

**COMPARATIVE QUANTITATIVE RISK ANALYSIS
OF MOTOR GASOLINE, LPG, AND
ANHYDROUS AMMONIA AS AN AUTOMOTIVE FUEL**

Prepared For

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SECTION 1

INTRODUCTION AND OVERVIEW

Quest Consultants Inc. was retained by Iowa State University to perform a quantitative risk analysis (QRA) that compared the risks associated with the bulk movement, storage, and dispensing of three automotive fuels. The fuels that were the subject of the study were automotive gasoline, liquefied petroleum gas (LPG) and anhydrous ammonia. The objective of the study was to compute the level of risk posed to the public near an average roadway along which the fuels would be transported in road tankers, and near an automotive fueling station.

The study was divided into three primary tasks.

Task 1 – Compare the potential consequences associated with an accidental release of anhydrous ammonia to the potential consequences associated with accidental releases of automotive gasoline and LPG, when used for automotive fuel.

Task 2 – Review of the frequencies associated with accidental releases of anhydrous ammonia, automotive gasoline, and LPG.

Task 3 – Evaluation of the risk level (consequence x frequency) associated with each material when used as an automotive fuel. The boundaries of the analysis will be defined by the transport of bulk material to the service station, storage of material at the service station, and loading of material into automobiles.

Figure 1-1 illustrates the steps in the QRA procedure required to complete the three primary tasks.

1.1 Hazards Identification

The potential hazards associated with the transport, storage, and fueling activities are common to similar flammable fluid handling facilities worldwide, and are functions of the materials being handled, handling systems, and the procedures used for operating and maintaining the road tankers and fueling facilities. The hazards that are likely to exist are identified by the physical and chemical properties of the materials being handled, and the process conditions. For the fuel handling activities considered in this study, the common hazards are:

- Exposure to toxic gas (e.g., ammonia)
- Torch (jet) fires
- Flash fires
- Pool fires
- Vapor cloud explosions

The hazards identification step is discussed in Section 3.

1.2 Failure Case Definition

The potential release sources of flammable and toxic materials are determined from a combination of site-specific information and past history of releases from similar facilities, including previous reports, accident data, and engineering analyses by system safety engineers.

QUANTITATIVE RISK ANALYSIS STEPS

TOOLS UTILIZED

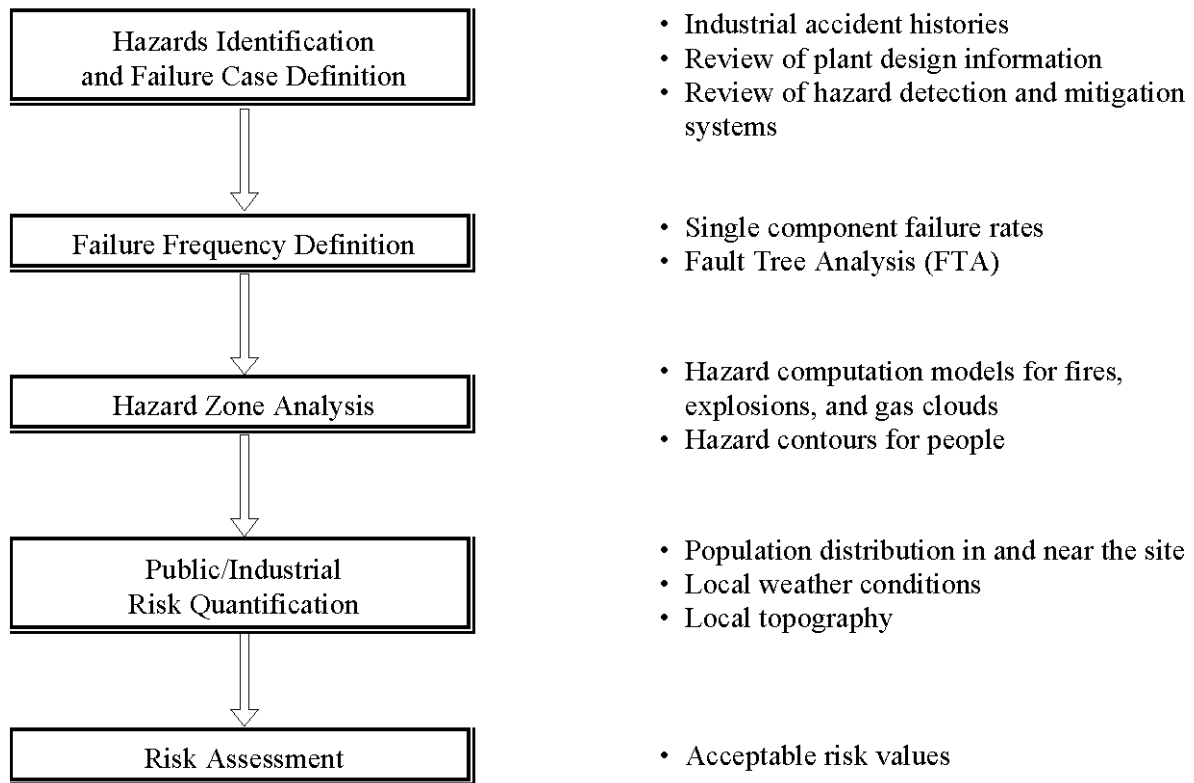


Figure 1-1
Overview of Risk Analysis Methodology

This step in the analysis defines the various release sources and conditions of release for each failure case. The release conditions include:

- Fluid composition, temperature, and pressure
- Release rate and duration
- Location and orientation of the release
- Type of surface over which released liquid (if any) spreads

The failure case definition step is included in Section 3.

1.3 Failure Frequency Definition

The frequency with which a given failure case is expected to occur can be estimated by using a combination of:

- Historical experience
- Failure rate data on similar types of equipment

- Service factors
- Engineering judgment

For single component failures (e.g., hose rupture), the failure frequency can be determined from industrial failure rate data bases. For multiple component failures (e.g., failure of an automatic system for preventing an uncontrolled release from a storage vessel), fault tree analysis (FTA) techniques can be used. The single component failure rates used in constructing the fault trees are obtained from industrial failure rate data bases.

The failure frequency step and the data base references are included in Section 4.

1.4 Hazard Zone Analysis

The release conditions (e.g., composition, pressure, temperature, hole size, inventory, etc.) from the failure case definitions are processed, using the best available hazard quantification technology, to produce a set of hazard zones for each failure case. The CANARY by Quest® computer software hazards analysis package is used to produce profiles for the toxic, fire, and overpressure hazards associated with each failure case. The models that are used account for:

- Release conditions
- Ambient weather conditions (wind speed, air temperature, humidity, atmospheric stability)
- Effects of the local terrain (diking, vegetation)
- Mixture thermodynamics

The hazard zone analysis step is discussed in Section 3.

1.5 Public/Industrial Risk Quantification

The methodology used in this study has been successfully employed in many QRA studies that have undergone regulatory review in several countries worldwide. This methodology is described in Section 5.

The result of the analysis is a prediction of the risk posed by the truck transport of the three fuels and the risk near a typical fueling station. Risk may be expressed in several forms (e.g., risk contours, average individual risk, societal risk, etc.). For this analysis, the focus was on the prediction of risk contours as a method of comparing the site-specific risk levels associated with the three fuels. Descriptions of this procedure are presented in Section 5.2.

1.6 Risk Assessment

Risk indicators enable decision makers (i.e., corporate risk managers and regulatory authorities) to compare the risks associated with the transport, storage and dispensing of each fuel. The results of the risk analysis, and conclusions drawn from this study, are presented in Section 6.

1.7 Motor-Vehicle Deaths by Type of Accident

It is important to note that this comparative risk analysis does not include the calculation of fatality risk while being transported in an automobile as a function of the type of fuel (gasoline, LPG, or anhydrous

ammonia) used to power the automobile. There are several reasons for this, the primary one being that the fuel used to power an automobile plays an insignificant part in the fatality risk due to automobile transportation.

The National Safety Council maintains an extensive data base covering injuries and fatalities due to accidents. One of the largest subsets of this data base pertains to accidents involving motor vehicles. A review of the data base indicates that most of the fatalities associated with motor vehicles are not due to the fuel in the vehicle. In short, whether the motor vehicle is powered by gasoline, LPG, natural gas, or some other fuel has little to do with whether a fatality occurs during an accident.

The National Safety Council data summary [2006] does not record whether the fuel for the motor vehicle was released during the accident. Certainly many accidents that resulted in fatalities did not involve a release of fuel. This can be seen by reviewing how the NSC categorizes the fatality data for motor-vehicle accidents. Using the 2004 calendar year as an example (many other years yield similar results), the following table provides a breakdown of motor-vehicle deaths by type of accident.

**Table 1-1
Motor-Vehicle Deaths by Type of Accident (2004)**

Total Deaths	Deaths Resulting From a Motor-Vehicle Collision With	Comments
20,600	Other vehicles	It is possible that some of these accidents resulted in a release of fuel. It is unknown whether the release of fuel contributed to the fatality.
200	Railroad trains	It would seem reasonable to assume that the fatalities in these accidents were caused by colliding with the train, not by a release of fuel.
13,300	Fixed objects	Collisions with guardrails, abutments, bridges, etc. Similar to train collisions in that the impact or rollover may have caused the majority of the fatalities.
5,900	Pedestrians	These are pedestrian fatalities, almost entirely expected to be by blunt force.
900	Pedal-cycles	Collisions with pedalcycles (e.g., bicycles). These collisions would not be expected to result in a release of fuel from the vehicle.
100	Animal drawn vehicle or animal	Similar to collisions with pedalcycles. These collisions would not be expected to result in release of fuel.
5,200	Non-Collision Accidents	Accidents as a result of rollover or jackknifing a truck would fall into this category. There may be some potential for a loss of fuel in some of these accidents.
46,200	Total Deaths	Total fatalities associated with motor vehicles

A review of the table shows the primary cause of death to the motor-vehicle occupants or persons outside the motor vehicle is most likely due to the force of the collision, not a release of fuel. This is easily seen for the accidents that involve pedestrians, bicycles, animals, and even collisions with trains.

Only in the collisions with other vehicles or fixed objects could a reasonable argument be made that some of the fatalities resulted from a release of fuel. The NSC data base does not list the cause of death in these accidents. Thus, if an accident occurred and an occupant were killed by the impact and then fuel was

released, the data base would only list the fatality without identifying whether blunt force trauma or exposure to the fuel (e.g., fire caused by ignition of gasoline vapors) was the cause of death.

Common news accounts support the assumption that most motor-vehicle accidents that result in one or more fatalities do not involve a release of fuel. The most common motor-vehicle fuels are gasoline, LPG, and compressed natural gas (CNG). Of these three, gasoline is the most common fuel. It is stored in the motor vehicle in a thinner walled tank than either LPG or CNG, which are stored in pressure vessels. Few news accounts describe a motor-vehicle accident that results in a fire, and fewer still report any fatalities associated with the accident involving a fire.

Thus, it can be concluded that the fuel used to power a motor vehicle does not contribute significantly to the fatality rate of motor-vehicle accidents. It appears that the fuel, by itself, is not a significant factor in the fatality rates. This conclusion is based on a simple review of the available NSC data and would be expected to be true if anhydrous ammonia were the automotive fuel since anhydrous ammonia would be carried in a pressure vessel similar to LPG.

SECTION 2

ROAD TANKER, STORAGE FACILITY, AND FUELING STATION DESCRIPTIONS

2.1 Project Description

The scope of the overall risk comparison study will contain three basic elements: transportation of the fuel from its point of origin to the local fueling station, the unloading and storage of bulk fuel in the fueling station, and the individual refueling of automobiles at the fueling station. A general description of each operation for the three fuels involved is presented in this section.

2.1.1 Road Transport

Automotive gasoline, LPG, and anhydrous ammonia are routinely transported by tank truck in the United States. Since LPG and anhydrous ammonia are gases at standard conditions (32 F and 1 atmosphere pressure), these materials are often liquefied by pressure and transported as liquefied gases. In some instances, such as is the case for the anhydrous ammonia in this study, the materials are transported as liquids due to refrigeration. Gases such as LPG and anhydrous ammonia liquefied by pressure or refrigeration are transported in pressure vessels. Automotive gasoline is a liquid at standard conditions and does not require road transport in a pressure vessel. The distinctions between the two transport vessels are briefly described in the following sections.

2.1.1.1 LPG and Anhydrous Ammonia Road Transport

The US Department of Transportation classifies propane and ammonia as hazardous materials, and requires them to be transported in containers that meet DOT specifications. Only one category of DOT-specification tank trucks is in common use for transporting propane and ammonia as liquefied gases. The DOT refers to this category of tanks as MC 331. The design and construction standards for MC 331 tanks are found in Title 49, Part 178, of the Code of Federal Regulations (49 CFR 178). (It is possible that a few tank trucks built to an earlier DOT specification, MC 330, are still in use, but these tanks would be more than forty years old, making their continued use unlikely.)

The typical propane/ammonia transport truck, whether built to the MC 330 or MC 331 specifications, carries the fluid in a steel tank with a circular cross section.

Typical parameters for the tank are as follows.

Design pressure	250 psig
Diameter of tank	86 inches
Wall thickness	0.4 inches
Cargo capacity	10,000 gallons
Shape of heads	hemispherical

The primary differences between tanks for transporting propane and those for transporting anhydrous ammonia are related to the metallurgy of tank components. A tank that is intended to transport ammonia

must be heat treated once the tank has been fabricated. In addition, pipe fittings, valves, etc., cannot be constructed of copper, zinc, silver, or their alloys (e.g., brass) if used in ammonia service. Tank trucks that are used for transporting propane are not used to transport ammonia, and vice versa. This is due not only to metallurgy issues, but also to product contamination issues.

The tank is not divided into compartments and has no internal bulkheads. The tank is fitted with a manway, usually at the center of or near the top of the rear head. This manway has no openings in it, and it is removed only if the tank needs to be entered for inspections or repairs. Pressure relief valves are located along the top of the tank. All liquid and vapor inlet and outlet connections to the tank are located along the centerline of the tank bottom. The pipes leading to and from these connections all terminate at the curb-side of the tank, or in a compartment at the rear of the tank.

There are typically four main connections at the bottom of the tank. One is a 2-inch diameter vapor inlet/outlet; one is a 3-inch diameter liquid inlet for spray filling the tank; one is a 3-inch diameter liquid outlet line (without a pump) that can also be used for bottom filling the tank, and one is a 4-inch diameter outlet that is connected to a power take-off (PTO) pump. The vapor and liquid outlet connections to the tank are required to be fitted with a remotely operable internal self-closing stop valves. These valves, which are normally held in the off position by springs, can be manually operated at the valves, and from diagonally opposite ends of the tank (typically accomplished by cables connected to operating levers). They also incorporate thermal devices that will close the valves in case of fire. These thermal devices are located near the valves and near the remote operators for the valves. In addition to the required functions, the type of valve actually used in the vapor line and liquid outlet line also incorporates an excess flow valve. The primary working and sealing parts of these valves are located within the tank, which provides protection from damage in case of a vehicular accident. The spray filling line can be equipped with either a simpler valving arrangement, but it is more common to install a remotely operable internal self-closing stop valve like those used on the other bottom connections.

The piping for the vapor inlet/outlet, spray filling, and liquid outlets must be grouped into the smallest practical space and protected from damage by structural elements. Each of these pipes will have a hose connection on the “non-tank” end of the pipe. Just inboard of the hose connections, each pipe will be fitted with a manually operable shut off valve. Between that valve and the nozzle flange on the tank, there is a section “that will break under undue strain.” The purpose of this shear section is to allow the piping to separate cleanly from the tank in case of a severe vehicular accident. This prevents damage to the internal valves and, if the internal valve is in the open position, it ensures the release will constitute excess flow, thus causing the excess flow valve to close and stop the release. These internal valves are closed while the truck is in transit.

When propane or ammonia is to be transferred from the truck’s tank to an above ground storage tank, a 3-inch diameter reinforced rubber hose is attached to the hose coupling on the end of the pipe on the discharge side of the PTO pump. The other end of the hose is attached to a hose coupling at the transfer area bulkhead. An emergency shutoff valve (ESV) will be installed on the transfer piping, on the back side of the bulkhead. A cable running from the actuating lever of the ESV, along the hose, to the truck, will cause the ESV to close if the hose is stretched – as would happen if the truck were to move while the hose is still connected. During the cargo transfer operation, a 2-inch diameter hose may be used to connect the vapor line on the truck’s tank to piping that passes through the bulkhead, on to the vapor space of the tank receiving the cargo. This equalizing hose is seldom used, primarily due to economic issues (i.e., how much vapor was transferred from the receiving tank to the truck’s tank, and what was the value of that vapor?).

When being transported in tank trucks, propane and ammonia are typically carried at ambient temperature, with the pressure in the tank being the vapor pressure that corresponds to that temperature.

By using appropriate steel alloys to construct the truck's tanks and installing insulation to the exterior of the tank, it is possible to carry propane and ammonia at temperatures near their boiling points, in which case the pressure in the tank is relatively low.

2.1.1.2 Automotive Gasoline Road Transport

The US Department of Transportation classifies gasoline as a hazardous material, and requires it to be transported in containers that meet DOT specifications. Although several containers meet the required specifications, only two types of DOT-specification tank trucks are in common use – MC 306 and DOT 406. The design and construction standards for DOT 406 tanks are found in Title 49, Part 178, of the Code of Federal Regulations (49 CFR 178). The standards for MC 306 tanks were found in the same part of 49 CFR 178, but construction of new MC 306 tanks has not been allowed since August 31, 1993. However, tanks built to that standard before that date can continue to be used to transport gasoline.

