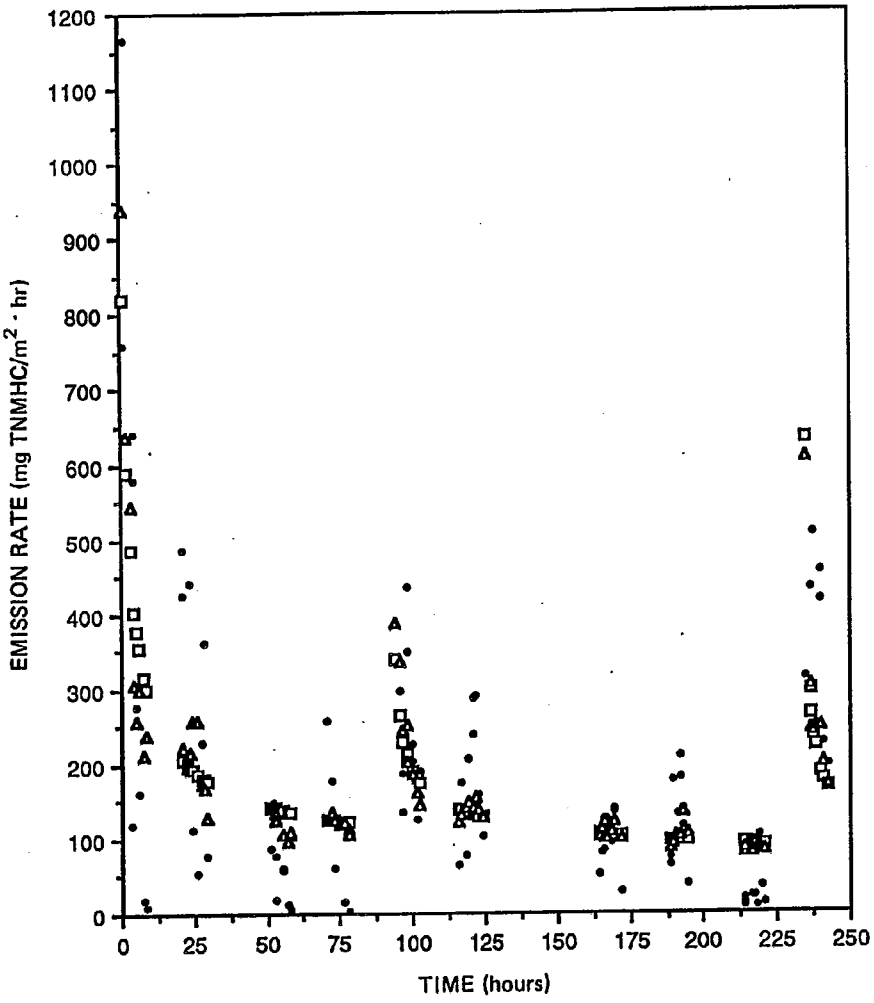
The two regression models for TNMHC emissions measurements obtained with the IFC are:

$$\text{Emission rate} = 32.017 + 504.671\ (t_a^{-\frac{1}{2}}) + 283.524\ (t_t^{-\frac{1}{2}}) + \text{unexplained variation}$$

Emission rate = 31.282
+ 15.444 (Surface soil temperature, °C) $(t_a^{-\frac{1}{2}})$
+ 11.826 (Surface soil temperature, °C) $(t_t^{-\frac{1}{2}})$
+ unexplained variation

The temperature factor improves the overall r^2 by only 4.5 percent, although it is clear from inspection of the daily IFC measurements that TNMHC emissions increased noticeably during the warm part of the day. Apparently, temperature was an important influence on short-scale (within-day) variability during this experiment, but it faded in comparison to time since waste application and time since tilling as an influence on long-term changes in TNMHC emission rates. Moreover, it was determined that incorporating surface soil temperature in units of °C achieved better results (in terms of r^2) in this model than units of °K or several other temperature terms that were investigated. It is possible that better chamber surface temperature measurements in the field could have increased the proportion of variation explained. Errors in the temperature measurements were not assessed during the experiment but presumably could have been decreased by averaging several spot measurements within each sampling collar.

Figure 3-2 shows a plot of measured and predicted TNMHC emission rates versus time for both IFC regression models. Vertical deviations about the predicted values, which include over half of the total variation in each case, are not normally distributed, are larger in absolute value where the predicted values are larger, and also show some autocorrelation in time. Hence, it would be inappropriate to attempt classical statistical hypothesis testing or the fitting of confidence intervals to these results. However, it is evident from the correlation coefficients and r^2 values in Table 3-4 that both of the variables used in each model are generally useful in predicting emissions rates as measured by the IFC.



KEY:

- ● Observed value
- □ Estimated value from regression against time only
- △ Estimated value from regression against time and surface soil temperature

Figure 3-2. COMPARISON OF MEASURED TNMHC EMISSIONS USING IFC WITH PREDICTIONS OF REGRESSION MODEL

The particular parameter values estimated for these models are very sensitive to individual data points and should not be generalized beyond this particular experiment. Nevertheless, the overall form of the models may be useful for prediction of emissions at other landfarms under other conditions. The large amount of unexplained variability (over 50 percent in each case) probably can be attributed to spatial variation in waste concentrations and emissions over the landfarm plot. It would be difficult to estimate the size of this effect quantitatively, because the individual measurement stations were visited in roughly the same sequence on several days and the spatial effect is somewhat confounded with clock time (and thus with temperature). Furthermore, both the exact locations of the stations and the local distributions of waste in the soil near each station were altered with tilling, so the spatial effect at each station could have changed considerably over the course of the study.

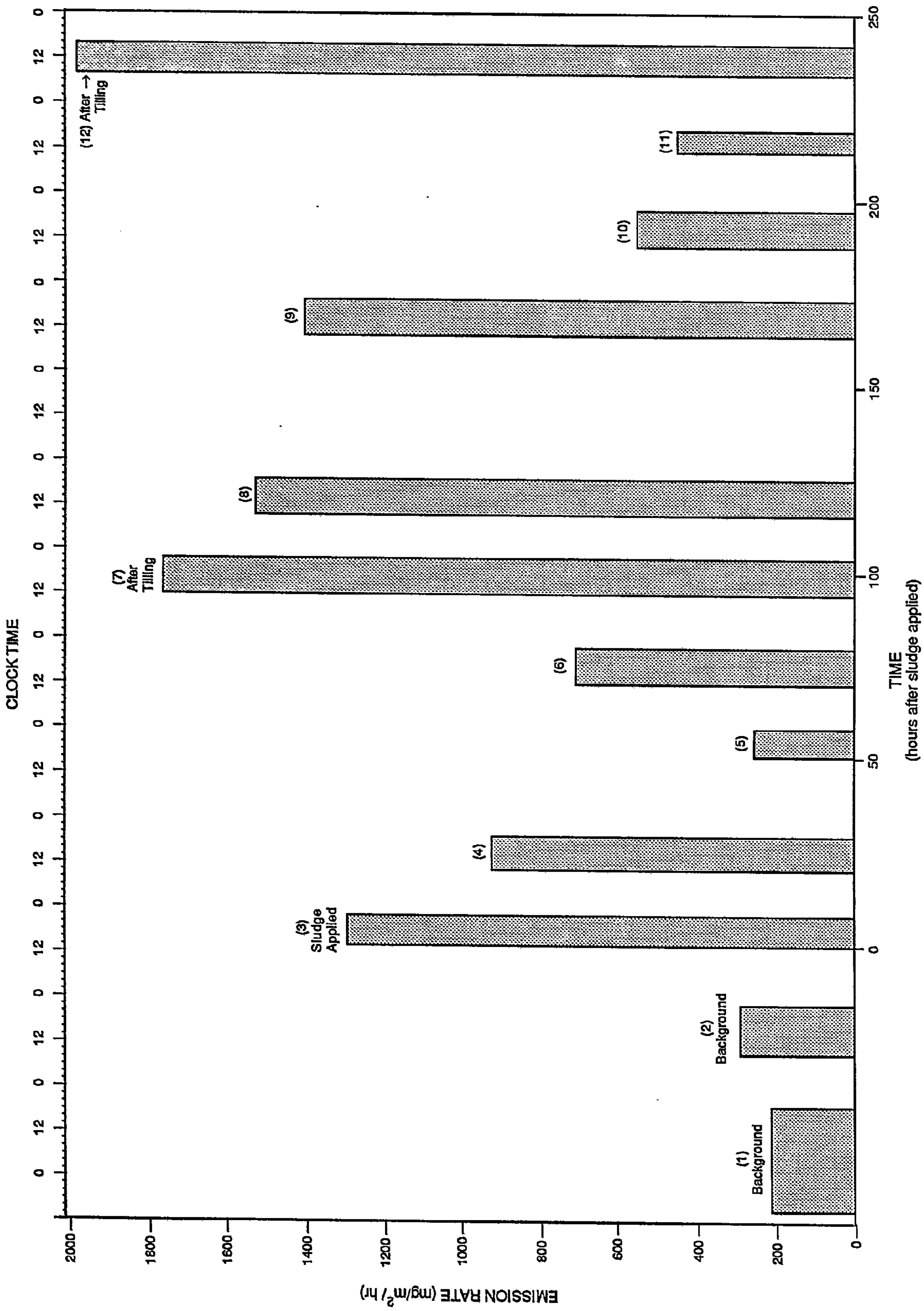
Field and laboratory duplicates do provide some information on the relative contributions of measurement errors to the total variation observed in the experiment. The total variance in the TNMHC emissions data obtained with the IFC is roughly 34,000 (mg TNMHC/m^2/hr)^2. Of this, 16,800 (mg TNMHC/m^2/hr)^2 is left as residual mean square error from the first model and 15,600 (mg TNMHC/m^2/hr)^2 is left from the second model (incorporating surface soil temperature). The analytical results from field and laboratory duplicates are quite variable, making estimates of these sources of variation uncertain. The variance also tends to increase with the mean, which changed in time and space during the experiment. Therefore, the following estimates are only rough generalizations. Laboratory variance averaged around 600 (mg TNMHC/m^2/hr)^2, and combined field and laboratory variance was about 900 (mg TNMHC/m^2/hr)^2. Clearly these sources of variation are small in comparison to the residual variance left by either model, suggesting that unquantified spatial variability has a major influence on the observed IFC emissions data.

Analysis of the IFC field blanks shows a mean blank emission rate of 3 mg TNMHC/m^2/hr. Actual field measurements at the same locations averaged about 139 mg TNMHC/m^2/hr and the mean of all the IFC data used in model fitting was 179 mg TNMHC/m^2/hr. Analyses of IFC blanks are strongly related to the field measurements taken at the same locations with a correlation coefficient of 0.62 (after averaging for duplicates). Although this suggests contamination in the IFC samples, the extent of contamination was clearly small in comparison to the TNMHC concentrations being assessed.

A number of other general observations were made regarding operation of the IFC in the field. While this device was very convenient to set up and transport around the test plot, it also tended to accumulate heat and moisture underneath the transparent dome. Similar phenomena have been noted by EPA (1986c) in technical guidance on the use of IFCs. For example, when sampling was done during the middle of the day, it was not unusual to observe condensation inside the IFC. This problem was particularly acute immediately after waste application and tilling when soil moisture levels were highest. As shown by the temperature data in Appendix G, surface soils within the IFC averaged 1.8°C warmer than corresponding soils outside the chamber. Surface temperature differences as high as 15°C were noted occasionally at some locations. Subsurface temperature differences were less apparent, probably because the device was not on the sampling collars long enough to appreciably heat the soil several inches below the surface.

3.3 TNMHC EMISSIONS - WTD

Average TNMHC emission rates measured with the WTD are plotted on Figure 3-3 for every day of the experiment. The complete WTD data base is provided as Appendix H. TNMHC emissions as measured by the WTD showed the same temporal trends as the IFC data discussed in Section 3.2.



Note: Number in parentheses above each bar indicates sampling round.

Figure 3-3. AVERAGE TNMHC EMISSION RATE: WIND TUNNEL DEVICE

Table 3-5 summarizes exploratory fits of two multiple linear regression models to the WTD data. The information contained in this table is identical to that provided in Table 3-4. The two WTD models shown are of the same form as the two IFC models. The inverse square roots of time since waste application ($t_a^{-\frac{1}{2}}$) and time since the most recent tilling ($t_t^{-\frac{1}{2}}$), or these variables multiplied by chamber surface soil temperature (°C), are used as predictors of TNMHC emission rates.

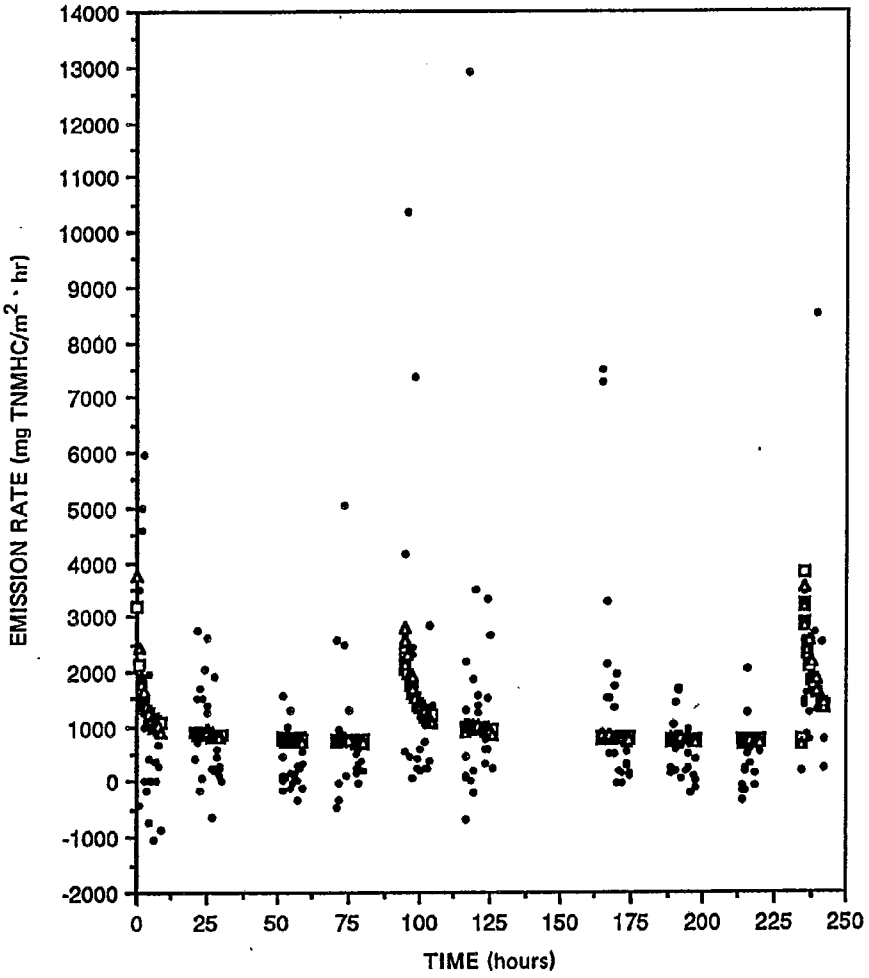
The means and variances of WTD emission rates are dramatically higher than those of the IFC, and the models explain much less of the total variation in the data (8.13 percent and 10.16 percent for WTD, versus 43.41 percent and 47.95 percent for IFC). As these measurements were taken at the same locations under comparable field conditions, it is likely that measurement uncertainty contributed relatively more variation to the WTD data base than to the IFC data base.

