CAPCOA
Air Toxics "Hot Spots" Program

Gasoline Service Station
Industrywide Risk Assessment Guidelines

Prepared by the:
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in consultation with the:
> Office of Environmental Health Hazard Assessment (OEHHA),
> California Air Resources Board (CARB), and
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EXECUTIVE SUMMARY

The Gasoline Service Station Industrywide Risk Assessment Guidelines were developed by a subcommittee of the California Air Pollution Control Officers Association's (CAPCOA) Toxics Committee. The Subcommittee included representatives of twelve air pollution control and air quality management districts (districts) and staff of the California Air Resources Board (CARB) and the Office of Environmental Health Hazard Assessment (OEHHA). The purpose of these guidelines is to provide the districts with <u>suggested</u> procedures for preparing gasoline station emissions inventories and risk assessments to meet the requirements of the Air Toxics "Hot Spots" Information and Assessment Act of 1987.

This methodology should be considered a screening methodology. Gasoline station owners or the district may want to prepare a site specific risk assessment to more accurately quantify risks if a significant risk is indicated using this methodology.

The dispersion modeling was prepared using the United States Environmental Protection Agency's (U.S. EPA) ISCST3 model. Two point sources at the center of the station represent the loading and breathing emissions. Two volume sources measuring 4 meters high x 13 meters wide x 13 meters long and centered on the property represent spillage and refueling emissions.

The results of these calculations show that the benzene in gasoline can cause a cancer risks to people living near gasoline stations greater than 10 per million when large amounts of gasoline are dispensed. Consequently, if the districts determine their significant risk level for notification at greater than 10 per million, then these stations will need to send public notifications to affected neighbors, and, in certain cases, will need to implement measures to reduce the risk.

In summary, the procedure for conducting a default risk assessment for a gasoline service station is presented below:*

1. Determine the annual throughput at the facility. A survey form to obtain this information is presented in Appendix K.

2. Determine the type of facility (underground or aboveground storage tank, Phase I vapor recovery, Phase II vapor recovery, vent valve), site characterization (rural or urban), and distance to the nearest receptor.

3. Using this information, and the Tables or Graphs in Appendix E, determine the cancer risk per million gallons of throughput.

4. Multiply the cancer risk per million gallons of throughput by the annual throughput to obtain the cancer risk.

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* Defaults include Screen3 meteorological data, with either rural or urban dispersion coefficients, and the low wind speed processing method. Site specific data may be used to improve the accuracy of the risk assessment.

Not all the emissions from gasoline stations are included in this effort. Listed below are some of the emissions sources not included:

- benzene and other emissions from vehicles operating at the gasoline station,
- gasoline cap removal emissions,
- station leakage from connectors and components,
- nozzle tip evaporative emissions occurring after refueling,
- loading spillage emissions,
- loading overfill catch basin evaporative emissions,
- seasonal variations in the fuels content,
- the effects of onboard canister controls, and
- nongasoline dispensing emissions, such as service and repair emissions.

CARB's current and planned research and testing efforts should provide additional data to more fully quantify the emissions and risks from gasoline stations.

Gasoline Service Station
Industrywide Risk Assessment Guidelines

I.   INTRODUCTION AND PURPOSE

The Gasoline Service Station Industrywide Risk Assessment Guidelines were developed by a subcommittee of the California Air Pollution Control Officers Association's (CAPCOA) Toxics Committee.   The Subcommittee included representatives of twelve air pollution control and air quality management districts (districts) and staff of the California Air Resources Board (CARB) and Office of Environmental Health Hazard Assessment (OEHHA). Additional input was provided by the full CAPCOA Toxics Committee, the public, and industry representatives.

The purpose of these guidelines is to provide the districts with suggested procedures for use in preparing gasoline station emissions inventories and risk assessments to meet the requirements of the Air Toxics "Hot Spots" Information and Assessment Act of 1987, California Health and Safety Code, Sections 44300-44394. Section 44323 states that a district shall prepare an industrywide emissions inventory for the facilities (facilities which emit less than 10 tons per year of criteria pollutants) that the district finds and determines meets all the following conditions.

1. All facilities in the class fall within one four-digit Standard Industrial Classification Code.
2. Individual compliance would impose severe economic hardships on the majority of the facilities within the class.
3. The majority of the class is composed of small businesses.
4. Releases from individual facilities in the class can easily and generically be characterized and calculated.

This effort was initiated to provide a cost effective and uniform method for calculating gasoline station emissions inventories and risk assessments for the thousands of gasoline stations throughout the State. However, districts may use other emissions information and modeling procedures appropriate in their district.

II.   SUMMARY OF ASSUMPTIONS AND MODELING CONSIDERATIONS

Assumption and modeling parameters to be used in preparing emissions inventories and risk assessments are outlined below. The United States Environmental Protection Agency's (U.S. EPA) ISCST3 (Industrial Source Complex Short Term, Version 3) dispersion model was used to determine downwind concentrations. [1] Most of the toxicity values from CAPCOA's Risk Assessment Guidelines were used to determine the risks; however, the toxicity value for MTBE and the Reference Exposure Concentrations for MTBE and ethyl benzene came from the U.S. EPA. [2]

A.   Emissions Profile

Assumptions:
- Gasoline stations emit vapors continuously (24 hours/day, 365 days/year).
- Hourly emissions = $\dfrac{\text{Annual emissions}}{8760 \text{ hours/year}}$

B.   Gasoline Station Scenarios

Assumptions:
- All gasoline storage tanks are equipped with submerged fill tubes.
- All Phase II vapor recovery systems were properly installed using CARB certified vapor recovery systems capable of achieving a 95% capture efficiency.
- The **overall control efficiency** for Phase II vapor recovery systems was assumed to be **90%**.
- Emissions from assist systems are equal to balance systems.

Modeling Scenarios:

	Scenario Number	Control Equipment
Aboveground Tanks	1	Submerged Fill Only
	2	Phase I Only
	3A	Phase I & II, without vent valves
	3B	Phase I & II, with vent valves
Underground Tanks	4	Submerged Fill Only
	5A	Phase I Only, without vent valves
	5B	Phase I Only, with vent valves
	6A	Phase I & II, without vent valves
	6B	Phase I & II, with vent valves

C. Gasoline Content & Density of Vapors

Assumptions:

- Gasoline vapor density = 0.105 lbs/ft^3

  (assumes a mixture of 70 vol% air and 30 vol% gasoline in the underground storage tank and car tank headspace, see Appendix D-2)

- Content of Reformulated Gasoline

Substance	Weight % In Liquid	Weight % In Vapor
Benzene	1.0	0.3
Ethyl Benzene	1.6	NA
Toluene	8.0	NA
Xylene	2.4	NA
Methyl Tertiary Butyl Ether	11.0	NA

NA - Information not available at this time

D. Toxicity Factors

Toxic Substance	URV[1] Cancer $(\mu g/m^3)^{-1}$	REL[2] Chronic $\mu g/m^3$	REL Acute $\mu g/m^3$	U.S. EPA RfC[3] Chronic $\mu g/m^3$
Benzene	2.9E-5	71	NR	NR
Ethyl Benzene	NC	NR	NR	1000
Toluene	NC	200	NR	NR
Xylene	NC	300	4400	NR
MTBE	7.5E-8 to 1.7E-7	NR	NR	3000

NC = Not identified as a carcinogen

NR = no REL or RFC currently available

[1] URV = Unit Risk Value

[2] REL = Reference Exposure Level

[3] RfC = Reference Exposure Concentration

E.   Modeling Parameters

Dispersion model ISCST3
Weather data . . . .   Site specific, or use SCREEN3 default
Low wind speed processing method . . .   Determined by district for site specific
    weather data, or use SCREEN3 default
Dispersion coefficients . . . .   Rural or urban to be determined by
    district
Building downwash . . . .   Not significant; see page 17
Modeling configuration . . . .   See Figure 1 (page 14)

    <u>1 spillage and 1 refueling volume source</u>
        Volume configuration . . . .   4 m high x 13 m long x 13 m wide
        Sigma y (dimensionless) . . . . . .   13 m / 4.3 = 3.02
        Sigma z (dimensionless) . . . . . .   4 m / 2.15 = 1.86
        Spillage release height . . . .   0 m
        Refueling release height . . . . . .   1 m

    <u>1 loading and 1 breathing point source</u>
        Release height . . . .   3.66 m (12 ft)
        Stack gas temperature . . . .   291 K (65 °F) aboveground tanks
    breathing and all loading emissions.
    289 K (60 °F) underground tanks
    breathing emissions.

    <u>Receptor Grid</u>
- Receptor grid begins 20 m from the center of the gasoline station
- Spaced from source every 10 m
- Radially spaced every 10 degrees

F.   Site Specific Data Options

A gasoline station owner or district staff may want to more precisely characterize the risks from an individual gasoline station using site specific data if the risk appears significant after using this screening methodology. Examples of parameters that may represent the emissions and risks from an individual gasoline station more precisely include:

- Actual pump islands and vent pipe locations relative to the property lines,
- Use of site specific weather data,
- Use of specific emissions profiles (time of day emissions occur in relation to actual weather data),
- Use of measured gasoline compositions,
- Use of additional or updated toxicity factors,
- Use of actual building dimensions for applying building downwash effects,
- Use of actual emissions test data for bootless nozzles,
- Applicable urban or rural site characteristics,
- Addition of emissions from a soil or water cleanup system on site,
- Addition of emissions from vehicle maintenance activities,
- Addition of emissions from the opening of the car gasoline cap,
- Addition of emissions from nozzle tips after refueling,
- Addition of emissions from vehicles entering and leaving station, or
- Use of new emissions factors due to vehicle onboard control systems.

III. STORAGE TANK AND VAPOR RECOVERY SYSTEMS

The quantity of gasoline vapors emitted from a gasoline station depends on the type of storage tank and type of vapor recovery systems in use. Nine basic gasoline station scenarios found throughout California are considered. These scenarios are listed below:

	SCENARIO #	CONTROL EQUIPMENT
Aboveground Tanks	1	Submerged Fill Only
	2	Phase I Only, without vent valves
	3A	Phase I & Phase II, without vent valves
	3B	Phase I & Phase II, with vent valves
Underground Tanks	4	Submerged Fill Only
	5A	Phase I Only, without vent valves
	5B	Phase I Only, with vent valves
	6A	Phase I & Phase II, without vent valves
	6B	Phase I & Phase II, with vent valves

All existing gasoline stations selling more than 480,000 gallons annually were required to install Phase I and Phase II vapor recovery systems by February 1991. The primary focus of the gasoline station risk assessments has been on Scenarios 6A and 6B, because the majority of gasoline stations in California are configured with underground storage tanks, Phase I and Phase II vapor recovery systems, with and without storage tank pressure release vent valves.

A. Aboveground or Underground Tank

Most gasoline stations have underground storage tanks to reduce the loss of gasoline vapors due to diurnal temperature changes. However, the emissions from both underground and aboveground tanks are described.

B. Submerged Fill Tubes

A submerged fill tube extends from the top of the storage tank to below the residual liquid level in the storage tank. This reduces splashing and emissions during the underground storage tank filling process. Submerged fill tubes are required by the California Health and Safety Code, Section 41950, for all storage tanks with a capacity greater than 250 gallons. It was assumed that all gasoline stations are equipped with submerged fill tubes.

C. Phase I Vapor Recovery Systems

Phase I vapor recovery refers to the collection of gasoline vapors displaced from storage tanks when cargo tank trucks make gasoline deliveries. CARB certifies Phase I vapor recovery systems to collect 95 percent of displaced vapors for return to the delivery truck. The spillage which can occur during delivery has not been quantified and is not included in the emissions factors.

D. Phase II Vapor Recovery Systems

Phase II vapor recovery systems control the vapors displaced from the vehicle fuel tanks during refueling. The vapors recovered from vehicle tanks are returned to the gasoline station's storage tanks. The Phase II vapor recovery systems certified by the CARB must capture at least 95 percent of the vapors resulting from fueling vehicles. Both balance and assist vapor recovery systems are currently certified to achieve 95 percent overall efficiency. However, the **overall control efficiency** was assumed to be **90%.**

1.   Balance Systems

CARB has certified balance systems to capture and return 95 percent of emissions during refueling when installed and operated properly. This efficiency can be decreased when cuts and tears occur on the boot or hose, when check valves are worn, or when the return vapor is blocked by condensate in the return line.

2.   Assist Systems

Assist systems draw a mix of vehicle gasoline tank vapors and ambient air from around the nozzle back to the underground storage tank, using vapor pumps. Some assist systems then move the excess vapors from the underground storage tank out the vent through an incineration device. Assist systems do not have cut and tear defects like balance systems. However, because these systems are under pressure, loose fittings or other leak points can be the cause of excess emissions. Vacuum pumps not operational will render the vapor recovery system ineffective.

CARB will develop new emission factors for assist systems to determine whether the 95 percent overall efficiency levels are being met on a continuous basis. In the meantime, CARB suggests assuming that the emission factors for assist systems are equivalent to balance systems. If it is later determined that the emissions factors for assist systems are significantly different from balance systems, then districts will need to identify which facilities have assist systems and which have balance systems, and apply the applicable emissions factors to the updated inventories and risk assessments. This difference may become larger as more cars with on-board controls enter the marketplace.

3.   Storage Tank Pressure Relief Vent Valves

Pressure/vacuum valves are sometimes installed on the vent pipes of storage tanks. With no vent valve, the vent pipe is open. Vent pipes with vent valves can effectively reduce emissions if they are leak tight and the nozzle vapor return line has a check valve to prevent vapors in the tank from escaping to the atmosphere out the nozzle between fuelings.

IV.   EMISSIONS FACTORS

The gasoline emissions identified in this effort originate from the following four processes:

Loading -   Loading emissions occur when a cargo tank truck unloads gasoline to the storage tanks at the gasoline station. Storage tank vapors are emitted from the vent pipe during the initial fuel transfer period. These emissions are significantly reduced when the vent pipe includes a pressure/vacuum valve.

Breathing -   Gasoline vapors are emitted from the storage tank vent pipe due to temperature and pressure changes within the storage tank vapor space.

Refueling -   During the refueling process, gasoline vapors are emitted at the vehicle/nozzle interface.

Spillage -   Spillage emissions occur from spills during vehicle fueling.

The existing CARB and EPA emission factors have been reexamined and updated for this report. The new emission factors are shown in **Appendix A**. The emissions factor changes resulted from Reid vapor pressure changes, and emissions tests. A more detailed explanation of the emission factor changes is shown in Appendix A.

V.   EMISSIONS PROFILE

It was assumed that the emissions occur continuously throughout the year, 365 days, 24 hours per day. This emissions profile was chosen because the risk results, generally, were not significantly different when different operating profiles were compared. South Coast Air Quality Management District (SCAQMD) meteorological data were used in the comparisons. Three scenarios were considered:

1)   The **annualized alternative** assumes that 100 percent of daily emissions occur equally each hour throughout the day.

2)   The **100/0 alternative** assumes that 100 percent of daily emissions occur equally each hour only from 6 a.m. to 10 p.m.

3)   The **80/20 alternative** assumes that 80 percent of daily emissions occur equally each hour from 6 a.m. to 8 p.m., while the remaining 20% of daily emissions occur equally each hour from 8 p.m. to 6 a.m.

For some meteorological data sets, the risks were nearly the same regardless of operating hours. For other meteorological data sets, the risks can be either increased or decreased. For example, when using the Redlands meteorological data, the risk for the 80/20 alternative was a third less than the annualized alternative; for the 100/0 alternative, the risk was half the risk of the annualized alternative.

Although most of the time an annualized emissions profile will be health protective, there can be times when it underestimates risks, and thus, it may be important to consider operating hours as a variable in the risk assessment. However, gathering this data would require surveying each facility. If districts or gasoline station owners want to refine the initial risk results, then alternative emissions profiles may give more precise risk values. However, the emissions profile should be based on actual test data. Preliminary vent pipe test data from San Diego shows that the greatest emission rate does not always coincide with the greatest period of gasoline pumping. The test data show that vent pipe emissions can be large when the liquid gasoline in the storage tank turns over at night due to temperature differences between the vapor space an the liquid. This process is not fully understood and warrants additional study.

It is not necessary to determine the one hour maximum downwind concentration of substances in gasoline vapors. Appendix I contains a discussion on the relative toxicity of substances in gasoline. It shows that benzene is the most important substance driving the risk assessment. It also shows that xylene is the only substance which is associated with acute adverse health effects. Not until the benzene emissions are three orders of magnitude above the 10 per million cancer risk threshold, do the emissions of xylene begin to cause acute adverse health effects. Therefore, it is not likely the downwind xylene concentrations will ever need to be determined unless the gasoline throughput caused the cancer risk to exceed 100 per million.
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VI.   TOXIC SUBSTANCES IN REFORMULATED GASOLINE

A.   Concentrations of Toxic Substances

Table 1 shows the average concentration of toxic substances in gasoline sold in the San Francisco Bay Area. [3] As a point of reference, **Table 2** shows the average speciation of gasoline produced before 1996. California reformulated gasoline may not exceed an average benzene content greater than 1.0 weight percent (0.80 volume percent) in the liquid, which results in a vapor concentration of 0.3 weight percent. **Appendix B** contains the section of the California Code of Regulations which limits the benzene content in gasoline.

TABLE 1.   Anticipated Speciation of Reformulated Gasoline

Toxic Substance	Weight % In Liquid	Weight % In Vapor
Benzene	1.0	0.3
Ethyl Benzene	1.6	NA
Toluene	8.0	NA
Xylene	2.4	NA
Methyl Tertiary Butyl Ether	11*	NA

NA - Information not available at this time

TABLE 2.   **Speciation of Pre-1996 Gasoline**

Toxic Substance	Weight % In Liquid	Weight % In Vapor
Benzene	2	0.7
Toluene	8	1
Xylene	11	1

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* Oxygen content requirements are specified in the California Code of Regulations. Reformulated gasoline typically contains approximately 2.0% oxygen by weight, which is equal to aproximately 11% by volume MTBE.

** Data from average weight percent in liquid between summer/winter blend, California Air Resources Board Identification of Volatile Organic Compounds Species Profile, Second Edition, Volume I, August 1991.

B.   Toxicity of Substances in Gasoline

The toxicity of the various substances in gasoline are listed in the table below. OEHHA has not determined Unit Risk Values (URV) or Reference Exposure Levels (REL) for all substances. However, OEHHA recommends using the U.S. EPA Reference Exposure Concentrations (RfC) for missing chronic RELs.

The U.S. EPA has recently estimated the inhalation URV for methyl tertiary butyl ether (MTBE) to range between 7.5E-8 to 1.7E-7 $(\mu g/m^3)^{-1}$. The cancer toxicity of MTBE does not significantly contribute to the overall cancer risk compared to the benzene content. It is not significant because the MTBE URV is two to three orders of magnitude less than the benzene URV. Even when considering that typical California RFG may contain 11% MTBE by volume and 0.80 benzene by volume, the two to three orders of magnitude URV difference still outweigh the content difference.

Appendix I shows that the cancer risk from benzene is by far the determining risk factor compared to the other substances identified in gasoline. Therefore, only benzene emissions are used in this risk assessment procedure.

TABLE 3.   Toxicity of Substances in Gasoline

Toxic Substance	URV[1] Cancer $(\mu g/m^3)^{-1}$	REL[2] Chronic $\mu g/m^3$	REL Acute $\mu g/m^3$	U.S. EPA RfC[3] Chronic $\mu g/m^3$
Benzene	2.9E-5	71	NR	NR
Ethyl Benzene NC	NR		NR	1000
Hexane	NC	NR	NR	200
MTBE	7.5E-8 to 1.7E-7	NR	NR	3000
Toluene	NC	200	NR	NR
Xylene	NC	300	4400	NR

NC = Not currently identified as a carcinogen
NR = no REL or RFC currently available

[1] URV = Unit Risk Value
[2] REL = Reference Exposure Level
[3] RfC = Reference Exposure Concentration

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VII. POINT AND VOLUME SOURCE EMISSIONS

A. Point Source Emissions (Loading and Breathing)

Point source modeling best characterizes the vent stack emissions due to loading and breathing. The point source modeling parameters chosen were based on the collective experience of State and district staff and are shown below:

Breathing (underground tanks):
stack height . . . . 12 feet

stack diameter . . . . 2 inches
stack gas temperature ($65°$ F aboveground tanks) . . . . $60°$ F
Loading (underground and aboveground tanks):
stack height . . . . 12 feet

stack diameter . . . . 2 inches
stack gas temperature . . . . $65°$ F

The loading emissions rate was determined during the loading process, then annualized to an average yearly emission rate. The breathing emission rate was calculated as if it occurs continuously throughout the year.

B. Volume Source Emissions (Refueling and Spillage)

1. Volume Source Dimensions Used for Refueling and Spillage Emissions

Refueling and spillage emissions were modeled as volume sources. Volume source modeling seems to most appropriately represent downwind concentrations influenced by turbulence factors due to cars and pump islands disrupting the flow of wind. The size of the volume sources was derived from the calculations in **Appendix C** and was determined to be:

4 meters high x 13 meters long x 13 meters wide

2.   Release Heights Used For Refueling and Spillage Emissions

In order to determine a release height for spillage, the information from the CARB Spillage Emission Factor study was used. [4] Results of the study indicated that approximately 93% of spilled gasoline lands on the ground, while 7% is spilled on the side of a vehicle, never touching the ground. Thus, a **ground level release height** (0 meters) was selected for **spillage** emissions.

For the **refueling** emissions, the **release height** was chosen to be **one meter.** This is the same height as most car nozzle receptors.

VIII.   PUMP ISLANDS AND VENT PIPES LOCATIONS

Ideally, the location of the pump islands and vent pipes should be determined on a site specific basis. Because it is very costly to gather this information and apply it to individual gasoline stations, a generic station configuration was assumed. Station owners or districts may want to refine the risk assessment results using actual rather than generic configurations if the risk appears significant.

The diagram on the next page shows the gasoline station configuration used to generically model emissions. Four multiproduct dispensers were assumed to be spaced four meters from the center point of the station. The average distance between multiproduct dispensers in the Monterey Bay Unified Air Pollution Control District is approximately 8 meters and is considered typical throughout the State.

The vent pipes were modeled as a single vent pipe located at the center of the property. Sometimes the vent pipes are located near the property boundary. Other times they are located towards the center of the property. Vent pipes positioned in the middle of the station will result in lower risks than vent pipes located near the property boundary. It may be appropriate to model the vent pipes using the actual location if the risk is near the 10 per million cancer risk threshold using this screening methodology and if people are located near the vent pipes.

The two volume sources, representing spillage and refueling emissions, are shown as the shaded area in the middle of the station. The spillage volume is superimposed over the refueling volume.
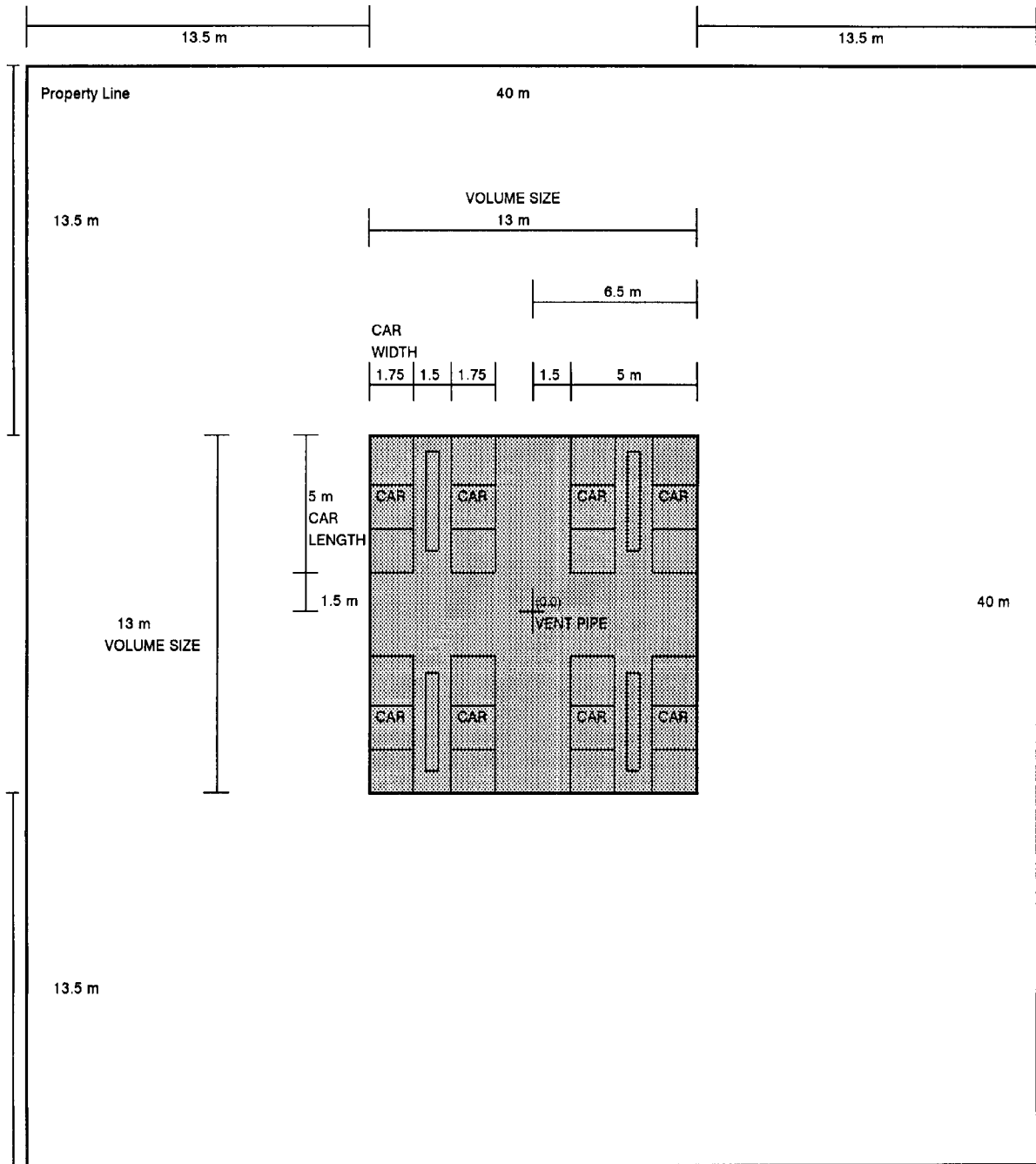
Plot Plan Showing Volume Source Size Relative to Cars and Gas Pump Location

(The Shaded Area Represents the Volumes Used For Modeling Spillage and Refueling Emissions)
(The Vent Pipe Represents the Points Used for Modeling Loading and Breathing Emissions)

Figure 1

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IX. MISCELLANEOUS MODELING PARAMETERS

The Industrial Source Complex Short Term (ISCST3) dispersion model was chosen to prepare the risk assessment modeling. The assumptions used for the modeling are described below:

A. Dispersion Coefficients (Rural Versus Urban)

EPA recommends two methods for determining whether the rural or the urban dispersion coefficients should be applied. One method is based upon EPA's Land Use Procedure, while the other is based upon a Population Density Procedure. These methods are further described below.

