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LANDFARM AIR EMISSIONS

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LANDFARM AIR EMISSIONS

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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-ft² 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

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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.

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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/ft³ 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)

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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.

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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

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

Compound	Applied To Test Plot (kg)	Cumulative Emissions ¹		Remaining in Soil ²		Biodegraded/ Experimental Error ¹	
		(kg)	Pct. of Applied	(kg)	Pct. of Applied	(kg)	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

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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 ft². See Table 3-8 for soil constituent concentrations at conclusion of test (September 24, 1987).

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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.

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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

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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 HWT 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 HWT facility.

1.1 HWT PRACTICES IN THE PETROLEUM REFINING INDUSTRY

A number of excellent review articles are available which discuss HWT 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 HWT 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

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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.

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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

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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 ft³ (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.

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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 HWT 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

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(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 ft² 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

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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 HWT 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 HWT 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

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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,

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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:

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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.

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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.

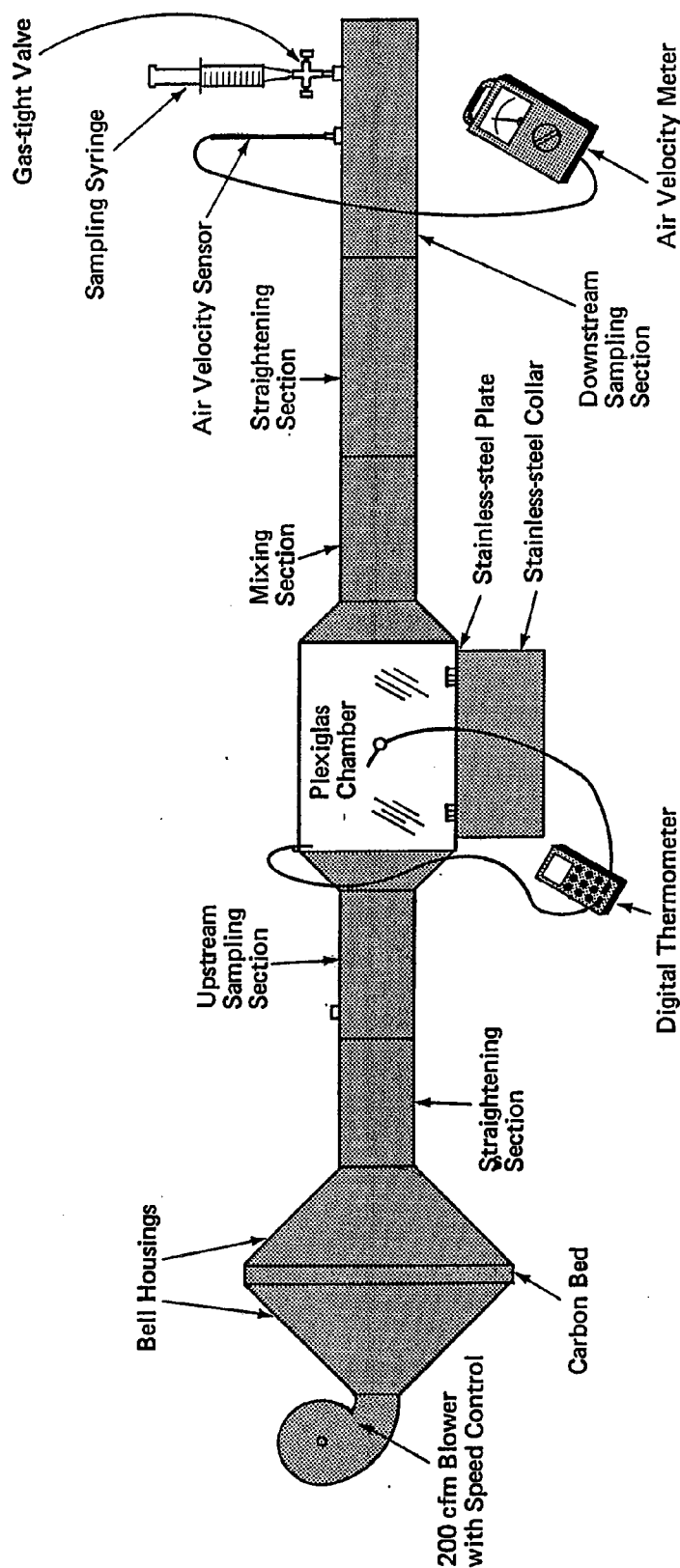


Figure 2-1. SCHEMATIC DIAGRAM OF WIND TUNNEL DEVICE (WTD)

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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 in³.

