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FACTORS INVOLVED IN
CARGO SIZE LIMITATIONS

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FACTORS INVOLVED IN CARGO SIZE LIMITATIONS

A Report Prepared by the
Panel on Cargo Size Limitations
of the
Committee on Hazardous Materials
Division of Chemistry and Chemical Technology
National Research Council
for the
U.S. Coast Guard Under
Contract No. Tcg-15559

July 29, 1970

Washington, D. C.

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PREFACE

The National Research Council's Committee on Hazardous Materials, Advisory to the U. S. Coast Guard, was requested by the Coast Guard to determine whether size limits can rationally be set on shipments of hazardous materials, aside from considerations of the mechanical strength and stability of the vessel. A panel of the Committee was assigned to study the question, and was assisted by advice from a number of specialists whom they consulted.

After considerable discussion of the various factors involved, the members of the panel were unable to quantify these factors in such a way as to set meaningful limits on the size of shipments. The consensus is that, in addition to cargo size and characteristics of the material, the degree to which appropriate safeguards, both mechanical and personal, are applied at all phases of shipment where uncontrolled release of cargo is possible, must be considered. There is no ready way to quantify the effects of such safeguards in reducing the incidence of accidental release or in controlling the area affected in the case of accidental release. However, the panel did assemble information on how the size of the shipment affects measures needed to control the consequences of accidental release of cargo to the surroundings.

Water pollution associated with release of petroleum has been of growing concern, and was briefly noted by the panel. Since numerous studies have been made and are underway by other groups, and since the technology of control measures is in a state of flux, the panel elected not to comment on this major specific problem in greater detail.

The Committee believes the information contained in this report, while not directly answering the specific question put to it, will be useful in stimulating further thought by others interested in the effects of cargo size. The report is transmitted to the Coast Guard with that end in mind.

ABSTRACT

Cargo size has been studied in the context of water transport of bulk chemicals, many of which have been previously identified as hazardous if accidentally released.

The panel concludes no firm or arbitrary size limits presently exist or can be scientifically justified with the present information. However, larger shipments, with greater potential hazard to the public domain, demand greater attention to:

- -- container integrity;
- -- adequate pre-shipment hazard evaluation and control;
- -- a higher level of technical monitoring, supervision, and escort;
- -- faster availability of emergency control information and procedures, and more complete two-way emergency reporting of near-misses, minor incidents, as well as casualties, with subsequent detailed analysis and feed-back, to protect the interests of the shipper, operating and emergency personnel, and the public.

Areas of incomplete knowledge and needed research have been delineated.

The existence of a practical mutual-assistance plan for prompt mobilization of all available facilities, manpower, and knowledge, backed by actual training and exercises in response, should be emphasized in appraising introduction of the larger cargoes into a port.

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I. INTRODUCTION

Container size is one of the pertinent factors to be considered by the Coast Guard in establishing regulations or approving shipments of hazardous materials. The problem of whether a maximum container size should be set involves questions of safety, possible hazard, and economics. Safety and possible hazard are of concern to the public and to the approving authority. Economics is primarily of concern to the shipper. All three facets are of general concern. The Coast Guard requested the NRC Committee on Hazardous Materials to consider the problem of container size, as a follow-up to the "Report on Movement of Dangerous Cargoes," an Interagency Study, coordinated by the Office of the Under Secretary of Commerce for Transportation (1963). This report concluded (pages 14 and 26):

> "It is recommended that an administrative review and evaluation be made of the adequacy and suitability of existing Federal Laws and regulations with respect to quantity of dangerous cargoes now permitted to move within a single ship, barge, or other vessel operating on inland waterways, such study to be made by the United States Coast Guard... The Coast Guard accepts responsibility for reviewing its controls over quantities of dangerous cargoes moving on navigable waters of the United States." (Letter August 18, 1963, signed by D. McG. Morrison, Vice Admiral, U.S. Coast Guard, Acting Commandant)

The Committee on Hazardous Materials established the Panel on Cargo Size Limitations to consider the problem in depth. After preliminary study, it was agreed that an analysis of the hazard situation should be made, with a view to providing the Coast Guard with such

criteria as would be devised or discovered for use as tools in making decisions regarding the approval of various container sizes.

CARGO SIZE LIMITATIONS

I. Purpose of Study

To answer the Coast Guard request for an orderly method of determining whether a given size cargo constitutes a potential hazard greater than that acceptable to the public, and to develop a formula or procedure for comparing or relating the inherent danger in two quantities of a cargo.

II. Approach of Study

To identify, where possible, the elements of risk which are common to all shipments of hazardous materials (such as fire, explosions, toxic release to air and/or water, excessive corrosion, etc.), with the objective of quantifying these with respect to their effects.

Table #1

Types of hazards include:
1. Fire
2. Explosion
3. Toxic vapor
4. Water contamination

Table #2

Key elements identified are:
1. the size of an accident that may occur;
2. the likelihood (probability) of an accident;
3. the damage that may result.

These parameters are discussed below.

III. FACTORS CONSIDERED

Evaluation of Degree of Accident Severity

Basic to considerations of accident severity are assumptions concerning the amount and type of cargo involved. Since the capacity of containers aboard barges and ships may vary from a few hundred gallons to many tons, and the possible combinations are unpredictable, the panel carefully considered the most serious incident or casualty that might occur. Coast Guard operating personnel questioned on this point suggested the most serious situations would involve the head-on collision of two loaded tankers while both were underway in restricted waters (such as a river, waterway, or ship channel). While the serious consequences of such a navigational accident cannot be minimized, they do not directly reflect the role of the cargo size.

As considered in subsequent sections of this report, the hazards may be fire, explosion, or release of toxic cargo to air or water, each or in combination, all of which require technical evaluation for prevention and control.

An evaluation of accident potential most useful to cargo size considerations should include:

1. An accurate assessment of the immediate danger to human health, to property, and of residual hazard to the environment.
2. Design and operation of a comprehensive protection situation aimed at preventing or limiting the consequences of accidents that release dangerous materials.
3. Accident analysis aimed at defining and re-defining the specifications of the system.

The panel discussed this evaluation concept in the light of accidents which might reasonably be expected to occur in water shipments of hazardous materials. For some time it was considered

that the expected or anticipated accident might be the catastrophic release of the entire contents of a single tank or pressure vessel, or the uncontrolled admixture of the contents of two adjacent integral tanks located on a vessel. After considerable study, and consideration of documented accidents on land and at sea, it was concluded that several tanks, or even the entire cargo of a single ship (vessel) might be involved simultaneously. It further appeared that adjacent barges in a single tow might be involved in a single accident, suggesting that technical monitoring be established to assign and maintain the order of assembly of such a mixed tow. Storage of dissimilar, incompatible (or reactive) substances aboard a single hull or in a single hold likewise could be prevented by application of competent technical supervision at the working level.

It is possible to design, engineer and operate a system to a certain specific level of operational safety. It is not possible with our present knowledge to reduce to zero the probability of accidents. Sooner or later, with sufficient exposure, the circumstances could occur which would yield a major catastrophe, no matter how remote or improbable the circumstance might be in one particular operating cycle.[1]

Analysis of Hazard

When application for an increase in cargo size is presented to the Coast Guard, it is obvious that the larger cargo represents a greater potential hazard to the public than the smaller one, if all other factors remain unchanged. However, the other factors usually do not remain constant. For example, a smaller number of large shipments will be required to carry a given quantity of cargo, resulting in a lesser number of shipments and hence, less total exposure to accident situations. Other factors may likewise change, such as differences in containment and degree of technical supervision.

The decision maker, faced with these facts, needs some overt means of handling many factors in as objective a fashion as possible, to supplement his experience and judgment where these are more applicable. One set of factors amenable to quantitative assessment is the extent of the "expected" hazard from an accident resulting in release of hazardous substances. The estimation of hazard involves assessment of the nature and quantitative effect of several factors which at times may be acting in diverse senses. Broadly speaking, the hazard can be defined as a function of the

1. likelihood that an accident will occur (probability)
2. effects resulting from the accident should it occur* (consequences) and any mitigating circumstances, as for example,
3. any actions taken subsequent to the accident to reduce damage (control).

The hazard may be expressed as:

$$H = P_a D \frac{1}{F_p}$$

Where P_a = probability of accident occurrence (minimized by strict, enforced precautions). The probability factor has been studied in the context of the highway accidents where release of radioactive material would follow highway accidents.[2] The magnitude of P_a is a function of safety devices, reduction of probability, construction, etc. It is also a function of traffic congestion on the water.[3]

D = extent of expected damage which could result or evolve from the accident if allowed to proceed unchecked.

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*The environment (atmosphere, water, etc.) greatly influences these effects; sometimes increasing and sometimes decreasing them.

F_p = the factor by which actions taken subsequent to the accident reduce damage or loss. This factor is extremely important in assessing the significance of practical emergency control measures.

This equation will apply to accidents in transit, as well as accidents under static situations, such as storage, if adequate information is available from which to evolve or calculate appropriate and meaningful factors.

To utilize the above expression in assessing a cargo size for purposes of evaluation of a given container, quantitative data are required on the various factors, including some criteria for judgment of relative degree of hazard. Criteria should be established for damage to life, to health, to property, or to a combination of these effects. Without common criteria, it is impossible to compare relative hazard from different types of potential damage, such as fire versus toxicity.

In a practical sense, when faced with a decision to approve or reject an application for a container for a certain size cargo of a potentially hazardous material, the decision maker may draw on precedents as a guide, with full appreciation that these precedents may not be sound or justifiable in view of present knowledge. He can compare the magnitude of the hazard from the proposed size (Situation 2) with the similar hazard from a previously approved size (Situation 1) (assuming that the previous approval in fact had adequate justification); and he can assess whether the overall hazard will be increased or decreased. For a new material, he can compare the expected hazard with the same size cargo of a material known to have equivalent potential for similar adverse effects. The new material must be systematically evaluated for its hazard potentials. In general, it will be possible to render the decision on the basis of relative hazard.

Evaluation must be as complete as current knowledge and testing procedures will permit, since estimations, guesses, or analogy frequently invalidate otherwise valid conclusions. The relative hazard, situation 2 versus situation 1, (neglecting actions taken subsequent to an accident) may be defined as:

$$H_r = \frac{Pa_2}{Pa_1} \times \frac{D_2}{D_1}$$

Where H_r = relative hazard, situation 2 as compared to situation 1

Pa_2, Pa_1 = probability of accident in the two situations

D_2, D_1 = expected damage in the two situations

The relative hazard may be considered as the product of the relative probability of accident Pa_2/Pa_1 and the relative expected damage D_2/D_1 assuming a similar degree of control for reducing damage after accidents. Even though exact quantitative estimates may not be possible for a given situation, the relative values appear more amenable to subjective or objective evaluation, or to a combination of the two. For example, as a practical measure, the relative expected damage can be replaced by the relative area over which damage of a given magnitude would be expected. Obviously, the amount of damage might be greater in a given area in one environment (a populated area) than in another environment (a rural area), but the relative area of damage would be the same. Density of population and value of property exposed hence become major considerations. Development of an analytical model will assist in assuring that such assessments consider all factors believed germane.[4]

Comparison cannot readily be made if either of the materials exhibits more than one hazardous property, as for example, both flammability and toxicity. In this case the damage can be reduced to probable cost, allowing for the estimate of relative hazard on the basis of likely losses or claims for deprivation in the event of an accident.

This will allow reduction of dissimilar hazards to a comparable basis, cost, so that multiple types of damage can be added together to assess the total damage potential.