The typical gasoline transport truck, whether built to the MC 306 or DOT 406 specifications, carries the gasoline in an aluminum tank with an elliptical cross section.

Typical parameters for the tank are as follows.

MAWP	3 psig
Test pressure	5 psig
Width of tank	96 inches
Height of tank	60 inches
Wall thickness	0.188 to 0.250 inches
Gasoline capacity	9,500 gallons
Shape of heads	slightly convex

Most of the tanks are divided into four compartments by internal bulkheads. This allows a single tank to carry multiple grades of gasoline. The bulkheads also reduce the effects of cargo movement when the truck is moving. Each compartment is fitted with a manway at the top of the tank, and with a 4-inch diameter liquid inlet/outlet pipe at the bottom. The liquid inlet/outlet pipes from all compartments are clustered together beneath the tank, on the right side (curb side), near the longitudinal center of the tank.

Each inlet/outlet pipe is fitted with an internal self-closing stop valve. The primary working and sealing parts of these valves are located within the tank, which provides some protection from damage in case of a vehicular accident. This type of valve is held closed by a spring. It is opened by the application of pressurized air. If air pressure is lost, the valve closes automatically. It can also be closed by operating a trip lever located at the end of the tank. In addition, each of these valves is fitted with a thermally activated device that will close the valve if the device reaches its set point temperature, which cannot exceed 250 degrees F. The closing time of the internal self-closing stop valve must not exceed 30 seconds.

At the other end of each loading/unloading pipe, there is another stop-valve, which is opened and closed manually. Beyond that valve it is common practice to have a fitting that conforms to API 1004. This fitting can be permanently connected or can be connected only when the truck is being filled. This fitting incorporates a spring-loaded plunger that keeps liquid from flowing through the fitting until the plunger is withdrawn manually, or another specialized fitting is attached (which is normally the case when the tank is being filled).

When gasoline is to be transferred from a tank compartment to an underground storage tank, a 4-inch diameter rubber hose (with special end fittings), is attached to the API fitting on the appropriate loading/unloading pipe at one end, and the fitting on the other end is attached to the inlet piping for the underground tank. All valves that must be open in order to allow gasoline to drain from the appropriate compartment are opened and gasoline flows (by gravity) from the compartment to the underground tank. Vapor displaced by gasoline entering the underground tank is either vented to the atmosphere at a safe location, or is transferred to the truck's tank through a 4-inch hose.

2.1.2 Fuel Unloading and Storage

In the comparative analysis, a generic automotive fueling station will be employed. This typical station will be located in a suburban area, near an intersection. General descriptions of each station based on the fuel stored and dispensed are described below.

2.1.2.1 Automotive Gasoline

The service station dispensing gasoline is assumed to unload gasoline from road tankers and store the fuel in underground storage tanks. The gasoline is pumped from the underground storage tanks, through the aboveground meter (the gas "pump") and into the fuel tank of the automobile. All fuel lines from the underground storage tanks to the gas pump are buried.

The service station gas pumps are equipped with break-away hose couplings to ensure that a "drive away" accident does not result in a continuous release of gasoline on the ground.

2.1.2.2 LPG

A typical service station dispensing LPG as an automotive fuel will unload the LPG from road tankers with the use of a pump on the road tanker. The LPG will be stored in an above ground pressurized vessel (typically a cylindrical vessel mounted horizontally on supports above ground). LPG is transferred from the storage vessel to the LPG dispensers by pumping the LPG through underground lines.

The LPG dispensers are equipped with pressure couplings to link the LPG fuel line from the dispenser to the automobile fuel tank. The LPG fuel lines from the dispenser to the automobile connection are equipped with break-away couplings as a safety measure to prevent the uncontrolled release of LPG if a drive away accident should occur.

2.1.2.3 Anhydrous Ammonia

A service station dispensing anhydrous ammonia as an automotive fuel would first unload the refrigerated ammonia from a tank truck in a manner similar to the unloading operations for LPG. The refrigerated ammonia would be pumped, via the tank truck's pump, to an insulated storage tank. This insulated storage tank will be housed in an above ground or below ground vault. The vault will serve as a secondary containment vessel for the refrigerated ammonia. The vault will be equipped with a vertical vent stack to facilitate the release of ammonia vapor into the atmosphere should a leak from the storage tank or associated equipment occur.

Unlike the gasoline or LPG storage systems, the transfer of ammonia to the fuel dispenser requires the ammonia to undergo a thermodynamic change. The automotive fuel tanks are designed to hold ammonia at ambient temperature. This requires the automotive fuel tanks to be pressure vessels. In many ways these automotive fuel tanks are identical to the LPG automotive fuel tanks. In order to load the automotive fuel tanks with ambient temperature ammonia, at a pressure well above atmospheric, the ammonia transferred out of the storage tank must be heated. This fluid temperature increase is accomplished by the use of an electric heater that is housed in the vault with the refrigerated storage tank.

Once the ammonia passes through the heater, the transfer lines are run underground until they arrive at the fuel dispenser. Once at the dispenser, the ammonia is loaded into the automobile fuel tank in a manner identical to that of LPG. The ammonia fueling hoses will have break-away connections such that if a drive away accident were to occur, a minimal amount of ammonia would be released.

2.2 System Components Included in Comparative Quantitative Risk Analysis

The following activities are included in the comparative QRA:

- Road transport
- Fuel unloading
- Fuel storage
- Fueling of individual automobiles

For the purposes of this analysis, a generic service station was employed. The basic service station layout is presented in Figure 2-1. A traditional service station is assumed to have six (6) automotive gasoline pumps. If LPG or anhydrous ammonia is available for automobile fueling, the service station is assumed to have one (1) fueling bay.

Every effort was made to make the comparative analysis as “even” as possible. This required a set of assumptions that did not influence the overall risk comparison. The primary assumptions used in this study are outlined below.

2.2.1 Road Transport Parameters

The road transport portion of this analysis assumed the following.

LPG transport truck (MC 331) had a cargo capacity of 10,000 gallons

Anhydrous ammonia transport truck (MC 331) had a cargo capacity of 10,000 gallons

Automotive gasoline transport truck (DOT 406) had a cargo capacity of 9,500 gallons

The comparative risk transport analysis is based upon 52 loaded road transits per year (i.e., 1 per week per product).

2.2.2 Service Station Parameters

The example service station would have the following major equipment.

One above ground LPG storage bullet with a capacity of 30,000 gallons

One above ground LPG fueling dispenser.

Or

One above ground or below ground refrigerated anhydrous ammonia storage tank with a capacity of 30,000 gallons housed in a vault with an elevated vent.

One above ground anhydrous ammonia fueling dispenser.

Or

Three below ground automotive gasoline storage tanks. Each with a capacity of 10,000 gallons.

Six above ground gas pumps.

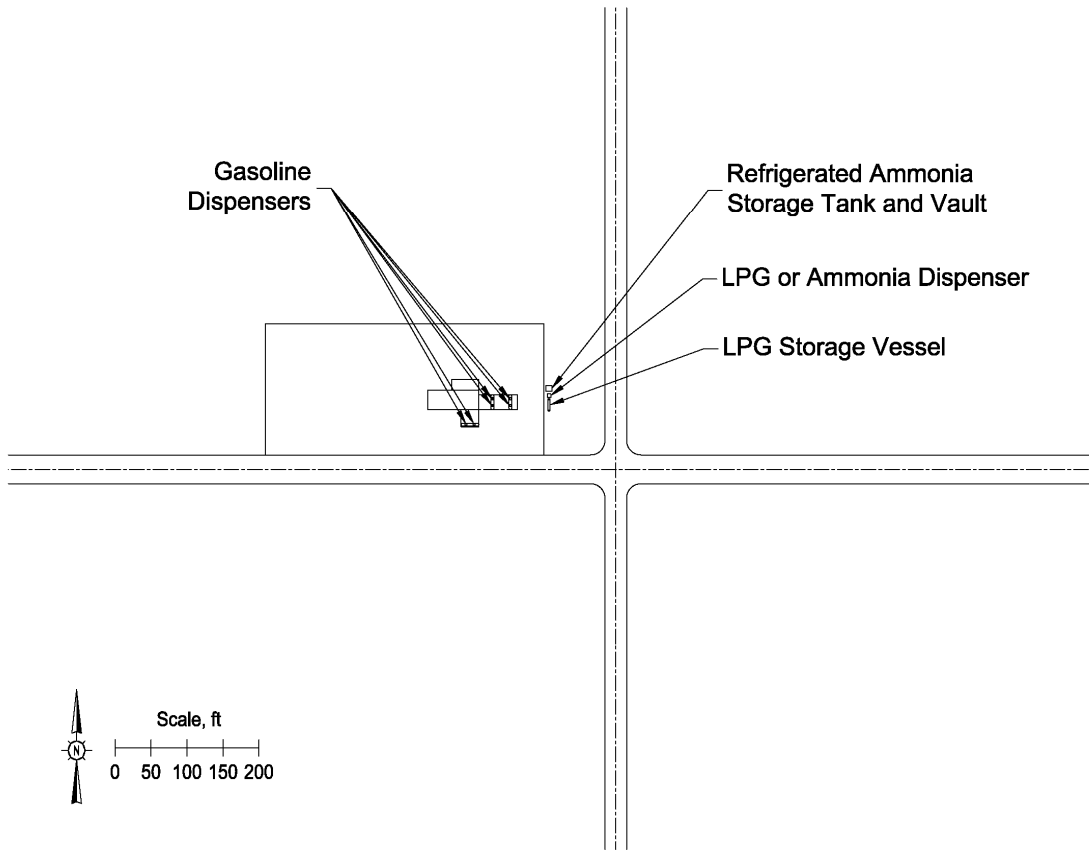


Figure 2-1
Basic Service Station Layout

2.3 Meteorological Data

Generic meteorological data were used in this study. The wind speed and direction data are summarized in the wind rose presented in Figure 2-2. The length and width of a particular arm of the rose define the frequency and speed at which the wind blows from the direction the arm is pointing. As an example, Figure 2-2 shows the predominant wind direction is from the northwest, blowing toward the southeast. Although a risk analysis is sensitive to the choice of weather data, a comparative analysis such as is the subject of this study will yield reasonable results since the analysis of each system will use the same weather data.

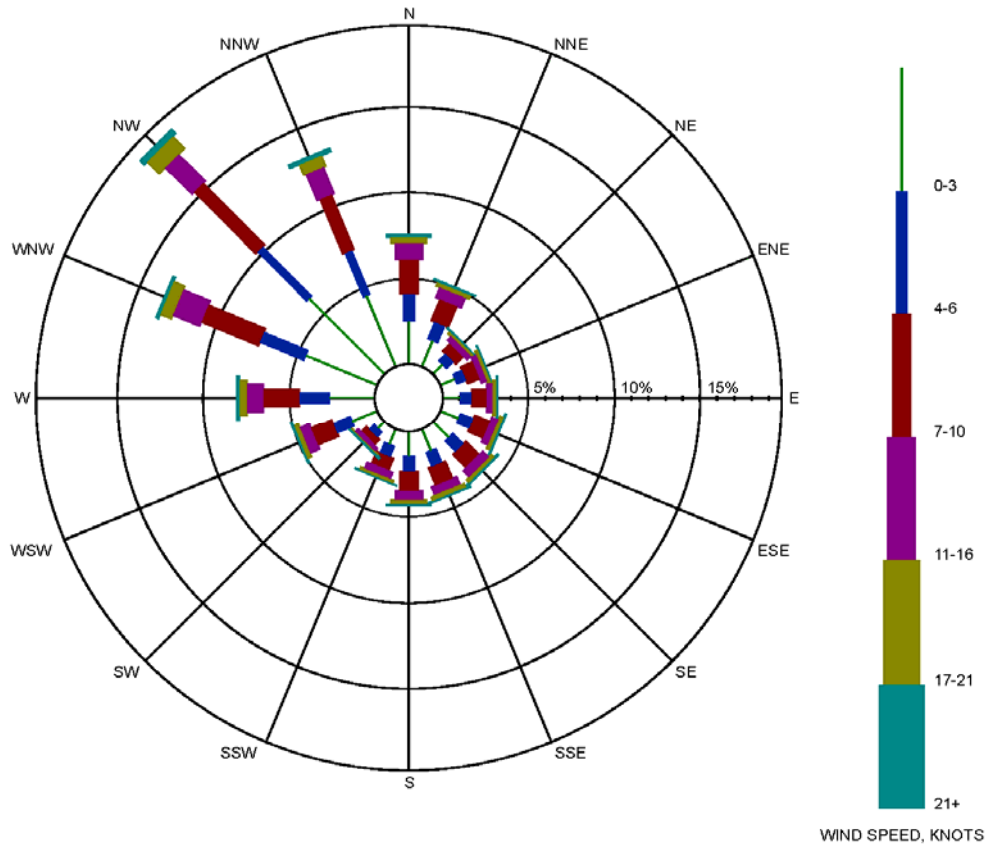


Figure 2-2
Annual Wind Rose

SECTION 3

POTENTIAL HAZARDS

3.1 Hazards Identification

Quest personnel developed a generic service station design and other public information related to the truck transport and storage of automotive gasoline, LPG, and anhydrous ammonia. Using that information, a review of applicable codes and standards, our knowledge of and experience with flammable fuels and liquefied gases, and good engineering practices; we determined the types of credible hazardous events that have some potential to occur in each phase of the transportation, storage, and fueling process. In general, these events can be divided into the following categories.

- (1) Small releases (leaks), characterized by a 1/4-inch (6.35 mm) diameter hole.
- (2) Moderate releases (punctures), characterized by a 1-inch (25.4 mm) diameter hole.
- (3) Large releases (ruptures), characterized by a hole with a diameter equal to the pipe diameter or, for vessels and associated equipment, a hole with a diameter equal to the diameter of the largest attached pipe.
- (4) Catastrophic failure of a vessel, characterized by a rapid release of its contents.

Potential releases of gasoline, LPG, and ammonia were considered for each phase of the study. For small, moderate, and large releases, each scenario was evaluated with and without emergency shutdown (ESD) activation. In the case where the ESD is activated, the release continues for no more than a set period of time (in the range of seconds for the ESD devices common to these types of fuel systems).

3.2 Introduction to Physiological Effects of Fires, Overpressure, and Ammonia

The QRA performed for use in comparing the risks associated with the three automotive fuels involved the evaluation of thousands of potential hazardous material releases. Each potential release may result in one or more of the following hazards.

- Exposure to thermal radiation from a torch fire, which is the result of ignition of a high velocity release of LPG.
- Exposure to the thermal radiation from a pool fire, which is the result of ignition of a pool of LPG or gasoline.
- Exposure to the heat of a flash fire, which is the result of delayed ignition of a flammable vapor cloud following a release of LPG or gasoline.
- Exposure to overpressure, which is the result of delayed ignition of a flammable vapor cloud created by a release of LPG or gasoline.
- Exposure to ammonia gas, which is the result of a release of anhydrous ammonia.

In order to compare the risks associated with each type of hazard listed above, a common measure of consequence must be defined. In risk analysis studies, a common measure for such hazards is their impact on humans. For each of the fire, overpressure, and ammonia hazards listed, there are data available that define the effect of the hazard on humans.

When comparing a flammable hazard to an overpressure hazard, the magnitude of the hazard's impact on humans must be identically defined. For instance, it would not be meaningful to compare human exposure to non-lethal overpressures (e.g., low overpressures that break windows) to human exposure to lethal thermal radiation (e.g., 37.5 kW/m² for one minute).

In this study, risk is defined as the potential exposure of humans to lethal hazards (i.e., radiant heat, overpressure or exposure to ammonia gas) that have the potential to occur as a result of accidents originating in the import terminal. The lethal exposure levels for the various hazards are discussed in the following sections.

3.2.1 Physiological Effects of Exposure to Thermal Radiation from Fires

The physiological effect of fire on humans depends on the rate at which heat is transferred from the fire to the person, and the time the person is exposed to the fire. Even short-term exposure to high heat flux levels may be fatal. This situation could occur when persons wearing ordinary clothes are inside a flammable vapor cloud (defined by the lower flammable limit) when it is ignited. Persons located outside a flammable cloud when it is ignited will be exposed to much lower heat flux levels. If the person is far enough from the edge of the flammable cloud, the heat flux will be incapable of causing fatal injuries, regardless of exposure time. Persons closer to the cloud, but not within it, will be able to take action to protect themselves (e.g., moving farther away as the flames approach, or seeking shelter inside structures or behind solid objects).

In the event of a continuous torch fire during the release of flammable gas or gas/aerosol, or a pool fire, the thermal radiation levels necessary to cause fatal injuries to the public must be defined as a function of exposure time. This is typically accomplished through the use of probit equations, which are based on experimental dose-response data.

$$Pr = a + b \cdot \ln(t \cdot K^n)$$

where: Pr = probit
 K = intensity of the hazard
 t = time of exposure to the hazard
 $a, b,$ and n = constants

The product $(t \cdot K^n)$ is often referred to as the “dose factor.” According to probit equations, all combinations of intensity K^n and time t that result in equal dose factors also result in equal values for the probit Pr and therefore produce equal expected fatality rates for the exposed population.

