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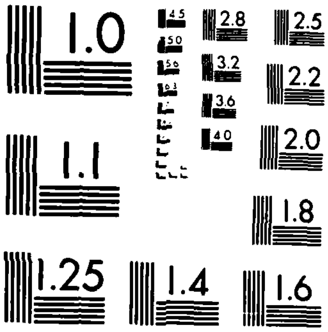

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INVESTIGATION OF THE HAZARDS POSED BY CHEMICAL VAPORS RELEASED IN MARINE OPERATIONS — PHASE II

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FINAL REPORT

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16. Abstract
The flammability and toxicity hazards associated with (1) chemical vapors emitted from tankers and barges during product loading, and (2) man entry into empty tanks was studied. Analytical models have been developed to describe (1) the downwind concentration contours of heavier-than-air product vapors emitted during tank loading, and (2) the vapor concentrations in an empty tank during ventilation and evaporation of residual chemicals. The analytical models have been validated through an extensive series of field tests on tankers and barges in marine terminals. For the plume model validation, 103 independent tests covering numerous products, loading rates, vent geometries, tank geometries, and atmospheric conditions were conducted. Source concentrations at the tank vent and downwind concentrations on the deck at man breathing height were measured for each test for both model validation and hazard assessment. Validation of the tank ventilation models was accomplished through 26 independent gas freeing tests. Tank gas concentrations were measured for a range of tanker and barge tank configurations, chemical products, blower flowrates, and residual cargo conditions. A hazardous chemical vapor handbook for marine tank vessels has been developed including a users manual which will allow Coast Guard specialists to integrate the analytical models into the USCG HACS system. Personal exposure and biological monitoring was also accomplished to provide a direct indication of occupational exposure. Over 200 exposure samples were obtained for various work activities including single and multiple event exposures during tank entry, tank gauging, and on-deck work activities. A pilot biological monitoring program was initiated where blood, breath, and urine samples were obtained concurrently with occupational exposure monitoring. A preliminary assessment of marine terminal occupational hazards is provided. A more comprehensive toxicological assessment of hazardous activities including additional biomonitoring and exposure data will be furnished in an addendum report.

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EXECUTIVE SUMMARY

Background

The term, "Marine Hazardous Chemical Worker" is used to encompass several diverse groups of workers whose marine-related work activities cause them to be exposed to potentially hazardous chemicals. These workers fall into four generic classes:

- Marine chemical transport workers (tankers and barges)
- Chemical terminal dock workers
- Offshore platform and service vessel workers
- U. S. Coast Guard personnel

Personnel in each of the four generic marine worker categories can be further subdivided into many specific work classes. For each of these worker subclasses, potential safety hazards from flammable and toxic substances in the work environment are inherent in job activities. Hazardous substances include vapors, gases, liquids, mists, and dust; and the sources of these substances may be encountered during both routine and nonroutine work situations. The exposure potential to these substances varies with work functions as do operational equipment and procedures. Thus, a simplified definition of hazardous sources, equipment and work practices for marine personnel is not possible. Furthermore, the work schedules do not follow the normal 8-hour day that is characteristic of other industries. Thus, worker exposures are difficult to interpret in terms of the usual OSHA/NIOSH threshold limit values.

With the realization of these complexities, the USCG is conducting research efforts to identify and characterize potentially hazardous safety and health situations in the marine work environment. The Coast Guard has formulated and is implementing a multi-element program which is summarized below.

Element No.	Project Title
1.	Investigation of the Hazards Posed by Chemical Vapors Released in Marine Operations - Phase I (Complete) - Reference 1.
2.	Investigation of the Hazards Posed by Chemical Vapors Released in Marine Operations - Phase II
3.	A Crew Exposure Study - Phase I (Complete) - Reference 2.
4.	A Crew Exposure Study - Phase II (Current)
5.	A Study to Improve the Health and Safety of the Marine Hazardous Chemical Worker (Current)

The emphasis in the first four program elements is on characterizing the work/exposure environment so that control methodology, be it engineering, administrative, or protective equipment, can be adequately considered in the fifth element.

This report describes the results of Phase II (Element 2) of the two-element USCG research project entitled "Investigation of the Hazards Posed by Chemical Vapors Released in Marine Operations."

Phase I Efforts

In Phase I, a background study was conducted to identify marine terminal work activities/operations that are potentially hazardous. This was accomplished through field studies, discussions with marine industry personnel and literature searches. The field studies included (1) the measurement of chemical vapor sources and work area concentrations, and

(2) the documentation of work activities in these areas such that a preliminary assessment of worker exposure could be undertaken. As a result of this background study, the following operations were identified as being potentially hazardous:

- Open venting of product vapors during tank loading,
- Washing and gas freeing of cargo tanks, and
- Product hose hookup and disconnect before and after product loading.

Specific work activities associated with these operations include:

- Cargo gauging during tank loading,
- Tank entry for cleaning or inspection,
- Various work activities on deck regions downwind of open vents during product loading, and
- Manual hose connecting (disconnecting) over open manifold drip trays.

The spatial and time dependent vapor concentration in the vapor plume downwind of a vent and in a tank during and after gas freeing are amenable to analytical modeling. Because of the large number of parameters affecting on-deck and in-tank concentration levels, the Phase I study included developing first generation analytical models to describe (1) the downwind dispersion and dilution of chemical vapor plume emissions during cargo loading and gas freeing, and (2) the in-tank vapor concentration environment during gas freeing with vapor regeneration. Concurrent with analytical model development, an experimental plan was developed which identified the methods and techniques for (1) acquiring vapor concentration and other supporting data for use in validating the analytical models, and (2) the direct measurement of occupational exposures through personnel monitoring.

Phase II Objectives

Based on the results of Phase I, the requirements for Phase II were identified. Phase II consists of five major task elements with Tasks I - IV identified in Phase I and Task V initiated during the conduct of Phase II.

- Task I - The objective of this task was to implement the experimental plan that had been designed in Phase I. Task I emphasized vapor dispersion and tank ventilation experimentation in support of model development as well as occupational exposure monitoring.

- Task II - The analytical models were evaluated and revised as indicated by the experimental data from Task I. Extension of these models to other chemical terminal operations was also accomplished.

- Task III - In this task, the data that had been collected was evaluated with respect to flammability and toxicity as they relate to analytical model predictions and occupational exposure monitoring.

- Task IV - The objective of this task was to develop a handbook that describes the analytical models and associated computer codes that can be used by the USCG Hazardous Materials Specialists to assess various aspects of tanker/terminal operations. The handbook was published in Reference 3, and the programs will be incorporated into the Coast Guard's Hazard Assessment Computer System (HACS).

- Task V - The objective of Task V was to initiate a pilot biological sampling study to determine the feasibility of collecting concomitant environmental and biological blood, breath, and urine data during novel work schedules associated with marine terminal operations.

This report contains the results of Tasks I, II, and IV as well as a preliminary interpretation of the initial biological monitoring tests and the occupational exposure data. Results of the remaining biological monitoring tests and an in-depth assessment of exposure data will be published in an addenda to this report.

Analytical Modeling and Experimental Validation

An analytical model for predicting the dispersion of chemical vapor plumes emitted from cargo tank vents during cargo loading and tank ventilation has been developed and experimentally validated. The model predicts the near-field (up to 100 m) downwind concentrations which depend on the following parameters:

- the vented gas flowrate,
- the vapor concentration in the vented gas stream,
- the height and diameter of the vent, and
- the ambient wind velocity, direction, and turbulence level.

Over one hundred separate tests were performed to provide model validation data for the chemical vapor concentration distribution downwind of the tank vents. These tests were performed during actual cargo loading operations on both tanker ships and barges, and during full-scale simulations of tank atmosphere venting. The tests covered the full range of conditions for vent gas concentrations, vent gas flowrate, vent height, and ambient wind velocity expected for shipboard operations.

Good agreement was found between plume model predictions and the experimental vapor concentration data for venting tests performed with vents ranging from 2 to 6 meters in height. Using the validated model, a parametric study was performed to evaluate the sensitivity of the downwind concentrations to model input parameters. The results of this study confirmed the importance of increased vent height in reducing chemical vapor concentration levels at breathing height downwind of tank vents. It also showed that even for increased vent heights to 6 m, deck concentrations on the order of 10 - 50 ppm can occur over some areas during moderate to low wind speeds.

Two tank ventilation models have been developed which describe the tank vapor concentration-time histories during gas freeing in the [illegible]esence of vapor regeneration from either pure product residues or post-w[illegible] residues of chemical and water solutions. Twenty-four full and model [illegible]e tests were conducted to collect gas freeing data for model valida[illegible] These tests involved 13 different products whose physical properties inc[illegible] a wide range of vapor pressures and aqueous solubilities. The full scale tests included tanks on parcel chemical carriers, product tankers and unmanned barges. Comparison of the model predictions and the experimental data indicate that the models adequately describe both evaporation processes and the concentration-time histories of the vapors that are discharged from the tank during dilution ventilation provided that certain key variables are known accurately and the tank does not have internal structure.

The response of the model with evaporation of chemical from solution was studied parametrically by systematically varying four key independent variables: the residual liquid thickness, initial chemical concentration in solution, the initial vapor phase concentration, and the blower flowrate. This parametric analysis indicated that the time to gas free to a given concentration is a strong function of residue thickness, solution concentration, and blower flowrate. The effects of residue thickness and liquid concentration were more dominant than blower flowrate. Initial tank vapor concentration had an insignificant effect on the time to gas free to a prescribed level because after the initial stages of purging of the vapor space, the evaporation process is controlled by the liquid phase resistance to mass transfer.

A similar parametric analysis was conducted on the model that incorporates evaporation of pure chemical residues. The results of this analysis confirmed the statistical sensitivity analysis that was performed in Phase I of this project. Blower flowrate and residue thickness have a strong effect on the gas freeing time, but initial vapor concentration has a negligible effect.

Model Programming and Use

To facilitate the use of the analytical models that were developed on this project, a step-by-step guide to the structure and usage of the three computer programs

- ONDEK - Atmospheric dispersion of cargo vapor that is discharged from a tank during product loading or gas freeing,
- TANKP - Gas freeing of a tank in the presence of evaporation of pure product residues,
- TANKM - Gas freeing of a tank in the presence of evaporation of residual chemical from a water solution,

is provided in Reference 3, "Hazardous Chemical Vapor Handbook for Tank Vessels - User's Manual." The manual is intended to provide both the USCG and marine industry personnel with analytical tools to evaluate potential hazards for actual and hypothetical operations. To this end, the manual will allow:

- The USCG to evaluate the effectiveness of proposed engineering controls and operational practices to minimize marine hazards.
- Industry to evaluate current company operational practices and engineering controls for their effect on worker exposure and flammability hazards.
- USCG and industry field personnel to assess the hazard potential before responding to routine inspections or emergencies.

Occupational Exposure Monitoring

Personnel exposures and biological monitoring was also accomplished to provide a direct indication of occupational exposures. Over 200 exposure samples were obtained for various work activities including single and multi-event exposures during tank entry, tank gauging, and on-deck work activities. Twenty-eight percent of all tank entries resulted in exposure concentrations that exceeded the TLV-STEL. In 5.5 percent of the entries, the 8-hour time-weighted average exposure exceeded the TLV-TWA. Tank entries on in-service vessels are relatively short term in duration and range from just a few minutes for a brief inspection to approximately one hour when manual cleaning and mucking are performed. In the majority of the entries (58 percent), the exposure concentration was less than one-half of the TLV-STEL or TLV-C. The highest exposure levels in excess of the TLV-STEL occur during open ullage gauging at top-off of fully loaded tanks.

Exposure to mixtures of chemical vapors does occur because multiple product vapors are emitted to the work environment during vessel loading. In the majority of the situations that were observed, individual component exposure levels were relatively low, and the mixture TLV based on additive effects was not exceeded. The reason for this behavior is due to the rapid dilution and dipersion of chemical vapors following discharge from tanks that are being loaded. The mixture TLV was exceeded in a limited number of instances in which there was one dominant vapor component, and this component of exposure resulted from open gauging or sampling of product tanks.

Concluding Remarks

In the course of this study (Phase I and Phase II), work activities have been identified where potentially significant exposure to chemical vapors can occur. These activities include:

- Open gauging during tank loading,
- Tank entry for cleaning or inspection,
- Work activities that are conducted in regions of the deck that are downwind of open vents during product loading, and
- Manual hose connecting (disconnecting) over open manifold drip trays that contain product accumulations.

The marine industry and responsible government regulatory agencies have recognized that occupational exposure to chemical vapors is inherent in these work activities. However, prior to the initiation of this project, a comprehensive definition of exposure levels for these work activities had not been published in the open literature.

In this project, one area of emphasis has included quantifying chemical exposures in the marine terminal work environment. This quantification has been accomplished through work area chemical vapor concentration measurements and through personal exposure monitoring in the field. Also, validated analytical models have been developed which allow a definition of work area vapor concentrations downwind of vents and in "gas freed" tanks for many more atmospheric and operational conditions than could practically be covered in field testing.

Extensive field measurements of the vapor discharge concentrations at the open ullage port and expansion trunk during product loading have shown that the concentrations range from levels of a hundred to a thousand ppm at the beginning of product loading into a clean tank to significantly higher values (10,000 to 100,000 ppm) at the start of loading into a dedicated, uncleaned tank. As product loading proceeds, vapors are liberated from the liquid surface and the vented concentrations can proceed through the flammable range to saturation as the tank is topped-off. Thus, the open gauging of tanks presents a potential for a significant exposure. Personal exposure data collected on this project during open gauging support this conclusion.

Vapor measurements downwind of the vent during product loading and analytical model predictions show that the concentrations dilute rapidly from the level at the vent. Therefore, when there is a flammable or higher concentration at the vent, the flammable boundaries may extend only a few meters downwind. This indicates that the potential for a flammable hazard is low. For low (ullage port level of $\sim$ 1 m) vent heights, the concentrations at man breathing height on the deck in regions from 5 to 20 meters downwind can be in the range from 10 to 500 ppm. Thus, for product chemical vapors with exposure limits in this concentration range, the potential for a significant occupational exposure exists. However, an effective method of minimizing this potential is to vent product vapors during loading from a height of at least 4 m which reduces both downwind concentration and the area on the deck where vapor concentration exists.

The necessity for proper monitoring of a tank atmosphere in preparation for man entry is also highlighted by the analytical and experimental results of this study. Proper monitoring includes measurement of oxygen content and product vapor concentration as it relates to both flammability and toxicity. Emphasis on gas freeing to safe occupational exposure levels will insure an additional margin of safety regarding flammability. Instrument measurements of tank vapor concentration during man entry and personal exposure monitoring have shown that accepted exposure limits are exceeded in some cases. The in-tank analytical models show that very small amounts of residual cargo (either pure chemical or soluble chemical/wash water solution) create enough vapor regeneration that the in-tank concentration can exceed a safe man entry level for extended periods of time. Thus, the models have shown the necessity of maintaining stringent cleaning requirements so that tank atmospheres do not present a potential toxicity hazard for man entry.

The personal exposure data obtained on this project have shown that both open gauging and tank entry as currently practiced in the industry do, on occasion, subject workers to exposures in excess of currently accepted TLV levels. Restricted gauging systems significantly reduce the exposure potential. The data also show that in the majority of cases, the measured levels are below currently accepted limits. Effective engineering and procedural methods of control to minimize the exposures that appear potentially hazardous have been identified.

Many of the regulations and operational practices in place on tankers are not followed or are circumvented because of conflicting requirements. For example, certain Subchapter O chemicals require vent heights of B/3, or 4 m, which the study results show to be effective in reducing exposure levels to vented vapors during tank loading. However, open gauging is permitted for these Subchapter O chemicals which results in vapor venting at the tank hatch and nullifies the effectiveness of the elevated vent. Also, the minimum vent height requirements which can reduce exposure hazards in tanker operations are not applied to barge operations. As a result, there is probably a higher level of occupational exposure during barge loading operations than for tankers.

Several factors are responsible for the continued practice of open gauging. First, there are significant penalties imposed on the ship's crew and owner if a spill occurs. Secondly, closed gauging systems have a reputation of being unreliable and ships crews are reluctant to accept their ullage indications. As a result, crewmen continue to "look" into the tank to establish an absolute indication of the ullage level at tank topoff. During the course of this project (Phases I and II) inert gas systems (which require closed gauging) have become more prevalent on crude oil and select product tankers as a result of new regulations which require IGS for petroleum products with certain flash points. Although most chemical products are carried in barges or ships which are currently not required to have IGS, it is possible that future trends will result in reliable IGS and/or closed gauging systems on a broader range of liquid bulk carriers. However, to effectively eliminate the practice of open gauging will require reliable closed gauging systems as common place on both barges and tankers, and it is not anticipated that this will occur in the immediate future.

The results presented in this study will allow both the government regulatory agencies and the marine industry to evaluate current operational practices and engineering controls as they affect worker exposure and flammability hazards. Effective controls are available to significantly reduce worker exposure during tank gauging and tank entry work activities. Even so, a continued exposure to multiple chemical vapors at low levels will be inherent in the work activity. An assessment of the implications of these low level multiple exposures will require further evaluation. As part of this evaluation, an environmental and medical monitoring activity may be considered as appropriate to insure the health and safety of these workers.

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GLOSSARY OF TERMINOLOGY

A/B = Able Bodied Seaman

ACGIH = American Conference of Governmental Industrial Hygienists

B/3 = One-third ship's breadth

CFR = Code of Federal Regulations

CHRIS = Chemical Hazards Response Information System

C/M = Chief Mate

F.I.D. = Flame ionization detector

GC = Gas chromatograph

HACS = Hazard Assessment Computer System

IDLH = Concentration that is immediately dangerous to life or health

I/O = Computer program input/output

LEL = Lower explosive limit

MHCW = Marine Hazardous Chemical Worker

NIOSH = National Institute for Occupational Safety and Health

η = Desorption efficiency

O_2/CGI = Oxygen/combustible gas indicator

ONDEK = Model name for atmospheric dispersion of vapors

O/S = Ordinary Seaman

OSH Act = Occupational Safety and Health Act

OSHA = Occupational Safety and Health Administration

OVA = Organic vapor analyzer

ppm = Concentration in parts per million by volume

PRO = Port Relief Officer

P/V = Pressure/vacuum

RH = Relative humidity

GLOSSARY OF TERMINOLOGY (CONTD)

Subchapter D = 46CFR, Parts 30-40

Subchapter O = 46CFR, Parts 150-155

SwRI = Southwest Research Institute

TANKM = Model name for gas freeing of cargo tanks that contain residues of chemical in wash water

TANKP = Model name for gas freeing of cargo tanks that contain residues of pure chemical

tℓv = Turbulence level value

TLV-C = Ceiling exposure limit

TLV-STEL = Short term exposure limit

TLV-TWA = 8-hour time weighted average threshold limit value

UEL = Upper explosive limit

USCG = United States Coast Guard

USC = United States Code

VLCC = Very large crude carrier

CHEMICAL ABBREVIATION GLOSSARY

ACT = Acetone

BAN = n-Butyl alcohol

BNZ = Benzene

BTC = n-Butyl acrylate

CBT = Carbon tetrachloride

CRF = Chloroform

DBO,P = o-Dichlorobenzene, p-Dichlorobenzene

DCM = Methylene chloride

DEA = Diethanolamine

EAC = Ethyl acrylate

EAL = Ethyl alcohol

EDC = Ethylene dichloride

EPC = Epichlorohydrin

HXA = Hexane

MAL = Methyl alcohol

MEK = Methyl ethyl ketone

MIK = Methyl isobutyl ketone

MMM = Methyl methacrylate

STY = Styrene

TCE = 1,1,1 Trichloroethane

TCL = Trichloroethylene

TOL = Toluene

TTE = Tetrachloroethylene

VAM = Vinyl acetate

XLM,O,P = m-Xylene, o-Xylene, p-Xylene

I. INTRODUCTION

The term "Marine Hazardous Chemical Worker" is used to encompass several diverse groups of workers whose marine-related work activities may cause them to be exposed to potentially hazardous chemicals. Marine Hazardous Chemical Workers (MHCW) fall into four generic classes:

- o Marine chemical transport workers (tankers and barges)
- o Chemical terminal dock workers
- o Offshore platform and service vessel workers
- o U. S. Coast Guard personnel
    - Marine Inspectors
    - Port Safety Teams
    - Pollution Response Teams
    - National Strike Force Teams.

In the United States, the U. S. Coast Guard has broad responsibility for the safety and health of these personnel. This responsibility is derived in part from the Ports and Waterways Safety Act of 1978, Outer Continental Shelf Lands Act of 1953, Marine Inspection Laws, and various other U. S. codes and public laws. In some cases OSHA's responsibility or authority, as stipulated in the OSH Act of 1980 (29 USC 651), overlaps the Coast Guard's for some MHCW classes. Memorandums of Understanding between the Coast Guard and OSHA have been published to (1) define cooperational guidelines between the two Agencies, (2) eliminate interagency conflicts, and (3) eliminate duplication of efforts while working to develop meaningful regulations to protect the MHCW.

Personnel in each of the four generic marine worker categories presented above can be further subdivided into many specific work classes or job classifications. For each of these worker sub-classes, potential safety hazards from flammable and toxic substances in the work environment are inherent in job activities. Hazardous substances include vapors, gases, liquids, mists, and dusts; and the sources of these substances may be encountered during routine and nonroutine work situations. For most of the job categories, exposure to these substances, either individually or in combination, can occur during the course of marine operations. In addition, operational equipment and procedures vary greatly. Thus, a simplified definition of hazardous sources, equipment, and work practices for marine personnel is not possible. Furthermore, the work schedules of most MHCW's do not follow the normal eight-hour day that is characteristic of other industries. Thus, the worker exposures may be difficult to interpret in terms of the usual OSHA/NIOSH threshold limit values.

With the realization of these complexities, the U. S. Coast Guard is conducting research efforts to identify and characterize potentially hazardous safety and health situations in the marine environment for marine chemical transport workers, offshore platform and service vessel personnel, chemical terminal dock workers, and U. S. Coast Guard field personnel.

The Coast Guard has formulated and is implementing a multi-element program, which is summarized below.

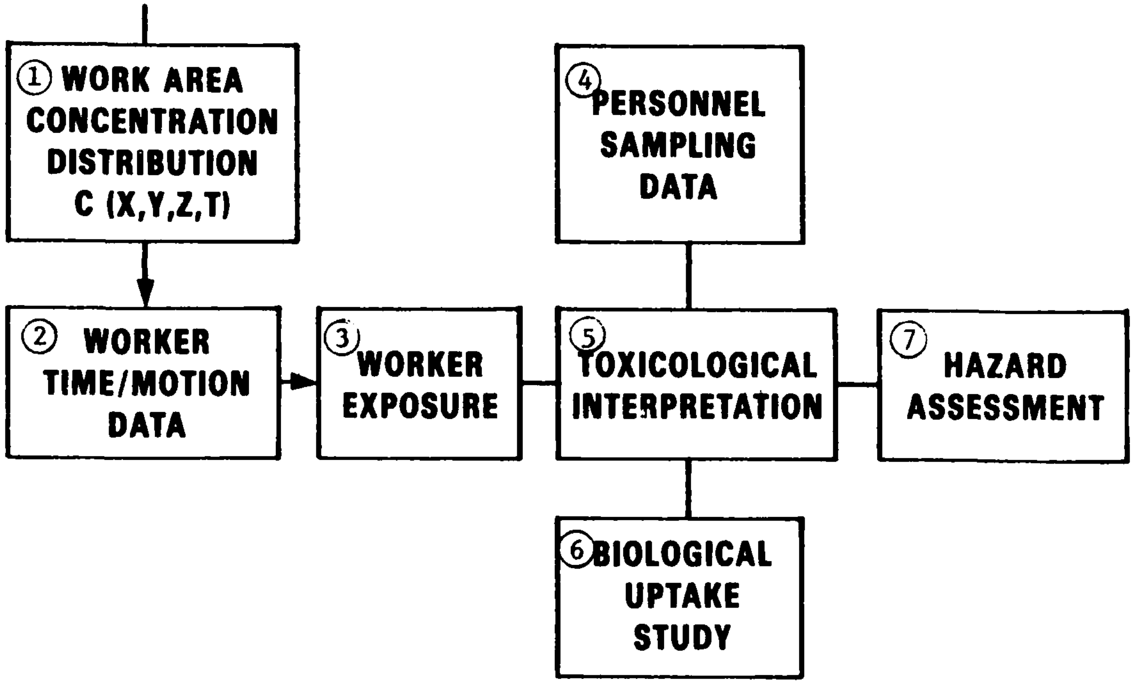
Element No.	Project Title
1	Investigation of the Hazards Posed by Chemical Vapors Released in Marine Operations - Phase I (Complete) - Reference 1.
2	Investigation of the Hazards Posed by Chemical Vapors Released in Marine Operations - Phase II.
3	A Crew Exposure Study - Phase I (Complete) - Reference 2.
4	A Crew Exposure Study - Phase II (Current)
5	A Study to Improve the Health and Safety of the Marine Hazardous Chemical Worker (Current).

In formulating this program and the element sequence, the Coast Guard recognized, and it was later substantiated through searches of the worldwide technical literature, that there was a lack of basic data on occupational exposures aboard marine tank vessels. A limited amount of data has been gathered by private industry, but this information was not in the public domain. Therefore, the emphasis in the first four program elements is on characterizing the work/exposure environment so that control methodology, be it engineering, administrative or protective equipment, can be adequately considered in the fifth element.

Program elements 1 and 2 deal with investigating potential hazards to workers involved in marine terminal operations. Program elements 3 and 4 deal with investigating potential hazards to offshore oil and gas facility (drilling and production) workers and to merchant tanker crews at sea. Program elements 1 - 4 all involve generating the data base necessary to provide input to the hazard assessment methodology presented in Figure I.1.

This report describes the results of Phase II (Element 2) of the two-element U. S. Coast Guard research project entitled "Investigation of the Hazards Posed by Chemical Vapors Released in Marine Operations."

HAZARD ASSESSMENT METHODOLOGY



CHEMICAL VAPOR HAZARD ASSESSMENT

FIGURE I.1

II. INVESTIGATIVE PLAN

II.1 Method of Approach

In Phase I, a background study was conducted to identify marine terminal work activities/operations that are potentially hazardous. This was accomplished through field studies, discussions with marine industry personnel and literature searches. The field studies included (1) the measurement of chemical vapor sources and work area concentrations, and (2) the documentation of work activities in these areas such that a preliminary assessment of Blocks ①, ②, and ③ in Figure I.1 could be undertaken. As a result of this background study, the following operations were identified as being potentially hazardous:

- Open venting of product vapors during tank loading,
- Washing and gas freeing of cargo tanks, and
- Product hose hookup and disconnect before and after product loading.

Specific work activities associated with these operations include:

- Cargo gauging during tank loading,
- Tank entry for cleaning or inspection,
- Various work activities on deck regions downwind of open vents during product loading, and
- Manual hose connecting (disconnecting) over open manifold drip trays.

The spatial and time dependent vapor concentration (Block ①, Figure I.1) in the vapor plume downwind of a vent and in a tank during and after gas freeing are amenable to analytical modeling. Because of the large number of parameters affecting on-deck and in-tank concentration levels, the Phase I study included developing first generation analytical models to describe (1) the downwind dispersion and dilution of chemical vapor plume emissions during cargo loading and gas freeing, and (2) the in-tank vapor concentration environment during gas freeing with vapor regeneration. Concurrent with analytical model development, an experimental plan was developed which identified the methods and techniques for (1) acquiring vapor concentration and other supporting data for use in validating the analytical models, and (2) the direct measurement of occupational exposures through personal monitoring. The experimental plan was partially implemented with tests of limited scope. Following these tests, the experimental data were compared to model predictions, and model and test plan modifications were identified where indicated.

Thus, at the conclusion of Phase I, analytical models were developed to provide work area concentration distribution predictions (Block ①, Figure I.1) and a feasible experimental plan was established to provide data to validate the models and to provide a preliminary assessment of worker exposure (Blocks ③ and ④, Figure I.1). Based on the results of Phase I, which are reported in Reference 1, the requirements for Phase II were identified. Under the initial plan, Phase II consisted of four major task elements.

- Task I - The objective of this task was to implement the experimental plan that had been designed in Phase I. Task I emphasized vapor dispersion and tank ventilation experimentation in support of model development as well as occupational exposure monitoring.

- Task II - The analytical models were evaluated and revised as indicated by the experimental data from Task I. Extension of these models to other chemical terminal operations was also considered.

- Task III - In this task, the data that had been collected was evaluated with respect to flammability and toxicity as they relate to analytical model predictions and occupational exposure monitoring.

- <u>Task IV</u> - The objective of Task IV was to develop a handbook that describes the analytical models and associated computer codes that can be used by the USCG Hazardous Materials Specialist to assess various aspects of tanker/terminal operations. The handbook was published in Reference 3, and the programs will be incorporated into the Coast Guard's Hazard Assessment Computer System (HACS).

Prior to and during the data evaluation process, it was recognized that the continuous 8-hour workday that is the basis for current occupational exposure guidelines is not frequently encountered in the marine industry. Work schedules aboard tankers range from the traditional 4-on, 8-off rotating shift to the 6-on, 6-off shift schedule. In addition, loading and tank cleaning operations may result in extended continuous work periods that may approach or exceed 24 hours. The technical literature contained several suggested mathematical models for adjusting existing Threshold Limit Values to reflect these novel or unusual work schedules. However, overall, the modeling assumptions were not consistent with the observed exposure patterns of merchant marine tankermen. To this end, Task V of this project was initiated. This task, entitled "Biological Sampling - A Pilot Study," was designed to determine the feasibility of collecting concommitant environmental and biological blood, breath and urine data during these novel work schedules. The long range objective of this task was to collect data that may indicate the feasibility and direction of TLV adjustment, and thus it relates to Blocks ⑥ and ⑦ in Figure I.1.

The method of approach to occupational exposure monitoring evolved from Phase I. In that initial phase, several cargo transfer operations were observed. Foremost among the work activities that posed the greatest potential for short-term vapor exposure were open tank gauging at top-off and tank entry.

Logically, the initial monitoring efforts in Phase II emphasized these activities on the vessels that had been included in the preliminary observations. As additional vapor venting, cargo gauging and operational procedures were encountered in Phase II, exposure monitoring during loading was expanded to include longer sampling durations that encompassed a complete shift or operation. Subsequently, exposure monitoring was extended to include multiple deck watches as well as 24-hour environmental monitoring for biological sampling purposes.

In a marine tanker terminal, ship tanks may be entered for two reasons and by two different classes of personnel.

- Land-based cargo surveyors or quality control personnel inspect tanks for cleanliness prior to loading. These tanks have been cleaned and gas freed at sea.
- Crew members enter tanks for final manual cleaning after the tank has been washed and ventilated in port but before quality control inspection.

Entry for quality control inspection occurs more frequently in port than does the latter type of entry because some terminal operators do not permit tank cleaning while the ship is tied up. Occupational exposures were monitored for both entry categories at each opportunity. The scope of tank entry exposure monitoring was expanded by including entries in chemical barge washing facilities and on tankers at sea where the majority of tanks are processed.

Exposure monitoring included both collection of breathing zone samples and documentation as to the source of the exposure, the work activities and how it was performed, and the duration of the work activity in proximity to the source. With minor exceptions, NIOSH recommended sampling media and analytical chemistry procedures were employed. Initially, where charcoal was the indicated adsorbent, the large tube (400 mg/200 mg) was used. Subsequently, both the large and the small (100 mg/50 mg) tubes were used; selection was based on experience and the anticipated vapor levels during the sampling interval.

Throughout Phases I and II, exposure monitoring was conducted within a research framework as opposed to a framework of compliance monitoring. This philosophy was adopted so that exposure levels could be quantified as an end objective and because the latter approach presumes the existence of a set of exposure standards that are applicable to marine work schedules.

II.2 Rationale

Throughout this project, emphasis has been placed on developing the data base which is required to allow the hazard assessment methodology implied by Figure I.1. Out of necessity, most of the emphasis has been placed on developing and validating analytical models which can be integrated into the U. S. Coast Guard Hazard Assessment Computer System (HACS).

The Coast Guard maintains the Hazard Assessment Computer System (HACS) which consists of a number of computer codes that describe various scenarios that pertain to chemicals and the environment. These codes can be exercised to study the impact of hypothetical releases or to provide emergency guidance to on-scene personnel immediately following an incident. The HACS system does not presently include codes for analytical models that describe

- the near-field dispersion and trajectory of heavier-than-air vapor plumes such as those that are emitted during cargo loading, or
- the gas freeing process that precedes man entry into a cargo tank.

To this end, the models that were developed on this project will be integrated into the HACS system to provide an expanded assessment capability.

Significant emphasis has also been placed on developing a comprehensive data base on marine occupational exposures, and a pilot biological monitoring effort has been initiated. The composite of this information is being subjected to a toxicological interpretation so that a hazard assessment based on current toxicological information can be accomplished.

This report contains the results of Tasks I, II, and IV as well as a preliminary interpretation of the initial biological monitoring tests and the occupational exposure data. The results of the remaining biological monitoring tests and an in-depth assessment of exposure data will be published in addenda to this report.

Section IV of this report presents the model development/validation results, and Section V the occupational exposure monitoring data.

III. CONCLUSIONS

III.1 Analytical Modeling

Plume (ONDEK) Model

- An analytical model for predicting the dispersion of chemical vapor plumes emitted from cargo tank vents during cargo loading and tank ventilation has been developed and experimentally validated.

- Over one hundred separate tests were performed to provide model validation data for the chemical vapor concentration distribution downwind of the tank vents. These tests were performed during actual cargo loading operations on both tanker ships and barges, and during full-scale simulations of tank atmosphere venting. The tests covered the full range of conditions for vent gas concentration, vent gas flowrate, vent height, and ambient wind velocity expected for shipboard operations.

- Good agreement was found between plume model predictions and experimental vapor concentration data for venting tests performed with low vents (within 2 m of the deck) and 4 m high vents. The plume model predicted higher (by a factor of 2 to 3) concentration levels for a 6.1 m vent (a typical B/3 vent height) than measured experimentally. However, since predictions are at man breathing height and since for 6.1 m vents the measured values are on the order of 10 ppm, the model accuracy is considered acceptable for hazard assessment.

- Plume dispersion tests were performed for situations in which (1) the wind was unobstructed as it passed over the tank vent, and (2) deck structures partially shielded the tank vent from the wind. The effect of upwind deck structure was to reduce the local wind speed near the vent and to increase the unsteadiness and/or turbulence of the wind field. This effect enhances the dilution of the plume, reduces the peak concentration levels, and causes the plume to cover a greater surface area than if upwind structure were not present. However, if structure completely shields the vent from the wind, then the concentration near the vent would be much greater than for cases 1 or 2 above.

- Venting of tank atmospheres from low vents, within 2 m of deck level, was found to give the highest levels of chemical vapor concentration at man breathing height. Vapor concentration values that exceeded the current accepted STEL and TLV-TWA limit values were predicted and measured at man breathing height during cargo loading of methanol and vinyl acetate.

- A parametric study was performed with the validated plume dispersion model. The results of this study confirmed the importance of increased vent height in reducing chemical vapor concentration levels at breathing height downwind of tank vents. It also showed that even for increased vent heights to 6 m , deck concentrations on the order of 10 - 50 ppm can occur over some areas during moderate to low wind speeds.

Tank Ventilation (TANKP, TANKM) Models

- Two tank ventilation models have been developed which describe the in-tank vapor concentration-time history during gas freeing in the presence of vapor regeneration from either pure product residues or post-wash residues of chemical in water solution.

- Twenty-four full and model scale tests were conducted to collect gas freeing data for model validation. These tests involved 13 different products whose physical properties included a wide range of vapor pressures and aqueous solubilities. The full scale tests included tanks on parcel chemical carriers, product tankers and unmanned barges.

- Comparison of the model predictions and the experimental data indicate that the models adequately describe both evaporation processes and the concentration-time histories of the vapors that are discharged from the tank during dilution ventilation provided that certain key variables are known accurately and the tank does not have internal structure.

- For tanks that have been washed prior to ventilation, the key variables that are not readily amenable to field measurement are (1) the initial thickness of the residual chemical/water solution on the tank bottom, and (2) the initial concentration of chemical in solution at the beginning of ventilation. Where these independent variables are not known, selection criteria or default options were developed which serve as a starting point for parameter estimation. Use of these estimation procedures results in good agreement between theory and experiment.

- The thickness of the pure chemical residue layer on the tank bottom, prior to gas freeing *without washing*, can only be estimated visually; it is not amenable to direct measurement. In this case, a selection criterion was developed for estimating the residual thickness. Perturbation of the selection criterion resulted in good agreement between theory and experiment.

- The response of the model with evaporation of chemical from solution was studied parametrically by systematically varying four key independent variables: the residual liquid thickness, initial chemical concentration in solution, the initial vapor phase concentration, and the blower flowrate. This parametric analysis indicated that the time to gas free to a given concentration is a strong function of residue thickness, solution concentration, and blower flowrate. The effects of residue thickness and liquid concentration were more dominant than blower flowrate. Thorough washing and efficient stripping operations will result in low initial chemical concentrations in solution and low residue thicknesses that minimize the gas freeing time to safe vapor levels for man entry into the tank. Use of the largest commercially-available blower will expedite the gas freeing process. Initial tank vapor concentration had an insignificant effect on the time to gas free to a prescribed level because after the initial stages of purging of the vapor space, the evaporation process is controlled by the liquid phase resistance to mass transfer.

- A similar parametric analysis was conducted on the model that incorporates evaporation of pure chemical residues. The results of this analysis confirmed the statistical sensitivity analysis that was performed in Phase I of this project. Blower flowrate and residue thickness have a strong effect on the gas freeing time, but initial vapor concentration has a negligible effect. This conclusion supports an efficient stripping operation and the use of the largest commercially-available blower.

- Both models assume that the vessel has double bottom tanks without internal structure, which is characteristic of parcel chemical carriers as well as product tankers that have been retrofitted and certified to carry specialty chemicals. Neither model includes the effect of tank internal structure that exists on vessels whose certification does not require double bottom construction. Tanks with internal structure were included in the full scale tests. Comparison of model predictions with experimental data suggests that two structure-related model modifications should be investigated. The first modification would take into account the reduced liquid surface area that is available for product evaporation in the bays immediately beneath the blower jet. The second modification would reflect the fact that bays that are remote to blower jet are shielded from the convective air currents and will gas free by slower physical processes. These physical processes delay or retard the overall gas freeing time relative to a tank without internal structure.

III.2 Occupational Exposures

A significant data base has been generated on occupational exposures to chemical vapors in marine operations, and the data base is presented in this report together with documentation of each exposure scenario. Full toxicological interpretation of these data will be published in an addendum to this report. However, the following conclusions can be stated at this time.

- Twenty-eight percent of all tank entries resulted in exposure concentrations that exceeded the TLV-STEL. In 5.5 percent of the entries, the 8-hour time-weighted average exposure exceeded the TLV-TWA. Tank entries on in-service vessels are relatively short term in duration and range from just a few minutes for a brief inspection to approximately one hour when manual cleaning and mucking are performed. In the majority of the entries (58 percent), the exposure concentration was less than one-half of the TLV-STEL or TLV-C.

- The highest exposure levels in excess of the TLV-STEL occur during open ullage gauging at top-off of fully loaded tanks.

- Gauging tubes which have the appearance of a restricted gauging system but which terminate at deck level are basically open gauging systems. These gauging tubes pose the same exposure potential as gauging through an open ullage port on an expansion trunk.

- Restricted gauging systems significantly reduce exposure levels during all phases of cargo loading including tank top-off. These reduced levels may approach the detection limits of analytical chemistry instrumentation.

- The operational procedure known as "shore-stop" loading effectively reduced exposure levels regardless of whether the tank is fully loaded or short-loaded. The reason is that, in shore-stop loading, there is less emphasis on manual tank gauging especially during the final stages of loading.

- Exposure to mixtures of chemical vapors does occur because multiple product vapors are emitted to the work environment during vessel loading. In the majority of the situations that were observed, individual component exposure levels were relatively low, and the mixture TLV based on additive effects was not exceeded. The reason for this behavior is due to the rapid dilution and dispersion of chemical vapors following discharge from tanks that are being loaded. The mixture TLV was exceeded in a limited number of instances in which there was one dominant vapor component, and this component of exposure resulted from open gauging or sampling of product tanks.

III.3 Concluding Remarks

In the course of this study (Phase I and Phase II), work activities have been identified where potentially significant exposure to chemical vapors can occur. These activities include:

- Open gauging during tank loading,
- Tank entry for cleaning or inspection,
- Work activities that are conducted in regions of the deck that are downwind of open vents during product loading, and
- Manual hose connecting (disconnecting) over open manifold drip trays that contain product accumulations.

The marine industry and responsible government regulatory agencies have recognized that occupational exposure to chemical vapors is inherent in these work activities. However, prior to the initiation of this project, a comprehensive definition of exposure levels for these work activities had not been published in the open literature.

In this project, one area of emphasis has included quantifying chemical exposures in the marine terminal work environment. This quantification has been accomplished through work area chemical vapor concentration measurements and through personal exposure monitoring in the field. Also, validated analytical models have been developed which allow a definition of work area vapor concentrations downwind of vents and in "gas freed" tanks for many more atmospheric and operational conditions than could practically be covered in field testing.

Extensive field measurements of the vapor discharge concentrations at the open ullage port and expansion trunk during product loading have shown that the concentrations range from levels of a hundred to a thousand ppm at the beginning of product loading into a clean tank to significantly higher values (10,000 to 100,000 ppm) at the start of loading into a dedicated, uncleaned tank. As product loading proceeds, vapors are liberated from the liquid surface and the vented concentrations can proceed through the flammable range to saturation as the tank is topped-off. Thus, the open gauging of tanks presents a potential for a significant exposure. Personal exposure data collected on this project during open gauging supports this conclusion. Vapor measurements downwind of the vent during product loading and analytical model predictions show that the concentrations dilute rapidly from the level at the vent. Therefore, when there is a flammable or higher concentration at the vent, the flammable boundaries may extend only a few meters downwind. This indicates that the potential for a flammable hazard is low. For low (ullage port level of ~ 1 m) vent heights, the concentrations at man breathing height on the deck in regions from 5 to 20 meters downwind can be in the range from 10 to 500 ppm. Thus, for product chemical vapors with exposure limits in this concentration range, the potential for occupational exposure exists. However, an effective method of minimizing this potential is to vent product vapors during loading from a height of at least 4 m which effectively reduces both downwind concentration and the area on the deck where vapor concentration exists.

The necessity for proper monitoring of a tank atmosphere in preparation for man entry is also highlighted by the analytical and experimental results of this study. Proper monitoring includes measurement of oxygen content and product vapor concentration as it relates to both flammability and toxicity. Emphasis on gas freeing to safe occupational exposure levels will insure an additional margin of safety regarding flammability. Instrument measurements of tank vapor concentration during man entry and personal exposure monitoring have shown that accepted exposure limits are exceeded in some cases. The in-tank analytical models show that very small amounts of residual cargo (either pure chemical or soluble chemical/wash water solution) create enough vapor regeneration that the in-tank concentration can exceed a safe man entry level for extended periods of time. Thus, the models have shown the necessity of maintaining stringent cleaning requirements so that tank atmospheres do not present a potential toxicity hazard for man entry.

The personal exposure data obtained on this project have shown that both open gauging and tank entry as currently practiced in the industry do, on occasion, subject workers to exposures in excess of currently accepted TLV levels. Restricted gauging systems significantly reduce the exposure potential. The data also show that in the majority of cases, the measured levels are below currently accepted limits. Effective engineering and procedural methods of control to eliminate the exposures that appear potentially hazardous have been identified.

Many of the regulations and operational practices in place on tankers are not followed or are circumvented because of conflicting requirements. For example, certain Subchapter O chemicals require vent heights of B/3, or 4 m , which the study results show to be effective in reducing exposure levels to vented vapors during tank loading. However, open gauging is permitted for these Subchapter O chemicals which results in vapor venting at the tank hatch and nullifies the effectiveness of the elevated vent. Also, the minimum venting requirements which can reduce exposure hazards in tanker operations are not applied to barge operations. As a result, there is probably a higher level of occupational exposure during barge loading operations than for tankers.

The results presented in this study will allow both the government regulatory agencies and the marine industry to evaluate current operational practices and engineering controls as they affect worker exposure and flammability hazards. Effective controls are available to significantly reduce worker exposure during tank gauging and tank entry work activities. Even so, a continued exposure to multiple chemical vapors at low levels will be inherent in the work activity. An assessment of the implications of these low level multiple exposures will require further evaluation. As part of this evaluation, an environmental and medical monitoring activity may be considered as appropriate to insure the health and safety of these workers.

IV. MATHEMATICAL MODELING AND EXPERIMENTAL VALIDATION

IV.1 Scope

As described in Section II, the Phase I research project identified two routine operations performed on tanker ships and barges that involve the emission of chemical vapors and the potential for worker exposure to vapor concentrations exceeding the hazard threshold level. These operations are (1) the open venting of tanks during cargo loading, and (2) the washing and ventilation of tanks after cargo discharge. Analytical models were developed during Phase I to simulate the emission, dilution and dispersion of chemical vapors during these operations. Particular attention was paid to predicting the vapor concentration level at breathing zone height in areas where workers perform their activities. An experimental plan was developed during Phase I to guide the collection during both actual and simulated operations of the vapor concentration data needed to test and validate the analytical models. The experimental test plan was given a trial implementation during Phase I to demonstrate the viability of the data collection and analysis methods and to provide a preliminary comparison of model predictions and experimental data.

The objective of the Phase II research project was to validate the analytical models developed during Phase I. This required performing the experiments indicated by the experimental test plan and collecting data for several model variables over a wide range of model conditions. The key elements of the Phase II model validation effort were the following.

(1) Setting up the experiments called for by the test plan. This involved identifying marine terminals and vessels that handled the chemicals of interest to this project and obtaining permission to perform vapor sampling activities during their operations. Where necessary, laboratory experiments were used to supplement the range of test conditions encountered during marine terminal observations.

(2) Calibrating instruments, collecting and reducing the data for the model variables for each experiment. Since some chemical cargos were industrial grade in purity, or blends of different chemicals, the vapor concentration analyzer was always calibrated with samples of known concentration prepared from a liquid sample obtained during the experiment.

(3) Using the analytical models to compute the chemical vapor concentration field predicted for each set of experimental conditions.

(4) Comparing the results of the model predictions with the experimental data, and determining the values for the empirical model parameters that give the best agreement.

(5) Reformulating the analytical models when necessary to improve the simulation of geometrical effects, operational procedures and the physical and chemical behavior of chemical cargos of interest.

The results of the model validation effort are described in Sections IV.2 and IV.3 of this report. In addition, it was the practice of the SwRI project team to observe and note the activities of crew members which involved their exposure to chemical vapors. Where appropriate, personal sampling was performed on crew members and/or SwRI project team members to establish chemical vapor exposure profiles during their work activity. The results of the vapor exposure monitoring activity are reported in Section V.

IV.2 Gas Freeing of Cargo Tanks

Tank cleaning is an integral part of operations on in-service chemical tankers. In one class of tanker, the parcel chemical carrier, every tank is cleaned prior to being loaded with product because of the need to eliminate cross-contamination and, thus, maintain product purity. The requirement for tank cleaning is somewhat less on product tankers and dedicated carriers although cleaning is generally performed as a prerequisite for a change of cargo grade.

Tank cleaning normally consists of a water wash and stripping operation followed by mechanical ventilation to gas free the tank. In a variation of this procedure there is no water wash. Two analytical models were developed to describe the gas freeing process with or without an initial water wash. Both of these models predict the concentration-time history of the vapors that are discharged from the tank during dilution ventilation. The motivation for developing these models is as follows:

- At some time following the beginning of ventilation, crew members will enter a tank to perform manual cleaning of the tank bottom, which can include sweeping of debris and hand mucking of residual liquid. The models provide a means of estimating potential occupational exposure levels to chemical vapors.
- During forced ventilation of a tank, product vapors are discharged into the work environment on-deck. These vapors may pose a potential exposure to the deck crew. The tank ventilation models predict a source concentration-time history that can be used by the plume dispersion model of Section IV.3 to estimate these exposure levels.

The two models that are presented in this section are entitled TANKM and TANKP. The TANKM model describes the ventilation of a product tank in the presence of evaporation of residual chemical from a binary chemical/water solution on the tank bottom following washing. In the majority of operations, the tanks are washed prior to ventilation. The TANKP model applies to the minority of situations where the tank is not washed and product residues are removed by evaporation of pure chemical product.

The model formulations that are described below form the basis for computer codes and a user's manual that will be incorporated into the U.S. Coast Guard Hazard Assessment Computer System (HACS).

IV.2.1 Model Formulation

TANKM Model

After a water wash, chemical/water residues will exist primarily on the tank bottom and to a much lesser degree on the tank walls, internal structure and the underside of the weather deck. The first two assumptions are that

- the tank does not have internal structure, and
- only the residues on the tank bottom contribute significantly to chemical evaporation during ventilation.

The first assumption is indeed valid for modern chemical tanker fleets with double bottom hull construction. The second assumption is appropriate for low viscosity products, especially those that are water soluble.

In reality, the air flow field inside the tank during ventilation is three-dimensional in nature. A complete analytical formulation of this complex flow field is feasible, but it is not warranted because there is experimental evidence (Reference 4) that, when dilution ventilation is properly applied, the vapor space approaches a state of homogeneous mixing. Therefore, the model assumes that mechanical, dilution ventilation produces a uniform vapor space that is characterized by the "well-mixed reactor." Under this assumption, there is no spatial variation of vapor concentration within the tank; concentration varies only with time.

As ventilation proceeds, mass transfer of chemical will take place between the vapor space and the binary residual solution on the tank bottom. Local variations in the concentration of chemical in solution would be expected because of the non-uniformity of the air flow field above the residual layer. Also, vertical concentration gradients in liquid layer are likely. The model further assumes that

- the local mass transfer flux between the vapor space and the binary layer does not vary over the surface area of the layer.

The area of the residual layer is equal to the area of the tank bottom.

- the concentration of chemical in solution is constant through the layer depth.

On the basis of the above assumptions, a mass balance can be formulated for the chemical in the vapor phase and the chemical in the liquid solutions.

Vapor Phase

$$\forall \frac{dC_V}{dt} = -C_V Q + AF \qquad (1)$$

Liquid Phase

$$\frac{dC_L}{dt} = -F/\delta \qquad (2)$$

where $\forall$ = tank volume

C_V = mass concentration of vapor in air

Q = blower flow rate

A = residual liquid surface area

F = net flux of chemical between liquid and vapor phases. F is positive when mass is transferred to the vapor phase from the aqueous solution.

C_L = mass concentration of chemical (solute) in water (solvent)

δ = residue thickness

These two differential equations are coupled through an interface condition that describes mass transfer flux between the liquid and vapor phases.

The interface condition that describes the flux term F is based on the two-layer film model in Reference 5.

$$F = K_{OL} (C_L - C_V/H) \qquad (3)$$

where K_{OL} = overall mass transfer coefficient referenced to the liquid phase

H = Henry's law constant or partition coefficient

This flux model assumes that both the bulk liquid and vapor phases are well mixed and concentration gradients exist only within the thin two-layer interface film.

A single initial value for the vapor and liquid concentrations at the beginning of ventilation completes the basic formulation.

$$\left.\begin{aligned} C_V &= C_{ov} \\ C_L &= C_{OL} \end{aligned}\right\} \quad \text{at} \quad t = 0 \tag{4}$$

The analytical expression for the mass transfer coefficient, K_{OL}, as derived by Liss and Slater in Reference 5, is as follows.

$$K_{OL} = \frac{k_\ell \, k_g \, H}{k_\ell + H \, k_g} \tag{5}$$

Equation (5) can be rearranged;

$$\frac{1}{K_{OL}} = \frac{1}{k_\ell} + \frac{1}{Hk_g} \tag{6}$$

In this form, the reciprocal of K_{OL} represents the total resistance to mass transfer referenced to the liquid phase. This total resistance consists of two parts: the resistance of the gas phase, $1/Hk_g$, and the resistance of the liquid phase, $1/k_\ell$. The relative magnitude of these two resistances indicates which phase, liquid or gas, controls the mass transfer. Expressions for the exchange rate constants, k_ℓ and k_g, are based on References 6 and 7, respectively. In these references, the exchange constants for CO_2 (molecular weight 44) and water vapor (molecular weight 18) mass transfer at the air-sea interface (Reference 5) were adapted to the volatilization of chemicals from water solutions.

$$k_{\ell} = 0.33\ (44/M)^{1/2} \tag{7}$$

$$k_g = 18.95\ U_{wind}\ (18/M)^{1/2} \tag{8}$$

where M = molecular weight of the chemical
U_{wind} = effective air velocity over the liquid surface.

As can be seen, the movement of ventilation air over the surface of the residue on tank bottom affects k_g but not k_{ℓ}. Theoretically, k_{ℓ} is influenced primarily by the gross motion of the liquid body; e.g., velocity currents in a river or stream. As the residues on the tank bottom are essentially stagnant or non-flowing, k_{ℓ} is unaffected by kinematic parameters.

One of the consequences of assuming a "well-mixed reactor" (homogeneous vapor space concentration) and a spatially-independent evaporative flux is that there are no local variations in the velocity of the air over any element of the residue surface area. This situation was addressed by adapting the blower jet impingement model in Reference 8 to generate an expression for U_{wind}.

The model in Reference 8 was derived for the normal impingement of a submerged jet (chemical vapor component neglected) onto a flat plate with a radially-symmetric flow field about the stagnation point. The jet in this model is analogous to the ventilation blower jet, and the flat plate is the tank bottom. Following impingement of the jet on the tank bottom, the maximum air velocity, V_m, parallel to the impingement surface increases linearly with distance, r, from the stagnation point. This relationship applies throughout the "jet deflection" region whose radial boundary is defined as αD where D is the tank depth. Determination of the constant, α, will be discussed later. Thus, the maximum jet deflection velocity is predicted by Equation (9):

$$V_{m,jd} = Kr, \quad 0 \leq r \leq \alpha D \tag{9}$$

where K is a constant. In this region, viscous effects are negligible. Immediately downstream of the "jet deflection" region is the "wall jet" region. This region is characterized by self-similar velocity profiles that also exhibit a maximum velocity, $V_{m,wj}$. This maximum velocity parallel to the tank bottom separates the boundary layer zone from a free jet zone. Experimental and theoretical studies substantiate that $V_{m,wj}$ decays monotonically with increasing radial distance.

$$V_{m,wj} = \frac{1.4\ U_o}{(r/d)^{1.12}} \quad \text{for} \quad r \geq \alpha D \tag{10}$$

where U_o = average jet velocity based on blower flow rate, Q, and jet inlet diameter, d.

A weighted average wall velocity was obtained by integrating these velocity profiles radially outward from the jet stagnation point.

$$\bar{U} r_2 = \int_0^{r_1} Krdr + \int_{r_1}^{r_2} \frac{C}{r^n}\ dr \tag{11}$$

where $C = 1.4\ U_o d^{1.12}$

$n = 1.12$

$r_1 = \alpha D$

r_2 = arbitrary radial distance from the stagnation point; $r_2 > r_1$

The resulting expression for U is

$$\bar{U} = \frac{K}{2}\ \frac{{r_1}^2}{r_2} + \frac{C}{1-n}\ {r_2}^{-n} \left[1 - \left(\frac{r_1}{r_2}\right)^{1-n}\right] \tag{12}$$

Matching of the velocity profiles at the boundary, r_1, between the jet deflection and wall jet regions resulted in an equation for K.

$$K = \frac{C}{{r_1}^{n+1}} \tag{13}$$

Equation (12) applies strictly to the unconfined radial expansion of the jet following impingement. This situation does not occur with respect to radial expansion of the jet along the tank bottom. The wall jet region is constrained by the tank walls, which limit the expansion, and the blower is not normally centered on a deck opening above the tank. These two factors will combine to produce an asymmetric velocity field over the residue layer that departs from the predicted value of $\overline{U}$. As a result, r_2 is not a well-defined geometrical parameter. Based on a review of ship planform drawings and full-scale experimentation, the best engineering estimate of r_2 was

$$r_2 = 0.75\ L \tag{14}$$

where L = tank length (fore-aft). Subsequent comparisons of model predictions and experimental data indicated that the assymmetry could be more closely taken into account by the following equation.

$$U_{wind} = \beta \overline{U} \tag{15}$$

Determination of the numerical value of β will be discussed later.

Reference 8 contains experimental measurements of the maximum radial velocity, V_m, in both the jet deflection and wall jet regions. In the jet deflection region, V_m generally follows Equation (9), and in the wall jet region, Equation (10) describes the experimental data after development of the wall jet. As shown by the experimental data in Figure IV.1, there is a gradual transition between these two regions. In this transition zone, the theory is a reasonable approximation to the experimental data. Figure IV.1 shows velocity profiles in the jet deflection region for constant values of the ratio, D/d. A typical value of D/d for a barge is approximately 15; the ratio increases to 40 for a tanker. These lines of constant D/d intersect the wall jet profile as described by Equation (10). The value of α that defines the boundary between these two regions was determined at the intersection of the lines of constant D/d with Equation (10). That is,

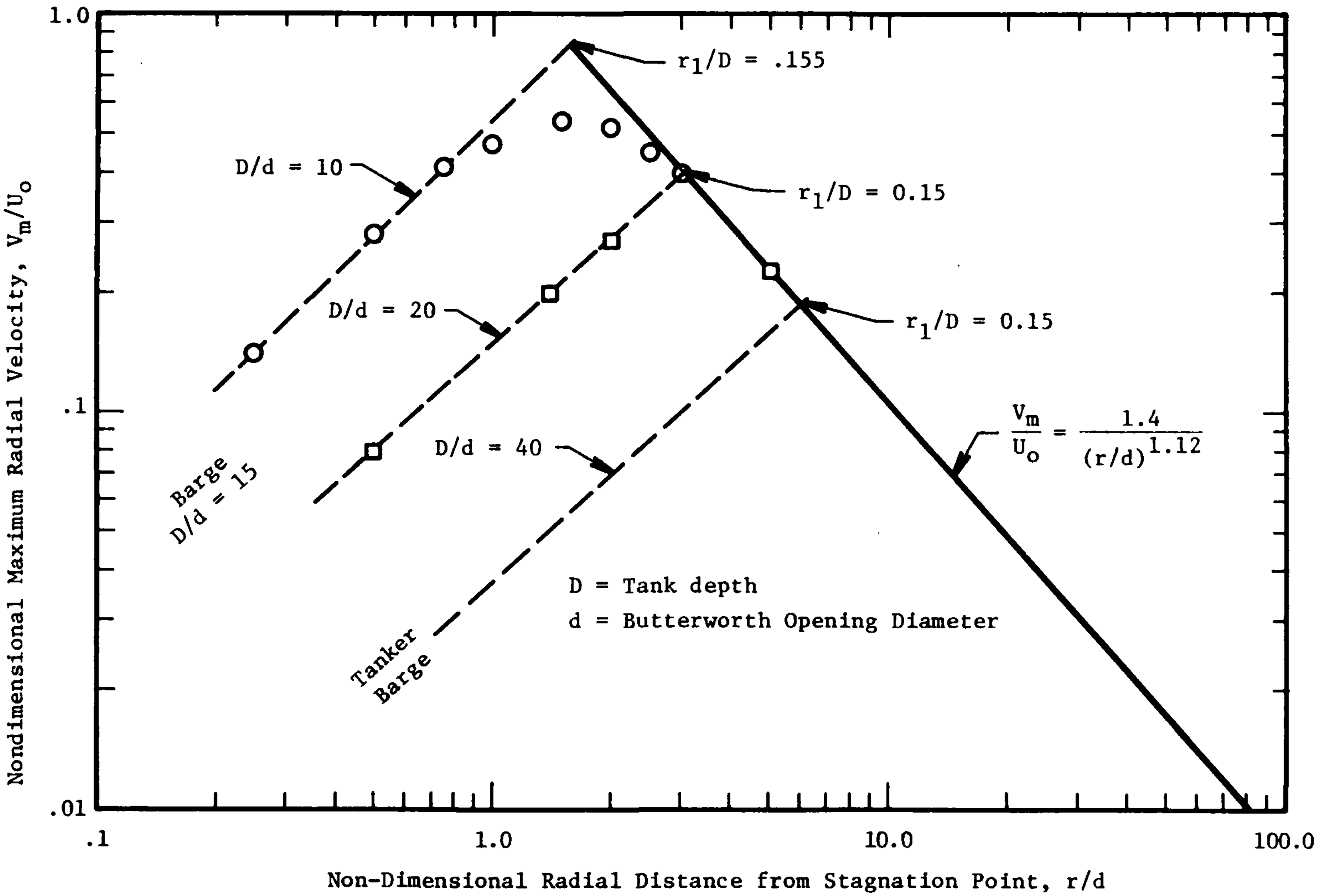


FIGURE IV.1 NONDIMENSIONAL RADIAL VELOCITY PROFILES FOLLOWING JET IMPINGEMENT (Reference 5)

$$\alpha = \frac{r/d}{D/d}\Bigg|_{\text{Profile Intersection}} \tag{16}$$

The indicated value of α is 0.15. Thus,

$$r_1 = 0.15\ D \tag{17}$$

This procedure is consistent with the previous requirement that $V_{m,jd}$ equal $V_{m,wj}$ for determination of K.

The final item in the TANKM formulation is the Henry's law constant or partition coefficient. Two methods are used to calculate H. For dilute, ideal solutions, H is calculated by Dilling's method in Reference 3.

$$H = 16.04\ \frac{p_V M}{TS} \tag{18}$$

where p_V = vapor pressure of the solute (chemical) at solution temperature T
M = solute molecular weight
S = solute solubility in water (finite)

For highly or infinitely water soluble chemicals, H is calculated by the method proposed by Mackay in Reference 9.

$$H = v_w\ p_V\ \gamma_1/RT \tag{19}$$

where v_w = molar volume of water
p_V = vapor pressure of solute at solution temperature T
γ_1 = solute activity coefficient
R = Universal gas constant

The activity coefficient, γ_1, is a thermodynamic quantity that applies to the solute component in a binary liquid mixture and accounts for non-ideal solutions, i.e., solutions that depart from Raoult's law.

There is a corresponding activity coefficient for the solvent component in the mixture. In deriving γ_1, Dalton's law is assumed to apply, e.g., the vapor phase follows the ideal gas law. The activity coefficients for each component in the binary mixture are interrelated through the relative volatility of the components and their component vapor pressures. Both coefficients are strong functions of liquid concentration and vary somewhat with temperature. In the TANKM model, which includes the γ_1 formulation, it is assumed that solution temperatures do not depart significantly from 20-25°C, although temperature effects can be taken into account.

The activity coefficient, γ_1, for a chemical (solute) in water (solvent) solution is based on the following approximation to the two-suffix van Laar equations of Reference 10.

$$\log \gamma_1 = \log \gamma_1^{\infty} \left(1 - x_1\right)^2 \tag{20}$$

where γ_1^{∞} = activity coefficient at infinite dilution
x_1 = mole fraction of chemical in solution

The full van Laar equations apply to all mole fraction concentrations, x_1, from zero to unity. Equation (20) was derived by noting first that the correlating constants in the van Laar equations are of the same order of magnitude so their ratio is roughly unity. Equation (20) results from (1) two binomial expansions in x_1 noting that the mole fraction of the solvent is equal to $1 - x_1$, and (2) retention of only terms that are less than second order in x_1. These expansions assume that x_1 is less than x_2. Beyond that there is no dilute solution approximation.

The mole fraction x_1, is related to the mass concentration of chemical in water

$$x_1 = \frac{1}{\left[1 + \frac{M_c}{M_w} \rho_w \left(\frac{1}{C_L} - \frac{1}{\rho_c}\right)\right]} \tag{21}$$

where M_c, M_w = molecular weight of chemical and water, respectively

ρ_c, ρ_w = mass density of chemical and water, respectively

C_L = mass concentration of chemical in solution.

This conversion assumes that the chemical and water volumes are additive in solution, and it gives the best representation of x_1 over a range of C_L from zero to ρ_c (Reference 11).

There are a number of systems of correlating equations that can be used in calculating γ_1^{∞} as indicated in Reference 9. All of these methods require varying amounts of basic data in order to perform the calculation. The most readily used method is presented in Table 8-17 of Reference 9. The elements of the method are outlined below.

1. The user identifies the functional group that includes the chemical (solute) of interest with water being the solvent. For example, ethanol is an n-primary alcohol and xylene is an n-alkyl benzene.

2. Table 8-17 of Reference 12 identified five correlating constants for each functional group and the appropriate correlating equation.

3. The last pieces of information are obtained from a two-dimensional representation of the chemical structure.
   N_1, N_2 = total number of carbon atoms in solute and solvent molecules, respectively,
   N',N'',N''' = number of carbon atoms in respective branches of branched compounds, including polar groups.

4. γ_1^{∞} is then calculated.

Table IV.1 illustrates the application of this method for several chemicals in water solution.

TABLE IV.1 CORRELATING CONSTANTS AND EQUATIONS FOR CALCULATING γ_1^∞

Solute Category	Solute	Eqn. No.	@25°C (Except As Noted)					N_1	N_2	N_1'	N_1''	$\log_{10}\gamma_1^\infty$
			α	ε	ζ	η	θ					
n-Primary Alcohols	n-Butanol	a	-0.995	0.622	0.558	-	0	4	0	-	-	1.6325
	Ethyl Alcohol	a	-0.995	0.622	0.558	-	0	2	0	-	-	0.528
n-Secondary Alcohols	Isopropyl-Alchol	b	-1.22	0.622	0.170	0	-	3	-	2	2	0.816
n-Ketones	Acetone	b	-1.475	0.622	0.500	0	-	3	0	2	2	0.891
	MEK	b	-1.475	0.622	0.500	0	-	4	0	2	3	1.4297
n-Esters	Vinyl Acetate	b(20°C)	-0.930	0.640	0.260	0	-	4	0	2	2	1.890
n-Monoalkyl Chlorides	Chloroform	a(20°C)	1.265	0.640	0.073	-	0	1	0	-	-	1.978
	EDC	a(20°C)	1.265	0.640	0.073	-	0	2	0	-	-	2.5815
n-Alkyl Benzenes	Toluene	f	3.554	0.622	-0.466	-	-	7	-	-	-	9.7054
	Xylenes	f	3.554	0.622	-0.466	-	-	8	-	-	-	10.3358

Eqn. a $\log_{10}\gamma_1^\infty = \alpha + \varepsilon N_1 + \zeta/N_1 + \theta/N_2$

Eqn. b $\log_{10}\gamma_1^\infty = \alpha + \varepsilon N_1 + \zeta\,(1/N_1' + 1/N_1'') + \eta\,(N_1 - N_2)$

Eqn. f $\log_{10}\gamma_1^\infty = \alpha + \varepsilon N_1 + \zeta\,(1/N_1 - 4)$

SUBSCRIPTS: 1 = Solute (Chemical)
2 = Solvent (Water)

SOURCE: Reference 12

NOTE: As a result of experimental errors, the correlating equation for n-alkyl benzenes overpredicts the numerical value of $\log_{10}\gamma_1^\infty$ (Reference 13). For chemicals in this class, use activity coefficients estimated from the aqueous solubility (Reference 9).

$\log_{10}\gamma_1^\infty = 3.997$ (Toluene)

$\log_{10}\gamma_1^\infty = 4.528$ (Xylenes)

The correlating equations for γ_1^∞ in Reference 12 have their origin in Reference 13. Reference 12 states that the accuracy of the predictive method is roughly eight percent as long as the numerical value of γ_1^∞ is less than two orders of magnitude. This statement apparently applies to all of the binary systems that were studied; i.e., chemical-chemical and chemical-water. For chemical-water systems, in which water is the solvent, the data in Reference 13 suggest that the prediction accuracy is closer to 12 percent on the average.

TANKP Model

The TANKP model applies to tank cleaning operations that do not involve an initial water wash before gas freeing commences. In this type of operation, the tank would contain residues of pure chemical that would evaporate during mechanical ventilation. As noted earlier, the majority of tank cleaning operations involve a water wash. Thus, the TANKP model would apply to the minority of operations where washing may be neither feasible nor practical, but the tanks need to be cleaned. It may be desirable to evaporate a pure chemical residue if the product is insoluble or only slightly soluble in water and the chemical is sufficiently volatile. It is also conceivable that trace quantities of highly volatile residues can be evaporated and the tank gas freed more rapidly than if the tank had been prewashed regardless of the water solubility of the chemical.

The TANKP model differs from the TANKM model in three main areas.

- The TANKP model includes chemical film on the vertical tank walls as well as a residual pool on the tank bottom. The film on the walls does not flow vertically under gravity during ventilation. There is no film on the underside of the weather deck.
- The temperature of the tank walls can vary from the weather deck to the tank bottom. The rationale for this assumption

is that tank bottom may be at or near water temperature while the walls beneath the weather deck would approach ambient temperature. Wall and tank bottom temperatures do not vary with time.

- The model for residue evaporation flux applies strictly to pure solvents and excludes solvent mixtures or aqueous solutions.

The assumption regarding homogeneity of vapor space concentration and the implications for air flow over the liquid surfaces are the same for TANKP as TANKM. As in TANKM, the ambient supply air to the blower is assumed to be vapor-free.

A detailed derivation of the TANKP model appears in Reference 1. The governing equations and additional assumptions are summarized below.

At any time, t, a mass balance on the vapor in the tank results in the following ordinary differential equation.

$$\forall \frac{dC}{dt} = \dot{m}_G - CQ \tag{22}$$

where $\forall$ = tank volume
C = mass concentration of vapor in air
Q = blower flow rate
$\dot{m}_G$ = instantaneous, total evaporation rate of pure chemical from residual films on the tank walls and bottom.

The evaporation rate model for $\dot{m}_G$ is based on Reference 14. Gray's model for the evaporative flux of vapor from an element of liquid surface can be reduced to the following equation.

$$\frac{d\dot{m}}{dA} = \frac{DMP_v}{RT_GF} \tag{23}$$

where $\dot{m}$ = local mass evaporation rate
A = local element of liquid surface area
D = diffusion coefficient
M = molecular weight
P_V = vapor pressure of chemical film corresponding to the local wall temperature or tank bottom temperature
R = Universal gas constant
T_G = temperature of in-tank vapor space, assumed equal to temperature of vapor discharged from tank during gas freeing
F = thickness of stagnant interface film that exists between the residual chemical layer and the air flow over the liquid layer.

Equation (23) contains the following assumptions

- a uniform concentration profile exists above the liquid surface, thus vapor mixing is instantaneous and uniform,
- the *air-vapor mixture within the film thickness*, F, *is stagnant*,
- mass transfer within the film is controlled by molecular diffusion,
- flow velocity profiles are laminar,
- a single component liquid evaporates into a mixture of its own vapor and air,
- the elements of liquid surface are continually presented with fresh, uncontaminated air,
- the moles of liquid evaporated per unit time are negligible compared to the number of moles of air that sweep the liquid surface per unit time, and
- the vapor pressure of the liquid is much greater than the partial pressure of the vapor in the tank.

Following Gray's approach, the diffusion coefficient, D, is represented by Equation (24).

$$D = \frac{0.425\ T_G^{3/2}}{P(MT_b/G)^{1/2}} \qquad (24)$$

where T_b = chemical boiling point at atmospheric pressure
G = liquid surface tension
P = atmospheric pressure

The film thickness, F, in Equation (23) is given by the following empirical expression.

$$1/F = 0.217\ Sc^{-0.9}\ (ScU)^{0.625}\ Sc^{0.3} \tag{25}$$

where Sc = Schmidt number, ν/D
ν = kinematic viscosity of air
U = effective air velocity over the liquid surfaces.

Note that the film thickness, F, that was used by Gray for pure product evaporation is analogous to the two-layer film model presented by Liss and Slater in Reference 5 for component mass transfer at a liquid-gas interface. The air velocity, U, in Equation (25) is identical to the quantity U_{wind} that was presented earlier for the TANKM model; the assumptions and equations are the same in both instances.

The TANKP model formulation is completed by specifying the thickness of the residue on the tank bottom, TPOOL, a uniform initial chemical film thickness on the tank walls, TFILM, and an initial vapor concentration in the tank at the beginning of ventilation, C_{ov}.

The local evaporative flux model is independent of vapor space concentration. The net effect of this decoupling is that local flux rates can be integrated over the liquid surfaces subject to prescribed local temperature variations to yield a total evaporation rate profile as a function of time. The time variation arises from the fact that local evaporation will continue at a constant rate until a time equal to

$$\tau_{\ell} = t_{film}\ \rho_F/(d\dot{m}/dA) \tag{26}$$

where τ_{ℓ} = local evaporation time
ρ_F = pure chemical density

Local evaporation ceases for times greater than τ_{ℓ}. Analogous statements apply to the pool of residual chemical on the tank bottom. The evaporative contribution from the walls and bottom are then summed to produce the total evaporation rate, $\dot{m}_G(t)$. At this point, Equation (22) can be integrated numerically subject to the initial condition and the evaporation rate schedule.

IV.2.2 Ventilation Test - Model and Full Scale

Summary of Test Conditions

A total of 26 ventilation tests were conducted to collect data on independent and dependent variables for use in validating the models described in Section IV.2.1. A composite list of the important conditions of these tests are shown in Table IV.2. The first 18 tests were conducted on full scale ship and barge tanks. The remaining eight tests were conducted in a model scale tank at SwRI. The majority of all tests (10 full scale and 8 model scale) were performed on tanks that did not have internal structure.

Extensive model scale tests of dilution ventilation in the presence of pure chemical residue evaporation were performed in Phase I. Consequently, five of the eight model scale tests during Phase II involved tank ventilation in the presence of a residual layer of chemical/water solution on the tank bottom. Only one of the model scale tests was performed with a residual layer of pure chemical. The remaining two model scale tests were run without a liquid layer to validate test equipment, procedures, and the assumption of a well-mixed vapor space that leads to exponential dilution ventilation without residue evaporation.

The chemical/water layer was also the predominant type of residue in the full scale tank ventilation tests. A total of 13 test tanks contained the two-component solution residue while five test tanks had a layer of pure chemical during ventilation.

TABLE IV.2. SUMMARY OF FULL AND MODEL SCALE TANK VENTILATION TEST CONDITIONS

TEST NO.	TERM-INAL	VESSEL TYPE	CHEMICAL	TANK NO.	INTERNAL TANK STRUCTURE	WASHED PRIOR TO VENT	TANK VOL. (m^3)	TANK DEPTH (m)	VENT FLOW RATE (m^3/min)	VENT DIAM. (m)	INITIAL CHEM. VAPOR CONC. (ppm)	INITIAL CHEM. LIQUID CONC. (mg/ℓ)	LIQUID RESIDUE HEIGHT (cm)	SOLU-BILITY OF CHEM. @ 20°C (mg/ℓ)	VAPOR PRES. @ 20°C (mm Hg)	SURFACE TENSION @ 20°D dynes/cm	MOLE-CULAR WT. g/mole	NORMAL BOILING POINT T_B (°K)
1	H	Tanker	Acetone	3CS	Yes	Yes	1099	14	99.4	.305	5000	NM①	NM	Infinite	176	NA	58.08	NA
2	"	"	n-Butanol	10CP	No	Yes	1246	14	99.4	.305	570	"	"	77,000	4.4	"	74.12	"
3	"	"	"	"	No	Yes	1246	14	99.4	.305	410	153	"	77,000	4.4	"	74.12	"
4	A	Barge	Ethylene Dichlo-ride	3	No	Yes	573	4.21	97.4	.305	65610	4505	"	8,690	61	"	98.97	"
5	"	"	Chloro-form	1	No	No	571	4.42	96.3	.368	39000	Pure Chem.	"	NA	155	27.1	119.39	334.3
6	B	Tanker	Xylenes	2S	Yes	Yes	1695	14.9	140	.305	9030	Pure③ Chem.	"	198②	6.5②	29.1②	106.16	411.4②
7	"	"	Methyl Ethyl Ketone	2CA	No	Yes	1425	14.9	110	.305	292	26130	"	213,000	78.6	NA	72.11	NA
8	"	"	Ethanol	3S	Yes	No	1891	14.9	101	.305	27700	Pure Chem.	"	NA	42.4	22.5	46.07	351.3
9	"	"	"	3C	No	No	1067	14.9	83	1.22	20000	"	"	"	42.4	22.5	46.07	"
10	"	"	"	3P	Yes	No	1891	14.9	120	.305	582	"	"	"	42.4	22.5	46.07	"
11	"	"	Regular Gasoline	2	Yes	Yes	2032	14.0	117.8	.321	110250	NM	"	50	325-④ 501	NA	72	NA
12	"	"	Unleaded Gasoline	4	Yes	Yes	2080	14.9	132.4	.321	13980		"	50	"	"	"	"

TABLE IV.2. SUMMARY OF FULL AND MODEL SCALE TANK VENTILATION TEST CONDITIONS (CONTD)

TEST NO.	TERM-INAL	VESSEL TYPE	CHEMICAL	TANK NO.	INTERNAL TANK STRUCTURE	WASHED PRIOR TO VENT	TANK VOL. (m^3)	TANK DEPTH (m)	VENT FLOW RATE (m^3/min)	VENT DIAM. (m)	INITIAL CHEM. VAPOR CONC. (ppm)	INITIAL CHEM. LIQUID CONC. (mg/ℓ)	LIQUID RESIDUE HEIGHT (cm)	SOLU-BILITY OF CHEM. @ 20°C (mg/ℓ)	VAPOR PRES. @ 20°C (mm Hg)	SURFACE TENSION @ 20°D dynes/cm	MOLE-CULAR WT. g/mole	NORMAL BOILING POINT T_B (°K)
13	K	Tanker	Chloro-form	5C	No	No	1903	15.3	NM	.305	2950	Pure Chem.	NM	NA	155	27.1	119.39	334.3
14	"	"	"	"	No	Yes	1903	15.3	"	.305	750	210	"	8,690	155	NA	"	NA
15	H	Barge	Toluene	1S	No	Yes	223	3.6	75.6	0.483	89	515	"	515	22.7	"	92.1	"
16	"	"	"	3P	No	Yes	223	3.6	45.0	0.305	620	4	"	515	22.7	"	"	"
17	"	"	88% Iso-propyl-Alcohol	1S	No	Yes	414	3.6	63.5	0.483	58	286	"	Infinite	33.6	"	60.1	"
18	"	"	Vinyl Acetate	4S	No	Yes	414	3.6	71.6	0.483	539	272	"	25,000	93	"	86.1	"
19	SwRI	Model Scale Tank	Acetone	NA	No	NA	48.9	3.66	4.76	0.102	19100	NA	NA	NA	176	"	58.08	"
20	"	"	"	"	No	Yes⑤	"	"	4.94	"	18400	11100	1.19	Infinite	"	"	"	"
21	"	"	Ethyl Acetate	"	No	NA	"	"	4.84	"	20200	NA	NA	NA	69	"	100.12	"
22	"	"	"	"	No	Yes⑤	"	"	4.94	"	18200	9500	1.19	79,000	"	"	"	"
23	"	"	"	"	No	"	"	"	4.93	"	39000	9900	0.76	"	"	"	"	"
24	"	"	"	"	No	"	"	"	5.02	"	18300	1600	1.26	"	"	"	"	"
25	"	"	"	"	No	"	"	"	4.98	"	2500	8500	1.19	"	"	"	"	"
26	"	"	"	"	No	No⑥	"	"	5.13	"	23700	Pure Chem.	1.19	"	"	25.4	"	350

① Not measured
② P-xylene
③ Two phase mixture of chemical and wash water
④ Estimated from Data Book on Hydrocarbons, by J. B. Maxwell.
⑤ Premix Chemical/Water Mixture Residue
⑥ Pure Chemical Residue
NA This physical property is not important to the applicable model

A total of 18 full and model scale ventilation tests resulted in data that was appropriate to the two-component ventilation model, and a total of six tests corresponded to the pure component model formulation. Table IV.2 illustrates that these tests involved a wide range of physical properties, tank geometries and initial tank conditions. With respect to physical properties, a total of 13 different pure chemicals and one mixture (gasoline) were encountered. An important physical property, vapor pressure, ranged from 4.4 mm Hg at 20°C for the two butanol tests to 176 mm HG for the two acetone tests, which does not include gasoline ventilation tests. For the two-component model, chemical solubilities ranged from 50 mg/ℓ for gasoline to infinitely soluble for the chemicals, acetone and isopropanol. Surface tension, which is used to calculate the diffusion coefficient in the pure component model, ranged from 22.5 to 29.1 dynes/cm for the ventilation of tanks that had contained ethanol and xylene, respectively.

A wide range of tank geometries were encountered. Tank volumes ranged from 1067 m^3 to 2082 m^3 for full scale shiptanks and from 223 m^3 to 573 m^3 for full scale barges. Tank heights in full scale varied from 14.9m to 3.6m for ship and barge tanks, respectively. The majority of the tank ventilation inlet diameters were 0.305m, which coincides with the diameter of the typical Butterworth opening. Blowers were normally positioned over the Butterworth opening. In the majority of the tests, these blowers supplied ambient air to the tank; tank vapors were exhausted through the open tank hatch. On a few tests, the air flow direction was reversed by inverting the blower, which was an operational procedure on the ship. Consequently, the tank hatch became the vent inlet and the Butterworth opening became the vent outlet.

The starting conditions of the full scale tests were dictated by the volatility and solubility of the chemical, the extent of tank washing, and the time lapse between the end of washing or product discharge and the beginning of ventilation. A broad range of initial conditions were encountered. Initial tank vapor concentration ranged from 58 ppm for isopropylalcohol to 110,250 ppm for gasoline. Initial chemical concentration in the binary liquid residue varied from 4 mg/ℓ for toluene to 26,130 mg/ℓ for methyl ethyl ketone. While accuract measurement of the initial thickness of the residual liquid layer on the tank bottom was not possible on full scale tanks, visual observation through the expansion trunk suggested that the residue thickness ranged from a very thin layer having the appearance of a "wet sidewalk" up to an estimated maximum thickness of approximately 4 - 6 cm. A much higher degree of control and measurability was achieved for initial liquid and vapor phase concentrations and initial residue thickness in the model scale tests. The range of these variables were within the ranges noted above for the full scale tests.

Test Equipment and Measurements

Model Scale Tank Tests

Figure IV. 2 illustrates the 12-foot cube model scale test tank and associated test apparatus. By virtue of its size, the 12-foot tank approximates the dimensions of a full scale barge or a 1/3-scale model of a ship tank. The test tank contains a 0.102m diameter vent inlet, which is 1/3 of the diameter of a full scale Butterworth opening (0.305m).

The test tank was fitted with four in-tank sampling ports and one exhaust vapor sampling port. During ventilation tests that included a residual chemical/water layer, liquid samples were withdrawn at the four locations noted in the top view of Figure IV.2. Tank vapor temperatures were measured at two vertical locations in the tank, T_1 and T_2. The temperature of the residual chemical/water mixture was measured at T_3. A graduated aluminum rod was positioned in front of each of the six observation windows to determine the initial depth of the residual liquid. A mixing fan was mounted at the top of the tank and was used to accelerate the evaporation of pure chemical for the initial vapor concentration in the tank prior to each ventilation test. Homogeneous mixtures of chemical/water solution, which simulated post washing residues in full scale, were added to the test tank from an external 55-gallon mixing drum. Ventilation air was directed to the tank vent inlet through a 0.102m diameter plastic pipe by a centrifugal blower. Flow rate was obtained from pitot-static tube readings taken in a long straight section of this pipe downstream of the blower. Chemical vapor concentrations as methane were measured with a

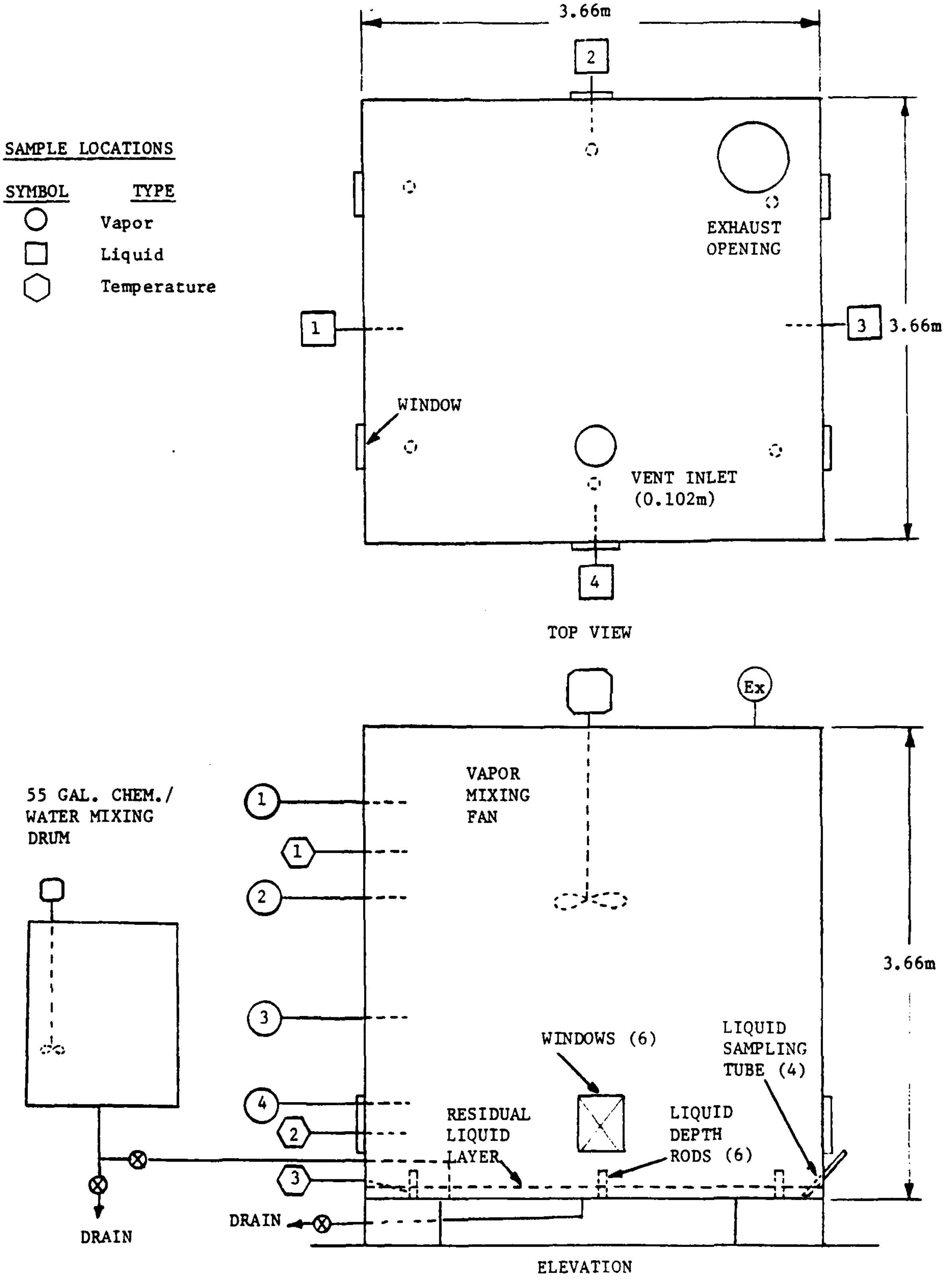


FIGURE IV.2 3.66 m CUBE VENTILATION TEST TANK APPARATUS

Century Systems OVA 128 Total Hydrocarbon Analyzer. Following a test, the OVA was calibrated to the specific chemical vapor. Liquid samples were gathered during the test and were analyzed with a Baseline 1030A Gas Chromatograph.

Initially, Test Nos. 19 and 21 were conducted without a residual layer of chemical or chemical/water solution to verify that complete vapor mixing was achieved in the model scale tank. All five vapor sampling points were utilized during these tests. The concentration time-histories at all sampling locations for both tests are shown in Figures IV.3 and IV.4. These figures illustrate that complete mixing was achieved because the concentration time-histories coincide with the theoretical dilution curve.

Full Scale Tank Tests

The measurement methodology that was used in full scale for vapor concentration measurements was similar to that which was described for the model scale tests. On the majority of the tests, the tank vapor concentrations were measured at the tank hatch where the vapors were being exhausted. In some instances, it was possible to obtain concentration-depth profiles prior to ventilation by using a dropline. For those tests in which air was drawn into the tank through the tank hatch, a dropline was used to retrieve samples from near the tank bottom so that the tank vapor concentration time-history could be measured.

Blower flowrate was measured with a hand-held vane anemometer. A multipoint velocity traverse was normally made over the entire cross-section of the discharge opening. The average velocity was calculated and multiplied by the cross-sectional area of the opening to give the ventilation flowrate. On a few of the initial tests, blower flowrate was estimated indirectly from the supply pressure (steam or compressor air) to the blower and the blower capacity curves.

Two methods were used to collect a sample of the residual chemical/water solution in the tank prior to beginning of ventilation.

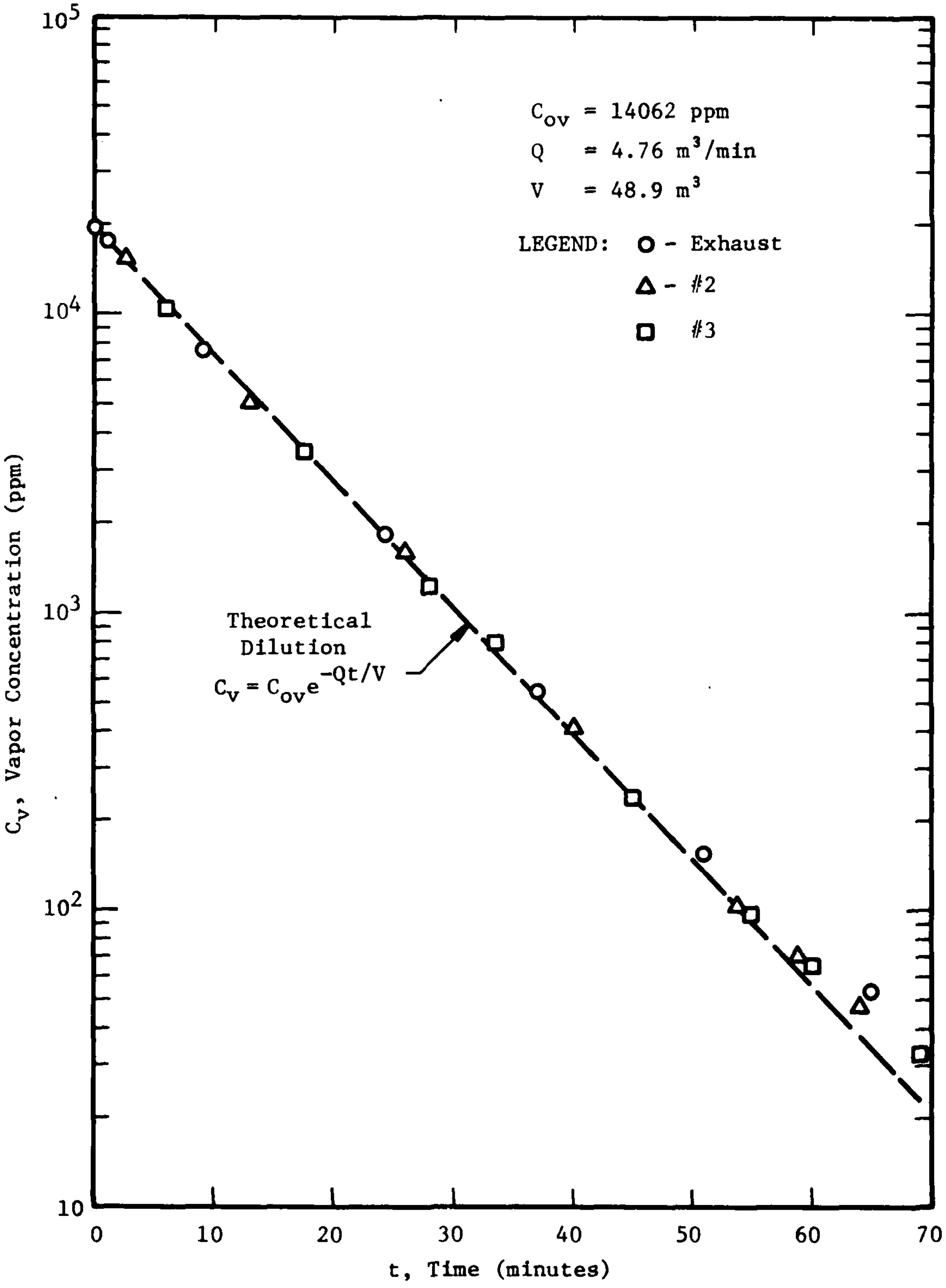


FIGURE IV.3 TEST NO. 19: VENTILATION OF ACETONE WITH NO RESIDUAL LIQUID LAYER

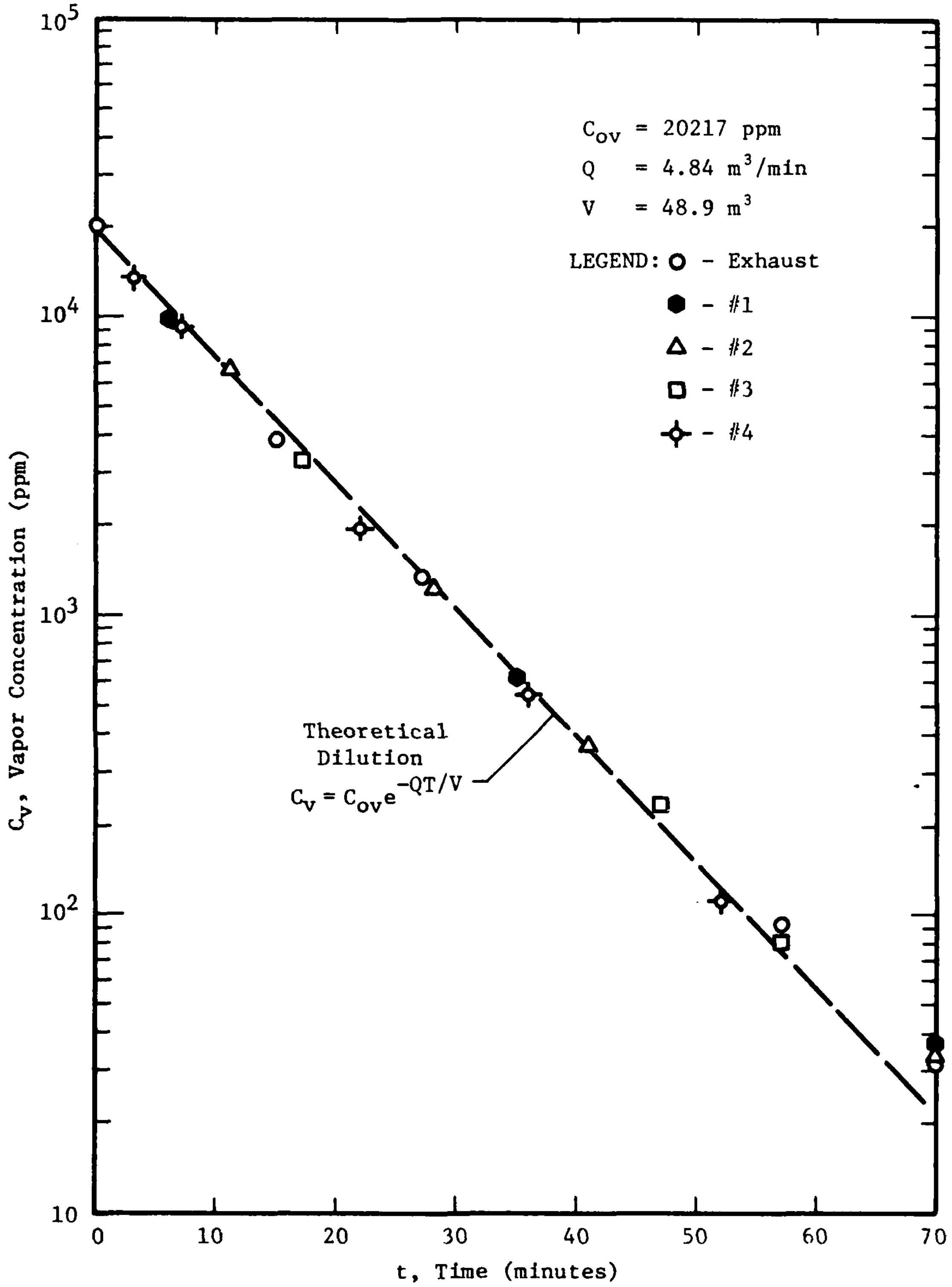


FIGURE IV.4 TEST NO. 21: VENTILATION OF ETHYL ACETATE WITH NO RESIDUAL LIQUID LAYER

This sample was analyzed to determine the initial chemical concentration in the solution. One method consisted of drawing a liquid sample of the wash slops from a sample valve immediately downstream of the tank discharge pump. This method proved to be the simplest when the discharge lines had this type of valve. The other method consisted of lowering a sample bottle on a line into the tank from the deck. This method was satisfactory for shallow barge tanks; however, it proved to be impractical for deep ship-tanks. In some instances, the tank depth or unavailability of sample valves precluded collection of a wash slop sample. For these cases, initial solute (chemical) concentration in water could not be determined.

Measurement of the residual liquid thickness proved to be the most difficult parameter to quantify in full scale. For the most part, only a quantitative estimate was obtained by visually observing the appearance of the tank bottom after washing had been completed. With the exception of Tests 4 and 6, the tank bottoms had the appearance of a "wet sidewalk".

The above discussion pertains to the major test parameters. Other variables and information were also measured or documented as indicated in the data acquisition forms that appear in Appendix A.

IV.2.3 Comparison of Theory and Experiment

Two analytical models were developed to describe dilution ventilation (gas freeing) of cargo tanks. The first model, TANKM, describes the gas freeing process in which chemical evaporates from the aqueous solution that remains on the tank bottom after an initial water wash. The second model, TANKP, applies to gas freeing operations in which there is no water wash, and it includes evaporation of pure chemical residues.

Ship or barge tanks may or may not contain internal structure. The majority of the tanks that were encountered during field operations did not have internal structure. Tanks with internal structure exist primarily on older vessels or vessels that are dedicated to non-chemical products. In their present form, neither model includes the effect of internal structure on the gas freeing and evaporation processes. Therefore, the models apply to the majority of tanks on barges and recently-constructed tankers that transport pure chemicals.

Two-Component Model TANKM - No Internal Tank Structure

Based on the comparison of experimental test data and model predictions, the two-component binary mixture model, TANKM, adequately predicts the concentration-time history of the vapors that are discharged from a tank without internal structure during dilution ventilation, provided that certain key variables are known to a reasonable accuracy. These variables are δ, the initial residue thickness on the tank bottom, and C_{OL}, the initial solute concentration in solution. This caveat cannot be overemphasized because, as has been stated previously, these parameters are not readily amenable to measurement in the field. The residue thickness can only be estimated visually from the deck above a 40-foot deep tank. A wash slop sample, if it can be collected, may not be totally representative of the remaining solution in the tank at the beginning of ventilation. In addition, solution samples collected and refrigerated in the field may not be analyzed for an extended period of time, and biodegradation of the chemical solute becomes a major concern.

In case that either or both of these two variables, δ and C_{OL}, are not known, the experimental data were used to develop a selection criterion that served as a guide in estimating their numerical values for input to the model prediction. That criterion is stated below.

$$\delta\, C_{OL}\, A = Q \int_0^{t_f} C_v(t)dt + V\,[C_v(t_f) - C_{ov}] \qquad (27)$$

where A = area of the tank bottom
C_v = experimentally-measured vapor concentration
t_f = time at which the last value of C_v was measured
C_{ov} = initial vapor concentration in the tank at the beginning of ventilation.

The lefthand side of that equation represents the initial mass of chemical in solution at the beginning of ventilation. The righthand side of the equation is an estimate of the solute mass that evaporated during the test period. This equation is an approximation because it does not include chemical that remains in solution and has not been evaporated at the end of the test, which normally was defined to be the time when crew members entered the tank to perform manual cleaning. The experimental $C_V(t)$ data were fitted to a nonlinear regression equation that permitted evaluation of the righthand side of the above equation. Thus, the criterion provided an estimate for the product of δ and C_{OL}. If neither δ nor C_{OL} were known, then the following procedure was applied.

- A reasonable range of δ values were defined based on visual observation.
- The corresponding values of C_{OL} were calculated using the selection criterion.
- Complementary $\delta - C_{OL}$ pairs were input to the model.
- The order pair of variables that produced the best visual fit was accepted.

If δ or C_{OL} were known, but not both, then the following procedure was used.

- The selection criterion and known variable were used to calculate the unknown variable.
- Model prediction was then compared to the experimental data.
- If the prediction was not acceptable, then the values of δ and C_{OL} were perturbed about their criterion value until an acceptable prediction was obtained. This step is justified because the selection criterion is an approximation, at best, and constitutes a starting point for parameter perturbation.

In the aggregate, 14 model and full scale tests were conducted for the TANKM model, which does not include the effect of internal structure. Based on these tests and the model predictions, the numerical values for the product, δC_{OL}, fell into two groups.

- Group I - Based on a review of the test documentation, values of δC_{OL} in this group represented tank cleaning operations where a longer washing period and/or more efficient stripping of slops would have reduced C_{OL} and/or δ. For this group, the average value of δC_{OL} was

$$\delta C_{OL}\Big|_{ave} = 1.16 \times 10^5 \text{ mg/m}^2$$

In this group, the values of δC_{OL} ranged from 0.099×10^5 to 3.96×10^5 mg/m^2.

- Group II - Tests in this group tended to reflect a very thorough tank washing and efficient stripping operations. The thoroughness of the washing was reflected in a relative reduction of C_{OL} while the stripping efficiency reflected use of portable stripping pumps after the limits of deepwell pumps on in-tank stripper lines had been reached. For this group

$$\delta C_{OL}\Big|_{ave} = 160.6$$

The values of δC_{OL} ranged from 16 to 380 mg/m^2.

Fourteen model and full scale tests were conducted for the TANKM model without internal structure. A comparison of theory and experiment is presented below for a subset of these tests. The remaining comparisons are presented in Appendix B.

Five ventilation tests (Tests 20, 22, 23, 24, and 25) were conducted in the model scale test tank in the presence of a residual liquid layer of chemical and water. These tests were conducted to (1) examine the effect of evaporation from a thin layer of dilute chemical in water on the experimentally measured concentration-time history curve, and (2) compare the experimental data with predictions generated by the two-component model derived in Section IV.2.1. By physically varying the key test parameters, such as chemical residual liquid layer thickness, initial chemical concentration in the liquid, and the initial tank vapor concentration, the validity of the model predictions could be demonstrated.

The conditions under which these tests were conducted were illustrated in Table IV.2. Tests 20 and 22 were run under identical conditions, with the exception of the type of chemical. The initial chemical concentration in the liquid was varied between Tests 22 and 24. The difference between Tests 22 and 25 was the initial tank vapor concentration. Last of all, the residual liquid layer, as well as the initial tank vapor concentration were adjusted between Tests 22 and 23.

The resulting experimental concentration-time histories for all five tests are illustrated in Figures IV.5 through IV.9. The experimental data indicate that, in all cases, evaporation is occurring, as evidenced by the divergence of the experimental data from the theoretical dilution curve (i.e., pure dilution ventilation with no evaporation, $C_v=C_{ov}e^{-Qt/V}$). The divergence is quite profound considering that for all tests, with the exception of Test 24, the chemical concentration in liquid was approximately 10% by volume or less. For Test 24, the liquid concentration was almost an order of magnitude lower.

Of even greater importance is the close agreement between the two-component model predictions and the experimental data. The tests which gave the best agreement were Tests 22 and 23. For the remaining tests, the predicted $C_v(t)$ histories are considered to be in quite good agreement with the experimental data because

- the model formulation does not include the complex, unsteady, three-dimensional flow field that exists in the tank, and
- decisions regarding time to man-entry into the tank will be conservative because the model overpredicts concentration at the end of the test.