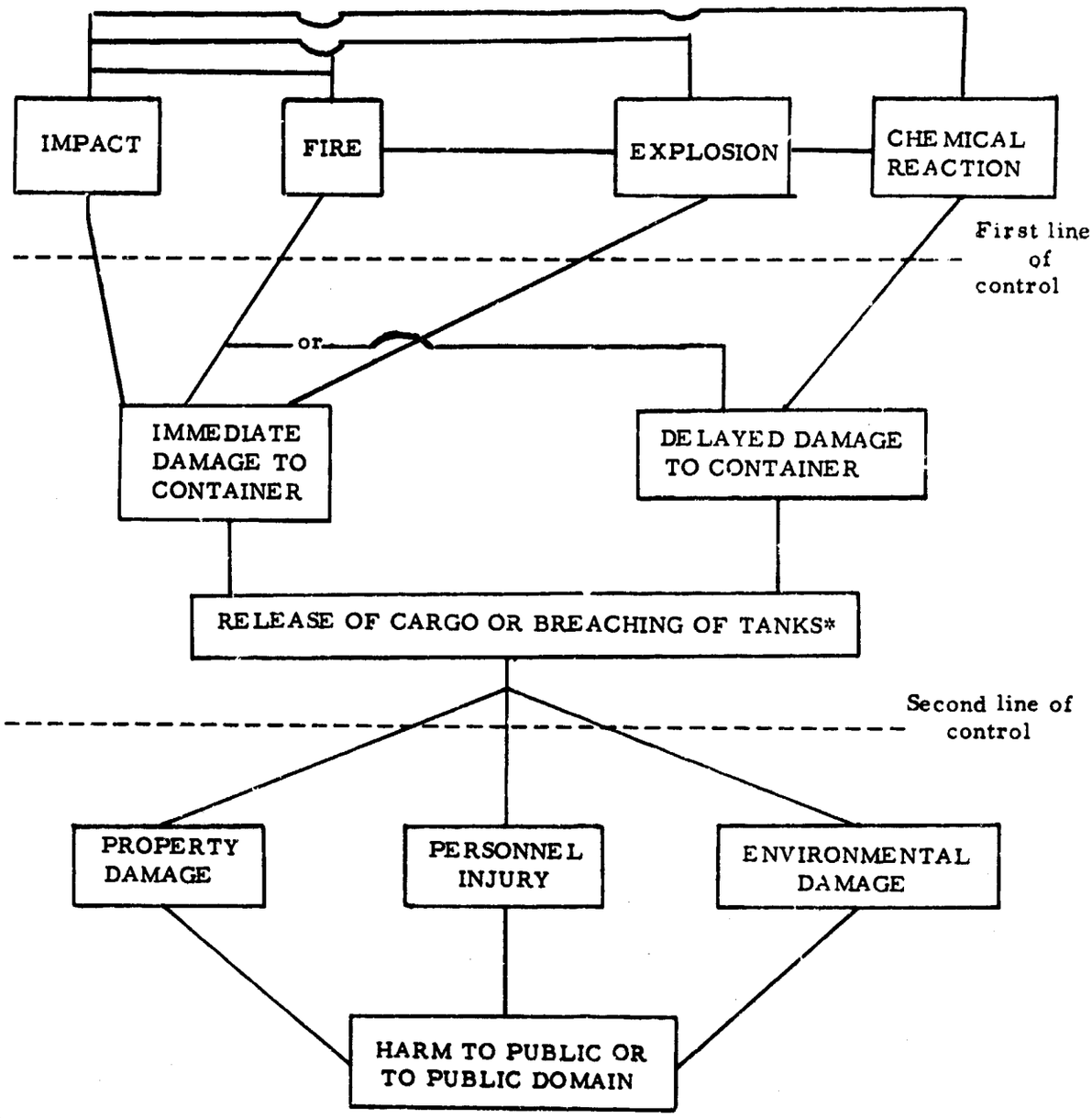
A practical example may be cited of the utility of this expression for the simple case of increase of size. Approval has been requested for shipment of a hazardous material in a container twice the capacity previously approved, on a barge equipped with certain specified safety devices. Assessment of the relative hazard would require an estimation of the relative likelihood of accident of the new system as compared to the old, and assessment of the relative area of damage, or cost of damage if an accident should occur.[5] If the material presented toxic hazards, twice the quantity released would create a hazard over somewhat less than twice the area. If the safety devices were such as to reduce the likelihood of accident by greater than a factor of two, then the relative hazard would be reduced. This simple approach must be tempered with judgment as to what degree of hazard one is willing to accept. Some levels of damage are considered unacceptable even if the likelihood is extremely low.[6]

This latter consideration will many times be overriding. In general the larger the shipment of a hazardous material, the greater the damage that might ensue if an accident were to occur, but this increase is not a linear relation.[7,8] Conversely the size of the shipment probably has less to do with the likelihood of an accident. Accident probability would seem to be a function of the number of shipments (reflecting the exposures in loading, unloading and collisions) and the preventative safety devices employed. If one were given the choice of shipping a given quantity of cargo in one large or several small shipments, the likelihood of an accident would be less for the one large shipment, assuming random statistical probability of occurrence. Furthermore, as a secondary

effect, the larger shipment would be more economical, and hence more attractive for the shipper to supply extra facilities, trained personnel, and technical supervision for the one large shipment than for several smaller ones.[9] The necessity for additional vigilance, both from the chemical and physical aspects, is emphasized by the increased chance of ship or barge collisions with increased traffic. "According to empirical analysis of the data, the distribution of ships on the water is Poissonian. This is to say, it has a structure characteristic of chance interactions. If the traffic flow doubles, and the triadic relationship of vessels is the dangerous one, then the rise in the risk of collision is $2^3 = 8$. So the risk of collision does not double, but is eight-fold in the circumstances proposed."[3] Preventive measures are important and should be considered at all levels of operations. Examples of preventive measures are considered on pages 25-31 of this report.

Hazards are incompletely understood in many cases and, even where available, the dissemination of knowledge to point-of-use is far from adequate. Chemical Abstract estimates that 4,500,000 chemicals are known. The U.S. Surgeon General testified before Congress that 6,000 of these are in common use. Specific published safety guides by recognized national authoritative organizations are available for only a few hundred. As a consequence, decisions may frequently be based on less than firm data,[10] even when made by qualified personnel. For example, exposure guidelines for a single exposure to the public have not yet been devised for most toxic materials which are now transported. The National Air Pollution Control Administration has solicited the assistance of the NAS-NRC Committee on Toxicology in developing community air quality criteria and standards for short-term exposures. (See Appendix III). The complexity of this task

TRANSPORTATION EMERGENCY



Sequence of events from time of emergency to time of harm to public or public domain. Dotted lines indicate critical times during which emergency action or controls would aid in reducing severity of incident.

*Release of cargo may occur due to other malfunctions.

for even the common substance, carbon monoxide, has been recently documented.[11] For industrial exposure, only a limited number of substances have been assigned exposure limits. Even though previous approval has been granted for a certain size container or a certain material, the approval was probably not based on an accurate appraisal of the toxic hazard. A relative relationship is only as good as the basis on which it is established. If the hazard is only vaguely documented (as is the general case), a probability estimate may give grossly inaccurate results. A totally unsupported sense of security, or an exaggerated idea of the degree of hazard, may result. The panel has not attempted to evaluate the potential hazard of existing-size cargoes. The availability of a more complete index of existing or programmed information systems for environmental quality control will facilitate such evaluations.*

Areas of Concern

Discussion of the various safety problems involved in evaluation of cargo size revealed several areas of concern. Data are needed on the probability of occurrence of an accident, a damage estimation from accidents of various sizes, and on possible protective responses or emergency control measures that might be taken which would serve to reduce the damage from the incident.

The damage assessment is a function of (a) the type of damage, or (b) effect on life and health of personnel. Survey of possible hazards revealed that areas of concern include the following:

1. explosion, immediate or delayed, as from flammable vapor-air mixtures
2. fire
3. release of toxic vapors
4. contamination of water and municipal water supplies by toxic substances.

The final area of concern is that of emergency control. This is a more diffuse area. In case of an explosion, only secondary damage can

* Proceedings of Workshop on Environmental Pollution Information Programs, May 18-19, 1970, Study of Environmental Quality Information Programs in the Federal Government (SEQUIP Committee), Office of Science and Technology, Executive Office of the President, Washington, D. C.

be mitigated. On the other hand, damage from a spill can be reduced by prompt communications to responsible authorities downstream; exposures to gross air contamination can be minimized by evacuation of personnel from downwind areas.[12] In general, common sense and realistic evaluation or prediction of the reaction to be expected in particular cases are the only apparent guides. This reaction may range from panic to apathy in the general public, and special information is needed to offset either extreme.[13, 14] Until effective instructions for emergency action are immediately available for each cargo, a coordinated national emergency control information system is activated, or some other technique or mechanism is provided for accurate, complete, and readily-available information retrieval, no assurance can be given that proper action will be taken in time to minimize the consequences of an emergency. As an absolute minimum, all cargoes must be plainly identified, with easily-recognized and understood names or symbols, so that properly equipped, trained emergency or operating personnel can promptly cope with the identified hazard. Administrative control cannot be relied upon entirely for the protection of the public. The peculiar circumstances of an incident often negate the intent of any regulation. On-the-scene evaluation by qualified personnel will always play an important part in emergency control.

Probability of Accident

Of all the information needed to estimate relative hazard, this topic yielded the least available data. As such, it constitutes an area of knowledge requirement being addressed by the Coast Guard. Efforts might well be expended to compile more complete information on accidents (casualties), on a continuing basis, including number and type of vessels involved, cargo involved and role of the cargo in the incident, extent and type of damage, and circumstances surrounding the incident. Parallel data must be obtained for the total number and tonnage of all similar shipments, to assess the percentage of shipments of a given

type suffering significant damage. Correlations of accident experience can then be made on some quantitative basis, as for example, total miles or hours in transit or at anchor, and for periods of significantly greater or less hazard, such as possible differences between daylight and night operations. Included in the study might be experience of operations under adverse visibility, such as fog.[15, 16, 17]

Relative Damage

The estimation of relative damage is amenable to some quantitative treatment if one ignores specific local situations and considers relative geographical areas that would be affected under similar environmental conditions. Damage estimation may be considered parametrically for each of the hazards discussed above: explosion, fire, release of toxic vapors, and water contamination.

IV. DAMAGE ESTIMATION

Methods of damage estimation do not exist yet in some areas of concern. For example, the greatest emphasis in fire and explosion has been on safety rather than on quantitative estimation of damage. Toxic gas clouds have been studied in considerable detail. Work is underway by the U.S. Geological Survey on the quantitative study of gross contamination of flowing streams. These topics are discussed below and in the appendices.

Explosion*

Quantitative estimation of damage from explosive materials is not readily available in open literature. The Military Services, particularly the Ballistics Research Laboratory and the Army Materiel Command Systems Analysis Agency, may be a source of information on damage from explosions beyond that available to the panel.

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*For definitions of the terms explosion, detonation, and deflagration, see Appendix VI, page 67.

For well-recognized explosives, a reasonable set of initial criteria are provided by the American Table of Distances,[18] and the DOD Ammunition and Explosives Safety Standards.[19] It is unfortunate that these tables pay little attention to the frequently-dramatic effects of missiles, created by the rupture of containers.[20] During its study, the panel made several observations of background data which appear as Appendix VIII.

Fire

Quantitative damage from fire is little better assessed than damage from explosives. Limited data are available for the burning rate of fuels on water. Several variables may be present in the many conceivable situations involving releases of fuels from barges and ships on waterways. Data are now available in translation from the Japanese oil pollution control tests at sea, July 18-19, 1968.[21,22] Similar data are needed for other liquid bulk cargoes. Even water-solubility itself does not insure complete safety, since very high dilution and mixing with water are required to reduce the vapor pressure of volatile substances so they will not burn if an ignition source is present. Released liquid fuels will quickly spread to a more or less circular, thin film on the surface of the water unless confined as by slips, locks, dams or other barriers. The shape of spills will be affected by winds, tide, and current.[23]

Based upon an average burning rate in tank fires of approximately one foot per hour, one authoritative source has extrapolated that a 10 gallon per minute spill rate of gasoline will be in equilibrium with 80 square feet of burning area. The same source cites an example of fire spread on water using this factor:

"Assuming that the rate of loading a barge is 3,000 barrels per hour (2100 gallons per minute) a broken hose would liberate gasoline sufficient to

involve some 16,800 square feet of fire area, which under intermediate conditions might easily spread on the water to a distance of about 260 feet (2 times the square root of the burning area.)" Intermediate conditions are described as a spill which is affected by wind or tide, and the fire area is four times as long as it is wide.[24]

The burning rates of several liquids and liquefied gases were determined and found to approach a maximum and constant value with increasing pool diameter.[25] This constant burning rate is proportional to the ratio of the net heat of combustion to the sensible heat of vaporization. However, it is pointed out that, with cryogenic fuels, heat conducted from the surface may be the dominant factor in the rate of vaporization of the fuel. This factor would probably also be true with those fuels on the surface of the water, but experimental verification is needed.[26,27,28] Additionally, in certain confined situations, one may no longer be dealing with a diffusion flame, but rather with a turbulent pre-mixed flame in which the flame temperature is hundreds of degrees higher than in diffusion flames.[29,30,31,32] "Average" incident heat flux (irradiation) within a fire has been observed to be approximately 47,000 BTU/(hr.) (sq. ft.). This heat-flux was achieved in fires fed with JP-4 fuel with a surface area of approximately 400 sq. ft. arranged in a circle or square. In smaller fires, irradiation from the flames was reduced, and in fires larger than 2,000 sq. ft., oxygen starvation occurred in the central core resulting in lower fire temperature. The average fire temperature of 1,850° F. was derived from a large number of tests. A fire model has been constructed and used for studies by computer simulation.[33]

Flammable Vapor Clouds

A gaseous flammable material released into the atmosphere will mix with the atmosphere to create a flammable vapor-air mixture. The initial concentration near the source will be determined by the rate of

release and by the ambient meteorological conditions. As the vapor-air (or gas-air) cloud travels downwind it will diffuse, and the flammable component may become diluted depending upon meteorological conditions. If the cloud concentration is within the flammable limits when it passes a source of ignition, it will ignite or explode if the ignition source has sufficient energy density. The incidence of ignition sources for clouds of any significant magnitude would appear to be quite high, with the result that clouds within flammable limits would have a high probability of ignition.