Work sponsored by the U.S. Coast Guard [Tsao and Perry, 1979] developed the following probit relationship between exposure time and incident heat flux.

$$Pr = -36.378 + 2.56 \cdot \ln(t \cdot I^{4/3})$$

where: t = exposure time, sec
 I = effective thermal radiation intensity, kW/m²

Table 3-1 presents the probit results for several exposure times that would be applicable for torch fires and pool fires. The mortality rates and corresponding thermal radiation levels are listed. The graphical form of the thermal radiation probit equation for different exposure times is presented in Figure 3-1.

Table 3-1
Hazardous Thermal Radiation Levels for Various Exposure Times

Exposure Time (sec)	Probit Value	Mortality Rate* (percent)	Incident Thermal Radiation Flux	
			(kW/m ²)	(Btu/(hr · ft ²))
5	2.67	1	27.87	8,833
	5.00	50	55.17	17,485
	7.33	99	109.20	34,610
15	2.67	1	12.22	3,873
	5.00	50	24.20	7,670
	7.33	99	47.39	15,178
30	2.67	1	7.27	2,304
	5.00	50	14.39	4,561
	7.33	99	28.47	9,025
60	2.67	1	4.32	1,369
	5.00	50	8.55	2,709
	7.33	99	16.93	5,365

*Percent of population fatally affected.

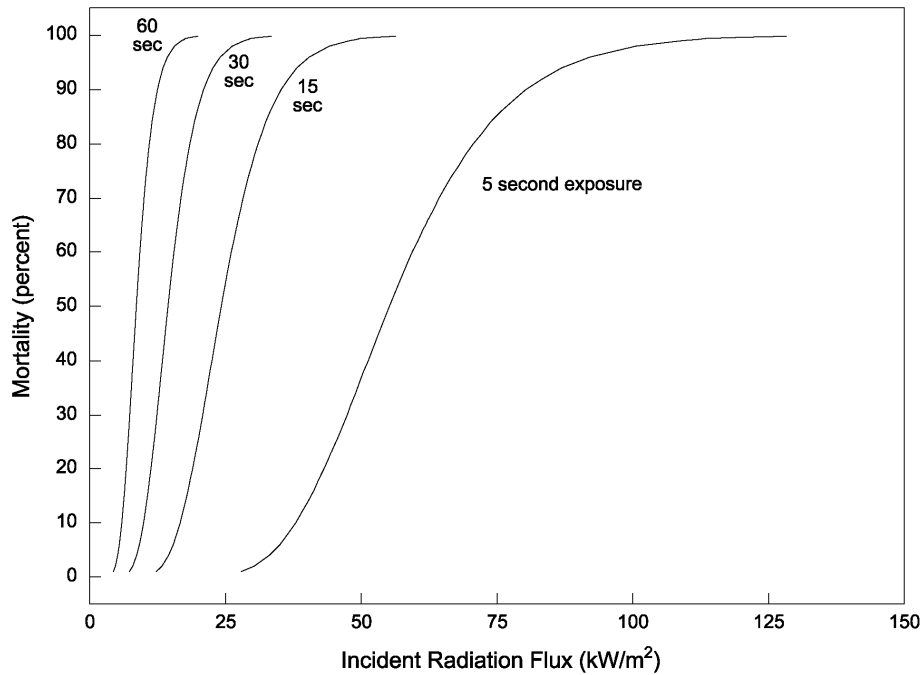


Figure 3-1
Thermal Radiation Probit Relations

The choice of thermal radiation flux levels is influenced by the duration of the fire and the potential time of exposure to the flame by an individual. All combinations of incident heat flux (*I*) and exposure time (*t*) that

result in equal values of “radiant dosage” ($t \cdot I^{4/3}$) produce equal expected mortality rates. An exposure time of 30 seconds was chosen for this analysis for torch fires and pool fires. People who are exposed to radiant hazards are aware of the hazards and know in which direction to move in a very short period of time.

3.2.2 Physiological Effects of Overpressures

The damaging effects of overpressures depend on the peak overpressure that reaches a given structure, and the method of construction of that structure, as illustrated by Table 3-2. Similarly, the physiological effects of overpressures depend on the peak overpressure that reaches the person. Exposure to high overpressure levels may be fatal. Persons located outside the flammable cloud when it ignites will be exposed to lower overpressure levels than persons within the flammable cloud. If the person is far enough from the edge of the burning cloud, the overpressure is incapable of causing fatal injuries.

**Table 3-2
Damage Produced by Blast Waves [Clancey, 1972]**

Overpressure		Damage
psig	kPag	
0.02	0.14	Annoying noise
0.04	0.28	Loud noise (143 dB)
0.15	1.0	Typical pressure for glass breakage
0.3	2.0	10% window glass broken
0.5 - 1.0	3.45-6.9	Large and small windows usually shattered; occasional damage to window frames
0.7	4.8	Minor damage to house structures
1.0	6.9	Partial demolition of houses, made uninhabitable
1.3	9.0	Steel frame of clad building slightly distorted
2.0	13.8	Partial collapse of walls and roofs of houses
2.3	15.8	Lower limit of serious structural damage
2.5	17.2	50% destruction of brickwork of houses
3.0	20.7	Steel frame building distorted and pulled away from foundations
3 - 4	20.7-27.6	Frameless, self-framing steel panel building demolished
4.0	27.6	Cladding of light industrial buildings ruptured
5.0	34.5	Wooden utility poles snapped
5.0 - 7.0	34.5-48.2	Nearly complete destruction of houses
7.0	48.3	Loaded railcars overturned
7.0 - 8.0	48.3-55.2	Brick panels, 8-12 inches (203-305 mm) thick, not reinforced, fail by shearing or flexure
9.0	62.1	Loaded train boxcars completely demolished

The vapor cloud explosion (VCE) calculations in this analysis were made with the Baker-Strehlow model. This model is based on the premise that the strength of the blast wave generated by a VCE is dependent on the reactivity of the flammable gas involved; the presence (or absence) of structures such as walls or ceilings that partially confine the vapor cloud; and the spatial density of obstructions within the flammable cloud [Baker, et al., 1994, 1998]. This model reflects the results of several international research programs on vapor cloud explosions and deflagrations, which show that the strength of the blast wave generated by a VCE increases as the degree of confinement and/or obstruction of the cloud increases. The following quotations illustrate this point.

“On the evidence of the trials performed at Maplin Sands, the deflagration [explosion] of truly unconfined flat clouds of natural gas or propane does not constitute a blast hazard.” [Hirst and Eyre, 1982] (Tests conducted by Shell Research Ltd. in the United Kingdom.)

“Both in two- and three-dimensional geometries, a continuous accelerating flame was observed in the presence of repeated obstacles. A positive feedback mechanism between the flame front and a disturbed flow field generated by the flame is responsible for this. The disturbances in the flow field mainly concern flow velocity gradients. Without repeated obstacles, the flame front velocities reached are low both in two-dimensional and three-dimensional geometry.” [van Wingerdan and Zeeuwen, 1983] (Tests conducted by TNO in the Netherlands.)

“The current understanding of vapor cloud explosions involving natural gas is that combustion only of that part of the cloud which engulfs a severely congested region, formed by repeated obstacles, will contribute to the generation of pressure.” [Johnson, Sutton, and Wickens, 1991] (Tests conducted by British Gas in the United Kingdom.)

Researchers who have studied case histories of accidental vapor cloud explosions have reached similar conclusions.

“It is a necessary condition that obstacles or other forms of semi-confinement are present within the explosive region at the moment of ignition in order to generate an explosion.” [Wiekema, 1984]

“A common feature of vapor cloud explosions is that they have all involved ignition of vapor clouds, at least part of which have engulfed regions of repeated obstacles.” [Harris and Wickens, 1989]

In the event of an ignition and deflagration of a flammable gas or gas/aerosol cloud, the overpressure levels necessary to cause injury to the public are often defined as a function of peak overpressure. Unlike potential fire hazards, persons who are exposed to overpressure have no time to react or take shelter; thus, time does not enter into the hazard relationship. Work by the Health and Safety Executive, United Kingdom [HSE, 1991], has produced a probit relationship based on peak overpressure. This probit equation has the following form.

$$Pr = 1.47 + 1.37 \cdot \ln(p)$$

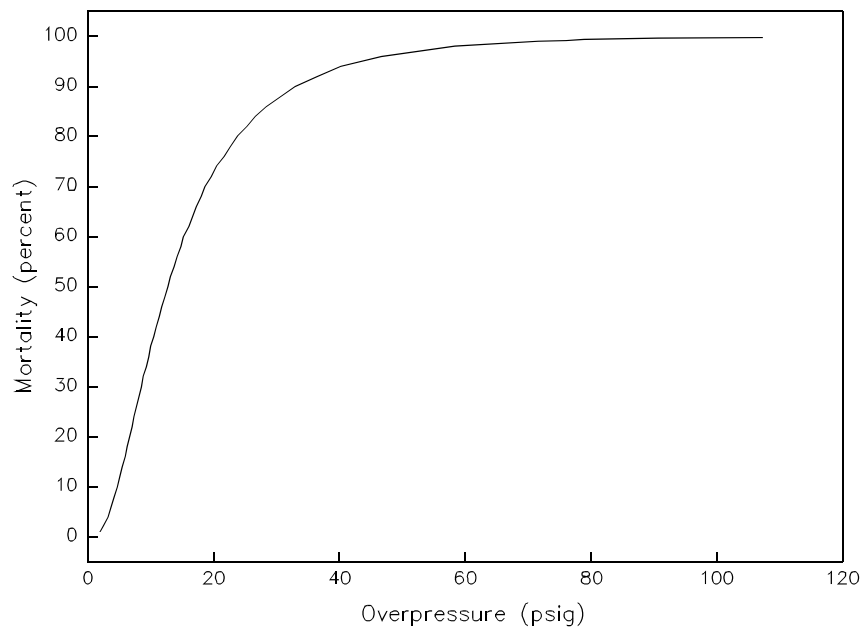
where: p = peak overpressure, psig

Table 3-3 presents the probit results for 1%, 50%, and 99% fatalities. The graphical form of the overpressure probit equation is presented in Figure 3-2.

**Table 3-3
Hazardous Overpressure Levels**

Probit Value	Mortality Rate* (percent)	Peak Overpressure	
		(psig)	(kPag)
2.67	1	2.4	16.55
5.00	50	13.1	90.73
7.63	99	72.0	496.83

*Percent of exposed population fatally affected.



**Figure 3-2
Overpressure Probit Relation**

3.2.3 Physiological Effects of Ammonia

Ammonia (NH₃) is a colorless, toxic gas with a low threshold limit value (TLV). NH₃ is detectable by odor at concentrations much less than those necessary to cause harm. This allows persons who smell the gas to escape. The most serious hazard presented by NH₃ is from a large release from which escape is not possible. Table 3-4 describes various physiological effects of NH₃.

**Table 3-4
Effects of Different Concentrations of Ammonia**

Description	Concentration (ppmv)	Reference
TLV (Threshold Limit Value)	25	ACGIH
The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hr without experiencing other than mild transient adverse health effects or perceiving a clearly defined objectionable odor.	25	ERPG-1
The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hr without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action.	150	ERPG-2
Concentration causing severe irritation of throat, nasal passages, and upper nasal tract.	400	Matheson
Concentration causing severe eye irritation.	700	Matheson
The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hr without experiencing or developing life-threatening health effects.	750	ERPG-3
Concentration causing coughing and bronchial spasms. Possibly fatal for exposure of less than one-half hour.	1,700	Matheson
Minimum concentration for the onset of lethality after 30-minute exposure (fatal to 1% of exposed population).	1,883	Perry and Articola
Minimum concentration for 50% lethality after 30-minute exposure (fatal to 50% of exposed population).	4,005	Perry and Articola
Minimum concentration for 99% lethality after 30-minute exposure (fatal to 99% of exposed population).	8,519	Perry and Articola

ACGIH (1995), *1995-1996 Threshold Limit Values (TLVs) for Chemical Substances and Physical Agents and Biological Exposure Indices (BEIs)*. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1995 (ISBN: 1-882417-11-9)

ERPG (2008), *Emergency Response Planning Guidelines*. American Industrial Hygiene Association, Akron, Ohio, 2008. <http://www.aiha.org/1documents/Committees/ERP-erpglevels.pdf>

Matheson (1961), - *Matheson Gas Data Book* (Matheson Company, 1961).

Perry, W. W., and W. P. Articola (1980), – “Study to Modify the Vulnerability Model of the Risk Management System.” U.S. Coast Guard, Report CG-D-22-80, February, 1980.

Physiological effects of airborne toxic gases depend on the concentration of the toxic vapor in the air being inhaled, and the length of time an individual is exposed to this concentration. The combination of concentration and time is referred to as “dosage.” In risk studies that involve toxic gases, probit equations are commonly used to quantify the expected rate of fatalities for the exposed population.

A probit equation for NH₃ uses the values of -28.33, 2.27, and 1.36 for the constants *a*, *b*, and *n*, respectively [Perry and Articola, 1980]. Substituting these values into the general probit equation yields the following probit equation for NH₃.

$$Pr = -28.33 + 2.27 \ln(C^{1.36} \cdot t)$$

Dispersion calculations are often performed assuming a one-hour exposure to the gas. This is particularly true with air pollution studies since these studies are typically concerned with long-term exposures to low concentration levels. For accidental releases of toxic gases, shorter exposure times may be warranted since the durations of many accidental releases are less than an hour. In this study, the calculations were performed for various exposure times (and concentration levels), dependent on the duration and nature of the release.

When using a probit equation, the value of the probit (*Pr*) that corresponds to a specific dose factor must be compared to a statistical table to determine the expected fatality rate. For example, if *Pr* = 2.67, the expected fatality rate is 1%. Using the Perry and Articola probit equation given above, the dose factor that equates to a 1% fatality rate is 1,131 ppmv for sixty minutes, or 1,883 ppmv for thirty minutes, or 3,135 ppmv for fifteen minutes, etc., as shown in Table 3-5. Table 3-5 presents the mortality rates, dosage levels, and NH₃ concentrations for various exposure times, while Figure 3-3 presents the same information in graphical form.

Table 3-5
Hazardous Ammonia Concentration Levels for Various Exposure Times

Exposure Time (minutes)	Probit Value	Mortality Rate* (percent)	NH ₃ Dosage (ppmv ^{1.36} -min)	NH ₃ Concentration (ppmv)
5	2.67	1	853,000	7,031
	5.00	50	2.38 x 10 ⁶	14,955
	7.33	99	6.64 x 10 ⁶	31,809
15	2.67	1	853,000	3,135
	5.00	50	2.38 x 10 ⁶	6,667
	7.33	99	6.64 x 10 ⁶	14,182
30	2.67	1	853,000	1,883
	5.00	50	2.38 x 10 ⁶	4,005
	7.33	99	6.64 x 10 ⁶	8,519
60	2.67	1	853,000	1,131
	5.00	50	2.38 x 10 ⁶	2,406
	7.33	99	6.64 x 10 ⁶	5,117

*Percent of exposed population fatally affected.

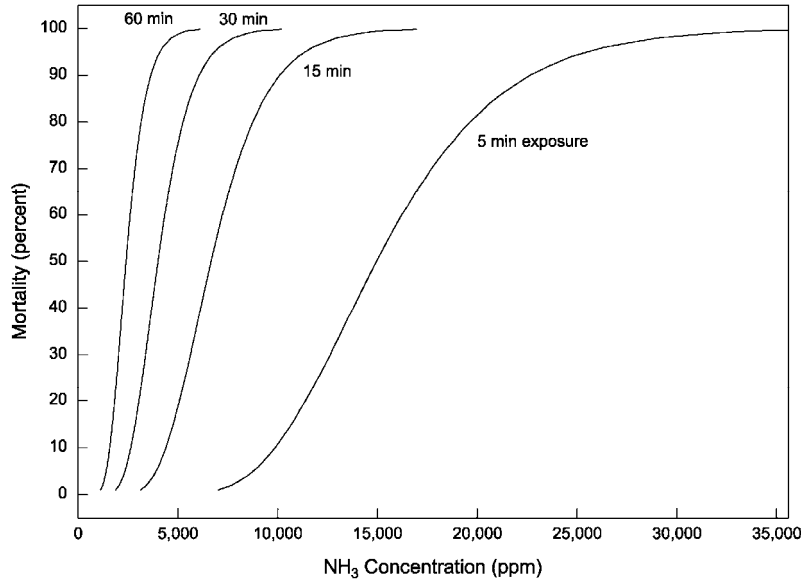


Figure 3-3
Ammonia Probit Relations

3.3 Consequence Analysis

3.3.1 Consequence Analysis Models

Each selected release scenario was evaluated to determine the extent and location of the hazards. When performing site-specific consequence analysis studies, the ability to accurately model the release, dilution, and dispersion of gases and aerosols is important if an accurate assessment of potential exposure is to be attained. For this reason, Quest uses a modeling package, CANARY by Quest®, that contains a set of complex models that calculate release conditions, initial dilution of the vapor (dependent upon the release characteristics), and the subsequent dispersion of the vapor introduced into the atmosphere. The models contain algorithms that account for thermodynamics, mixture behavior, transient release rates, gas cloud density relative to air, initial velocity of the released gas, and heat transfer effects from the surrounding atmosphere and the substrate. The release and dispersion models contained in the QuestFOCUS package (the predecessor to CANARY by Quest) were reviewed in a United States Environmental Protection Agency (EPA) sponsored study [TRC, 1991] and an American Petroleum Institute (API) study [Hanna, Strimaitis, and Chang, 1991]. In both studies, the QuestFOCUS software was evaluated on technical merit (appropriateness of models for specific applications) and on model predictions for specific releases. One conclusion drawn by both studies was that the dispersion software tended to over predict the extent of the gas cloud travel, thus resulting in too large a cloud when compared to the test data (i.e., a conservative approach).