The total variance in WTD emissions during the experiment is about 3.0×10^6 (mg TNMHC/m^2/hr)^2, of which about 2.8×10^6 (mg TNMHC/m^2/hr)^2 remains as mean square error from the first model and 2.7×10^6 (mg TNMHC/m^2/hr)^2 remains from the second model that incorporates surface soil temperature. As in the case of the IFC data, the duplicate analyses are quite variable and contain some apparently anomalous values, making the overall contributions of field and laboratory errors difficult to assess reliably. Laboratory and field variance combined are around 1.0×10^6 (mg TNMHC/m^2/hr)^2, whereas laboratory variance alone, based on a different set of data, is approximately the same value. (In principle, laboratory variance alone should be somewhat less). These values are only a portion of the total residual variance, but are nevertheless much more important than comparable measurement errors in the IFC data.

Figure 3-4 plots measured and predicted TNMHC emission rates versus time for the regression models developed from the WTD data. It is apparent that the data base includes a number of extreme values that considerably

Table 3-5. SUMMARY OF LINEAR MODELS FIT TO TNMHC EMISSIONS DATA OBTAINED BY WTD

Model	Number of Data Points	Linear Variable	Mean Value	Std Dev.	Simple Correlation	Partial Correlation	Parameter Estimate	r^2
1	227							0.0813
		$t_a^{-1/2}$	0.159	0.202	0.0977	-0.0923	-1017.848	
		$t_t^{-1/2}$	0.262	0.258	0.2698	0.2679	2308.735	
		Intercept	---	---	---	---	621.190	
		TNMHC Emission Rate	1063.987	1729.008	---	---	---	
2	226							0.1016
		(Temp) $(t_a^{-1/2})$	4.292	5.884	0.1283	-0.1103	-45.101	
		(Temp) $(t_t^{-1/2})$	6.980	7.063	0.2990	0.2917	99.391	
		Intercept	---	---	---	---	568.557	
		TNMHC Emission Rate	1068.677	1731.398	---	---	---	



KEY:

- • Observed value
- □ Estimated value from regression against time only
- △ Estimated value from regression against time and surface soil temperature

Figure 3-4. COMPARISON OF MEASURED TNMHC EMISSIONS USING WTD WITH PREDICTIONS OF REGRESSION MODEL

influence the parameter estimates. These extreme values also affect the percent TNMHC emissions variation (r^2) explained by the models in Table 3-5. For example, removal of emission rates greater than 5000 mg/m^2/hr (9 out of 227 observations) increases r^2 in the first model from 8.13 percent to 15.75 percent, suggesting that these high measurements may incorporate a large amount of random measurement error.

The mean of the WTD blanks is about 248 mg TNMHC/m^2/hr, and the variability in the blank data is quite high. (Note that the mean value for the WTD blanks corresponds to a concentration change of about 0.03 ppmv hexane across the sampling device under typical operating conditions.) There is some linear relationship between WTD blanks and associated emissions measurements, with a correlation coefficient of 0.29 after averaging of duplicates. Furthermore, WTD blanks with anomalous values tend to be associated with anomalous emissions measurements. The relationship between the absolute values of blanks and emissions had a correlation coefficient of 0.46, suggesting that both WTD blanks and actual emissions measurements were unstable (in one direction or another) at many of the same locations.

Several other observations can also be made from the WTD emissions data reported in Appendix H. First, negative emission rates were measured at a number of points during the study. These negative values generally occurred when the difference between the upstream and downstream gas concentrations was much less than the absolute values of the measurements themselves. As noted in Appendix H, it was not at all uncommon to obtain concentration changes across the WTD that were less than the estimated detection limit of the TNMHC analytical procedure used in the field laboratory (estimated as 0.05 ppmv hexane). This problem of computing mass emission rates on the basis of small differences between relatively large numbers undoubtedly contributed to the variability in the WTD data noted above.

A second observation from Appendix H is that the upstream WTD gas samples were not completely free of hydrocarbons. This was true despite the fact that the carbon in both WTD filters was fresh at the beginning of the study and was replaced once during the field program. Samples taken at the blower intakes and at the upstream sampling ports indicated that the carbon filters were removing approximately 50 percent of the TNMHC in the ambient air. However, it is apparent from the upstream data in Appendix H that the WTD design should be modified to include a larger carbon filter that will attain greater removals of ambient TNMHC upstream of the collection chamber if this device is to be used for any future studies of low-level hydrocarbon emissions from refinery landfarms.

3.4 COMPARISON OF WTD AND IFC

A comparison of Figures 3-1 and 3-3 shows that TNMHC emission rates measured with the WTD were significantly and consistently higher than those obtained with the IFC. These differences were probably a result of the much greater air flow rate in the WTD (4350 L/min) compared to the IFC (1.86 L/min) in conjunction with the TNMHC analytical detection limits. For example, a concentration difference across the WTD of 0.05 ppmv hexane, which is the estimated TNMHC method detection limit, would be equivalent to a volatile hydrocarbon mass emission rate of 370 mg TNMHC/m^2/hr. This probably represents a realistic lower limit for obtaining reliable emissions data from the WTD as configured for this study. It is noteworthy that this limiting value is within a factor of 3.2 of the highest TNMHC emission rate measured at any individual IFC station. It is also greater than the average IFC value obtained on any day of the test.

Several factors inherent in the IFC design could also contribute to the relative bias in measured TNMHC emissions rates. First, as noted above, condensation on the IFC dome was observed on some days. This would act to reduce measured emissions to the extent that volatile organics were dissolved in the condensate, a point that has also been noted by EPA

(1986c). Second, the data in Appendix G indicate that TNMHC levels inside the IFC were as much as two to four orders of magnitude above ambient values. It is possible that high gas phase TNMHC concentrations inside the IFC dome could approach equilibrium levels in the soil vapor space. This would suppress emissions from the enclosed soil surface and thereby impose a low bias on measured flux rates.

Finally, there are a number of practical differences between the IFC and the WTD that should be mentioned. While the IFC was an easy instrument to use under field conditions and only required one operator, the WTD required two operators and proved to be unwieldly to move around the landfarm. Moreover, the WTD also reduced productivity in the field laboratory since, by the very nature of its operation, it required at least two gas sample injections per station compared to one for the IFC.

3.5 EMISSIONS OF VOLATILE ORGANIC CONSTITUENTS

Table 3-6 presents gas canister concentration data obtained with the IFC along with calculated emission rates for volatile organic constituents. Supporting laboratory documentation is provided in Appendix I.

With the exception of naphthalene and phenol, which were not detected in any of the IFC canister samples, the general trend of emissions for each of the individual organics followed the expected pattern of extremely low background levels with an immediate rise on the day of sludge application (September 14, 1987). Emissions declined with time for the next several days and rose again after the initial tilling (September 18, 1987). The same pattern was repeated prior to the second tilling (September 24, 1987), when emissions were again elevated.

TABLE 3-6. API LANDFARM STUDY - EMISSIONS OF VOLATILE ORGANIC CONSTITUENTS MEASURED USING THE IFC

ROUND:	1	3	4	5	5D	6	7	8	9	9D	10	12
DATE:	9/11-12/87	9/14/87	9/15/87	9/16/87	9/16/76	9/17/87	9/18/87	9/19/87	9/21/87	9/21/87	9/22/87	9/24/87
TIME:	-	1430-2215	1215-1915	1645-2345	1645-2345	1215-1945	1145-1945	0930-1815	1000-1730	1000-1730	1000-1630	0830-1545
HOURS SINCE SLUDGE APPLIED:	BACKGROUND	4.9	26.1	54.8	54.8	74.5	98.3	120.4	168.3	168.3	191.8	238.6
RMAL SAMPLE ID:	64548-035	64548-041	64546-066	64548-070	64548-072	64548-091	64548-093	64548-108	64548-112	64548-111	64548-123	64548-127
COMPOUND	IFC CONCENTRATION (ppbv)											
2-METHYLPENTANE	14	2400	990	180	250	210	1100	360	210	65	190	2000
3-METHYLPENTANE	ND	1200	470	120	130	140	660	240	140	40	130	1400
n-HEXANE	ND	1800	600	130	140	140	970	240	150	160	140	1800
BENZENE	ND	640	96	13	7	13	140	17	16	19	20	210
2,2,4-TRIMETHYLPENTANE	17	1000	440	94	96	130	590	190	110	130	120	740
3-METHYLHEXANE	11	930	430	86	86	120	550	180	110	120	120	1300
TOLUENE	7	1800	420	28	24	34	460	58	45	49	55	840
m,p-XYLENE	4	600	200	24	16	25	210	35	25	26	27	310
o-XYLENE	4	360	180	28	21	38	170	42	27	29	30	260
TOTAL XYLENES	8	960	380	52	37	63	380	77	52	55	57	570
1,2,4-TRIMETHYLBENZENE	5	370	200	23	13	33	180	42	29	31	36	300
PHENOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
NAPHTHALENE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
ETHYLBENZENE	ND	270	87	12	5	12	95	15	10	11	11	ND

COMPOUND	MOLE. WT.	EMISSION RATE (mg/m2/hr.)										
2-METHYLPENTANE	86.16	0.043	7.407	3.055	0.556	0.772	0.648	3.395	1.111	0.648	0.201	0.586	6.173
3-METHYLPENTANE	86.16	NA	3.704	1.451	0.370	0.401	0.432	2.037	0.741	0.432	0.123	0.401	4.321
n-HEXANE	86.16	NA	5.555	1.852	0.401	0.432	0.432	2.994	0.741	0.463	0.494	0.432	5.555
BENZENE	78.12	NA	1.791	0.269	0.036	0.020	0.036	0.392	0.048	0.045	0.053	0.056	0.588
2,2,4-TRIMETHYLPENTANE	114.23	0.070	4.092	1.800	0.385	0.393	0.532	2.414	0.777	0.450	0.532	0.491	3.028
3-METHYLHEXANE	100.21	0.039	3.338	1.543	0.309	0.309	0.431	1.974	0.646	0.395	0.431	0.431	4.666
TOLUENE	92.15	0.023	5.941	1.386	0.092	0.079	0.112	1.518	0.191	0.149	0.162	0.182	2.773
m,p-XYLENE	106.17	0.015	2.282	0.761	0.091	0.061	0.095	0.799	0.133	0.095	0.099	0.103	1.179
o-XYLENE	106.17	0.015	1.369	0.685	0.106	0.080	0.145	0.647	0.160	0.103	0.110	0.114	0.989
TOTAL XYLENES	106.17	0.030	3.651	1.445	0.198	0.141	0.240	1.445	0.293	0.198	0.209	0.217	2.168
1,2,4-TRIMETHYLBENZENE	120.2	0.022	1.593	0.861	0.099	0.056	0.142	0.775	0.181	0.125	0.133	0.155	1.292
PHENOL	94.11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
NAPHTHALENE	128.19	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
ETHYLBENZENE	106.17	NA	1.027	0.331	0.046	0.019	0.046	0.361	0.057	0.038	0.042	0.042	NA

ND - Not Detected
NA - Not Analyzed

Emission rates for each compound were calculated as follows:

$$E_i = \frac{C_i Q}{AV} \times (MW_i) \times (0.0930)$$

where:

E_i = mass emission rate of compound i ($mg/m^2/hr$)
Q = purge gas flow rate (1.86 L/min)
C_i = concentration of compound i in IFC (ppbv)
A = surface area of test chamber (200 in^2)
MW_i = molecular weight of compound i (ng/nmol)
V = molar volume of air at 70°F and 1 atm (24.15 L/mol)
0.0930 = conversion factor ($min \cdot in^2 \cdot mg/hr \cdot m^2 \cdot ng$)

Note that this equation assumes an ideal gas at standard conditions of 1 atm and 70°F. These were the same reference conditions used to calibrate the rotameter connected to the IFC purge gas inlet line.

Mass emissions of volatile organics, as measured with the IFC, are reported in Table 3-7. For each compound, these values were computed for nine different time periods spanning each sampling event. The following equation was used:

$$M_{i,j} = (E_{i,j}) \times (t_j) \times (TA) \times (9.29 \times 10^{-8})$$

where:

$M_{i,j}$ = mass emissions (kg) of compound i during period j.
$E_{i,j}$ = emission rate ($mg/m^2/hr$) of compound i during period j.
t_j = elapsed time of period j (hr)
TA = total area of test plot (96,000 ft^2)
9.29×10^{-8} = conversion factor ($m^2 \cdot kg/ft^2 \cdot mg$)

TABLE 3-7. API LANDFARM STUDY - CUMULATIVE MASS EMISSIONS OF VOLATILE ORGANICS

PERIOD:	1	2	3	4	5	6	7	8	9
START-HRS. SINCE SLUDGE APPLIED:	0.00	15.75	40.50	64.75	93.00	109.13	144.63	180.25	234.75
END-HRS. SINCE SLUDGE APPLIED:	15.75	40.50	64.75	93.00	109.13	144.63	180.25	234.75	242.25
ELAPSED TIME (HRS.):	15.75	24.75	24.25	28.25	16.13	35.50	35.62	54.50	7.50

COMPOUND	MOLE. WT.	EMISSION RATE (mg/m2/hr.)								
2-METHYLPENTANE	86.16	7.407	3.055	0.664	0.648	3.395	1.111	0.424	0.586	6.173
3-METHYLPENTANE	86.16	3.704	1.451	0.386	0.432	2.037	0.741	0.278	0.401	4.321
n-HEXANE	86.16	5.555	1.852	0.417	0.432	2.994	0.741	0.478	0.432	5.555
BENZENE	78.12	1.791	0.269	0.028	0.036	0.392	0.048	0.049	0.056	0.588
2,2,4-TRIMETHYLPENTANE	114.23	4.092	1.800	0.389	0.532	2.414	0.777	0.491	0.491	3.028
3-METHYLHEXANE	100.21	3.338	1.543	0.309	0.431	1.974	0.646	0.413	0.431	4.666
TOLUENE	92.15	5.941	1.386	0.086	0.112	1.518	0.191	0.155	0.182	2.773
m,p-XYLENE	106.17	2.282	0.761	0.076	0.095	0.799	0.133	0.097	0.103	1.179
o-XYLENE	106.17	1.369	0.685	0.093	0.145	0.647	0.160	0.106	0.114	0.989
TOTAL XYLENES	106.17	3.651	1.445	0.169	0.240	1.445	0.293	0.203	0.217	2.168
1,2,4-TRIMETHYLBENZENE	120.2	1.593	0.861	0.078	0.142	0.775	0.181	0.129	0.155	1.292
PHENOL	94.11	NA	NA	NA	NA	NA	NA	NA	NA	NA
NAPHTHALENE	128.19	NA	NA	NA	NA	NA	NA	NA	NA	NA
ETHYLBENZENE	106.17	1.027	0.331	0.032	0.046	0.361	0.057	0.040	0.042	NA

COMPOUND	MOLE. WT.	MASS EMISSIONS (kg)									TOTAL
2-METHYLPENTANE	86.16	1.040	0.674	0.143	0.163	0.488	0.352	0.135	0.285	0.413	3.694
3-METHYLPENTANE	86.16	0.520	0.320	0.083	0.109	0.293	0.234	0.088	0.195	0.289	2.132
n-HEXANE	86.16	0.780	0.409	0.090	0.109	0.431	0.234	0.152	0.210	0.372	2.787
BENZENE	78.12	0.252	0.059	0.006	0.009	0.056	0.015	0.016	0.027	0.039	0.480
2,2,4-TRIMETHYLPENTANE	114.23	0.575	0.397	0.084	0.134	0.347	0.246	0.156	0.239	0.203	2.381
3-METHYLHEXANE	100.21	0.469	0.341	0.067	0.109	0.284	0.205	0.131	0.209	0.312	2.126
TOLUENE	92.15	0.835	0.306	0.019	0.028	0.218	0.061	0.049	0.088	0.185	1.789
m,p-XYLENE	106.17	0.320	0.168	0.016	0.024	0.115	0.042	0.031	0.050	0.079	0.845
o-XYLENE	106.17	0.192	0.151	0.020	0.036	0.093	0.051	0.034	0.055	0.066	0.699
TOTAL XYLENES	106.17	0.513	0.319	0.037	0.060	0.208	0.093	0.065	0.105	0.145	1.544
1,2,4-TRIMETHYLBENZENE	120.2	0.224	0.190	0.017	0.036	0.111	0.057	0.041	0.075	0.086	0.838
PHENOL	94.11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
NAPHTHALENE	128.19	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
ETHYLBENZENE	106.17	0.144	0.073	0.007	0.011	0.052	0.018	0.013	0.020	NA	0.339

This equation assumes constant emissions rates during each period and is thus a conservative overestimate. As noted in Section 3.2, the TNMHC data indicate that actual emissions of volatile organics after sunset were probably lower than the predominantly daytime measurements reported on Table 3-7.