The concentration of such clouds downwind can be calculated from the source strength in mass of volatile material released to the atmosphere per unit time (pounds per minute) and the conditions of wind speed, wind velocity, and atmospheric stability. Charts indicating concentration as a function of downwind distance are given in Appendices I and II. The total area covered by the clouds can also be calculated.[34]

The atmospheric situation as well as the terrain and ground cover also affect the results of explosions. The energy in blast waves may be focused, dissipated and absorbed by the atmosphere, terrain and ground cover. Such knowledge has limited application before the actual occurrence of an accident. However, these effects should be considered in order to obtain reliable hazard estimates. They are probably second-order effects in that a blast is much more damaging locally than at a distance. These effects must be considered at the time and place of an explosion in order to obtain a reliable estimate of the total damage and the degree of possible legal liability.

The calculations of TNT equivalent values, in which a substance is compared by its potential energy of combustion to the equivalent amount of TNT, is considered one index of hazard, but should be viewed as only one of several insights into the actual damage potential. With

confinement and specialized situations, it is possible to realize significant energy. In actual practice, only a small percent of this calculated release is realized.[35]

The studies by E. A. Farber, in which he compared the theoretical maximum energy with observed yields from propellants when missiles failed, showed 1% to 18% yields.[36] Another study of five major space vehicle explosions involved accidents ranging from 231,000 lbs. of LO_2/LH_2 with 3.5% yield (3200 lb. TNT equivalency) down to 25,000 lbs. LO_2/RP-1 with a 4% yield (or 1000 lb. TNT). Maximum fragment range with a few exceptions was 1200 feet, with 90% of the material falling within 700 feet. The fragment densities outside the major fragment radius ranged from 0.31 to 0.80 fragments per 10,000 sq. ft. The overpressure radius of 0.65 PSI in all cases exceeded the major (90%) fragment radius.[37]

Severe destructive forces from blasts fall off very rapidly as distance from the cloud increases, and can be ignored to a first approximation when estimating relative hazard.

An equation has been suggested for calculation of yield from a vapor cloud,

$$\text{Equivalent Energy Yield of Hydrocarbons (In lbs. of TNT)} = \alpha \frac{(\Delta H\text{-Combustion})\ W}{1800}$$

where α is an empirical factor, (ΔH-Combustion) is the standard heat of combustion in BTU/lb., and W is the weight of available vapor in pounds. Values of α [minimum (0.008-0.014) to maximum (0.03-0.04)] are given, with the value for hydrogen of 0.3. Recommended approaches are given for estimation of the effects from vapor cloud explosions.[38]

Liquid Release and Water Pollution

When a liquid is released into water, the extent of flammable and/or toxic hazard will be determined by several variables. These variables include: quantity of material, characteristics of the material,

solubility in water, mixing, evaporation rates, air and water temperatures, density of liquid, effects of winds, stream flow, tidal action, and localized obstruction (such as dams, locks, or other barriers).

Information to assist in establishing the extent of the hazard created by a specific incident is often limited or non-existent.

Two separate Rhine River barge incidents, both involving the cargo cyclohexane, illustrate the importance of local conditions and the value of technical data and response. Cyclohexane is a flammable liquid, with a flash point of -4°F (-20°C), flammable limits of 1.3 to 8% by volume in air, vapor density of 2.9 (vs air), and a specific gravity (vs water) of 0.8. It has a melting point of 43°F (6.5°C), boils at +176°F or 80°C, and is insoluble in water. On July 14, 1964, TMS Eiltank 17, carrying 632 tons of cyclohexane, collided with another ship, releasing about 200 tons of cyclohexane which floated on the warm river, evaporating to a sweet-smelling, steam-like vapor. Two barges tied together sailed into this released liquid. The fire in the galley of one barge served as an ignition source for the flammable vapor-air mixture and started a fire on the water, which caused serious damage to the vessels and the loss of five lives. By contrast, on January 5, 1967, the TMS Viking, carrying 1070 tons of cyclohexane, struck the piling of the street bridge at Worms, and released 1-1/2 tons of cargo. Cooled by the river temperature of 5.2°C (41.4°F), the leaking cyclohexane crystallized and plugged the leak. Another favorable factor was the immediate response of the River Patrol, with special oil-removal equipment. Measurements with a combustible gas indicator at the point of leakage and over the water downstream showed only small traces of cyclohexane vapors. No fire occurred, and no personal injuries resulted. Quantities, the temperatures of the water and air, and the prompt response of trained personnel with knowledge and equipment, were important factors

in explaining the difference in damage between the two incidents. Unless all necessary technical data, combined with operational response, can be promptly applied to evaluation and control of a release, there is little prospect for limiting the effects of emergency situations.

In commenting on emergency control for petroleum spills, the Japanese suggest:

> "If the site of a marine fire is an open area free of industrial installations and such other facilities that might suffer from secondary hazards, it would be best to let the oil burn off, from the viewpoint of preventing sea pollution as well as from cost considerations. However, spilled oil which has been left on the sea for a fairly long time and has lost most of its volatile components may have to be diluted with gasoline in order to catch fire and burn itself out. Also, the fire cannot go on burning when the oil layer has been reduced to less than 1.5 mm thickness, and the remaining oil will have to be disposed of by some other means..."[21] See also (21a).

In considering the harmful effects of the release of a liquid cargo into a stream, the panel considered time-of-travel measurements for streams, which have been conducted by the U.S. Geological Survey. Tests have been made on the lower Missouri River,[39] and on the Mississippi River from Baton Rouge to New Orleans.[40] The reports of these tests provide the basis for a technique for predicting the time of travel of a spilled contaminant to downstream water users.[41]

Recent studies by the U.S. Geological Survey indicate that even for streams of vastly different sizes and discharge rates, a method of predicting approximate downstream concentrations is available. Appendix V discusses the concept of unit concentration and provides a

single curve, Figure 1, sufficiently accurate to predict downstream concentrations with reasonable confidence. The unit concentration is defined as the peak concentration to be expected per unit of pollutant spilled, multiplied by the rate of flow of the stream. Given the rate of streamflow,[42] the weight of contaminant spilled, and the time of travel, it is possible to calculate the maximum probable peak concentration which would arrive at any point downstream. Additional study is required on the broadening of the concentration distribution function, to estimate the arrival of the leading and trailing edges of the contamination wave (defined as the arrival of an undesirable concentration), and the subsequent reduction of contamination below this value. In addition, there is a vital need for field data on other navigable streams, as well as complementary tests on those studied.

Toxic Clouds

The hazard downwind from the release of hazardous vapors is a function of the total amount of release, the toxicity of the vapor, the time over which it is released, the time required to remove or evacuate personnel from the path, and the atmospheric conditions prevalent during the release. The study of catastrophic releases of large quantities of material is complicated by the lack of experimental information on vaporization rates. This is even more complex in a water environment, where the solubility of the chemical may be a significant factor.

The estimation of source strength (release rate of the toxic material) is the single factor which must be estimated roughly on the basis of reasonable judgment for the specific incident. Information on toxicity and downwind cloud travel is available.[43,44,45] These topics are discussed below.

Toxicity is usually studied from one of two viewpoints, and toxicity data are given for two modes of consideration. The easiest estimates to

obtain, and the most rigorous, are the acute figures for the median effect, either lethal or sublethal. Usually these data are of little use in setting hazard limits, since some fraction of the general population will be significantly affected at much lower levels. Data on acute toxicity are usually expressed as the dose in milligrams of agent per kilogram of body weight required to exhibit an effect on the exposed population. Since the dose varies between individuals, either the median lethal dose (LD_{50}) or the median incapacitating dose (ID_{50}) for a population is used. For gases or vapors, the dose received is the product of the breathing rate and the "dosage" to which exposed. The dosage is the integrated product of the concentration and the time,

$$D = \int_0^t C \, dt$$

or summation over the whole time of the concentrations at a given point, frequently spoken of as the "Ct." Acute toxicity data for human beings are usually evaluated at an assumed standard breathing rate (or minute volume) of 10 liters per minute; the resulting median dosages are designated respectively LCt_{50} and ICt_{50}, for lethality and incapacitation. Downwind hazard is frequently expressed in terms of the distance at which an unacceptable dosage will occur for a given release and specified meteorological situation. A detailed discussion of this system, with definitions, is contained in the Army-Air Force Manual on Military Chemistry.[46]

In the alternative system for measuring experimental data, toxicity for common industrial vapors is usually expressed as allowable concentrations for continuous exposure, 8 hours per day, for an indefinite employment period. These are referred to as TLV (Threshold Limit Values) by the American Conference of Governmental Industrial Hygienists; or as Maximum Allowable Concentration (MAC) by the American National Standards Institute. The terms and concepts are not interchangeable. MAC's and TLV's are long-term exposure limits

developed for industry, and are conservative since they presuppose repeated exposure over a long period of time. Accidents typically involve relatively short-term, once-in-a-lifetime (or very infrequent) exposures. Until short-term exposure limits for the general public are established, estimation of public hazard is difficult. Such limits are urgently needed.

The figure which represents the concentration one would be willing to accept as a calculated risk for accidental one-time exposure is somewhere between the two levels discussed above. It is probably nearer to the acute figure than to the long-term exposure value. In considering the practical aspects, one should also question the type of action such exposure will produce:

1. is recovery rapid with no residual effects?
2. is action delayed, possibly producing serious effects later?
3. are residual effects likely?
4. are irritant effects, odor, color, or opacity (restriction of visibility) likely to cause panic?
5. are carcinogenic effects known or suspected?
6. is specific medical treatment available and widely known by the physicians and nurses who will be called upon for treatment?

Short-term emergency exposure limits have been set for certain military chemicals by the NAS-NRC Advisory Committee on Toxicology, and short-term limits for certain industrial chemicals are published by the Pennsylvania Department of Health.* Pennsylvania defines short-term limit as the maximum atmospheric concentration of a contaminant to which a workman may be exposed for a specified short-term period. The concentration represents an upper limit of exposure for the specified time and assumes that there are sufficient recovery periods between episodes for recuperation. The average daily exposure to the contaminant, including these episodes, shall be such that the threshold limit value shall not be exceeded. The figure considered for short-term higher level

*Note that neither the NAS-NRC or Pennsylvania limits are intended to be applied to the general public, nor are the TLV or MAC values noted previously.

exposures may differ by orders of magnitude from the TLV and MAC limits of long-term exposures. This problem is being addressed by the National Air Pollution Control Administration with guidance from the NAS-NRC Advisory Committee on Toxicology, as noted previously.

Downwind travel of gas and vapor clouds has been extensively studied for many years by various agencies of the U.S. Government, including the Weather Bureau (now a part of Environmental Science Services Administration), the Atomic Energy Commission, and branches of the Military Services. A set of tables and charts reflecting the behavior of clouds from a single instantaneous (or short-term) release or from a continuous source are given in Appendices I and II, and published data on toxicity of representative compounds with high volatility from the list of bulk cargoes in bulk transportation are given in Appendix III.

These data may be used in connection with the procedure set out in Appendices I and II to estimate relative hazard for toxic gas or vapor released.

V. LEGAL ASPECTS OF SIZE LIMITATIONS

The authority under which the Coast Guard regulates hazardous cargoes originates in the "Commerce Clause" of the Federal Constitution, and is vested in the Commandant of the Coast Guard by the Reorganization Act of 1945 (P.L. 63, 79th Congress) and subsequent statutory authority. A long series of legal actions has established that where federal action, taken under constitutional authority, has provided statutes and regulations governing shipments in interstate and foreign commerce, any state or local law (even though involving exercise of the police powers) which is inconsistent or conflicting, must give way to the federal authority. This pre-emption has been held to extend to intrastate activities where they have a substantial effect upon interstate commerce.

In cases where local and federal regulations are complementary rather than conflicting, local prescriptions are to be recognized to the extent possible [e.g., see 46 USCA 170 (7)(d)]. However, there are areas where the purpose, scope, and extent of federal involvement is such as to indicate that Congress intended the federal authority to pre-empt the field except where the contrary is specifically stated. (Decisions by the Advisory Committee on Reactor Safeguards of the A.E.C. regarding the safe siting of reactors are thought to come under this description.)