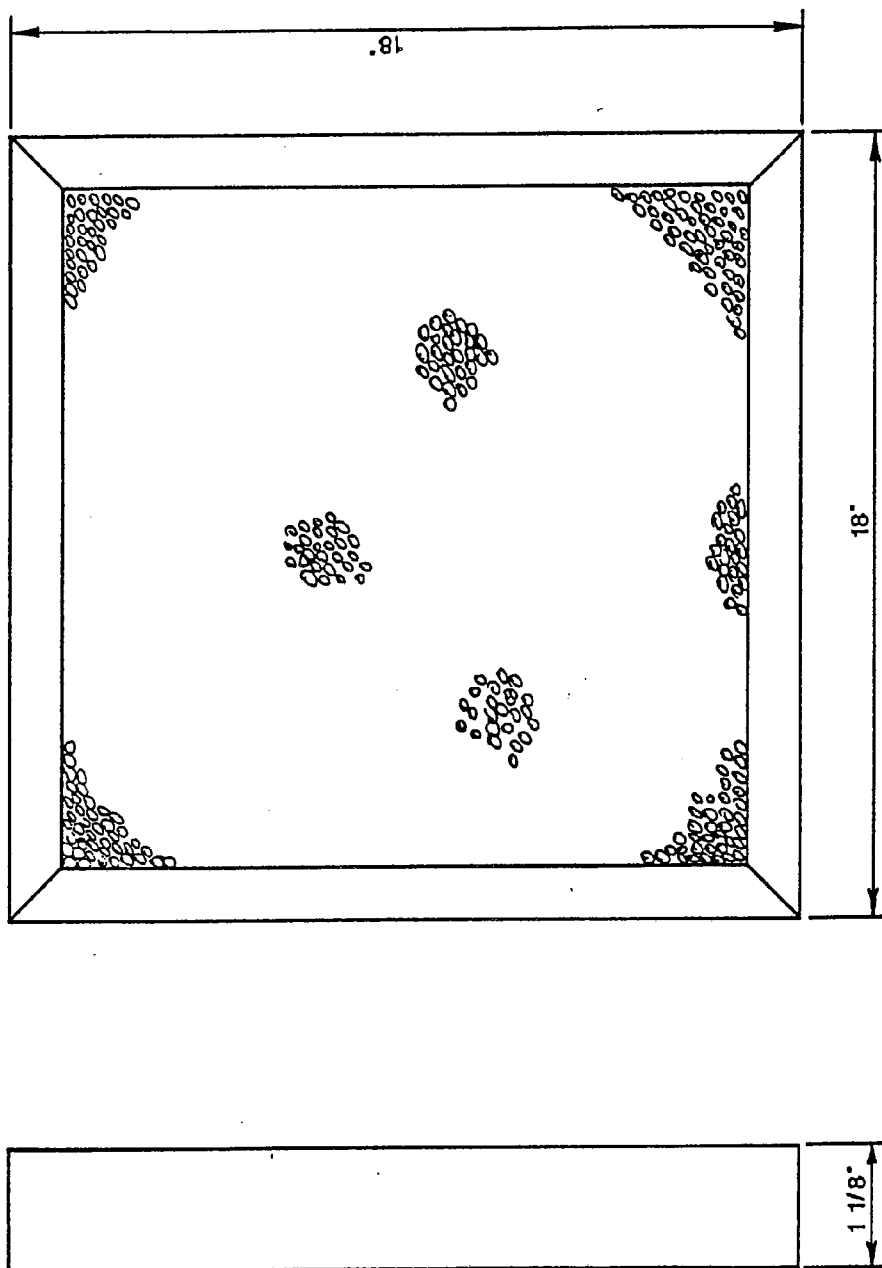


Figure 2-2. WIND TUNNEL DEVICE:
CARBON FILTER

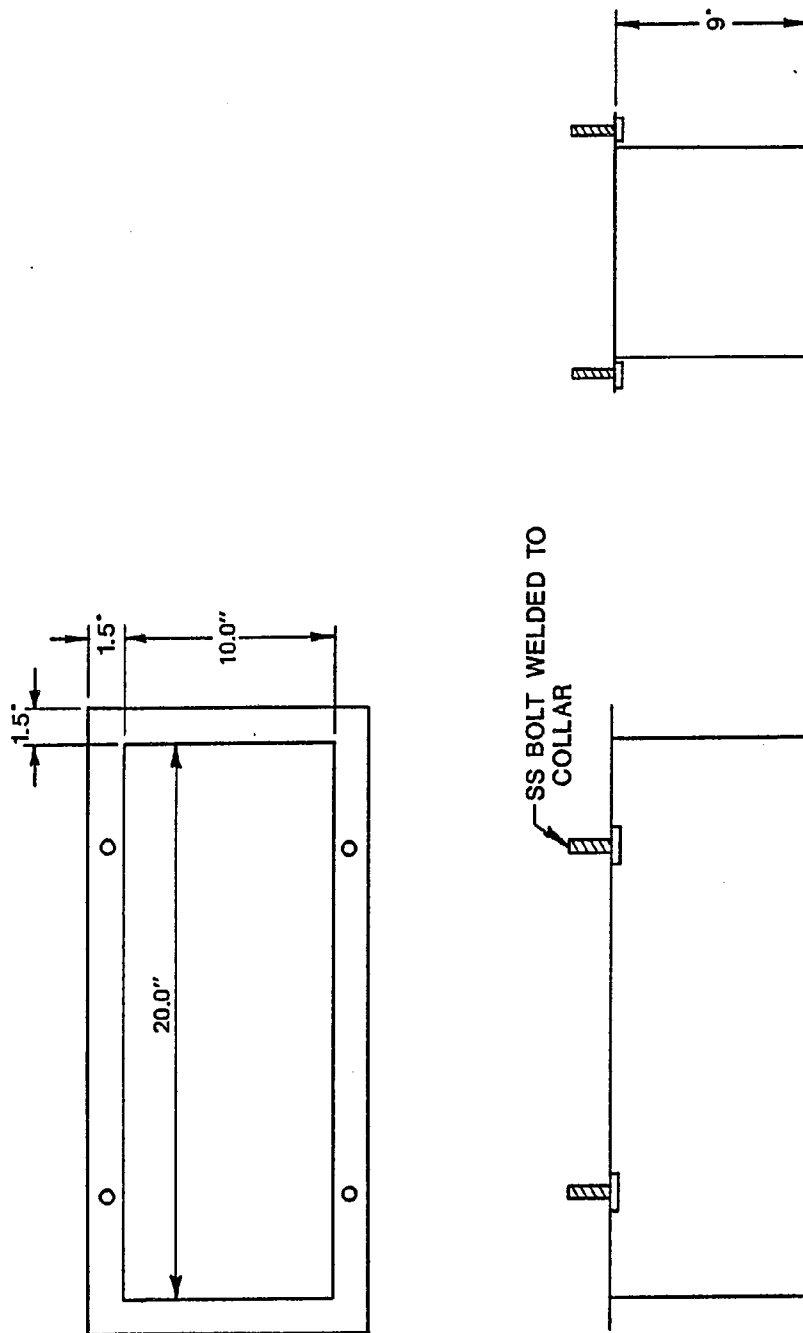
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2.1.1.6 Sampling Collar. The sampling collars were rectangular stainless steel boxes, open on the top and bottom and inserted into the soil at approximately 20 fixed locations across the test plot. As shown in Figure 2-3, each collar was designed to capture emissions from a defined surface area of 200 in². 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.

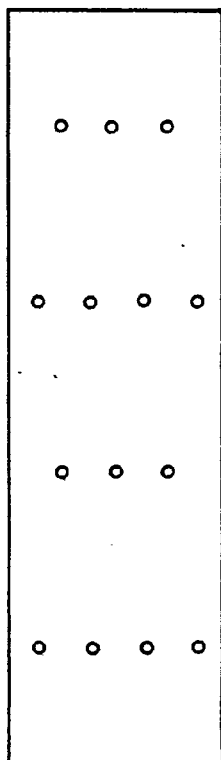
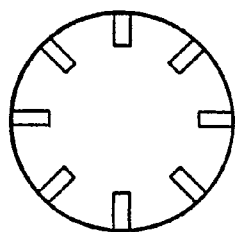
Before going to the field, a series of calibration runs was performed in the laboratory to test the air velocity measurement equipment and the WTD air speed control system. The carbon filter was removed and a standard gas mixture containing isobutylene was introduced through a mass flow controller at 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