Laboratory reports for the WTD canister samples are provided in Appendix J. No WTD sample showed any volatile organic compound above 1.0 ppbv, the detection limit for gas samples reported by RMAL. The reason for this is apparent when one considers that the air flow in the WTD was greater than that in the IFC by a factor of 2340. Only one IFC measurement exceeded 2340 ppbv (2-methylpentane measured at 2400 ppbv on September 14, 1987). The expected result for a parallel WTD sample would be 1.03 ppbv, right at the detection limit. Thus, it is not surprising that no WTD canister samples were reported above 1.0 ppbv.

3.6 SOILS CHARACTERIZATION

A complete set of laboratory reports for the soil samples is provided as Appendix K. Results for the background analyses show that the landfarm soil contained residual inorganic nitrogen (600-1200 mg/kg), phosphorus (4.5 mg/kg), and potassium (100 mg/kg). The soil was at pH 7.1-7.2 prior to waste application and had a bacterial count of approximately 4.0×10^9 organisms/g. Soil pH, nitrogen, and potassium were at levels adequate to support hydrocarbon biodegradation, based on data reported by Bossert, Kachel, and Bartha (1984) and Raymond, Hudson, and Jamison (1976). However, the test plot may have been deficient in phosphorus. Soil moisture was maintained at 9.5-13.5 percent (wet weight basis) throughout the study, typical of operating practices at this HWLT facility. As noted in Section 2.2, the oil loading to the test plot was within the range of reported values for the refining industry.

Soil data for the organic constituents, OSW, and TNMHC are summarized on Table 3-8. There is considerable scatter in some of the soil results, as evidenced by the large relative differences between several of the replicate pairs. Based on a review of these data with RMAL, WCC believes that much of the variability observed in the soil data reflects difficulties in obtaining a representative sub-sample for analysis from the soil samples submitted to the lab. WCC's field notes state that the oily waste had a tendency to form clumps of tar-like material when mixed into the sandy soil at the test site. Despite efforts to composite and homogenize the soils collected in the field, the samples sent to RMAL did contain "tar balls" that would be difficult to sub-sample in a representative manner.

Even with the scatter observed between individual samples, average soil concentrations showed an apparently decreasing trend with time, especially after September 19-20, 1987. During the entire study, average soil concentration decreases were 60-75 percent for the alkanes and 40-75 percent for the monoaromatics. Naphthalene declines were negligible.

To determine the statistical significance of these apparent trends, WCC computed linear least squares regression statistics for each soil parameter versus time, excluding background data collected before waste application. Nine replicate pairs for each chemical were available for this analysis. All data were used in the regression except the first replicate of the organic constituent results from Round 4 (September 15, 1987), which appeared to be anomalous.

Regression statistics for the soils data are shown on Table 3-9. Tabulated information includes:

- Number of data points

TABLE 3-8. API LAND TREATMENT STUDY - SOILS DATA

ROUND:	1	3	4	5	6	7	8	9	10	12
DATE:	9/11/87	9/14/87	9/15/87	9/16/87	9/17/87	9/18/87	9/19/87	9/21/87	9/22/87	9/24/87
CLOCK TIME:	1430	2130	1230	1430	1200	1200	1000	1030	0900	1000
HRS SINCE SLUDGE APPLIED:	BACKGROUND	8	23	49	70.5	94.5	116.5	165	187.5	236.5
CONTAMINANT ANALYSES										
RMAL SAMPLE ID:	64548-001/002	64548-009/010	64548-017/018	64548-046/047	64548-050/051	64548-058/059	64548-074/075	64548-082/083	64548-099/100	64548-115/116
2-METHYLPENTANE (ug/kg)										
REPLICATE 1	4.2	1200	66	1100	1400	1200	1400	1200	820	790
REPLICATE 2	1.1	1000	1700	1100	1700	910	1600	1600	1100	880
AVERAGE	3.2	1100	883	1100	1550	1055	1500	1400	960	835
RANGE	3.1	200	1634	0	300	290	200	400	280	90
3-METHYLPENTANE (ug/kg)										
REPLICATE 1	3.2	930	55	740	910	770	890	730	530	530
REPLICATE 2	1	740	300	700	1100	590	1000	980	720	570
AVERAGE	2.6	835	178	720	1005	680	945	855	625	550
RANGE	2.2	190	245	40	190	180	110	250	190	40
n-HEXANE (ug/kg)										
REPLICATE 1	2.8	1400	4.5	1200	340	1100	1300	1100	760	770
REPLICATE 2	ND	1200	2000	1400	1800	870	1500	1400	1000	790
AVERAGE	NC	1300	1002	1300	1070	985	1400	1250	880	780
RANGE	NC	200	1996	200	1460	230	200	300	240	20
BENZENE (ug/kg)										
REPLICATE 1	ND	440	ND	500	ND	400	270	310	240	180
REPLICATE 2	ND	350	610	430	850	260	290	320	260	200
AVERAGE	NC	395	305	465	425	330	280	315	250	190
RANGE	NC	90	610	70	850	140	20	10	20	20
TOLUENE (ug/kg)										
REPLICATE 1	3.2	3300	5.2	4700	530	3500	2700	2500	1700	1600
REPLICATE 2	ND	2600	4900	3300	6500	2400	2800	2800	2000	1600
AVERAGE	NC	2950	2453	4000	3515	2950	2750	2650	1850	1600
RANGE	NC	700	4895	1400	5970	1100	100	300	300	0
ETHYLBENZENE (ug/kg)										
REPLICATE 1	0.7	1100	ND	1700	240	1300	910	910	610	750
REPLICATE 2	ND	880	1500	1500	2100	880	1100	1200	770	760
AVERAGE	NC	990	750	1600	1170	1090	1005	1055	690	755
RANGE	NC	220	1500	200	1860	420	190	290	160	10
TOTAL XYLENES (ug/kg)										
REPLICATE 1	18	7300	ND	12000	2800	8800	7700	6900	4700	5900
REPLICATE 2	1.1	5900	10000	10000	14000	6300	9400	9300	6100	5200
AVERAGE	9.6	6600	5000	11000	8400	7550	8550	8100	5400	5550
RANGE	16.9	1400	10000	2000	11200	2500	1700	2400	1400	700
PHENOL (ug/kg)										
REPLICATE 1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
REPLICATE 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
AVERAGE	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
RANGE	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
NAPHTHALENE (ug/kg)										
REPLICATE 1	1.9	1100	ND	2100	680	1500	1300	1300	810	1200
REPLICATE 2	ND	1000	1100	1700	2900	1100	2000	1800	1300	940
AVERAGE	NC	1050	550	1900	1790	1300	1650	1550	1055	1070
RANGE	NC	100	1100	400	2220	400	700	500	490	260

TABLE 3-8. API LAND TREATMENT STUDY - SOILS DATA (CONCLUDED)

ROUND:	1	3	4	5	6	7	8	9	10	12
DATE:	9/11/87	9/14/87	9/15/87	9/16/87	9/17/87	9/18/87	9/19/87	9/21/87	9/22/87	9/24/87
CLOCK TIME:	1430	2130	1230	1430	1200	1200	1000	1030	0900	1000
HRS SINCE SLUDGE APPLIED:	BACKGROUND	8	23	49	70.5	94.5	116.5	165	187.5	236.5
CONTAMINANT ANALYSES										
RMAL SAMPLE ID:	64548-001/002	64548-009/010	64548-017/018	64548-046/047	64548-050/051	64548-058/059	64548-074/075	64548-082/083	64548-099/100	64548-115/116
TOTAL NONMETHANE HC (ug/kg)(a)										
REPLICATE 1	36000	190000	110000	150000	100000	240000	140000	280000	270000	220000
REPLICATE 2	23000	220000	230000	180000	230000	140000	160000	240000	240000	170000
AVERAGE	29500	205000	170000	165000	165000	190000	150000	260000	255000	195000
RANGE	13000	30000	120000	30000	130000	100000	20000	40000	30000	50000
SOLIDS, OIL and WATER ANALYSES										
RMAL SAMPLE ID:	64548-005/006	64548-029/030	64548-025/026	64548-042/043	64548-054/055	64548-062/063	64548-078/079	64548-086/087	64548-103/104	64548-119/120
SOLIDS (%)										
REPLICATE 1	81.3	81.6	80.6	80.1	84.2	81.1	80.1	79.6	79.4	82.1
REPLICATE 2	83	81.6	80.8	79.7	83.6	81.9	78.6	80	81.1	80.8
AVERAGE	82.2	81.6	80.7	79.9	83.9	81.5	79.4	79.8	80.3	81.5
RANGE	1.7	0	0.2	0.4	0.6	0.8	1.5	0.4	1.7	1.3
WATER (%)										
REPLICATE 1	6.6	11.6	12.4	11.8	11.8	14.4	11.4	11.8	13	13.4
REPLICATE 2	12.9	12.4	10.8	14.9	11	14.9	14.3	13.2	8.9	13.6
AVERAGE	9.8	12	11.6	13.4	11.4	14.7	12.9	12.5	11.0	13.5
RANGE	6.3	0.8	1.6	3.1	0.8	0.5	2.9	1.4	4.1	0.2
TOTAL OIL (%)										
REPLICATE 1	11.4	7.5	6.8	8.4	4.9	4.2	7.2	8.6	7.3	5.2
REPLICATE 2	4.1	7.2	8.4	8	5.7	3.5	7.4	7.0	10.1	6.2
AVERAGE	7.8	7.4	7.6	8.2	5.3	3.9	7.3	7.8	8.7	5.7
RANGE	7.3	0.3	1.6	0.4	0.8	0.7	0.2	1.6	2.8	1
VOLATILE OIL (%)										
REPLICATE 1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
REPLICATE 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
AVERAGE	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
RANGE	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
NON-VOLATILE OIL (%)										
REPLICATE 1	11.4	7.5	6.8	8.4	4.9	4.2	7.2	8.6	7.3	5.2
REPLICATE 2	4.1	7.2	8.4	8	5.7	3.5	7.4	7	10.1	6.2
AVERAGE	7.8	7.4	7.6	8.2	5.3	3.9	7.3	7.8	8.7	5.7
RANGE	7.3	0.3	1.6	0.4	0.8	0.7	0.2	1.6	2.8	1

(a) TNMHC DATA REPORTED AS HEXANE
(b) ND = NOT DETECTED
(c) NC = NOT CALCULATED

Table 3-9. LINEAR REGRESSION STATISTICS FOR CONCENTRATION OF SOIL PARAMETERS VS. TIME (HOURS) SINCE WASTE APPLICATION

Soil Parameter	Number of Data Points	Mean	Std. Deviation	Regression Intercept	Regression Slope	r^2	F	Probability Level[a]
2-Methylpentane, µg/kg	17	1218	302	1400	-1.73	0.152	2.68	0.122
3-Methylpentane, µg/kg	17	749	206	811	-0.59	0.039	0.60	0.450
n-Hexane, µg/kg	17	1172	408	1481	-2.94	0.241	4.75	0.046
Benzene, µg/kg	17	348	189	493	-1.39	0.249	4.98	0.041
Toluene, µg/kg	17	2908	1429	4062	-11.01	0.274	5.67	0.031
Ethylbenzene, µg/kg	17	1071	448	1382	-2.97	0.203	3.81	0.070
Total Xylenes, µg/kg	17	7147	3011	7969	-7.84	0.031	0.49	0.496
Phenol, µg/kg	17	ND	--	--	--	--	--	--
Naphthalene, µg/kg	17	1402	556	1543	-1.35	0.027	0.42	0.527
TNMHC, mg/kg	18	195	53.7	168.5	0.026	0.115	2.07	0.170

[a] Probability that true slope of regression is zero.

- Mean and standard deviation for each parameter analyzed in soil composites

- Estimated slope and intercept of a least-squares regression line relating soil concentrations to time since waste application

- Coefficient of variation (r^2) showing the fraction of total variance in the soil data explained by the regression line

- An F-statistic used to test the significance of the linear regression against the null hypothesis that the slope is zero

- The percent probability that the reported F-statistic could be achieved if the true slope were zero

Compared to the TNMHC emissions measurements discussed in Section 3.2 and Section 3.3, the soil data were relatively "well behaved" from a statistical standpoint. Therefore, it was considered appropriate to make the various assumptions required for hypothesis testing (i.e., all residuals normally distributed with mean zero and all observations independent).

A review of data in the right hand column of Table 3-9 shows that the probability of a true zero slope is relatively high for most of the soil constituents evaluated in this study. Thus, there appears to be little statistical basis for rejecting the null hypothesis (no measurable trend in soil concentration with time) for all soil parameters except n-hexane, benzene, toluene, and ethylbenzene. Slopes for these four parameters were all significantly less than zero ($p \leq 0.10$).

It is possible that statistically significant decreases in soil levels would have been detected for some of the other constituents as well if variability in the daily soil replicates could have been reduced.

Moreover, because only a small number of separate lab and field soil replicates were analyzed, it is not possible to determine whether the variability in the soil data base arose primarily from field sampling and compositing or from the laboratory.

3.7 FATE OF VOLATILE ORGANICS DURING LANDFARM OPERATIONS

The cumulative emissions estimates calculated from the IFC canister samples were combined with the waste and soil data to evaluate the fate of each constituent in the test plot. These calculations are shown on Table 3-10. Note that a plow depth of 10 in was assumed in these calculations, based on operating practices at the test site. Overall conclusions regarding constituent fate are quite sensitive to this assumption.

Except for naphthalene, Table 3-10 shows that the amount of each compound remaining in the soil plus the mass emitted during the experiment did not exceed the loading applied to the test plot. Thus, it can be stated at a minimum that the organic constituent data obtained during this study do not violate conservation of mass principles. Separate biodegradation experiments, which were not done, would be required to compute a material balance and actually differentiate the amount of material biodegraded from that unaccounted for due to experimental error.

A second observation from Table 3-10 concerns the fate of the various classes of waste constituents. For the aliphatics (all were C_6 compounds), volatilization and biodegradation plus experimental error appeared almost equally important as fate pathways. About 30-35 percent of the applied wasteload remained in the test plot 10 days after waste had been applied. Naphthalene was essentially inert in the test plot during the 10-day study.

Among the monoaromatics, benzene showed the greatest tendency to volatilize, with 16.9 percent of the applied mass apparently emitted. Biodegradation/experimental error accounted for a reduction of 60 percent

Table 3-10. API LANDFARM STUDY - FATE OF ORGANIC CONSTITUENTS APPLIED TO TEST PLOT

Compound	Applied To Test Plot[1] (kg)	Cumulative IFC Emissions[2] (kg)	Cumulative IFC Emissions[2] Pct. of Applied	Remaining in Soil[3] (kg)	Remaining in Soil[3] Pct. of Applied	Biodegraded/ Experimental Error[4] (kg)	Biodegraded/ Experimental Error[4] Pct. of Applied
2-Methylpentane	9.648	3.694	38.3	2.875	29.8	3.079	31.9
3-Methylpentane	5.548	2.132	38.4	1.894	34.1	1.522	27.4
n-Hexane	9.045	2.787	30.8	2.686	29.7	3.572	39.5
Benzene	2.834	0.480	16.9	0.654	23.1	1.700	60.0
Toluene	18.090	1.789	9.9	5.509	30.5	10.792	59.7
Ethylbenzene	4.462	0.339	7.6	2.600	58.3	1.523	34.1
Xylenes (Total)	31.356	1.544	4.9	19.110	60.9	10.702	34.1
Naphthalene	2.231	0	0.0	3.684	165.1	0.0	0.0

1. See Table 3-3.

2. See Table 3-7.

3. Assumes 10 in plow depth, soil density = 1.52 and test plot = 96,000 ft^2. See Table 3-8 for soil constituent concentrations at conclusion of test (September 24, 1987).