A comprehensive, detailed, complete system of regulations and supervision such as that found in the Coast Guard regulations relative to explosives and other dangerous articles (e.g. 46 CFR 146.01-1 et seq., 33 CFR 126-09 and 126-17) prevails, therefore, against conflicting local prescription. The test seems to be whether the federal scheme is so completely elaborate and pervasive as to "make reasonable the inference that Congress left no room for the States to supplement it." (DuPont vs. Board of Standards and Appeals of N.Y.) However, it should be noted that where the federal government has once undertaken to exercise such supervision, "the duty is devolved upon the government to complete it in a manner reasonably free from carelessness." (Penn RR vs. U.S.)

Within the pertinent regulations there is a specification [46 USCA 170(7)(e)] that for Class A Explosives (those requiring Coast Guard permits) such limits as to maximum quantities, isolation and remoteness which are established by "local, municipal, and territorial or state authorities for each port shall not be exceeded." As to such explosives, therefore, the federal regulations are subservient to local limitations of the type described. However, it is important to note that this does NOT subordinate the federal prerogative to classify the various products in whatever manner it deems proper under existing regulations.

An unanswered question is whether the clause requiring adherence to local limitations of quantity, isolation, and remoteness for Class A explosives could be interpreted, on the basis of intent and public policy, to include "other dangerous articles" (if any). These may be determined to represent a danger of equal gravity as that presented by Class A explosives. The DuPont case (E.I. DuPont de Nemours & Co., Inc. vs. Board of Standards and Appeals of New York City) exempted "Nitramon" from loading restrictions sought to be imposed by the City Fire Marshal under local administrative ordinances on the basis that the conflicts apparent between the New York and the Federal (Coast Guard) regulations were governed by the latter, which were pre-emptive for "Class B and C" explosives and "other dangerous articles." The Court was primarily intent here on distinguishing the regulations classifying "Nitramon," an oxidizing agent, under "other dangerous articles," and further classified in 1954 as category (c)(2), dynamite-grade ammonium nitrate, from the Class A explosive limitations which under federal proscriptions were subject to specified local controls. It may be contended that the Court overstated its argument, and that, since there are several categories of "other dangerous articles," those which represent dangers equal to Class A explosives may also be subject to the local prerogatives granted by 170(7)(e). This argument would be particularly apt for any other materials requiring loading permits. It would also be substantiated by the procedure whereby authorization from local officials is obtained before loading radioactive materials within a community.

In summary, any Coast Guard regulation limiting hazardous cargo on the basis of size of quantity would be subject only to the constitutional safeguards. As long as such restrictions were not arbitrary and were reasonable, they should survive challenge to their propriety. The more

dependable, effective and comprehensive the criteria of determination, the more likely are they to be held reasonable on contest, with doubts being resolved on the side of federal authority. As to the federal-state (local) area of conflict, resolutions will be in favor of the federal government except in areas which have been specifically reserved to the state, or where there is a question as to whether the regulations are complementary rather than conflicting. The only specific question area presently moot involves the applicability of 46 USCA 170(7)(e) to such "other dangerous articles" as may be at least as dangerous as Class A explosives.[47]

VI. MEASURES TO PREVENT OR MINIMIZE CASUALTIES (OR ACCIDENTS)

Engineering and Maintenance

The integrity of the vessel-tank system should be maintained under all circumstances. The following suggestions are advanced to increase the probability of cargo containment:

1. The design of barge or ship, which takes into consideration such factors as adequate strength, collision barriers, and double skin construction, should also reflect the relative hazard expected from cargo release. This is already under active study by the Coast Guard, using the relative criteria developed by the NRC Committee on Hazardous Materials.[48] Incompletely-defined cargoes have not yet been evaluated but will be as soon as required information on their composition is available.[49] (Refer to discussion of chemical reactions in Appendix VIII and on pages 28 and 29 of this report.)

2. Systems of high reliability for automatic location of position (e.g. mechanical or electronic) should be included on each barge or ship, to assist in immediate location in the event of sinkage or other disappearance. Immediate identification of location will improve the safety and efficiency of casualty control measures. (One thousand barges and ships were reported scattered at random during hurricane

Betsy in the New Orleans area in 1965.) "Finding and securing" all hazardous cargoes should have high priority during and following any major emergency.

3. Construction-inspection, in-service instrumentation, certification, and periodic re-inspection of the cargo container should be continued or established. Specifications have been established for pressure vessels. The adequacy of construction specifications for non-pressure hazardous cargo containers should be reviewed, with particular reference to the systems involved. This would include wall-thickness, properties of materials of construction, welds, protection of connective piping, valves, pumps, and other auxiliary equipment. Frequent inspection would help prevent in-use failures.

4. Pressure venting systems should be reviewed. Existing formulae for calculating pressure relief on cargo tanks containing volatile cargoes have been reviewed by the Cargo Containment Panel of the NRC Committee on Hazardous Materials. The report of this panel is in preparation.

Operational Aspects (Responsibilities of Crews)

1. Identification of Cargo

a. Adequate identification of cargoes is of paramount importance. Without adequate identification, plainly visible and understandable to all personnel who may be involved, no intelligent control measures can be taken.[50]

b. This identification must be supplemented with sufficient information on properties, hazards, and recommended emergency action of the type currently available for 20 cargoes under the WIC (Water Information Card) program. It should be extended to describe all hazardous cargoes (both those with chemical names and those with mixture or trade names), such as the Material Safety Data Sheet requirements of the U.S. Department of Labor, Bureau of Standards.

c. Appendix IX lists emergency telephone numbers which several chemical manufacturers have established for

immediate emergency control information on their products. This information must be made available on the barge or at the tank-hold opening, as well as in the quarters of the Captain and First Officer on the tow-boat or ship. Similar information should be made available to deck crews. Without ready access to this information by trained persons who can take intelligent and immediate action, any information for emergency control action has limited value. Sufficient copies of CG-388 (Chemical Data Guide for Bulk Shipment by Water - 1970 Edition) and other Coast Guard instruction or information publications should also be readily available.[51] Consideration should be given to the very real barrier posed by language differences among ship personnel as well as confusion caused by trivial names or initials used to describe cargoes.

2. Supervision by Competent Personnel. The trade-off to reduce the overall hazard when an increase in cargo size is requested, may include provision for a higher level of training and instruction than is usually required by personnel operating vessels carrying relatively non-hazardous cargoes. This might include at least one person in the crew with sufficient technical training to supervise chemical operations and to advise the master on technical aspects. Whether or not the man should have a technical certification by the Coast Guard, based on study and examinations analogous to the "tankerman rating," has not been considered by this panel. However, unless some crew member on the ship or tow-boat has sufficient background knowledge to understand and to interpret regulations and instructions in view of the specific emergency involved, the probability of prompt and effective action which will relate to the public interest is doubtful. The panel suggests that the curriculum of those institutions which train personnel for maritime service, including the U.S. Coast Guard Academy, the several state Maritime

Academies, and the proposed National River Academy, be reviewed to insure that personnel handling hazardous cargoes have an adequate understanding of their responsibilities.[52]

Efficient emergency two-way radio communications, promptly channelled to the proper authority, has been demonstrated to be of inestimable value in any situation where additional data or knowledge is needed.[56]

3. Operating Procedures. Barges and ships carrying hazardous cargoes should be given special consideration at all times. A review of the tow-boat operating procedures should insure that the barge is located in the tow in such a way as to have minimum exposure and yet be accessible to emergency or deck crews. The lead positions should be avoided (to minimize sinkings and groundings), as should the positions immediately in contact with the tow-boat (to reduce possible exposure to crews in case of spills or release by excessive pressure). Locking procedures should avoid placing two barges of known reactive chemicals in one lock at the same time, since confinement would increase the possibility of hazard due to reactivity or fire. Hazardous cargoes should be extended priority over non-hazardous cargoes in locking and other traffic flow operation in order to minimize the potential exposure to personnel.[53]

When dealing with adjacent cargoes, vessels carrying substances which are known or suspected of chemical reactivity on contact should be isolated from each other by a distance of at least one barge. The Panel on Chemical Reactivity of the NRC Committee on Hazardous Materials has developed guides on adjacent loading.[54] The literature of chemical safety also contains considerable guidance for immediate application.[55] For example, such combinations as fuel oil spilling on ammonium nitrate, or of strong oxidizers such as liquid oxygen (LOX),

chlorine, and nitric acid contacting flammable or combustible liquids or solids, should be avoided by physical separation. Special attention should be given to the isolation of vessels carrying substances which are known to be capable of detonating. These substances include, among others:

ethylene oxide
nitromethane
n-propyl nitrate
propargyl bromide
methyl ethyl ketone peroxide

(See Appendix VIII for evaluation parameters of high-energy materials.)

Reporting

1. The tow-boat captain or ship master should have a clear understanding of standard operating procedures detailing to whom he should report any incident involving dangerous cargoes regardless of the severity of the incident. Reports should be made of exposure of any personnel, whether crew, passenger, or shore-based; the spillage or accidental release of cargo; the sinking, grounding or other damage to the barge or vessel; fire; explosion; or other misadventure. A report of the incident should be made to the U.S. Coast Guard by the fastest means available (usually 2-way radio),[56] and should contain sufficiently detailed information to enable the Captain of the Port or other Coast Guard officer to take appropriate action where necessary. Details of what to report and to whom should be formalized, and should be revised or updated as often as experience warrants. A clearer definition of reportable incident, in the context used here, is needed to insure adequate emergency reporting both for immediate action as well as for long-range analysis and feedback.[57]

2. The Coast Guard office receiving the report should know what response to give, by whom and for what purpose. This may involve other Coast Guard units, including Search and Rescue, AMVERS, the Interagency Joint Oil (and Chemical) Pollution Center, U.S. Army Corps of Engineers, state or local water and air pollution control authorities, as well as the more obvious response of harbor or river patrol, fire departments and others.[58]

3. Proper authority, procedures, and authorization for response must have been agreed to in writing by all agencies in advance, and actual drills or simulated exercises conducted at frequent intervals or confusion and misunderstanding will occur.[14] Several area-wide mutual assistance organizations exist in various ports, including the Kanawha Valley and the Houston Ship Canal. The role of the Coast Guard as an essential and unique element in such plans, should be further explored in the context of the local areas involved. Disparities should be studied, and the relationship between the vessel, the water-front facility, the Coast Guard and other federal, state, regional or local agencies should be clarified.

Coast Guard officers participating in the deliberations of this panel have stated that the Coast Guard has no legal requirement or mandate to fight fires, except for protection of Coast Guard property. How widely this limitation of authority and responsibility is recognized has not been reviewed by the panel, but a frank and realistic understanding between the Coast Guard and the harbor and river port authorities would seem to be mandatory. Fire and police units are usually the first response to emergencies. The loan and use of specialized Coast Guard equipment, including fire hoses, pumps, extinguishers, personal protective equipment (such as self-contained breathing apparatus or other appropriate respiratory protective devices[59], helmets, boots, analytical instruments, and other items necessary for the safe and efficient deployment of emergency control personnel should be reviewed. One step in the direction of placing more

responsibility on the shipper for on-scene emergency control would be to install and maintain fire-pumps and other emergency control devices on tow-boats handling hazardous cargoes.[60]

Refloating or Retrieval

The panel has discussed the need for a survey or inventory of cranes and other lifting devices which are available on short notice for lifting all or parts of sunken or damaged ships, barges, and cargo tanks. It may be noted that, even if the location of a sunken barge or ship is immediately known, considerable time may elapse before equipment may be brought to the scene to effect retrieval. The survey should also include state-of-the-art references to alternate lifting by pontoons, air inflation, plastic beads, and other salvage techniques. The transfer of cargo to another vessel, while leaving the hull submerged, may also be considered. Neutralization is another possibility. Cargoes could be classified into those which can be left on submerged ships or barges, and those which, in the public interest, must be removed regardless of effort expended.

The Coast Guard, on request and at the option of the Captain of the Port, provides escort service for certain quantities of explosives and other cargoes when these are passing through restricted waterways. The Army Technical Escort Service escorts in transit unusual substances, the release of which might be detrimental to the public. Escort service insures on-the-scene presence of personnel, specifically briefed or trained on emergency control measures, and having instrumentation, neutralizing agents, and personal protective equipment adequate for the specific cargo involved. It is possible that an extension of the escort service concept might be helpful for especially hazardous cargoes, in restricted waterways, areas of heavy concentration of water traffic, or near areas of high population density.[9]

VII. CONCLUSIONS

1. In order to make a valid decision on permissible cargo container size, it is essential that an estimation be made of the relative hazard to the community from shipments at the proposed size as compared to shipments of a size previously approved for the same commodity or for one with a similar hazard potential. In fact, little data exists on the potential hazard of "accepted" cargoes of existing size, and the panel has made no assessment of the level of hazard. The components of the hazard evaluation are the likelihood of accident, the expected damage if an accident occurs, and the possibility of taking mitigating action to lessen the damage subsequent to the accident. In some cases, the expected damage will be greater than that acceptable under any circumstances, even if the likelihood of occurrence is very low.

