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A METHOD FOR DEFINING DOWN-WIND EVACUATION AREAS FOR TRANSPORTATION ACCIDENTS INVOLVING TOXIC PROPELLANT SPILLS

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SUMMARY

Evacuation areas for accidental spills of toxic propellants along the rail and highway shipping routes are defined to help local authorities reduce risks to people from excessive vapor concentrations. These criteria along with other emergency information are shown in Propellant Spill Cards being prepared by the Joint Army Navy NASA, Air Force (JANNAF) Safety and Environmental Protection Working Group. The evacuation areas are based on current best estimates of propellant evaporation rates from various areas of spill puddles. These rates are used together with a continuous point-source, bi-normal model of plume dispersion. The rate at which the toxic plume disperses is based on a neutral atmospheric condition. This condition, which results in slow plume dispersion, represents the widest range of weather parameters which could occur during the day and night-time periods. Evacuation areas are defined by the ground level boundaries of the plume within which the concentrations exceed the toxic Threshold Limit Value (TLV) or in some cases the Emergency Exposure Limit (EEL). A margin of safety was used to estimate propellant evaporation rates since research-data for spills on various surfaces is very limited.

INTRODUCTION

Transportation accidents involving the spill of toxic or volatile chemicals pose a threat to the health and safety of populations adjacent to rail or highway shipping routes. The frequency of these types of accidents will increase as more ton-miles for hazardous chemicals are logged each year. The initial reaction to these types of accidents within the first several minutes by local emergency services probably has the greatest effect upon reducing hazards from fire, explosion and airborne toxic vapors. Accordingly, the Joint Army-Navy-NASA-AIR FORCE (JANNAF) Safety and Environmental Protection Working Group has prepared emergency procedures in the form of Propellant Spill Cards for use by shippers and local fire/police departments.

These spill cards include several item of procedure and information, some of it quite similar to material developed by others concerned with such types of accidents. However, prior efforts did not deal in any quantitative fashion, with an important question: "What size area in the vicinity of a toxic chemical spill should be evacuated to protect people from excessive concentrations of airborne vapors?" This report describes the approach used to answer that question.

Evacuation areas are defined by making use of evaporation rate data for spilled propellants (refs. 1 and 2), their toxicity limits (ref. 3), and an atmospheric diffusion model. This model incorporates standard deviations of Gaussian distributions of plume concentrations in the cross wind and vertical directions (ref. 4). These deviations, based on field experiments are related to the more commonly observed weather parameters describing conditions of atmospheric turbulence which affect the rate of toxic plume dispersion. In transportation accidents where a propellant spill is likely to occur or is in progress, there would not ordinarily be anyone available to interpret these weather parameters which affect plume dispersion rate and the size of evacuation areas. Consequently, an assumed set of weather parameters was used which will, it is thought, cover a very wide range of situations which conservatively define evacuation areas required for propellant spill evaporation rates. These evaporation rates have been referenced to various areas of spill puddles. Thus the only observations that emergency forces need make in selecting an evacuation area are the type of propellant and the estimated area of its spill puddle.

It should be emphasized that the lead time required to establish an evacuation area may not always be reasonable, especially if the propellant is extremely toxic and has a high evaporation rate. Thus the application of criteria described here will not always eliminate, entirely, risks to people adjacent to toxic propellant spills. Nevertheless, use of these areas should certainly reduce the number of people exposed to danger and should, moreover, help the emergency forces to avoid ether over- or under-reacting to the threat of airborne toxic vapors.

ATMOSPHERIC DISPERSION OF SPILLED PROPELLANTS

The plume dispersion model used to estimate concentrations of vapor from a toxic propellant spill is given in equation (1) (ref. 4). This equation applies to a continuous point-source release.

$$\chi_{(xy)} = \frac{Q}{2\pi\sigma_y\sigma_z U} \text{EXP}\left[-\frac{1}{2}\left(\frac{y}{\sigma y}\right)^2\right] \qquad (1)$$

where

$\chi_{(xy)}$ is the concentration at the cross-wind and down-wind distances of interest

Q is the evaporation rate from a spilled toxic propellant

σ_y is the standard deviation of plume concentration distribution cross-wind

σ_z is the standard deviation of plume concentration distribution with elevation

U is the mean surface wind speed

y is the cross-wind distance

The values of σ_y and σ_z vary with plume elevation and downwind distances, turbulent structure of the atmosphere, the mean surface wind speed, and the surface roughness over which the plume is dispersed.