4. During 10 days between waste application and end of experiment.

of the benzene in the waste. Mass emissions of the alkyl-substituted monoaromatic hydrocarbons were all less than 10 percent of the waste application, with biodegradation/experimental error presumed to be the fate of 59.7 percent of the toluene and 34.1 percent of both ethylbenzene and the combined xylene isomers.

Assuming that biodegradation is more significant than experimental error in these data, the relative rate of monoaromatics biodegradation (with zero order kinetics) appears to be as follows:

toluene > xylenes > benzene > ethylbenzene

The finding that toluene is the most biodegradable of the monoaromatics is consistent with previous data reported by API (1984, 1987). The relative degradability of the other monoaromatics in soils is disputed in the literature and appears to depend on the form of the kinetic expression (zero order or first order) assumed when laboratory biodegradation data are analyzed. While most of the literature analyzes monoaromatics biodegradation data using a first order kinetic model, API (1987) has presented results which suggest that an assumption of zero order kinetics in a landfarm operation may be equally if not more valid for volatile aromatics heavier than benzene.

3.8 EMISSIONS MODELING

Measured volatile organic emissions rates were compared with estimates from two theoretical models which have been developed to predict hazardous constituent volatilization following application of wastes to a HWLT unit. The two models considered were the CHEMDAT6 model, as presented by EPA (1987a), and the Thibodeaux-Hwang (T-H) model, as presented by Thibodeaux and Hwang (1982) and EPA (1986d). CHEMDAT6 was received from EPA already encoded as a Lotus 123 spreadsheet program. The T-H model equations were used by WCC as the basis for preparing a Fortran program suitable for execution on a personal computer.

A general discussion of the problems of modeling landfarm air emissions is presented as an introduction to this section. The two individual models used in this paper are then discussed. For each model, the technical development is first presented, followed by a discussion of required input data and specific parameter values used for this study. The results obtained for each model are then evaluated and compared to the experimental measurements.

3.8.1 Modeling Landfarm Air Emissions

At HWLT facilities, wastes are either spread onto or injected into the soil, after which they are normally tilled at periodic intervals. Other activities that may occur include waste storage in tanks, loading and unloading of wastes in vacuum trucks or dump trucks, and waste dewatering. All these operations have associated emissions, but only waste application and tilling will be discussed in this report.

Estimating emissions from HWLT units depends on operating practices at a particular site. If waste is applied from a vacuum truck, allowed to remain on the soil surface for a period of time, and then tilled, emissions can be estimated over three separate intervals. These include application of waste onto soil, the time period after waste application and before tilling, and the time period after tilling. If waste is applied by surface or subsurface injection and immediately tilled, only the last step is required to estimate emissions.

This latter case applies when attempting to model landfarm emissions for this study. As noted in Section 2.3.1, waste at the test site was spread onto the soil and immediately tilled. As a consequence, the only process which must be modeled is the emission rate following tilling. This is exactly the case for which CHEMDAT6 and the T-H model were developed.

Both CHEMDAT6 and the T-H model are based on solutions to mass transfer and mass balance equations. CHEMDAT6 includes two mechanisms to explain the observed disappearance of volatile compounds from the soil, volatilization to the atmosphere and biological degradation. The T-H model only considers volatilization. Neither model includes other potential environmental fate pathways such as adsorption or chemical and photochemical decomposition. It has been suggested (EPA 1986d, 1987a) that these other routes will be of little importance compared to volatilization or biodegradation.

3.8.2 CHEMDAT6

3.8.2.1 Technical Development. The CHEMDAT6 air emissions model was developed as the solution to analytical and material balance equations describing the rate of volatilization and biological degradation of an individual waste constituent applied to a land treatment area. It is based on the premise that emissions from HWLT facilities are limited solely by vapor diffusion in the soil, except immediately after tilling or waste application. At those times, resistance to mass transfer at the soil surface is also considered. The model further assumes that an equilibrium concentration of organic vapors exists at all times within the soil pores. The governing equations are based on Fick's second law of diffusion applied to a flat slab as described by Crank (1970) and include a term to estimate biological degradation assuming a decay rate that is first order with respect to soil constituent concentrations. The technical development of the CHEMDAT6 land treatment model presented in the following paragraphs was taken directly from the manual provided by EPA (1987a) with the Lotus 123 spreadsheet program.

The solution to the Fickian diffusion equation assumes an initial uniform concentration of diffusing material throughout a slab with equal concentrations at each surface. The general solution for these conditions, as presented by Crank (1970), is:

$$F_t = \frac{M_t}{M_o} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(\frac{-D\,(2n+1)^2\pi^2 t}{4l^2}\right) \qquad (3\text{-}1)$$

where:

F_t = fraction of initially applied material that has diffused out of the slab at time t
M_t = mass of material that has diffused out of the slab at time t
M_o = initial mass of material present
D = diffusion coefficient
l = distance from center to surface of slab
t = time after initial distribution of diffusing material into the slab

This series solution converges very slowly for $Dt/l^2 < 0.213$. Because of this slow convergence at short times (i.e., immediately after waste application or tilling), Crank (1970) presented an alternative solution that is valid during the initial period. The following equation was obtained for the alternative solution:

$$F_t = \frac{M_t}{M_o} = \frac{2}{\sqrt{\pi}} \left(\frac{Dt}{l^2}\right)^{1/2} \quad (\text{for } Dt/l^2 < 0.213) \qquad (3\text{-}2)$$

Equation (3-2) approximates the Crank (1970) solution but excludes a small error function correction originally used.

The full series solution to Equation (3-1) has been compared by EPA (1987a) to the solution of Equation (3-2) and to values obtained for only the first series term in Equation (3-1):

$$F_t = 1 - \frac{8}{\pi^2} \exp\left(\frac{-D\pi^2 t}{4l^2}\right) \qquad (3\text{-}3)$$

For a range of values of the dimensionless parameter (Dt/l^2), it was demonstrated that Equation (3-2) is a valid solution for $Dt/l^2 < 0.213$ and that the truncated Equation (3-3) is a valid solution for $Dt/l^2 > 0.213$. Thus, sufficient accuracy can be attained under all conditions if the appropriate equation is used to correspond to values of the dimensionless parameter. It was also observed that the fraction of material that diffuses out of the slab is linear with respect to the square root of time up to the point where approximately 50 percent of the diffusing material is lost.

The conditions defined for the above solutions by Crank (1970) are analogous to diffusion of volatile organics out of a surface soil layer as happens in HWLT operations. Because the boundary conditions for the above solutions are symmetrical, an impenetrable plane could, in theory, be inserted at the midpoint of the slab without changing the result. One-half of the slab with an impenetrable boundary layer on the bottom would represent the surface layer of soil into which waste is mixed during land treatment.

In an HWLT facility, only volatile material in the soil vapor phase is available for diffusion to the atmosphere. Therefore, to apply the above equations to land treatment, the amount of material in the vapor phase must be known. This can be estimated by calculating equilibrium conditions as defined by Keq, the ratio of the mass of organics in the vapor phase to the total mass of organics in the soil. The instantaneous emission rate, E, at any time, t, can be estimated by the following equations, which are obtained by differentiating Equations (3-2) and (3-3) with respect to time and adding the equilibrium constant as well as a term to account for constituent biodegradation:

(short times) $$E = \frac{M_o}{l}\left(\frac{KeqD}{\pi t}\right)^{1/2} exp^{-t/t_b} \quad (3\text{-}4)$$

and

(longer times) $$E = M_o\left(\frac{2KeqD}{l^2}\right) \exp\left(\frac{-KeqD\ \pi^2 t}{4l^2}\right) \exp^{-t/t_b} \quad (3\text{-}5)$$

where:

t_b = biodegradation time constant

Note that the above equations imply that volatilization and biodegradation are the only important fate pathways for organics in a landfarm operation.

Biodegradation at HWLT sites is generally considered to be first-order with respect to waste concentration in the soil up to the point where saturation is achieved (EPA 1987a). The integrated form of a first-order decay process has the following form:

$$M_t = M_o exp^{-k_b t}$$

The rate constant, k_b, has units of reciprocal time and can be expressed as the reciprocal of the biological decay time constant, $1/t_b$. The exponential is introduced directly into the rate relationships, Equations (3-4) and (3-5), to reduce the amount of material available for air emissions by the fraction removed by biodegradation.

When oily wastes are applied to a land treatment area, volatile materials in the soil have the potential for partitioning into four different phases--vapor, oil, soil-pore water, and the soil itself, where volatile material is adsorbed by humic materials. Volatile hydrocarbons will preferentially dissolve in oil rather than water so that the fraction

of volatile materials in the soil-pore water is estimated to be very small (EPA 1987a). Partitioning of volatiles into the soil phase by adsorption is a function of the amount of organic carbon in the soil but is also estimated by EPA (1987a) to account for only a small fraction of the applied organics at the high loading rates normally used in oily waste land treatment. An equation can be written that takes all four phases into account in the estimation of equilibrium vapor concentration in the soil (see, for example, Short [1986] and EPA [1986a]). However, the equilibrium equation in the CHEMDAT6 land treatment model considers only two phases, oil and air, in the soil pores.

Calculations presented by EPA (1987a) evaluated the differences between estimated emissions using two-phase partitioning of waste into an oil phase and vapor phase and using four-phase partitioning as described above. It was found that for soils having an organic carbon content up to 10 percent, the estimated fraction of applied organics emitted using four-phase partitioning is only about 10 percent less than the estimated fraction emitted assuming two-phase partitioning.

In any given situation, the amount of volatile material adsorbed by organic carbon in the soil is relatively constant. Thus, in soils with high humic content, adsorption of volatiles in the soil may become significant if low waste loading rates are used. Furthermore, as one of the products of biodegradation is organic carbon, land treatment sites that have been active for an extended time may have elevated concentrations of organic carbon. Even so, with the normal oil loading used in land treatment, it has been assumed by EPA (1987a) that a large fraction of the available soil adsorption sites would be occupied by the oil itself, thus limiting the effects of adsorption on emissions of the lighter hydrocarbon constituents.

Using 1 cm^3 of soil as a basis for calculation, the total volume of gas (i.e., void space) is described by the air porosity of the soil, ε_a. According to the ideal gas law, the number of moles of gas in the 1 cm^3 of soil is $P\varepsilon_a/(RT)$, where P is the partial pressure of a constituent in the gas phase. Assuming that Raoult's Law is applicable for volatile hydrocarbons in oily wastes, the CHEMDAT6 land treatment model sets P equal to xP* (x is the mole fraction of the constituent in the oil phase and P* is the pure component vapor pressure). The moles of volatile constituent in the gas phase in 1 cm^3 of soil is thus $xP^*\varepsilon_a/(RT)$.

Oil loading in units of grams of oil per cm^3 of soil is L, and the total constituent loading is thus xL/MW_{oil}. The equilibrium coefficient, Keq, is defined as the moles of constituent in the gas phase per unit volume of soil divided by the total moles of constituent per unit volume of soil. Therefore, the following equation can be written:

$$Keq = \frac{xP^*\varepsilon_a/(RT)}{x\ L/MW_{oil}} = \frac{P^*MW_{oil}\varepsilon_a}{RTL}$$

This equation differs from the usual expression for equilibrium coefficients by the factor ε_a, which is included to account for the limited air space available within the soil pores. In the CHEMDAT6 land treatment model, Keq for volatile constituents in oily wastes is calculated using only pure compound vapor pressures and oil loading and does not consider the water content of the waste.

The diffusivity of volatile organic compounds reported in the literature assumes that diffusion occurs in free air. In a HWLT facility, diffusion of vapors from the soil must take place within the confines of the air-filled voids of the soil column. The ratio of effective diffusivity of a constituent in the soil to its free air diffusivity can be described by the following equation (Farmer, Igue, and Spencer 1973):

$$\frac{D_e}{D_a} = \frac{\varepsilon_a^{10/3}}{\varepsilon_T^2}$$

where:

D_e = effective diffusivity of constituent in soil vapor

D_a = diffusivity of constituent in air

ε_a = air porosity of soil

ε_T = total porosity of soil.

Total porosity refers to the fraction of the land treatment medium that is made up of nonsoil (or nonsolid) materials, i.e., the sum of the void space, water-filled space, and space occupied by oil from the applied waste. When air porosity and total porosity are the same (i.e., for dry soil), the preceding equation reduces to:

$$\frac{D_e}{D_a} = \varepsilon_a^{4/3}$$

Soil air porosity undergoes substantial changes over time as soil dries out and when moisture is added by rainfall or by watering. As a result, accurately accounting for soil porosity in an analytical model is difficult. The use of average or typical values for soil porosity is considered by EPA (1987a) to be the most practical approach for purposes of modeling.

With the preceding as background, F_t can be estimated by integrating Equation (3-4) from time 0 to time t:

$$F_t = \left(\frac{Keq\ D_e}{\pi\ l^2}\right)^{1/2} \int_o^t t^{-1/2} e^{-t/t_b} dt$$

The exponential term is replaced by a convergent series which is substituted into the above equation and integrated. The result of this integration is:

$$F_t = \left(\frac{Keq\ D_e}{\pi\ l^2}\right)^{1/2} 2t^{1/2} \left[1 - \frac{1}{3}\left(\frac{t}{t_b}\right) + \frac{1}{10}\left(\frac{t}{t_b}\right) - \frac{1}{42}\left(\frac{t}{t_b}\right)^3 + \ldots\right]$$

This series solution converges after only a few terms for values of t/t_b less than 1. Therefore, the following simplification is used in the CHEMDAT6 land treatment model to estimate the mass fraction emitted at short times:

$$F_t = \left(\frac{Keq\ D_e}{\pi\ l^2}\right)^{1/2} 2t^{1/2} \left(1 - \frac{1}{3}\frac{t}{t_b}\right) \qquad (3\text{-}6)$$

The above equation is used to predict the fraction of a constituent emitted to the air when t/t_b is less than 0.5 and when $(Keq\ D_e t/l^2)$ is less than 0.25.

For longer times, when most of the constituent is not present in the soil, the short-term solution overestimates emissions. Under these conditions, Equation (3-5) is integrated to estimate the fraction removed by volatilization. Prior to the integration, Equation (3-5) is first simplified by defining the constant K_d:

$$\frac{Keq\ D_e\ \pi 2}{4\ l^2} = K_d$$

and:

$$E = \frac{M_o 8 K_d}{\pi^2} \exp\ (\ -\ K_d t\ -\ t/t_b) \qquad (3\text{-}7)$$

Integrating from time 0 to t gives:

$$F_t = \frac{8}{\pi^2}\ (1 + \frac{1}{K_d t_b})^{-1}\ [1\ -\ \exp\ [-K_d t\ -\ t/t_b])\ +\ 0.1878 \qquad (3\text{-}8)$$

In the above equation, all terms after the first in the convergent series solution are replaced by the constant 0.1878. This equation is used in the CHEMDAT6 land treatment model for estimating air emissions when $K_d t_b$ is greater than or equal to 0.22.

When $K_d t_b$ is less than 0.22, the following simplification is used to estimate air emissions at long times. An exponential decay factor is established to relate the fraction emitted at any time, t, to the fraction emitted at very long times (i.e., $t \rightarrow \infty$) as estimated using Equation (3-11), which follows. The resulting equation is:

$$F_t = F_a\ [1\ -\ \exp\ (-K_d t\ -\ t/t_b)] \qquad (3\text{-}9)$$

where:

F_a = fraction of constituent emitted at very long times ($t \rightarrow \infty$).