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



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

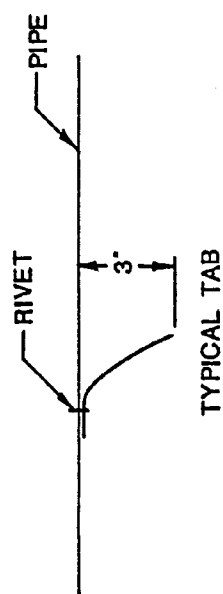


Figure 2-4. WIND TUNNEL DEVICE:
MIXING SECTION

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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

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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 ft³/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.

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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

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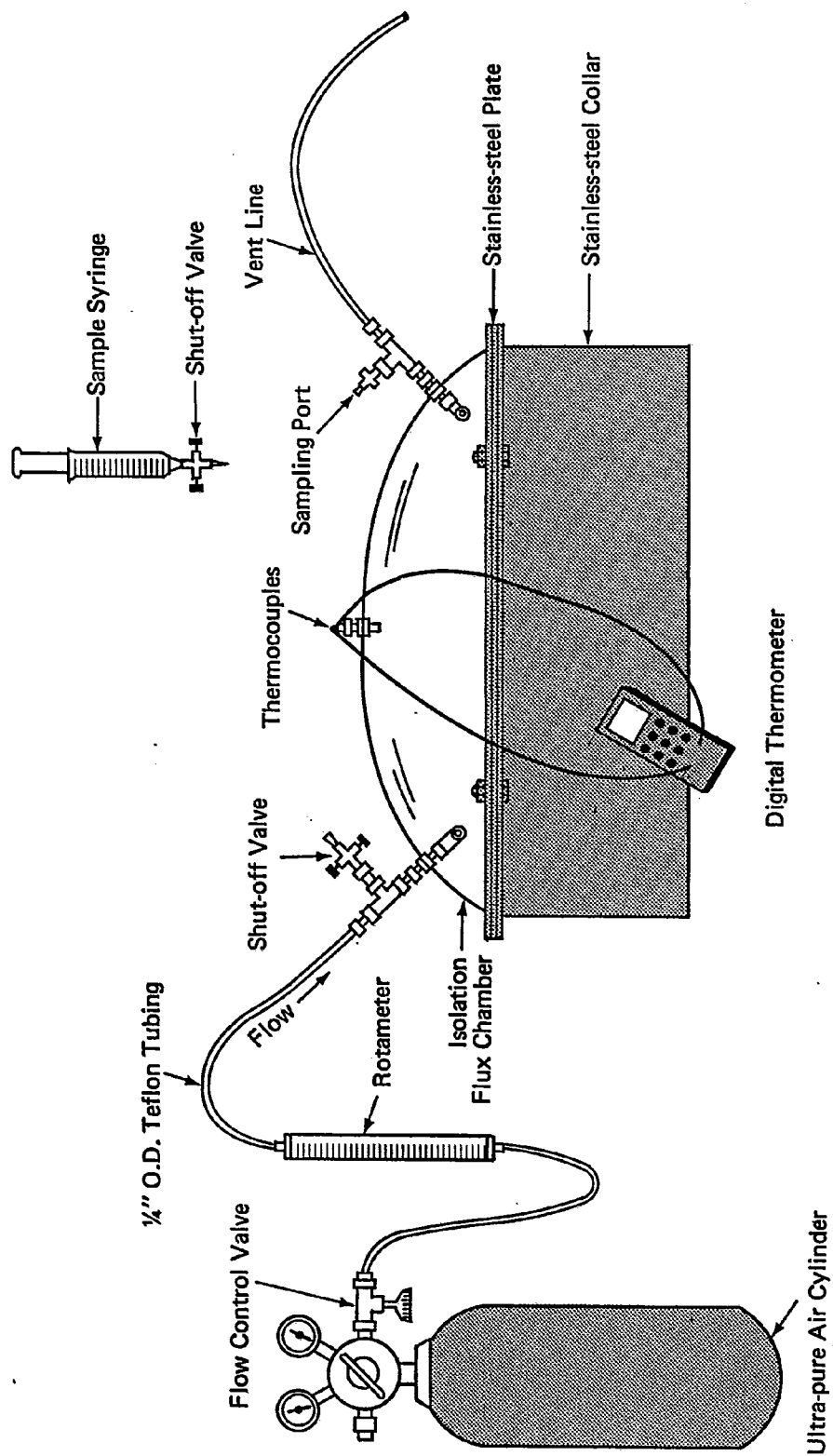