Atmospheric Stability

Categories of atmospheric stability as related to the more commonly observed weather conditions are shown in figure 1 (ref. 4).

It will be noted that the neutral category "D", which has very little atmospheric turbulence, covers a wide range of weather parameters during the day and night period. These parameters result in slow plume dispersion rates. Categories "A," "B," and "C" are unstable atmospheric conditions which enhance plume dispersion whereas "E" and "F" are very stable atmospheric conditions which suppress plume dispersion.

The neutral condition, D, was assumed for the following reasons:

1. The "D" category covers the widest range of meteorological parameters that are adverse for plume dispersion.

2. The very stable conditions prevailing under inversion conditions E and F tend toward the neutral condition D in the vicinity of highly populated urban areas, due to the turbulence-promoting effects of the city's surface roughness and the convective effects of its heat loss to the air.

PLUME SHAPE EQUATION FOR ATMOSPHERIC STABILITY CATEGORY "D"

The values of standard deviation of plume concentration σ_y and σ_z for neutral atmospheric conditions were estimated in terms of downwind distance, d (ref. 4). These values are given in equations (2) and (3).

$$\sigma_y = 70(d)^{0.894} \tag{2}$$

$$\sigma_z = 31(d)^{0.783} \tag{3}$$

where:

σ_y is the standard deviation of plume concentration distribution, cross wind (m)

σ_z is the standard deviation of plume concentration distribution with elevation (m)

d is downwind distance (km)

Selecting a mean surface wind speed of 5 m/sec from figure 1 and substituting the values of σ_y and σ_z and U into equation (1), downwind distances can be expressed in terms of propellant evaporation rate "Q" and plume concentrations χ as given in equation (4).

$$d = 0.001916\left(\frac{Q}{\chi_x}\right)^{0.6} \qquad (4)$$

where

Q is the propellant evaporation rate (g/sec)

χ_x is the plume concentration on the center line of the plume (g/m^3)

Cross-wind distances of the plume, $\pm y$ are given in equation (5).

$$\pm y = 99.12(d)^{0.894}(\ln \chi_x - \ln \chi_y) \qquad (5)$$

where

$\pm y$ is cross-wind distance (m)

χ_y is the plume concentration at a distance "y" off the center line of the plume

ESTIMATED PROPELLANT EVAPORATION RATES

Data on evaporation rate, Q, for an average wind speed of 5 m/sec associated with neutral stability condition "D" have been measured for UDMH/N_2H_4, N_2O_4 and LOX (ref. 1) and for anhydrous ammonia (ref. 2). It has been found that these data, representing highest evaporation rates, plot almost linearly against the normal boiling points of the four propellants. This is shown in figure 2, where the data has been referenced to a spill puddle area of 55 m^2 (600 ft^2). The remaining propellants are keyed by their normal boiling points to the line established by the data from reference 1 and confirmed by that of reference 2.

Inspection of figure 2 shows that the propellants fall into five distinct groups. In view of the fact that errors in estimating evaporation rates significantly affect downwind concentrations (eq. 4), and that the correlation of figure 2 is based on a limited amount of data a cautious approach seemed to be required. Consequently, it was decided to assign the highest evaporation rate for each group of propellants to all members of the group. For instance, nitrogen tetroxide ethylene oxide and chlorine trifluoride were all assumed to evaporate at the rate predicted for chlorine pentafluoride (Group II, fig. 2). These group evaporation rates are summarized in table I.