For very long times (i.e., $t \rightarrow \infty$), the fraction emitted is estimated using the following procedure. The integrated form of the general solution without dropping terms is:

$$F_a = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1 - \exp\{-(2n+1)^2 K_d t - t/t_b\}}{(2n+1)^2 + \frac{1}{t_b K_d}}$$

For large values of t, the exponential terms are negligibly small, and for large values of n, $1/(t_b K_d)$ also becomes negligibly small with respect to $(2n+1)^2$. The simplified equation is:

$$F_a = \frac{8}{\pi^2} \left(\frac{K_d t_b}{K_d t_b + 1} + 0.2317\right)$$

The value of 0.2317 was obtained by EPA (1987a) by evaluating the first 125 terms of the series for n > 0 with negligibly small values of $1/(t_b K_d)$:

$$\sum_{n=1}^{125} \frac{1}{(2n+1)^2} = 0.2317$$

Combining terms and simplifying, the equation becomes:

$$F_a = \frac{0.81057 K_d t_b}{K_d t_b + 1} + 0.1878 \qquad (3\text{-}10)$$

The assumptions used in developing Equation (3-10) are not valid at very long times for small values of $K_d t_b$ ($K_d t_b < 0.62$). The solution under these conditions is approximated by the following relationship:

$$F_a = \sqrt{\frac{Keq\ D_e}{l^2} t_b} \qquad (3\text{-}11)$$

This relationship was established by using multiple terms of the general solution to calculate values of F_a for a series of input values for the

parameters $K_{eq}D_e/l^2$ and t_b and then using a curve-fitting routine to derive the relationship in Equation (3-11) for $K_d t_b < 0.62$ (EPA 1987a).

To calculate the amount of waste constituent remaining in the soil, it is necessary to know both the amount emitted to the air and the amount biodegraded. At very long times (i.e., $t \rightarrow \infty$), all waste is assumed to disappear from the soil. Thus, the cumulative fraction of waste emitted plus the cumulative fraction biodegraded must be equal to 1 if other removal mechanisms are ignored:

$$F_b = 1 - F_a \qquad (3\text{-}12)$$

where:

F_b = fraction of constituent that is biodegraded after a long time (i.e., $t \rightarrow \infty$).

To apply the CHEMDAT6 land treatment model to a situation where the HWLT unit is retilled after the initial waste application and tilling, estimates of the amount of constituent emitted to the air and the amount biodegraded are required. When retilling occurs, the amount of material remaining in the soil at the time of retilling is estimated using the following equation:

$$F_S = (1 - F_{t'})\, e^{-t/t_b} \qquad (3\text{-}13)$$

where:

F_S = fraction of constituent remaining in the soil

$F_{t'}$ = fraction of material emitted to the air at time t' assuming no biodegradation ($F_{t'}$ can be estimated by setting $t/t_b = 0$ in Equation (3-6) or (3-8), whichever is appropriate)

For modeling emissions after retilling occurs, M_o is set equal to $F_S M_o$ and t is reset to zero.

If a reapplication of waste occurs, the total waste loading is the sum of the waste remaining in the soil and the newly applied waste:

$$M_o = F_S M_o + M_n \qquad (3\text{-}14)$$

where:

M_n = amount of constituent newly applied to the land treatment site.

To continue the modeling after waste reapplication and tilling, t is reset to zero and the calculations are repeated.

3.8.2.2 Programming. A Lotus 123 spreadsheet program which incorporates the model equations developed above was obtained from EPA and used to calculate the results presented later in this report. Sample output from this program is shown on Table 3-11. The program requires input data specific to the landfarm site and the applied waste. Compound-specific physical parameters, with the exceptions noted later, were included in a data base supplied with the spreadsheet program. The EPA program was used without modification except as described below.

3.8.2.3 Data Input. Execution of the CHEMDAT6 land treatment model requires a data set describing the land treatment site, the waste application, and waste-related properties. Input values used in this study, and the sources for those values, are described on Table 3-12.

Waste loading was determined from the experimental data, including the volume of waste applied, the dimensions of the test plot, and an assumed plow depth of 10 in (25.4 cm). The waste loading term used in the CHEMDAT6 land treatment model is the amount of oil phase waste, not total waste, applied per unit area across the land treatment site. Note that this

90397-T311 CON-1

Table 3-11. SAMPLE OUTPUT FROM CHEMDAT6 LAND TREATMENT MODEL

LAND TREATMENT MODEL DATA (land treatment)	
L,Loading (g oil/cc soil)	0.00666
Enter Ci x 10^6 VO ppmw	1
l,Depth (cm)	25.4
Total porosity	0.43
Air Porosity (default=0)	0.25
MW oil	282.6
VO diss. in water, enter 1	0
Time of calc. (days)	5.94
Biodegradation, enter 1	1
Temperature (Deg. C)	26
Wind Speed (m/s)	4.47
Area (m2)	8918

	LANDTREATMENT EMISSION RATES (g/cm2-s) TIME (hours)				
COMPOUND NAME	0.25	1	4	12	48
N-HEXANE	3.86E-12	1.93E-12	9.60E-13	5.46E-13	2.55E-13
2-METHYLPENTANE	4.54E-12	2.27E-12	1.14E-12	6.56E-13	3.28E-13
3-METHYLPENTANE	4.32E-12	2.16E-12	1.07E-12	6.11E-13	2.87E-13
BENZENE	2.04E-12	1.02E-12	5.08E-13	2.90E-13	1.38E-13
TOLUENE	1.14E-12	5.68E-13	2.80E-13	1.54E-13	6.29E-14
XYLENE(-M)	5.28E-13	2.64E-13	1.31E-13	7.38E-14	3.30E-14
ETHYLBENZENE	6.11E-13	3.06E-13	1.52E-13	8.55E-14	3.82E-14
NAPHTHALENE	8.03E-14	4.08E-14	2.04E-14	1.16E-14	5.17E-15

Table 3-12. INPUT DATA FOR CHEMDAT6 LAND TREATMENT MODEL

Datum	Value	Units	Reference and Comments
Waste loading	0.00666	g oil/cm^3 soil	Calculated from waste application data and dimensions of test plot
Area	8918	m^2	Area of test plot
Compound concentration	various	mg compound/ kg oil	Waste analysis data
Tilling depth	25.4	cm	Site operation characteristic
Total soil porosity	0.43	Dimensionless	Calculated from equation given by Ehrenfeld et al. (1986) assuming soil bulk density of 1.5 g/cm^3 and soil particle density of 2.65 g/cm^3
Soil air porosity	0.25	Dimensionless	Calculated from equation given by Ehrenfeld et al. (1986) and average bulk water content in soil of 12 percent
Molecular weight of oil phase	282.6	g/mole	Value for eicosane ($C_{20}H_{42}$)
Temperature	26	°C	Experimental measurement
Wind speed	4.47	m/s	Default program value

initial oil loading value does not consider the fact that the applied waste will mix to some extent with residual oil remaining in the plot from previous applications. As this oil is generally devoid of volatile constituents (see background soils data on Table 3-8), any mixing that occurs will effectively dilute the applied waste and thus reduce estimated emissions rates. However, it cannot be assumed that tilling with agricultural equipment will completely mix the freshly applied oil into the residual oil, especially as the latter may be present in clumps and "tar balls" within the soil column. For this reason, WCC chose to ignore the presence of residual oil in the test plot when applying the CHEMDAT6 land treatment model. It is recognized that this choice may result in conservatively high emissions predictions, especially for the time period immediately following waste application.

A single value for the concentration of each volatile compound in the waste was input into the model. Calculated emissions are directly proportional to initial constituent concentrations.

The total soil porosity and soil air porosity were calculated using equations provided by Ehrenfeld et al. (1986), with an assumed soil bulk density of 1.5 g/cm^3, an assumed soil particle density of 2.65 g/cm^3, and the average soil water content determined in the test plot. Use of typical values such as these is consistent with guidance provided by EPA (1987a) for the CHEMDAT6 land treatment model.

The molecular weight of the oil phase was set equal to that of eicosane ($C_{20}H_{42}$; molecular weight = 282.6) since it was assumed that the waste oil would be approximately similar in physical and chemical properties to a high molecular weight aliphatic hydrocarbon. The soil temperature was measured during the course of the field experiments. An average value was used as input to the model. The program default value for wind speed of 4.47 m/s (10 mi/hr) was used, which is also a typical ambient value for the test site according to data presented on Table 2-4.

As stated above, the CHEMDAT6 land treatment model includes a data base of physical properties for the individual compounds considered, including diffusion coefficients in air, pure compound vapor pressure data, molecular weights, and biodegradation time constants. It is not at all clear from the spreadsheet or supporting documentation (EPA 1987a) how biodegradation rates were obtained or calculated. Nevertheless, the spreadsheet values for physical properties were used without modifications for n-hexane, benzene, toluene, xylene, and naphthalene. The supplied data base did not include this information for 2-methylpentane and 3-methylpentane. Data for these two compounds were added to the spreadsheet by WCC. The values used and the methods employed to obtain them were the same as those described in Section 3.8.3.2 under the discussion of the T-H model.

3.8.2.4 Results. The CHEMDAT6 land treatment model was run for each of the three relevant time intervals of this study. These included waste application to first tilling at 92 hours, 92 hours to second tilling at 234.75 hours, and 234.75 hours to the end of experimental measurements at 242.5 hours. Partition coefficients describing the equilibrium distribution of volatile compounds between the waste oil phase and air in the soil pores were calculated as described in Section 3.8.2.1. The model was run both with and without inclusion of a biodegradation term.

Predictions of the CHEMDAT6 land treatment model for the case including biodegradation are presented in Table 3-13. For each time interval, the fraction of each compound lost by volatilization and biodegradation was calculated. Rates of volatilization at intermediate times were also calculated. Initial concentrations of each compound were determined by the analysis of the applied waste and are expressed as concentration in the waste oil phase. Final concentrations at the end of each time interval were calculated by reducing the initial concentration by the fraction determined to have volatilized or biologically decomposed. These final concentrations were used as initial concentrations for the next time interval.

Table 3-13. CHEMDAT6 LAND TREATMENT MODEL RESULTS WITH BIOLOGICAL DEGRADATION CONSIDERED

Input Data:

Waste Loading (g oil/cc soil) =	0.00666
Tilling Depth (cm) =	25.4
Soil Bulk Density (g/cm3) =	1.5
Total Soil Porosity =	0.5
Air Filled Soil Porosity =	0.25
MW of Oil (g/gmole) =	282.6
Temperature (C) =	26
Wind Speed (m/s) =	4.47
Area (m2) =	8918

Period from Initial Waste Application to Tilling at 92 Hours

Compound	Initial Concentration in Oil (mg/kg oil)	Initial Concentration in Soil (mg/kg soil)	Final Concentration in Oil (mg/kg oil)	Final Concentration in Soil (mg/kg soil)	Percent Lost by Volatilization	Percent Lost by Biodegradation	Emission Rate at Indicated Elapsed Time (mg/h-m2) 0.25 hours	1 hours	4 hours	12 hours	48 hours
n-Hexane	600	2.664	123.40	0.548	71.91	7.52	88.422	41.681	20.732	11.795	5.517
2-Methylpentane	640	2.842	98.76	0.439	84.57	.00	104.685	52.373	26.194	15.125	7.563
3-Methylpentane	368	1.634	56.39	0.250	78.18	6.50	57.224	28.591	14.223	8.096	3.796
Benzene	188	0.835	95.63	0.425	39.92	9.21	13.812	6.905	3.439	1.963	0.931
Toluene	1200	5.328	545.87	2.424	14.00	40.51	49.219	24.548	12.077	6.666	2.718
Xylenes (as m-Xylene)	2080	9.235	1388.21	6.164	4.91	28.35	39.508	19.776	9.812	5.528	2.469
Ethylbenzene	296	1.314	193.75	0.860	5.85	28.69	6.514	3.259	1.617	0.911	0.407
Naphthalene	148	0.657	108.92	0.484	0.71	25.70	0.428	0.218	0.109	0.062	0.028

Period from Tilling at 92 Hours to Tilling at 234.75 hours

Compound	Initial Concentration in Oil (mg/kg oil)	Initial Concentration in Soil (mg/kg soil)	Final Concentration in Oil (mg/kg oil)	Final Concentration in Soil (mg/kg soil)	Percent Lost by Volatilization	Percent Lost by Biodegradation	Emission Rate at Indicated Elapsed Time (mg/h-m2) 92.25 hours	93 hours	96 hours	104 hours	140 hours
n-Hexane	123.40	0.548	11.95	0.053	81.43	8.88	17.157	8.573	4.264	2.426	1.135
2-Methylpentane	98.76	0.439	6.17	0.027	93.75	.00	16.155	8.082	4.042	2.384	1.167
3-Methylpentane	56.39	0.250	3.47	0.015	86.43	7.41	8.769	4.381	2.180	1.241	0.582
Benzene	95.63	0.425	37.39	0.166	48.86	12.04	7.026	3.512	1.749	0.998	0.474
Toluene	545.87	2.424	172.37	0.765	18.53	49.90	22.389	11.167	5.494	3.032	1.237
Xylenes (as m-Xylene)	1388.21	6.164	766.36	3.403	7.02	37.78	26.368	13.198	6.548	3.689	1.648
Ethylbenzene	193.75	0.860	104.32	0.463	8.33	37.82	4.264	2.134	1.058	0.596	0.266
Naphthalene	108.92	0.484	68.06	0.302	1.02	36.50	0.315	0.160	0.080	0.045	0.020

Period from Tilling at 234.75 Hours to End of Experiment at 242.5 Hours

Compound	Initial Concentration in Oil (mg/kg oil)	Initial Concentration in Soil (mg/kg soil)	Final Concentration in Oil (mg/kg oil)	Final Concentration in Soil (mg/kg soil)	Percent Lost by Volatilization	Percent Lost by Biodegradation	Emission Rate at Indicated Elapsed Time (mg/h-m2) 235 hours	235.75 hours	238.75 hours
n-Hexane	11.95	0.053	9.05	0.040	23.09	1.23	1.662	0.830	0.413
2-Methylpentane	6.17	0.027	4.49	0.020	27.28	.00	1.010	0.505	0.253
3-Methylpentane	3.47	0.015	2.54	0.011	25.83	1.17	0.540	0.270	0.134
Benzene	37.39	0.166	32.42	0.144	12.22	1.06	2.747	1.373	0.684
Toluene	172.37	0.765	153.49	0.681	1.61	9.35	7.070	3.526	1.755
Xylenes (as m-Xylene)	766.36	3.403	723.65	3.213	0.49	5.08	14.556	7.286	3.615
Ethylbenzene	104.32	0.463	98.00	0.435	0.58	5.48	2.296	1.149	0.570
Naphthalene	68.06	0.302	66.05	0.293	0.07	2.88	0.197	0.100	0.050

CHEMDAT6 land treatment model output with biological degradation not included is presented in Table 3-14. Rates of compound volatilization at intermediate times are inversely proportional to the square root of the time since last tilling, which is consistent with the model development given in Section 3.8.2.1.

3.8.3 T-H Model

The T-H model was developed using the concept of a dried out zone through which the volatile compounds must diffuse to reach the surface. (Thibodeaux and Hwang 1982). The depth of the dried out zone is assumed to increase with time as material is released from the landfarm. Equilibrium partitioning of volatile components is assumed between air in the soil pores and the waste oil phase below the lower plane of the evaporating zone. The only removal mechanism for volatile compounds considered in this model is volatilization. The technical development of the T-H model presented below was taken largely from EPA (1986d).