1. **Land Use Procedure** - Draw a 3 kilometer radius circle between the source and the receptor, and define the actual land use according to Table 4 below. If the land use for more than 50 percent of the area is categorized as: 1) heavy or medium industrial (I1 or I2), 2) commercial (C1), or 3) multi-family residential (R2 and R3), use **urban** dispersion parameters; otherwise, use **rural** dispersion coefficients.

2. **Population Density Procedure** - Compute the resident population in the area enclosed by a 3 kilometer radius circle. If the population exceeds 21,200 (750 people per square kilometer), use **urban** dispersion parameters; otherwise, use **rural** dispersion coefficients. Most municipalities can provide detailed population data for periods more recent than the 10-year Federal census.

Of the two methods, the Land Use Procedure is considered more accurate. In heavily industrialized areas in the core of a city, the residential population may be quite low, thus indicating a rural area by the population procedure. However, the area may be sufficiently built-up that the urban land use criteria would be satisfied. In these cases, the area should be classified as urban.

In general, rural dispersion coefficients yield risks more than three times larger than urban coefficients at distances between 20 and 60 meters from the center of the facility.

Due to the diversity of land use throughout California, each district should select the appropriate dispersion coefficient appropriate for the location of each gasoline station. If a district is unsure which coefficient to use, then the EPA default, rural dispersion coefficients should be used as an initial screen.

TABLE 4.   Identification and Classification of Land Use Types [5]

Type	Use and Structures	Vegetation
I1	*Heavy Industrial* Major chemical, steel and fabrication industries; generally 3-5 story buildings, flat roofs	Grass and tree growth extremely rare; <5% vegetation
I2	*Light-moderate industrial* Rail yards, truck depots, warehouses, industrial parks, minor fabrications; generally 1-3 story buildings, flat roofs	Very limited grass, trees almost totally absent; <5% vegetation
C1	*Commercial* Office and apartment buildings, hotels; >10 story heights, flat roofs	Limited grass and trees; <15% vegetation
R1	*Common residential* Single family dwelling with normal easements; generally one story, pitched roof structures; frequent driveways	Abundant grass lawns and light-moderately wooded; >70% vegetation
R2	*Compact residential* Single, some multiple, family dwelling with close spacing; generally <2 story, pitched roof structures; garages (via alley), no driveways	Limited lawn sizes and shade trees; <30% vegetation
R3	*Compact residential* Old multi-family dwellings with close (<2 m) lateral separation; generally 2 story, flat roof structures; garages (via alley) and ashpits, no driveways	Limited lawn sizes, old established shade trees; <35% vegetation
R4	*Estate residential* Expansive family dwelling on multi-acre tracts	Abundant grass lawns and lightly wooded; >80% vegetation
A1	*Metropolitan natural* Major municipal, state, or federal parks, golf courses, cemeteries, campuses; occasional single story structures	Nearly total grass and lightly wooded; >95% vegetation
A2	*Agricultural rural*	Local crops (e.g., corn, soybean); >95% vegetation
A3	*Undeveloped* Uncultivated; wasteland	Mostly wild grasses and weeds, lightly wooded; >90% vegetation
A4	*Undeveloped rural*	Heavily wooded; >95% vegetation
A5	*Water surfaces* Rivers, lakes	

B.   Building Downwash

The ISCST3 model includes algorithms to model the effects of building downwash on emissions from nearby or adjacent point sources. However, building downwash algorithms do not apply to volume or area sources. Thus, only the emissions from the vent pipe are affected.

To determine how building downwash affects risk, three building downwash scenarios were run using Salinas and default meteorological data:

*   No building present,
*   A 10m long x 5m wide x 4 m high building, 15 meters from the center point of the property, symmetrically spaced 8 volume sources, and 2 point sources located at the center point,
*   A building placed at the center point of the property with all the sources arranged as described above.

Results of the modeling indicated that the placement of the buildings and their subsequent potential to create downwash have very little effect on the resultant risks from the vent pipes. For the scenarios where a building is present, the risks increase by 5% at 20 meters from the vent pipes. As the distance increased further, the risks became equal to the risks with no building downwash. This occurred at distances around 50 meters. Thus, it was concluded that it is not necessary to include the building downwash when determining the dispersion from the vent pipes.

X.   PARAMETERS CAUSING UNCERTAINTY

Some modeling parameters may cause significant uncertainties in the modeling calculations. The effect of turbulence created by vehicle traffic within the station, the effect of buoyant forces due to temperature differences between gasoline vapors and air, and the effect due to density differences between gasoline vapors and air were studied.

A.   Turbulence

Initially it was thought that the dispersion of gasoline vapors from refueling and spillage may also be dependent on the turbulence created by cars entering and leaving the service station. It can be assumed that turbulence caused by moving cars is insignificant if cars are stationary for longer than they are moving within the station boundary. To determine the parameters needed to perform such a calculation, several gasoline stations in the Monterey Bay area were observed to determine the minimum time required to driving to and from a pump based on the measured average driving speed, and the time required to pay after a fill up. [6] The calculations below show that cars are moving and creating turbulence within the station boundary only 13% of the time. Therefore, turbulence due to car movement is not likely to significantly affect risk results.

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Maximum gasoline dispensing rate	=	10 gal/min
Average fill volume [7]	=	8 gal/car
Minimum time required to pay	=	1 minute
Average driving length through station	=	40 meters
Measured average driving speed	=	2-3 mph
Measured average time driving to pump	=	8 seconds
Measured average time driving from pump	=	8 seconds
Measured total driving time	=	16 seconds

Calculations:

Minimum time to fill car: $= \dfrac{(8 \text{ gal})}{(\text{car})} \dfrac{(\text{minute})}{(10 \text{ gal})}$ = 0.8 min/fill = 1 min/fill

Minimum stopping time: = pay time + fill time   = 2 minutes or 120 seconds

$\dfrac{\text{driving time}}{\text{time car is stopped}}$ $= \dfrac{16 \text{ seconds}}{120 \text{ seconds}}$ = 13%

B.   Buoyant Forces

Buoyant forces may have some influence on spillage losses since the gasoline liquid released may be warmer than the ambient air. Temperature measurements of gasoline vapors and liquid stored in underground double walled tanks in the San Diego County APCD were found to be on the average 5 to 10 degrees Fahrenheit warmer than the ambient air. Although the measurements were taken at inland sites in San Diego County, the temperature differential rather than actual temperatures are of interest. The 5 to 10 degree temperature differential may be representative of the entire State. However, the temperature of the pavement the spill lands on can be above or below the ambient air temperature. The heat transferred to or from the spill will also affect evaporative vapor temperature and the buoyancy of the vapors.

C. Dense Gas Characteristics of Gasoline Vapors

Gasoline vapors are four times heavier than air. Therefore, it is important to know whether the ISCST3 model adequately calculates the dispersion of gasoline vapors at gasoline stations. To determine whether emitted gasoline vapors are neutrally buoyant, two different calculation methods were used. The first method calculates the Richardson number. If the resulting Richardson number is above 32, then gasoline vapors should be treated as a dense gas. The second method uses the EPA model TSCREEN. Results of both these calculations are shown in **Appendix H**. They indicate that gasoline vapors emitted from the gasoline stations can be modeled as a neutrally buoyant gas using the ISCST3 model.

XI. METEOROLOGICAL DATA

A. Meteorological Data Set Selection

Each district should model emissions based upon the weather data set most applicable to the location of each gasoline station. The following list shows the order of preference with regard to meteorological data sets. The top set is the most preferred, while the bottom set would be the least preferred.

- Three consecutive years of meteorological data.

- Five nonconsecutive years of meteorological data.

- If multiple years of meteorological data exist, only one year of meteorological data could be used if it is the worst case year.

- If no meteorological data exists, use ISCST3 with the default SCREEN3 meteorological data. Run ISCST3 to estimate the one hour maximum concentration, then multiply this concentration by a factor of 0.08 (ARB suggested default) to estimate annual average concentrations. The 0.08 default factor is the midpoint of the range recommended in EPA's Guidelines (0.06-0.10) for estimating annual concentrations from one hour maximums. Some districts use the high end of the range (0.10) because a factor of 0.08 underestimates the annual concentration for some of the meteorological data sets in their district. [8]

B.   Meteorological Data Containing Low Wind Speeds (<1 Meter/Second)

Wind speeds less than 1.0 m/s pose a special problem in model applications, because Gaussian models assume that the downwind concentrations are inversely proportional to wind speed. Because of this reason, the concentrations can become unrealistically large when wind speeds less than 1.0 m/s are input into the model. This issue is very significant in districts such as the SCAQMD where hourly wind speeds are less than 1 m/s for a significant fraction of the year.
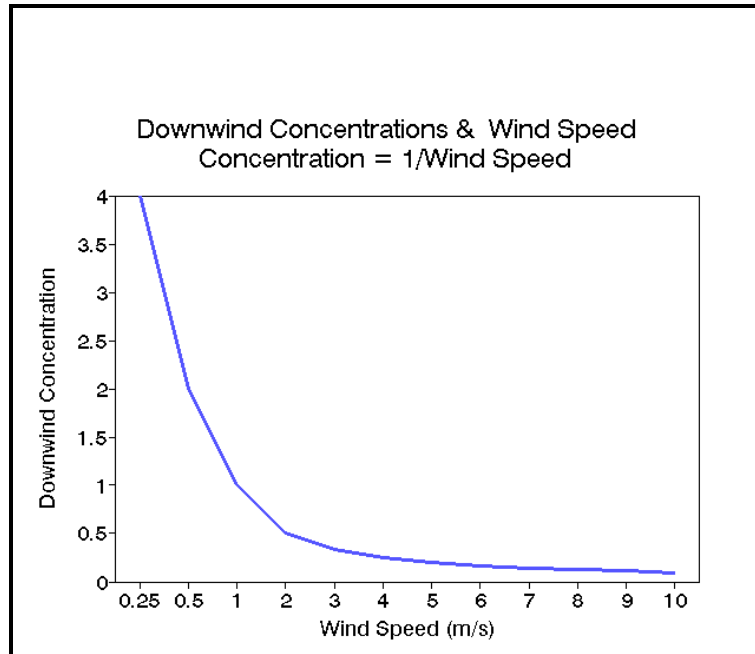
Figure 2. Example Downwind Concentrations Compared to Wind Speeds

There are three ways to handle data representing hourly wind speeds <1m/s:

1.   The EPA "calm off" processing method assumes that the wind speed is equal to 1 m/s for hours when the wind speed is less than 1 m/s, and assumes the wind direction is that of the previous hour. The downside of assuming a 1 m/s wind speed is that actual downwind concentrations will be higher than those calculated at 1 m/s, and the actual wind directions may be different from the previous hour's wind direction.

2.   The EPA "calm on" processing method removes the hours with wind speeds less than 1 m/s. "Calm on" is the EPA default. The disadvantage of this processing method is that the hours with the highest risk are not included in the calculations.

3.   The SCAQMD applies the actual wind direction recorded during the hour when the wind speed was less than 1 m/s, then assumes a 1 m/s wind speed. This is without regard to whether the wind speed instrument is recording windspeeds

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below the instrument threshold for accuracy. This may underestimate hourly downwind concentrations some, but at least it does not ignore them, or unrealistically over predict them. The CAPCOA Committee recommended that if a significant fraction of the year (30%) includes hourly wind speeds of less than 1 m/s, and the actual wind directions are known, then the SCAQMD method should be used.

Risk results will vary greatly depending upon the processing method applied due to the vast diversity of meteorological wind patterns throughout California. If the data exists, it is best to use the SCAQMD processing method if over 30% of the time the wind speeds are less than 1 m/s. If the actual wind directions are not known, then the EPA default calm on processing method should be used. (Note: Appendix E results are from screening default meteorological inputs. The three options above do not apply for Appendix E results.)

XII.   SUMMARY OF PROCEDURE FOR CALCULATING CANCER RISKS

The procedure below outlines how to apply the tables and graphs in Appendix E to determine the cancer risk from individual gas stations using default weather data. This procedure uses the ICST3 model and SCREEN3 default weather data. SCREEN3 default weather data are 33 different combinations of wind speed and stability class designed to represent a wide range of meteorological conditions. For the case of gasoline station modeling in Appendix E, maximum 1-hour concentrations were determined by a wind speed of 1 m/s and a stability of E or F depending on the gas station configuration. The cancer risk values in Appendix E are based on stations with a throughput of 1,000,000 gallons per year. The actual risks must be factored to account for actual throughputs.

1.   Determine the annual gasoline throughput at the facility. Note: Appendix K includes a survey form that can be used to obtain this information.

2.   Determine the type of facility and assign the proper scenario. Assume Scenario 6A if the facility has an underground storage tank and Phase I and II vapor recovery systems, but it is not known whether the facility has a vent valve.

3.   Determine if the facility is characterized as being located in a rural or urban area, using the procedures described in Section IX.A., Dispersion Coefficients (Rural versus Urban).

4.   Determine the location of the nearest receptor to the facility. Assume 20 meters as a default.

5.   When using the Appendix E <u>tables</u> to determine the cancer risk, move down the column labeled risk per million for the applicable station scenario and dispersion coefficients until the distance from the middle of the station to the nearest receptor is reached. This risk is based on a station throughput of 1,000,000 gallons per year. Go to step 6.

When using the <u>graphs</u> to determine the cancer risk, identify the graph which applies to the applicable station scenario and dispersion coefficients. Identify the distance from the middle of the station to the nearest receptor along the x-axis. Move up from the distance point on the x-axis until the line representing the applicable station scenario is crossed. Move over to the left margin of the graph to identify the cancer risk per million. This risk is based on a station throughput of 1,000,000 gallons per year. Go to step 6.

6.   Determine the actual cancer risk by factoring the risk based on a station with a throughput of 1,000,000 gallon per year as follows:

$$\text{Cancer Risk} = \frac{\text{(throughput in gal/yr)}}{(\ 1{,}000{,}000 \text{ gal/yr}\ )} * \text{(Cancer Risk from Appendix E)}$$

7.   The cancer risk will be less for people exposed for periods less than 70 years. The method for factoring for exposure times is determined by each district.

XIII.   CURRENT STATUS AND PROBLEMS TO BE RESOLVED IN THE FUTURE

As this report was being prepared, it became apparent that some emissions from gasoline stations have not been quantified. If these additional emissions were added to the emissions inventories and risk assessments, then an increased cancer risk would result. The following paragraphs describe what is known of these emissions and what further efforts are needed to further quantify these emissions. As additional data becomes available, it should be used in the emissions inventory and risk assessment updates.

A.   Nozzle Tip Emissions Occurring After Refueling

The risk assessment results shown in Appendix E assume insignificant evaporative emissions from the interior of nozzles after fueling. Some evaporation is occurring but it has not been quantified. Some test data from the BAAQMD and presented to CARB indicated that the **Emco Wheaton 4000 series nozzles**, the most popular nozzle installed during 1984 to 1991, may emit **20% greater emissions** than other nozzles due to the location of the check valve. The problem with the Emco Wheaton nozzle is that the check valve, also referred to as a remote check valve, is located between the hose and the pump, instead of between the hose and the nozzle. Therefore, any residue left in the hose

will escape out the nozzle, because there is no nozzle check valve to prevent its release. Other nozzles emissions are proportional to the wetted surface within the interior of the nozzle. Additional testing is needed to accurately determine nozzle tip emissions.

B.   Federal Spitback Measures

Federal spitback measures, 40 CFR Parts 80 and 86, require vehicle fill pipes to be designed such that less than one gram of liquid per refueling is spit from the nozzles/vehicle interface when refueling at a dispensing rate of 10 gallons per minute. This requirement became effective January 1, 1996 on 1996 vehicles. It also limits vehicle refueling to no more than 10 gallons per minute per nozzle. If the refueling rate is faster than 10 gallons per minute, then greater amounts of spillage tends to occur. The risk assessment results in Appendix E assume that stations do not dispense at rates higher than allowed.

C.   "Whoosh" Emissions

"Whoosh" emissions are the emissions released when the gasoline cap on the car tank is removed prior to refueling. The term "whoosh" was coined by the BAAQMD. It is the sound of vapors rushing out of the tank when the car gasoline cap is removed. The calculations in **Appendix J** indicate that these emissions may significantly contribute to the total risk. The resulting emission factors range from **0.26 to 0.66** lbs emitted/1000 gal dispensed. This compares to a total emission rate of **1.68** lbs/1000 gallons (Scenario 6A). If these initial calculations are confirmed, then whoosh emissions may be more significant than loading, spillage or breathing emissions. However, these emissions have not been added to the emissions inventory and risk assessment procedure described in this report.

More information is needed before these emissions are added to gasoline station risk assessments, because many variables affect the emission rate. Newer cars tend to have well sealed gasoline tanks and emit vapors when the gasoline cap is removed. Older cars tend to leak gasoline vapors continuously. New cars with on-board control systems are designed not to emit any vapors. CARB data from their 100 car certification tests tend to show that approximately 10% of cars cannot be pressurized to meet the standards of the certification test. This mean that 10% of cars would not have whoosh emissions because the gasoline tank is not under pressure. Other factors that affect whoosh emissions include the ambient temperature and pressure, the time and average speed the car has been driven prior to fill up, the condition of the gasoline cap, whether the car is fuel injected or carbureted, the amount of headspace in the fuel tank, the time period since the car was last filled, and perhaps other factors not yet identified.

Actual emissions may be determined by applying the CARB shield test used to certify nozzles. It may be feasible to remove the gasoline cap by hand under the hood while measuring total hydrocarbon emissions without significantly affecting results. The results

may show a fairly accurate accounting of average whoosh emissions. A research effort to measure these emissions is needed.

D.   Vapor Return Blockage

The vapor return line to the underground storage tank can become filled with condensate such that the returning vapor flow is blocked by the condensate. This can occur when the vapor return line is bowed from the weight of the fill over the return lines, or when the slope of a return line is not adequate to drain the condensate. These design problems are common, but can only be found by performing a blockage test. Districts that have not tested for blockage may find a large number of stations experience this problem. When vapor blockage occurs, the Phase II vapor recovery system becomes ineffective. If a district has not tested for blockage, then it may be appropriate to assume scenario 5A or 5B (Phase I only, with or without vent valves) rather than scenario 6A or 6B (Phase I and II, with or without vent valves).

E.   Leakage Emissions

Leakage emissions due to loose fittings, valves, and damaged components reduce the effectiveness of vapor recovery systems. This is especially important for stations with vent valves, when the system is pressurized.   Currently, no leakage emission factors are available. However, a June 1995 CARB report contains the results of leakage testing at stations equipped with Phase I and II vapor recovery systems without vent valves. [9] Over 90% of tested stations leaked vapors to varying degrees. A 2-inch water column pressurization could not be sustained by 43% of gasoline stations, while 48% of stations could not be pressurized to the 2-inch water column mark. Only 9% of facilities could demonstrate leak tightness.

This survey shows that most stations are not maintained well enough to eliminate fugitive emissions. The results also indicate that the emissions factors used for stations with vent valves, Scenario 3B, 5B, and 6B may be underestimated. In this report the risks are based on an **overall control efficiency of 90%** to take into account leakage and other emissions not fully quantified. A research project to quantify the leakage emissions from different types of stations is needed.

F.   Loading Spillage Emissions

Some amount of spillage occurs after the underground storage tanks are filled, and as the hoses from the tank truck are removed and returned to the truck. These emissions have never been estimated. Further study is needed to quantify these emissions and determine their risk contribution.

G. Loading Overfill Catch Basin Emissions

Sometimes gasoline is spilled into the catch basin that rings the underground storage tank loading port. Some of this evaporates into the air, while most of it is returned from a drain valve into the underground storage tank. Additional gasoline vapors are released if the drain valve does not close properly, or when the basin has water in it which operators do not want to return to the underground tank. When the gasoline is not returned, it is evaporated. Here too, is an area where further study is needed.

H. Assist System Emissions Controls

The emission factors developed for this report assume that the emissions from assist systems are equal to the emissions from balance systems. It was assumed that each system has equivalent emissions, because both can meet CARB's certification standards. However, the following design and maintenance factors may result in greater emissions from assist systems compared to balance systems.

- Greater amounts of spillage have been observed with assist systems, particularly at throughputs greater than the 10 gallons per minute (gpm) certification limit. Even though this limit must be met, inspectors continue to observe stations operating with fill up rates above 10 gpm.

- If the volumetric flowrate of the air/gasoline mixture being returned to the underground storage tanks is greater than the fuel dispensing flowrate, then the system pressure can increase to the level which causes the pressure relief valves to open and release vapors. Also, if the system contains leaks, as they frequently do, then greater emissions will be emitted from these leak points due to the greater system pressure.

- When excess air leaks into an assist system with an incinerator, the incinerator may not ignite. This will cause a system wide failure.

- If the vent valves become stuck in the open position, or otherwise leak, greater emissions will occur.

- Although the emissions have not been measured, field staff have observed what appears to be greater amounts of density gradient waves emanating from vent valves at assist system stations during loading operations compared to balance stations. The visual observations indicate that greater amounts of emissions are being released at stations with assist systems compared to stations with balance system.

Further efforts are needed to determine whether stations with assist systems have greater actual emissions compared to balance systems.

I. Effects of On-Board Canisters on Gasoline Station Vapor Recovery Systems

On-board vapor recovery canisters have been added to new vehicles starting in September 1997. CARB studied the impact of onboard controls applied to Phase II equipped stations, and found that the emissions may be significantly increased. [10] This means that the cancer risk will also increase. CARB will be studying this issue further. When the full impact of on-board canisters is realized, the impact should be included in risk assessments prepared in future years.

J. Effects of Seasonal Variations in the Volatility of Gasoline

The volatility and oxygen content of gasoline is higher in the winter compared to the summer. However, the benzene content is limited regardless of the season and cannot exceed an average of 0.80% by volume in reformulated gasoline.   Because the benzene content used to prepare risk assessments is based on the maximum allowable level, the maximum cancer risks from benzene should remain the same throughout the year.

K. OEHHA Risk Assessment Guidelines

In 1992, Senate Bill (SB) 1731 amended the Air Toxics "Hot Spots" Information and Assessment Act of 1987, which in part requires OEHHA to prepare risk assessment guidelines using a full public process. Pursuant to SB 1731, OEHHA is developing risk assessment guidelines for use in the "Hot Spots" program. In the future, OEHHA's Risk Assessment Guidelines may affect the Gasoline Service Station Industrywide Risk Assessment Guidelines by adding or changing health effects values and exposure assumptions. As a result, the Gasoline Service Station Industrywide Risk Assessment Guidelines may need to be updated, where appropriate, per changes in OEHHA's Risk Assessment Guidelines.

XIV. CONCLUSIONS

The information in this report can be used for preparing an industrywide risk assessment for gasoline stations. If the results of the industrywide risk assessment indicate a significant risk is occurring, a refined risk assessment using site specific information may show a lower risk. The information in this report should be revised to include the new developments in emission estimates and modeling capabilities as they become available.

REFERENCES

1.   U.S. Environmental Protection Agency, <u>User's Guide for the Industrial Source Complex (ISC3) Dispersion Models</u>, EPA-454/B-95-003a, September 1995.

2.   CAPCOA Air Toxics "Hot Spots" Program, <u>Revised 1992 Risk Assessment Guidelines</u>, October 1993.

3.   Memo from Rob Harley, Assistant Professor, Department of Civil and Environmental Engineering, University of California at Berkeley, August 27, 1997, Testing performed for the Bay Area Air Quality Management District in the Summer of 1996.

4.   James J. Morgester, Robert L. Fricker, G. Henry Jordan, "Comparison of Spill Frequencies and Amounts at Vapor Recovery and Conventional Service Stations in California", <u>Journal of Air & Waste Management Association</u>, Vol. 42, No. 3, pp. 284-289, March 1992.

5.   Auer, Jr., A.H., 1978, "Correlation of Land Use and Cover with Meteorological Anomalies", <u>Journal of Applied Meteorology</u>, pp. 636-654.

6.   MBUAPCD Field Observations, December 23, 1994.

7.   American Petroleum Institute, "A Survey & Analysis of Liquid Gasoline Released to the Environment During Vehicle Refueling at Service Stations", June 1989, p. 3-6.

8.   EPA-454/R-02-019, <u>Screening Procedures for Estimating the Air Quality Impact of Stationary Sources Revised</u>, U.S. Environmental Protection Agency, OAQPS, Research Triangle Park, North Carolina, October 1992, pp. 4-16.

9.   CARB, "Investigation of Balance Vapor Recovery System Leak Tightness at a Random Sample of Gasoline Dispensing Facilities", July 28, 1995.