2. It does not appear valid to restrict shipment of cargoes on the basis of size alone. Presently accepted shipments cannot be used as a reference point, since little evaluation has been made of the potential effects of present-size cargoes. Factors acting to restrict accidents and resulting damage have been extremely effective, as attested to by the low incidence of damage from many large shipments. For some commodities little or no adverse effects have been experienced, suggesting the success of procedures and devices in restricting the probability of accident and of resulting damage. For approval of future requests for shipments of a larger size, the trade-off to be realized is the further development of such procedures and devices, of ship and barge design, and of supervisory and on-the-deck personnel, adequately trained and informed in technical details of safe handling and emergency control procedures.

3. Past experience and incident reports of previous accidents are of limited usefulness to the decision-maker, since incomplete details minimize the quality and validity of such reports.

4. Methods for estimating possible damage and threat to life and property can be obtained on a quantitative basis for fire, explosion, and release of toxic gas. (See pages 12-14 and 19-22 of this report). These estimates would then serve as a means of comparison and as a basis for shipment approval. Stream pollution calculations will be subject to quantitative treatment in the near future.

5. Certain information required for the assessment of the quantitative nature of hazards is lacking or inadequate. The panel has identified the following areas where such information is needed:

a. Information is needed on the type of shipment and on the frequency of accidents which, directly or indirectly, involve cargo size. This would provide a means for assessing the probability of an accident occurring, at least on a relative or actuarial basis. (See pages 11-12 of this report).

b. Information is lacking on permissible toxicity guide-lines for human exposure of the general public. (See pages 19-22 of this report). These guidelines must be based on the assumption that there will be no lasting residual injury from a one-time exposure to the accidental release of a chemical vapor or gas.

c. Stream flow data is incomplete for navigable streams. This data should relate volume flow on a daily basis to arrival and duration of the contaminant at various points downstream from the point of accidental release. (See Appendix V of this report).

d. An appreciation is lacking of tidal flow pollution as it relates to spills in harbors or bays.[28, 61, 62, 63, 64]

e. Basic data are needed on leaks from damaged containers for various cargoes, including compressed and liquefied gases, and liquids.

f. The hazard created by release of flammable and/or toxic liquids on water has not been adequately quantified for various conditions.

6. The available information, though sparse, can be utilized to guide intelligent action to minimise hazard in the case of some types of accident. For example:

a. Examination of the tables in Appendix I will indicate that downwind hazard from release of toxic gas or vapor is lowest during lapse meteorological conditions. This would indicate that many dangerous operations (such as the historic raising of the chlorine barges in the Mississippi) should preferably be carried out on bright, sunny days with moderate winds.

b. In the event of a catastrophic release of toxic gas or vapor, the same appendix will indicate the area to be warned and temporarily evacuated.

c. Using Appendix V, supplemented by additional knowledge of navigable rivers, charts can be developed to predict the arrival of dangerous concentrations of soluble contaminants downstream of a spill. These charts may then be used to warn water users downstream of the time periods during which it would be undesirable to take water from the river for potable supply. Since the time of travel in many cases ranges from several hours to days, sufficient time may be available to muster trained personnel to conduct sequential chemical analyses as a further aid to decision making.

7. In view of the fact that explosion and fire damage criteria are not readily available in the open literature for use in estimating relative hazard, the appropriate military organizations should be queried for such pertinent information they may have developed, but not yet published.

APPENDIX I

Calculation of Hazard from Vapor or Gas Clouds

A. Flammable Vapor Clouds

A flammable vapor cloud will ignite if the concentration reaches the lower flammable limit, as the cloud moves with the wind. The combustion will flash back to the point at which the upper flammable limit is reached, or to the source of the flammable substance. If the leak rate is small enough that the lower flammable limit is not reached at any point, no combustion or explosion would be expected.

To estimate the downwind distance reached by a given concentration, first determine or estimate the leak rate (or evaporation rate from a pool of flammable liquid resulting from a spill). Then follow the step-by-step procedure given below for toxic clouds, Case II (pages 39-41), using the lower flammable limit concentration for the "allowable" concentration, Cp.

B. Toxic Clouds

Exposure to toxic vapor causes physiological effects depending in large measure upon the quantity inhaled, which in turn depends largely upon the dosage (Ct) to which one is exposed. The dosage at a remote point will be a function of the source concentration, distance from the source, wind speed, atmospheric turbulence, and time. The cloud will travel in the general direction of the prevailing wind, but will wander from a straight line due to gustiness of the wind and to terrain features. Generally it will broaden and become more dilute the farther it travels. The area of hazard will be roughly elliptical or tear-drop in shape for any dose level of concern. That level is a function of the toxicity of the compound released. Since

the wind may be from any direction at the time of accidental release of a toxic material, the danger area will be within a circle centered on the release point and with a radius equal to the calculated downwind travel distance.

Two basically different modes of accidental release may be cited. The first is the total spill of a given quantity of material at one instant, or over a short period of time, arising from a rupture, such that little control can be exercised within the spill time. This time may range from several minutes to perhaps an hour. The second limiting case would be relatively constant, continuous release of material from a leak over a more extended period of time. All variations between this might occur, but these two situations will define the limits of the problem. Solutions for both situations are outlined below. For the first case, the allowable dosage would be required. This is the "public exposure" limit previously mentioned. This limit may be quoted in various units. It will be necessary to convert it to units of mg min/m^3. It may be derived from values of mg/person or mg/kg of body weight. To convert from milligrams per person to dosage units, divide by the standard breathing (resting) rate of 10 liters per minute and multiply by 1000 (liters per m^3).

$$\frac{\text{mg}}{\text{10 liters/minute}} \times \frac{\text{1000 liters}}{\text{m}^3} = \frac{\text{mg min}}{\text{m}^3}$$

This is tantamount to multiplying dose in mg by 100 to give the "Ct" units of mg min/m^3.

Tables 1, 2, and 3, pages 42-43, give the downwind distance to which any given dosage will carry under a range of meteorological conditions. If the release of vapors is over a longer period of time, the distance will be somewhat less and the cloud width greater, but the relative areas will remain approximately the same. For

purposes of relative hazard estimation, the distances would probably suffice.

For the second case, a continuous leak over a long period of time, the concentration to which one could be safely exposed would be needed. If data are available in other units, they can be converted as discussed below. Figures 1 and 2, pages 44-45, give the source strength (lbs/min), or C_p/Q. The source strength is located on the abscissa and the distance is read from the ordinate using the appropriate curve depending upon the meteorological conditions. In every case, maximum hazard will obtain with moderate wind speed and inversion (temperature increasing with height above ground--a situation regularly expected on calm, clear nights.) It will be necessary to ascertain the leak rate or source strength of a gaseous material, or to estimate the evaporation rate of a pool of liquid, if that is the source of the vapor.*

In both cases, it will be necessary to establish a toxic dosage or concentration limit. In the absence of public exposure limits, the most useful reference found to be applicable in the intermediate range of concentration was Industrial Hygiene and Toxicology, Patty, F. A., Ed., 2nd Revised Edition, Vol. 2, Toxicology, Interscience, John Wiley & Sons, N.Y., 1963. This compilation

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*In a 7 ft. diameter tray, 1/2 ton liquid chlorine at 3 inch depth was observed to evolve 5.6 lb./hr. sq. ft. of gas. After an initial increase in vapor release, the rate was significantly reduced by application of mechanically produced protein foam, but was significantly increased by water fog. Control of Chlorine Spillages, 16mm, sound, color, 10 minute movie, Mond Division, I.C.I. New York, Inc., Stamford, Connecticut.

appears to include all figures in previous standard references, plus a larger amount of more recent data from the general literature. This source has been compiled in Appendix III giving, where possible, concentrations and time data quoted. The compounds selected are those listed in U.S. Coast Guard Circular No. 10-64 which boil below 150° F. This arbitrary limit was chosen because the bulk of liquids boiling above this value would be expected to evaporate only slightly before clearing operations could take place, although some operations should be conducted by experts wearing protective gear appropriate for the specific exposure.

STEP-BY-STEP PROCEDURE

Case I. Sudden Massive Release

1. Establish or estimate quantity of agent released.
2. Determine hazardous toxicity dosage for the compound of concern in units of mg min/m^3. Use toxicity Appendix III.
3. Estimate atmospheric dispersivity. As a reasonable approximation use the following guide:
   a. Clear cool nights over land (inversion) and all cases of light winds over water bodies more than 1/2 mile wide - Use Table 1.
   b. Cloudy skies and/or moderate winds day or night over land or over water (neutral) - Use Table 2.
   c. Bright day with light winds over land - Use Table 3.
4. From the appropriate table, for the quantity released (1 above) and toxic dose (2 above) estimate the hazard distance in miles.
5. Note: Table 2 also applies over land with light winds as a transitional condition following sunrise and a brief period on either side of sunset. The length of the

transition period is shortest (45 minutes or less) with open level terrain and very light winds, and longer (2 hours or more) in urban areas or hilly, wooded areas.

6. Note: The hazard dosage-distance relationship is a function of the wind speed. Tables 1, 2, and 3 are given for reasonable usual speeds expected. Higher winds will reduce the downwind hazard distance. Correction can be made, if desired, by considering that the dose at any point downwind will be inversely proportional to wind speed. Thus, if a toxic dosage would travel to 50 miles under a given set of conditions at 4 miles per hour wind speed, the dose at 50 miles would be only half as great at 8 miles per hour. This is not equivalent to saying the toxic dosage would travel only to 25 miles downwind.

Case II. Continuous Leak

Since the leak is continuous, the dosage to which a person would be exposed varies with the time he spends in the cloud. The total dosage to which he would be exposed would be the product of the concentration and the time he spent in the cloud at a given point, since dosage is defined as the integral of this product.

Proceed as follows:

1. Estimate the allowable concentration from tables for the compound of concern, or by dividing the allowable toxic dosage by the estimated time of exposure (until the victim would be removed from the cloud, or could leave the area).

   Allowable concentration = C_p = Dosage ÷ Time

   Units = milligrams/cubic meter

2. Estimate or determine the spill rate in pounds of material released per minute.

   Q = lbs/min

3. Divide C_p by Q.

4. Estimate atmospheric turbulence. As a reasonable approximation use the following guide:

   a. Clear cool nights over land (inversion) and all cases of light winds over water bodies more than 1/2 mile wide - Use Figure 1, line labeled A (stable).

   b. Cloudy skies and/or moderate winds day or night over land or over water (neutral) - Use Figure 1, line labeled B (neutral). See note 7.

   c. Bright day with light winds over land - Use Figure 1, line C (unstable).

5. Reading down from C_p/Q (3 above) on the abscissa to the relevant curve, read downwind distance on the ordinate. This is the distance to which the allowable concentration would reach. Upwind the concentrations would be greater; downwind they would be less.

6. Note: The distance to which any concentration of interest would travel can be determined by the same procedure, merely by dividing C by Q and repeating steps 4 and 5 above.

7. Note: Line B (neutral) also applies over land with light winds as a transitional condition following sunrise and a brief period on either side of sunset. The length of the transition period is shortest (45 minutes or less) with open level terrain and very light winds, and longer (2 hours or more) in urban areas or hilly, wooded areas.

8. Note: The concentration-distance relationship is a function of the wind speed. The curves are drawn for reasonable usual speeds expected. Higher winds will reduce the concentration. Correction can be made, if desired, by considering that the concentration at any point

downwind will be inversely proportional to wind speed. Thus, the concentration at 25 miles downwind under a given set of conditions with a 4 mile per hour wind would be reduced by half if the wind speed were 8 miles per hour.

Table 1

Downwind Hazard - Dosage

Meteorological Conditions: Inversion (+2° F.T.G. 2-1/2 m)
4 mph Wind Speed
Downwind Hazard Distance, Statute Miles

Source Strength Tons	Distance in miles for						
	Hazard Dosage mg min/cu m						
	1	10	100	1000	10,000	100,000	300,000
10	(4300)	(800)	(125)	25	4	0.7	0.3
20	(6800)	(1200)	(200)	35	6	1	0.5
50	-	(2200)	(420)	(75)	12	2	1
100	-	(4300)	(800)	(125)	25	4	1.6
200	-	(6800)	(1200)	(200)	(35)	6	2.8
500	-	-	(2200)	(420)	(75)	12	5.6
1000	-	-	(4300)	(800)	(125)	25	10

Figures in parenthesis - Note 1.