3.8.3.1 Technical Development. The T-H HWLT air emissions model assumes an isothermal soil column, no capillary action through the soil layer, no adsorption in the soil pore space, and no biodegradation of applied organics within the soil column. The description of vapor movement through the soil is valid for surface or subsurface waste applications through the use of surface injection depth, h_s, and penetration or plow slice depth, h_p (Figure 3-5).

Under steady-state conditions, the time for the initial applied mass to completely volatilize into the soil pore space, t_E, and the mass flux rate of each component, F_A, are determined through a mass balance on the component assuming Fickian diffusion. Neglecting mass transfer resistance at the soil surface and assuming no component vapor concentration at the air/soil interface, the following relationship for evaporation time can be developed:

Table 3-14. CHEMDAT6 LAND TREATMENT MODEL RESULTS WITH BIOLOGICAL DEGRADATION NOT CONSIDERED

Input Data:

Waste Loading (g oil/cc soil) =	0.00666
Tilling Depth (cm) =	25.4
Soil Bulk Density (g/cm3) =	1.5
Total Soil Porosity =	0.5
Air Filled Soil Porosity =	0.25
MW of Oil (g/gmole) =	282.6
Temperature (C) =	26
Wind Speed (m/s) =	4.47
Area (m2) =	8918

Period from Initial Waste Application to Tilling at 92 Hours

Compound	Initial Concentration in Oil (mg/kg oil)	Initial Concentration in Soil (mg/kg soil)	Final Concentration in Oil (mg/kg oil)	Final Concentration in Soil (mg/kg soil)	Percent Lost by Volatilization	Percent Lost by Biodegradation	Emission Rate at Indicated Elapsed Time (mg/h-m2) 0.25 hours	1 hours	4 hours	12 hours	48 hours
n-Hexane	600	2.664	146.33	0.650	75.61	.00	83.461	41.759	20.887	12.061	6.031
2-Methylpentane	640	2.842	98.76	0.439	84.57	.00	104.685	52.373	26.194	15.125	7.563
3-Methylpentane	368	1.634	66.48	0.295	81.93	.00	57.250	28.643	14.326	8.272	4.136
Benzene	188	0.835	109.43	0.486	41.79	.00	13.817	6.915	3.459	1.998	0.999
Toluene	1200	5.328	919.28	4.082	23.39	.00	49.289	24.687	12.354	7.135	3.569
m-Xylene	2080	9.235	1854.03	8.232	10.86	.00	39.539	19.838	9.936	5.741	2.872
Ethylbenzene	296	1.314	258.77	1.149	12.58	.00	6.520	3.270	1.637	0.946	0.473
Naphthalene	148	0.657	145.47	0.646	1.71	.00	0.428	0.218	0.110	0.064	0.032

Period from Tilling at 92 Hours to Tilling at 234.75 hours

Compound	Initial Concentration in Oil (mg/kg oil)	Initial Concentration in Soil (mg/kg soil)	Final Concentration in Oil (mg/kg oil)	Final Concentration in Soil (mg/kg soil)	Percent Lost by Volatilization	Percent Lost by Biodegradation	Emission Rate at Indicated Elapsed Time (mg/h-m2) 92.25 hours	93 hours	96 hours	104 hours	140 hours
n-Hexane	146.33	0.650	18.46	0.082	87.38	.00	20.355	10.185	5.094	2.941	1.471
2-Methylpentane	98.76	0.439	6.17	0.027	93.75	.00	16.155	8.082	4.042	2.334	1.167
3-Methylpentane	66.48	0.295	5.29	0.023	92.05	.00	10.342	5.174	2.588	1.494	0.747
Benzene	109.43	0.486	52.73	0.234	51.81	.00	8.042	4.025	2.013	1.163	0.581
Toluene	919.28	4.082	651.46	2.892	29.13	.00	37.759	18.912	9.464	5.466	2.734
m-Xylene	1854.03	8.232	1603.19	7.118	13.53	.00	35.244	17.683	8.857	5.117	2.560
Ethylbenzene	258.77	1.149	218.24	0.969	15.66	.00	5.700	2.858	1.431	0.827	0.414
Naphthalene	145.47	0.646	142.38	0.632	2.13	.00	0.421	0.215	0.108	0.063	0.032

Period from Tilling at 234.75 Hours to End of Experiment at 242.5 Hours

Compound	Initial Concentration in Oil (mg/kg oil)	Initial Concentration in Soil (mg/kg soil)	Final Concentration in Oil (mg/kg oil)	Final Concentration in Soil (mg/kg soil)	Percent Lost by Volatilization	Percent Lost by Biodegradation	Emission Rate at Indicated Elapsed Time (mg/h-m2) 235 hours	235.74 hours	238.75 hours
n-Hexane	18.46	0.082	14.24	0.063	22.85	.00	2.568	1.285	0.643
2-Methylpentane	6.17	0.027	4.51	0.020	26.87	.00	1.010	0.505	0.253
3-Methylpentane	5.29	0.023	3.94	0.017	25.55	.00	0.823	0.412	0.206
Benzene	52.73	0.234	46.36	0.206	12.08	.00	3.875	1.939	0.970
Toluene	651.46	2.892	607.41	2.697	6.76	.00	26.758	13.402	6.707
m-Xylene	1603.19	7.118	1552.85	6.895	3.14	.00	30.475	15.290	7.658
Ethylbenzene	218.24	0.969	210.30	0.934	3.64	.00	4.807	2.411	1.207
Naphthalene	142.38	0.632	141.67	0.629	0.49	.00	0.412	0.210	0.106

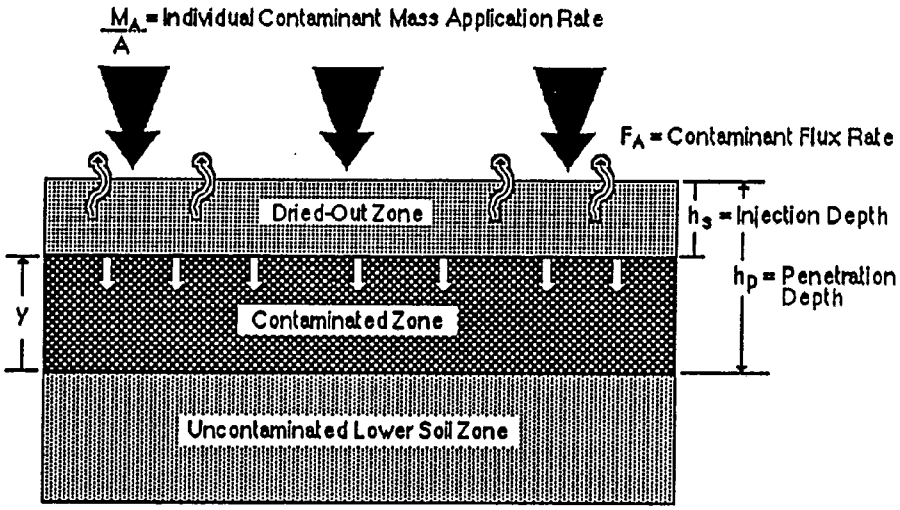


Figure 3-5. THEORETICAL CONTAMINANT BEHAVIOR DESCRIBED BY THE THIBODEAUX-HWANG (1982) MODEL. ADAPTED FROM EPA (1986d)

$$t_E = \frac{M_o(h_p + h_s)}{2AD_eC_A^*} \quad (3\text{-}15)$$

where:

A = surface area of land treatment plot
M_o = mass of component applied to the contaminated zone
C_A^* = equilibrium concentration of component in soil pore spaces at the evaporating plane
D_e = effective component soil air diffusion coefficient

Mass flux rate is given as:

$$F = \frac{D_eC_A^*}{\left(h_s^2 + \frac{2D_etA(h_p - h_s)C_A^*}{M_o}\right)^{1/2}} \quad (3\text{-}16)$$

where:

t = time after component application
F = mass flux rate

The component pore space concentration, C_A^*, is related to the component concentration within the applied oil by equating diffusion through the oil phase to that through the dry soil column. The transfer rate equality takes the form:

$$a_sAy\frac{D_o}{Z_o}(C_o - C_L) = \frac{D_eA}{(h_p - y)}(C_A^* - 0) \quad (3\text{-}17)$$

where:

a_s = interfacial area per unit volume of soil
D_o = component diffusion coefficient in the oil phase
Z_o = oil layer diffusion length
C_o = initial component concentration in the oil
C_L = component concentration on the oil side of the air/oil interface
y = average thickness of the wet zone
0 = assumed concentration of constituent in ambient air above soil surface

The concentration of the component in the air and oil phases within the soil pore space is related by a modified Henry's Law constant to yield:

$$C_A^* = H_{C'} C_L \tag{3-18}$$

where:

$H_{C'}$ = Modified Henry's Law constant (cm^3 oil/cm^3 air)

Substitution of Equation (3-17) into Equation (3-18) allows for expression of the concentration of the component in the soil vapor phase in terms of its initial concentration within the oil as:

$$C_A^* = \frac{H_{C'} C_o}{1 + \frac{H_{C'} D_e Z_o}{D_o a_s y(h_p - y)}} \tag{3-19}$$

An average value for the term $y(h_p - y)$ is estimated by taking its integral from 0 to $h_p - h_s$ divided by $h_p - h_s$:

$$y(h_p - y) = \frac{h_p^2 + h_p h_s - 2h_s^2}{6} \tag{3-20}$$

Substitution of Equation (3-20) into Equation (3-19) results in:

$$C_A^* = \frac{H_{C'}C_o}{1 + \frac{H_{C'}6D_eZ_o}{D_oa_s(h_p^2 + h_ph_s - 2h_s^2)}} \qquad (3\text{-}21)$$

The importance of the oil layer diffusion term in Equation (3-21) is highly dependent upon the oil layer diffusion length, Z_o, and the interfacial area, a_s, both of which are tied to the waste application rate and the nature of the soil in the land treatment system. Thibodeaux and Hwang (1982) present equations for Z_o and a_s for oil/soil interactions that result in either "film" forms or "lump" forms within the soil column. A thin coating of oil around soil particles results in film forms, while soil aggregation and clumping result in the entrapment of oil lumps within the soil matrix. Based on simple geometry and an assumed orthogonal arrangement of soil particles, these physical parameters take the following mathematical form:

Film Form: $Z_o = \frac{d\rho_p f}{6\rho_o}$ Lump Form: $Z_o = \frac{d}{2}$ (3-22)

$a_s = 6/d$ $a_s = 2.7/d$ (3-23)

where:

d = particle diameter
ρ_p = soil particle density
ρ_o = oil density
f = fraction of air filled pore space in soil

If a thin oil diffusion length, on the order of soil particle diameter, can be assumed, Equation (3-21) can be simplified to Equation (3-24):

$$C_A^* = H_{C'}C_o \qquad (3\text{-}24)$$

If the land treatment unit is tilled at a time t less than the volatilization lifetime of the constituents of interest, the equations developed above must be modified for the new geometry which results. The mass of contaminant lost during the period prior to tilling, M_t, is determined from the integration of Equation (3-16) from t = 0 to t = time of tilling, resulting in Equation (3-25):

$$M_t = \frac{M_o}{(h_p - h_s)} \left[(h_s^2 + \frac{2D_e A t (h_p - h_s) C_A^*}{M_o})^{\frac{1}{2}} - h_s\right] \qquad (3\text{-}25)$$

The mass remaining after time t, M_r, is calculated as the difference between M_o and M_t. This value is then used in Equations (3-15) and (3-16) above to determine the evaporation time and mass flux rate for the residual mass from the tilled soil, assuming uniform mass distribution within a soil column of dimensions h_p = tilling depth and h_s = 0.

With the use of Equations (3-15) through (3-25), the organic compound emissions rate from land treatment sites before and after tilling can be estimated once three sets of parameters are determined. These are soil parameters (bulk density, particle diameter, and particle density), compound parameters (air and oil molecular diffusivity and modified Henry's Law constant), and operational parameters (surface injection and plow slice depth, tilling depth, waste application surface area, mass of oil and volatile constituents applied, and time).

3.8.3.2 Parameter Calculation and Estimation. A number of critical model parameters must be calculated or estimated for the soil and waste system under consideration. However, only a limited theoretical base exists for determining the majority of these soil/waste/component characteristics. The approach taken in this study was to use correlation equations presented by EPA (1986d) and others for estimation of parameters that could not be determined experimentally or from operating data for the test plot.

The compound property most affecting vapor diffusion within a soil system is the effective diffusion coefficient, D_e. This parameter has been correlated with physical properties of the soil, namely soil total porosity and soil air porosity. One such correlation has been presented by Farmer, Igue, and Spencer (1973), and was also used in development of the CHEMDAT6 land treatment model (see Section 3.8.2.1).

Component partitioning within the complex environment of a contaminated soil system will also significantly affect volatilization. The partition parameter of concern in the T-H model is a modified Henry's Law constant which describes equilibrium between an oil film and the soil vapor phase. Modified Henry's constants were calculated assuming that each compound would partition only between the soil vapor and the waste oil phase. In such a case, the equation for equilibrium partitioning may be written as:

$$P = x \gamma P^* \qquad (3\text{-}26)$$

where:

P = partial pressure of component in soil vapor
x = mole fraction of component in oil phase
γ = activity coefficient of component in oil phase
P^* = saturation vapor pressure of pure component at temperature of experiment

Pure component saturation vapor pressures were obtained from Perry and Chilton (1973). Activity coefficients were obtained using regular solution theory as described by Prausnitz (1969). The value of the modified Henry's constant can be obtained from Equation (3-26) by converting P to a concentration in the soil vapor (assuming ideal gas behavior) and converting x to a concentration in the oil phase. The ratio of the first concentration to the second is the modified Henry's constant. The oil phase was assumed to be eicosane for this study.

Values for diffusion coefficients of waste constituents in the oil phase were estimated using the equation of Wilke and Chang (1955):

$$D_o = \frac{7.4 \times 10^{-8} (M)^{1/2} T}{\mu V^{0.6}} \qquad (3\text{-}27)$$

where:

D_o = diffusion coefficient of component in oil
M = molecular weight of component
T = absolute temperature
μ = viscosity of oil
V = molar volume of component at boiling point

The viscosity of the oil phase was estimated to be 20 cP based on typical values for oily refinery wastes reported by EPA (1986d). Molar volumes of the volatile components of concern to this study were estimated using the additive method of Le Bas as described by Reid et al. (1977).

Values for free air diffusion coefficients of the compounds of concern were estimated using the form of the Wilke-Lee equation presented by Reid et al. (1977):

$$D_a = \frac{[3.03 - 0.98/(2[1/M + 1/M_A])^{\frac{1}{2}}]\ [10^{-3} \times T^{3/2}]}{P_T[2(1/M + 1/M_A)]^{1/2}\ \sigma^2\ \Omega_D} \qquad (3\text{-}28)$$

where:

D_a = diffusion coefficient for component in air
M_A = molecular weight of air
T = absolute temperature
P_T = atmospheric pressure
σ = interaction length
Ω_D = collision integral

Values of the interaction length and collision integral were estimated using methods described by Reid et al. (1977). Effective diffusivity (D_e) in the soil vapor was estimated from D_a and assumed soil air and total porosities using the equation of Farmer, Igue, and Spencer (1973).

3.8.3.3 Data Input. Section 3.8.3.2 has described methods used to estimate compound-specific data for input to the T-H model. Computed values for the required constituent data are listed in Table 3-15.

Site-specific input data used for this study are listed in Table 3-16, together with explanation of how the values were estimated. The waste application rate was based on field measurements and waste analysis data and included total waste mass. Input constituent concentrations were based on the total waste mass and include a value of 250,000 mg/kg for the oil phase.

The tilling depth and area of waste application were determined from site operating practices and the dimensions of the test plot, respectively. The initial depth of waste penetration was set equal to zero immediately following tilling, which is the starting point for the model calculations.