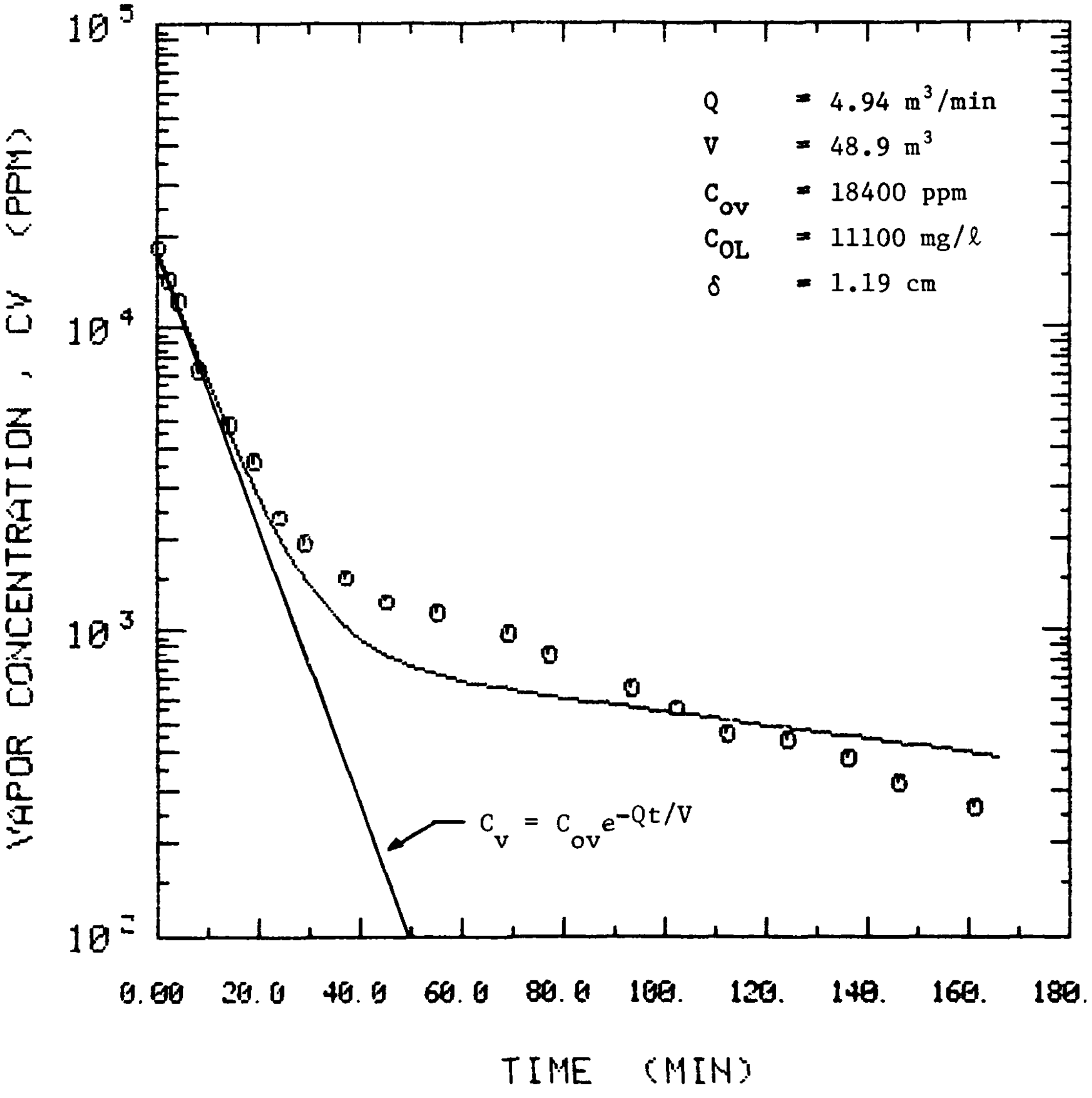


FIGURE IV. 5. VENTILATION TEST NO. 20 CONDUCTED IN A MODEL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF ACETONE AND WATER

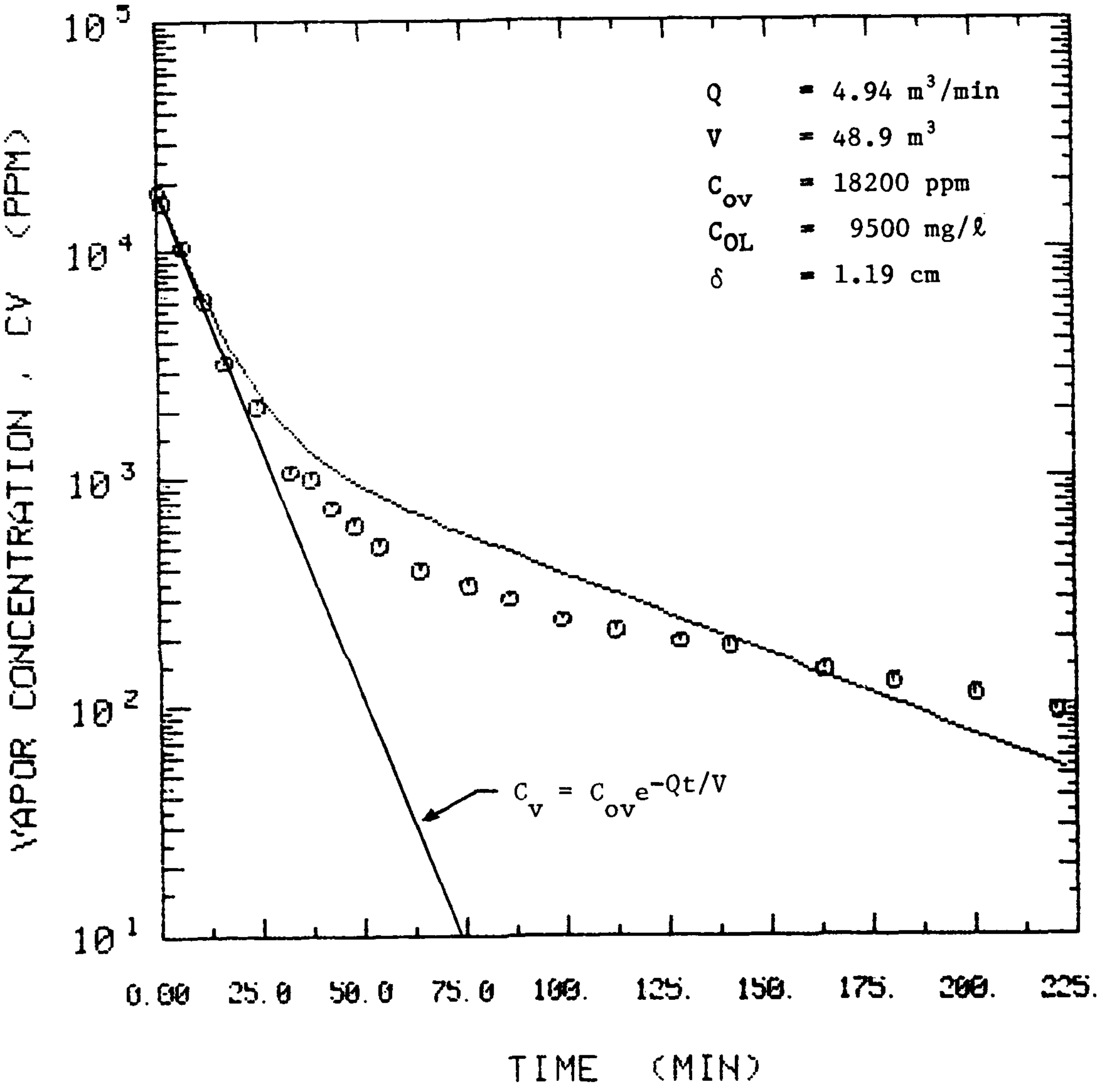


FIGURE IV. 6. VENTILATION TEST NO. 22 CONDUCTED IN A MODEL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF ETHYL ACETATE AND WATER

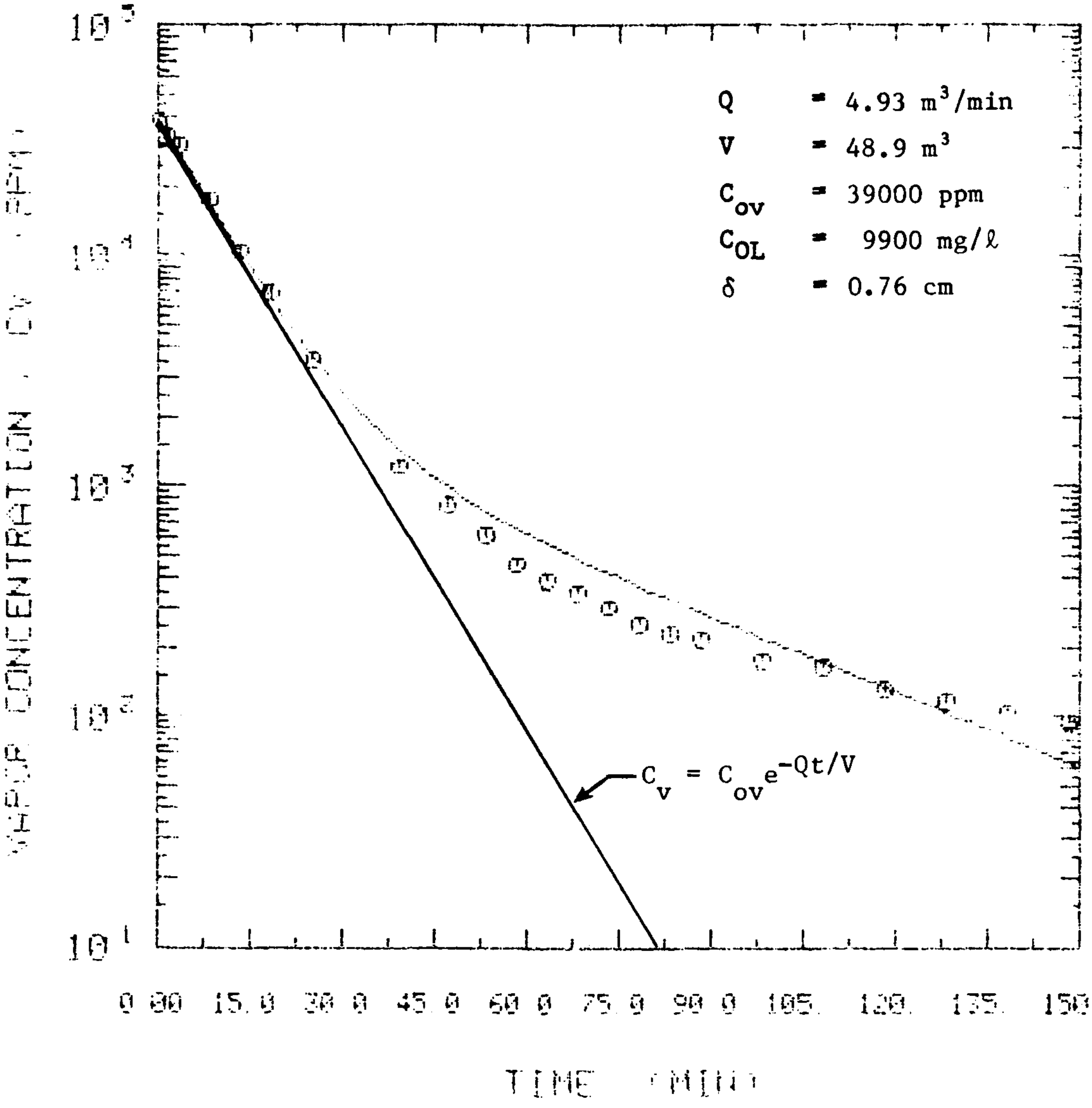


FIGURE IV. 7. VENTILATION TEST NO. 23 CONDUCTED IN A MODEL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF ETHYL ACETATE AND WATER

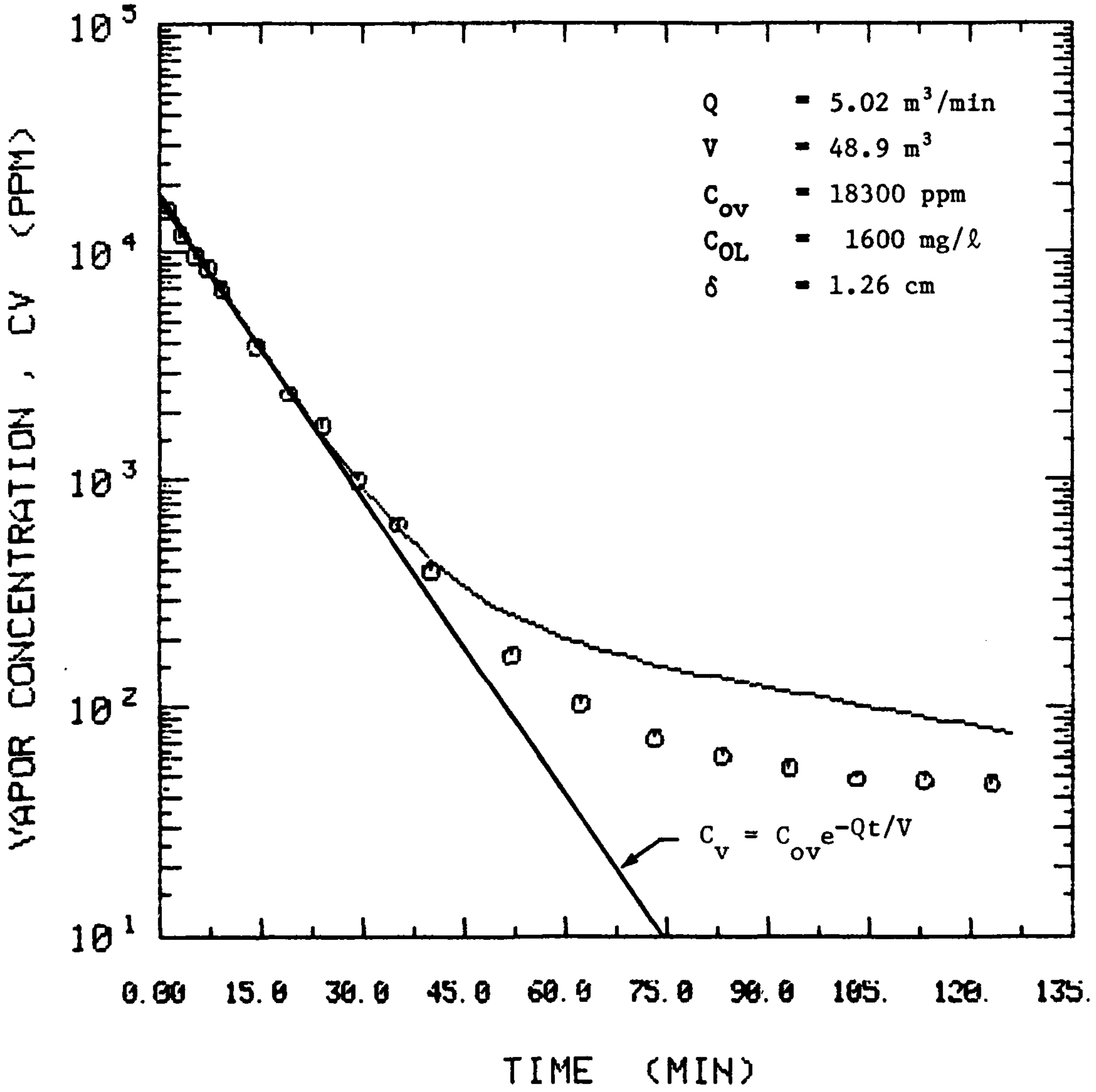


FIGURE IV. 8 . VENTILATION TEST NO. 24 CONDUCTED IN A MODEL SCALE TANK WITH STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF ETHYL ACETATE AND WATER

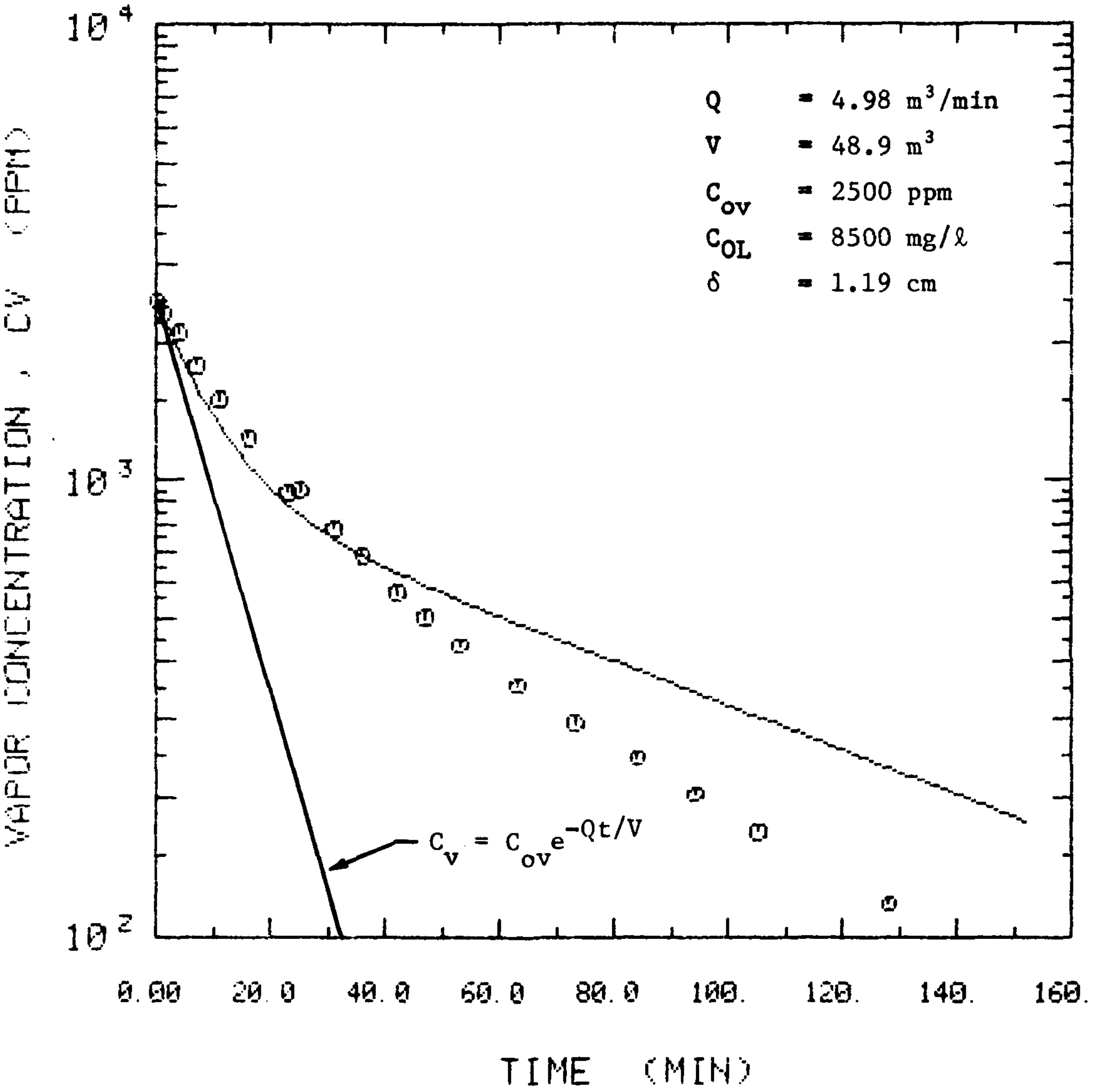


FIGURE IV. 9. VENTILATION TEST NO. 25 CONDUCTED IN A MODEL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF ETHYL ACETATE AND WATER

Note, that in these five model predictions, measured values of δ and C_{OL} were used; the selection criterion was inappropriate, and the product δC_{OL} could be classed as Group I.

Comparison of the TANKM predictions with the experimental full scale ventilation test data for Tests 2, 3, 4, and 18 are presented below to illustrate certain key features. The comparisons for the other full scale tests in which there was no internal structure are shown in Appendix B. Tests 2 and 3 were selected to show the effect of evaporation on the tank ventilation process in the presence of an aqueous solution of a relatively soluble chemical with low vapor pressure in a tank having a low initial tank vapor concentration. Test 4 contained a chemical whose physical properties were exactly opposite to those of Tests 2 and 3. In addition, the initial tank vapor concentration of Test 4 was relatively high. Tests 2, 3, and 4 are included in Group I. Lastly, Test 18 was chosen to illustrate the characteristics of a number of tank ventilation tests, including Tests 14, 15, 16, and 17 in Appendix B, which were performed under conditions of reduced liquid and vapor concentrations as a result of efficient washing and *stripping operations* that characterize Group II. The four tests indicated above utilized the δC_{OL} selection criterion to varying degrees.

As shown in Table IV.3, Tests 2 and 3 were conducted with the same chemical in the same tank but on two separate occasions. In fact, the washing procedure and the length of the washing period that was used prior to tank ventilation was identical in both cases. Since the same blower and blower flowrate was used during each ventilation, these two tests approximate a replication of a tank ventilation. Neither C_{OL} nor δ was measured in Test 2, and only C_{OL} was measured in Test 3. Consequently, the method that described the analytical determination of the selection criterion was used to provide the model with reasonable input values for these parameters.

Three values of δ (1, 0.5, and 0.2 cm) were selected because they best described the estimated range of residual liquid thicknesses that were visually observed prior in each test. Based on the experimental concentration-time histories for these two tests, a range of C_{OL} values were calculated that satisfied the integral expression for the selection criterion and were also below the solubility limit of butanol. These estimates are shown in Table IV.3.

TABLE IV.3. RANGE OF JUSTIFIABLE VALUES FOR C_{OL} AND δ FOR TESTS 2 AND 3

TEST NO.	M_{evap} (mg)	TANK AREA (m^2)	$C_{OL} \times \delta$ (mg/m^2)	C_{OL} (mg/m^3)	δ (cm)
2	0.57×10^7	94.81	0.60×10^5	0.60×10^7	1.0
				0.12×10^8	0.5
				0.30×10^8	0.2
3	0.50×10^7	94.81	0.53×10^5	*0.153×10^6	34.3
				0.530×10^7	1.0
				0.106×10^8	0.5
				0.265×10^8	0.2

*Measured from single sample collected prior to start of ventilation.

In addition, δ was calculated based on the measured value of C_{OL} for Test 3. The experimental concentration time histories for Tests 2 and 3 and the model predictions generated by the three $C_{OL} - \delta$ combinations are shown in Figures IV.10 and IV.11, respectively. The divergence between the experimental data for both tests and the theoretical dilution curve ($C_v = C_{ov} e^{-Qt/V}$) definitely illustrates the effect of evaporation on the ventilation of both tanks.

The values of C_{OL} and δ that yield the best agreement in each case are the pair with the highest C_{OL} and lowest δ. The poorest agreement was obtained for the combinations having the lowest C_{OL} value for both tests. It is apparent that the $C_{OL} \times \delta$ pair, based on the measured C_{OL} value for Test 3 would also yield poor results. In fact, an unrealistically large δ value would be required to maintain the δC_{OL} product calculated by the selection criterion. The reason that a low

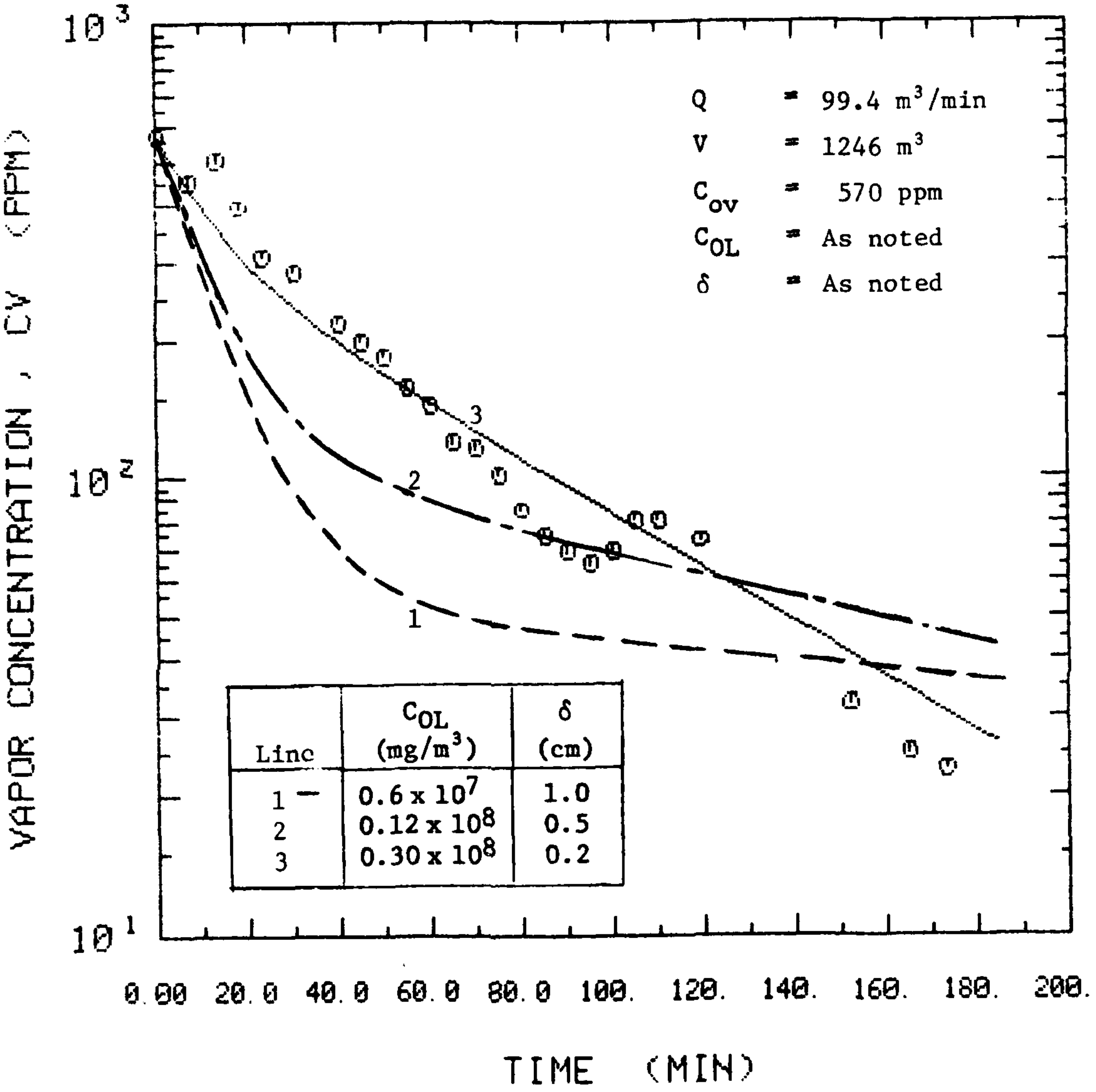


FIGURE IV.10. VENTILATION TEST NO. 2 CONDUCTED IN A FULL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF n-BUTANOL AND WATER

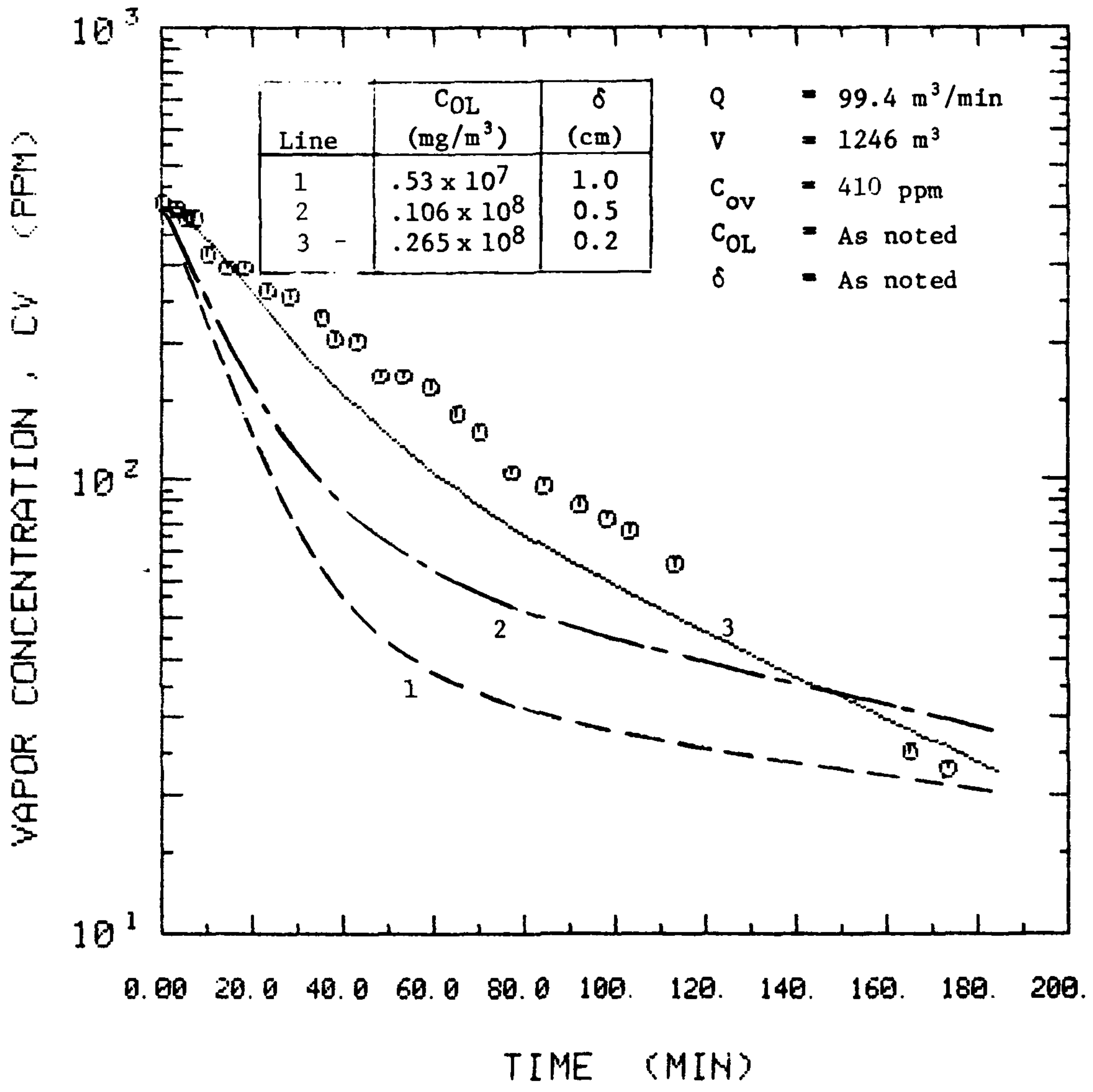


FIGURE IV.11. VENTILATION TEST NO. 3 CONDUCTED IN A FULL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF n-BUTANOL AND WATER concentration of chemical in the liquid may have been measured in Test 3, is attributed to an extended length of time between liquid sample collection and analysis. Biodegradation of the wash water sample was suspected.

The tank in which Test 4 was conducted underwent two separate ventilation operations. The first ventilation operation, which will be discussed here, was conducted in the presence of an unusually thick residual layer (estimated visually to be between 4 - 6 cm). Ethylene dichloride, a low solubility chemical, had been carried in the tank prior to washing. Because the actual residual liquid thickness was not measured, the selection criterion was estimated using the previously defined procedure for integrating the experimental data. For this test, the measured value for C_{OL} was felt to be accurate because the wash water sample was analyzed shortly after collection. The estimated value of δ was 8.8 cm. The model prediction using these two values is shown in Figure IV.12, and it is apparent the model overpredicted the actual response during the latter stages of ventilation. Based on the previously stated logic that the selection criterion is a guide for first estimation of variables and a starting point for parameter perturbation, the value of δ was varied holding the measured value of C_{OL} constant. Using this procedure, the best model prediction was obtained with a value of δ equal to 4.0 cm, which was within the visually estimated range.

Comparison of the experimental data for the two butanol tests (Tests 2 and 3) with that of the ethylene dichloride test (Test 4) indicates that initial conditions have a pronounced effect on solute evaporation. In Test 4, a high initial tank vapor concentration coupled with a low chemical liquid concentration tends initially to retard the evaporation of solute from the residual layer. This observation is illustrated by the fact that the initial slope of the experimental data approximates the theoretical dilution curve. As the test proceeds, C_V is reduced through ventilation to a level where the driving force for mass transfer of chemical from solution is large enough to result in sufficient evaporation to produce a departure of the $C_V(t)$ profile from the ideal dilution curve. In contrast, the experimental ventilation data for Tests 2 and 3 illustrate

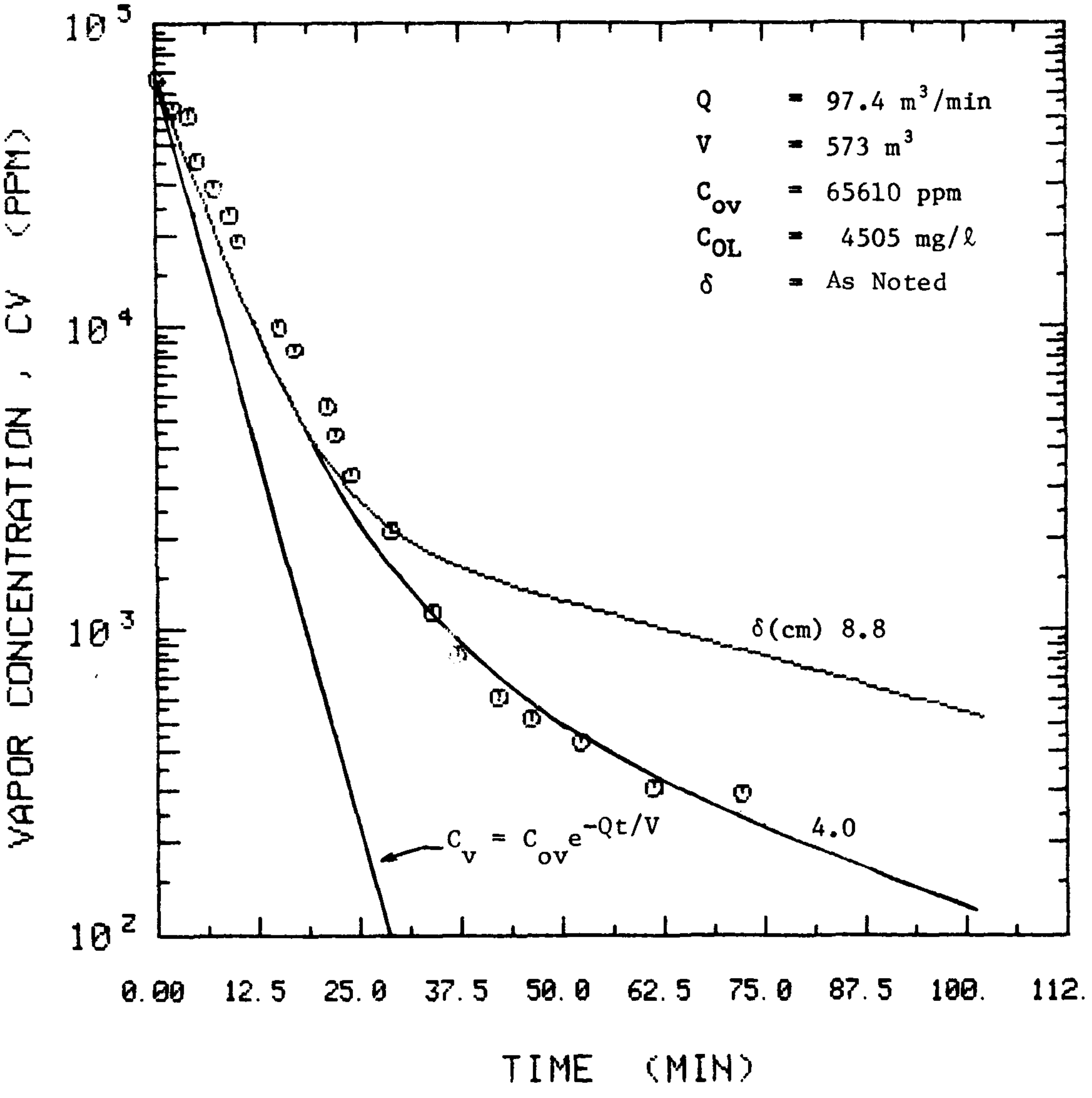


FIGURE IV.12. VENTILATION TEST NO. 4 CONDUCTED IN A FULL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF ETHYLENE DICHLORIDE AND WATER that evaporation of the chemical/wash water layer begins with the initiation of ventilation as a result of a low tank vapor concentration and an estimated high initial liquid concentration. In other words, the driving force for evaporation is positive at the beginning of ventilation. These same trends have been shown to be predicted by the two-component model.

The last group of two-component residue tests conducted in a tank without structure can be characterized by the ventilation Test 18. This series included Tests 14 through 18. Prior to each test, the tanks were subjected to a very rigorous washing procedure. The washing procedure utilized prior to Tests 15 through 18 consisted of a 15-minute hot water wash. During the final 2 minutes of this wash, a soap solution was added. The final step consisted of a 30-minute cold water rinse. For Test 14, a normal cold water wash was used; however, prior to the washing step the tank was ventilated to reduce the initial amount of pure chemical. In all cases, the stripping operation was quite efficient. As a result, the initial concentration of chemical in both the aqueous solution and the vapor space and the residue thickness prior to the start of ventilation (shown in Table IV.2) was substantially lower than in the previous tests that have been discussed.

The experimental data for Test 18 are shown in Figure IV.13. These data approximate the ideal or theoretical dilution curve which suggests that little or no evaporation was occurring. As C_{OL} was measured on this test but δ was not, the procedure for estimating the selection was attempted. The calculation produced a negative mass of evaporated chemical, which indicates that mass transfer was from the vapor phase to the liquid phase, i.e., no evaporation. This fact reinforces the observed behavior of the experimental data with respect to the theoretical dilution curve (which contains no evaporation effects). The model prediction, when evaluated with the measured C_{OL} and an estimated value of δ of 0.14 cm, coincided with the theoretical dilution curve and supported all of the above observations. The experimental data and the model predictions for Tests 14 and 16 exhibited essentially the same characteristics as Test 18.

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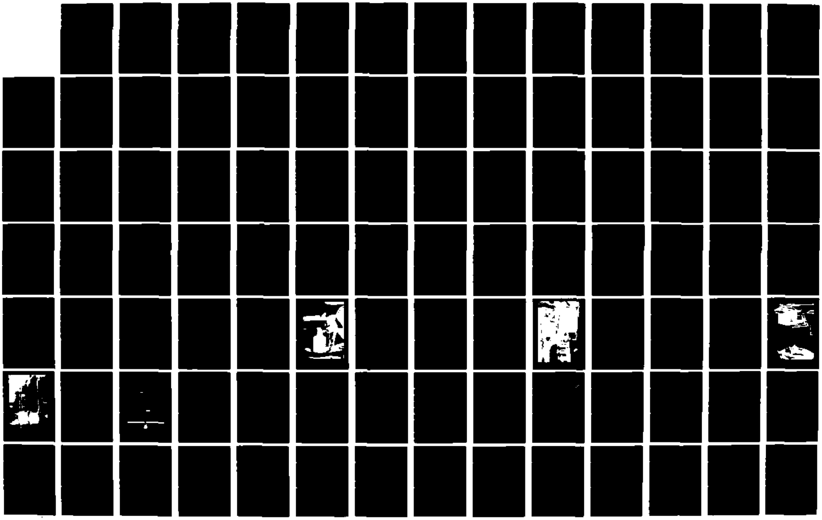

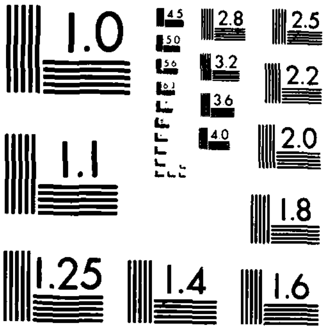

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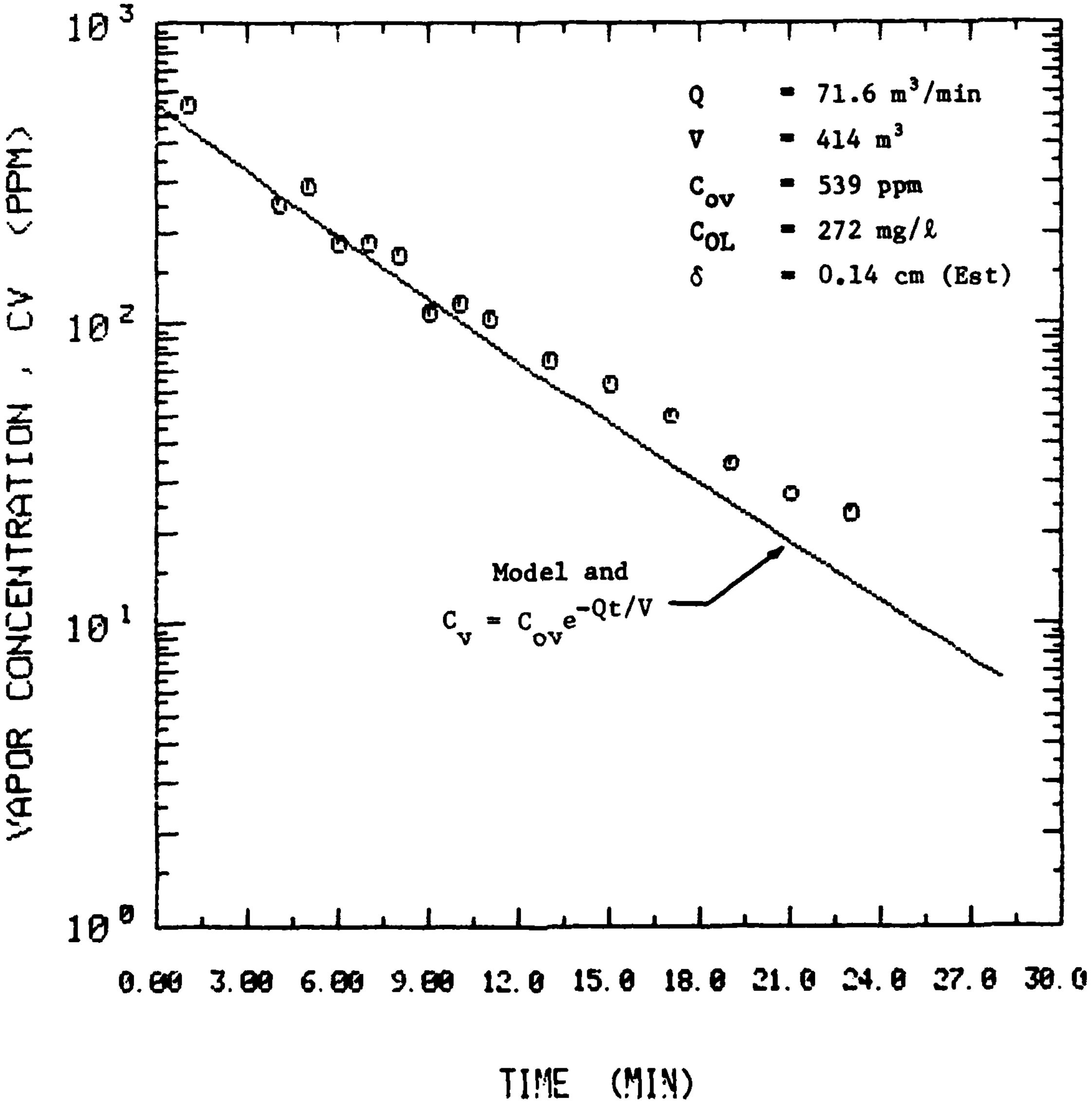


FIGURE IV.13. VENTILATION TEST NO. 18 CONDUCTED IN A FULL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF VINYL ACETATE AND WATER

In Tests 15 and 17, the thoroughness of the washing and stripping operations resulted in initial vapor concentrations of less than 100 ppm, which were lower than on any other tests. The ensuing experimental $C_v(t)$ measurements exhibited a fair amount of data scatter, which may have resulted from a combination of the low initial concentration and local changes in the hydrocarbon background level of the ambient ventilation air. Assuming that this hypothesis is correct, then the fact that the agreement between experiment and theory was not as good for these two tests as in the other tests is attributed to the model formulation, which does not include non-zero vapor concentrations in the ventilation inlet air.

In the case of Test 7, which is shown in Appendix B, the selection criterion, δC_{OL}, was generated using the experimental data. The model prediction, using the measured C_{OL} and calculated δ, did not agree well with the experimental data. As the measured value of C_{OL} had some degree of uncertainty, both δ and C_{OL} were perturbed from their original values holding the values of the selection criterion constant. The final values of δ and C_{OL} that produced good agreement between predicted $C(t)$ and the experimental data were reasonable deviations from the original values given the uncertainty in C_{OL} and that δ could not be measured.

Pure Component Model TANKP - No Internal Tank Structure

As in the two-component tank ventilation tests, the thickness of the residual chemical layer on the tank bottom can be estimated visually, but not measured. In the nomenclature of the TANKP model, this thickness is t_{pool}. Consequently, a selection criterion was established for estimating this independent variable. For the pure chemical case, the analogy to the two-component criterion is

$$t_{pool}\, \rho_c\, A = Q \int_0^{t_f} C_v(t)dt + V\, [C_v(t_f) - C_{ov}] \tag{28}$$

where ρ_c = mass density of the pure chemical. The other quantities were defined previously. The righthand side of this equation represents the mass of evaporated chemical and is evaluated from the experimental data as defined earlier. As all of the initial mass of chemical, $t_{pool} \rho_c A$, may not have evaporated at the end of ventilation, the criterion yields an approximation to the true value of t_{pool}. In addition, the criterion does not include the effect of chemical film on the tank walls, which is an option that is incorporated into the TANKP model formulation. This criterion was imposed on the full scale tests in the same manner as described for the two-component tests. Note, again, that the criterion represents a base for estimating physical variables.

The experimental data and model predictions for selected tests are presented below. Data for additional tests are presented in Appendix B.

One ventilation test (Test 26) was conducted in the model scale test tank in the presence of a residual liquid layer of pure chemical, ethyl acetate. The primary purpose of this test was to determine the value of a free parameter or multiplier that could be applied to the evaporation air velocity that is calculated by the jet deflection and spreading model in order to account for the effects of wall constraints and off-center blower locations. In its original form, the jet model was suitable only for unconfined jets.

The experimental data for Test 26 is shown in Figure IV.14. A reasonably thick layer of chemical was used to insure that a steady-state mass transfer condition would be achieved such that

$$V \frac{dC_v}{dt} = 0 = \dot{m}_g - C_v Q \qquad (29)$$

where $\dot{m}_g$ = total mass evaporation rate of pure chemical.

Based on initial conditions, the original TANKP model was used to predict the experimental response. The prediction produced the

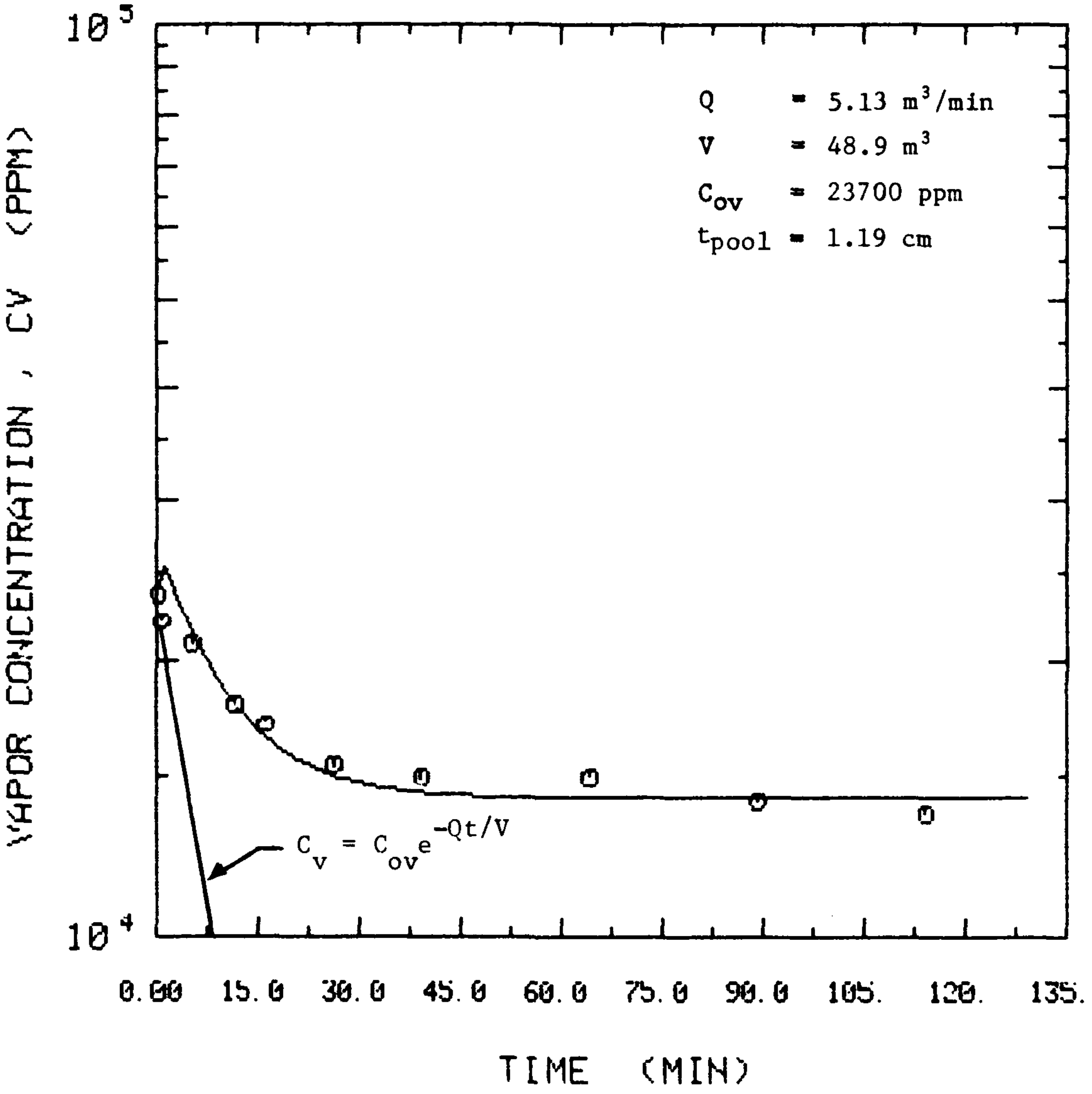


FIGURE IV.14. VENTILATION TEST NO. 26 CONDUCTED IN A MODEL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF ETHYL ACETATE observed steady-state mass transfer condition but at an elevated concentration level. In this original model, the blower jet was assumed to spread symmetrically about the impingement or stagnation point on the tank bottom. Clearly, this condition does not occur because of the presence of the tank walls and the fact the blower is not normally centered on the tank top. To account for these flow modifying effects, the experimental data in Figure IV.14 were used to calculate $\dot{m}_g$ according to the above equation. Using this experimentally-determined $\dot{m}_g$, physical properties of the chemical and Gray's evaporation rate model in Reference 14, an empirical value of the effective air velocity over the liquid surface was calculated. This velocity was compared to the velocity generated by the jet deflection and spreading model for unconfined spaces. The ratio of these two velocities was 0.33, which corresponds to the free parameter β in Equation (15). Incorporating this free parameter into the jet deflection model produced the TANKP prediction that is shown in Figure IV.14. This empirical free parameter β was used in all single and two-component model predictions.

Three full scale, pure chemical tests (5, 9, and 13) were conducted on tanks without internal structure. The results for Tests 5 and 9 are presented and discussed below. Test 13 is presented in Appendix B.

Figure IV.15 presents the experimental data and two model predictions for the chloroform Test 5. At the measured flowrate of 96.3 m^3/min and a residue thickness, t_{pool}, of 0.034 cm as calculated by the selection criterion, the model underpredicted the experimental data. In this test, the measured flow rate was based on a single velocity measurement at the center of the open expansion trunk. As such, it approximates the maximum velocity across the open area. Using the analogy between maximum and average velocity in pipe or orifice flow, a reduction in flowrate was justified. Further, the residue thickness was perturbed from its criterion estimate. The result was a blower flowrate-residue thickness combination that resulted in good agreement between theory and experiment.

All tests with the exception of Test 9 were dilution ventilation tests. The ventilation process in Test 9 was one of displacement

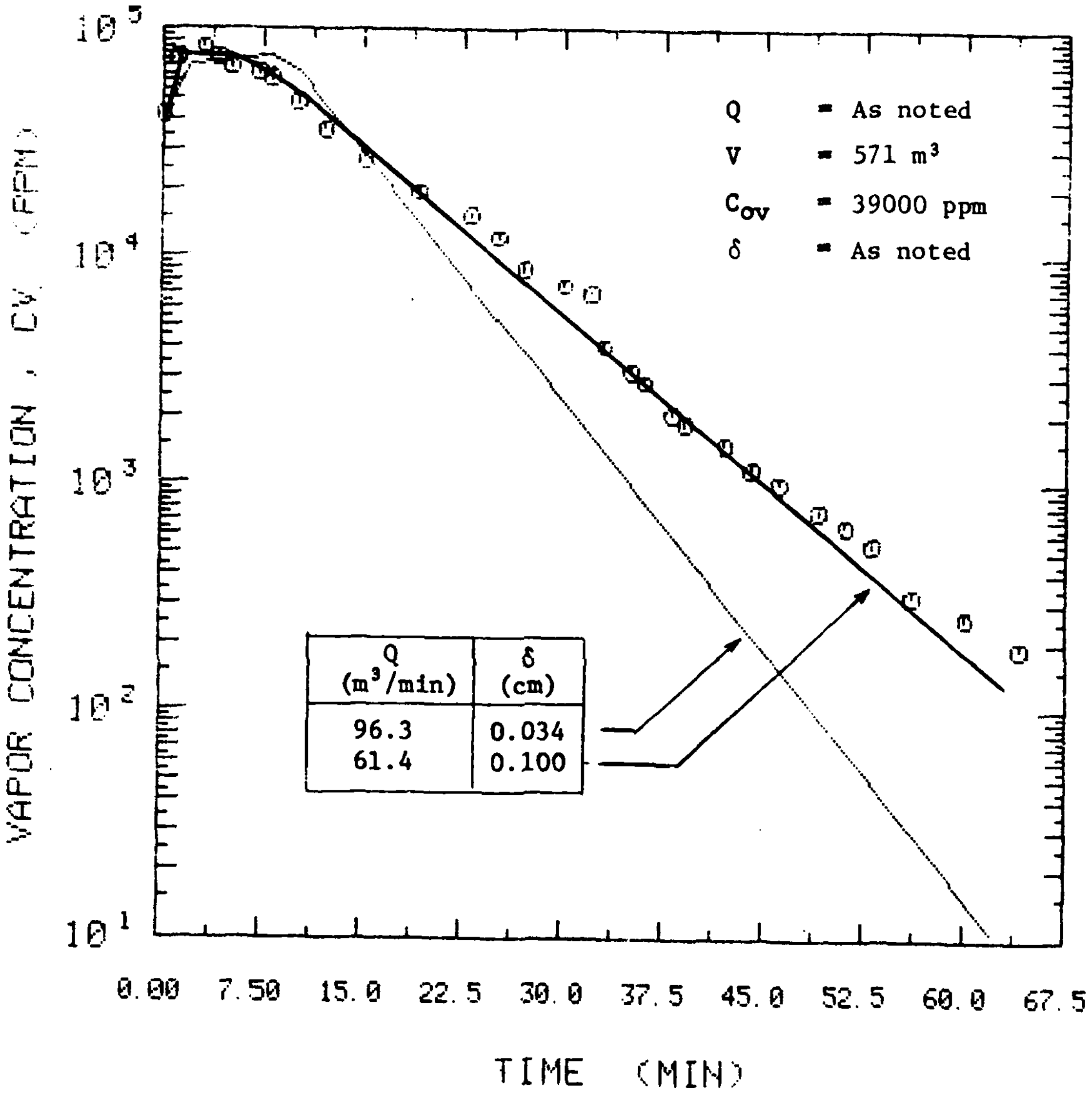


FIGURE IV.15. VENTILATION TEST NO. 5 CONDUCTED IN A FULL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF CHLOROFORM rather than dilution. The open expansion trunk was the air inlet and the restricted tank gauging standpipe was the air outlet. Air was drawn into the tank by means of an eductor set on top of the standpipe. Prior to the test a dilution gas freeing process was anticipated because other vessel tanks on this voyage had utilized this method even for the same chemical. However, a procedural change resulted in displacement gas freeing. Estimates of the densimetric Froude number suggested that the inlet air through the expansion trunk did not penetrate to the tank bottom; thus, a well-mixed vapor space would not be anticipated. In view of the difference in ventilation mechanics between the dilution and displacement methods, the model prediction using the measured flowrate and selection criterion value for the initial residual thickness produced quite good agreement with the experimental data as shown in Figure IV.16. Displacement ventilation would normally be encountered on product tanks with internal structure, i.e., crude oil tanks. It is plausible that the eductor flow rate combined with the inlet air and suction removal of vapors near the residue surface resulted in a flow field in the tank that approached the well-mixed state.

Tanks With Internal Structure

The following tests were conducted on tanks that contained internal structure.

Test Nos.	Residue State
6, 8, 10	Pure Chemical
1, 11, 12	Chemical-Water Solution

The level of predictability of the TANKM and TANKP models cannot readily be determined for this type of tank because neither model includes the flow-modifying effect of the internal structure or additional physical processes that may result from its presence.

Internal tank structure, in the form of webframes, divides the tank bottom into a number of separate compartments. During dilution ventilation, only those compartments directly under the inlet opening

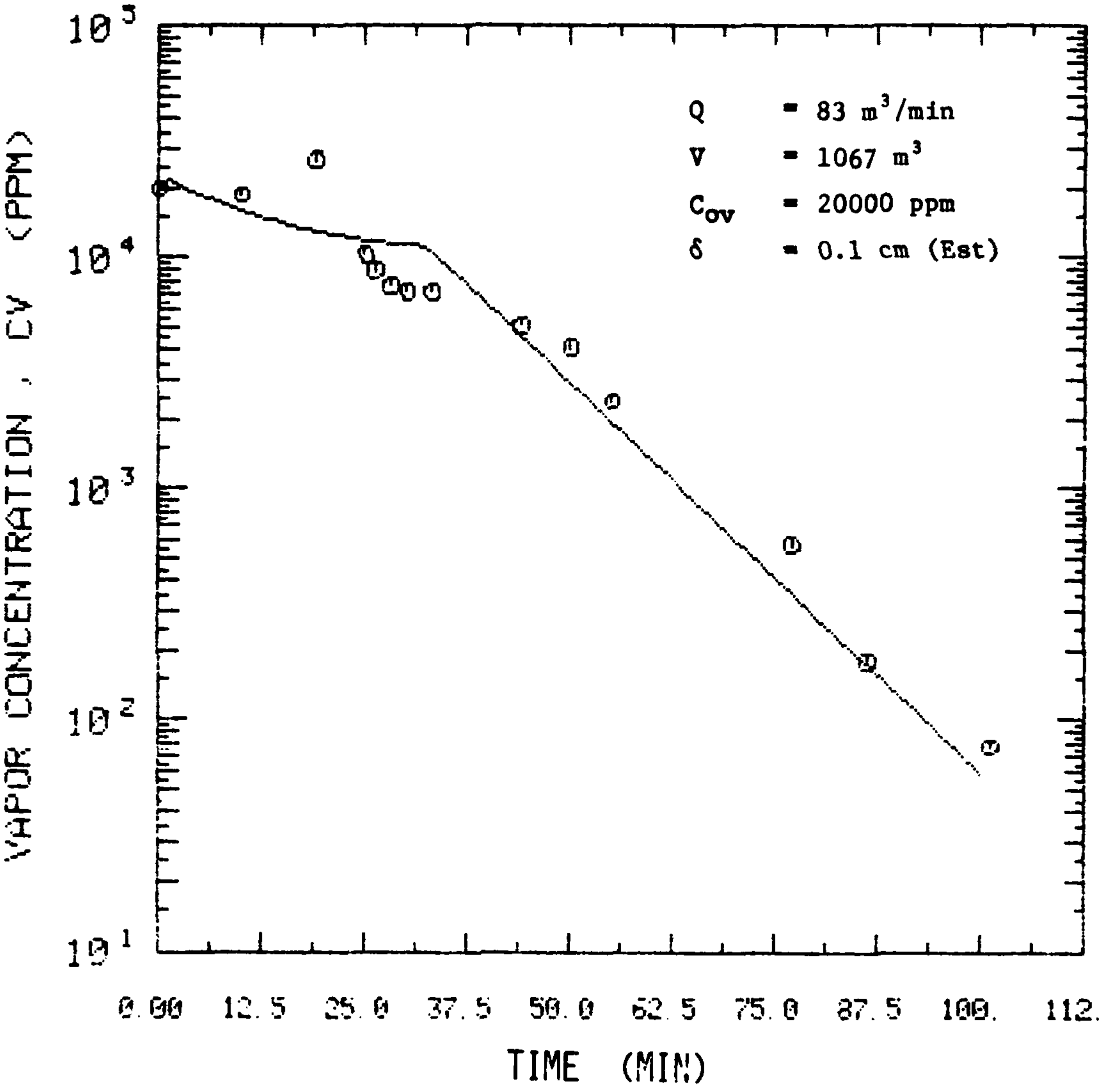


FIGURE IV.16. VENTILATION TEST NO. 9 CONDUCTED IN A FULL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF ETHANOL actually see the inlet air jet. The webframes of adjacent compartments essentially block off the spreading of the jet. Consequently, one obvious effect of internal structure is to change the velocity flow field over the bottom surface where evaporation is occurring as well as to reduce the available evaporation area. These are both key parameters in the model formulations. Consequently, one of the effects of structure on the predictions of the model may be accounted for by reducing the surface area calculation in the model as well as increasing the evaporative velocity. However, this approach would not account for the mass transfer processes in the shielded areas of the tank where high concentration vapors are not exposed to the convective flow field. The relative rate at which these compartments gas free by mechanisms other than mechanical dilution will affect the overall gas freeing time and the vapor discharge concentration.

For each of the above six tests, the appropriate models were exercised using measured data and best estimates for variables that could not be measured. The selection criterion was not used because of the issue of appropriate liquid surface area. The resulting predictions are quite variable as compared to experimental data, but they do suggest conceptual modifications that may improve model predictability for this class of tank. The results for tests 11 and 10 are presented and discussed below. Tests 6, 8, 1, and 12 are presented in Appendix B.

Test No. 11 involved gasoline. The washing and stripping procedure suggested that a layer of this low solubility product was not floating on the residual layer. It was assumed that the wash water was saturated with this product, and the TANKM model was employed. The results in Figure IV.17 indicate that the model underpredicts the time to gas free to a given concentration. This delay time effect due to structure was observed in Reference 4 in conjunction with model scale ventilation tests of VLCC tanks with internal structure. This similarity suggests that an experimentally-determined, structure-time delay correlation for chemical tanks with aqueous solutions may improve the model's predictability.

In Test 10, the tank had contained ethanol but was not washed prior to gas freeing. Hence, the TANKP model was exercised, and

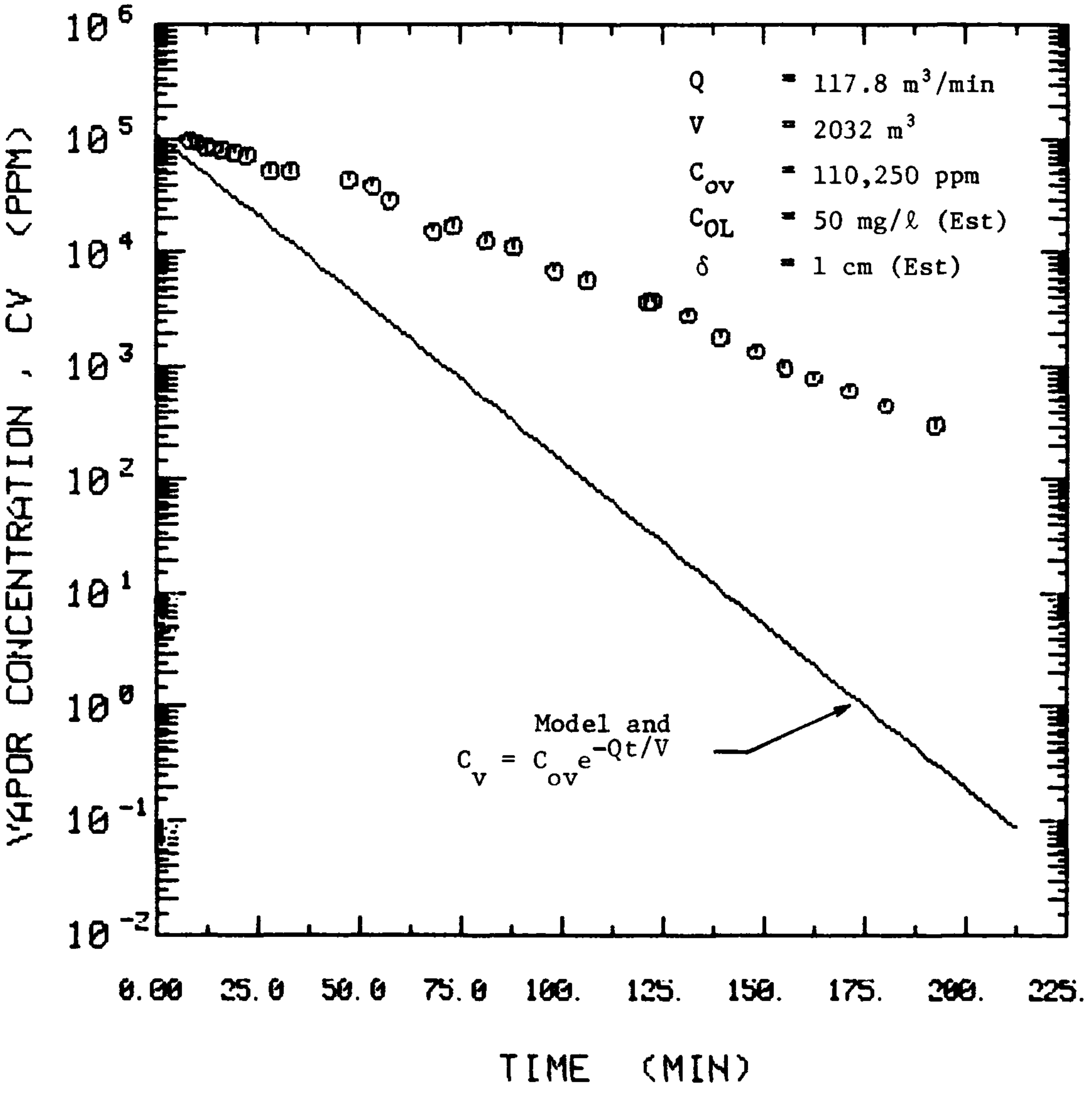


FIGURE IV.17. VENTILATION TEST NO. 11 CONDUCTED IN A FULL SCALE TANK WITH STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF GASOLINE AND WATER the results that are shown in Figure IV.18 overpredict the experimental data at all times. The shape of the model curve compared to the experimental data does not imply that the form of the model is incorrect. What is incorrect is the application of the calculated evaporation velocity over the entire tank bottom as if no structure was present. In order to obtain more reasonable predictions for the pure component model in tanks containing structure it would be necessary to modify the estimate of the evaporative velocity within the compartments directly under the jet as well as the liquid surface area that is directly subjected to this air flow. Since evaporation rate is directly proportional to surface area, the area reduction suggested above should, qualitatively, result in a reduced concentration prediction and closer agreement with experiment.

The presence of tank internal structure increases the complexity of the gas freeing process. Even though tanks with internal structure appear to be in the minority as far as chemical transport is concerned, additional analytical and experimental investigation is needed to quantify the suggested conceptual modifications to the models.

IV.2.4 Parametric Results

The two ventilation models developed in Section IV.2.1 predict the vapor concentration-time history in a tank during evaporation of residual layers of liquid containing either an aqueous solution of chemical in water or pure chemical. The comparisons made in Section IV.2.3 between the model predictions and experimental tank ventilation data, obtained over a wide range of conditions, have shown that certain independent variables have a strong affect on the model responses. The purpose of this section is to identify these independent variables and to investigate the sensitivity of the models to changes in these variables.

Two-Component Model

The significant independent variables in the two-component model are (1) the thickness of residual liquid layer, δ, (2) the initial

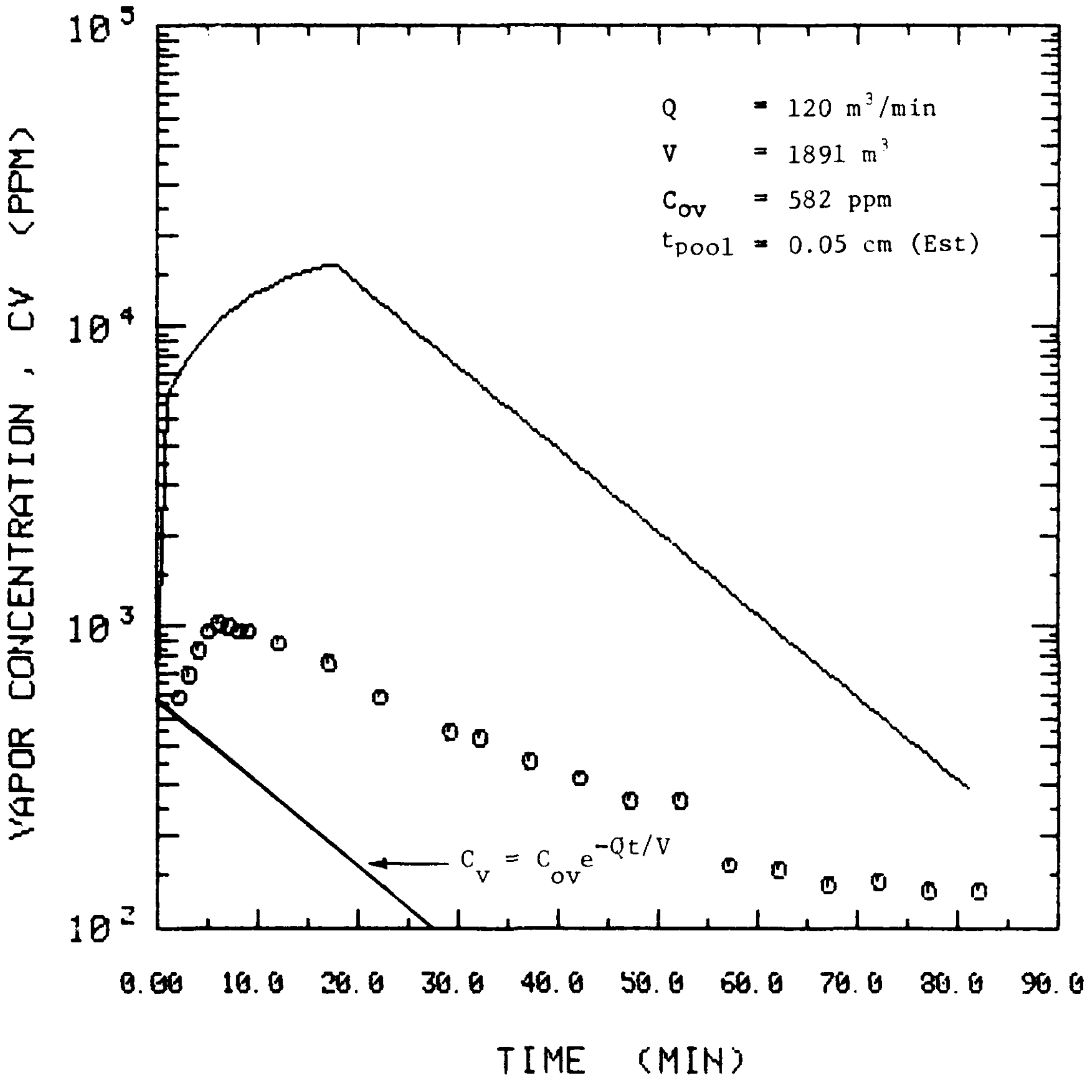


FIGURE IV.18. VENTILATION TEST NO. 10 CONDUCTED IN A FULL SCALE TANK WITH STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF ETHANOL concentration of chemical in the liquid layer, C_{OL}, (3) the ventilation flowrate, Q, (4) the initial chemical concentration in the tank vapor space, C_{ov}, and (5) the physical properties of the chemical. To investigate how each of these variables affects the response of the model, a series of computer runs were made by varying one of the above parameters while holding the others constant. The tank geometry and temperature conditions chosen for the parametric analysis were those of Test 3. Butanol, which was the chemical that had been carried in the tank during Test 3, was used to investigate the effect of the first four parameters. The effect of the chemical's physical properties, primarily vapor pressure, was evaluated by replacing butanol with acetone while holding the first four parameters constant. Table IV.4 illustrates the parametric combinations that were examined.

Figure IV.19 illustrates the effect of δ variation on the concentration-time history. From the figure, the thicker the layer of chemical/water residue, the longer it takes to ventilate the tank down to a given concentration level. At the beginning of ventilation, the evaporative flux is the same in all cases because C_{OL} and C_{ov} are constant. However, the rate of change of solute concentration is inversely proportional to δ. Thus, at any time, smaller values of δ will correspond to lower values of C_L and evaporation rate because the driving force for evaporation is proportional to C_L. Conversely, for a given C_{OL}, there is more chemical mass to evaporate from a thick layer compared to the thin layer, and the gas freeing time is correspondingly longer. Evaporation is occurring in all cases as evidenced by the departure of the gas freeing curves from the ideal dilution curve. This parametric exercise demonstrates that, in actual tank cleaning operations, the more efficiently the tank is stripped of residual wash slops, the faster will be the gas freeing time and the higher the probability that the occupational exposure during tank entry will be acceptable.

The next parameter investigated was the variation of initial concentration of chemical in the residual layer. The model response for three different C_{OL} concentrations is shown in Figure IV.20. In contrast to the effect of δ, changes in C_{OL} yield different responses in the concentration-time histories immediately after the start of ventilation.

TABLE IV.4. PARAMETRIC CONDITIONS FOR TWO-COMPONENT MODEL

RUN NO.	CHEMICAL	P_v mm Hg @ 20°C	Q (m^3/min)	C_{ov} (ppm)	C_{OL} (mg/m^3)	δ (cm)	PARAMETER ADJUSTED
1	Butanol	4.4	100	410	20000	1.0	δ
2	"	"	"	"	"	0.5	
3	"	"	"	"	"	0.2	
4	"	"	"	"	50000	0.5	C_{OL}
5	"	"	"	"	20000	"	
6	"	"	"	"	5000	"	
7	"	"	150	"	20000	"	Q
8	"	"	100	"	"	"	
9	"	"	50	"	"	"	
10	"	"	100	4100	"	"	C_{ov}
11	"	"	"	410	"	"	
12	"	"	"	41	"	"	
13	"	"	"	410	"	"	Physical Properties
14	Acetone	176	"	"	"	"	

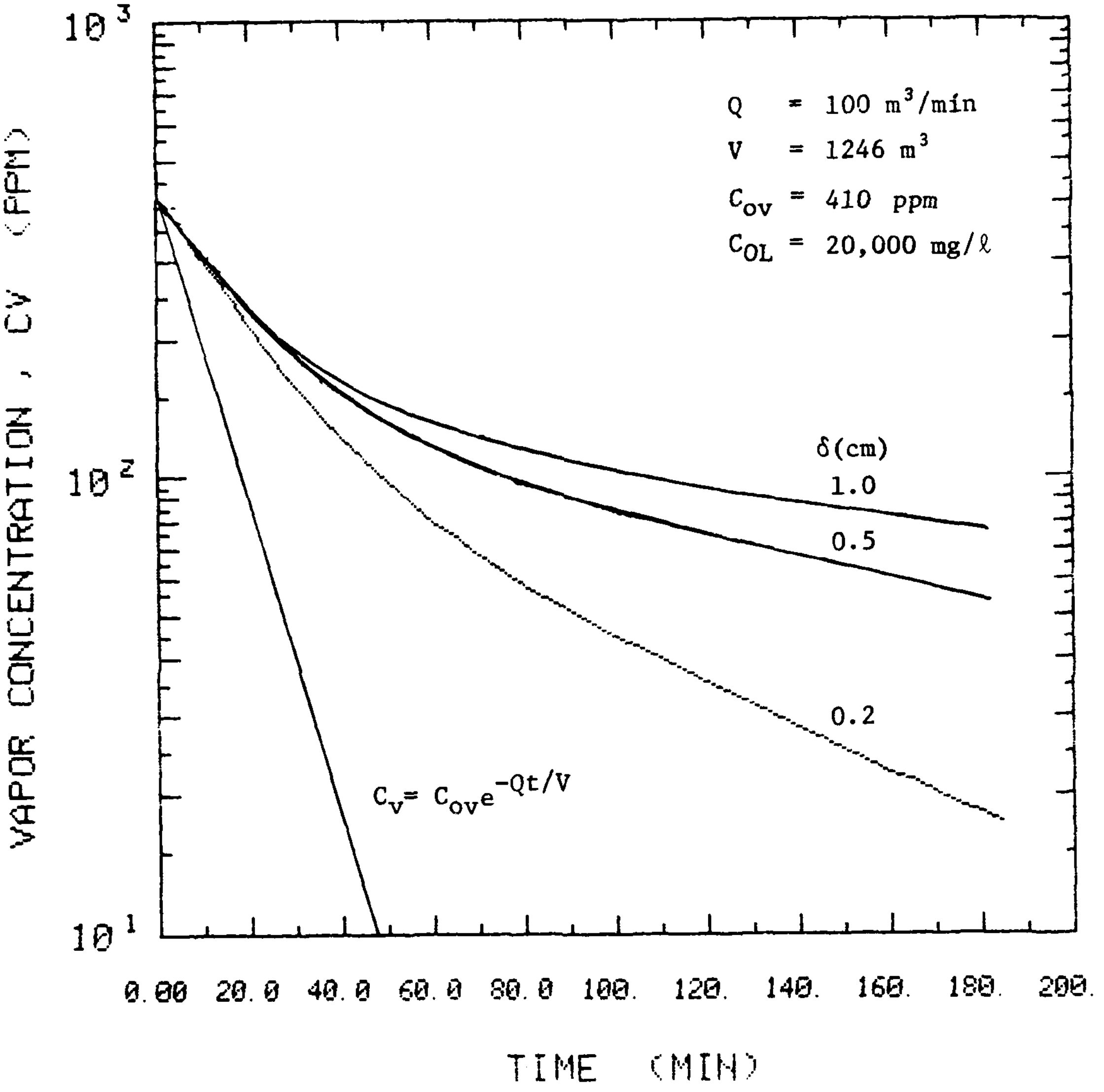


FIGURE IV.19. TWO COMPONENT VENTILATION/EVAPORATION MODEL CONCENTRATION TIME HISTORIES FOR CHANGES IN RESIDUAL LIQUID THICKNESS, δ

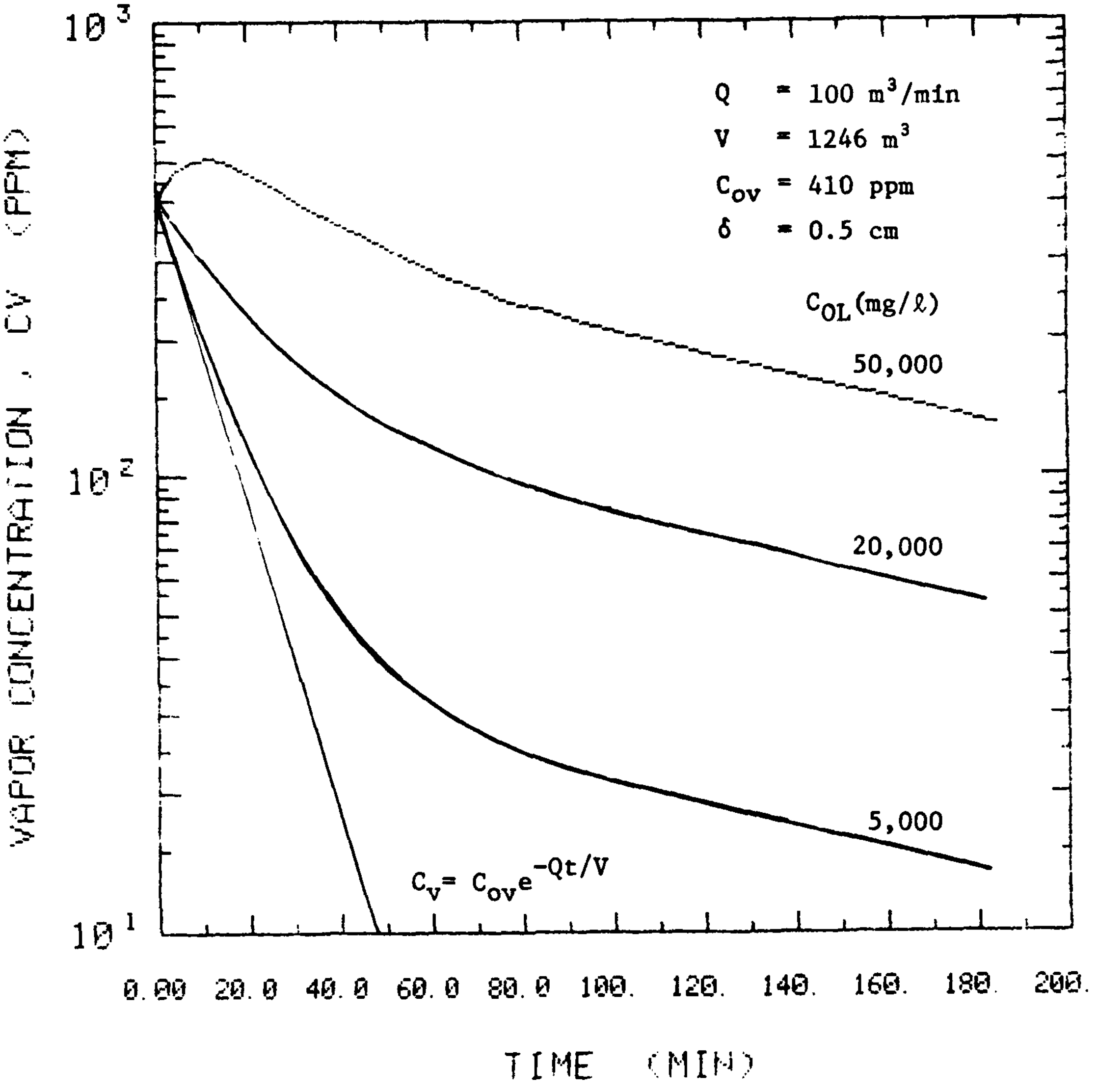


FIGURE IV.20. TWO COMPONENT VENTILATION/EVAPORATION MODEL CONCENTRATION TIME HISTORIES FOR CHANGES IN INITIAL CHEMICAL CONCENTRATION IN RESIDUAL LIQUID, C_{OL}

As C_{OL} increases, the initial evaporation rate is greater due to the increase in the initial concentration driving force $(C_{OL} - C_{ov}/H)$. This is demonstrated by the relative difference in the starting slope of each curve as compared to the slope of the theoretical dilution curve. At the highest indicated value of C_{OL}, mass is transferred to the vapor space faster than it can be discharged from the tank. In addition, higher initial values of C_{OL} correspond to relatively higher levels of C_L at a given time and higher evaporation rates. However, in all cases as time increases, C_L decreases exponentially to a point beyond which the solute concentration does not have a dominant effect on the evaporation flux; the flux is controlled by the vapor phase concentration, and the result is a log-linear rate of decay of vapor concentration that is independent of the initial value of C_{OL}. Another observation is that the relative time to gas free this tank to a given concentration is longer for roughly a two-fold increase in C_{OL} as compared to a comparable increase in δ. For water soluble chemicals, the parametric effect of C_{OL} indicates that a rigorous washing procedure will reduce the gas freeing time and the subsequent tank entry exposure levels. Obviously, an efficient stripping operation will improve this result. Water insoluble products will present a more difficult gas freeing situation.

Three values of Q, the blower flowrate, were selected to determine the effect on tank ventilation time in the presence of chemical evaporation from solution. The values chosen approximate the range of blower flowrates in the marine industry. The effect of blower flowrate on the ventilation process is shown in Figure IV.21. Changes in Q affect the overall mass transfer coefficient, K_{OL}, through its dependence on the gas phase resistance term, $1/Hk_g$, which reflects the blower-induced air velocity over the liquid surface. Another term in the mass balance on the vapor phase is $Q\ C_v$, the rate of discharge from tank vapor. By its functional form, it is directly proportional to Q. These two effects act in combination to give the resulting model response shown in Figure IV.21. The parametric affect of Q is to reduce gas freeing time by increasing blower flowrate. However, intuitively there is a practical limit to the benefits of increasing blower flowrate beyond which there is a disproportionately smaller increase in the

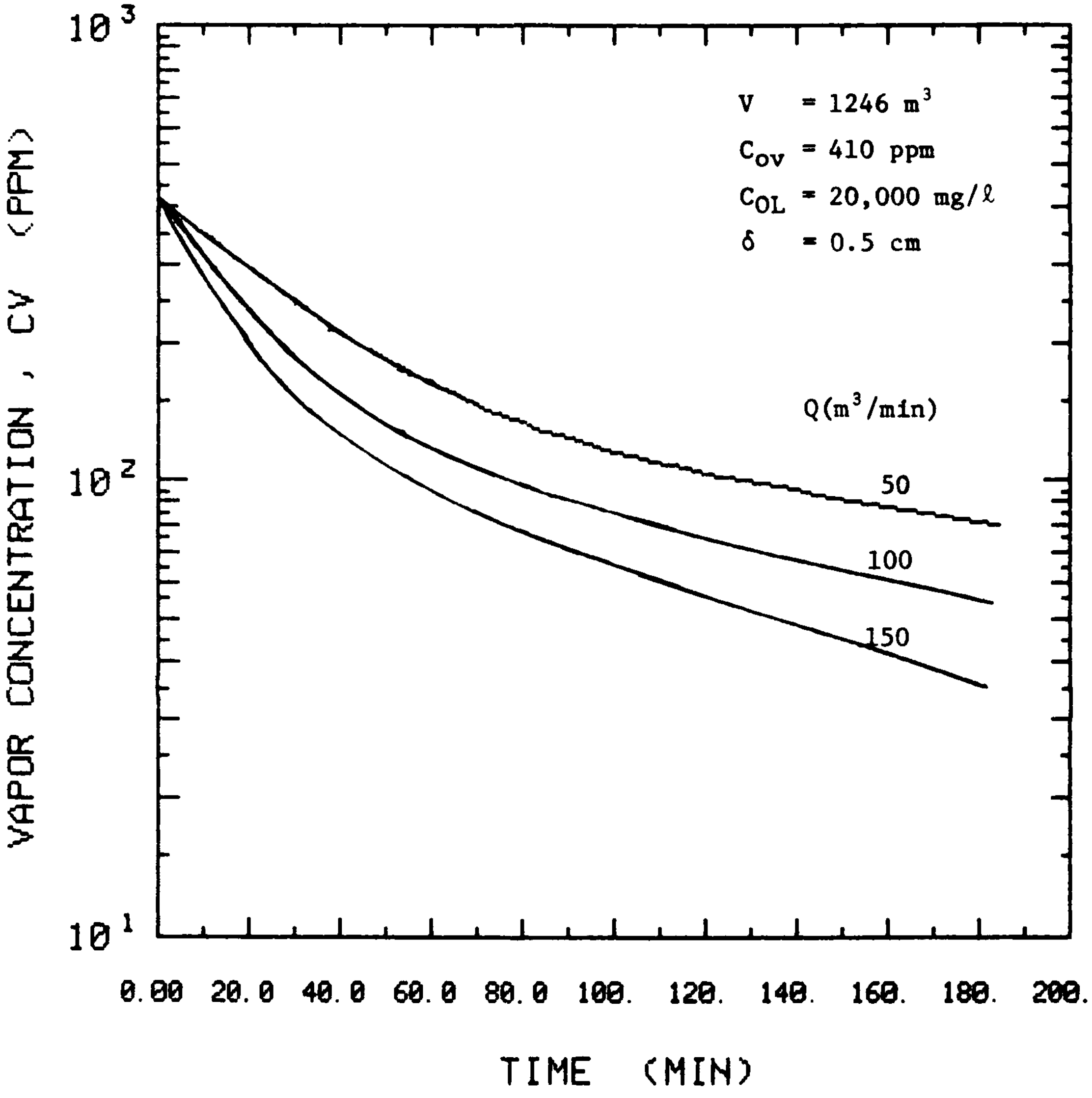


FIGURE IV.21. TWO COMPONENT VENTILATION/EVAPORATION MODEL CONCENTRATION TIME HISTORIES FOR CHANGES IN BLOWER FLOWRATE, Q level of vapor space mixing and the mass transfer of solute to the vapor phase. In the latter case, the gas phase exchange constant is proportional indirectly to blower flowrate; but in the limit as blower flowrate increases without bound, the evaporation process is controlled by liquid phase resistance, $1/k_{\ell}$. The above logic combined with the parametric effects of δ, C_{OL}, and Q indicate that gas freeing time is more sensitive to residual product conditions than to Q. That is, small improvements in tank cleaning will have a greater impact on reducing gas freeing times or concentration at a given time than will increasing blower flowrate.

Figure IV.22 shows the model response for initial values of tank vapor concentration that range over three orders of magnitude. An immediate observation is that, after approximately 80 minutes into the ventilation, the vapor concentration predicted by the model is essentially the same in all cases. Only during the initial part of the ventilation do the model predictions reflect the effect of C_{ov}. At high initial values of C_{ov}, the driving force for evaporation has an insignificant effect on chemical mass transfer from solution. Hence, gas freeing approximates the ideal dilution curve. The fact that all three curves asymptotically approach the same gas freeing profile regardless of the initial value of C_{ov} indicates that for this chemical, butanol, the evaporation process is controlled by the liquid phase. It further indicates that the residual product conditions would dominate the practicalities of gas freeing to safe limits.

Figure IV.23 illustrates the concentration-time history predictions during ventilation of the same tank but with a different residual chemical in solution - acetone. The model response for butanol is also shown. Butanol is highly soluble in water, and acetone is infinitely soluble. The independent variables of Q, C_{ov}, C_{OL}, and δ are the same in both cases, and the predictions were made using the activity coefficient approach to evaluate the partition coefficient, H. In this comparison, the primary effect of the higher vapor pressure of acetone was to produce a partition coefficient that was roughly three to ten times larger than the corresponding value of H for butanol. For both of these chemicals, solute evaporation from solution is controlled by the liquid phase. That is, the liquid phase resistance,

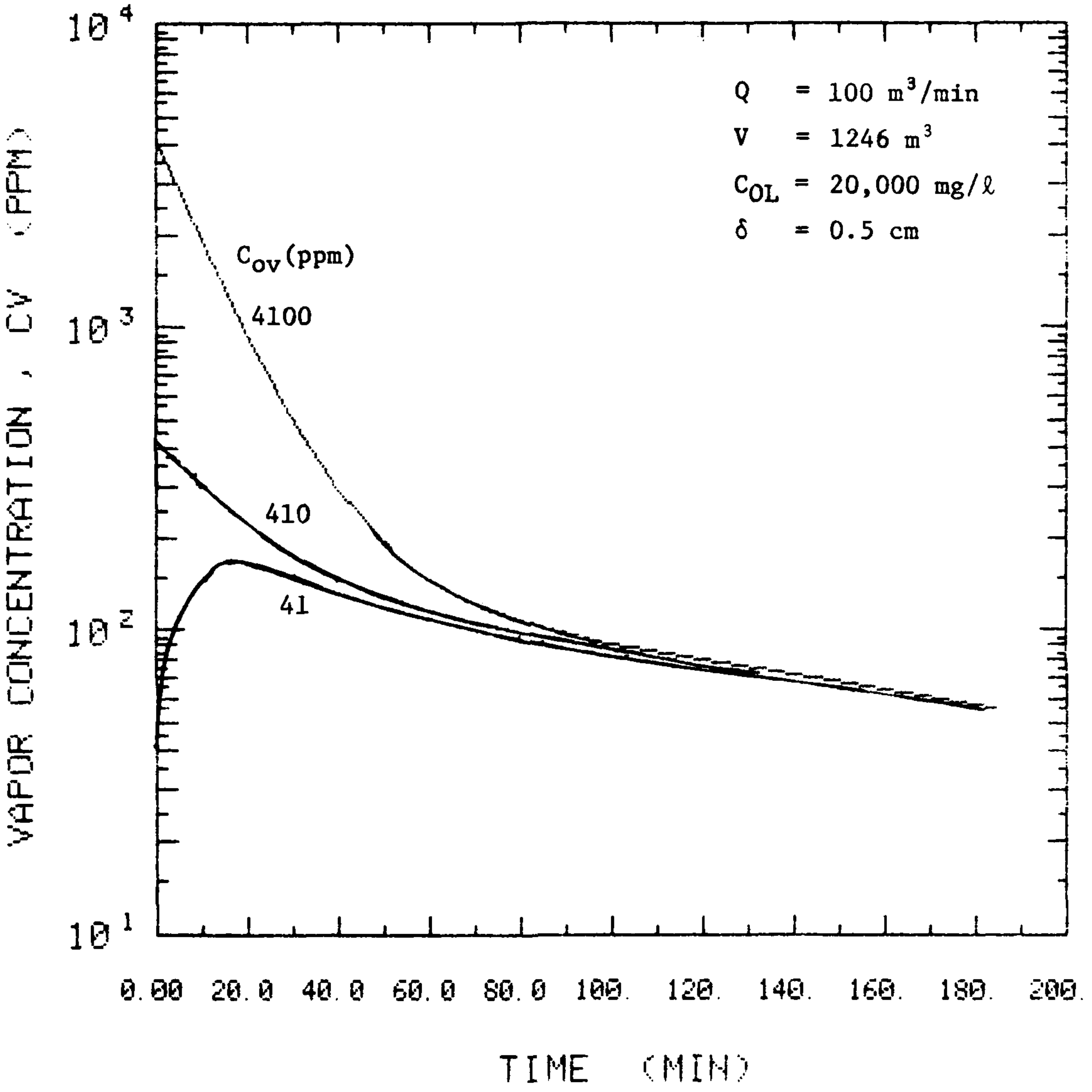


FIGURE IV.22. TWO COMPONENT VENTILATION/EVAPORATION MODEL CONCENTRATION TIME HISTORIES FOR CHANGES IN INITIAL TANK VAPOR CONCENTRATION, C_{OV}

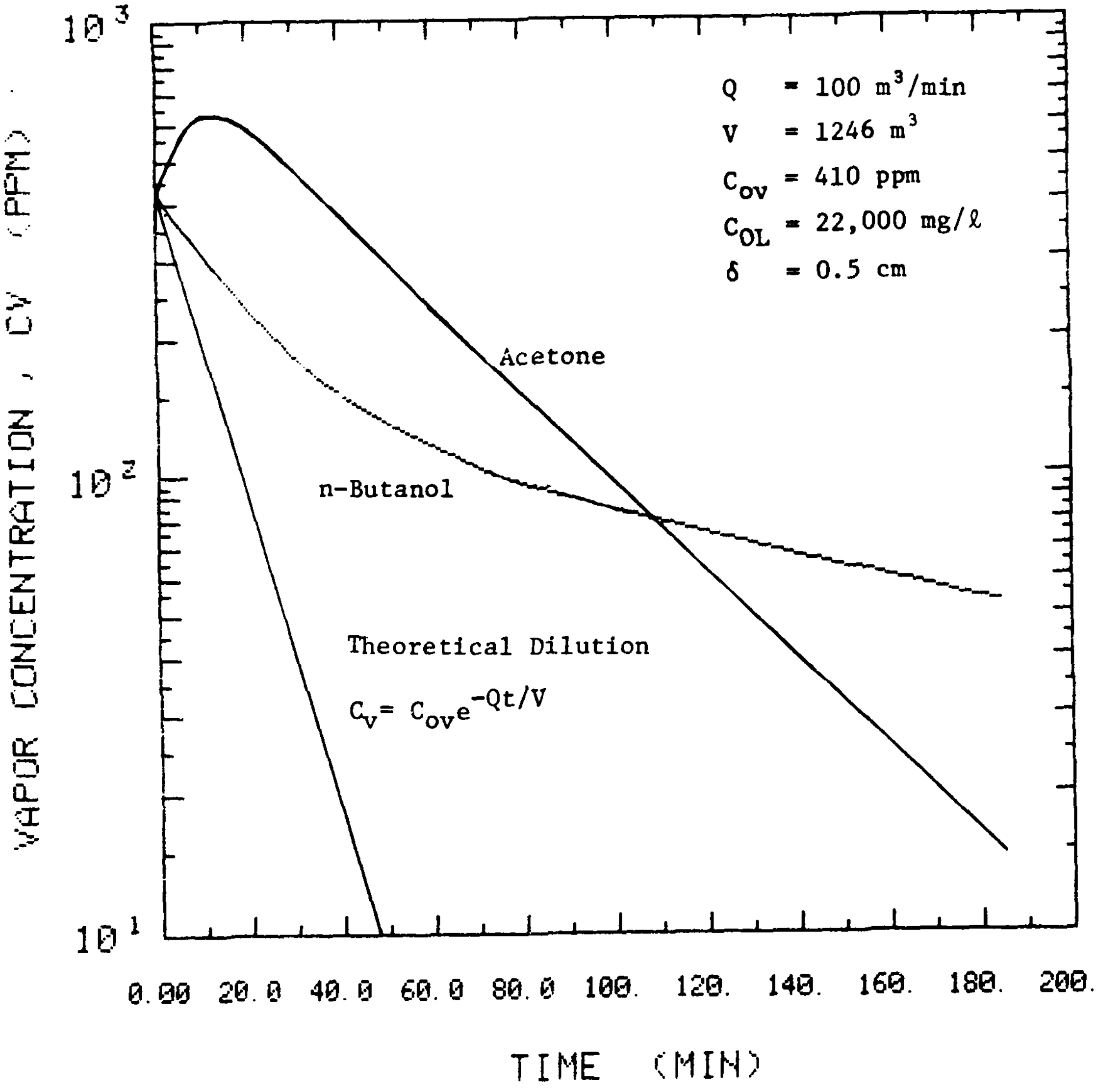


FIGURE IV.23. TWO COMPONENT VENTILATION/EVAPORATION MODEL CONCENTRATION TIME HISTORIES FOR CHANGES IN PHYSICAL PROPERTIES

$1/k_\ell$ is greater than the gas phase resistance, $1/Hk_g$. The resistance to mass transfer was initially greater for butanol than for acetone, which resulted in a higher evaporation rate for acetone during the first half of the ventilation. During the latter half of ventilation, the combined effect of K_{OL} and H resulted in a larger evaporation rate for butanol than for acetone. This parametric evaluation indicates that for a given set of initial conditions, gas freeing to low level concentrations will require the least amount of time for binary chemical/water residues that have the largest value of $p_v \gamma_1^\infty$, where p_v is the solute vapor pressure and γ_1^∞ is the solute activity coefficient at infinite dilution.

Pure Component Model

A statistical sensitivity analysis was conducted on the original version of the TANKP model in Phase I. The results of that analysis are reproduced below from Reference 1.

1. The following parameters and parameter combinations do not have a statistically significant effect on the evaporation/ventilation time required to achieve a 1% LEL concentration:
   a. initial concentration,
   b. initial liquid thickness on the vertical walls,
   c. the combination of initial concentration with either flow rate, residue thickness on the tank bottom, or wall temperature,
   d. the combination of flowrate and wall film thickness, and
   e. the combination of wall film thickness with either residue thickness, or wall temperature.
2. The following parameters and parameter combinations do have a statistically significant effect on the evaporation/dilution time criterion:
   a. ventilation flowrate,
   b. residue thickness on tank bottom,
   c. wall temperature,

d. the combination of initial concentration with wall film thickness (significant at 90% confidence level),

e. the combination of ventilation rate and either pool depth or wall temperature, and

f. the combination of pool depth and wall temperature.

The only difference between the original version of this model and the version that appears in this report is that this latest version included the empirical parameter β, which accounts for the confined, nonsymmetrical spreading of the blower jet following impingement as a result of the presence of the tank walls.

In view of this change, three independent variables were parameterized to determine if the sensitivities had been altered. These variables were t_{pool}, Q, and C_{ov}. The tank geometry, temperature and chemical (chloroform) in experimental Test 5, were selected to investigate the model response to variations in t_{pool}, Q, and C_{ov}. Xylene was then chosen to illustrate the effect of physical property changes while holding the other variables constant. The parametric conditions used in the study are shown in Table IV.5. The parameter t_{pool}, which is the thickness of the pure chemical residue on the tank bottom, is analogous to the parameter δ in the two-component model.

Figure IV.24 shows the ventilation concentration-time histories for three values of residual liquid thickness. Initially, the model predicts a rise in the tank concentration followed by a period of constant vapor concentration. This concentration plateau represents an equilibrium state in which the mass rate of evaporation is equal to the mass rate of discharge of tank vapor. Mathematically, the dC_v/dt term in the pure component mass balance equation is zero, and the equation reduces to

$$\dot{m}_g = C_v \, Q \qquad (30)$$

The constant concentration period persists until all of the chemical has been evaporated. Consequently, the larger the initial thickness of the

TABLE IV.5. PARAMETRIC CONDITIONS FOR PURE COMPONENT MODEL

RUN NO.	CHEMICAL	P_v mm Hg @ 20°C	Q (m^3/min)	C_{ov} (ppm)	t_{pool} (cm)	PARAMETER VARIED
1	Chloroform	155	150	42100	1.0	t_{pool}
2	"	"	"	"	0.5	
3	"	"	"	"	0.2	
4	"	"	"	"	0.5	Q
5	"	"	100	"	"	
6	"	"	50	"	"	
7	"	"	100	"	"	C_{ov}
8	"	"	"	4210	"	
9	"	"	"	421		
10	"	"	"	15000	"	Physical Properties
11	Xylene	6.5	"	"		

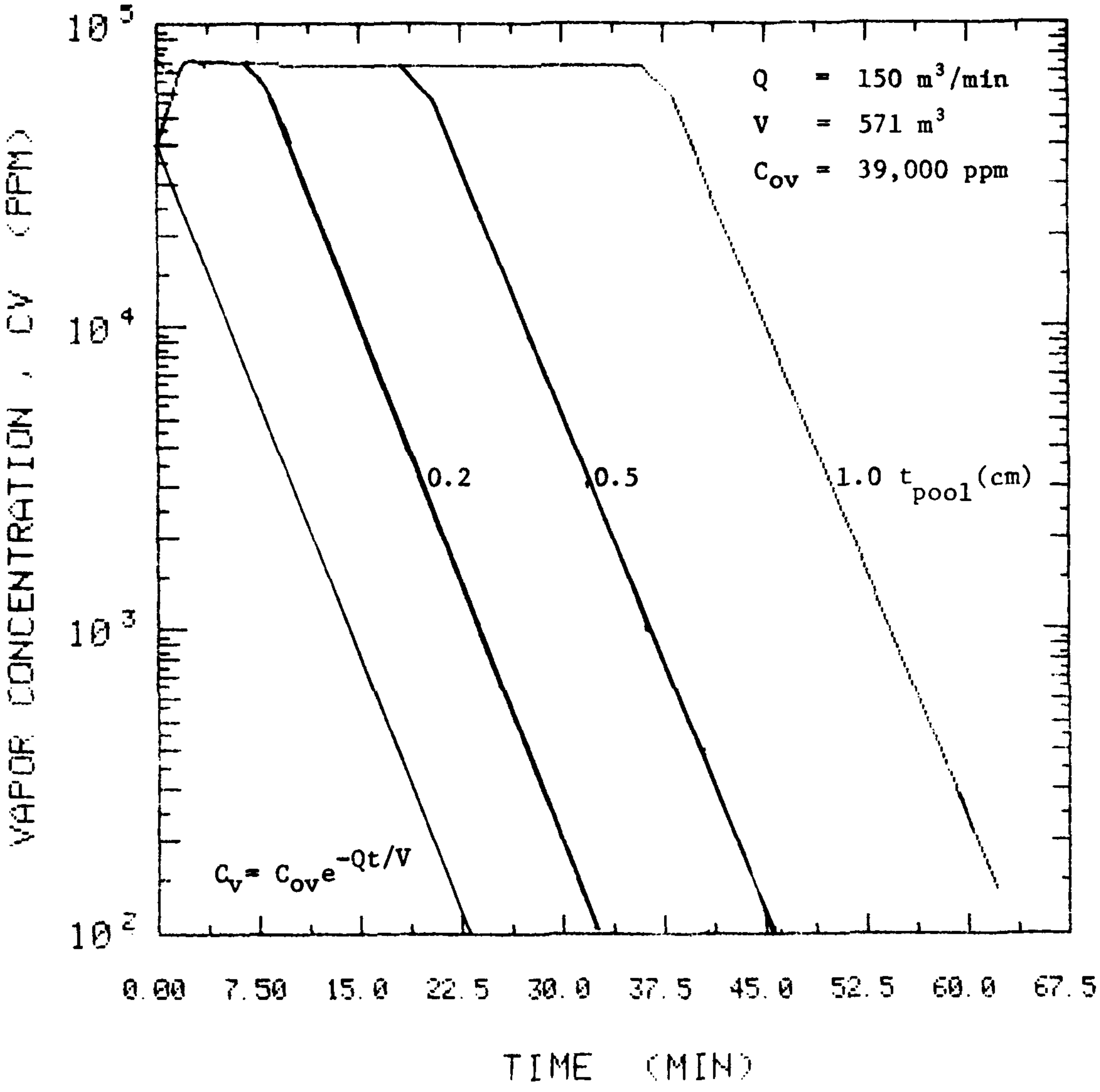


FIGURE IV.24. PURE COMPONENT VENTILATION/EVAPORATION MODEL CONCENTRATION TIME HISTORIES FOR CHANGES IN RESIDUAL LIQUID THICKNESS, δ

residual layer the longer is the duration of constant rate evaporation. After evaporation ceases, the concentration-time history is described by the theoretical dilution curve. Since identical blower flowrates and tank volumes were used in this parametric exercise, all post-evaporation concentration-time histories have the same theoretical slope. The results in Figure IV.24 confirm the statistical sensitivity analysis that residue thickness has a significant effect on gas freeing time.

The response of the model to changes in blower flowrate, Q, are shown in Figure IV.25. The three blower flowrates were 150, 100, and 50 m^3/min. A residual product thickness of 0.5 cm was used. The concentration plateau described previously was reached in each case. However, the value of the equilibrium concentration is different for each flowrate. The reason is that the mass discharge rate, QC_V, is proportional to Q, but the mass evaporation rate is proportional to Q to a fractional power. After the mass of chemical is depleted, the ventilation of the tank proceeds at a rate described by the theoretical dilution curve. The slopes of these curves after evaporation, however, are different because the flowrates are not the same. As in the sensitivity analysis, Q is a significant variable in the gas freeing process. As anticipated, larger values of Q accelerate the evaporation and gas freeing processes, but the relationship is nonlinear.

The response of the two-component model was not overly sensitive to variations in C_{ov}, the initial vapor concentration. A similar conclusion resulted from the response of the pure component model to C_{ov} variations as shown in Figure IV.26. The variation of C_{ov} results in different model responses only during the initial portion of the ventilation. In all cases, the tank vapor concentration increases to an equilibrium concentration corresponding to the same flowrate in Figure IV.25. Evaporation proceeds until the chemical residue is exhausted. Because the blower flowrate and the amount of chemical were the same for all three runs, the period of evaporation and the remaining portion of the ventilation profile are identical. Following evaporation, tank vapor concentration decays exponentially. This parametric exercise confirms that initial vapor concentration has no significant effect on the time to gas free to safe levels.

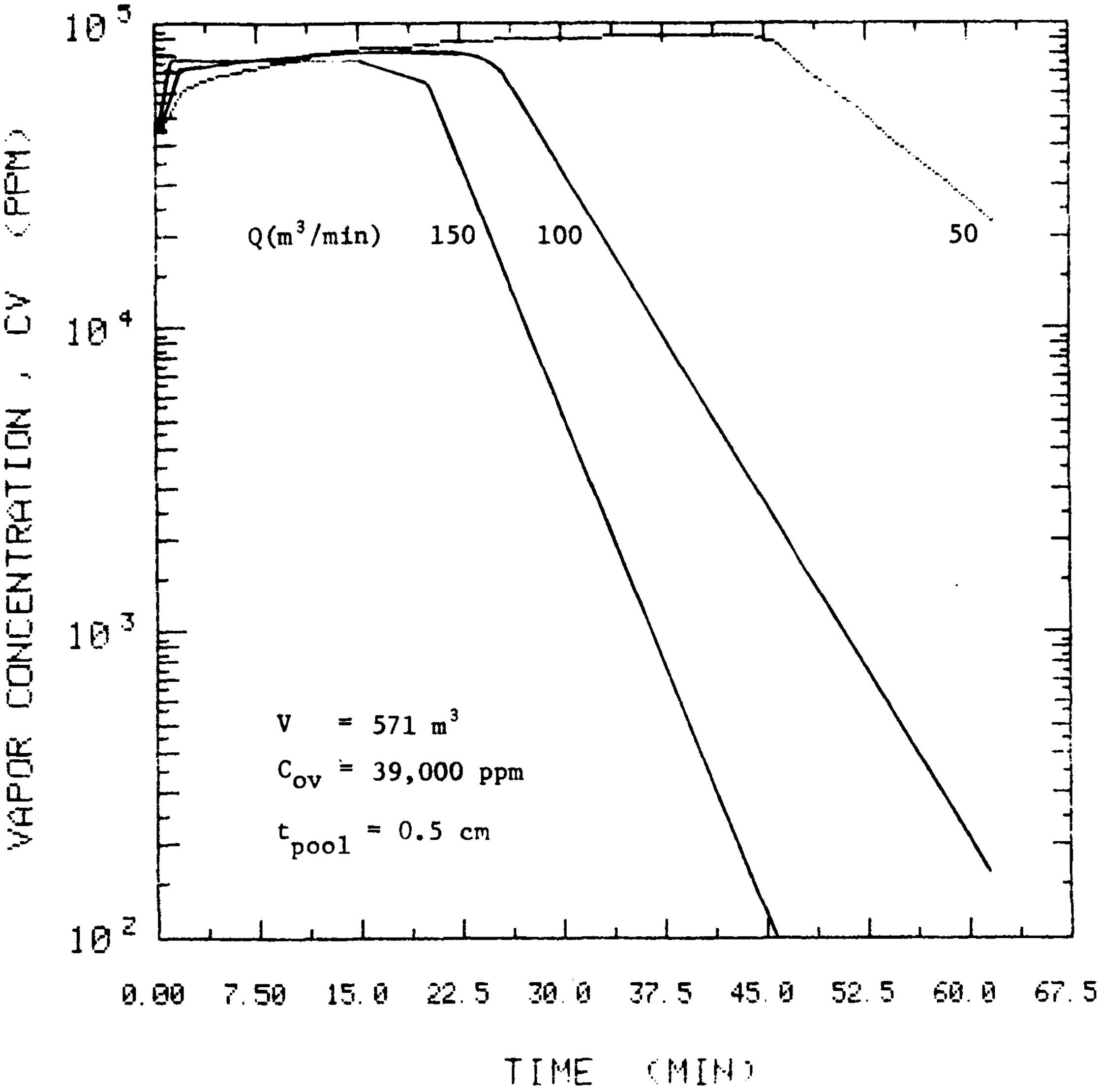


FIGURE IV.25. PURE COMPONENT VENTILATION/EVAPORATION MODEL CONCENTRATION TIME HISTORIES FOR CHANGES IN BLOWER FLOWRATE, Q

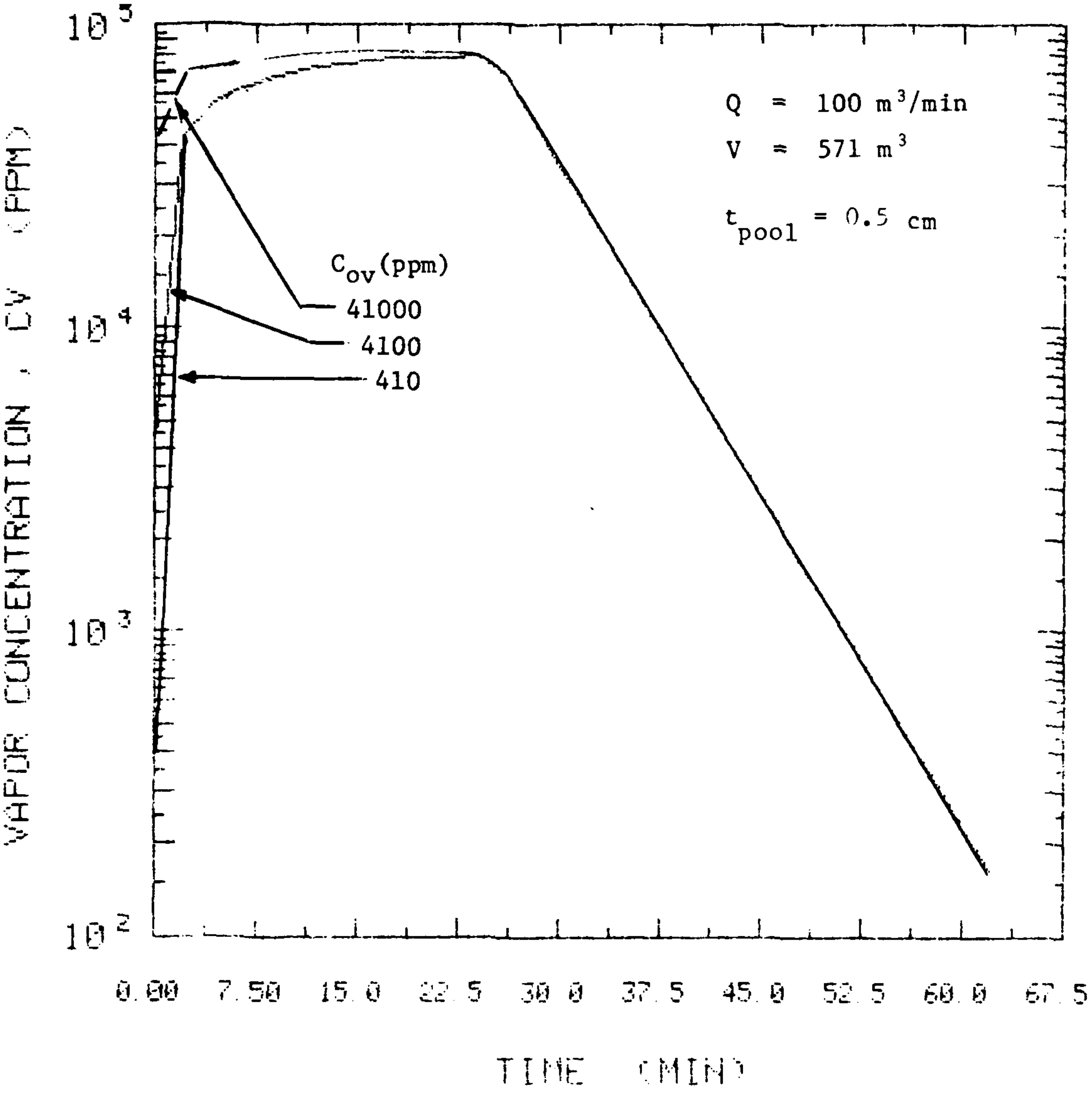


FIGURE IV.26. PURE COMPONENT VENTILATION/EVAPORATION MODEL CONCENTRATION TIME HISTORIES FOR CHANGES IN INITIAL TANK VAPOR CONCENTRATION, C_{ov}

Figure IV.27 demonstrates the cumulative effect of a different set of chemical properties on the gas freeing profile when other parameters (t_{pool}, Q, C_{ov}, V) are held constant. The two chemicals involved in Figure IV.27 are chloroform and p-xylene. At 20°C, the vapor pressure of the more volatile chloroform is approximately 24 times larger than the vapor pressure of p-xylene. The diffusion coefficient is inversely proportional to the square root of the property combination MT_b/G. The diffusion coefficient for chloroform is roughly an order of magnitude greater than that of p-xylene. As a result of the vapor pressure and diffusion coefficient effects, chloroform has a higher evaporation rate than p-xylene. Based on Equation (30) and the fact that blower flowrate is the same, it follows that the xylene concentration curve should reach equilibrium at a lower plateau level than chloroform during the evaporation period. This feature is also shown in Figure IV.27. Due to the lower evaporation rate, a longer time is necessary to evaporate the same amount of xylene relative to chloroform. In fact, over the ventilation period, the chloroform had completely evaporated and the vapor concentration had decreased exponentially while evaporation of xylene was still occurring. This example demonstrates that for a given set of conditions, chemicals with low evaporation rates require a significantly longer gas freeing time. Thus, low evaporation rate chemicals require more thorough tank stripping in order to minimize residue thickness prior to gas freeing for man entry into the tank.

IV.2.5 Model Limitations

Gas freeing of ship/barge tanks is a complex physical process regardless of whether or not it is accompanied by evaporation of chemical product residues. The assumptions that were made in formulating the models and the degree to which the complexities can be reasonably modeled result in limitations that must be recognized.

1. Neither model accounts for the presence of internal tank structure such as web frames, buttresses, etc. Internal structure increases the time required to gas free a tank to a given concentration relative to a clean wall tank. An empirical correlation was developed in Reference 4 for estimating this structure-related time increment through a nondimensional quantity known as

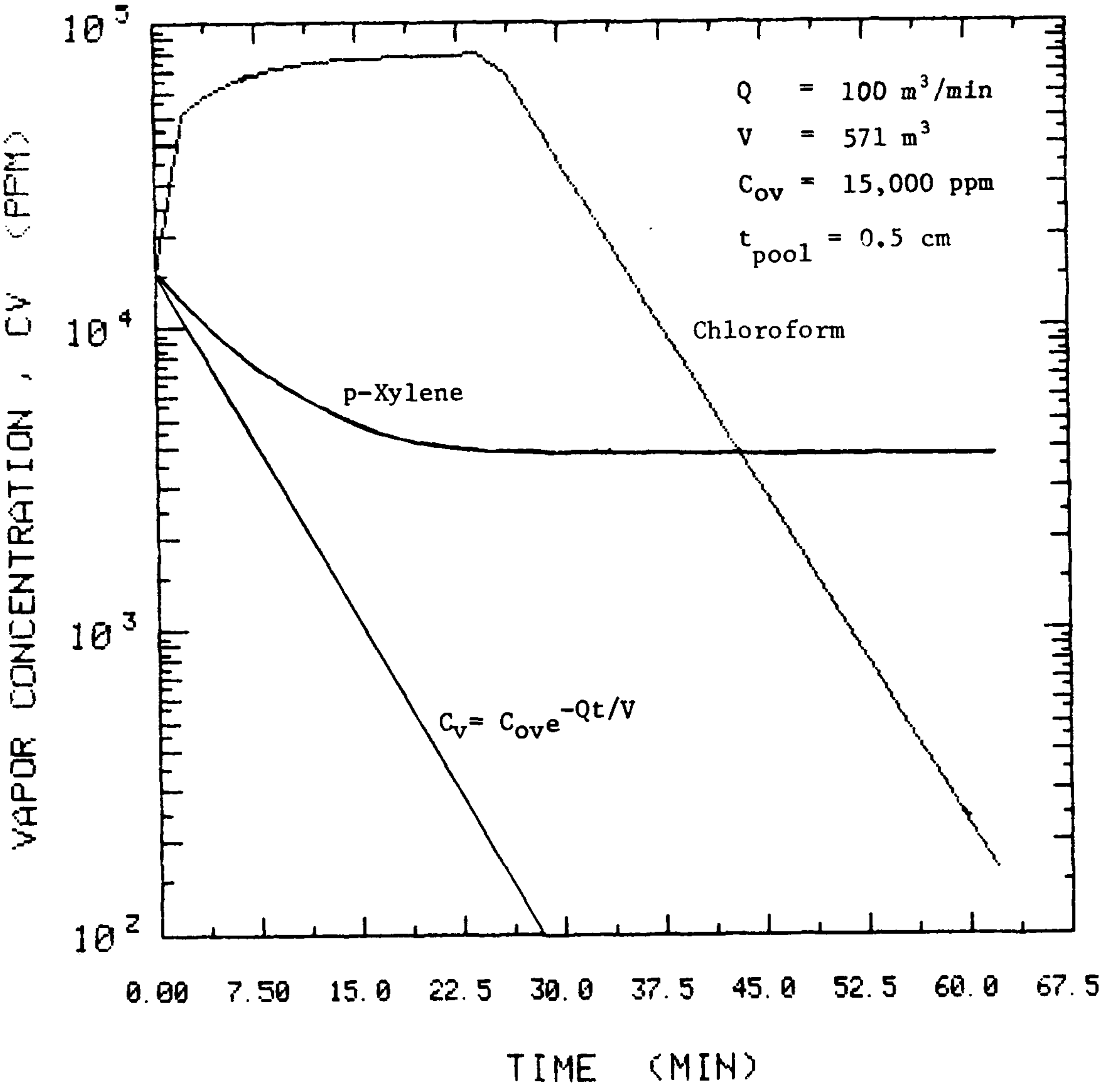


FIGURE IV.27. PURE COMPONENT VENTILATION/EVAPORATION MODEL CONCENTRATION TIME HISTORIES FOR CHANGES IN PHYSICAL PROPERTIES the "tank drainage number." The "tank drainage number" which can be calculated from a knowledge of various geometric parameters for the internal structure, ventilation flow rate and initial vapor density, is proportional to the additional number of tank turnovers, Qt/V, that are then added to the gas freeing time for a clean wall tank. This correlation could be used to give a first estimate of the effect of internal structure, but it must be recognized that the correlation is based on a final concentration equal to 20 percent of the initial value. As this final level may still exceed the levels of interest, e.g., TLV-TWA or TLV-STEL, additional experimental work would be needed to extend the validity of the correlation.

2. Both models assume that the blower jet penetrates the tank atmosphere and impinges onto the tank bottom at all times during ventilation. This assumption, which ensures that the dilution air and chemical vapor are uniformly mixed at all times, is valid if the following Froude number criterion is satisfied:

$$\frac{V^2}{gH(\bar{\rho}-1)} > 50$$

where V = blower jet velocity

g = acceleration due to graviry

H = tank depth

$\bar{\rho}$ = ratio of vapor density at beginning of ventilation to the density of air.