Table 2

Downwind Hazard - Dosage

Meteorological Conditions: Neutral (Z.T.G.)
7 mph Wind Speed
Downwind Hazard Distance, Statute Miles

Source Strength Tons	Distance in miles for						
	Hazard Dosage mg min/cu m						
	1	10	100	1000	10,000	100,000	300,000
10	(140)	40	10	2.8	.8	0.2	0.1
20	(225)	60	15	4.3	1.3	0.3	0.2
50	(370)	(100)	25	8.1	1.9	0.5	0.3
100	(500)	(140)	40	10	2.8	0.8	0.4
200	(850)	(225)	60	15	4.3	1.3	0.6
500	(1500)	(370)	(100)	25	8.1	1.9	1.2
1000	(2000)	(500)	(140)	40	10	2.8	1.6

Table 3

Downwind Hazard - Dosage

Meteorological Conditions: Lapse (-2° F.T.G. 2-1/2 m)
7 mph Wind Speed
Downwind Hazard Distance, Statute Miles

Source Strength Tons	Distance in miles for						
	Hazard Dosage mg min/cu m						
	1	10	100	1000	10,000	100,000	300,000
10	1.7	0.9	0.5	0.3	0.14	0.08	0.06
20	2	1.1	0.6	0.32	0.2	0.1	0.07
50	2.5	1.4	0.7	0.4	0.22	0.12	0.1
100	3.0	1.7	0.9	0.5	0.3	0.14	0.11
200	3.7	2	1.1	0.6	0.32	0.2	0.12
500	4.7	2.5	1.4	0.7	0.4	0.22	0.17
1000	5.6	3.0	1.7	0.9	0.5	0.3	0.19

Notes to Tables 1-3.

1. For the inversion and neutral cases, hazard distances greater than 50 miles cannot be considered as accurate for many reasons.

a. At a low wind speed of 4 mph in any 8 hour period the cloud would traverse only 32 miles. In most 8 hour periods there would be a change of atmospheric stability conditions thereby subjecting the cloud to different diffusion conditions. The effect of variable atmospheric conditions should be considered for any case that results in large hazard distances (> 50 miles) especially since any distance that great represents an extreme hazard.

b. Little is known about the degree of terrain absorption of an airborne chemical cloud. This factor would reduce hazard distances but no quantitative data are available.

c. The diffusion equation used for the hazard table is based on relatively short distance data (on the order of 1-1/2 to 2 miles).

2. The hazard distance is thus conservative in nature and contains a rather large safety factor.

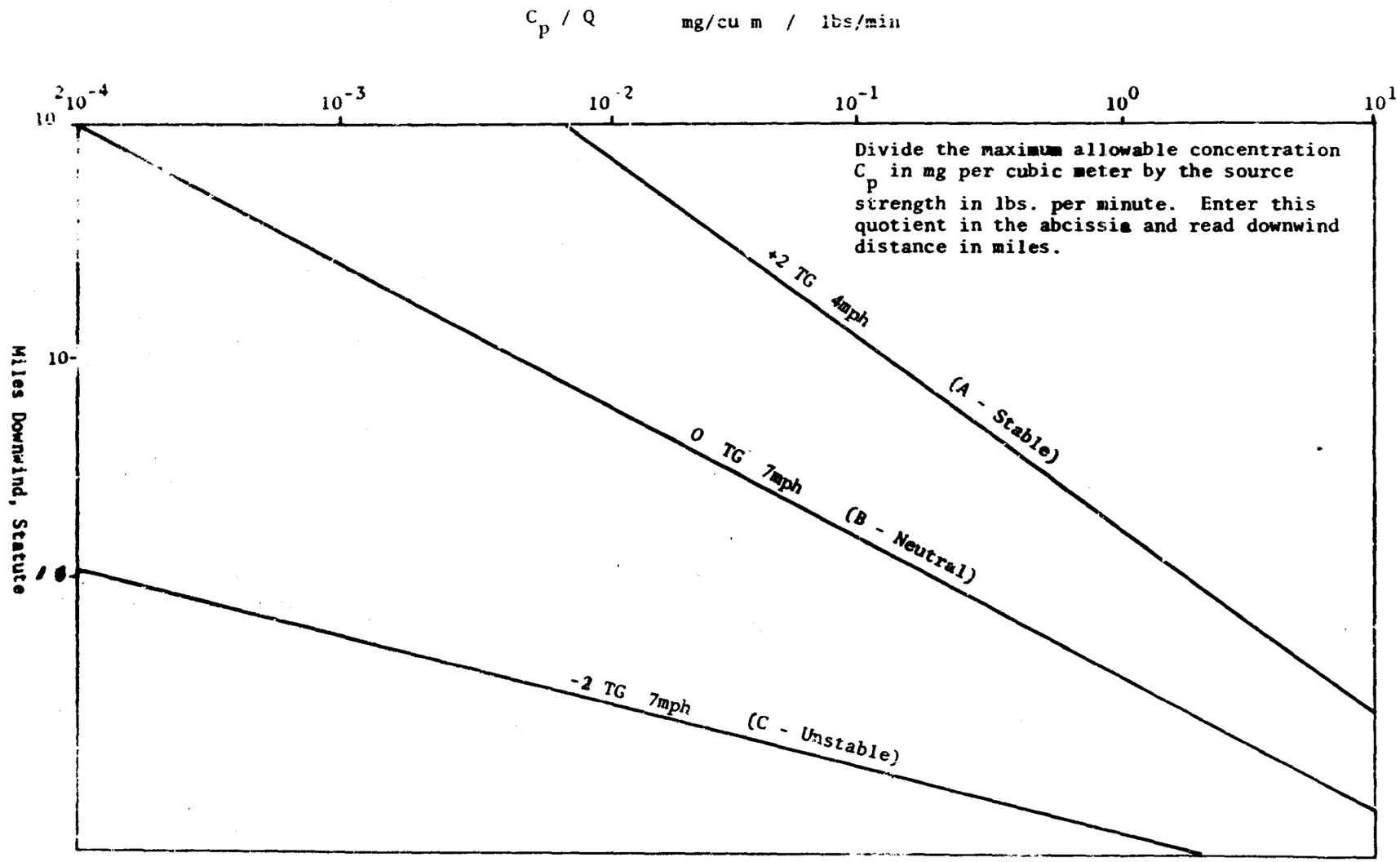

C_p / Q mg/cu m / lbs/min
10^2
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
10
1
Miles Downwind, Statute
Divide the maximum allowable concentration C_p in mg per cubic meter by the source strength in lbs. per minute. Enter this quotient in the abcissia and read downwind distance in miles.
+2 TG 4mph
(A - Stable)
0 TG 7mph
(B - Neutral)
-2 TG 7mph
(C - Unstable)

FIGURE 1.

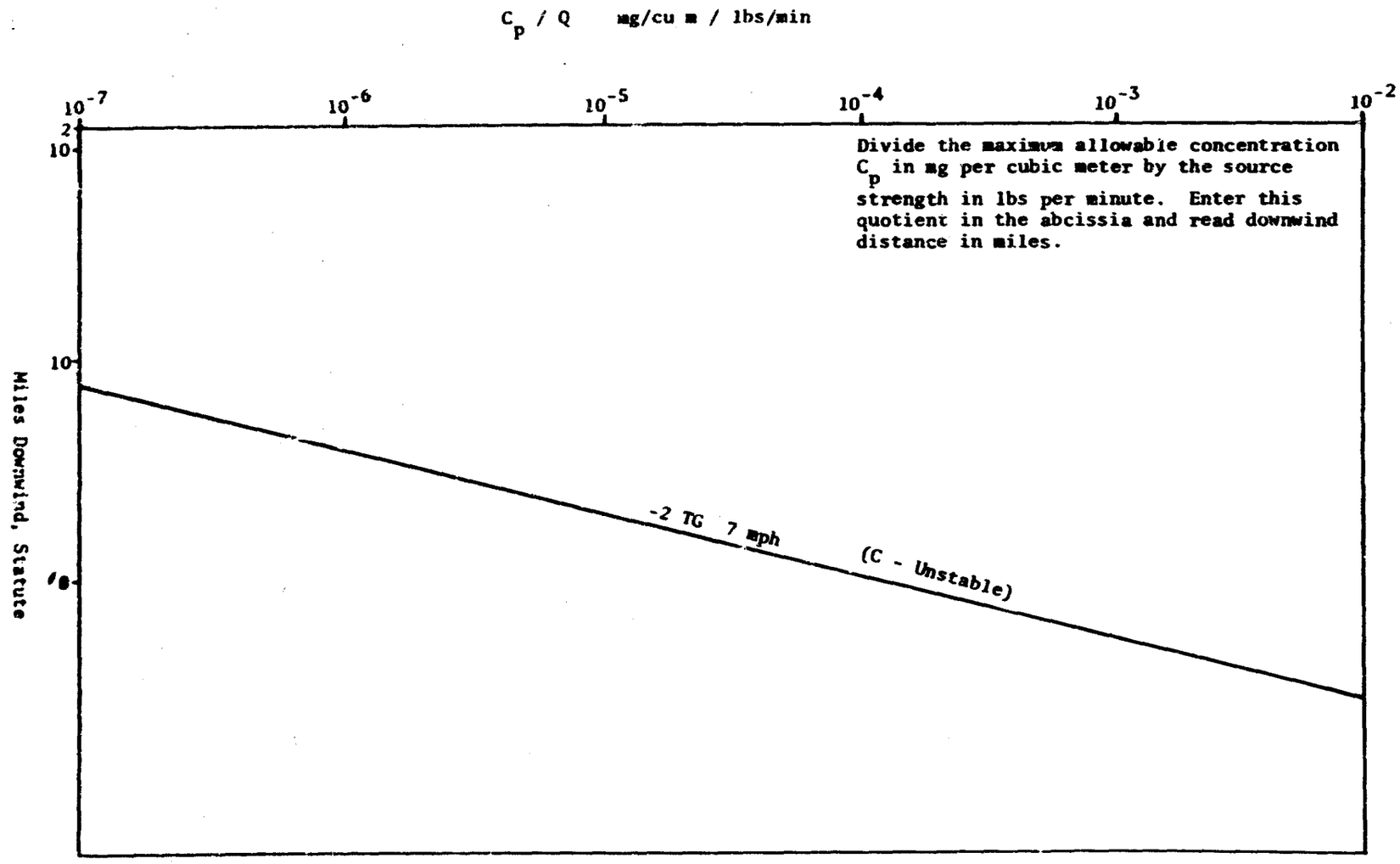


FIGURE 2. (FIGURE 1 Extended)

APPENDIX II

Computations for Concentration of Chlorine Release*

Conditions

Stable conditions (Pasquill Type E)

Wind speed = 2m/sec

Distances of 10^2, 10^3, 10^4m

Initial diameter of chlorine pool = 20m, 100m

Source strengths 1000 lb = 4.5×10^5 gm

10,000 lb = 4.5×10^6 gm

Release times 10 min, 180 min

1.0 gm/m^3 = 350 ppm (Cl_2) (by volume)

Equation

Concentration for centerline (peak) is:

$$\bar{X} = \frac{Q'}{\pi \left(\sigma_{y_o}^2 + \sigma_y^2\right)^{1/2} \sigma_z \bar{u}}$$

where

Q' = gm/sec (for dose use Q (total release in gms)

σ_{y_o} = 1/4 of initial pool diameter

σ_y = standard deviation, lateral

σ_z = standard deviation, vertical

$\bar{u}$ = average wind speed

NOTE: The equation used gives the concentration on the time-mean plume centerline. Off axis concentrations will decrease as an approximately normal distribution with distance from the axis.

* These calculations were made independently of the method and tables used in Appendix I, and are included as a method of cross-check.