Table 3-15. COMPOUND-SPECIFIC INPUT DATA FOR THE T-H LANDFARM EMISSIONS MODEL

Compound	Diffusion Coefficient in Air (cm^2/s)	Diffusion Coefficient in Oil (cm^2/s)	Modified Henry's Coefficient (cm^3 oil/cm^3 air)
n-Hexane	8.97E-03	5.18E-07	3.00E-03
2-Methylpentane	9.01E-03	5.18E-07	4.16E-03
3-Methylpentane	8.96E-03	5.18E-07	3.84E-03
Benzene	1.05E-02	6.18E-07	4.23E-03
Toluene	9.35E-03	5.95E-07	1.18E-03
Total Xylenes	8.47E-03	5.76E-07	3.55E-04
Ethylbenzene	8.48E-03	5.76E-07	4.18E-04
Naphthalene	7.85E-03	6.13E-07	3.81E-05

Table 3-16. SITE-SPECIFIC INPUT DATA FOR T-H MODEL

Datum	Value	Units	Reference and Comments
Waste loading	0.6765	g/cm^2	Calculated from experimental data
Area	8918	m^2	Area of test plot
Tilling depth	25.4	cm	Site operating characteristic
Injection depth	0.0	cm	Injection depth equal 0 cm immediately after tilling
Soil bulk density	1.5	g/cm^3	Ehrenfeld et al. (1986)
Soil particle density	2.65	g/cm^3	Ehrenfeld et al. (1986)
Soil percent moisture	12.3	percent	Experimental measurement
Temperature	26	°C	Experimental measurement
Fraction void space filled with air	0.582		Calculated from equations in Ehrenfeld et al. (1986)
Oil phase density	0.833	g/cm^3	Density of non-volatile oil recovered from waste by MODT analysis (Appendix K)

Percent moisture content in the soil was measured during the experiment. The soil particle and soil bulk densities used were typical values reported in the literature (Ehrenfeld et al. 1986). The fraction of soil pore space filled with air was calculated from these numbers. The oil phase density was set equal to that of the measured value for the non-volatile oil recovered from the waste during the MODT analysis (see Section 2.4.1.3 and Appendix K).

3.8.3.4 Results. Equations presented in the previous sections were used to prepare a Fortran program which calculated constituent emission rates and soil concentrations from the time of waste application on. Modeling results are presented in Appendix L. The model was run twice for those compounds which were not predicted to have completely volatilized before the first tilling 92 hours after waste application. Final waste concentrations predicted from the first run were used as inputs for the second run.

The film form model described in Equations (3-22) and (3-23) was used for estimation of the oil layer diffusion length and interfacial area. However, the choice of the film form over the lump form did not influence the results obtained from the T-H model. This is because the second term in the denominator of Equation (3-19) is much less than 1.0 for the range of physical parameters assumed. Therefore, Equation (3-19) was effectively simplified to Equation (3-24) in this study. This condition corresponds to negligible resistance to mass transfer in the liquid (oil) phase in the soil system.

3.8.4 Comparison of Modeling Results with Measured Emissions

The purpose of predicting volatilization rates using the CHEMDAT6 and the T-H land treatment models was to compare these estimates to the experimental results reported in Section 3.5. Data presented in Tables 3-13 and 3-14 show that the CHEMDAT6 model is a reasonably good emissions predictor immediately after waste application or tilling but in general

predicts higher emission results than those measured in the field experiments. The model including the biodegradation component overpredicts actual short-term emissions by a factor of 1.4-3.4. This overprediction at short times may reflect the fact that mixing of applied oily waste with residual oil in the soil was neglected (see Section 3.8.2.3). In addition, actual wind speed at the soil surface may have been substantially less that the 10 mi/hr velocity assumed in CHEMDAT6. This would result in greater resistance to mass transfer, and therefore lower emissions, than accounted for by the model immediately following sludge application.

As illustrated for toluene emissions in Figure 3-6 and all the volatile compounds of interest in Table 3-17, relative discrepancies between the CHEMDAT6 model and experimental results increase with time after initial waste application. Except over very long time intervals (longer than 200 hours), emission rates predicted by the model with biodegradation included were not substantially different from predictions when biodegradation was not included. This appears to contradict the field measurements, especially for the monoaromatics, which indicate that biodegradation was an important loss mechanism for many of the volatile compounds of concern to this study.

The T-H model results in Table 3-17 and Appendix L show much higher predicted rates of volatilization than were observed in these experiments. Predicted emissions rates were 8-50 times greater than experimental results. This leads the T-H model to predict that n-hexane, 2-methylpentane, 3-methylpentane, benzene, and toluene would be completely volatilized from the soil before tilling at 92 hours. This prediction is at odds with the field data presented in Sections 3.6 and 3.7, which show measurable emissions and residual soil concentrations for these same components even at the end of the experiment, over 240 hours after the initial waste application.

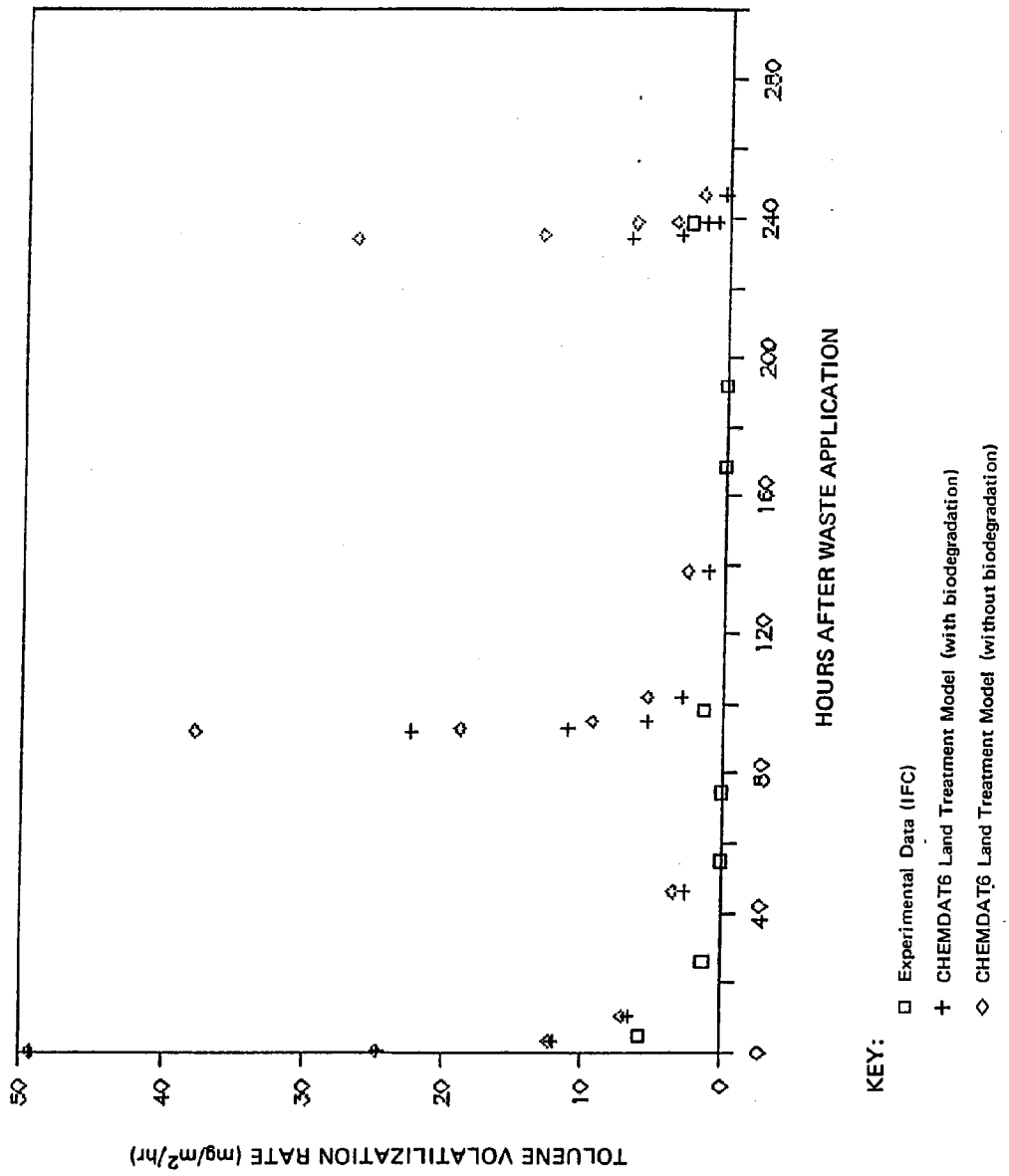


Figure 3-6. VOLATILIZATION OF TOLUENE FROM LANDFARM SURFACE: COMPARISON OF EXPERIMENTAL RESULTS TO CHEMDAT6 LAND TREATMENT MODEL PREDICTIONS

Table 3-17. COMPARISON OF EXPERIMENTAL RESULTS FOR VOLATILE COMPOUND EMISSION RATES WITH MODEL PREDICTIONS AT A TIME SHORTLY AFTER WASTE APPLICATION AND AT A TIME LONG AFTER WASTE APPLICATION

Compound	Values of Volatilization Rate (mg/m^2-h) After Waste Application			
	Experimental Value[1]	CHEMDAT6 Land Treatment Model with Biodegradation[2]	CHEMDAT6 Land Treatment Model without Biodegradation[2]	Thibodeaux-Hwang Model
4.9 Hours After Waste Application				
n-Hexane	5.56	18.72	18.87	44.47
2-Methylpentane	7.41	23.67	23.67	56.00
3-Methylpentane	3.70	12.85	12.94	30.85
Benzene	1.79	3.11	3.13	17.91
Toluene	5.94	10.91	11.16	57.07
Xylenes (Total)	3.65	8.87	8.98	51.50
Ethylbenzene	1.03	1.46	1.48	7.96
Naphthalene	0.00	0.10	0.10	1.16
74.5 Hours After Waste Application				
n-Hexane	0.43	4.43	4.84	0.00[3]
2-Methylpentane	0.65	6.07	6.07	0.00[3]
3-Methylpentane	0.43	3.05	3.32	0.00[3]
Benzene	0.04	0.75	0.80	0.00[3]
Toluene	0.11	2.18	2.86	0.00[3]
Xylenes (Total)	0.24	1.98	2.31	14.06
Ethylbenzene	0.05	0.33	0.38	2.18
Naphthalene	0.00	0.02	0.03	0.32

1 Obtained with IFC.

2 Values interpolated from model output results

2 T-H model predicts n-hexane, 2-methylpentane, 3-methylpentane, benzene, and toluene to be completely volatilized before 74.5 hours.

3.9 AMBIENT LEVELS OF VOLATILE CONSTITUENTS

Appendix M provides laboratory reports for the ambient air samples collected in and around the test landfarm on the day of waste application and immediately after the first tilling. Only trace levels (1-2 ppbv) of several volatile hydrocarbon constituents were found downwind of the landfarm on the day waste was applied. All other samples, including those collected in the breathing zone of WCC personnel working within the test plot itself, were below the method detection limit (1.0 ppbv) reported by RMAL. These results suggest that refinery HWLT operations do not contribute significantly to ambient levels of air toxics. However, this conclusion is very preliminary and should be confirmed with a more rigorous sampling and analytical program.

4.0
CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

The following conclusions are made based on experimental results presented in Section 3.0:

- Volatilization of TNMHC and specific waste constituents followed the expected pattern based on previous investigations of refinery landfarm emissions. From low background levels prior to waste application, emissions increased significantly when waste was first applied by surface spreading followed immediately by tilling. Emissions then declined with time and subsequently increased upon tilling of the test plot. Individual data points collected with the IFC and the WTD both showed that instantaneous emission rate measurements are sensitive to changes in the temperature of surface soils throughout the day. The one round of sampling conducted after dark also showed reduced TNMHC emissions compared to levels that would be expected from daytime measurements.

- A comparison of waste loadings to cumulative mass emissions measured with the IFC and residual constituent concentrations in the soil at the end of the test can be used to assess the environmental fate of trace hydrocarbons in this experiment. Volatilization and biodegradation/experimental error each accounted for 30-40 percent of the C_6-aliphatics applied to the test plot. Benzene mass emissions were 17 percent of the applied

load, while volatilization of the other monoaromatics evaluated was less than 10 percent. Biodegradation/experimental error was conservatively estimated to account for 35-60 percent of the monoaromatics contained in the original waste application. Naphthalene was apparently neither degraded nor volatilized during the 10 days of the field program.

- Under the conditions of this experiment, the CHEMDAT6 land treatment model was found to be a reasonably accurate predictor of emission rates for volatile waste constituents immediately after sludge application and tilling. However, CHEMDAT6 overpredicted emissions at longer time intervals and thus tended to overestimate cumulative mass emissions during the experiment. Inclusion of the biodegradation coefficients provided with CHEMDAT6 had little effect on predicted emission rates over the 10 days of this experiment. Since the field data suggest that biodegradation was an important fate pathway for hydrocarbons in this test, the discrepancy between model and field results over longer time intervals suggests that additional effort is needed to accurately estimate biological decay coefficients for use with the this model.

- The Thibodeaux-Hwang model consistently and significantly overestimated volatile emissions during all phases of the experiment. As the field data indicate biodegradation to be an important fate process for volatiles in refinery landfarms, even over periods as short as this experiment, the lack of a biological decay term in the Thibodeaux-Hwang model must be regarded as a serious deficiency.

- As configured for this experiment, the WTD appeared to offer no advantage over the IFC for measurement of organics volatilization from soil surfaces. Comparative TNMHC emissions data showed that

results from the WTD were more variable and of consistently greater magnitude than mass flux rates determined with the IFC at the same sampling stations. These differences were due primarily to the much larger air flow rate passed through the WTD and the inability of the field analytical procedure used for TNMHC gas measurements to accurately quantify small concentration changes (often less than 0.5 ppmv as hexane) observed across the WTD. High air flow rates also precluded measurement of organic constituent emissions with the WTD. In addition, the WTD proved to be an unwieldy and inefficient instrument under field conditions. Substantial design changes should be made to the WTD if it is to be used again in a field study to monitor low-level hydrocarbon emissions from refinery landfarms (see Section 4.2).

- Ambient air samples collected around the landfarm on the day of sludge application and on the first day of tilling contained only trace (1-2 ppbv) concentrations for several volatile constituents in one downwind sample. All other samples, including those collected in the breathing zone of WCC personnel working in the test plot, showed non-detectable levels of the organic compounds evaluated for this study. However, it should be noted that these findings are the result of only a very preliminary sampling program and therefore should be supported by data from a more extensive monitoring network around an active refinery HWLT unit.

4.2 RECOMMENDATIONS

The following recommendations are offered for future studies of refinery landfarm emissions:

- If the WTD is to be used again in a similar study, it could be improved by several design changes. To more effectively reduce hydrocarbon levels in the upstream samples, the depth of the

carbon filter should be increased to provide more contact time with the inlet air stream. In addition, the blower intake should be raised several feet above the soil surface to take advantage of dilution provided in the natural environment. Finally, the WTD should be re-designed to include handles and light-weight structural support that would make it easier for operators to carry the instrument around an operating landfarm.

- The WTD is designed to simulate the effect of typical wind conditions on emissions of volatile organic compounds from the soil surface. It is intended to avoid some of the features of the IFC that could introduce measurement bias, such as artificial heating of the enclosed soil surface and accumulation of moisture and volatile hydrocarbons underneath the chamber dome. However, the practical utility of the WTD as a field device is limited by the ability of the supporting analytical methods to accurately quantify very small changes in TNMHC levels as air is passed over the enclosed surface area. For this reason, serious consideration should be given in future studies with the WTD to the use of sampling and analytical procedures with lower TNMHC detection limits than could be attained in this experiment.