A study prepared for the Minerals Management Service [Chang, et al., 1998] reviewed models for use in modeling routine and accidental releases of flammable and toxic gases. CANARY by Quest received the highest possible ranking in the science and credibility areas. In addition, the report recommends CANARY by Quest for use when evaluating toxic and flammable gas releases. The specific models (e.g., SLAB) contained in the CANARY by Quest software package have also been extensively reviewed.

CANARY also contains models for pool fire and torch fire radiation. These models account for impoundment configuration, material composition, target height relative to the flame, target distance from the flame,

atmospheric attenuation (includes humidity), wind speed, and atmospheric temperature. Both are based on information in the public domain (published literature) and have been validated with experimental data.

For vapor cloud overpressure calculations, CANARY employs the Baker-Strehlow method. It accounts for the reactivity of the fuel in the vapor cloud, the size of the flammable vapor cloud, and the degree to which the vapor cloud is obstructed or confined. The model is based on experimental and historical observations of vapor cloud explosions and deflagrations, with relation to the amount of confinement and obstruction present in the volume occupied by the vapor cloud.

Technical descriptions of the CANARY models used in this study are presented in Appendix A.

All releases were fully evaluated with the CANARY software. A partial list of the release scenarios identified for this analysis is given in Table 3-6. For each case identified, several potential hazardous outcomes might be possible. These outcomes were identified by the construction of event trees for each release.

**Table 3-6
Initial Fluid Conditions for Selected Release Scenarios**

Description	Fluid Temperature (°F)	Fluid Pressure (psia)
Road transport of gasoline	80	14.7
Road transport of LPG	80	145
Road transport of anhydrous ammonia	-28	14.7
Storage of gasoline	80	14.7
Storage of LPG	80	145
Storage of anhydrous ammonia	-28	14.7
Automobile fueling of gasoline	80	25
Automobile fueling to LPG	80	200
Automobile fueling of anhydrous ammonia	80	210

3.3.2 Release Event Trees

For any single release from a vessel or piping system, several different hazards may occur, dependent on such factors as availability of ignition sources and the reactivity of the material (for overpressure potential). The chance that any single event will result from a release of material is dependent on these factors, as well as the “size” of the release. For this work, the release size was divided into three categories.

- (1) Small releases (leaks), characterized by a 1/4-inch (6.35 mm) diameter hole.
- (2) Moderate releases (punctures), characterized by a 1-inch (25.4 mm) diameter hole.
- (3) Large releases (ruptures), characterized by a hole with a diameter equal to the pipe diameter or, for vessels and certain process equipment, a hole with a diameter equal to the diameter of the largest attached pipe.

One of the event trees prepared for this study is presented in Figure 3-4. It begins with the release of LPG from a welded metal pipe associated with the storage bullet on the service station property. Moving from left

to right, the tree first branches into three leak sizes, each being identified by the diameter of the hole through which the fluid is being released. Each of these three branches divides into three branches based upon the ignition timing and probability. Immediate ignition of the release results in a pool fire and/or a torch fire. Each delayed ignition branch divides again into two branches: flash fire (and subsequent pool/torch fire) and vapor cloud deflagration (explosion). If the release does not find an ignition source, the outcome is dissipation of the hazardous fluid. The far right of the event tree shows twelve “outcomes” that have some probability of occurring if the release occurs. The probabilities of the event outcomes are developed in Section 4.

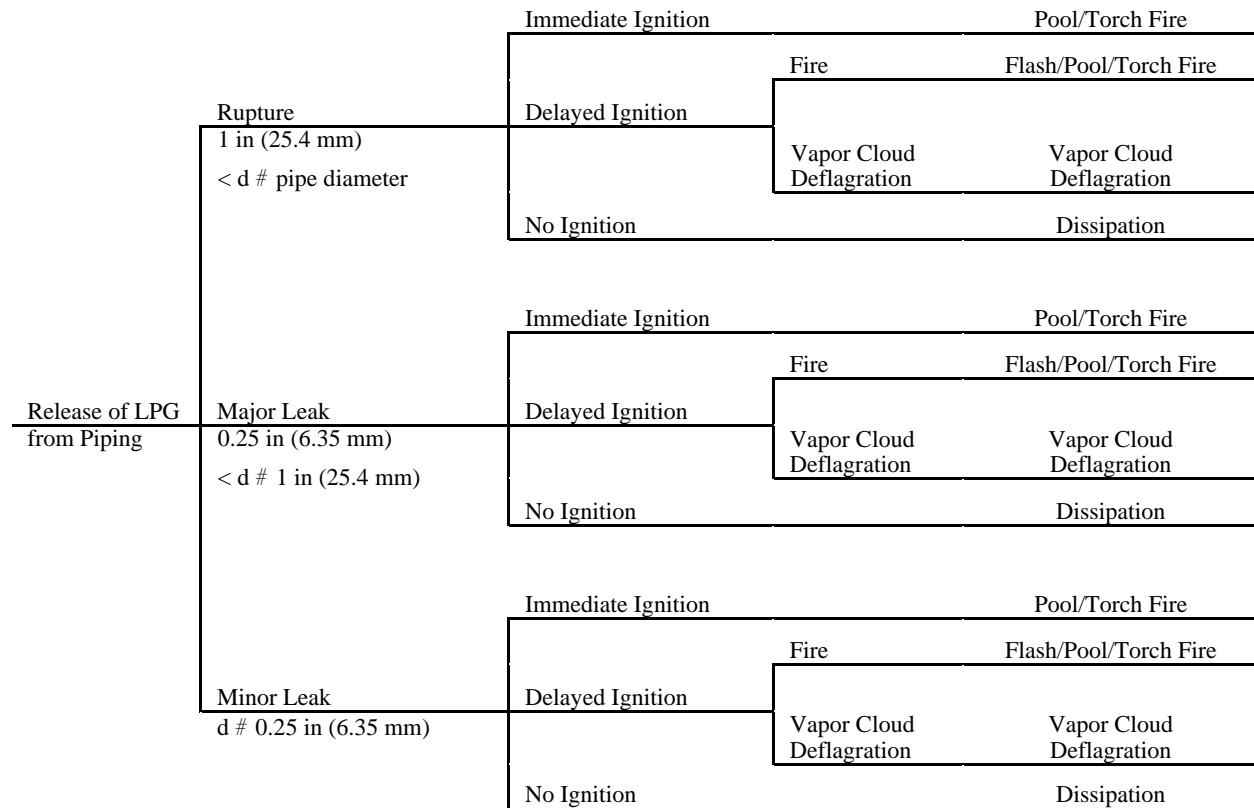


Figure 3-4
Event Tree for a Flammable Release

A similar event tree could be constructed for a release of anhydrous ammonia from a storage bullet on the service station property. Although ammonia/air mixtures can be ignited, it is difficult to do so in an open environment. Thus, for the purposes of this study, all anhydrous ammonia releases were assumed to disperse without ignition and form a toxic cloud hazard.

3.4 Summary of Consequence Analysis Results

Table 3-7 presents a summary of the rupture scenario hazard distances for three fuels under two different weather conditions for a range of releases associated with the road transport, storage, and fueling activities. The table lists the downwind ground level distances to the specified hazard endpoints for a low wind and stable atmosphere condition (1.03 m/s and F stability) and an average atmospheric case (4.63 m/s and D stability).

**Table 3-7
Hazard Distances for Rupture Releases Associated with the Road Transport, Storage, and Fueling
of Gasoline, LPG, and Anhydrous Ammonia**

Release Description	Weather Conditions: Wind Speed (m/s) and Stability	Distance (ft) from Release to Fatality Level							
		Flash Fire (LFL)	Ammonia Toxicity				Pool/Torch Fire Thermal Radiation		
			100%	1%	50%	99%	1%	50%	99%
Catastrophic failure of gasoline road tanker	1.03/F	20	-	-	-	50	35	25	
	4.63/D	15	-	-	-	70	55	40	
Catastrophic failure of LPG road tanker	1.03/F	970	-	-	-	480	470	465	
	4.63/D	720	-	-	-	480	470	465	
Catastrophic failure of refrigerated anhydrous ammonia road tanker	1.03/F	-	560	265	155	-	-	-	
	4.63/D	-	125	60	25	-	-	-	
BLEVE of LPG road tanker	all	-	-	-	-	400	245	220	
Unloading hose failure during gasoline unloading	1.03/F	10	-	-	-	20	15	10	
	4.63/D	10	-	-	-	25	20	15	
Unloading hose failure during LPG unloading	1.03/F	80	-	-	-	20	10	5	
	4.63/D	45	-	-	-	30	20	5	
Unloading hose failure during refrigerated anhydrous ammonia unloading	1.03/F	-	80	75	15	-	-	-	
	4.63/D	-	15	10	5	-	-	-	
Piping rupture on LPG storage vessel	1.03/F	180	-	-	-	70	50	20	
	4.63/D	125	-	-	-	75	60	50	
Piping rupture refrigerated anhydrous ammonia storage vessel (in vault)	1.03/F	-	*	*	*	-	-	-	
	4.63/D	-	*	*	*	-	-	-	
Gasoline automobile fueling hose failure	1.03/F	<5	-	-	-	<5	<5	<5	
	4.63/D	<5	-	-	-	<5	<5	<5	
LPG automobile fueling hose failure	1.03/F	<5	-	-	-	<5	<5	<5	
	4.63/D	<5	-	-	-	<5	<5	<5	
Anhydrous automobile fueling hose failure	1.03/F	-	<5	<5	<5	-	-	-	
	4.63/D	-	<5	<5	<5	-	-	-	

SECTION 4

ACCIDENT FREQUENCY

The likelihood of a particular accident occurring within some specific time period can be expressed in different ways. One way is to state the statistical probability that the accident will occur during a one-year period. This annual probability of occurrence can be derived from failure frequency data bases of similar accidents that have occurred with similar systems or components in the past.

Most data bases (e.g., CCPS [1989], OREDA [1984]) that are used in this type of analysis contain failure frequency data (e.g., on the average, there has been one failure of this type of equipment for 347,000 hours of service). By using the following equation, the annual probability of occurrence of an event can be calculated if the frequency of occurrence of the event is known.

$$p = 1 - e^{(-\lambda \cdot t)}$$

where: p = annual probability of occurrence (dimensionless)
 λ = annual failure frequency (failures per year)
 t = time period (one year)

If an event has occurred once in 347,000 hours of use, its annual failure frequency is computed as follows.

$$\lambda = \frac{1 \text{ event}}{347,000 \text{ hours}} \cdot \frac{8,760 \text{ hours}}{\text{year}} = 0.0252 \text{ events/year}$$

The annual probability of occurrence of the event is then calculated as follows.

$$p = 1 - e^{(-0.0252 \cdot 1)} = 0.0249$$

Note that the frequency of occurrence and the probability of occurrence are nearly identical. (This is always true when the frequency is low.) An annual probability of occurrence of 0.0249 is approximately the same as saying there will probably be one event per forty years of use.

Due to the scarcity of accident frequency data bases, it is not always possible to derive an exact probability of occurrence for a particular accident. Also, variations from one system to another (e.g., differences in design, construction, operation, maintenance, or mitigation measures) can alter the probability of occurrence for a specific system. Therefore, variations in accident probabilities are usually not significant unless the variation approaches one order of magnitude (i.e., the two values differ by a factor of ten).

The following subsections describe the basis and origin of failure frequency rates used in this analysis. In general, industry databases were used due to the absence of equipment-specific failure rate data for operations in the service station.

4.1 Process Piping Failure Rates

WASH-1400 [USNRC, 1975] lists the failure rates for piping as 1.0×10^{-10} /hour for pipes greater than 3 inches (76 mm) in diameter, and 1.0×10^{-9} /hour for smaller pipes. These rates are based on a “section” of pipe, i.e., 1.0×10^{-10} failures per section of > 3 inch (76 mm) pipe/hour. A section of pipe is defined as any straight portion of pipe of welded construction between any two fittings (such as flanges, valves, strainers, elbows, etc.). CCPS [1989] gives a mean pipe failure rate of 2.68×10^{-8} /mile/hour (4.31×10^{-8} /km/hour). This would be approximately the same as the WASH-1400 rate, 1.0×10^{-9} /section/hour (8.76×10^{-6} /section/year), if the average section of pipe were about 200 feet (61 meters) in length.

Most data bases of pipe failure rates are not sufficiently detailed to allow a determination of the failure frequency as a function of the size of the release (i.e., size of the hole in the pipe). However, British Gas has gathered such data on piping releases [Fearnough, 1985]. The data show that well over 90% of all failures are less than a 1-inch (25-mm) diameter hole, and only 3% are greater than a 3-inch (76-mm) diameter hole. Since most full ruptures of piping systems are caused by outside forces, full ruptures are expected to occur more frequently on small-diameter pipes.

Based on the above discussion, the expected failure rates for aboveground, metallic piping with no threaded connections are assumed to be as follows.

For pipes from 1 inch (25 mm) to 3 inches (76 mm) in diameter:

<u>Hole size</u>	<u>up to ¼ inch</u>	<u>¼ inch to 1 inch</u>	<u>1 inch to full rupture</u>
Expected failure rate	2.25×10^{-8} /foot/year (7.30×10^{-8} /m/year)	1.8×10^{-8} /foot/year (5.91×10^{-8} /m/year)	4.5×10^{-9} /foot/year (1.47×10^{-8} /m/year)

For pipes greater than 3 inches (76 mm) in diameter:

<u>Hole size</u>	<u>up to ¼ inch</u>	<u>¼ inch to 1 inch</u>	<u>1 inch to full rupture</u>
Expected failure rate	2.25×10^{-8} /foot/year (7.38×10^{-8} /m/year)	2.0×10^{-8} /foot/year (6.56×10^{-8} /m/year)	2.5×10^{-9} /foot/year (8.20×10^{-9} /m/year)

4.2 Valves

WASH-1400 [USNRC, 1975] lists a failure rate of 1.0×10^{-8} failures/hour for external leakage or rupture of valves. Assuming continuous service, the annual leakage/rupture rate is approximately 8.8×10^{-5} /year. Unfortunately, this number includes very small leaks, as well as valve body ruptures. This reduces the usefulness of this failure rate since the probability of a small leak from a valve bonnet gasket is obviously much greater than the probability of a 1-inch (25-mm) hole in the valve body. To overcome this difficulty, the valve body can be considered similar to pipe, and the valve bonnet gasket can be treated like other gaskets. To be conservative, each flanged valve is considered to have a failure rate equal to a 10-foot (3-m) section of pipe and one gasket. Similarly, a threaded valve is treated like 10 feet (3 m) of pipe, one gasket, and one screwed fitting.

4.3 Pressure Vessel Failure Rates

CCPS [1989] reports a failure rate of 1.09×10^{-8} /hour for pressure vessels. For continuous service, the annual expected failure rate for pressure vessels would be 9.5×10^{-5} failures/year. Bush [1975] made an

in-depth study of pressure vessels of many types, including boilers. In Bush's study, the rate of "disruptive" failures of pressure vessels was 1.0×10^{-5} /year, i.e., a factor of ten less than the CCPS value. The explanation for this difference lies in the definition of "failure." Bush's number is based on "disruptive" failures which are assumed to be failures of such magnitude that the affected vessel would need to be taken out of service immediately for repair or replacement. The data base reported by the CCPS most likely includes smaller leaks that Bush categorized as "non-critical."

Smith and Warwick [1981] analyzed the failure history of a large number of pressure vessels (about 20,000) in the United Kingdom. They present a short description of each failure, thus allowing the failures to be categorized by size. Most of the failures were small leaks (approximately half can be categorized as smaller than a 1-inch diameter hole).

Based on the previous discussion, the following failure rates are proposed for pressurized process vessels.

Hole size	up to ¼ inch	¼ inch to 1 inch	1 inch to full rupture
Expected failure rate	3.0×10^{-5} /year	4.0×10^{-5} /year	5.0×10^{-6} /year

4.4 Pump Failure Rates

Green and Bourne [1972] list the failure rate for "rotating seals" as 7.0×10^{-6} /hour. Assuming continuous operation (i.e., 8,760 hours/year), the annual expected failure rate is 6.0×10^{-2} failures/year/seal. For pumps fitted with double mechanical seals, a major seal leak occurs only if both seals fail. If the two seal failures were always caused by independent events, the failure rate for a double seal configuration would be the square of the single seal failure rate, i.e., about 3.6×10^{-3} failures/year. However, some causes of seal failure can result in the simultaneous failure of both seals (e.g., bearing failures, excessive vibration, improper installation, etc.). Thus, the failure rate is somewhere between 6.0×10^{-2} /year and 3.6×10^{-3} /year. In the absence of hard data, we have assumed the failure rate for double mechanical seals is 5.0×10^{-3} /year.

4.5 Road Tanker Accident Rates

Battelle produced a report titled *Comparative Risks of Hazardous Materials and Non-Hazardous Materials Truck Shipment Accidents/Incidents* in March, 2001 [Battelle, 2001]. This report covers a wide range of topics and materials and does contain sufficient information to develop an accident rate for each class of materials and data defining what fraction of accidents result in a release of material. Since this report contained data for the truck transport of gasoline, LPG, and anhydrous ammonia, it can be relied upon to produce a consistent evaluation of the relative accident frequencies needed for this comparative risk analysis.