Step-Wise Presentation of Concentrations from Releases of Gases

RELEASE TIME: 10 min, 180 min

SOURCE STRENGTH: 4.5×10^5 gm (1 ton); 4.5×10^6 gm (10 tons)

INITIAL DIAMETER OF POOL: 20m, 100m

DISTANCE FROM SOURCE: 10^2 m, 10^3, 10^4

		4.5×10^5 gm, 20m, 10^2 m	4.5×10^5 gm, 20m, 10^3	4.5×10^5 gm, 20m, 10^4	4.5×10^5 gm, 100m, 10^2	4.5×10^5 gm, 100m, 10^3	4.5×10^5 gm, 100m, 10^4	4.5×10^6 gm, 20m, 10^2	4.5×10^6 gm, 20m, 10^3	4.5×10^6 gm, 20m, 10^4	4.5×10^6 gm, 100m, 10^2	4.5×10^6 gm, 100m, 10^3	4.5×10^6 gm, 100m, 10^4
		NOT COMPUTED									NOT COMPUTED		
DOSAGE (gm sec/m^3)	10 Min RELEASE				9.5×10^2	8.0×10^1	2.6	3.6×10^4	9.0×10^2	25			
PEAK CONCENTRATION (gm/m^3)	10 Min RELEASE				1.6	0.13	0.004	60	1.5	0.04			
PEAK CONCENTRATION (PPM)	10 Min RELEASE				560	46	1.4	2.1×10^4	530	14.0			
DOSAGE (gm sec/m^3)	180 Min RELEASE				8.9×10^2	5.0×10^1	1.3	2.3×10^4	4.8×10^2	13			
PEAK CONCENTRATION (gm/m^3)	180 Min RELEASE				8.2×10^{-2}	4.6×10^{-3}	1.2×10^{-4}	2.1	4.5×10^{-2}	1.2×10^{-3}			
PEAK CONCENTRATION (PPM)	180 Min RELEASE				29	1.6	0.04	735	15.7	0.42			

D. H. SLADE
2/15/68

APPENDIX III

Compound	Short term Exposure Values	B.P. (°F)	1969 Vapor TLV Hazard Concentration ppm	mg/m^3	Remarks
Acetaldehyde		70	200	360	Odor detected at 25-50 ppm; LCt_{50} (Rats) = 1.08×10^6 mg min/m^3; 1 ppm≃1.8 mg/m^3.
*Acetone	15,000 ppm 60 min NRC 1,000 ppm 30 min Pa.	134	1,000	2,400	Industrial limit: 1,000 ppm; LCt_{50} (Rats) 1.8×10^7 mg min/m^3; unacclimated persons experience eye, nasal, and throat irritation at 500 ppm; acclimated persons - up to 3,000 ppm with minor irritation; 1 ppm≃2.37 mg/m^3.
Acrolein	0.5 ppm 5 min Pa.	125	0.1	0.25	1 ppm causes marked eye, nose, and throat irritation within 5 min; 0.25 ppm is moderately irritating; LCT_{50} (Rats) ≃ 8.97×10^3 mg min/m^3; 1 ppm≃2.3 mg/m^3.
Allyl Chloride		115	1	3	Odor detected at 3-25 ppm; nose and pulmonary irritation at <25 ppm; eye irritation at 50-100 ppm; LCt_{50} (Rats)> 1.63×10^5 mg min/mg^3; 1 ppm≃3.13 mg/m^3.
Ammonia Anhydrous	400 ppm 60 min NRC 100 ppm 30 min Pa.	-28	50	35	Odor detected at ~5 ppm; 300-500 ppm may be tolerated for less than 1 hr; 400 + ppm cause immediate irritation to eyes, nose, and throat; LCt_{50} (Rabbits)≃ 3.15×10^5 mg min/mg^3; 1 ppm≃ 0.7 mg/m^3.
Butadiene (1,3 Butadiene)		24	1,000	2,200	Humans survived 8,000 ppm for 8 hrs without serious effect; hazard concentration is probably conservative, but data are sparse; 1 ppm≃ 2.22 mg/m^3.

* Asterisk indicates hazard concentration exceeds industrial limit for chronic exposure.
Short term values from Pennsylvania, except where shown as NRC limits. (January 25, 1968)

Compound	Short term Exposure Values	B. P. (°F)	1969 Vapor TLV Hazard Concentration ppm	1969 Vapor TLV Hazard Concentration mg/m^3	Remarks
Butane (n-Butane)		31	3,700	8,790	Odor detected at ~ 5,000 ppm; hazard concentration is based upon 1/5 of lower flammable limit, not physiological effects; 10 min. exposure to 10,000 ppm results in drowsiness, no other effects; 1 ppm ≃ 2.38 mg/m^3.
*Carbon Disulfide	200 ppm 10 min 100 ppm 30 min 50 ppm 60 min NRC 300 ppm 30 min Pa.	115	20	60	Odor not adequate warning; industrial limit: 20 ppm; LCt_{50} (Man) ≃ 4.5 x 10^5 mg min/m^3; 1 ppm ≃ 3.12 mg/m^3.
Carbon Tetrachloride	25 ppm 30 min Pa.	168	10	65	Odor detected at ~ 79 ppm; LCt_{50} (Rats) > 1.13 x 10^6 mg min/m^3; 1 ppm ≃ 6.29 mg/m^3.
*Chlorine	3 ppm 5 min Pa.	-29	1		Industrial limit: 1 ppm; 3-6 ppm causes definite irritation to eyes, nose, and throat; exposures to 14-21 ppm for 1/2 hr + are dangerous; 1 ppm ≃ 2.9 mg/m^3.
Chloroform	400 ppm 30 min Pa.	142	50 ceiling	240	Odor detected at ~ 200-300 ppm; 389 ppm can be endured for 30 min without complaint; 1 ppm ≃ 4.89 mg/m^3.
Dimethylamine	20 ppm 5 min Pa.	45	10	18	High to moderate toxicity, methylamines are irritating to eyes, throat and lungs at < 100 ppm; little irritation at < 10 ppm; 1 ppm ≃ 1.84 mg/m^3. The odor of dimethylamine is readily detected at less than 10 ppm; brief exposures of 20 to 100 ppm cause irritation to eyes, nose and throat; no irritation at less than 10 ppm.

* Asterisk indicates hazard concentration exceeds industrial limit for chronic exposure.

Compound	Short term Exposure Values	B. P. (°F)	1969 Vapor TLV Hazard Concentration ppm	mg/m^3	Remarks
Ethyl Chloride		54	1,000	2,600	The anesthetic effect of high concentrations might create hazardous situations; LCt_{50} (Guinea Pigs) $\cong 1.41 \times 10^7$ mg min/m^3; 1 ppm $\cong$ 2.64 mg/m^3.
Ethyl Ether	1000 ppm 30 min Pa.	94	400	1,200	Exposure to 2,000 ppm for more than a brief period may lead to illness; there is a large margin of safety between the concentration causing nasal irritation and that causing anesthesia, permanent damage, and death; 1 ppm $\cong$ 3.03 mg/m^3.
Ethylene		-115			Greatest industrial hazards are flammability and possible asphyxia. Patty suggests maximum limit in workroom of 5,500 ppm, which is 1/5 of lower flammable limit; 1,000 ppm is recommended industrial limit for chronic exposure; 1 ppm $\cong$ 1.15 mg/m^3.
*Ethylene Oxide	200 ppm 30 min Pa.	51	50	90	Industrial limit = 50 ppm; odor detected at 700 ppm; Patty claims 150 ppm probably safe for single exposures not exceeding 7 hrs once per week; 500 ppm probably safe for single exposure not exceeding 1 hr; 1 ppm $\cong$ 1.8 mg/m^3.
Ethylenimine (Ethyleneimine)	5 ppm 30 min Pa.	132	0.5	1	Poor warning properties and delayed symptoms accentuate hazard; eye, nose, and throat irritation at $>$100 ppm; odor detected at 2 ppm, but similar to ammonia; LCt_{50} (Mice) $\cong 3.93 \times 10^4$ mg min/m^3; 1 ppm $\cong$ 1.8 mg/m^3.
Isobutyraldehyde		142 147 (Commercial 97%)			Toxicity relatively low - definite value not established.** LCt_{50} (Rats) $>5.57 \times 10^6$ mg min/m^3; 1 ppm $\cong$ 2.9 mg/m^3; See attachment #2.

* Asterisk indicates hazard concentration exceeds industrial limit for chronic exposure.

** "Chemical Safety Data Sheet", SD-78; Mfg. Chemists Association; 1960.

Compound	Short term Exposure Values	B.P. (°F)	1969 Vapor TLV Hazard Concentration ppm	1969 Vapor TLV Hazard Concentration mg/m^3	Remarks
Isoprene		93			Toxicity probably similar to Butadiene - definite value not established. Qualitatively, its pharamacological activity is similar to Butadiene; animal studies indicate it is a more potent anesthetic. LCt_{50} (Mice) $> 1.51 \times 10^7$ mg min/m^3; 1 ppm $\simeq 2.79$ mg/m^3.
Methane		-259	Toxicity low - definite value not established.		Chief danger is explosion hazard; methane may accumulate in upper strata of poorly ventilated areas to produce asphyxiating atmosphere; 10,000 ppm is a suggested maximum limit based upon 1/5 lower flammable limit; 1 ppm $\simeq$ 0.66 mg/m^3.
* Methyl Alcohol	1,000 ppm 60 min NRC	147	200	260	Industrial limit = 200 ppm; 2,000 ppm is barely detectable by odor; 400 ppm is probably safe for a limit exposure $<$(8 hrs.); LCt_{50} (Cats) $\simeq 1.58 \times 10^7$ mg min/m^3; 1 ppm $\simeq 1.31$ mg/m^3
Methyl Bromide	20 ppm 5 min Pa.	40	20 ceiling	80	No warning properties, even at hazardous concentrations; LCt_{50} (Rats) $> 1.22 \times 10^5$ mg min/m^3; 1 ppm $\simeq 3.89$ mg/m^3.
Methyl Chloride	100 ppm 5 min Pa.	-11	100 ceiling	210	No warning properties; single exposure of 150,000 to 300,000 ppm kills most animals in a short time; 1 ppm $\simeq 2.09$ mg/m^3.
Methylene Chloride	1,000 ppm 30 min Pa.	104	500	1,740	Excessive exposure may create "drunkeness", leading to hazardous situations. Odor can be detected at pre-dangerous concentrations; LCt_{50} (Mice) $\simeq 2.4 \times 10^7$ mg min/m^3; 1 ppm $\simeq 3.48$ mg/m^3.

* Asterisk indicates hazard concentration exceeds industrial limit for chronic exposure.

Compound	Short term Exposure Values	B. P. (°F)	1969 Vapor TLV Hazard Concentration ppm	mg/m^3	Remarks
Monochlorodi-fluoromethane		-40			Low toxicity - definite value not established. LCt_{50} (Guinea Pigs) $\approx 1.64 \times 10^7$ mg min/m^3; 1 ppm $\approx$ 3.54 mg/m^3.
Nitrous Oxide		-130			Low toxicity - definite value not established. Compound is of little interest to industrial hygienists.
Pentane			500	1,500	See notice of intended change - Threshold Limit Values of Airborne Contaminants, Adopted by A.C.G.I.H. for 1969, page 17.
n - Pentane		97	1,000	2,950	Humans have been exposed to 5,000 ppm for 10 min without irritation or ill effects; 1 ppm $\approx$ 2.95 mg/m^3.
iso - Pentane		82			Similar to, and less toxic than n-pentane.
Petroleum Ether	500 ppm 30 min Pa.	68	500*		Based upon industrial limits of components (C_4 to C_6), hazard concentration is probably not less than ~500 ppm (hexane).

* By analogy with Petroleum Distillates (Naptha).

Compound	Short term Exposure Values	B. P. (° F)	1969 Vapor TLV Hazard Concentration ppm	1969 Vapor TLV Hazard Concentration mg/m^3	Remarks
Propane (Commercial)		-44	1,000	1,800	Brief exposures to 10,000 ppm cause no symptoms in man; odor is not detectable at < 20,000 ppm; 100,000 ppm is not very irritating to eyes, nose, or throat, but will produce dizziness in a few minutes; 1 ppm ≅ 1.80 mg/m^3.
Propionaldehyde		120			Toxicity relatively low - definite value not established. LCt_{50} (Rats) = 1.79×10^6 mg min/m^3; 1 ppm ≅ 2.3 mg/m^3.
Propylene		-54			Toxicity low - definite value not established. A suggested maximum limit is 4,000 ppm based upon 1/5 of lower flammable limit; 1 ppm ≅ 1.72 mg/m^3.
* Propylene Oxide		95	100	240	Industrial limit = 100 ppm; 400 ppm is probably safe for single exposures not exceeding 7 hrs. once per week; 1 ppm ≅ 2.38 mg/m^3.
Vinyl Chloride	500 ppm 5 min Pa.	7	500 ceiling	1,300	Odor is not adequate warning for excessive exposure, odor detected at ~4,100 ppm; human exposure to 6,600 ppm for 1/2 hr results in dizziness and sleepiness; 1 ppm ≅ 2.56 mg/m^3.
Vinylidene Chloride		99			Odor detected at 500 - 1,000 ppm, not adequate warning; 4,000 ppm will rapidly produce "drunkeness" progressing to unconsciousness if exposure is continued. Hazard concentration is suggested by Patty and is not an industrial standard; 1 ppm ≅ 3.97 mg/m^3.

* Asterisk indicates hazard concentration exceeds industrial limit for chronic exposure.