EVACUATION AREAS

Propellant Toxicity Limits

The final parameter needed to define the boundary of a dangerous plume by means of equations (4) and (5) is the maximum allowable concentration, χ, of the toxic vapor from the spilled propellant. Here again, as in the case with evaporation rates, information is not as complete as would be desirable. The criterion that should be applied is the maximum safe concentration which can be tolerated by the general public for time durations which would make evacuation of an area a fesible procedure. Unfortunately, such a criterion has yet to be established for chemical propellant vapors. Thus it is necessary to fall back on other toxicity level standards. One of these standards is a peak concentration limit set by the American Industrial Hygene Association (AIHA) for workers customarily exposed during their normal work routine. This standard is called, "Theshold limit Value" (TLV). The other standard is an upper limit dosage of short time duration for a once-in-a lifetime exposure. This standard is intended for personnel who must be exposed to accomplish highly essential tasks in emergency situations. This standard was established for chemical propellants by the National Academy of Sciences for chemical propellants and it is called, "Emergency Exposure Limit" (EEL).

Admittedly, industrial workers, exposed to a toxic environment, are medically examined periodically to assure health requirements for their job. Consequently, they are better able to withstand toxic fumes which may even slightly exceed the TLV when compared to the general public with its infants and aged, infirm, or ill people. Offsetting is the fact that a transportation accident involving a toxic spill will be a rare event within a lifetime and morever, the exposure will be of limited duration particularly if areas are evacuated as recommended in this report. Therefore, substitution of the TLV's (ref. 3) for χ_x and χ_y (eqs. 4 and 5) should define the ground level plume boundaries in a conservative manner.

This procedure was followed for all but three propellants. Fluorine, oxygen difluoride and diborane have such low TLV's and high evaporation rates that their use in equations (4) and (5) defines extremely large toxic plumes extending many kilometers downwind from the spill. The small lead time available in event of large spill of these propellants would make evacuation of such an area unrealistic. In fact, these situations may call for immediate rescue and first aid followed by medical attention. Thus, the ten-minute EEL's (ref. 3) were used instead of the TLV's to arrive at more realistic boundaries of the evacuation and/or rescue areas. Counteracting, this seemingly unconservative approach is the extreme reactivity of all three materials. This makes it very likely that spills will result in fire, the combustion products of which are less toxic than the propellants themselves. Other compensating factors are that the fire often induces sufficient atmospheric turbulence to dilute the plume concentrations and that both fluorine and diborane react with water vapor in the air, again with the formation of less toxic products.

Determination of Evacuation Areas

The evacuation area for a given propellant was constructed as shown in figure 3 by first defining the ground level boundaries of the cigar shaped plume consistant with the TLV (or the EEL). The plume area was then rotated $\pm 15^{\circ}$ off the center line of wind direction to account for possible wind fluctuations associated with the neutral, D, atmospheric conditions. A line was then drawn tangent to the largest width of the plume at an azimuth of 15° relative to wind direction. Finally, an exclusion area around the point of spill was defined by a radius equal to half the largest width of the toxic plume. Typical evacuation areas are compared in figure 4. In figure 5, one of the proposed spill cards is represented to show how the information on evacuation areas is presented.

CONCLUDING REMARKS

The motivation for the present work was a desire to provide something better than the general instruction, often found in safety documents, to clear downwind areas in the event of a toxic spill. In the process of defining reasonable areas to be evacuated, three sources of uncertainty were encountered and in each case an attempt was made to deal with the uncertainty in such a way as to provide an added margin of safety. The first source of uncertainty is weather conditions, but this can be dealt with by assuming that conditions will always be unfavorable for rapid dilution and dispersion. The other two problem areas are evaporation rates and toxicities. More work is needed in both cases to reduce uncertainty in establishing evacuation areas, not only for liquid propellants, but also in the event that the methods presented here are extended to other toxic chemicals shipped in bulk quantities. Evaporation rates should be measured for more chemicals, on various spill surfaces, and the substances measured should have a wide range of boiling points. Perhaps the most pressing need is to define a level of toxicity for each chemical that can be tolerated by the general public in the typical environment of a transportation accident.