10.   CARB, "Estimated Hydrocarbon Emissions of Phase II and On-Board Vapor Recovery Systems", Amended May 24, 1994.

APPENDIX A

EMISSION FACTORS FOR
GASOLINE STATIONS

EMISSION FACTORS FOR GASOLINE STATIONS

Gasoline station emission factors vary depending on the type of loading, refueling, and maintenance procedures used at each facility. Before selecting an emission factor from the following categories, see the definitions on the last page of this appendix for a description of the various loading, refueling, and inspection frequency categories. Each of the scenarios include submerged fill pipes.[a]

ABOVEGROUND TANKS

Scenario 1 - No Controls

Historical Emission Factors (lbs/1000 gal)	Current Emission Factors (lbs/1000 gal)	Process	Method of Derivation
10.0[2]	8.4[1]	Loading	From BAAQMD Test Data[1]
2.5[5]	2.1	Breathing	Assumes the same ratio as previously published emission factors[2] $$\frac{10.0}{2.5} = \frac{8.4}{X} \qquad X = 2.1$$
10.0[2]	8.4[1]	Refueling	Same as loading, from BAAQMD Test Data[1]
	0.61[3]	Spillage	JAWMA[3]
	19.5	**Total**	

Scenario 2 - Phase I Only

Historical Emission Factors (lbs/1000 gal)	Current Emission Factors (lbs/1000 gal)	Process	Method of Derivation
0.5	0.42	Loading	Assumes 95% Control 8.4 x 0.05 = 0.42
2.5[5]	2.1	Breathing	Assumes the same ratio as previously published emission factors[2], same as scenario 1, breathing. $$\frac{10.0}{2.5} = \frac{8.4}{X} \qquad X = 2.1$$
10.0[2]	8.4	Refueling	Same as Scenario 1, loading, from BAAQMD Test Data[1]
	0.61[3]	Spillage	JAWMA[3]
	11.5	**Total**	

ABOVEGROUND TANKS
(CONT'D)

Scenario 3A - Phase I and II, without Vent Valves
90% Overall Efficiency for Breathing and Refueling

Historical Emission Factors (lbs/1000 gal)	Current Emission Factors (lbs/1000 gal)	Process	Method of Derivation
0.5	0.42	Loading	Assumes 95% Control 8.4 x 0.05 = 0.42
0.25	0.21	Breathing	Assumes the same ratio as previously published emission factors[2] $\frac{1.0}{0.1} = \frac{2.1}{X}$ X = 0.21
10.0[2]	0.63	Refueling	Uncontrolled x [100-90%] - Breathing = Refueling [8.4 x 0.10] - 0.21 = 0.63
	0.42[3]	Spillage	JAWMA[3]
	1.68	**Total**	

Scenario 3B - Phase I and II, with Vent Valves
90% Overall Efficiency for Breathing and Refueling

Historical Emission Factors (lbs/1000 gal)	Current Emission Factors (lbs/1000 gal)	Process	Method of Derivation
0.5	0.42	Loading	Assumes 95% Control 8.4 x 0.05 = 0.42
0.25	0.053	Breathing	Aeroenvironment Study[4]. It was assumed that vent valves on aboveground tanks perform similar to underground tanks. Vent valves on underground tanks reduce the emissions from 0.08 to 0.02, a difference of 0.06, a resultant 75% reduction. (0.21)(100-75%) = 0.053
	0.63	Refueling	Same as Scenario 3A
	0.42[3]	Spillage	JAWMA[3]
	1.52	**Total**	

UNDERGROUND TANKS

Scenario 4 - No Controls

Historical Emission Factors (lbs/1000 gal)	Current Emission Factors (lbs/1000 gal)	Process	Method of Derivation
10.0[2]	8.4[1]	Loading	From BAAQMD Test Data[1]
1.0	0.84	Breathing	Assumes the same ratio as previously published emission factors[2] $$\frac{10.0}{1.0} = \frac{8.4}{X} \qquad X = 0.84$$
	8.4	Refueling	Same as Scenario 1, loading, from BAAQMD Test Data[1]
	0.61[3]	Spillage	JAWMA[3]
	18.2	**Total**	

Scenario 5A - Phase I Only

Historical Emission Factors (lbs/1000 gal)	Current Emission Factors (lbs/1000 gal)	Process	Method of Derivation
0.5	0.42	Loading	Assumes 95% Control 8.4 x 0.05 = 0.42
1.0	0.84	Breathing	Same as Scenario 5, breathing. Assumes the same ratio as previously published emission factors[2] $$\frac{10.0}{1.0} = \frac{8.4}{X} \qquad X = 0.84$$
10.0[2]	8.4	Refueling	Same as Scenario 1, loading, from BAAQMD Test Data[1]
	0.61[3]	Spillage	JAWMA[3]
	10.3	**Total**	

Scenario 5B - Phase I with Vent Valves

Historical Emission Factors (lbs/1000 gal)	Current Emission Factors (lbs/1000 gal)	Process	Method of Derivation
	0.084	Loading	Aeroenvironment Study[4] indicated no emissions, but assumes emissions of 1% of uncontrolled emissions due to equipment failures or defects. 1% x 8.4 = 0.084
	0.21	Breathing	Even though the Aeroenvironment Study[4] was not a leak tight test, it was assumed that the reported 75% emissions reductions (00.8 down to 0.02 lbs/gal) can be used to derive the effectiveness of vent valves. Thus, the breathing loss reduced by 75% equals (0.84) (100-75%) = 0.21
10.0[2]	8.4	Refueling	Same as Scenario 1, loading, from BAAQMD Test Data[1]
	0.61[3]	Spillage	JAWMA[3]
	9.30	**Total**	

Scenario 6A - Phase I and Phase II, without Vent Valves
90% Overall Efficiency for Breathing and Refueling

Historical Emission Factors (lbs/1000 gal)	Current Emission Factors (lbs/1000 gal)	Process	Method of Derivation
0.5	0.42	Loading	Assumes 95% Control 8.4 x 0.05 = 0.42
0.1	0.1	Breathing	Historical emissions factor
	0.74	Refueling	Uncontrolled x [100-90%] - Breathing = Refueling [8.4 x 0.10] - 0.1 = 0.74
	0.42[3]	Spillage	JAWMA[3]
	1.68	**Total**	

UNDERGROUND TANKS
(CONT'D)

Scenario 6B - Phase I and Phase II, with Vent Valves
90% Overall Efficiency for Breathing and Refueling

Historical Emission Factors (lbs/1000 gal)	Current Emission Factors (lbs/1000 gal)	Process	Method of Derivation
	0.084	Loading	Aeroenvironment Study[4] indicated no emissions, but assumes emissions of 1% of uncontrolled emissions due to equipment failures or defects. 1% x 8.4 = 0.084
	0.025	Breathing	Even though the Aeroenvironment Study[4] was not a leak tight test, it was assumed that the reported 75% emissions reductions (0.08 down to 0.02 lbs/gal) can be used to derive the effectiveness of vent valves. Thus, the breathing loss reduced by 75% equals (0.1) (100-75%) = 0.025
	0.74	Refueling	Same as Scenario 6A
	0.42[3]	Spillage	JAWMA[3]
	1.27	**Total**	

NOTES

a) Submerged loading - Submerged loading is a type of filling method. There are two types of submerged loading methods, either the fill pipe descends almost to the bottom of the storage tank (submerged fill method) or the fill pipe enters the storage tank from the bottom (bottom loading method).

b) Phase I - Phase I refers to control methods used for reducing emissions when tank trucks unload into underground storage tanks. A Phase I vapor balance system employs a vapor return hose which returns gasoline vapor displaced from the underground storage tank to the tank truck storage compartment being emptied.

c) Phase II - Phase II refers to control methods used for reducing vehicle/equipment refueling emissions. The Phase II systems are designed to convey the vapors displaced from vehicle fuel tanks to underground storage tanks vapor space. Both balance systems and assist systems were assumed to capture 95% control of the vapors released from the vehicle fuel tank, with an overall efficiency of 90%.

REFERENCES

1.   BAAQMD continuous testing from 1/5/93-1/25/93 and from 2/11/93-2/22/93.

2.   California Air Resources Board, "A Report to the Legislature on Gasoline Vapor Recovery Systems for Vehicle Fueling at Service Stations (Phase II Systems)", March, 1983.

3.   James J. Morgester, Robert L. Fricker, G. Henry Jordan, "Comparison of Spill Frequencies and Amounts at Vapor Recovery and Conventional Service Stations in California", Journal of Air & Waste Management Association, Vol. 42, No.3, pp.284-289, March 1992.

4.   Aerovironment, Inc., Prepared for WSPA, "Underground Storage Tank Vent Line Emissions form Retail Gasoline Outlets", Report # AV-FR-92-01-204R2, p. 3-23, May 1994.

5.   Based on discussions among experts, the breathing emission factor for aboveground tanks should be higher than underground tanks due to the effects of diurnal changes, temperature fluctuations, sun and wind exposure that doesn't occur for underground tanks. The value chosen was not based on empirical data.

APPENDIX B

CONTENT OF PHASE 2
REFORMULATED GASOLINE

CALIFORNIA AIR RESOURCES BOARD

EXCERPTS FROM
THE CALIFORNIA REFORMULATED GASOLINE REGULATIONS

Title 13, California Code of Regulations, Sections 2250-2272
(As last amended July 2, 1996)

NOTE: This is a compilation of California Air Resources Board (ARB) motor vehicle gasoline regulations that are applicable in all or some circumstances on March 1, 1996. They are collectively referred to as the California reformulated gasoline (CaRFG) regulations.

Title 13, California Code of Regulations, Division 3, Chapter 5 (Standards for Motor Vehicle Fuels), Article 1 (Standards for Gasoline) consists of two Subarticles. Subarticle 1 (commencing with section 2250) contains standards that became applicable before 1996. Subarticle 2 (commencing with section 2260) contains the phase 2 reformulated gasoline regulations that became applicable starting in March and April, 1996. Section 2261(b) identifies the preexisting subarticle 1 regulations that continue to apply to all California gasoline after April 1, 1996: section 2253.4 (Lead/Phosphorus in Gasoline), section 2254 (Manganese Additive Content), and section 2257 (Required Additives in Gasoline). Two additional regulations in subarticle 1 -- section 2250 (Degree of Unsaturation of Gasoline) and section 2252 (Sulfur Content of Gasoline) -- continue to apply until March 1, 1998 *only* to small refiners who have qualified under section 2272 for temporary exemptions from the CaRFG standards for sulfur content, olefin content, T50 and T90. One other subarticle 1 regulation -- section 2259 -- establishes a mechanism under which exemptions from the ARB fuels requirements may be granted for motor vehicle fuels being used in test programs; it applies to all of the CaRFG standards (see section 2267).

This compilation contains all of the regulations mentioned in the preceding paragraph. It does not include the following subarticle 1 gasoline regulations that were sunsetted February 29, 1996: section 2251.5 (Reid Vapor Pressure of Gasoline Sold After January 1, 1992 and Before March 1, 1996), and section 2258 (Oxygen Content of Gasoline in the Wintertime). It also does not include sections 2296 (Motor Fuel Sampling Procedures) and 2297 (Test Method for the Determination of RVP Equivalent).

In the latter part of 1995 the ARB conducted three rulemakings amending parts of the CaRFG regulations. The amendments, pertaining to test methods, variances, and downstream blending of oxygenates and "housekeeping" matters, are incorporated in the text below.

At a November 16, 1995 hearing, the ARB approved amendments to section 2257 (Required Additives in Gasoline). These amendments were formally adopted July 2, 1996, and became effective October 13, 1996. They are also reflected in this compilation, as is an editorial clarification of the title of Subarticle 1 (starting with section 2250), which was transmitted to OAL November 19, 1996.

Section 2262.3. Standards for Benzene Content.

(a) *Maximum benzene standard for all California gasoline.* No person shall sell, offer for sale, supply, offer for supply, or transport California gasoline which has a benzene content exceeding 1.20 percent by volume.

(b) *Additional flat benzene standard for producers and importers.* No producer or importer shall sell, offer for sale, supply, or offer for supply from its production facility or import facility California gasoline which has a benzene content exceeding 1.00 percent by volume, unless the transaction occurs during a period for which the producer or importer has elected to be subject to section (c), or unless the gasoline has been reported as a PM alternative gasoline formulation pursuant to section 2265(a) or as an alternative gasoline formulation pursuant to section 2266(c).

(c) *Benzene averaging compliance option for producers and importers.* No producer or importer shall, during a period for which the producer or importer has elected to be subject to this section (c), sell, offer for sale, supply, or offer for supply from its production facility or import facility California gasoline which has a benzene content exceeding 0.80 percent by volume, unless the gasoline has been reported as a PM alternative gasoline formulation pursuant to section 2265(a) or as an alternative gasoline formulation pursuant to section 2266(c), or unless:

(1) A designated alternative limit for benzene content has been established for the gasoline in accordance with the requirements of section 2264(a), and

(2) The benzene content of the gasoline does not exceed the designated alternative limit, and

(3) Where the designated alternative limit exceeds 0.80 percent by volume, the excess benzene content is fully offset in accordance with section 2264(d).

NOTE: Authority cited: sections 39600, 39601, 43013, 43018, and 43101, Health and Safety Code; and Western Oil and Gas Ass'n. v. Orange County Air Pollution Control District, 14 Cal.3d 411, 121 Cal.Rptr. 249 (1975). Reference: sections 39000, 39001, 39002, 39003, 39010, 39500, 39515, 39516, 41511, 43000, 43016, 43018, and 43101, Health and Safety Code; and Western Oil and Gas Ass'n. v. Orange County Air Pollution Control District, 14 Cal.3d 411, 121 Cal.Rptr. 249 (1975).

To: David Craft
    Monterey Bay APCD

From: Rob Harley
      Assistant Professor
      Dept. Of Civil and Environmental Engineering
      UC Berkeley

Re: Your request for information on gasoline properties

Date: August 27, 1997

Below are weight fractions of selected individual hydrocarbons found in summer 1996 gasoline sampling in the Bay Area. These data reflect a composite of regular and premium grade gasoline samples. They are appropriate for the composition of the liquid gasoline; headspace vapors emitted to the atmosphere during refueling will be enriched in benzene, and have less of the heavier compounds (esp. xylene and heavier).

Compound:	Wt% in Liquid Gasoline:
benzene	0.6
toluene	8.0
ethylbenzene	1.6
o-xylene	2.4
m-ethyltoluene	1.5
1,2,4-trimethylbenzene	2.4

APPENDIX C

MODELING, REFUELING, AND SPILLAGE AS VOLUME SOURCES - LORAX REPORT

ANALYSIS OF WAKE EFFECTS AT RETAIL GASOLINE OUTLETS

APRIL 1997

Prepared for:
WESTERN STATES PETROLEUM ASSOCIATION
Glendale, California

...

Prepared by:
LORAX ENVIRONMENTAL, INC.
Pasadena, California

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INTRODUCTION

The Western States Petroleum Association (WSPA) has been working with the Gasoline Risk Assessment Committee (GASRAC) of the AB2588 Toxics Committee of the California Air Pollution Control Officers Association (CAPCOA) in developing screening risk assessment procedures for evaluating the health impacts caused by retail gasoline outlets (RGOs). LORAX Environmental, Inc. (LORAX) is assisting WSPA in evaluating the technical issues surrounding the preparation of a screening risk assessment for this industry.

One of the major factors in the evaluation of risk from RGOs is the choice of source characteristics for use in the Industrial Source Complex Short Term dispersion model (ISCST3). The draft report issued by CAPCOA in May, 1996 [1] recommended that emissions be modeled as four volume sources each with dimensions 1.3 meters high by 3 meters long by 3 meters wide. These dimensions were developed based on a standardized gasoline service station plot plan and an analysis of the size of the wake cavity that will be produced as wind travels over the dispensers and the vehicles being refueled.

It is WSPA's position that the volume sources presented in the draft CAPCOA report do not adequately represent the source characteristics of emissions from a typical RGO. The presence of dispensers, standards, the canopy, nearby buildings, trees, and other objects will result in enhanced mixing of benzene vapors with air at the source thereby greatly reducing near-receptor impacts. WSPA recommends that emissions be modeled using a single volume source with dimensions roughly equivalent to the volume beneath a typical gas station canopy, i.e.: 5 meters high by 13 meters long by 13 meters wide.

In order to help resolve this issue and develop a better understanding of the behavior of these emissions once they are released during refueling operations, LORAX retained Dr. Anthony Leonard, a professor of aeronautical science at the California Institute of Technology in Pasadena. Dr. Leonard submitted a preliminary report on the results of his investigation in November of 1996 [2]. The GASRAC committee reviewed his analysis and requested additional information from Dr. Leonard as well as from LORAX. This document summarizes the work originally reported by Dr. Leonard in November as well as the results of additional investigation carried out in response to issues raised by the GASRAC. This report also summarizes work carried out by LORAX in applying the results of Dr. Leonard's work to dispersion modeling at a typical RGO.

2

WAKE EFFECTS

The movement of air across a structure such as a cube is often illustrated by a series of flow vectors similar to those shown in Figure 1. The vectors illustrate the presence of a wake in which air flows up and over the body and a recirculation zone or wake cavity created on the leeward side of the cube. Diagrams such as this imply that the wake cavity is a well-mixed zone with little mixing or exchange occurring between it and the outer wake flow.
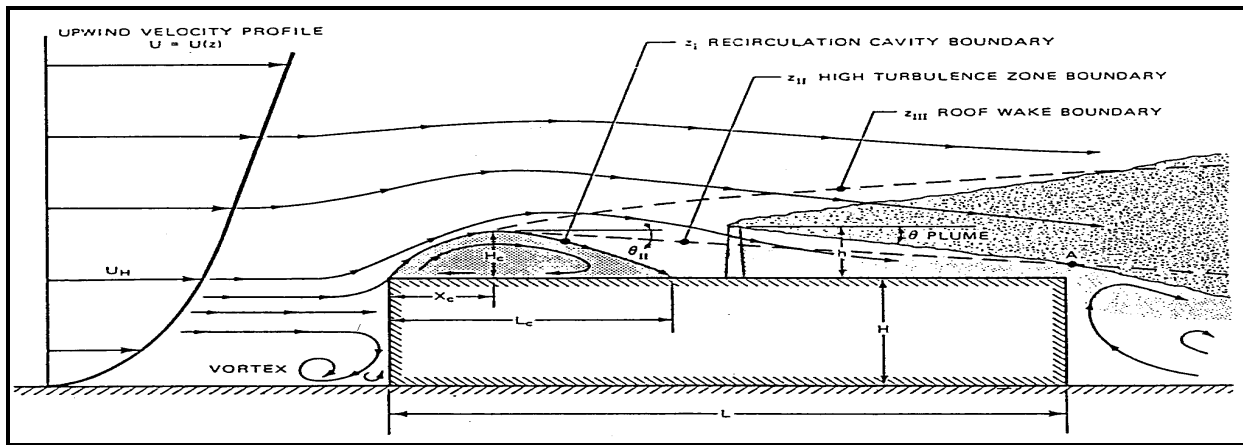

Figure 1: Two dimensional representation of wake effects (from Wilson [3])

The draft risk assessment guidelines prepared by CAPCOA determined the size of the well-mixed zone brought about by the presence of bluff bodies such as cars, dispensers, and the canopy at an RGO by considering the dimension of the wake cavity. In his preliminary report, however, Dr. Leonard pointed out that wake effects were much more complex.

> "As the wind first approaches an object in its path, individual parcels of air at first slow down due to the slightly increasing air pressure caused by the presence of the object but they then accelerate to speeds higher than the original approach velocity as they move around the body. However, the air immediately adjacent to the wall of the body is strongly affected by viscous forces that retard the flow. As a result, this boundary layer fluid does not have the energy to continue along the body into the higher pressure leeward side of the body. This boundary layer fluid then separates from the body at some point on the leeward side of a smooth body, or before then if a sharp radius of curvature is encountered. The separating boundary layer fluid carries with it the fluid vorticity generated at the boundary producing a vigorous, unsteady mixing process with the outer flow.

The Wake Envelope

This vortical fluid then moves downstream of the object in an unsteady manner with the outermost excursions in the lateral directions serving to define the edge or envelope of the wake. The vortical fluid acts as a vigorous stirring agent so that any effluent, along with the non-vortical fluid within the wake, is mixed rapidly laterally throughout the wake. As one moves downstream, the wake increases in lateral dimension and the turbulent kinetic energy of the wake fluid decreases.

The Wake Cavity

If one considers a time-averaged wake flow, assuming a constant incoming wind speed and direction, there exists a recirculation zone, or wake cavity, immediately downstream of the object. For two dimensional or axisymmetric objects, there is a dividing stream surface that separates the outer, time-averaged flow from the wake cavity and defines the fluid boundary of the wake cavity. In a general three dimensional bluff body flow, a dividing stream surface may or may not exist but one can still define a region where some recirculation takes place. In dispersion problems, the wake cavity is sometimes defined as that region outside of which no effluent is observed to recirculate back to the base of the object (Huber and Snyder, [4])."

These effects are illustrated by Figure 2.
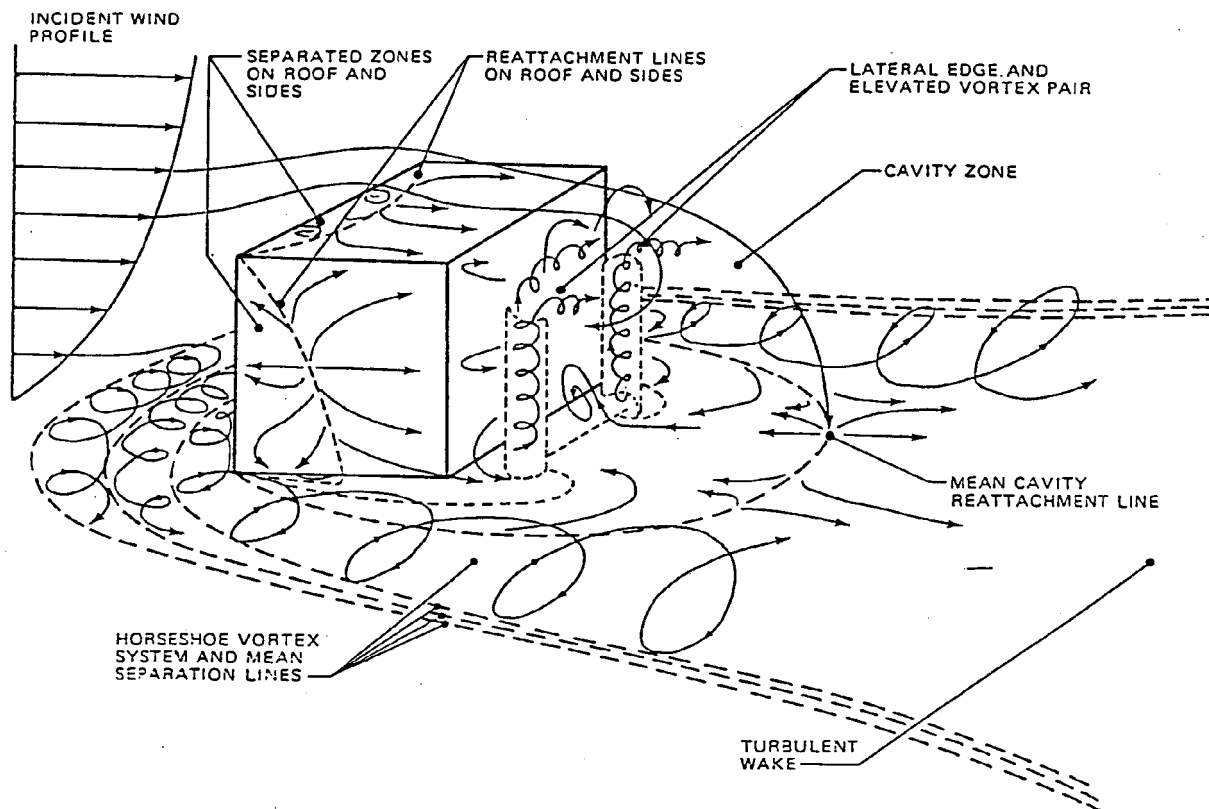

Figure 2:   Model of flow near a sharp-edged building in a deep boundary layer
             (from Hosker, [5])

The end result of this mixing is that any pollutant that is released within a wake is rapidly mixed in the lateral and vertical direction throughout the wake envelope, not just within the recirculating cavity.

The effectiveness of mixing of an effluent introduced into the wake was also discussed by Dr. Leonard in his preliminary report paraphrased below:

> The recirculating, closed streamline pattern of the time-averaged flow within the wake cavity gives the impression of poor mixing or exchange with the outer wake flow. However, this notion is misleading. Because of flow unsteadiness for all **Reynolds Numbers (Re)>100**, there is considerable exchange of fluid between the wake cavity and the surroundings, as mentioned above. For example, for Re=190 flow past a circular cylinder, a case that can be in some detail using computational fluid dynamics, 49% of the fluid in the cavity is exchanged ever **Strouhal period**, or every **5D/U** seconds [6].

> These exchange rates are expected to hold roughly independent of Re and of body geometry if **D** is taken to be an **effective lateral dimension** of the body and **U** is the **upwind velocity**.

> Huber & Snyder [4], for example, in studying the dispersion of effluents in the wake of a rectangular-shaped object, noted that "for the ground-level source, rapid spreading of the effluent was observed to fill the wake in both the vertical and horizontal planes." The Re for their studies were at least 36,000. Below an Re of 36,000 they indicate that there may be some quantitative changes in the degree of mixing but they will be very small.

To give an example of interest to the present study, consider a **1 m/sec wind speed** past an object with a **5 ft. (1.5 m) lateral dimension**. The Reynolds number is calculated as:

$$\begin{aligned} \text{Re} \quad &= \quad \text{Wind Speed x Lateral Dimension / Kinematic Viscosity} \\ &= \quad UD/K \\ &= \quad (1 \text{ m/sec}) (1.5 \text{ m}) / (0.000015 \text{ m}^2/\text{sec}) \\ &= \quad 100,000 \end{aligned}$$

The Strouhal period where 50% of the cavity is exchanged is calculated as:

$$\begin{aligned} \text{Strouhal period} \quad &= \quad 5 \, D/U \\ &= \quad 5 \, (1.5 \text{ m}) / (1 \text{ m/sec}) \\ &= \quad 7.5 \text{ sec} \end{aligned}$$

In summary, as long as you have an unsteady wake (which occurs at Reynolds numbers >100), there will be good mixing. The Reynolds number remains above 100 even with wind speeds as low as 0.001 m/sec.

$$\begin{aligned} \text{Re} \quad &= \quad (\text{Wind Speed}) (\text{Lateral Dimension}) / (\text{Kinematic Viscosity}) \\ &= \quad UD/K \\ &= \quad (0.001 \text{ m/sec}) (1.5 \text{ m}) / (0.000015 \text{ m}^2/\text{sec}) \\ &= \quad 100 \end{aligned}$$

3

MATHEMATICAL DESCRIPTION OF THE WAKE REGION

WAKE GEOMETRY

In his preliminary report, Dr. Leonard pointed out that theories of turbulent wakes lead to a one third power law describing the lateral spreading of an axisymmetric wake and a one half power law describing a two-dimensional wake [7],[8]. A two-dimensional problem is one involving a structure whose height is very small compared to its length and width. Given the situation described by Figure 3:
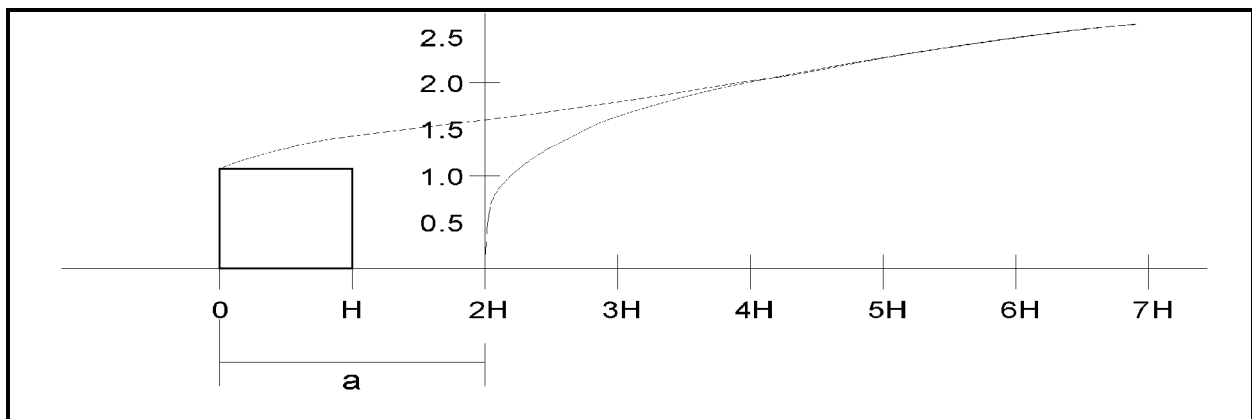

Figure 3: Growth of a wake envelope for an axisymetric wake

the growth of the wake envelope at a distance beyond 4H can be described by:

$$Z = 2L[\frac{(x+a)}{2L}]^{1/3}$$

(1)

where Z =   height of wake envelope
             x =   downwind distance

Here, a is the virtual origin and L is the body radius for a circular cross-section above the ground plane, or a semicircular object on the ground plane. An O(1) constant can be used, multiplying the right-hand side of the equation, for fine tuning. In experiments with disks Carmody [9] found good agreement with a=-R for x+ a>20R. The experiments of Huber and Snyder [4] for flow past a rectangular object of height H show a vertical spreading of ground level emissions to 2H at x = 4H downstream, where x is measured from the windward side of the object, and a lateral spread to 2.5H at that same location. The object width normal to the wind was 2H and the width in the wind direction was H. (In their study, the wake envelope was determined as the maximum

spread of smoke that was emitted from a point within the wake cavity.) If the 1/3 power law is fitted to the data at x=4H we find a corresponding of -0.1H in the lateral direction and a = -2H in the vertical direction, using L=H in the above formula. Huber and Snyder [4] give results for 4H<x<11H. Their fit to the data in this range show an additional growth of the wake width by a factor of 1.67. Using this fact only in the 1/3 power law above leads to a virtual origin of a = -2.1H, in good agreement with the virtual origin found above for vertical spreading. We expect the near wake spreading rate and the virtual origin, a, in the asymptotic rate to be only a weak function of the other non-dimensional parameters of the body geometry, e.g., the width normal to the wind to height ratio and the width in the wind direction to height ratio, for the case of a rectangular object.