Figure 2-5. SCHEMATIC DIAGRAM OF ISOLATION FLUX CHAMBER(IFC)

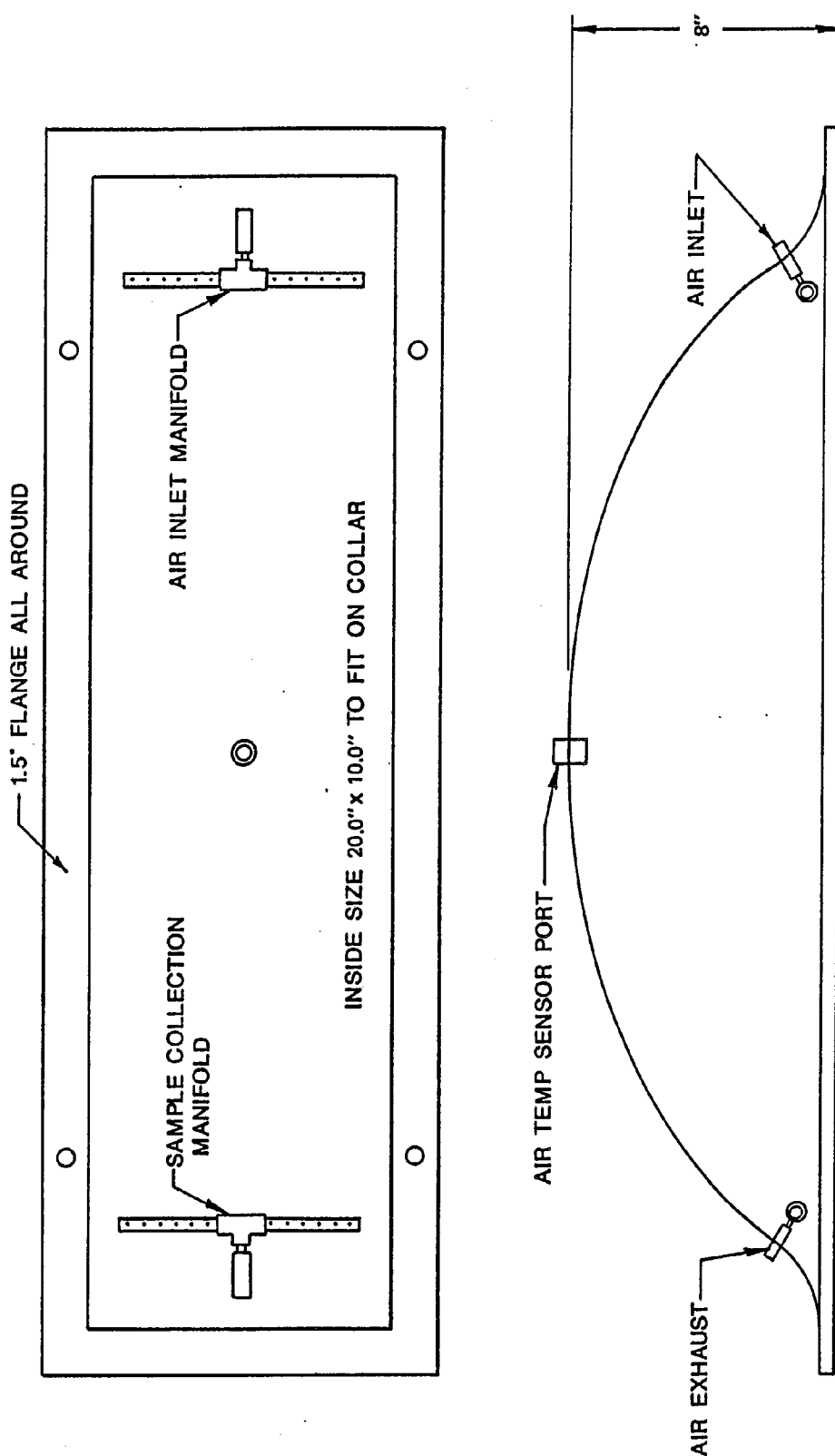


Figure 2-6. CONSTRUCTION DETAILS FOR ISOLATION FLUX CHAMBER DOME

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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 ($\text{mg}/\text{m}^2/\text{hr}$)
- 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 ($\mu\text{g}/\mu\text{mol}$)
- 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 ($1000 \mu\text{g}/\text{mg}$)

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.