4.5.1 Gasoline Road Tanker Accident Rates

Gasoline is included in Hazardous Material Category 3 (HM 3). According to the 2001 Battelle report, the truck transport of this class of materials (flammable and combustible liquids) during 1997 (data from the Commodity Flow Survey for 1997) covered 2,800,000,000 miles. During 1997, there were a total of 1,379 tank truck accidents involving gasoline (the primary component of HM Class 3) and other flammable and combustible liquids. Of these 1,379 road tanker accidents, 889 did not result in a release of material. The remaining 490 road tanker accidents did result in a release of material from the road tanker. Using the number of road tanker accidents that resulted in a release of material (490) and the total

number of tank truck miles (2,800,000,000), an accident rate for HM 3 can be calculated as $1.75 \times (10)^{-7}$ releases per mile traveled per truck.

4.5.2 LPG Road Tanker Accident Rates

LPG is classified as a flammable gas and is contained in Hazardous Material Category 2.1 (HM 2.1). During the same 1997 calendar year, HM 2.1 tank trucks traveled a total of 805,000,000 miles. During 1997 there were 276 road tanker accidents involving HM 2.1 tank trucks, with 47 of these accidents resulting in a release of material. Thus, the accident rate for HM 2.1 is found to be $5.84 \times (10)^{-8}$ releases per mile traveled per truck.

4.5.3 Anhydrous Ammonia Road Tanker Accident Rates

Anhydrous ammonia (shipped as a liquefied gas by pressure or by refrigeration) is classified as a non-flammable gas in the United States and is contained in Hazardous Material Category 2.2 (HM 2.2). During 1997, HM 2.2 tank trucks traveled a total of 1,400,000,000 miles and were involved in 178 accidents. Of the 178 accidents, 26 resulted in a release of material. Using this data results in a HM 2.2 tank truck release rate of $1.9 \times (10)^{-8}$ releases per mile traveled per truck. This rate is approximately half the rate for than HM 2.1 which includes LPG. It should be expected that the release rates for LPG tank trucks and anhydrous ammonia tank trucks are similar since they use nearly identical pressure vessels for the tanks.

4.6 Effect of Noncontinuous Use

Components such as tanks, pipelines, heat exchangers, etc., are typically in continuous use. The annual probability of failure of such a component should be based on 8,760 hours of operation per year (365 days/year \times 24 hours/day = 8,760 hours/year).

Some components are used only intermittently. Examples of such components include hoses and articulated metal “arms” that are used for loading or unloading ships, tank trucks, and railcars. The annual probability of failure of such a component should be based on the actual number of hours the component is used during one year.

$$\lambda = \frac{4.5 \text{ failures}}{1,000,000 \text{ hours}} \cdot \frac{1,460 \text{ hours}}{\text{year}} = 6.57 \times 10^{-3} \text{ failures/year}$$

The standard equation is then used to compute the annual probability of failure of the hose.

$$p = 1 - e^{(-\lambda \cdot t)}$$

where: p = annual probability of occurrence (dimensionless)

λ = annual failure frequency (failures per year)

t = time period (one year)

$$p = 1 - e^{(-0.00657 \cdot 1)} = 6.57 \times 10^{-3}$$

4.7 ESD System Failure Rate

Emergency shutdown (ESD) systems are often activated in response to an accidental release of hazardous fluid. Depending on the design of the ESD system and the operating/control philosophy of the facility, the ESD might be activated automatically in response to hazard detectors (such as combustible gas detectors or fire detectors) or process alarms (such as loss of pressure within a pipe), or they might be activated by an operator pushing an ESD button. Such systems typically have little effect on the failure rate of plant equipment since they normally operate only in response to a release, but they can affect the duration of the release, thereby affecting the consequences of the release.

4.8 Human Error

The probability of occurrence of any specific accident can be influenced by human error. However, in most situations, it is not possible to quantify this influence. Fortunately, it is seldom necessary to attempt such quantification.

There are two general forms in which human error can contribute to the failure of a component or system of components. The first form, which is implicit in nature, includes poor component design, improper specification of components, flawed manufacturing, and improper selection of materials of construction, and similar situations that result in the installation and use of defective components or the improper use of non-defective components. The second form, which is explicit in nature, includes improper operation and improper maintenance.

Most of the available equipment failure rate data bases do not categorize the causes of the failures. Whether the rupture of a pipe is due to excessive corrosion, poor design, improper welding procedure, or some other cause, the rupture is simply added to the data base as one "pipe failure." Thus, since implicit human errors manifest themselves in the form of component failures, they are already included in the failure rate data bases for component failures.

Many types of explicit human errors also manifest themselves in the form of component failures. Therefore, like implicit human errors, component failures caused by explicit human errors are already included in the failure rate data bases for component failures. For example, if a pump seal is improperly installed (improper maintenance) and it begins to leak after several hours of operation, it would simply be recorded in a failure rate data base as one "pump seal failure." Similarly, if an operator responds improperly (improper operation) to a high pressure alarm and the pressure continues to increase, ultimately resulting in the rupture of a pipe, the event is recorded in a failure rate data base as a "pipe rupture."

Except in rare cases, there is little reason to believe that equipment failures due to implicit or explicit human errors will occur more often or less often in a specific facility than in the facilities that contributed failure rate data to the data bases. Therefore, component failure rates obtained from historical data bases can nearly always be used without being modified to account for human error.

Accidents that are the result of explicit human errors, but do not involve failures of components, are not included in typical failure rate data bases. Examples of such accidents include overfilling a tank (resulting in a liquid spill), opening a flanged connection on a piping system that has not been properly drained and purged (resulting in a leak of gas or liquid), opening a water-draw-off valve on an LPG tank and then walking away (resulting in a release of LPG), etc.

The contribution of explicit human error to the frequency of accidents that do not involve the failure of components can sometimes be estimated by techniques such as fault tree analysis or event tree analysis. These techniques are used to illustrate how the occurrence of an accident is the result of a chain of events or the simultaneous occurrence of several events. These events can be component failures or human failures. Using these techniques, the probability of occurrence of the accident can be quantified if the probability of occurrence of every event that contributes to the accident can be quantified. In many cases, there is insufficient historical data for some of the events. (This is particularly true for human error events.) Thus, assumed values must often be used. This inevitably leads to questions regarding the accuracy or applicability of the estimated probability of occurrence of the accident.

In the analysis that is the subject of this report, the accidents of interest all involve the failure of a physical component of a process system. Thus, frequencies of occurrence of these accidents (which are based on component failure rates obtained from historical data bases) need not be increased or decreased to account for human error.

SECTION 5

RISK QUANTIFICATION

The trucks and service station facilities handling automotive gasoline, LPG, and anhydrous ammonia pose no danger to people as long as toxic/flammable liquid or gas is not released into the environment. In the event of an accident that results in a release of toxic/flammable fluid, persons near the release point may be at risk due to the potential impacts following a release.

5.1 Risk Quantification Methodology

The risk posed by hazardous materials is often expressed as the product of the probability of occurrence of a hazardous event and the consequences of that event. Therefore, in order to quantify the risk associated with hazardous fluids, it is necessary to quantify the probabilities of accidents that would release the fluids into the environment, and the consequences of such releases. The release frequencies and potential consequences must then be combined using a consistent, accepted methodology that accounts for the influence of weather conditions and other pertinent factors.

The risk quantification methodology used in this study has been successfully employed in QRA studies that have undergone regulatory review in several countries worldwide. The following is a brief description of the steps involved in quantifying the risk due to the transportation and use of the three automotive fuels that are the subject of this work.

Conceptually, performing a risk analysis is straightforward. For example, for releases of flammable fluid such as LPG, the analysis can be divided into the following steps.

- Step 1. Within each “area” (e.g., truck transport or service station) being considered in the study, identify the full range of potential releases that would create a flammable gas cloud, torch fire, or pool fire.
- Step 2. Determine the frequency of occurrence of each of these releases.
- Step 3. Calculate the size of each potentially fatal impact zone created by each of the releases identified in Step 1.
 - i. The hazards of interest are:
 - a. Exposure to flash fires.
 - b. Thermal radiation from torch fires, pool fires, and BLEVE fireballs.
 - c. Overpressure from vapor cloud explosions.
 - ii. The size of each impact zone is a function of one or more of the following factors.
 - a. Orientation of the release (e.g., vertical or horizontal).
 - b. Wind speed.
 - c. Atmospheric stability.
 - d. Local terrain (including diking and drainage).
 - e. Composition, pressure, and temperature of fluid being released.
 - f. Hole size.
 - g. Vessel inventories.
 - h. Diameter of the liquid pool.

Step 4. Determine the risk to people in the vicinity of the roadway (truck accidents) or service station (storage and fueling accidents).

- i. The potential exposure of any individual to a specific impact zone depends on the following factors.
 - a. Size (area) of the impact zone.
 - b. Location of the individual, relative to the release location.
 - c. Wind direction.
- ii. Determine the exposure of each person to each potential impact zone.
 - a. Perform flash fire (flammable vapor dispersion) impact zone calculations for all wind directions, wind speeds, atmospheric stabilities, terrain conditions, and release orientations.
 - b. Perform vapor cloud explosion (following flammable vapor dispersion) impact zone calculations for all wind directions, wind speeds, atmospheric stabilities, terrain conditions, and release orientations.
 - c. Perform torch fire and pool fire thermal radiation zone calculations for all wind speeds and wind directions.
- iii. Modify each of the above exposures by its probability of occurrence. Probabilities are divided into the following groups.
 - a. $P(wd,ws,stab)$ = probability that the wind blows from a specified direction (wd), with a certain wind speed (ws), and a given atmospheric stability class, A through F (stab). Meteorological data are generally divided into sixteen wind directions, six wind speed classes, and six Pasquill-Gifford atmospheric stability categories. Although all 576 combinations of these conditions do not exist, a significant number will exist for each release studied. Figure 5-1 represents a representative wind speed versus stability distribution for the many sites in the central United States.

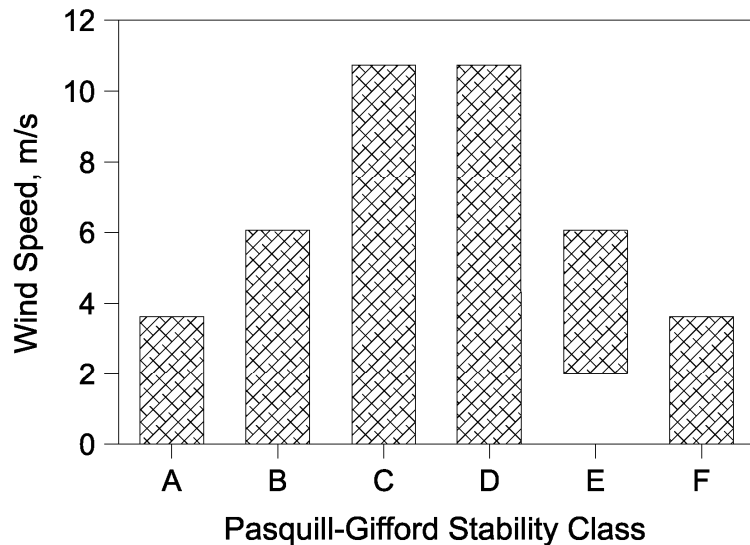


Figure 5-1
Wind Speed Versus Stability for the Central United States

- b. $P(acc)$ = probability of occurrence of each release identified in Step 2.
- c. $P(ii)$ = probability of immediate ignition (i.e., probability that ignition occurs nearly simultaneously with the release).

- d. $P(di)$ = probability of delayed ignition (i.e., probability that ignition occurs after a vapor cloud has formed).
 - e. $P(orientation)$ = probability that hazardous fluid is released into the atmosphere in a particular orientation.
- iv. Sum the potential exposures from each of the hazards for all releases identified in Step 1. This summation requires modifying each potential impact zone by its probability of occurrence (for example, the probability of a delayed torch fire is $P(acc) \cdot P(orientation) \cdot P(ws,wd) \cdot P(di)$.)

The methodology for calculating the risk due to a toxic material such as ammonia is similar. The hazard listed in Step 1 and Step 3(i) is simply exposure to toxic gas. The remaining steps are modified accordingly.

5.2 Risk Presentation

Professionals in risk analysis realize there is no single measure that completely describes the risk a project poses to the public or the project's workers. Measures that have been used by risk analysts include hazard footprints, risk contours, and f/N curves.

5.2.1 Hazard Footprints and Vulnerability Zones

When conducting a quantitative risk analysis, it is necessary to determine the probability of occurrence and the consequences of each possible combination of:

- hole size,
- release orientation,
- release outcome,
- wind speed,
- atmospheric stability, and
- wind direction

for each potential release that is included in the study. For each potential release, each combination of these factors results in a "unique accident."

A hazard footprint can be defined as the area over which a given unique accident is capable of producing some level of undesirable consequences (e.g., 1% mortality). A vulnerability zone is defined as the area within the circle created by rotating a hazard footprint around its point of origin. Any point within that circle could, under some set of circumstances, be exposed to a hazard level that equals or exceeds the endpoint used to define the hazard footprint. Except for accidents that produce circular hazard footprints, the whole area within a vulnerability zone cannot be simultaneously affected by the effects of a unique accident. This is illustrated in Figure 5-2 by a generic example of a flammable vapor cloud hazard footprint (cross-hatched area) and its vulnerability zone. In addition, many "smaller" accidents might be capable of producing hazard footprints that would affect parts of the vulnerability zone associated with a "large" accident.

Vulnerability zones can be used to define the size and shape of the area around a release within which there is a finite probability of exposure to a fatal hazard. Persons located outside this area would not be at risk from accidents involving flammable materials released from that location.

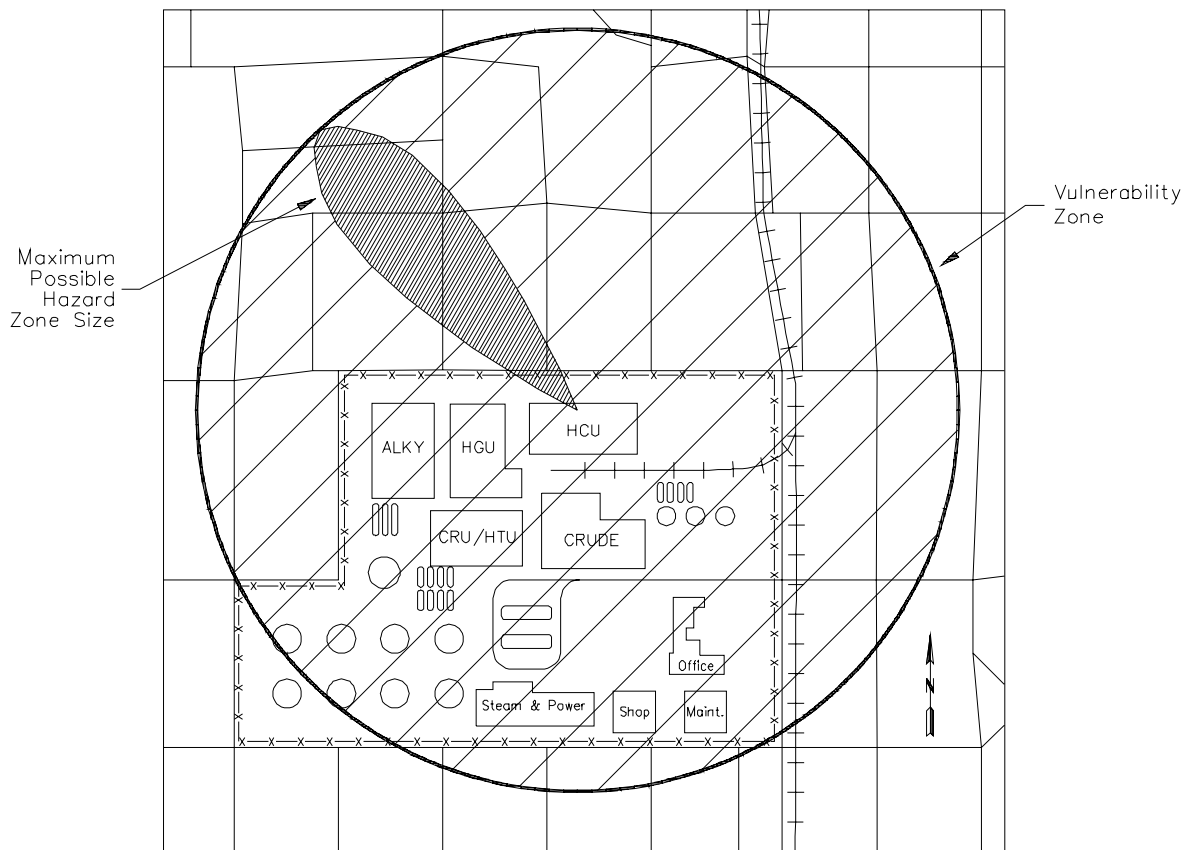


Figure 5-2
Example Hazard Footprint and Vulnerability Zone

5.2.2 Risk Contours

The results of all possible unique accidents can be combined to produce a measure of the overall risk presented by the subject of the study. The measure of risk must be in a form that is easy to interpret and can be compared to risk criteria and/or risks associated with ordinary human activities.

One presentation method that meets these criteria is the use of risk contours. An example of risk contours is presented in Figure 5-3. If early fatality is the measure of risk, then each risk contour is the locus of points where there exists a specific probability of being exposed to a fatal hazard, over a one-year period. The level of risk illustrated by a particular risk contour is the risk of lethal exposure to any of the acute hazards associated with many possible releases. Because the risk contours are based on annual data, the risk level for a given contour is the risk to an individual who remains at a specific location for 24 hours a day, for 365 consecutive days.