MIXING DOWNSTREAM OF A WAKE

One of the results suggested by Dr. Leonard's preliminary report was that the wake from a dispenser would intersect that from the canopy. GASRAC committee members raised questions concerning the ability of the two plumes to mix since they only reached each other at some distance from the formation of the wake. In a related question, Dr. Leonard was asked how well a source located downwind of the bluff body would be mixed. Upon further review of the literature, Dr. Leonard proposed the following analysis.
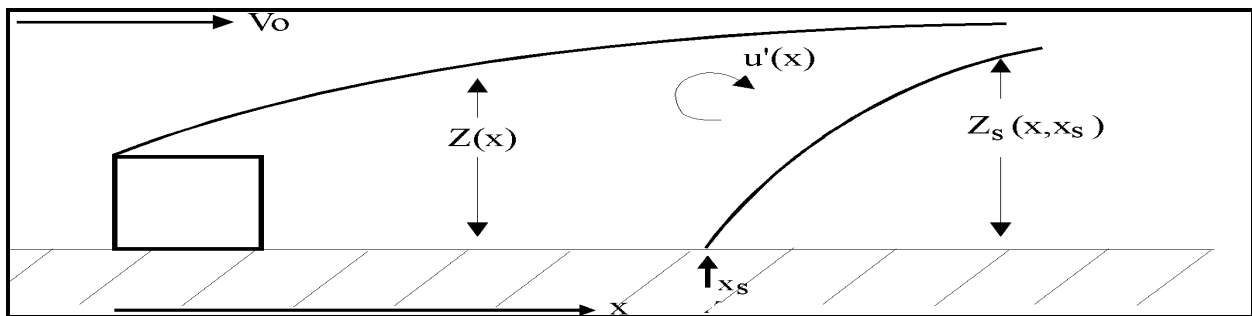Given the scenario described by Figure 4:

Figure 4: Mixing of a downstream release into a wake

where:

v_o	=	free stream velocity
$u'(x)$	=	velocity fluctuation in the wake
$Z(x)$	=	wake envelope for bluff body
$Z_s(x, xs)$	=	plume envelope at x for source at $x = x_s$
$K_T(x)$	=	turbulent diffusiveness in wake
x_s	=	downstream location of the source

According to eddy diffusiveness theory, growth in gaussian width can be expressed as:

$$V_o \frac{d\sigma^2}{dx} \propto K_T(x) \qquad (2)$$

where a reasonable estimate for K_T is provided by:

$$K_T(x) \propto Z(x) * u'(x) \qquad (3)$$

For axisymetric wakes:

$$\frac{u'}{Vo} \propto (\frac{2L}{x+a})^{2/3} \qquad (4)$$

where
$$-a = \text{apparent origin}$$
$$L = \text{characteristic length}$$

From before:

$$Z(x) = 2L(\frac{x+a}{2L})^{1/3} \qquad (5)$$

In addition, the gaussian width and the plume envelope are proportional to each other:

$$Z_s \propto \sigma \qquad (6)$$

To obtain equation 7, first substitute theta for Z and Zu' for K_T into equation 2.

$$V_o \frac{d^2 Z_s}{dx} \propto k_T \propto Zu'$$

Next, substitute equation 5 into Z and equation 4 into u', to get

$$V_o \frac{d^2 Z_s}{dx} \propto 2L(\frac{x+a}{2L})^{1/3} * V_o(\frac{2L}{x+a})^{2/3}$$

$$V_o \frac{d^2Z_s}{dx} \propto 2L \frac{(x+a)^{1/3}}{(2L)^{1/3}} \ast V_o \frac{(2L)^{2/3}}{(x+a)^{2/3}}$$

$$V_o \frac{d^2Z_s}{dx} \propto 2L \frac{(x+a)^{1/3}}{(x+a)^{2/3}} \ast V_o \frac{(2L)^{2/3}}{(2L)^{1/3}}$$

$$V_o \frac{d^2Z_s}{dx} \propto 2L(x+a)^{1/3-2/3} \ast V_o(2L)^{2/3-1/3}$$

$$V_o \frac{dZ_s^2}{dx} = C \ast 2L \left(\frac{2L}{x+a} \right)^{1/3}$$

(7)

where C is a constant to be determined.
Integrating this expression yields:

$$\int_x^{x_s} \frac{dZ_s^2}{dx} = C(2L)^{4/3} \int_x^{x_s} \frac{dx'}{(x'+a)^{1/3}}$$

$$Z_s^2(x,x_s) - Z_s^2(x_s,x_s) = \frac{3}{2}C(2L)^{4/3}[(x+a)^{2/3} - (x_s+a)^{2/3}]$$

where $Z_s^2(x_s,x_s) = 0$

$$Z_s^2(x,x_s) - 0 = \frac{3}{2}C(2L)^{4/3}[(x+a)^{2/3} - (x_s+a)^{2/3}]$$

(8)

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Using equation (5), we find:

$$Z(x) = 2L\left(\frac{x+a}{2L}\right)^{1/3}$$

$$Z(x) = 2L\frac{(x+a)^{1/3}}{(2L)^{1/3}}$$

$$Z(x) = (2L)^{2/3}(x+a)^{1/3}$$

Square $Z(x)$ to create the term $(x+a)^{2/3}$:

$$Z^2(x) = (2L)^{4/3}(x+a)^{2/3}$$

$$(x+a)^{2/3} = \frac{Z^2(x)}{(2L)^{4/3}}$$

Now solve equation (8) in terms of $(x+a)^{2/3}$:

$$Z_s^2(x,x_s) = \frac{3}{2}C(2L)^{4/3}[(x+a)^{2/3}-(x_s+a)^{2/3}] \qquad (8)$$

$$Z_s^2(x,x_s) = \frac{3}{2}C(2L)^{4/3}\left[\frac{Z^2(x)}{(2L)^{4/3}}-\frac{Z^2(x_s)}{(2L)^{4/3}}\right]$$

$$Z_s^2(x,x_s) = \frac{3}{2}C[Z^2(x)-Z^2(x_s)] \qquad (9)$$

To determine C, let: $\qquad x_{s=} -a$

Then solve for $x_s = -a$ in equation (5)

$$Z(-a) = 2L\left(\frac{-a+a}{2L}\right)^{1/3}$$

This results in $Z(x_s) = 0$ when $x_{s=}$ -a

Because -a is the virtual origin that defines the wake envelope $Z(x)$, then

$Z_s^2(_{x,\,xs}) = Z_s^2(x,-a) = Z^2(x)$

and that

$Z^2(x_s) = Z^2(-a) = 0$

Using these facts in equation 9 we find

$$Z_s^2(x,x_s) = \frac{3}{2}C[Z^2(x) - Z^2(x_s)]$$

$$Z_s^2(x,-a) = \frac{3}{2}C[Z_s^2(x,-a) - 0\,]$$

$$\frac{Z_s^{\sim}(x,-a)}{Z_s^2(x,-a)} = \frac{3}{2}C$$

$$1 = \frac{3}{2}C,\ C = \frac{2}{3}$$

Substitute $C = 2/3$ into equation 9 to get

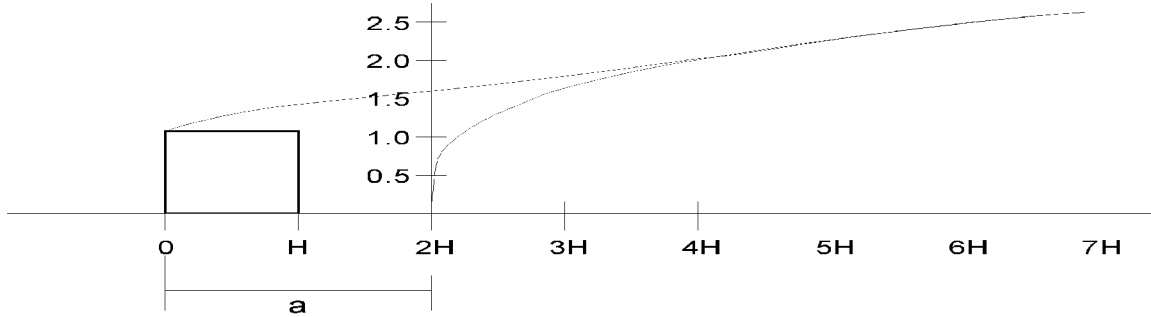$$Z_s^2(x,x_s) = \frac{3}{2}(\frac{2}{3})[Z^2(x) - Z^2(x_s)]$$

$$Z_s^2(x,x_s) = [Z^2(x) - Z^2(x_s)]$$

$$Z_s(x,x_s) = \sqrt{Z^2(x) - Z^2(x_s)}$$ (10)

C-10

For example, assume a release takes place at a distance $x_s = 4H$ from a body of height H. As before:

$$a = -2H$$
$$L = H$$

From equation (5)

$$Z(x) = 2L(\frac{x+a}{2L})^{1/3}$$

$$Z(x_s) = 2H(\frac{4H-2H}{2H})^{1/3} = 2H$$

$$Z(6H) = 2H(\frac{6H-2H}{2H})^{1/3}$$

$$= 2*2^{1/3}H$$

$$= 2.52H$$

The well mixed plume height for the release at x_s can be calculated from equation (10)

$$Z_s(6H,4H) = \sqrt{4H^2(\frac{6H-2H}{2H})^{2/3}-4H^2)}$$

$$= 2H\sqrt{2^{2/3}-1}$$

$$= 1.53H$$

4

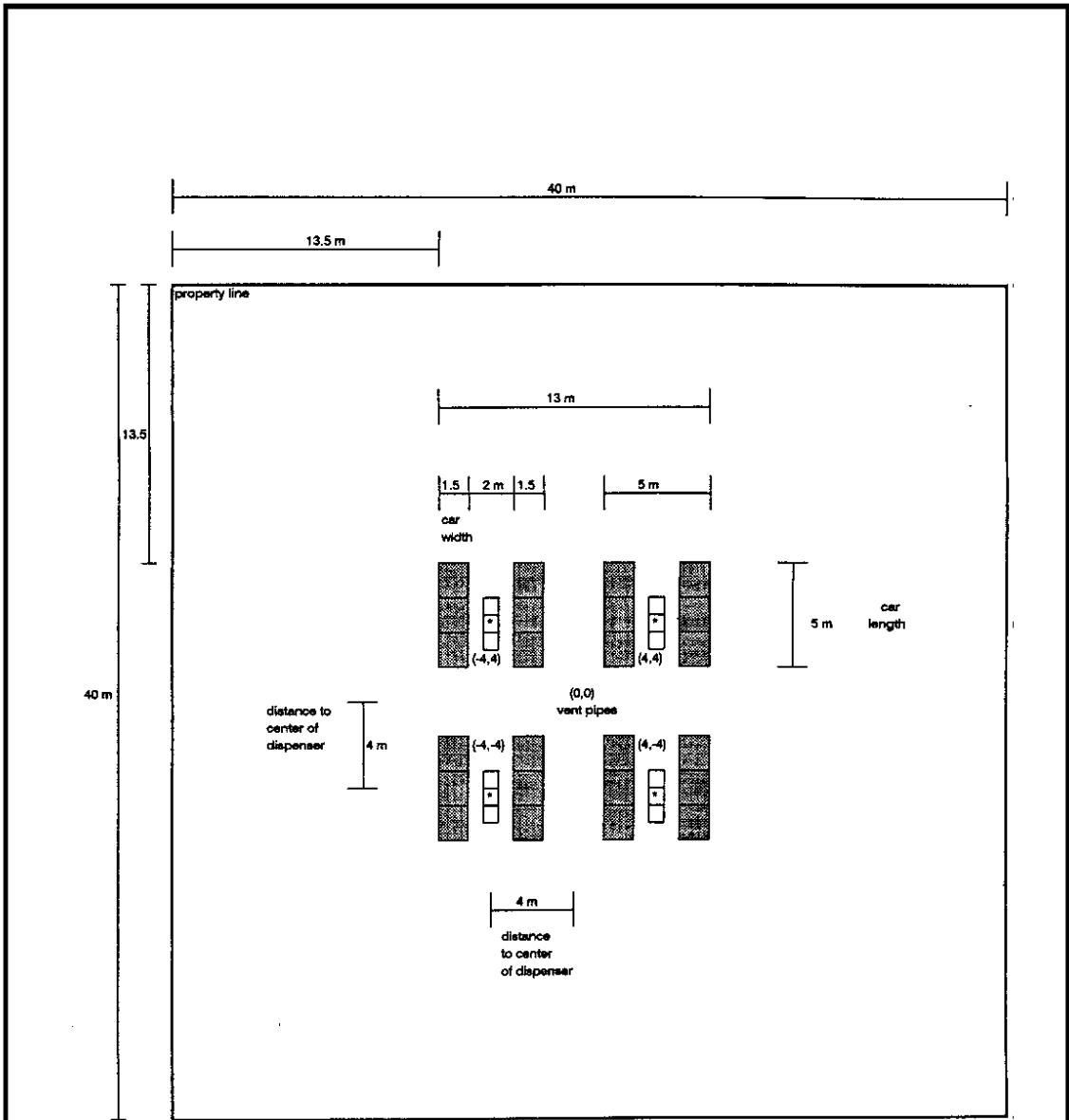# APPLICATION TO A TYPICAL GAS STATION

MIXING AT A TYPICAL RGO

The results described above allow us to estimate the effectiveness of various bluff bodies in enhancing the mixing process at a typical RGO. The dimensions of a typical RGO were established in the draft Risk Assessment Guideline Document and are described by **Figure 5**.

From **Figure 3**, the wake caused by the presence of a dispenser 1.5 meters in height (Ha = 1.5 m) can be estimated as 1.6 Ha (2.4 m) at 2Ha, and as 2.0Ha (3m) at 4Ha. Further downwind, the height of the wake can be estimated from equation (1). The dispenser wake is represented by curve (1) on Figure 6. The effective height of the canopy was estimated as ½ of its overall height of 1m (Hb = 0.5 m). Again, the wake height can be estimated as 1.6 Hb at 2Hb downwind and as 2Hb at 4Hb downwind. Since the canopy is almost a two dimensional structure (Hb is small compared to its length and width), the growth of the wake might actually follow a ½ power law. In order to be conservative, growth was calculated using a 1/3 power law instead. The canopy wake is described by curve (2) in **Figure 6**.   The two wakes intersect at about 12 Hb and 2.6 Ha.

The rate at which the dispenser wake mixes into the canopy wake can be calculated using equation (12) where x_s equals 12 Hb. This results in the following values of $Z_s(_{x, xs})$:

Distance	$Z(x)$ m	$Z(x_s)$ m	$Z_s(_{x, xs})$ m
14 Hb	1.817	1.71	0.615
16 Hb	1.913	1.71	0.857
20 Hb	2.180	1.71	1.184
24 Hb	2.224	1.71	1.422
28 Hb	2.351	1.71	1.614

The predicted mixing into the canopy wake is described by curve (3) in **Figure 6**. This demonstrates that the interaction of the two wakes causes vertical mixing of emissions to occur more rapidly than it would without the canopy wake but that ultimately there is not much difference in the final well mixed height which reaches about 4m at 10 Ha.

Plotplan for a typical retail gasoline outlet

40 m

13.5 m

property line

13.5

40 m

13 m

1.5 | 2 m | 1.5

car width

5 m

(-4,4)

(4,4)

5 m

car length

distance to center of dispenser

4 m

(0,0) vent pipes

(-4,-4)

(4,-4)
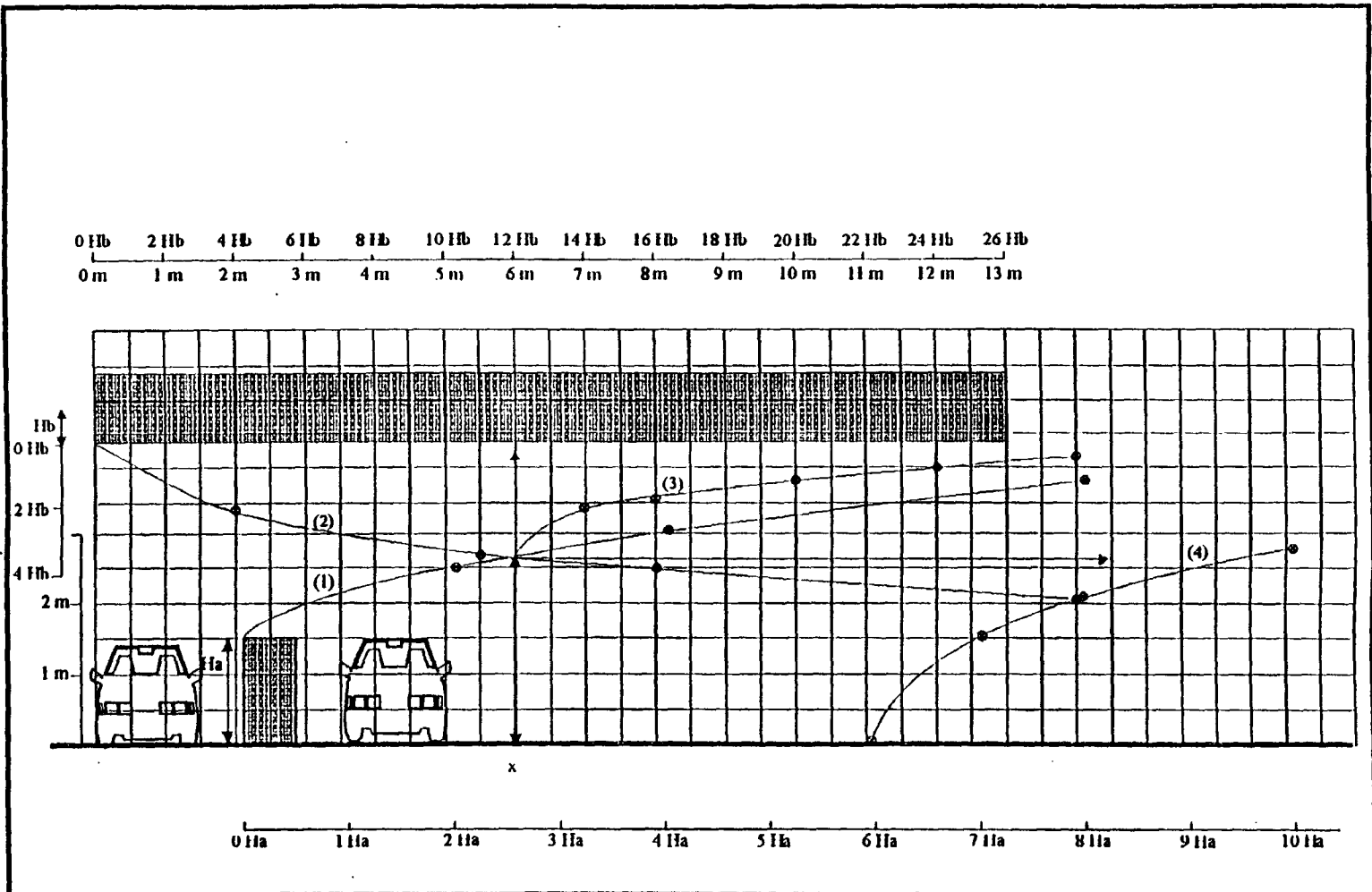
4 m

distance to center of dispenser

LORAX
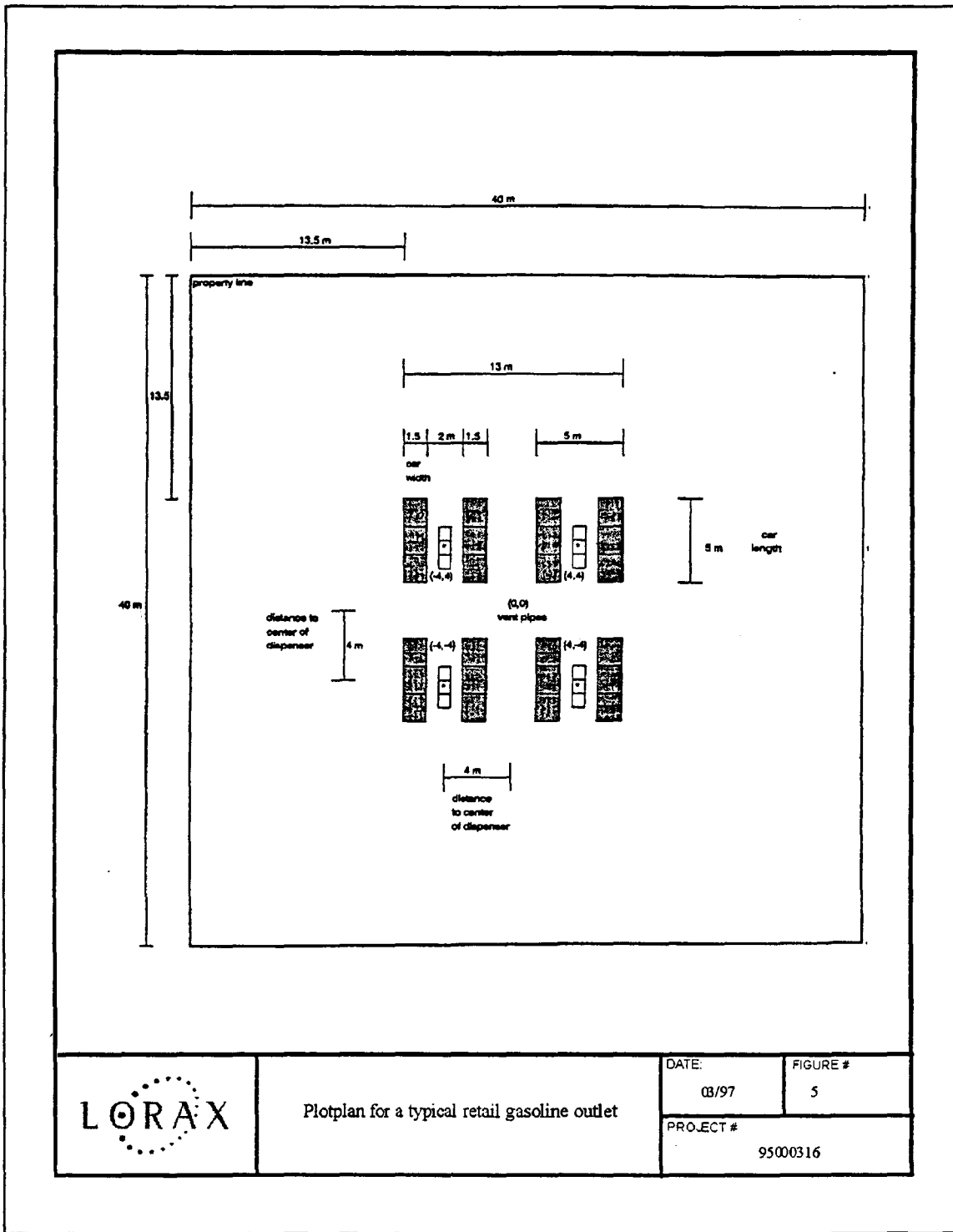
Plotplan for a typical retail gasoline outlet

| DATE: 03/97 | FIGURE # 5 |
| PROJECT # | 95000316 |

LORAX

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Wake envelopes developed by a dispenser and canopy at a typical retail gasoline outlet

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DATE: 03/97

FIGURE # 6

PROJECT # 95000316

LORAX

Equation (12) can also be used to predict how quickly emissions released some distance downwind of the dispenser will mix. In this case, x_s is equal to 6Ha.

Distance	Z(x) m	Z(x$_s$) m	Z$_s$(x, xs) m
7Hb	4.072	3.78	1.514
8Hb	4.327	3.78	2.106
10 Hb	4.762	3.78	2.897

These results are represented by curve (4) of Figure 6. If mixing at the downwind location relies solely on the presence of the upstream dispenser wake, the well mixed height would be limited to about 3 meters.
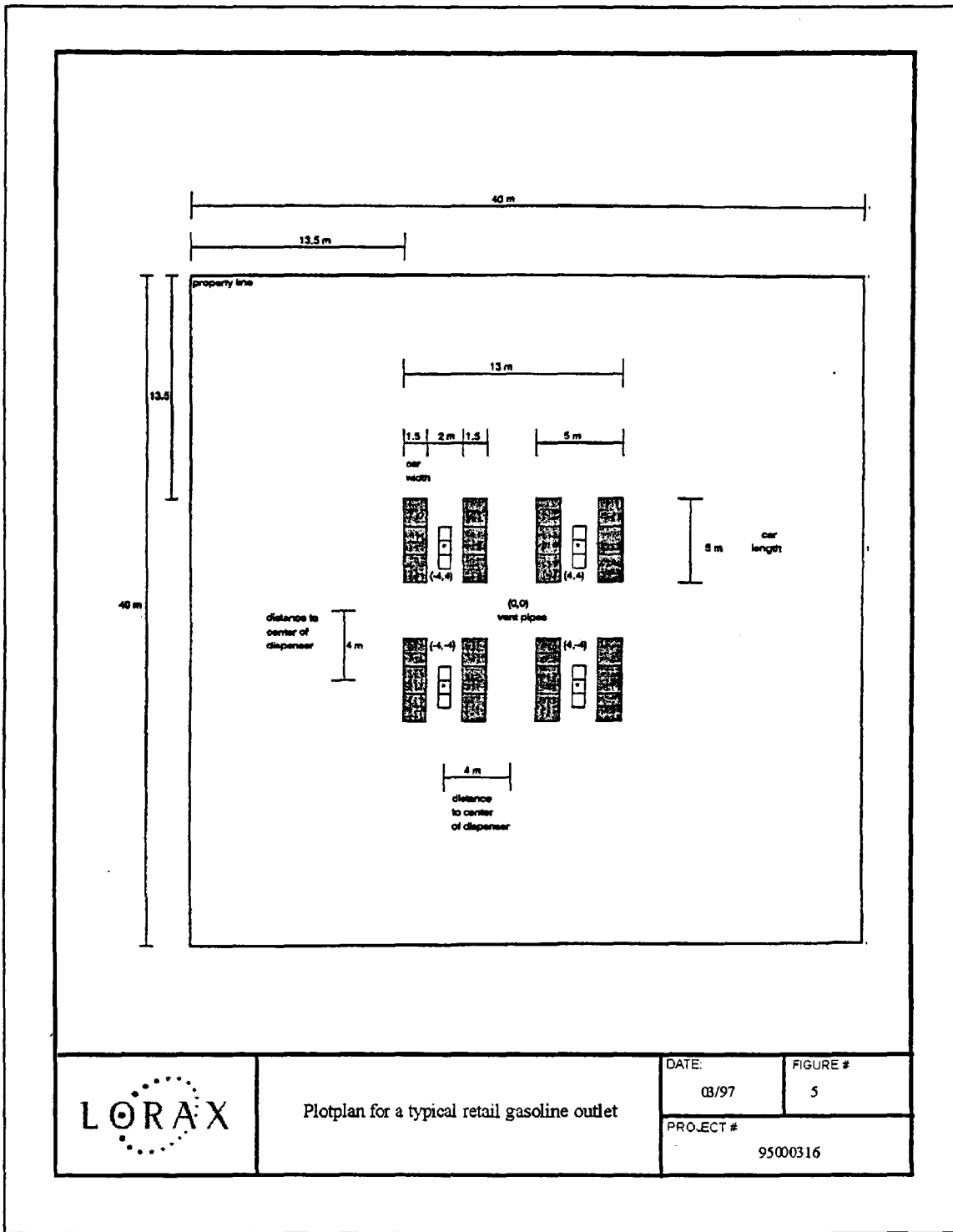
According to Dr. Leonard, however, there will also be a wake associated with the downstream dispenser. This wake is described by Figure 7 which demonstrates that the mixing height will reach about 2.5 m at the canopy edge. The wake envelope will continue to grow, ultimately reaching a height of about 4.8 meters at a distance of 10 H.