REFERENCES

1. Henderson, W. Paul; and Brown, Ralph H.: Evaporation Rate Studies of Liquid Oxygen and 50/50 Mixture of Unsymmetrical-Dimethylhydrazine and Hydrazine. Rep. EA-TR-4425, Edgewood Arsenal (AD-874737), Sept. 1970.

2. Matsak, V. G.: Vapor Pressure and Evaporation of Substances in Movable Air. Rep. FTD-TT-63-1044/1+2, Air Force Systems Command (AD-425608), Nov. 8, 1963.

3. Jensen, Andreas V.: Chemical Rocket/Propellant Hazards. Vol. III. Liquid Propellant Handling, Storage, and Transportation. Rep. CPIA-Pub.-194, vol. 3, Johns Hopking Univ. (AD-870259L), May 1970.

4. Turner, D. Bruce: Workbook of Atmospheric Dispersion Estimates. Publ. 999-AP-26, Environmental Science Services Adm., 1968.

TABLE I. - ESTIMATED PROPELLANT EVAPORATION RATES FROM AT 55 m^2 PUDDLE FOR ATMOSPHERIC CATEGORY "D"

Group	Propellants	Evaporation rates (lb/sec)	Evaporation rates (g/sec)
I	Hydrazine, monomethylhydrazine (MMH), unsymmetrical dimethyl-hydrazine/diethylenetraimine/ acetonitrile (MAF-1), unsymmetrical dimethylhydrazine (UDMH), unsymmetrical dimethylhydrazine/ diethylene triamine (MAF-4), and fuming nitric acids (WFNA, IWFNA, RFNA, IRFNA)	0.2	90
II	Nitrogen tetroxide (N_2O_4), Ethylene oxide Chlorine trifluoride (CTF) Chlorine pentafluoride (CPF)	0.6	270
III	Anhydrous ammonia Perchloryl fluoride (PF) Unsymmetrical dimethylhydrazine/ Diethylenetriame (MAF-4)	1.3	590
IV	Diborane	1.5	680
V	Methane Liquid fluorine Oxygen difluoride	2.2	1000

SURFACE WIND (SPEED AT 10 m ELEV), $m\,SEC^{-1}$	KEY TO STABILITY CATEGORIES				
	DAY			NIGHT	
	INCOMING SOLAR RADIATION			≥4/8 LOW CLOUD	≤3/8 CLOUD COVER
	STRONG	MODERATE	SLIGHT		
<2	A	A-B	B		
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	D
>6	C	D	D	D	D

Figure 1. - Atmospheric stability categories.