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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 $\tau = 3.7$ 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

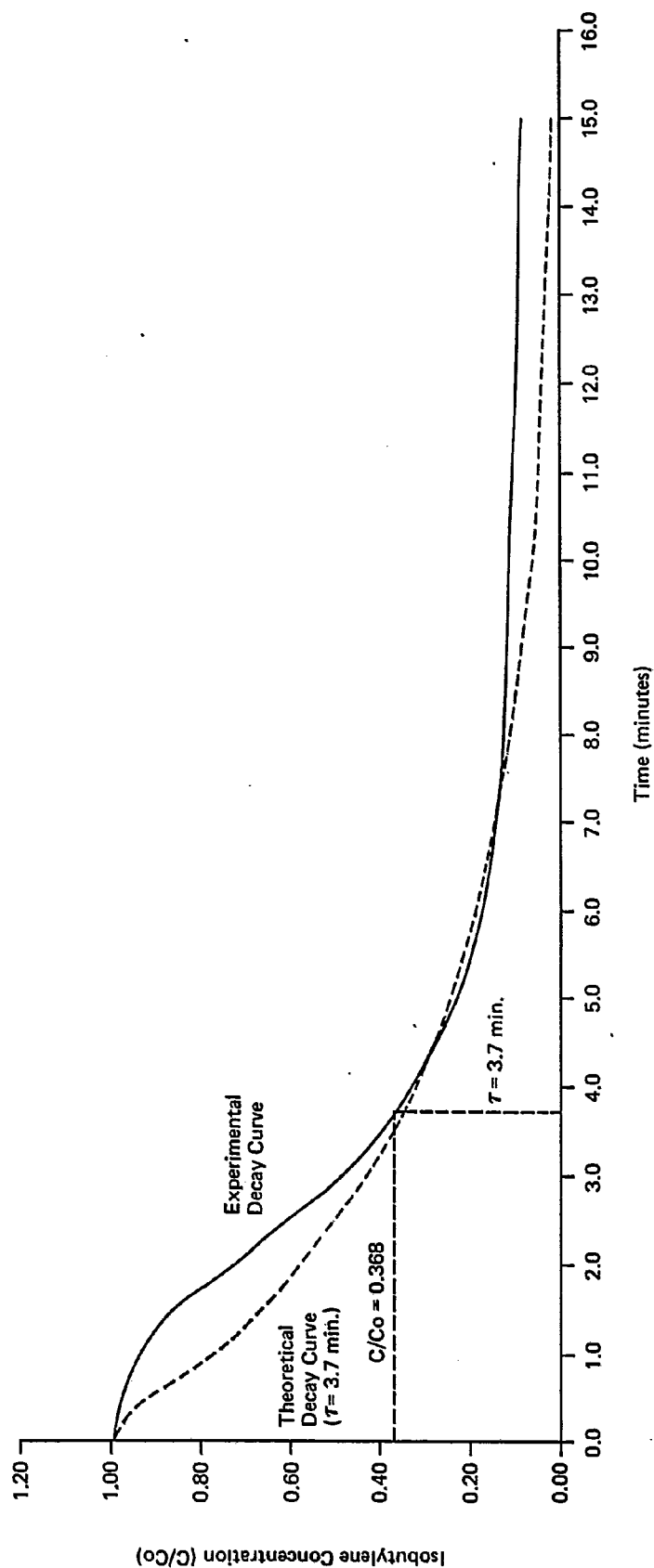


Figure 2-7. DECAY CURVE FOR ISOBUTYLENE IN ISOLATION FLUX CHAMBER

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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 $\mu\text{g-C/m}^2/\text{sec}$) 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.

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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

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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 ft². 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.