If this criterion is not satisfied initially, complete penetration will not be achieved. Partial penetration and short circuiting will occur; gas freeing will take place but not according to the dilution theory until the Froude number at a later time exceeds the criterion level of 50.

3. The assumption of a well-mixed vapor atmosphere implies that all parts of the tank gas free uniformly. Accordingly, the models do not predict spatial variations in concentration that would be expected in a complex three-dimensional flow field.

4. The evaporation model for chemical/water solutions does not include water evaporation. Chemical solute evaporates from a water solvent. As such, the model does not reflect a time for complete dryness. Binary solution (solute and solvent) evaporation can be modeled by relating the moles of solution to the solute mole fraction through the relative volatility of chemical and water. As the number of moles of solution decreases with time, so does the residue thickness. This approach, while feasible, requires reverse solubility data for water as the solute in order to calculate relative volatility. The uncertainties posed by lack of such data did not justify a "drying" formulation in the model. A review of the solute evaporation equations suggests that the consequence of this limitation is a conservative model prediction of the solute evaporation time because the decay rate of solute concentration is not affected by a decreasing residue thickness.

5. If a tank that has carried a low solubility chemical is washed prior to ventilation, it is possible that the residue will consist of a layer of saturated water solution beneath a layer of pure chemical. Neither model can handle this situation independently. As an alternative, the TANKP model could be applied during evaporation of the pure chemical layer. The final conditions after evaporation of that layer together with a chemical concentration equal to the saturation limit would constitute the initial conditions for applying the TANKM model. The predicted concentration-time histories could then be combined to form a composite history.

6. Gas freeing tests were conducted on 14 tanks that had no internal structure and which contained binary solution residues of chemical in wash water. These tests included ketones, aromatics, esters, alcohols and chlorinated hydrocarbons. In each case, TANKM model predictions were generated. These predictions were based on measured initial conditions or best estimates of critical, unmeasurable initial conditions (δ and C_{OL}) from the selection criteria. For all tests, the last measured vapor concentration was assumed to represent the initial exposure level on many-entry into the tank. The ability of the TANKM model to predict these measured concentrations was assessed by performing a regression analysis on 14 ordered pairs of data which consisted of the last experimental data points and the corresponding analytical predictions. The regression analysis indicated that the analytical prediction correlated log-linearly with the expeirmental data at a coefficient of determination (R^2) of 0.87 and a variance ($\hat{\sigma}^2$) of 0.06. That is,

$$\log C_{exp} = \log a + b \log C_{anal}$$

where $\log a = 0.0755$ (intercept)
$\log b = 0.951$ (slope)

A Student t-test was performed to determine if the slope, b, was equal to unity, i.e., does the analytical model predict the experimental result. At the 95 percent confidence level, the hypothesis was accepted that b equals unity. Therefore, 95 percent of the time, the analytical model predicted the vapor concentration at man-entry. In addition to the above considerations, the analytical predictions of tank entry concentration agreed with the experimental data within a factor of two.

A comparable analysis for the TANKP model was not feasible because of the small number of tests in which the tank was gas free without washing.

IV.3 Dispersion of Chemical Vapor Plumes

Plumes of gas containing vapors from chemical cargos are emitted from cargo tank vents into the air above the deck of tankerships and barges during cargo loading and tank ventilation operations. During cargo loading, vapor evaporates at the gas/liquid interface to form a "vapor blanket" above the liquid surface. Some of the chemical vapor moves away from the interface, either by molecular diffusion or through the action of convection currents, and mixes with the gas atmosphere initially inside the tank. As the liquid level rises, the tank gas atmosphere is displaced from the tank through a tank vent, or an open ullage hatch as shown schematically in Figure IV.28. This stream of displaced gas containing chemical vapor is bent over by the wind, and transported and dispersed in the downwind direction as a chemical vapor plume.

During tank ventilation fresh air is blown into the tank to dilute or replace the tank gas atmosphere which contains the vapor of the previous chemical cargo. The stream of displaced tank gas is often vented to the air above the deck through a vent, ullage hatch or expansion trunk opening. It is also transported and dispersed by the wind as a chemical vapor plume.

Crewmen who are working in the vicinity of a tank vent during cargo loading and tank ventilation operations may be enveloped by the plume of air and chemical vapor. As a result, they may inhale, or experience irritation from contact with air containing chemical vapor. The next section describes the analytical model used to predict the size and concentration distribution of chemical vapor plumes produced during cargo loading and tank ventilation operations.

IV.3.1 Model Formulation

The size of the vapor plume downwind of a tank vent, and the level of vapor concentration at man breathing height, depend upon several factors such as

- the vented gas flowrate,

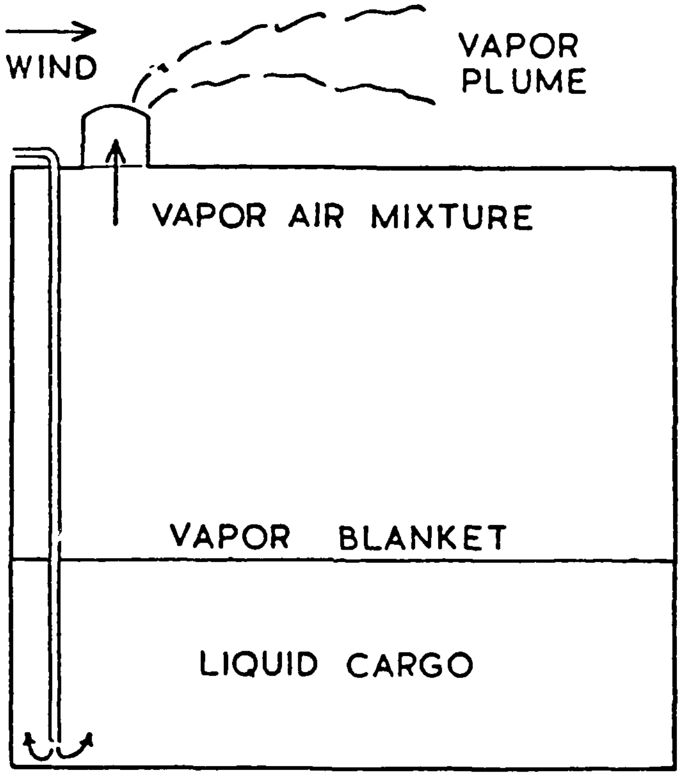


FIGURE IV.28. EMISSION OF A CHEMICAL VAPOR PLUME DURING CARGO LOADING

- the vapor concentration in the vented gas stream,
- the height and the diameter of the vent used to emit the vented gas stream, and
- the ambient wind velocity.

Usually, during an operation such as cargo loading, the vented gas flowrate and the vapor concentration in the vented gas stream vary rather slowly with time. However, the ambient wind above the deck of a ship or barge varies randomly in both speed and direction. These turbulent velocity fluctuations affect the trajectory and the dilution of the plume and cause the instantaneous vapor concentration at downwind locations to fluctuate with time.

For hazard analysis it is the mean, or time average value of the fluctuating vapor concentration value that is of interest. Therefore, it was necessary to define a basis for time averaging of all plume variables, and to include the effect of the wind turbulence directly in the plume dispersion model. An averaging time of 10 minutes was found to give statistically reliable estimates for mean wind speed and turbulence intensity. Also, variations in vent gas flowrate and vent gas concentration were usually observed to be small during periods of 10-minute duration. The major exception occurred near the end of loading when the product flowrate into a tank was adjusted frequently to avoid overfilling or to reach a particular level.

The discussion in the following sections describes the formulation and validation of the ONDEK model for predicting the dispersion of a chemical vapor plume emitted continuously from a tank vent. The HACS Manual (Reference 3), which is a companion volume to this report, gives a listing of the FORTRAN computer program for the ONDEK model and instructions on the use of this program.

The ONDEK chemical vapor plume dispersion model is based upon the numerical integration of a set of conservation equations for mass and momentum along the axis of the plume. Ooms' method (Reference 15) is used to compute the behavior of plumes that are elevated above deck level.

In those circumstances (emission of a very dense plume at low wind speeds) where it is possible for the plume axis to descend to deck level, teRiele's method (Reference 16) is used to compute plume behavior downwind of the transition point. References 15 and 16 should be consulted for the derivations and detailed descriptions of these models.

Ooms considers the development of plumes that are bent over by the wind but remain symmetrical about their axis. Ooms writes four equations for the conservation of mass, chemical species and momentum within the plume. These equations are:

- Conservation of mass

$$\frac{d}{ds}\left(\int_0^{b\sqrt{2}} \rho u 2\pi r \, dr\right) = 2\pi b \rho_a \left\{\alpha_1 \left|u^*(s)\right| + \alpha_2 U_a \left|\sin\theta\right| \cos\theta + \alpha_3 u'\right\} \quad (31)$$

- Conservation of chemical species

$$\frac{d}{ds}\left(\int_0^{b\sqrt{2}} c \, u \, 2\pi r \, dr\right) = 0 \quad (32)$$

- Conservation of momentum in the x (downwind) direction

$$\frac{d}{ds}\left(\int_0^{b\sqrt{2}} \rho u^2 \cos\theta \; 2\pi r \, dr\right) = 2\pi b \rho_a U_a \left\{\alpha_1 \left|u^*\right| + \alpha_2 U_a \left|\sin\theta\right| \cos\theta + \alpha_3 u'\right\}$$

$$+ C_d \pi b \rho_a U_a^2 \left|\sin^3\theta\right| \quad (33)$$

- Conservation of momentum in the z (vertical) direction

$$\frac{d}{ds}\left(\int_0^{b\sqrt{2}} \rho u^2 \sin\theta \, 2\pi r \, dr\right) = \int_0^{b\sqrt{2}} g(\rho_a - \rho) \, 2\pi r \, dr \pm C_d \pi b \rho_a U_a^2 \sin^2\theta \cos\theta \quad (34)$$

where the variables and parameters in these equations are:

b = plume characteristic radius, m

C_d = plume drag coefficient, dimensionless

c = vapor concentration, kg/m^3
g = acceleration of gravity = 9.8 m/sec^2
r = plume radius, m
s = distance along the plume centerline, m
U_a = time average wind speed, m/s
u = local velocity in the plume, m/s
u' = turbulent entrainment velocity, m/s
u^* = velocity on the plume axis, m/s
α_1 = entrainment parameter for shear, dimensionless
α_2 = entrainment parameter for buoyancy, dimensionless
α_3 = entrainment parameter for turbulence, dimensionless
θ = angle of the plume axis with respect to the horizon, radians
ρ = plume density, kg/m^3
ρ_a = ambient air density, kg/m^3

The plume density depends upon the plume concentration and the plume temperature. In most cases, the temperature of the cargo tank atmosphere is very close to the ambient air temperature, and the plume dispersion process can be assumed to be isothermal. This allows eliminating the plume density as an independent variable in favor of the plume concentration through

$$\rho = \rho_a + \frac{(\rho_o - \rho_a)}{\rho_o} c \tag{35}$$

where ρ_o = density of pure chemical vapor, kg/m^3. The isothermal plume dispersion assumption is discussed in more detail in Section IV.3.5.

In order to solve Equations (31) through (34), Gaussian similarity profiles are assumed for both the plume concentration distribution and the plume velocity "defect" (the difference between the plume velocity and the velocity component of the ambient wind speed along the direction of the plume axis).

$$c = c^* \; e^{-r^2/\lambda^2 b^2} \tag{36}$$

$$u - U_a \cos\theta = u^* \; e^{-r^2/b^2} \tag{37}$$

In these equations,

c^* = plume centerline concentration, kg/m^3, and
λ^2 = turbulent Schmidt number squared = 1.35

These similarity profiles are substituted into the conservation Equations (31) - (34), and the equations are integrated to give four simultaneous, ordinary differential equations to be integrated numerically. The dependent variables for these four equations are c^*, b, u^*, and θ. Two additional equations are included to compute the trajectory of the plume axis

$$\frac{dz}{ds} = \sin\theta \tag{38}$$

$$\frac{dx}{ds} = \cos\theta \tag{39}$$

where z and x are the vertical and horizontal coordinates of the plume axis, respectively.

The ordinary differential equations that result from the integration of Equations (31) through (34) still contain four empirical parameters, α_1, α_2, α_3, and C_d. These values are to be determined by experiment. Listed below are the values of these parameters suggested by Ooms, et al. (Reference 15) and Petersen and Cermak (Reference 17). The values of α_1, α_2, and C_d recommended by Ooms and Petersen are quite similar. However, the difference in values of α_3 deserves more discussion.

VALUES OF EMPIRICAL PLUME ENTRAINMENT AND DRAG PARAMETERS

	α_1	α_2	α_3	C_d
Ooms, Mahieu and Zelis (Ref. 15)	.057	0.5	1.0	0.3
Petersen and Cermak (Ref. 17)	$.057\left(\frac{\rho_{soo}}{\rho_{so}}\right)\left(\frac{\rho_{aoo}}{\rho_{soo}}\right)^{\frac{1}{2}}$	0.65 to 1.34	2.84	0.3
This work	.057	0.5	2 to 3	0.3

Ooms, et al. (Reference 15) modeled the entrainment of air into the plume due to atmospheric turbulence in Equation (31) as

$$\alpha_3 \quad u' \tag{40}$$

where u' represents a characteristic "entrainment velocity." The entrainment velocity was modeled either as

$$u' = (\overline{u_a^2})^{1/2} \qquad \text{or as} \tag{41}$$

$$u' = (\varepsilon b)^{1/3} \tag{42}$$

where ε = eddy energy dissipation. In response to a question, Ooms (Reference 18) interpreted $(\overline{u_a^2})^{1/2}$ to be the root mean square of the sum of the velocity component fluctuations in all three directions.

$$u' = (\overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2})^{1/2} \tag{43}$$

However, for emissions from industrial stacks he favored the use of Equation (42).

Petersen (Reference 17) performed wind tunnel experiments in which he measured the trajectory of plumes in a turbulent boundary layer, and compared the measured plume trajectories with predictions using Ooms' model. Petersen defined the entrainment velocity as

$$u' = U_a * \frac{(i_x + i_y)}{2} \tag{44}$$

where $i_x = \sqrt{\overline{u_x^2}} / U_a$ is the turbulence intensity in the longitudinal direction,

and $i_y = \sqrt{\overline{u_y^2}} / U_a$ is the turbulence intensity in the lateral (crosswind) direction.

One set of laboratory experiments were performed with neutral density stratification and low levels of turbulence intensity, $u'/U_a < 5\%$. Petersen assumed that his entrainment relation for α_1 was valid and then varied α_2 to minimize the error between his model predictions and all of the experimental data. He found the range for the expected value of α_2 was between 0.65 and 1.34 with the value of $\alpha_2 = 0.9$ giving the best fit. He assumed that the turbulence level was low enough that it did not contribute significantly to plume entrainment. A second set of experiments performed with stable density stratification and low levels of turbulence indicated that the values of α_1 and α_2 used for neutral stratification were adequate for stable stratification as well.

Petersen (Reference 17) performed an analysis of the plume dispersion equations for the region in which atmospheric dispersion should dominate the entrainment process. This analysis gives a derived value of $\alpha_3 = 2\sqrt{2} = 2.83$ for the turbulence entrainment parameter.

Two additional sets of plume rise experiments were performed by Petersen with neutral density stratification and both moderate ($5\% < u'/U_a \leq 10\%$) and high ($u'/U_a > 10\%$) levels of turbulence. He assumed that the values of α_1 and α_2 determined previously for low turbulence levels still applied, and he sought to confirm experimentally the analytical value of $\alpha_3 = 2.83$.

The moderate turbulence level tests were performed in a relatively "clean" wind tunnel with surface roughness elements added to increase the turbulence level. Good agreement between model predictions and experimental data for plume trajectory was found using $\alpha_3 = 2.83$. However, the high turbulence level tests were conducted with simulated terrain topography including ridges and hills. The terrain topography simulation produced downdrafts as well as increased turbulence, and the agreement between model prediction and experiment was poor for plumes with low rise heights (low values of stack exit velocity).

Petersen, et al. (Reference 17) recommend use of a value of $\alpha_3 = 2\sqrt{2}$ for the turbulence entrainment parameter when the ambient turbulence dominates the mixing process. They note that if Ooms' recommended value of $\alpha_3 = 1$ were applied to their tests, the plume rise height would be overpredicted. However, the definitions of entrainment velocity given in Equations (42), (43), and (44) are not the same. Thus, the proper value of α_3 for use in a dispersion model should be linked to the definition of entrainment velocity, u'.

When the distance from the plume centerline to the vessel deck is less than the plume characteristic width, b, entrainment is reduced. This effect is simulated by including an "image" plume at $z = z_{C\ell}$ in the equation for concentration distribution. Then, Equation (36) is replaced by

$$C(x,y,z) = C^* \left[\exp - \left(\frac{(z-z_{C\ell})^2 + y^2}{\lambda^2 b^2}\right) + \exp - \left(\frac{(z+z_{C\ell})^2 + y^2}{\lambda^2 b^2}\right)\right] \tag{45}$$

In this equation, y and z are the lateral (crosswind) and vertical coordinates of the point at which concentration is predicted, and $z_{C\ell}$ is the height of the plume centerline above the deck.

If the plume is very much denser than air, and if the wind speed is very low, the predicted elevation of the plume centerline could become negative. Physically, the plume centerline cannot pass through the deck of the vessel. Instead, the plume would continue to disperse along the deck with the maximum concentration at deck level. To simulate the dispersion of a chemical vapor plume along the deck, a transition is made to a simplified version of teRiele's model (Reference 16) for heavier-than-air gas plumes emitted near the ground.

TeRiele's model was developed to predict the downwind dispersion of dense gas emissions from area sources. It consists of three integral equations for the conservation of mass and one integral equation for conservation of momentum. The integral equations for conservation of mass are identical except for Y_L, the limit of integration in the crosswind, y, direction.

$$\int_0^{Y_L} \left[\frac{\partial}{\partial x}\left[\int_0^{\infty} cu \, dz\right]\right] dy = \left[\int_0^{\infty} K_y \frac{\partial c}{\partial y} \, dz\right]_{y=Y_L} \tag{46}$$

In this equation, K_y is an atmospheric dispersion coefficient and the limit of integration, Y_L, can take on three different values

$Y_L = b$, at the edge of a region near the source where the concentration is constant in the crosswind direction,

$Y_L = b + \sqrt{2}\,\sigma_y/2$, outside the region of constant concentration, but within the dense gas plume,

$Y_L = \infty$, outside the vapor cloud.

Since we intend to match teRiele's model to Ooms model downwind of a vent, the value of b will be equal to 0. Thus, the set of integral equations for conservation of mass is reduced to two equations with integration limits of

$Y_L = \sqrt{2}\,\sigma_y/2$, and

$Y_L = \infty$.

The integral equation for conservation of mass is written as

$$\frac{d}{dx}\left[\int_0^\infty\int_0^\infty cu^2\,dy\,dz\right] = \int_0^\infty \frac{c_{gr}}{\rho_{gr}}\cdot\tau_o\,dy \qquad (47)$$

where c_{gr} = concentration at ground (deck) level, kg/m^3

ρ_{gr} = density of the plume at ground (deck) level, kg/m^3

τ_o = wind shear stress at ground (deck) level, kg/m^2

Equations (46) and (47) can be integrated analytically if the shape of the concentration and velocity profiles are specified. A Gaussian-type profile is assumed for the concentration distribution, and a power law profile for the wind velocity.

$$c = c_a \exp\left[-\left(\frac{y}{\sigma_y}\right)^2 - \left(\frac{z}{\sigma_z}\right)^{1+2\alpha}\right] \tag{48}$$

$$u = u_o \left(\frac{z}{z_o}\right)^{\alpha} \tag{49}$$

where c_a = concentration on the plume axis at deck level, kg/m^3
u_o = wind speed at reference height, m/s
z_o = reference height, m
α = velocity profile parameter, dimensionless
σ_y = horizontal dispersion coefficient, m
σ_z = vertical dispersion coefficient, m

Substituting these profile formulas into the conservation equations and performing the integrations determines the form of the atmospheric dispersion coefficient. TeRiele gives

$$K_y = K_o^* \left(\frac{W}{B}\right)^{\gamma} \left(\frac{z}{z_o}\right)^{\alpha} \tag{50}$$

where K_o^* = a function of wind velocity, atmospheric stability class and area source width
W = $b + \sqrt{\pi}\ \sigma_y/2$ = characteristic width of the concentration profile
B = width of the area source
γ = $2 - 1/\beta$, where β is a coefficient in the formula for point source dispersion
σ_y^* = δx^{β}. Both δ and β depend upon atmospheric stability class.

Using Equation (50) for K_y, we obtain three simultaneous, ordinary differential equations for C_a, σ_y and σ_z. Concentration profiles must be matched at the point of transition from Ooms' to teRiele's model. The following matching equations can be derived to relate c_a and σ_y to c^* and b.

$$c_a = 2\ c^* \tag{51}$$

$$\sigma_y = \lambda b \tag{52}$$

Since the form of the concentration profiles for Ooms' and teRiele's method are different (they are the same only if $\alpha = 0.5$), it is necessary to estimate a value of σ_z that gives a good "global" match to the concentration profiles. We have required that the integral

$\int_0^\infty c\ dz$ be equal for both methods along the $y = 0$ plane.

This gives a relation between σ_z and b

$$\sigma_z = \lambda b\ \frac{\sqrt{\pi}}{2}\ \frac{(1+2\alpha)}{\Gamma(1/1+2\alpha)} \tag{53}$$

With these values of c_a, σ_y, and σ_z as starting conditions, teRiele's equations are integrated numerically without further reference to Ooms' variables.

The procedures used to solve the plume dispersion equations numerically are discussed in detail in Reference 3.

IV.3.2 Vapor Dispersion Experiments - Laboratory and Field Tests

Table IV. 6 lists the experimental conditions for the 103 separate tests that were performed to provide the experimental data used for plume model validation. Of this number, 49 tests were performed during actual cargo loading operations on tankerships and barges, and 54 tests were full scale cargo loading simulations performed out-of-doors at SwRI.

The field tests were performed in four different marine terminals, and consist of 3 observations of cargo loading on barges and 7 observations of cargo loading on tankerships. Seven different chemical cargos were loaded during these operations:

TABLE IV.6. SUMMARY OF ON-DECK FULL SCALE TESTS

OBSERVATION	TERMINAL	VESSEL TYPE	PRODUCT	TANK NO.	TANK VOL. m^3	LOADING RATE m^3/hr	VENT C_o Kg/m^3	VENT TYPE	VENT HEIGHT m	VENT DIAM m	VENT EXIT VELOCITY m/s	WIND VELOCITY m/s	TURBULENCE LEVEL %	TYPE OF CONCENTRATION MEASUREMENTS		
														SOURCE	AREA	PERSONNEL
1	H	TANKER	ETHANOL	2CP	1040	155	.0141	OPEN ULLAGE HATCH	0.86	0.21	1.25	4.02	17.2	Yes	Yes	Yes
2	H	"		"	"	"	.0177		"	"	"	4.42	21.4	"	"	"
3	H	"		"	"	"	.0227		"	"	"	4.20	18.9	"	"	"
4	H	"		"	"	"	.0375		"	"	"	4.62	22.6	"	"	"
5	H	"		"	"	"	.0445		"	"	"	5.11	19.8	"	"	"
6	H	"		"	"	"	.0541		"	"	"	4.41	17.0	"	"	"
7	H	"		"	"	"	.0815		"	"	"	5.17	21.2	"	"	"
8	H	TANKER	ISOPROPANOL	3CS	1096	158	.00364	OPEN ULLAGE HATCH	0.86	0.21	1.27	3.01	13.0	Yes	Yes	Yes
9	H	"		"	"	131	.00847		"	"	1.06	2.59	11.3	"	"	"
10	H	"		"	"	102	.00954		"	"	0.82	2.78	4.9	"	"	"
11	H	"		"	"	"	.0140		"	"	"	3.02	8.2	"	"	"
12	H	"		"	"	"	.0154		"	"	"	3.21	6.3	"	"	"

NOTES: * C_o uncertain due to presence of methane in tank atmosphere.

** Vent in wake of deckhouse, vapor transported upwind.

TABLE IV.6. SUMMARY OF ON-DECK FULL SCALE TESTS (CONTD)

OBSERVATION	TERMINAL	VESSEL TYPE	PRODUCT	TANK NO.	TANK VOL. m^3	LOADING RATE m^3/hr	VENT C_o Kg/m^3	VENT TYPE	VENT HEIGHT m	VENT DIAM m	VENT EXIT VELOCITY m/s	WIND VELOCITY m/s	TURBU-LENCE LEVEL %	TYPE OF CONCENTRATION MEASUREMENTS		
														SOURCE	AREA	PERSONNEL
13	H	BARGE	DENATURED ETHANOL	1S	797	94.7	.136*	OPEN ULLAGE HATCH	0.76	0.197	0.864	2.46	9.1	Yes*	Yes	No
14	H	"		"	"	"	"		"	"	"	3.40	10.1	"	"	"
15	H	"		"	"	"	"		"	"	"	4.14	11.6	"	"	"
16	H	"		"	"	"	"		"	"	"	4.36	21.8	"	"	"
17	H	"		"	"	"	"		"	"	"	5.40	17.0	"	"	"
18	H	"		"	"	"	"		"	"	"	5.05	17.3	"	"	"
19	H	"		"	"	"	"		"	"	"	6.42	16.1	"	"	"
20	H	"		"	"	"	"		"	"	"	6.03	18.1	"	"	"
21	H	"		"	"	"	"		"	"	"	6.68	16.3	"	"	"
22	F	TANKER	n-HEPTANE	10C	1270	127	.0063	OPEN ULLAGE HATCH	1.07	0.25	0.719	**	**	Yes	Yes	Yes
23	F	"		"	"	"	"		"	"	"	**	**	"	"	"

TABLE IV.6. SUMMARY OF ON-DECK FULL SCALE TESTS (CONTD)

OBSERVATION	TERMINAL	VESSEL TYPE	PRODUCT	TANK NO.	TANK VOL. m^3	LOADING RATE m^3/hr	VENT C_o Kg/m^3	VENT TYPE	VENT HEIGHT m	VENT DIAM m	VENT EXIT VELOCITY m/s	WIND VELOCITY m/s	TURBU-LENCE LEVEL %	TYPE OF CONCENTRATION MEASUREMENTS		
														SOURCE	AREA	PERSONNEL
24	H	TANKER	ISOPROPANOL	3CS	1096	272	.00927	OPEN ULLAGE HATCH	0.86	0.21	2.19	0.67	28.8	Yes	Yes	No
25	H	"		"	"	"	.01346		"	"	"	0.68	30.2	"	"	"
26	H	"		"	"	"	.01884		"	"	"	0.62	27.0	"	"	"
27	H	"		"	"	"	.02410		"	"	"	0.47	36.4	"	"	"
28	H	TANKER	VINYL ACETATE	10CP	1245	228	.00976	OPEN ULLAGE HATCH	0.86	0.21	1.83	0.57	22.4	Yes	Yes	No
29	H	"		"	"	"	.03674		"	"	"	0.62	32.7	"	"	"
30	H	"		"	"	"	.1449		"	"	"	0.49	23.5	"	"	"
31	H	"		"	"	"	.1924		"	"	"	1.29	33.4	"	"	"

TABLE IV.6. SUMMARY OF ON-DECK FULL SCALE TESTS (CONTD)

OBSERVATION	TERMINAL	VESSEL TYPE	PRODUCT	TANK NO.	TANK VOL. m^3	LOADING RATE m^3/hr	VENT C_o Kg/m^3	VENT TYPE	VENT HEIGHT m	VENT DIAM m	VENT EXIT VELOCITY m/s	WIND VELOCITY m/s	TURBU-LENCE LEVEL %	TYPE OF CONCENTRATION MEASUREMENTS		
														SOURCE	AREA	PERSONNEL
32	G	BARGE	METHANOL	3	563	193	.1039	OPEN ULLAGE HATCH	0.76	0.48	0.30	2.02	27.3	Yes	Yes	Yes
33	G	"		"	"	"	.1080		"	"	"	1.45	32.6	"	"	"
34	G	"		"	"	"	.1095		"	"	"	1.72	26.5	"	"	"
35	G	"		"	"	"	.1380		"	"	"	2.28	36.5	"	"	"
36	G	"		"	"	"	.1383		"	"	"	1.95	22.8	"	"	"
37	G	"		"	"	"	.1785		"	"	"	1.41	30.6	"	"	"
38	H	BARGE	ETHANOL	3S	816	122	.15676	OPEN ULLAGE HATCH	0.74	0.20	1.08	4.30	15.7	Yes	Yes	No
39	H	"		"	"	"	.14842		"	"	"	3.69	15.1	"	"	"
40	H	"		"	"	121	.14075		"	"	1.07	4.14	14.6	"	"	"
41	H	"		1S	797	114	.17397		"	"	1.01	3.99	13.0	"	"	"
42	H	"		"	"	"	.17454		"	"	"	4.03	12.6	"	"	"
43	H	"		"	"	151	.18353		"	"	1.33	3.59	11.4	"	"	"
44	H	"		"	"	"	.17169		"	"	"	4.01	11.5	"	"	"

TABLE IV.6. SUMMARY OF ON-DECK FULL SCALE TESTS (CONTD)

OBSERVATION	TERMINAL	VESSEL TYPE	PRODUCT	TANK NO.	TANK VOL. m^3	LOADING RATE m^3/hr	VENT C_o Kg/m^3	VENT TYPE	VENT HEIGHT m	VENT DIAM m	VENT EXIT VELOCITY m/s	WIND VELOCITY m/s	TURBU-LENCE LEVEL %	TYPE OF CONCENTRATION MEASUREMENTS		
														SOURCE	AREA	PERSONNEL
45	SwRI	VENT SIMULATION	PROPANE/AIR	--	--	728.	.04543	ULLAGE HATCH	1.60	.202	6.32	4.19	24.9	Yes	Yes	No
46	"			--	--	722	.05491		"	"	6.27	4.44	22.0	"	"	"
47	"			--	--	734	.05122		"	"	6.37	4.24	21.7	"	"	"
48	"			--	--	461	.04302		"	"	4.00	4.64	23.0	"	"	"
49	"			--	--	456	.04484		"	"	3.96	4.20	26.8	"	"	"
50	"			--	--	455	.05350		"	"	3.95	5.74	29.8	"	"	"
51	"			--	--	454	.05487		"	"	3.95	5.07	23.6	"	"	"
52	"			--	--	155	.07653		"	"	1.35	4.37	19.8	"	"	"
53	"			--	--	166	.08196		"	"	1.44	5.18	25.3	"	"	"
54	"			--	--	196	.10576		"	"	1.70	5.41	31.6	"	"	"
55	"			--	--	222	.11046		"	"	1.93	4.35	31.6	"	"	"

TABLE IV.6. SUMMARY OF ON-DECK FULL SCALE TESTS (CONTD)

OBSERVATION	TERMINAL	VESSEL TYPE	PRODUCT	TANK NO.	TANK VOL. m^3	LOADING RATE m^3/hr	VENT C_o Kg/m^3	VENT TYPE	VENT HEIGHT m	VENT DIAM m	VENT EXIT VELOCITY m/s	WIND VELOCITY m/s	TURBULENCE LEVEL %	TYPE OF CONCENTRATION MEASUREMENTS SOURCE	AREA	PERSONNEL
56	SwRI	VENT SIMULATION	PROPANE/AIR	--	--	899	.08800	4m VENT	4.01	.202	7.81	3.94	28.7	Yes	Yes	No
57	"			--	--	913	.09074		"	"	7.93	3.86	32.1	"	"	"
58	"			--	--	529	.10744		"	"	4.59	3.89	31.1	"	"	"
59	"			--	--	501	.10967		"	"	4.35	3.26	32.8	"	"	"
60	"			--	--	533	.12110		"	"	4.62	2.76	34.4	"	"	"
61	"			--	--	215	.27122		"	"	1.86	3.04	33.5	"	"	"
62	"			--	--	197	.25552		"	"	1.71	3.32	27.0	"	"	"
63	"			--	--	197	.25100		"	"	1.71	2.71	23.8	"	"	"
64	"			--	--	869	.09942		"	"	7.53	2.66	39.0	"	"	"
65	"			--	--	923	.09939		"	"	8.00	2.28	28.6	"	"	"
66	"			--	--	922	.10952		"	"	7.99	2.18	30.4	"	"	"
67	"			--	--	528	.12311		"	"	4.58	2.04	33.2	"	"	"
68	"			--	--	526	.12145		"	"	4.56	1.42	42.8	"	"	"
69	"			--	--	209	.24624		"	"	1.81	0.68	52.0	"	"	"
70	"			--	--	188	.25729		"	"	1.63	2.86	27.2	"	"	"
71	"			--	--	182	.25093		"	"	1.58	3.18	27.2	"	"	"

TABLE IV.6. SUMMARY OF ON-DECK FULL SCALE TESTS (CONTD)

OBSERVATION	TERMINAL	VESSEL TYPE	PRODUCT	TANK NO.	TANK VOL. m^3	LOADING RATE m^3/hr	VENT C_o Kg/m^3	VENT TYPE	VENT HEIGHT m	VENT DIAM m	VENT EXIT VELOCITY m/s	WIND VELOCITY m/s	TURBU-LENCE LEVEL %	TYPE OF CONCENTRATION MEASUREMENTS		
														SOURCE	AREA	PERSONNEL
72	SwRI	VENT SIMULATION	PROPANE/AIR	--	--	213	.23017	4m VENT	4.01	.202	1.85	2.81	24.7	Yes	Yes	No
73	"			--	--	545	.14038		"	"	4.72	3.32	35.5	"	"	"
74	"			--	--	568	.10690		"	"	4.92	3.68	31.8	"	"	"
75	"			--	--	915	.10811		"	"	7.93	5.40	24.8	"	"	"
76	"			--	--	915	.11147		"	"	7.93	4.95	25.4	"	"	"
77	"			--	--	923	.12385		"	"	8.00	5.02	25.7	"	"	"
78	"			--	--	463	.15993		"	"	4.01	4.96	23.1	"	"	"
79	"			--	--	565	.16348		"	"	4.90	4.02	28.8	"	"	"
80	"			--	--	570	.18424		"	"	4.94	4.33	30.8	"	"	"
81	"			--	--	570	.17662		"	"	4.94	3.62	34.6	"	"	"
82	"			--	--	287	.33065		"	"	2.49	3.64	34.4	"	"	"

TABLE IV.6. SUMMARY OF ON-DECK FULL SCALE TESTS (CONTD)

OBSERVATION	TERMINAL	VESSEL TYPE	PRODUCT	TANK NO.	TANK VOL. m^3	LOADING RATE m^3/hr	VENT C_o Kg/m^3	VENT TYPE	VENT HEIGHT m	VENT DIAM m	VENT EXIT VELOCITY m/s	WIND VELOCITY m/s	TURBU-LENCE LEVEL %	TYPE OF CONCENTRATION MEASUREMENTS		
														SOURCE	AREA	PERSONNEL
83	"	VENT SIMULATION	PROPANE/AIR	--	--	569	.20090	B/3 VENT	6.10	.202	4.93	3.90	27.0	"	"	"
84	"			--	--	618	.21661		"	"	5.36	3.02	29.0	"	"	"
85	"			--	--	272	.28042		"	"	2.36	3.24	40.0	"	"	"
86	"			--	--	255	.28731		"	"	2.21	2.86	34.7	"	"	"
87	"			--	--	908	.16573		"	"	7.87	3.52	25.7	"	"	"
88	"			--	--	608	.26276		"	"	5.27	3.44	27.3	"	"	"
89	"			--	--	616	.24494		"	"	5.34	4.30	20.3	"	"	"
90	K	TANKER	MEK	7CP	625	116	.00753	OPEN ULLAGE HATCH	0.93	0.15	1.01	0.54	--	Yes	Yes	Yes
91	"			"	"	116	.01011		"	"	1.01	0.59	--	"	"	"
92	"			"	"	116	.02877		"	"	1.01	0.74	--	"	"	"

TABLE IV.6. SUMMARY OF ON-DECK FULL SCALE TESTS (CONTD)

OBSERVATION	TERMINAL	VESSEL TYPE	PRODUCT	TANK NO.	TANK VOL. m^3	LOADING RATE m^3/hr	VENT C_o Kg/m^3	VENT TYPE	VENT HEIGHT m	VENT DIAM m	VENT EXIT VELOCITY m/s	WIND VELOCITY m/s	TURBU-LENCE LEVEL %	TYPE OF CONCENTRATION MEASUREMENTS		
														SOURCE	AREA	PERSONNEL
93	SwRI	VENT SIMULATION	PROPANE/AIR	--	--	908	.39960	B/3 VENT	6.10	.202	7.87	3.27	34.3	Yes	Yes	No
94	"			--	--	908	.19980		"	"	7.87	3.33	37.7	"	"	"
95	"			--	--	908	.14708		"	"	7.87	3.57	37.9	"	"	"
96	"			--	--	618	.22760		"	"	5.36	3.68	28.6	"	"	"
97	"			--	--	272	.37740		"	"	2.35	3.10	41.4	"	"	"
98	"			--	--	272	.55500		"	"	2.35	3.81	23.0	"	"	"
99	"			--	--	618	.12770		"	"	5.36	2.69	30.9	"	"	"
100	"			--	--	618	.12770		"	"	5.36	4.00	28.0	"	"	"
101	"			--	--	272	.42740		"	"	2.35	3.65	28.6	"	"	"
102	F	TANKER	GASOLINE	2P	1217	591	.03813	OPEN ULLAGE HATCH	1.04	.203	4.89	3.32	33.9	Yes	Yes	No
103	"			2P	1217	591	.04452		1.04	.203	4.89	3.75	45.3	"	"	"

- ethanol (denatured), 3 observations
- gasoline (unleaded grade)
- n-heptane
- isopropanol, 2 observations
- methanol
- methyl ethyl ketone
- vinyl acetate

The cargo loading rates encountered in these observations ranged from 95 m^3/hr (600 bbl/hr) to 272 m^3/hr (1712 bbl/hr) for the pure chemicals and 591 m^3/hr (3723 bbl/hr) for gasoline. The loading rate was governed primarily by the capacity of the product transfer pumps located onshore that take product from storage tanks in the tank farm and pump it to the loading dock. In some cases, the flow of product received by the vessel was split and transferred to 2 or more cargo tanks simultaneously.

In every one of the field observations, the tank atmosphere displaced by incoming cargo was vented through open ullage hatches located close to deck level. Vent heights ranged from 0.74m (29 inches) to 1.07m (42 inches) above deck level. Vent diameters ranged from 0.15m (6 inches to 0.48m (19 inches).

In order to properly validate the plume dispersion model it was necessary to acquire additional data at higher loading rates and for different vent geometries. For this purpose, a set of 54 laboratory tests were performed at SwRI to simulate (in full scale) the emission of chemical vapors during cargo loading. These tests were performed in the open air, away from laboratory buildings and other obstructions. Plume emission was simulated by releasing a mixture of propane and air through a 0.20m (8 inch) diameter vent at heights of 1.6m (5.25 ft), 4.0m (13.1 ft) and 6.1m (20 ft) above the ground. The propane and air emission rates were adjusted to simulate the complete range of low (155 to 287 m^3/hr), medium (454 to 618), and high (722 m^3/hr to 923 m^3/hr) cargo loading rates anticipated in marine terminal operations.

All of the plume model validation experiments were designed to take advantage of the model's sensitivity to α_3, the turbulence entrainment parameter. Other researchers have used measurements of plume rise height for the determination of entrainment coefficients. However, for the range of conditions anticipated for most tank atmosphere venting operations, the plume rise height would have been too small to measure accurately. Also, for chemical vapor plumes that are heavier than air, the effects of increasing plume momentum flux and buoyancy flux cancel each other. Increasing the momentum flux causes the plume to rise, while increasing the buoyancy flux causes the plume to sink. These combined effects could be mistaken for the effect of ambient turbulence which limits plume rise through quicker dilution. Thus, plume rise height could not be used to provide an unambiguous determination of the plume model entrainment parameters.

Instead of plume rise height, the crosswind concentration distribution was used in this study for determining the appropriate value of α_3, the turbulence entrainment parameter, for each test condition. Figure IV.29 compares the behavior of the crosswind concentration distribution predicted for values of α_3 between 1 and 4 for the set of vapor emission conditions listed in Table IV. 7. Both the peak concentration value in the center of the plume and the width of the plume in the crosswind direction are strongly sensitive to the value of α_3 used in the prediction. Not only is the crosswind concentration distribution a sensitive function of model parameters, it is the variable that must be predicted correctly to give realistic predictions of chemical vapor hazards.

During each vapor dispersion test several variables were measured and recorded.

- Vent geometry and receptor arrangement
- Ambient wind speed and direction
- Plume emission rate
- Vapor concentration at the vent
- Vapor concentration distribution downwind of the vent.

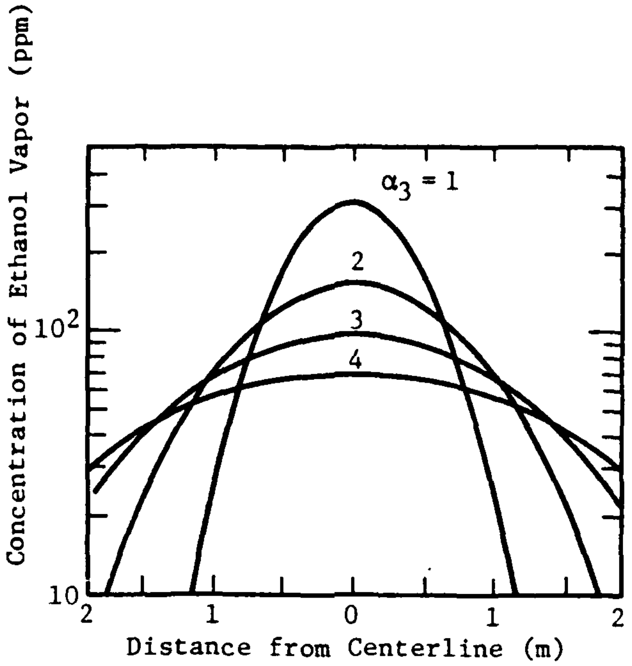


FIGURE IV.29. CROSSWIND CONCENTRATION DISTRIBUTION PREDICTED FOR 4 VALUES OF α_3 AT 4m DOWNWIND OF VENT

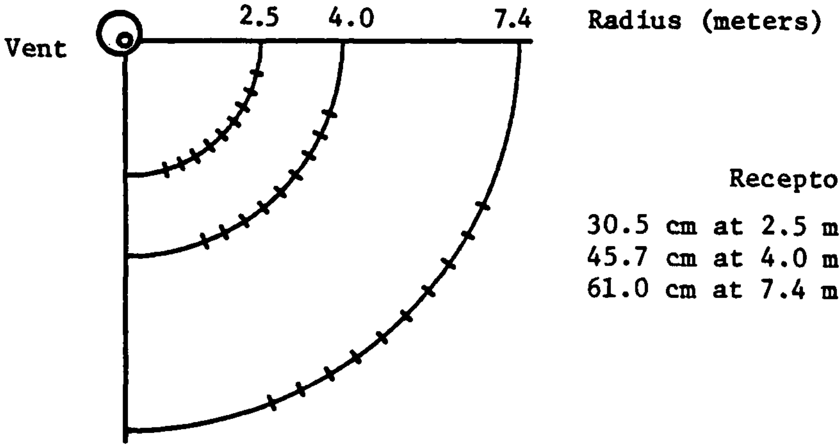
TABLE IV. 7. VAPOR EMISSION CONDITIONS FOR THE EXAMPLE IN FIGURE IV.29

Vented Gas	:	Ethanol vapor and air
Concentration at the Vent	:	43,050 ppm (0.0815 kg/m^3)
Cargo Loading Rate	:	155 m^3/hr
Vent Diameter	:	21 cm
Vent Height	:	86 cm above deck level
Wind Speed	:	4.9 m/s at 10 m height
Turbulence Entrainment Velocity	:	1.04 m/s (21.2% of wind speed)
Ambient Temperature	:	24°C
Concentration Prediction Height	:	1.67 m above deck level

The methods used to measure each of these variables are described below.

Vent Geometry and Receptor Location

Both the diameter of the vent and its height above the deck were measured and recorded. A circular arc, with the vent at its center, was scribed onto the deck of the vessel with chalk. Vapor sampling receptors were arranged along the arc as shown schematically in Figure IV.30. The height of each receptor above the deck, and the separation distance between receptors were measured and recorded for each test. A photograph or sketch was made showing the vent and receptor arrangement. The proximity of on-deck structures (such as piping, pumphouses or a deckhouse) that might influence the dispersion of the plume was also recorded.



Receptor Spacing

30.5 cm at 2.5 m Radius
45.7 cm at 4.0 m Radius
61.0 cm at 7.4 m Radius

FIGURE IV.30. TYPICAL ARRANGEMENT OF VAPOR SAMPLING RECEPTORS FOR MEASUREMENT OF CROSSWIND CONCENTRATION DISTRIBUTION

Ambient Wind Speed and Direction

Wind speed measurements were made at two locations, (1) on the deck of the vessel, and (2) on a 10m meteorological tower located in the marine terminal area. Ambient wind speed was measured continuously during the tests with either a propeller/vane or a cup/vane anemometer placed atop the meteorological tower. The continuous wind speed indications were sampled and recorded every 15 seconds by a data logger. Thus, during a 10-minute vapor sampling run wind speed and direction were measured and recorded 40 times. The set of wind speed values was used to form statistical estimates of the mean and standard deviation of wind speed during the 10-minute-long test. The estimates of the standard deviation of wind speed was used as the measured value of turbulence entrainment velocity, u', for plume model predictions. This method was also used for the simulation tests performed at SwRI.

In some of the field tests on tanker ships, the velocity close to the tank vent was affected by on-deck structure, and the local wind speed and direction were different from the values measured at the meteorological tower. Thus, it was necessary to obtain another measurement of average wind speed close to the vent on the deck of the vessel. This was obtained with a mechanical wind velocity meter that indicated the total flow of air (in linear meters) passing through the meter during the 10-minute vapor sampling test. This method gave a value for average wind speed only. An estimate of turbulence entrainment velocity, u', was obtained by multiplying the on-deck average velocity by the ratio of the standard deviation to the mean velocity obtained from the meteorological tower record.

Plume Emission Rate

During the field tests on tankerships and barges, the emission rate of air and cargo vapor was usually determined from liquid level measurements made every 15 minutes during cargo loading as shown in Figure IV.31. A typical graph of indicated ullage (the vertical distance from the liquid surface to the rim of the ullage hatch on the expansion trunk) versus time is shown in Figure IV.32 for the loading of denatured ethanol during Tests 1 through 7. Cargo loading tables, or cargo tank plan drawings were used to give the tank volume per foot of depth. Multiplying the tank volume per unit of depth by the rate of ullage change gives a value for the volumetric flowrate of chemical product into the cargo tank. If the tank is vented directly to the air through an open ullage hatch, or individual tank vent, the plume emission flowrate can be equated to the cargo volumetric flowrate.

FIGURE IV.31. ULLAGE MEASUREMENT DURING CARGO LOADING TO DETERMINE LOADING RATE

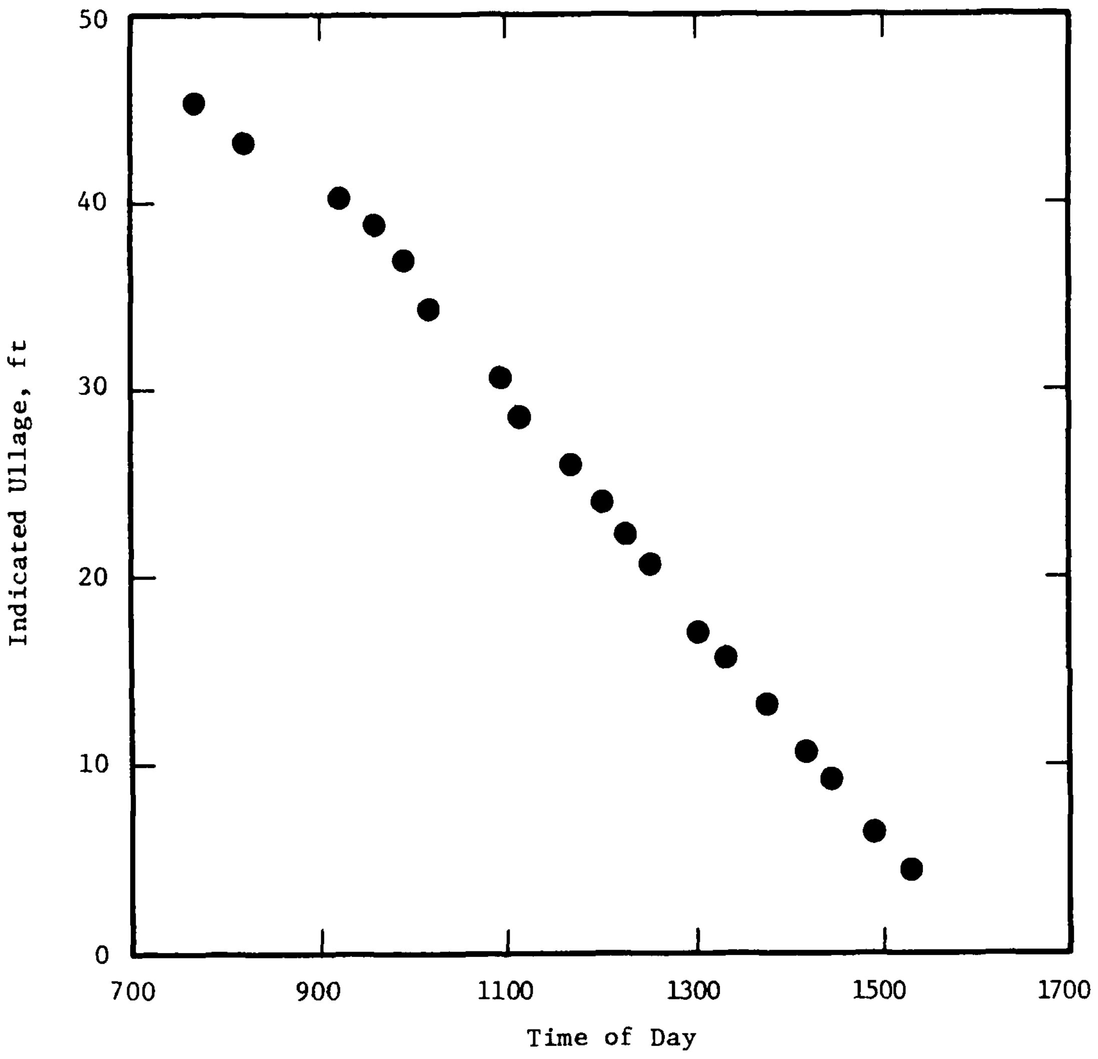


FIGURE IV.32 INDICATED ULLAGE DURING THE LOADING OF DENATURED ETHANOL FOR TESTS 1 THROUGH 7

For Tests 102 and 103 on a gasoline tanker, the vent lines from several cargo tanks were connected. In this case, the plume emitted from a vent may contain gas from other tanks. For these two tests, the plume emission velocity was measured directly at the vent with the mechanical velocity meter used for on-deck wind velocity measurements.

For the vent simulation tests performed at SwRI, a different procedure was used. A fan, with a nominal flowrate rating of 850 m^3/hr, was connected directly to a length of 0.20m (8 inch) diameter PVC pipe as shown in Figure IV.33. The flowrate of air through the fan was adjusted by placing a flow restricting orifice across the fan inlet. Propane was added to the airflow to produce a propane/air plume. The flow of propane was metered through a series of five rotameters and controlled by adjusting a set of needle valves. The propane gas flow was added to the airflow through ports drilled into the wall of the PVC vent line. In this way, propane concentrations as high as 0.56 kg/m^3 (30% by volume) were obtained in the propane/air plume.

Vapor Concentration at the Vent

The concentration of chemical vapor in the stream of gas emitted from a tank vent was measured directly with an Organic Vapor Analyzer, as shown in Figure IV.34. In general, the level of vapor concentration in a cargo tank gas atmosphere depends on whether or not the tank has been washed and gas freed before loading.

On some vessels, particular cargo tanks are "dedicated" to transporting one product and they do not require washing and ventilating to prepare them for cargo loading. Also, certain liquid bulk cargos do not have critical purity requirements and can tolerate contamination from liquid and vapor residue of a chemically compatible cargo carried previously in the tank. In these circumstances, when the cargo tank has not been washed and ventilated before loading, the level of vapor concentration in the tank from the previous cargo may be high. Figure IV.35 shows a graph of vapor concentration measured at a tank vent during the loading of methanol into a

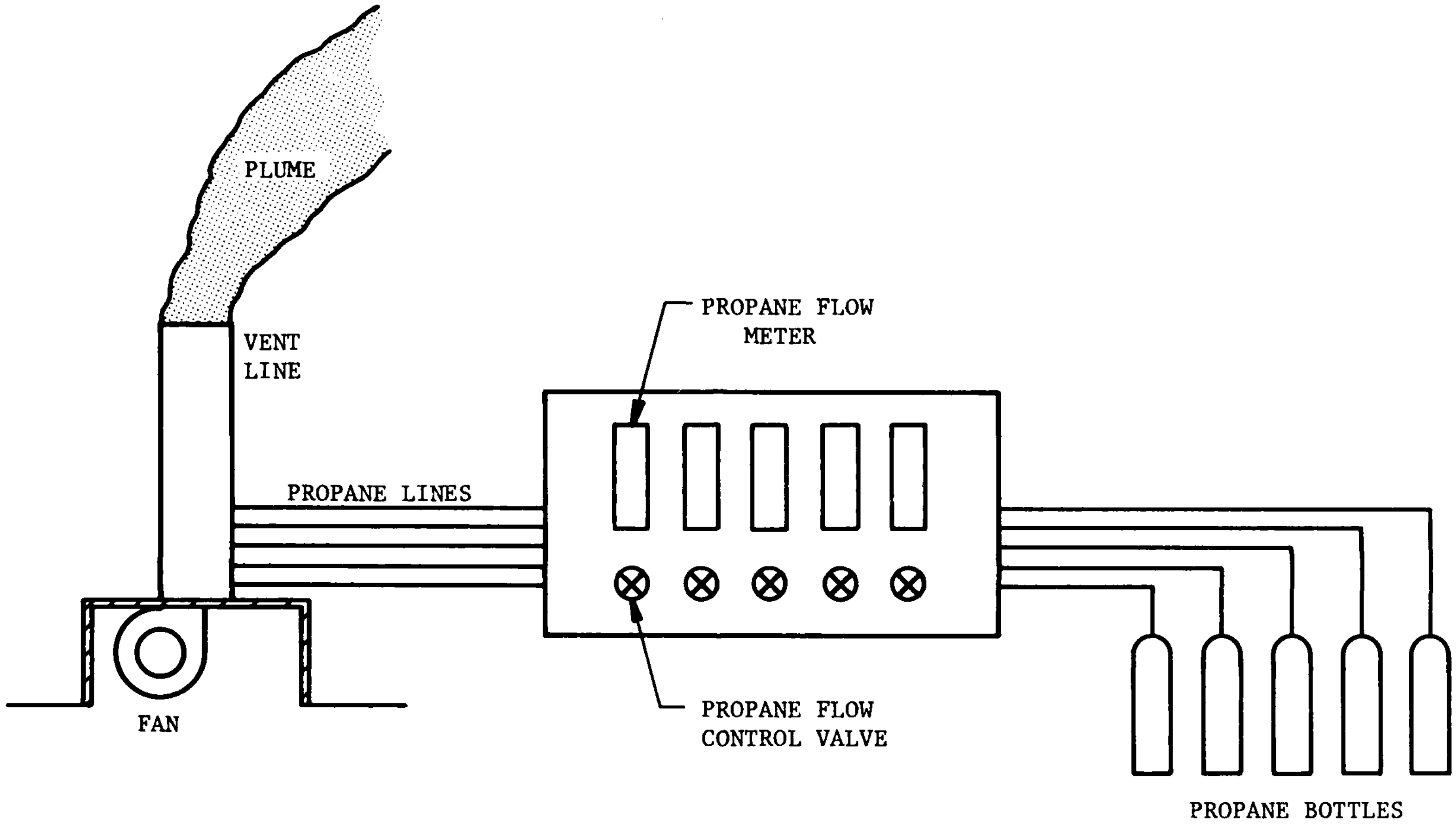


FIGURE IV.33 SCHEMATIC OF VENTING SYSTEM USED FOR FULL SCALE VENTING SIMULATION TESTS AT SwRI

FIGURE IV.34. MEASUREMENT OF VENT CONCENTRATION DURING CARGO LOADING

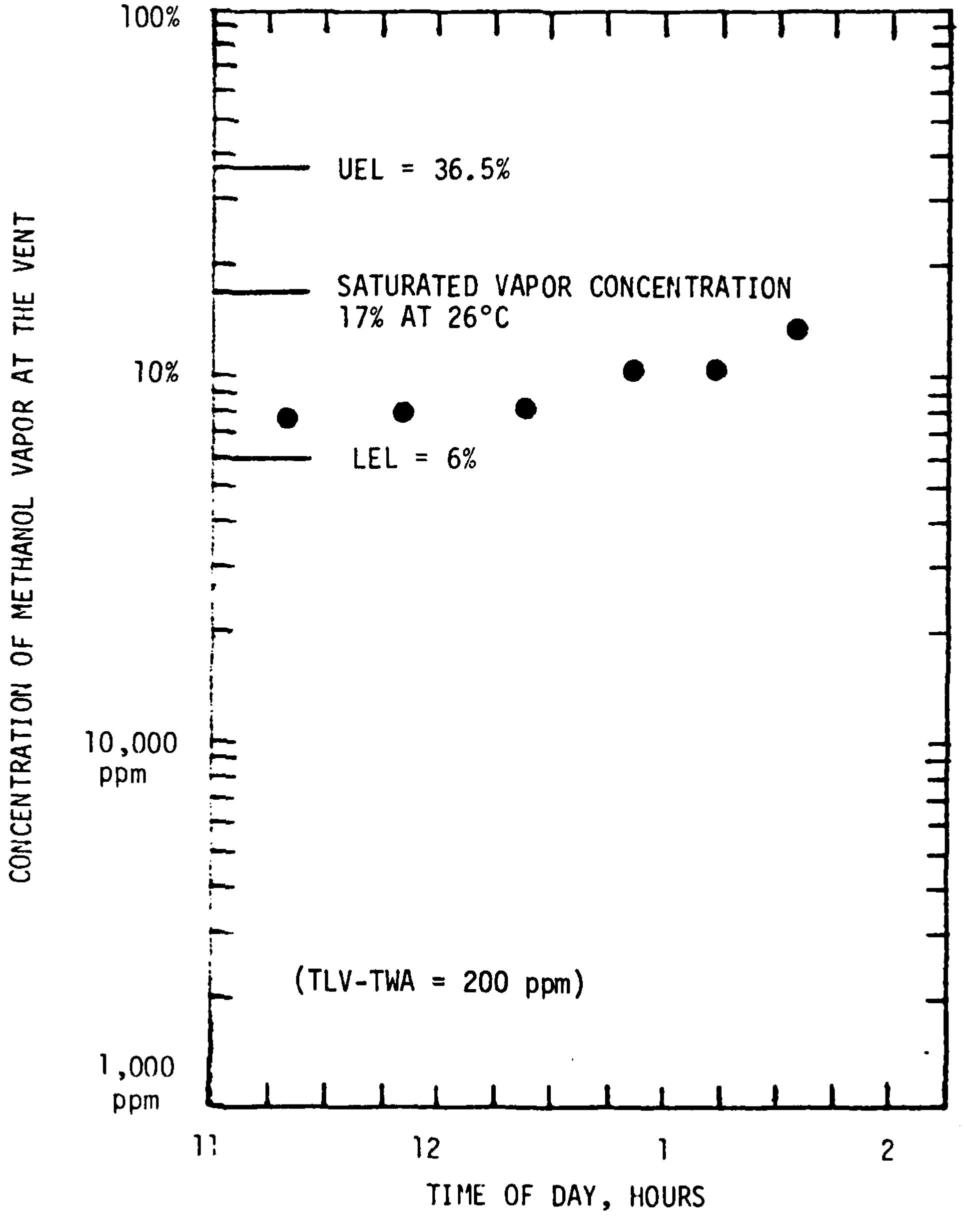


FIGURE IV.35. VAPOR CONCENTRATION AT THE TANK VENT MEASURED DURING LOADING OF METHANOL INTO A DEDICATED TANK "dedicated" tank for test numbers 32 through 37 in Table IV. 6. Note that at the start of cargo loading the methanol vapor concentration in the tank, formed from the residue of previous cargos, exceeded the LEL. During loading the vapor concentration increased slowly, and approached the saturation vapor concentration for methanol vapor in air near the end of loading.

Cargo tanks are routinely washed and gas freed to remove all residue from the previous cargo when it is required to meet product quality standards or when the previous cargo is not chemically compatible with the cargo to be loaded. In this case, the chemical vapor concentration in the tank can be low at the start of loading. Figure IV.36 shows a graph of vent concentration during the loading of 200-proof denatured ethanol into a clean, gas-free tank. Note that the vapor concentration increased steadily during cargo loading, but that the concentration level exceeded the LEL only during the final stage of loading. As in Figure IV.35, the vapor concentration approaches the saturation concentration value when the liquid level nears the top of the tank.

Except at the start and end of cargo loading, the vapor concentration at the vent varies slowly enough that an average value of vent concentration can be used for plume model validation. Thus, the vent concentration was measured at 15-minute intervals during loading, and at both the start and end of each 10-minute-long vapor sampling run.

Vapor Concentration Distribution Downwind of the Vent

The method used to determine the spatial vapor concentration distribution was to obtain and analyze air samples at 9 or more receptor locations usually arranged along a circular arc downwind of the vent as described earlier in this section. The wind direction above the deck of the vessel close to the vent was indicated reliably by the wind vane shown in Figure IV.37. Receptor stations were rearranged along the sampling arc between runs in response to shifts in wind direction. The typical arrangement of receptors used for Tests 22 and 23 during the loading of n-heptane is shown in Figure IV.38. During some tests, on-deck structure prevented the

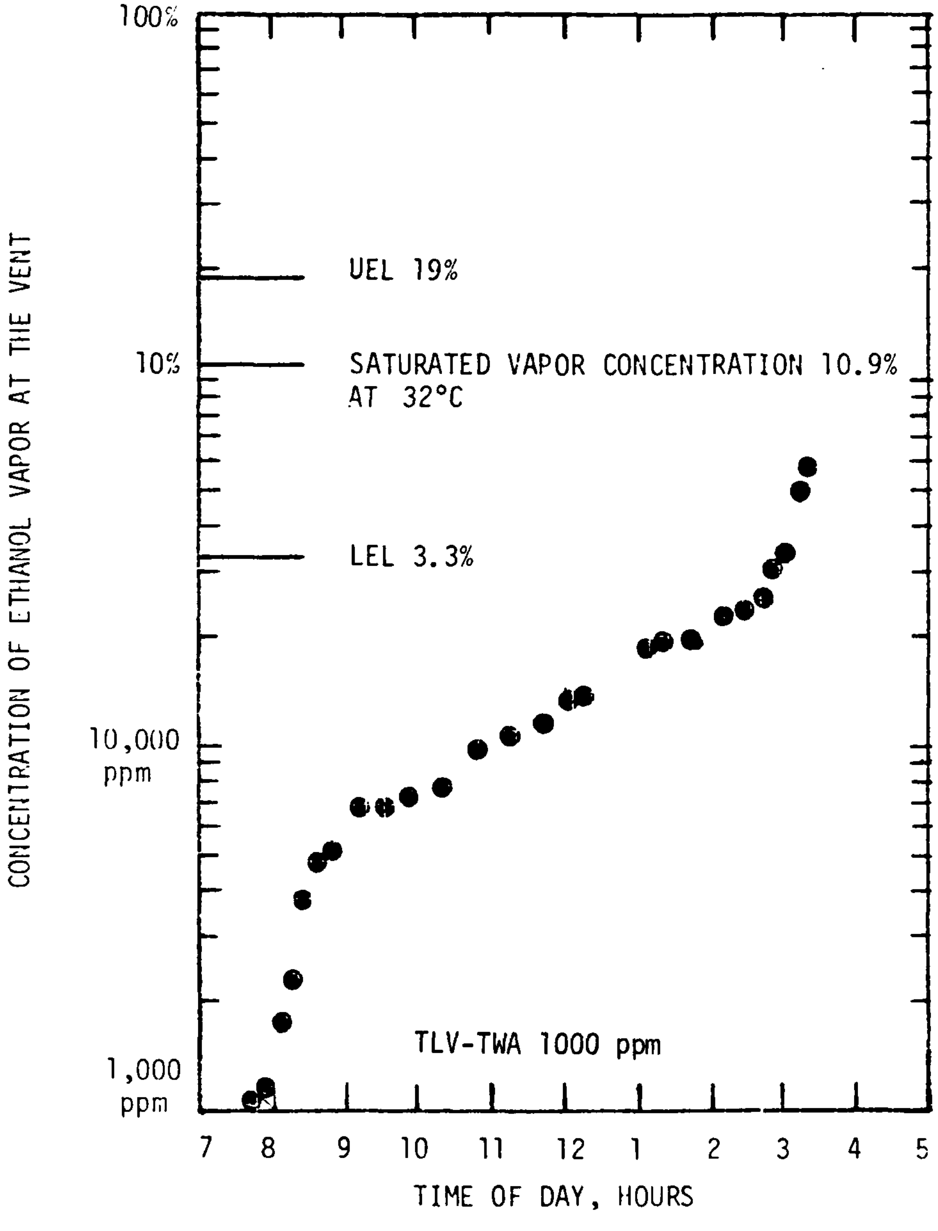


FIGURE IV.36. VAPOR CONCENTRATION AT THE TANK VENT MEASURED DURING LOADING OF ETHANOL INTO A CLEAN, GAS FREE TANK

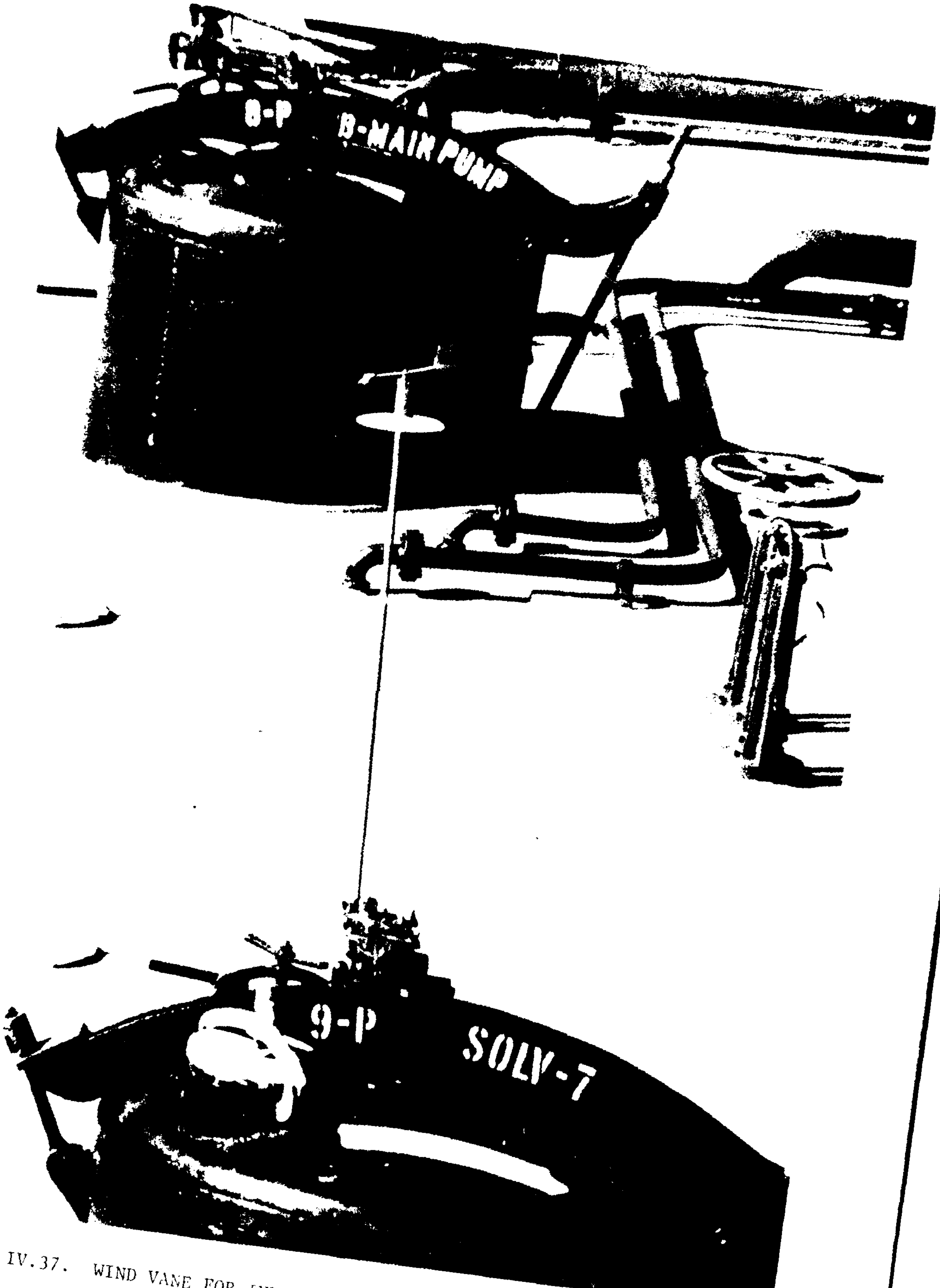


FIGURE IV.37. WIND VANE FOR INDICATING WIND DIRECTION CLOSE TO THE VENT

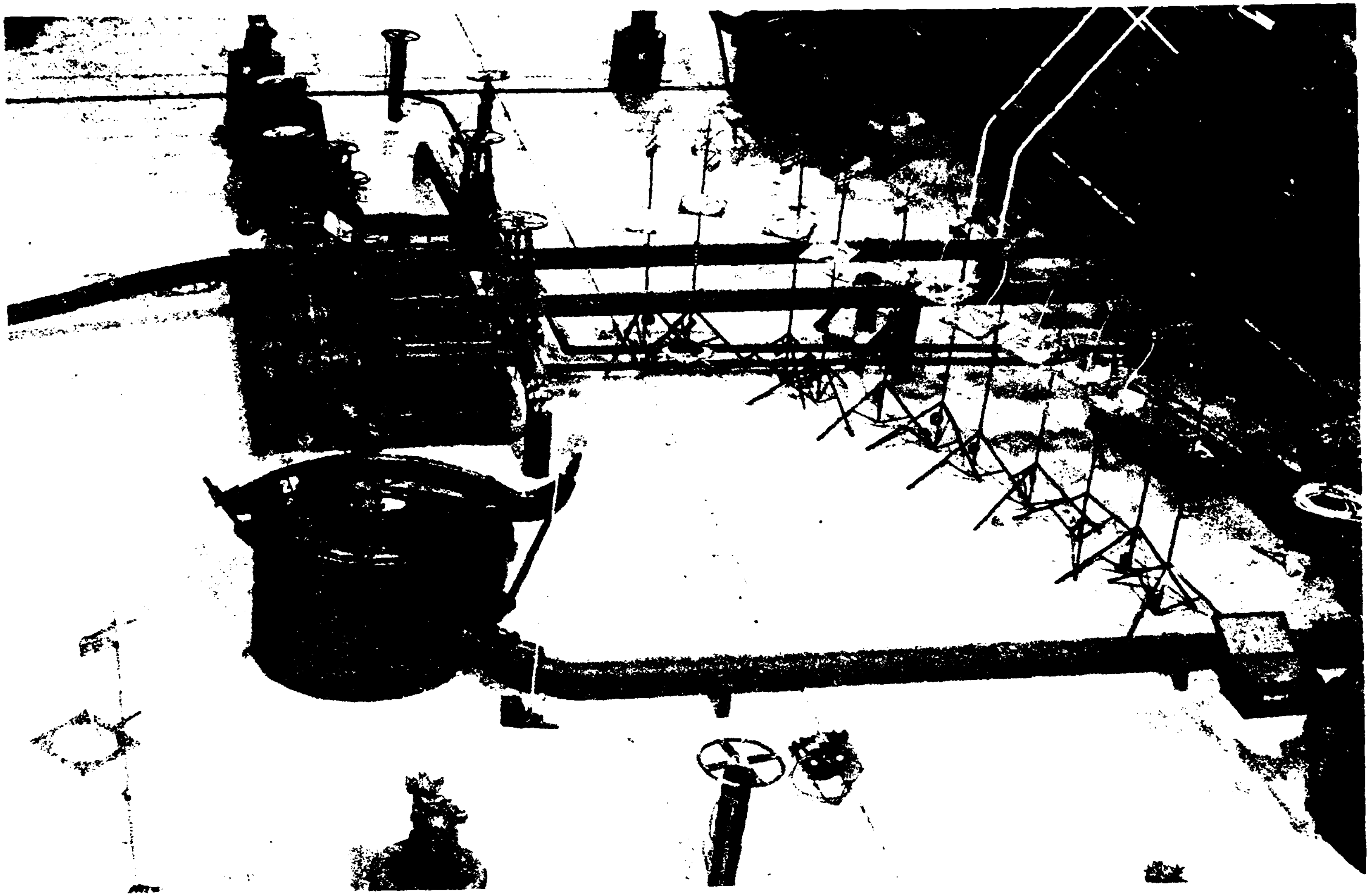


FIGURE IV.38. ARRANGEMENT OF VAPOR SAMPLING RECEPTORS DOWNWIND OF A TANK VENT DURING CARGO LOADING placement of receptors along a circular arc. When this occurred, alternate receptor locations were chosen and recorded on a sketch of the deck region.

Each receptor station consisted of an MSA Model C-200 sampling pump connected to an inert collection bag as shown in Figure IV.39. The nose of the sampling pump was usually set at a height of 1.67m (5.5 ft) in order to obtain samples of air at breathing height. Each collection bag was identified by number and both the bag number and the receptor location were recorded on a data sheet for each run. All collection bags were purged with nitrogen and evacuated before use. A valve at the bag inlet was closed to prevent entry of ambient air.

At the start of a vapor sampling run, the collection bag valves were opened and the sampling pumps were turned on. After 10 minutes the pumps were turned off and the valves were closed. Soon after the collection bags were removed from the receptor stations. A small sample of gas was drawn off for measurement of the "total hydrocarbon" concentration with an Organic Vapor Analyzer. This reading identified the approximate level of concentration and guided further analysis with a gas chromatograph. Each vapor sample was analyzed again with a portable F.I.D. gas chromatograph within 0 - 4 hours of collection. This procedure minimized the possible loss of chemical vapor by diffusion through the collection bag walls. GC traces were recorded on a strip chart recorder for further analysis by peak height or integrated area methods. Liquid samples of the chemical cargo were collected and used for post-test calibrations. After the vapor concentration data were reduced and plotted, it was compared with plume model predictions as described in the next section.

IV.3.3 Comparison of Model Predictions and Experimental Data

Of the total of 103 chemical vapor plume dispersion tests listed in Table IV. 6 , many are replicate tests that were performed during the same loading operation. Although plume dispersion model predictions were made for the recorded conditions of all of the dispersion tests, it is not necessary to show all of the comparisons in this report. Instead,

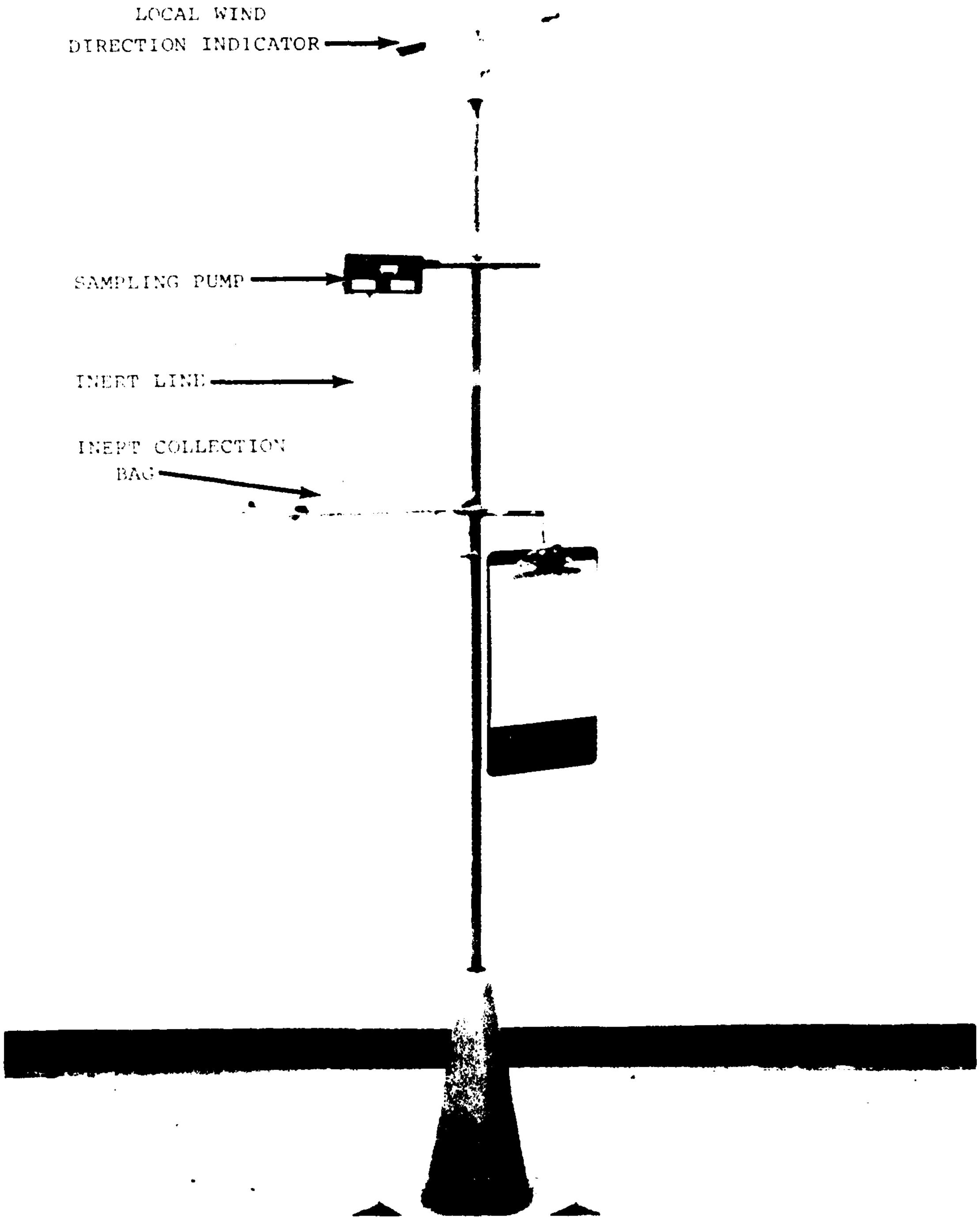


FIGURE IV.39. AIR SAMPLING RECEPTOR STATION one or two representative tests have been selected from key loading observations for presentation and discussion in this section.

The comparisons of plume model predictions with experimental data show clearly the situations where the plume model gives good results, and where it works poorly. In general, the agreement between predictions and data is good whenever the ambient wind field was unimpeded by on-deck structure. Poorer agreement was found when the cargo tank vents were shielded from the wind by on-deck structure. Examples of both situations are presented and discussed in this section.

Ethanol Loading into a Washed and Ventilated Tank, Tests 2 and 6

These tests were performed during a cargo loading observation on a chemical product tanker. The cargo tank had been washed, ventilated and inspected prior to loading. The cargo loading rate was maintained constant during loading at approximately 155 m^3/hr. Figure IV.40 shows the values of vapor concentration measured at the open ullage port which was used to vent the tank gas atmosphere during loading. The vent was located close to the edge of the "trunk" deck which was elevated above the main deck. As a result, the path of the wind over the vent was clear and unobstructed. During this observation the wind speed on the deck of the vessel was not measured. However, the meteorological tower was located close to the vessel and the meteorological tower measurements have been used for plume model predictions.

Seven vapor sampling runs were performed during this observation as indicated in Table IV. 6 . Good agreement between model predictions and experimental data was found for all seven runs. The results of tests 2 and 6 are presented here. Test number 2 was performed relatively early during loading as shown in Figure IV.40. The average ethanol vapor concentration was 0.0177 kg/m^3 (9350 ppm) during the 10-minute-long vapor sampling run. The time average wind velocity was 4.42 m/s (9.9 mile/hr) with an estimated turbulence level (defined as the ratio of the standard

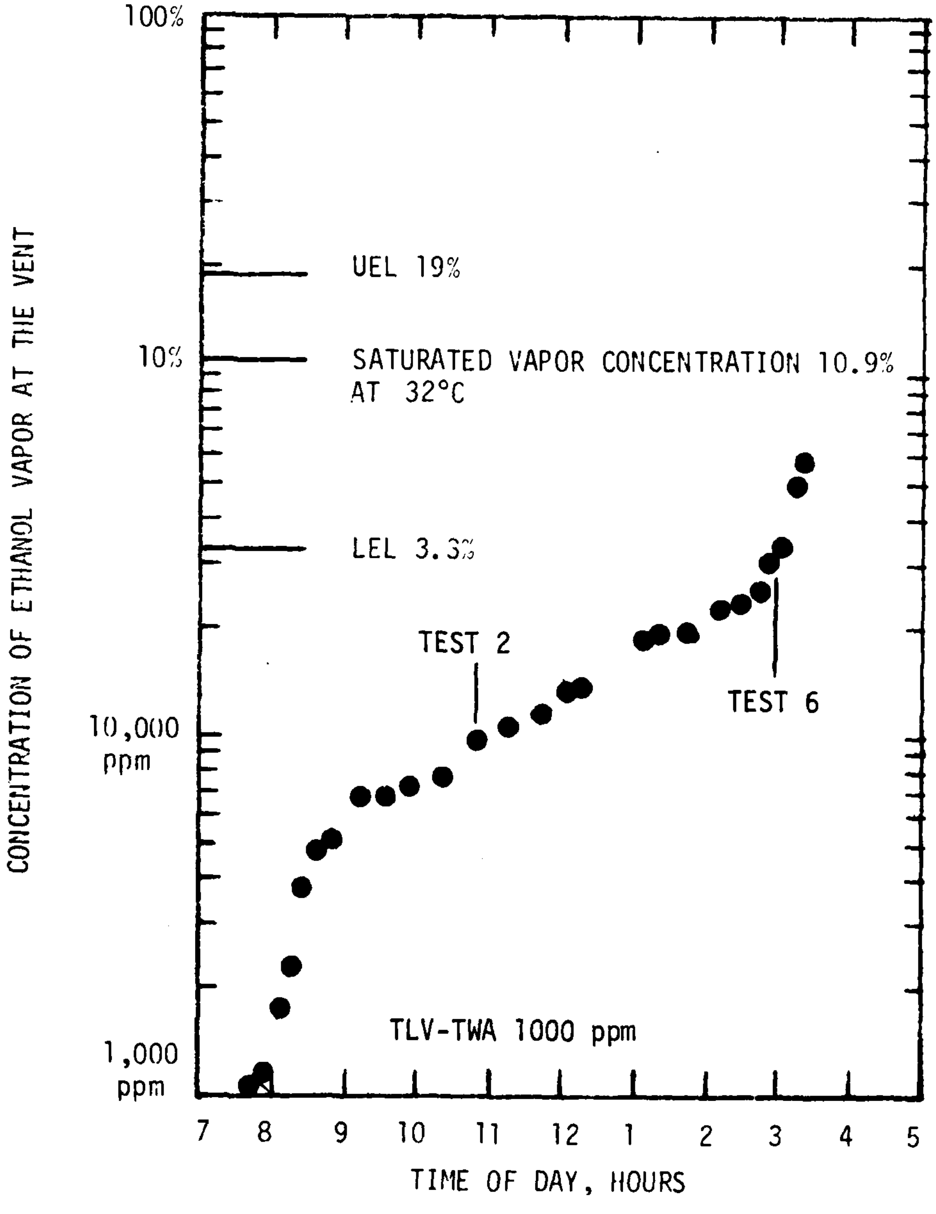


FIGURE IV.40. VAPOR CONCENTRATION AT THE TANK VENT MEASURED DURING LOADING OF ETHANOL INTO A CLEAN, GAS FREE TANK deviation to the mean value calculated from wind velocity samples) of 21.4%. Receptors were placed at man breathing height along an arc at a radial distance of 2.51m (8.2 ft) downwind of the vent. Figure IV.41 compares the measured concentration data for Test No. 2 with plume model predictions for two values of α_3, the turbulence entrainment parameter, equal to 2 and 3, respectively. The experimental data matches the concentration distribution predicted for $\alpha_3 = 3$ quite well.

Test number 6 was performed during the last 45 minutes of cargo loading as shown in Figure IV.40. The average ethanol vapor concentration was 0.054 kg/m^3 (28,600 ppm) during the vapor sampling run. The average wind velocity was 4.41 m/s (9.9 mile/hr) with an estimated turbulence level of 17.0%. For this test, receptors were placed at man breathing height along an arc at a radial distance of 4.0m (13.3 ft) downwind of the vent. Figure IV.42 compares the vapor concentration values measured at the receptor stations with plume model predictions for $\alpha_3 = 2$ and $\alpha_3 = 3$. Again, the experimental data matches the predicted concentration distribution well for $\alpha_3 = 3$.

The maximum ethanol vapor concentrations predicted at man breathing height along the arc of receptors were about 27 ppm for test 2 and about 55 ppm for test 6. These two values are well below the accepted STEL value of 5000 ppm for 15 minutes and the TLV-TWA value of 1000 ppm for ethanol.

Isopropanol Loading into a Washed and Ventilated Tank
Tests 8, 9, 10, 11, 12

These tests were performed on the same chemical product tanker as tests 1 through 7. However, the tanker moved to a different dock before the start of tests 8 through 12. The cargo tank to be loaded had been washed, ventilated and inspected earlier in the day, so that the vapor concentration was very low ($\sim$68 ppm as CH_4). During this loading observation, the incoming flow of isopropanol was split between two tanks. The flowrate to these tanks was adjusted from time to time to maintain the trim of the vessel. As a result, the loading rate into tank 3CS decreased from

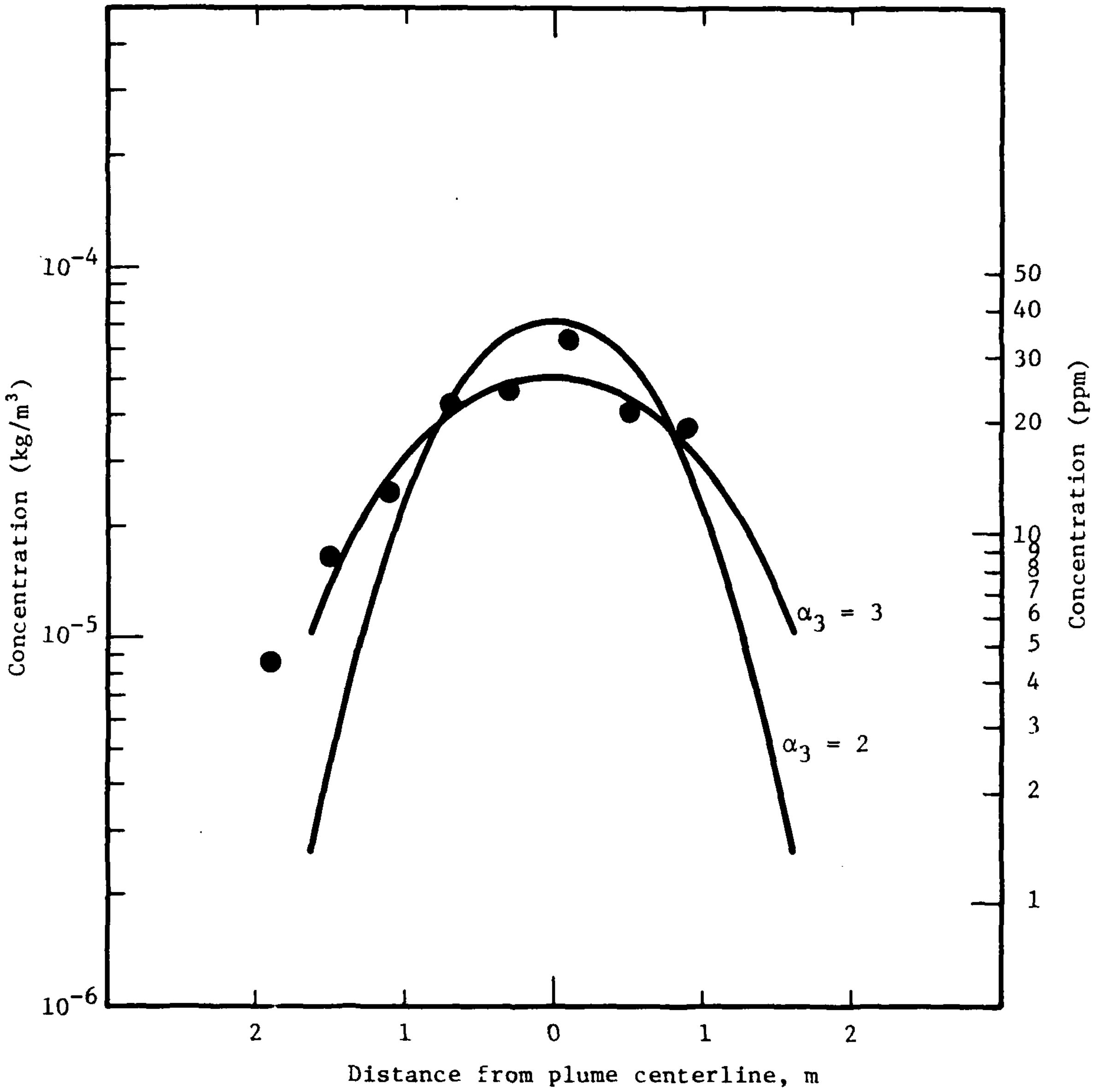


FIGURE IV.41 COMPARISON OF EXPERIMENTAL CONCENTRATION DATA FOR RUN 2 WITH PREDICTED CONCENTRATION DISTRIBUTION FOR $\alpha_3 = 2$ AND $\alpha_3 = 3$

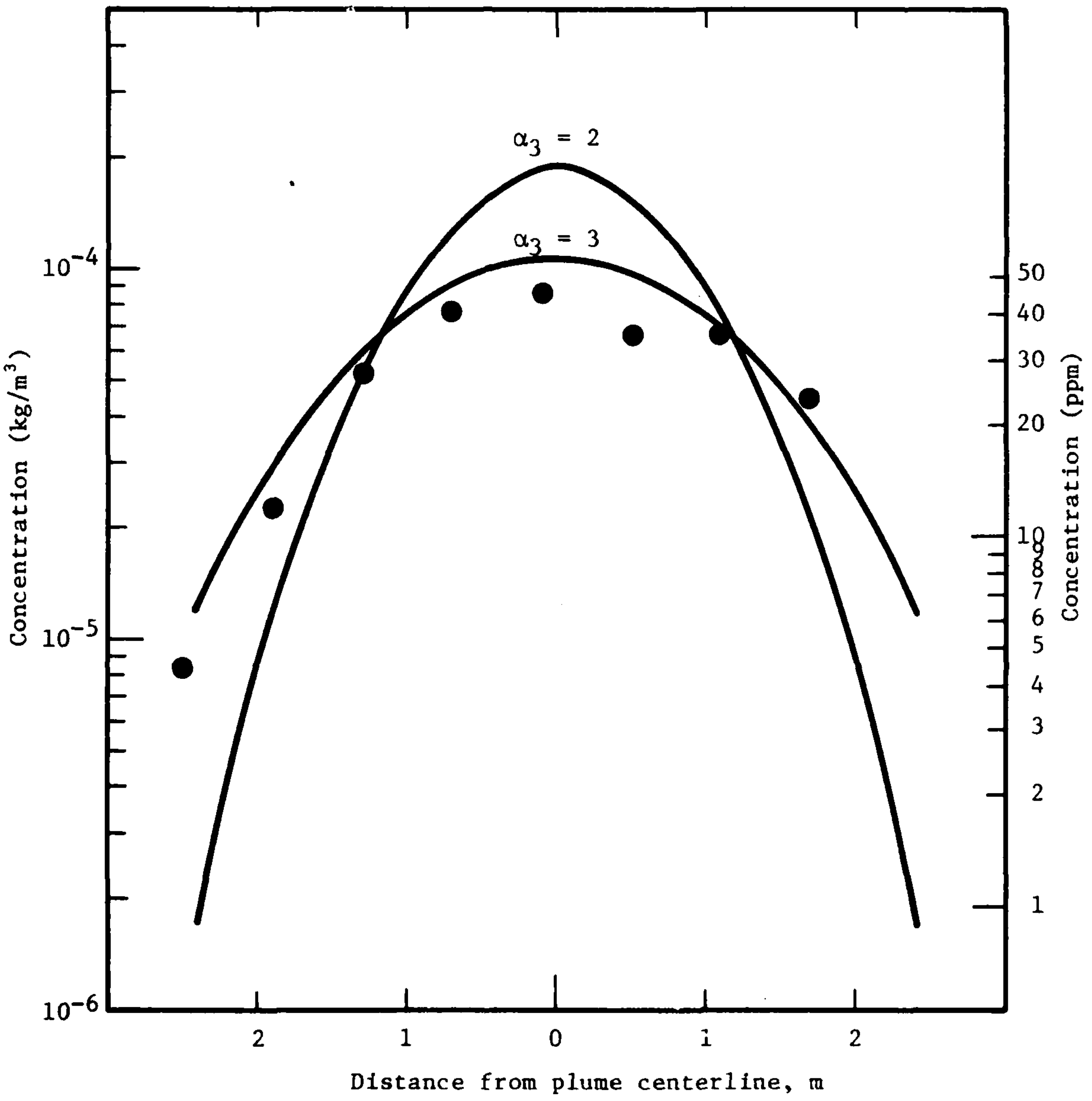


FIGURE IV.42 COMPARISON OF EXPERIMENTAL CONCENTRATION DATA FOR RUN 6 WITH PREDICTED CONCENTRATION DISTRIBUTION FOR α_3 = 2 AND α_3 = 3

158 m^3/hr to 102 m^3/hr during loading. Figure IV.43 shows the measured variation of isopropanol vapor at the ullage port used to vent the tank atmosphere. This vent was located on the upwind side of the ship and close to the edge of the "trunk" deck so that the wind was relatively unobstructed by on-deck structures. The wind speed at deck level close to the vent was not measured, and the meteorological tower was situated over 800m (1/2 mile) away from the vessel at a remote location where an electrical supply was available. The tower was located near the top of a sea wall, and the base of the tower was elevated more than 6m (20 ft) above the dock area.

Five vapor sampling tests were performed during a three-hour period during the middle stage of cargo loading, as shown in Figure IV.43 and Table IV.6. The values of the mean wind speed and the average turbulence level were measured by the meteorological tower for these runs as listed in Table IV.6. However, when these data were used for plume model predictions, the vapor concentration distribution was considerably underpredicted as described below.

The results for test number 8 are typical and they reveal the problem that occurred. The average isopropanol vapor concentration at the vent was 0.00364 kg/m^3 (1490 ppm) for this run. The measured values of mean wind velocity and average turbulence level were 3.01 m/s (6.73 mile/hr) and 13.0%, respectively. Receptors were placed at breathing height along an arc at a radial distance of 2.51m (8.2 ft) from the vent. Figure IV.44 shows that the measured values of concentration were between 2 and 6 times higher than the level predicted by the plume model for receptor locations. Because of the remote location of the meteorological tower, it was reasonable that the wind speed at vessel deck level could be different from the recorded value. Plume model predictions were repeated using a 50% lower value of wind speed, and the same value of turbulence intensity. The results are shown in Figure IV.44. The measured and predicted values of vapor concentration are much closer, generally within a factor of 2 for a value of $\alpha_3 = 5$.

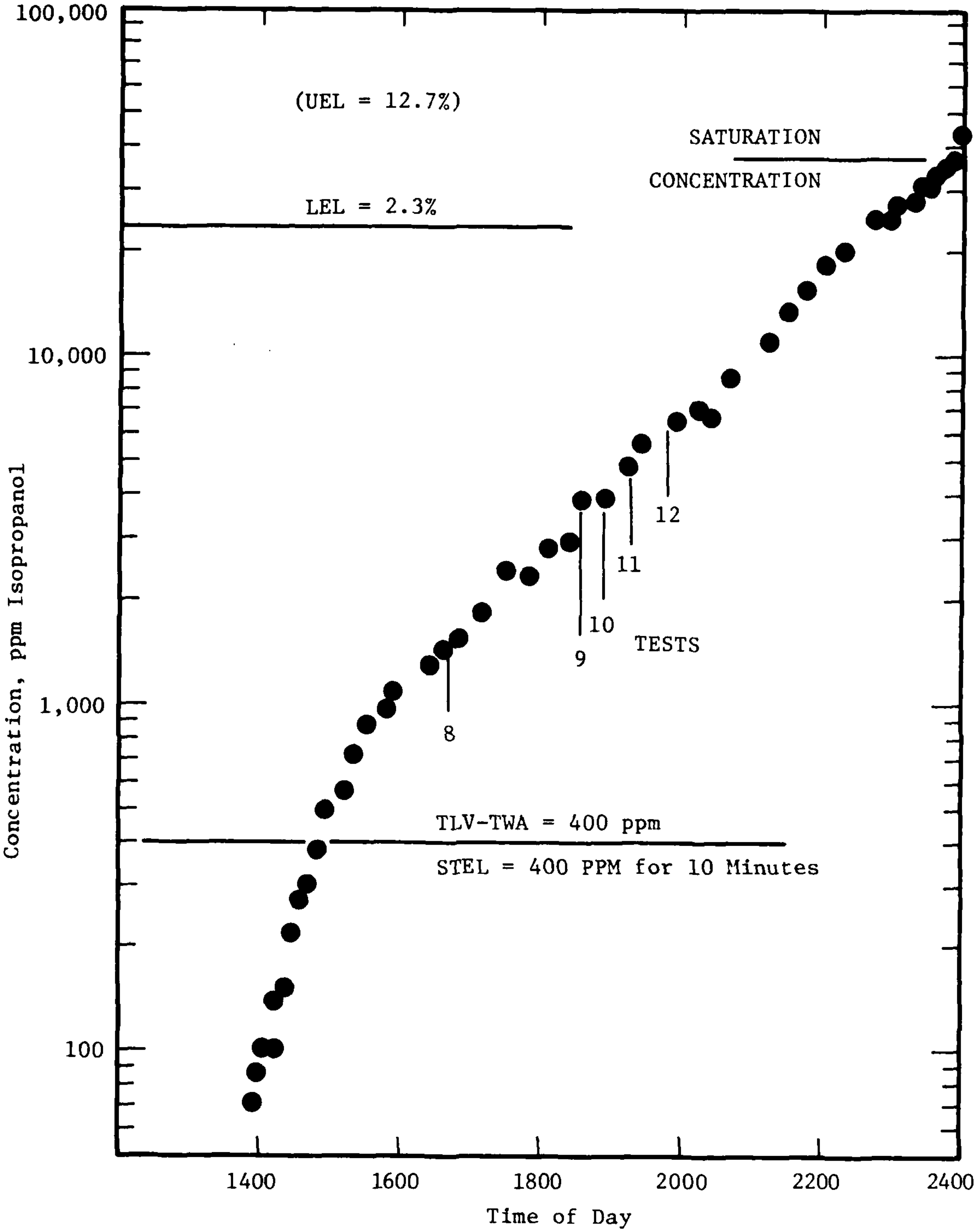


FIGURE IV.43 VAPOR CONCENTRATION AT THE ULLAGE HATCH DURING LOADING OF 99% ISOPROPANOL INTO TANK 3CS

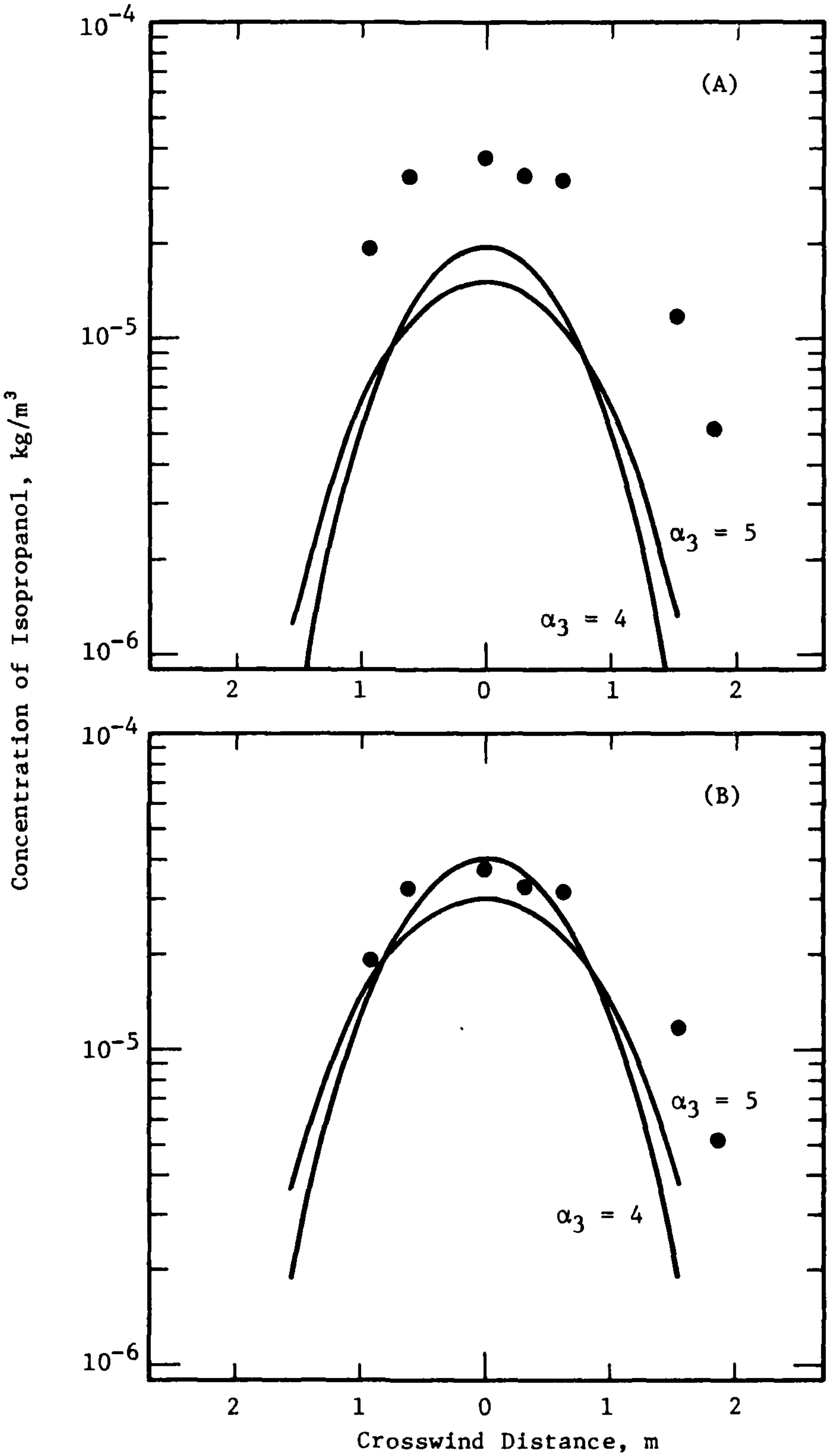


FIGURE IV.44 A COMPARISON OF PREDICTED AND MEASURED CONCENTRATIONS OF ISOPROPANOL VAPOR FOR TEST NO. 8, USING TWO VALUES OF WIND SPEED (A) 3.01 m/s, (B) 1.51 m/s

Plume model computations for runs 9 through 12 also underpredicted the level of vapor concentration at receptor locations. As for test number 8, the agreement between the model predictions and the experimental data was improved considerably when the value of the mean wind velocity was reduced by 50%. Table IV. 8 lists the set of experimental conditions for these tests.

Figures IV.45(A) and (B) compare the experimental data for tests 9 and 10 along an arc 3.73m (12.2 ft) downwind of the vent with plume model predictions using 50% of the measured wind speed values. Referring to Table IV. 8 we see that the vent concentration values and the wind speeds were fairly similar for these two runs. However, the estimated value of turbulence level dropped sharply from 11.3% for run 9 to 4.9% for run 10. Yet, Figures IV. 45 (A) and (B) show clearly that the measured concentration distributions were very similar for these two runs. Figure IV.45(B) shows that the value of α_3 had to be increased from 6 to 12 in order to compensate for the lower estimated value of tlv, the turbulence level.

Figure IV.46 compares the predicted and measured concentration distributions for observations 11 and 12, which employed a circular arc located 7.39m (24.2 ft) from the vent. As with Figure IV.45, the agreement between predicted and measured concentration values is good when a 50% value of the measured wind speed is used. Note also that a higher value of $\alpha_3 \sim 8$ or 9 is required in Figure IV. 46 (B) than in Figure IV. 46 (A), where $\alpha_3 \sim 6$ or 7. The increase in α_3 goes hand-in-hand with the decrease in turbulence level from 8.2% to 6.3% from run 11 to run 12.

Table IV. 8 shows that the product of α_3 and turbulence level was nearly constant for runs 8 to 12, having a mean of

$$\alpha_3 \cdot \text{tlv} = 0.61$$

with a standard deviation of .05. It is interesting that when the values of α_3 and turbulence level for tests 1 to 7 (discussed above) are multiplied together, they give a value of $\alpha_3 \cdot \text{tlv} \sim 0.59$.

TABLE IV. 8 . EXPERIMENTAL CONDITIONS FOR VAPOR SAMPLING TESTS 8 TO 12

TEST NO.	TIME OF DAY hr	VENT CONCENTRATION ISOPROPANOL		RECEPTOR RADIUS m	METEOROLOGICAL CONDITIONS		50% WIND SPEED m/s	BEST FIT $\alpha_3 \cdot tlv$
		kg/m^3	ppm		WIND SPEED m/s	TURBULENCE LEVEL tlv		
8	16:40	.00364	1490	2.51	3.01	0.13	1.51	0.65
9	18:26	.00847	3460	3.73	2.59	0.113	1.30	0.678
10	18:45	.00954	3900	3.73	2.78	0.049	1.39	0.588
11	19:22	.0140	5700	7.39	3.02	0.082	1.51	0.574
12	19:42	.0154	6300	7.39	3.21	0.063	1.61	0.567

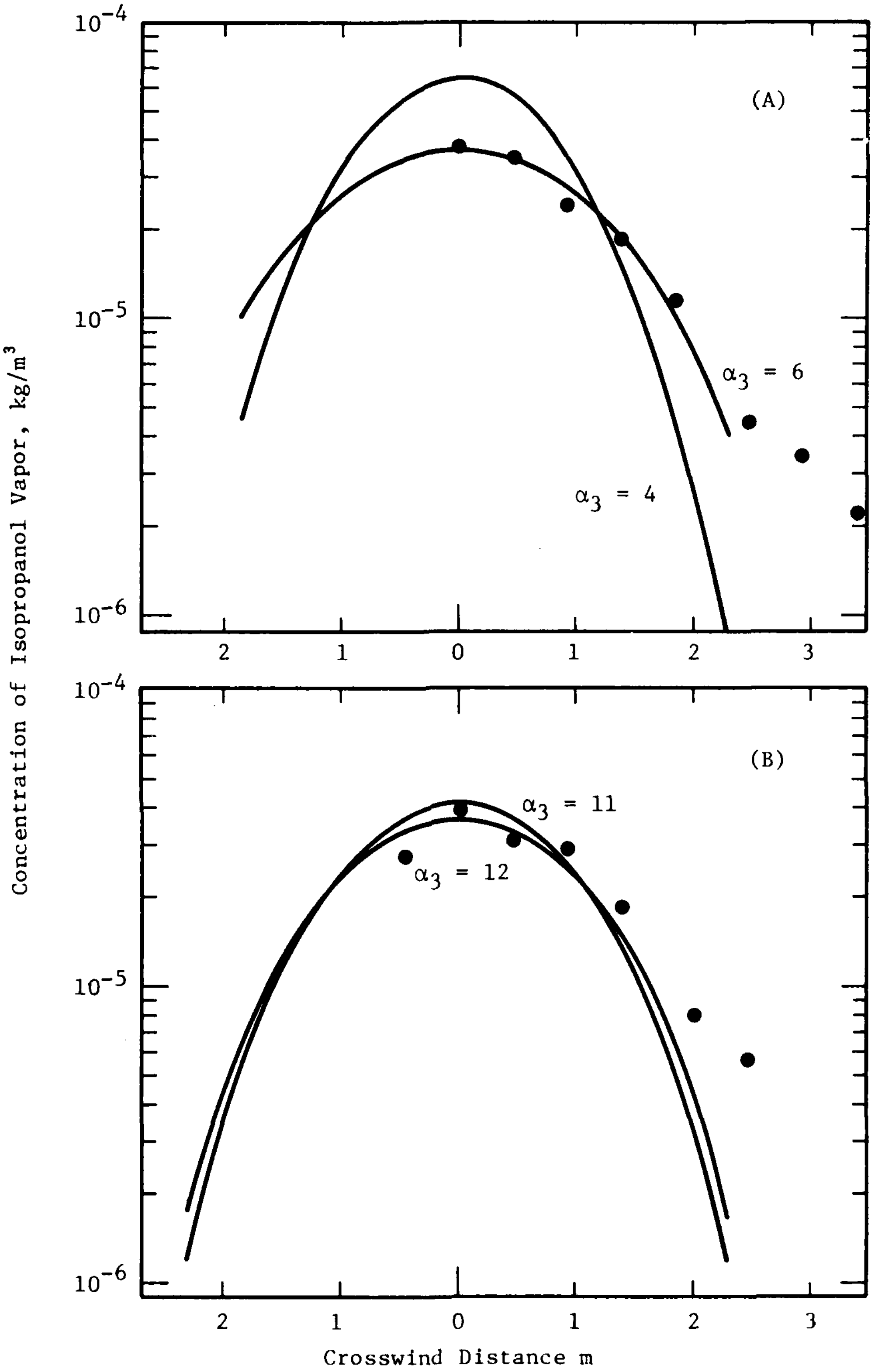


FIGURE IV.45 A COMPARISON OF PREDICTED AND MEASURED CONCENTRATIONS OF ISOPROPANOL VAPOR FOR (A) TEST NO. 9 AND (B) TEST NO. 10 USING 50% OF MEASURED WIND SPEED

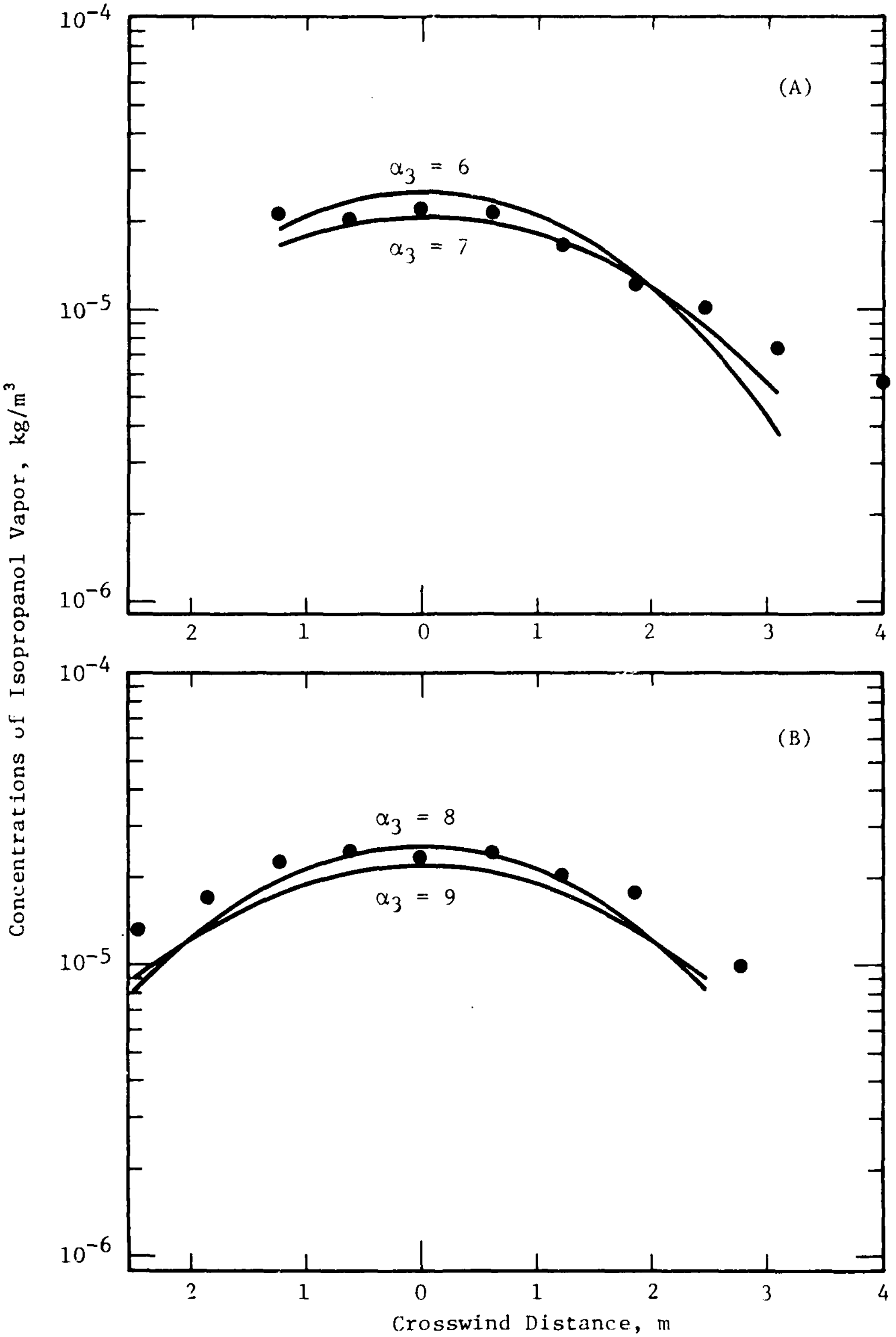


FIGURE IV.46 A COMPARISON OF PREDICTED AND MEASURED CONCENTRATIONS OF ISOPROPANOL VAPOR FOR (A) TEST NO. 11 AND (B) TEST NO. 12 USING 50% OF MEASURED WIND SPEED

This series of tests pointed out the need to base plume model predictions on the value of velocity closest to the vent. It also indicated that there was a problem with the meteorological instrumentation during tests 8 through 12 (also for tests 13 through 21 which were performed during the same period of time). The meteorological instrumentation was replaced with new equipment beginning with test 24.