  As an example of an alternative approach, McElroy et al. (1986), Dayton et al. (1986), and McAllister et al. (1986) have all reported on the use of 6.0 L stainless steel canisters (such as those employed in this study for measurement of individual organic compounds) to collect samples of ambient air for analysis of TNMHC. The canisters were transported to a remote laboratory and analyzed using a cryogenic preconcentration-direct FID method similar to that used in this study. Gas sample volumes were larger, however, generally on the order of 1.5-2.0 L, as opposed to the 25-50 mL gas volumes used here. Using this improved procedure, accurate TNMHC quantification has been reported at

concentrations at least an order of magnitude lower than those achieved in the field laboratory established by WCC for this project.

- Published documentation for the CHEMDAT6 land treatment model (EPA 1987a) should be revised to provide more information (including references) on the volatile organic biodegradation time constants used in the spreadsheet program. In addition, the spreadsheet should be modified to allow the user to incorporate site-specific biodegradation constants if available.

- TNMHC emissions data from this study can be used to make a first estimate of spatial variability within an HWLT unit. This information should be used in conjunction with statistical procedures provided by EPA (1986c) to select the number of sampling locations needed to obtain representative estimates of average emission rates from a landfarm test plot.

- Additional research should be conducted to evaluate and perhaps modify EPA Method 8240 for the analysis of complex oily wastes. In particular, the effect of the waste:methanol extraction ratio on quantification of volatile aromatic and aliphatic hydrocarbons should be investigated further.

5.0
REFERENCES

American Petroleum Institute. 1983. Land Treatment Practices in the Petroleum Industry. Washington, DC.

American Petroleum Institute. 1984. The Land Treatability of Appendix VIII Constituents Present in Petroleum Industry Wastes. API Publication No. 4379. Washington, DC.

American Petroleum Institute. 1987. Land Treatability of Appendix VIII Constituents Present in Petroleum Refinery Wastes: Laboratory and Modeling Studies. API Publication No. 4455. Washington, DC.

American Petroleum Institute. Undated. Land Treatment: Safe and Efficient Disposal of Petroleum Waste. Washington, DC.

Bossert, I., W.M. Kachel, and R. Bartha. 1984. Fate of Hydrocarbons During Oily Sludge Disposal in Soil. Applied and Environmental Microbiology. 47:763-767.

Brown, K.W., G.B. Evans, Jr., and B.D. Frentrup. 1983. Hazardous Waste Land Treatment. Butterworth Publishers. Boston.

Chevron Corporation. 1987. Summary Report: 1986 Landfarm Simulator Program. Richmond, CA

Crank, J. 1970. The Mathematics of Diffusion, Oxford University Press, London.

Dayton, D.P., et al. 1986. An Air Sampling System for Measurement of Ambient Organic Compounds. Proceedings of the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants. APCA Publication VIP-7.

DuPont, R.R. 1986. Evaluation of Air Emission Release Rate Model Predictions of Hazardous Organics from Land Treatment Facilities. Environmental Progress. 5:197-206.

DuPont, R.R. 1987. Measurement of Volatile Hazardous Organic Emissions from Land Treatment Facilities. Journal of the Air Pollution Control Association. 37:168-176.

Eklund, B.M., W.D. Balfour, and C.E. Schmidt. 1985. Measurement of Fugitive Volatile Organic Emission Rates. Environmental Progress 4:199-202.

Ehrenfeld, J.R., et al. 1986. Controlling Volatile Emissions at Hazardous Waste Sites. Noyes Publications. Park Ridge, N.J.

Environmental Protection Agency. 1981. Factors Influencing the Biodegradation of API Separator Sludges Applied to Soils in Land Disposal of Hazardous Wastes. Proceedings of 7th Annual Research Conference. EPA-600/9-81-026.

Environmental Protection Agency. 1983a. Preparation of Soil Sampling Protocols, Techniques, and Strategies. EPA-600/4-83-020.

Environmental Protection Agency. 1983b. Land Treatability of Refinery and Petrochemical Sludges. EPA-600/2-83-074.

Environmental Protection Agency. 1983c. Land Treatment Field Studies - Volume 1. Petroleum Wastewater Pond Bottoms. EPA-600/2-83-057a.

Environmental Protection Agency. 1983d. Land Treatment Field Studies - Volume 2. Oily Waste from a Petroleum Refinery. EPA-600/2-83-057b.

Environmental Protection Agency. 1984a. Laboratory Assessment of Potential Hydrocarbon Emissions from Land Treatment of Refinery Oily Sludges. EPA-600/2-84-108.

Environmental Protection Agency. 1984b. Evaluation and Selection of Models for Estimating Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities. EPA-450/3-84-020.

Environmental Protection Agency. 1984c. Evaluation of Emission Controls for Hazardous Waste Treatment, Storage, and Disposal Facilities. EPA-450/3-84-017.

Environmental Protection Agency. 1984d. Annotated Literature References on Land Treatment of Hazardous Waste. EPA-600/52-84-098.

Environmental Protection Agency. 1984e. Compendium of Methods for the Determination of Toxic Organic Compounds in Air. EPA-600/4-84-041. (Updated periodically.)

Environmental Protection Agency. 1985a. Evaluation of Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities. EPA-600/2-85-057.

Environmental Protection Agency. 1985b. Land Treatment of Petroleum Refinery Sludges. EPA-600/2-84-193.

Environmental Protection Agency. 1985c. Movement of Contaminants from Oily Wastes During Land Treatment. EPA-600/D-86-005.

Environmental Protection Agency. 1985d. Hazardous Waste Ranking - Assessment of Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities. EPA-450/3-85-006.

Environmental Protection Agency. 1985e. Land Treatment of an Oily Waste-Degradation, Immobilization, and Bioaccumulation. EPA-600/2-85-009.

Environmental Protection Agency. 1986a. Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations. EPA-530/SW-86-032.

Environmental Protection Agency. 1986b. Background Information Document - Hazardous Waste Treatment, Storage, and Disposal Facilities: Land Treatment. Draft Report. Prepared by Office of Air Quality Planning and Standards.

Environmental Protection Agency. 1986c. Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber: User's Guide. EPA-600/8-86-008.

Environmental Protection Agency. 1986d. Evaluation of Volatilization of Hazardous Constituents at Hazardous Waste Land Treatment Sites. EPA-600/2-86-071.

Environmental Protection Agency. 1986e. Preliminary Assessment of Hazardous Waste Pretreatment as an Air Pollution Control Technique. EPA-600/2-86-028.

Environmental Protection Agency. 1986f. Field Evaluation of Hazardous Waste Pretreatment as an Air Pollution Control Technique. EPA-600/2-86-048.

Environmental Protection Agency. 1986g. Test Methods for Evaluating Solid Waste. Third Edition. SW-846.

Environmental Protection Agency. 1987a. Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) - Air Emission Models. EPA-450/3-87-026.

Environmental Protection Agency. 1987b. Waste-Soil Treatability Studies for Four Complex Industrial Wastes: Methodologies and Results. EPA-600/S6-86-003.

Environmental Protection Agency. 1987c. Field Assessment of Air Emissions and Their Control at a Refinery Land Treatment Facility. Volume 1. EPA-600/2-87-086a.

Environmental Protection Agency. 1987d. Field Assessment of Air Emissions and Their Control at a Refinery Land Treatment Facility. Volume 2. EPA-600/2-87-086b.

Environmental Protection Agency. 1987e. Hazardous Waste Treatment, Storage, and Disposal Facilities. Assessment of Air Emissions from a Laboratory Land Treatment Facility. Volumes I and III. EMB Report 87-HWS-6.

Ettre, L.S., B. Kolb, and S.G. Hurt. 1983. Techniques of Headspace Gas Chromatography. American Laboratory. October. pp. 76-83.

Farmer, W.J., K. Igue, and W. F. Spencer, 1973. Effects of Bulk Density on the Diffusion and Volatilization of Dieldrin from Soil. J. Envir. Qual. 2:107-118.

Fuller, W.H., and A.W. Warrick. 1985. Soils in Waste Treatment and Utilization - Volume 1. Land Treatment. CRC Press, Inc. Boca Raton, FL.

Grove, G.W. 1978. Use Land Farming for Oily Waste Disposal. Hydrocarbon Processing. May, 1978. pp. 138-140.

Hornick, S.B., R.H. Fisher, and P.A. Paolini. 1983. Petroleum Wastes. Land Treatment of Hazardous Wastes. J.F. Parr, P.B. Marsh, and J.M. Kla, eds. Noyes Data Corporation. Park Ridge, NJ.

Huddleston, R.L., C.A. Bleckmann, and J.R. Wolfe. 1986. Land Treatment Biological Degradation Processes. Land Treatment: A Hazardous Waste Management Alternative. R.C. Loehr and J.F. Malina, Jr., eds. Water Resources Symposium Number Thirteen. University of Texas. Austin, TX.

Hwang, S.T. 1985. Model Prediction of Volatile Emissions. Environmental Progress. 4:141-144.

Kaufman, D.D. 1983. Fate of Toxic Organic Compounds in Land-Applied Wastes. Land Treatment of Hazardous Wastes. J.F. Parr, P.B. Marsh, and J.M. Kla, eds. Noyes Data Corporation. Park Ridge, NJ.

Kincannon, D.F., and Y.S. Lin. 1985. Microbial Degradation of Hazardous Wastes by Land Treatment. Proceedings of the 40th Industrial Waste Conference, May 14, 15, 16, 1985. Purdue University. West Lafayette, Indiana. Butterworth Publishers. Boston.

Knowlton, H.E., and J.E. Rucker. 1979. Landfarming Shows Promise for Refinery Waste Disposal. Oil and Gas Journal. May 14, 1979. pp. 108-116.

Kolb, B., and P. Pospisil. 1977. A Gas Chromatographic Assay for Quantitative Analysis of Volatiles in Solid Materials by Discontinuous Gas Extraction. Chromatographia. 10:705-711.

Lindstrom, F.T., and W.T. Piver. 1985. Mathematical Model for the Transport and Fate of Organic Chemicals in Unsaturated/Saturated Soils. Envir. Health Perspectives. 60:11-28.

Loehr, R.C. 1986. Land Treatment as a Waste Management Technology: An Overview. Land Treatment: A Hazardous Waste Management Alternative. R.C. Loehr and J.F. Malina, Jr., eds. Water Resources Symposium Number Thirteen. University of Texas. Austin, TX.

Martin, J.P., R.C. Sims, and J. Matthews. 1986. Review and Evaluation of Current Design and Management Practices for Land Treatment Units Receiving Petroleum Wastes. Haz. Wastes and Haz. Materials. 3:261-280.

McAllister, R.A., et al. 1986. 1984 and 1985 Nonmethane Organic Compound Sampling and Analysis Program. Proceedings of the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants. APCA Publication VIP-7.

McElroy, F.F., et al. 1986. Cryogenic Preconcentration - Direct FID Method for Measurement of Ambient NMOC: Refinement and Comparison with GC Speciation. Journal of the Air Pollution Control Association. 36:710-714.

Minear, R.A., et al. 1981. Atmospheric Hydrocarbon Emissions from Land Treatment of Refinery Oil Wastes. American Petroleum Institute. Report No. DCN 81-219-060-06. Washington, D.C.

Morrill, L.G., B.C. Mahilum, and S.H. Mohiuddin. 1982. Organic Compounds in Soils: Sorption, Degradation, and Persistence. Ann Arbor Science Publishers, Inc. Ann Arbor, MI.

Myers, J.D., and R.L. Huddleston. 1980. Treatment of Oily Refinery Wastes by Landfarming. Proceedings of the 34th Industrial Waste Conference, May 8, 9, 10, 1979. Purdue University. West Lafayette, Indiana. Ann Arbor Science Publishers, Inc. Ann Arbor, MI.

Norris, D.J. 1981. Landspreading of Oily and Biological Sludges in Canada. Proceedings of the 35th Industrial Waste Conference, May 13, 14, and 15, 1981. Purdue University. West Lafayette, Indiana. Ann Arbor Science Publishers, Inc. Ann Arbor, MI.

Oliver, K.D., J.D. Pleil, and W.A. McClenny. 1986. Sample Integrity of Trace Level Volatile Organic Compounds for Ambient Air Stored in SUMMA Polished Canisters. Atmospheric Environment. 20:1403-1411.

Overcash, M.R., and D. Pal. 1979. Design of Land Treatment Systems for Industrial Wastes - Theory and Practice. Ann Arbor Science Publishers, Inc. Ann Arbor, MI.

Perry, R.H., and C.H. Chilton, eds. 1973. Chemical Engineer's Handbook. Fifth Edition. McGraw-Hill. New York.

Pfeffer, F.M., G.M. Myers, R.C. Loehr, and D.F. Kincannon. 1985. Small-Scale Evaluation of Land Treatment of an Oily Hazardous Waste. Proceedings of the 39th Industrial Waste Conference, May 8, 9, 10, 1984. Purdue University. West Lafayette, Indiana. Butterworth Publishers. Boston.

Pransnitz, J.M. 1969. Molecular Thermodynamics of Fluid-Phase Equilibrium. Prentice-Hall. Englewood Cliffs, NJ.

Radian Corporation. 1986. Draft Final Report: Assessment of Air Emissions from a Laboratory Land Treatment Facility. Prepared for EPA Under Contract No. 68-02-4338.

Raymond, R.L., J.O. Hudson, and V.W. Jamison. 1976. Oil Degradation in Soil. Applied and Environmental Microbiology. 31:522-535.

Reid, R.C., J.M. Pransnitz, and T.K. Sherwood. 1977. The Properties of Gases and Liquids. Third Edition. Mc-Graw Hill. New York.

Rhoderick, G.C., and W.L. Zielinski, Jr. 1988. Preparation of Accurate Multicomponent Gas Standards of Volatile Toxic Organic Compounds in the Low-Parts-per-Billion Range. Analytical Chemistry. 60:2454-2460.

Ryan, J.F. 1986 The Land Treatability of Appendix VIII Organics Present in Petroleum Industry Wastes. Land Treatment: A Hazardous Waste Management Alternative. R.C. Loehr and J.F. Malina, eds. Water Resources Symposium Number Thirteen. University of Texas. Austin, TX.

Ryan, J.F., M.L. Hanson, and R.C. Loehr. 1986. Land Treatment Practices in the Petroleum Industry. Land Treatment: A Hazardous Waste Management Alternative. R.C. Loehr and J.F. Malina, Jr., eds. Water Resources Symposium Number Thirteen. University of Texas. Austin, TX.

Short, Thomas E. 1986. Modeling of Processes in the Unsaturated Zone. Land Treatment: A Hazardous Waste Management Alternative. R.C. Loehr and J.F. Malina, Jr., eds. Water Resources Symposium Number Thirteen. University of Texas. Austin, TX.

Sprehe, T.G., L.E. Streebin, J.M. Robertson, and P.T. Bowen. 1985. Process Considerations in Land Treatment of Refinery Sludges. Proceedings of the 40th Industrial Waste Conference, May 14, 15, 16, 1985. Purdue University. West Lafayette, Indiana. Butterworth Publishers. Boston.

Thibodeaux, L.J., and S.T. Hwang. 1982. Landfarming of Petroleum Wastes-Modeling the Air Emission Problem. Environmental Progress. 1:42-46.

Weldon, R.O. 1979. Biodisposal Farming of Refinery Oily Wastes. Proceedings 1979 Oil Spill Conference (Prevention, Behavior, Control, Cleanup). API Publication No. 4308. Washington, DC.

Wetherold, R.G., and W.D. Balfour. 1986. Volatile Emissions from Land Treatment Systems. Land Treatment: A Hazardous Waste Management Alternative. R.C. Loehr and J.F. Malina, Jr., eds. Water Resources Symposium Number Thirteen. University of Texas. Austin, TX.

Wilke, C.R., and P. Chang. 1955. Correlations of Diffusion Coefficients in Dilute Solutions. AIChE J. 1:264-270.

Order No. 841-45000