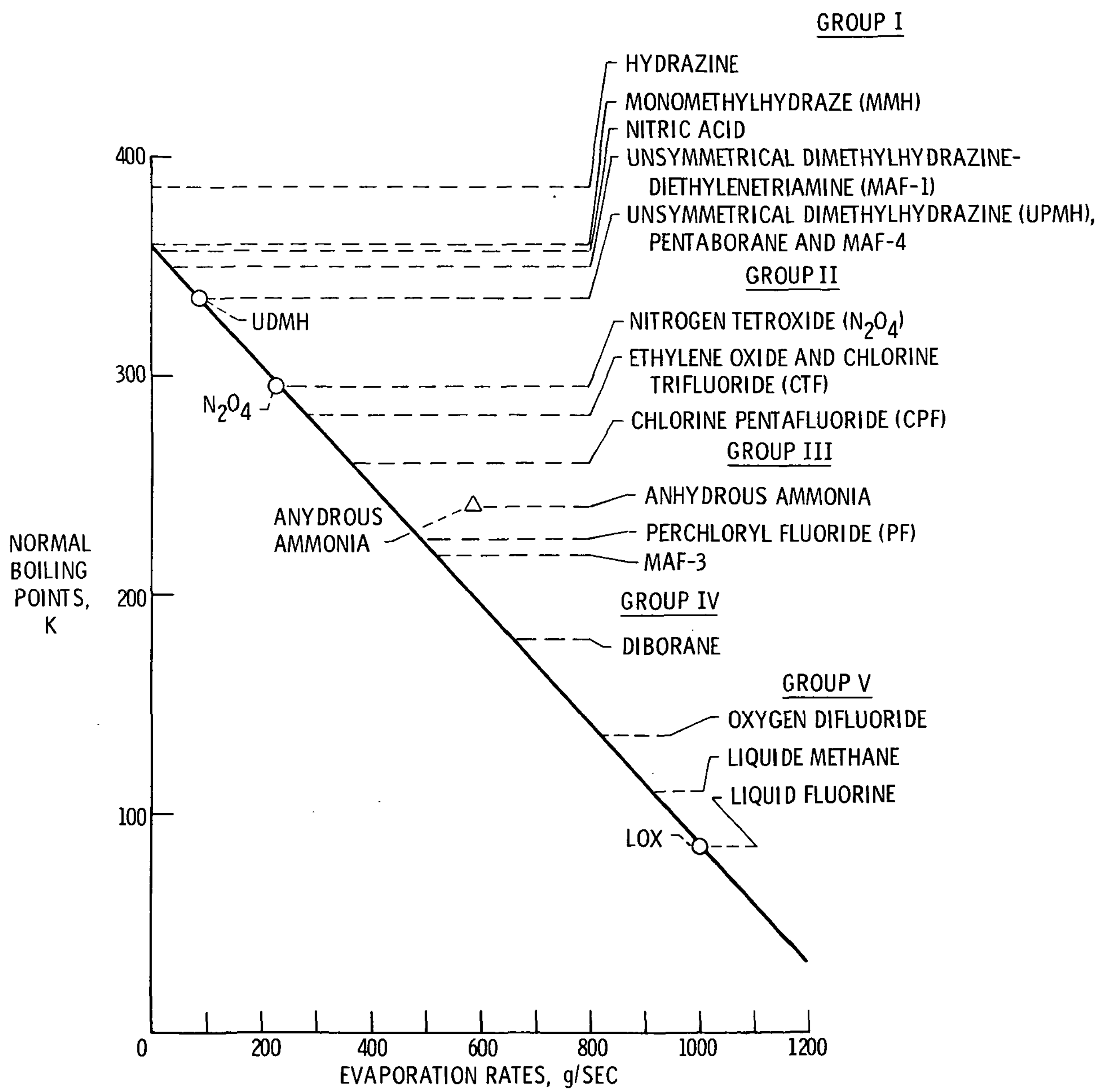


Figure 2. - Estimated evaporation rates versus normal boiling points hazardous for propellants. Wind velocity, 5 m/sec; puddle area, 55 m^2.