During tests 8 through 12, the maximum isopropanol vapor concentrations measured at man breathing height were about 0.004 kg/m^3 (16.4 ppm). This value is well below the accepted STEL and TLV-TWA value of 400 ppm for isopropanol.

Isopropanol Loading into a Washed and Ventilated Tank
Tests 24, 25, 26

Because of the uncertainty in the results of tests 8 - 12 caused by problems with the meteorological instrumentation, a second set of plume dispersion tests was performed during an isopropanol loading. Tests 24-27 repeated the isopropanol loading observation (at a later date) on the same tanker.

During tests 8 - 12, isopropanol had been loaded into tanks 3CS and 3CP simultaneously. During tests 24 - 27, isopropanol was loaded only into tank 3CS. As a result, the cargo loading rate was approximately 272 m^3/hr for tests 24 - 27 compared with 102 - 158 m^3/hr for tests 8 - 12.

During tests 8 - 12, the wind speed had been measured only at the meteorological tower located about 800m (1/2 mile) away from the marine terminal area. During tests 24 - 27, the meteorological tower was located within 50 meters (160 ft) of the vessel Also, the wind speed on the deck of the vessel was measured with a mechanical wind meter.

Figure IV.47 shows the arrangement of expansion trunks, platforms, etc. for the chemical product tanker. During tests 8 - 12, the wind direction had been from starboard to port and the wind was unobstructed

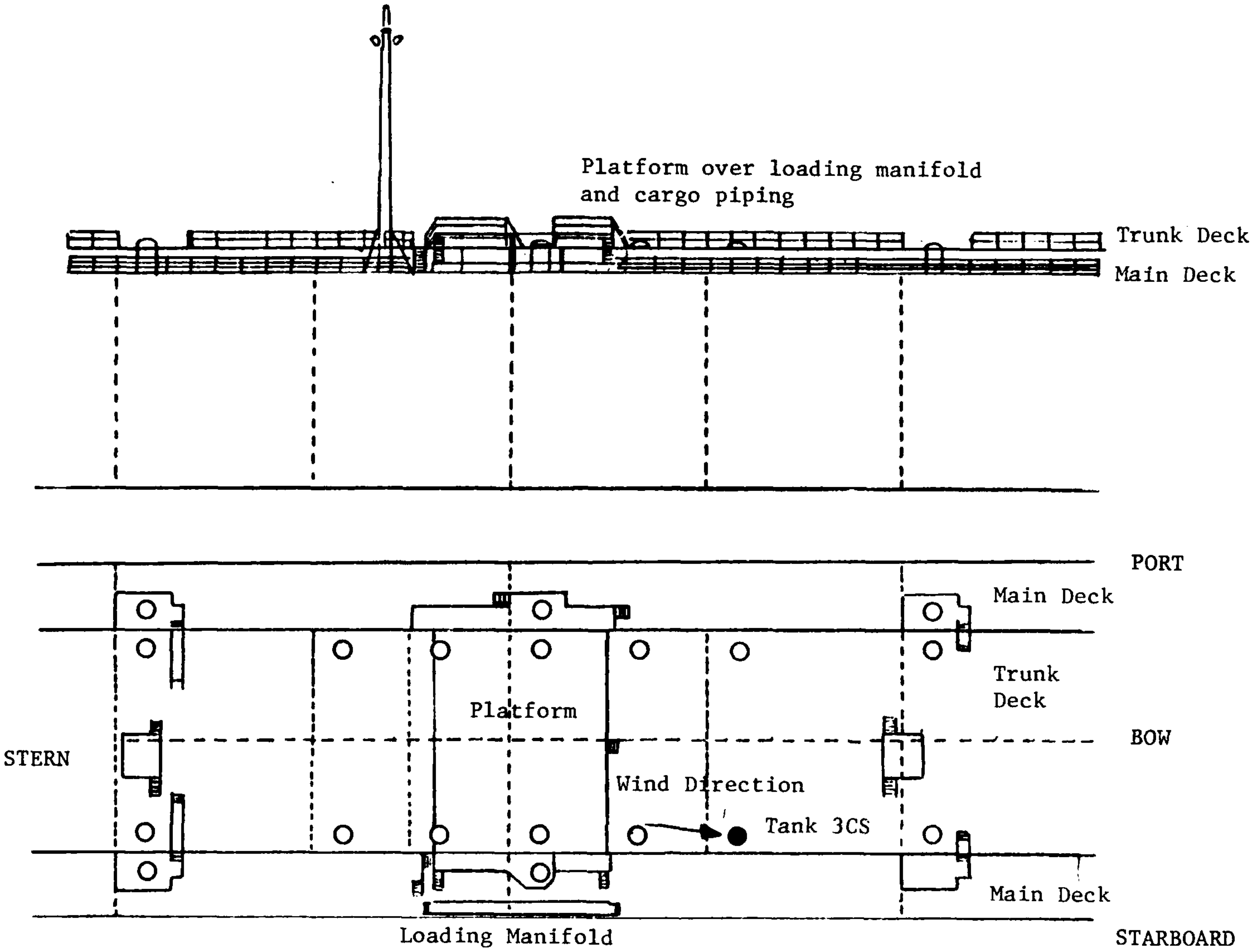


FIGURE IV.47. SKETCH OF DECK ARRANGEMENT FOR CHEMICAL TANKER as it passed over the tank vent. However, during tests 24 to 27, the wind direction was from the stern of the vessel towards the bow. A raised platform over the cargo loading manifold and on-deck piping lay directly upwind of the expansion trunk and tank vent for tank 3S. This structure partially shielded the tank vent from the wind. As a result, the wind speed readings made on the deck of the vessel were considerably lower than the wind speed readings at the meteorological tower only 50m away. Table IV.9 lists both the meteorological tower wind speed and on-deck wind speed readings for runs 24 to 26. Run 27 was strongly affected by wind obstruction. The propeller in the on-deck wind meter stopped and reversed direction during part of that run.

Figures IV.48 and IV.49 compare the predictions for crosswind concentration distribution with the experimental concentration data using the meteorological tower wind speed value and the on-deck wind speed value. As expected, the higher value of wind speed used in Figure IV.48 caused the concentration distribution to be underpredicted. Surprisingly, using the lower on-deck value of wind speed caused the concentration distribution to be overpredicted as shown in Figure IV.49. This could be caused either by inaccuracy in the wind meter readings or by inaccuracy in the plume model predictions at low wind speed.

As a compromise, the average of the on-deck and the meteorological tower wind speed readings has been used for the value of wind speed in the plume dispersion model with good results. Figures IV.50, IV.51, and IV.52 compare the experimental concentration data for runs 24, 25, and 26 with the predicted concentration distribution for values of α_3 equal to 2 and 3. The agreement is quite good when a value of $\alpha_3 = 3$ is used. Table IV.9 lists the best fit values of $\alpha_3 \cdot \text{tlv}$ as 0.86, 0.91, and 0.81 for these three tests. These values are 50% higher than the values of $\alpha_3 \cdot \text{tlv} \sim 0.6$ found for tests 1 - 7 and 8 - 12. The difference is probably due to (1) interference by the on-deck structure upwind of the vent and (2) greater randomness in wind direction at low wind speeds.

TABLE IV. 9 . EXPERIMENTAL CONDITIONS FOR VAPOR SAMPLING TESTS 24 TO 26

TEST NO.	VENT CONCENTRATION ISOPROPANOL		RECEPTOR RADIUS m	METEOROLOGICAL CONDITIONS		ON-DECK m/s	AVERAGE m/s	BEST FIT $\alpha_3 \cdot$ tlv
	kg/m^3	ppm		TURBULENCE tlv	METEORO.TOWER m/s			
24	.0093	3800	2.67	0.288	2.67	0.67	1.67	0.86
25	.0135	5500	2.67	0.302	2.57	0.68	1.63	0.91
26	.0188	7700	2.67	0.270	2.40	0.62	1.51	0.81

CONCENTRATION DISTRIBUTION ALONG RECEPTOR ARC
DOWNWIND OF OPEN ULLAGE HATCH

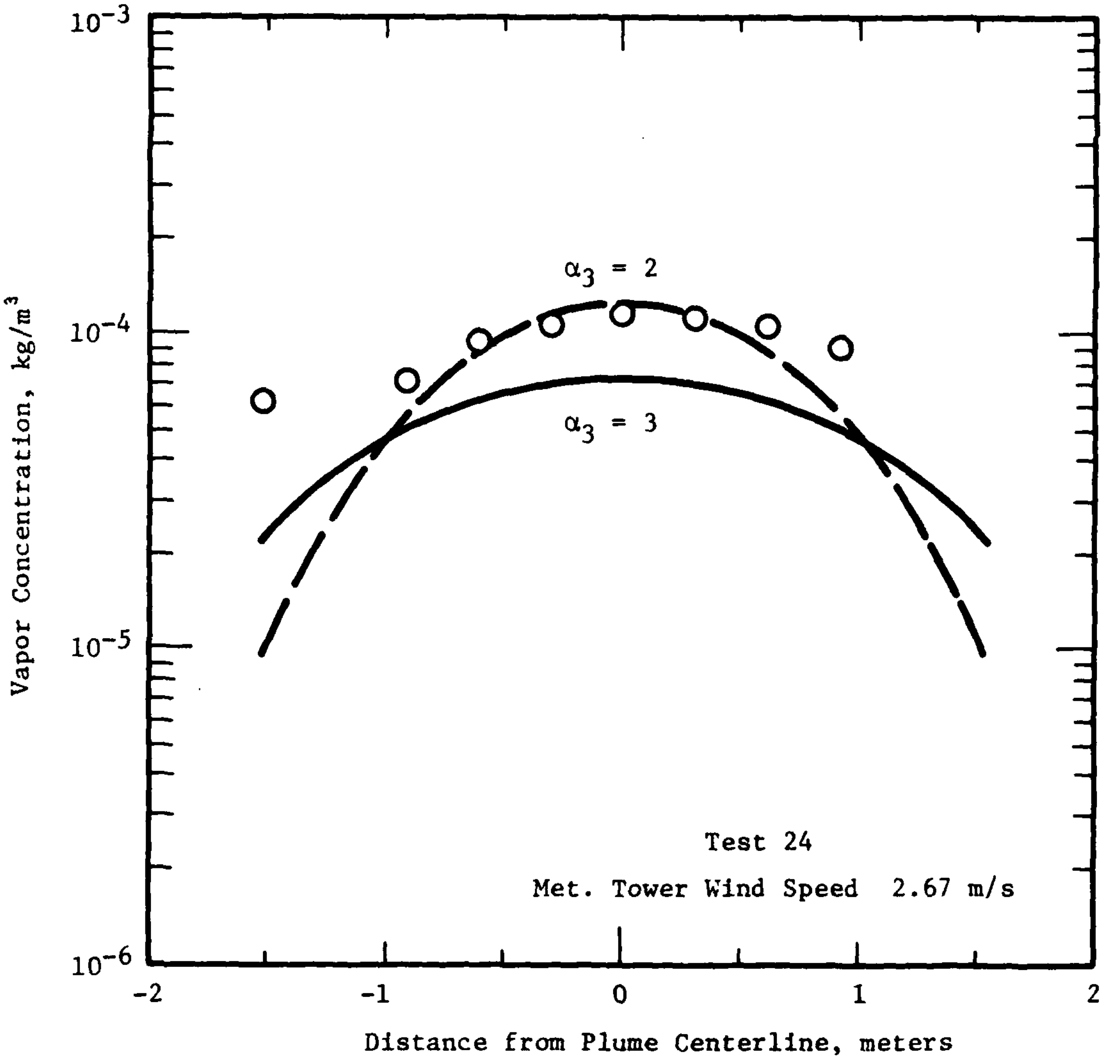


FIGURE IV.48 CROSSWIND CONCENTRATION DISTRIBUTION FOR TEST 24 DURING ISOPROPANOL LOADING

CONCENTRATION DISTRIBUTION ALONG RECEPTOR ARC
DOWNWIND OF OPEN ULLAGE HATCH

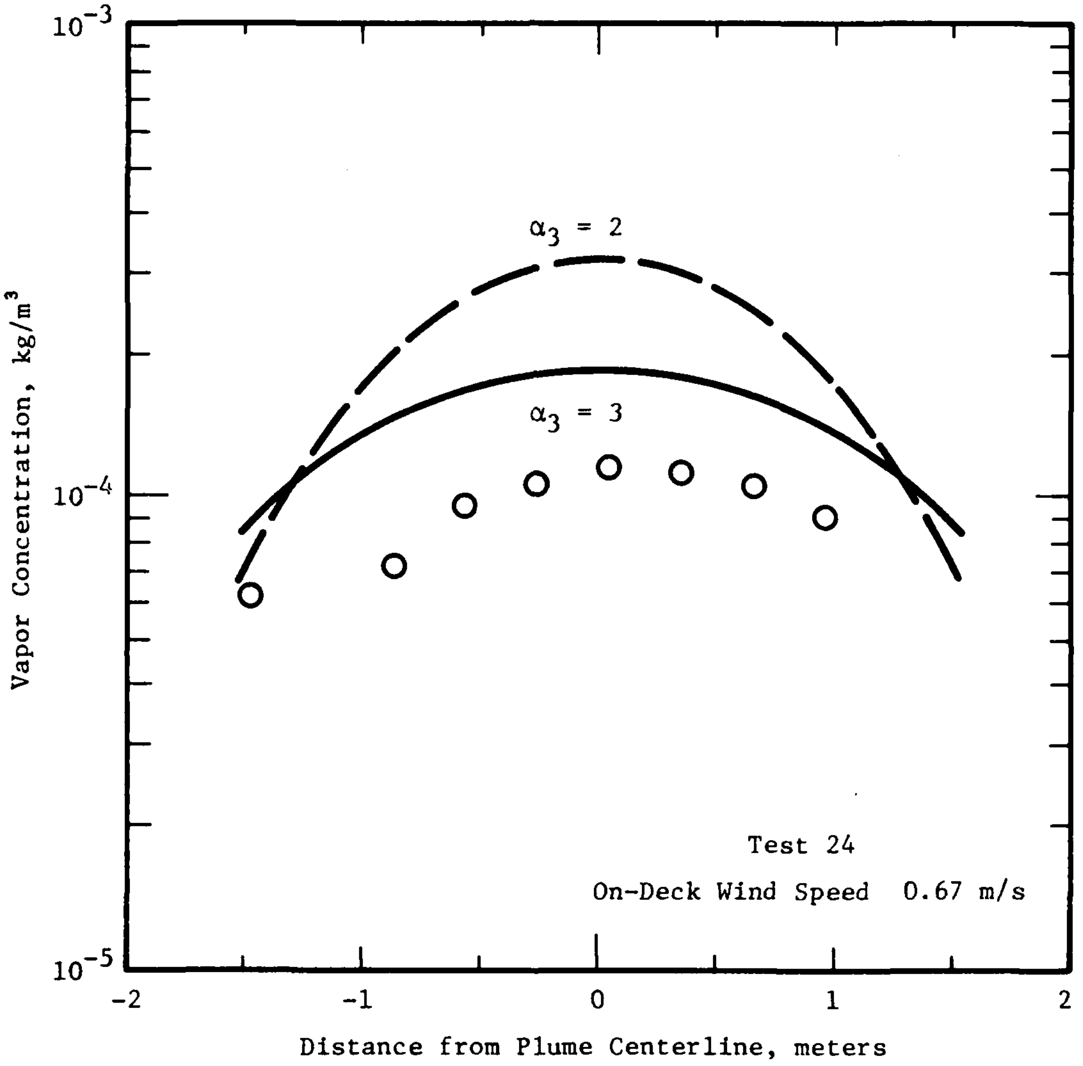


FIGURE IV.49 CROSSWIND CONCENTRATION DISTRIBUTION FOR TEST 24 DURING ISOPROPANOL LOADING

CONCENTRATION DISTRIBUTION ALONG RECEPTOR ARC
DOWNWIND OF OPEN ULLAGE HATCH

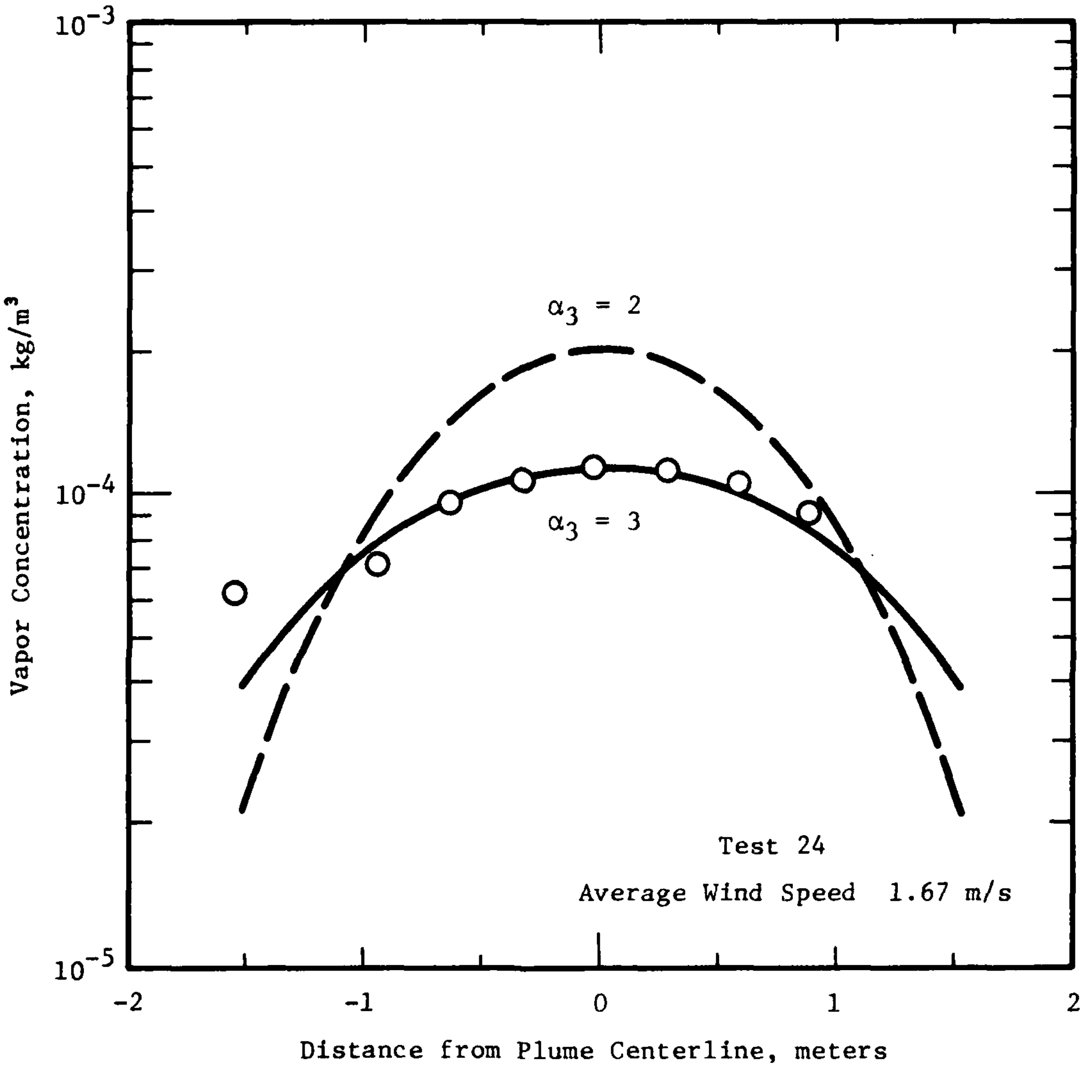


FIGURE IV.50 CROSSWIND CONCENTRATION DISTRIBUTION FOR TEST 24 DURING ISOPROPANOL LOADING

CONCENTRATION DISTRIBUTION ALONG RECEPTOR ARC
DOWNWIND OF OPEN ULLAGE HATCH

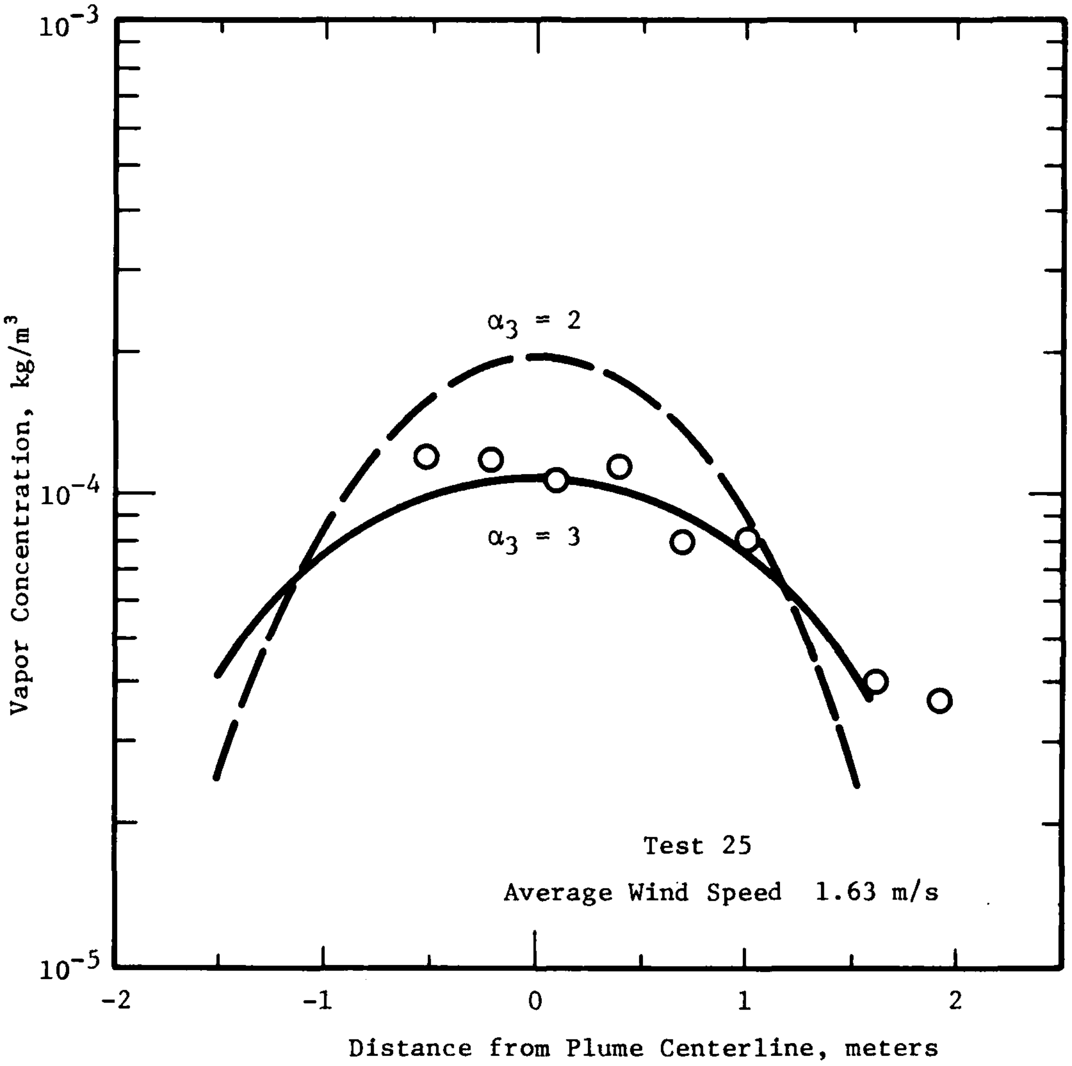


FIGURE IV.51 CROSSWIND CONCENTRATION DISTRIBUTION FOR TEST 25 DURING ISOPROPANOL LOADING

CONCENTRATION DISTRIBUTION ALONG RECEPTOR ARC
DOWNWIND OF OPEN ULLAGE HATCH

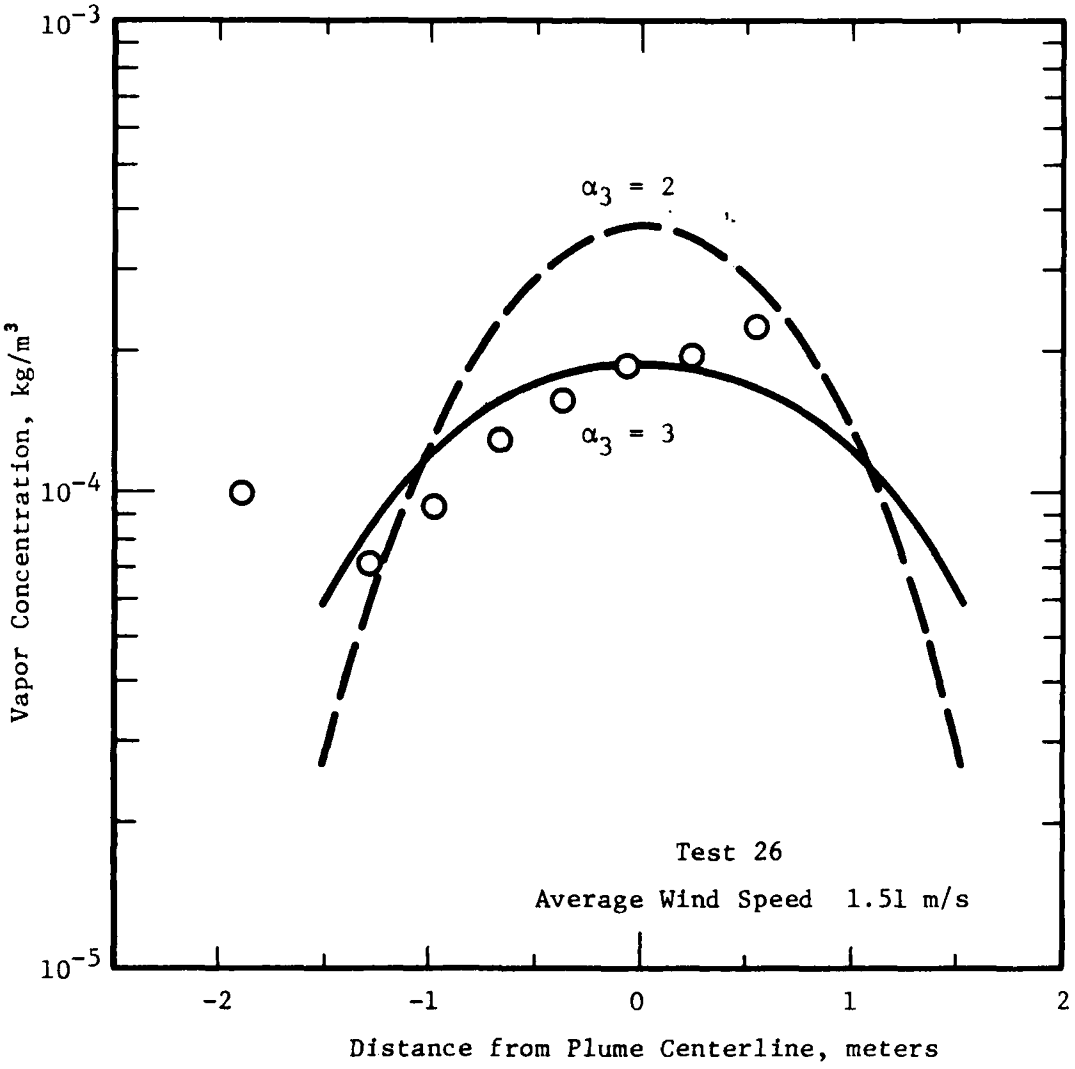


FIGURE IV.52 CROSSWIND CONCENTRATION DISTRIBUTION FOR TEST 26 DURING ISOPROPANOL LOADING

Although the vent concentrations measured during tests 8 - 12 and 24 - 26 were similar (compare Tables IV. 8 and IV. 9) the maximum values of isopropanol concentration measured for tests 24 - 26 were higher because the loading rate was higher and the receptors were closer to the vent. For tests 24 - 26, the highest values measured were about 10^{-4} kg/m^3 (41 ppm), 1.2×10^{-4} kg/m^3 (49 ppm), and 2.3×10^{-4} kg/m^3 (94 ppm). However, these values are still lower than the accepted STEL and TLV-TWA value of 400 ppm for isopropanol.

Methanol Loading into a Dedicated Tank

Tests 32, 34, 35, 36

These tests were performed during a cargo loading observation on a barge that is dedicated to carrying of methanol. The barge contained three separate tanks, each with a capacity of about 564 m^3 (149,000 gallons). The tanks are not washed or ventilated between discharge and loading operations. All three tanks were loaded simultaneously, but topped off sequentially. The average loading rate for each tank was about 227 m^3/hr (1000 gpm). The tank gas atmosphere was vented through an open ullage hatch with the hatch cap resting on pins.

During loading operations, the wind was fairly steady both in strength and direction, passing across the barge from river towards shore. Measurements of wind velocity were made both with the 10 meter meteorological tower (located ∿300 meters downwind from the barge) and with a mechanical air meter located on the barge deck, next to the wind direction indicator. The meteorological tower wind speeds were generally higher than those measured on the deck of the barge, and the on-deck wind speeds have been used for the average wind speed in the plume model calculations. An estimate of the turbulence intensity (rms velocity fluctuation divided by mean wind speed) was obtained from the meteorological tower record.

A total of 6 plume dispersion runs were made (see Table IV. 6 , tests 32 to 37). Nine receptors were arranged along a circular arc at a radius of 3.66m (12 ft) from the center of the ullage hatch. The spacing along the arc between receptors was 0.46m (18 in.). For runs 32 and 33, the receptors were located at 1.68m (5.5 ft) above the deck of the barge. For runs 34 - 37, the receptor height was reduced to 1.07m (3.5 ft) above the deck.

During each test, a 10-minute sample of the tank gas atmosphere at the ullage hatch was drawn off and stored in a bag. Each source concentration sample was analyzed together with the 9 area bag samples collected during each 10-minute observation. The source concentration values are shown in Figure IV.53. The methanol concentration level was high, exceeding the lower explosive limit, throughout the entire loading period.

The plume dispersion model was used to predict the crosswind concentration distribution for each run using the measured values of loading rate, on-deck wind speed, turbulence level and source concentration. To simplify the computation of initial plume conditions, it was assumed that the ullage hatch was fully open. Good agreement was obtained between the model predictions and experimental data for all six tests. The results of tests 32, 34, 35 and 36 are presented here. The set of experimental conditions for these tests are summarized in Table IV.10.

Figure IV.54 compares the measured concentration distribution along the arc of receptors at a height of 1.68m (5.5 ft) above the deck of the barge for test 32 with the predicted concentration distribution for values of α_3 equal to 2 and 3. The experimental data match the predicted concentration distribution predicted for $\alpha_3 = 2$ fairly well. The combination of $\alpha_3 \cdot \text{tlv}$ is equal to 0.55 for this run.

Figures IV.55, IV.56 and IV.57 compare the measured concentration distributions along the arc of receptors at a height of 1.07m (3.5 ft) above the deck for tests 34, 35 and 36 with concentration distribution predictions for values of α_3 equal to 1, 2, or 3. Note that the experimental data match the predicted concentration distribution for a value of $\alpha_3 = 2$ for runs 34 and 35, and for a value of $\alpha_3 = 3$ for run 36.

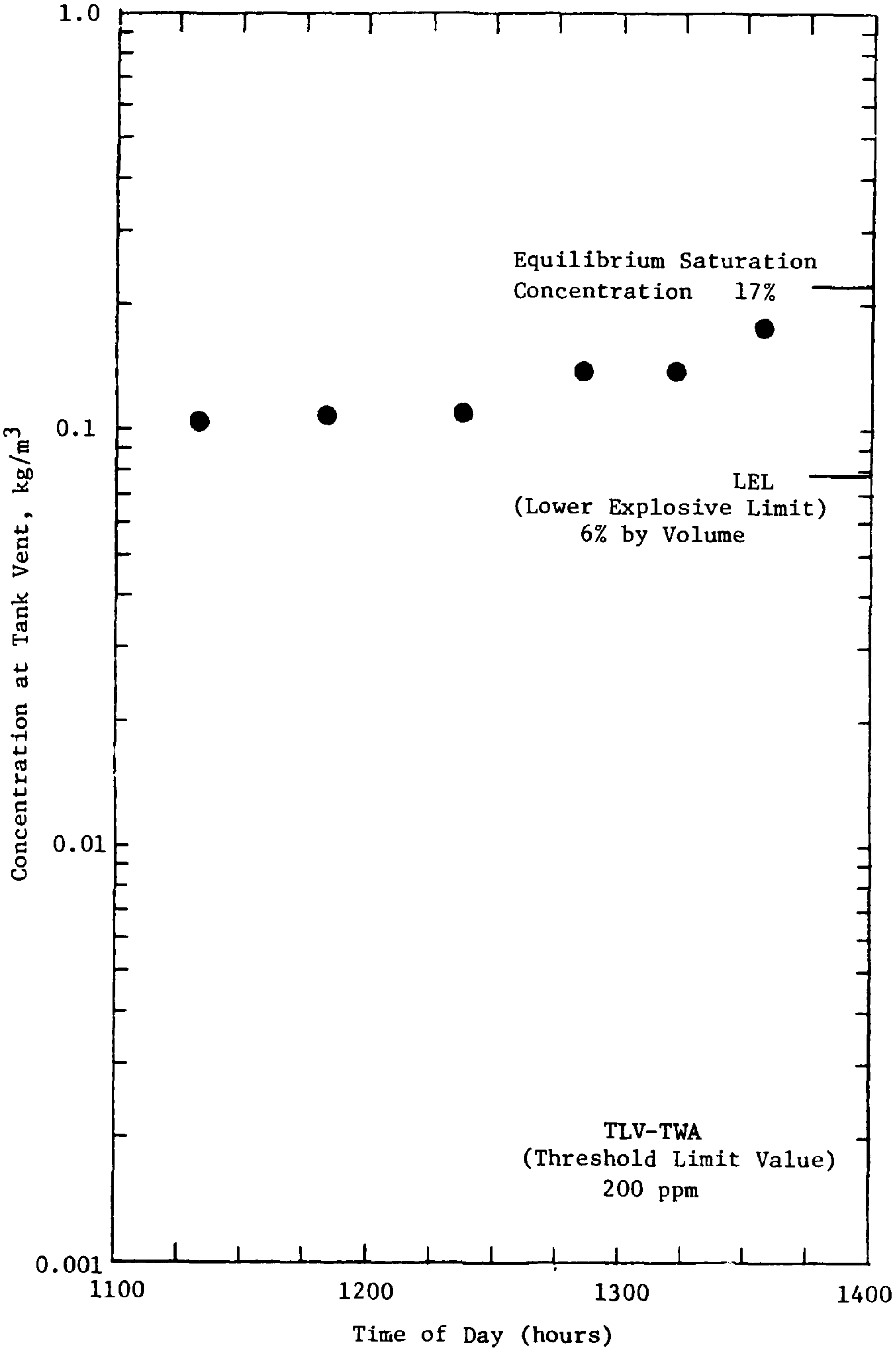


FIGURE IV.53. SOURCE CONCENTRATION VALUES MEASURED AT OPEN ULLAGE HATCH DURING BARGE LOADING WITH METHANOL

TABLE IV.10. EXPERIMENTAL CONDITIONS FOR VAPOR SAMPLING TESTS 32, 34, 35, 36

TEST NO.	VENT CONCENTRATION METHANOL		RECEPTOR		METEOROLOGICAL CONDITIONS		BEST FIT
	kg/m^3	ppm	RADIUS m	HEIGHT m	WIND SPEED m/s	TURBULENCE LEVEL tlv	$\alpha_3 \cdot$ tlv
32	0.104	80,000	3.66	1.68	2.02	.273	.55
34	0.110	85,000	3.66	1.07	1.72	.265	.53
35	0.138	106,000	3.66	1.07	2.28	.365	.73
36	0.138	106,000	3.66	1.07	1.95	.228	.68

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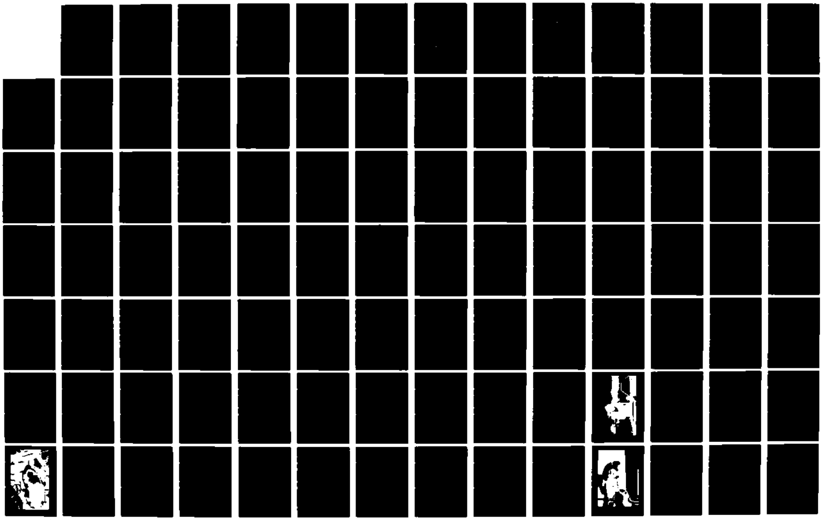

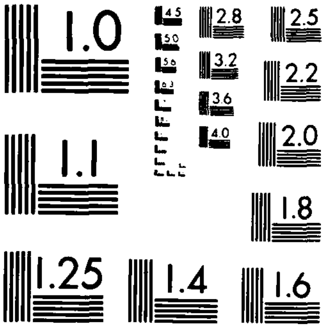

MICROCOPY RESOLUTION TEST CHART
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CONCENTRATION DISTRIBUTION ALONG RECEPTOR ARC
DOWNWIND OF OPEN ULLAGE HATCH

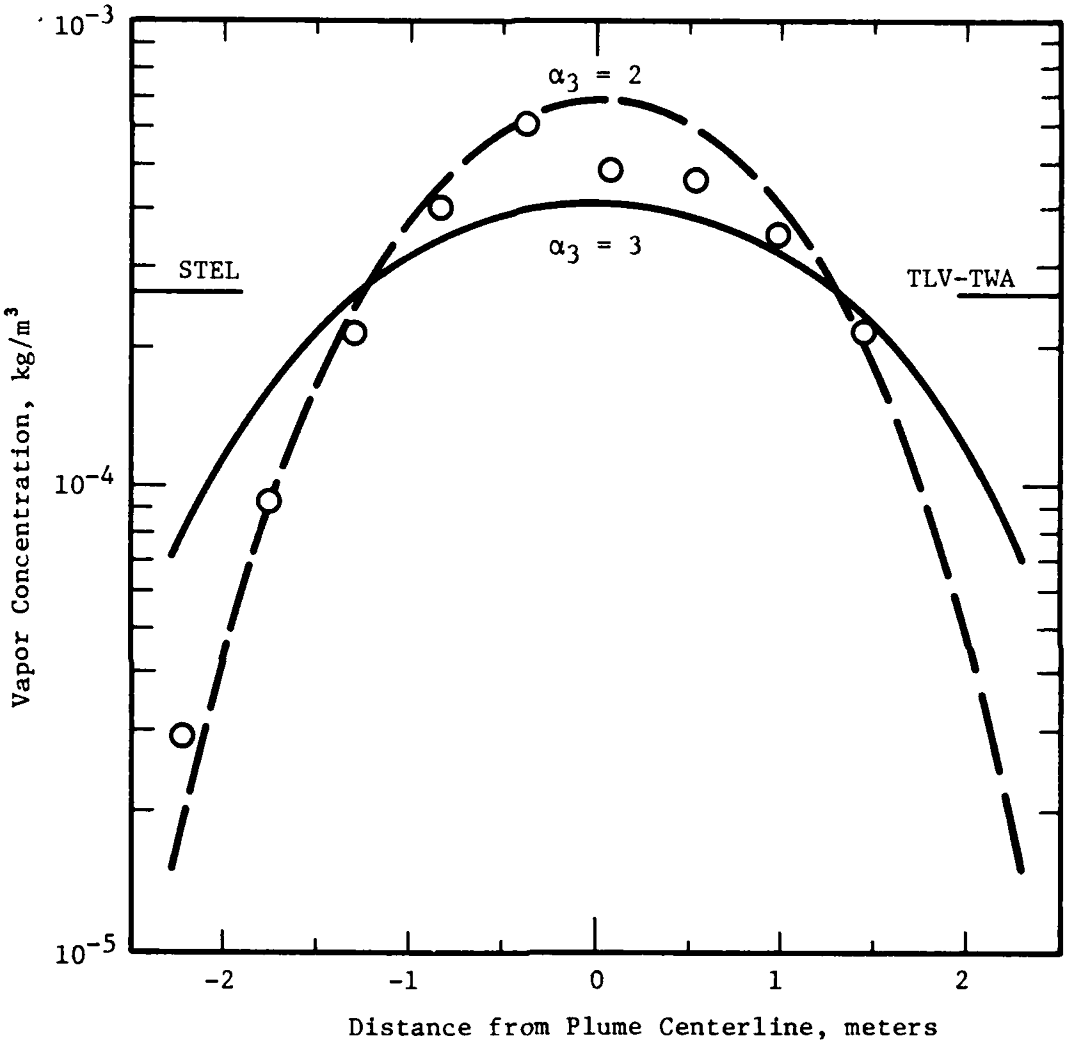


FIGURE IV.54 CROSSWIND CONCENTRATION DISTRIBUTION FOR TEST 32 (OBSERVATION 32) DURING METHANOL LOADING

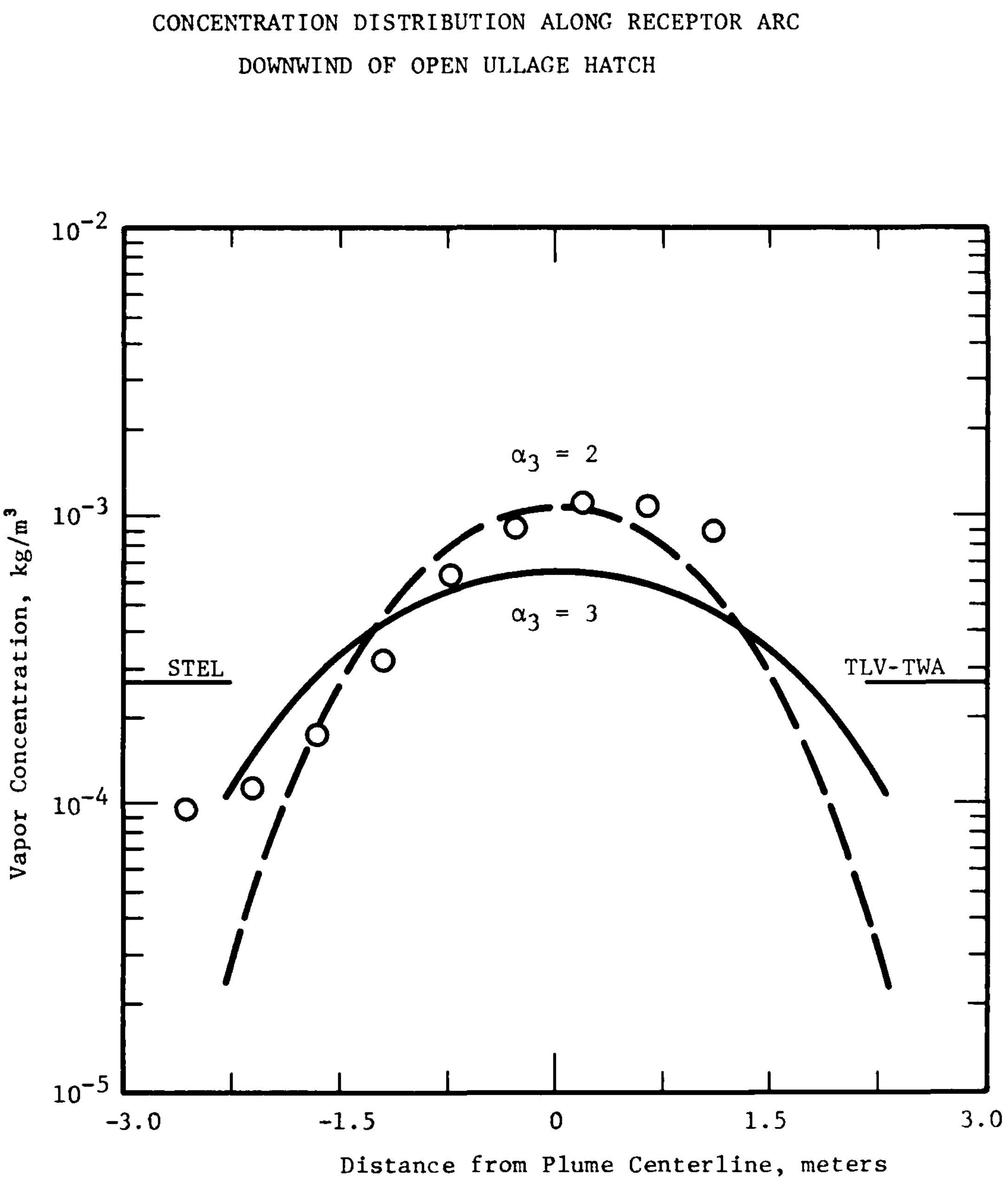


FIGURE IV.55 CROSSWIND CONCENTRATION DISTRIBUTION FOR TEST 34 (OBSERVATION 34) DURING METHANOL LOADING

CONCENTRATION DISTRIBUTION ALONG RECEPTOR ARC
DOWNWIND OF OPEN ULLAGE HATCH

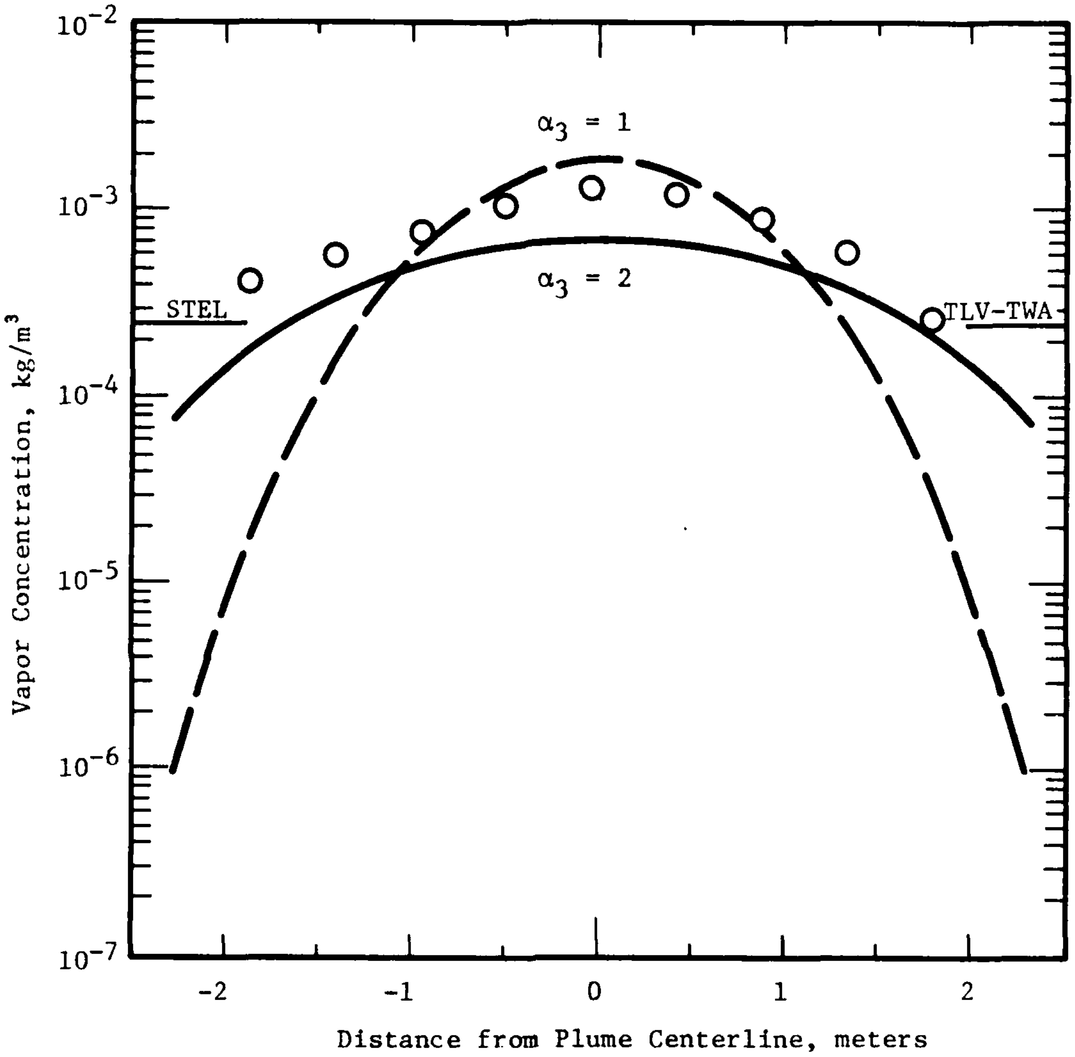


FIGURE IV.56 CROSSWIND CONCENTRATION DISTRIBUTION FOR TEST 35 (OBSERVATION 35) DURING METHANOL LOADING

CONCENTRATION DISTRIBUTION ALONG RECEPTOR ARC
DOWNWIND OF OPEN ULLAGE HATCH

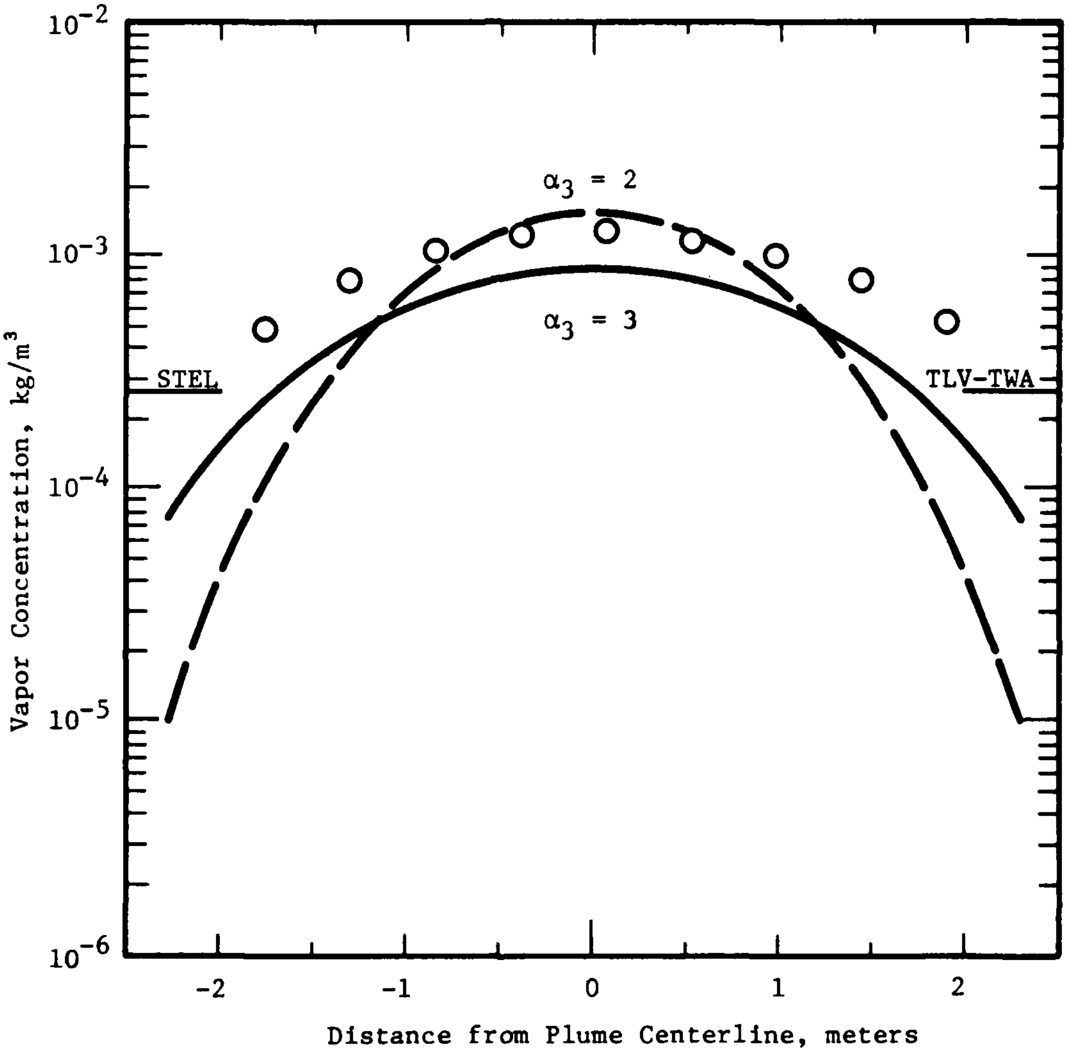


FIGURE IV.57 CROSSWIND CONCENTRATION DISTRIBUTION FOR TEST 36 (OBSERVATION 36) DURING METHANOL LOADING

Table IV.10 shows that the experimental conditions for runs 35 and 36 were very similar except for the estimated values of turbulence intensity which were 0.365 for run 35 and 0.228 for run 36. Comparing Figures IV.56 and IV.57 shows that the measured concentration distributions were actually very similar for the two runs. Thus, the higher value of $\alpha_3 = 3$ required for run 36 to match the data has compensated for the lower estimated value of turbulence intensity. In fact, the combinations of $\alpha_3 \cdot \text{tlv}$ for runs 35 and 36 are equal to 0.73 and 0.68, respectively. The average value of $\alpha_3 \cdot \text{tlv}$ for all <u>six</u> tests was 0.63, which is quite close to the values of 0.59 calculated for tests 1 - 8, and the value of 0.61 for tests 8 - 12. In all of these particular tests, the wind field above the vent was unobstructed by on-deck structure.

The current accepted concentration values for the STEL inhalation limit is 260 mg/m^3 for 60 minutes. This is equal to a value of 2.6×10^{-4} kg/m^3 or 200 ppm. The value of the TLV-TWA for methanol vapor is also 200 ppm. Figures IV.54 through IV.57 show that the vapor concentration in the central region of the plume exceeded these concentration limits at the receptor locations. While only run number 32 measured the vapor concentration at breathing height, it is likely that the TLV-TWA and STEL limits were exceeded at breathing height for the other runs also since the vent concentration, wind speed and loading rate conditions changed only slightly during the tests. Figure IV.58 shows the concentration contours downwind of the tank vent at a height of 1.07m (3.5 ft) above the deck predicted for a wind speed of 1.41 m/s and a value of $\alpha_3 \cdot \text{tlv}$ equal to 0.61. The contour lines are shown superposed onto an outline sketch of the barge. It is interesting to note that the concentration contour line corresponding to the 200 ppm STEL and TLV-TWA limit values extends beyond the side of the barge, and nearly reaches a walkway on shore.

Vinyl Acetate Loading into a Washed and Ventilated Tank

Tests 29 and 31

These tests were performed during a loading of vinyl acetate into tank 10CP, close to the deckhouse, on a chemical product tanker. The

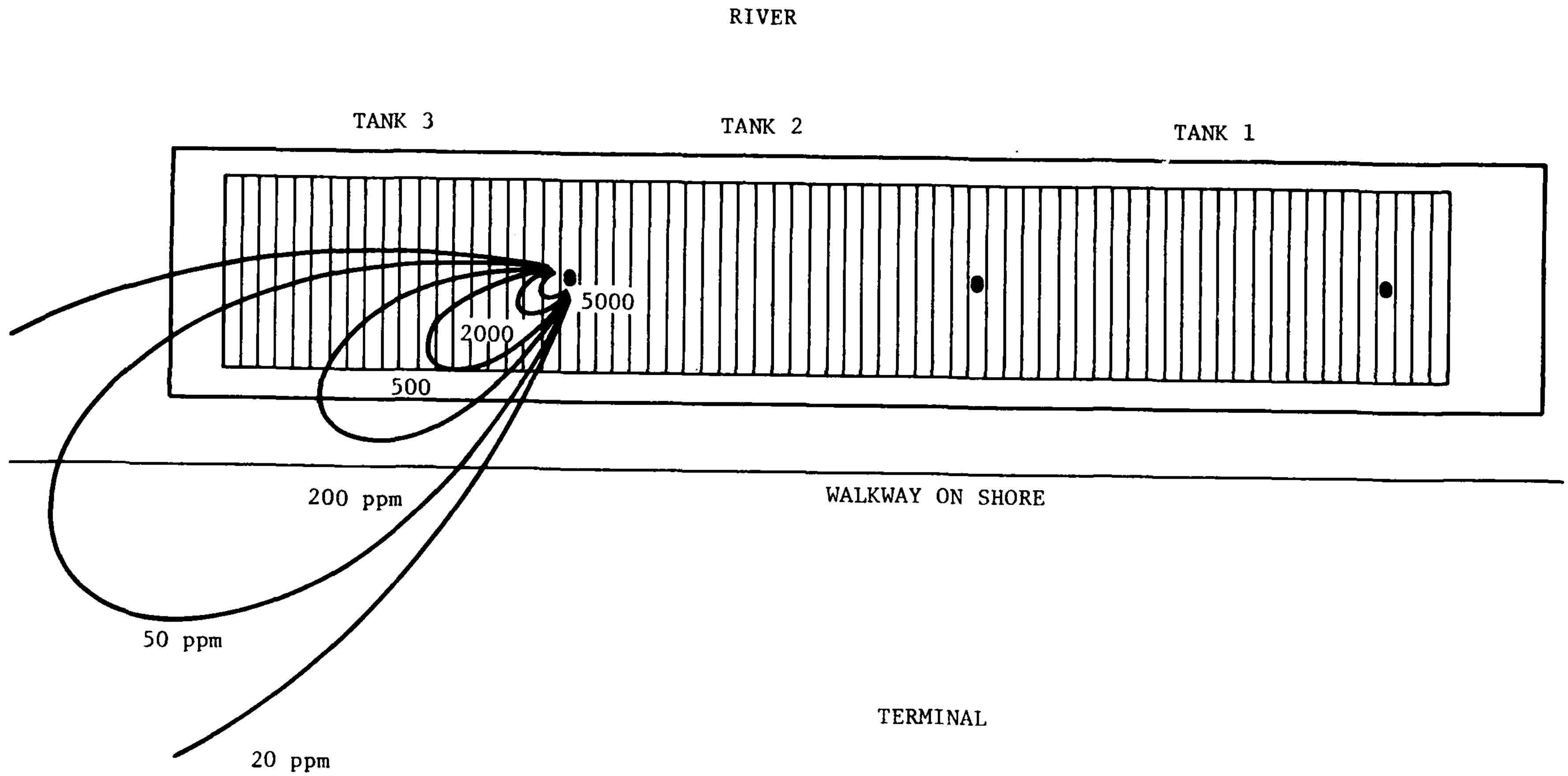


FIGURE IV.58 CONCENTRATION CONTOURS DOWNWIND OF TANK #3 DURING TEST 37 FOR METHANOL BARGE LOADING

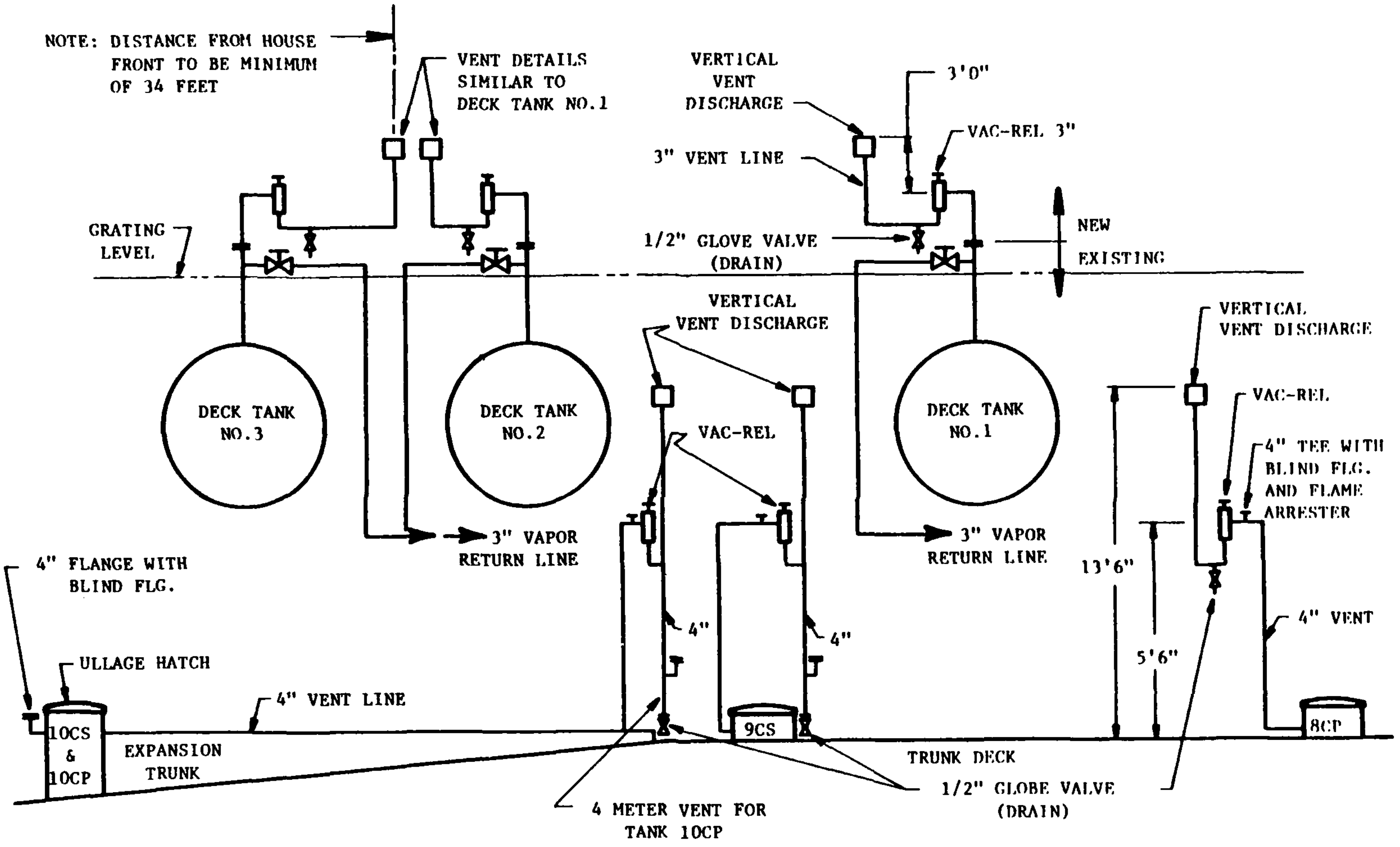
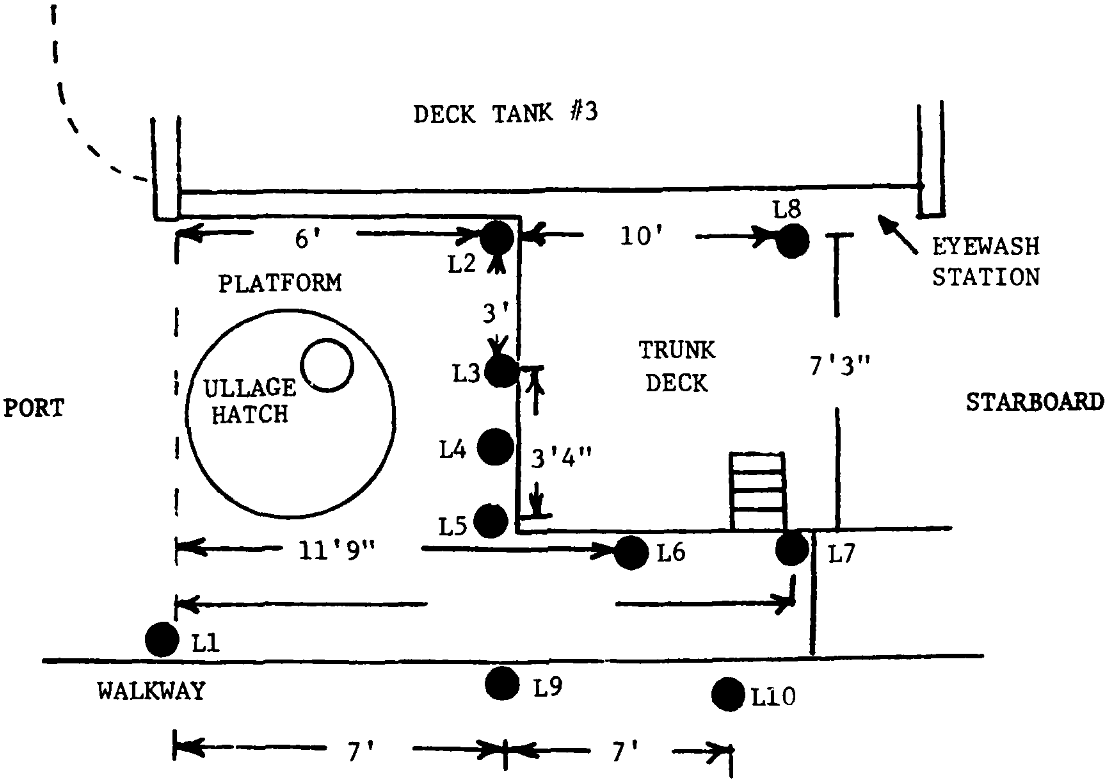


FIGURE IV.59 TANK VENTING ARRANGEMENT FOR TANK 10CP



NOTE: Receptors L1 through L7 were situated on a platform raised above the top of the trunk deck. The pump noses were all at 5'6" above the platform.

Receptor L8 was placed on the sloping trunk deck next to an eyewash station.

Receptors L9 and L10 were placed on a walkway above the platform. Pump nose elevation was 11'3" above the platform.

FIGURE IV.60. SKETCH OF RECEPTOR LOCATIONS FOR VINYL ACETATE LOADING IN TANK 10 CP starboard through the passage between deck tank #3 and the deckhouse. Thus, receptor L1 was in a nominally upwind location, and the other nine receptors were downwind of the ullage hatch. Vapor concentration measurements at location L1 serve to indicate reversals in wind direction.

Figure IV.61 shows the vinyl acetate vapor concentration measured at the ullage hatch during loading. The concentration remained below 1000 ppm until 2:00 PM when the vapor blanket began to appear at the vent. From then until the end of loading at 3:15 PM, the source concentration varied quickly, reaching a peak of approximately 8% at 2:55 PM, then decreasing when some air entered the tank as the loading rate was decreased.

Table IV.11 lists the vinyl acetate concentration values determined at receptors L1 through L10 for observations 28 - 31. A blank entry indicates that the bag had become deflated before it could be sampled. All concentration values in this table were determined from the measurement of peak height on an Organic Vapor Analyzer used in its gas chromatograph mode. The vapor concentration data measured during test 28 are relatively low, and the data for test 30 was incomplete. Therefore, only tests 29 and 31 have been used for comparison with plume model predictions.

Tests 24 - 26 had indicated that the value of α_3, the turbulence entrainment parameter, should be increased in order to properly account for the effects of upwind structure. However, for tests 29 and 31, the primary effect of structure was to make the wind speed through the passage very unsteady in speed and direction.

A special version of the plume dispersion model was prepared to determine least square error estimates of two parameters, α_3 and the angle of the wind relative to the longitudinal axis of the ship. The coordinates and concentration values for receptor stations L2 through L8 (see Figure IV.60) were used for tests 29 and 31. Receptor L1 was not used since it was upwind of the ullage hatch and receptors L9 and L10 were not used because they were at an elevation about 2 meters higher than L2 to L8. The results from the least squares estimate of α_3 and plume angle for these tests are:

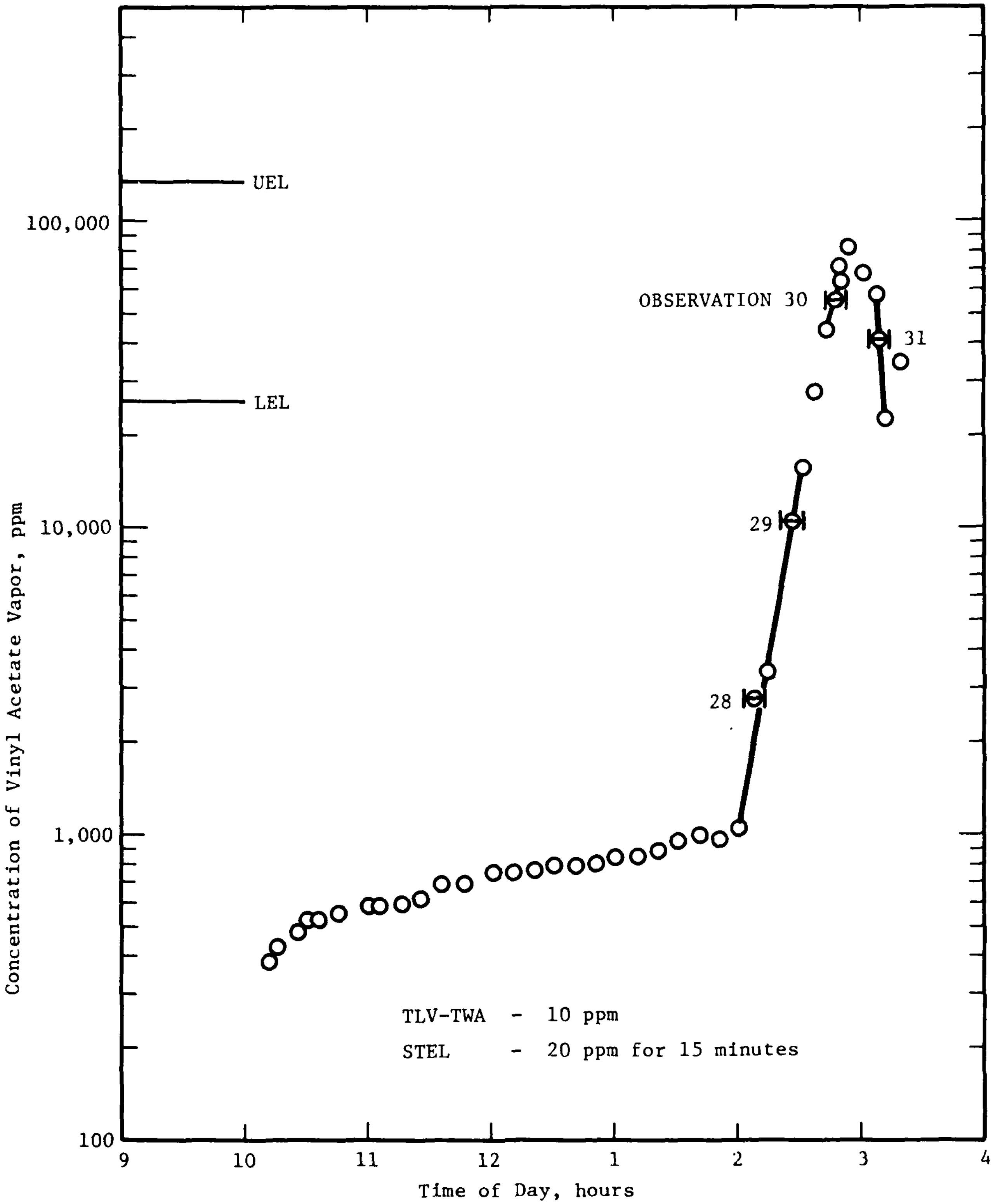


FIGURE IV.61 SOURCE CONCENTRATION VALUES MEASURED AT ULLAGE HATCH DURING LOADING OF TANK 10CP WITH VINYL ACETATE

TABLE IV.11. MEASURED VALUES OF VINYL ACETATE VAPOR CONCENTRATION (ppm)

RECEPTOR NUMBER	OBSERVATION NUMBER			
	#28	#29	#30	#31
L1	14	24	158	14
L2	12	16	30	55
L3	17	271	---	494
L4	26	432	1249	1051
L5	16	133	---	358
L6	13	57	174	717
L7	14	31	81	340
L8	12	20	---	148
L9	14	57	531	85
L10	13	46	---	222

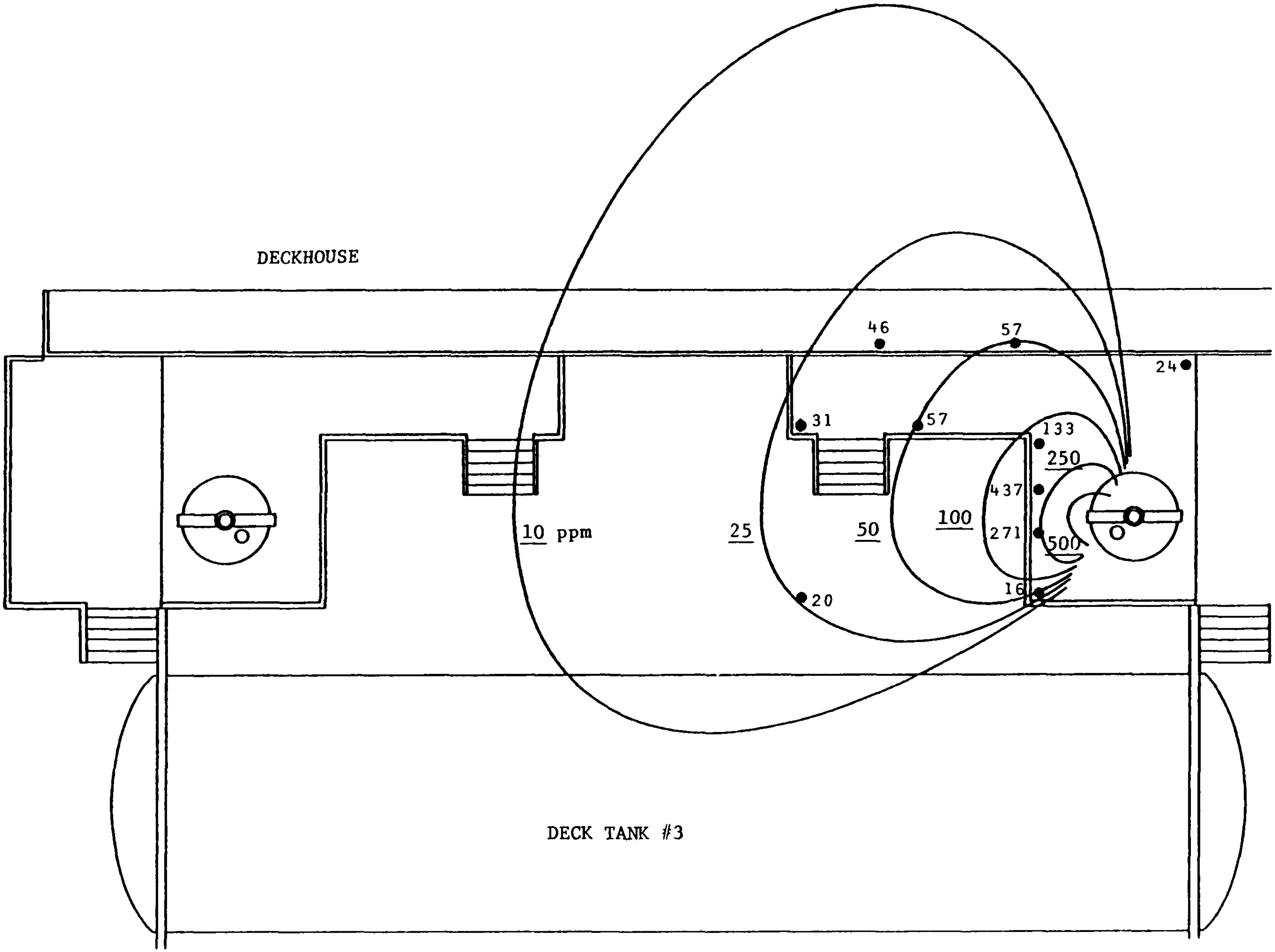
Test No.	α_3	Wind Angle
29	5.55	64.2°
31	4.75	70.9°

Figures IV.62 and IV.63 compare the concentration values measured at the receptors and the concentration contours predicted for tests 29 and 31, respectively. Figure IV.62 shows very good agreement between predicted and measured concentrations while Figure IV.63 shows general, order of magnitude, agreement.

A possible explanation for the poorer agreement between actual and predicted concentrations for test 31 may be due to the wind speed. From Table IV. 6 , it can be seen that the wind speed was reported to be much higher for this test than for tests 28, 29, and 30. An artificially high wind speed could cause the underpredicted concentrations such as those seen in Figure IV.63.

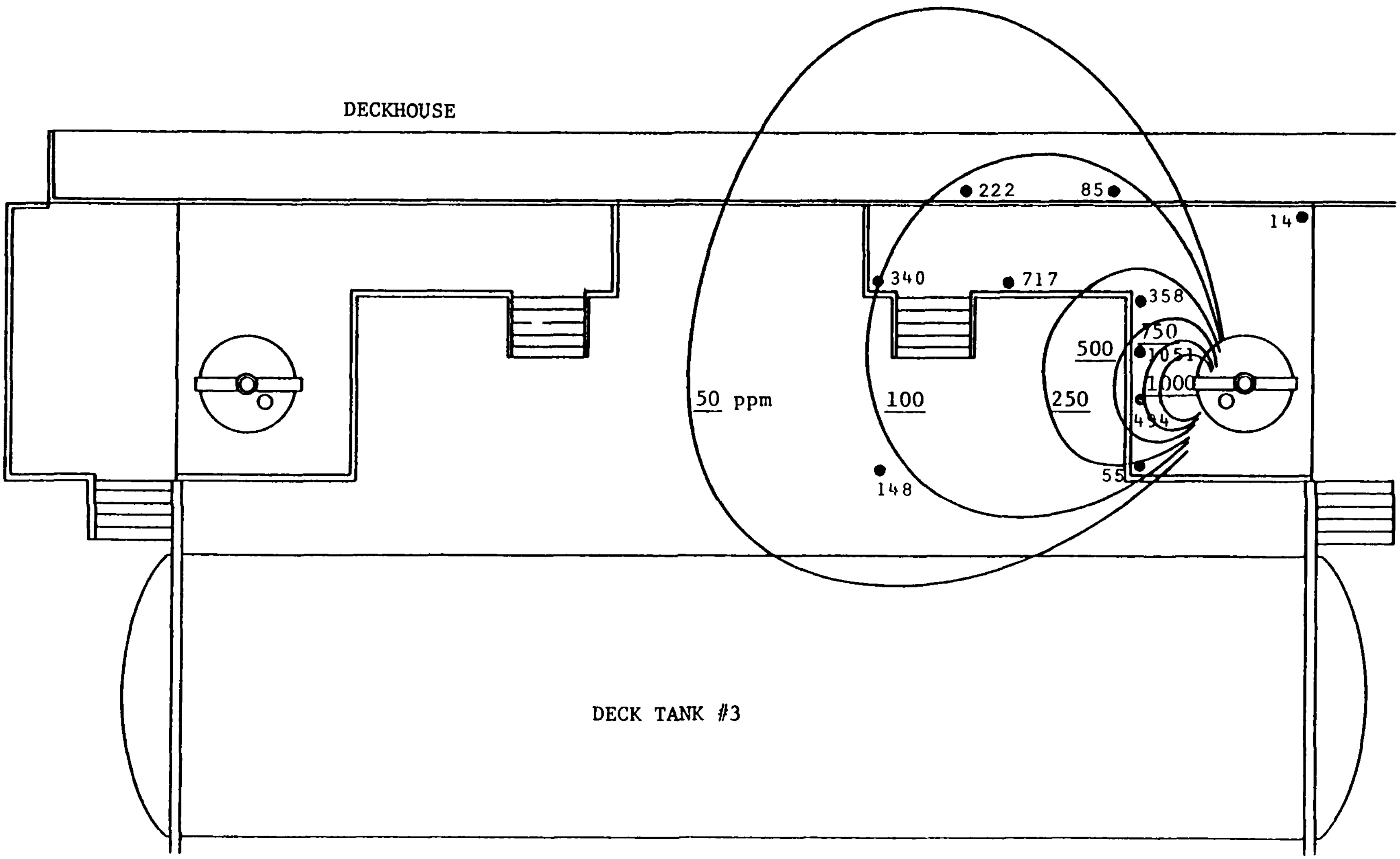
Nevertheless, these observations demonstrate the usefulness of the on-deck plume model even in regions between the deckhouse and on-deck structures such as deck tanks. In general, we may conclude:

- The local wind speed between the deck tank and deckhouse will probably be lower and less steady in magnitude and direction than the wind speed measured by a meteorological tower in the terminal area.
- If a "standard" estimate of wind turbulence based upon meteorological tower readings is used, the appropriate value of α_3, entrainment coefficient for the turbulence, is larger (~ 5) than the usual value of 2 to 3.
- The combined effect of lower local wind speed and higher effective turbulence level, $\alpha_3 U'$, serves to make the plume broader and to increase the width of the deck area within the STEL or TLV-TWA concentration contour.



NOTE: Concentration Contour Values are Underlined, e.g., 25

FIGURE IV.62. CONCENTRATION CONTOURS FOR OBSERVATION #29 AND α_3 = 5.55 COMPARED WITH MEASURED CONCENTRATION VALUES AT RECEPTORS



NOTE: Concentration Contour Values are Underlined, e.g., 50

FIGURE IV.63. CONCENTRATION CONTOURS FOR OBSERVATION #31 and α_3 = 4.75 COMPARED WITH MEASURED CONCENTRATION VALUES AT RECEPTORS

The current accepted values for the STEL and TLV-TWA inhalation limits are 20 ppm for 15 minutes and 10 ppm, respectively. Table IV.11 shows that the actual concentration values measured at the ten receptor locations exceeded one or both of these values during all four tests. Even along the elevated walkway next to the deckhouse, receptors L9 and L10 indicated vapor concentrations above the TLV-TWA for test 28 and above the STEL for tests 29, 30, and 31.

Cargo Loading Simulation Tests with a 1.6m Vent
Tests 45, 47, 48, 50, 53, 55

As discussed in Section IV.3.2, an extensive set of outdoor plume dispersion tests was designed and performed to simulate a wider range of cargo loading rates and tank vent heights than had been encountered in the marine terminal tests.

The first set of simulation tests used a 1.6m (5.25 ft) tall vent. All of the field tests on tankerships and barges had observed tank venting from low vents less than 2m in height. Therefore, the results from this set of simulation tests could be compared directly with the field tests.

A total of eleven tests (numbers 45-55 in Table IV. 6) were performed with the 1.6m vent. Of these, the results of six tests (numbers 45, 47, 48, 50, 53, and 55) are presented in this section. Table IV.12 lists the experimental conditions recorded for these tests. For each test an array of vapor sampling receptors was set up at a radial distance of 10m (32.8 ft) downwind of the vent. The height of the receptors was 1.67m above the ground and the spacing between receptors was 1m. Wind measurements were performed with the 10m meteorological tower located less than 20m from the test site.

Tests 45 and 47 were performed with high venting rates, 728 and 734 m^3/hr, and vent concentrations of approximately 2.5% by volume of propane. The concentration values measured at the receptors are compared with plume model predictions in Figures IV.64 and IV.65. The agreement is

TABLE IV.12. EXPERIMENTAL CONDITIONS FOR CARGO LOADING SIMULATION TESTS WITH 1.6m VENT AND LOW, MEDIUM AND HIGH VENTING RATES

TEST NO.	VENT CONCENTRATION PROPANE IN AIR		VENTING RATE	METEOROLOGICAL CONDITIONS		BEST FIT
	kg/m^3	ppm	m^3/hr	Wind Speed m/s	Turbulence tlv	$\alpha_3 \cdot tlv$
45	.0454	24,900	728	4.19	.249	0.50
47	.0512	28,100	734	4.24	.217	0.66
48	.0430	23,500	461	4.64	.230	0.46
50	.0535	29,300	455	4.74	.298	0.60
53	.0820	45,000	166	5.18	.253	0.50
55	.1105	60,600	222	4.35	.316	0.62

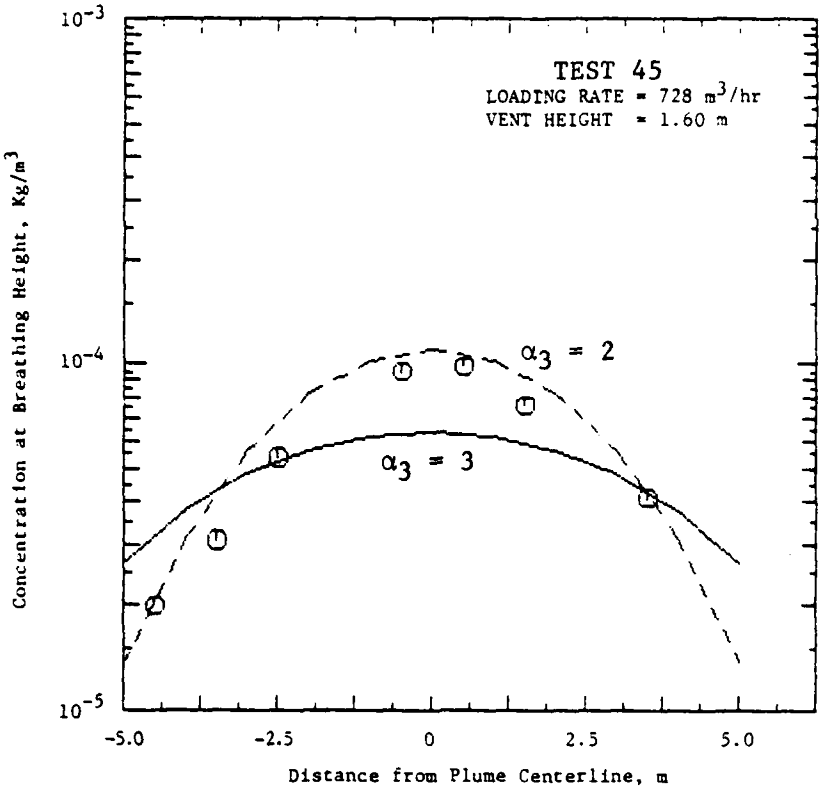


FIGURE IV.64. TEST 45 - PLUME DISPERSION FROM A 1.6m VENT AT HIGH LOADING RATE

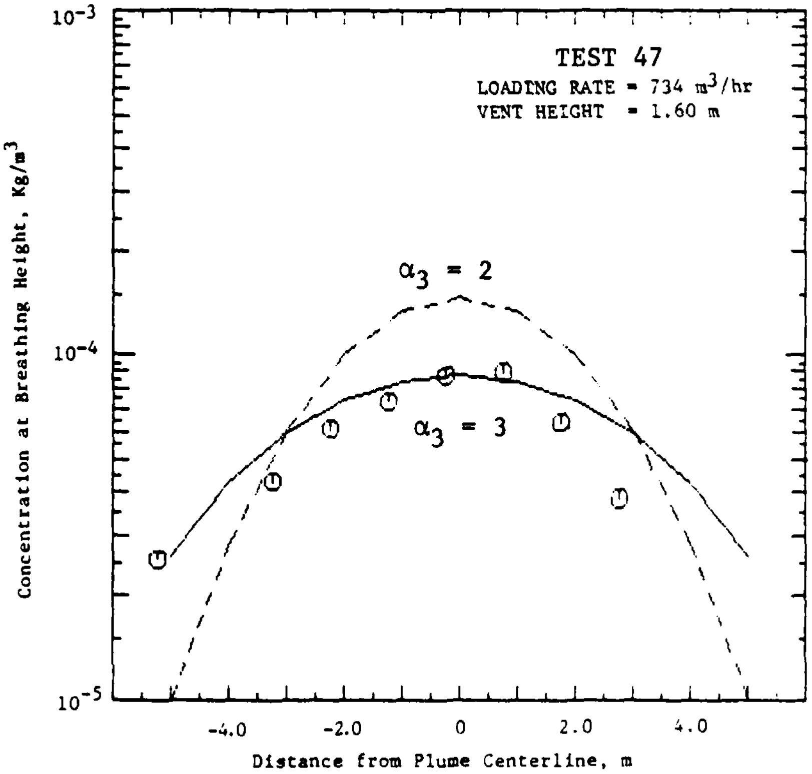


FIGURE IV.65. TEST 47 - PLUME DISPERSION FROM A 1.6m VENT AT HIGH LOADING RATE good for both runs. Best fit values of $\alpha_3 \cdot tlv$ are 0.50 and 0.66, respectively. Since comparisons were made only for integer values of α_3 for these tests, it will be necessary to calculate an "ensemble" average for $\alpha_3 \cdot tlv$ over all tests in this series.

Tests 48 and 50 were performed with medium venting rates, 461 and 455 m^3/hr, and vent concentrations of about 2.4% and 2.9% by volume. Predicted and measured concentration distributions are shown in Figures IV.66 and IV.67. Again, the agreement is good. Best fit values of $\alpha_3 \cdot tlv$ are 0.46 and 0.60, respectively.

Tests 53 and 55 were performed with low venting rates, 166 m^3/hr and 222 m^3/hr. To compensate for the reduced volume of gas being vented, it was necessary to increase the vent concentration to 4.5% and 6.1% of propane. Figures IV.68 and IV.69 compare the predicted and measured concentration distributions. Again, agreement is good (although a value of $\alpha_3 \sim 2.4$ would improve agreement even more in Figure IV.68). Best estimated values of $\alpha_3 \cdot tlv$ are 0.50 and 0.62, respectively.

Taking all six tests together, the average value of $\alpha_3 \cdot tlv$ from Table IV.12 is 0.56. The average value of $\alpha_3 \cdot tlv$ for all eleven tests performed with a 1.6m vent is 0.61. These estimates agree well with the results of the field tests ($\alpha_3 \cdot tlv = 0.59$ for tests 1 - 8, 0.61 for tests 8 - 12, and 0.63 for tests 32 - 37).

Thus, the plume model has been shown to correctly predict the vapor concentration distribution downwind of low tank vents for venting rates ranging from 100 to 700 m^3/hr. The appropriate value of $\alpha_3 \cdot tlv$ is about 0.60 when the wind passing over the vent is not obstructed by on-deck structures. When the vent is partially shielded from the wind (as in tests 24 - 27 and 28 - 31), higher values of $\alpha_3 \cdot tlv$ ranging from 0.9 to as high as 1.5 should be used.

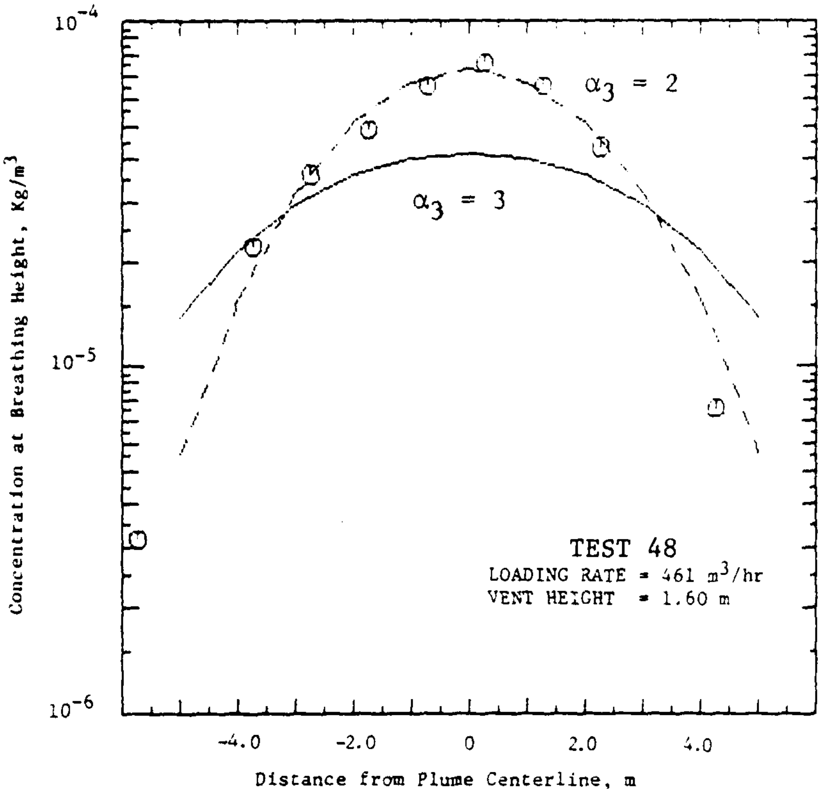


FIGURE IV.66. TEST 48 - PLUME DISPERSION FROM A 1.6m VENT AT MEDIUM LOADING RATE

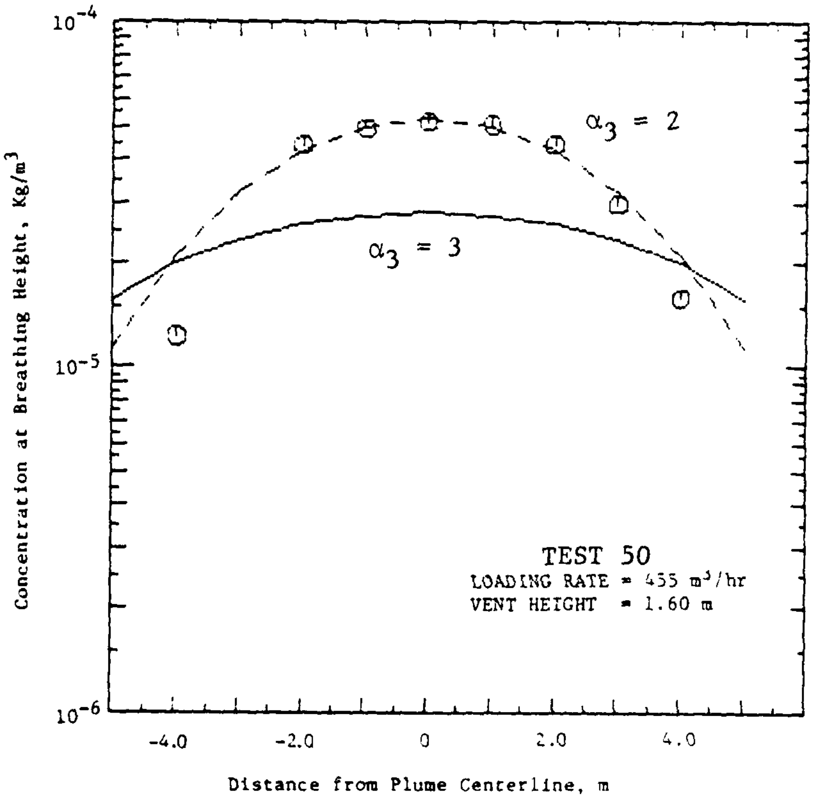


FIGURE IV.67. TEST 50 - PLUME DISPERSION FROM A 1.6m VENT AT MEDIUM LOADING RATE

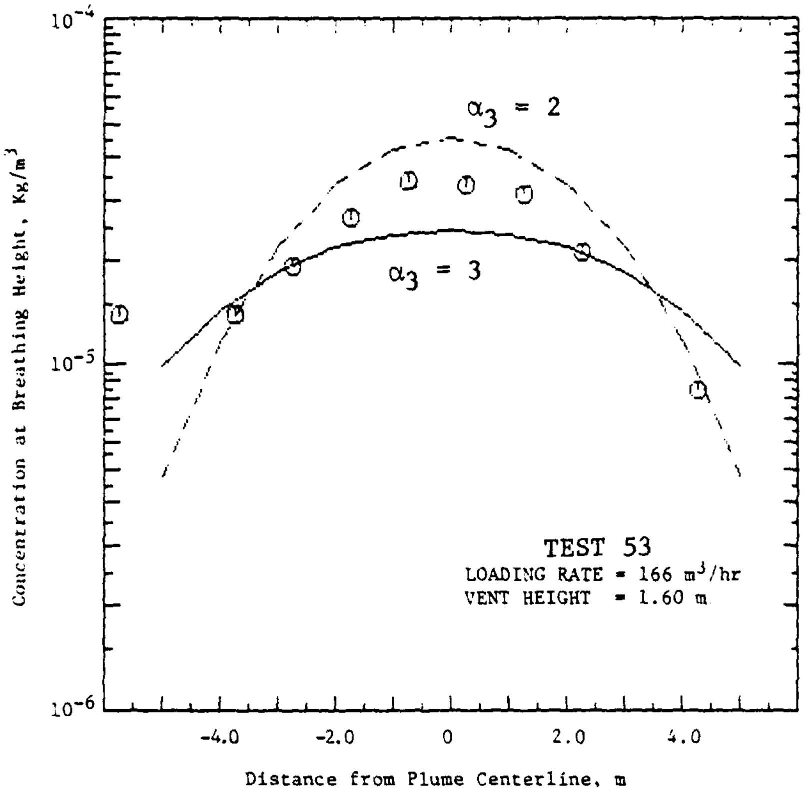


FIGURE IV.68. TEST 53 - PLUME DISPERSION FROM A 1.6m VENT AT LOW LOADING RATES

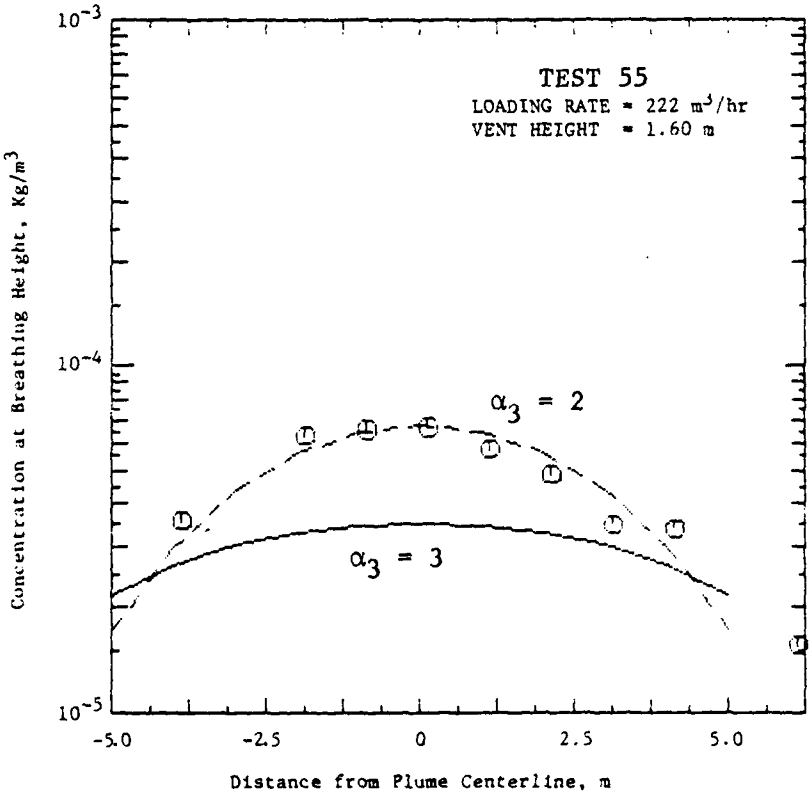


FIGURE IV.69. TEST 55 - PLUME DISPERSION FROM A 1.6m VENT AT LOW LOADING RATES

Cargo Loading Simulation Tests With a 4.0m Vent

Tests 61, 67, 71, 75, 77, 79

The next series of outdoor venting simulation tests used a 4.0m (13.1 ft) tall vent. A total of 27 tests (numbered 56 to 82 in Table IV. 6) were performed with this vent. In this section the results of six tests are presented for discussion. Table IV.13 lists the experimental conditions recorded for these tests. For each test an array of vapor sampling receptors was set up at a radial distance of 10m (32.8 ft) downwind of the vent. Receptor height was 1.67m above the ground and receptor spacing was 1m. Wind measurements were recorded for the 10m meteorological tower.

Tests 75 and 77 were performed at high venting rates, 915 and 923 m^3/hr, respectively. The propane concentration at the vent exit was about 7.1 and 8.1% by volume. The concentration data measured at receptor locations for these runs are compared with plume model predictions in Figures IV.70 and IV.71. The agreement between model predictions and data is only fair. Although the concentration distribution data has about the same shape as the plume model predictions for $\alpha_3 = 3$, the predicted concentration values are too high by a factor of about 2.

Tests 67 and 79 were performed at medium venting rates, 528 and 565 m^3/hr, respectively. The propane concentration at the vent was 8.1% and 10.8%, respectively. Figures IV.72 and IV.73 compare the concentration data at receptor locations with plume model predictions. The agreement between the data and the model predictions for $\alpha_3 = 2$ is good on the side of the concentration distribution curve and fair in the center. The level of concentration was predicted well. The maximum differences were within a factor of 2.

Tests 61 and 71 were performed at low venting rates, 215 and 182 m^3/hr, respectively. The propane concentration at the vent exit was about 17.8 and 16.5% by volume. Figures IV.74 and IV.75 compare the measured concentration data with plume model predictions. The agreement

TABLE IV.13. EXPERIMENTAL CONDITIONS FOR CARGO LOADING SIMULATION TESTS WITH 4.0m VENT AND LOW, MEDIUM AND HIGH VENTING RATES

TEST NO.	VENT CONCENTRATION PROPANE IN AIR		VENTING RATE m^3/hr	METEOROLOGICAL CONDITIONS		BEST FIT $\alpha_3 \cdot tlv$
	kg/m^3	ppm		Wind Speed m/s	Turbulence tlv	
75	.1081	59,300	915	5.40	.248	0.74
77	.1239	67,900	923	5.02	.257	0.77
67	.1231	67,500	528	2.04	.332	0.66
79	.1635	89,600	565	4.02	.288	0.58
61	.2712	149,000	215	3.04	.335	0.67
71	.2509	138,000	182	3.18	.272	0.54

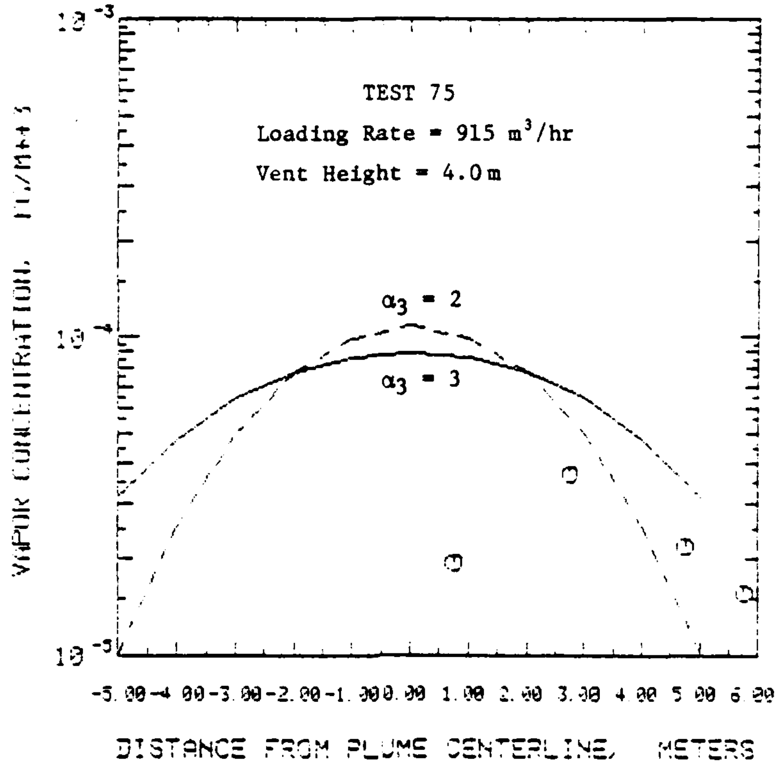


FIGURE IV.70. TEST 75 - PLUME DISPERSION FROM A 4.0 m VENT AT HIGH LOADING RATE

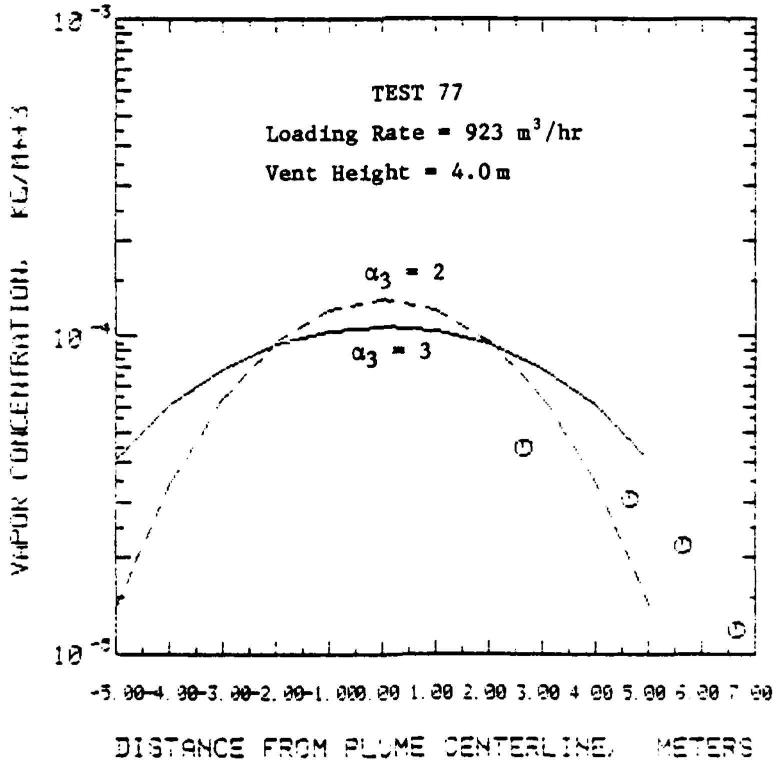


FIGURE IV.71. TEST 77 - PLUME DISPERSION FROM A 4.0 m VENT AT HIGH LOADING RATE

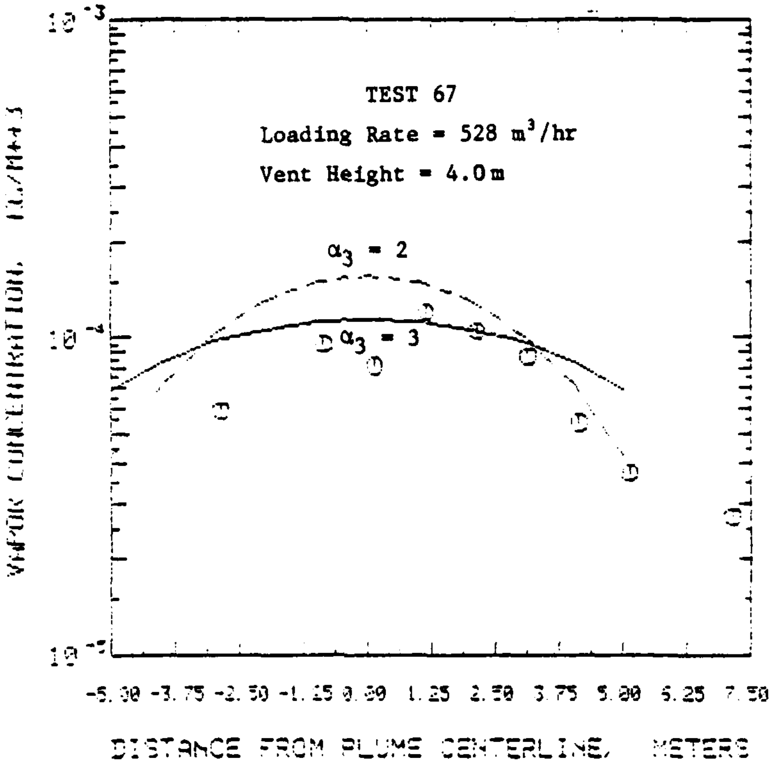


FIGURE IV.72. TEST 67 - PLUME DISPERSION FROM A 4.0 m VENT AT MEDIUM LOADING RATE

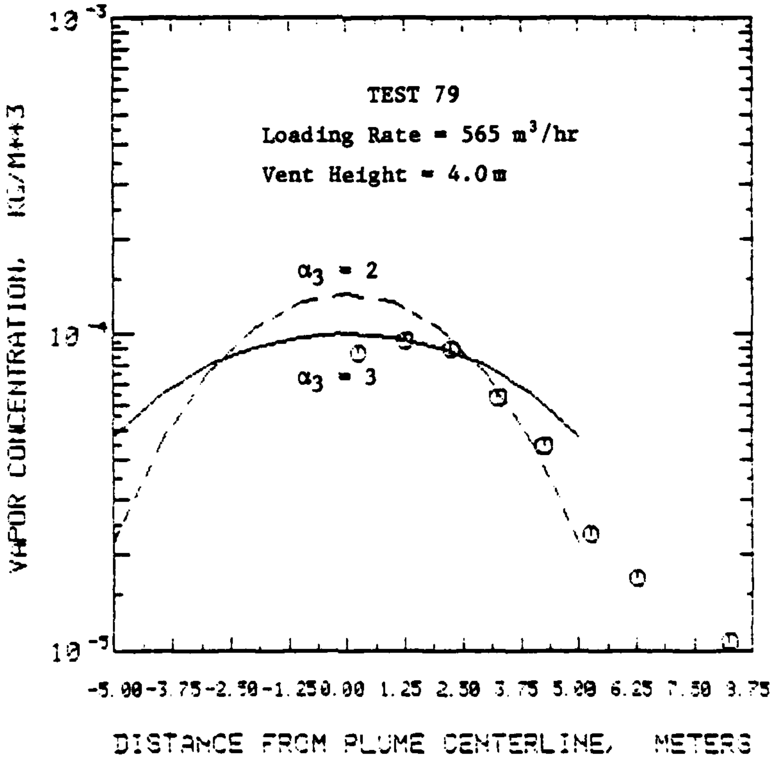


FIGURE IV.73. TEST 79 - PLUME DISPERSION FROM A 4.0 m VENT AT MEDIUM LOADING RATE

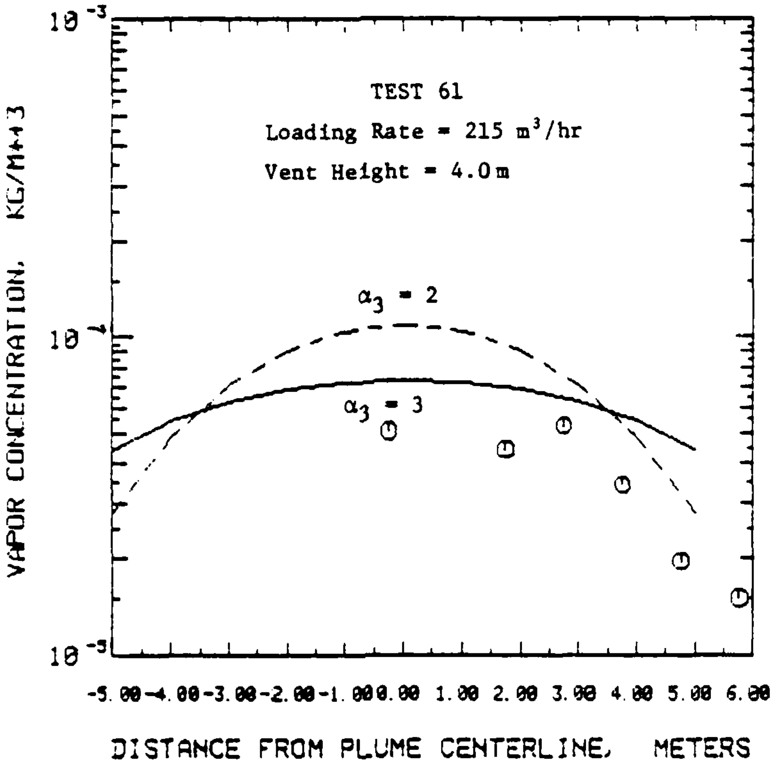


FIGURE IV.74. TEST 61 - PLUME DISPERSION FROM A 4.0 m VENT AT LOW LOADING RATE

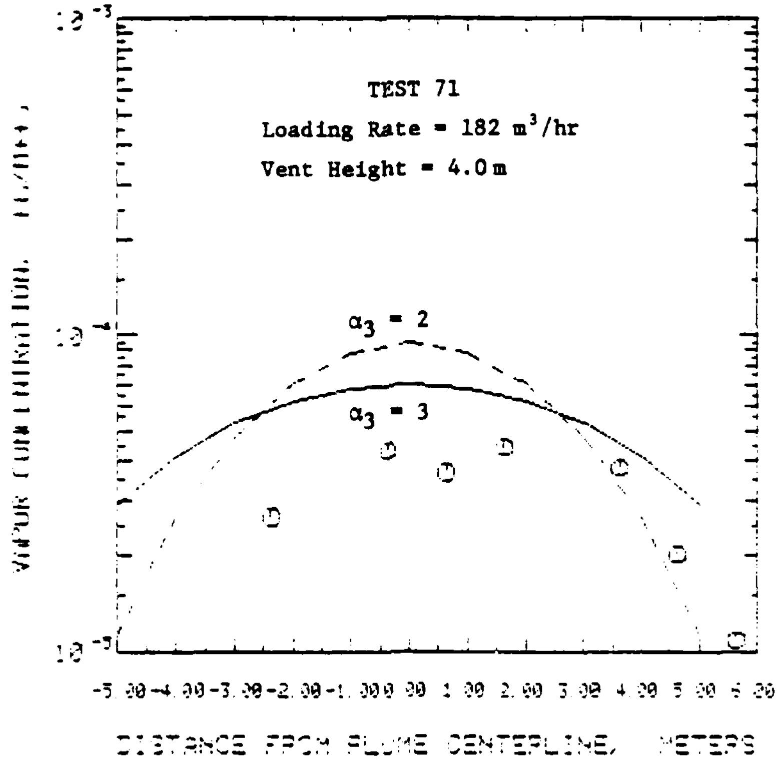


FIGURE IV.75. TEST 71 - PLUME DISPERSION FROM A 4.0 m VENT AT LOW LOADING RATE between model predictions and data is fair. As in the previous two figures, the overall shape of the concentration profile is predicted well by a value of $\alpha_3 = 2$. However, the propane concentration level predicted for the center of the concentration distribution curve is too high by a factor of from 2 to 2.5.