The amount of mixing brought about by wake effects is even more impressive if an additional structure such as a spanner is present. This is illustrated by Figure 8. The interaction of the various wakes will result in rapid mixing within the canopy volume for all release scenarios.

Figure 9 considers the effect of bluff body wakes on mixing when the wind direction is parallel rather than perpendicular to the dispensers. Since under these conditions the dispenser becomes a tall thin body, air will primarily move around the dispenser rather than up and over it. In this case, the dominant wake will be that caused by the vehicle itself. For a relatively streamlined vehicle, Dr. Leonard suggests that the effective height will be about 1 meter. The resulting wake is presented as curve (1) on Figure 9. The wake will intersect that from the canopy at about 14 Hb downwind. Applying equation 12 to estimate mixing into the canopy plume yields the following:

Distance	Z(x) m	Z(x$_s$) m	Z$_s$(x, xs) m
16 Hb	1.913	1.817	0.598
20 Hb	2.080	1.817	1.012
24 Hb	2.224	1.817	1.282
28 Hb	2.351	1.817	1.492

	DATE: 03/97	FIGURE # 5
LORAX	Plotplan for a typical retail gasoline outlet	
	PROJECT # 95000316	

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C-14

0 Hb	2 Hb	4 Hb	6 Hb	8 Hb	10 Hb	12 Hb	14 Hb	16 Hb	18 Hb	20 Hb	22 Hb	24 Hb	26 Hb
0 m	1 m	2 m	3 m	4 m	5 m	6 m	7 m	8 m	9 m	10 m	11 m	12 m	13 m

DATE:	FIGURE #
03/97	6

LORAX

Wake envelopes developed by a dispenser and canopy at a typical retail gasoline outlet

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95000316

Impact of downwind dispensers on mixing

LORAX

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FIGURE # 7

PROJECT # 95000316

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Plotplan for a typical retail gasoline outlet

	DATE: 03/97	FIGURE # 5
LORAX	PROJECT # 95000316	

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Wake envelopes developed by a dispenser and canopy at a typical retail gasoline outlet

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FIGURE # 6

PROJECT # 95000316

LORAX

Impact of downwind dispensers on mixing

LORAX
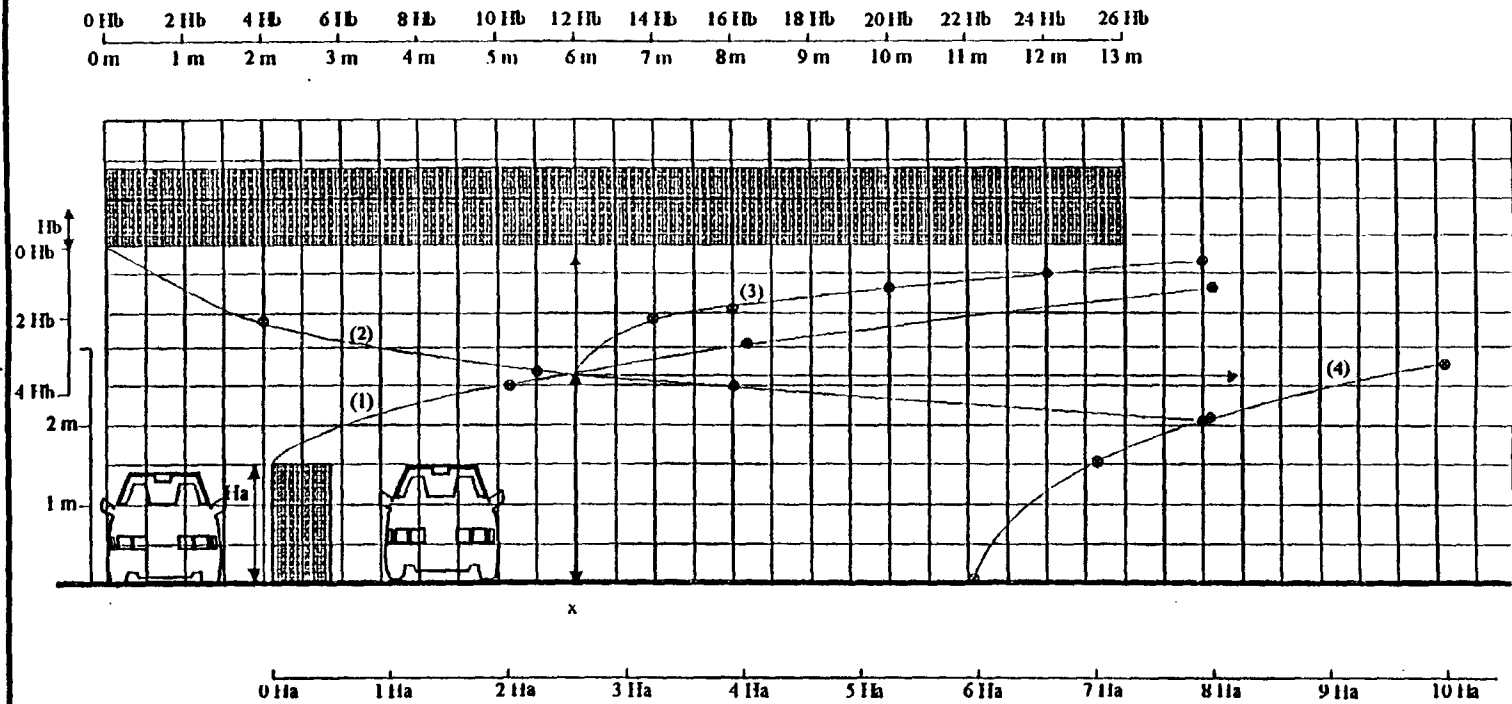
DATE: 03/97

FIGURE # 7

PROJECT # 95000316

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0 Hb	2 Hb	4 Hb	6 Hb	8 Hb	10 Hb	12 Hb	14 Hb	16 Hb	18 Hb	20 Hb	22 Hb	24 Hb	26 Hb
0 m	1 m	2 m	3 m	4 m	5 m	6 m	7 m	8 m	9 m	10 m	11 m	12 m	13 m

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Hb
0 Hb
2 Hb
4 Hb
2 m
Hc
1 m
Ha

x
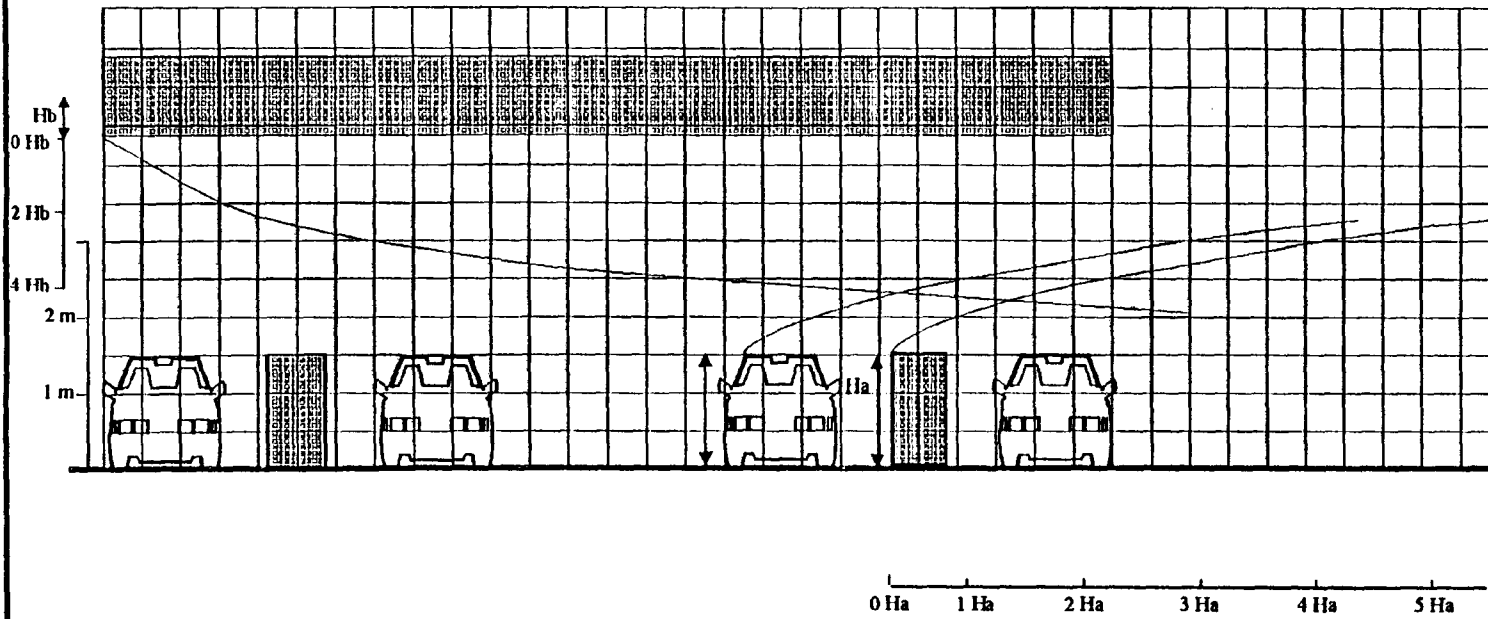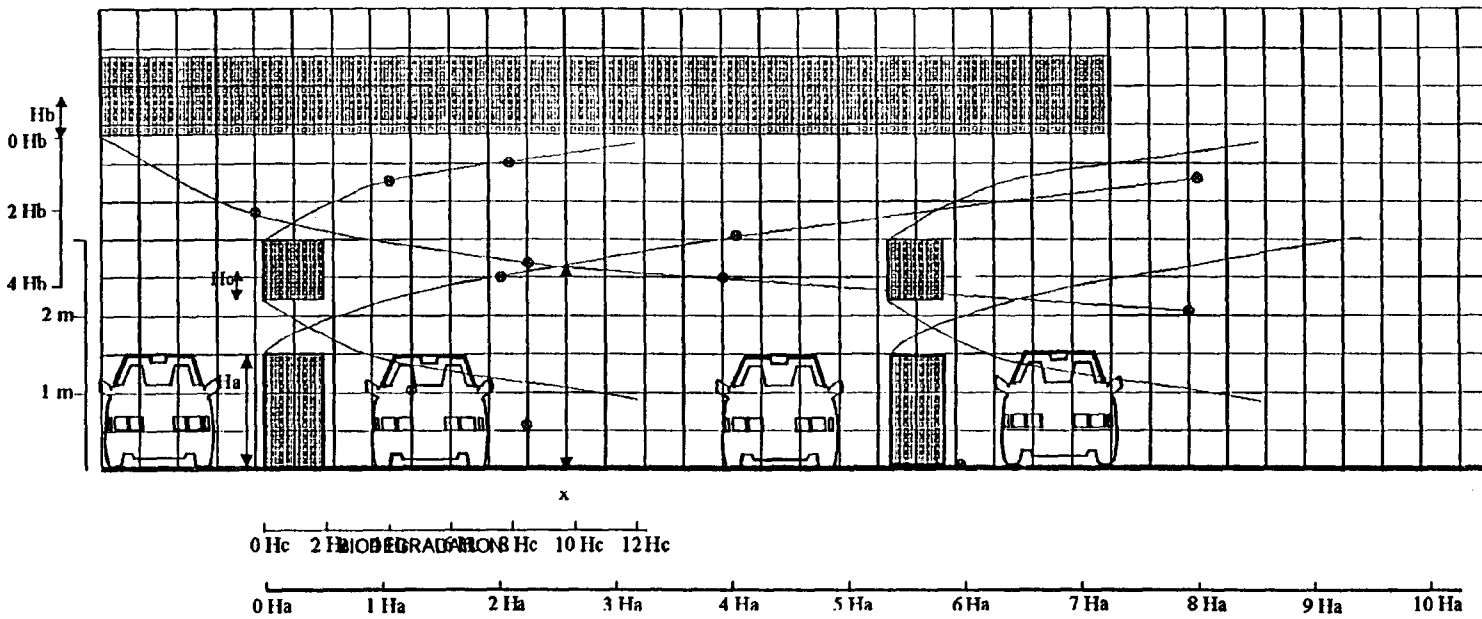
0 Hc 2 Hc 4 Hc 6 Hc 8 Hc 10 Hc 12 Hc
BIODEGRADATION

0 Ha 1 Ha 2 Ha 3 Ha 4 Ha 5 Ha 6 Ha 7 Ha 8 Ha 9 Ha 10 Ha

LORAX

Impact of spanners on mixing

DATE: 03/97	FIGURE # 8
PROJECT # 95000316	

Plotplan for a typical retail gasoline outlet

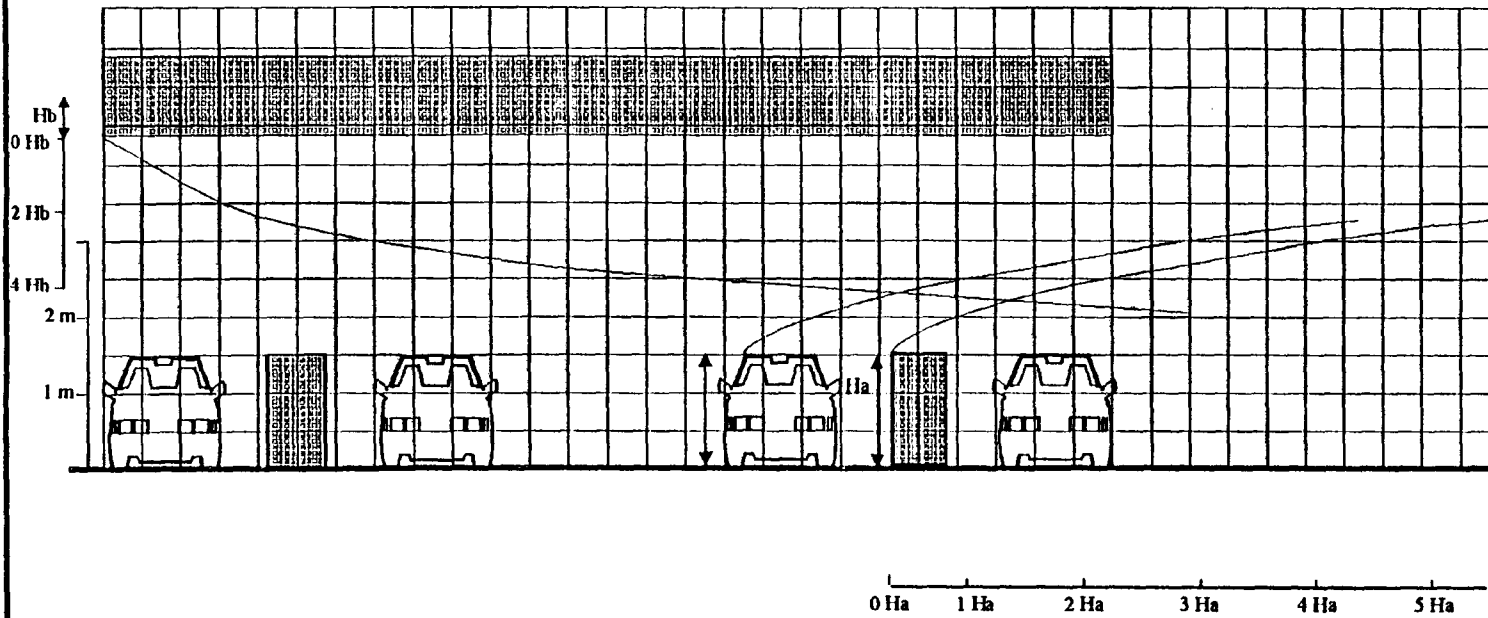|	DATE: 03/97	FIGURE # 5
LORAX	PROJECT #	95000316

C-13

0 Hb   2 Hb   4 Hb   6 Hb   8 Hb   10 Hb   12 Hb   14 Hb   16 Hb   18 Hb   20 Hb   22 Hb   24 Hb   26 Hb

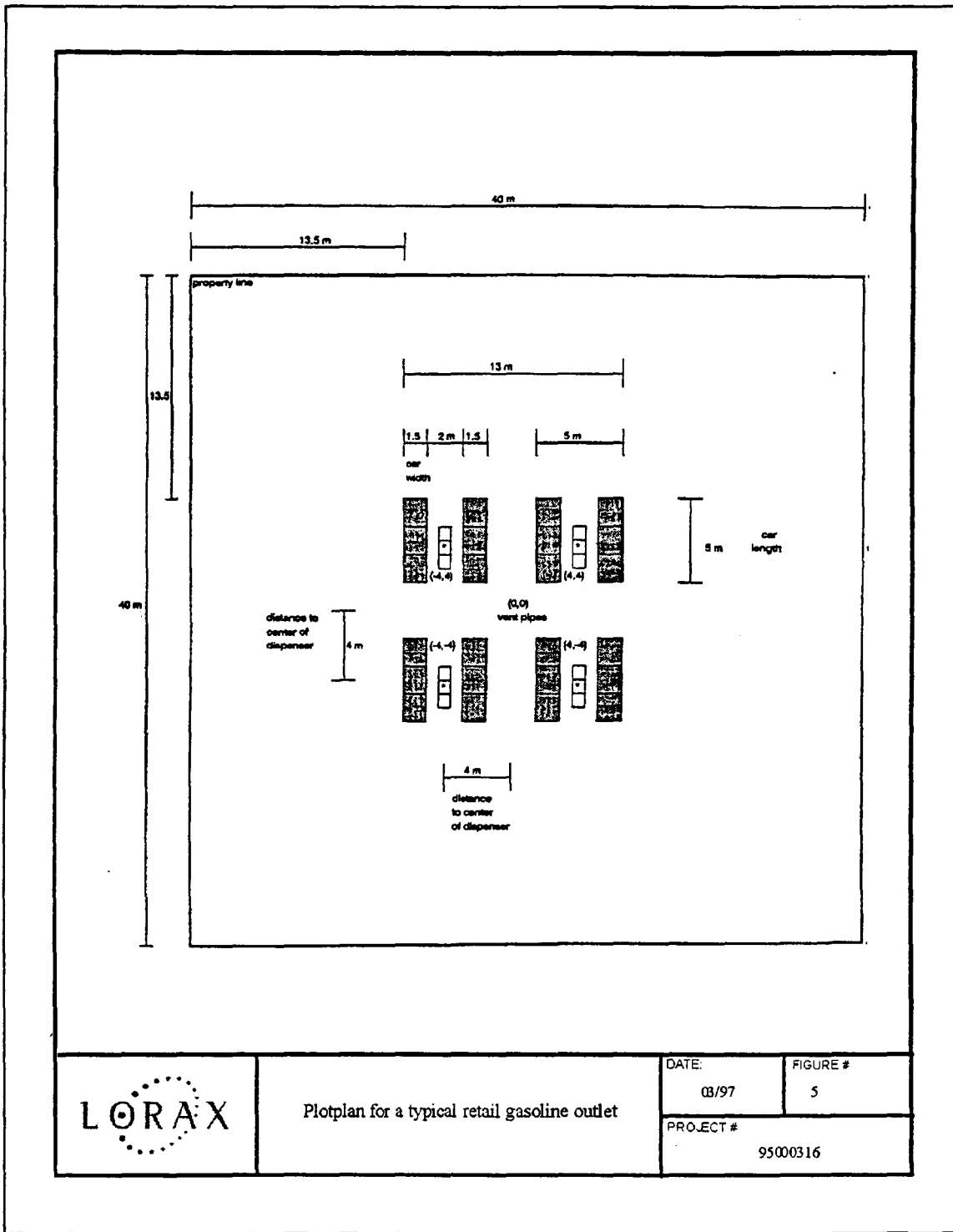0 m   1 m   2 m   3 m   4 m   5 m   6 m   7 m   8 m   9 m   10 m   11 m   12 m   13 m
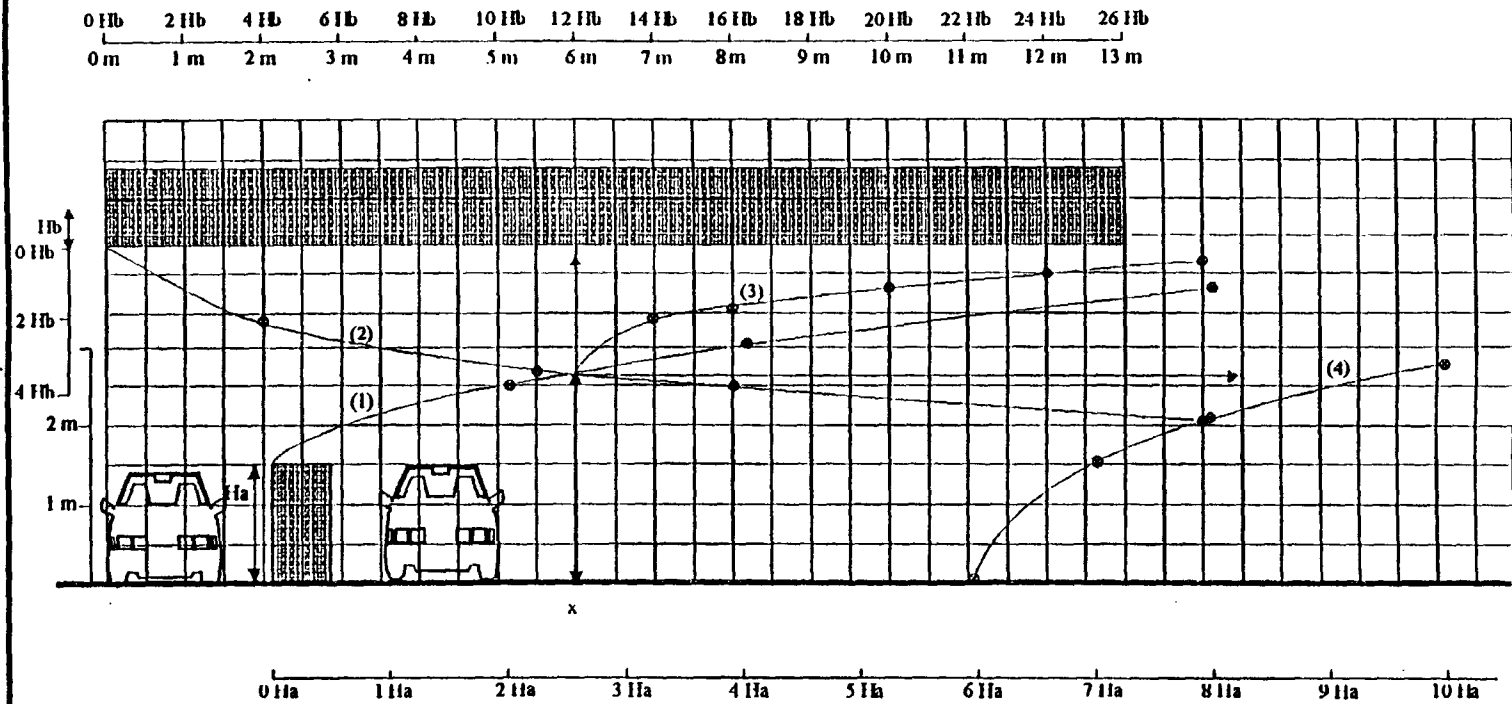
Hb
0 Hb
2 Hb
4 Hb
2 m
1 m

(1)
(2)
(3)
(4)
Ha
x

0 Ha   1 Ha   2 Ha   3 Ha   4 Ha   5 Ha   6 Ha   7 Ha   8 Ha   9 Ha   10 Ha

C-14

LORAX

Wake envelopes developed by a dispenser and canopy at a typical retail gasoline outlet

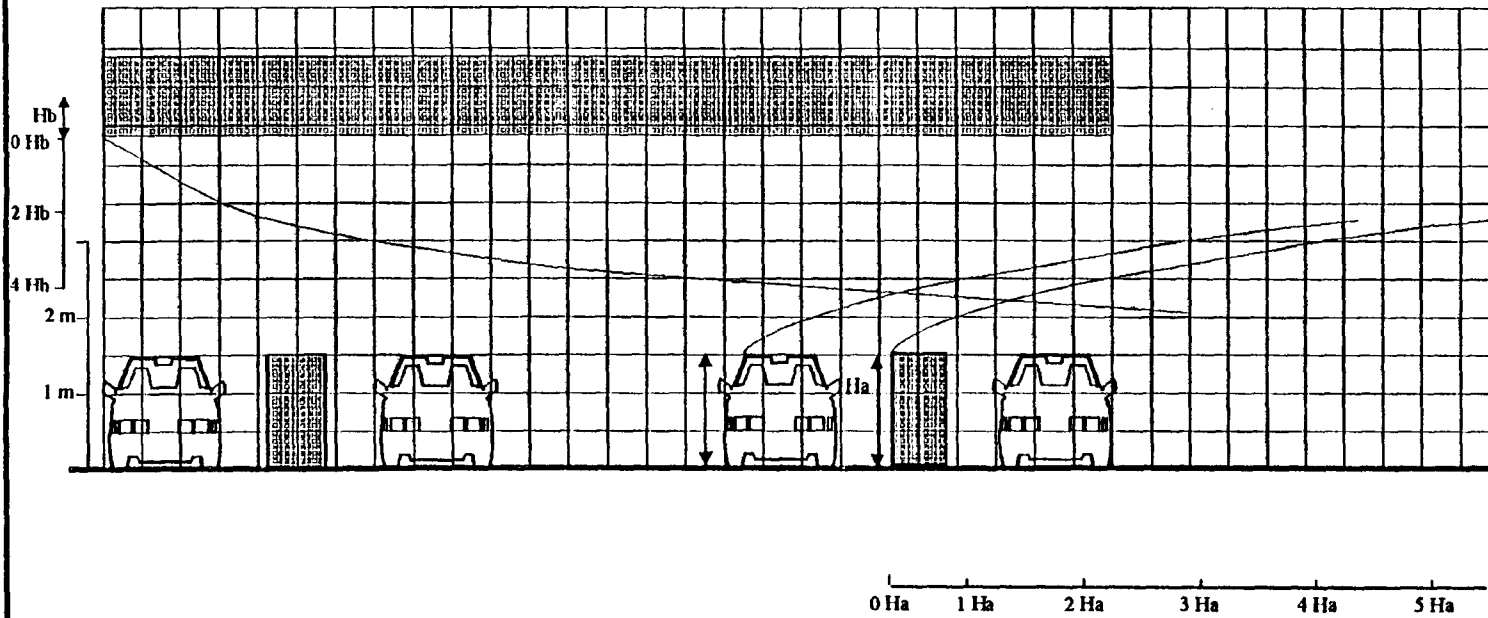| DATE: 03/97	FIGURE # 6
PROJECT # 95000316	