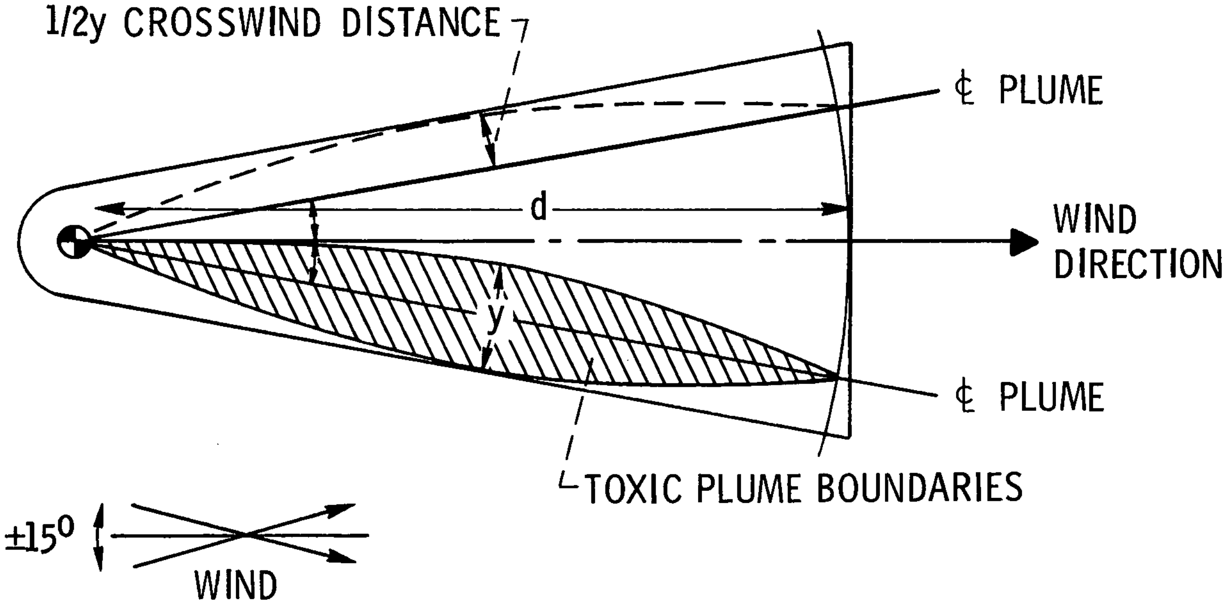


Figure 3. - Evacuation area development for toxic propellant spills.