Taking all six tests together, the mean value of $\alpha_3 \cdot \text{tlv}$ is estimated to be 0.66 with a standard deviation of 0.09. This value is from 5% to 10% higher than the values obtained from the previous tests, but cannot be distinguished from them statistically.

This series of tests showed that the chemical vapor plume dispersion model gives a reasonably good simulation of the dispersion of gas released from a 4m vent. The model predictions were generally conservative. In the central region of the concentration profile (at breathing height), the concentration level was overpredicted by as much as a factor of two. In none of the 27 tests performed with the 4m vent was the peak propane concentration underpredicted significantly.

Cargo Loading Simulation Tests With a 6.0 m Vent
Tests 85, 86, 93, 95, 96, 99

The last series of outdoor venting simulation tests used a 6.0 m (19.7 ft) tall vent. A total of 16 tests (Nos. 83 to 89 and 93 to 101) were performed with this vent. The results of six of these tests are presented here for discussion. Table IV.14 lists the experimental conditions for these tests. Tests 85 and 86 were performed with an array of vapor sampling receptors set up at a radial distance of 13 m (42.7 ft) downwind of the vent with a spacing of 1.3 m (4.25 ft) between receptors. Tests 93, 94, 96, and 99 were performed with the receptor array located at a radial distance of 20 m (65.6 ft) from the vent with a spacing of 2 m (6.6 ft) between receptors. The height of the receptors above ground was 1.67 m (5.5 ft) for each test. Wind measurements were recorded from the 10 m meteorological tower.

TABLE IV.14. EXPERIMENTAL CONDITIONS FOR CARGO LOADING SIMULATION TESTS WITH 6.1 m VENT AND LOW, MEDIUM AND HIGH VENTING RATES

TEST NO.	VENT CONCENTRATION PROPANE IN AIR		VENTING RATE m^3/hr	METEOROLOGICAL CONDITIONS		BEST FIT $\alpha_3 \cdot$ tlv
	kg/m^3	ppm		Wind Speed m/s	Turbulence tlv	
93	.3996	219,000	908	3.27	.343	--
94	.2000	110,000	908	3.57	.379	0.75
96	.2276	125,000	618	3.68	.286	0.57
99	.1277	70,000	618	2.69	.309	0.62
85	.2804	154,000	272	3.24	.400	1.20
86	.2873	157,000	255	2.86	.347	1.04

Tests 93 and 94 were performed at a high venting rate, 908 m^3/hr. The propane concentration at the vent was about 21.9% and 11.0% by volume for Tests 93 and 94, respectively. Figures IV.76 and IV.77 compare the concentration data with plume model predictions. The agreement is poor for Test 93 in Figure IV.76. The plume model predicted significantly higher values of concentration than were measured. However, the agreement in Figure IV.77 for Test 94 is much better for nearly the same test conditions as in Test 93. The reason for this discrepancy is not known, but it is probably related to a shift in wind direction away from the array of receptors during the test.

Tests 96 and 99 were performed at a medium venting rate of 618 m^3/hr. The propane concentration at the vent was about 12.5% and 7.0%, respectively for Tests 96 and 99. Figures IV.78 and IV.79 compare the concentration distribution data with the plume model predictions. The agreement is fair in both tests. The concentration data lies below the predicted values in the central region of the plume for Test 99. However, Test 96 concentration data matches the plume predictions rather well.

Tests 85 and 86 were performed at low venting rates of 272 and 255 m^3/hr, respectively. The propane concentration levels at the vent were about 15.4% and 15.7%, respectively for these tests. Figures IV.80 and IV.81 compare the measured concentration data with plume model predictions. The agreement is fair for both tests. The plume model overpredicted the level of propane concentration by about a factor of two for both tests. The general shape of the concentration distribution data agrees reasonably well with plume model predictions for $\alpha_3 = 3$.

The agreement between the predicted and measured concentration distributions for these 6 m vent tests is not as good as was found for the other vent heights. There are two plausible reasons for this. The centerline of a plume emitted from the 6 m vent is considerably higher than the height of the receptors. Thus, the region of the plume being sampled at breathing height is at least 4 m or more away from the center of the plume. In this region the instantaneous concentration is subject to

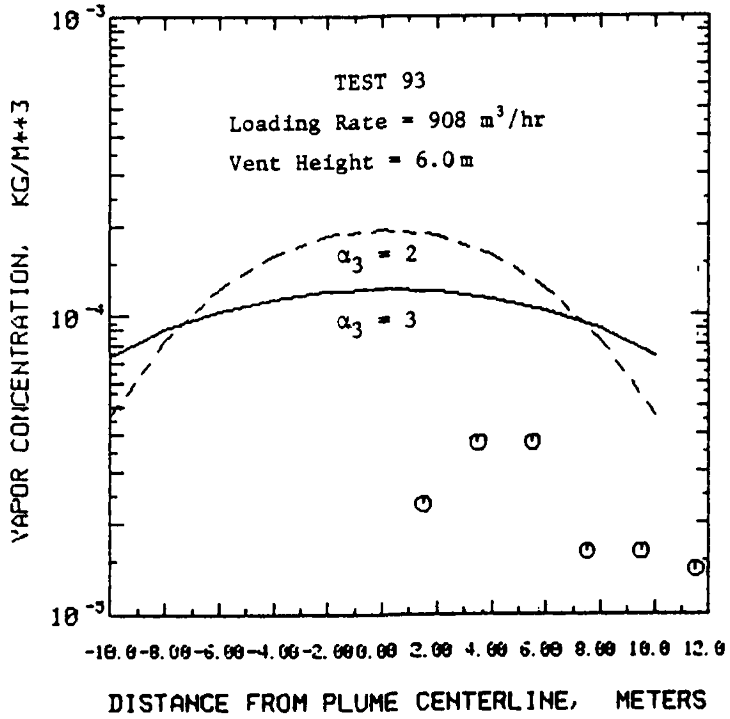


FIGURE IV.76. TEST 93 - PLUME DISPERSION FROM A 6.0 m VENT AT HIGH LOADING RATE

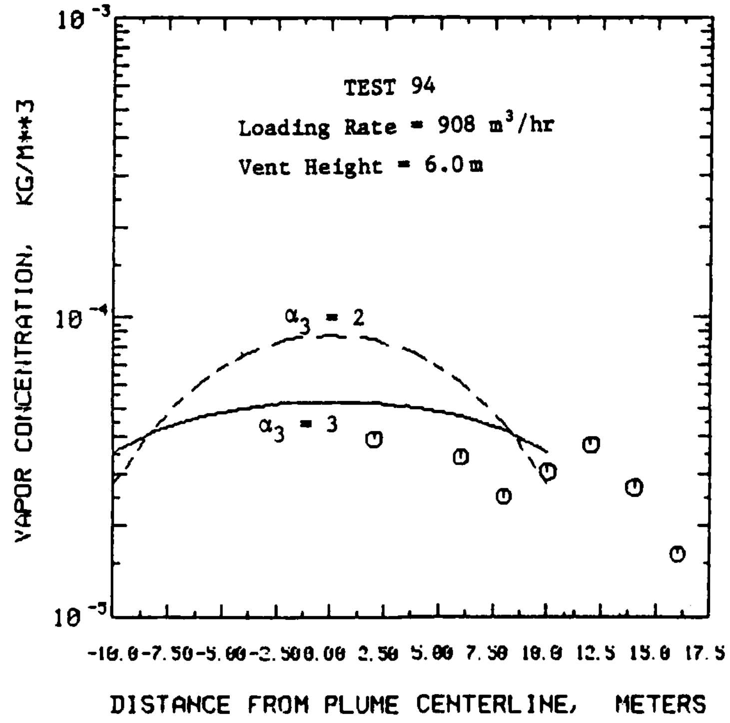


FIGURE IV.77. TEST 94 - PLUME DISPERSION FROM A 6.0 m VENT AT HIGH LOADING RATE

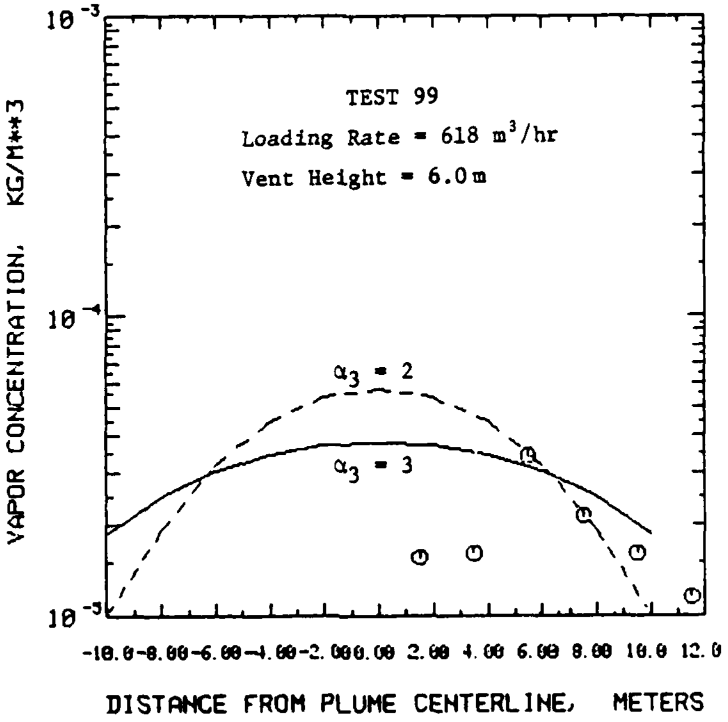


FIGURE IV.78. TEST 99 - PLUME DISPERSION FROM A 6.0 m VENT AT MEDIUM LOADING RATE

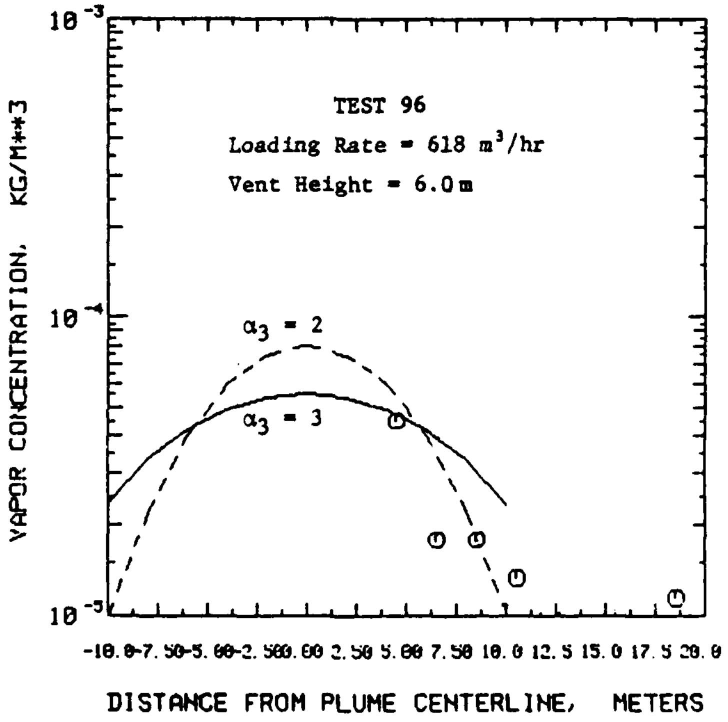


FIGURE IV.79. TEST 96 - PLUME DISPERSION FROM A 6.0 m VENT AT MEDIUM LOADING RATE

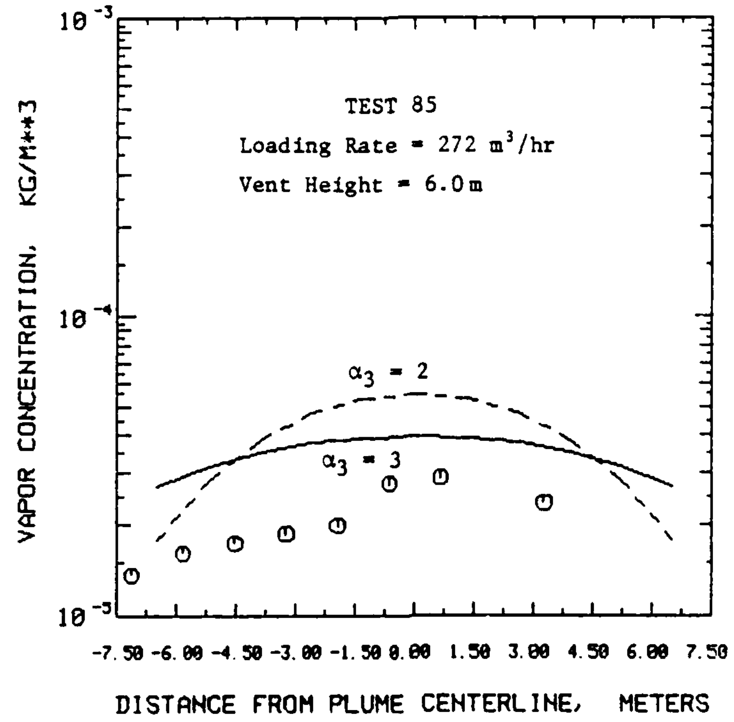


FIGURE IV.80. TEST 85 - PLUME DISPERSION FROM A 6.0 m VENT AT LOW LOADING RATE

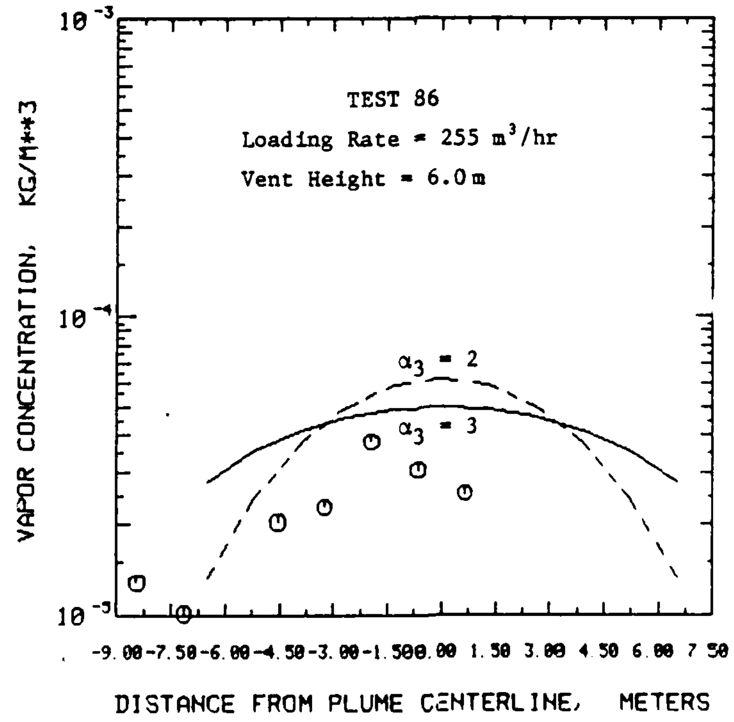


FIGURE IV.81. TEST 86 - PLUME DISPERSION FROM A 6.0 m VENT AT LOW LOADING RATE strong fluctuations caused by fluctuations in wind velocity and direction. The irregular behavior of the concentration distribution data is an indication that sampling times longer than 10 minutes might have been needed to give a true representation of the mean concentration field.

Another possible reason for discrepancies between measured and predicted concentration profiles may be the assumption of a symmetric concentration profile in both vertical and crosswind directions. To validate the plume model, a value of the turbulence entrainment parameter was determined that gave the best agreement between the measured and predicted concentration profiles in the crosswind direction. When the plume centerline elevation and the receptor height are nearly the same (as they are for low vents close to the ground) this comparison is not sensitive to the spatial variation of concentration in the vertical direction. However, for the 6 m vent (and also for the 4 m vent, but to a lesser degree), the comparison of predicted and measured concentration distributions is very sensitive to spatial variation of concentration in the vertical direction. The fact that the plume model appears to overpredict the concentration level at breathing height, but gives reasonable agreement for profile width or shape in the crosswind direction seems to indicate that the plume radius, b, must be smaller in the vertical direction than in the crosswind direction. This conclusion is consistent with the standard estimates of horizontal and vertical dispersion coefficients that are used in point source air pollution models. For atmospheric stability Class D, Turner's Workbook (Reference 31) suggests values of $\sigma_y \sim 8$m and $\sigma_z \sim 4.7$m for the horizontal and vertical dispersion coefficients at a distance of 100 m downwind of an elevated point source.

Therefore, it can be concluded that the plume model gives a reasonably good simulation of the dispersion of gas released from a 6 m vent. It is anticipated that the concentration distribution predicted at man breathing height will be conservative. Based upon the tests reported in this section, the concentration predictions should not exceed the actual concentration level by a factor of more than 3.

Gasoline Loading Into a Dedicated Tank

Tests 102 and 103

A final set of plume dispersion tests were performed during a loading of unleaded grade gasoline into a tanker dedicated to transporting gasoline. This test was selected because gasoline is often loaded at rates that are higher than those observed for pure chemicals in the previous marine terminal field tests. Thus, it provided an opportunity to validate the plume model during actual loading operations in the higher venting rate range that had been covered only by the outdoor venting simulation tests at SwRI.

On this particular vessel an enclosed gauging system was used to measure cargo level in the tank. The tank gas atmosphere was vented through both an open ullage hatch on the expansion trunk and a vent line connected to a mast riser vent common to several tanks. The Chief Mate explained that their usual practice was to load the cargo tank with the ullage cap down on its seat (not propped open on pins). The weight of the cap holds a small backpressure on the tank and forces the tank gas atmosphere into a vent line leading from the expansion trunk to a common header which then leads to the mast riser vent. While some of the tank atmosphere did escape from beneath the ullage hatch cap, most of the gas appeared to be discharged from the mast riser. This method of tank venting had not been observed on other gasoline tankers, but it did seem to be an effective method for minimizing gasoline vapor concentration levels near the deck.

The cargo loading rate was determined to be about 591 m^3/hr (3723 bbl/hr) from ullage measurements. The wind speed and direction were fairly steady during loading operations, and the wind was unimpeded by on-deck structure as it passed across the vessel from port to starboard.

Vapor sampling receptors were arranged 0.46 m (18 inches) apart along a circular arc at a radial distance of 4.6 m (15 ft) from the vent. One vapor sampling run was performed with the ullage hatch cap down, and the hydrocarbon vapor concentration in the vapor sampling bags was measured and recorded. Not surprisingly, the vapor concentration levels were low, and of the same order of magnitude as the "background" concentration in the terminal area. This supported the observation that most of the tank gas atmosphere was being diverted to the mast riser vent when the ullage hatch cap was resting on its seat.

At our request, the Chief Mate permitted us to lift the ullage hatch cap for vapor sampling tests of 10 minutes duration. Two tests were performed with the hatch cap open, and they gave readings of total hydrocarbon vapor concentration at the receptors that are 10 times higher than the values obtained with the hatch cap down. The test conditions for these two tests (Nos. 102 and 103) are listed in Table IV.6 .

Wind speeds were measured both at the meteorological tower located on shore about 50 m upwind of the vessel, and with a hand-held wind meter on the deck of the vessel. The wind speeds measured by the wind meter were higher than the wind speed values calculated from the meteorological tower readings for both tests. For Tests 102 and 103, the wind speeds recorded by the tower were 1.64 m/s with a turbulence level of 0.34, and 1.50 m/s with a turbulence level of 0.45, and the wind meter values were 3.32 m/s and 3.75 m/s, respectively.

During each test, a sample of the tank gas atmosphere at the ullage hatch was drawn off and stored in a bag. These source concentration samples were analyzed together with the receptor samples with a F.I.D. gas chromatograph. A value of 68 for the average molecular weight for gasoline vapor was estimated from the G.C. traces.

Plume model computations were performed for both tests using (1) both the on-deck and meteorological tower values for wind speed, and (2) both the measured value of vent velocity and the value determined from the loading rate. The difference in wind speed values proved to be significant while the differences in venting rate measurements were of minor importance. Therefore, results are presented for both wind speed values for each test.

Figure IV.82 compares the measured concentration distribution along the arc of receptors at a height of 1.67 m (5.5 ft) above the deck for Test 102 with tl predicted concentration distribution for $\alpha_3 = 1$ and $\alpha_3 = 2$ when the on-deck value of wind speed is used. The predicted concentration distribution for $\alpha_3 = 2$ comes closest to the data, but the level of concentration is underpredicted. Figure IV.83 shows that the predicted concentration distribution for $\alpha_3 = 2$ matches the data quite well when the meteorological tower value of wind speed is used. The value of $\alpha_3 \cdot$ tlv for this run is 0.68, which is very close to the values ranging from 0.59 to 0.66 that were determined from the previous tests.

Figure IV.84 compares the measured concentration distribution for Test 103 with the predicted concentration distribution for $\alpha_3 = 1$ and $\alpha_3 = 2$ using the on-deck value of wind speed. In this figure, the concentration data come quite close to the predicted concentration distribution for $\alpha_3 = 1$. However, the profile width predicted with $\alpha_3 = 1$ seems too narrow. Figure IV.85 shows that the predicted concentration level for $\alpha_3 = 2$ comes close to many of the data points when the meteorological tower value of wind speed is used. However, the profile width predicted for $\alpha_3 = 2$ in Figure IV.85 is too wide. A value of α_3 between 1 and 2 is needed to match the concentration data in both Figure IV.84 and IV.85. Since the estimated value of tlv for this test was relatively high (0.45), the proper value of $\alpha_3 \cdot$ tlv must be between 0.45 and 0.9. The average of these two values is 0.68; this is also the value determined from Test 102.

This test series confirms the validity of the chemical plume dispersion model for predicting the vapor concentration distribution downwind of tank vents during loading. Based upon the results of the plume dispersion tests the following values of $\alpha_3 \cdot$ tlv are recommended:

- $\alpha_3 \cdot$ tlv = 0.6 - This combination of values should be used whenever the wind speed and wind direction are not altered by on-deck structure.
- $\alpha_3 \cdot$ tlv = 0.9 - This value should be used when on-deck structure partially shields the vent from the wind, but does not alter the wind direction significantly.

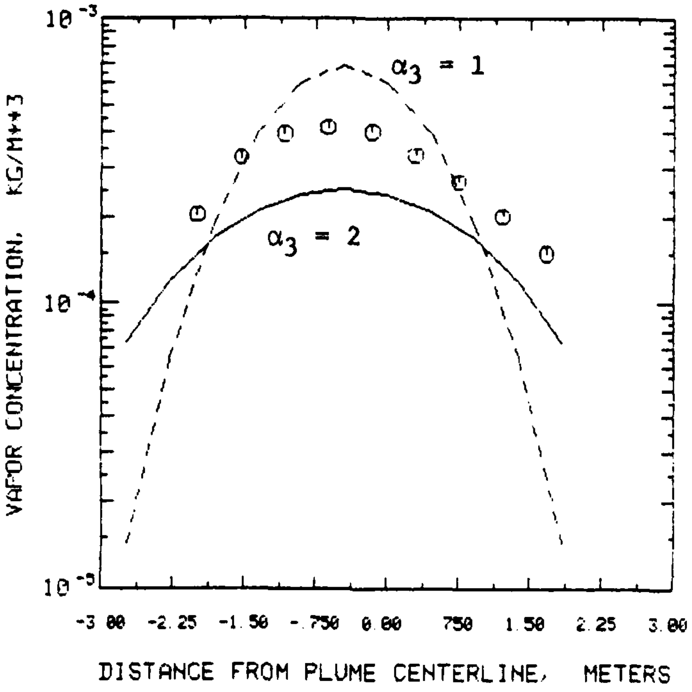


FIGURE IV.82. CROSSWIND CONCENTRATION DISTRIBUTION FOR TEST 102 USING ON-DECK VALUE OF WIND SPEED

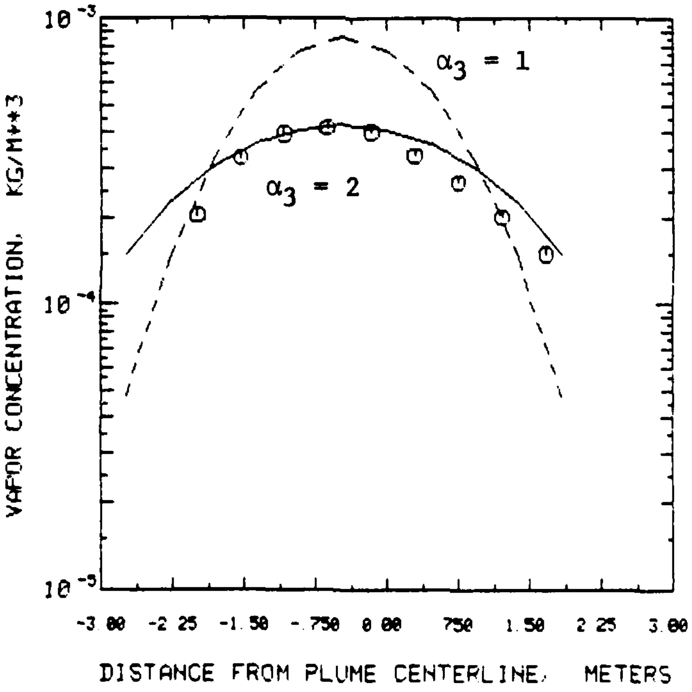


FIGURE IV.83. CROSSWIND CONCENTRATION DISTRIBUTION FOR TEST 102 USING METEOROLOGICAL TOWER VALUE OF WIND SPEED

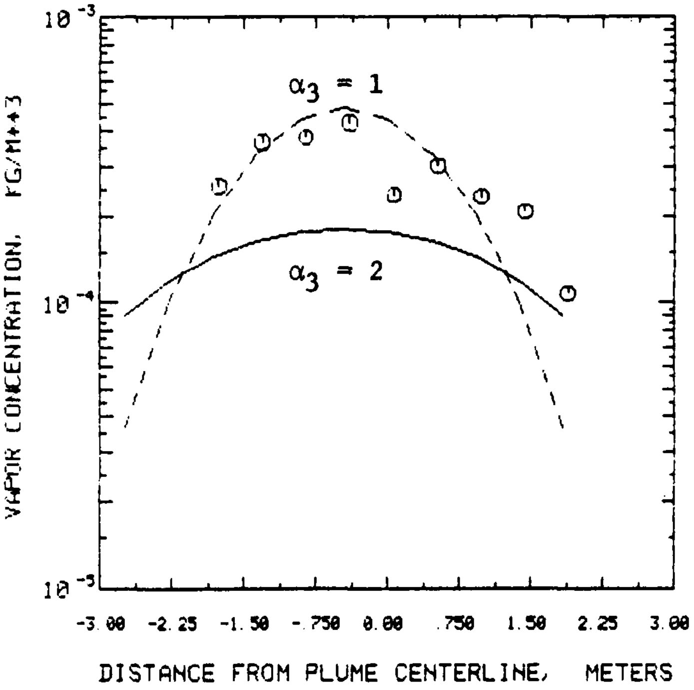


FIGURE IV.84. CROSSWIND CONCENTRATION DISTRIBUTION FOR TEST 103 USING THE ON-DECK VALUE OF WIND SPEED

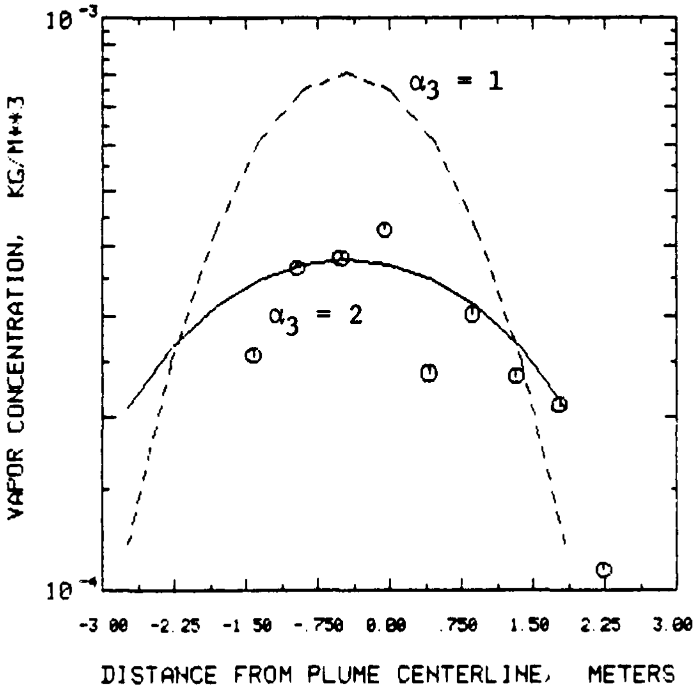


FIGURE IV.85. CROSSWIND CONCENTRATION DISTRIBUTION FOR TEST 103 USING THE METEOROLOGICAL TOWER VALUE OF WIND SPEED

- $\alpha_3 \cdot tlv = 0.9$ to 1.5 - These values can be used when the on-deck structure alters the wind direction and enhances the unsteadiness of both the wind direction and wind speed.

IV.3.4 Results of Parametric Computations

The validated model for chemical plume dispersion was exercised in a set of parametric computations. The purpose of these computations was (1) to test the sensitivity of the model to changes in the values of the model variables, and (2) to demonstrate the utility of the model in assessing the effects of different operational and geometrical conditions on the level of chemical vapor concentration downwind of tank vents.

The computations were performed to simulate the venting of vinyl acetate vapor during cargo loading. Vinyl acetate was selected because it is a hazardous chemical cargo that is regulated by U. S. Coast Guard regulations in Title 46, Subchapter O. These regulations require the installation of a 4 m high vent for tanks containing vinyl acetate on self-propelled vessels. Vinyl acetate is a volatile chemical with a vapor pressure of 1.65 psia at 20°C, and has low threshold concentration levels for toxicity, 20 ppm for the STEL and 10 ppm for the TLV-TWA.

Three sets of parametric computations were performed. These consisted of (1) variation of the cargo loading rate, (2) variation of the ambient wind speed, and (3) variation of the height of the vent used to release the tank gas atmosphere. One common base scenario was included in each set of parametric computations. The base scenario is

- Vent height = 4 m above the vessel deck.
- Ambient wind speed = 2.24 m/s (5.0 mile/hr).
- Venting rate = 159 m^3/hr (700 gallon/minute or 1000 barrel/hr)
- Vinyl acetate vapor concentration = 0.41 kg/m^3 (11.3% by volume, equal to the saturation concentration of vinyl acetate vapor in air at 20°C).

This vapor concentration is the maximum concentration when air and vapor are in equilibrium at a temperature of 20°C. Measurements of vent concentration during cargo loading for Tests 28 - 31 indicated that the vent concentration came very close to this value near the end of loading. The cargo loading rate of 159 m^3/hr is lower than the actual loading rate of 228 m^3/hr observed during Tests 28 - 31.

The results of the parametric computations are shown as graphs of the maximum vapor concentration at breathing height (1.67 m above the deck) as a function of distance downwind of the vent, and as graphs of vapor isoconcentration contour curves at breathing height downwind of the vent. Figures IV.86 through IV.90 show the results for vapor concentration at breathing height as a function of venting rate. The following variables were held constant

- vent height = 4 m above the deck
- wind speed = 2.24 m/s
- vent concentration = 0.41 kg/m^3

while the venting rate was given values of 79 m^3/hr, 159 m^3/hr, 318 m^3/hr, and 794 m^3/hr. Figure IV.86 shows that the maximum vapor concentration downwind of the vent exceeds both the STEL and TLV-TWA level for all four venting rates. Figure IV.87 shows that for the lowest venting rate the deck region lying within the STEL = 20 ppm contour is relatively small, less than 4 m in width and 10 m in length. However, at higher venting rates the deck area within the toxicity threshold concentration levels grows progressively larger, as shown in Figures IV.88 through IV.90. At the highest venting rate of 794 m^3/hr, breathing height concentrations can exceed 100 ppm, 5 times the STEL level, at distances from 8 to 18 m from the vent.

These examples show that venting rate is an important variable that affects vapor concentration levels in the breathing zone downwind of tank vents. By itself, the 4 m vent height required by current regulations is not sufficient to prevent vapor concentration levels from exceeding toxicity threshold levels downwind of the vent. However, reduced

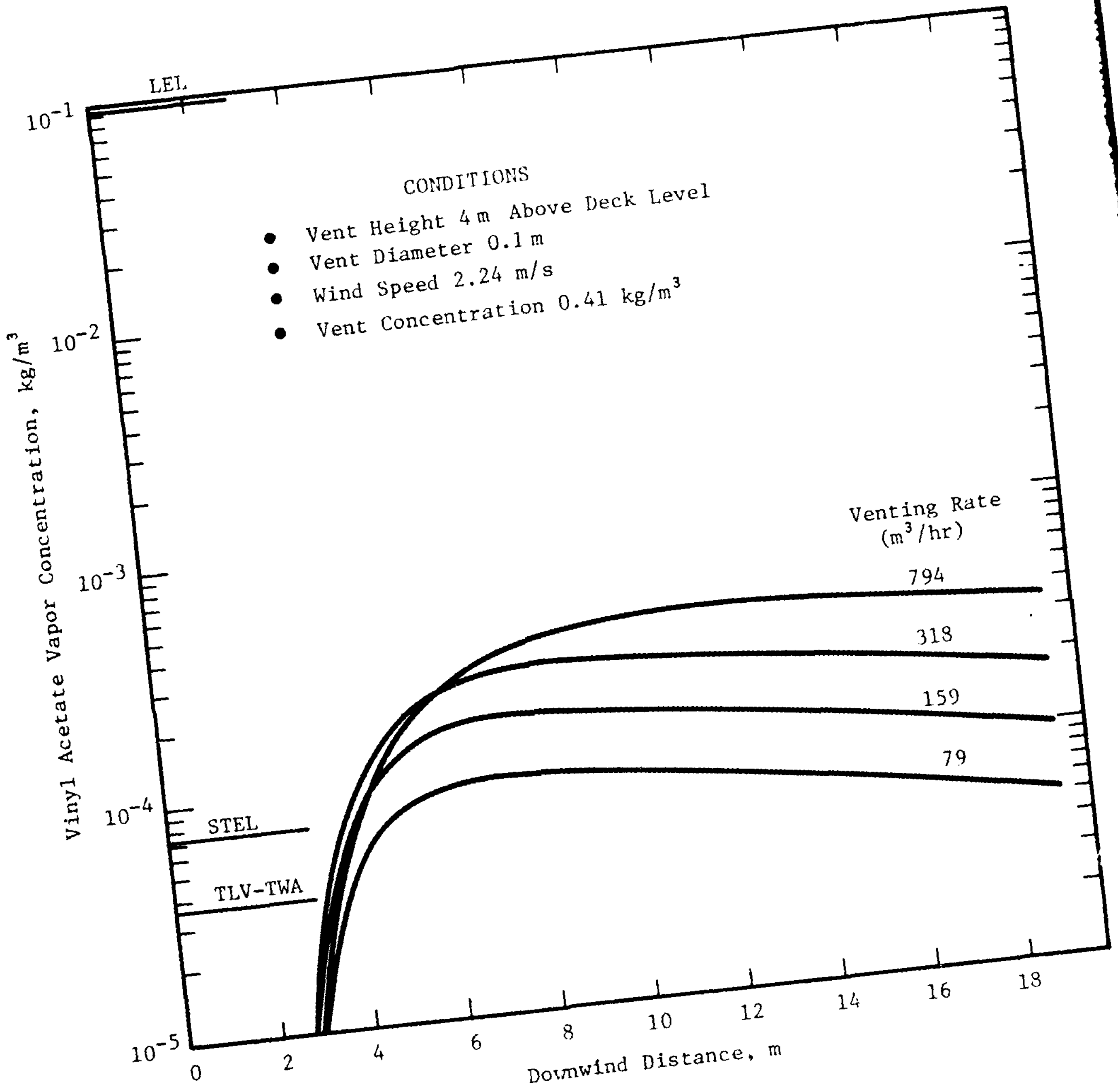


FIGURE IV.86 VINYL ACETATE VAPOR CONCENTRATION AT MAN BREATHING HEIGHT DOWNWIND OF A 4 m VENT AS A FUNCTION OF VENTING RATE

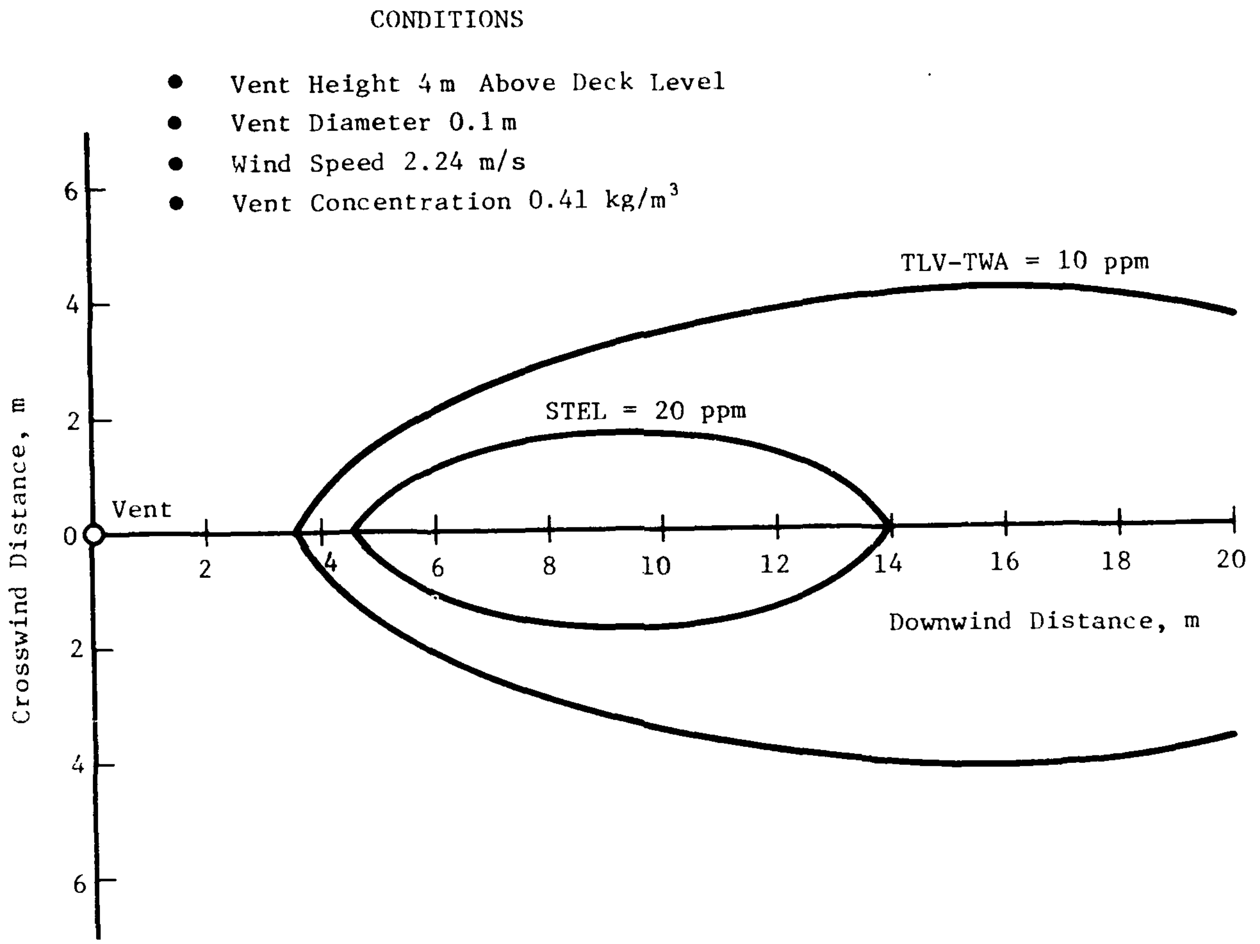


FIGURE IV.87 LOCATION OF VINYL ACETATE VAPOR CONCENTRATION CONTOURS AT MAN BREATHING HEIGHT FOR A VENTING RATE OF 79 m^3/hr

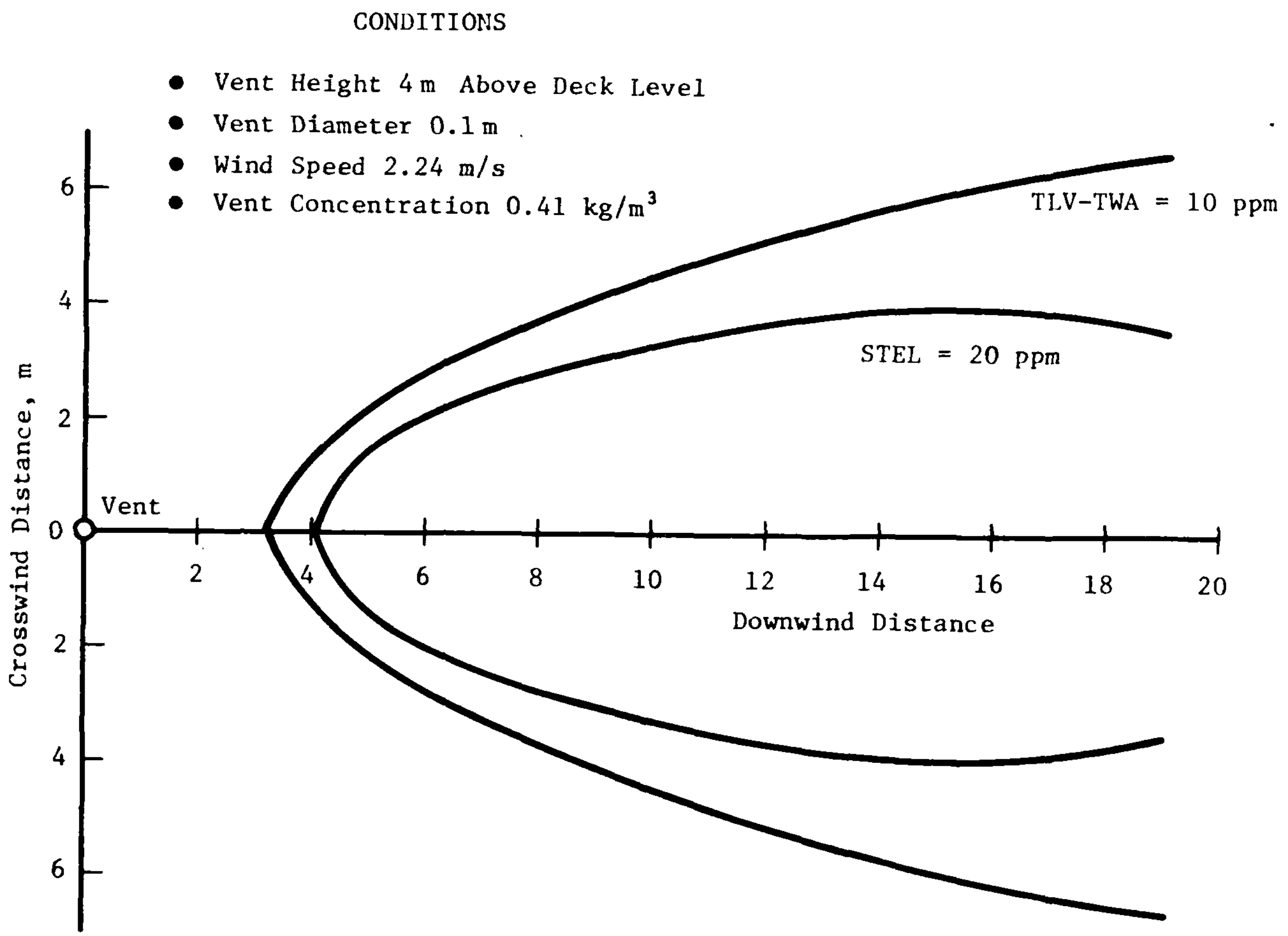
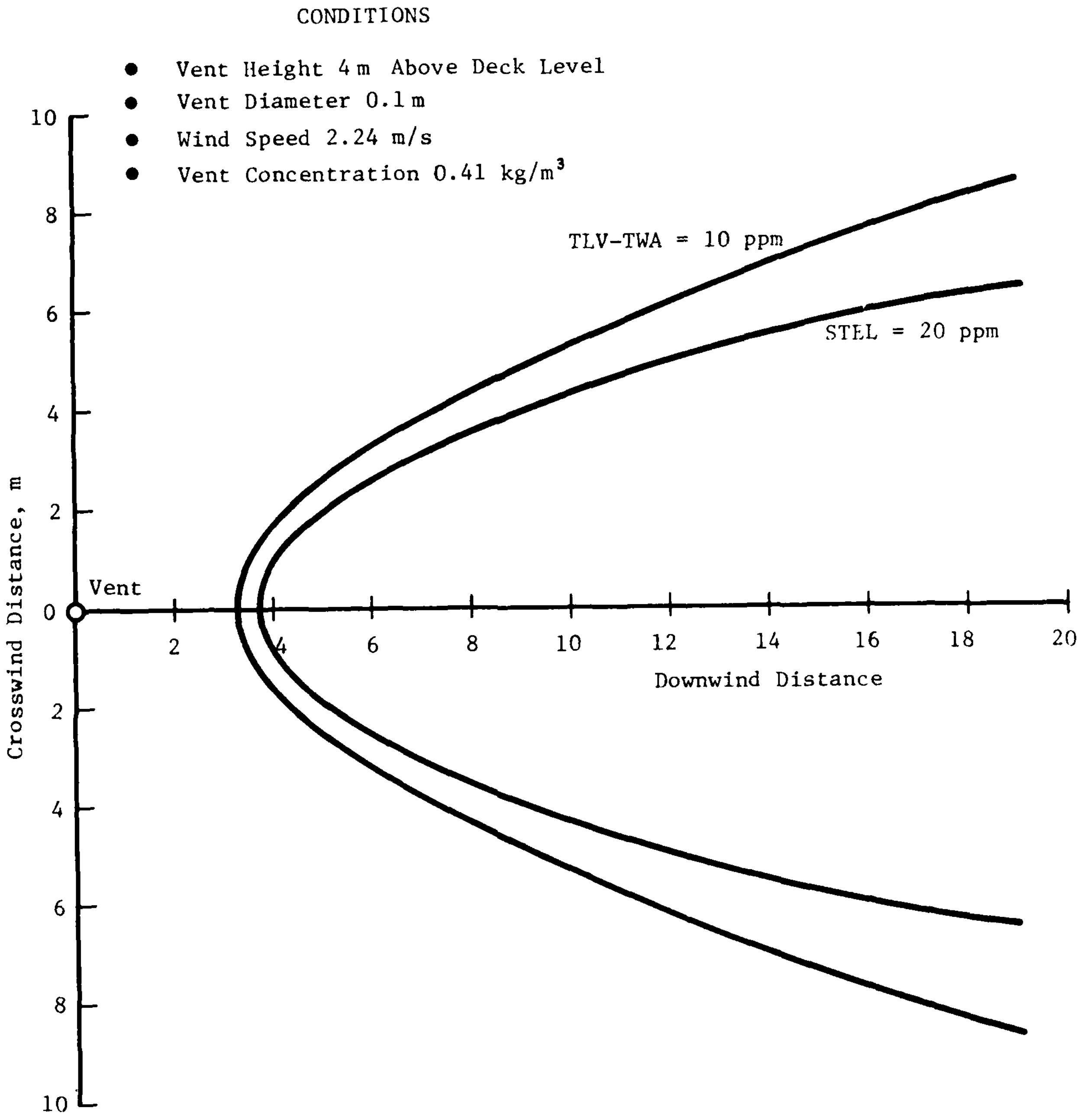


FIGURE IV.88 LOCATION OF VINYL ACETATE VAPOR CONCENTRATION CONTOURS AT MAN BREATHING HEIGHT FOR A VENTING RATE OF 159 m^3/hr



CONDITIONS

- Vent Height 4 m Above Deck Level
- Vent Diameter 0.1 m
- Wind Speed 2.24 m/s
- Vent Concentration 0.41 kg/m^3

Figure IV.89 LOCATION OF VINYL ACETATE VAPOR CONCENTRATION CONTOURS AT MAN BREATHING HEIGHT FOR A VENTING RATE OF 318 m^3/hr

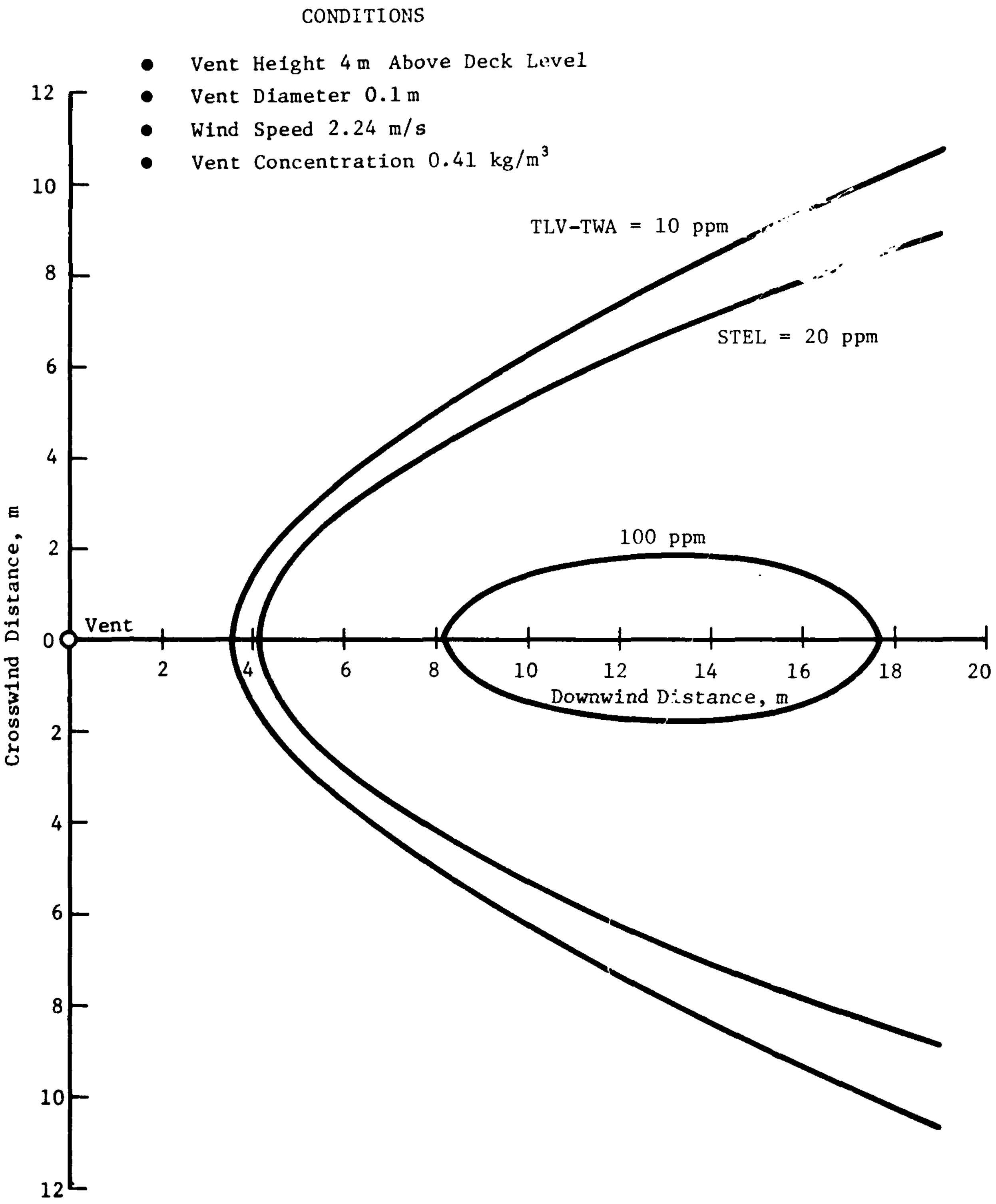


FIGURE IV.90 LOCATION OF VINYL ACETATE CONCENTRATION CONTOURS AT MAN BREATHING HEIGHT FOR A VENTING RATE OF 794 m^3/hr loading rates, of the order of 80 m^3/hr, together with the use of a 4 m vent will minimize the concentration level, and the potential risk of vapor inhalation to crew members.

Figures IV.91 through IV.95 show the results for vapor concentration at breathing height for the set of variable wind velocity computations. For this set the vent height, vent concentration, and venting rate were held constant

- vent height = 4 m above the deck
- vent concentration = 0.41 kg/m^3
- venting rate = 159 m^3/hr

while the wind speed was given values of 1.12, 2.24, 4.47, and 6.71 m/s. Figure IV.91 shows that the maximum vapor concentration downwind of the vent exceeded the TLV-TWA at all wind speeds and the STEL at all wind speeds except the highest value of 6.71 m/s. Figures IV.92 through IV.95 show that the area of the deck contained within the STEL = 20 ppm contour curve shrinks noticeably as the wind speed increases from 1.12 to 6.71 m/s. Although the ambient wind speed cannot be controlled during cargo loading operations, it is still an important variable to consider when trying to minimize the risk of vapor inhalation exposure to crew members.

These results suggest that on-deck structures that may shield the tank vent from the wind and reduce the effective wind velocity will adversely affect plume dispersion and lead to higher vapor concentration levels in the breathing zone downwind of the vent. Therefore, tank vents ought to be located away from on-deck structures whenever possible. Vents for tanks located close to the deckhouse should be located forward of the deckhouse and above other deck level structures. In this way the maximum effect of wind velocity in promoting dispersion of the chemical vapor plume may be realized.

The final set of parametric computations shows the direct effect of tank vent height on the vapor concentration level at breathing

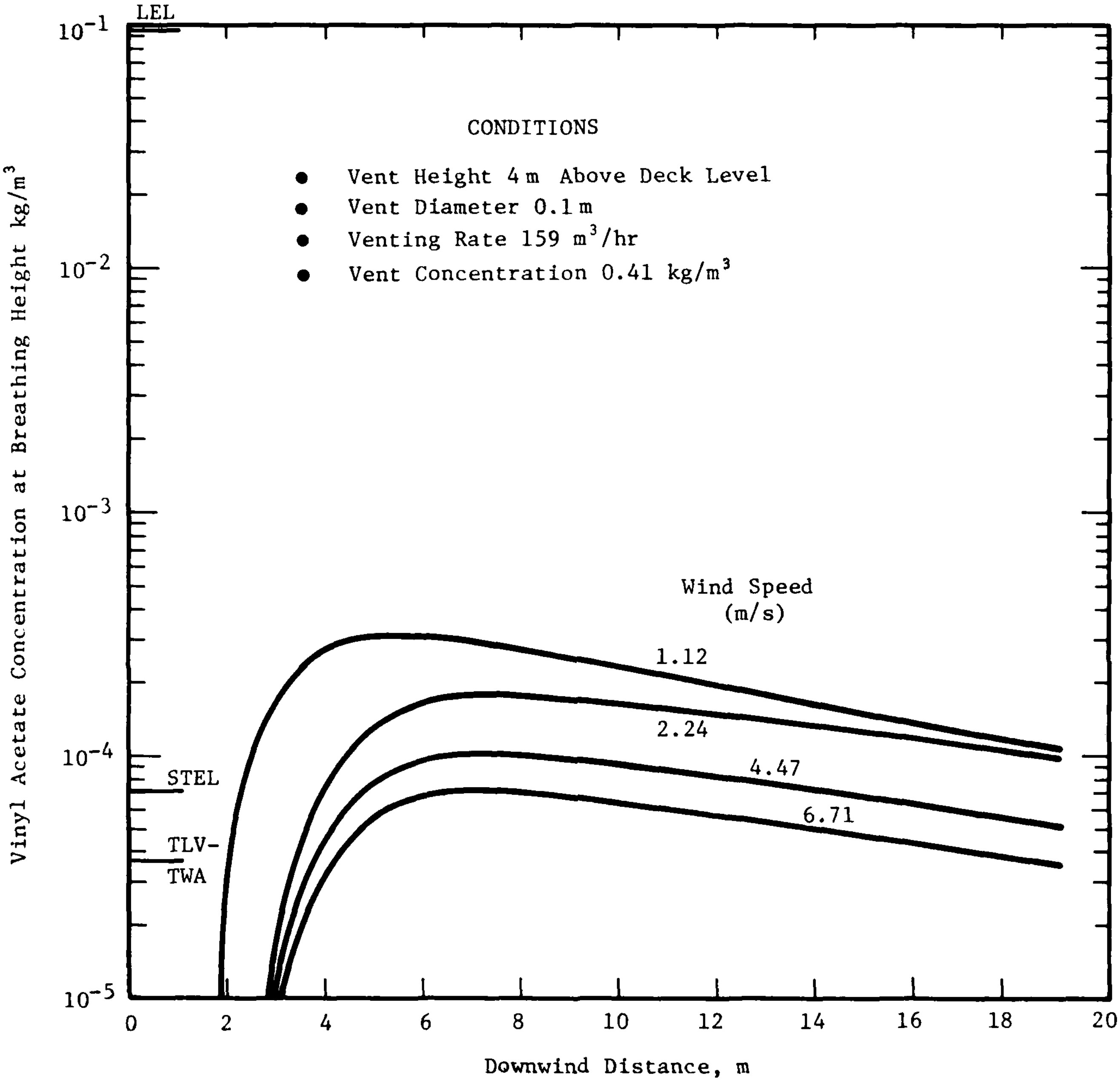


FIGURE IV.91 VINYL ACETATE VAPOR CONCENTRATION AT MAN BREATHING HEIGHT DOWNWIND OF A 4 m VENT AS A FUNCTION OF WIND SPEED

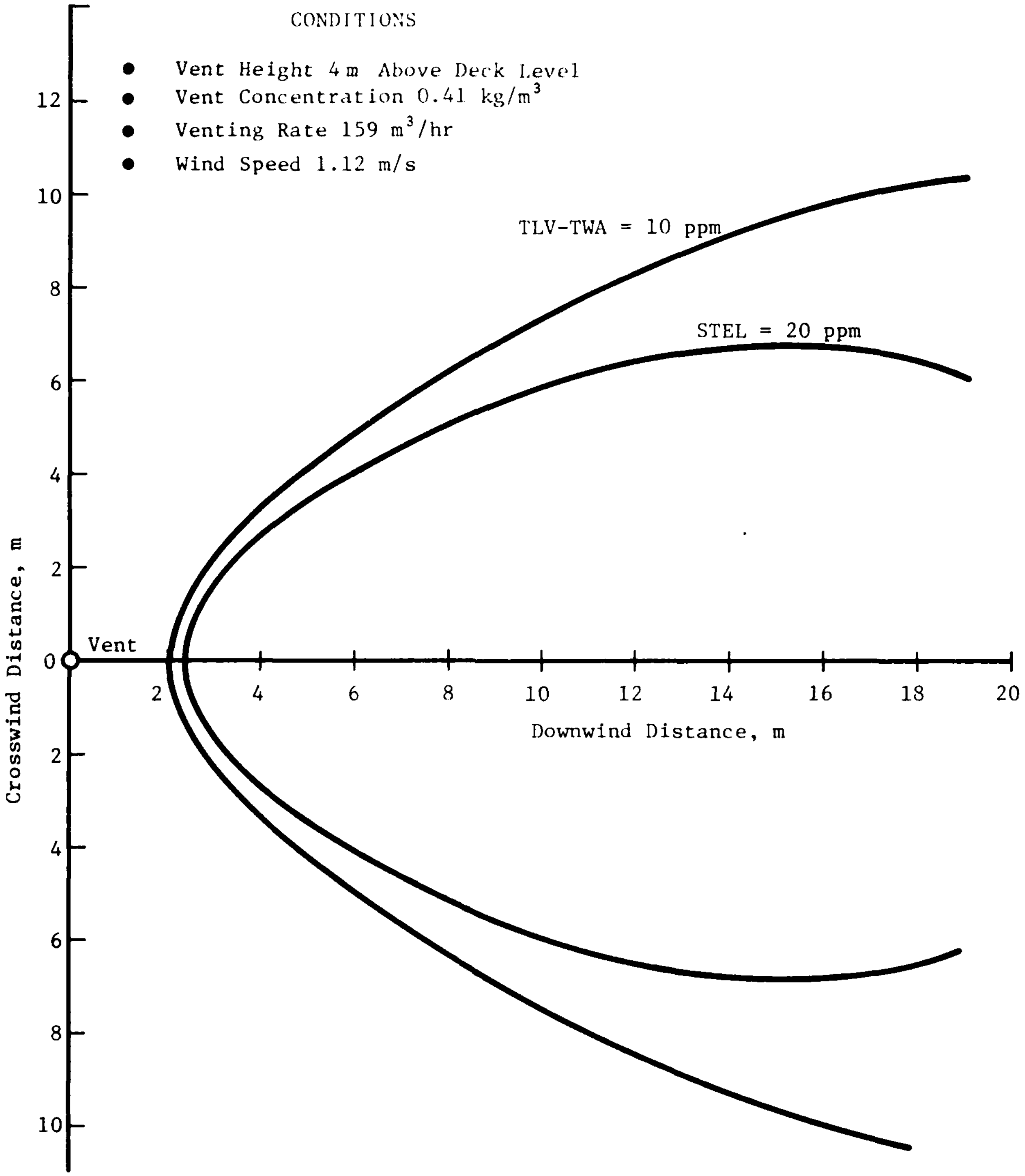


FIGURE IV.92 LOCATION OF VINYL ACETATE CONCENTRATION CONTOURS AT MAN BREATHING HEIGHT FOR A WIND SPEED OF 1.12 m/s

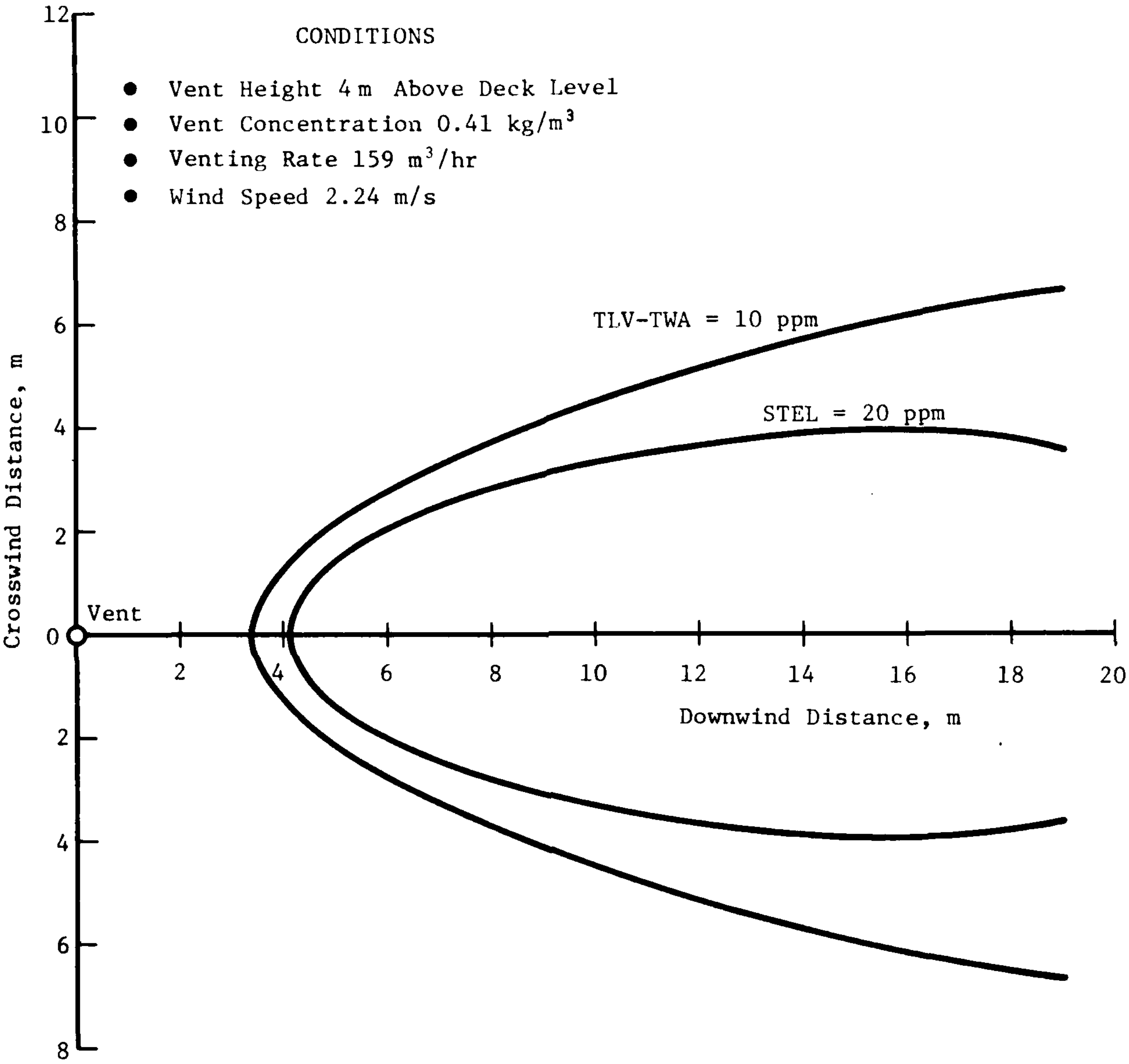


FIGURE IV.93 LOCATION OF VINYL ACETATE CONCENTRATION CONTOURS AT MAN BREATHING HEIGHT FOR A WIND SPEED OF 2.24 m/s

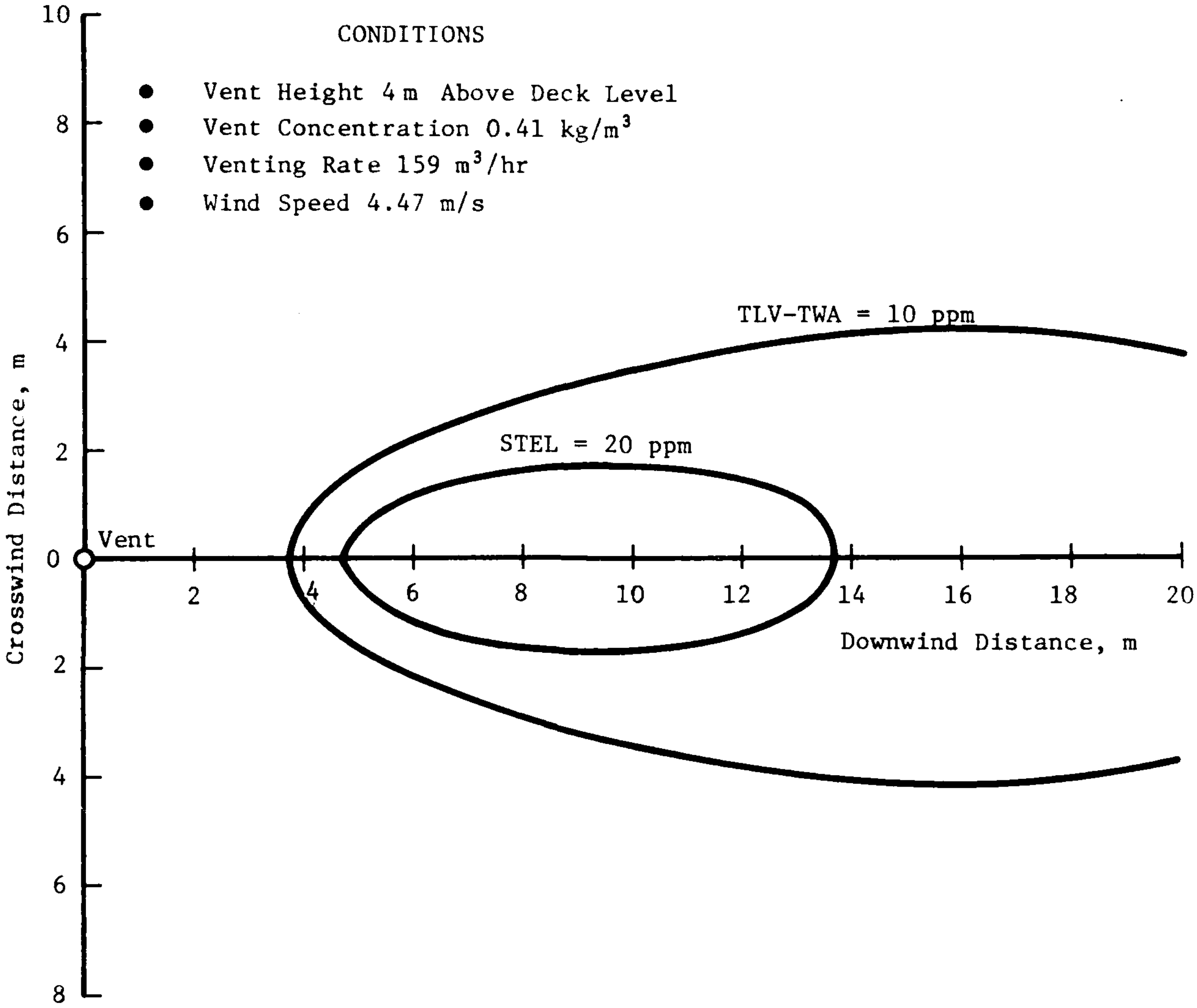


FIGURE IV.94 LOCATION OF VINYL ACETATE CONCENTRATION CONTOURS AT MAN BREATHING HEIGHT FOR A WIND SPEED OF 4.47 m/s

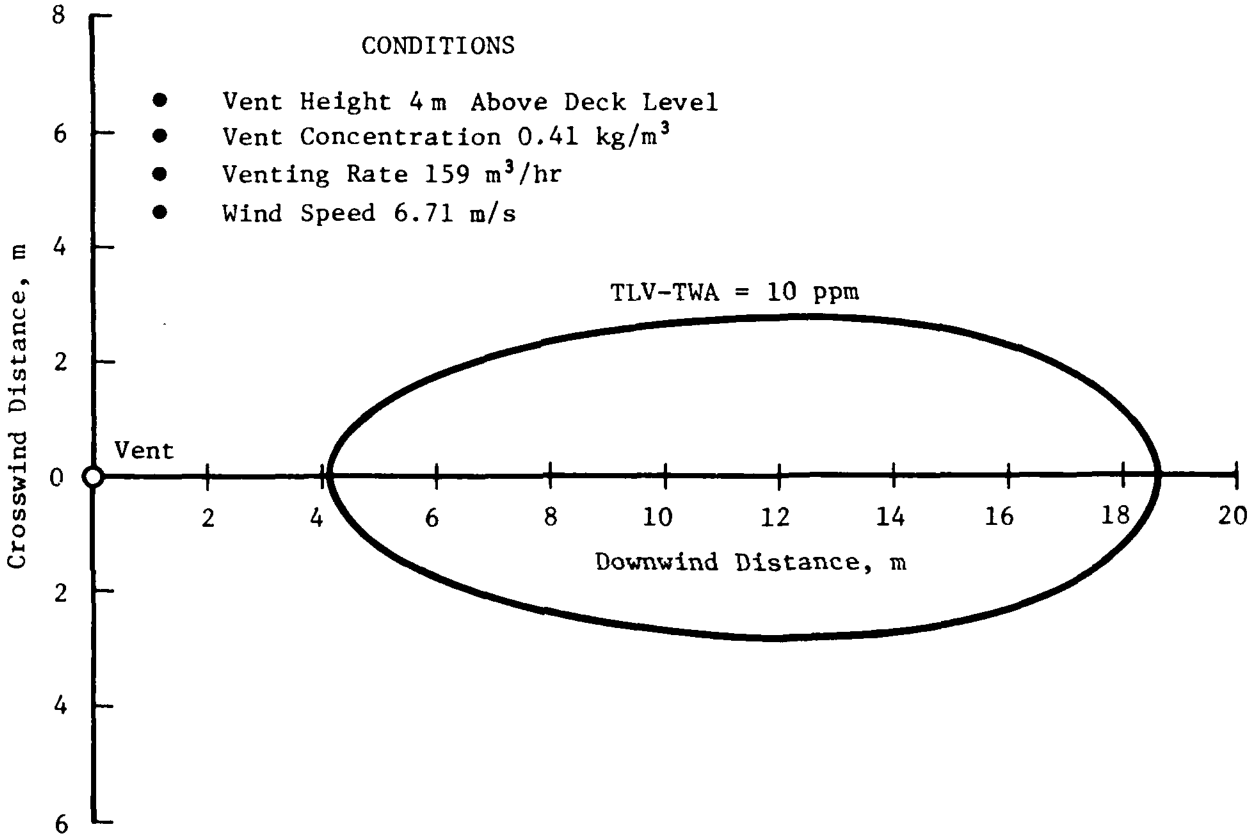


FIGURE IV.95 LOCATION OF VINYL ACETATE CONCENTRATION CONTOURS AT MAN BREATHING HEIGHT FOR A WIND SPEED OF 6.71 m/s

height downwind of a tank vent. For these computations the venting rate, wind speed, and vent concentration were held constant

- venting rate = 159 m^3/hr
- vent concentration = 0.41 kg/m^3
- wind speed = 2.24 m/s

while the vent height was given values of 1 m, 4 m, and 6 m above the deck. Figure IV.96 shows that the maximum vapor concentration at breathing height exceeds 7.2×10^{-3} kg/m^3 (2000 ppm) within one meter downwind of the 1 m high vent, and exceeds 3.6×10^{-4} kg/m^3 (100 ppm) for the first 10 m downwind of this vent. On the other hand, the highest concentration level at breathing height downwind of the 4 m vent is about 1.8×10^{-4} kg/m^3 (50 ppm), and for the 6 m vent only 5.4×10^{-5} kg/m^3 (15 ppm). Figures IV.97 through IV.99 show the concentration contours corresponding to the STEL and TLV-TWA toxicity threshold limit values for vinyl acetate vapor. As expected, a greater area of the deck lies within the toxicity threshold values for the 1 m vent than for the 4 m or 6 m vent.

These results show that the most significant effect of vent height is to raise the chemical vapor plume above the heads of crew members standing on deck. Very far downwind (greater than 20 m, the maximum distance shown on these figures) the plume radius becomes much larger than the vent height and the breathing height concentrations for all three vent heights merge together. However, when this occurs the plume will have been diluted by a factor of 10,000 or more, and vapor concentration levels will be on the order of 10 ppm or less.

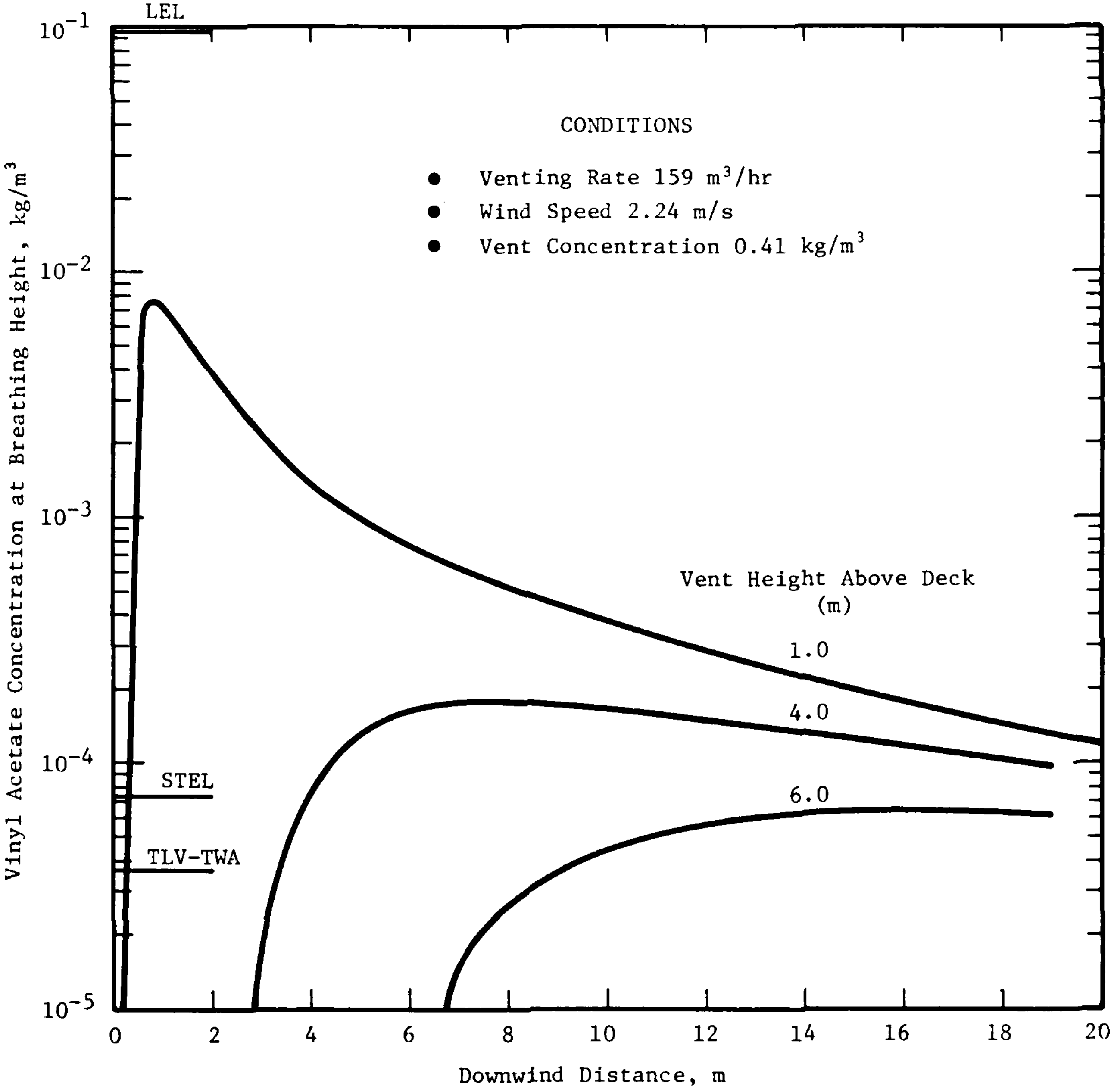


FIGURE IV.96 VINYL ACETATE VAPOR CONCENTRATION AT MAN BREATHING HEIGHT DOWNWIND OF A VENT AS A FUNCTION OF VENT HEIGHT

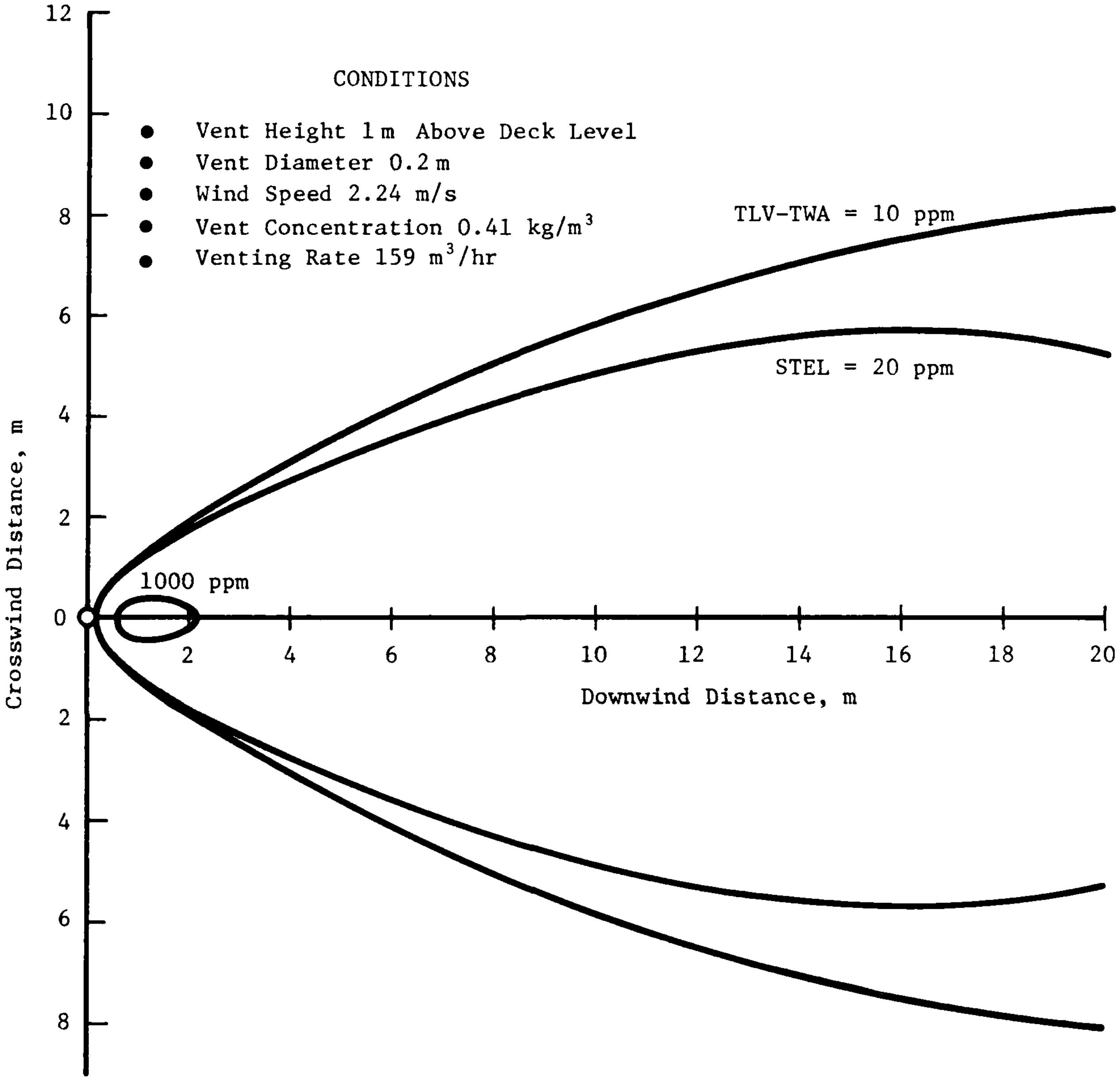


FIGURE IV.97 LOCATION OF VINYL ACETATE CONCENTRATION CONTOURS AT MAN BREATHING HEIGHT DOWNWIND OF A 1.0 m HIGH VENT

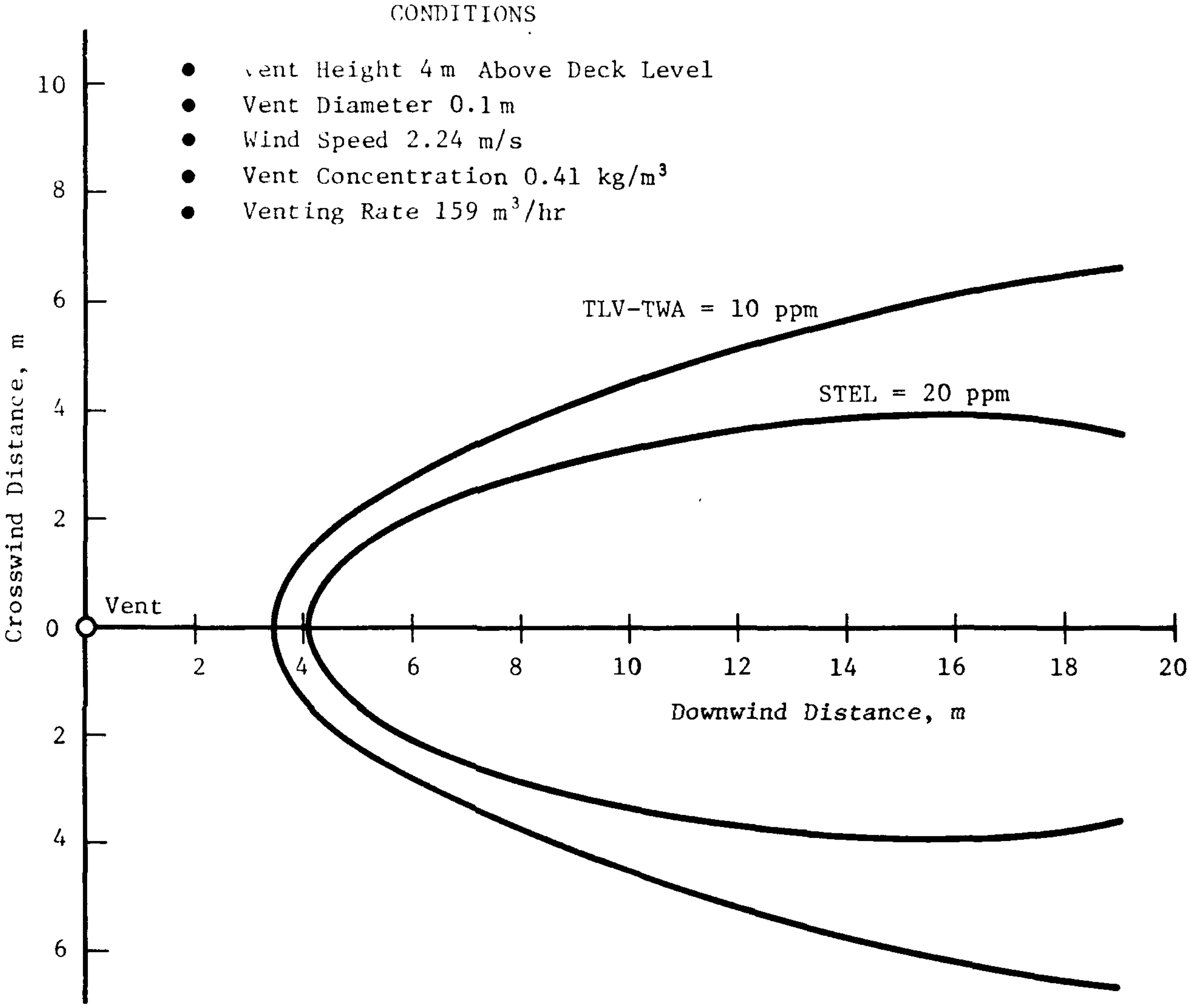


FIGURE IV.98 LOCATION OF VINYL ACETATE CONCENTRATION CONTOURS AT MAN BREATHING HEIGHT DOWNWIND OF A 4.0 m VENT

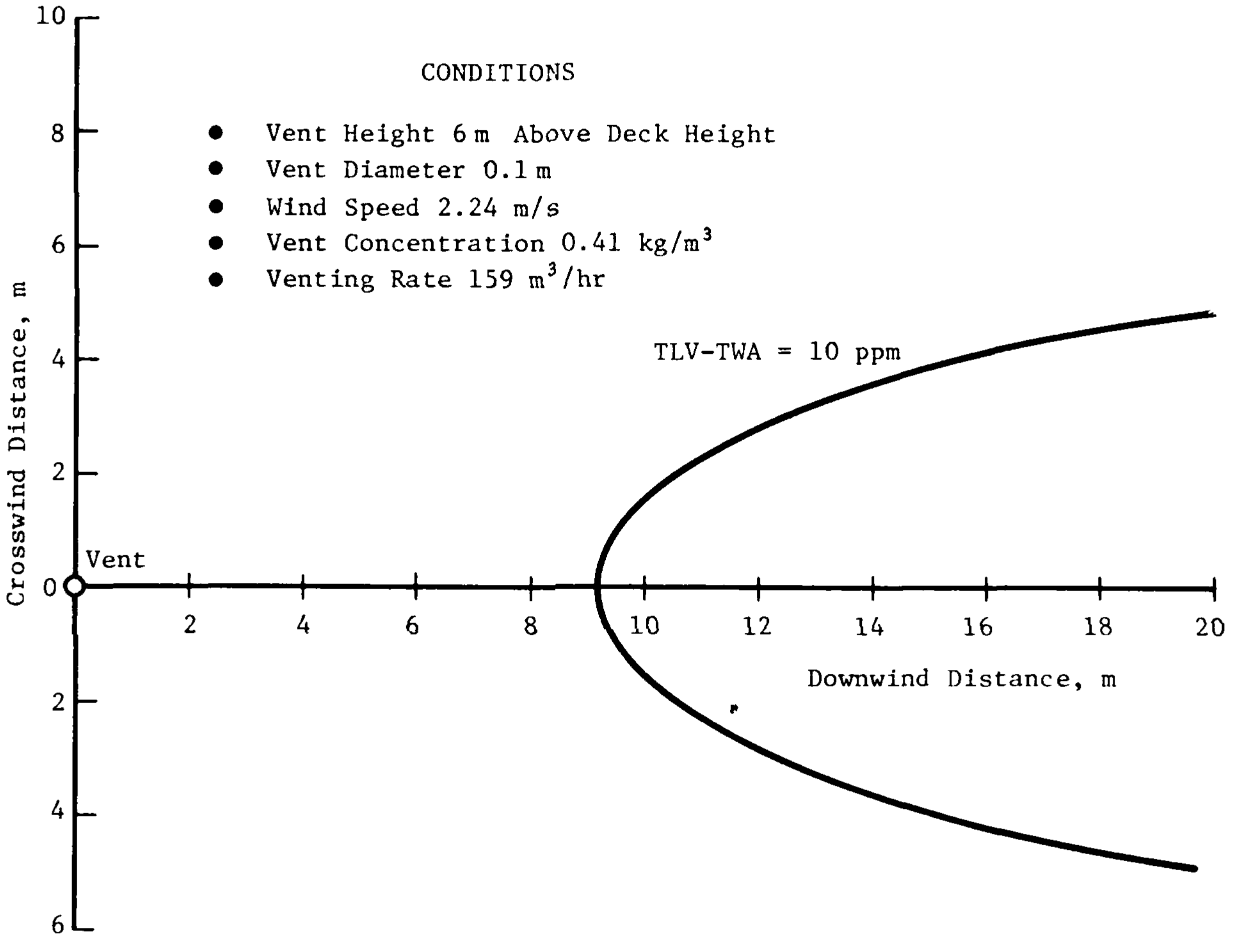


FIGURE IV.99 LOCATION OF VINYL ACETATE CONCENTRATION CONTOURS AT MAN BREATHING HEIGHT DOWNWIND OF A 6 m VENT

IV.3.5 Model Limitations

Despite the success in validating the chemical plume dispersion model shown in Section IV.3.3, the model does have some important limitations as outlined below.

- Asymmetry of plume concentration profile - One important limitation of the plume model is that it assumes the time average concentration profile is axisymmetric. This assumption is fairly good close to a vent, and may also be good further downwind for short averaging times. However, fluctuations in wind direction with periods of a minute (more or less) cause the plume to change direction and disperse over a larger arc than if the wind direction were fixed. Thus, far downwind the standard deviation of the Gaussian concentration distribution (called the dispersion coefficient) will be greater in the crosswind, y, direction than in the vertical, z, direction.

  The plume validation test program was designed to match the predicted concentration profile in the crosswind direction to the experimental data measured in outdoor tests. For all tests with vent heights within 1 m of breathing height, this comparison was not sensitive to the vertical dispersion coefficient. However, the tests performed with 4 m and 6 m vents showed that the plume model predictions for distances from 10 to 20 m from the vent overestimated the concentration distribution data by a factor of 2 or 3. This indicates that the predicted value of the vertical dispersion coefficient is slightly too large. Still farther downwind the sensitivity to the vertical dispersion coefficient diminishes when the value of the plume radius becomes as large as the vent height.

  Thus, for practical vent heights between 4 m and 6 m above the deck, the assumption of plume symmetry could lead to overprediction of the concentration level at breathing height by less than a factor of 3. For vent heights of from 1m to 2.5m above the deck, the error caused by the plume symmetry assumption should be negligible.

- Isothermal plume dispersion - In developing the set of conservation equations to be solved in computing plume dispersion, it was assumed that the vapor plume emitted from the tank vent was at essentially the same temperature as the ambient air. This assumption was true for all of the cargo loading tests performed on this project. However, it need not be true in all cases. If the cargo is heated before transfer to the vessel, or if the cargo tank is being washed with hot water during ventilation, the vapor plume could have a temperature significantly higher than the ambient temperature.

  The plume temperature may be significant if it changes the plume density, and the buoyancy force. The plumes emitted during cargo loading are often negatively buoyant because the density of the chemical vapor is greater than the density of air. Increasing the plume temperature decreases the plume density and offsets the buoyancy force produced by the dense vapor concentration.

  Ooms, et al. (Reference 15) include the temperature as a plume model variable and present an equation for the conservation of energy that may be solved together with the conservation equations for mass, momentum, and chemical species. For situations where the plume concentration and temperature both affect the plume buoyancy significantly, it might be necessary to incorporate the additional equation into the chemical vapor plume model.

- Effect of on-deck structure on plume dispersion - The field tests performed on tanker ships provided some examples of situations where the wind speed was reduced and the wind direction was made unsteady by on-deck structures lying upwind of the vent. However, we did not observe another possible situation where the vent was completely shielded from the wind by on-deck structure. The latter situation almost occurred in Test 30 during the vinyl acetate loading. During this test the wind direction was more closely aligned with the axis of the vessel, and the wind speed through the passage between the deck tank and the deckhouse dropped to nearly zero for part of the 10-minute sampling period. Thus, there was no wind to disperse the vented gas stream and it began to accumulate in the vent region. The dispersion of chemical vapor plumes in a wind of less than about 0.5 m/s cannot be modeled accurately with this plume dispersion model.

Ideally, gas atmosphere venting operations should be halted, if possible, when the ambient wind velocity becomes still and/or less than 0.5 m/s.

- Uncertainty in Estimating Plume Variables - In practice, the accuracy of the plume model predictions for chemical vapor concentration profile is limited by the uncertainty in measuring or estimating the actual values of (1) cargo loading rate, (2) vapor concentration at the tank vent, and (3) time average wind speed close to the tank vent. It is possible to estimate the uncertainty in the model predictions for vapor concentration by means of a sensitivity analysis. For example, consider the sensitivity analysis results in Figure IV.91. Assuming the actual mean wind speed to be 2.24 m/s, errors of +100% and -100% in the estimated value of wind speed would lead to errors of -45% and +40%, respectively in the predicted values of vapor concentration at breathing height and a distance of 10m downwind of the tank vent. Similar results can be determined for uncertainty in the estimation of the other model variables for other chemicals and other operational conditions.

In summary, the validated plume model predictions for the "near-field" chemical vapor concentration distribution may be used with confidence in health and safety analyses. In particular, the plume model validation experiments have shown that the model predictions for vapor concentration distribution are good for the following range of conditions:

- cargo loading rates from 100 to 90 m^3/hr
- tank vent heights from 0.5 to 4m above the deck
- vent concentrations from 0.01 kg/m^3 to 0.3 kg/m^3
- wind speeds from 0.5 m/s to 6.0 m/s
- downwind distances from 3m to 20m from the tank vent.

(The model predictions may also be good for conditions outside the range of the model validation experiments).

The validation experiments have also shown that

- for vent heights of 6m or more above the deck, the model overpredicts the vapor concentration at breathing height (1.67m) by approximately a factor of 2.
- the effect of on-deck structure is generally to increase the effective level of wind turbulence and reduce the mean wind speed. These effects enhance plume dilution, except as described above when the vent is shielded from the wind.

IV.4 Hazardous Chemical Vapor Handbook for Marine Tank Vessels - User's Manual

To facilitate the use of the analytical models that were developed on this project, a step-by-step guide to the structure and usage of the three computer programs

- ONDEK - Atmospheric dispersion of cargo vapor that is discharged from a tank during product loading or gas freeing,
- TANKP - Gas freeing of a tank in the presence of evaporation of pure product residues,
- TANKM - Gas freeing of a tank in the presence of evaporation of residual chemical from a water solution,

is provided in Reference 3 , "Hazardous Chemical Vapor Handbook for Tank Vessels - User's Manual."

This manual is organized in the following format:

- Model Description Summary - This section describes the model, the technical basis for the model both in theory and practice, the scenarios for which the model is designed and the model limitations. Detailed analytical derivations and sets of governing equations are not contained in this manual but are presented in this Final Report.
- Input Data Requirements - All input data are presented in tabular form in the order that they are requested of the user by an interactive driver. The tabulation includes the physical variable name, the equivalent program code and the expected units.
- Default Options - Certain pieces of input data are assumed to be known, e.g., chemical properties. Other inputs that pertain to ship/barge operations may or may not be available. In these latter cases, the interactive driver asks the user a question regarding the availability of data. If the user responds negatively, the interactive driver will present a series of default

options from which the user can make a selection. These sections of the manual present the various default options and their basis in the order in which they may be encountered.

- Program Output - Program output consists of tabular data and computer-generated graphs. The tables may contain the plotted variables and other internally computed variables. In this section of the manual, the output variables are defined by physical name, corresponding program code and the applicable units.
- Hazard Assessment - The basic program outputs are either chemical vapor concentration-time histories or vapor concentration profiles in space. In the case of tank entry following tank cleaning, the programs make an interpretation of the in-tank work environment based on accepted occupational exposure guidelines. A similar assessment of the on-deck environment is neither warranted nor entirely feasible due to the unconstrained, random nature of deck work.
- Examples - Each program description includes a computer-generated example. Each example is preceded by a brief discussion of the problem that is being simulated, followed by an I/O listing and finally discussion of the results as appropriate.
- Flow Charts - Each program is flow-charted to indicate primary decision points and the major program operations. For clarity, minor IF statements and DO loops have been omitted.
- References - Primary references are cited to support the model description.
- Program Listings - Hard copy listings of all programs are presented in the appendices.

The manual was written specifically for the USCG Hazardous Material Specialist. However, the manual is intended to provide both the USCG and marine industry personnel with analytical tools to evaluate potential hazards for actual and hypothetical operations. To this end, the manual will allow:

- The USCG to evaluate the effectiveness of proposed engineering controls and operational practices to minimize marine hazards.

- Industry to evaluate current company operational practices and engineering controls for their affect on worker exposure and flammability hazards.

- USCG and industry field personnel to assess the hazard potential before responding to routine inspections or emergencies.

V. OCCUPATIONAL EXPOSURE MONITORING AND BIOLOGICAL MONITORING

The occupational exposure environment in the marine chemical transport industry differs substantially from that in most land-based industries. In a land-based industry, the exposure environment is relatively constant from day to day; process-related fluctuations about some norm are recognized. In addition, the number and types of chemical substances in the land-based work environment is process-dependent, but within a given process some stability of contaminant composition would be anticipated. Conversely, on a parcel chemical or product tanker, the exposure environment is not constant either in concentration level or composition. The composition may vary with each voyage in accordance with the mix of chemical products that are transferred to and from the ship. Within a given voyage, short-term, high-level exposures may be combined with longer-term, low-level exposures to multiple product vapors followed by periods of non-detectable exposures. The occupational exposure environment on chemical tank vessels and its impact on the seafarer's health is of primary concern to the U. S. Coast Guard.

This project included both occupational exposure monitoring and biological monitoring. The measured occupational exposures, which were collected using accepted industrial hygiene monitoring techniques, represent a wide range of chemicals, work activities, vessel operations and ship equipment. This broad data base assists in identifying those activities, operations or equipment items that enhance or reduce the potential for vapor exposure.

Existing exposure limits, principally the TLV-TWA, reflect conventional land-based work schedules, i.e., 8-hour days and 40-hour weeks. Maritime work schedules do not follow this convention; they may be classed as novel or unusual work schedules. A series of biological monitoring tests was conducted to obtain data to aid in interpretation of vapor exposures during the novel work schedules of the maritime industry.

V.1 Occupational Exposure Monitoring

V.1.1 Philosophy and Scope

As discussed previously in Section I, the U. S. Coast Guard has formulated and implemented a multi-element program regarding the occupational health and safety of maritime workers which is summarized below:

Element No.	Project Title
1	Investigation of the Hazards Posed by Chemical Vapors Released in Marine Operations - Phase I (Complete).
2	Investigation of the Hazards Posed by Chemical Vapors Released in Marine Operations - Phase II
3	A Crew Exposure Study - Phase I (Complete)
4	A Crew Exposure Study - Phase II (Current)
5	A Study to Improve the Health and Safety of the Marine Hazardous Chemical Worker (Current)

The emphasis in the first four program elements has been on characterizing the work/exposure environment so that control methodology, be it engineering, administrative or protective, can be adequately considered in the fifth element.

The project reported here is Element No. 2, Investigation of the Hazards Posed by Chemical Vapors Released in Marine Operations - Phase II. The occupational exposure data that are presented in this report were collected in Elements Nos. 1, 2, and 3. The Crew Exposure Study - Phase I was conducted concurrently with this project, and it afforded opportunities to monitor exposures to a larger number of chemical cargo vapors, thereby expanding the data base of this project for interpretation or characterization purposes. These data represent chemical vapor exposures received by Deck Department personnel on tankers and tankermen involved in barge operations.

The monitoring philosophy is summarized below.

- Element No. 1 emphasized monitoring during single event or short duration work activities. This class of activity, which includes tank top-off and tank entry, was defined as having a high probability of exposure.
- In Element No. 2, exposure monitoring was expanded to include longer duration sampling during single shift or operations oriented to work activities. Tank cleaning and periodic tank gauging through top-off are represented in this exposure class. The occupational exposures during the biological monitoring tests are also included in this category.
- Element No. 3 expanded the scope of the monitoring efforts and emphasized characterization of exposure profiles of selected crew members over a period of several days that included multiple loading, discharging, tank cleaning and ballasting operations.

The merchant marine tankerman does not have a fixed work station on a tanker or barge. His work station may include all or a large part of the deck area depending upon the phase of vessel operations. As a result of this requirement for mobility and his responsibilities, the tankerman may be directly exposed to the cargo vapors from multiple work-related sources, e.g., periodic gauging of cargo ullage on several tanks. He may also be indirectly exposed to the chemical vapors from sources that are not related to his work activity, e.g., setup of tank washing equipment downwind of vapor discharge ports on tanks that are being loaded. Because of this complex interaction between the work activities and the exposure sources, documentation is required which will facilitate an understanding of the cause of the exposures. The following documentation was collected during exposure monitoring.

- Work activity
- Duration of work activity
- Source of exposure
- Proximity of the tankerman to the vapor source.

Without this information, the work activity that produced the exposure could not be adequately defined.

V.1.2 Sampling and Analytical Methods

Tankers and barges transport a wide range of liquid cargos. The following guidelines or criteria were employed in selecting the cargos for occupational exposure or area monitoring.

- Products that represented proprietary blends or mixtures were excluded from consideration. The only exception was monitoring of vapor exposures to the benzene fraction in gasoline. This criterion eliminated those products that could require development of sampling and analysis methods or extensive analytical chemistry.

- Chemicals that require liquid impinger collection equipment were excluded because this sampling system is not compatible with a crew member's cargo-related work activities. Toluene diisocyanate is an example of a chemical in this category.

- Chemicals were excluded where published sampling and analysis methods required special, high-cost equipment that did not have a broader application beyond one specific chemical. Vinyl acetate (VAM) is an example of this type of chemical. It should be noted that, in the future, this criterion need not apply to VAM as more cost effective methods have recently been published.

Those chemicals that were not excluded according to the above criteria were sampled using intrinsically safe, battery-operated pumps and solid sorbent collection tubes. For each chemical, sampling flow rate and sorbent type was based on NIOSH-recommended methods. Pre- and post-test pump calibration included five replicate determinations of flow rate using a bubble meter with a representative load in-line.

Three solid sorbents were used during the study: activated charcoal, silica gel and XAD-2 resin. Activated charcoal was indicated for the majority of the chemical vapors. Where high tube loading was anticipated, the large charcoal tube (400/200) was used; the smaller NIOSH-approved tube (100/50) was used when lower loading levels were anticipated. The recommended tube size was used when samples were collected with silica gel and XAD-2. For each sampling scenario, a blank tube was broken, capped and submitted with the exposed tubes for analysis.

All samples were refrigerated from the time of collection through analysis. This time frame was governed by the requirements of the field test, which ranged from roughly three days for a terminal test to nearly three weeks for an at-sea voyage.

Chemical analysis of adsorbed vapors were based on NIOSH-recommended desorption and gas chromatography methods. Samples of the liquid chemicals, which were collected during cargo transfer, were used for determination of desorption efficiencies and preparation of calibration standards. Desorption efficiencies were determined analytically for each combination of chemical, adsorbent, adsorbent size, and lot number that was used. Desorption efficiency was determined at two loading levels (one-half and two times the TLV-TWA for a representative sample volume) with three recplicates at each level.

All vapor concentrations were calculated by the following equation:

$$C = \frac{(W_{CF} + W_{CB}) - (W_{BF} + W_{BB})}{\eta Q t} \left(\frac{24.45}{MW}\right) \left(\frac{T+273}{298}\right) \left(\frac{760}{P}\right) \tag{54}$$

where W_{CF} = analyte weight on front section of sample tube, µg
W_{CB} = " " " back " " " " , µg
W_{BF} = " " " front " " blank tube, µg
W_{BB} = " " " back " " " " , µg
η = desorption efficiency
Q = average sample flow rate, L/min
t = sample duration, min
MW = analyte molecular weight
T = sampling temperature, °C
P = atmospheric pressure, mm Hg

Sampling temperature was routinely documented. The pressure correction was applied where such data were readily accessible.

All samples were assessed for possible analyte breakthrough, i.e., $W_{CB} > 0.3\,(W_{CB} + W_{CF})$. In the majority of the samples, breakthrough was not indicated. However, breakthrough was suspected on a small number of samples. For this group of samples, the indication is not conclusive because of the potential for analyte migration during the period between sample collection and analysis.

On two occasions, exposure monitoring was conducted for methanol vapors. The recommended procedure uses a silica gel trap; this material in combination with the high humidity marine environment can impose severe constraints on sampling duration. In an attempt to avoid this constraint, a sampling and analysis method was used, which was developed by the E. I. DuPont Company. The method, which employs conventional large charcoal tubes and desorption with acetonitrile followed by GC analysis, is used by this company for internal methanol monitoring.

Pre-test preparations included identification of the chemicals that were to be handled and calibration of pump/tube combinations at flow rates that were appropriate to these chemicals. During these preparations, details of the cargo transfer plan are not known, i.e., the sequence in which the chemicals will be loaded or discharged from the ship. This information is developed by the ship in coordination with the terminal. Many factors influence this plan, e.g., ship trim, availability of product from shore tanks, etc., and it is not uncommon for the plan to change during the docking. Consequently, the mix of cargo vapors in the work place is not known apriori. As a consequence, two situations may arise.

- A crew member can be conveniently instrumented with up to two pump/tube combinations without interfering with his work. The adsorptive medium and sampling rate for one pump/tube combination may be appropriate for several cargo vapors that are present in the work place, but the procedures for desorbing the analytes may be different. In these cases, a decision must be made as to the analytes that will be retained and those that will be sacrificed with due regard for toxicity and maximizing data output. This situation was encountered during one monitoring activity. To avoid such situations, it would be necessary to use a third pump/tube combination, which may interfere with the crew member's ability to work efficiently.

- A similar situation exists when the sample collection medium and desorptive methods are appropriate for a subset of the vapors that coexist in the work environment, but the recommended sampling rates are different. The crew member may already be wearing a full complement of sampling equipment, and it would be prohibitive to add another device. In these cases, a primary compound that had a consistent set of sampling requirements was identified. Other vapors that had the same collection medium and desorption method were sampled at the primary rate, but were identified as secondary analytes for chemical and computational analysis purposes.