0 Hb   2 Hb   4 Hb   6 Hb   8 Hb   10 Hb   12 Hb   14 Hb   16 Hb   18 Hb   20 Hb   22 Hb   24 Hb   26 Hb

0 m   1 m   2 m   3 m   4 m   5 m   6 m   7 m   8 m   9 m   10 m   11 m   12 m   13 m

Hb
0 Hb

2 Hb

4 Hb

2 m

1 m

Ha

0 Ha   1 Ha   2 Ha   3 Ha   4 Ha   5 Ha

LORAX	Impact of downwind dispensers on mixing	DATE: 03/97	FIGURE # 7
		PROJECT # 95000316	

Impact of spanners on mixing

LORAX

| DATE: 03/97 | FIGURE # 8 |
| PROJECT # 95000316 | |

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C-18

BIODEGRADATION

0 Hb   2 Hb   4 Hb   6 Hb   8 Hb   10 Hb   12 Hb   14 Hb   16 Hb   18 Hb   20 Hb   22 Hb   24 Hb   26 Hb

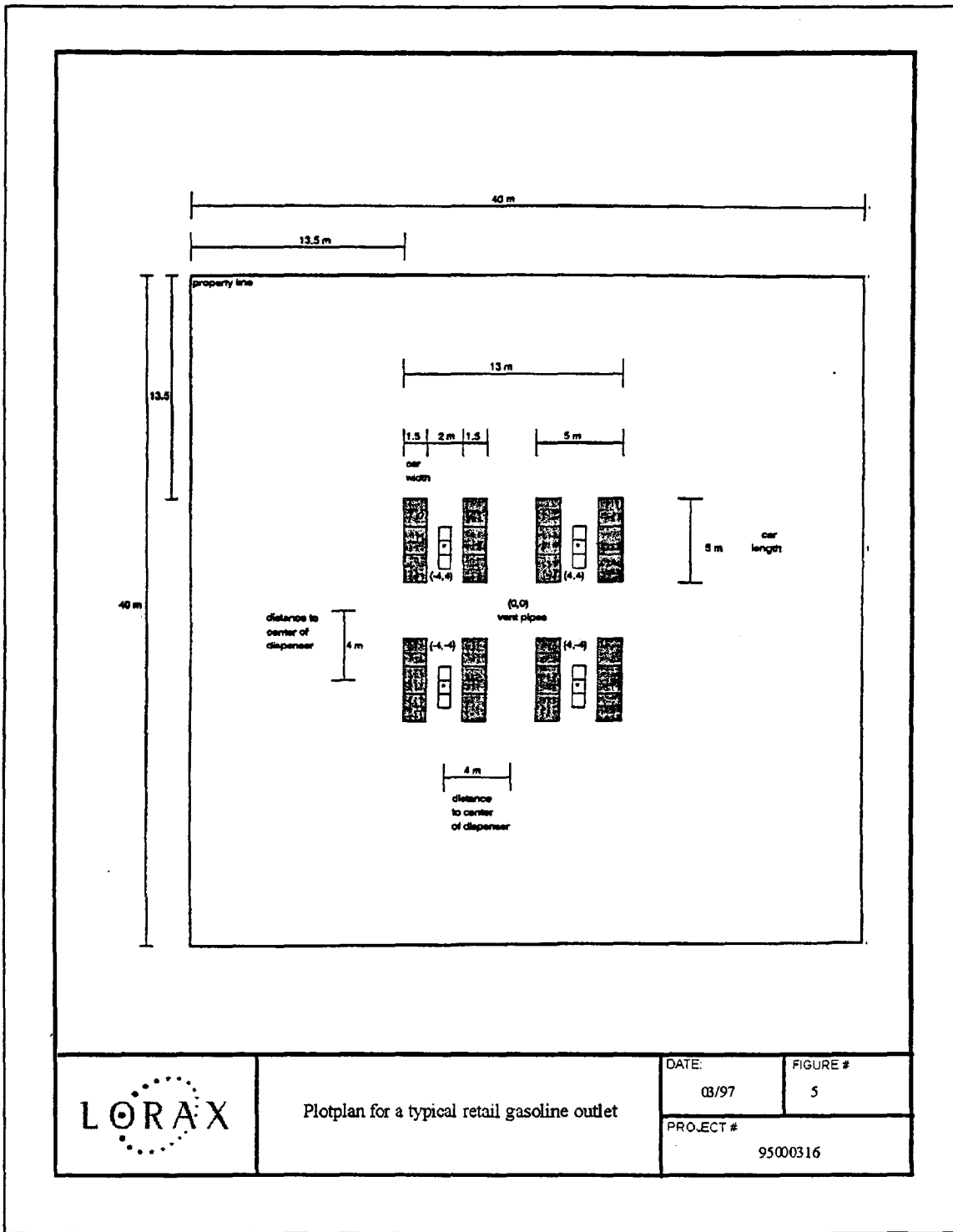0 m   1 m   2 m   3m   4 m   5 m   6 m   7 m   8 m   9 m   10m   11 m   12m   13 m
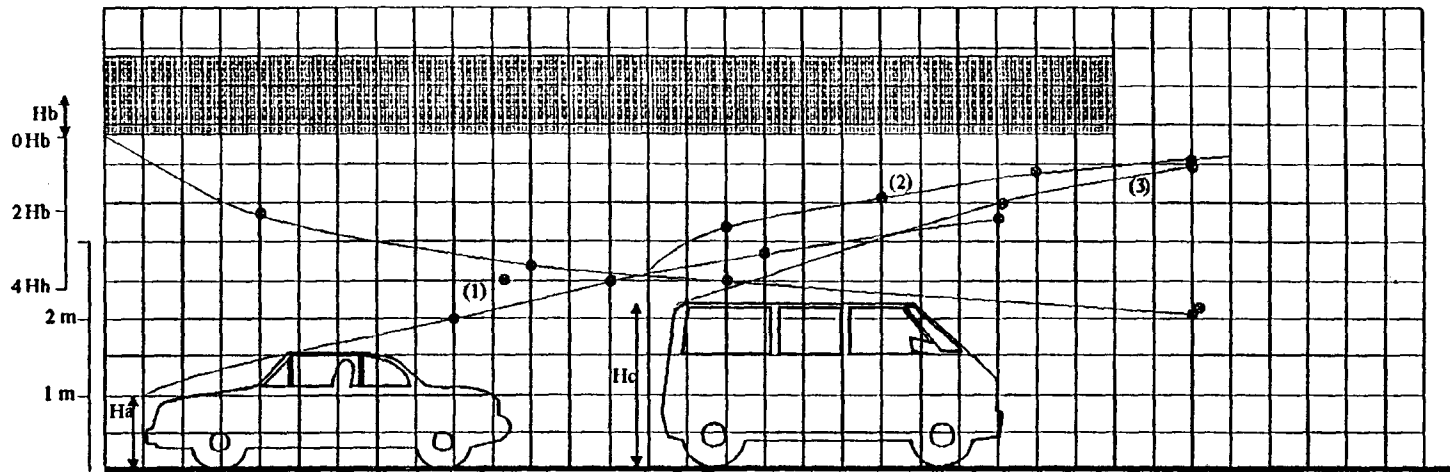
0 Ha   1 Ha   2 Ha   3 Ha   4 Ha   5 Ha   6 Ha   7 Ha   8 Ha   9 Ha   10 Ha   11 Ha   12 Ha   13 Ha

Impact of vehicles on mixing

LORAX

DATE: 03/97

FIGURE # 9

PROJECT # 95000316

Mixing of the vehicle wake into the canopy wake is represented by curve (2). The presence of a larger vehicle such as a sport utility vehicle or a van will result in a more prominent wake. The wake for a body with an effective height of two meters is shown as curve (3) on Figure 9.

EFFECT OF NEARBY BUILDINGS

The work done by Dr. Leonard has demonstrated that there is a great deal more mixing brought about by the presence of the dispenser and vehicles than originally considered in the draft guidelines. The presence of a dispenser, canopy, and vehicles will result in mixing up to a height of from three to five meters depending on the location of the release, the wind direction, and the type of vehicles present. The presence of additional components such as spanners will further enhance the mixing process. The same can be said for nearby buildings such as a service bay or mini-mart. In order to demonstrate this effect, refueling and spillage emissions from a station equipped with Phase II controls (scenario 7) were modeled using point sources located near a five meter high building. Results are compared to those obtained with the GASRAC configuration and the WSPA-recommended volume sources in Figure 10. Use of a large volume source as recommended by WSPA provides a good representation of dispersion that will result in the presence of nearby buildings.

VOLUME SOURCES

One of the concerns raised by the GASRAC was whether the use of a large volume source such as that advocated by WSPA would accurately represent dispersion from a gasoline station as described by Dr. Leonard. They requested that Dr. Leonard prepare an estimate of the vertical concentration profile that would result from this source as a result of the mixing brought about by the wake effects previously described. This profile could then be compared to the profile predicted by the model.

Unfortunately, Dr. Leonard found that there were very little experimental data available particularly for a situation as complex as that of a gasoline station. The use of a theoretical analysis would result in so much uncertainty as to be pointless. Some limited data on concentration profiles developed by Huber and Snyder are presented in Figure 11.

Based on this information, the vertical concentration profile resulting from a ground level effluent release on the leeward side of a bluff body is quite flat with significant concentrations appearing at elevations up to about 2.5 H. The lateral profile is also quite flat downwind of the structure.
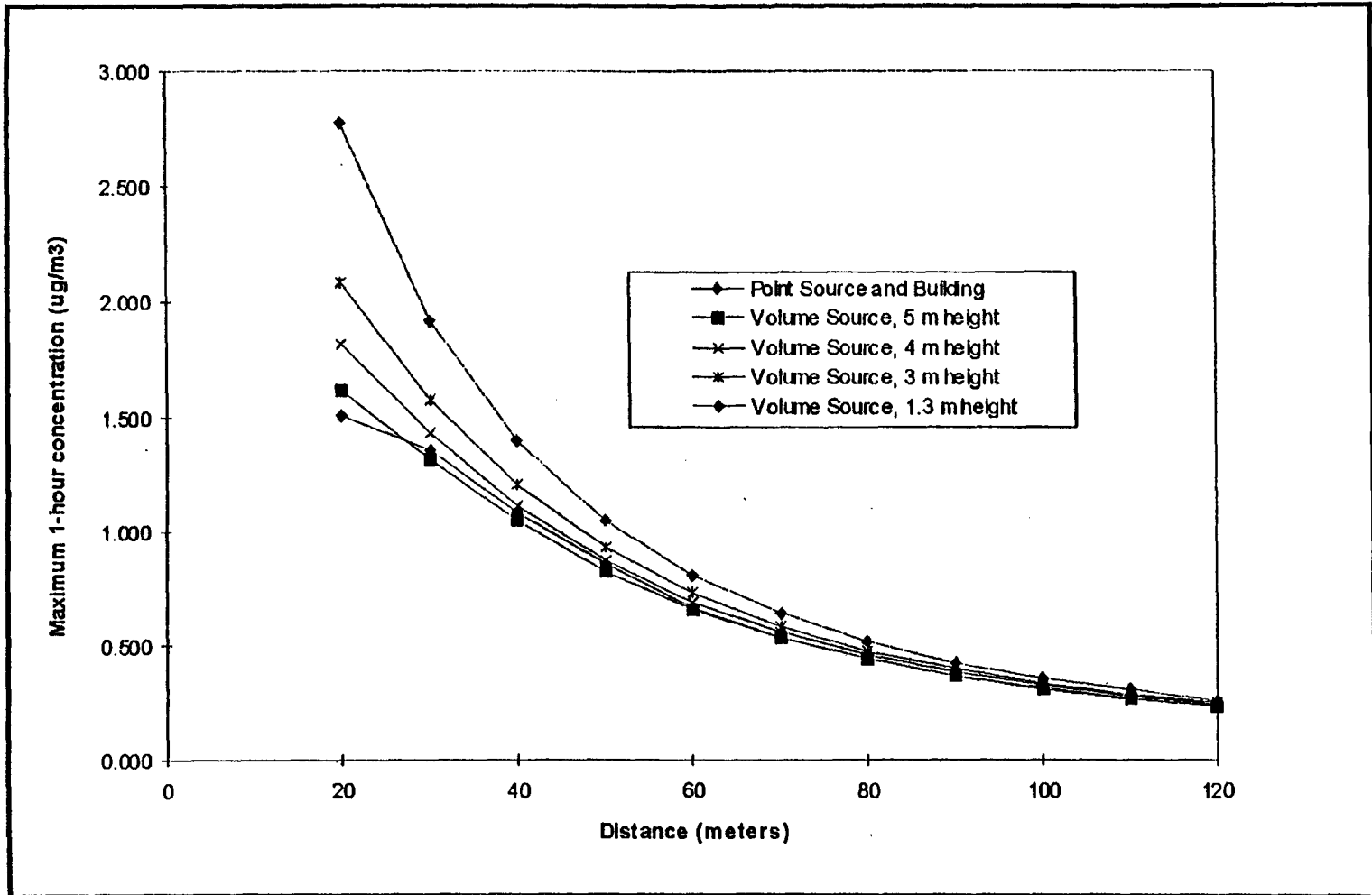
Impact of a nearby building on dispersion
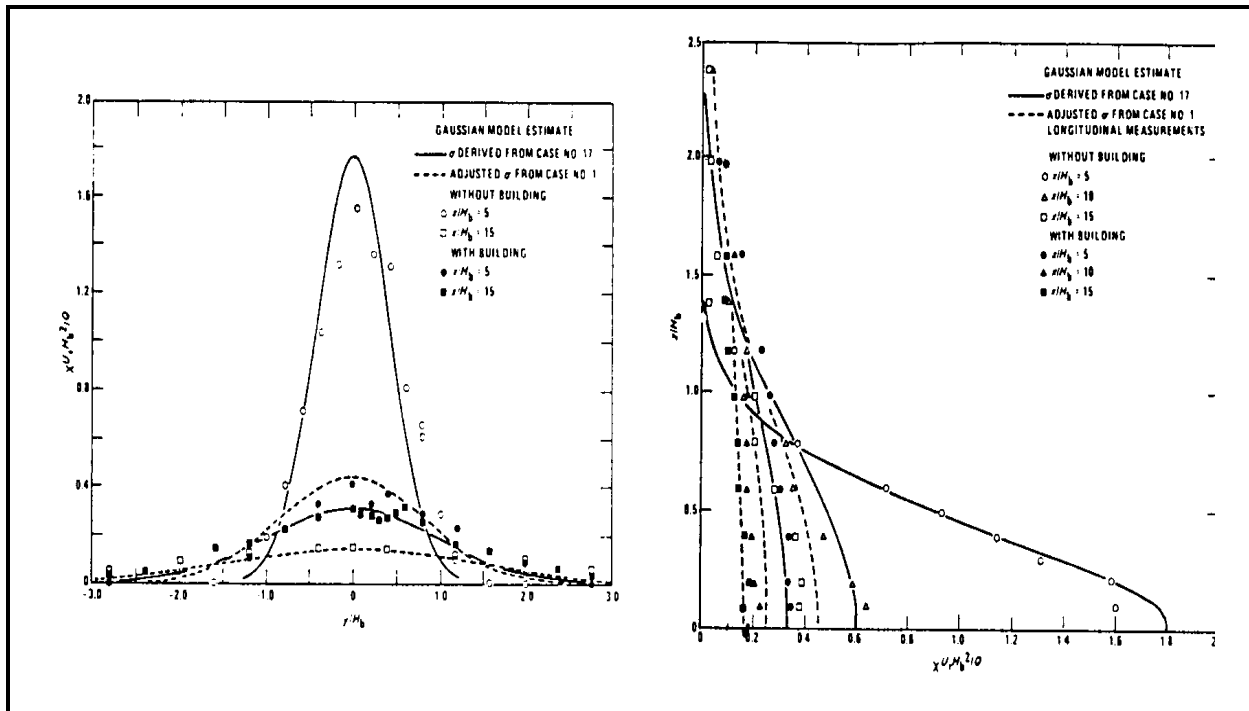
Figure 11: Lateral and vertical concentration profiles with and without the presence of a building (from Huber and Snyder, [4])

In order to further develop this analysis, two model runs were carried out based on the typical gas station layout developed by GASRAC. One run was carried out using the GASRAC volume source dimensions, the other using the WSPA volume source. Concentrations were estimated at a distance of 8.5 meters from the center of the facility (0.5 meters beyond the edge of the canopy and about 6H from the upwind release point), and at elevations ranging from 0 to 15 meters. Results are compared in Figure 12. It appears that neither approach results in an accurate prediction of the expected vertical or lateral concentration profiles. In the case of the GASRAC volume source, the concentration profile is very pronounced with concentrations near the ground much higher than those at elevated receptors. Use of the larger volume source results in an improved profile but also results in the presence of emitted material at higher elevations than might be expected.

The problem is that the ISC model is not designed to mimic the type of complex behavior exhibited by this source. It is at best an estimate. One approach to resolving this issue is to simply apply the procedure suggested by the ISC manual, namely, to estimate the size of the volume source and divide by 2.15 to estimate σ_z. It appears that the height of the volume source (or well mixed area) could be between 3.5 and 5 meters for even the simplest configuration. The use of an average of these two might be appropriate for a screening assessment. The lateral extent of the various wakes under consideration has not been examined in great detail, however, given the size of the vehicles and the fact that the wake will expand laterally as well as vertically, the area of the canopy also appears to be a reasonable choice for use in estimating σ_y.

C-21
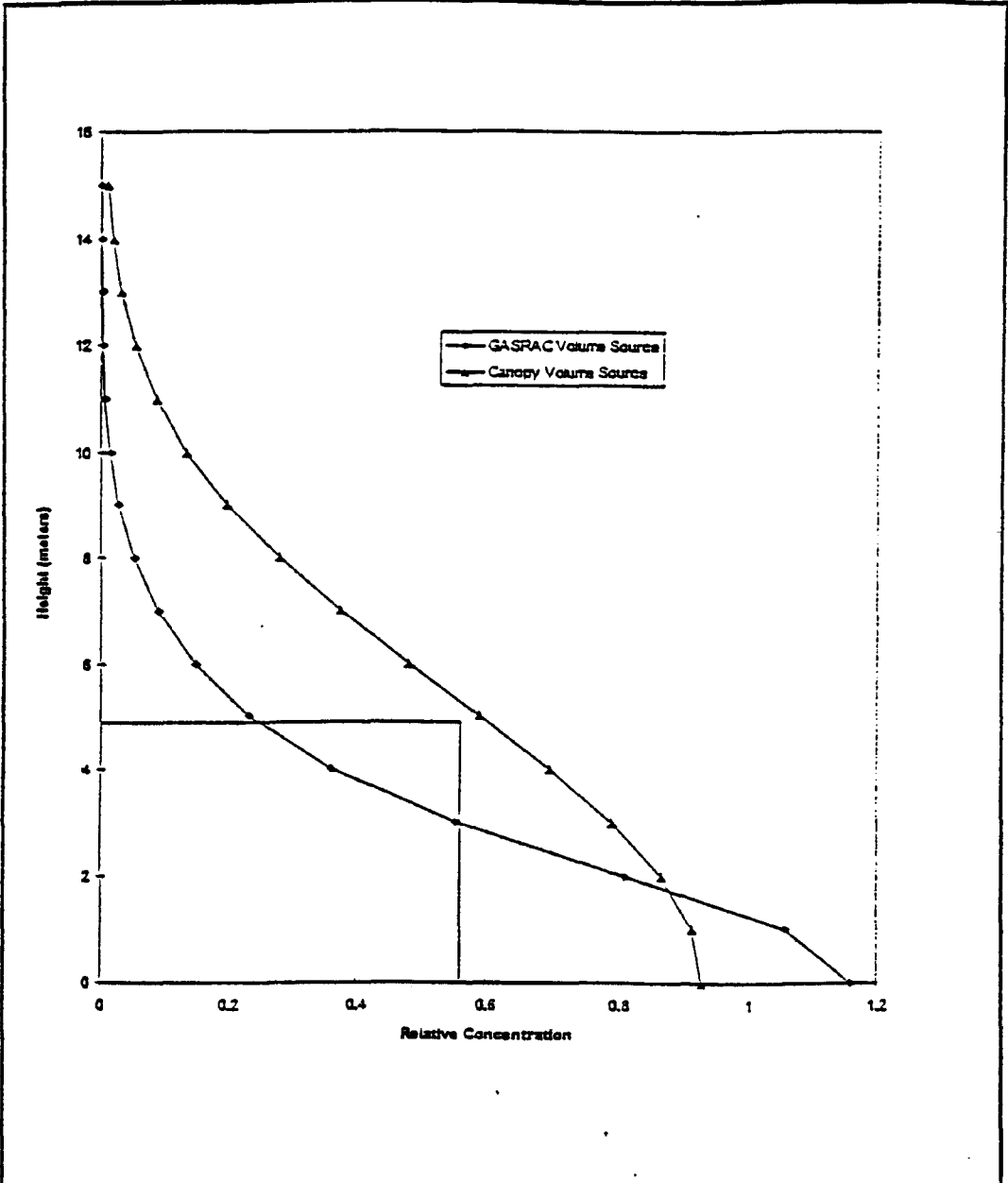
Effect of volume source configuration on the vertical concentration profile 0.5 meters beyond the edge of the canopy

LORAX

DATE:	FIGURE #
03/97	12
PROJECT #	
95000316	

C-22

5
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5. Hosker, R.P., Jr., *Methods for Estimating Wake Flow and Effluent Dispersion Near Simple Block-Like Building*, NOAA Technical Memorandum ERI, ARI-106, Air Resources Laboratories, Silver Spring, Maryland (May 1981).

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8. Tennekes, H. And J.L. Lumley, *A First Course in Turbulence*, The MIT Press, 1972, pp. 113-124.

9. Carmody, T., *"Establishment of the Wake Behind a Disk"*, J. Basic Engng. Trans. A.S.M.E. Vol. 86D, p. 869, 1964.

APPENDIX D

MODELING PARAMETERS

MODELING PARAMETERS

The parameters for modeling gasoline stations are described on the following pages.

A)   **Loading - Point Source**

Stack Height	=	12 Ft	=	3.66 meters
Stack Temperature	=	65°F	=	291 K
Stack Diameter	=	2"	=	0.0508 m

B)   **Breathing - Point Source**

Stack Height	=	12 Ft	=	3.66 m
Stack Temperature	=	60°F	=	289 K
Stack Diameter	=	2"	=	0.0508 m

C)   **Refueling - Volume Source**

Volume	=	4 m high x 13 m long x 13 m wide	
Height of Release	=	1 meter	
Lateral Dimension	=	13 meters / 4.3	= 3.02
Vertical Dimension	=	4 meters / 2.15	= 1.86

D)   **Spillage - Volume Source**

Volume	=	4 m high x 13 m long x 13 m wide	
Height of Release	=	0 meter	
Lateral Dimension	=	13 meters / 4.3	= 3.02
Vertical Dimension	=	4 meters / 2.15	= 1.86

GASOLINE VAPOR DENSITY

The molecular weight of liquid gasoline is nominally 126 lbs/lbmole (Lindbeburg, Michael R., Mechanical Engineering Reference Manual, Eighth Edition, 1990, Professional Publications). But, the molecular weight of the vapors in the storage tank headspace is approximately 65 lbs/lbmole. This is determined as follows:

CARB's has measured the vapors in the headspace of underground storage tanks using a composite carbon number of 4.5 for gasoline vapors for current gasoline. To determine the molecular weight of the vapor mixture, it was assumed that the gasoline fraction is an alkane similar to butane or pentane. Alkanes have a formula of $C_n + H_{2n+2}$. If $n = 4.5$, then resultant molecular weight = $[(12)(4.5)] + [(2)(4.5)+2] = 65$ lbs/lbmole.

> MW = 65 lbs/lbmole gasoline
> MW = 29 lbs/lbmole air

According to CARB, the average yearly temperature of the gasoline vapors in the headspace varies between 58-62 degrees F. An average temperature of 60 degrees F (519 R) was used.

> T = 60 F, (519 R)

The density of the gasoline/air mixture in the vapor space above the liquid gasoline in an underground storage tank must account for the air and gasoline fraction in the headspace. According to API Bulletin 25-13, at the average annual RVP of 7.8, at 65 F, the headspace consists of 29.1 volume % gasoline vapors/70.9 volume % air. This is rounded to 30% gasoline/70% air.

> Volume % gasoline vapors = molar % = 30%
> Volume % air = molar % = 70%

The density of the mixture is calculated as follows:

$$\frac{M_{mix}}{V} = \frac{(n\% \text{ gasoline}) (MW \text{ gasoline}) + (n\% \text{ air}) (MW \text{ air})}{(\text{standard volume gas at STP})}$$

$$= \frac{(0.3) (65 \text{ lbs/lbmole gasoline}) + (0.7) (29 \text{ lbs/lbmole air})}{(379 \text{ ft}^3/\text{lbmole gasoline and air mixture})}$$

$$= 0.105 \text{ lbs/ft}^3 \text{ gasoline and air mixture}$$

STACK EXIT VELOCITIES

Stack exit velocities were determined for the four emissions sources at gasoline stations: Loading, Breathing, Refueling, and Spillage.