Risk contours define the summation of all hazard zones for all accident scenarios combined with all respective probabilities. The set of risk contours in Figure 5-3 illustrates how the probability of fatal exposure from a release within an HCU (Hydrocracking Unit) varies with location around the facility. It is important to note that the risk contours are independent of the local population density and distribution. Thus, whether there are 2, 20, or 200 persons at a specific location outside the facility, and they are there continuously for one year, the risk of exposure to a fatal hazard would be the same for each of the persons at that location.

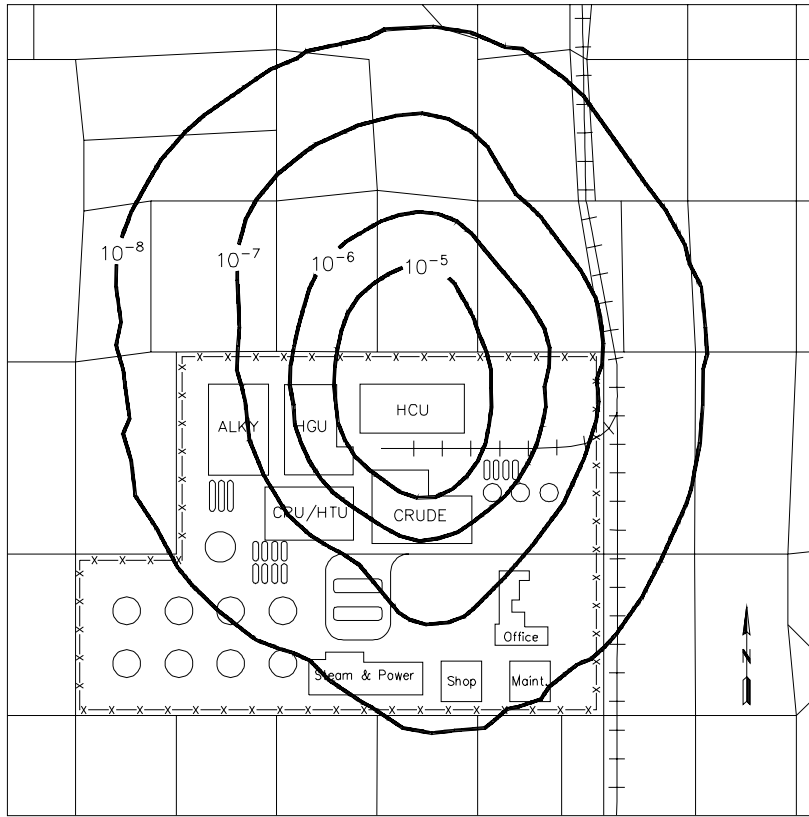


Figure 5-3
Example Risk Contours

SECTION 6

RESULTS AND CONCLUSIONS

This section presents the results of the comparative quantitative risk analysis for the three automotive fuels; gasoline, LPG, and anhydrous ammonia.

6.1 Hazard Footprints and Vulnerability Zones

For each release of gasoline, LPG, or anhydrous ammonia from a tank truck during transport, or from a piece of equipment associated with the storage and dispensing of fuel in the automotive fueling station, one particular combination of conditions will create the largest potentially lethal hazard zone for that area. For the release of anhydrous ammonia from a road tanker, the largest toxic vapor cloud is associated with a catastrophic rupture of the road tanker. Under worst-case atmospheric conditions, the toxic vapor cloud, defined by the 1% fatality limit, extends 730 feet from the point of release. The toxic impact zone associated with this unique event is illustrated in two ways in Figure 6-1. One method presents it as a vulnerability corridor along the roadway, with an offset distance of 730 feet. This presentation is misleading since all locations along the roadway cannot be simultaneously exposed to the toxic cloud from any single release. A more realistic presentation of the maximum potential toxic impact zone associated with the road transport of refrigerated anhydrous ammonia is the cross-hatched area in Figure 6-1, which is the hazard footprint that would be expected if the road tanker were to rupture, and the wind is blowing perpendicular to the roadway, and the wind speed is low (1 m/s), and the atmosphere is extremely stable (Pasquill F). The probability of the simultaneous occurrence of these conditions is approximately 5.63×10^{-14} per truck per mile of roadway per year. Thus, the probability of generating the toxic cloud exactly as shown in Figure 6-1 is about one chance in 17 trillion per year, per mile of roadway for each refrigerated ammonia truck transport.

When the vulnerability corridor on Figure 6-1 is presented, there is no associated probability since the toxic cloud cannot cover the entire area at one time. In addition, there are many other possibilities of cloud formation from the same accident scenario that would fill part of the vulnerability corridor. This risk analysis considered 21 combinations of wind speed and atmospheric stability and 64 wind directions for each unique release. These conditions are combined with three release hole sizes and several event outcomes (flash fires, torch fires, and vapor cloud explosions for gasoline and LPG, and toxic clouds for anhydrous ammonia). The scenario presented in Figure 6-1 is just one of the thousands of possible outcomes following a release from the refrigerated ammonia tank truck. Thus, vulnerability corridors are not a meaningful measure of risk. Vulnerability corridors simply provide information about which areas could potentially be exposed to one unique accident, but provide no information about the probability of exposure.

The vulnerability corridors for the three fuels are presented in Figure 6-2. The gasoline tank truck vulnerability zone is defined by the largest pool fire following a release of gasoline on the roadway. The LPG vulnerability zone is defined by the largest flash fire following a release of LPG on the roadway.

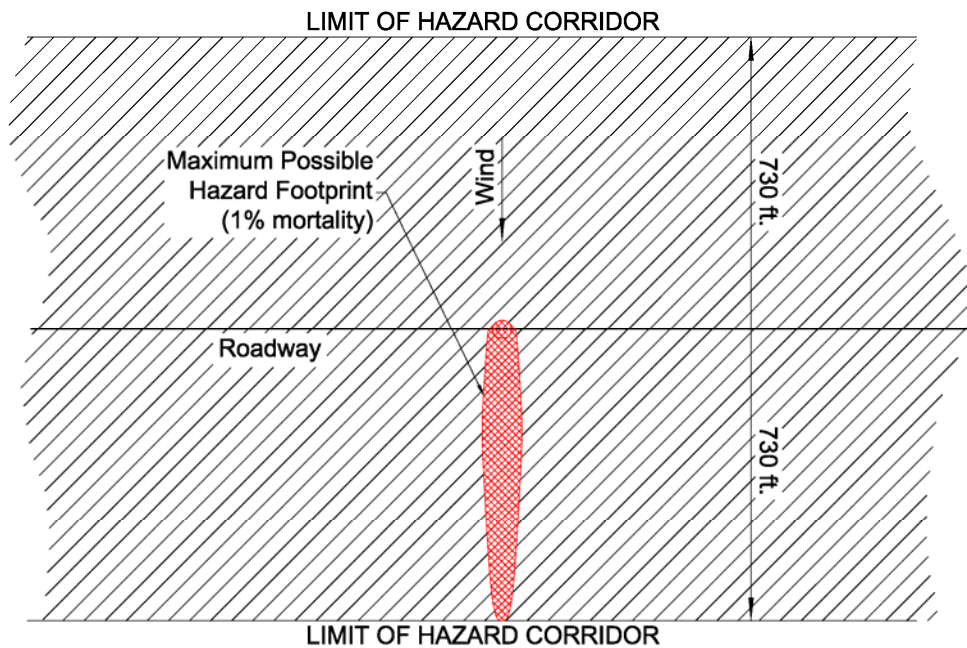


Figure 6-1
Vulnerability Corridor and Toxic Gas Hazard Footprint for a Rupture of the Production Pipeline

6.2 Risk Contours

6.2.1 Terminology and Numerical Values for Representing Risk Levels

The risk an individual is potentially exposed to by events that originate along the roadways where the automotive fuels are transported, or from an individual fueling station, can be represented by a numerical measure. This numerical measure represents the chance, or probability, that an individual will be exposed to a fatal hazard during a year-long period. Table 6-1 lists the numerical value, the short-hand representation of that value as it is used in this report, and the value expressed in terms of chances per year.

Table 6-1
Risk Level Terminology and Numerical Values

Numerical Value	Shorthand Notation	Chance per Year of Fatality
$1.0 \times 10^{-3}/\text{year}$	10^{-3}	One chance in 1,000 of being killed per year
$1.0 \times 10^{-4}/\text{year}$	10^{-4}	One chance in 10,000 of being killed per year
$1.0 \times 10^{-5}/\text{year}$	10^{-5}	One chance in 100,000 of being killed per year
$1.0 \times 10^{-6}/\text{year}$	10^{-6}	One chance in 1,000,000 of being killed per year
$1.0 \times 10^{-7}/\text{year}$	10^{-7}	One chance in 10,000,000 of being killed per year
$1.0 \times 10^{-8}/\text{year}$	10^{-8}	One chance in 100,000,000 of being killed per year

6.2.2 Risk Results for the Truck Transport of Automotive Fuels

The vulnerability zones presented in Figures 6-1 and 6-2 show the maximum extent of a fatal impact along the roadways for the three automotive fuels being transported by tank truck. Although this provides an overall picture of the maximum potential hazard, it is not helpful in determining the risk contribution from any one of the fuels being transported by any location along their route. Another method of presenting the risk posed by the truck transport of the fuels is the risk transect. A risk transect plot shows the annual risk of fatality due to a release from the tank trucks against the perpendicular distance from the roadway. This method of risk presentation accounts for all the possible releases and hazards and provides a simple method of risk comparison for multiple fuels being transported by truck.

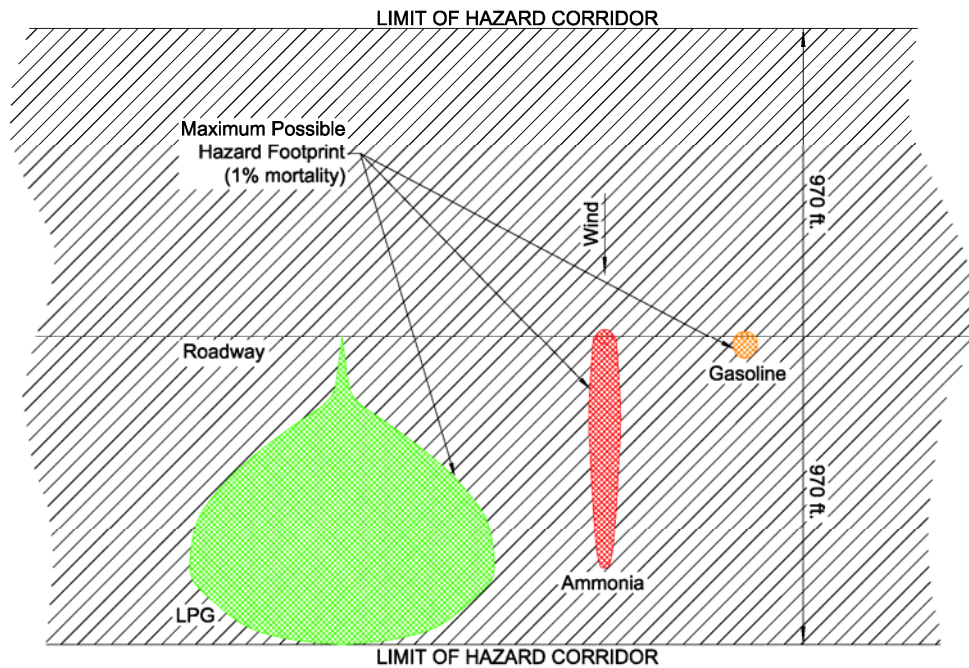


Figure 6-2
Vulnerability Corridors and Zones for the Truck Transport of Gasoline, LPG, and Refrigerated Ammonia

Figure 6-3 presents the risk transects for gasoline, LPG, and refrigerated ammonia along a common roadway. For this comparison, each fuel was assumed to be transported by truck along the roadway once a week (for a total of 52 trips per year). The number of trips is not a critical factor in the comparative analysis as long as the number of trips for each fuel is the same.

As can be seen from Figure 6-3, the risk of fatality decreases as the distance from the roadway increases. This is particularly true for automotive gasoline, whose largest hazards are associated with a pool fire of gasoline. The extent of a fatal radiant flux from the pool of gasoline is limited by the size of the base of the pool. Historically, fire hazards generated by these events have not affected large areas.

In comparison to the risk transects for gasoline, the risk transect for the road transport of refrigerated ammonia shows a lower risk level on the roadway. This is due in part to the fact that vessel containing refrigerated ammonia is a pressure vessel identical to those transporting LPG, whereas the gasoline tank truck is a thinner-walled atmospheric pressure vessel. The road tanker accident data show a lower

incidence of failure for these thicker-walled vessels than those transporting gasoline. However, if a release occurs, the potential extent of the fatal ammonia toxic hazard is larger than that of the fatal fire hazard following a gasoline tank truck release.

The risk transect for the third fuel evaluated, LPG, is also shown in Figure 6-3. Even though LPG and refrigerated ammonia are transported in the same type of road tanker pressure vessels, a comparable release of LPG from a road tanker has the potential to generate a larger overall hazard impact than the same sized release of refrigerated ammonia. This is partially due to the nature of LPG as it can produce both a radiant and explosive hazard. The extent of a flash fire hazard is often larger than the extent of a toxic ammonia gas hazard given identical atmospheric conditions. Thus, when all the possible combinations of failure mechanisms and hazard maps are combined, the risk transect for LPG is “broader” (extends further away from the roadway) than the transects for gasoline or refrigerated ammonia.

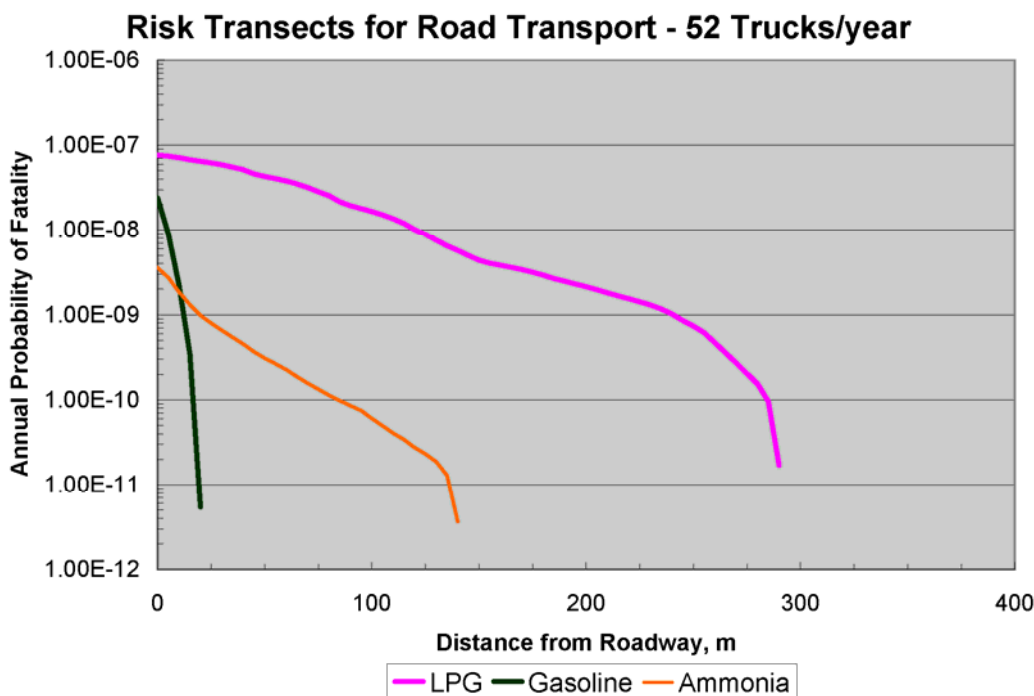


Figure 6-3
Risk Transects for the Truck Transport of Gasoline, LPG, and Refrigerated Ammonia

6.2.3 Risk Results for an Automotive Refueling Facility

Figures 6-4, 6-5, and 6-6 present the risk contours for an automotive refueling station dispensing gasoline, LPG, and anhydrous ammonia, respectively. Each contour on each plot illustrates the annual risk to persons in the area as a function of their location. Risk contours define the risk of lethal exposure to any of the hazards associated with all fuel releases originating within the refueling facility. For example, the contour labeled 10^{-6} in Figure 6-4 represents one chance in one million per year of being exposed to a fatal hazard from any of the possible releases associated with the unloading, storage, and dispensing of gasoline within the station. Because the risk contours are based on annual data, this level of risk is dependent on an individual being in the location where the 10^{-6} contour is shown 24 hours a day, 365 consecutive days per year.