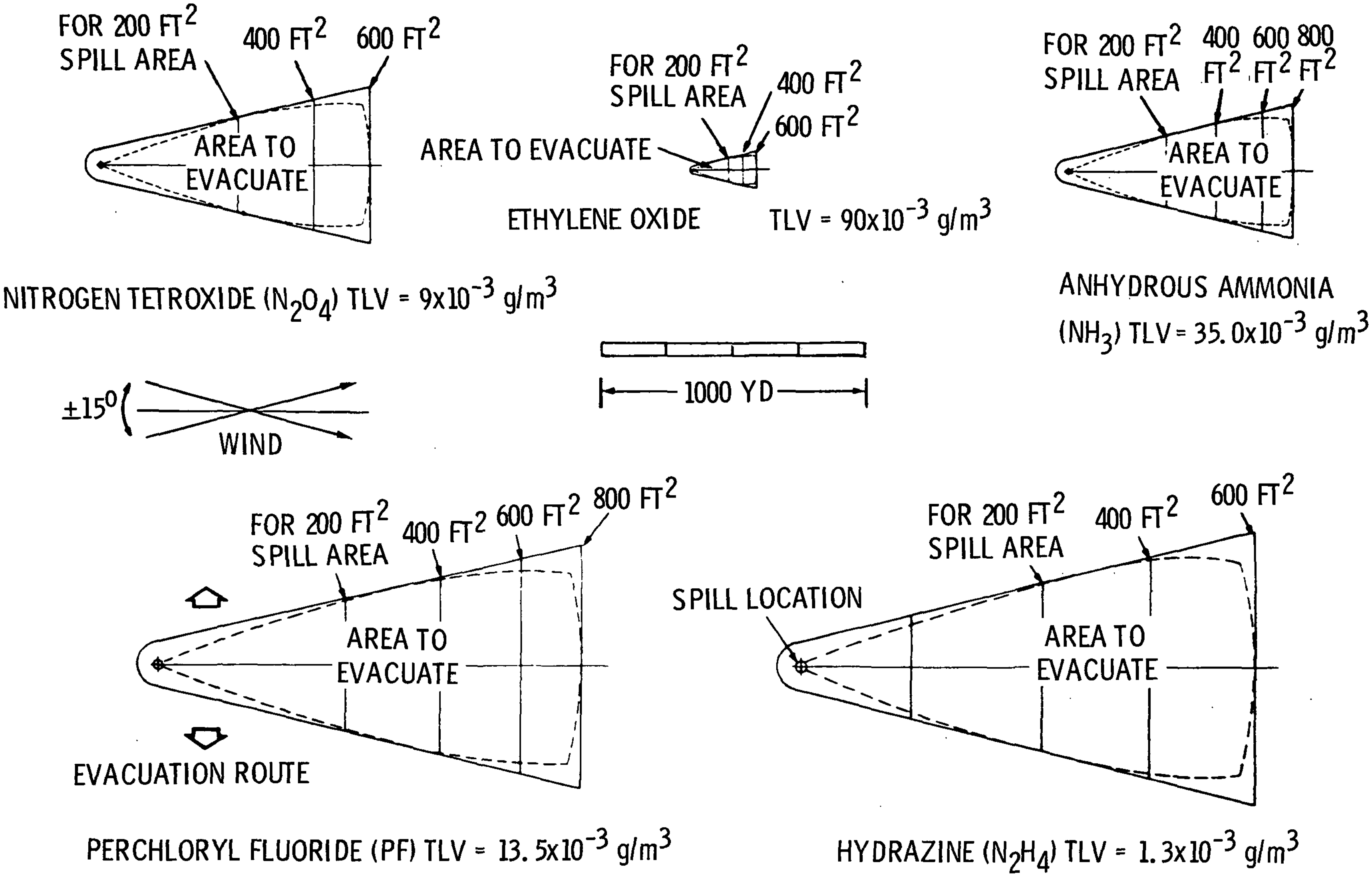


Figure 4. - Propellant spill card evacuation areas for several liquid propellants.

NITROGEN TETROXIDE

(OXIDIZER, POISON, CORROSIVE)

FOR ASSISTANCE CALL 800 424 9300

POTENTIAL HAZARDS

FIRE	May cause fire on contact with combustibles. Reaction with fuels may be violent.
HEALTH	Vapor may cause severe lung and eye damage. Contact with liquid may cause severe burns to skin and eyes. Contaminated water or material runoff may pollute water supply.

IMMEDIATE ACTION INFORMATION

NO UNNECESSARY PERSONNEL. KEEP UPWIND. IDENTIFY AND ISOLATE HAZARD AREA. WEAR SELF-CONTAINED BREATHING APPARATUS AND FULL PROTECTIVE CLOTHING.

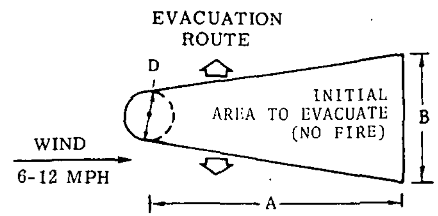
FIRE	Use water spray or fog. Cool containers with water from maximum distance. Use water spray to protect surrounding area.
SPILL or LEAK	Evacuate in accordance with the Table of Distances. Stop leak if without risk. Avoid contact with spilled material. Keep spilled material away from combustibles. Use water spray to reduce vapors. Dilute spill with large amounts of water. Dike for later disposal.
FIRST AID	Remove to fresh air. Call physician. If not breathing give artificial respiration. If breathing is difficult give oxygen. Remove contaminated clothing and shoes. In case of contact with material or its water solution, immediately flush skin or eyes with running water for at least 15 minutes. Keep patient at rest. Effects of contact or inhalation may be delayed.

DO THIS NOW

- ☐ 1. Get a Helper
- ☐ 2. Start Evacuation with circle
- ☐ 3. Follow immediate action info
- ☐ 4. For assistance call (800) 424-9300 with:
  - a) your location and phone no.
  - b) incident location
  - c) label color and no.
  - d) name of product and shipper, if known
  - e) weather conditions
  - f) Populated area?
  - g) Water nearby?
- ☐ 5. Advise local authority to control evacuation
- ☐ 6. Adjust Evacuation Area:
  - a) According to wind changes
  - b) According to observed effects on population

TABLE OF DISTANCES TO EVACUATE

EVACUATE	Observed Sq. Ft. Area Of The Spill 200	400	600	800
(D) Circle, Yds.	126	126	126	126
(A) Downwind, Yds.	528	800	980	1280
(B) Crosswind, Yds. (Based on TLV)	375	480	600	650



WATER POLLUTION CONTROL

Direct runoff of spill to a stream or body of drinking water should be prevented by diking for later disposal. Evaporation of the material to the air at its slow natural rate is preferable to flooding which will produce large clouds of fumes. Nitrogen Tetroxide may kill fish, it reacts with water to produce toxic products. Residue may be flushed to storm sewers or sanitary system.
Advise the EPA or U. S. Coast Guard that a water incident is in progress.

Figure 5.