A.   LOADING EMISSIONS:

Scenario	Loading Emission Factors lb / 1000 gal
1	8.4
2	0.42
3A	0.42
3B	0.42
4	8.4
5A	0.42
5B	0.084
6A	0.42
6B	0.084

Annual Gasoline Throughput	= 1,000,000 gal/yr
Density of Liquid Gasoline	= 6 lbs / gal
Density of Gasoline/Air Vapor Mixture	= 0.105 lb / ft^3
Radius of Stack	= 1" = 0.0833 ft
Area of Stack	= Πr^2 = 0.0218 ft²

Example Calculation for Scenario 6A:

Average Emission Rate   = (emission factor) (1,000,000 gal/yr throughput)

$$= \frac{(\ 0.42\ lbs)}{(1000\ gal)} \frac{(1,000,000\ gal)}{(\qquad\qquad yr)} \frac{(\qquad yr)}{(8760\ hr)} \frac{(\qquad hr)}{(3600\ sec)}$$

$$= \frac{(0.0000133\ lbs)}{(\qquad\qquad sec)} \frac{(454\ grams)}{(\qquad lb)}$$

$$= 0.00605\ g/sec$$

Average Vent Stack Exit Velocity $\quad = \dfrac{\text{(mass emission rate)}}{\text{(area) (density of gas)}}$

$$= \frac{(0.0000133 \text{ lbs/sec})}{(0.0218 \text{ ft}^2) (0.105 \text{ lbs/ft}^3)}$$

$$= (0.0058 \text{ ft/sec}) (0.3048 \text{ m/ft})$$

$$= 0.00177 \text{ m/sec}$$

Thus, for each scenario the average annual velocity for a 1,000,000 gal/yr throughput gas station is:

Scenario	Velocity (m/sec)
1	0.035
2	0.00177
3A	0.00177
3B	0.00177
4	0.035
5A	0.00177
5B	0.00035
6A	0.00177
6B	0.00035

B. BREATHING EMISSIONS:

Scenario	Breathing Emission Factor lb / 1000 gal
1	2.1
2	2.1
3A	0.21
3B	0.053
4	0.84
5A	0.84
5B	0.21
6A	0.1
6B	0.025

Example Calculation for Scenario 6A:

Radius of Stack $= 1" = 0.0833$ ft

Area of Stack $= \Pi r^2 = 0.0218$ ft²

Density of Gasoline/Air Vapor Mixture $= 0.105$ lb / ft^3

Mass Emission Rate = (emission factor) (1,000,000 gal/yr throughput)

$$= \frac{(0.1 \text{ lbs})}{(1000 \text{ gal})} \frac{(1,000,000 \text{ gal})}{(\quad)} \frac{(\quad \text{yr})}{(\text{yr})} \frac{(\quad 1 \text{ hr})}{(8760 \text{ hr})} \frac{(\quad)}{(3600 \text{ sec})}$$

$= (0.00000317$ lbs/sec) (454 grams/lbs)

$= 0.00144$ g/s

Vent Stack Exit Velocity $= \dfrac{\text{(mass emission rate)}}{\text{(area) (density of gas)}}$

$$= \frac{(0.00000317 \text{ lbs / sec})}{(0.0218 \text{ ft}^2) \ (0.105 \text{ lb / ft}^3)}$$

$= (0.00138$ ft / sec) (0.3048 m / ft)

$= 0.000422$ m / sec

Thus, for each scenario the average annual velocity for a 1,000,000 gal/yr throughput gas station is:

Scenario	Velocity (m / sec)
1	0.00886
2	0.00886
3A	0.000886
3B	0.000224
4	0.00355
5A	0.00355
5B	0.000886
6A	0.000422
6B	0.000106

C.   REFUELING EMISSIONS:

Because refueling is being modeled as a volume source there are no stack velocities required.

D.   SPILLAGE EMISSIONS:

Because spillage is being modeled as a volume source there are no stack velocities required.

CALCULATING EMISSION RATES

The calculations below show how to calculate the emission rates from a 1,000,000 gal/year throughput station with underground storage tanks and phase 2 vapor recovery systems, 90% overall control efficiency (Scenario 6A).

A.   Loading Mass Emissions Rate:

$$= \frac{(0.42 \text{ lbs})}{(1000 \text{ gal})} \frac{(1{,}000{,}000 \text{ gal})}{(\qquad \text{yr})} \frac{(454 \text{ g})}{(\quad \text{lb})} \frac{(\quad 1 \text{ yr})}{(8760 \text{ hr})} \frac{(\quad 1 \text{ hr})}{(3600 \text{ sec})}$$

$$= (0.00605 \text{ g gasoline / sec}) \ (0.3\% \text{ benzene})$$

$$= 0.0000181 \text{ g benzene / sec}$$

B.   Breathing Mass Emissions Rate:

$$= \frac{(0.1 \text{ lbs})}{(1000 \text{ gal})} \frac{(1{,}000{,}000 \text{ gal})}{(\qquad \text{yr})} \frac{(454 \text{ g})}{(\quad \text{lb})} \frac{(\quad 1 \text{ yr})}{(8760 \text{ hr})} \frac{(\quad 1 \text{ hr})}{(3600 \text{ sec})}$$

$$= (0.00144 \text{ g gasoline / sec}) \ (0.3\% \text{ benzene})$$

$$= 0.00000432 \text{ g benzene / sec}$$

C.   Refueling Mass Emissions Rate:

$$= \frac{(0.74 \text{ lbs})}{(1000 \text{ gal})} \frac{(1{,}000{,}000 \text{ gal})}{(\qquad \text{yr})} \frac{(454 \text{ g})}{(\quad \text{lb})} \frac{(\quad 1 \text{ yr})}{(8760 \text{ hr})} \frac{(\quad 1 \text{ hr})}{(3600 \text{ sec})}$$

$$= (0.0107 \text{ g gasoline / sec}) \ (0.3\% \text{ benzene})$$

$$= 0.000032 \text{ g benzene / sec}$$

D.   Spillage Mass Emissions Rate:

$$= \frac{(0.42 \text{ lbs})}{(1000 \text{ gal})} \frac{(1{,}000{,}000 \text{ gal})}{(\qquad \text{yr})} \frac{(454 \text{ g})}{(\quad \text{lb})} \frac{(\quad 1 \text{ yr})}{(8760 \text{ hr})} \frac{(\quad 1 \text{ hr})}{(3600 \text{ sec})}$$

$$= (0.00605 \text{ g gasoline / sec}) \ (1.0\% \text{ benzene})$$

$$= 0.0000605 \text{ g benzene / sec}$$

The other scenarios were calculated using the same method as for Scenario6A. Table 1 lists the emission factors used in calculating the gasoline emission rates and benzene emission rates. Table 2 lists the gasoline emission rates and Table 3 lists the benzene emission rates.

Table 1: Emission Factors (lb/1000 gal)

Scenario	Loading	Breathing	Refueling	Spillage
1	8.4	2.1	8.4	0.61
2	0.42	2.1	8.4	0.61
3A	0.42	0.21	0.63	0.42
3B	0.42	0.053	0.63	0.42
4	8.4	0.84	8.4	0.61
5A	0.42	0.84	8.4	0.61
5B	0.084	0.21	8.4	0.61
6A	0.42	0.1	0.74	0.42
6B	0.084	0.025	0.74	0.42

Table 2: Gasoline Emission Rates (g/sec)

Annualized for a 1,000,000 gal/year station

Scenario	Loading	Breathing	Refueling	Spillage
1	0.121	0.0302	0.121	0.00878
2	0.00605	0.0302	0.121	0.00878
3A	0.00605	0.00302	0.0091	0.00605
3B	0.00605	0.000763	0.0091	0.00605
4	0.121	0.0121	0.121	0.00878
5A	0.00605	0.0121	0.121	0.00878
5B	0.00121	0.000302	0.121	0.00878
6A	0.00605	0.00144	0.0107	0.00605
6B	0.00121	0.00036	0.0107	0.00605

Table 3: Benzene Emission Rates (g/sec)

Annualized for a 1,000,000 gal/year station

Scenario	Loading	Breathing	Refueling	Spillage
1	0.000363	0.0000907	0.000363	0.0000878
2	0.0000181	0.0000907	0.000363	0.0000878
3A	0.0000181	0.0000091	0.0000273	0.0000605
3B	0.0000181	0.0000023	0.0000273	0.0000605
4	0.000363	0.0000363	0.000363	0.0000878
5A	0.0000181	0.0000363	0.000363	0.0000878
5B	0.0000036	0.000000907	0.000363	0.0000878
6A	0.0000181	0.00000432	0.0000321	0.0000605
6B	0.00000363	0.00000108	0.0000321	0.0000605

APPENDIX E

CANCER RISKS:
TABLES AND GRAPHS
BY SCENARIO

TABLE 1A
SCENARIOS 1, 2, 3A, 3B - **RURAL** DISPERSION COEFFICIENTS

Distance from station center (meters)	Scenarios							
	1		2		3A		3B	
	Conc. * (ug/m^3)	Risk per million	Conc. * (ug/m^3)	Risk per million	Conc. * (ug/m^3)	Risk per million	Conc. * (ug/m^3)	Risk per million
20	15.66	36.33	15.66	36.33	3.20	7.42	3.20	7.42
30	13.30	30.86	13.28	30.81	2.70	6.26	2.69	6.24
40	11.71	27.17	11.49	26.66	2.32	5.38	2.32	5.38
50	11.02	25.57	10.19	23.64	2.06	4.78	2.05	4.76
60	10.86	25.20	9.24	21.44	1.88	4.36	1.84	4.27
70	10.81	25.08	8.47	19.65	1.73	4.01	1.68	3.90
80	10.68	24.78	7.82	18.14	1.60	3.71	1.54	3.57
90	10.41	24.15	7.22	16.75	1.49	3.46	1.42	3.29
100	10.03	23.27	6.68	15.50	1.38	3.20	1.31	3.04

TABLE 1B
SCENARIOS 4, 5A, 5B, 6A, 6B - **RURAL** DISPERSION COEFFICIENTS

Distance from station center (meters)	Scenarios									
	4		5A		5B		6A		6B	
	Conc. * (ug/m^3)	Risk per 10e6	Conc. * (ug/m^3)	Risk per 10e6	Conc. * (ug/m^3)	Risk per 10e6	Conc. * (ug/m^3)	Risk per 10e6	Conc. * (ug/m^3)	Risk per 10e6
20	15.66	36.33	15.66	36.33	15.66	36.33	3.37	7.82	3.37	7.82
30	13.29	30.83	13.28	30.81	13.28	30.81	2.84	6.59	2.84	6.59
40	11.68	27.10	11.45	26.56	11.42	26.49	2.44	5.66	2.43	5.64
50	10.89	25.26	10.06	23.34	9.94	23.06	2.15	4.99	2.11	4.90
60	10.61	24.62	8.98	20.83	8.75	20.30	1.95	4.52	1.86	4.32
70	10.45	24.24	8.11	18.81	7.76	18.00	1.78	4.13	1.66	3.85
80	10.23	23.73	7.36	17.07	6.95	16.12	1.64	3.80	1.49	3.46
90	9.91	22.99	6.71	15.56	6.25	14.50	1.51	3.50	1.34	3.11
100	9.50	22.04	6.15	14.27	5.66	13.13	1.39	3.22	1.21	2.81

* 1 hour maximum benzene concentration

TABLE 2A
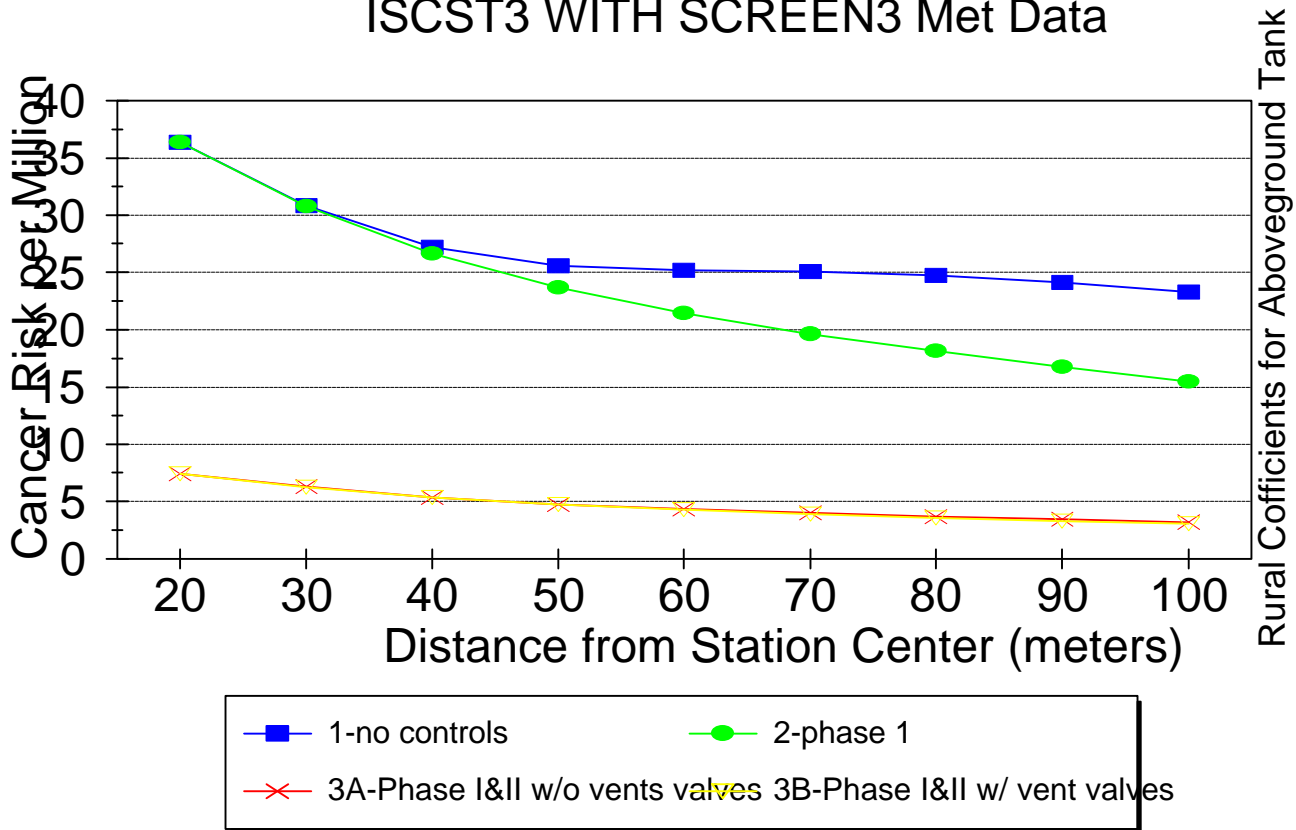SCENARIOS 1, 2, 3A, 3B - **URBAN** DISPERSION COEFFICIENTS

Distance from station center (meters)	Scenarios							
	1		2		3A		3B	
	Conc. * (ug/m^3)	Risk per million	Conc. * (ug/m^3)	Risk per million	Conc. * (ug/m^3)	Risk per million	Conc. * (ug/m^3)	Risk per million
20	11.86	27.52	8.61	19.97	1.74	4.04	1.70	3.94
30	11.04	25.61	6.83	15.85	1.40	3.25	1.32	3.06
40	9.34	21.67	5.30	12.30	1.10	2.55	1.02	2.37
50	7.45	17.28	4.12	9.56	0.85	1.97	0.79	1.83
60	5.93	13.76	3.27	7.59	0.68	1.58	0.62	1.43
70	4.78	11.09	2.64	6.12	0.55	1.28	0.50	1.16
80	3.92	9.09	2.18	5.06	0.45	1.04	0.41	0.95
90	3.27	7.59	1.82	4.22	0.38	0.88	0.35	0.81
100	2.76	6.40	1.55	3.60	0.32	0.74	0.29	0.67

TABLE 2B
SCENARIOS 4, 5A, 5B, 6A, 6B - **URBAN** DISPERSION COEFFICIENTS

Distance from station center (meters)	Scenarios									
	4		5A		5B		6A		6B	
	Conc. * (ug/m^3)	Risk per 10e6	Conc. * (ug/m^3)	Risk per 10e6	Conc. * (ug/m^3)	Risk per 10e6	Conc. * (ug/m^3)	Risk per 10e6	Conc. * (ug/m^3)	Risk per 10e6
20	10.94	25.38	8.23	19.09	7.92	18.37	1.79	4.15	1.68	3.90
30	10.30	23.90	6.08	14.11	5.47	12.69	1.40	3.25	1.19	2.76
40	8.63	20.02	4.59	10.65	4.00	9.28	1.08	2.51	0.87	2.02
50	6.87	15.94	3.54	8.21	3.06	7.10	0.84	1.95	0.67	1.55
60	5.46	12.67	2.80	6.50	2.41	5.59	0.66	1.53	0.53	1.23
70	4.41	10.23	2.26	5.24	1.95	4.52	0.54	1.25	0.43	1.00
80	3.61	8.38	1.87	4.34	1.62	3.76	0.44	1.02	0.35	0.81
90	3.01	6.98	1.57	3.64	1.36	3.16	0.37	0.86	0.30	0.70
100	2.55	5.92	1.33	3.09	1.16	2.69	0.32	0.74	0.25	0.58

* 1 hour maximum benzene concentration

Cancer Risk - 1,000,000 gal/yr thruput
ISCST3 WITH SCREEN3 Met Data

Cancer Risk per Million

Rural Cofficients for Aboveground Tank

Distance from Station Center (meters)

- ■ 1-no controls
- ● 2-phase 1
- ✕ 3A-Phase I&II w/o vents valves
- ✕ 3B-Phase I&II w/ vent valves

Cancer Risk - 1,000,000 gal/yr thruput
ISCST3 With SCREEN3 Met Data

Y-axis (left): Cancer Risk per million

X-axis: Distance from Station Center (meters)

Y-axis (right): Rural Cofficients for Underground Tank

Legend:
- 4-no controls
- 5A-Phase I
- 5B-Phase I with vent valves
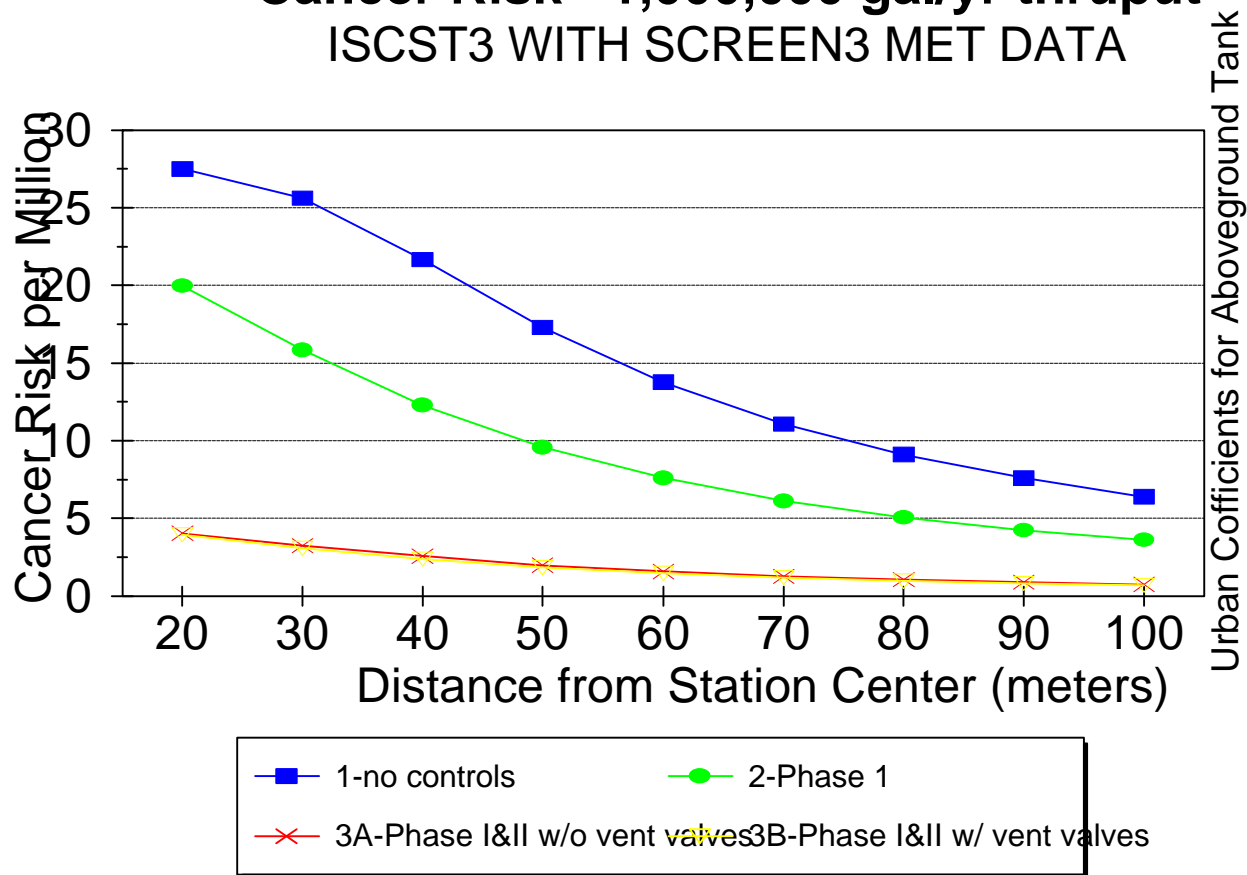- 6A-Phase I&II w/o vent valves
- 6B-Phase I&II w/ vent valves

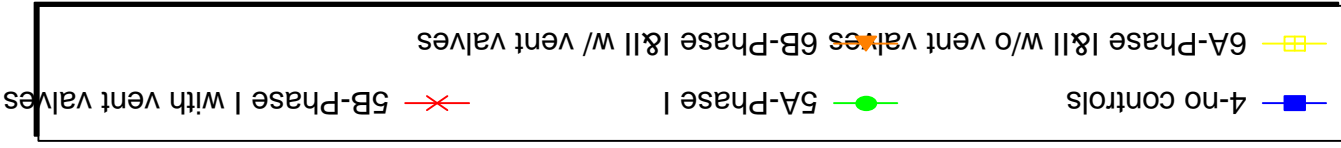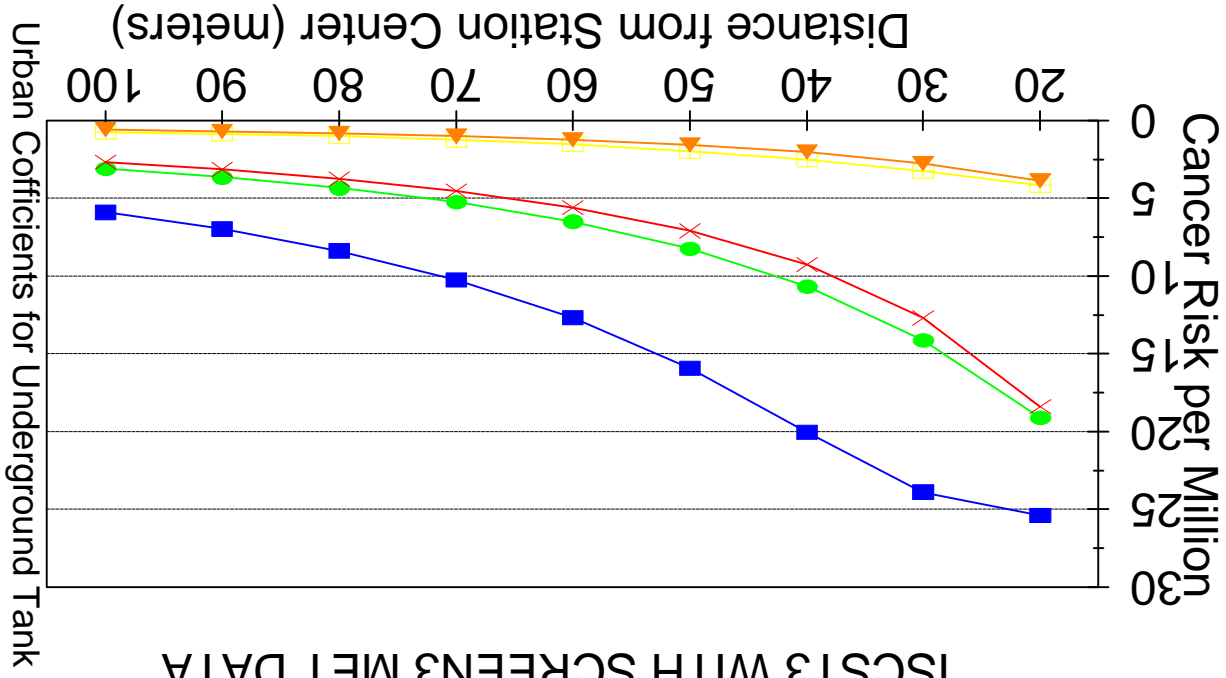**Cancer Risk - 1,000,000 gal/yr thruput**
ISCST3 WITH SCREEN3 MET DATA

Cancer Risk - 1,000,000 gal/yr thruput
ISCST3 WITH SCREEN3 MET DATA

Distance from Station Center (meters)

Urban Cofficients for Underground Tank

Cancer Risk per Million

Legend:
- 4-no controls
- 5A-Phase I
- 5B-Phase I with vent valves
- 6A-Phase I&II w/o vent valves
- 6B-Phase I&II w/ vent valves

X-axis (Distance from Station Center): 20, 30, 40, 50, 60, 70, 80, 90, 100

Y-axis (Cancer Risk per Million): 0, 5, 10, 15, 20, 25, 30

Influences on the Shapes of the Graphs

An explanation regarding the shape and magnitude of some of the risk curves may be needed.

Risk Graphs Using Rural Dispersion Coefficients

1. Why are the risk curves for **scenarios 1 and 2** equal out to 50 meters and then begin to diverge? The risks are equal out to 50 meters because the total risk is more influenced by the refueling and spillage emissions modeled as volume sources, rather than the loading and breathing emissions modeled as point sources. The influence of reduced loading emissions will not appear until the point source plume touches the ground at 50 meters.

2. Why are the risk curves for **scenarios 3A and 3B** nearly equal with only a slight divergence around 100 meters? The application of vent valves does not reduce the total risk significantly compared to the risk from the volume sources (spillage and refueling).

3. Why are the risk curves for **scenarios 4, 5A and 5B** equal out to 50 meters and then begin to diverge? See question #1.

Risk Graphs Using Urban Dispersion Coefficients

4. Why does the risk curve for **scenario 1** have a bump at the 30 meters point? With greater mixing due to urban dispersion coefficients, the vent pipe plume touches the ground at 30 meters and begins to significantly contribute to the overall risk.

5. Why is the risk curve for **scenario 2** much lower than **scenario 1** for urban coefficients when the risk curves are nearly equal with rural coefficients? Greater mixing occurs using urban coefficients than with rural coefficients. Using urban dispersion coefficients, the plume from the point source emissions are well mixed, impacting the ground, and contributing significantly to the total risk at 20 meters and beyond. By using phase I controls, the total risk is significantly reduced, because the emissions are significantly reduced, and the vent pipe risks significantly contributing to the total risk at 20 meters and beyond.

6. Why are the risk curves for **scenarios 5A and 5B**, and **scenarios 6A and 6B** nearly equal? Scenarios 5A and 5B, as well as scenarios 6A and 6B, are nearly equal because the total risks are driven more by the volume source (refueling and spillage) risks than the point source (loading and breathing) risks.