V.1.3 Single Event Exposures

Table V.1 summarizes a series of single event exposures. The work activities that resulted in these exposures meet one or more of the

TABLE V.1. SINGLE EVENT EXPOSURES

SEQUENCE NO.	SAMPLE NO.	CHEMICAL	SAMPLING RATE (L/min)	SAMPLING DURATION (min)	W_c (μg)	η	T (°C)	P (mm Hg)	RH (%)	EXPOSURE CONC. (ppm)	TLV-TWA (ppm)	TLV-STEL (ppm)	TLV-C (ppm)	COMMENTS
1	PS-1	MIK	0.099	20.5	341	0.363	20.8	763	NM	111	50	75	--	TANK ENTRY
	PS-2	MIK	0.074	20.9	111	0.363	20.8	763	NM	47	50	75	--	TANK ENTRY
	PS-3	MIK	0.264	21.5	733	0.363	20.8	763	NM	85	50	75	--	TANK ENTRY
1	PS-4	TOL(Skin)	0.099	37.3	2872	0.881	20.8	763	NM	230	100	150	--	TANK ENTRY
	PS-5	TOL(Skin)	0.074	36.1	1775	0.881	20.8	763	NM	197	100	150	--	TANK ENTRY
	PS-6	TOL(Skin)	0.264	38.4	7850	0.881	20.8	763	NM	229	100	150	--	TANK ENTRY
2	UCC-110	BAN(Skin)	0.101	26.0	104.3	0.653	37.6	764	NM	21	--	--	50	TANK ENTRY
	UCC-100	BAN(Skin)	0.098	27.0	32.2	0.653	37.6	764	NM	6	--	--	50	TANK ENTRY
	UCC-101	ACT	0.107	29.0	45.2	0.317	31.2	762	NM	20	750	1000	--	TANK ENTRY
3	UCC-105	BAN(Skin)	0.199	34.0	145.2	0.712	32.6	761	NM	10	--	--	50	TANK ENTRY
	UCC-102	BAN(Skin)	0.204	34.0	224.3	0.712	32.6	761	NM	15	--	--	50	TANK ENTRY
4	--	EDC	--	85.0	REAL TIME MEASUREMENTS WITH ORGANIC VAPOR ANALYZER (OVA)					≥700	10	15	--	TANK ENTRY
5	DW-2	EDC	0.196	7.0	541.7	0.693	19.8	760	85	138	10	15	--	TANK ENTRY
	DW-10	TCL	0.196	8.7	323	1.190	19.8	760	85	29	50	150	--	TANK ENTRY
	DW-3	TCE	0.196	5.0	136	0.937	19.8	760	85	45	350	450	--	TANK ENTRY
6	SB-30	BNZ	0.203	82.0	173	0.867	32.5	760	NM	3.8	10	25	--	TANK ENTRY; BNZ IN GASOLINE
7	PE-1	TOL(Skin)	0.092	35.4	1917	0.739	9.5	768	NM	199	100	150	--	TANK TOP-OFF, OPEN GAUGING TOL TANK
		HXA	0.092	35.4	25	0.989	9.5	768	NM	2	50	--	--	HXA FROM ADJACENT TANK
	PE-5	HXA	0.092	34.9	11220	0.989	9.8	766	NM	944	50	--	--	TANK TOP-OFF; OPEN GAUGING HXA TANK
	PE-4	HXA	0.092	40.8	912	0.989	9.8	766	NM	66	50	--	--	TOP-OFF ASSISTANT, HXA TANK
8	UCC-104	EAL	0.051	21.0	46.2	0.209	30.5	763	NM	112	1000	--	--	TANK TOP-OFF, OPEN GAUGING EAL TANK
		ACT	0.051	21.0	61.1	0.317	30.5	763	NM	78	750	1000	--	ACT FROM ADJACENT TANK
9	UCC-103	BAN(Skin)	0.226	49.5	27.8	0.712	26.4	762	NM	1.2	--	--	50	DECKSIDE, TANK WASHING CREW
	UCC-106	BAN(Skin)	0.204	50.5	17.1	0.712	26.4	762	NM	0.8	--	--	50	DECKSIDE, TANK WASHING CREW

NOTES:
1. W_c = Weight of analyte corrected for blank
2. NM = Not measured
3. ND = Not detectable

TABLE V.1. SINGLE EVENT EXPOSURES (CONTD)

SEQUENCE NO.	SAMPLE NO.	CHEMICAL	SAMPLING RATE (L/min)	SAMPLING DURATION (min)	W_c (µg)	η	T (°C)	P (mm Hg)	RH (%)	EXPOSURE CONC. (ppm)	TLV-TWA (ppm)	TLV-STEL (ppm)	TLV-C (ppm)	COMMENTS
10	SB-10	BNZ	0.186	6	ND	0.867	27	760	61	ND	10	25	--	OPEN ULLAGE PORTS & GAUGING TUBES ON 18 TANKS AT DISCHARGE PORT: BNZ IN GASOLINE
	SB-11	BNZ	0.186	9	ND	0.867	19.2	760	63	ND	10	25	--	SAME AS SB-14 BUT AT SECOND DISCHARGE PORT: BNZ IN GASOLINE
11	VF-7	BNZ	0.205	22	10	0.965	31.1	760	76	0.5	10	25	--	MUCK PUMPROOM BILGE, EMPLOYEE NO. 1, BNZ IN GASOLINE
	VF-8	BNZ	0.198	22	14	0.965	31.1	760	76	0.8	10	25	--	MUCK PUMPROOM BILGE, EMPLOYEE NO. 2 WITH NO. 1, BNZ IN GASOLINE
12	VF-10	MEK	0.204	13	10.8	0.801	16.7	760	90	1.2	200	300	--	COLLECT PRODUCT SAMPLE THROUGH ULLAGE PORT
		XLO,M,P (Skin)	0.204	13	2	0.992	16.7	760	90	0.1	100	150	--	COLLECT PRODUCT SAMPLE THROUGH ULLAGE PORT
13	VF-100	BNZ	0.204	17	ND	0.965	30.3	760	70	ND	10	25	--	ENTER FRESH WATER BALLAST TANK TO CHECK FOR GASOLINE LEAK
14	VF-102	EAL	0.204	84	>1436	0.68	31.1	760	74	>67	1000	--	--	ENTER EAL TANK, REMOVE COVERPLATE TO ACCESS DOUBLE BOTTOM OF ADJACENT ECH TANK; POSSIBLE BREAKTHROUGH ON EAL
		EPC(Skin)	0.204	84	16	0.68	31.1	760	74	0.4	2	5	--	
15	VF-103	EAL	0.203	30	>1842	0.68	29.4	760	77	>239	1000	--	--	TANK ENTRY, MUCKING, POSSIBLE ANALYTE BREAKTHROUGH
16	VF-11	BNZ	0.196	144	ND	0.965	27.9	760	87	ND	10	25	--	TANK ENTRY - FORWARD BALLAST TANK, TWO CREWMEN CHECK POTENTIAL AV GAS LEAK FROM ADJACENT TANK
	VF-13	BNZ	0.209	165	ND	0.965	26.9	760	85	ND	10	25	--	
17	107	CRF	1.067	15	2518	0.978	14.2	760	62	31.7	10	50	--	TANK ENTRY FOR CLEANUP, CREW MEMBER NO. 1
	108	CRF	1.067	15	1780	0.978	14.2	760	62	22.4	10	50	--	
	109	CRF	1.067	10	743	0.978	14.2	760	62	14.0	10	50	--	
	524	CRF	0.936	15	1873	0.978	14.2	760	62	26.9	10	50	--	TANK ENTRY FOR CLEANUP, CREW MEMBER NO. 2
	525	CRF	0.936	15	1190	0.978	14.2	760	62	17.1	10	50	--	
	526	CRF	0.936	10	346	0.978	14.2	760	62	10.6	10	50	--	
	110	CRF	1.067	15	2401	0.978	16.2	760	54	30.4	10	50	--	TANK ENTRY FOR CLEANUP, CREW MEMBER NO. 3, 19 HOURS AFTER EXIT OF CREW MEMBERS NO. 1 AND 2
	112	CRF	1.067	26	3692	0.978	16.2	760	54	28.6	10	50	--	
18	113	XLOMP (Skin)	0.149	6	10.7	0.981	16.2	760	54	2.74	100	150	--	TANK ENTRY, DECK CREW
19	504	XLM(Skin)	0.201	5	18.3	0.981	18.1	760	93	4.2	100	150	--	TANK ENTRY, CARGO SURVEYOR
	505	XLM(Skin)	0.201	4	< 3	0.981	18.1	760	93	< 0.86	100	150	--	TANK ENTRY, CARGO SURVEYOR

NOTES:
1. W_c = Weight of analyte corrected for blank
2. NM = Not measured
3. ND = Not Detectable

following criteria.

- The work activity is relatively short in duration.
- The work activity was suspected apriori of having a high probability for elevated exposure levels.
- The work activity was confined to a single work station during the exposure period.

A comparison of these criteria with the data in Table V.1 indicates that the majority of the exposures involved confined space entry and tank top-off. In general, the work activity involved a single chemical or product.

Confined spaces include both product/ballast tanks and pumprooms. Tank entry on product/chemical tankers and barges is an integral part of normal operations. Following cleaning (washing and gas freeing), product tanks are entered to accomplish one or more of the following objectives:

- Sweep debris from the tank floor.
- Hand-muck residual chemical/water solutions that could contaminate the next cargo.
- Inspect a tank for dryness and odor before loading the next cargo.
- Check condition of tank coatings and measure coating thickness.

Non-routine entries may be required if there is a question of tank integrity, i.e., leaks that may result in subsequent product contamination or other difficulties. The trend in ship design and retrofit is to eliminate the decentralized discharge of products through a pumproom by installing independent deepwell pumps on cargo tanks. Some older vessels contain pumprooms, and cleaning product leaks from the pumproom bilge is an accepted operation. If more than one crew member enters the confined space at the same time, the exposure levels will not necessarily be constant; they reflect the work that each individual performs.

Each entry or group of entries in Table I bears a sequence number. The remainder of this subsection consists of brief descriptions of the work scenarios corresponding to each sequence number. These scenario descriptions are included as aids in interpreting the exposure environment. The chemical names correspond to the USCG CHRIS abbreviation system.

Sequence No. 1

The scenario for the in-tank vapor exposures was as follows. The vessel arrived in port with two tanks that had been washed, ventilated, and manually cleaned during the ballast voyage. Other than identification of the previous contents of the tank and the fact that the clean tanks had been sealed for five days prior to docking, there was little documentation of the particulars of washing and ventilating. Before sealing the tanks, the Chief Mate had sampled the tanks with an explosimeter and had determined that the vapor concentrations were zero on the instrument scale. Upon opening, the tanks appeared to be clean and void of any liquid residual. The Chief Mate again tested the tanks with an explosimeter; the vapor sampling line was introduced into the tank through an open hatch, and it terminated near the tank bottom. A zero concentration was again indicated on the tanks of interest—one had carried toluene and the other methyl isobutyl ketone. Two SwRI personnel entered both tanks along with the Third Mate. In both instances, each individual wore personal sampling equipment (pump and charcoal tube). In addition, a portable organic vapor analyzer (OVA) and recorder were also taken into each tank.

The lower exposure level of PS-2 (SwRI) relative to PS-1 (SwRI) and PS-3 (Third Mate) is attributed to the fact that, while in the tank, these personnel performed individual familiarization and inspection activities, but not as a group. This diversity of movement is reflected in the variation of exposure concentration. The OVA instrumentation that accompanied this man-entry recorded a mean MIK concentration of 67 ppm with excursions to 47 and 96 ppm. The Third Mate did not perform any sweeping or mucking operations. Man-entry into the toluene tank indicated that all three personnel were exposed to vapor concentrations that exceeded the STEL by 46%

on the average. The OVA instrumentation substantiated these levels with a mean recorded toluene concentration of 240 ppm and excursions to 200 and 273 ppm. These results are particularly interesting because concentration levels were apparently below the detection limit of the explosimeter whose readings are used as a basis for decisions regarding man-entry. In the case of this toluene tank, the explosimeter was insensitive to vapor concentrations that were hygienically significant. Sample No. PS-6 was collected on the Third Mate while PS-4 and 5 represent samplers worn by SwRI personnel.

Sequence No. 2

This sequence includes two tank entries on the same vessel in port. Both tanks had been washed and gas freed on the ballast voyage. Two crew members entered a tank that had carried butanol. A third crew member entered an acetone tank.

The butanol tank was entered to remove any debris and wash residue from the tank bottom prior to backloading of another chemical. The tank bottom was essentially dry upon entry except for a small amount of wash residue beneath the product drop line. The terminus of the drop line was directly beneath the open expansion trunk. One crew member (UCC-110) wiped this residue with rags. His exposure level agreed quite closely with OVA vapor concentrations measured at the expansion trunk and 30 feet into the tank prior to entry. The second crew member (UCC-100) used an eductor vacuum to remove debris from the tank bottom. This activity was performed in an area of the tank beneath the on-deck blower.

The work performed by the third crew member in the acetone tank was the same as in the butanol tank.

Sequence No. 3

This sequence involved entry by two crew members into the same butanol tank as in Sequence No. 2 but on a different voyage. The tank had again been washed and ventilated at sea. The work activities did not include debris removal; entry was accomplished to inspect the tank for product-contaminating rust on the internal structure which included wall buttresses and longitudinal stringers.

Sequence No. 4

An EDC barge tank had been washed and partially ventilated by the end of the work shift on Day 1. At that time, a considerable amount of residue remained on the tank floor. The following morning, two workers entered the tank at 0700 to perform cleanup operations. The tank was tested via drop-line through the hatch and was certified gas free (0% LEL and 21% O_2) by Marine Department personnel. Cleaning consisted of mopping the main tank floor with towels and removing buckets of EDC/water/rust sludge from the pump sump. In all, 18 five-gallon buckets of sludge were removed from the tank. The in-tank workers wore neither respirators nor protective gloves. An intense odor of EDC was present in the sludges that were dumped on deck. During the mucking operation, the Coppus blower was positioned over the aft butterworth opening, but it was not operating. The only ventilation was provided by the shore-based air system through the loading line. The workers exited the tank at 0825 for a total in-tank work time of 85 minutes.

As the project team was detained at the main terminal gate, there was no opportunity to monitor exposures with personal dosimeters. As an alternative, the cleaning and residue removal operations were observed as indicated above. Following worker egress from the tank, project personnel entered the tank with an OVA, chemical goggles and respirators. During a 25-minute survey of the tank, the following EDC vapor concentrations were recorded:

- 700 ppm top to bottom of tank during descent.
- 1170-1780 ppm directly above a wet spot along a wall-floor seam on one side of the barge.
- 20,763 ppm directly above a wet spot along a wall-floor seam on the other side of the barge.

- 2000-6000 ppm directly above a fore-aft weld bead on the tank floor.

At the time of this test, the ACGIH TLV-TWA and TLV-STEL were 50 and 75 ppm, respectively. The ACGIH now recommends limits of 10 and 15 ppm. It is probable that these measured concentrations, particularly the 700 ppm, represent a lower bound on the exposure levels that the two employees encountered.

Sequence No. 5

Many of the tanks on the 17,272 Dwt drugstore tanker had been cleaned at sea during the ballast voyage. The hatches on these tanks had then been dogged down for periods of five days or more. The tanks may have been tested for a gas free condition at sea, but vapor regeneration during the time that the hatches had been dogged down had altered the tank gas concentrations. Upon docking at the terminal, the cleaned tanks were entered by dock personnel for the purpose of inspecting the tanks for cleanliness and ability to receive the next cargo.

For each tank inspected, the dock inspector requested that the tank hatch be opened. Using a combination O_2/combustible gas indicator, he sampled the tank atmosphere with a dropline that was 7 ft long, even though the tank was 40 ft deep. If acceptable O_2 and combustible vapor concentration levels were found, the inspector attempted entry with a helper remaining on deck. If irritating or objectionable odors were encountered, he exited the tank, requested that it be further ventilated, later repeated the testing procedure, and then entered the tank if the situation had been remedied. Tank entry took place without the wearing of a respiratory protective device, or the availability of such a device close to the point of tank entry. Also, toxic gas detector tubes were not taken into the tanks. The entries into the EDC and TCE tanks were standard entries as described above with no further ventilation necessary. When the inspector went down only a few steps into the TCL tank, he quickly came back out and requested that the tank be further ventilated. Although the tank had passed the test with the O_2/combustible gas indicator, the inspector said he could not inspect the tank because the smell of chemical was too strong. In this case, the additional ventilation and entry criterion of odor did produce an acceptable tank environment, but odor is not a primary indicator of concentration level.

This scenario, which is frequently encountered with terminal personnel, indicates the need for specifying and using instrumentation that is reliable and sensitive to vapor concentrations that are hygienically significant. That two of the three tanks had acceptable atmosphere on this observation may not be representative.

Sequence No. 6

This sequence describes entry into three consecutive tanks on a tanker that transports mixed grades of motor gasoline.

Upon docking, a Marine Chemist boarded the ship and tested the atmosphere in Tank Nos 2P, 2C, 2S, 3C, 4P, 4C, and 4S, which had been either washed and ventilated or deballasted at sea. Testing consisted of in-tank measurements of O_2 level and % LEL (as methane) using a combination oxygen meter and explosimeter and a dropline that was inserted into the tank through the open expansion trunk. A gas free certificate was issued for these tanks.

Two SwRI personnel accompanied three ship's personnel into Tank Nos. 3C, 2C, and 2S. The purpose of the entry was to inspect the condition of tank coatings and measure their thicknesses. OVA surveys were made of the tank atmospheres and a charcoal tube dosimeter was worn by one of the SwRI project team members. The duration of each inspection and elapsed time between entries is given below. The dosimeter pump was turned off between entries, and the personal exposure sample was analyzed for benzene.

Tank No.	Inspection Time (min.)	Pump Off Time (min.)
3C	45	4
2C	22	5
2S	15	
	82 min. total sample time	

The results of the OVA surveys produced the following total gasoline vapor concentrations. All concentrations are referenced to breathing zone height unless otherwise noted.

Tank 3C
First level into tank = 390 ppm
Second level into tank = 355 ppm
Tank bottom = 395 ppm
Above wet spot on floor = 430 ppm
Deposits on web frames = 660 ppm

Tank 2C
First level down = 300 ppm
Second level down = 320 ppm
Tank bottom = 355 ppm
Above wet spot on floor = 1600 ppm
Above wet spot after disturbing it = greater than 4200 ppm
Behind loose chip of coating material on wall = greater than 4200 ppm
Deposits on hand rail = greater than 4200 ppm

Tank 2S
First level down = 110 ppm
Second level down = 118 ppm
Tank bottom = 220 ppm
Mud on bottom = 1150 ppm

Sequence No. 7

This scenario describes top-off of two product tanks on the same vessel, i.e., the final phase of loading where ship personnel control the cessation of product delivery. Both tanks were loaded to near capacity, and the top-off was accomplished by open gauging. In this phase of the operation, the concentration of vapor that is discharged from an open ullage port on an expansion trunk increases rapidly and approaches a saturation level. During these latter stages of loading, a deck officer is assigned the responsibility of visually gauging the ullage depth through an open ullage port. The breathing zone may be located two feet or less from the vapor discharge port and directly in the vapor plume, as illustrated in Figure V.1. If the ship has a list or pitch as a result of differential product loading, the deck officer may be assisted by a deckhand whose job is to call out indicated ullage from a tape gauging system that is located some distance from the expansion trunk. The perceived ullage is then a mean of the two indications.

Shortly after hexane loading had commenced in Tank 3C, the shore-based pump was shut down. Loading of toluene in Tank 4C was initiated and proceeded without interruption to tank top-off. The topping operation was monitored continuously by the Third Mate (PE-1) beginning at an indicated tape ullage of 10 ft (3.05m) and ending at an approximate ullage of 4.5 ft (1.37m). Although the primary exposure was to toluene, the sample was analyzed for the presence of hexane from the adjacent tank.

Following top-off of Tank 4C, the hexane loading was completed. Since the ship had a port list, the Second Mate was assisted in the topping operation as described above. The Second Mate (PE-5) performed the topping operation in the same fashion as had been done on the toluene tank. The Mate's assistant (PE-4) manned the closed gauging system that was located roughly 10m downwind of the open ullage port where the Mate was positioned.

It is noteworthy that both of these tanks were open-loaded, but with vent covers on their pins. The hinge line was on the starboard side of the vent cover. This reduction of discharge area relative to a full open vent produced a jet of high velocity, high concentration vapor that was projected upwind at the Mate when the vent cover was opened and reseated.

The duration of all personal exposure samples coincided with the length of the topping operation.

Sequence No. 8

The Port Relief Officer (PRO) was monitored during top-off of a denatured ethanol loading. The top-off was accomplished by open gauging the product ullage. While gauging, the PRO took up a position that was downwind and slightly to the port side of the ullage hatch where the vapor

FIGURE V.1. EXAMPLE OF OPEN GAUGING THROUGH OPEN ULLAGE PORT FROM DECK LEVEL was being discharged from the tank. In this position, his breathing zone was removed from direct exposure to the vapor plume. His exposure sample, UCC-104, was also analyzed for acetone content as this product was stored in an adjacent tank with the ullage cap open. This sequence demonstrated that other peripheral vapor sources can contribute to a simultaneous, multiple exposure.

Sequence No. 9

Tank washing, which is normally the first step in the cleaning operation, involves manual lowering of water washing machines into the tank through one or more access openings on the deck. Each machine may be positioned at various depths in the tank for specified periods of time.

This scenario involves two crew members who were responsible for lowering the washing machines and attached hoses into the tank according to specified depth-time plan. The actual lowering of the machines is accomplished quickly; i.e., within one minute. When the crew members were not performing this manual operation, they took up positions well away from the butterworth openings and the open expansion trunk, but they remained on the deck area over the tank being washed.

The tank contains the vapor of the previous cargo, which is discharged at a low flow rate through the on-deck tank openings during the washing operation. The low vapor discharge rate coupled with rapid atmospheric dilution and the worker locations produced the measured exposures.

Sequence No. 10

In transit, cargo tanks are sealed. Upon docking, certain access ports on each tank are manually opened in preparation for cargo sampling and product discharge. These ports are opened on slack and empty tanks as well. Before opening these ports, the pressure in the ullage space above the cargo may range essentially from atmospheric pressure up to a pressure that is controlled by a relief valve on each tank venting system.

As these access ports are opened and the pressure is relieved, there may be a transient release of cargo vapor that could pose a potential inhalation exposure.

The samples in this sequence were collected on the same crew member who opened the ullage ports and gauging tubes on all tanks at two consecutive discharge terminals. At the first terminal, all tanks were full; at the second terminal, the majority of the tanks were either full or slack. The sample durations include both the time required to open the ports on 18 tanks and the walking time between tanks. These samples indicate a non-detectable exposure to the benzene fraction in gasoline during this specific observation.

Sequence No. 11

This sequence was observed on a tanker on which gasoline products are normally discharged through a pumproom. Two members of the Deck Department entered the pumproom to muck bilge residues with buckets and shovels. Ventilation of this confined space consisted of an on-deck blower that operated in suction mode. Attached to the blower suction inlet was an "elephant trunk" that extended down into the pumproom and terminated at the bilge level. One additional crew member stood safety watch on deck. The occupational exposure samples that were collected during this brief work period were analyzed for the benzene fraction in gasoline.

Sequence No. 12

Prior to product discharge, a quality control sample of the bulk liquid was obtained from the tanks that were to be off-loaded. Before these samples could be retrieved, the tank P/V valves were opened. Once pressure was relieved, the pins on the ullage ports were removed, and a quart sample bottle connected to a chain was lowered through the ullage port to withdraw the sample. Dermal exposure occurred during this activity. The dermal exposure occurs as a result of skin contact with the chain and bottle which have been immersed in the chemical and are then withdrawn from the tank.

No gloves or protective clothing were worn by the crewmen performing this activity.

The inhalation exposures that were monitored on one crew member, who sampled two tanks, were quite low because passive diffusion is the primary mechanism for vapor discharge under these circumstances; the vapors are not forceably discharged from the tank.

Sequence No. 13

Some tankers, by design or retrofit, have segregated, fresh water, ballast tanks. Because these tanks do not carry products, there is relatively infrequent need to discharge the ballast for the purpose of tank entry. This particular sequence did require entry for two reasons. The tank was entered to accomplish a needed cleaning and to inspect the tank for a suspected gasoline leak from an adjacent tank. Consequently, the exposure sample was analyzed for benzene in gasoline, but none was detected.

During entry, a deck ventilator was in operation, and there was a safety watch at the tank hatch.

Sequence No. 14

An ethanol tank that had previously been ventilated but not washed was entered by one crew member. The in-tank work activities consisted of placing a portable stripping line in the sump of the main cargo pump and removing a vertical coverplate that provided access to the double bottom for the adjacent epichlorohydrin tank. This plate was removed to facilitate gas freeing of the double bottom beneath the EPC tank prior to biennial inspection.

Respiratory protection was not worn. Tank ventilators were in operation, and there was a deck safety watch as illustrated in Figure V.2.

The analytical analysis of the charcoal tube indicated possible ethanol breakthrough. Given the low exposure level relative to the TLV-TWA,

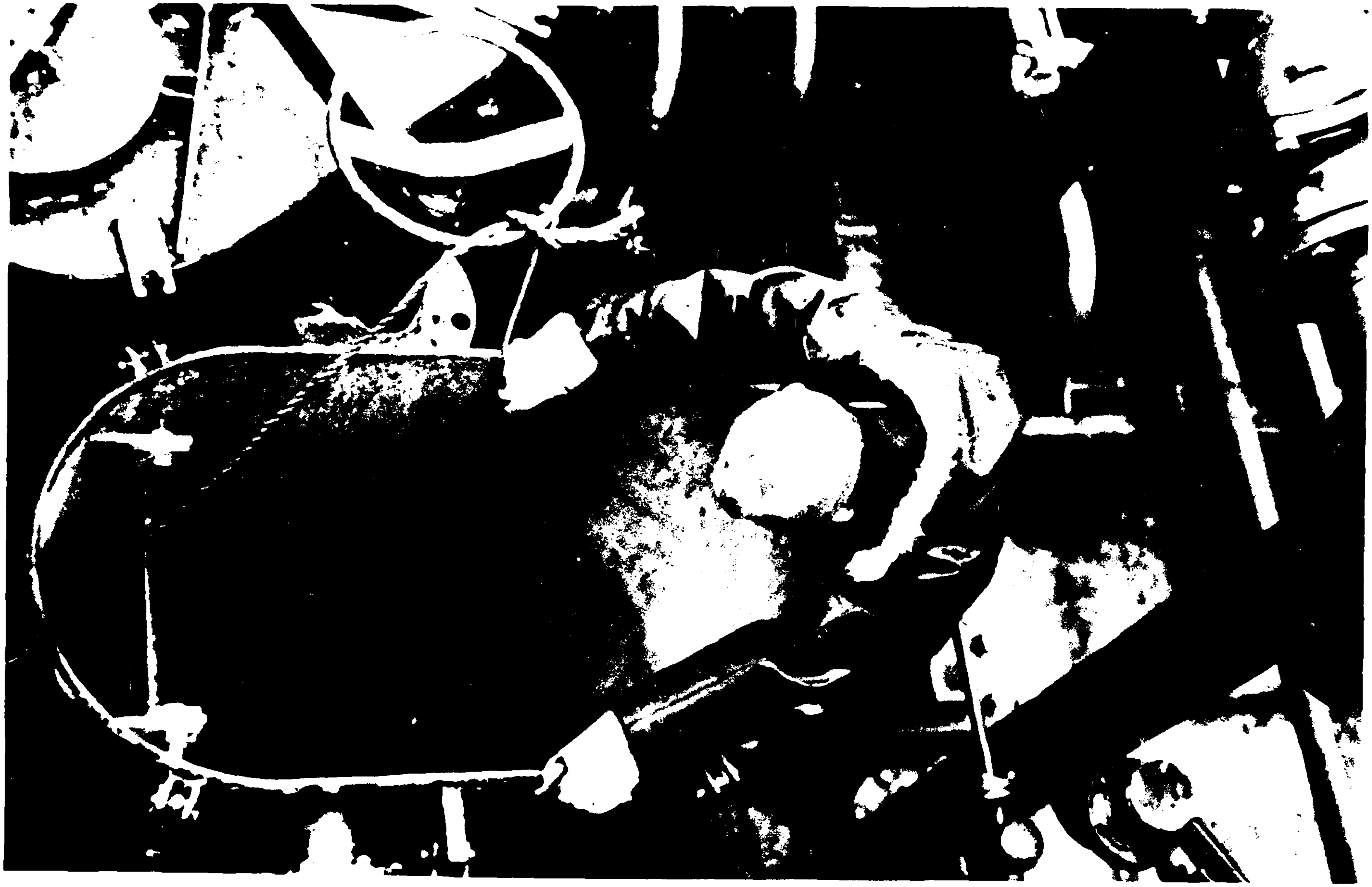


FIGURE V.2. CREWMEMBER ON SAFETY WATCH DURING TANK ENTRY the perceived breakthrough is believed to represent, in actuality, migration of the analyte between sample collection and chemical analysis.

Sequence No. 15

One crew member entered an ethanol wing tank to mop up residual pure chemical on the tank floor. The tank had not been washed, but had been ventilated. At the end of pre-entry ventilation, the ethanol concentration at the hatch and throughout the tank was 132 ppm as determined by OVA surveys. The increase in exposure level above this background is a result of localized evaporation of ethanol during the mopping operation.

The comments in Sequence 14 that pertain to respiratory protection, ventilation during work, safety watch and analyte breakthrough are also applicable to this scenario.

Sequence No. 16

This sequence is similar to Sequence No. 13 in that another ballast tank was entered for cleaning and inspection for gasoline leaks from adjacent tanks. The entry, which involved two crew members, lasted roughly 1.5 hours. During this time, no detectable benzene from gasoline leaks was found.

Sequence No. 17

This sequence is concerned with two separate entries into the same tank separated by approximately 19 hours. All tank entries were permitted without prior testing of the tank atmosphere for oxygen and combustible gas levels or potentially toxic levels. It should be noted that the combustible gas test would have been irrelevant because chloroform is not combustible. The purpose of these entries was to clean up any solid debris and/or liquid residues on the tank floor and in the pump sump. Cleanup materials included a broom, shovel, dust pan, bucket, and rags.

Two crew members made the first entry immediately after the tank had been washed and ventilated. Both of these crew members wore full-face respirators with organic vapor cartridges, rubber boots, and cotton coveralls, but did not wear gloves. One individual (Sample Nos. 524-526) was primarily concerned with sweeping dry debris on the tank bottom; the other individual (Sample Nos. 107-109) concentrated on shoveling wet debris from the pump sump and mucking the remaining liquid by hand with the rags. This latter activity resulted in definite dermal contact with the liquid residue. Despite the fact that respirators were being used, potential environmental exposure levels were monitored; the NIOSH procedure for collecting "ceiling concentration" samples was used. Deck blowers were operating during this entry. For each of the two crew members, the samples were collected sequentially in time. The decline in vapor concentration during the 40-minute work period reflects the expected dilution effect of the on-deck tank ventilation blower.

The second entry into the chloroform tank was made by a third crew member. His clothing complement was the same as that which the previous two crew members had used with the exception that he did not use a respirator. During this entry, vapor concentrations were nearly the same as were encountered at the beginning of the preceding entry. This situation is indicative of chemical vapor regeneration over a prolonged period of time (19 hours) when the tank is not continually ventilated between entries.

Sequence No. 18

Following exit from the chloroform tank (Sample Nos. 110 and 112), the same crew member entered a tank that had carried mixed xylenes (Sample No. 113). He wore a respirator in addition to the other items cited in Sequence No. 17. The in-tank time was minimal and indicates that there was little need for additional cleanup as the primary manual cleaning had been performed five days earlier on the ballast voyage.

Sequence No. 19

Before a tank is loaded with a given chemical, the usual procedure is that a cargo surveyor, who is retained by and represents the purchaser of the chemical, will enter and inspect the tank for the presence of moisture, debris, odor, or previous product residues. All of these factors can influence the product purity and its compatibility with its intended use.

Two surveyors boarded the ship for a pre-loading inspection of two tanks, both of which had previously held m-xylene. These tanks had been cleaned prior to docking. The inspectors tested each tank atmosphere with an O_2/combustible gas indicator before entering. These tests were made at one location in the tank with a drop line through the open dome on the expansion trunk. Vessel personnel witnessed the tests, but did not conduct an independent evaluation.

One inspector entered each tank and was accompanied by one member of the project team who wore personal dosimeters and walked with the inspector during his survey. Ventilating blowers were not operated during entry; the Second Mate and the remaining surveyor stood safety watch at the expansion trunk. The duration of each entry is fairly representative of this class of work activity.

V.1.4 Single Shift or Operations Oriented Exposures

The exposures in this category resulted from work activities associated with operations, in general, that are somewhat longer in duration than those that produced the single event exposures. Certain ship operations may extend over one or more deck watches. For example, tank cleaning or the loading of several large parcels of chemicals may include one 4-hour watch and part of the succeeding watch. Deck watch personnel changes may be made on schedule or certain crew members will continue to work until the operation is completed. A barge loading or cleaning operation can normally be accomplished within a conventional 8-hour workday.

The occupational exposure data for this exposure category are summarized in Table V.2. In the aggregate, these data reflect operations that result in exposures to single chemicals as well as mixtures of several chemical

TABLE V.2. SINGLE SHIFT OR OPERATIONS ORIENTED EXPOSURES

SEQUENCE NO.	SAMPLE NO.	CHEMICAL	SAMPLING RATE (L/min)	SAMPLING DURATION (min)	W_c (µg)	η	T (°C)	P (mm Hg)	RH (%)	EXPOSURE CONC. (ppm)	TLV-TWA (ppm)	TLV-STEL (ppm)	TLV-C (ppm)	COMMENTS
1	DD-1	MAL(Skin)	0.156	58	163.4	0.95	24.2	760	59	14	200	250	--	BARGE LOADING, INITIAL TANK SAMPLING, EMPLOYEE #1
	DD-3	↓	0.154	12	560.0	0.95	32.0	760	37	249	↓	↓	--	BARGE LOADING, TANK TOP-OFF, EMPLOYEE #1, OPEN GAUGING
	DD-5	↓	0.154	20	120.9	0.95	32.0	760	37	32	↓	↓	--	BARGE LOADING, FINAL TANK SAMPLING, EMPLOYEE #1
	DD-2	↓	0.149	56	223.7	0.95	24.2	760	53	21	↓	↓	--	BARGE LOADING, INITIAL TANK SAMPLING, EMPLOYEE #2
	DD-4	↓	0.158	21	169.0	0.95	32.0	760	37	42	↓	↓	--	BARGE LOADING, FINAL TANK SAMPLING, EMPLOYEE #2
2	EX-16	TCE	0.200	122	563	0.937	20.9	760	85	4.5	350	450	--	SAMPLE NOS. EX-16 THROUGH DW-8 REPRESENT FOUR SEQUENTIAL SAMPLES COLLECTED ON ONE EMPLOYEE DURING REPETITIVE GAUGING ROUNDS. ALL GAUGING INCLUDING TOP-OFF PERFORMED THROUGH RESTRICTED SYSTEMS
		TCL	↓		117.6	1.19	↓	↓	↓	0.7	50	150	--	
		TTE	↓		190	0.91	↓	↓	↓	1.2	50	--	--	
		STY	↓		57.7	0.68	↓	↓	↓	0.8	50	100	--	
	DW-1	TCE	0.200	116	1019	↓	26.4	↓	65	8.6	↓	↓	↓	
		TCL	↓		26.1	↓	↓	↓	↓	0.2	↓	↓	↓	
		TTE	↓		3643	↓	↓	↓	↓	25.6	↓	↓	↓	
		STY	↓		ND	↓	↓	↓	↓	ND	↓	↓	↓	
	DW-6	TCE	0.194	126	1127	↓	↓	↓	65	9.0	↓	↓	↓	
		TCL	↓		13.1	↓	↓	↓	↓	0.1	↓	↓	↓	
		TTE	↓		1088	↓	↓	↓	↓	7.2	↓	↓	↓	
		STY	↓		ND	↓	↓	↓	↓	ND	↓	↓	↓	
	DW-8	TCE	0.194	46	201	↓	24.2	↓	58	4.4	↓	↓	↓	
		TCL	↓		ND	↓	↓	↓	↓	ND	↓	↓	↓	
		TTE	↓		ND	↓	↓	↓	↓	ND	↓	↓	↓	
		STY	↓		ND	↓	↓	↓	↓	ND	↓	↓	↓	
	UCC-114	TCE	0.198	121	778	↓	20.9	↓	85	6.3	↓	↓	↓	SAME AS SAMPLE NOS. EX-16 THROUGH DW-8 EXCEPT FOR SECOND TANK GAUGER
		TCL	↓		39.2	↓	↓	↓	↓	0.3	↓	↓	↓	
		TTE	↓		271.9	↓	↓	↓	↓	1.8	↓	↓	↓	
		STY	↓		155.6	↓	↓	↓	↓	2.2	↓	↓	↓	
	DW-5	TCE	0.198	116	1046	↓	26.4	↓	65	8.9	↓	↓	↓	
		TCL	↓		39.2	↓	↓	↓	↓	0.3	↓	↓	↓	
		TTE	↓		2773	↓	↓	↓	↓	19.7	↓	↓	↓	
		STY	↓		ND	↓	↓	↓	↓	ND	↓	↓	↓	
	DW-4	TCE	0.195	116	429	↓	26.4	↓	65	3.7	↓	↓	↓	
		TCL	↓		ND	↓	↓	↓	↓	ND	↓	↓	↓	
		TTE	↓		229.4	↓	↓	↓	↓	1.7	↓	↓	↓	
		STY	↓		ND	↓	↓	↓	↓	ND	↓	↓	↓	
	DW-9	TCE	0.195	48	ND	↓	24.2	↓	58	ND	↓	↓	↓	
		TCL	↓		↓	↓	↓	↓	↓	↓	↓	↓	↓	
		TTE	↓		↓	↓	↓	↓	↓	↓	↓	↓	↓	
		STY	↓		↓	↓	↓	↓	↓	↓	↓	↓	↓	

NOTES:
1. W_c = weight of analyte corrected for blank
2. NM = not measured
3. ND = not detectable

TABLE V.2. SINGLE SHIFT OR OPERATIONS ORIENTED EXPOSURES (CONTD)

SEQUENCE NO.	SAMPLE NO.	CHEMICAL	SAMPLING RATE (L/min)	SAMPLING DURATION (min)	W_c (µg)	η	T (°C)	P (mm Hg)	RH (%)	EXPOSURE CONC. (ppm)	TLV-TWA (ppm)	TLV-STEL (ppm)	TLV-C (ppm)	COMMENTS
3	SB-14	BNZ	0.187	89	189	0.867	19.6	760	80	3.6	10	25	--	DECKSIDE, TANK CLEANING CREW, BNZ IN GASOLINE
	SB-20	BNZ	0.196	387	348	0.867	23.8	760	80	1.6	10	25	--	DECKSIDE, TANK CLEANING CREW, BNZ IN GASOLINE
4	SB-1	BNZ	0.202	194	576	0.867	18.7	760	83	5.2	10	25	--	PERIODIC OPEN TANK GAUGING, EMPLOYEE #1, BNZ IN GASOLINE
	SB-2	↓	0.188	165	207	0.867	19.5	↓	70	2.4	↓	↓	--	PERIODIC OPEN TANK GAUGING, EMPLOYEE #2, BNZ IN GASOLINE
	SB-3	↓	0.171	254	940	0.867	25.6	↓	52	7.8	↓	↓	--	PERIODIC OPEN TANK GAUGING PLUS TOP-OFF OF FOUR TANKS, EMPLOYEE #2, BNZ IN GASOLINE
	SB-4	↓	0.172	232	557	0.867	27.0	↓	49	5.1	↓	↓	--	PERIODIC OPEN TANK GAUGING, EMPLOYEE #1, BNZ IN GASOLINE
	SB-5	↓	0.190	201	670	0.867	22.8	↓	65	6.3	↓	↓	--	PERIODIC OPEN TANK GAUGING PLUS TOP-OFF OF THREE TANKS, EMPLOYEE #2, BNZ IN GASOLINE
5	SB-12	BNZ	0.186	81	37	0.867	17.8	760	72	0.9	10	25	--	DECK CREW, PRODUCT DISCHARGE, BNZ IN GASOLINE, EMPLOYEE #1
	SB-13	BNZ	0.208	225	23	0.867	17.8	760	72	0.2	10	25	--	DECK CREW, PRODUCT DISCHARGE, BNZ IN GASOLINE, EMPLOYEE #2
6	SS-1	MEK	0.198	77	< 1	0.89	33.4	760	58.5	<< 1	200	300	--	SEQUENTIAL SAMPLES ON ONE DECK CREW MEMBER, INTERMEDIATE PHASES OF MEK LOADING
	SS-2	↓	0.198	97	< 20	↓	33.4	↓	58.5	< 0.5	↓	↓	--	
	SS-10	↓	0.201	82	110	↓	33.4	↓	58.5	2.6	↓	↓	--	SEQUENTIAL SAMPLES ON SECOND DECK CREW MEMBER, INTERMEDIATE PHASES OF MEK LOADING
	SS-11	↓	0.201	60	< 20	↓	33.4	↓	58.5	< 0.6	↓	↓	--	
	SS-30	↓	0.198	67	55	↓	29.9	↓	70	1.6	↓	↓	--	TWO DECK CREW MEMBERS, FINAL STAGES OF MEK LOADING INCLUDING LINE BLOWING
	SS-40	↓	0.201	52	108	↓	29.9	↓	70	4.0	↓	↓	--	
7	PS-7	EAL	0.099	261.5	24.6	0.02	26.1	763.9	NM	25	1000	--	--	RESTRICTED TANK GAUGING DURING LOADING, THREE EMPLOYEES
		TOL(Skin)			60.2	0.881		↓	↓	0.7	100	150	--	
		MEK			ND	0.144		↓	↓	ND	200	300	--	
	PS-8	EAL	0.074	133.3	22.9	0.02	25.4	↓	↓	61	1000	--	--	
		TOL(Skin)			10.9	0.881		↓	↓	0.3	100	150	--	
		MEK			ND	0.144		↓	↓	ND	200	300	--	
	PS-9	EAL	0.264	255.5	49.9	0.02	26.1	↓	↓	20	1000	--	--	
		TOL(Skin)			97.9	0.881		↓	↓	0.4	100	150	--	
		MEK			2.6	0.144		↓	↓	0.1	200	300	--	

NOTES: 1. W_c = weight of analyte corrected for blank
2. NM = not measured
3. ND = not detectable

TABLE V.2. SINGLE SHIFT OR OPERATIONS ORIENTED EXPOSURES (CONTD)

SEQUENCE NO.	SAMPLE NO.	CHEMICAL	SAMPLING RATE (L/min)	SAMPLING DURATION (min)	W_c (µg)	n	T (°C)	P (mm Hg)	RH (%)	EXPOSURE CONC. (ppm)	TLV-TWA (ppm)	TLV-STEL (ppm)	TLV-C (ppm)	COMMENTS
8	UCC-115	CRF	0.200	94.5	2250	0.51	22	760	71	47	10	50	--	TANK CLEANING, PRODUCT STRIPPING AND VENTILATION, EMPLOYEE NO. 1
	UCC-112	↓	0.200	33	344	0.51	22	↓	NM	21	↓	↓	↓	TANK CLEANING, VENTILATION, EMPLOYEE NO. 1
	DW-14	↓	0.200	5	ND	0.51	26	↓	NM	ND	↓	↓	↓	TANK ENTRY, EMPLOYEE NO. 1 } See Scenario
	DW-12	↓	0.196	3	ND	0.51	26	↓	NM	ND	↓	↓	↓	TANK ENTRY, EMPLOYEE NO. 2 } Description
9	VF-5	MEK	0.201	172	77.8	0.801	28.8	760	72	0.92	200	300	↓	PERIODIC TANK GAUGING DURING LOADING
		EPC(Skin)	↓	↓	40.0	0.679	28.8	↓	72	0.47	2	5	↓	RESTRICTED GAUGING ON MEK AND EAL
		EAL	↓	↓	7.0	0.68	28.8	↓	72	0.16	1000	--	↓	CLOSED GAUGING ON EPC
	VF-6	XLO,M,P (Skin)	0.197	106	26	0.992	25.6	760	83	0.28	100	150	↓	RESTRICTED TANK GAUGING DURING LOADING
10	VF-14	MEK	0.204	202	9	0.801	18.3	760	90	0.09	200	300	↓	
		EPC(Skin)	↓	↓	11	0.679	↓	↓	↓	0.10	2	5	↓	PREDISCHARGE ULLAGE AND PRODUCT *TEMPERATURE MEASUREMENTS*
		EAL	↓	↓	22	0.68	↓	↓	↓	0.41	1000	--	↓	
		XLO,M,P (Skin)	↓	↓	46	0.992	↓	↓	↓	0.25	100	150	↓	
	VF-12	MEK	0.194	110	40	0.801	19.2	760	85	0.78	200	300	↓	
		EPC(Skin)	↓	↓	21	0.679	↓	↓	↓	0.38	2	5	↓	
		EAL	↓	↓	77	0.68	↓	↓	↓	2.76	1000	--	↓	RESTRICTED TANK GAUGING DURING DISCHARGE
		XLO,M,P (Skin)	↓	↓	20	0.992	↓	↓	↓	0.21	100	150	↓	
12	VF-15	BNZ	0.194	141	12	0.965	28.6	760	59	0.14	10	25	↓	RESTRICTED TANK GAUGING; BALLASTING INTO GASOLINE CARGO TANKS
14	VF-18	BAN	0.208	176	423	0.859	19.7	760	67	4.40	--	--	50	
	VF-20	MEK	0.208	93	ND	0.801	20.6	760	85	ND	200	300	--	RESTRICTED TANK GAUGING DURING DISCHARGE; TWO CREWMEN
		EPC(Skin)	↓	↓	12	0.679	↓	↓	↓	0.12	2	5	↓	
		EAL	↓	↓	20	0.68	↓	↓	↓	0.80	1000	--	↓	
		XLO,M,P (Skin)	↓	↓	ND	0.992	↓	↓	↓	ND	100	150	↓	

NOTES:
1. W_c = weight of analyte corrected for blank
2. NM = not measured
3. ND = not detectable

vapors. The data are indexed by a sequence number. For each sequence number, a work activity/operation description is included in this subsection. Standard atmospheric pressure was assumed during sampling when actual pressure was not available. Relative humidity determinations were made where they were compatible with the sampling and work documentation activities.

Sequence No. 1

The loading of a methanol barge was accomplished by two workers that will be referred to as Worker No. 1 and Worker No. 2. Worker time on deck was minimal. There were three principal boardings for the purpose of collecting initial and final product samples and final tank top-off. At all other times during the loading, both individuals remained in the dock house. A description of work activities is indicated below.

METHANOL BARGE LOADING

TIME	ELAPSED TIME (min)	EVENT
0919	0	Worker No. 1 boards barge to open tank hatches and deck valves.
0925	6	Worker No. 1 disembarks to dock house.
0930	11	Standby in dock house for delivery of product from tank farm.
0952	33	Loading of tank heels commences.
0953	34	Worker No. 1 boards barge; Worker No. 2 in dock house.
1007	48	Heel loading terminates.
1008	49	Worker No. 2 boards barge to collect liquid heel samples from three tanks and is assisted by Worker No. 1
1017	58	Sample collection completed, and both workers disembark to dock house. Samples sent to laboratory for purity analysis.
1103	104	Product purity verified; pumping resumed. All personnel in dock house.
1351	272	Worker No. 1 boards barge and commences to top-off all three tanks.
1403	284	Worker No. 1 disembarks.
1419	300	Worker No. 2 boards barge, disconnects hoses at barge manifold, and prepared to collect final product sample
1420	301	Worker No. 1 disconnects loading hoses on dock, boards barge and assists Worker No. 2 with sample collection.
1440	321	Sample collection and loading complete; workers disembark to dock house.

Since Worker No. 2 performed the actual collection, his exposure level is consistently higher than that of the assistant (Worker No. 1). The exposure concentrations for both workers at the final sampling are higher, as expected, than at the initial product sampling. The final sampling reflects the discharge of a rich vapor blanket, whereas the initial sampling reflects a nearly empty tank and the arrival concentration. The sampling intervals for exposure monitoring are given below.

PERSONAL SAMPLING FOR METHANOL

TASK	WORKER NO.	SAMPLE NO.	TIME START	TIME STOP
Initial Tank Sampling	1 2	DD-1 DD-2	0919 0921	1017 1017
Tank Top-off	1	DD-3	1351	1403
Final Tank Sampling	2 1	DD-4 DD-5	1419 1420	1440 1440

Sequence No. 2

Restricted tank gauging systems differ from the open gauging methods that were described in the previous section. The restricted system is basically a small diameter sounding tube or standpipe that extends from roughly two feet above the deck, through the weather deck and terminates approximately one foot above the tank bottom. Because this tube penetrates the product liquid surface during all but the initial stages of loading, there is a minimal chemical surface area in the tube for product evaporation. Thus, vapor discharge concentrations and flow rates are lower than in open gauging systems. The exposure data for this sequence and subsequent restricted gauging sequences clearly indicates that this gauging system results in lower exposure levels than does the open gauging method.

This scenario includes restricted tank gauging by two crew members during loading of four products. The time frame for loading of each tank is summarized below.

TANK NO.	CONTENTS	LOADING TIME START	STOP	RESUME	FINISH
2A	Perchloroethylene	0820	0830	1112	1400
2F	Perchloroethylene	0820	0830	1115	1400
2B	Perchloroethylene	0820	0830	1115	1235
2C	Trichloroethylene	0720	0730	0820	0909
2E	Trichloroethane	0705	0715	1008	1245
3A	Styrene	0520	0535	0900	>1400*
3B	Styrene	0520	0535	0900	>1400*
4A	Trichloroethane	0705	0715	1125	1525

*Loading rate reduced to correct trim.

In general, each of these two crew members gauged product ullage on each tank in a regular rotation. This gauging, which included tank top-off, was performed by inserting a Lufkin tape into the sounding tube as shown in Figure V.3. Approximately 20 to 30 seconds was needed to gauge each tank; during this time the breathing zone was two to three feet directly above the end of the standpipe. Both crew members worked independently; roughly 10 minutes separated the gauging round of one crew member from the gauging round of the second crew member.

The styrene tanks, which were adjacent to the chlorinated hydrocarbon tanks, had been retrofitted with a vapor return system. Simplistically, this system consisted of aluminum housings that rested on the riser plates of butterworth openings on each tank. Attached to these castings were flexible conduits that manifolded together into a common line that returned the vapor to shore via an air eductor. The principal point of interest is that the flex-lines had leaks and the housings were not positively seated on the riser plates. These conditions permitted escape of styrene vapors into the tank gauging area. All product tanks were loaded with the expansion trunk hatch covers cracked.

During the nearly seven-hour monitoring period, one crew gauged the perchloroethylene tanks a total of 10 times, styrene tanks 10 times, trichloroethane tanks 15 times and trichloroethylene tank twice. This encounter frequency was also representative of the second crew members gauging activities.

FIGURE V.3. EXAMPLE OF RESTRICTED TANK GAUGING THROUGH A SOUNDING TUBE

Sequence No. 3

Normally, with clean petroleum products such as gasoline, there is not a recurring need to clean product tanks on every ballast voyage. In this sequence, nine gasoline tanks were cleaned in preparation for hotwork on the hull exterior during the next docking, and the exposure samples were collected on the Chief Mate.

The Chief Mate has responsibility for all tank cleaning. Because of this responsibility, he was present continuously during the cleaning of seven tanks with the exception of a 4-hour navigation watch. The work unit consisted of the C/M, an A/B, and an O/S. The A/B's and the O/S's rotated watches with their counterparts so that no individual A/B or O/S was present continually during tank cleaning.

The tank cleaning operation can be characterized by major work tasks, but the duration and frequency of the elements of these work tasks may vary in a random fashion. The following scenario is a composite of the work activities that were observed during the tank cleaning period.

- The initial activity involved hookup of the water hoses to the main supply line and the washing head. The blower was positioned near the butterworth opening that would be used.

- The expansion trunk hatch was opened, as was the butterworth opening for the first drop of the washing machine.

- The wash water was then turned on.

- At this point, the Chief Mate's position was at the open expansion trunk. The other two members of the work crew may man the deck valve that controls pump discharge, or one member may be on that valve with the other member on the water supply valve.

- During the initial stages of washing, it is important to balance the water inflow rate with the water discharge rate to yield a liquid free surface level on the tank bottom slightly above the inlet of the product discharge nozzle. If the liquid surface is too high, the pump will remove only water since the gasoline rides on the water surface. If the liquid level is too low, the pump may cavitate and lose suction head.

- To achieve this balancing, the C/M used a flashlight (night) or mirror (day) at the open-expansion trunk to view the location of the liquid surface. This viewing was accomplished, generally, with the neck resting on the expansion trunk rim and the head over the open trunk. He remained in this position for two to three minutes, during which time he gave hand signals to the A/B and O/S to indicate the amount and direction of movement of deck valve or water supply valve. The C/M may alternate between two tanks being washed, spending two to three minutes viewing into each tank trunk. The time duration between successive viewings is a random variable that is governed by his experience, the distance between tanks, and the indicated need for additional balancing.

- Characterization of the C/M exposure presents some practical problems. Lapel-mounted samplers are an approximation to the breathing zone. With his head in the indicated position, the sampler is outside of the expansion trunk and is not exposed to the breathing zone atmosphere. Shirts are frequently not worn during warm weather, and this presents an additional monitoring problem. These considerations are important because the total vapor concentrations are significant during washing.

- After the water balance had been set, the three crew members worked together to lower the washing head according to the washing plan and switch the head to the next deck opening for the second drop.

- During the intermediate stages of washing a tank, there is considerably less emphasis on viewing the liquid surface through the expansion trunk. The work crew tended to stand upwind of the expansion trunk during this time.

- Toward the end of washing, the viewing frequency increases, but viewing duration decreases. This increased activity by the C/M is needed to ensure that the maximum amount of liquid is stripped from the tank before gas freeing is initiated. A portion of this activity was conducted after the wash water was turned off. Viewing durations ranged from 22 seconds to 70 seconds, with an average of 54 seconds. In between viewings, the C/M may take charge of discharge valve adjustments.

- The A/B and O/S normally do not take part in the tank viewing activity. Their potential for high concentration exposure is reduced significantly. Their low level exposure is dictated by whether the deck valves are downwind or upwind of the expansion trunk.

- At the conclusion of washing, the C/M, A/B, and O/S remove the washing hoses, install the blower in a deck opening, attach the water hose to the blower, and turn the water on.

- After ventilation is initiated, the three-man work crew may begin a washing operation on another tank. The above description of work activities would be applicable to all tank washings.

- The C/M continues his in-tank observation during ventilation. He assumes the previously described position at the expansion trunk or he lays on the deck to view through an open butterworth plate using a flashlight or mirror. The purpose of this viewing is to observe the status of the residual liquid and the state of dryness of the tank walls. The frequency and duration did not appear to be predictable. In one instance, four viewings were conducted within a five-minute period, with an average viewing time of 39 seconds. Earlier, three viewings were conducted

AD-A128 537 INVESTIGATION OF THE HAZARDS POSED BY CHEMICAL VAPORS RELEASED IN MARINE..(U) SOUTHWEST RESEARCH INST SAN ANTONIO TX W J ASTLEFORD ET AL. APR 83 DOT-CG-904571-A 4/5

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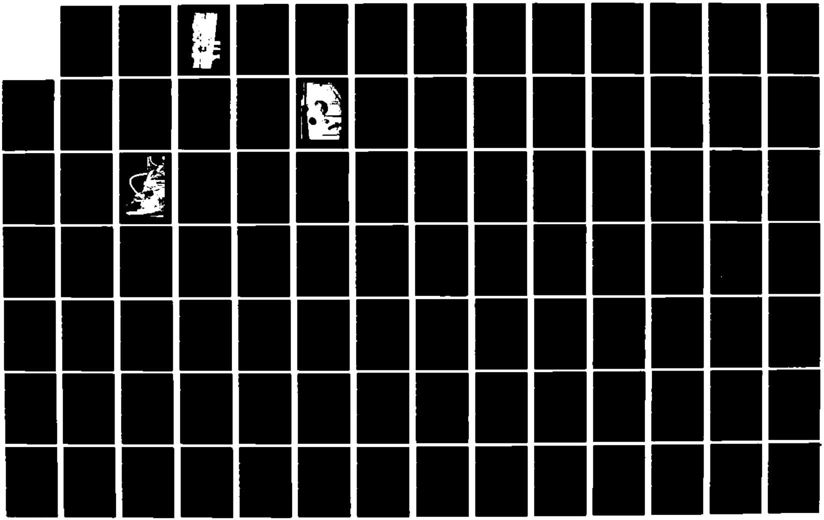
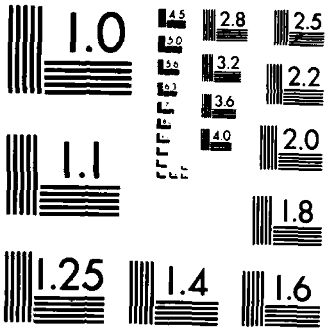



1.0
4.5
5.0
5.6
6.3
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

in roughly two minutes with an average viewing time of 20 seconds.

- The potential for exposure during these viewings is greatest during the initial stages of ventilation.

Sequence No. 4

This sequence is concerned with open tank gauging and exposure to the benzene fraction in motor gasoline. The entire ship was loaded with three grades of gasoline.

Normally, open gauging is accomplished through the ullage port on the expansion trunk. On this vessel, the gauging was performed through a tube that had the appearance of a restricted gauging system, but the tube terminated at deck level and did not penetrate into the tank. Thus, this tube constitutes an open gauging system that poses the same exposure potential as the more conventional open gauging method. Figure V.4 illustrates this method of open gauging at tank top-off.

The exposures in this sequence were collected on three Mates whose responsibilities included periodic ullage gauging of the tanks being loaded and tank top-off. Where more than one sample is indicated for a given employee, the samples were collected on consecutive deck watches.

Routine or periodic gauging was performed with a Lufkin tape inserted into the tube, and it necessitated direct viewing into the open tube. The breathing zone was immersed in the vapor discharge plume approximately two to three feet above the discharge point.

This periodic gauging was a definite pattern that is characterized by the "gauging round." The gauging round consists of sequentially measuring and recording the ullages on all tanks that are being loaded. Initially, the gauging rounds are performed on almost an hourly basis. The ullage measurements were used to calculate loading rates and to estimate the times to complete tank filling. The frequency of periodic gauging increased as the

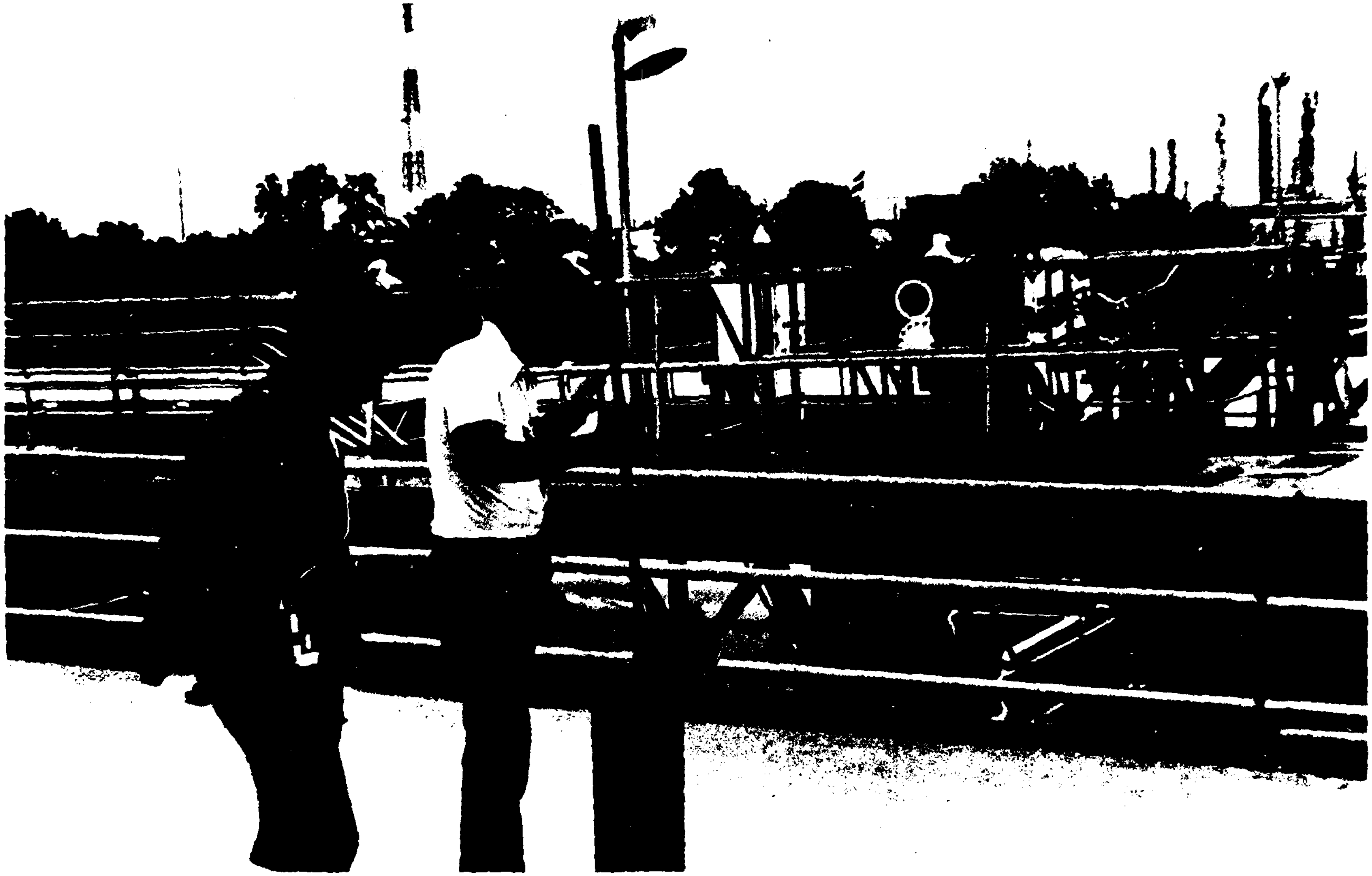


FIGURE V.4. EXAMPLE OF OPEN TANK GAUGING AT TOP-OFF. GAUGING TUBE RESEMBLES A RESTRICTED GAUGING SYSTEM, BUT IT TERMINATES AT THE WEATHER DECK time approached to top off selected tanks. In this case, the emphasis was placed on the tanks that were nearly full, and the other tanks were temporarily eliminated from the gauging round. A summary of the observed periodic gauging frequency is tabulated below. The elapsed time for a gauging round is a function of the number of tanks to be gauged and the distances between the gauging ports. Within a gauging round, each ullage measurement takes approximately one minute, which includes walking time between tanks. Actual gauging time is also variable, but it is roughly 30 seconds per tank. Interspersed between gauging rounds is random gauging of individual tanks.

FREQUENCY OF PERIODIC GAUGING ROUNDS

CLOCK TIME START	NO. OF TANKS	APPROXIMATE ELAPSED TIME (min.)
0030	11	10
0100	3	5
0130	9	7
0200	3	5
0309	11	16
0500	3	10
0900	3	5
1000	3	10
1230	4	4
1311	2	2
1321	2	2
1330	4	4
1334	3	3
1340	9	9
1355	2	2
1415	6	5
1615	3	3
1800	3	3

A single product may eventually be loaded into as many as nine tanks. Normally, the product flow rates are adjusted so that the wing tanks (port and starboard tanks) are filled first, but at different rates. This staggering of delivery rates eliminates the possibility that two tanks will top off at identically the same time. Top-off of a single tank requires two workers. The Mate gauged the tank using a crucifix, and the gauging frequency was every minute initially and increased to every 15 seconds as the final ullage was approached. The Mate was assisted by an A/B or an O/S who manned the deck valves. Either of these two workers closed the valve to reduce product flow in response to the Mate's directions. When two wing tanks were being topped, the Mate gauged the tank that would finish first while the A/B gauged the other wing tank. When the first wing tank had been filled, the Mate relieved the A/B on the other tank. The O/S's function was to again man the delivery valves to each tank. The duration of crucifix gauging on selected tanks is summarized below. The duration of final top-off gauging was quite variable and ranged from 5 to 37 minutes per tank.

DURATION OF CRUCIFIX GAUGING DURING TANK TOP-OFF

TANK NO.	CLOCK TIME/DURATION (min.)	INDIVIDUAL INVOLVED
5S	0928-0933 = 5 min.	3M
5P	0928-1005 = 37 min.	AB
1S	1045-1115 = 30 min.	3M
1P	1045-1118 = 33 min.	AB
2S	1250-1300 = 10 min.	2M
2P	1250-1307 = 17 min.	AB
3S	1420-1445 = 25 min.	2M
3P	1420-1447 = 27 min.	AB
	1447-1457 = 10 min.	2M
4S	1519-1526 = 7 min.	2M
4P	1519-1526 = 7 min.	AB

During both periodic gauging and top-off, no consistent attempts were made to stand upwind or crosswind of the vapor plume so as to minimize exposure. Consequently, there were direct, downwind exposures to the product vapors. Neither respiratory protection nor goggles were worn during gauging.

Sequence No. 5

During product discharge, ambient air is ingested into the tank. If the discharge proceeds without interruption, vapor concentrations at the ullage ports are insignificant compared to the levels during loading. After the pumps are shut down, either because discharge is completed or there is a need to correct the ship's trim, ullage port concentrations will rise as a result of product evaporation and the mechanisms of molecular diffusion and free convection that work to equilibrate ullage space vapor levels. Therefore, vapors can be passively discharged on deck.

In this sequence, the occupational exposures of two unlicensed crew members were monitored for the benzene fraction in gasoline during product discharge. Their responsibilities, which were substantially the same, were to man the deck valves on each tank that control bulk discharge rate and the stripping suction. These valves are located several feet from the expansion trunk. As they do not visually site into the tank, their exposures reflect the cumulative effect of the deck environment and cannot be associated with high level vapor sources.

Sequence No. 6

The work scenario during loading of MEK into Tank 7CP was considerably different from the scenarios that were observed on previous loadings. The entire loading was under the control of the tank farm. As such the termination of product delivery was based upon flow totalizers in the tank farm metering station. This loading method contrasts with the more common procedure where the ship has control of the loading including the signal for termination of delivery. In the "ship stop" loading method, there is more emphasis on tank gauging particularly as the tank is topped-off to the final ullage. Conversely, in this "shore stop" method of loading the MEK, tank gauging does not follow an observable pattern, and there were no ullage readings taken during the latter stages of loading. In addition, the tank was loaded to only 80 percent of capacity; thus, the majority of the vapor blanket above the liquid remained in the tank and was not discharged to the atmosphere at the end of loading.

The bulk of the MEK was loaded during the 6-hour period from 1200 to 1800 hours. On four occasions, the tank was either manually gauged or the liquid level was sited visually by the Ordinary Seaman on duty. The duration of these activities were as follows:

TIME	DURATION	ACTIVITY
1346	10 sec	view liquid with mirror
1358	90 sec	manually gauge ullage with tape
1437	3 sec	view liquid with mirror
1456	37 sec	manually gauge ullage with tape

The loading overlapped two deck watches. The individuals that were monitored were selected on the basis that their work stations included the deck area of the tank being loaded with MEK. Because this was a "shore stop" loading, the majority of their time was devoted to activities that were unrelated to Tank 7CP. The first four exposure samples in this sequence were collected on two crew members that worked on the port side of the ship. Two additional crew members (SS-30 and SS-40) worked on the starboard side of the vessel during the final stages of loading which included blowing of the loading lines with nitrogen from the dock. Their exposure levels reflect a port-starboard wind that diluted and transported the vapors to their work area.

Sequence No. 7

This sequence includes restricted tank gauging of two product tanks by three crew members. Each individual performed his duties independently of the other crew members. Two of the exposure samples were collected over a 4-hour watch, and the third sample was collected during the latter half of the shift. The actual gauging method and the equipment involved were described in a previous sequence.

During the monitoring periods, each individual did not perform gauging rounds; the majority of their deck watch time was spent upwind of the loading tanks in the vicinity of the manifold with brief excursions to gauge a tank and then return to the manifold area.

MEK and TOL were the products being loaded. EAL was included in the analysis because this chemical had been carried in the tank in which MEK was being loaded.

Sequence No. 8

This sequence involves the cleaning of one tank on a 3-tank chloroform barge. The cleaning procedure consisted of a 67-minute stripping operation followed by a 64-minute ventilation period. Stripping of residual cargo was accomplished using a hand-held vacuum line inserted through the open hatch and extending into the pump sump. Two workers were involved in this operation. At the beginning of stripping, the residual liquid depth on the tank bottom was approximately 0.125 inches as determined by using a dipstick from the deck. At the end of stripping, the residual depth could not be measured; the tank bottom had the appearance of wet sidewalk, and the liquid layer was estimated to be 0.1 cm or less. The presence or amount of unstripped cargo in the pump sump could not be determined.

The tank was then gas freed using a Coppus CP-20 blower on the aft Butterworth opening plus auxiliary ventilation through the product discharge line into the pump sump. Vapors were exhausted through the open hatch and also through an open gauging standpipe during the latter half of gas freeing. The latter half of the gas freeing was characterized by one worker on deck at the open hatch. His primary presence on deck was to monitor the odor of the discharged vapors. The termination of odor was his signal that the tank had been gas freed and that it could now be tested for man-entry by responsible marine department personnel. This procedure is faulty because, in the case of chloroform, the odor threshold, (205-307 ppm per Verschueren) is substantially above the ACGIH/TWA-TLV and STEL-TLV of 10 and 50 ppm, respectively. The tank was subsequently tested for O_2 and combustible gas levels using a combination O_2/CGI and a dropline and was found to be "acceptable". The zero combustible gas reading is misleading because (1) chloroform is non-combustible and (2) the instrument that was used is based upon the principle of catalytic combustion on a wire wound filament and the corresponding increase in electrical resistance of the wire at elevated tamperatures. Thus, the instrument is inappropriate for use with chloroform, and zero readings would be obtained regardless of concentration level.

Following marine department approval, two workers entered the tank for three and five minutes, respectively, which included descent and ascent times. Entry activities consisted of a brief inspection of tank surfaces; no cleanup activities were conducted. The workers did not have respirators available during entry, and there was no standby worker on deck.

Chloroform concentrations at the open hatch during stripping, as measured with an OVA, are summarized below:

TIME (min)	CONCENTRATION (ppm)
0	26,500
5	26,500
10	68,000
15	62,000
21	39,000
29	39,000
31	34,500
36	39,000
41	39,000
48	34,500
54	41,000
66	30,000

The concentrations are reasonably constant in time with the exception of the excursion at 10 to 15 minutes into the stripping. This fluctuation is believed to be the result of agitation of the sump contents by the stripping line as the workers attempted to ensure that the suction inlet was actually positioned in the sump. This positioning was accomplished by feel since the inlet position could not be observed visually.

It is interesting to note that termination of ventilation at 64 minutes was based on the absence of vapor odor. The discharge concentration, measured with the OVA, was less than 200 ppm which in turn is slightly less than the odor threshold for chloroform.

Employee No. 1 did receive detectable exposures during stripping and ventilation. These exposures are quite probably lower than the actual exposures that were received for the following reason. The OSHA/NIOSH representative breathing zone sample is obtained with the collector inlet located on the shirt lapel not at the nose. The work pattern of Employee No. 1 included frequent visual sightings into the tank. During these sightings, his head was over the hatch while his chin rested on the hatch riser. In this position, the collector inlet was outside the hatch and was shielded from the high concentration exhaust.

The exposure levels during tank entry were not detectable. The explanation is that the exposure time was insufficient to yield an adsorbed weight greater than the detection limit. This situation may also have been influenced by a sampling rate that was less than the recommended rate of 1.00 Lpm. Even at the recommended rate, the entry duration would not have satisfied the sample volume requirements.

Following the brief tank entry by the barge workers, SwRI personnel entered the tank with an OVA and appropriate respiratory protective devices. Another SwRI team member stood watch at the open tank hatch. The measured chloroform concentrations were:

- 57-65 ppm from top to bottom of the tank
- 49-65 ppm at breathing level on the tank bottom
- 820-2400 ppm above rust piles in the pump sump.

As was noted above, the sampling time for the in-tank occupational exposures was insufficient to adsorb a weight of chloroform vapor that exceeded the GC threshold of sensitivity. The in-tank OVA data, however, suggest the likelihood that both workers received chloroform exposures that exceeded the ACGIH TLV-STEL.

Sequence No. 9

This sequence involves exposure monitoring of one crew member on two consecutive deck watches during product loading. Work activities during collection of the first sample, VF-5, included restricted tank gauging of two Subchapter D chemicals, MEK and EAL; and closed gauging of EPC, which is a Subchapter O chemical. The equipment and techniques that are used in restricted gauging have been described earlier.

For certain hazardous materials, the USCG specified minimum equipment or procedure requirements for ullage gauging and vapor venting during loading. EPC is a chemical that requires closed gauging; vented vapors must be released at a minimum distance of B/3 (one-third the width of the ship's beam) above the deck. With a closed gauging system, the ullage can be read without directly exposing the tankerman to vented tank vapors; in this example, the closed system consisted of a sealed, flotation tape device.

The exposure levels for MEK and EAL on Sample No. VF-5 are consistent with the concentrations that were for other restricted gauging activities. The EPC concentration represents the contribution to the deck work environment that results from EPC vapor discharge at elevation and the subsequent atmospheric dilution.

The second sample, VF-6, represents the integrated exposure to a mixed xylenes chemical during restricted gauging on the subsequent deck watch.

Sequence No. 10

The sequence of work activities during discharge is initiated with the hookup of the loading hoses by the dock crew. While this is being performed, one of the dock inspectors comes aboard to obtain tank samples, initial ullage readings and tank temperatures, for each of the product tanks. This activity is accomplished in the presence of the mate on watch.

Sample No. VF-14 represents the integrated exposure of this mate as he accompanied the dock inspector. The sampling duration included not only the contact time with the indicated chemical tanks but also the time needed to perform the same operations on the majority of the tanks that contained proprietary solvents and gasolines. Similar operations were conducted on an n-butanol tank, but the exposure sample was not analyzed for this chemical because it required a different desorption procedure than did the four indicated chemicals.

As during loading, restricted tank gauging became the dominant work activity once discharging operations were underway. Gauging rounds were performed in the same way as observed for loading. The personnel involved in gauging consisted of the pumpman and the mate. In some cases, the AB on watch was allowed to take ullage measurements. Sample No. VF-12 represents the pumpman's exposure during restricted discharge ullage gauging. The four chemicals on this sample are the same as on Sample No. VF-14.

As anticipated, the exposure to chemical vapor was [illegible]w during gauging or discharging tanks because of the inflow of fresh a[illegible]o the tanks as the product level drops. Elevated chemical concentrati[illegible] levels were measured with an OVA on deck during discharge, and the source was traced to a number of leaking drain valves located in various product lines. During product discharge, the line pressure is much higher than during product loading. As opposed to seeing near atmospheric pressures during loading, the product line pressures reach upwards to 100 psig because they are just downstream of the cargo pump discharge. The leaks from the drain valves fall to the deck where they may accumulate and evaporate. The mate on watch indicated that leaks are typical during discharge. They are usually contained by placing a coffee can under the leaking valve. Accumulation of raw product on the deck could contribute substantially to localized high vapor concentrations and potentially the breathing environment. The measured exposure levels suggest that in this case, the leaks, while important, did not result in a quantitative increase in the exposure during the pumpman's gauging activities. Rapid evaporation and atmospheric dilution probably negated a higher exposure level.

Sequence No. 11

This sequence is a continuation of the restricted tank gauging during discharge aboard the same vessel that was represented in Sequence No. 10.

As mentioned previously, gauging rounds may overlap; two crew members may each begin an independent round but the rounds are separated in time by roughly one-half hour.

Sample No. VF-20 was collected on the Third Mate who gauged the same tanks as the Pumpman (Sample No. VF-12) in the previous sequence. The consistent trend toward low exposure levels with restricted tank gauging is again apparent in Sample No. VF-20.

Sample No. VF-18 was collected on the same Third Mate when n-butanol and other products were discharged at a second terminal. His gauging rounds included the butanol tank as well as the other tanks that were being discharged. The exposure level was low, but it was slightly higher than would be expected based on vapor pressure considerations and the other restricted gauging results. The reason is not conclusive, but on-deck leakage from product line valving may have contributed to the exposure level.

Sequence No. 12

Following product discharge, two center tanks and two wing tanks were ballasted. These tanks had previously carried motor gasoline; the tanks were not washed and ventilated prior to ballasting. During ballasting, product vapors are discharged from the tanks into the work place. The concentration-time history is influenced by:

- the extent to which a tank is ballasted, i.e., the volume of ballast introduced relative to tank capacity, and
- the elapsed time from completion of product discharge to the beginning of ballasting. The longer this elapsed time, the more homogeneous will be the concentration profile in the tank during ballasting.

In this sequence, the tanks were not completely ballasted, and discharge gasoline vapor concentrations ranged from 2.5 to 6.0 percent by volume. Complete ballasting would likely have resulted in final vapor concentrations that approached the maximum values encountered at the end of product loading, i.e., upwards of 40 percent by volume.

This sequence involved restricted tank gauging during the ballasting operation. The frequency of gauging is reduced during ballasting in comparison to loading because the exact quantity of ballast is not critical. The pumpman gauged the ullage on each tank approximately once an hour. In between gauging rounds, the pumpman either checked the operation of the ballast pump in the pumproom or was idle.

The measured exposure during restricted gauging of ballasting operations is consistent with other measured exposures during loading where the same gauging system is used.

V.1.5 Sequential and Simultaneous Exposures During Multiple Terminal Loading Operations

The occupational exposure data that are presented in Table V.3 were collected over a 7-day period that included eight terminal dockings during which 19 chemicals were loaded and one chemical was discharged from the tanker. These data were obtained in support of another USCG-sponsored research project, and complete documentation is contained in Reference 2. Over the 7-day period all of the operations that were monitored could be classed as marine terminal operations as opposed to those operations that are more normally conducted at sea. Therefore, inclusion of the data in this report is appropriate because

- it reflects a variation in ship operations that had not been observed on previous monitoring tests,
- the majority of the chemicals had not been encountered on previous tests,
- it provides a broader perspective of ship operations from the standpoint of data interpretation, and
- it represents a substantial contribution to the exposure data base at the time that this report was written.

TABLE V.3. SEQUENTIAL AND SIMULTANEOUS EXPOSURES DURING MULTIPLE TERMINAL LOADING OPERATIONS

SAMPLE NO.	CHEMICAL	SAMPLING RATE (L/min)	SAMPLING DURATION (min)	W_c (μg)	η	T (°C)	P (mm Hg)	RH (%)	EXPOSURE CONC. (ppm)	TLV-TWA (ppm)	TLV-STEL (ppm)	TLV-C (ppm)	COMMENTS(4)
500	DCM	0.201	121	191	0.983	22.6	760	62	2.3	100	500	--	DECK WATCH NO. 1, A/B1
	CBT(Skin)			<40	0.980				<0.3	5	20	--	
501	DCM	0.048	133	45	0.983	22.6	760	62	2.1	100	500	--	
	CBT(Skin)			<40	0.980				<1.0	5	20	--	
503	DCM	0.201	140	<20	0.983	19.8	760	88	<0.2	100	500	--	DECK WATCH NO. 2, A/B1
	CBT(Skin)			<40	0.980				<0.2	5	20	--	
	TCE			<15	1.006				<0.1	350	450	--	
507	EAC(Skin)	0.201	69	<6	0.936	16.4	760	86	<0.1	5	25	--	DECK WATCH NO. 3, A/B1
508	DEA	0.936	66	<100	0.664	16.4	760	86	<0.6	3	--	--	
511	EAC(Skin)	0.201	151	<6	0.936	14.2	760	76	<0.1	5	25	--	
512	DEA	0.936	93	<100	0.664	14.2	760	76	<0.4	3	—	--	
517	DBO	0.048	63	<6	0.910	4.8	760	85	<0.3	--	--	50	DECK WATCH NO. 7, A/B1
	DBP			<6	0.882				<0.4	75	110	--	
518	DBO	0.201	16	<6	0.910	4.8	760	76	<0.3	--	--	50	
	DBP			<6					<0.3	75	110	--	
519	EAC(Skin)	0.048	70	<6	0.936	7.0	760	68	<0.4	5	25	--	
	CRF			135	0.978				7.9	10	50	--	
	DBO			<6	0.910				<0.3	--	--	50	
	DBP			<6	0.882				<0.3	75	110	--	
521	EAC(Skin)	0.048	60	<6	0.936	11.4	760	70	<0.5	5	25	--	
	CRF			<25	0.978				<1.7	10	50	--	
	DBO			<6	0.910				<0.4	--	--	50	
	DBP			<6	0.882				<0.4	75	110	--	
528	EAC(Skin)	0.207	73	<6	0.936	18.1	760	95	<0.1	5	25	--	DECK WATCH NO. 11, A/B3
	TOL(Skin)			91	0.984				1.6	100	150	--	
	BTC			<5	0.882				<0.07	10	--	--	
529	MMM	0.048	59	<23	0.968	18.1	760	95	<2.0	100	125	--	
530	EAC(Skin)	0.207	71	64	0.936	18.1	760	95	1.1	5	25	--	
	TOL(Skin)			<3	0.984				<0.05	100	150	--	
	BTC			<5	0.882				<0.07	10	--	--	
531	MMM	0.048	71	<23	0.968	18.1	760	95	<1.7	100	125	--	
532	EAC(Skin)	0.207	59	<6	0.936	18.1	760	98	<0.1	5	25	--	
	TOL(Skin)			23	0.984				0.5	100	150	--	
	BTC			<5	0.882				<0.09	10	--	--	
533	MMM	0.048	59	<23	0.968	18.1	760	98	<2.0	100	125	--	

NOTES:
1. W_c = weight of analyte corrected for blank
2. 500 Series Samples are sequential
3. 100 Series Samples are sequential
4. Within a Sample Series, sample sets may be separated by Off-Watch periods or watch periods having no exposure potential

TABLE V.3. SEQUENTIAL AND SIMULTANEOUS EXPOSURES DURING MULTIPLE TERMINAL LOADING OPERATIONS (CONTD)

SAMPLE NO.	CHEMICAL	SAMPLING RATE (L/min)	SAMPLING DURATION (min)	W_c (μg)	η	T (°C)	P (mm Hg)	RH (%)	EXPOSURE CONC. (ppm)	TLV-TWA (ppm)	TLV-STEL (ppm)	TLV-C (ppm)	COMMENTS(4)
100	CBT(Skin)	0.049	126	401	0.980	22.4	760	62	10.4	5	20	--	DECK WATCH NO. 1, A/B2
	DCM			<20	0.983				<0.9	100	500	--	
	TCE			73	1.006				2.1	350	450	--	
101	CBT(Skin)	0.201	117	1360	0.980	22.4	760	62	9.2	5	20	--	
	DCM			<20	0.983				<0.25	100	500	--	
	TCE			299	1.006				2.3	350	450	--	
102	CBT(Skin)	0.201	134	91	0.980	19.6	760	88	0.5	5	20	--	DECK WATCH NO. 2, A/B2
	DCM			<20	0.983				<0.2	100	500	--	
	TCE			78	1.006				0.5	350	450	--	
104	DEA	1.01	107	<100	0.664	16.4	760	87	<0.3	3	--	--	DECK WATCH NO. 3, A/B2
105	EAC(Skin)	0.201	102	<6	0.936	16.4	760	87	<0.07	5	25	--	
106	EAC(Skin)	0.201	110	<6	0.936	14.4	760	77	<0.07	5	25	--	
114	EAC(Skin)	0.149	68	96	0.936	18.1	760	94	2.4	5	25	--	DECK WATCH NO. 11, A/B4
	TOL(Skin)			590	0.984				15.4	100	150	--	
	BTC			124	0.882				2.6	10	--	--	
115	MMM	0.049	54	<23	0.968	18.1	760	94	<2.1	100	125	--	
116	EAC(Skin)	0.149	82	<6	0.936	18.1	760	94	<0.1	5	25	--	
	TOL(Skin)			147	0.984				3.2	100	150	--	
	BTC			89	0.882				1.5	10	--	--	
117	MMM	0.049	82	<23	0.968	18.1	760	94	<1.4	100	125	--	
120	EAC(Skin)	0.149	54	43	0.936	18.1	760	94	1.1	5	25	--	
	TOL(Skin)			217	0.984				5.7	100	150	--	
	BTC			15	0.882				0.3	10	--	--	
121	MMM	0.049	54	<23	0.968	18.1	760	94	<2.1	100	125	--	

NOTES:
1. W_c = weight of analyte correcte for blank
2. 500 Series Samples are sequential
3. 100 Series Samples are sequential
4. Within a Sample Series, sample sets may be separated by Off-Watch periods or watch periods having no exposure potential

A significant expansion of the data base will be generated under the project in Reference 30.

As in previous monitoring tests, the data in Table III are supported by the following documentation:

- identity of vapor sources,
- work activities and their proximity to the sources, and
- the duration of these work activities.

Detailed documentation appears in Reference 2. Due to length, it is not practical to reproduce that documentation in this report; therefore, the reader should consult Reference 2.

The following narrative provides a perspective on ship operations and work practices during the 7-day monitoring period.

The data that were presented in previous sections indicate that occupational exposure potential is reduced when ullage gauging is performed through restricted gauging systems as opposed to the open gauging method. This statement applies generally to all phases of loading, especially tank top-off. The vast majority of the data in Table III were collected during tank gauging. As with restricted gauging exposures, the data in Table III tend toward low, frequently non-detectable levels. However, this vessel did not have restricted gauging systems; tanks were open-loaded and open-gauged. These low level exposures are attributed to three factors:

- Shore-stop loading
- Short-loading, and
- Work practices.

The first factor was "shore-stop" loading. In this loading method, the tank farm has responsibility for terminating product delivery when the scheduled quantity of a cargo has been taken aboard. This mode of operation relieves the crew from the necessity of continuously gauging a tank to its final ullage, as is the procedure for "ship-stop" loading where the crew assumes the responsibility for terminating delivery. This scenario would apply to either a tank that is loaded to capacity or a tank that is "short-loaded."

The second factor is "short-loading." This term indicates that the volume of product that is loaded into the tank is intentionally less than the rated capacity of the tank, which is usually 95 to 98 percent full. The majority of the chemicals on this vessel were short-loaded. The average fill fraction was 54 percent with a range of 30 to 78 percent. As such, the loading is terminated before the high concentration vapor blanket above the liquid surface is vented from the tank. These first two factors combined to produce a reduced exposure potential.

The third factor pertains to the procedure that was used in open gauging the tanks. Normally, a crew member stands on the deck when the tank is gauged. At this location, his breathing zone would be roughly one to two feet above the open ullage port. During this 7-day period, the crew members stood on top of the expansion trunk when gauging, as shown in Figure V.5. In this practice, the separation distance of the breathing zone from the ullage port is increased to three to five feet. Over this increased distance, there is additional time for dispersion and dilution of the discharged vapors, and the breathing zone may be totally removed from the vapor plume. If the tanks had all been loaded to capacity (no short-loading), then it would be expected that open-tank gauging from on top of the expansion trunk would have produced higher occupational exposures but which would be less than if the tank was open-gauged from deck level.

Finally, on this vessel, gauging rounds were conducted every 30 minutes, which is representative of the practice on other vessels. The time required to gauge each tank was also consistent with gauging operations that had been observed previously.

The data in Table III reflect the operational and work practice procedures on one vessel. These procedures consistently resulted in analyte

FIGURE V.5. EXAMPLE OF OPEN TANK GAUGING FROM ON TOP OF EXPANSION TRUNK weights that were not detectable analytically; where this situation occurred, concentrations were quantified at the detection limit of the gas chromatograph for the sampling duration.

V.1.6 Occupational Exposures During Biological Monitoring Tests

One aspect of this program included concomitant biological and occupational exposure monitoring over 24-hour period during which two preselected chemicals were loaded onto different tankers. The specific details pertaining to rationale, methodology and results are presented in Section V.2.

Each of the two biological monitoring tests involved three crew members whose job functions indicated the highest potential for exposure during the loading operations. The objective of this section is to summarize their occupational exposures to the chemical vapors and to discuss the work activities that occurred in each sampling interval.

The environmental monitoring data are presented in Table V.4. Sequence Nos. 1, 2, and 3 pertain to three separate crew members on a methanol loading while Sequence Nos. 4, 5, and 6 were collected on three different crew members during a toluene loading.

Methanol Loading

Two wing tanks of methanol were open-loaded onto a vessel. The starboard tank was filled to 95 percent of capacity while the port wing tank was loaded to 82 percent of capacity. This differential in loading resulted in maximum vapor discharge concentrations at top-off of roughly 85,000 ppm on the starboard tank and 70,000 ppm on the port tank. Both tanks were located directly forward of the deckhouse.

The crew member in Sequence No. 1 open-gauged product ullage on both wing tanks during loading and was involved in the entire top-off operation on the port tank. His pre-top-off contact time, during periodic gauging

TABLE V.4. OCCUPATIONAL EXPOSURES DURING BIOLOGICAL MONITORING TESTS

SEQUENCE NO.	SAMPLE NO.	CHEMICAL	SAMPLING RATE (L/min)	SAMPLING DURATION (min)	W_c (μg)	η	T (°C)	P (mm Hg)	RH (%)	EXPOSURE CONC. (ppm)	TLV-TWA (ppm)	TLV-STEL (ppm)	TLV-C (ppm)	COMMENTS
1	01-P1	MAL(Skin)	0.155	28	112	0.957	29.2	760	69	21	200	250	--	OPEN TANK GAUGING
	01-P2		0.155	59	804		28.7		67	71				OPEN TANK GAUGING
	01-P3		0.155	33	5400		28.1		63	850				TANK TOP-OFF
	01-P4		0.152	350	<15		24.2		NM	<0.22				OFF WATCH
	01-P5		0.150	208	<15		28.1		83	<0.39				POST LOADING DECKWORK
	01-P6		0.151	105	<15		30.9		71	<0.77				POST LOADING DECKWORK
														} SEQUENTIAL EXPOSURE SAMPLES COLLECTED FROM ONE EMPLOYEE IN SUPPORT OF BIOLOGICAL MONITORING TEST
2	02-P2	MAL(Skin)	0.150	64	<15	0.957	27.6	760	69	<1.26				OPEN TANK GAUGING
	02-P3		0.150	42	>921		28.1		67	>118				OPEN TANK GAUGING, POSSIBLE ANALYTE BREAKTHROUGH OR MIGRATION
	02-P4		0.150	60	25		27.0		63	2				OPEN TANK GAUGING, TANK TOP-OFF
	02-P5		0.150	10	<15		27.0		63	<8				POST LOADING DECKWORK
	02-P6		0.154	364	<15		24.2		NM	<0.2				OFF WATCH
	02-P7		0.150	106	<15		28.1		78	<0.8				POST LOADING DECKWORK
	02-P9		0.150	103	<15		28.1		84	<0.8				POST LOADING DECKWORK
	02-P10		0.150	135	<15		30.9		71	<0.6				POST LOADING DECKWORK
														* SEQUENTIAL SAMPLES FROM SECOND CREW MEMBER DURING BIOLOGICAL MONITORING TEST
3	03-P3	MAL(Skin)	0.152	45	<15	0.957	29.2	760	65	<1.8	200	250		WORK UNRELATED TO MAL LOADING
	03-P2		0.152	66	19		28.4		70	1.5				WORK UNRELATED TO MAL LOADING
	03-P10		0.152	92	165		28.1		61	9.5				COLLECT SAMPLE FROM PRODUCT LINE DRAIN VALVE
	03-P8		0.152	73	<15		28.1		63	<1.1				REMOVE MAL HOSE AND BOLT MANIFOLD FLANGE BLIND
	03-P9		0.152	400	<15		24.2		NM	<0.2				OFF WATCH
	03-P1		0.148	69	>1194		28.7		78	>94				DISCONNECT MAL CROSSOVER PIPING AT STARBOARD MANIFOLD, POSSIBLE ANALYTE MIGRATION OR BREAKTHROUGH
	03-P7		0.148	96	>375		28.1		84	>21				MAINTENANCE AT STARBOARD MANIFOLD, POSSIBLE ANALYTE MIGRATION OR BREAKTHROUGH
	03-P12		0.148	126	17		30.9		70	0.7				MAKE READY CROSSOVER PIPING, STARBOARD MANIFOLD
														** SEQUENTIAL SAMPLES FROM THIRD CREW MEMBER DURING BIOLOGICAL MONITORING TEST

NOTES:
1. W_c = weight of analyte corrected for blank
2. NM = not measured
3. ND = not detectable

TABLE V.4. OCCUPATIONAL EXPOSURES DURING BIOLOGICAL MONITORING TESTS (CONTD)

SEQUENCE NO.	SAMPLE NO.	CHEMICAL	SAMPLING RATE (L/min)	SAMPLING DURATION (min)	W_c (µg)	η	T (°C)	P (mm Hg)	RH (%)	EXPOSURE CONC. (ppm)	TLV-TWA (ppm)	TLV-STEL (ppm)	TLV-C (ppm)	COMMENTS
4	06-P2	TOL(Skin)	0.201	54	63	0.975	27.6	760	92	1.6	100	150	--	OPEN TANK GAUGING, TOLUENE
	06-P3		0.201	49	95		27.6		92	2.7				OPEN TANK GAUGING AND TANK TOP-OFF, TOLUENE
	06-P4		0.201	100	96		27.6		92	1.3				SHORE-STOP, TOLUENE TANK TOP-OFF AND POST LOADING DECKWORK *
	06-P6		0.200	444	12		24.2			0.03				OFF WATCH
	06-P7		0.193	218	<5		28.7		78	<0.03				OPEN TANK GAUGING ETHYL BENZENE
	06-P8		0.198	473	<5		24.2			<0.01				OFF WATCH
														* SEQUENTIAL EXPOSURE SAMPLES COLLECTED FROM ONE CREW MEMBER DURING BIOLOGICAL MONITORING TEST
5	07-P1	TOL(Skin)	0.207	27	30	0.975	27.2	760	92	1.5	100	150		OPEN TANK GAUGING, TOLUENE
	07-P5		0.207	45	61		27.2		92	1.8				OPEN TANK GAUGING, TOLUENE
	07-P9		0.207	60	38		28.3		87	0.84				POST LOADING DECKWORK
	07-P7		0.201	307	<5		23.9			<0.02				OFF WATCH
	07-P6		0.202	124	<5		27.8		80	<0.05				OPEN TANK GAUGING ETHYL BENZENE **
	07-P8		0.207	190	17		30.6		71	0.12				OPEN TANK GAUGING ETHYL BENZENE
	07-P2		0.201	303	<5		23.9			<0.02				OFF WATCH
	07-P3		0.201	147	<5		28.3		73	<0.05				POST LOADING DECKWORK
														** SEQUENTIAL EXPOSURE SAMPLES COLLECTED FROM SECOND CREW MEMBER DURING BIOLOGICAL MONITORING TEST
6	08-P1	TOL(Skin)	0.200	58	229	0.975	27.6	760	92	5.4	100	150		OPEN TANK GAUGING, TOLUENE
	08-P2		0.200	35	240		27.6		92	9.4				OPEN TANK GAUGING, TOLUENE
	08-P3		0.200	75	554		27.6		92	10.1				OPEN TANK GAUGING, TOLUENE AND POST LOADING DECKWORK
	08-P4		0.193	133	<5		27.6		92	<0.05				WHEELHOUSE WATCH ***
	08-P5		0.193	118	<5		24.2			<0.06				HOSE HOOKUP FOR ONBOARD CARGO TRANSFER
	08-P6		0.201	410	<5		28.7		78	<0.02				OFF WATCH
	08-P7		0.200	443	14		24.2			0.04				OPEN TANK GAUGING ETHYL BENZENE
														*** SEQUENTIAL EXPOSURE SAMPLES COLLECTED FROM THIRD CREW MEMBER DURING BIOLOGICAL MONITORING TEST

NOTES: 1. W_c = weight of analyte corrected for blank
2. NM = not measured
3. ND = not detectable

of each tank, is summarized below. The gauging activities occurred during collection of the indicated gauging sample numbers.

TANK	BEGIN TIME	DURATION (sec)	SAMPLE NO.
P	1901	140	01-P1
P	1934	60	01-P2
S	1935	60	01-P2
P	2028	86	01-P2
S	2030	60	01-P2

In performing these tank gaugings, the crew member stood on the hatch cover with his breathing zone three to four feet above the ullage port in the vapor plume. The top-off operation on the port tank commenced at 2136 and lasted for 16 minutes. Sample No. 01-P3 was collected during the top-off operation. The tank was gauged seven times in 16 minutes. Gauging time ranged from 10 to 88 seconds with an average of 37 seconds. Because top-off gauging is a critical part of the loading, the crew member remained on the tank hatch for the entire 16 minutes. While performing the top-off gauging his breathing zone was one to two feet above the ullage port in the vapor plume. In between gaugings, his breathing zone was roughly five feet from the ullage port and out of the main vapor plume. There was minimal wind movement in the vicinity of the port tank due to shielding by the deckhouse, deck piping and deckside tank reinforcement structure. The last three samples in Sequence No. 1 indicate that there were no further exposures to methanol for the remainder of the 24-hour period. Samples bearing the "less than" symbol were quantified at the detection limit of the analysis equipment.

The crew member in Sequence No. 2 also periodically gauges both the starboard and port wing tanks during loading, and he was the individual that was most involved in the top-off of the starboard tank. The pre-top-off gauging times are summarized below along with the sample numbers. The sampling durations are shown in Table IV.4.

TANK	BEGIN TIME	GAUGING DURATION (sec)	SAMPLE NO.
S	1857	120	02-P2
P	1954	30	02-P3
S	1956	30	02-P3
S	2100	60	---
P	2110	60	---

This crew member did not wear a monitor during the last two gaugings because of logistics related to the biological monitoring effort. Each ullage reading was obtained in the same manner as described in Sequence No. 1 including the proximity of the breathing zone to the ullage port. Top-off of the starboard tank began at 2156 and continued for 30 minutes. During that period, the tank was gauged five times. Gauging time ranged from 10 to 50 seconds with an average of 24 seconds. For all but two of the 30 minutes the tankerman stood on the expansion trunk hatch cover. From this location, the majority of the top-off ullage measurements were made with the breathing zone three to six feet from the ullage port and out of the main vapor discharge plume. Following top-off of the starboard tank, this individual's work activities did not result in any further exposure to methanol as indicated by the last five personal samples.

Sequence No. 3 contains the exposure monitoring results for the pumpman whose work responsibilities did not include gauging and top-off of the methanol tanks. His work activities, which posed a potential for methanol exposure, are summarized below. Each of the indicated activities took place during a sampling interval.

SAMPLE NO.	ACTIVITY	DURATION (min)
03-P3	In pumproom adjacent to starboard methanol tank	10
03-P2	On deckhouse walkway above port methanol tank	4
	On deckhouse walkway above starboard methanol tank	2
	In pumproom adjacent to starboard methanol tank	4

(continued on next page)

SAMPLE NO.	ACTIVITY	DURATION (min)
03-P10	On deckhouse walkway above port methanol tank	3
	On deckhouse walkway above port methanol tank	5
	Collect methanol sample from product line drain valve near port methanol tank	2
03-P8	On deckhouse walkway above port methanol tank	1
	On deck near starboard methanol tank	2
	Near methanol loading hose on starboard manifold	1
	In pumproom adjacent to starboard methanol tank	4
	Standby at starboard manifold for disconnect of methanol loading hose	10
	Remove loading hose and secure flange blind to manifold	9
03-P1	Disconnect and remove cross-over piping from methanol loading; stand on drip pan grating; stand on manifold walkway above drain valve	24
03-P7	Standby adjacent to starboard manifold drip pan	4
03-P12	Make ready cross-over piping on starboard manifold in preparation for next loading terminal	22

Where samples indicated a non-detectable level of methanol, the concentration was quantified at the detection limit of the analytical instrumentation.

Toluene Loading

Toluene was loaded simultaneously into a port and a starboard tank through one loading hose. Both tanks had been cleaned prior to docking. The port tank was manually gauged through top-off. When the desired final ullage had been reached on the port tank, the entire flow of toluene was diverted into the starboard tank. Manual top-off gauging was not conducted on the starboard tank because product delivery to the ship was terminated by the tank farm (this type of loading control is known as a shore-stop). The port tank was loaded to 85 percent capacity while the starboard tank contained 73 percent of rated capacity. Thus, both tanks were short-loaded; a full load would occupy 95 to 98 percent of rated tank capacity. When a clean tank is short-loaded, the concentration of the vapor that is discharged from the tank at the end of loading is less than the nearly saturated vapor concentration that would exist if the tank was fully loaded. Consequently, the potential for occupational exposure is reduced under short loading conditions. The monitoring results substantiate this conclusion.

During loading, vapors were vented through an ullage port and a butterworth plate, both of which rested on their pins in between ullage measurements. The ullage port was opened when the tank was gauged. If a crew member felt that the vapor concentrations were objectionable, the butterworth plate was also opened.

The crew member in Sequence No. 4 gauged both port and starboard tanks during the initial stages of loading. He also performed the top-off on the port tank. He spent most of his time on the deck just upwind of one of the tanks being loaded. Very rarely he would go on the center walkway or stray from the tanks being loaded. Gauging was accomplished from deck level. While not gauging, he stood to one side of the expansion trunk separated from the ullage port by a diagonal distance of approximately 5 feet. When gauging, the crew member's breathing zone was about 2 feet above the ullage port and slightly off to one side. After loading had been terminated on the port tank, the crew member gauged the tank three additional times ostensibly to check the validity of the final ullage. Three sequential occupational exposure samples were collected during the period when the crew member in Sequence No. 4 performed the ullage measurements. A record of his gauging activities is summarized below. Note the increase in gauging frequency as top-off is approached.

SAMPLE NO.	BEGIN TIME	DURATION (sec)
06-P2	2114	20
	2218	30
	2130	120
	2133	60
06-P3	2215	60
	2222	40
	2227	30
	2237:20	20
	2238:20	13
	2238:23	5
	2239:38	11
	2240:10	7
	2241:00	6
	2241:21	7
	2241:38	6
	2242:05	3
	2242:16	11
	2242:45	5
06-P4	2256	20
	2315	60
	2330	10

The crew member in Sequence No. 6 was also actively involved in periodic gauging of ullage on both toluene tanks. His gauging activities are summarized below.

SAMPLE NO.	BEGIN TIME	DURATION (sec)
08-P1	2048	5
	2049	30
	2058	5
	2100	10
08-P2	2145	20
	2148	15
	2148	30
	2151	20
	2157	180
	2210	18
08-P3	2247	52
	2258	480
	2307	45

Recall that termination of loading was controlled by shore stop. During the latter stages of loading of the starboard tank, the crew member gauged this tank on three occasions (Sample No. 08-P3) even though he had no control over the termination of loading. On all of these gauging encounters, he consistently stood upwind of the ullage port with his breathing zone 18-24 inches from the vapor source.

Note that the loading-related exposures to toluene are quite low for both Sequence Nos. 4 and 6 because of the lower concentration levels associated with short loading. After the toluene loading was completed, their work continued on other parts of the ship, and in this time there was no meaningful encounter with toluene. Large quantities of ethyl benzene were loaded after the toluene. The ethyl benzene did not interfere or interact with the environmental or biological samples for toluene.

The occupational exposure samples in Sequence No. 5 were collected on the pumpman. He has a wide range of responsibilities during a loading operation; he may gauge tanks occasionally, but this is not his main function. Initially, his main task is to participate in hose hookup. Exposure monitoring was not practical during this activity as it would have interrupted and interferred with his work. There is some evidence in the biological monitoring data to suggest that a toluene exposure may have occurred during hose hookup or the loading of the heel. Exposure monitoring was initiated with Sample No. 07-P1 at the first practical opportunity after hose hookup. Summarized below are the pumpman's work activities that posed a potential exposure to toluene.

SAMPLE NO.	ACTIVITY	DURATION (min)
07-P1	Gauge port toluene tank	0.67
07-P5	Man product deck valve near port toluene tank	9
07-P9	At starboard drip pan grating	2

V.1.7 Area Monitoring

The results obtained from area monitoring cannot be used to infer occupational exposure levels. The results can, however, provide an insight into (1) vapor concentrations at various locations on a vessel, and (2) the potential for contribution to the overall exposure if work is performed in the vicinity of a stationary monitor.

Table V.5 summarizes the results from several area samples. The remainder of this subsection contains a brief description of each monitoring sequence. In each of these descriptions, no attempt should be made to correlate employee contact time with the duration of the monitoring interval.

Sequence No. 1

At the end of a loading operation, raw product may collect in the drip pan when hoses are disconnected from the manifold. Generally, this product will remain in the pan during the laden voyage. Additional quantities of product may collect in the pan when the manifold flanges are subsequently removed in preparation for hose hookup at the discharge port. Evaporation of the product in the drip pan represents a potential source of exposure. Figure V.6 illustrates a hose hookup crew working at the manifold above the drip pan that contained product accumulations.

During discharge, there is a tendency for crew members on watch to congregate near the drip pan as they can communicate with and have access to the dock from this location.

Sample No. EX-11 was collected during a gasoline discharge operation in which there were product accumulations in the drip pan. The sampling equipment was located at breathing zone height on the aft end of the starboard manifold and above the product drip pan. This location was on the downwind end of the drip pan and in the proximity to the site where crewmen congregated. The sample was analyzed for the benzene content in gasoline.

FIGURE V.6. CREWMEMBERS PREPARING SHIP'S MANIFOLD FOR PRODUCT DISCHARGE. VOLATILIZATION OF RESIDUAL PRODUCTS IN THE DRIP PAN MAY RESULT IN AN INHALATION EXPOSURE

TABLE V.5. AREA MONITORING

SEQUENCE NO.	SAMPLE NO.	CHEMICAL	SAMPLING RATE (L/min)	SAMPLING DURATION (min)	W_c (µg)	η	T (°C)	P (mm Hg)	RH (%)	EXPOSURE CONC. (ppm)	TLV-TWA (ppm)	TLV-STEL (ppm)	TLV-C (ppm)	C O M M E N T S
1	EX-11	BNZ	0.198	338	502	0.987	28.1	760	60	2.1	10	25	--	MANIFILD DRIP PAN; BNZ IN GASOLINE
2	VF-4	EPC(Skin)	0.199	188	21	0.679	28.8	760	72	0.22	2	5	--	DOWNWIND OF EPC TANK AT BREATHING ZONE HEIGHT, PRODUCT LOADING
3	VF-1	BNZ	0.207	208	>711	1.003	30.4	760	69	>5.23	10	25	--	PUMPROOM EXHAUST FAN DISCHARGE, PRODUCT DISCHARGE, BNZ IN GASOLINE, POSSIBLE ANALYTE BREAKTHROUGH
	VF-2	BNZ	0.199	193	492	1.003	30.6	760	69	4.07	10	25	--	IN PUMPROOM DURING GASOLINE DISCHARGE
4	VF-16	BNZ	0.192	566	7	0.965	21.9	760	79	0.02	10	25	--	PUMPROOM FOLLOWING MUCKING OF BILGE, BNZ IN GASOLINE
5	513	EAC(Skin) CRF	1.038 1.038	61 61	<6 <25	0.936 0.978	9.2 9.2	760 760	60 60	<0.02 <0.08	5 10	25 50	-- --	LOADING MANIFOLD
	514	EAC(Skin) CRF	1.038 1.038	43 43	<6 <25	0.936 0.978	10.9 10.9	760 760	40 40	<0.03 <0.10	5 10	25 50	-- --	LOADING MANIFOLD
6	515	EAC(Skin) CRF	1.038 1.038	96 96	<6 210	0.936 0.978	9.2 9.2	760 760	40 40	<0.01 0.40	5 10	25 50	-- --	ULLAGE BOARD ON MIDSHIP CATWALK
7	520	DBO DBP	0.048 0.048	69 69	70 232	0.91 0.88	7.0 7.0	760 760	68 68	3.6 12.4	-- 75	-- 110	50 --	BREATHING ZONE HEIGHT, DICHLOROBENZENE TANK EXPANSION TRUNK
	522	DBO DBP	0.048 0.048	69 69	47 150	0.91 0.88	7.6 7.6	760 760	70 70	2.5 8.1	-- 75	-- 110	50 --	
8	UCC-117	DCM	0.1825	84	>27975	0.60	24.2	760	NM	>873	100	500	--	ULLAGE PORT ON EXPANSION TRUNK, POSSIBLE ANALYTE BREAKTHROUGH

NOTES: 1. W_c = weight of analyte corrected for blank
2. NM = not measured

Sequence No. 2

Epichlorohydrin is a Subchapter O chemical that requires closed loading, closed gauging and venting of product vapors at a minimum height of B/3 above the deck. The objective of B/3 venting is to promote rapid atmospheric dilution and dispersion of potentially hazardous vapors, thus preventing high level concentrations in the workplace, i.e., at deck level.

The area sample in this sequence was collected roughly 5m downwind of the expansion trunk on the EPC tank and on the ship's elevated longitudinal catwalk (wind starboard to port). There is generally a considerable amount of fore-aft foot traffic on the catwalk. Two sources may have contributed to the measured EPC concentration.

- The most probable source was vapor leakage past the sealed expansion trunk and ullage port.
- The least probable source would be the vapors that were diluted after being vented through the B/3 riser. This contribution could occur if the diluted vapors were entrained in a recirculating flow field and were transported upwind toward the sampling station as a result of an air flow separation on the starboard side of the vessel.

Sequence No. 3

The pumproom is used primarily during product discharge, ballasting, and tank cleaning. The large centrifugal pumps in this room may develop cargo leaks that accumulate in the bilge. Bilge cleaning is generally performed when the leaks are substantial or the ship is scheduled for inspection. The pumpman's responsibilities require that he enter this confined space during product discharge, and the bilge accumulations and leaks can generate a work atmosphere that is a potential source of exposure. Area Sample VF2 was collected to characterize the benzene vapor environment in the pumproom. This sample was collected during gasoline discharge and at a location where the pumpman would work. Although the pumpman spends a small portion of his time in this space, the measured benzene level of 4 ppm is meaningful because it is of the same order of magnitude as the exposure levels that were monitored during open gauging of gasoline tanks during loading. While the 4-ppm level is below ACGIH TWA and STEL limits, it would represent a contribution to the pumpman's total occupational exposure.

Sample No. VF2 represents conditions when products are flowing through the pumproom. The pumproom has its own mechanical exhaust ventilation systems. The ventilation discharge was located on deck adjacent to the deckhouse superstructure and near the walkway that provided access to the second level of the deckhouse. Crew members, specifically the Mate on watch, frequently walked past this pumproom ventilation discharge. Sample No. VF1 was collected in the vicinity of the pumproom exhaust and walkway. The measured area concentration of 5 ppm benzene with gasoline flowing through the pumproom is consistent with the benzene level of 4 ppm (Sample No. VF2) in the pumproom during this same operation.

Possible BNZ breakthough is indicated on Sample No. VF1 because analyte loading on the backup section of the charcoal tube exceeded 30 percent of the total loading. As gasoline vapor has multi-components, the breakthrough may have resulted because of adsorption of other vapor components. The breakthrough may also be an artifact that resulted from post-collection analyte migration.

Sequence No. 4

Sequence No. VF-16 was collected in the pumproom after the bilge had been cleaned. As gasoline was the only product that was transferred through the pumproom the sample was analyzed for the benzene component in gasoline. A comparison of this sample with Sample Nos. VF-7 and 8 (see Table V.1 in Section V.1.3) indicates that the manual cleaning reduced the BNZ level in the pumproom by an order of magnitude.

Sequence No. 5

This sequence was monitored during preparations for CRF discharge. At 1235, the starboard manifold flange to the CRF tank was removed, and hose hookup proceeded. During this operation, the wake from a passing vessel caused a stern spring line to snap and the ship to move away from the dock. As the ship recoiled toward the dock, the discharge hose was damaged when it became trapped between the hull and the dock bumper. The damaged hose was removed from the ship's manifold at 1340. During this period of time, an area sample (Sample No. 513) was collected by taping the pump and sampling medium to the manifold flange for Tank 4S, which was located directly adjacent to the CRF flange. The separation distance between flanges was approximately 2 feet. This sampler was placed in that work location because of the presence of CRF odor from the exposed manifold ball valve and the presence of EAC odor from Tank 9S, which was adjacent to the manifold. A new hose was then delivered to the dock; reconnect was resumed at 1413, and the discharge began at roughly 1500. Sample No. 514 was collected during this 43-minute period and at the same location as Sample No. 513. Between 1239 and 1500, a Mate and an A/B were present in that work area for a majority of their time.

The odor of a chemical vapor is not a reliable indicator of exposure potential or concentration. This is clearly demonstrated by the low EAC concentrations and the fact that the EAC odor threshold is in the sub-ppm range. CRF, on the other hand, has an odor threshold of 200-300 ppm, and that odor was perceived only at the valve ball and flange directly adjacent to the sampler location. A low vapor release rate coupled with rapid atmospheric dilution resulted in the measured sub-ppm concentrations of CRF, which are not detectable by odor alone.

Sequence No. 6

During a discharge operation, a record is normally kept of tank ullage vs. time. This record is used by the deck watch crew to estimate the time when the discharge will be completed. On this particular tanker, the record was kept on a chalkboard that was located on the ship's longitudinal catwalk. An area sampler was placed at the chalkboard because

- o . it was an established work station between tank gauging,
- o the catwalk was a main fore-aft traffic lane for loading stores onto the ship,
- o the ullage board was directly downwind of the CRF discharge pump and manifold, and
- o there was a perceptable EAC odor from a previously-loaded tank that was located adjacent to the catwalk.

Low level concentrations of EAC and CRF were obtained at this monitoring location. These results suggest that the sources were primarily fugitive emissions as opposed to sustained releases at elevated concentrations.

Sequence No. 7

The nature of tanker operations dictates that many activities be conducted simultaneously. In this sequence, the watch crew performed a variety of tasks on the forward half of the deck. These tasks required crew members to make several trips to a deckhouse storeroom in the aft end of the vessel to retrieve equipment and supplies. The traffic lane that was used passed adjacent to and downwind of a DBO/DBP tank that was being open-loaded. The contact time with the dichlorobenzene vapor was minimal and was limited to the time to walk through the plume.

To characterize the environment in the vicinity of this traffic lane, monitoring equipment was taped to the tank hatch structure at breathing zone height. In this position the sampler was located between the open ullage port and the traffic lane. Two sequential samples were collected, i.e., Sample Nos. 520 and 522, and analyzed for both the ortho and para isomers.

Sequence No. 8

Many first generation product/parcel tankers have a midship deckhouse in addition to an aft or stern deckhouse. Deck level passageways in the midship deckhouse provide access to the forward and aft sections of the deck. In addition, it is not uncommon for an expansion trunk on a tank to be located within a few feet of the deckhouse structure and in proximity to the passageways. In this position, the deckhouse may shield the expansion trunk from the ambient wind; high concentration vapors that are discharged during loading may be retained in the vicinity of the expansion trunk without substantial dilution. This situation could result in a potential exposure to crew members working in the area of that expansion trunk or using the passageway next to the trunk.

The above situation was encountered during loading of DCM into a tank whose expansion trunk was next to the deckhouse and adjacent to the passageway. The tank was open-loaded. DCM is extremely volatile; to avoid any possibility of overpressuring the tank, vapors were vented through the open ullage port, and the hatch cover was cracked. Area Sample No. UCC-117 was collected in anticipation of work activity and foot traffic in the area. As there was no convenient location at breathing zone height, the sampling apparatus was set up on the expansion trunk flange roughly 2.5 feet above deck level. The sample was collected during the latter stages of loading when vapor discharge concentrations approach the saturation level.

In the final analysis, there was little work activity in the area on this particular observation. However, the concentration level that was monitored should be recognized for its exposure potential.

The analytical results from this sample suggest that both breakthrough and post-sampling analyte migration may have occurred.

V.1.8 Equipment, Cargo Transfer Procedures and Work Practices That Influence Exposure Levels

The objective of this section is to present and discuss various aspects of cargo transfer and tanker/barge operations that impact on the potential for occupational exposure. This presentation is based on field observations and measurements, and no attempt is made to generalize beyond actual experience to situations that have not been encountered to date, nor is it implied that all operations are consistently conducted as described.