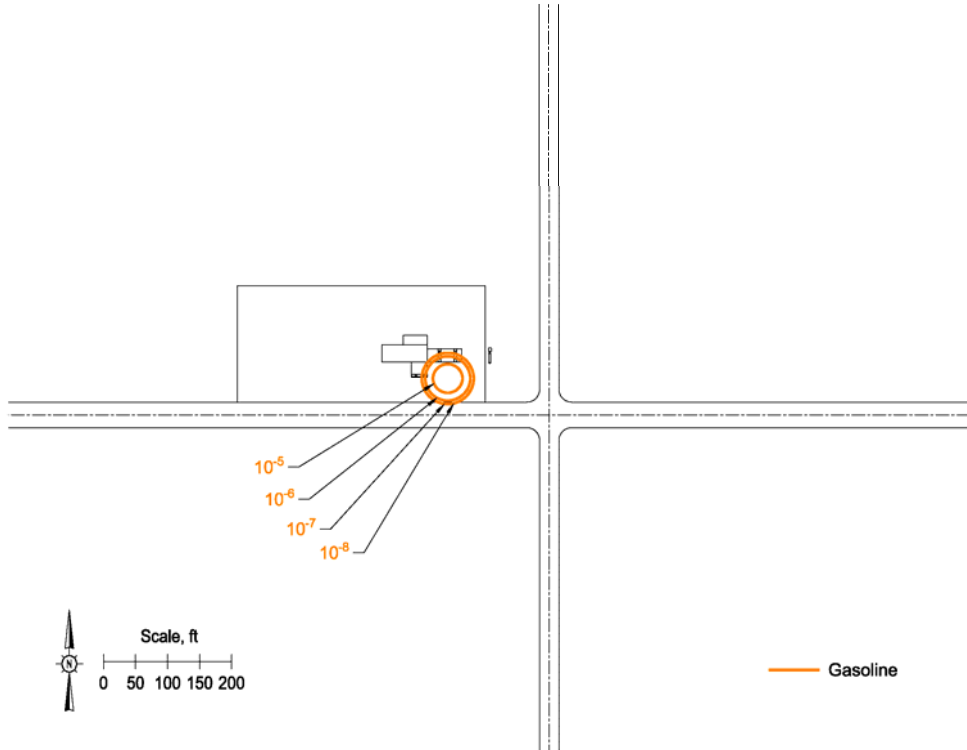


Figure 6-4
Risk Contours for a Service Station Storing and Dispensing Gasoline

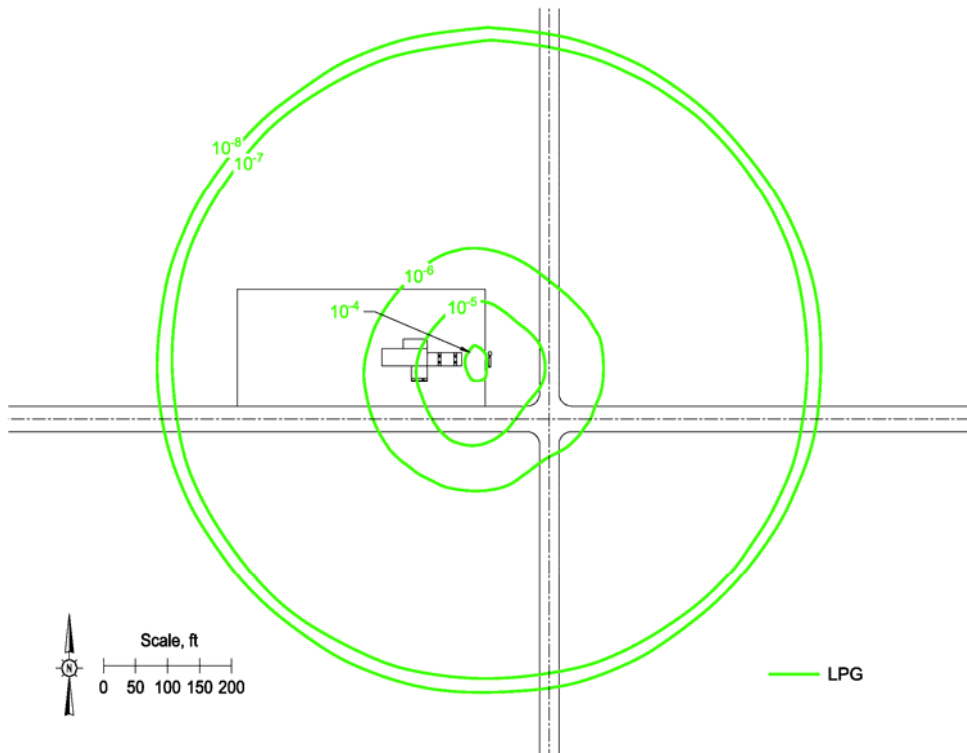


Figure 6-5
Risk Contours for a Service Station Storing and Dispensing LPG

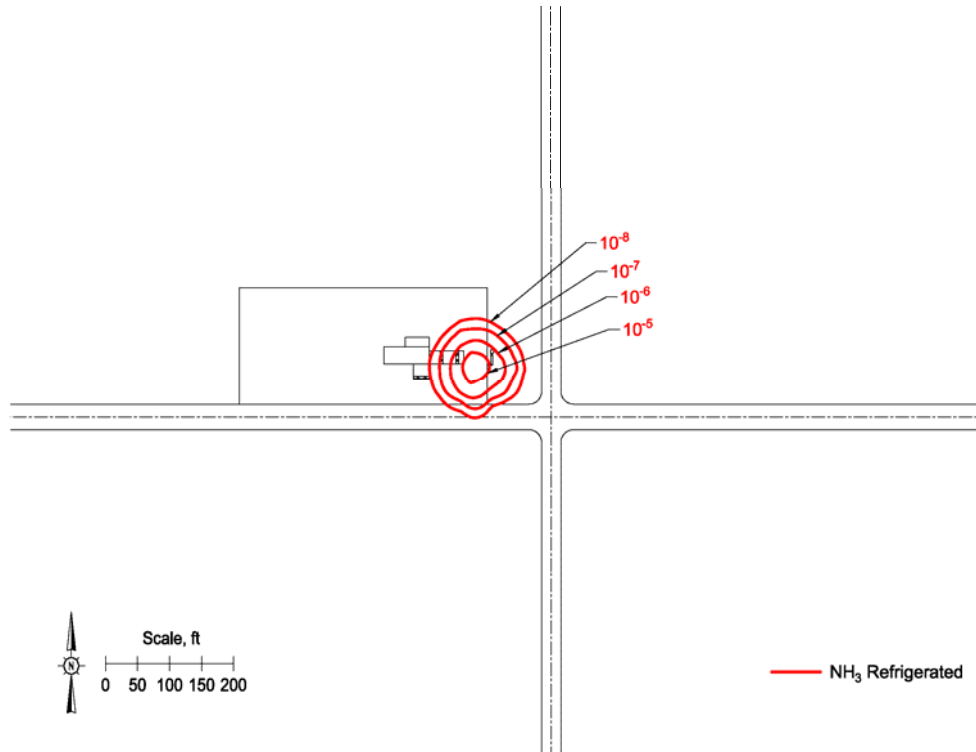


Figure 6-6
Risk Contours for a Service Station Storing and Dispensing Anhydrous Ammonia

When the automotive refueling station is evaluated with LPG as the fuel, the risk contours are larger, as shown in Figure 6-5. Since LPG is stored under pressure and is more volatile than gasoline, it has the potential to generate larger fatal hazard zones than gasoline. This behavior is seen when Figures 6-4 and 6-5 are compared.

Figure 6-6 presents the risk contours for a station in which refrigerated ammonia is unloaded, stored, and dispensed. This risk impact due to the storage and use of ammonia is smaller than the comparable LPG station but larger than the risk associated with gasoline. There are several reasons for this, the most important being that fact that LPG is commonly stored as a liquefied gas by pressure in current automotive refueling station layouts, whereas ammonia would be unloaded and stored as refrigerated ammonia in this comparative analysis. The volatility of refrigerated ammonia is larger than that of gasoline, thus the risks associated with refrigerated ammonia are larger than those for gasoline.

6.3 Risk Acceptability Criteria

In this comparative risk analysis, there are no defined project-specific risk criteria. Thus, a determination of risk acceptability using recognized international risk criteria is not possible. However, it is instructive to review the available criteria in order to determine whether the automotive refueling options would be considered acceptable for varying delivery rates (i.e., number of fuel trucks per year) and overall usage rates (i.e., the amount of fuel dispensed per year). In this manner, the risk associated with the three fuels can be compared if the same number of fuel road transports, unloadings and automobile fuelings are assumed.

There have been a few attempts to define acceptability criteria for the public. In general, the risk criteria have been developed to help regulatory agencies define where permanent housing should be developed near industrial areas. Several recognized international standards are described below.

Western Australia

The Environmental Protection Authority of Western Australia [EPA of Western Australia, 2000] uses the following definitions of acceptable and unacceptable public risk limits for new industrial installations.

- Risk levels lower than 1.0×10^{-6} per year are defined as acceptable.
- Risk levels greater than 1.0×10^{-5} per year are defined as unacceptable.

The use of a “band” between the two limits suggests there is some uncertainty in the calculation of absolute risk. This band (between 1.0×10^{-5} and 1.0×10^{-6}) allows for some judgment in what is acceptable or unacceptable.

Hong Kong

Risk guidelines have been developed by the government of Hong Kong [HKGPD, 2008] for potentially hazardous installations. The guidelines are to be applied to new facilities and the expansion of existing facilities. The purpose of the guidelines was to limit the expansion of housing developments near potentially hazardous installations.

In general, development of new housing near an existing facility, or expansion of a facility near existing housing, would be restricted if the risk of fatality contour of 1.0×10^{-5} per year encroaches onto the housing development. Thus, the Hong Kong criteria can be defined as:

- Risk levels lower than 1.0×10^{-5} per year are defined as acceptable.
- Risk levels greater than 1.0×10^{-5} per year are defined as unacceptable.

United Kingdom

The Health and Safety Executive (HSE) is the regulatory authority for hazard identification and risk assessment studies in the United Kingdom. In 1989, the HSE published a document entitled *Risk Criteria for Land Use Planning in the Vicinity of Major Industrial Hazards*. The risk criteria proposed by the HSE are:

- Risk levels lower than 1.0×10^{-6} per year are defined as acceptable.
- Risk levels greater than 1.0×10^{-5} per year are unacceptable for small developments.
- Risk levels greater than 1.0×10^{-6} per year are unacceptable for large developments.

The HSE has also published a document that discusses their process for risk-based decision making. In *Reducing Risks, Protecting People* (2001), the HSE presents another set of risk tolerability limits that are intended as guidelines to be applied with common sense, not with regulatory rigidity.

- Risk levels lower than 1.0×10^{-6} per year for any population group are defined as acceptable.
- For members of the public, risk levels greater than 1.0×10^{-4} per year are unacceptable.

- Risk levels between 1.0×10^{-4} and 1.0×10^{-6} for the public are considered tolerable if the risk is “in the wider interest of society” and the risk is demonstrated to be as low as reasonably practicable (ALARP).

Netherlands

The Directorate General for Environmental Protection in the Netherlands published a document entitled *Premises for Risk Management, Dutch Environmental Policy Plan, 1989*. This plan requires companies to quantify the risks associated with industrial activities and then determine their acceptability. For facility siting, the regulatory requirements are:

- Risk levels lower than 1.0×10^{-8} per year are defined as acceptable.
- Risk levels greater than 1.0×10^{-5} per year are unacceptable for existing facilities.
- Risk levels greater than 1.0×10^{-6} per year are unacceptable for new facilities.

Petróleos de Venezuela, S.A.

Petróleos de Venezuela, S.A. (PDVSA), the state-owned petroleum arm of the Venezuelan government, published a document entitled *Crterios para el Análisis Cuantitativo de Riesgos* (Criteria for Quantitative Risk Analysis). The document requires companies to evaluate public and worker risk levels posed by a project and compare them to the following criteria.

- Public risk levels lower than 1.0×10^{-6} per year are defined as acceptable.
- Public risk levels greater than 1.0×10^{-5} per year are defined as unacceptable.
- Public risk levels between 1.0×10^{-6} and 1.0×10^{-5} per year are considered reducible, and a cost-benefit analysis should be applied to ensure the risk is as low as reasonably practicable (ALARP).

6.3.1 Individual Risk Criteria Summary

Figure 6-7 presents a summary of the risk acceptability criteria. The most common acceptable level of risk for members of the public is 1.0×10^{-6} . A review of Figure 6-7 shows that an individual risk level less than 1.0×10^{-6} would be acceptable by all authorities, with the possible exception of the more restrictive guidelines published in the Netherlands. Thus, 1.0×10^{-6} could be suggested as an acceptable public risk standard for the fuels evaluated in this study.

6.4 Public Risk Associated with the Three Automotive Fuel Options

The production of individual risk contours is based upon the assumption that “people” are located everywhere within the reach of each outcome following a release. Therefore, every single release has the potential to affect (in this case fatally injure) anyone in its impact area. Since individual risk is, by its nature, a summation of the products of frequency and impact (consequence), if there were no people to be impacted, the product would be zero for that calculation. In the calculation of risk contours, this is not an option as almost every calculation creates a non-zero product of frequency and impact (for ground level releases for instance) and the risk is calculated for that location (as though someone were standing there).

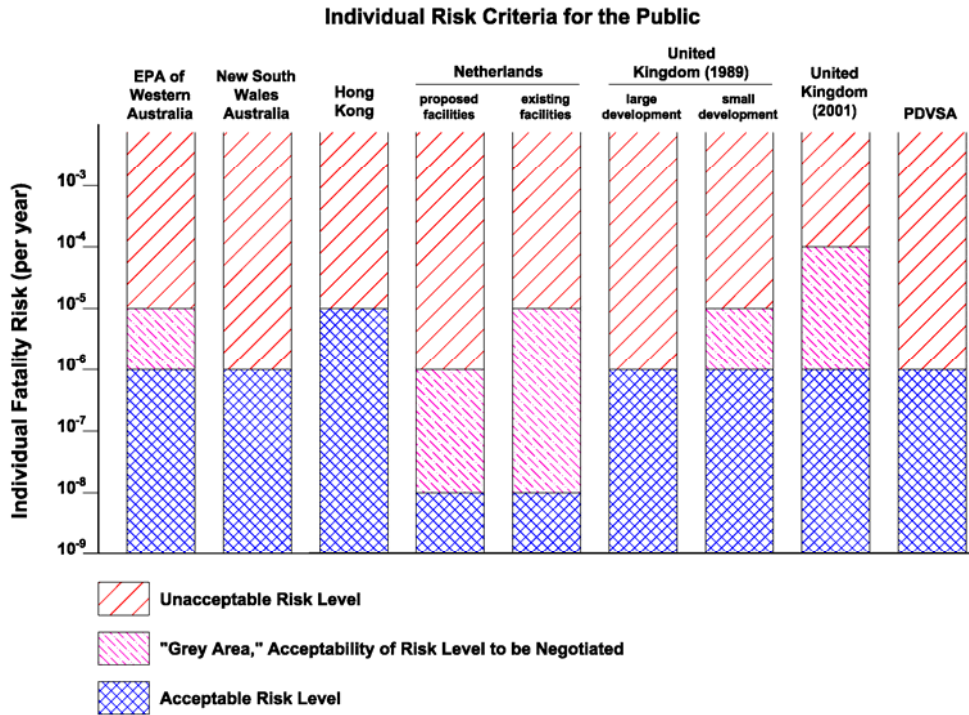


Figure 6-7
Acceptability Standards for Individual Risk

Based on the assumption that people are continuously present near the roadways and service stations, the risk contours and risk transects were generated and are presented in Figures 6-3 through 6-6. Ordinarily, when reviewing a risk contour figure, the reader will mentally note that people might not be present 24 hrs/day, 365 days/year in a particular area. Thus, the reader may think of an individual risk level, for example the 10^{-7} contour, as the “potential” risk and forget that the 10^{-7} was based on assuming that people were present everywhere in this area (in order to generate a non-zero risk value). If it is argued that people only “occupy” the area where the 10^{-7} contour is located one-half of the time, then the risk to those individuals is $0.5 \times 10^{-7}/\text{yr}$. This is particularly true when reviewing the risk transect results along a common roadway. Since the populations along most roadways are not present 24 hours a day and 365 days a year, the risks associated with these areas are most certainly overpredicted.

For the risk contours associated with the service station, this approach, and the errant thinking about what the numbers mean, are often overlooked as the risk values are fairly low and the reader will justify a slightly “high” risk level by saying “that spot will not be occupied 24 hrs/day and 365 days/year, thus the risk is somewhat lower.” In many cases this rationale works.

In order to perform a comparative analysis of the three automotive fuels, many of the same assumptions were used in each fuel’s risk calculations (e.g., weather, number of truck transports, fueling station storage capacity, etc.). In this manner, the risks posed by each system can be reasonably compared. There are three primary factors affecting the comparison that define the study’s outcome.

1. The consequence analysis is dominated by the volatility of the released fuel. LPG stored as a pressurized liquid at ambient temperature. Under the assumed storage conditions for the three

fuels, LPG is the most volatile. Gasoline, a liquid at atmospheric pressure and temperature, is the least volatile. The volatility of refrigerated ammonia falls in between these two fuels.

2. The road tanker accident rates and subsequent hazardous material release frequencies are similar but not the same for all three fuels. The thinner walled gasoline tankers are more likely (per mile transported) to have an accident that results in a release of material than the thicker walled pressure vessels used to transport LPG and refrigerated ammonia. This results in a higher frequency of release of gasoline per mile traveled when compared to LPG and refrigerated ammonia.
3. At the service station, the largest hazards are associated with the unloading and storage of the fuel. An unloading or storage accident that results in a release of material is dominated by the volatility of the fuel. Since LPG is transported and generally stored in aboveground pressurized vessels, a release of LPG from the pressure vessel has the potential to generate a large aerosol cloud that could travel a significant distance before diluting below the LFL. All areas within the LFL have the potential to be affected if the flammable cloud finds an ignition source.