APPENDIX F

EXAMPLE ISCST3 INPUT FILE

Example ISCST3 Input File

```
CO STARTING
CO TITLEONE GASOLINE DISPENSING (GAS6BM-I) - SCENARIO 6A WITH 4MX13MX13M, 2 POINT SOURCES & 2 VOLUME SOURCES
CO MODELOPT CONC    RURAL      NOSTD    NOBID
CO AVERTIME          1
CO POLLUTID OTHER
CO DCAYCOEF     .000000
CO RUNORNOT RUN
CO ERRORFIL ERRORS.OUT
CO FINISHED

SO STARTING

** SOURCE LOCATION CARDS:
**         SRCID SRCTYP     XS         YS         ZS

SO LOCATION    1 POINT    .0000      .0000      .0000
               2 POINT    .0000      .0000      .0000
               3 VOLUME   .0000      .0000      .0000
               4 VOLUME   .0000      .0000      .0000

** SOURCE PARAMETER CARDS:
** POINT:   SRCID     QS      HS      TS      VS      DS
** VOLUME:  SRCID     QS      HS    SYINIT  SZINIT
** AREA:    SRCID     QS      HS    XINIT

SO SRCPARAM    1  0.0000181   3.66    291.0   .001773   0.051
               2  0.0000043   3.66    289.0   .000422   0.051
               3  0.0000321   1.00     3.02   1.86
               4  0.0000605   0.00     3.02   1.86

SO EMISUNIT    .100000E+07 (GRAMS/SEC)         (MICROGRAMS/CUBIC-METER)
SO SRCGROUP ALL
SO FINISHED

RE STARTING
RE GRIDPOLR POL STA
RE GRIDPOLR POL ORIG    0.0      0.0
RE GRIDPOLR POL DIST   10.0     20.0     30.0     40.0     50.0     60.0
RE GRIDPOLR POL DIST   70.0     80.0     90.0    100.0    110.0    120.0
RE GRIDPOLR POL GDIR    36      10.0     10.0
RE GRIDPOLR POL END
RE FINISHED

ME STARTING
ME INPUTFIL SCRNMET.ASC
ME ANEMHGHT 10.000 METERS
ME SURFDATA 99999  1999 SCREEN
ME UAIRDATA 99999  1999 SCREEN
ME WINDCATS    1.54    3.09    5.14    8.23    10.80
ME FINISHED

OU STARTING
OU RECTABLE ALLAVE FIRST SECOND
OU FINISHED

**********************************
*** SETUP FINISHES SUCCESSFULLY ***
**********************************
```

APPENDIX G

CALCULATION OF CANCER RISK

APPENDIX G

CALCULATION OF CANCER RISK

This is an example calculation showing how to calculate cancer risk.

1. Identify the 1 hour maximum benzene concentration in air using the ISCST3 model.

    ▸   Example 1 hour maximum benzene concentration $= 15.66\ \mu g/m^3$

2. Convert the 1 hour maximum benzene concentration to the annual benzene concentration by multiplying the 1 hour maximum benzene concentration by 0.08.

    ▸   Annual benzene concentration $= (15.66\ \mu g/m^3)(0.08)$
    $= 1.2528\ \mu g/m^3$

3. Look up the Unit Risk Value for benzene in the CAPCOA Risk Assessment Guidelines.

    ▸   Unit risk value for benzene $= 2.9E\text{-}05\ (\mu g/m^3)^{-1}$

4. Calculate the cancer risk by multiplying the unit risk value for benzene by the annual benzene concentration in air.

    ▸   Cancer risk $=$ (annual benzene concentration) (unit risk value)

    $= (1.2528\ \mu g/m^3)(2.9E\text{-}05\ (\mu g/m^3)^{-1})$

    $= 3.63E\text{-}05$

    ▸ $\underline{\text{Cancer risk}}$ $= (3.63E\text{-}05)(1,000,000)$
    million

    ▸   Cancer risk $= 36.3$ in a million

APPENDIX H

CALCULATIONS FOR DETERMINING WHETHER GASOLINE VAPORS SHOULD BE MODELED AS A DENSE GAS OR A WELL MIXED GAS

APPENDIX H

**CALCULATIONS FOR DETERMINING WHETHER
GASOLINE VAPORS SHOULD BE MODELED AS A
DENSE GAS OR A WELL MIXED GAS**

The density of gasoline vapors is four times heavier than air. Therefore, it is important to know whether the ISCST3 model adequately calculates the dispersion of gasoline vapors at gasoline stations. To determine whether emitted gasoline vapors are neutrally buoyant, two different calculation methods were used. Each method calculates the Richardson number. If the resulting Richardson number is above 30 using the TSCREEN model or above 32 using the EPA DEGADIS model, then gasoline vapors should be treated as a dense gas. Results of both these calculations indicate that gasoline vapors emitted from the gasoline stations can be modeled as a neutrally buoyant gas using the ISCST3 model.

I.   EPA DEGADIS 2.1 Air Dispersion Model

The Richardson number (Ri) is used to evaluate the characteristics of a dense gas in the EPA DEGADIS 2.1 air dispersion model (Trinity Consultants, Custom Air Modeling Workshop for San Diego County APCD, August 24-26, 1992). The concept of the Richardson number is described below:

$$Ri \ = \ \frac{\text{(potential energy of cloud)}}{\text{(turbulent energy of environment)}}$$

For purposes of determining whether gasoline emissions from gas stations should be considered a dense or well mixed gas, continuous emissions were assumed. For continuous releases, the formula for the Richardson number is:

$$Ri = \left(\frac{9.8}{u_f^2}\right)\left(\frac{\rho_i - \rho_a}{\rho_a}\right)\sqrt{\frac{Q}{2\rho_i u}}$$

u	= wind speed	(m/s)
u_f	= friction velocity $\approx 0.1\ u$	(m/s)
ρ_i	= density of gasoline/air mixture leaving vent	(kg/m^3)
ρ_a	= density of ambient air	(kg/m^3)
Q	= emission rate of gasoline vapors	(kg/s)

If Ri > 32, then the gas should be considered to have dense gas characteristics and requires special attention in the air dispersion modeling.

To determine the wind speed and friction velocity used in the equation, a minimum wind speed is 1.0 meters per second was used. The maximum Ri number is found when the wind speed is minimized.

$$u = 1.0 \text{ m/s minimum wind speed}$$
$$u_f = (1.0 \text{ m/s})(0.1) = 0.1 \text{ m/s}$$

To determine the density of the gasoline being emitted, assume that the molecular weight of the vapor is the molecular weight of the vapors in the storage tank headspace. This is approximately 65 lbs/lbmole. See Appendix D, page 2 for the calculation.

Also needed in the density calculation is the average temperature of the gasoline vapors emitted. Assume an average temperature of 60 degrees F (289 K). The ambient temperature used in the calculations ranges from 20-110 degrees F (266-316 K). The density of the gasoline and ambient air is calculated as follows.

$$T_i = 60 \text{ F} \quad (289 \text{ K})$$
$$T_a = 20\text{-}110 \text{ F} \quad (266\text{-}316 \text{ K})$$

$$\rho_i = \frac{M}{V} = \frac{P \cdot MW_i}{R \cdot T_i} = \frac{(1 \text{ atm}) \ (65 \text{ g/gmole})}{(82.05 \text{ atm*cm}^3/\text{gmole*K}) \ (289 \text{ K})}$$

$$= \frac{(0.0027 \text{ g})}{(\quad \text{cm}^3)} \frac{(1,000,000 \text{ cm}^3)}{(\quad \text{m}^3)} \frac{(\quad \text{kg})}{(1000 \text{ g})}$$

$$= 2.74 \text{ kg/m}^3$$

$$\rho_a = \frac{M}{V} = \frac{P \cdot MW}{R \cdot T} = \frac{(1 \text{ atm}) \ (29 \text{ g/gmole})}{(82.05 \text{ atm*cm}^3/\text{gmole*K}) \ (266 \rightarrow 316 \text{ K})}$$

$$= \frac{(0.00133 \rightarrow 0.00112 \text{ g})}{(\quad \text{cm}^3)} \frac{(1,000,000 \text{ cm}^3)}{(\quad \text{m}^3)} \frac{(\quad \text{kg})}{(1000 \text{ g})}$$

$$= 1.33 \rightarrow 1.12 \text{ kg/m}^3$$

For a gas station with phase 2 vapor recovery and no vent valves (scenario 6A) and 1,000,000 gal/year gasoline throughput, the total emissions factor is 1.68 lbs/1000 gal throughput (see Appendix A). The total mass emissions rate is 0.0242 g/sec (see Appendix D).

$$Q \quad = \quad 0.0242 \text{ g/s gasoline vapors}$$
$$= \quad (0.0242 \text{ g/s}) (\text{kg/1000 g})$$
$$= \quad 0.0000242 \text{ kg/s}$$

$$\rho_i \quad = \quad 2.74 \text{ kg/m}^3$$
$$\rho_a \quad = \quad 1.12 \rightarrow 1.33 \text{ kg/m}^3$$

$$u \quad = \quad 1.0 \text{ m/s}$$
$$u_f \quad = \quad 0.1 \text{ m/s}$$

$$Ri = \frac{(9.8)}{(.1 m/s)^2} \frac{(2.74 - 1.33 \; kg/m^3)}{(1.33 \; kg/m^3)} \sqrt{\frac{(0.0000242 \; kg/s)}{(2) \; (2.74 \; kg/m^3) \; (1 \; m/s)}} = 0.212$$

$$Ri = \frac{(9.8)}{(.1 \; m/s)^2} \frac{(2.74 - 1.12 \; kg/m^3)}{(1.12 \; kg/m^3)} \sqrt{\frac{(0.0000242 \; kg/s)}{(2) \; (2.74 \; kg/m^3) \; (1 \; m/s)}} = 0.298$$

Thus, for a 1,000,000 gallon/year throughput station, the Richardson number ranges from 0.212-0.298, given ambient temperatures between 20-110 degrees F. These Richardson numbers are less than 32 which is when the gas should be considered to have dense gas characteristics and requires special attention in the air dispersion modeling.

The Richardson number continues to remain below 32 even when the gas throughput is at an unrealistically high 30,000,000 gallons/year. At this throughput the Richardson number is between 1.63 -1.2.

$$Q \quad = \quad (30) (0.0242 \text{ g/s gasoline vapors})$$
$$= \quad (0.726 \text{ g/s}) (\text{kg/1000 g})$$
$$= \quad 0.000726 \text{ kg/s}$$

$$\rho_i \quad = \quad 2.74 \text{ kg/m}^3$$
$$\rho_a \quad = \quad 1.2 \rightarrow 1.33 \text{ kg/m}^3$$

$$u \quad = \quad 1.0 \text{ m/s}$$
$$u_f \quad = \quad 0.1 \text{ m/s}$$

$$Ri \; = \; \frac{(9.8)}{(.1 m/s)^2} \; \frac{(2.74 - 1.33 \; kg/m^3)}{(1.33 \; kg/m^3)} \; \sqrt{\frac{(0.000726 \; kg/s)}{(2) \; (2.74 \; kg/m^3) \; (1 \; m/s)}} \; = \; 1.2$$

$$Ri \; = \; \frac{(9.8)}{(.1 \; m/s)^2} \; \frac{(2.74 - 1.12 \; kg/m^3)}{(1.12 \; kg/m^3)} \; \sqrt{\frac{(0.000726 \; kg/s)}{(2) \; (2.74 \; kg/m^3) \; (1 \; m/s)}} \; = \; 1.63$$

II. TSCREEN Model

Another resource for evaluating dense gas properties is the EPA model TSCREEN.
TSCREEN is used to determine if the gasoline vapors should be modeled as a dense gas or a
neutrally buoyant source by calculating the Richardson number. It defines a vapor release as a
dense gas if the Richardson number exceeds 30.

The following are the inputs to the TSCREEN model.

T_a = ambient air temperature
T_s = gasoline vapor temperature
MW   = molecular weight of gasoline
Q   = emission rate
D   = stack tip diameter

The Richardson number of 30 is not exceeded until more than 1.1 grams/sec are emitted. This
emission rate converts to a gasoline throughput of 36,000,000 gallons per year. No stations
in California have been identified as having a throughput this large.

Using the DEGADIS method, gas stations should be modeled as a dense gas if the throughput
is greater than 30,000,000 gallons/year. But using the TSCREEN method, gas stations
should be modeled as a dense gas if the throughput is greater than 36,000,000 gallons/year.
The reasons for the differences include the use of different formulas and input parameters.
TSCREEN accounts for stack diameter, while the DEGADIS method does not. The
DEGADIS method accounts for wind speed, while the TSCREEN method does not. Both
approaches indicate gasoline vapors from gasoline stations should be modeled as neutrally
buoyant gases.

APPENDIX I

CALCULATIONS TO DETERMINE THE
RELATIVE TOXICITY OF SUBSTANCES IN GASOLINE

RELATIVE TOXICITY OF SUBSTANCES IN GASOLINE

When considering downwind concentrations of the components in gasoline emissions, the concentrations of gasoline vapors which cause adverse health effects (other than cancer) are reached after the concentration required to cause a 10 per million cancer risk is exceeded. The calculations to determine this are shown below. They are based on the assumption that the concentrations of toluene and xylene in reformulated gasoline are the same as in pre-1996 gasoline, because the actual formulations of current gasoline have not been measured yet by the ARB.

	Post-96 Gas (%wt.) Liquid	Post-96 Gas (%wt.) Vapor	Pre-96 Gas (%wt.) Liquid	Pre-96 Gas (%wt.) Vapor	Cancer Unit Risk Value $(\mu g/m^3)^{-1}$	Chronic REL $(\mu g/m^3)$	Acute REL $(\mu g/m^3)$	EPA's Reference Conc. (RfC) $(\mu g/m^3)$
Benzene	**1**	**0.3**	**2**	**0.7**	**2.9E-5**	**71**	NA	NA
Toluene	**8**	N/A	NA	NA	NA	**200**	NA	NA
Xylene	**2.4**	N/A	NA	NA	NA	**300**	**4400**	NA
MTBE	**11**	N/A	**<15**	NA	**7.5E-8 to 1.7E-7**	NA	NA	**3000**
Ethyl Benzene	NA	NA	NA	NA	NA	NA	NA	**1000**

NA - Not Available

BENZENE:
Calculate the downwind concentrations of benzene representing a 10 per million cancer risk.

(10 per million cancer risk) = (Benzene Unit Risk Factor) (Benzene Concentration)

(Benzene Concentration) = $\dfrac{\text{(10 per million cancer risk)}}{\text{(Benzene Unit Risk Factor)}}$

$= \dfrac{\text{10 per million cancer risk}}{2.9\text{E-5 } (\mu g/m^3)^{-1}}$

$= 0.345 \ \mu g/m^3$

The Chronic Hazard Index equals 1 when the downwind concentration of benzene equals 71 $\mu g/m^3$. The cancer risk of 10 per million is reached at 0.345 $\mu g/m^3$, but the Hazard index is reached at 71 $\mu g/m^3$. This is a difference of three orders of magnitude. Therefore, the benzene cancer risk of 10 per million will be exceeded far sooner than the chronic hazard index for benzene.

TOTAL HYDROCARBONS:

Knowing the concentration of benzene which causes a cancer risk of 10 per million (0.345 $\mu g/m^3$), determine the concentration of the other gasoline components in the air.

First, determine the total hydrocarbon (THC) concentration from the benzene concentration.

This is done by determine the benzene fraction emitted from refueling, loading, breathing, and spillage.

The headspace of underground storage tanks contain 0.3% by weight benzene in the vapors. Assume that this is the same benzene fraction as in breathing, loading, and refueling emissions.

Liquid gasoline contains 1% by weight benzene. Assume that this is the same benzene fraction as in spillage emissions.

Also needed is the fraction of risk due to breathing, loading, and refueling compared to spillage. Modeling results for Scenario 6A indicated approximately 50% of the risk is due to breathing, loading, and refueling and 50% of the risk is due to spillage.

Benzene concentration due to spillage   = (0.345 $\mu g/m^3$) (50% spillage risk)
       =   0.172 $\mu g/m^3$

Benzene concentration due to breathing, loading, & refueling

       = (0.345 $\mu g/m^3$) (50% nonspillage risks)
       = 0.172 $\mu g/m^3$

THC concentration due to breathing, loading, & refueling

$$= \frac{0.172 \ \mu g/m^3}{0.3\% \ benzene}$$

$$= \textbf{57.3 } \boldsymbol{\mu} \textbf{g/m}^3$$

THC concentration due to spillage $\quad = \dfrac{0.172 \ \mu g/m^3}{1\% \ benzene}$

$$= \textbf{17.2 } \boldsymbol{\mu} \textbf{g/m}^3$$

TOLUENE:
The corresponding toluene concentration can be calculated assuming the concentration of toluene in post-96 gasoline is equal to the concentration in pre-96 gasoline. Pre-96 liquid gasoline emissions contained 8% by weight toluene and tank headspace emissions contained 1% by weight toluene.

Toluene concentration due to spillage
$= $ (THC concentration due to spillage) (8% toluene)
$= $ (17.2 $\mu g/m^3$) (0.08)
$= $ 1.38 $\mu g/m^3$

Toluene concentration due to breathing, loading, & refueling
$= $ (THC concentration due to breathing, loading, & refueling) (1% toluene)
$= $ (57.3 $\mu g/m^3$) (0.01)
$= $ 0.573 $\mu g/m^3$

Toluene concentration total
$= $ 1.38 $\mu g/m^3$ + 0.573 $\mu g/m^3$
$= \textbf{1.95 } \boldsymbol{\mu} \textbf{g/m}^3$

Compare how the total toluene concentration (**1.95 µg/m³**) compares with the Chronic REL for toluene (**200 µg/m³**). The difference is a little more than two orders of magnitude. Therefore, the cancer risk threshold of 10 per million for benzene will be exceeded far sooner than the chronic hazard index threshold of one for toluene.

XYLENE:
Using the same method as above, the corresponding xylene concentration can be calculated knowing the pre-96 liquid gasoline emissions contained 2.4% by weight xylene and the tank headspace emissions contained 1% by weight xylene.

Xylene concentration due to spillage
$$= \text{(THC concentration due to spillage) (2.4\% xylene)}$$
$$= (17.2 \ \mu g/m^3) \ (0.024)$$
$$= 0.41 \ \mu g/m^3$$

Xylene concentration due to breathing, loading, & refueling
$$= \text{(THC concentration due to breathing, loading, \& refueling) (1\% xylene)}$$
$$= (57.3 \ \mu g/m^3) \ (0.01)$$
$$= 0.57 \ \mu g/m^3$$

Xylene concentration total
$$= 0.41 \ \mu g/m^3 + 0.57 \ \mu g/m^3$$
$$= \mathbf{0.98 \ \mu g/m^3}$$

Compare how the total xylene concentration (**0.98 μg/m³**) compares with the Chronic and Acute REL for xylene (**300 μg/m³, 4400 μg/m³**). The difference is a little less than two orders of magnitude for the chronic comparison and a little more than three orders of magnitude for the acute comparison. Therefore, the cancer risk threshold of 10 per million for benzene will be exceeded far sooner than the chronic and the acute hazard index threshold of one for xylene. Even when the chronic hazard index for xylene is added to the hazard index for toluene, the total hazard index is not exceeded before the 10 per million cancer risk level for benzene is exceeded.

METHYL TERTIARY BUTYL ETHER (MTBE):
Although the MTBE toxicity data is still being debated, the EPA chronic reference exposure value is available to compare the concentrations of MTBE which is present when the benzene risk is 10 per million. Assume that the 11% by volume is also 11% weight MTBE in the liquid, and is also 11% weight in gasoline vapors.

MTBE concentration due to spillage
$$= \text{(THC concentration due to spillage) (11\% MTBE)}$$
$$= (17.2 \ \mu g/m^3) \ (0.11)$$
$$= 1.9 \ \mu g/m^3$$

MTBE concentration due to breathing, loading, & refueling

$$= \text{(THC concentration due to breathing, loading, \& refueling) (11\% MTBE)}$$
$$= (57.3 \ \mu g/m^3) \ (0.11)$$
$$= 6.3 \ \mu g/m^3$$

MTBE concentration total

$$= 1.9 \ \mu g/m^3 + 6.3 \ \mu g/m^3$$
$$= \textbf{8.2 } \boldsymbol{\mu} \textbf{g/m}^3$$

Compare how the total MTBE concentration **(8.2 µg/m³)** compares with the Chronic RfC for MTBE **(3000 µg/m3).** The difference is a little less than three orders of magnitude. Therefore, the cancer risk threshold of 10 per million for benzene will be exceeded far sooner than the chronic reference concentration threshold for MTBE.

APPENDIX J

GAS CAP "WHOOSH" EMISSIONS

APPENDIX J
GAS CAP "WHOOSH" EMISSIONS

Below are the calculations used to determine the significance of "Whoosh", gas cap removal, emissions:

Assumptions used to determine whoosh emissions:

Gasoline dispensed per vehicle	12 gallons
Molecular weight of the gasoline/air vapor mixture	65 lb/lbmole
Gasoline carbon number	4.5 (approximately isobutane)
Atmospheric pressure (1 atm)	406.9 inches water
Temperature of the car gas tank headspace range	80-120 F
(20 F above ambient)	average 100 F, 560 R

The equilibrium concentrations of isobutane at various temperatures are:

Temperature (F)	Equilibrium Pressure (psia)
60	4.3
65	4.7
80	5.8
100	7.4
120	10.5

Notice that at 100 degrees F the equilibrium pressure is approximately equal to the average summer blend RVP, 7. Thus it follows that the winter blend equilibrium pressures would be an additional 4 psia at various temperatures, because the RVP is 11 at 100 F for winter blends.

Headspace pressures were measured by BAAQMD in the Spring of 1995 in a preliminary survey. Cars are currently designed so that the headspace pressure will not exceed 28 inches of water (1 psig). The table below shows the pressures measured by the BAAQMD:

Tank Size (gallons)	Tank Vapor Space (gallons)	Vapor Space Pressure (inches water)
16	12	10
16	12	15
16	12	20
16	12	25

J-1

To determine the concentration of gasoline vapors in the car gas tank headspace, assume the headspace contains equilibrium concentrations of gasoline to air. To determine the concentration of gasoline to air, assume that the partial pressure at equilibrium of isobutane over the atmospheric pressure, equals the molar volume of isobutane over the molar volume of air.

$$\frac{n_i}{n_t} = \frac{v_i}{v_t} = \frac{p_i}{p_t}$$

Thus, the molar concentration of gasoline at 100 F is:

$$\frac{n_i}{n_t} = \frac{v_i}{v_t} = \frac{p_i}{p_t} = \frac{7.4 \text{ psia}}{14.7 \text{ psia}} = 0.50 = 50\% \text{ gasoline}$$

The range of gasoline concentrations will be 29% at 60 F to 90% at 120 F. To determine the average gasoline concentration, assume that most cars are fuel injected and the temperature of the headspace for fuel injected cars is about 20 F above ambient when they arrive at gas stations. In the summer, assume an average ambient temperature of 80 F when most people fill up. In the winter assume an average ambient temperature of 50 F when most people fill up.

Thus, the equilibrium pressure is 7.4 at 100 F for summer blends, and the concentration is 50% gasoline. And, at 50 F for winter blends, when the RVP is 4 psia above the summer blend RVP, the partial pressure is about 7.4 psia, and the concentration is also about 50% gasoline.

To determine the molar volume of vapors released when the gas cap is opened, determine the molar volume of the headspace under pressure prior of opening the gas cap, then subtract the molar volume of the headspace immediately after the cap has been opened and the pressure is stabilized.

P = ambient pressure + gage pressure   =406.9 + 10→25 inches water
R = ideal gas law constant   =0.7302 atm ft^3/lbmole R
T = ambient temperature   =560 R
V = headspace of empty gas tank   =12 gal

Initial Molar Volume$_1$:
$$n_1 = PV/RT$$

$$= \frac{(406.9 + 10\rightarrow25 \text{ inches of water}) \ (12 \text{ gal headspace})}{(0.7302 \text{ atm ft}^3/\text{lbmole R}) \ (560 \text{ R})}$$

$$= \frac{(1.0246\rightarrow1.0614 \text{ atm}) \ (1.6044 \text{ ft}^3 \text{ headspace})}{(0.7302 \text{ atm ft3/lbmole R}) \ (560 \text{ R})}$$

= 0.004020→0.004164 lbmoles in the headspace

= 50% gasoline (0.004020→0.004164 lbmoles)

= 0.00201→0.002082 lbmoles gasoline

m_1 = n_1 * mw
= (0.00201→0.002082 lbmoles) (65 lb/lbmoles)
= 0.1306→0.1354 lbs gasoline in headspace

Final Molar Volume$_2$:

n_2 = PV/RT

$$= \frac{(406.9 \text{ in water})\ (12 \text{ gal headspace})}{(0.7302 \text{ atm ft}^3/\text{lbmole R})\ (560 \text{ R})}$$

$$= \frac{(1 \text{ atm})\ (1.6044 \text{ ft}^3 \text{ headspace})}{(0.7302 \text{ atm ft3/lbmole R})\ (560 \text{ R})}$$

= 0.003924 lbmoles vapor in the headspace

= 50% gasoline (0.003924 lbmoles)

= 0.001962 lbmoles gasoline

m_2 = n_2 * mw
= (0.001962 lbmoles) (65 lb/lbmoles)
= 0.1275 lbs gasoline in headspace

m_o = m_1 - m_2

= 0.1306→0.1354 - 0.1275 lbs

$$= \frac{0.0031 \rightarrow 0.0079 \text{ lbs gasoline emitted}}{12 \text{ gal headspace}}$$

= 0.000258 → 0.000658 lbs/gal

= **0.258 → 0.658 lbs emitted/1000 gal dispensed**

This compares to a total emission rate of **1.68 lbs/1000 gallons** (Scenario 6A). If these initial calculations are confirmed, then whoosh emissions may be more significant than loading, spillage or breathing emissions.

APPENDIX K

INDUSTRYWIDE TOXIC EMISSIONS INVENTORY SURVEY FORM

(DISTRICT NAME & ADDRESS)
INDUSTRYWIDE TOXIC EMISSIONS INVENTORY SURVEY
GASOLINE SERVICE STATION

Dear Permit Holder:

Pursuant to sections 42303 and 40701(g) of the California Health & Safety Code, we hereby request that you provide the following information. It will be used to estimate your station's gasoline vapor emissions and potential health impacts. Please return the form to the district by **(date)**. If you have any questions, please call (district contact person) at (telephone number). Thank you for your cooperation.

Gas station permit holder's name: _____

Gas station name: _____

Air Pollution Control District permit number: _____

Person filling out this form: (print) _____ Title: ____ _____

Signature: _____

Phone number of person filling out form for follow up information, if necessary: _____

Gas Station Address: _____

_____

City: _____ Zip: _____

Number of gallons of gasoline dispensed during last calendar year: _____ _____ gallons

Distance from the **center** of the station to the edge of nearest: Residential building _____ feet
Commercial building _____ feet

Storage tank type (check): ❒ underground
❒ aboveground

Type of vapor recovery equipment used (check): ❒ Phase I
❒ Phase II
Assist system: ❒ (bootless nozzle)
❒ (booted nozzle)
Balance system: ❒ (booted nozzle)

Storage Tank Vent Valves (check): ❒ yes
❒ no

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