The minimum venting and gauging requirements for Subchapter O chemicals are identified in 29CFR, Parts 151 and 153 for unmanned barges and tankships, respectively. To be licensed to transport this class of chemical, the vessel must be equipped with venting and gauging systems that meet or exceed these minimum requirements. These requirements represent engineering controls that are intended to minimize exposure potential. Restricted and closed gauging systems avoid the direct exposure to high concentration vapors that exist during open gauging. Venting at elevation allows product vapors to be diluted and dispersed, thus reducing the potential for vapor concentrations of health significance to occur in the workplace. In practice, however, the requirements may be circumvented for a variety of reasons. For example, chemicals in this category may be intentionally open-loaded (vented) and open-gauged even though minimum equipment is available for closed gauging and P/V venting at 4m or B/3 above the deck. Open gauging of these cargos cannot be justified from an occupational health standpoint, but it can be justified on operational grounds since closed gauging systems frequently malfunction, respond sluggishly or are inoperable. For these reasons, the tankerman will rely on open gauging so as to avoid a deck spill and ensure that the correct quantity of cargo is loaded aboard the ship. The use of open loading (venting) may be (1) the result of an inoperable P/V valve, (2) a precaution against overpressuring a tank, or (3) due to the fact that the minimum requirements do not clearly state if P/V venting at elevation applies during loading, while the ship is underway, or both. On one occasion, the operational variances described above existed for four out of eight Subchapter O chemicals that required at least restricted gauging and venting at elevation. A more uniform adherence to these minimum requirements would contribute to a reduced exposure potential.

Minimum gauging requirements are not specified for Subchapter D chemicals. Depending upon the vessel's equipment, ullages will be gauged through restricted sounding tubes, open ullage ports or gauging tubes that terminate at deck level. The occupational exposure data that were presented in the preceding sections confirm the ability of restricted gauging systems to minimize exposure to Subchapter O chemicals relative to either of the open gauging methods. Therefore, a phased retrofit program to install restricted gauging systems would be beneficial.

Tankships and barges have drip pans beneath the manifold. Raw products can accumulate in the pan beneath an open grating during hose connect/disconnect or as a result of flange leaks during pumping. Single products and mixtures can evaporate and result in an inhalation exposure potential to the crew members that are involved in manifold-related work. Depending upon the number and size of hoses to be handled at a single docking, as many as six crew members may be exposed to these product accumulations. In addition, ship procedures may or may not require that the drip pan be drained and flushed with water between consecutive dockings. In the latter case, there may be a continued accumulation of products on successive dockings that would compound the inhalation exposure potential. This overall situation could be addressed from two directions:

- As an administrative control, the drip pan could be drained and flushed at sea between dockings. This procedure would minimize the initial exposure potential from past cargos at the next terminal. Permanently installed water wash equipment is currently available and in use on some vessels for flushing the manifold and drip pan areas.
- Currently, raw products accumulate in the pan beneath an open grating. Installation of a funnel-shaped insert between the grating and the pan would permit liquids to drain into the pan and would reduce the evaporation potential. The contents could be drained during the above water flush operation.

During open gauging of product ullage, there does not appear to be a consistent awareness among the deck crew of the exposure potential and a work practice that could reduce that potential. An integral part of a training program should stress standing upwind or at least crosswind of the ullage port, if it is possible. Gauging from a downwind position will enhance the exposure potential. In some cases, there may be no wind or it may not be possible to stand upwind because of the expansion trunk configuration or adjacent deck piping. For these situations, protective equipment should be considered. Those crew members that do stand upwind appear to have learned through experience rather than training.

Man-entry into cargo tanks occurs frequently on board chemical tankers and barges. Tank entry also occurs on product and crude oil tankers, but the necessity is much less frequent than on chemical tankers. Under normal operations, the tank will have been washed and ventilated before entry is considered. The decision to permit entry should be based on tank atmosphere tests for oxygen deficiency, vapor explosibility and toxicity. The following discussion pertains to these three tests and the safety procedures during man-entry.

Oxygen Deficiency and Explosibility

Excluding the Marine Chemist's activities, these two tests are usually performed by the "responsible individual" who may be a member of the ship's crew, an independent cargo surveyor, or an employee of the marine terminal. Separate or combined O_2/CGI (combustible gas indicator) instruments may be used. The determinations are usually made with a drop line through an open tank hatch and at one depth into the tank. In some cases the drop line length is considerably less than the tank depth. As this procedure may erroneously conclude that the tank atmosphere is homogeneous, additional determinations at various depths into the tank through both the expansion trunk and a butterworth opening at the opposite end of the tank would appear to be in order. Such a modified procedure would require a drop line length of the order of the tank depth, but that procedure would provide additional assurance that the tank has sufficient oxygen throughout and that there are no high concentration pockets of vapor particularly on tanks that have internal structure.

Toxicity

Assessment of toxic vapor levels should include sampling at several depths into the tank and through multiple openings as suggested above. In practice, assessment of toxic vapor levels is made with the CGI at one location in the tank. The CGI is not suited for toxic concentration measurements for two reasons.

- The CGI can provide a measurement of high concentration levels in the percent LEL range, which would indicate that additional ventilation is required. However, from a health standpoint, the potential exposure concentrations should be less than the TLV-TWA, TLV-STEL, or TLV-C, but the CGI is insensitive to these very low level concentrations. The result is a zero concentration reading that may provide a false indication of the acceptability of the tank atmosphere. Situations have been encountered in the field where entry was permitted on the basis of a non-detectable CGI reading, but subsequent occupational exposure monitoring and OVA vapor concentration measurements during entry indicated that concentrations were not acceptable.
- In addition to the above limitation of the CGI, on occasion it is used to test atmospheres that are not combustible, e.g., chloroform. In this situation, the CGI gave a non-detectable reading that would have been the same regardless of the actual vapor concentration. This practice, which could result in a high risk exposure, should be addressed through administrative controls.

More definitive determinations of toxic vapor levels can be made with colorimetric indicator tubes where they are available for specific chemicals. Use of this equipment for pre-entry assessments was not observed at any time even though the equipment may be available on the ship. Administrative controls, including training, would promote use of this equipment and increase the probability of an acceptable in-tank work environment.

Tank entry by ship personnel and cargo inspectors does occur without pre-entry testing of the tank atmosphere. The extent of this practice is unknown. Cargo inspectors tended to base entry decisions on the presence or absence of chemical odor. It is widely recognized that odor intensity or lack of odor are not reliable indicators of concentration level especially when the odor threshold is above accepted exposure limits. Ship personnel may wear a cartridge respirator when entering a tank that has not been tested. Without testing, there is no assurance that the performance limits of the cartridge will not be exceeded. It should be noted, however, that the majority of the observed tank entries were preceded by pre-entry tests.

Safety Procedures and Work Practices

If a tank is tested and the atmosphere is acceptable, no further tests are conducted while in-tank work is in progress. This observation applies only to in-service vessel operation and does not include out-of-service entry for repairs or inspection. Additional tests during the entry period, either by deck or in-tank personnel, would indicate the status of the work environment and whether or not the work activities or chemical residue evaporation had changed the acceptability of the atmosphere.

Tanks are ventilated in preparation for entry. Following tank entry, ventilation may or may not continue. Exposure monitoring during tank entry has indicated, as anticipated, that workplace concentrations continue to decline with time when the tank is ventilated. The environment becomes increasingly acceptable. If the tank is not ventilated during entry, the potential for exposure increases with in-tank work time as a result of evaporation of product residues from the tank walls and bottom. Any mucking or sweeping operations can enhance the vapor generation rate. This situation is similar to the buildup of vapor concentration that occurs in a tank that has been sealed after cleaning; as a result of experience, nearly all Deck Department personnel recognized this phenomenon. Ventilation during tank entry should be a standard operating procedure.

Cartridge and canister respirators provide a means of reducing exposure potential. In actual usage, these devices may not provide the anticipated protection and may enhance the exposure potential.

- Respirators and attached cartridges that are stored on deck are subjected to a wide range of chemical vapors. When needed, the integrity of the cartridge (prior loading, breakthrough) is unknown, and the cartridge may not have been replaced on a regular basis.
- One respirator may be used by several crew members. Incompatabilities in fit can nullify respiratory protection.

V.2 Biological Monitoring

V.2.1 Background and Scope

Background

Historically, the Coast Guard's efforts to promote safety and health in worker populations have focused on the prevention of explosive and oxygen deficient atmospheres as well as acute exposures to toxic chemicals that can result in an immediate hazard to life or health. Relatively little attention has been given to the health impact of chronic low to moderate level exposures. Nor has there been a great deal of concern about the health effects due to synergism or additive effects of low level multiple chemical exposures.

Some of the bulk chemicals carried in the marine trade are inorganic chemicals such as sulfuric acid. Some are highly corrosive acid or caustic agents and many are highly reactive. Health effects related to spills or respiration of fumes from such chemicals tend to be acute in nature for which safety procedures and protective gear are well understood and are generally adequately employed. The least well understood hazard is that related to low level exposure potentially related to chronic effects, where no apparent acute effect occurs. The majority of the chemicals carried in bulk are liquid organic solvents which tend to produce significant vapor levels at ordinary temperatures. Some have fairly low TLV-TWA's of 10 ppm or less. Examples include benzene, phenol, formaldehyde, and vinyl chloride.

As documented in Section V.1, levels in the air can exceed accepted TLV and STEL values for workplace environments. These TLV values are based on health effects determined from land based operations. Concern about chemical exposures is certainly not limited to maritime operations. As an example, acrylonitrile, one of the substances carried in bulk, has recently been reported to be related to respiratory cancer among workers employed in rubber manufacturing plants (Reference 19). Continuing research in land based occupational environments serves as major input to evaluation of the maritime occupational environment. Unfortunately, however, that research deals largely with hazard control in an industrial situation, not in the unique environment of maritime transportation. "Because of the vastly different hazards and working conditions of the maritime industry, the marine environment does not compare with that of shore-based industry, and the direct adoption of the standards of the Occupational Safety and Health Administration would seem inappropriate. Recognizing that many of the chemicals routinely shipped pose substantial risks to the members of the maritime community, the Coast Guard has decided that these risks must be systematically evaluated." (Reference 32).

Traditional occupational studies in the marine industry have examined only the environmental concentrations of hazardous substances. Unusual work conditions in the marine chemical industry make it desirable to assess biological concentrations simultaneously with environmental concentrations. These unusual work conditions include the workplace itself, the frequent occurrence of multiple exposures, and the duration of exposures. The workplace is typically the open deck of a ship or a closed compartment which needs cleaning or inspection. During a shift, a worker may be involved in the loading of several chemicals, all having different properties, and the worker's shift may extend from 4 to 24 hours and include different types of duties and different types of exposures. Because of these complexities in the working conditions in the marine chemical industry, hazard evaluation based on environmental data alone is incomplete. The augmentation of environmental sampling with biological sampling provides additional data to enhance the hazard assessment process.

Scope

The biological monitoring study reported here is a pilot study to better define occupational hazards with respect to exposures to hazardous chemicals in the marine chemical industry. The objectives of this pilot study are: (1) to determine whether reliable measurements of the test substances can be obtained under practical conditions, (2) to provide data for correlation of blood, urine, and breath concentrations with environmental concentrations, and (3) to provide a basis for estimating biologic effects utilizing existing information as available in literature. In order to focus the study efforts, three specific chemicals were selected from the broad range of hazardous chemicals carried in the marine chemical industry. Some key considerations which entered the selection of chemicals are discussed as follows. The chemical should be important in terms of volumes shipped, and, therefore, significant in terms of potential shipboard personnel exposures. The chemical should be one for which metabolic pathways are known, thus enhancing the likelihood of obtaining reliable analytical data. Analytical methods of reasonable precision and accuracy should be available for the chemicals and/or metabolites. The several chemicals selected should present a range of structural types and a range of toxic manifestations.

Based on the general considerations in the foregoing, the chemicals selected for the pilot program were toluene ($C_6H_5CH_3$), methanol (CH_3OH), and dichloroethane (ethylene dichloride), $ClCH_2CH_2Cl$. All three chemicals have been characterized toxicologically to a substantial degree in that metabolic pathways and excretion rates are known with some precision. Suitable analytical methods for the chemicals and metabolites (or at least the principal metabolites) are known. Toluene is a widely used aromatic. The volume shipped in 1977 was well over a billion pounds. Toluene is a central nervous system depressant. Methanol is the first member of a series of aliphatic alcohols (alkanols) that are widely used in industry in large amounts. The 1977 quantity of this chemical shipped by water exceeded 300 million pounds. Methanol is neurotoxic, with special activity in the optic system. Ethylene dichloride is a chlorinated aliphatic, with a 1977 water shipment quantity approaching 400 million pounds. In addition to a number of systemic effects, it is strongly hepatotoxic, and renal toxicity has been documented.

The general design of this pilot investigation has been to obtain environmental (workplace) measurements and personal dosimetry under various work activities for two of the three chemicals listed previously. Work conditions considered of highest interest include (1) loading of a significant amount of cargo (duration of several hours) with ship-stop, open manual gauging, and full tank loading, and (2) entry of tanks for tank cleaning operations over an extended time period. These work conditions were considered to offer potentially high exposures and present a worst case for study observation. For each of two selected chemical/work activity combinations, the experimental design required environmental and biological sampling operations for 24 hours after the initiation of chemical exposures. During this 24-hour period, blood, urine, and breath samples were collected at designated times from each of the three persons most highly exposed and personal dosimetry was obtained continuously for the same 24 hours. In addition, environmental measurements were also obtained in the workplace, and background health history information was collected from the subjects. Blood, breath, urine, and personal dosimetry samples were analyzed for the specific chemical compound of exposure; additionally, urine samples were analyzed for a pertinent metabolite. A more complete description of the sampling and analysis design is presented in the discussion of experimental protocol.

V.2.2 Experimental Protocol

Human Subjects

The subjects of this experiment were human volunteers who were members of the ship's crew, i.e., deck officers and seamen. The objective was to recruit and obtain participation of those individuals most closely associated with activities with the highest exposure potentials.

The volunteers were recruited freely in a manner so situated that the individual was able to exercise free power of choice without undue inducement or any element of force or any other form of constraint or coercion. Informed consent was obtained and documented on a written consent form, properly developed and approved specifically for this purpose. The subject was not made to waive any of his legal rights or release the conducting institution from liability for negligence.

Volunteers were informed that blood, urine, and breath samples would be collected over a 24-hour period from three workers on their vessel and that compensation would be provided, based on the number of blood samples obtained from the volunteer. Volunteers were further informed that if they decided to participate, they were free to withdraw consent and discontinue participation at any time, without prejudice. Payment would be based on the number of samples provided prior to withdrawal.

Personal Factors

Personal factors which could have an impact on the investigation of biological sampling results were obtained through informal conversation with the workers. Topics of interest include medical history, medication usage, smoking, alcohol and caffeine consumption patterns, personal hygiene habits, exercise program, avocations or hobbies that may involve use of chemical substances such as solvents and volatiles, length of time in present occupation, and occupation previous to present employment. A more detailed breakdown of the topics covered is presented in the table on the following page.

Work Practices

The activities of the experimental subjects were recorded chronically to provide data relating to exposure characterization and interpretation. This documentation was obtained by a dedicated one-on-one observer, and provides a time-motion analysis for the monitoring period. Specific attention was directed to the identity and duration of high-interest work tasks such as tank top-off and tank entry. The duration and

PERSONAL FACTORS AND HEALTH HISTORY

History of Medical Problems

- liver
- kidney
- respiratory
- other

Use of Medicine

- prescription drugs

Smoking History

- ever smoked
- now smoke
- quantity (packs per day)

Alcohol Consumption

- ever consumed
- now consume
- quantity (amount per day - beers, drinks)

Caffeine Consumption

- ever consumed
- now consume
- quantity (cups per day)

Personal Hygiene Habits

- wash hands before eating
- frequency of baths

Exercise Program

- ever exercise
- frequency (times per week)
- type of exercise

Hobbies/Avocations

- solvents
- volatile chemicals

Occupation

- length of time in present occupation
- previous occupations and lengths of time employed.

proximity of the worker to other sources of chemical vapors was also noted, e.g., open hatches during tank ventilation, steam eductors used for sump pumping. Any situations that could enhance the overall exposure characterization, e.g., handling of food following skin contact with a chemical, infrequent changes of clothing, etc., were documented.

Sampling Schedules

In order to obtain information relating to the absorption and excretion of a volatile cargo material, a planned schedule of sampling was followed. The time intervals used were based on the assumption that the test chemical of interest is rapidly absorbed and that a majority of it will be excreted within a 24-hour period. Also, compounds can be excreted unchanged or as one or more metabolites. This study measured the compound and/or the metabolite(s) in three major body systems: breath, blood, and urine. In addition, ambient concentrations (occupational exposures) of the test material were measured by accepted active dosimetry procedures at frequencies at least as often as when body fluid samples are obtained. Ambient concentrations were also measured by the use of passive dosimeters attached to the subject's clothing.

Whole blood samples were obtained, ideally, at 30 to 60 minutes prior to an exposure, and then at 1, 2, 4, 6, 12, 18, and 24 hours after the subject was first exposed. Two urine aliquots were collected at each urination during the 24-hour period following initial exposure. Breath samples were collected at the same time as the blood samples. In general, occupational exposure samples covered the intervals between the blood samples.

Sampling and Analysis

Blood Blood samples were collected, ideally at intervals of 1, 2, 4, 6, 12, and 24 hours after initial exposure. A baseline blood sample was also collected prior to exposure. The blood samples were collected by venipuncture in 10 ml vaccutainer tubes containing anticoagulant. One 10 ml vacutainer tube was utilized at each sample collection, and the tube was filled as completely as possible, with a minimum of at least one-third full (at least 3 ml blood). Vacutainers containing blood samples were immediately stored at 4°C and transported to the laboratory in this refrigerated condition. At the laboratory, the blood samples were frozen until analyzed.

Blood samples containing methanol were analyzed by direct injection of 5 μℓ of the whole blood into a gas chromatographic column. A mass spectrometer was used for detection of the methanol.

For toluene, 0.5 cc of the whole blood was mixed with DI water and a dilute antifoam silicon emulsion. The mixture was injected into a purging chamber, sparged with helium, trapped in tenax absorbent, and thermally desorbed for injection into a gas chromatograph. A photoionization detector was used to detect the toluene.

Urine Urine samples were collected over the same 24-hour period in which blood and breath samples were obtained. Immediately after collection in a beaker, urine samples were transferred into a graduated cylinder and volume was recorded. Two subsamples were placed in preacidified (0.1 ml nitric acid) 10-ml vials and septum sealed with a crimping tool. Specific gravity was determined and recorded with the use of a hydrometer and pH was measured and recorded with use of Hydrion paper. The two 10-ml septum sealed vials were stored at 4°C and transported to the laboratory in this refrigerated condition. At the laboratory, urine samples were frozen until analyzed.

For the urine samples, analysis procedures for methanol and for toluene were identical to those for blood samples, discussed, separately for methanol and for toluene, in the previous section.

The urine samples were also analyzed for metabolites of methanol and toluene, formic acid and hippuric acid, respectively. For formic acid, the method was similar to that presented for methanol analysis in blood and urine samples: direct injection of 2 μℓ of preserved urine into a gas chromatographic column with mass spectrographic detection. For hippuric acid, the preserved urine was processed to yield a hippuric acid ester, methyl hippurate. The derivative was injected into a gas chromatograph with flame ionization detection. A more detailed discussion of the procedure for the hippuric acid analysis is presented in Appendix B.

Breath Breath samples were taken at the same intervals as blood samples and were generally obtained immediately before or immediately after completing the blood sample. End tidal breath samples were collected using Looman's method (Reference 20). In brief, the subject blew into a mouthpiece having a Y-tube fixed to an exit bypass and an inert bag. The first two-thirds exhalation was allowed to bypass the collection bag. In the last portion of the exhalation, the bypass was closed and expelled air was collected in the inert bag. The process was repeated until the bag was slightly puffed so that it contained in excess of 100 cc of expelled air. The bag was then closed off (by rotating a valve) and the air-filled bags were stored at room temperature during transport to the analytical laboratory.

Air sample bags were analyzed for methanol by first heating the bag to 90°C and withdrawing 50 cc of the air mixture through a septum seal by syringe. The sample was injected into a purging chamber, sparged with helium, trapped on a combination of silica gel and tenax absorbent, and thermally desorbed for injection into a gas chromatographic column. A mass spectrometer was used for detection of the methanol.

For toluene, 30 cc of the air mixture were withdrawn at ambient temperature (23-24°C) through the septum seal by syringe. The sample was injected into a purging chamber, sparged with helium, trapped in tenax absorbent and thermally desorbed for injection into a gas chromatograph. A photoionization detector was used to detect the toluene.

V.2.3 Methods and Procedures

Informed Consent

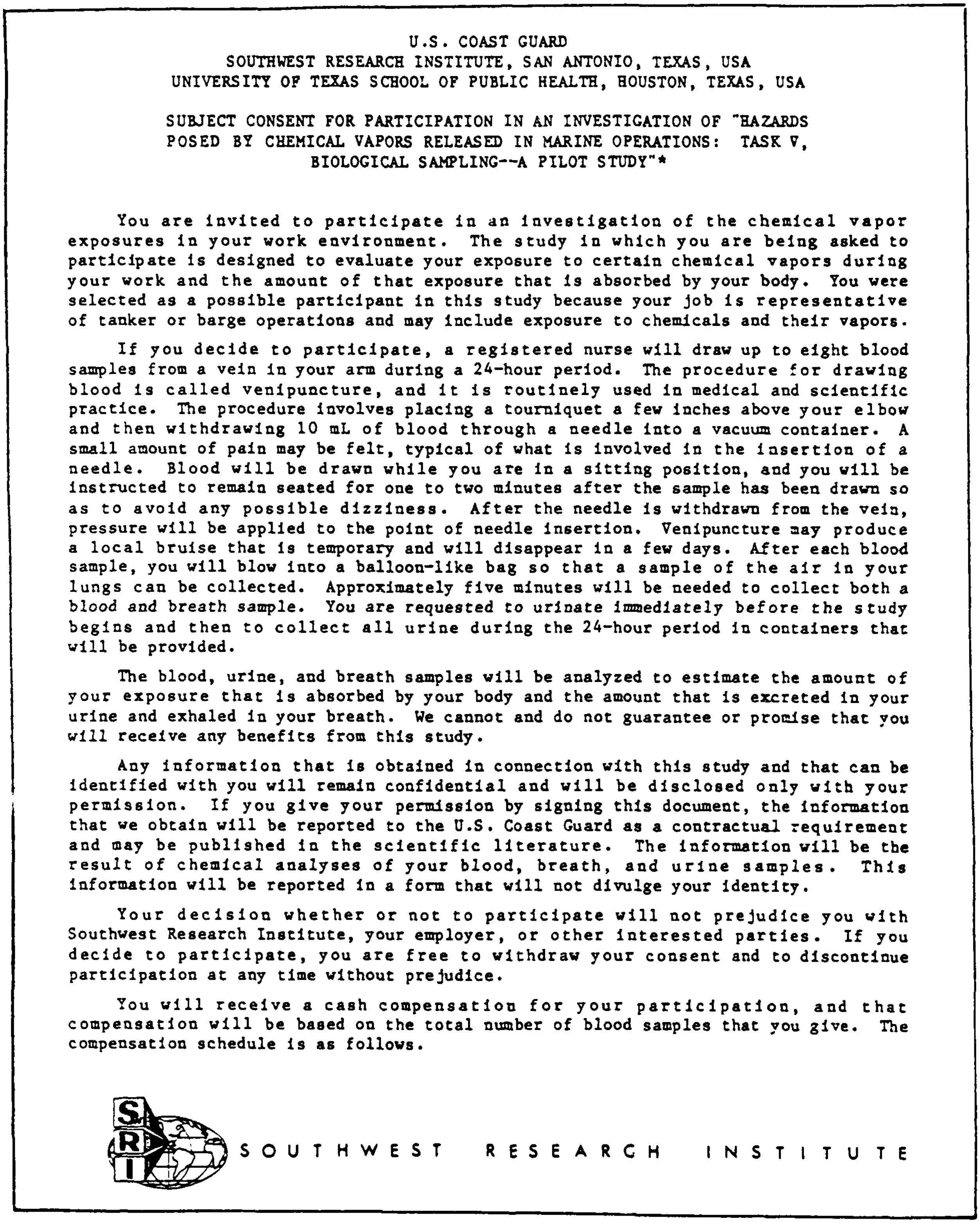
Two forms were developed to obtain and record informed consent of the human subjects in this pilot test: a subject consent form to record the informed consent of each participant, and a participation discussion form used during recruitment activities. Each of these forms is presented and discussed as follows.

The subject consent form shown in Figure V.7 was developed to document the informed consent of each participant. The form was designed to provide potential participants with a brief summary of the study purpose, a description of the study requirements for information and biological sampling from each participant, and an indication of any potential risk or hazard to the individual. The form is self-explanatory and was reviewed in person with each participant at the time of their enrollment into the study to ensure their understanding of the study requirements and hazards. A signed and witnessed informed consent was obtained from all participants in this study. A copy of the consent form was given to each participant.

The participant discussion form shown in Figure V.8 was developed to use during recruitment activities. The form was designed to be used during informal discussions with potential recruits and was also provided prior to recruitment meetings to provide a general description of the study and, hopefully, generate interest in participation.

Review Committee Regarding Human Subjects

Because the pilot test documented here involved use of human subjects, the experimental protocol and the forms used to collect information were subject to review and approval by an appropriate review committee. Accordingly, the study protocol and copies of the consent form and participation discussion form were submitted to the Institutional Review Board of the University of Texas Health Science Center at San Antonio, Texas.



U.S. COAST GUARD
SOUTHWEST RESEARCH INSTITUTE, SAN ANTONIO, TEXAS, USA
UNIVERSITY OF TEXAS SCHOOL OF PUBLIC HEALTH, HOUSTON, TEXAS, USA

SUBJECT CONSENT FOR PARTICIPATION IN AN INVESTIGATION OF "HAZARDS
POSED BY CHEMICAL VAPORS RELEASED IN MARINE OPERATIONS: TASK V,
BIOLOGICAL SAMPLING--A PILOT STUDY"*

You are invited to participate in an investigation of the chemical vapor exposures in your work environment. The study in which you are being asked to participate is designed to evaluate your exposure to certain chemical vapors during your work and the amount of that exposure that is absorbed by your body. You were selected as a possible participant in this study because your job is representative of tanker or barge operations and may include exposure to chemicals and their vapors.

If you decide to participate, a registered nurse will draw up to eight blood samples from a vein in your arm during a 24-hour period. The procedure for drawing blood is called venipuncture, and it is routinely used in medical and scientific practice. The procedure involves placing a tourniquet a few inches above your elbow and then withdrawing 10 mL of blood through a needle into a vacuum container. A small amount of pain may be felt, typical of what is involved in the insertion of a needle. Blood will be drawn while you are in a sitting position, and you will be instructed to remain seated for one to two minutes after the sample has been drawn so as to avoid any possible dizziness. After the needle is withdrawn from the vein, pressure will be applied to the point of needle insertion. Venipuncture may produce a local bruise that is temporary and will disappear in a few days. After each blood sample, you will blow into a balloon-like bag so that a sample of the air in your lungs can be collected. Approximately five minutes will be needed to collect both a blood and breath sample. You are requested to urinate immediately before the study begins and then to collect all urine during the 24-hour period in containers that will be provided.

The blood, urine, and breath samples will be analyzed to estimate the amount of your exposure that is absorbed by your body and the amount that is excreted in your urine and exhaled in your breath. We cannot and do not guarantee or promise that you will receive any benefits from this study.

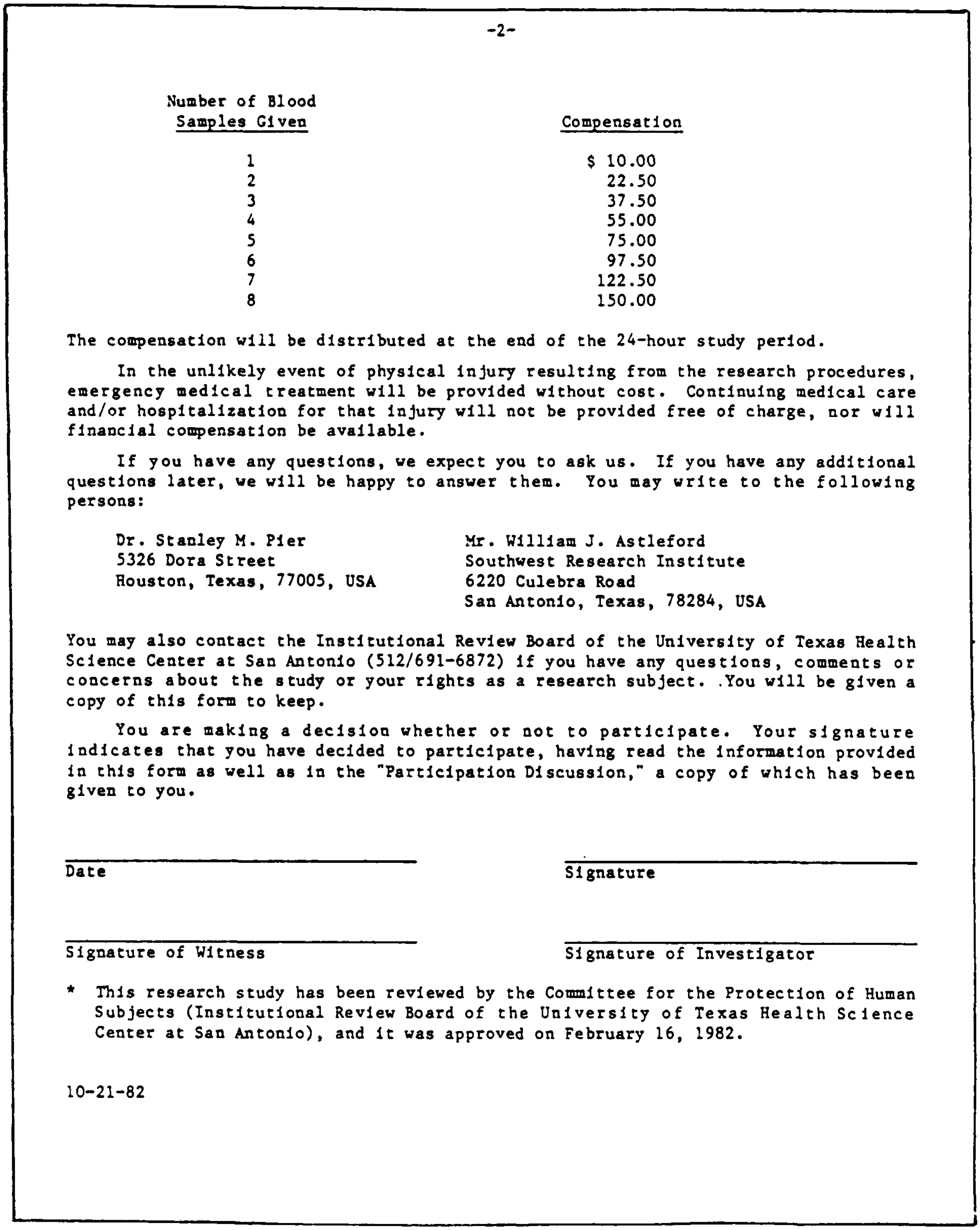
Any information that is obtained in connection with this study and that can be identified with you will remain confidential and will be disclosed only with your permission. If you give your permission by signing this document, the information that we obtain will be reported to the U.S. Coast Guard as a contractual requirement and may be published in the scientific literature. The information will be the result of chemical analyses of your blood, breath, and urine samples. This information will be reported in a form that will not divulge your identity.

Your decision whether or not to participate will not prejudice you with Southwest Research Institute, your employer, or other interested parties. If you decide to participate, you are free to withdraw your consent and to discontinue participation at any time without prejudice.

You will receive a cash compensation for your participation, and that compensation will be based on the total number of blood samples that you give. The compensation schedule is as follows.

SOUTHWEST RESEARCH INSTITUTE

FIGURE V.7 SUBJECT CONSENT FORM



-2-

Number of Blood Samples Given	Compensation
1	$ 10.00
2	22.50
3	37.50
4	55.00
5	75.00
6	97.50
7	122.50
8	150.00

The compensation will be distributed at the end of the 24-hour study period.

In the unlikely event of physical injury resulting from the research procedures, emergency medical treatment will be provided without cost. Continuing medical care and/or hospitalization for that injury will not be provided free of charge, nor will financial compensation be available.

If you have any questions, we expect you to ask us. If you have any additional questions later, we will be happy to answer them. You may write to the following persons:

Dr. Stanley M. Pier
5326 Dora Street
Houston, Texas, 77005, USA

Mr. William J. Astleford
Southwest Research Institute
6220 Culebra Road
San Antonio, Texas, 78284, USA

You may also contact the Institutional Review Board of the University of Texas Health Science Center at San Antonio (512/691-6872) if you have any questions, comments or concerns about the study or your rights as a research subject. .You will be given a copy of this form to keep.

You are making a decision whether or not to participate. Your signature indicates that you have decided to participate, having read the information provided in this form as well as in the "Participation Discussion," a copy of which has been given to you.

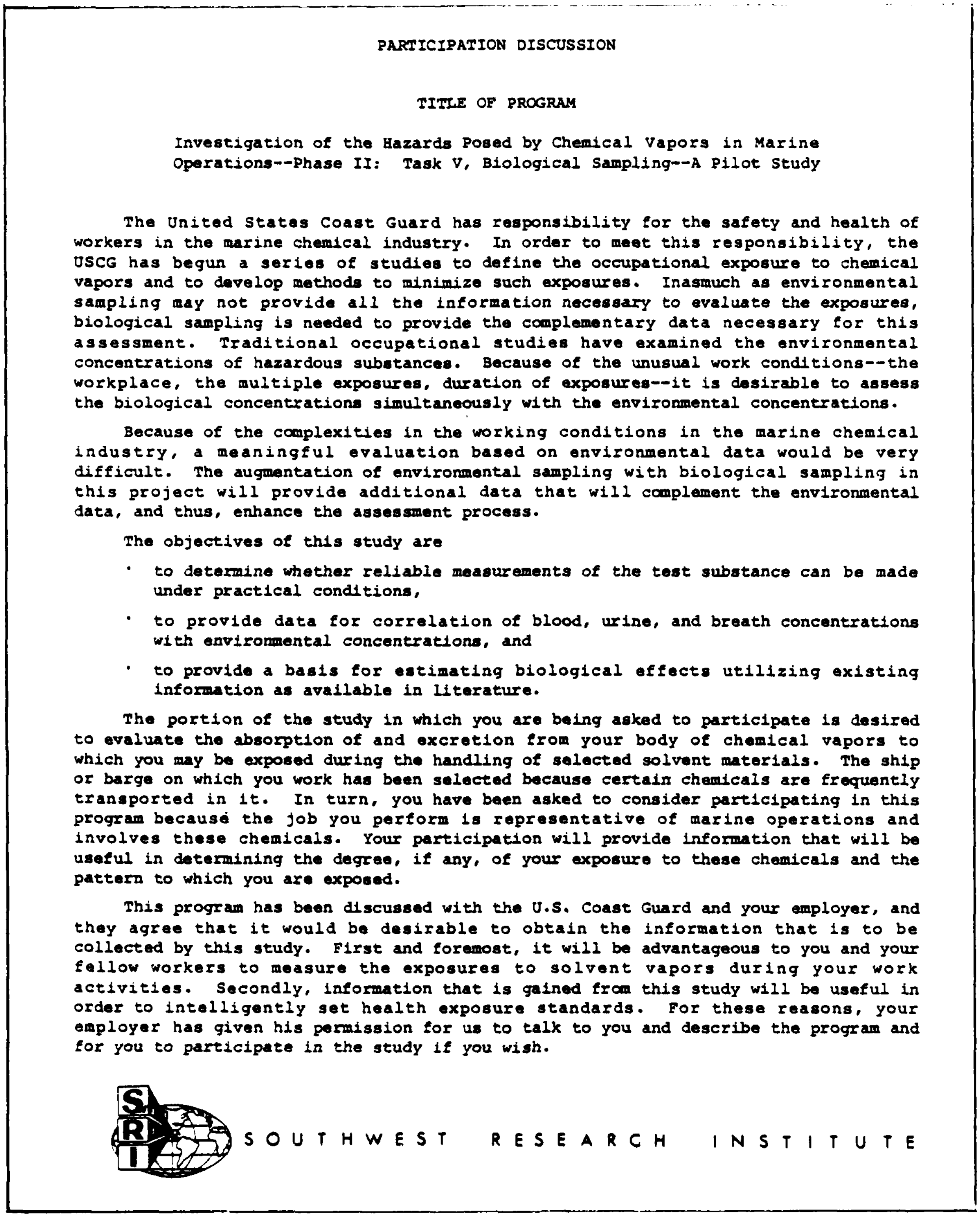
Date ________________________ Signature ________________________

Signature of Witness ________________________ Signature of Investigator ________________________

* This research study has been reviewed by the Committee for the Protection of Human Subjects (Institutional Review Board of the University of Texas Health Science Center at San Antonio), and it was approved on February 16, 1982.

10-21-82

FIGURE V.7 (CONTD.)



PARTICIPATION DISCUSSION

TITLE OF PROGRAM

Investigation of the Hazards Posed by Chemical Vapors in Marine Operations--Phase II: Task V, Biological Sampling--A Pilot Study

The United States Coast Guard has responsibility for the safety and health of workers in the marine chemical industry. In order to meet this responsibility, the USCG has begun a series of studies to define the occupational exposure to chemical vapors and to develop methods to minimize such exposures. Inasmuch as environmental sampling may not provide all the information necessary to evaluate the exposures, biological sampling is needed to provide the complementary data necessary for this assessment. Traditional occupational studies have examined the environmental concentrations of hazardous substances. Because of the unusual work conditions--the workplace, the multiple exposures, duration of exposures--it is desirable to assess the biological concentrations simultaneously with the environmental concentrations.

Because of the complexities in the working conditions in the marine chemical industry, a meaningful evaluation based on environmental data would be very difficult. The augmentation of environmental sampling with biological sampling in this project will provide additional data that will complement the environmental data, and thus, enhance the assessment process.

The objectives of this study are

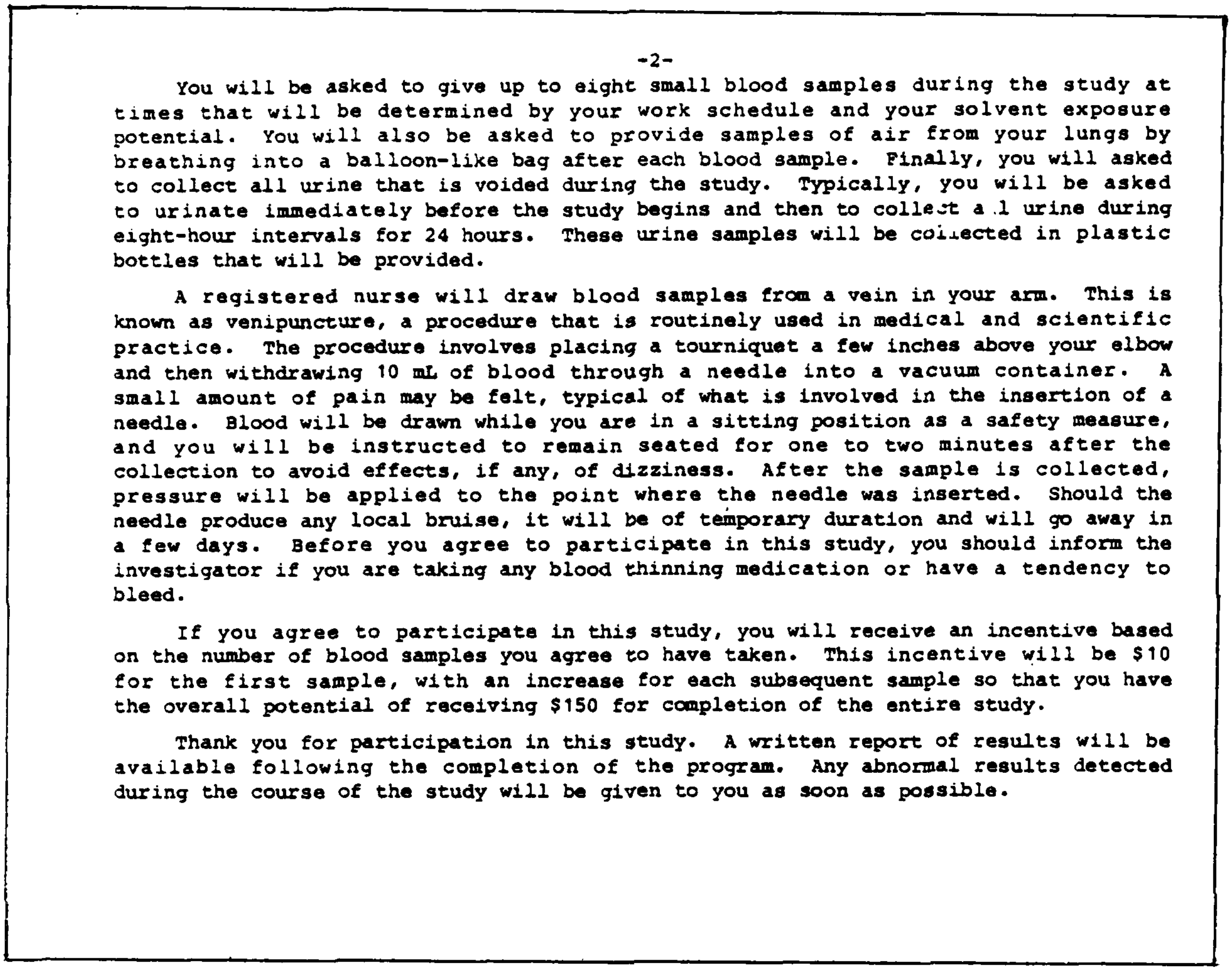
- to determine whether reliable measurements of the test substance can be made under practical conditions,
- to provide data for correlation of blood, urine, and breath concentrations with environmental concentrations, and
- to provide a basis for estimating biological effects utilizing existing information as available in literature.

The portion of the study in which you are being asked to participate is desired to evaluate the absorption of and excretion from your body of chemical vapors to which you may be exposed during the handling of selected solvent materials. The ship or barge on which you work has been selected because certain chemicals are frequently transported in it. In turn, you have been asked to consider participating in this program because the job you perform is representative of marine operations and involves these chemicals. Your participation will provide information that will be useful in determining the degree, if any, of your exposure to these chemicals and the pattern to which you are exposed.

This program has been discussed with the U.S. Coast Guard and your employer, and they agree that it would be desirable to obtain the information that is to be collected by this study. First and foremost, it will be advantageous to you and your fellow workers to measure the exposures to solvent vapors during your work activities. Secondly, information that is gained from this study will be useful in order to intelligently set health exposure standards. For these reasons, your employer has given his permission for us to talk to you and describe the program and for you to participate in the study if you wish.

SOUTHWEST RESEARCH INSTITUTE

FIGURE V.8 PARTICIPATION DISCUSSION FORM



You will be asked to give up to eight small blood samples during the study at times that will be determined by your work schedule and your solvent exposure potential. You will also be asked to provide samples of air from your lungs by breathing into a balloon-like bag after each blood sample. Finally, you will asked to collect all urine that is voided during the study. Typically, you will be asked to urinate immediately before the study begins and then to collect all urine during eight-hour intervals for 24 hours. These urine samples will be collected in plastic bottles that will be provided.

A registered nurse will draw blood samples from a vein in your arm. This is known as venipuncture, a procedure that is routinely used in medical and scientific practice. The procedure involves placing a tourniquet a few inches above your elbow and then withdrawing 10 mL of blood through a needle into a vacuum container. A small amount of pain may be felt, typical of what is involved in the insertion of a needle. Blood will be drawn while you are in a sitting position as a safety measure, and you will be instructed to remain seated for one to two minutes after the collection to avoid effects, if any, of dizziness. After the sample is collected, pressure will be applied to the point where the needle was inserted. Should the needle produce any local bruise, it will be of temporary duration and will go away in a few days. Before you agree to participate in this study, you should inform the investigator if you are taking any blood thinning medication or have a tendency to bleed.

If you agree to participate in this study, you will receive an incentive based on the number of blood samples you agree to have taken. This incentive will be $10 for the first sample, with an increase for each subsequent sample so that you have the overall potential of receiving $150 for completion of the entire study.

Thank you for participation in this study. A written report of results will be available following the completion of the program. Any abnormal results detected during the course of the study will be given to you as soon as possible.

FIGURE V.8 (CONTD.)

Southwest Research Institute is one member of a consortium of research establishments and universities in the San Antonio area which coordinates all review and approval of human research projects through the referenced review board. Approval of the study protocol was granted by the review board on February 16, 1982.

Chemicals and Work Activities Observed

The pilot test was designed to include two specific chemical/work activity combinations. As discussed previously, the chemical cargos of interest included toluene, methanol, and ethylene dichloride and the work activities of highest interest were loading operations or tank cleaning operations. Loading operations with ship-stop, open manual gauging, and full tank loading were selected for the pilot test. A shipping company which routinely loads the chemicals of interest at ports on the U. S. Gulf Coast was recruited and permission to perform the study aboard ship was obtained. Opportunities for observing a loading operation were monitored over a period of months. During the summer and fall of 1982, opportunities for such observations occurred and pilot test activities were accomplished for loading of 1500 metric tons of methanol during the period May 29 to June 2, 1982. A second biological monitoring test was accomplished for loading of 1000 metric tons during the period September 28 to October 1, 1982. A more detailed description of the field activities and procedures for each of these two biological monitoring tests is presented in Appendix C.

Participant Recruitment

Volunteer participants in this study were recruited freely from the crew aboard vessels selected for study. Recruitment was accomplished in the following manner. After selection of a particular ship and scheduled loading activity, a package of study materials was forwarded to the ship's captain at a port of call prior to the port at which pilot test activities were scheduled. The package contained copies of the subject consent form and the participation discussion form presented previously.

In addition, copies of the hand-out information sheet shown in Figure V.9 were also included. The ship's captain was requested to make the materials available to the crew and to post the hand-out information sheet and participant discussion form, if possible.

At a docking prior to the docking where the pilot test was scheduled, the project team member responsible for recruitment and a registered nurse boarded the vessel to begin recruitment activities. After meeting with the ship's captain and principal officers, the recruitment team began to meet with potential subjects. Presentations were given in the crew's lounge to instruct the crew regarding all aspects of the study and questions of the crew were answered by the recruitment team. Informal conversations were held with the potential subjects and copies of the participation discussion form and the informed consent form were provided to interested parties. The requirements for blood, breath, and urine samples from subjects and compensation based on the number of blood samples provided were clearly described and discussed. The value of the pilot test to themselves and to maritime workers in general was stressed during recruitment. It was pointed out that provision of samples, particularly blood samples, by the participants was a significant inconvenience. The reason for provision of samples by a participant must clearly be that he was convinced that he was doing a service to his own health and to that of his fellow workers. Compensation was offered, not as payment for such services, but as a token reward for the valuable services rendered by the participant.

During recruitment, it was stressed that the volunteers of interest to the study were those most likely to encounter the highest exposures during cargo transfer. It was pointed out that only three of the volunteers would be selected for the study, and that the basis for selection was exposure potential. It was further pointed out that limiting the study to only the three subjects with highest exposure potential did not imply that the study was not concerned with the health of all persons aboard the vessel. Potential subjects were told that the study was concerned with the health of all aboard the vessel but was limited to the

HOW ABOUT AS MUCH AS $150

SUMMARY

To evaluate exposure to certain chemical vapors a study is being conducted for the U.S. Coast Guard. You were selected as a possible participant because your job is representative of tanker or barge operations and may include exposure to chemicals and their vapors.

PARTICIPANTS NEEDED

3 members of the crew of a tanker or barge who perform tank loading or tank cleaning operations

SAMPLES NEEDED FROM EACH VOLUNTEER PARTICIPANT

as many as 8 blood samples
as many as 8 breath samples
as many as 3 urine samples

SAMPLE COLLECTION

These samples will be collected during a normal tank loading or tank cleaning operation by a registered nurse trained in taking blood samples. The total of 8 samples would be needed over a 24 hour period beginning at the start of the loading or clearing operation.

PAYMENT FOR VOLUNTEER PARTICIPANTS

Participants will be compensated according to the total number of blood samples given:

No. of Blood Samples Given	Compensation
1	$10.00
2	22.50
3	37.50
4	55.00
5	75.00
6	97.50
7	122.50
8	150.00

The compensation will be immediately provided at the end of the 24-hour study period. If you decide to participate, you are free to withdraw your consent and to discontinue participation at any time without prejudice. You would be paid according to the number of samples provided prior to your withdrawal.

MORE COMPLETE INFORMATION

For more details see the accompanying written materials. For those who might prefer, the materials have been translated into Tagalog and Spanish languages.

FIGURE V.9 HAND-OUT INFORMATION SHEET

worst exposures in order to focus the study to make the results more easily understood.

Subject consent forms were completed for all persons who volunteered for the study. The completed forms bear the signature of the volunteer and that of a witness on the project team. Health and personal factors information which could have an impact on interpretation of biological sampling results was obtained through informal conversation with each volunteer. Once docking had been accomplished for the scheduled cargo loading and specific crew assignments during the actual loading operation were known, a specific set of participants was selected from the list of volunteers. The participants were notified of their selection and enrolled as study subjects by obtaining an initial set of biological samples.

Biological and Occupational Exposure Monitoring

Immediately before cargo transfer operations began for loading of the cargo of interest to this study, biological sampling and occupational exposure monitoring operations were initiated for the study subjects. For each subject, a project team member was assigned to follow and record all pertinent activities of the subject which might relate to occupational exposures. A personal dosimeter was placed on the subject with the sample pickup attached to the shirt lapel in the breathing zone. The personal dosimeter was monitored routinely by the project team member assigned to the subject. Sample tubes were changed and readings were recorded at intervals which coincided with the biological sampling periods.

Biological sampling activities were conducted in the ship's hospital. A blood sampling area was set up with a table and two chairs, one for the subject and one for the nurse. Supporting materials including vacutainers and holders, disposable needles, antiseptic and cleansing materials, and band-aids were laid out, and the area was made as comfortable and private as possible. Apparata for obtaining the breath samples were laid out on a nearby hospital bed so as to be convenient during the sampling operation. The hospital bathroom was set up for collection of the urine samples. A collection beaker was marked for each of the participants and placed in the bathtub with a graduated cylinder and the hydrometer equipment needed for the specific gravity measurement.

Procedures for collection, preparation, labeling, and storage of biological samples are shown in Figure V.10. At the initial sampling period, the subject was instructed to enter the bathroom and provide a urine sample in the beaker marked with his name. For the next 24 hours, the subject was asked to proceed to the hospital bathroom and urinate in the beaker marked with his name each and every time he urinated. The subjects were reminded again and again about this need for urine sample collection for all urinations over the 24-hour test period. At each sampling period, a breath sample was taken from the subject by either the nurse or a properly trained member of the project team and a blood sample was obtained by the nurse. If the nurse experienced difficulty in obtaining an adequate blood sample (10-ml vacutainer, one-third full or more) with a given venipuncture, she was instructed to try further only if the subject did not object. In most cases the subject readily allowed a second try for the few times this occurred. If there was an obvious problem with obtaining an adequate sample, the subject was given full credit for participation once a venipuncture was initiated.

The urine samples were processed immediately after the sample was provided in the beaker marked with the subject's name. The urine sample was transferred into a graduated cylinder and the volume was observed and recorded. Acid was added to each of two 10-ml septum vials and the two vials were filled completely with urine and sealed with the crimping tool. The sample vials were labeled, stored in ice chests, and maintained in refrigerated condition until transfer to the analytical laboratory. Remaining urine was poured into a hydrometer cylinder and specific gravity was observed and recorded. The pH was measured with hydrion paper and recorded. After completion of the measurements, excess urine was discarded in the toilet and the equipment was cleaned and rinsed with deionized water.

PROCEDURES FOR COLLECTION, PREPARATION, LABELING, AND STORAGE OF BIOLOGICAL SAMPLES

BLOOD SAMPLES

1. Use vacutainer to collect sample
2. Obtain a minimun of 3 cc blood sample
3. Label and store in refrigerated space

BREATH SAMPLES

1. Attach bag valve to end of rubber tubing of sampler T
2. Turn valve on bag full counter clockwise to open
3. Place removable mouthpiece in subject's mouth
4. Instruct subject to exhale
5. Place thumb over fixed end of tee after subject has exhaled about 60% of his lung capacity
6. Repeat 4 and 5 until sample bag is slightly puffed
7. Close bag valve by turning valve clockwise until it offers resistance to turning
8. Remove rubber tubing by twisting clockwise
9. Label and store bag - do not refrigerate, store in shaded area
10. Remove movable mouthpiece and replace with clean unit

URINE SAMPLES

1. Collect urine in beaker
2. Pour sample into graduated cylinder - measure and record volume
3. Add two drops of acid to each of 10 ml septum vials
4. Fill the two vials completely full with urine - seal with septum using tool provided, black side of seal inside
5. Label and store in refrigerated space
6. Pour remaining urine into hydrometer cylinder
7. Measure and record specific gravity
8. Measure and record pH with Hydrion paper.

FIGURE V.10 PROCEDURES FOR COLLECTION, PREPARATION, AND STORAGE OF BIOLOGICAL SAMPLES

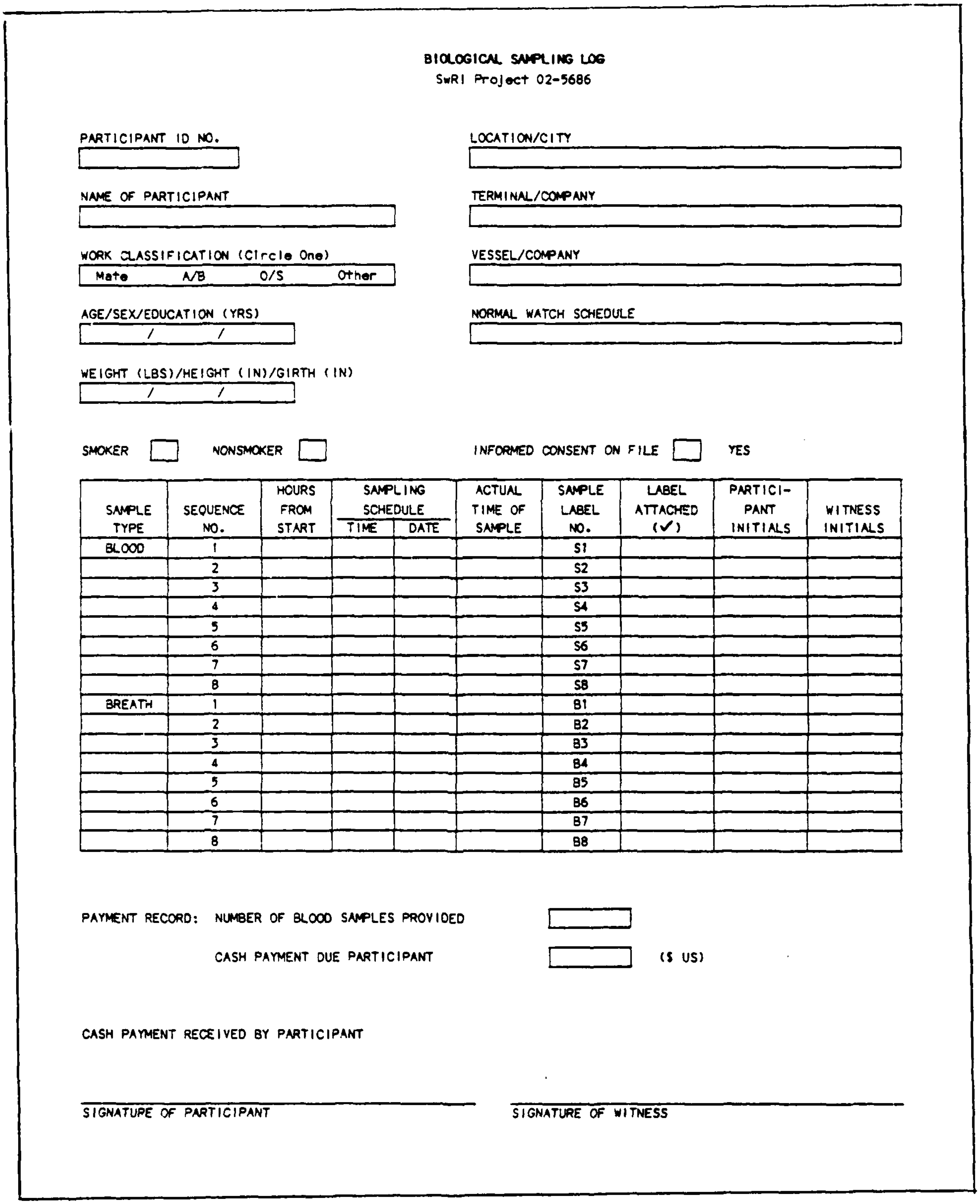
Blood samples in the 10-ml vaccutainer were labeled and stored in ice chests immediately after collection. The blood samples were maintained in refrigerated condition until transfer to the analytical laboratory. Breath samples collected in the air bags were labeled and maintained at room temperature so as to minimize condensation inside the bag.

Pre-coded, peel-off labels were used to label the blood, urine and breath samples. A set of labels such as that shown in Figure V.11 was prepared in advance for each participant. The label coding included a two-digit participant identification number followed by a sample type and sequence code. The sample type was indicated by a single letter: B = Breath, S = Blood/Serum, and U = Urine. A one- or two-digit sample sequence number completed the label coding. The labels shown in Figure V.11 are a complete set for participant number 09 and include eight blood/serum sample labels, eight breath sample labels, and ten duplicate urine sample labels.

For ease of record keeping purposes and, ultimately, to insure confidentiality of individual data, a two-digit participant identification number was assigned to each participant upon enrollment as a study subject. This identification number was used in all records maintained for the specific subject and provides an anonymous cross-reference among the various records. A complete record of the blood and breath sampling activities for each participant was maintained with the sampling log shown in Figure V.12. At a convenient time, the participant was weighed and his height and girth were measured and these measurements were recorded on the log. A sampling schedule was developed for each participant and entered into the log. The actual time of collection was recorded immediately after each sample collection. The log also specified the sample label identification to be used with the sample and provided a record check mark to indicate that the label had indeed been attached to the sample container. Because the log form served as a record for purposes of determining the compensation due each participant, initials of the participant and of a witness (usually the nurse who obtained the sample) were included for each blood sample.

09-S1	09-S2	09-S3
09-S4	09-S5	09-S6
09-S7	09-S8	
09-B1	09-B2	09-B3
09-B4	09-B5	09-B6
09-B7	09-B8	
09-U1	09-U2	09-U3
09-U4	09-U5	09-U6
09-U7	09-U8	09-U9
09-U10	09-U11	09-U12
09-U13	09-U14	09-U15
09-U16	09-U17	09-U18
09-U19	09-U20	

FIGURE V.11 PRE-CODED SAMPLE LABELS



BIOLOGICAL SAMPLING LOG
SwRI Project 02-5686

PARTICIPANT ID NO. ☐

LOCATION/CITY ☐

NAME OF PARTICIPANT ☐

TERMINAL/COMPANY ☐

WORK CLASSIFICATION (Circle One): Mate A/B O/S Other

VESSEL/COMPANY ☐

AGE/SEX/EDUCATION (YRS): / /

NORMAL WATCH SCHEDULE ☐

WEIGHT (LBS)/HEIGHT (IN)/GIRTH (IN): / /

SMOKER ☐ NONSMOKER ☐ INFORMED CONSENT ON FILE ☐ YES

SAMPLE TYPE	SEQUENCE NO.	HOURS FROM START	SAMPLING SCHEDULE		ACTUAL TIME OF SAMPLE	SAMPLE LABEL NO.	LABEL ATTACHED (✓)	PARTICIPANT INITIALS	WITNESS INITIALS
			TIME	DATE					
BLOOD	1					S1			
	2					S2			
	3					S3			
	4					S4			
	5					S5			
	6					S6			
	7					S7			
	8					S8			
BREATH	1					B1			
	2					B2			
	3					B3			
	4					B4			
	5					B5			
	6					B6			
	7					B7			
	8					B8			

PAYMENT RECORD: NUMBER OF BLOOD SAMPLES PROVIDED ☐

CASH PAYMENT DUE PARTICIPANT ☐ ($ US)

CASH PAYMENT RECEIVED BY PARTICIPANT

SIGNATURE OF PARTICIPANT

SIGNATURE OF WITNESS

FIGURE V.12 BIOLOGICAL SAMPLING LOG

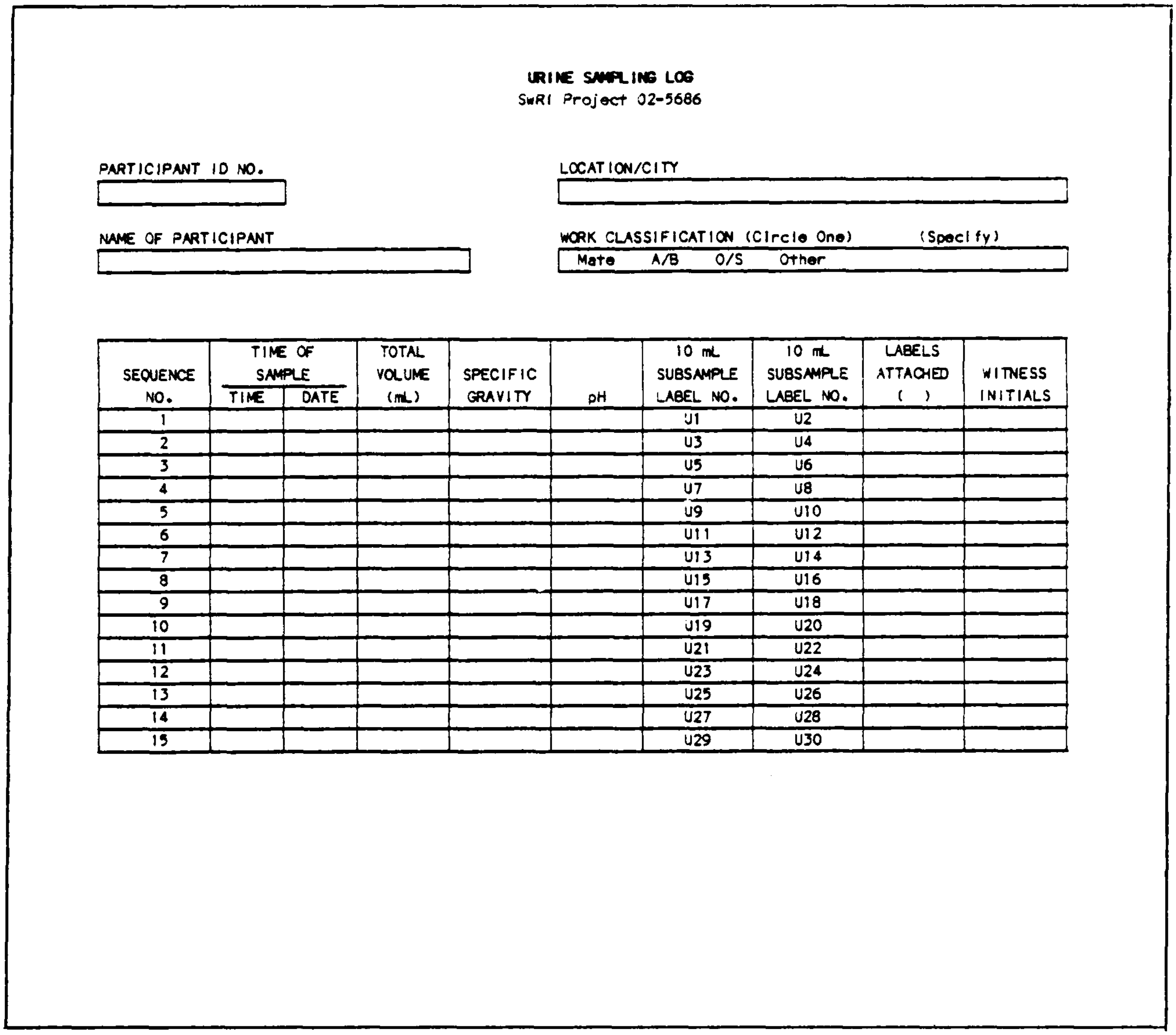
A record of the urine sampling activities was maintained with the form shown in Figure V.13. The time of sample collection was recorded immediately after collection and the volume, specific gravity, and pH measurements were recorded for each sampling sequence. The form specified the sample label identifications to be used with each sample sequence and provided a record check mark to indicate that the proper labels had been attached to each of the two 10-ml subsample containers. Provision was also made on the form for initials of the person responsible for labeling and storing the samples after each collection sequence.

V.2.4 Results

Recruitment and Sampling

The results of the recruitment and sampling operations may be summarized as follows. Two ships were visited and two different chemicals were monitored during loading: methanol and toluene. Nineteen volunteers were recruited and eight participants were selected and sampled: five for the methanol loading and three for the toluene loading. Two of the five participants during the methanol loading were sampled only at an initial sampling and were subsequently terminated from active participation due to a change of watch at which they were relieved by the remainder of the participants. The participant identification number assigned to these study subjects and the number of samples obtained from each are presented in Table V.6.

A summary of important personal characteristics of the study subjects is presented in Table V.7. No data are presented for participants 01 and 02 because of their involvement in so few samples. From the table, it is observed that the study subjects were relatively young seamen with average age of 30 years. Only one of the participants had been a seaman for more than five years. The group was relatively well educated with four of the six having completed high school and some formal education beyond high school. One-half of the group were current smokers and the preponderance indicated occasional or daily use of alcohol.



URINE SAMPLING LOG
SwRI Project 02-5686

PARTICIPANT ID NO.

LOCATION/CITY

NAME OF PARTICIPANT

WORK CLASSIFICATION (Circle One) (Specify)
Mate A/B O/S Other

SEQUENCE NO.	TIME OF SAMPLE		TOTAL VOLUME (mL)	SPECIFIC GRAVITY	pH	10 mL SUBSAMPLE LABEL NO.	10 mL SUBSAMPLE LABEL NO.	LABELS ATTACHED ( )	WITNESS INITIALS
	TIME	DATE							
1						U1	U2		
2						U3	U4		
3						U5	U6		
4						U7	U8		
5						U9	U10		
6						U11	U12		
7						U13	U14		
8						U15	U16		
9						U17	U18		
10						U19	U20		
11						U21	U22		
12						U23	U24		
13						U25	U26		
14						U27	U28		
15						U29	U30		

FIGURE V.13 URINE SAMPLING LOG

TABLE V.6. BIOLOGICAL AND OCCUPATIONAL EXPOSURE SAMPLES COLLECTED

CHEMICAL	PARTICIPANT I.D.	NUMBER OF SAMPLES COLLECTED			
		BLOOD	BREATH	URINE	OCCUPATIONAL
Methanol	01	1	1	0	0
	02	1	1	0	0
	03	6	8	9	6
	04	8	8	6	8
	05	8	8	6	8
	TOTAL	24	26	21	22
Toluene	06	8	10	6	6
	07	8	8	6	8
	08	8	8	4	7
	TOTAL	24	26	16	21
GRAND TOTAL		48	52	37	43

TABLE V.7. PARTICIPANT CHARACTERISTICS

CHEMICAL	PARTICIPANT I.D.	WORK * CLASS	AGE (yrs)	EDUCATION (yrs)	OCCUPATION (yrs)	WEIGHT (lbs)	HEIGHT (in)	SMOKE * (Y/N)	ALCOHOL * (Y/N)	CAFFEINE* (Y/N)
Methanol	03	A/B	24	12.5	1	128	63	1	1	1
	04	P/M	31	13	8	146	66.5	1	0	1
	05	A/B	33	13	2	164	65	1	1	0
	AVE	-	29	13	3.5	146	65	3/3	2/3	2/3
Toluene	06	M	27	14	5	190	69	0	1	1
	07	P/M	33	6	5	172	65	0	1	1
	08	O/S	34	6	1	168	64.5	0	1	0
	AVE	-	31	8.5	3.5	177	66	0/3	3/3	2/3
TOTAL AVERAGE			30	11	3.5	162	65.5	3/6	5/6	4/6

* Work Class:
A/B = Able bodied seaman
P/M = Pumpman
M = Mate
O/S = Ordinary seaman

Smoke/Alcohol/Caffeine: Y/N = Yes/No = 1/0

Biomonitoring

Analysis reports prepared by the analytical laboratory for chemical analysis of blood, breath, and urine samples are presented in Appendix D. These results have been summarized for each of the study participants and the summary data are presented in Tables V.8 through V.13. The format of these tables is designed to display data for air (occupational), breath, blood, and urine samples chronologically for each of the participants. The intent is to provide a visual display of the interrelationship between exposure (air) and response (breath, blood, and urine). It is significant to note that for participant 07, the initial sampling occurred after, rather than before, initiation of his work activities in which exposure may have occurred. This was inadvertently due to his being called to work before the initial sampling could be performed and the passage of more than thirty minutes before he was free to provide the initial samples.

Discussion

The results of the Phase I, pilot study recruitment and sampling activities have demonstrated the feasibility of biomonitoring of marine operations. The response of the marine workers was overwhelmingly positive toward the study and a more than adequate participation rate was provided for study purposes.

The exposure levels encountered during the Phase I biomonitoring activities were generally low. The biological sample analyses were consistent with low exposure levels. A short term higher exposure to methanol (33 minutes; 850 ppm air; participant 03) produced no obvious excursions in the biological data. Previous methanol monitoring data as presented in Section V.1 were of the same order of magnitude as those collected in the biomonitoring test. Higher exposure levels to toluene have been observed in previous occupational exposure studies as presented in Section V.1.

TABLE V.8. BIOMONITORING RESULTS: PARTICIPANT 03/METHANOL EXPOSURE

ANALYTE: Methanol METABOLITE: Formic Acid

	AIR				BREATH			BLOOD			URINE			
DATE	SAMPLE NO.	ANALYTE CONC (ppm)	TIME START-FINISH	DURATION (min)	SAMPLE NO.	ANALYTE CONC (μg/L)	TIME COLLECTED	SAMPLE NO.	ANALYTE CONC (μg/L)	TIME COLLECTED	SAMPLE NO.	ANALYTE CONC (μg/L)	METABOLITE CONC (μg/L)	TIME
6/1/82					B1	0.7	1850	S1	ND(<2)	1842	U1,U2	ND(<0.5)	120	1841
	01-P1	21	1852-1920	28	B2	0.9	1920	S2	ND	1917				
	01-P2	71	1929-2001 2020-2047	59	B3	1.2	2050				U3,U4	ND	130	2100
	01-P3	850	2135-2208	33	B4	1.0	2240				U5,U6	ND	140	2203
					B5	1.0	2330	S3	ND	2320	U7,U8	0.7	130	2330
6/2/82											U9,U10	ND	98	0040
	01-P4	ND	0000-0550	350	B6	0.9	0635	S4	ND	0635	U11,U12	ND	130	0510
	01-P5	ND	0834-1202	208	B7	1.3	1250	S7	ND	1250	U13,U14	ND	180	0950
											U15,U16	ND	180	1415
	01-P6	ND	1322-1507	105	B8	1.2	1530	S8	ND	1535	U17,U18	ND	160	1525

TABLE V.9. BIOMONITORING RESULTS: PARTICIPANT 04/METHANOL EXPOSURE

ANALYTE: Methanol   METABOLITE: Formic Acid

	AIR				BREATH			BLOOD			URINE			
DATE	SAMPLE NO.	ANALYTE CONC (ppm)	TIME START-FINISH	DURATION (min)	SAMPLE NO.	ANALYTE CONC (μg/L)	TIME COLLECTED	SAMPLE NO.	ANALYTE CONC (μg/L)	TIME COLLECTED	SAMPLE NO.	ANALYTE CONC (μg/L)	METABOLITE CONC (μg/L)	TIME
6/1/82					B1	0.8	1750	S1	ND(<2)	1747	U1,U2	ND(<0.5)	170	1805
	03-P3	ND	1824-1909	45	B2	ND(<.5)	1905	S2	ND	1855				
	03-P2	1.5	1918-2024	66	B3	ND(<.5)	2026	S3	ND	2021	U7,U8	ND	130	2040
	03-P10	9.5	2038-2210	92	B4	0.5	2213	S4	ND	2210	U3,U4	ND	140	2209
	03-P8	ND	2222-2335	73										
6/2/83					B5	4.7	0010	S5	ND	0007	U5,U6	2.5	150	0030
	03-P9	ND	2030-0710	400	B6	0.8	0750	S6	ND	0745	U9,U10	ND	130	0712
	03-P1	94	0815-0924	69										
	03-P7		0935-1000 1022-1133	96	B7	1.2	1113	S7	ND	1129	U11,U12	ND	130	1140
	03-P12		1309-1515	126	B8	1.0	1518	S8	ND	1515				

TABLE V.10. BIOMONITORING RESULTS: PARTICIPANT 05/METHANOL EXPOSURE

ANALYTE: Methanol METABOLITE: Formic Acid

	AIR				BREATH			BLOOD			URINE			
DATE	SAMPLE NO.	ANALYTE CONC (ppm)	TIME START-FINISH	DURATION (min)	SAMPLE NO.	ANALYTE CONC (μg/L)	TIME COLLECTED	SAMPLE NO.	ANALYTE CONC (μg/L)	TIME COLLECTED	SAMPLE NO.	ANALYTE CONC (μg/L)	METABOLITE CONC (μg/L)	TIME
6-1-82					B1	ND(<0.5)	1802	S1	NS(<2)	1753	U1,U2	ND(<0.5)	110	1800
	02-P2	ND	1824-1928	64	B2	ND	1940	S2	ND	1931				
	02-P3	117.7	1945-2027	42	B3	3.7	2143	S3	ND	2140				
	02-P4	2.2	2156-2256	60	B4	4.3	2305	S4	ND	2305				
	02-P5	13.3	2325-2335	10										
6-2-82					B5	1.0	0018	S5	ND	0014	U3,U4	ND	91	0020
	02-P6	0.4	0007-0611	364										
					B6	ND	0805	S6	ND	0805	U6,U7	0.7	95	1030
	02-P7	1.3	0805-0951	106							U8,U9	ND	100	1210
	02-P9	ND	1017-1200	103										
					B7	ND	1245	S7	3.3	1235	U10,U11	ND	88	1255
	02-P10	ND	1250-1505	135	B8	ND	1520	S8	ND	1525	U12,U13	ND	90	1315

TABLE V.11. BIOMONITORING RESULTS: PARTICIPANT 06/TOLUENE EXPOSURE

ANALYTE: Toluene METABOLITE: Hippuric Acid

	AIR				BREATH			BLOOD			URINE			
DATE	SAMPLE NO.	ANALYTE CONC (ppm)	TIME START-FINISH	DURATION (min)	SAMPLE NO.	ANALYTE CONC (μg/L)	TIME COLLECTED	SAMPLE NO.	ANALYTE CONC (μg/L)	TIME COLLECTED	SAMPLE NO.	ANALYTE CONC (μg/L)	METABOLITE CONC (μg/L)	TIME
9/30/82					B1	0.5	2035	S1	2.3	2039	U1,U2	ND	589	2036
	06-P2	1.59	2048-2142	54										
	47745	1.47	2047-2142	55										
					B2	0.4	2145	S2	25.8	2147				
	06-P3	2.72	2157-2246	49	BX	0.6	2245							
	47746	9.7	2157-2246	49										
					B3	1.2	2251	S3	32.9	2249				
	06-P4	1.31	2256-0036	100	BY	0.4	2315							
	47747	5.4	2256-0036	100										
					B4	0.5	0032	S4	8.2	0030	U3,U4	ND	902	0028
	06-P6	0.03	0100-0824	444										
					B5	0.4	0245	S5	7.1	0246	U5,U6	ND	687	0248
					B6	0.9	0757	S6	9.4	0802	U7,U8	ND	256	0755
	06-P7	ND	0826-1204	218										
					B7	0.3	1127	S7	7.1	1130	U9,U10	ND	169	1232
	06-P8	ND	1204-1957	473										
					B8	0.3	1957	S8	ND	2002	U11,U12	ND	43	1705

TABLE V.12. BIOMONITORING RESULTS: PARTICIPANT 07/TOLUENE EXPOSURE

ANALYTE: Toluene METABOLITE: Hippuric Acid

	AIR				BREATH			BLOOD			URINE			
DATE	SAMPLE NO.	ANALYTE CONC (ppm)	TIME START-FINISH	DURATION (min)	SAMPLE NO.	ANALYTE CONC (μg/L)	TIME COLLECTED	SAMPLE NO.	ANALYTE CONC (μg/L)	TIME COLLECTED	SAMPLE NO.	ANALYTE CONC (μg/L)	METABOLITE CONC (μg/L)	TIME
9/30/82					B1	1.8	2109	S1	104.1	2114	U1,U2	4.6	1750	2112
	07-P1	1.47	2133-2200	27										
	63860	2.69	2136-2200	24										
					B2	1.4	2204	S2	47.0	2207				
	07-P5	1.80	2215-2300	45										
	63841	2.38	2216-2300	44										
					B3	0.9	2305	S3	61.1	2303				
	07-P9	0.84	2315-0015	60										
10/1/82					B4	0.4	0017	S4	41.1	0020	U3,U4	2.3	690	0019
	07-P7	ND	0048-0555	307										
											U5,U6	ND	365	0200
					B5	0.4	0504	S5	22.3	0506	U7,U8	3.5	214	0502
	07-P6	ND	0618-0823	124										
	63842	ND	0618-0823	125										
					B6	0.2	0810	S6	17.6	0814				
	07-P8	0.12	0850-1200	190										
					B7	ND	1223	S7	14.1	1225	U9,U10	ND	299	1102
	07-P2	ND	1230-1733	303										
	07-P3	ND	1738-2005	147										
											U11,U12	ND	581	1750
					B8	0.3	2010	S8	11.8	2012				

TABLE V.13. BIOMONITORING RESULTS: PARTICIPANT 08/TOLUENE EXPOSURE

ANALYTE: Toluene METABOLITE: Hippuric Acid

	AIR				BREATH			BLOOD			URINE			
DATE	SAMPLE NO.	ANALYTE CONC (ppm)	TIME START-FINISH	DURATION (min)	SAMPLE NO.	ANALYTE CONC (μg/L)	TIME COLLECTED	SAMPLE NO.	ANALYTE CONC (μg/L)	TIME COLLECTED	SAMPLE NO.	ANALYTE CONC (μg/L)	METABOLITE CONC (μg/L)	TIME
9/30/82					B1	0.2	2008	S1	21.2	2011				
	08-P1	5.42	2026-2124	58										
	48959	5.87	2025-2124	59										
					B2	ND	2129	S2	45.8	2135	U1,U2	ND	457	2127
	08-P2	9.41	2140-2215	35										
	48958	9.36	2144-2215	31										
					B3	0.9	2020	S3	32.9	2022				
	08-P3	10.13	2230-2345	75										
	48957	12.63	2231-2345	74										
					B4	0.3	2350	S4	62.3	2353	U3,U4	ND	974	2348
10/1/82	08-P4	ND	0001-0214	133										
					B5	0.4	0249	S5	15.2	0252	U5,U6	7.1	781	0254
	08-P5	ND	0257-0455	118										
					B6	0.6	0455	S6	11.8	0458				
	08-P6	ND	0500-1150	410										
					B7	ND	1211	S7	5.8	1221				
	08-P7	0.04	1225-1948	443										
					B8	0.2	1948	S8	3.5	1952	U7,U8	ND	52	1903

V.2.5 Plan for Additional Tests

Phase II biomonitoring efforts will focus on operations where higher exposures are anticipated over longer periods of time. Extended exposures at or above the accepted 8-hour time weighted average TLV will be sought. A high priority will be placed on monitoring short-term (or longer) high exposure levels if appropriate occupational activities can be located. Plans for additional tests include observation of tank entry and cleaning operations involving exposures to methanol, toluene or ethylene dichloride and observation of a loading operation of ethylene dichloride which includes ship-stop, open gauging, and full tank loading.

Because of the generally low exposure levels encountered in Phase I biomonitoring, it is imperative that higher exposures be monitored in Phase II. A preliminary determination will be made prior to any scheduled biomonitoring field activities to insure a high likelihood of finding adequately high exposure levels to provide the study with meaningful data.

V.3 Evaluation of the Data

The work environment in the marine chemical transport industry differs substantially from that of land-based industries. Work schedules do not conform to the conventional 8-hour day and 5-day week that typifies most industries and which forms the work/rest basis for current occupational exposure guidelines. The traditional maritime work schedule consists of 4-hour watches separated by 8-hour rest periods seven days per week. A variation on this schedule is the 6-hours-ON, 6-hours-OFF routine. The exposure environment, during these novel work schedules, is quite variable. Product loading poses the potential for exposure to both low level concentrations of vapor mixtures with higher level excursions for individual chemical vapors. As the loading may encompass more than one deck watch, the composition of the vapors in the work environment may be different on each watch. Similar considerations apply during product discharge. These marine terminal operations may be separated by extended periods of time where the potential for exposure is minimal except during tank cleaning, which is normally performed at sea.

These novel work schedules and the day-to-day variability of the exposure environment are issues that must be considered in interpreting the occupational exposure data. The occupational exposure data that are presented in this report were collected on individual vessel loadings, but it must be recognized that exposure to other combinations of these same chemicals could also occur in response to changing ship operations. While evaluation of the data relative to existing exposure guidelines can provide a first level of interpretation, a more in-depth, second level of toxicological interpretation was indicated. To this end, a panel of project consultants identified the toxicological factors and issues that are relevant to chemical exposures. Their report entitled "Perspective on the Toxicology of Chemical Exposures" is presented in Appendix E . Using that report as a starting point, a detailed toxicology-industrial hygiene data assessment effort was undertaken, and the results of that interpretation will be published as an addendum to this final report.

In order to assess the results of the occupational and biological exposure monitoring data presented in this report, the concept of what comprises a hazard in the maritime occupational environment must be addressed. The specification of a hazard level for a given chemical substance and a given exposure scenario is a complex task. In his text on safety (Reference 21), the author, William A. Lowrance, presents the idea that an operation or environment is said to be safe if its risks are judged to be acceptable. Because nothing can be said to be absolutely free of risk, nothing can be said to be absolutely safe. Determination of a specific level of risk which is judged to be unacceptable, and thus a hazard, is a subjective judgement.

Evaluation of the hazard of occupational exposures to toxic chemical substances requires consideration of three basically different types of potential toxic response: acute health effects, chronic health effects, and carcinogenic effects. Acute effects are those which yield no long term health effects. Examples include irritants or intoxicants which cause irritation or narcosis during or immediately after exposure, but which tend to require only removal of the insult to mediate the effects. Chronic health effects deal with insults which cause organ damage, either reversible or irreversible, and require not only removal of the insult but other health measures to mediate the effects. Carcinogenic effects are a very special case of chronic effects, where the insulting substance is known or suspected to be a carcinogen. A given chemical substance can induce one or more of these three major toxicological responses and all three must be considered in establishing an acceptable or a hazard level for a given chemical. In evaluating the hazard level of acute effects in the occupational setting, an additional concept must be considered. The comfort level of the environment can and does affect productivity and efficiency. Allowable levels of irritant substances or narcotic substances which can affect the worker's ability to function must be accounted for.

In general the TLV and STEL levels established by ACGIH, NIOSH, and OSHA consider the potential for acute, chronic, and/or carcinogenic effects. In evaluating the maritime exposures reported in this document, the specific basis of the TLV and STEL levels for given substances will be examined regarding the potential for application to the circumstances existing in the marine environment. This evaluation and assessment will be accomplished on a one-by-one basis for each chemical substance where significant exposures have been observed.

The remainder of this section provides some preliminary observations regarding both occupational and biological exposures as well as an overview of the evaluation plan. Interpretation of the results of this project must always keep in mind that the observations reported here are but a sampling of the real world. That sampling may not include many important exposure events which simply did not occur during the operations observed by the study team. Although it is impossible to completely sample the entire population, an attempt must and will be made to extend the conclusions and comments to include other aspects not observed but known to occur.

V.3.1 Preliminary Observations Regarding Occupational Exposure Levels

Discussion

Occupational exposures were monitored either indirectly using conventional dosimetry techniques or directly using continuous, direct reading instrumentation, i.e , the OVA. A wide range of exposure levels was measured, and the equipment, work practice and operational procedure factors that account for this variability have been documented. Independent of these factors, the following observations can be made regarding the exposure environment.

A total of 36 confined space exposures were monitored. These confined spaces included entry into cargo tanks, ballast tanks and pumprooms. Of this number, 28 percent of these entries resulted in exposure concentrations that exceeded the TLV-STEL or TLV-C. In 14 percent of the entries, the exposure level was between 1/2 TLV-STEL (or TLV-C) and the TLV-STEL (or TLV-C). The majority or 58 percent of the entry exposures were less than 1/2 TLV-STEL (or TLV-C). In two of the 36 entries (5.5 percent), the exposure dose was sufficient to produce an 8-hour TWA exposure that exceeded the appropriate TLV-TWA.

Qualitatively, the exposure environment during cargo loading operations consists predominantly of low level concentrations of one or more chemical vapors, e.g., sub-TLV levels that may approach the limits of detection. High level concentrations do not persist through terminal operations. Where high concentrations are encountered, they are short-term in nature and are superimposed upon the low level profile. Excursions above the TLV-STEL were observed during cargo loading operations when tank top-off and certain other equipment and operational criteria were met.

The mixture TLV for multiple chemical vapors, based on the ACGIH additive effect formula, was exceeded in a limited number of instances. In these cases there was one predominant mixture component, and the exposure scenario involved gauging or sampling of fully loaded tanks. On multiproduct tankers, the specific compounds of vapor mixtures vary with each deck watch as a result of sequential cargo loading.

The occupational exposure data discussed in the foregoing indicate that tank entry and tank top-off both present a potentially toxic hazard to maritime workers. During these activities, personnel were sometimes exposed to chemicals at average concentrations in excess of ACGIH STEL values. Even when concentrations only approached STEL values, such exposures should not necessarily be considered "safe" because of the possibility of biological interactions of these chemicals with others to which the personnel were also exposed.

For certain of the chemicals, the data indicate that in-depth toxicological assessment is warranted. For others, the observed concentrations were generally low, and apparently below levels at which any toxic effects or symptoms would be anticipated unless the potential additive effects are considered. Those chemicals whose concentrations were sufficiently high during tank entry or tank top-off to warrant an in-depth toxicological assessment on the basis of the single chemical substance include methyl isobutyl ketone (MIK), toluene (TOL), ethylene dichloride (EDC), chloroform (CRF) and hexane (HXA). The assessment should consider the potential hazard of exposure to the individual chemicals and, also, to mixtures of these chemicals and others whose toxic effects and concentrations, as indicated by the occupational exposure data, might result in potentiating interactions.

A further analysis of additive effects is warranted by the potential for hazards due to mixtures. Those substances for which the observed concentrations were below levels at which any toxic effects or symptoms would be anticipated when the substance is considered alone will be reevaluated under the consideration of simultaneous exposures with one or more other substances for which concentrations have been observed. The combinations will include combinations actually observed, and other combinations not observed during this study but known to occur at times in the maritime industry. Analysis and interpretation of the results of this study must always bear in mind that the occurrences observed are but a sampling of those actually occurring in the industry.

An assessment of only single exposures to individual chemicals has been initiated and is presented in the following section. Analysis of the potential effects of mixtures will await further progress in the study activities.

Assessment

In-depth toxicological assessments of single exposures to individual chemicals have been initiated for those chemicals for which significantly high concentrations were observed. Preliminary assessments of the occupational exposure data relevant to single exposures to MIK, TOL and EDC are given below. Analysis of the effects of successive or repeated exposures to single chemicals and of single and repeated exposures to mixtures of chemicals are also underway. These types of exposure may represent a greater hazard to the health of maritime workers than single exposures to a chemical, even at elevated concentrations, because of possible cumulative effects and biological interactions. However, analyses of effects of repeated exposures and of mixtures are more complex and require an integrated application of relevant toxicological, pharmacological and toxicokinetic data. Therefore, in the following preliminary assessments of MIK, TOL and EDC, discussions are limited to single exposures of personnel to these chemicals at the significantly high concentrations encountered during tank entry and top-off.

Methyl Isobutyl Ketone (MIK)

Entry of personnel into tanks containing residual MIK resulted in exposures of 111, 47 and 85 ppm of MIK for approximately 20 minutes. Thus, two of the concentrations (111, 85 ppm) for these time periods exceeded the ACGIH STEL value of 75 ppm. Since the exposure values are averages for sampling periods, it is likely that initial MIK concentrations were even higher than the sampling period averages.

The exposure of maritime personnel to concentrations of MIK, or of any chemical, in excess of the STEL value should be regarded as "potentially toxic." STEL values are recommended by the ACGIH to ensure that workers do not suffer from (1) irritation, (2) chronic or irreversible tissue damage, or (3) narcosis of sufficient degree to increase the likelihood of accidental injury, impair self-rescue or materially reduce work efficiency. MIK is an irritant and is also capable of producing central nervous system depression and narcosis, although at relatively high concentrations, i.e., approximately 1000 ppm (Reference 22). Silverman, et al. (Reference 23) reported that 12 persons exposed to MIK for 15-minute periods found that 200 ppm had an objectionable odor and definitely caused eye irritation. These findings have been supported by other studies (Reference 22) in which 200 to 400 ppm produced eye irritation in 50 percent of exposed volunteers and 400 ppm caused nasal irritation in 50 percent. In recognition of the irritating effects of MIK and possible nephrotoxic effects from chronic exposure, the TLV for MIK was recently reduced from 100 ppm to 50 ppm and an STEL value of 75 ppm was adopted (Reference 22).

Although inhalation of MIK vapors is the most likely route of exposure of maritime personnel, exposure by skin and/or eye contact may be possible. Skin contact should be avoided because the defatting property of MIK produces a dermatitis. Also, direct contact of the eyes with this chemical may produce painful irritation.

Conclusion

The occupational exposure data for MIK indicate that even single exposures of workers, for relatively short periods, to the concentrations encountered during tank entry and tank top-off are potentially toxic. The primary toxic effect anticipated at these concentrations is eye irritation, the severity of which would depend on the exposure concentration and duration. Although a single exposure may not by itself be considered hazardous, the activities of maritime workers may involve repeated exposures to MIK and/or exposures to other chemicals. In such exposure sequences, the toxicity of MIK encountered during tank entry or top-off may be considerably exacerbated by cumulative effects and/or biological interactive effects and result in a potentially hazardous environment. Therefore, it is most important that a toxicological assessment of MIK address the effects of repeated exposures and of mixtures in addition to those of single exposures.

Toluene (TOL)

Entry of personnel into tanks containing residual toluene resulted in exposures of 230, 197 and 229 ppm average concentrations for periods from approximately 36 to 38 minutes. All of these averages exceed the ACGIH STEL level of 150 ppm. Since these values are averages, it is likely that initial concentrations exceeded these average concentrations.

Toluene, at high concentrations, is a narcotic and may produce parethesia, disturbances of vision, dizziness and nausea, narcosis and collapse (Reference 24). Such effects are generally associated with exposures to concentrations of approximately 1000 ppm or greater. Symptoms reported at various concentrations are: psychological effects and transient irritation at 100 ppm; transitory mild upper respiratory tract irritation and central nervous system effects at 200 ppm; mild irritation, lacrimation and hilarity at 400 ppm; lassitude, hilarity and slight nausea at 600 ppm; and rapid irritation, nasal mucous secretion, metallic taste, drowsiness and impaired balance at 800 ppm (References 25, 26). Because of the irritant effects of toluene, NIOSH (Reference 27) recommended a ceiling of 200 ppm for toluene for a 10-minute sampling period.

Chronic exposure to toluene has been reported to affect a number of organ systems and produce a variety of symptoms and effects. Thus, the literature contains reports of cardiotoxic, hepatotoxic, nephrototoxic and neurotoxic effects as well as hemotologic abnormalities. These effects have generally been limited to industrial workers and habitual "glue sniffers."

Chemical-biologic interactions of toluene with other chemicals, including trichloroethylene, tetrachloroethane, benzene and xylene, have been reported in the literature. The significance of these interactions to maritime worker exposures needs to be assessed.

Conclusions

The occupational exposure data indicate that tank entry and top-off may result in exposures of workers to toxic concentrations of toluene. Effects and symptoms that may be anticipated at the concentrations measured during these activities include eye and upper respiratory tract irritation, headache and nausea. In the event of repeated exposures to this chemical and its accumulation in the body, pronounced central nervous system (CNS) effects may result. Additionally, exposures to other chemicals, particularly other CNS depressants, may potentiate the narcotic effects of toluene. Therefore, an in-depth toxicological assessment should include detailed analyses of cumulative effects from repeated exposures and interactive effects of exposures to toluene and other chemicals.

There is no evidence that suggests that chronic effects observed in industrial workers would result from the intermittent exposures encountered by maritime workers. However, periodic medical examinations and laboratory tests recommended for industrial workers may be advisable for those maritime workers who are frequently exposed to toluene vapors.

Ethylene Dichloride (EDC)

Average concentrations of ethylene dichloride during two tank entries were greater than 700 ppm (85 minutes) and 138 ppm (7 minutes), which are in excess of the ACGIH STEL value of 15 ppm. The latter concentration is also the 15-minute ceiling value recommended by NIOSH as a workplace air standard (Reference 27). NIOSH subsequently revised its recommendation to a TWA of 1 ppm, with a 2-ppm ceiling for a 15-minute exposure in consideration of possible carcinogenic effects (Reference 27).

Although the concern with this chemical is its toxic effects from chronic exposure in the industrial workplace, EDC is considered one of the more toxic of the common chlorinated hydrocarbons. EDC is irritating to the eyes, nose and throat and produces symptoms related to CNS depression or gastrointestinal upset, such as mental confusion, dizziness, nausea and vomiting. Definite liver, kidney and adrenal injury may also result from exposure to EDC. These effects have been reported in literature reviews of EDC toxicity as resulting from "very high concentrations" or "subacute" levels without specific data as to the actual concentrations and durations of exposure (Reference 28). A review of reports of human exposures to EDC needs to be conducted before an assessment can be made of the potential toxicity of exposures during tank entry.

Several studies of the toxic effects of repeated exposures of animals to EDC have been reported. The findings from these studies should also be reviewed in order to assess the potential toxicity of repeated exposures of maritime workers to EDC.

Conclusions

The occupational exposure data indicate that the potential exists for exposure of maritime workers during tank entry to significantly high concentrations of EDC. The measured average concentration of 700 ppm EDC for 85 minutes is considerably higher than the STEL value and represents a toxic, and possibly hazardous, environment. Toxic effects of at least eye and upper respiratory tract irritation may be anticipated at this concentration. Of more importance are possible carcinogenic effects associated with this chemical. Therefore, an in-depth toxicological assessment of various exposure sequences to EDC during maritime operations is warranted.

V.3.2 Preliminary Observations on the Toxicology of Biological Monitoring

Loading of 1500 Metric Tons of Methanol

With one exception, all exposures were measured to be less than the eight-hour time weighted average TLV of 200 ppm air. One short term (33 minute) exposure was observed at 850 ppm. The ACGIH has established an STEL of 250 ppm. NIOSH, however, has recommended a 15-minute ceiling of 800 ppm, which is considerably higher than the STEL.

Although review of the literature is not complete, there appears to be little information relevant to acute human inhalation exposures to methyl alcohol (MAL). There are many reports of injuries or fatalities from the chronic inhalation of high concentrations of MAL by persons engaged in a variety of industries. These reports often differ considerably as to the concentrations of MAL at which symptoms occurred. These differences are probably due to the fact that concentrations in these work environments vary greatly and reported concentrations were often estimated values. In a study of the wood heat industry in Massachusetts, vapor concentrations ranged from 160 to 780 ppm, with no evidence of injury to exposed workers (Reference 27). A report by Kingsley and Hirsch (Reference 27) indicated headaches in workers exposed to MAL in concentrations between 200 and 375 ppm and diminution of vision at 1200 to 8300 ppm. In a fatal case of occupational MAL intoxication by inhalation, it was estimated that the individual was exposed to vapor concentrations ranging from 4000 to 13,000 ppm for about 12 hours (Reference 27). In a controlled human experimental study, Leaf and Zatman (Reference 29) exposed individuals to 500 ppm to 1100 ppm for periods of 3 to 4 hours in order to study the metabolism of methanol. In another study, headache, eye irritation and fatigue have been reported (Reference 29) for one hour exposures at 1000 ppm.

In the biological samples, measurable levels of methanol were found in breath, blood, and urine. Values as high as 4.7 μg/ℓ were found in breath samples; no data for comparison were located in the literature sources. In blood samples, values as high as 3.3 μg/mℓ were observed. These values compare favorably with 2-5 μg/mℓ reported (Reference 29) for exposures to 125 ppm air. In urine samples, values as high as 2.8 μg/mℓ were found. These compare with 3-6 μg/mℓ reported (Reference 29) for exposures to 125 ppm air. Formic acid levels in urine were measured as high as 180 μg/mℓ.

In summary, generally low exposure levels were encountered, with one short term higher exposure. The biological sample analyses were consistent with low exposure levels. Preliminary indications are that methanol levels found in biological samples were within normal, acceptable limits.

Conclusions

Although the 850-ppm exposure to MAL for 33 minutes exceeds the ACGIH STEL value, available data indicates that this single exposure would not cause serious toxic effects. Methyl alcohol is slowly eliminated from the body so that, under repeated or chronic exposure conditions, accumulation of the chemical or metabolites could occur. However, the basis of the TLV-STEL was prevention of toxic effects. Therefore, the observed exposure should be considered a potential toxic exposure when other factors such as multiple exposures or exposures to mixtures are considered.

Loading of 1000 Metric Tons of Toluene

All exposures were measured to be less than the eight-hour time weighted average TLV of 100 ppm air. All personal dosimetry samples were found to be less than 13 ppm time weighted average durations ranging 24 - 473 minutes. Literature for toluene toxicology was discussed earlier in Section V.3.1. From that discussion the 13 ppm exposure measured during the biological monitoring would be considered to be quite low.

In the biological samples, measurable levels of toluene were found in breath, blood, and urine. Values as high as 1.8 μg/ℓ were found in breath samples; no data for comparison were located in the literature sources. In blood samples, values as high as 104 μg/ℓ were observed. These compare with values in excess of 2000 μg/ℓ reported (Reference 24) for exposures to 100 ppm air, and 5,500 μg/ℓ for exposures to 200 ppm air. In urine samples, values as high as 7.1 μg/ℓ toluene were found. No data for comparison were located in the literature sources. With one exception, hippuric acid levels in urine were measured to be less than 975 μg/mℓ. In one case, a value of 1780 μg/mℓ hippuric acid was observed. The urinary biologic threshold for hippuric acid has been reported (Reference 24) to be 1100 μg/mℓ. This is the level used to check exposed workers. At urine levels of 4000 μg/mℓ, increased coagulation time and decrease in prothrombin level has been reported (Reference 24).

In summary, the biological sample analyses were consistent with low exposure levels. Preliminary indications are that toluene levels found in biological samples were within normal, acceptable limits. In one case, hippuric acid levels in urine were above the reported biologic threshhold level: 1780 μg/mℓ measured versus biologic threshold of 1100 μg/mℓ. The biologic threshold level is used as an indication of exposure and not necessarily an indication of detrimental health effects. Known health effects associated with urinary hippuric acid levels are generally at levels greater than the values observed here.

Conclusions

Hazardous concentrations of toluene were not encountered during the biological monitoring and there is no evidence in the biological data to suggest concern for chronic health effects from the exposures measured. However, occupational toluene exposure levels significantly higher than those observed during the biomonitoring activities have been observed and are reported and discussed in Section V.1.

V.3.3 Plan for Comprehensive Assessment

The comprehensive toxic assessment of occupational exposure and biological monitoring data from maritime operations will make use of all available and pertinent toxicity data, both from animal experimentation and human exposures. Toxicity data from human exposures will, naturally, be of major importance. However, most of these data have been obtained from exposures of workers in the industrial environment, typically 8-hours per day, 5 days per week. ACGIH limit values were established principally from these industrial data, under the assumption of daily, continuous 8-hour exposures or frequent repeated exposures. In contrast, exposures of maritime workers may be to single and/or mixtures of chemicals at frequent and infrequent intervals or continuously for prolonged periods of time. This does not mean that these toxicity data and ACGIH values cannot or should not be used for assessing the toxic hazards of chemical exposures of maritime workers. On the contrary, this information must be used in these assessments. However, application of these data and values and their interpretations, must be made with caution in view of the considerable differences in exposure conditions between the industrial workplace and the maritime environment.

The toxicological assessment of maritime occupational and biological exposure data will consist of a two-tier approach. In the first phase, ACGIH limit values will be used to identify those chemicals and exposure activities/sequences which can unequivocally be considered nontoxic. ACGIH values are set for the chronic 8-hour exposure conditions of the industrial workplace; maritime exposure concentrations and durations below these values will be regarded as safe exposures. For those activities involving exposure of workers to mixtures of chemicals, the ACGIH additive effect formula will be used to determine whether the exposure can be considered safe. It is anticipated that exposure concentrations/durations of chemicals during many shipboard activities will fall into this category and will require no further evaluation.

Those exposures which exceed ACGIH limit values of either individual chemicals or mixtures of chemicals will require further evaluation in a second phase. In this phase, all available and relevant toxicity and chemical information will be applied to the occupational and biological monitoring data for an assessment of toxicological hazard. Relevant information will include chemical and physical properties of the chemicals, reported toxic effects in humans and in animal studies, biological interactions with other chemicals, effects of these chemicals on metabolizing enzymes, biological half-lives of the chemicals, routes of metabolism and elimination, target organs and mechanisms of action, correlation of concentration-time constants with toxic effects and correlation of concentrations in biological fluids with exposure concentrations and symptomatology.

It is anticipated that for many of the documented exposures, the second phase assessment will enable the determination of whether an exposure is potentially hazardous, toxic and to what degree, or without adverse effects. The rationale for this assessment, including relevant literature toxicity data and sources, will also be presented. However, it is also anticipated that, for some exposures, sufficient relevant data will not be available to enable a definitive toxicological assessment. In such cases, available information will be presented and the reasons why this information does not allow an assessment will be discussed.

VI. ENUMERATION OF AREAS OF CONCERN - POTENTIALLY HAZARDOUS SITUATIONS

Hazards may be rated and ranked by degree. Throughout this project, on only one occasion was there an operation that could be classed as approaching an immediately dangerous to life or health situation. This isolated event involved hand mucking of chemical residues in an EDC barge tank without protective clothing, respiratory protection or adequate ventilation of the confined space. In-tank concentrations were of the order of 70 percent of the 1000 ppm IDLH level. This concentration, which is roughly one percent of the LEL for EDC, could have been detected with a combustible gas indicator even though 700 ppm is on the low end of the instrument scale. The tank atmosphere was tested with such an instrument and was approved for man-entry.

The above scenario demonstrates that the extent to which work practices, protective equipment, engineering controls and instrumentation are effectively implemented can have a profound impact on the exposure potential. These same factors interacted to varying degrees on other observed operations that were not life-threatening but nevertheless were capable of posing a potential exposure hazard. These operations or areas of concern, which have been noted in this report, are summarized below.

- Open gauging of open loaded (vented) tanks results in a potential exposure hazard particularly when the tanks are filled to near capacity. The potential is greatest when the tank is gauged from deck level where the separation distance between the breathing zone and the open ullage port is minimum. The potential can be reduced by standing on the expansion trunk which effectively increases the breathing zone separation distance. From each of the positions, an additional relative reduction in exposure potential can be achieved by standing upwind or crosswind of the ullage port, if possible, as opposed to downwind. Work practices during open gauging would be most effectively addressed through training and administrative controls. Alternatively, retrofit installation of restricted gauging systems can significantly reduce potential exposures during all phases of tank loading.

- Dress codes in the Deck Department vary from ship to ship, and they are somewhat seasonal in nature. In the aggregate, work clothing is not uniformly consistent with the potential for occupational exposure to chemical cargos. For many chemicals, the primary route of entry into the body is through the skin. Therefore, clothing that is worn should reflect an awareness of the potential for cutaneous absorption. Working without a shirt and in shorts is not appropriate. Footwear, such as sandles, that does not have chemical-resistant soles ignores another site of dermal exposure.

- Single cargos and mixtures of chemicals do accumulate in manifold drip pans. As these products evaporate, there is a potential inhalation exposure to personnel working in the area. A reduction in this potential may be feasible through a combination of (1) administrative controls that define draining and flushing procedures, and (2) engineering controls to effect a low-cost redesign of the pan configuration.

- There are several aspects of the tank entry procedure that could be modified to reduce exposure potential.

  (1) Tanks should not be entered until the tank atmosphere has been thoroughly tested and evaluated.

  (2) Product odor is not a reliable indicator of a safe or unsafe condition. Therefore, odor should be used as a supplemental piece of information to instrument evaluations.

  (3) The instrumental pre-entry testing procedure should be expanded to include additional tests at multiple depths into the tank and through multiple deck openings. The current procedure of single opening-single depth testing assumes that the tank atmosphere is homogeneous, which may not be the case.

(4) The combustible gas indicator is not accurate at low vapor concentrations. Colorimetric detector tubes should be used where appropriate to assess toxic vapor levels. Similarly, the CGI is ineffective when the products are not flammable.

(5) Tank atmosphere testing should be expanded to include additional tests during in-tank work. Under current methods, an increase in tank atmosphere concentrations would go undetected.

(6) Ventilation of a tank should be a standard operating procedure while in-tank work is in progress. Without ventilation, regeneration of product vapors from residues will occur, and these vapors will not be diluted and removed from the tank.

Tank entry is an area of concern because in each of the above six categories operations have been observed which enhance the exposure potential.

- Present usage of organic vapor cartridge respirators is not conducive to reducing exposure potential. When needed, the level of protection may be unknown because respirators stored on deck can adsorb product vapors to the extent that the service life may be exceeded and respirators are not fit-tested to the individual but are shared by several crew members.

- Current regulations define the minimum requirements for gauging and venting of Subchapter O chemicals. In practice, open gauging and open venting is conducted during loading even though equipment is available to meet a minimum requirement of closed gauging and venting at elevation. Circumventing the minimum requirements enhances the exposure potential. Monitoring of loading operations would be one means of promoting a more uniform adherence to these minimum requirements and a reduction in this area of concern.

- For certain Subchapter O chemicals, open gauging is permitted, but the minimum requirements call for P/V venting at elevation. It is not clear if the P/V venting requirements apply to loading and the laden voyage or if open venting is acceptable during loading. If the former interpretation is correct, then the ullage port must be opened during gauging. The pressure relief on the tank when the ullage port is opened could enhance the potential for a short-term high concentration exposure.

VII. RECOMMENDATIONS

Based on work reported herein, the following recommendations are appropriate.

- The minimum gauging and venting requirements for Subchapter O chemicals should be reviewed for continuity and their impact on occupational exposure potential. To this end, the plume dispersion model in this report would be a useful tool in assessing the trade-off between vent height and deck level concentrations during loading under a range of atmospheric conditions.

- In parallel with the above review, the minimum venting and gauging requirements for unmanned barges should be consistent with the tankship requirements.

- Subchapter D commodities should be reviewed as new health effects data become available. Where such data support a reduction in the applicable exposure limits, these commodities should be considered for inclusion in Subchapter O.

- The benefits of restricted gauging systems in reducing exposures have been demonstrated. Consistent with a vessel's intended service, future ship designs could incorporate restricted systems for tanks that will carry Subchapter D and certain Subchapter O chemicals. The cost savings relative to closed systems on all tanks, where they are not needed or used, would be appreciable. For current tonnage, the estimated cost of retrofitting a barge tank with a restricted gauging tube is roughly $500; the cost per ship tank would be slightly higher. Development of a time-phased retrofit program should be investigated.

- Cargo tanks on pure parcel chemical carriers are independent as opposed to integral. Structural rigidity and support for independent tanks are provided by external members in cofferdams, double bottoms, and on deck. The tank ventilation model is well suited to this clean structural configuration. A method has been developed for estimating the ventilation delay time for tanks with internal structure. The model is based on the incremental time required to achieve a local concentration equal to 20 percent of preventilation concentration. As this level may locally exceed current exposure limits, it is recommended that this delay time model be investigated further to extend its applicability to sub-TLV concentrations. The anticipated results would be recommended incremental ventilation times for internally-structured tanks relative to structureless tanks.

- A preliminary design study should be initiated to investigate alternative designs for the manifold drip pan that would minimize product evaporation and exposure potential.

- A major recommendation pertains to crew training, which is an administrative control function. For crew members in the Deck Department of chemical tankers, it is recommended that study materials for licensing include sections that emphasize an increased awareness and appreciation of chemical hazards, work practices and procedures that reduce exposure potential and the applicability and limitations of vapor detection equipment. This recommendation is based on an accumulation of observations.

- The marine work environment includes the potential for both short-term, high-level exposures to single chemicals as well as low level exposures to several chemicals, either sequentially or simultaneously. As the long term health effects of this work environment are not completely known, it is recommended that continued environmental monitoring be complemented by a well-designed, concomitant medical monitoring program. The combination of these two programs would aid in early identification of cause-effect relationships that could be attributed to the work environment and which indicate the route for remedial medical treatment.

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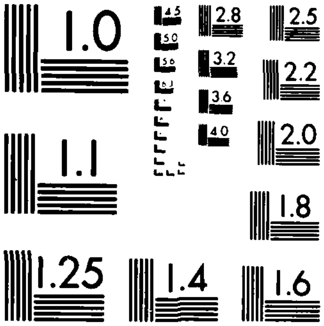

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APPENDIX A

DATA COLLECTION FORMS
FOR
TANK WASHING, GAS FREEING,
AND MAN ENTRY

TANK WASHING

1. Tank No.__________ Voyage No.__________ Date____________

Vessel___________________________

2. Contents Being Washed____

3. Prewash Measurements

a.

Time	Ft↓*	CH4(PPM)	Diluter I.D.	Bag No.
	0			

*Drop Line Length from Measurement Point

b. Measurement Point (Circle One)

Ullage Point Standpipe Expansion Trunk

c. Distance of Measurement Point Above Deck________Inches

4. Wash Profile

Time		Feet Down Into Tank	Wash Liquid				T(°F)	Detergent	Surfactant
Begin	End		Hot*	Cold	Fresh	Sea		Type	Type

*How Generated

5. Washing Machine Data

a. Make

b. Model No.

c. Optional Equipment

d. No. of Nozzles

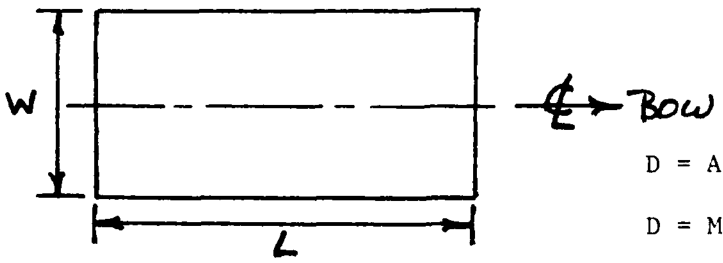
e. Nozzle Diameter

f. Water Pressure

g. GPM/Machine

6. Tank Data

a.



L =
W =
D =

D = Actual Tank Depth or

D = Max. True Ullage (ft)______
Minus Item 3C (ft)_______

Show B/W, Expansion Trunk & Pump Locations (ft) on Drawing

b. No. B/W Openings__________

c. B/W Opening Diameter__________In.

d. No. Washing Machines__________, On Which Openings_______F, C, A

e. Status of Openings with No Wash Machine

f. Blow While Wash (Circle One) Yes No

g. Ullage Cap Open (Circle One) Yes No

h. Hatch Cracked (Circle One) Yes No

If Yes, Crack Gap__________In.

7. Pump Capacity__________GPM

Eductor Capacity__________GPM

8. Previous Cargo (This Voyage)______________________________

Next Cargo (Next Voyage)______________________________

Copy of To/From Wash Procedure Obtained (Circle One) Yes No

9. Previous Cargo Data

Previous Cargo	Voyage No.

10. Tank Coating Material

11. Personnel Locations on Deck WRT B/W, ET, Eductor

12. Personal Sampling Pumps on Wash Personnel

TANK WASHING

Tank No.__________ Contents____________________ Date__________

Vessel________________________ Voyage No.______ OVA ID________

Time	CH4(PPM)	Diluter I.D.	T(°F)	Pump On/Off	Eductor On/Off	Comments

GAS FREEING

1. Tank No.__________ Voyage No.__________ Date___________

2. Chemical Being Ventilated____

3. Pre-Vent/Post-Vent Wash Measurements

a.

Time	Ft ↓*	CH4(PPM)	Diluter I.D.	Bag No.
	0			

*Drop Line Length from Measurement Point

b. Measurement Point (Circle One)

Ullage Cap Standpipe Expansion Trunk

c. Distance of Measurement Point Above Deck________Inches

4. Collect Solution Sample from Tank Bottom

a. Drop Line W/Bottle or

b. Slip Stream Off of Pump

5. Blower Data

a. Make

b. Model No.

c. Rating__________cfm on (Circle One)

Steam Compressed Air

d. Details of Optional Equipment (Modified Nozzle Throat, Etc.)

e. No. of Blowers__________

f. Blower Locations: F C A

g. Status of Remaining B/W Openings (Circle One)

Open Closed

h. Blower Line Pressure__________psig (Circle One)

Compressed Air Steam

i. Status of Hatch (Circle One)

Open Closed

6. Personnel Locations on Deck WRT

7. Sampling Pumps on Deck Personnel

GAS FREEING

Tank No.__________ Contents____________________ Date__________

Vessel________________________ Voyage No.______ OVA ID________

Time	CH_4 (IND) PPM	Diluter I.D.	T(°F)	Pump On/Off	Eductor On/Off	Comments

MAN-ENTRY

1. Tank No.__________ Voyage No.__________ Date____________

Vessel___________________________

2. Chemical Ventilated____

3. Pre-Entry/Post-Vent Measurements

a.