In contrast, the gasoline unloading accident results in a pool of gasoline that, if ignited, would create a dangerous radiant zone very near the spill location. The volatility of gasoline is low enough to prevent it from forming a significant flammable vapor cloud that could travel much beyond the liquid pool. In addition, most gasoline tanks at service stations are buried underground, making a release of gasoline from storage an environmental concern rather than an acute safety concern.

The unloading of refrigerated ammonia involves pumping the liquid from the truck to the storage tank. If a release were to occur, the ammonia on the ground would rapidly vaporize, warm, and disperse downwind. The ammonia vapor would not form as large a cloud as the aerosol cloud produced by an LPG release, but it would be a larger cloud than one created by an unloading release of gasoline.

The refrigerated ammonia storage system is designed such that if a small or significant release of ammonia were to occur in the storage, heating, or pumping systems, the released ammonia liquid and vapor would be contained in a vault and vented through a vertical stack extending upward. As the ammonia vapors warm and disperse from the elevated stack, the ammonia/air plume will be positively buoyant and will have no ability to slump back to grade. This storage method essentially eliminates the grade-level risk associated with the storage of refrigerated ammonia.

When the risks associated with each of the three fuels are calculated, it is reasonable to compare the risk level most often associated with acceptability, $1.0 \times (10)^{-6}$ per year. Figure 6-8 presents this risk level for the service station for each of the three automotive fuels studied. The results are consistent with the findings described in this report. The gasoline station has the smallest risk area (measured by area within the $1.0 \times (10)^{-6}$ risk contour) and the LPG system has the largest risk area defined by the $1.0 \times (10)^{-6}$ risk contour.

The findings for the service station are consistent with the risk transects for the road transport. Both analyses demonstrate the importance of the volatility of the fuel when evaluating the impact of a release.

6.4.1 Effect of Number of Truck Transports on the Analysis

Since this study was a comparative analysis, the actual number of tank truck transports and total number of automobile fueling events were assumed to be identical for all three fuels. While this is most likely not true if a detailed analysis were to be conducted, it is doubtful that moderate changes in the truck transport frequencies and automobile fueling frequencies would change the conclusions of the study. This can be seen by reviewing Figure 6-3, the risk transects for the truck transport of the three fuels. If the number of gasoline tank truck trips were increased by a factor of ten (from 52 to 520 per year), the gasoline risk transect line would simply move up the x-axis by one decade (a factor of ten). The decay of risk (the y-axis) would not change as this is a function of the consequences following a release, not the frequency of a release. This behavior is presented in Figure 6-9

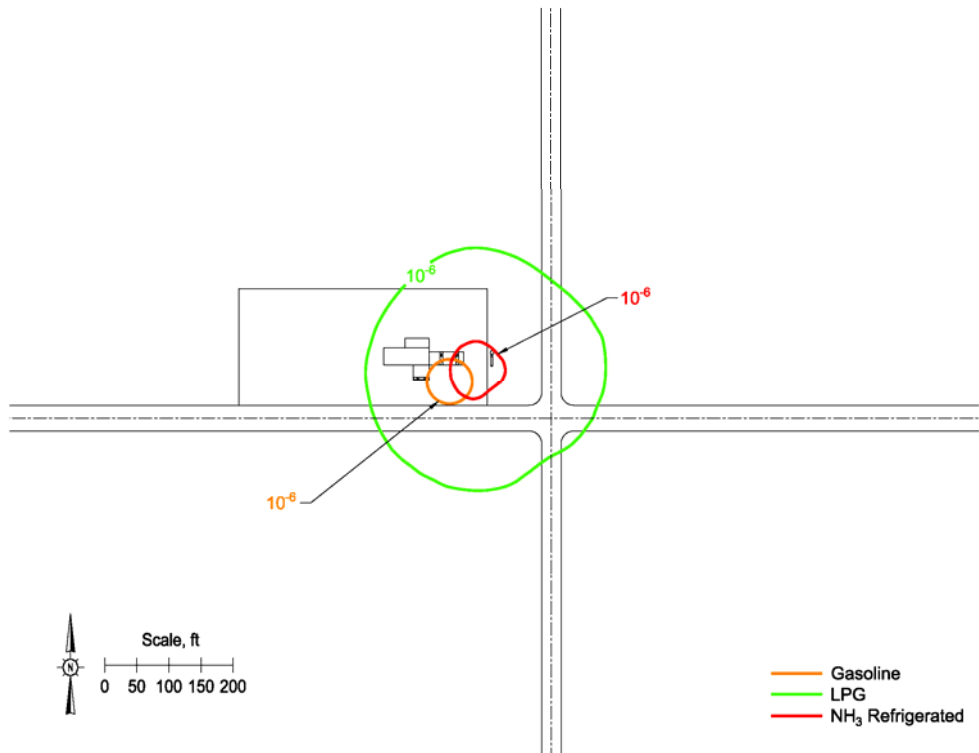


Figure 6-8
1.0 x (10)⁻⁶ Risk Contours for Three Automotive Fuels

As can be seen by this example, if the number of tank truck trips continues to increase (for any of the fuels), the 1.0 x (10)⁻⁶ risk threshold could be exceeded on the roadway. It should be remembered that the risk transect calculations are based on people being continuously present along the roadway (not in moving cars, but in fixed locations past the roadway proper) 24 hours a day and 365 days a year. In most instances this assumption is not true, thus leading to an overprediction of the risk.

6.4.2 Modeling Assumptions

There are several modeling assumptions that serve to overestimate the risk, thus providing a conservative risk analysis result. Several are listed below, while others have been incorporated into the risk calculations methodology presented in Section 5.

- All fuel dispensing equipment was assumed to be in operation at all times. This overestimates the frequency of a possible release if the station is closed during all or part of the day or evening.
- All releases were assumed to be oriented horizontally (parallel to the ground) in the direction the wind is blowing. This results in the maximum distance to any possible hazard.
- If a release did not ignite immediately upon release, it was assumed to grow (travel) to its full extent (maximum downwind distance) before igniting, if it ignites. This overestimates the risk by not allowing for intermediate ignition and subsequently smaller hazard zones.

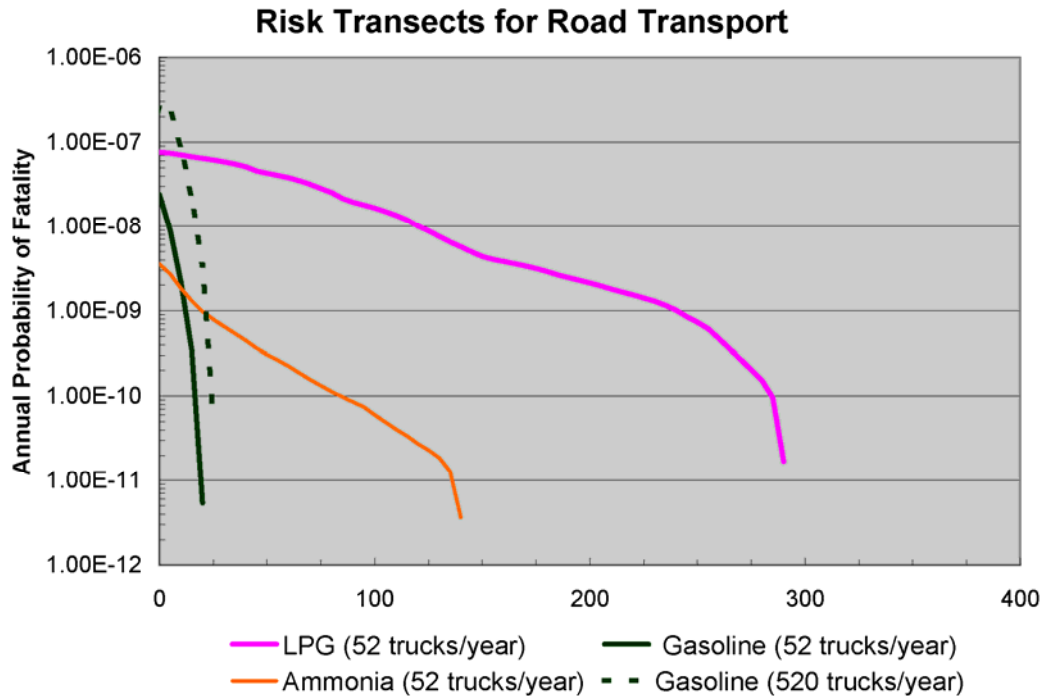


Figure 6-9
Risk Transects for the 52 Truck Transports per year of Gasoline, LPG, and Refrigerated Ammonia and 520 Truck Transports of Gasoline per year

6.5 Summary

With these conservative assumptions in mind, the following conclusions can be drawn from this comparative risk analysis.

- The road transport of any of the three fuels poses no risk to the public greater than 1.0×10^{-6} at distances beyond the roadway as presented in Figures 6-3 and 6-8. Dramatic increases in the number of truck transports made can raise the frequency of an event, but not increase the size of an impact.
- The risks associated with the transport, storage and dispensing of the three fuels is dominated by the volatility of the fuel. The least volatile fuel is gasoline and the most volatile fuel is LPG.
- The relative risk ranking of the three fuels can be summarized as follows:
 - Lowest risk option (travel, storage and dispensing) is gasoline
 - Medium risk option (travel, storage and dispensing) is refrigerated anhydrous ammonia
 - Highest risk option (travel, storage and dispensing) is LPG

It should be noted that the overall risk levels posed by the use of the anhydrous ammonia as an automotive fuels are closer to those posed by gasoline than those posed by LPG.

- (d) Using an assumed transportation and unloading frequency of 52 trucks per year for all three fuels finds that the risks associated with all three fuels would fall into the acceptable category for all referenced risk criteria (with the possible exception of the stringent requirements of the Netherlands). If occupancy factors were considered in the analysis, the Netherlands criteria may be satisfied as well.

In summary, the hazards and risks associated with the truck transport, storage, and dispensing of refrigerated anhydrous ammonia are similar to those of gasoline and LPG. The design and siting of the automotive fueling stations should result in public risk levels that are acceptable by international risk standards. Previous experience with hazardous material transportation systems of this nature and projects of this scale would indicate that the public risk levels associated with the use of gasoline, anhydrous ammonia, and LPG as an automotive fuel will be acceptable.

It is also important to note that the risk associated with traveling in a vehicle powered by any one of these fuels is dominated by accidents that do not result in a release of the fuel. As described in the National Safety Council database referenced in Section 1, very few traffic accidents result in a release of the fuel powering the automobile. Since anhydrous ammonia and LPG are stored in similar pressurized tanks, there is no reason to believe that the risks associated with the passengers in an automobile would go up or down due the use of anhydrous ammonia as the fuel.

SECTION 7

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SECTION 8 GLOSSARY

The following definitions are intended to apply to Consequence Analysis and Quantitative Risk Analysis studies of facilities that produce, process, store, or transport hazardous materials. Due to the limited scope of such studies, some of these definitions are narrower than the common definitions.

ACCIDENT. An unplanned event that interrupts the normal progress of an activity and has undesirable consequences, and is preceded by an unsafe act and/or an unsafe condition.

ACCIDENT EVENT SEQUENCE. A specific series of unplanned events that has specific undesirable consequences (e.g., a pipe ruptures, allowing flammable gas to escape; the gas forms a flammable vapor cloud that ignites after some delay, resulting in a flash fire).

ACCIDENT SCENARIO. The detailed description of an accident event sequence.

AIR DISPERSION MODELING. The use of mathematical equations (models) to predict the rate at which vapors or gases released into the air will be diluted (dispersed) by the air. The purpose of air dispersion modeling is to predict the extent of potentially toxic or flammable gas concentrations, in air, by calculating the change in concentration of the vapor or gas in the air as a function of distance from the source of the vapor or gas.

BLAST WAVE. An atmospheric pressure pulse created by an explosion.

BLEVE (Boiling Liquid–Expanding Vapor Explosion). The sudden, catastrophic failure of a pressure vessel at a time when its liquid contents are well superheated. (BLEVE is normally associated with the rupture, due to fire impingement, of pressure vessels containing liquefied gases.)

CONDITIONAL PROBABILITY. The probability of occurrence of an event, given that one or more precursor events have occurred (e.g., the probability of ignition of an existing vapor cloud).

CONSEQUENCES. The expected results of an incident outcome.

CONSEQUENCE ANALYSIS. Selection and definition of specific accident event sequences, coupled with consequence modeling.

CONSEQUENCE MODELING. The use of mathematical models to predict the potential extent of specific hazard zones or effect zones that would result from specific accident event sequences.

DEFLAGRATION. See explosion.

DETONATION. See explosion.

EFFECT ZONE. The area over which the airborne gas concentration, radiant heat flux, or blast wave overpressure is predicted to equal or exceed some specified value. In contrast to a hazard zone, the endpoint for an effect zone need not be capable of producing injuries or damage.

ENDPOINT. The specified value of airborne gas concentration, radiant heat flux, or blast wave overpressure used to define the outer boundary of an effect zone or hazard zone. Endpoints typically correspond to specific levels of concern (e.g., IDLH, LFL, onset of fatality, 50% mortality, odor threshold, etc.).

EVENT TREE. A diagram that illustrates accident event sequences. It begins with an initiating event (e.g., a release of hydrogen sulfide gas), passes through one or more intermediate events (e.g., ignition or no ignition), resulting in two or more incident outcomes (e.g., flash fire or toxic vapor cloud).

EXPLOSION. A rapid release of energy, resulting in production of a blast wave. There are two common types of explosions—physical explosions (sudden releases of gas or liquefied gas from pressurized containers) and chemical explosions (rapid chemical reactions, including rapid combustion). Chemical explosions can be further subdivided into deflagrations and detonations. In a deflagration, the velocity of the blast wave is lower than the speed of sound in the reactants. In a detonation, the velocity of the blast wave exceeds the speed of sound in the reactants. For a given mass of identical reactants, a detonation is capable of producing more damage than a deflagration. Solid and liquid explosives, such as dynamite and nitroglycerine, typically detonate, whereas vapor cloud explosions are nearly always deflagrations.

FIRE RADIATION. See thermal radiation.

FLAMMABLE VAPOR CLOUD. A vapor cloud consisting of flammable gas and air, within which the gas concentration equals or exceeds its lower flammable limit.

FLASH FIRE. Transient combustion of a flammable vapor cloud.

HAZARD. A chemical or physical condition that presents a potential for causing injuries or illness to people, damage to property, or damage to the environment.

HAZARD ZONE. The area over which a given incident outcome is capable of producing undesirable consequences (e.g., skin burns) that are equal to or greater than some specified injury or damage level (e.g., second-degree skin burns). (Sometimes referred to as a “hazard footprint.”)

INCIDENT OUTCOME. The result of an accident event sequence. The incident outcomes of interest in a typical study are toxic vapor clouds; fires (flash fire, torch fire, pool fire, or fireball); and explosions (confined, unconfined, or physical).

INITIATING EVENT. The first event in an accident event sequence. Typically a failure of containment (e.g., gasket failure, corrosion hole in a pipe, hose rupture, etc.).

INTERMEDIATE EVENT. An event that propagates or mitigates the previous event in an accident event sequence (e.g., operator fails to respond to an alarm, thus allowing a release to continue; excess flow valve closes, thus stopping the release).

ISOPLETH. The locus of points at which a given variable has a constant value. In consequence modeling, the variable can be airborne gas concentration, radiant heat flux, or blast wave overpressure. The value of the variable is equal to the specified endpoint. The area bounded by an isopleth is an effect zone.

LOWER FLAMMABLE LIMIT. The lowest concentration of flammable gas in air that will support flame propagation.

MISSILES. See shrapnel.

POOL FIRE. Continuous combustion of the flammable gas emanating from a pool of liquid.

QUANTITATIVE RISK ANALYSIS. The development of a quantitative estimate of risk based on engineering evaluation and mathematical techniques for combining estimates of incident consequences and frequencies.

RISK. A measure of economic loss or human injury in terms of both the incident likelihood and the magnitude of the loss or injury.

RISK ASSESSMENT. The process by which the results of a risk analysis are used to make decisions, either through relative ranking of risk reduction strategies or through comparison with risk targets.

SHRAPNEL. Solid objects projected outward from the source of an explosion. Sometimes referred to as missiles or projectiles.

SUPERHEATED LIQUID. A liquid at a temperature greater than its atmospheric pressure boiling point.

THERMAL RADIATION. The transfer of heat by electromagnetic waves. This is how heat is transferred from flames to an object or person not in contact with or immediately adjacent to the flames. This is also how heat is transferred from the sun to the earth.

TORCH FIRE. Continuous combustion of a flammable fluid that is being released with considerable momentum.

TOXIC. Describes a material with median lethal doses and/or median lethal concentrations listed in OSHA 29 CFR 1910.1200, Appendix A.

TOXIC VAPOR CLOUD. A vapor cloud consisting of toxic gas and air, within which the gas concentration equals or exceeds a concentration that could be harmful to humans exposed for a specific time.

VAPOR CLOUD. A volume of gas/air mixture within which the gas concentration equals or exceeds some specified or defined concentration limit.

VAPOR CLOUD EXPLOSION. Extremely rapid combustion of a flammable vapor cloud, resulting in a blast wave.

VULNERABILITY ZONE. The area within the circle created by rotating a hazard zone around its point of origin. Any point within that circle could, under some set of circumstances, be exposed to a hazard level that equals or exceeds the endpoint used to define the hazard zone. However, except for accidents that produce circular hazard zones (e.g., BLEVEs and confined explosions), only a portion of the area within the vulnerability zone can be affected by a single accident.