Time	Ft ↓*	CH4(PPM)	Diluter I.D.	Bag No.
	0			

*Drop Line Length from Measurement Point

b. Measurement Point (Circle One)

Ullage Cap Standpipe Expansion Trunk

c. Distance of Measurement Point Above Deck__________Inches

4. Safety Checks

a. O_2 Level__________, Sampling Point__________, Instr.__________________

b. THC Level__________, Sampling Point__________, Instr.__________________

5. Purpose of Man-Entry

If No Man-Entry, Criteria for Acceptance

6. Blower On During Entry (Circle One) Yes No

Which B/W Opening; F , C , A

7. Status of Remaining B/W Openings

Status of Hatch

8. Crewman on Deck for Safety (Circle One) Yes No

SwRI on Deck for Safety (Circle One) Yes No

9. Safety Equipment

Crew

SwRI

10. Sampling Pump on Crew (Circle One) Yes No

11. Intank OVA Readings

a. Down Ladder

Top = __________PPM CH4

Mid = __________PPM CH4

Bot = __________PPM CH4

b. On Bottom

● = Reading Locations

Show Pump Sump & B/W Blower Opening

12. Note Details of Intank Structure

D/B or No D/B, Web Frames, Cutouts, Drain Stringer Holes, Etc.

APPENDIX B

FULL SCALE TANK VENTILATION TESTS EXPERIMENTAL DATA AND MODEL COMPARISONS

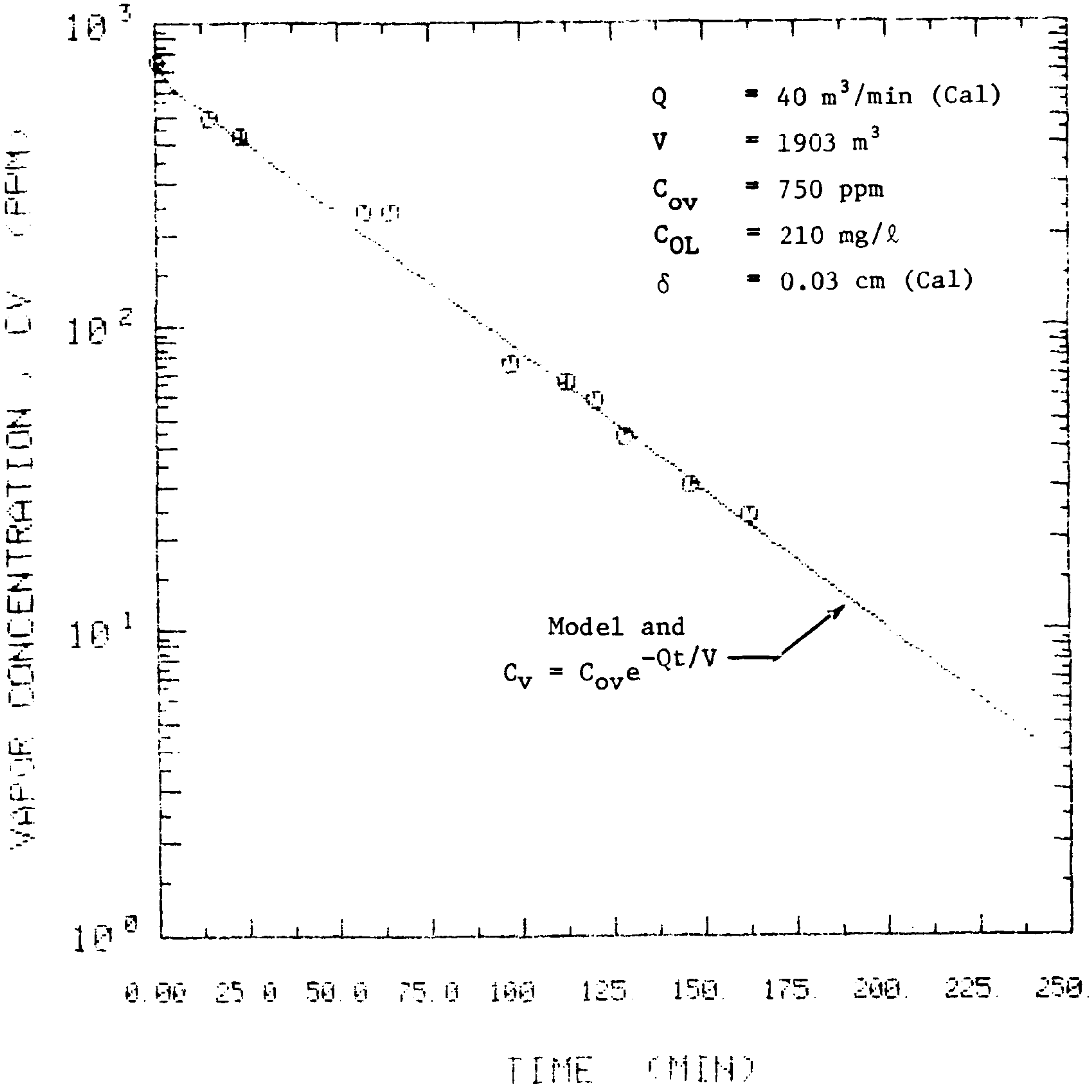


FIGURE B.1. VENTILATION TEST NO. 14 CONDUCTED IN A FULL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF CHLOROFORM AND WATER

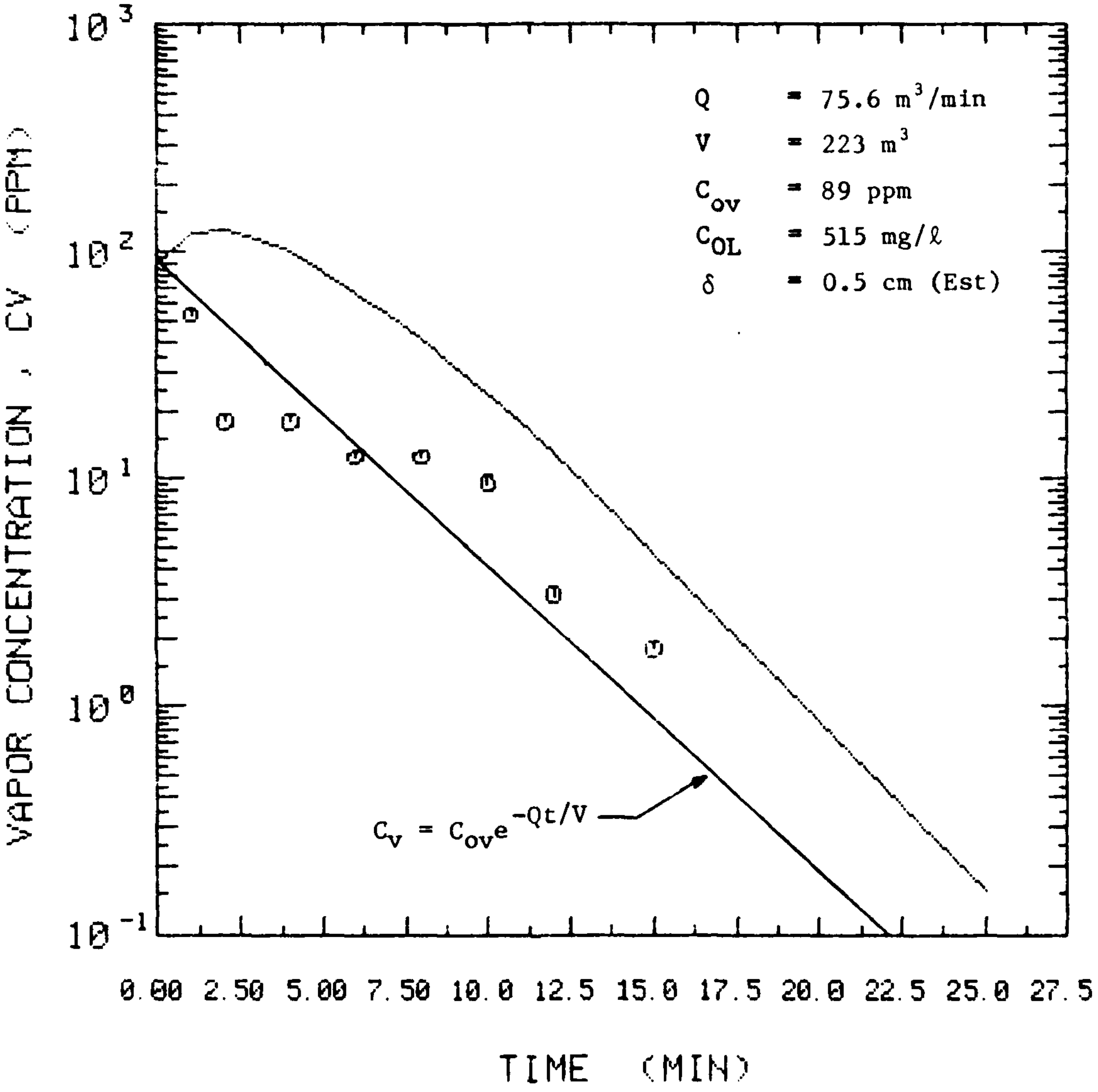


FIGURE B.2. VENTILATION TEST NO. 15 CONDUCTED IN A FULL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF TOLUENE AND WATER

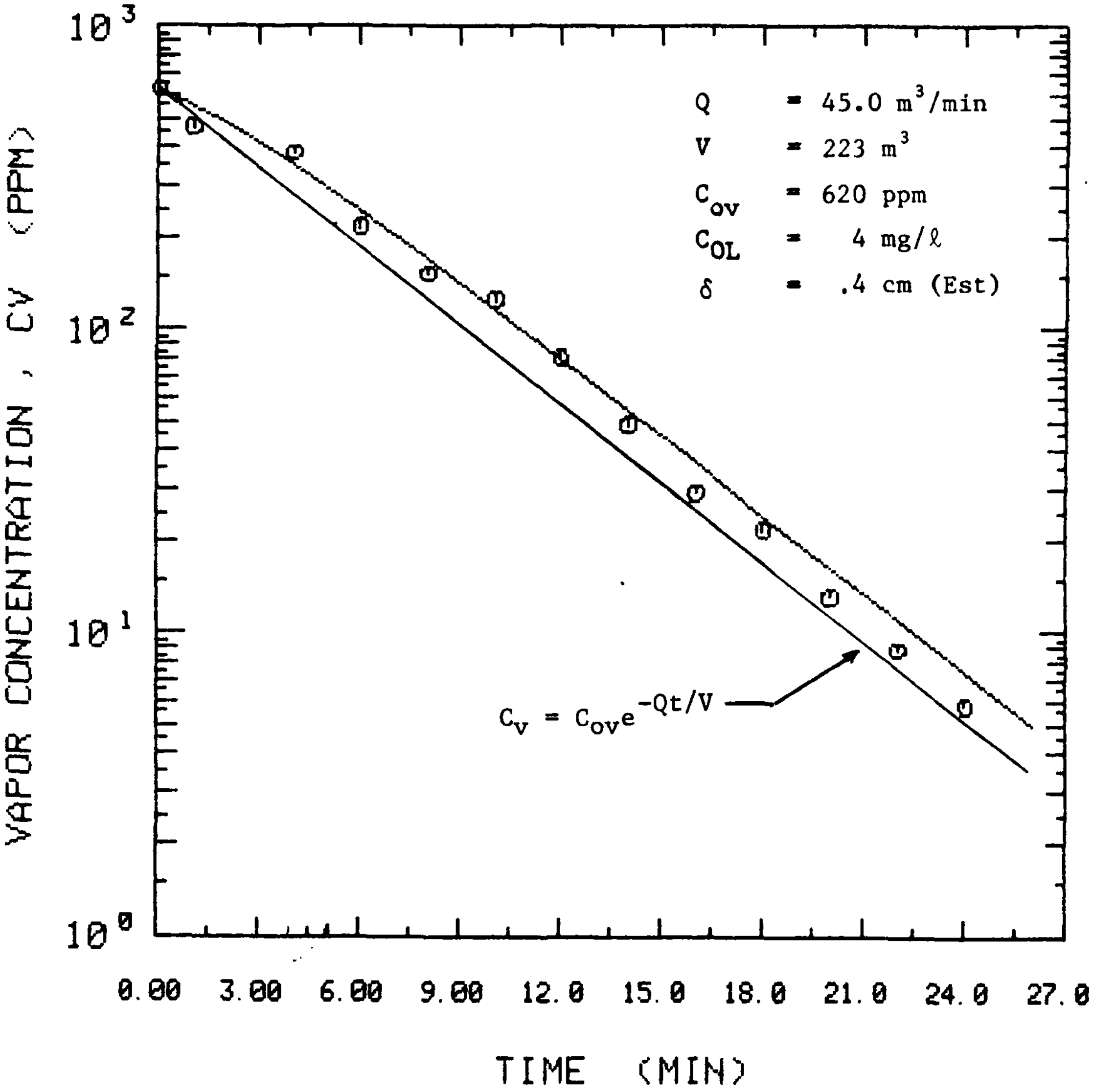


FIGURE B.3. VENTILATION TEST NO. 16 CONDUCTED IN A FULL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF TOLUENE AND WATER

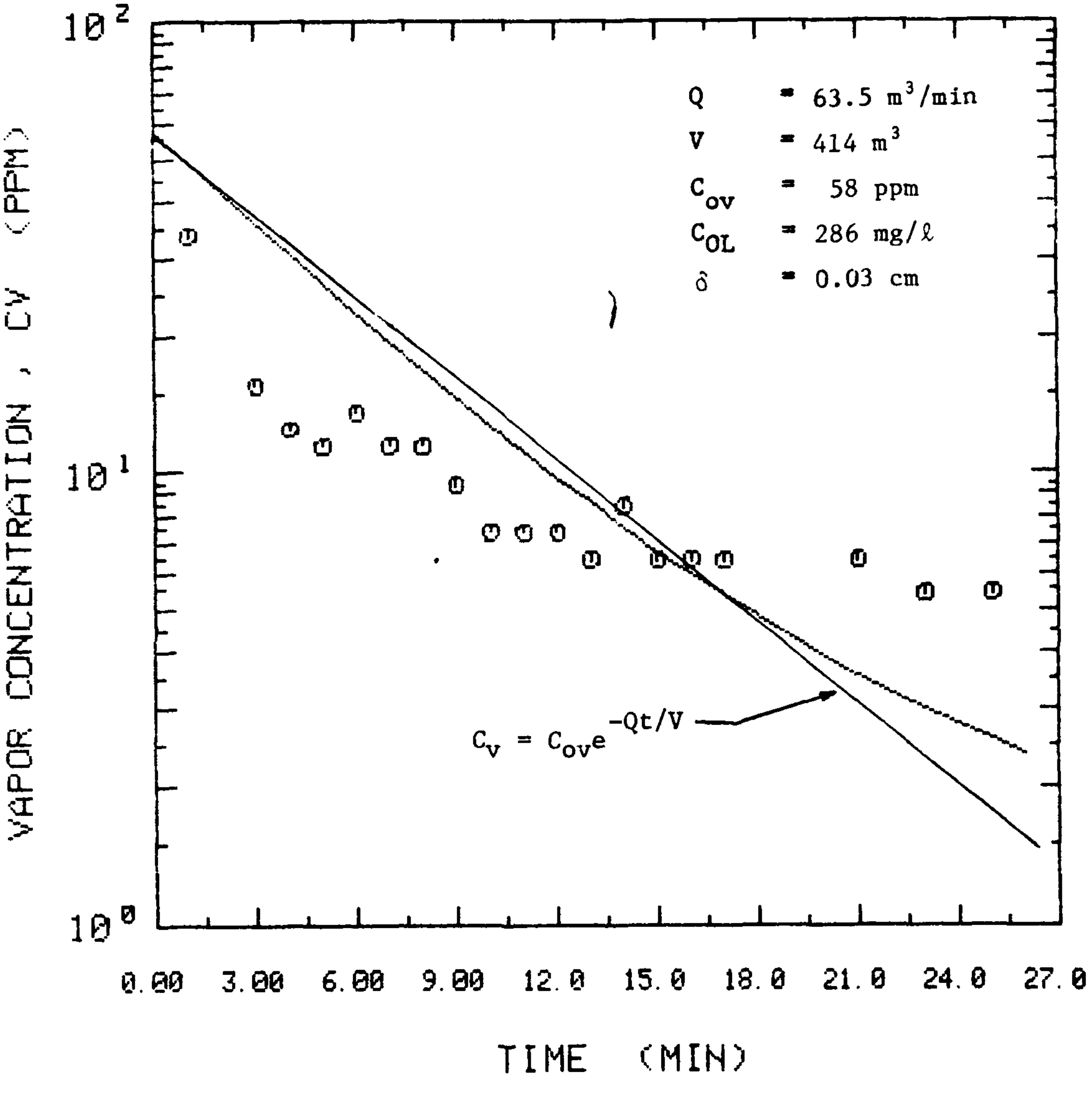


FIGURE B.4. VENTILATION TEST NO. 17 CONDUCTED IN A FULL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF ISOPROPANOL AND WATER

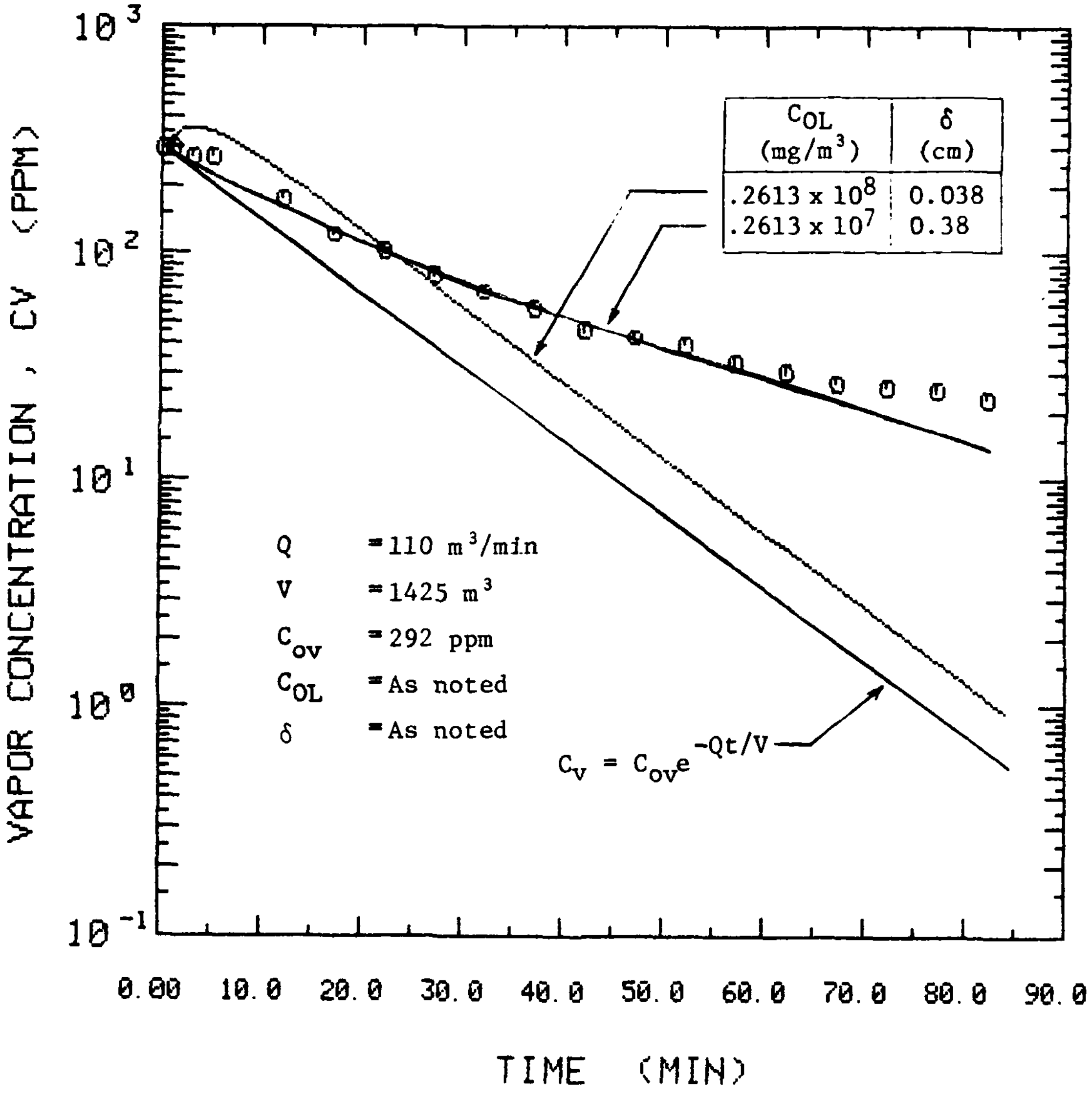


FIGURE B.5. VENTILATION TEST NO. 7 CONDUCTED IN A FULL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF METHYLETHYL KETONE AND WATER

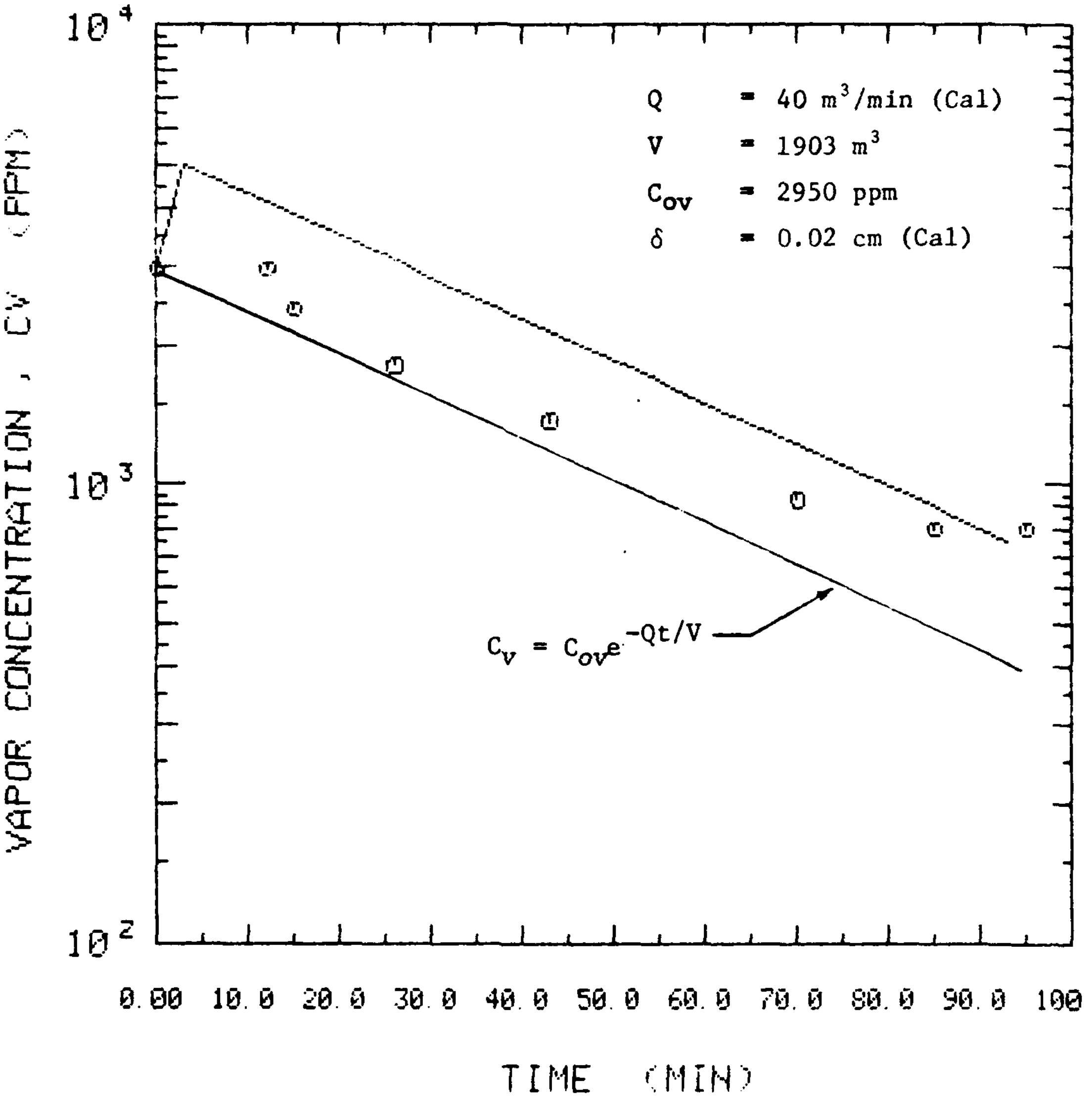


FIGURE B.6. VENTILATION TEST NO. 13 CONDUCTED IN A FULL SCALE TANK WITHOUT STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF CHLOROFORM

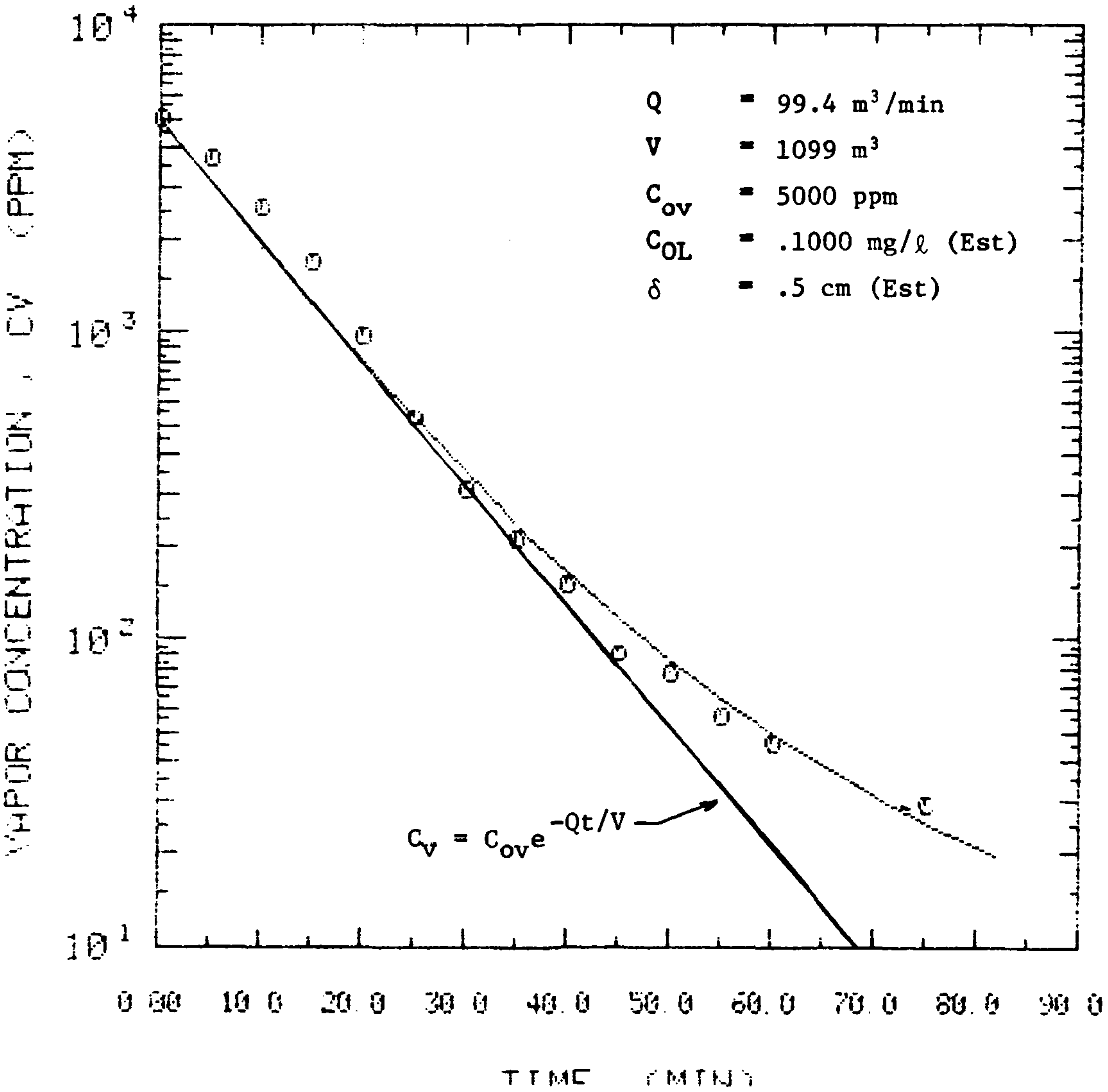


FIGURE B.7. VENTILATION TEST NO. 1 CONDUCTED IN A FULL SCALE TANK WITH STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF ACETONE AND WATER

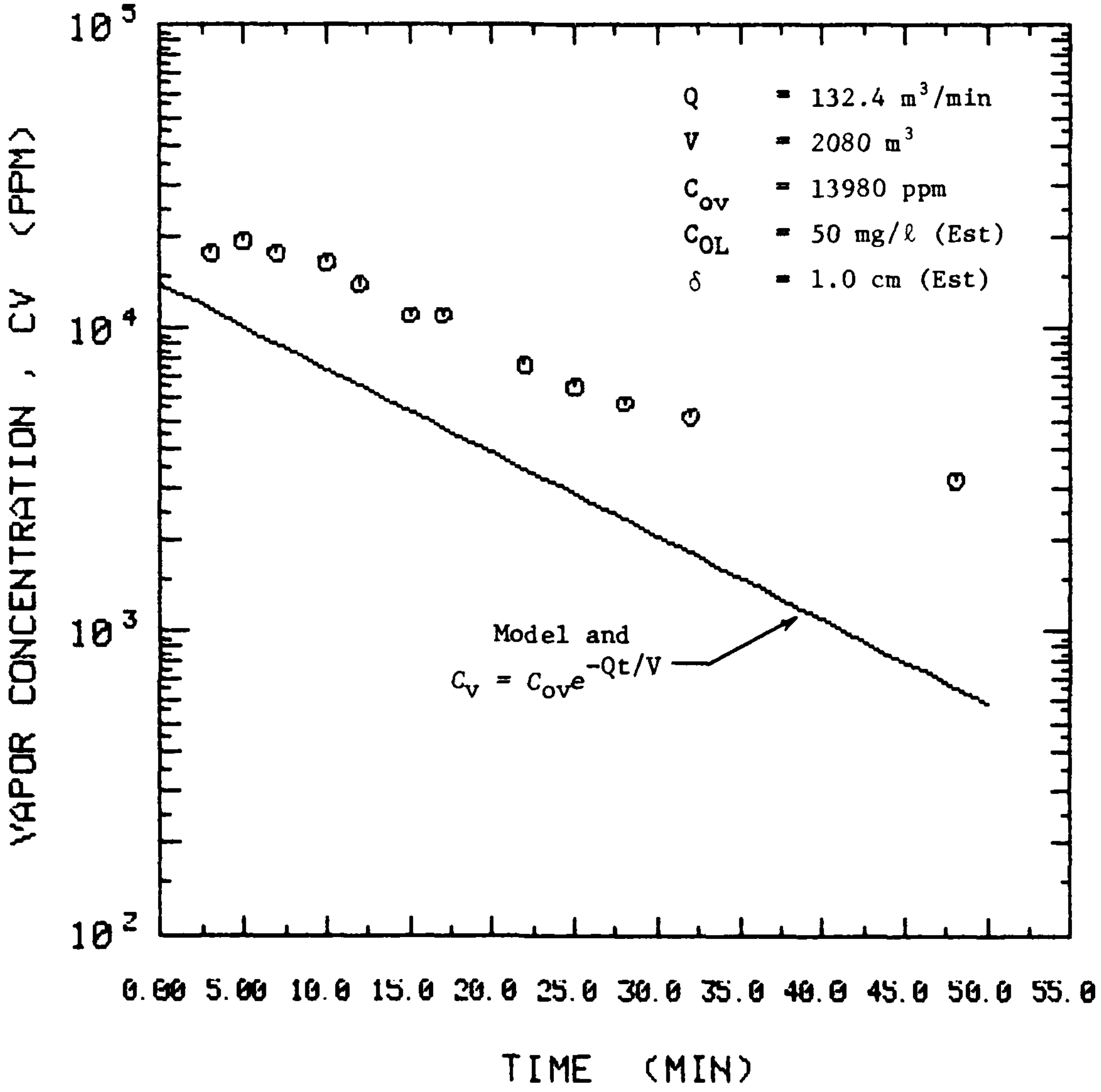


FIGURE B.8. VENTILATION TEST NO. 12 CONDUCTED IN A FULL SCALE TANK WITH STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF GASOLINE AND WATER

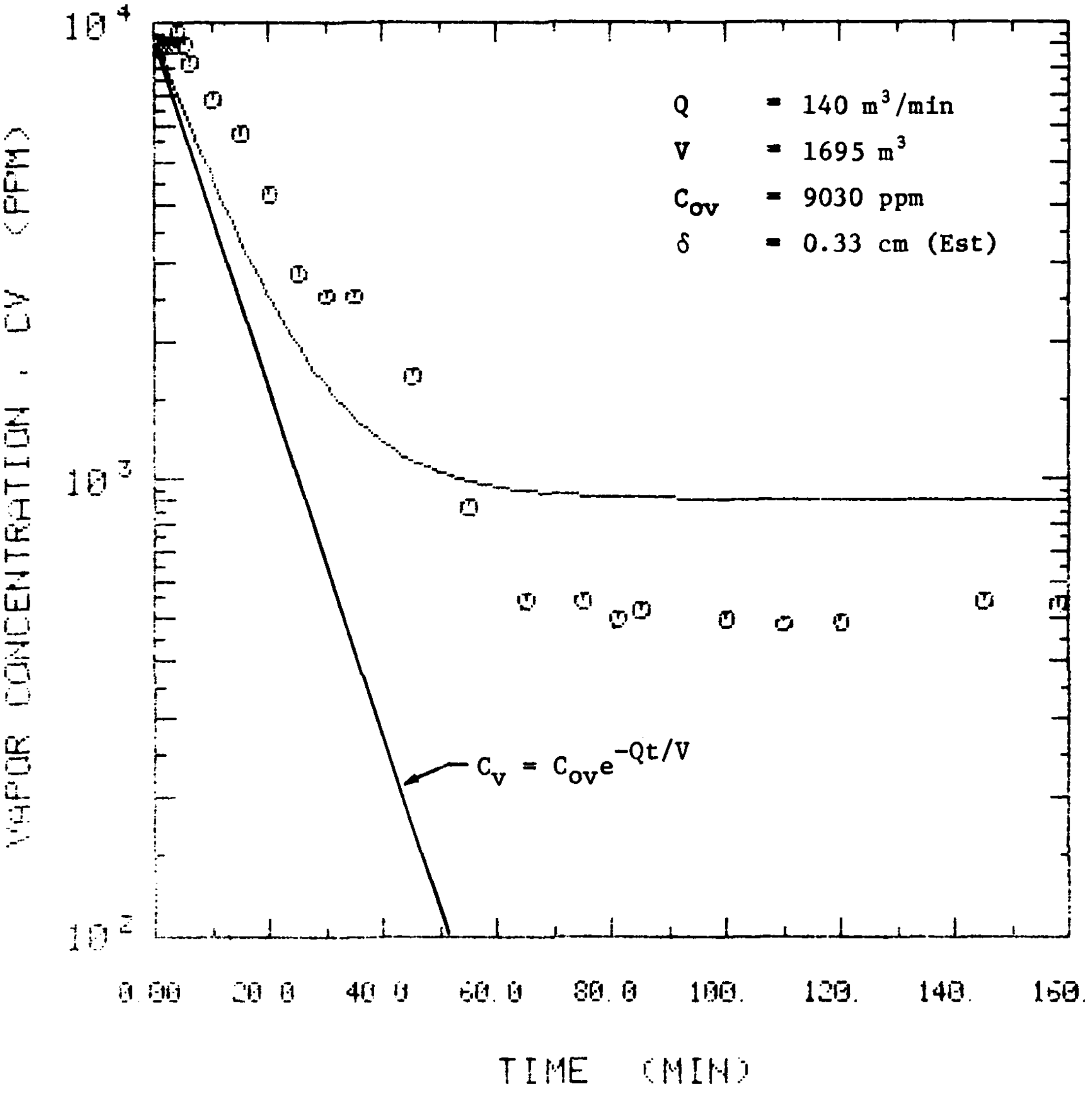


FIGURE B.9. VENTILATION TEST NO. 6 CONDUCTED IN A FULL SCALE TANK WITH STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OR XYLENE

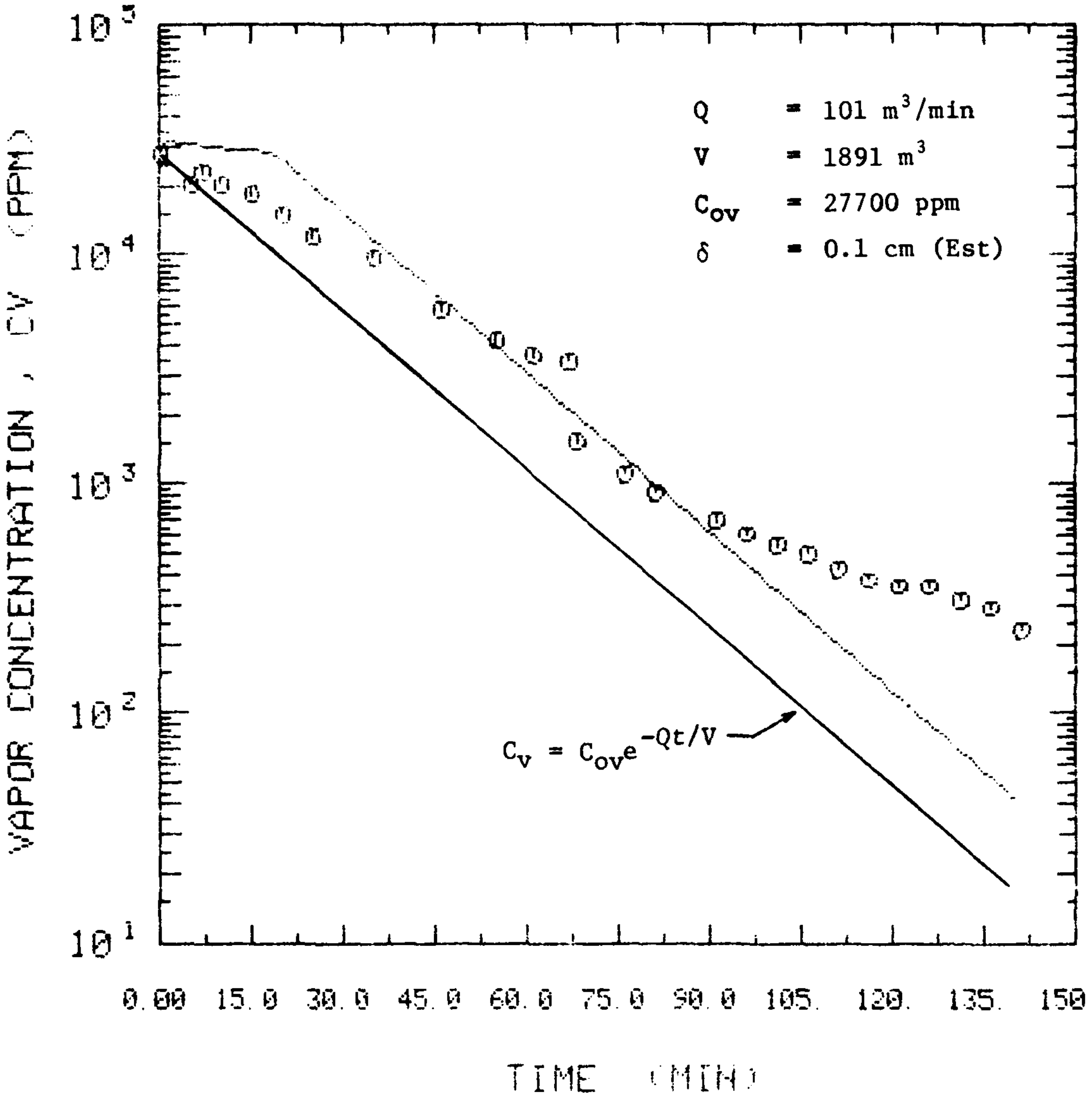


FIGURE B.10. VENTILATION TEST NO. 8 CONDUCTED IN A FULL SCALE TANK WITH STRUCTURE IN THE PRESENCE OF A RESIDUAL LAYER OF ETHANOL

APPENDIX C

DETAILED DOCUMENTATION OF BIOLOGICAL MONITORING TESTS

APPENDIX C

DETAILED DOCUMENTATION OF BIOLOGICAL MONITORING TESTS

The details of two biomonitoring tests conducted during the pilot study are documented in this appendix.

Biological Monitoring Test No. 1

The scheduled test on a ship during the period May 12-14 was cancelled due to terminal rotation changes that precluded boarding the vessel at a point prior to the terminal where toluene was to be loaded. Accordingly, another ship was selected, and a methanol loading test was conducted during the period May 29 - June 2. Officers and crewmen on the cargo transfer watches were recruited and enlisted in the study, and blood, urine, breath, and occupational exposure samples were collected from the three volunteers considered to be the most highly exposed during the loading of 1500 metric tons of methanol. In addition, work scenario activities for each of the three participants were monitored for a period of 24 hours after their initial exposure to the methanol transfer activities.

Mr. R. J. Prevost and a nurse, Ms. T. C. Carter, boarded the ship on May 29th at a terminal preceding the methanol loading. Recruitment activities were initiated on May 30th, and a total of eleven of the ship's crew, including one officer, volunteered for the study. An informed consent form was completed for each of the volunteers, and original copies bearing the signatures of the volunteer and a witness were placed on record in the confidential project files at SwRI.

The watch schedule involved two watches with alternating six-hours ON and six-hours OFF. Accordingly, volunteers were recruited and obtained for both watches. Final selection of the principal study participants was not made until the actual transfer of cargo began and the volunteers with greatest potential exposures to methanol could be determined. During the recruiting effort, the volunteers were informed that only those individuals that were most closely associated with the actual loading of methanol would be selected for the study.

On June 1, Messrs. W. J. Astleford, R. J. Magott, and J. C. Buckingham of SwRI, Ms. M. Hornyack, R.N. (retained through the Milby Clinic, Houston, Texas), and Lt. G. R. Colonna of the Coast Guard, boarded the ship at the loading terminal. Once the cargo loading schedule was determined, two crewmen of the first cargo transfer watch were selected and enrolled in the study on a tentative basis. It was explained that delays in cargo transfer could make members of the second cargo transfer watch more appropriate candidates to study. If such a delay occurred, participation of members of the first transfer watch would be terminated, and participants would be selected from the second transfer watch. The participants agreed to this condition, and initial blood and breath samples were obtained from these participants.

Delays in the methanol loading precluded the use of the participants on the first cargo transfer watch. Three members of the second cargo transfer watch (two A/B's and one pumpman) were selected from the list of volunteers and were enrolled in the study. Blood, urine, breath, and occupational exposure samples were collected on these three participants over the 24-hour period beginning with their initial duties at 1800 hours on June 1. The occupational exposure samples were collected at intervals between successive blood/breath samples, and a record of the scenario of work activities was maintained for each participant over a 24-hour period.

Upon completion of the sampling activities, the study team left the ship, and the biological and environmental samples were transported to the appropriate analytical laboratories.

The results of the field sampling activities regarding the loading of 1500 metric tons of methanol can be summarized as follows:

- 11 volunteers
- 5 participants selected and utilized
- 24 blood samples

- 26 breath samples
- 42 urine samples (21 duplicate samples)
- 22 occupational exposure samples
- 1500 metric tons of methanol loaded into two tanks filled to roughly 82% and 95% capacity.

Biological Monitoring Test No. 2

The second of two biological monitoring tests planned for the pilot study was conducted during the period September 28 - October 1, 1982. Officers and crewmen on the cargo transfer watches were recruited and enlisted in the study, and blood, urine, breath, and occupational exposure samples were collected from the three volunteers considered to be the most highly exposed during the loading of 1000 metric tons of toluene. In addition, work scenario activities for each of the three participants were monitored for a period of 24 hours after their initial exposure to the toluene transfer activities.

Mr. R. J. Prevost of SwRI and a nurse, Ms. T. C. Carter, boarded the ship on September 28th at a terminal preceding the toluene loading. Recruitment activities were initiated on September 29th, and a total of eight of the ship's crew, including two officers, volunteered for the study. An informed consent form was completed for each of the volunteers, and original copies bearing the signatures of the volunteer and a witness were placed on record in the confidential project files at SwRI.

During the recruiting effort, the volunteers were informed that only those individuals that were most closely associated with the actual loading of toluene would be selected for the study. The ship's Captain addressed the men and informed them that those men who volunteered and were selected would be assigned to the transfer watch for the duration of the toluene loading (approximately 3-4 hours) in order to provide no interruption of the biological monitoring activities. The Captain enthusiastically encouraged the men to participate in the study and to provide all the desired samples. The deck officer scheduled for watch during the anticipated loading period volunteered to work with the study team to completion of all samples and was tentatively selected for the study. On this ship, the deck officer personally takes the final ullages during tank topping and therefore is a prime candidate for study. The deck officer is assisted by a pumpman and an O/S during the loading operations. Accordingly, the two crew members to be assigned to these positions during loading of the toluene were sought for the study. Two of the deck crew particularly enthusiastic about the study volunteered to work with the study team to completion of all samples and these two men were tentatively selected for the study.

On September 30th, Messrs. J. C. Buckingham, R. J. Magott, J. P. Riegel, and J. Stout of SwRI boarded the ship at the loading terminal. Once the cargo loading schedule was determined, the tentatively selected officer and crewmen were enrolled in the study. These three men (one officer, one pumpman, and one O/S) were on duty throughout the loading of the toluene. Blood, urine, breath, and occupational exposure samples were collected from these three participants over the 24-hour period beginning with the initial loading at approximately 2000 hours on September 30th. The occupational exposure samples were collected at intervals between successive blood/breath samples, and a record of the scenario of work activities was maintained for each participant over the 24-hour period. In addition to the scheduled breath sampling, two additional breath samples were obtained on deck immediately after tank topping.

Upon completion of the sampling activities, the study team left the ship, and the biological and environmental samples were transported to the appropriate analytical laboratories.

The results of the field sampling activities regarding the loading of 1000 metric tons of toluene can be summarized as follows:

- 8 volunteers
- 3 participants selected and utilized
- 24 blood samples

- 26 breath samples
- 32 urine samples (16 duplicate samples)
- 21 occupational exposure samples
- 1000 metric tons of toluene loaded into two tanks filled to roughly 85% and 73% capacity, the latter of which was shore stopped.

APPENDIX D

ANALYSIS REPORTS FOR
BREATH, BLOOD, AND URINE ANALYSES

APPENDIX D

ANALYSIS REPORTS FOR BREATH, BLOOD, AND URINE ANALYSES

Analysis reports received from the analytical laboratory responsible for methanol, toluene, and metabolite analyses of the biological samples are presented in this appendix. Separate reports are presented for

(1) Methanol content of breath samples
(2) Methanol content of blood samples
(3) Methanol and formic acid content of urine samples
(4) Toluene content of breath, blood, and urine samples
(5) Hippuric acid content of urine samples.

NON-ROUTINE ANALYSIS REPORT
BREATH ANALYSIS

1.0 OBJECTIVE

The objective of this analysis was to quantitate the methanol content in breath samples collected from personnel exposed to methanol during ship loading operations.

2.0 SAMPLE COLLECTION AND DESCRIPTION

The breath samples were collected by SWRI personnel using methods described elsewhere. Twenty-six samples were submitted for analysis in mylar-aluminized air bags.

3.0 ANALYSIS PROCEDURES

The sample bags were first heated to 90 degrees C. by partial immersion in hot water to insure that any condensed water from the breath revrrted to the vapor phase. Fifty cc volume samples were withdrawn from the bags through the septum seal using a syringe. The breath samples were injected into the purging chamber of a Tekmar concentrator, trapped on a combination silica gel-OV101-Tenax adsorbent, and thermally desorbed for injection onto the gas chromatographic column. A mass spectrometer was used for detection of the methanol to increase sensitivity and shorten analysis time. (Charges for these samples, however, are being made according to GC-FID prices.)

Analysis conditions for methanol in breath were as follows:

Sample size: 50 cc
Purge: 100 cc/min of Helium for 4.0 min.
Trap desorption temp.: 180 degrees C.
Trap cooldown time: 4.0 min.
GC Column: 6′ X 1/8" SP1000 on 60/80 Carbopak B

GC Program: 100 degrees C. isothermal
Carrier Gas: Helium at 30 cc/min.
Analysis Time: 10 min.

Quantitation of the methanol was performed by comparing mass chromatogram areas of mass 31 of the methanol peak of the samples to that of a standard. The standards were prepared by injection of water solutions of methanol into bags containing 0.5 liter of air, adding another 0.5 liter of air and then heating the bag as above. Standards were run twice a day to concntration levels approximating those found in the samples. System blanks were run to establish cleanliness of the system prior to beginning the analyses. Several samples and standards were run in duplicate to establish reproducibility. All values are corrected to 25 degrees C. All analyses were completed by June 10, 1982.

4.0 RESULTS

The following are the results of the methanol analyses:

SAMPLE ID	METHANOL ug/L	SAMPLE ID	METHANOL ug/L
03-B1	0.7	04-B7	1.2
03-B2	0.9	04-B8	1.0
03-B3	1.2	05-B1-1	ND <0.5
03-B4	1.0	05-B1-2	ND <0.5
03-B5	1.0	05-B2	ND <0.5
03-B6	0.9	05-B3	3.7
03-B7	1.3	05-B4	4.3
03-B8-1	1.0	05-B5	1.0
03-B8-2	1.4	05-B6	ND <0.5
04-B1	0.8	05-B7	ND <0.5
04-B2	ND <0.5	05-B8	ND <0.5
04-B3-1	ND <0.5	01-B1	ND <0.5
04-B3-2	0.5	02-B1	ND <0.5
04-B4	0.5	SYSTEM BLANKS - Day 1	ND <0.5
04-B5	4.7	Day 2	ND <0.5

04-B6	0.8	Day 3	ND <0.5

ND = Not detected at the indicated limit.

NOTE: The measurement limit for these analyses is 0.5 ug/L. Values reported below 1.0 ug/L are estimated to be accurate to only +- 25%.

METHANOL CONTENT OF BLOOD SAMPLES

NON-ROUTINE ANALYSIS REPORT

1.0 OBJECTIVE

The objective of this analysis was to quantitate methanol in blood samples collected from personnel exposed to methanol during ship loading operations.

2.0 SAMPLE COLLECTION AND DESCRIPTION

The blood samples were collected by Southwest Research Institute personnel using 10 ml Vacutainers (C). Twenty-four (24) samples were submitted for analysis.

3.0 ANALYSIS PROCEDURES

The blood saples were analyzed by direct injection of the whole blood into a GC/MS. Analysis conditions were as follows:

SAMPLE VOLUME:	5.0 ul
GC COLUMN:	8' X 1/8" nickel with 60/80 Carbopack C coated with 0.2% Carbowax 1500
GC PROGRAM:	125 deg. C. isothermal
CARRIER GAS:	Helium at 30 cc/min.

Quantitation of methanol was performed by comparing mass chromatogram areas of mass 31 of the methanol peak of the samples to that of external standards.

4.0 RESULTS

The following are the results of the analysis of the blood samples for methanol content:

Same as 1mg/L = 1 ppm

SAMPLE ID	METHANOL CONTENT (ug/ml)	SAMPLE ID	METHANOL CONTENT (ug/ml)
01-S1	ND <2 (1)	04-S5	ND <2
02-S1	ND <2	04-S6	ND <2
03-S1	ND <2	04-S7	ND <2
03-S2	ND <2	04-S8	ND <2
03-S3	ND <2	05-S1	ND <2
03-S4	ND <2	05-S2	ND <2
03-S7	ND <2	05-S3	ND <2
03-S8	ND <2	05-S4	ND <2
04-S1	ND <2	05-S5	ND <2
04-S2	ND <2	05-S6	ND <2
04-S3	ND <2	05-S7	3.3 (2)
04-S4	ND <2	05-S8	ND <2

(1) Standards were run at the beginning, at the halfway point, and at the end of the analyses to demonstrate a detection limit of 2 ug/ml.

(2) Average of two duplicate runs (values were 3.4 and 3.2).

METHANOL AND FORMIC ACID CONTENT OF URINE SAMPLES

NON-ROUTINE ANALYSIS REPORT

1.0 OBJECTIVE

The objective of these analyses was the quantitative determination of methanol and its metabolite formic acid in urine samples collected from personnel exposed to methanol during a ship loading operation.

2.0 SAMPLE COLLECTION AND DESCRIPTION

Samples were collected by Southwest Research Institute personnel in 10 cc septum vials provided by Spectrix. 0.1 ml of nitric acid was added to each sample as a preservative. Twenty-one (21) samples were submitted in duplicate. One of each pair of samples was analyzed. The remaining set of samples is being retained.

3.0 ANALYSIS PROCEDURES

Analysis procedures for methanol are the same as those previously reported for blood (82-06-012 report). Analysis of formic acid was accomplished by direct injection GC/MS of the preserved urine. Analytical conditions for formic acid were as follows:

SAMPLE SIZE:	2.0 ul
GC COLUMN:	6' X 1/8" glass; 10% SP-1000/1% H3PO4 on 100/120 Chromasorb W AW
GC PROGRAM:	155 deg. C. isothermal
GC CARRIER GAS:	Helium at 70 ml/min.
MS SCAN RANGE:	25 - 50 amu

The samples were quantitated by comparing the areas of the M/Z 46 mass chromatograms in the unknowns to those of external standards.

4.0 RESULTS

The following are the results for the methanol and formic acid analyses of the urine samples:

SAMPLE ID	METHANOL ug/ml	FORMIC ACID ug/ml (4)
03-U1	ND <0.5 (3)	120
03-U3	ND <0.5	130
03-U5	ND <0.5	140
03-U7	0.7	130
03-U9	ND <0.5	98
03-U11	ND <0.5	130
03-U13	ND <0.5	180
03-U15	ND <0.5	180
03-U15 (2)	ND <0.5	Not measured
03-U17	ND <0.5	160
04-U1	ND <0.5	170
04-U3	ND <0.5	140
04-U5	2.8	150
04-U7	ND <0.5	130
04-U9	ND <0.5	130
04-U11	ND <0.5	130
05-U1	ND <0.5	110
05-U3	ND <0.5	91
05-U6 (1)	0.7	95
05-U8	ND <0.5	100
05-U10	ND <0.5	86
05-U10 (2)	ND <0.5	89
05-U12	ND <0.5	90

(1) Field report showed samples were labeled 05-U1 through 05-U12, but there is no Sample 05-U5 and there is a Sample 05-U13.

(2) Duplicate injection.

(3) Not detected at indicated measurement limit demonstrated by injection of external standard of 10 ug/ml methanol every fifth sample analysis.

(4) Laboratory water blanks for tap water, deionized water and

Super Q water contain formic acid at levels of 100 to 150 ug/L. Injection of 2.0 ul methanol produces no formic acid peak demonstrating formic acid is not in the GC/MS system. Since no formic acid free water was available for making formic acid standards, the average value for eight water blanks was subtracted from the average value of three 100 ug/ml formic acid standards to provide the response factors used in these calculations. Accuracies of values below 200 ug/ml are probably no better than +- 25% while precision was shown to be +- 5% by repeated injections of standards.

TOLUENE CONTENT OF BREATH, BLOOD, AND URINE SAMPLES

NON-ROUTINE ANALYSIS REPORT
BREATH, BLOOD AND URINE ANALYSES

1.0 OBJECTIVE

The objective of these analyses was to quantitate the toluene content in breath, blood and urine samples collected from personnel exposed to toluene during ship loading operations.

2.0 SAMPLE COLLECTION AND DESCRIPTION

The samples were collected by SWRI personnel using methods described elsewhere. Samples were stored under refrigeration.

2.1 BREATH SAMPLES

26 samples were submitted for analysis in mylar-aluminized air bags.

2.2 BLOOD SAMPLES

24 samples were submitted for analysis in septum-stoppered test tubes.

2.3 URINE SAMPLES

32 samples were submitted for analysis in septum-sealed serum vials.

3.0 ANALYSIS PROCEDURES

3.1 BREATH SAMPLES

The sample bags were at ambient laboratory temperature (23 - 24 deg. C.) during analysis. Thirty cc volume samples were withdrawn from the bags through the septum seal using a syringe. The breath samples were injected into the purging chamber of a Tekmar concentrator. Volatile organic compounds were trapped on Tenax absorbent and then thermally desorbed for injection onto the gas chromatographic column. The gas chromatographic column was installed in a Perkin-Elmer 900 gas chromatograph and connected to a hnu Systems photoionization detector (10.2 EV lamp).

Analysis conditions for toluene were as follows:

SAMPLE SIZE: 30 cc breath; 0.5 cc blood or urine.
PURGE: 20 cc/min. of Helium for 11.0 minutes.
TRAP DESORPTION TEMP: 180 degrees C.
TRAP COOLDOWN TIME: 4.0 minutes.
GC COLUMN: 10 X 1/8" 10% SP-1000 on 100/120 mesh Chromosorb W AW.
GC PROGRAM: 65 degrees C. isothermal.
CARRIER GAS: Helium at 30 cc/min.

3.2 BLOOD AND URINE SAMPLES

The samples, at or near ambient laboratory temperature, were thoroughly mixed by vigorous shaking. An aliquot of each sample was mixed with 1.0 cc of DI water and 0.1 cc of dilute Antifoam B Silicone Emulsion. The mixture was then injected into the purging chamber of a Tekmar Concentrator. The remaining procedure is as described for the breath samples.

3.3 QUANTITATION OF TOLUENE

Quantitation of toluene was performed by comparing the area of the toluene peak (retention time of toluene established by injecting standards) of the samples to that of standards. Standards for the breath analysis were prepared by injecting methanol solutions of toluene into septum-sealed vials (115 ml) containing air. Aliquots were then diluted in air to give concentrations in the range found in the samples. Standards for the blood and urine analysis were prepared by injecting methanol solutions of toluene into DI water containing antifoam agent to give concentrations in the sample range. Standards were run daily. System blanks were run to establish cleanliness of the system prior to beginning of analysis. In all cases, toluene was not detected. A sample of blood (07-S7) was spiked with 104 ug/L toluene; recovery was 80%. A sample of urine (07-U4) was spiked with the same amount of toluene; recovery was 84%. Selected samples and standards were analyzed in duplicate, i.e., a second aliquot of urine was taken from the same bottle. The breath analyses were completed by October 21, 1982; the blood analyses by November 5, 1982; and the urine analyses by November 10, 1982.

4.0 RESULTS

4.1 The results, not corrected for recovery, of the toluene analyses are given below:

BREATH SAMPLES

SAMPLE ID	TOLUENE ug/L	SAMPLE ID	TOLUENE ug/L
06-B1	0.5	07-B6	0.2
06-B2	0.4	07-B7	ND <0.1 *
06-B3	1.2	07-B8	0.3
06-B4	0.5	08-B1	0.2
06-B5	0.4	08-B2	TR <0.1 **
06-B6	0.9	08-B3	0.9
06-B7	0.3	08-B4	0.3
06-B8	0.3	08-B5	0.4
07-B1	1.8	08-B6	0.6

07-B2	1.4	08-B7	TR <0.1
07-B3	0.9	08-B8	0.2
07-B4	0.4	06-BX	0.6 ***
07-B5	0.4	06-BY	0.4 ****

BLOOD SAMPLES

SAMPLE ID	TOLUENE ug/L	SAMPLE ID	TOLUENE ug/L
06-S1	2.3	07-S5	22.3
06-S2	25.8	07-S6	17.6
06-S3	32.9	07-S7	14.1
06-S4	8.2	07-S8	11.8
06-S5	7.1	08-S1	21.2
06-S6	9.4	08-S2	45.8
06-S7	7.1	08-S3	32.9
06-S8	TR <2	08-S4	62.3
07-S1	104.1 *****	08-S5	15.2
07-S2	47.0	08-S6	11.8
07-S3	61.1	08-S7	5.8
07-S4	41.1	08-S8	3.5

URINE SAMPLES

SAMPLE ID	TOLUENE ug/L	SAMPLE ID	TOLUENE ug/L
06-U1	ND <2	08-U1	TR <2 ******
06-U2	TR <2	08-U2	ND <2
06-U3	ND <2	08-U3	TR <2
06-U4	ND <2	08-U4	2.3
06-U5	ND <2	08-U5	7.1
06-U6	ND <2	08-U6	ND <2
06-U7	ND <2	08-U7	ND <2
06-U8	ND <2	08-U8	ND <2

07-U1	4.6	06-U9	ND <2
07-U2	7.1	06-U10	ND <2
07-U3	2.3	06-U11	ND <2
07-U4	ND <2	06-U12	ND <2
07-U5	ND <2	07-U9	ND <2
07-U6	ND <2	07-U10	ND <2
07-U7	3.5	07-U11	ND <2
07-U8	ND <2	07-U12	ND <2

* = ND; not detected at the indicated detection limit.
** = TR; trace amount; detected but not measurable.
*** = Represents duplicate analyses; 0.6 and 0.6 ug/L.
**** = Represents duplicate analyses; 0.5 and 0.4 ug/L.
***** = Represents duplicate analyses; 102.4 and 105.8 ug/L.
****** = Represents duplicate analyses; TR <2 and TR <2 ug/L.

4.2 STATEMENT OF PRECISION AND ACCURACY

Duplicate runs, referring to *** through ****** above, give agreement better than 5% of the mean at concentrations of 100 ug/L down to 0.5 ug/L. Accuracy of values reported can be expected to be += 20% (1 sigma) based on the measured recovery for toluene and statistical data published by the USEPA for this method. For example, if a value of 100 ug/L were reported, there is a 66% chance (1 sigma) that it is between 80 and 120 ug/L.

Comparison of the results for duplicate urine samples analyzed from separate sample vials (i.e., odd number urine samples are duplicates of the next higher even number) doesnot show comparable agreement. This disagreement is probably the result of sample handling and storage, since we are dealing with very small amounts. For example, simply pouring the urine from a large container into the two septum vials may result in the loss of significant amounts of toluene when such low concentrations are involved. Consideration of all types of sampling and storage problems results in a measurement limit of 10 ug/L even though instrumental measurement reproducibility is good at lower values.

HIPPURIC ACID CONTENT OF URINE SAMPLES

NON-ROUTINE ANALYSIS REPORT
URINE ANALYSIS

1.0 OBJECTIVE

The objective of this analysis was to quantitate the hippuric acid content in urine samples collected from personnel exposed to toluene during ship loading operations. Hippuric acid is the metabolite of toluene. Earlier correspondence and documents (Spectrix quotes dated 4/10/80 and 3/16/82; UTHSCSA Protocol dated 12/16/80, page 9) mistakenly indicate that benzoic acid would be the analyte.

2.0 SAMPLE COLLECTION AND DESCRIPTION

The samples (32 in septum-sealed serum vials) were collected by Southwest Research Institute personnel and submitted for analysis. The samples were stored under refrigeration until analyzed.

3.0 ANALYSIS PROCEDURE

The procedures used to obtain the results given in this report are summarized below. Additional work on the development of the analysis procedure for urine for hippuric acid is in the Appendix.

3.1 EXTRACTION AND DERIVITIZATION

The procedure used was a modification of that described by Caperos and Fernandez (British Journal of Industrial Medicine, 1977, 34, 329 - 233) with the following changes:

1) Dimethylformamide dimethylacetal (Esterate from Supelco) was used instead of 3-methyl-1-p-polytriazene as the methylating agent.

2) Due to the change in methylating agent, the derivitized product was in a mixed solvent (dimethylformamide dimethylacetal, ethylacetate and methanol) instead of chloroform.

Our procedure may be summarized as follows:

Urine (0.5 ml, thoroughly mixed) or deionized water was transferred to an 8-ml vial and acidified with 0.1 ml of 10 N. HCL. After introduction of 5 ml of ethyl acetate containing 200 ug (400 mg/L of urine) of tridecanoic acid (internal standard), the vial was sealed with a teflon -lined cap and shaken for 5 minutes. Three mls of the ethyl acetate extract were transferred to a 4 ml vial and carefully blown to dryness (no heat was applied) under blowing nitrogen. Blowdown was continued until no HCL could be detected in the vial as checked with pH paper. The residue in the vial was treated as follows:

100 ul dimethylformamide dimethylacetal, 100 ul ethyl acetate and 50 ul methanol were added to the vial. The vial was sealed

and then heated 45 minutes at 60 degrees C. in an incubating oven. The reaction mixture, after cooling, was then ready for analysis without further treatment.

3.2 GC ANALYSIS

The instrument used was a Perkin-Elmer 900 gas chromatograph, FID, fitted with a 1.8 m X 2 mm ID glass column packed with 10% OV-101 on 100/120 mesh Chromosorb W-HP. Analysis conditions for the hippuric acid ester were as follows:

AMOUNT INJECTED:	3 ul
CARRIER GAS:	Helium at 20 ml/min.
INJECTION PORT TEMPERATURE:	250 deg. C.
MANIFOLD TEMPERATURE:	250 deg. C.
GC PROGRAM:	120 deg. C. for 4 min., then programmed to 270 deg. C. at 8 deg. C./min.

3.3 QUANTITATION OF HIPPURIC ACID

Quantitation of hippuric acid was carried out by the internal standard method. Response factors for the internal standard and hippuric acid were obtained by analyzing esterified tridecanoic acid (methyl tridecanoate) and hippuric acid (methyl hippurate) that were in the concentration range of hippuric acid found in the samples. The calculation is as follows:

$$\text{Hippuric acid, mg/L} = \frac{PA(MH)}{PA(IS) \times RRF} \times C(IS)$$

where:
PA = Peak area;
MH = Methyl·hippurate;
IS = Internal standard (methyl tridecanoate);

C = Concentration of IS in mg/L; and

$$\text{RRF} = \text{Relative response factor} = \frac{\text{RF(IS)}}{\text{RF(MH)}} = 1.0$$

Standards were run daily. System blanks were run to establish the cleanliness of the system. Selected samples were analyzed in duplicate. Deionized water and selected samples were spiked with hippuric acid to determine recoveries. The analyses of urine for hippuric acid were completed by December 10, 1982.

4.0 RESULTS

The results of the hippuric acid analyses, not corrected for recovery factor, are given in Table 1:

TABLE 1
HIPPURIC ACID RESULTS

A. SAMPLE RESULTS

SAMPLE ID	LAB ID	HIPPURIC ACID mg/L	SAMPLE ID	LAB ID	HIPPURIC ACID mg/L
06-U1	-01A	589	07-U5	-17A	365
06-U3	-03A	902	07-U7	-19A	214
06-U5	-05A	719	07-U9	-21A	299
06-U6	-06A	654	07-U11	-23A	581
06-U7	-07A	256	08-U1	-25A	433
06-U9	-09A	169	08-U2	-26A	481
06-U11	-11A	43	08-U3	-27A	974
07-U1	-13A	1.72X10(3)	08-U5	-29A	781
07-U2	-14A	1.78X10(3)	08-U7	-31A	52
07-U3	-15A	690			

B. DUPLICATE EXTRACT DATA

EXTRACT PAIR	MEAN, mg/L	RANGE	% DEVIATION
-05A, -06A	686	65	+- 4.8
-13A, -14A	1.75 X 10(3)	60	+- 1.7
-25A, -26A	457	48	+- 5.3

Average Pair Agreement +- 3.9% of Mean

C. SPIKE DATA

LAB ID	CONC. MEASURED	INITIAL CONC.	AMT. SPIKED	RECOVERY
Lab Water-SS	1.16 X 10(3) mg/L	0 mg/L	1.00 X 10(3) mg/L	116%
Lab Water-SS-Duplicate	1.14 X 10(3) mg/L	0 mg/L	1.00 X 10(3) mg/L	114%
-06A - SS	1.13 X 10(3) mg/L	654 mg/L	600 mg/L	79.8%
-26A - SS	2.08 X 10(3) mg/L	481 mg/L	1.60 X 10(3) mg/L	100%

Average Recovery = 102%

D. REPLICATE INJECTION DATA

SAMPLE	AVE.	RANGE	% DEVIATION
-26A - SS	2.08 X 10(3) mg/L *	182	+- 4.3

* = Average of two values, 1.99 X 10(3) and 2.18 X 10(3)

5.0 PRECISION AND ACCURACY STATEMENT

The duplicate extract data given in Table 1 indicate that the combined errors of the extraction, derivitization and analysis result in agreement of better than 5% of the average value when two duplicate urine samples are compared. There seems to be better precision as the concentration of hippuric acid increases over the range encountered. The precision of replicate injections of the same extract is comparable to that for duplicate extracts. The average recovery for four spiked samples is 102% and ranges from 79.8% to 116% with urine samples giving lower recoveries than lab water. The relative standard deviation of the spike recoveries is 17.0% (1 sigma) preliminarily indicating an accuracy of better than +- 20% of the reported values. A verification of this accuracy and more definitive accuracy and precision statements will require additional duplicate extract and spike recovery data from subsequent sample sets.

6.0 APPENDIX

In our efforts to analyze for hippuric acid, we have used two articles as references:

1) Caparos and Fernandez, British Journal of Industrial Medicine, 1977, 34, 229-233; and
2) Kiro, British Journal of Industrial Medicine, 1977, 34, 305-309.

We first tried to use the procedure of Caperos and Fernandez with the exception that a 1 m X 3 mm ID glass column packed with 3% OV-101 (Applied Science, High Efficiency Column Series 3000-3) was used instead of the column specified (4.5 m X 2 mm ID glass column packed with 4% Apiezon M on 80/100 mesh Chromosorb G AW-DMLS). These results were negative because the 3-methyl-1-p-tolyltriazene used would not form the methyl derivative.

Our second effort to analyze hippuric acid in urine is described in our report of November 19, 1982. These results were generally lower than expected and were characterized by poor repeatability.

A portion of this work was repeated using the same procedure (Kiro) except the sodium sulfate drying step was omitted, a 1.8 m X 0.2 mm glass column packed with 10% OV-101 on 100/110 W-HP was used and the reaction mixture was analyzed. These results were in general agreement with the previous report. However, repeatability was much improved.

A summary of the results follows:

SAMPLE ID	HIPPURIC ACID, mg/L
07-U1	865
07-U2	936
07-U7	103
07-U8	101
07-U7 Spiked *	574
07-U8 Spiked *	550

* = Spiked with 1000 mg/L hippuric acid. Recovery = 47.1 and 44.9%, respectively.

After discussing the results tabulated above and our previous report with Mr. John Prevost, the decision was made to repeat the analysis of all the samples except that only selected duplicates would be run. We used the procedure of Caperos and Fernandez instead of Kiro because we thought the poor recovery could be caused by the short extraction period. However, subsequent experience has indicated that the major difficulty was probably in the esterification step. When the residue was esterified either in pure dimethyl formamide or 50/50 dimethyl formamide, the product was turbid. By adding a small amount of methanol, the turbidity of the reaction mixture was removed. To test the effect of methanol, methanol was added to run 07-U1 and 07-U2, tabulated above. There was about a 15% increase in the internal standard response and a 100% increase in the hippuric acid response. The use of methanol was incorporated in the procedure used.

APPENDIX E

PERSPECTIVE ON THE TOXICOLOGY OF CHEMICAL EXPOSURES

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I. INTRODUCTION AND BACKGROUND

Water transportation is generally recognized as an economical mode of transport for bulk commodities. Consequently, large quantities of bulk liquids - crude oil, petroleum products, petrochemical feedstocks and finished petrochemicals - are moved by water. Movement is accomplished in vessels of all sizes from small barges to large tankers. Most vessels have multiple tanks so that a number of quite different products can be transported at the same time in a single vessel.

A. Activities Offering Exposure Potential

It is possible to distinguish three primary categories of activities and personnel that might come into contact with chemical vapors in consequence of these water movements. These are:

1. Deck Department personnel who are involved in the loading and discharging of the liquid cargoes,
2. personnel who enter tanks for cleaning purposes, and,
3. personnel who enter cleaned tanks for inspection purposes. This category would also include Marine Chemists and Coast Guard inspection personnel.

These three major potential exposure situations will be discussed in more detail.

Cargo Transfer

Several operations in the normal handling of chemical cargoes offer at least the potential for significant chemical exposures.

1. Shipboard personnel who handle hoses during loading and discharging operations may be exposed to vapors when lines are being coupled or uncoupled, i.e., lines from the dock to manifold onboard the ship. Exposures may involve cargoes left in the lines or manifold or liquids dripping from lines. Further, there is always the possibility of line ruptures in which substantial exposures may be involved to both vapors and liquids.

2. Personnel involved in tank gauging operations may be exposed to appreciable amounts of vapor. It has been observed that visual observations are frequently used even when vessels are equipped with mechanical or electronic automated gauging systems.

Tank Cleaning Personnel

Cleaning of tanks may be undertaken for a variety of reasons. These include cleaning necessitated by a change of cargo, cleaning to remove residues, cleaning required before maintenance operations can be undertaken, and cleaning required for biennial inspections for certification purposes.

Cleaning of chemical tanks, which includes washing and gas freeing, is performed before any human entry is permitted into the tank. Entry into chemical tanks is frequent, and is generally required after gas freeing to accomplish additional cleaning because tanks have areas in which liquids can accumulate and cannot be totally removed by pumps. In the case of tanks that have held heavy products such as crude petroleum, heavy fuels, etc., man entry may be less frequent because these tanks are normally dedicated to carriage of a single product, or compatible products, and there is a lesser concern for product contamination.

Tank cleaning personnel may obtain exposures to a variety of chemicals because a given tank may have retained residues of several chemicals in trace quantities. It has been reported that the rusty scale that may be present in tanks can absorb chemicals, from which vapors may be released following gas freeing.

Inspection Personnel

In many cases, shipboard personnel will enter and inspect a cleaned tank. The ship personnel may accompany a quality control inspector or surveyor to inspect the tank for residues and odor of previous cargoes before approving the loading. Marine chemists also enter to perform tests for parameters such as oxygen content, explosive mixtures, and toxic agents.

These tests are necessary before maintenance, inspection, and similar activities may be undertaken. Coast Guard personnel enter tanks to perform inspections relating to vessel safety and seaworthiness in connection with the certification process. It has been indicated that Coast Guard personnel may enter the tanks some time after the Marine Chemist's measurements have been made. This offers the possibility that the level of toxic agents may be considerably different from values determined at the time of measurements. Indications are that this is particularly a problem when the ambient temperature is higher at the time of the inspection than when the tank atmosphere tests were performed.

B. Pathways of Exposure

Chemicals of concern to this study are in the form of liquids, although some chemicals require pressurization to preserve the liquid state under ambient conditions. Consequently, the exposures of interest will be in the form of:

1. Gases, in the case of cargoes that would normally be in the gaseous state under ambient temperature and pressure,
2. vapors, in the case of cargoes that would normally be in the liquid state under prevailing environmental conditions,
3. aerosols, in the form of liquid droplets dispersed in air when a liquid is mechanically agitated by splashing, bubbling, rapid flowing, etc., and
4. bulk liquids that contact unprotected skin.

Toxic agents enter the body through three primary pathways:

1. Ingestion, in which the contact occurs via the gastrointestinal tract,
2. inhalation, in which the contact occurs via the pulmonary system,
3. dermal, in which the chemical comes into direct contact with the skin. A special case also of interest is contact of chemicals with the eye which is an especially critical and sensitive tissue.

With respect to ingestion and dermal contacts, bulk materials are most generally involved. Intoxication by ingestion is not a major concern with adult occupational exposures, the assumption being that adults are usually not prone to ingest foreign substances. Therefore, ingestion will not be a major consideration in this report.

Dermal contact with bulk liquid or spray may occur during normal operations and accident conditions. Chemicals vary widely in their ability to pass through the skin and enter the circulation. Some chemicals which may not readily pass through the skin may be damaging because of their lipophilic nature. This results in the removal of protective fats and oils from the skin, rendering the skin less effective as a defensive barrier.

Eyes and mucous membranes may be especially sensitive to the whole range of common chemicals. Sensitivity may be due to the acidity or alkalinity of the chemical. There can be little quarrel with the common view that contact between eyes and mucosa and chemicals should be avoided insofar as possible.

The inhalation contact is generally the pathway of greatest concern because contact with the chemical may be continuous and unrecognized. In addition, the amount of air inhaled, especially by an actively working adult, is substantial, so that the appearance of a contaminant even at low concentrations can result in a significant dose.

Inhalation of vapors and gases can result in deep respiratory penetration because of the small sizes of the contaminants: atoms and molecules. Finely divided aerosols are also capable of deep penetration. Particles under 10μ would be expected to penetrate the pulmonary system, with particles in the range of 1-5μ penetrating to the alveoli where the gas exchange process takes place.

When a chemical enters the gastrointestinal (GI) tract, the pulmonary system, or is in contact with the skin, it is still outside of the body. For systemic intoxication to occur, the chemical must be absorbed; it must pass the GI, lung, or skin barrier. This absorption process may involve metabolic or other chemical changes of the contacting chemical, thereby offering possibilities of intoxication by derivatives or metabolites of the original chemical. This complicates the problem of assessing the potential for intoxication.

C. Exposure Duration

Shipboard work schedules are frequently quite different from those that are characteristic of land-based industries. This is especially true for personnel involved in the loading or unloading of cargoes.

The typical industrial worker will work 8-10 hours per shift each day, working four or five days a week for about 50 weeks a year. Exposures to chemicals will then occur for 8-10 hours each day, with a "purge time" during the remaining 14-16 hours of each day. This purge time enables the system to dispose of potentially hazardous agents.

On board vessels, work is much more concentrated during the critical loading, tank cleaning, and unloading operations. A Deck Department crew member may work continuously for an extended period, sometimes 24 hours or more. During the work period, a variety of chemicals may be contacted as different cargoes are handled, and short-term exposures to very high levels of chemical vapors may be involved. Once the operation has been completed and the vessel is in transit between ports, there may be essentially no exposure. The no-exposure condition may persist for days or weeks - a very long purge time after several hours of exposure to varying levels of many substances.

The problem of multiple exposures, i.e., exposure to a variety of chemicals at varying concentrations in differing sequences, is not unique to shipboard personnel, but it probably represents an extreme case, especially when consideration is given to the range of concentrations of chemicals encountered during certain operations. A deck hand participating in vessel loading may be exposed to several chemicals at quite high concentrations during peak operating periods.

II. CONTROL OF EXPOSURES TO CHEMICALS

A. Assumptions

Certain basic assumptions are necessary for a rational approach to controlling workplace exposures. These have been stated succinctly by Hatch (see Cralley, et al, 1968):

1. There exists a systemic dose-response relationship between the magnitude of exposure to the hazardous agent and the degree of response in the exposed individual.
2. There is a graded decrease in the risk of injury as the level of the exposure goes down, and the risk becomes negligible when exposure falls below a certain tolerable level.

If these assumptions are correct, then chemicals in the workplace can be dealt with safely at some acceptable level of exposure to the worker above zero, and, therefore, it is not necessary to eliminate exposure completely to assure the worker's health.

Although there has been general agreement within the biomedical community on the validity of the above assumptions for most substances, there is continuing concern that these assumptions may not be valid for materials that produce either direct or secondary effects on genetic material. The concern is that <u>any</u> exposure to substances that produce such effects can initiate a course of action leading, eventually, to a carcinogenic or mutogenic response, far removed in time from the original insult. For this reason, it has been proposed by one sector of the biomedical community to work toward complete elimination of these specific agents from the working environment.

The converse position, supported by a maturing research base, is that the assumptions outlined above hold for all materials and for all effects, and, therefore, that a safe working environment <u>can</u> be maintained without complete removal of contaminants.

B. Sources of Data

The data base upon which to establish workplace standards can be derived from (a) the workplace experience, (b) human and/or animal experimentation or (c) analogy between chemicals.

When dealing with an unfamiliar chemical, animal or human health effects data are usually minimal or not available. Therefore, the prevailing principle is that the quality of response of a chemical may be assumed to be similar to that produced by chemically analogous substances.

It is generally presumed that chemicals that are structurally similar should produce similar biological responses so that a first estimate of toxic potential can be obtained. There are serious limitations on this procedure. First, there is no assurance that a particular chemical in a series will respond in a manner consistent with its relatives. An important example of this is found in the simple aliphatic hydrocarbon series. Hexane has a spectrum of toxicity that is qualitatively distinct from either pentane or heptane (Couri and Milks, 1982)*. Prediction of quantitative effects on the basis of chemical analogy is also difficult since the differences in the physico-chemical properties conveyed by addition of even one carbon radical to a molecule can markedly alter the biochemical availability of this material. However, despite the obvious limitations of this procedure, almost one out of every four of the Threshold Limit Values originally adopted for regulation under the Occupational Safety and Health Administration were based upon chemical analogy (Stokinger, 1970).

Animal experimentation, and to a lesser extent human experimentation, has formed the basis for the majority of current workplace health standards. There are, of course, limitations to the use of either of these approaches for evaluating the toxicity and/or hazard of materials in the workplace.

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*References are presented at the end of each major section.

First, for ethical considerations, any deliberate human exposures to foreign materials must be, by definition, at levels that are free from producing any permanent or delayed disease, i.e. safe. This precludes most experimentation using humans. However, considerable information can be obtained for many chemicals on uptake distribution and excretion of materials that is of vital importance in the establishment of rational standards.

Although the ethical consideration is more relaxed in regard to experimentation with animals, so that the full range of deleterious effects can be investigated, two serious limitations exist. First, the design of animal experiments should reflect the condition of industrial exposure to the substance in question. Most animal investigation does not reflect the expected conditions of industrial usage.

Secondly, there is a problem of extrapolation of animal information to man. This problem has been addressed by first seeking toxicological information on a variety of animal species on the premise that consistent responses across a variety of species increases the chance that man will respond in a similar manner. Further, no one species consistently reacts to foreign materials as does man. Therefore, in responding to a foreign chemical, man should be considered to be at least as sensitive as the most sensitive animal model tested. Three problems remain.

1. Whether man will respond as the most reactive or least reactive species tested cannot be universally predicted.
2. The question as to whether the most sensitive species has been tested is never completely resolved.
3. The problem of whether the animal response has any parallel to the human disease process cannot be completely answered.

Nevertheless, in the absence of data based on appropriate human experience, extrapolation from animal experimentations must be utilized in establishing workplace standards.

There remains the need for data on the toxicity of materials in several areas that cannot be obtained from animal experiments including assessment of

1. irritation and nausea,
2. allergic response,
3. odor evaluation,
4. higher nervous function effects, and
5. human metabolic pathways for specific chemicals.

This information can usually be derived from careful utilization of data from the occupational or workplace experience.

C. Standards

Until passage of the Occupational Safety and Health Act, the majority of workplace standards used in the United States were based on recommendations from one or more concensus committees (Dinman, 1973). These organizations, which include the American Conference of Governmental Industrial Hygenists (ACGIH) and the American National Standards Institute (ANSI) offered, and continue to offer, recommendations for Threshold Limit Values (TLV's) for contaminants in the workplace. TLV values refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be exposed eight hours a day for a forty-hour week over a working lifetime without adverse effect. These values are established by consensus of a number of experts in industrial hygiene and toxicology and are reviewed periodically. Information for their judgment is obtained from available literature data and personal information known to committee members.

Since adoption of the Occupational Safety and Health Act (OSH Act) of 1970, the National Institute for Occupational Safety and Health (NIOSH) has had the responsibility for developing criteria and recommended standards, and the Department of Labor has the responsibility for enforcement in the majority of work environments through the Occupational Safety and Health Administration (OSHA).

Current standards, whether voluntary or regulatory, still relate only to the 8-hour a day and 40-hour week, work-rest cycle. They do not adequately reflect the marine industry from either the work schedule or work conditions. There is, therefore, considerable need to obtain information regarding these "unusual" circumstances so that marine operations workers can be adequately protected.

Several methods have been proposed for adjusting the "normal" workday standards and limits to reflect the novel or unusual work schedule, i.e., Brief and Scala, Roach, Hickey and Reist, and Mason and Dershin. These are, for the most part, based on limitation of body burden and depend on mathematical adjustment of the current standards. However, the data base from which these proposals have been derived is very limited and pending verification, these methods should not be relied upon (see Calabrese, 1977). The occupational exposure data base for the novel marine work schedule is being developed under U. S. Coast Guard sponsored research projects*. The merits and limitations of these adjustment models are also being investigated.

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*"A Crew Exposure Study-Phases I and II," USCG Contract No. DTCG23-80-C-20015, Southwest Research Institute Project No. 06-6177.

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III. FACTORS INFLUENCING TOXICITY

A. Physical and Chemical Properties

This section is concerned with chemicals produced in the U. S. in significant quantities each year. It is presumed that chemicals produced in such high volume would be most likely to present potential health hazards under certain conditions of exposure. A recent EPA document, "Perspectives on the Top 50 Production Volume Chemicals", (July 1980), lists these chemicals, which are reproduced in Table E.1. Many of these are recognized as being shipped in bulk by barge or tanker. Thirty-one of the 50 are organic substances and are mostly monomers of plastics, rubbers or fibers.

The organic substances in Table E.2 are listed in increasing order of their boiling points. Only 19 are liquids that may be used as solvents although that may not be their sole use.

It is important to recognize that chemicals, even when they start as relatively pure material, being chemicals or solvents, are generally contaminated with other material. In use, chemicals or solvents consist of mixtures of varying composition, and the effects noted in studies of single solvent vapor exposure may, at best suggest likely target organ specificity, or minimal toxicity (Couri and Abdel Rahman, 1977). Furthermore, most of the literature dealing with volatile agents is derived from studies of single agent exposure (or administration) aimed at providing safety data and hazard evaluation for the work environment. Consequently, these studies often describe results of either acute, high dose mortality data (LD_{50}, LC_{50}) or long-term (chronic) low concentration exposures. In either case, the data provide guidelines for establishing relative hazard indices. Animal studies coupled with any known human exposures at various safe and sometimes lethal levels of chemicals are compiled, evaluated and used as a basis for recommended short-term exposure limits (STEL); or the time weighted average threshold limit value (TLV - TWA).

Two factors are important in considering chemical volatility. The vapor pressure determines the maximum concentration that can be reached at equilibrium; evaporation rates indicate how fast the maximum

TABLE E.1. CHEMICALS PRODUCED IN EXCESS OF ONE MILLION POUNDS PER YEAR

1. sulfuric acid
2. lime*
3. oxygen*
4. ammonia
5. nitrogen*
6. ethylene
7. chlorine
8. sodium hydroxide
9. phosphoric acid
10. nitric acid
11. sodium carbonate*
12. ammonium nitrate
13. propylene
14. benzene
15. urea*
16. ethylene dichloride
17. toluene
18. ethyl benzene
19. vinyl chloride
20. styrene
21. formaldehyde
22. methanol
23. xylenes (mixed)
24. terephthalic acid*
25. hydrochloric acid
26. ethylene oxide
27. carbon dioxide*
28. ethylene glycol
29. ammonium sulphate*
30. butadiene
31. p-xylene
32. carbon black
33. cumene
34. acetic acid
35. phenol
36. sodium sulfate*
37. calcium chloride*
38. aluminum sulfate*
39. cyclohexane
40. acetone
41. propylene oxide
42. acrylonitrile
43. isopropyl alcohol
44. adipic acid*
45. vinyl acetate
46. sodium silicate*
47. acetic anhydride
48. sodium tripolyphosphate*
49. titanium dioxide*
50. ethanol

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* Not permitted to be transported by water.

TABLE E.2. ORGANIC CHEMICALS IN TOP 50 RANKED BY BOILING POINTS

Organic Substance	TWA ppm	TWA mg/m3	STEL mg/m3	Flash Point °C	M.P. °C	B.P. °C	Mol.Wt. g/mole	TWA* grams	Vap.Pres. mm Hg
ethylene					-169	-104	23		52400
propylene					-182	- 47	42		8666
formaldehyde	2	3			- 92	- 20	30	6	4177
vinyl chloride	5	10			-160	- 14	63	20	3214
butadiene	1000	2200	2750		-109	- 5	54	4400	2260
ethylene oxide	10	20			-111	11	44	40	1290
propylene oxide	20	50	360	- 37	-112	34	58	100	532
acetone	750	1780	2375	- 20	- 94	57	58	3560	221
methanol	200	260	310	12	- 98	65	32	520	122
vinyl acetate	10	30	60	- 6	- 93	72	86	60	108
acrylonitrile	2	4.5		0	- 84	77	53	9	110
ethanol	1000	1900		9	-114	79	46	3800	57
benzene	10	30	75	10	6	80	78	60	95
cyclohexane	300	1050		- 18	6	81	84	2100	98
isopropyl alcohol	400	980	1225	12	- 89	83	60	1960	43
ethylene dichloride	10	40	60	15	- 35	83	99	40	82
toluene	100	375	560	6	- 95	111	92	750	28
acetic acid	10	25	37	40	17	118	60	50	3
ethyl benzene	100	435	545	20	- 95	136	106	870	10
p-xylene	100	435	655	30	13	137	106	870	9
acetic anhydride	5	20	16	54	- 73	139	102	40	5
xylenes	100	435	655	29	- 47	139	106	870	8
styrene	50	215	425	32	- 31	145	104	430	7
cumene	50	245	365	46	- 96	152	120	490	4
ethylene glycol	125	125	325	115	- 13	198	62	250	0
phenol	5	19	38	79	43	182	94	38	
adipic acid				196	152	338	146		

*The quantity of chemical required to achieve the TLV-TWA if evenly dispersed in a $2000 m^3$ product tank.

can be reached. Table E.3 compares the TWA in ppm with the concentration of saturated vapor in ppm as determined by the vapor pressure. The ratio of saturated vapor concentration to the TWA is a measure of the potential inhalation hazard. This ratio can be designated as the Inhalation Hazard Potential (IHP). Note that it varies from 72,000 for acrylonitrile, to one for ethylene glycol. Note also that vapor pressure correlates well with boiling point; only ethyl and isopropyl alcohols, acetic acid and its anhydride are lower than expected.

Although p-xylene is "7-1/2 times as toxic" as acetone, acetone has 27 times the vapor pressure of xylene and is potentially a greater hazard. Acetone also evaporates 4.5 times as fast as p-xylene. Evaporation rates vary greatly with ambient conditions, and they depend upon temperature, air velocity, as well as the vapor pressure and surface tension of the solvent. In general, evaporation rates correlate well with vapor pressure. Only methanol and acetic anhydride evaporate slower than expected from their vapor pressures, while toluene and acetic acid evaporate faster.

While focusing on toxicity, the hazards of fire or explosion should not be ignored. Table E.3 also lists the lower and upper explosive limits in ppm. All the TWA's are well below the LEL.

B. Host Factors

In the recent literature, there has been extensive research reported by many investigators to correlate chemical exposure to alterations in bodily function such as enzyme levels, organ damage, changes in the central and peripheral nervous system, alterations in bodily fluid components, urinary component and metabolites, and many other vital functions of the body. Work has been done to determine the levels of chemical exposure at which these alterations will occur. Investigators have also attempted to determine at what levels of exposure the damage is reversible, at what levels the damage is not reversible, and the time frame at which point the damage can no longer be reversed. It has become clear that the status of the receptor is a factor of major importance.

TABLE E.3. ORGANIC SOLVENT INHALATION AND FLAMABILITY HAZARD POTENTIAL

Substance	TWA	C_s	LEL	UEL	C_s/TWA*	LEL/TWA**	C_s/LEL
propylene oxide	20	700250	20000	220000	35013	1000	35
acetone	750	290237	25500	128000	387	34	11
methanol	200	160531	67200	365000	803	336	2
vinyl acetate	10	142632	26000	134000	14263	2600	5
acrylonitrile	2	144763	30500	170000	72382	15250	5
ethanol	1000	75237	32800	189500	75	33	2
benzene	10	124999	4000	71000	12500	400	31
cyclohexane	300	128605	12600	77500	429	42	10
isopropyl alcohol	400	56645	20200	118000	142	51	3
ethylene dichloride	10	108012	62000	159000	10801	6200	2
toluene	100	37164	12700	67500	372	127	3
acetic acid	10	4157	54000		416	5400	0
ethyl benzene	100	12500	10000	67000	125	100	1
p-xylene	100	11519	11000	70000	115	110	1
acetic anhydride	5	6658	29000	103000	1332	5800	0
xylenes	100	10851	10000	60000	109	100	1
styrene	50	9599	11000	61000	192	220	1
cumene	50	5906	9000	65000	118	180	1
ethylene glycol	125	175			1		

TWA = Threshold Limit Value-Time Weighted Average in ppm
C_s = Concentration of Saturated Vapor in ppm
LEL = Lower Explosive Limit in ppm
UEL = Upper Explosive Limit in ppm

* Index of inhalation hazard potential
** Flamability hazard = the rates of LEL/TWA

1. Age

It is generally felt that as an individual ages there is a gradual decrement in physiological processes, especially between the ages of 40 and 70 years. This could result in greater susceptibility to intoxication upon exposure to chemicals. Age, in and of itself, is not of any great significance in the evaluation of an individual's response to chemical exposure(s) (Couri and Milks, 1982). Yet, of great importance to the worker is an effect such as the potential impairment of their reproductive capacities which would result from exposure to certain solvents or chemicals, e.g. dibromochloropropane (DBCP) and ethylene oxide crown ethers. Relative to age is the state of preservation of healthy organ function. Persons beyond 40 years of age develop degenerative disease symptoms which are sometimes difficult to differentiate from those symptoms resulting from chemical exposure (Dyro 1978; Browning 1968). For example, complaints such as weakness, fatigue, headaches, malaise could represent physiological defects attributable to either natural processes or exposure to a variety of solvents and/or chemicals (Couri et al, 1976).

2. Health Status

Workers with healthy, well functioning physiological systems are better able to handle chemical exposures. The uptake, distribution, metabolism and excretion of most chemical exposures at low to moderate concentrations are such that they are readily processed and excreted with little or no consequences (Carpenter et al, 1949). In contrast to this, individuals exposed to the same chemicals but having impaired respiratory, hepatic and/or renal function would show severe and possibly irreversible adverse effects attributable to the decreased organ function(s) (Kleinhnecht et al, 1980).

There are many solvents capable of altering the rate of liver biotransformation activity and subsequent excretion of chemicals (Odkuist et al, 1979). These alterations may then produce an increase or decrease in the impact of chemical exposure.

The factor of health status can be approached from several vantage points when discussed in relationship to exposure to chemicals. First, it can be viewed from the aspect of the ability to metabolize and

and inactivate compounds that are considered harmful to the body. For instance, the inability to metabolize the solvent xylene, would lead to many complications in an individual such as severe fatigue, weakness, headache, and G.I. discomfort (Dyro, 1978). Liver function is a very significant factor in relationship to health status. In conjunction with liver function, kidney function is also vital and similar in many respects to liver in relationship to the metabolism and excretion of chemical compounds. Further important considerations relate to the presence or exacerbation of disease by exposure to chemicals (Kronevi et al, 1979). It is possible that a disease that might have been silent for many years can be induced to surface and cause significant discomfort and illness. Another possibility is that these compounds may manifest actions via the CNS and may cause any alteration in the nervous system to proceed to a higher level of discomfort, agitation or confusion. Thus, it is important when conducting a study on exposure to chemicals that a complete history and physical be given to an individual prior to the study. As would be expected, many alterations in bodily function will bias the data and yield incorrect conclusions. If any system in the body is not functioning properly, chemical exposure may or may not cause an increased alteration in the systems mentioned.

3. Immune System

For many years investigators thought that toluene was the substance that caused bone marrow suppression. It was not until Hamilton and Hardy in 1974 proposed from available data that toluene was not the cause of the bone marrow damage but rather the contaminant benzene which was present in toluene. This finding spurred many years of research into the capacity of benzene and analogs to induce damage to the immune system. Studies have been able to link solvent exposure with leukemia in rubber workers. McMichael et al, 1975, showed in an epidemiologic study that there was an association between leukemia and work involving exposure to chemical solvents. Other studies (Aksoy et al, 1974, Wolf et al, 1981) have shown that chemical solvents, mainly benzene and its homologues, were able to cause neutropenia and anemia. Therefore, if an individual did have any preexisting immune system disturbance, exposure to chemicals and solvents could exacerbate these disturbances (Moszcynski, 1980). These individuals would then be more susceptible to microbial infection.

4. Fatigue

It might be inferred intuitively that a fatigued person would be more susceptible to chemical intoxication. An individual who works 12-16 hours might be stressed and fatigued considerably more than an individual who only worked an 8-hour shift (Capurro, 1979). An individual who worked 12-16 hours would be exposed to a chemical for a longer time and would likely not be able to sense the chemical effects because of fatigue (Pederson et al, 1980). This is not to say that an individual who only worked eight hours would not be fatigued; his relative fatigue would probably be significantly less than the individual who worked 12-16 hours. Further, the individual who worked more than eight hours would be proven to have more damage on the whole than the individual who only worked eight hours in the same chemical environment (Capurro, 1980).

5. Life Style

Life style factors include smoking, drug and other chemical abuse, alcohol consumption, malnutrition, lack of exercise, and multiple medication use. The individual who can be characterized by one or more of these factors would be at a significantly greater risk than the individual who possesses none of these habits and is in excellent health. This is similar to many diseases afflicting man such as atherosclerosis, lung cancer, and cancer in general. A smoker has a greater risk of lung and other organ cancers than the non-smoker. Similarly in atherosclerosis, the individual who eats less cholesterol is at lesser risk than an individual who eats foods with very high contents of cholesterol and saturated fats. The individual who works in chemical processing has a greater risk of cancer than the individual who works in a non-chemical occupation, e.g. office worker (Moszczynski, 1980); on the other hand, the office worker would be at a greater risk of heart disease related to such sedentary work.

6. Race

A review of the literature with respect to toxicities of particular chemicals revealed no differences existed in observed effects among different races from Europe, Asia, Russia and the U. S. A. The commonality of effects suggests that no differences in response to toxicants exist among the races and various ethnic groups. However, individuals within the races may exhibit differences dependent upon genetic and epigenetic traits.

7. Sex

There seems to be no difference between males and females in the relative amounts of chemical retention. A study performed by Nomiyama and Nomiyama (1974) showed that the retention time of benzene following exposure was similar in both sexes. After exposure to benzene women had a greater blood concentration for the first two hours. Following the 2-hour period, men and women converged to identical blood levels. There is some evidence suggesting that women may have a tendency to have smaller uptake and excretion of organic solvents than men. This may be attributed to the difference in adipose tissue and water content between men and women (Sato et al, 1972, Bartonicek, 1962), but at this time, there is no hard evidence confirming this suggestion.

8. Genetic History

Individuals that demonstrated toxic responses upon exposure to chemicals and solvents were once termed "hypersensitive" or "idiosyncratic". Further studies revealed that these individual susceptibilities could be explained by genetic makeup, i.e. genetic deficiencies such as glucose-6-phosphate dehydrogenase deficiency (G6PD). These otherwise healthy persons, when exposed to aniline or aromatic nitro or amine (nitrobenzene) derivatives would suffer erythrocytic damage and lysis resulting in hemolytic anemia, a life endangering condition. Individuals having the G6PD trait must be identified and protected from such exposures. Several other enzyme deficiencies can be recognized by pre-employment history and/or blood tests, e.g. atypical cholinesterases, slow/fast acetylators, endowing susceptibility to esters and hydrazine derivatives, respectively.

C. Single and Mixed Chemical Exposures

In reviewing the literature, many investigators have demonstrated that exposure to a chemical, such as a single solvent, can and may lead to a variety of alterations in vital bodily functions as mentioned previously.

In 1978, Engstrom et al, demonstrated that with the solvent xylene, a component used in paint thinners, there was a high correlation between urinary methylhippuric acid levels (expressed in terms of mg/g of creatine) and the time weighted average exposure to xylene, via inhalation. It is well known that xylene is biotransformed by the body to toluic acid, which is then conjugated with glycine and excreted in the urine as methylhippuric acid. Engstrom showed that after three hours following a single exposure to xylene, a high concentration of methylhippuric acid was present in the urine, and elimination of methylhippuric acid continued for the next 10 hours following the exposure to xylene. He was able to demonstrate low levels of excretion of methylhippuric acid for at least 72 hours following exposure. This indicated that xylene was accumulated in the body and was slowly released and metabolized for days following the initial exposure. This behavior suggests a secondary excretion phase of methylhippuric acid and supports the idea that xylene was indeed being accumulated by the body after the initial exposure.

As mentioned earlier, Engstrom was able to correlate the methylhippuric acid concentration with the amount of creatine present in the urine. For example, at 25 ppm of xylene exposure, a level of approximately 350 mg methylhippuric acid per gram of creatine in urine was present. At 50 ppm of xylene exposure, a level of 665 mg/g of creatine in urine was present. From his data, it can be concluded that the amount of methylhippuric acid per gram of creatine was nearly a linear function of exposure and can be used as an indicator of xylene exposure. Engstrom was not able to correlate the blood level of xylene to expired air due to the fact that xylene is highly soluble in blood, so the exchange was in favor of xylene entering the blood circulation and leaving insignificant amounts to be expired into the atmosphere. Exhaled air samples can be used only for a rough estimation of momentary exposure in the work environment. Since xylene is highly soluble in blood, this would account for the levels of accumulation of xylene in the body mentioned earlier. Engstrom was able to use the blood level of xylene as an indicator of the body burden levels for different concentrations of xylene. Neither exhaled air samples nor venous blood taken at given intervals during or after a termination of exposure in a work day produced particularly accurate information on the average amount of xylene in ambient air. The best indicator for xylene exposure was the level of excreted methylhippuric acid expressed as mg per gram of creatine.

Having now discussed the effects of a single solvent, attention should now be focused on two or more chemicals and/or solvents interacting together. In recent years, investigations have been conducted of polyneuropathies in acute and chronic inhalers of glues and paint thinners in industry. Dyro (1978) investigated solvents acting independently of other solvents and then acting together. His objective was to determine whether or not solvents acting together will cause more damage than either solvent acting alone. He established the fact that many agents such as n-hexane, acrylamide, and methylbutyl ketone will cause nerve damage, thus effecting nerve conduction velocities and prolonged distal motor latencies (Allen et al, 1975; Herskowitz et al, 1971; Garland et al, 1968). Duro investigated the mixed solvent effects of methylethyl ketone (MEK) with acetone and toluene via the inhalation route. He based his studies on the finding of Altenkirch et al (1979) which showed that methylethyl ketone was capable of synergizing the effects of methylbutyl ketone and n-hexane in sufficient concentration. Dyro first studied a glue composed of 51% MEK and 27% toluene as the solvents. The patients he studied were exposed to 10 ppm MEK and 25 ppm toluene. The threshold limit values (TLV) for MEK and toluene were then 100 ppm and 200 ppm, respectively. Dyro found that workers had significant neuropathies. Dyro proposed that MEK was not the cause of neuropathy. He suggested that MEK was enhancing the effects of toluene, an agent known to cause neuropathies. It was noted that when the workers ceased employment, the symptoms persisted for a year. On follow-up examinations, the majority of the symptoms gradually disappeared within two years with the exception of a few symptoms, which could be attributed to other sources. It should be stated that the values for MEK and toluene were estimated and that the solvent concentrations at times reached the TLV.

In a second study, Dyro examined a glue composed of MEK and acetone. The workers were exposed to 21-180 ppm MEK and 36-250 ppm acetone. The TLV limits were then 200 ppm for MEK and 1000 ppm for acetone. From the study of these workers Dyro was able to show that an MEK and acetone combination caused more neurological damage than either solvent acting independently. Two years after cessation of exposure to these solvents, some workers still showed mild neuropathy, suggesting that the combination of MEK and acetone was more damaging than the combination of MEK and toluene. There have been several other reports of industrial toxicities which involved the presence of MEK in a mixture with other solvents; examples include (1) 10% 2-nitropropane and MEK (Elkins, 1959) and (2) MEK and an unsaturated ketone impurity (Smyth, 1956). In each of these cases, workers presented symptoms which were of greater severity than could be accounted for by any of the individual components.

Similar findings have been reported for ketones in combination with butyl, ethyl, and amyl acetates and other solvents (cited in Browning, 1965, Couri et al, 1974, Couri et al, 1976). Other studies have indicated that workers exposed to 1000 to 2000 ppm acetone for many years show no injury or, at worst, a dull headache with temporary anorexia. The well-known bone marrow injury related to benzene exposure was in some reports also thought to be a toxicity of toluene. It was later proven to be the presence of benzene contamination in toluene which was responsible for the myelotoxic events (Hamilton and Hardy, 1974). This example of marrow toxicity caused by very low levels of benzene in toluene can be looked upon as an enhanced toxicity of low concentrations of benzene when combined with toluene.

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IV. POTENTIAL CHEMICAL AND ENVIRONMENTAL INTERACTIONS

A definition of toxicological interactions, accepted by many investigators is as follows: "A toxicological interaction is a circumstance in which exposure to two or more chemicals results in a qualitatively or quantitatively altered biological response, relative to that predicted from the actions of a single chemical acting alone." Multiple-chemical exposures may be simultaneous or sequential in time while the altered response may be greater or smaller in magnitude."[1]

Injury produced by a chemical in a living organism is proportional to the quantity of the biologically active form of the chemical that is available for reaction with critical responsive sites, i.e., the targets. Thus, toxicological interactions can be considered as taking two forms:

1. The quantity of an active form of one or more chemicals which will be available for target-site interaction may be altered by the presence of one or more other chemicals, or
2. the reactivity of the target molecule with the active form(s) of one or more chemicals may be altered by the presence of one or more other chemicals that may or may not be capable of causing a response.

The first form cited above primarily involves sites of activation or loss of a chemical (i.e., sites of detoxification, excretion, storage, or neutralization). The second form involves interaction at sites of action. Here, either affinity for or intrinsic activity at the site of action may be altered. Three general reaction mechanisms involved in toxicological interactions among chemicals are discussed briefly here.

A. Chemical-Chemical Reactions

As a result of a combined exposure, one chemical may react with another in such a way that potentially injurious chemicals never reach target sites in an active form. Examples of such interactions might include:

1. Neutralization reactions among acids and bases,
2. chelation reactions, such as those with heavy metals, and
3. direct reactions between organophosphates and aldoximes.

Here, reduced injury might be expected if workers were exposed to combinations of such chemicals in relation to the effects produced by a single chemical.

On the other hand, enhanced injury might arise from these types of chemical-chemical reactions. An example is the formation in the stomach of nitrosamines from secondary amines and nitrites. Because certain nitrosamines are carcinogenic, this chemical-chemical interaction could be classified as yielding enhanced risk of injury.

B. Chemical Competition at Molecular Sites

This general mechanism of chemical interaction is probably the most frequently encountered and the most thoroughly studied. It involves the affinities of foreign chemicals for a limited number of reaction sites on cellular macromolecules. These may be molecular sites of absorption, activation, detoxification, injurious action, or excretion. Competition for binding or reaction at such sites may result in either enhanced or in reduced toxicity. This type of interaction generally requires that the interacting chemicals or their reactive derivatives be present in the organism at the same time.

C. Altered Cellular Reactivity

A third general mechanism for toxicological interaction is one in which the cells are altered by the first chemical in such a way that the cells' response to a second chemical is altered, even if the first chemical is no longer present. The first two classes of chemical interaction require concomitant exposure or simultaneous presence of the agents in order to effect a biological response. In contrast, this third type is more likely to result when exposures are separated in time, i.e., a sequential exposure to the chemicals.

D. Time Relationships in Chemical Interactions

When an organism is subjected to multiple-chemical exposures, the nature and degree of toxicological interaction will be dependent in part on the temporal relationships between or among exposures. Pretreatment with or inadvertent exposure to a variety of agents can profoundly modify the response to a second chemical. Toxic manifestations of the second, challenging agent can be enhanced, prevented, or be shifted from one target to another. Interactions of this type are most often investigated and interpreted in terms of altered metabolic pathways.

Although classical considerations of toxicological interactions have dealt with simultaneous exposures to combinations of two or more chemicals, an equally likely situation would be that exposures to more than one chemical would be sequential. The order in which these exposures occur and the length of time between them determine the likelihood of a toxicological interaction.

When exposures occur simultaneously, or very close in time, the occurrence of toxicological interactions very likely depends upon competition for sites of absorption, biotransformation, reaction with target tissue, and excretion. When exposure to different chemicals are separate in time, the mechanism of the interaction, the biological half-life of each chemical or its metabolites, the duration of binding to tissue macromolecules, and the rate at which injury is repaired may assume a greater importance than their relative binding affinities and intrinsic activities.

Where exposure to two agents is not necessarily simultaneous, toxicological interactions may be classified as follows:

1. Interactions where unanticipated biological effects are the result of altered metabolism, and
2. interactions where cell and tissue responsiveness is modified.

In other situations, toxicological interactions occur only when exposures take place in a certain order. The frequency of an exposure also can determine whether or not a toxicological interaction will occur. The more often there is an xposure to a chemical, the greater is the statistical probability that it will occur in the presence of or close in time to the exposure to another, possibly interacting, chemical. Other factors of importance are the influences of frequency of exposure on the accumulation of a body burden of a particular chemical, the accumulation of cellular injury with or without accumulated body burden, and the opportunity for reversal of action or repair of injury.

E. Examples of Relevant Chemical Interactions

Increased toxicity to humans from chemical interactions need not be limited to only the interaction of environmentally present materials. It also can be a problem when an individual has recently taken a chemical for health reasons or perhaps as an abused drug. In addition, ethanol has been shown to potentiate the toxicity of numerous industrial solvents. Cornish and Adefuin [2] demonstrated in rats the potentiation of toxicity by ethanol with carbon tetrachloride or trichlorethylene (TCE). This toxicity has been described as "degreaser's flush" in humans exposed to TCE and who have recently ingested ethanol. Also, ethanol given orally, followed 18 hours later by an inhalation exposure to the halogenated hydrocarbons, caused marked increases in serum-oxalacetic transaminase (evidence of liver damage) when the chemicals were studied in combination, but not when given singly. However, enhanced toxicity was not noted with combinations of ethanol and perchlorethylene or 1,1,1-trichlorethane. Interactive toxic effects also can be demonstrated with other aliphatic alcohols. These same authors [3] produced even greater toxicity when methanol, isopropanol, secondary butyl alcohol, or tertiary butyl alcohol were administered 16-18 hours before inhalation of carbon tetrachloride. Sequential exposure with only two hours between alcohol ingestion and carbon tetrachloride exposure did not produce enhanced toxic effects.

The importance of ethanol as a potentiating agent for halogenated hydrocarbon toxicity has been demonstrated by Kutob and Plaa [4]. These studies with mice demonstrated that pretreatment with ethanol followed by a challenge with chloroform caused increased hepatotoxicity and abnormal liver function. It is surmised that alcohol stress produced higher levels of liver lipids and thus greater chloroform retention.

Similar potentiation of toxicity in humans from another chlorinated hydrocarbon, trichlorethylene, has been demonstrated in industrial workers. Repeated exposure to trichloroethylene can cause vasodilitation of the face, neck, shoulders, and back, and, in some cases, dermatitis. These effects are sometimes accentuated if a person has been known to consume alcoholic beverages within a few hours of exposure to the solvent [5,6].

Numerous studies have demonstrated the toxicity of toluene to humans. The toxic effects, however, have been shown to be due to the presence of methylethyl ketone (MEK) in the toluene. Also, enhanced toxic responses have been demonstrated with combinations of MEK and methylbutyl ketone (MBK). All of these solvent combinations produce peripheral neuropathy in both animals and humans. A comprehensive review on this subject has been presented by Prockop and Couri [7]. The same types of nervous system toxicities have been demonstrated for n-hexane, with enhancement of the neuropathy when there are combinations or sequential exposure with MEK or MBK [8,9,10].

Recent clinical studies of the interactions of the solvent m-xylene, with ethanol, demonstrate the reality of organic solvent exposure and alcohol consumption. Ingestion of ethanol four hours prior to xylene inhalation caused a 1.5- to 2-fold increase in xylene blood concentration and decreased metabolite excretion over that of xylene exposure alone. Some of these patients experienced dizziness and nausea during exposure [11].

Chemical interactions may also pose potential long-term toxicities. A study conducted by Radike et al [12] showed enhanced incidences of hepatic angiosarcomas (malignant tumors of the liver) when rats were given drinking water containing five percent ethanol throughout their life, and were exposed to 600 ppm of vinyl chloride for four hours per day, five days per week for one year. Although these are laboratory animal studies, vinyl chloride is a known human carcinogen and alcohol is a known enhancer of toxic responses in other chemical toxicity situations.

These examples of chemical-chemical or chemical-modified target interactions were selected for presentation here since all of these chemicals are frequently transported by water. The demonstrated toxic effects of these materials in mammalian systems strongly suggest that safe work practices and control methods should be implemented to minimize human exposure.

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