APPENDIX III (Cont'd)

Sources

1. Rules and Regulations, Commonwealth of Pennsylvania, Department of Health, Chapter 4, Article 432, Regulations Establishing Threshold Limits in Places of Employment. (Revised January 25, 1968). Table 2, pp 17-20. Documentation of Pennsylvania limits.

2. Threshold Limit Values of Airborne Contaminants and Intended Changes, Adopted by the American Conference of Governmental Industrial Hygienists for 1969. Dr. Herbert E. Stokinger, Chairman.

3. Smyth, Henry F. "Military and Space Short-Term Inhalation Standards." Archives of Environmental Health. 12:488-490. April 1966.

APPENDIX IV

Hazardous Chemical Criteria

FLAMMABILITY

Flash Point: The flash point of a flammable liquid is the lowest temperature at which the liquid gives off sufficient vapors to form a flammable mixture when mixed with air near the surface of the liquid. Stated another way, the flash point is the lowest temperature at which a flammable liquid, when heated in the presence of a source of ignition and sufficient air, will flash but not continue to burn. The flash point figures may be arrived at by the closed cup method or by an open cup method. The open cup flash point is usually somewhat higher than the closed cup flash point for the same substance.

Fire Point: The fire point is the lowest temperature at which a flammable liquid, when exposed to a source of ignition and in the presence of sufficient air, will give off sufficient vapors to ignite and continue to burn. The fire point is usually a few degrees above the flash point.

Flammable Limits: The explosive or flammable limits include all concentrations of a mixture of flammable vapor or gas in air, usually expressed in per cent by volume, in which a flash will occur or a flame will travel if the mixture is ignited. The lowest percentage at which this occurs is the lower explosive limit, and the highest percentage, the upper explosive limit. If such a mixture is confined and ignited, an explosion results. Many common flammable liquids and gases have very wide explosive ranges. Mixtures outside these limits are either too "lean to burn" or too "rich to burn". The first mentioned mixture is below the lower explosive limit since it does not have sufficient flammable vapor or gas in proportion to the amount of air while the latter mixture has too much flammable vapor or gas in proportion to the available air.

Specific Gravity: The specific gravity of a material is the ratio of the density of the material to the density of some standard substance. The specific gravity of a liquid expresses the density of the liquid with reference to the density of water. Liquids with a specific gravity greater than one are heavier than water, and liquids with a specific gravity less than one are lighter than water.

Vapor Density: The vapor density of a flammable vapor or gas is the relative density of the vapor as compared with air when the density of air is taken as one.

Vapor Pressure: The pressure exerted by a vapor when a state

of equilibrium has been reached between a liquid, solid, or solution, respectively, and its vapor, is called the vapor pressure of a liquid, solid or solution. When the vapor pressure of a liquid exceeds that of the confining atmosphere, the liquid is said to be boiling.

Boiling Point: The boiling point of a liquid is the temperature of a liquid at which the vapor pressure of the liquid equals the atmospheric pressure. Therefore, the lower the boiling point the more volatile and generally the more hazardous is the flammable liquid.

Ignition Temperature: The ignition temperature of a flammable liquid or gas is the lowest temperature required to initiate or cause self-sustained combustion in the absence of a spark or flame. This is also known as the auto or autogenous ignition temperature. This temperature varies considerably, depending upon the nature, size, and shape of the igniting surface, container or other factors.

Spontaneous Heating: Spontaneous heating is the ability of a flammable liquid to combine readily at ordinary temperatures with the oxygen of the air to produce heat. When these liquids are present on rags or other material under conditions in which heat is produced faster than it is dissipated, the temperature rises and spontaneous ignition may occur.

REACTIVITY (INSTABILITY)

Thermal Stability Test: A weighed amount of a compound in a loosely covered glass vessel is placed in a ventilated drying oven at a constant temperature of 167°F (75°C). The sample is permitted to remain at this constant temperature for 48 hours to determine the loss of weight. Considerable care is necessary in the application os this test. The oven should be constructed without internal sparking mechanisms or other sources of ignition to prevent the possibility of internal explosions.

Detonation With a Blasting Cap: Samples are tested for detonation possibilities with a Number 8 blasting cap. The blasting cap is inserted into a container, specified by the Department of Transportation, or some other acceptable test container, which is filled with the material to be tested. The quantity of material and the type of container used will vary. The blasting cap is electrically exploded from a distance and any detonation is noted. As a further check, liquid materials are soaked into a small wad of cotton and the blasting cap is exploded while in contact with the saturated cotton.

Impact Test: This test is designed to show the shock or impact sensitivity of various products to a measured force. The

sample consisting of several grams of material is contained in an 0.26 diameter hole which has been drilled into a steel block. A closely fitting steel piston is placed in the hole, just touching the test sample. The impact is provided by dropping an 8-pound weight, with the help of a vertical guide, directly onto the piston head. The minimum distance to which the weight must be raised before an explosion, if any is obtained, is the criterion for determining the sensitivity to impact for each material.

Drop Weight or Hammer Test: This test is similar to the "Impact Test". It may be influenced by extraneous factors such as the presence of inert diluents or solvents, bubbles and grit. These factors either increase or decrease the actual sensitivity.

Card Gap Test: This test evaluates the sensitivity of liquid explosives or unstable chemicals by means of a stack of standardized plastic cards between a sample and a standard "booster" charge of high explosive. The desired sensitivity value is taken as the number of cards which weaken the shock of the charge and consists of just enough cards to allow the test material to detonate 50% of the time. It is recommended for determining the sensitivity and for establishing the shock tolerance limit of the sample to hydrodynamic shock.

The test measures the minimum hydrodynamic shock required to produce a stable propagation of a high order detonation in a 1-inch standard steel pipe. The pipe is closed on the bottom by a thin flat diaphragm and rests directly on a stack of plastic cards which separates it from the booster charge. The booster charge consists of a cylindrical graphited-tetryl pellet, nominally 1-inch by 1 5/8-inch in diameter, weighing about 50 grams. Detonation of the booster pellet is initiated by an electric blasting cap. The variable gap between the booster and test material is built from circular cellulose acetate cards 1.55 inches in diameter and 0.010 inches thick. The entire test assembly is lined up by the use of a cardboard tube which is held in a steel base firing pedestal.

A target plate gives evidence as to whether the liquid explosive or unstable chemical was detonated. Detonation results in a hole or dent in this plate The first shot is made with zero gap (no cards). If detonation occurs, the next shot is made at an arbitrary value of 32 cards. If no detonation takes place, fewer cards are utilized until a symmetrical distribution of detonations and failures becomes evident, having as its midpoint the desired sensitivity value.

Thermal Decomposition Test:

a. Liquids--The temperature at which rapid decomposition of a liquid is observed is the thermal decomposition point.

The sample liquid is put into test tubes which are immersed in an oil bath the temperature of which is gradually raised.

b. Solids--The lowest temperature at which vigorous decomposition of a solid occurs is the thermal decomposition point. Slow and controlled temperature rise is imperative.

Lead Block Test: This test is designed to group explosions in terms of its potential "destructive force" for classification purposes. A cylindrical lead block approximately 2 inches in diameter and 6 inches in length is used for this test. A cardboard tube about 8 inches in length and slightly over 2 inches in diameter is slid into position over the end of the upright block. The major part of the cardboard tube which extends over the block is filled with the organic peroxide to be tested. A number 8 blasting cap is placed in the test material, and this is exploded from a safe distance. A specific damage effect of the explosion on the lead block is an indication of a detonation type of explosion.

Influence Test: In this test, the test sample is subjected to the stimulus from the detonation of a standard primary high explosive charge. The measure of relative sensitivity is the minimum spacing distance between the primary charge and the test sample which can be maintained without initiating the test sample.

In testing a subject sample, about 50 c.c. of material is poured into a 1 1/8-inch diameter x 9-inch length polyethylene bag which is then tied into a wooden frame. The wooden frame is then attached to a metal bar of an I-frame and the desired alignment between it and the primary charge established. The primary charge used consisted of a 32-gram pressed tetryl pellet (density 1.6) which is detonated by means of a No. 6 electric blasting cap.

Self-Accelerating Decomposition Temperature (SADT): To determine the SADT, the largest commercial package of the test substance is placed in a specially designed oven at a selected temperature. Thermocouples are set to record the temperatures of the oven and the test sample. The nominal test period is arbitrarily set for seven days. Testing continues until the time and temperature at which no rapid decomposition occurs is determined. Testing at or above the SADT is terminated after the samples decompose. The minimum number of tests required to demonstrate an SADT is two, if the sample survives the test at the lower temperature, fails at the higher temperature, and if the difference in the test temperatures is not grater than 10°C. In some cases, several separate tests must be performed before this property is determined.

Differential Thermal Analysis (DTA): DTA curves using a differential thermal analyzer can be obtained for all suspected exotherms involving

raw materials, process mixtures, products, byproducts, waste streams and residues. It is important in process design and operational procedures to know at what temperatures an exothermic reaction or release of heat may be expected. A DTA utilizing higher pressures may be necessary to determine the properties under pressurized conditions. The test is conducted under the procedures of the Joint Army Navy Air Force (JANAF) Thermal Stability Tests.

Critical Diameter: Critical diameter is the minimum diameter of the test material mass, below which a propagating detonation cannot occur. Critical diameters have been established for many unstable materials, such as dinitrotoluene, n-propyl nitrate, and hydrogen peroxide (90%) or more).

Other Tests: Pressure Vessel Test, Ballistic Mortar, Ignitability Device, Flame Ignition Test, Rate of Burning Test are described in American Insurance Association Research Report No. 11, "Fire, Explosion and Health Hazards of Organic Peroxides".

TOXICITY

Threshold Limit Values: The Threshold Limit Value is the average eight hour per day concentration in air of a vapor, gas, dust or fume, to which persons may be exposed without injury to health, as determined by the American Conference of Governmental Industrial Hygienists (ACGIH). These values should be interpreted by experts and should not be misunderstood as having similar effects with higher concentrations for shorter periods, such as could be encountered under emergency conditions.

TLV's are measured as "parts per million" (ppm) at standard conditions or milligrams per cubic meter of air (mg/M^3), or in the case of respirable dusts, millions of particles per cubic foot (m.p.p.c.f.). Note that ppm are usually given by volume at 25°C and 760 mm.Hg. pressure. These values may not be accurate for elevated temperatures and pressures.

Lethal Concentration and Lethal Dose

(LC_{50} and LD_{50} Values)

These tests are employed to determine what quantity of material given to a test group of any species of animals will produce death in one half of the group.

LC_{50} (Lethal Concentration)

The LC_{50} refers to the inhalation of a specified concentration of air borne material which likewise results in death in 50% of the group of test animals. The period of exposure for evaluating the

LC_{50} for industrial gases is usually four hours and is followed by a 14-day observation period.

LD_{50} (Lethal Dose)

The LD_{50} is that quantity of material given to a test group of any species of animals which produces death in one-half of the group. In determining the LD_{50} of a material, several different dose levels are given, and the results used to determine the LD_{50}. The dosage is calculated in terms of milligrams test material per kilogram weight of the animal. Effects are observed for the next 14 days. Material may be given orally or by skin absorption.

Exposure Effects

Inhalation--The effects of inhalation of hazardous materials can briefly be classified as follows:

Respiratory Irritation: The irritation caused by the inhalation of irritant materials may cause pneumonitis. Unfortunately, not all irritants cause sufficient irritation at the time of exposure to warn of the potentially hazardous effects. Examples would be NO_2, SO_2, cadmium fumes.

Pneumoconiosis: The inhalation of certain dusts can cause changes to take place in the lungs which may adversely effect lung function. Examples would be silica containing dusts, asbestos dust and beryllium dust.

Narcosis: Hydrocarbon gases and vapors typically cause narcotic effects, (depress the central nervous system), which tends to make the exposed individual accident prone, and a less productive employee. Severe exposure may paralyze the respiratory center and stop breathing.

Asphyxiation: Gases may cause asphyxiation by simply displacing oxygen in the atmosphere to concentrations which are inadequate to maintain consciousness, (e.g. CO_2, N_2, etc.). However, chemical asphyxiants act specifically to block an adequate supply of oxygen from reaching the tissues, (e.g. CO, HCN, etc.).

Toxic Effects: Certain materials may cause systematic damage upon exposure which may or may not be reversible. Examples would be liver damage with carbon tetrachloride, blood forming system damage with benzene, and kidney damage with methyl cellosolve.

Ingestion: Ingestion, the process of taking material into the body through the mouth, may be measured approximately by the oral toxicity data on animals (LD_{50}). If the LD is in the range of 50 mg/kg to kill 50% of the test animals, human exposure

through unclean hands and inadvertent ingestion by tobacco or food may be a problem. Significant chemical illness could occur at exposure levels of one-tenth the LD_{50} determined for the test animals.

Skin Irritant: For skin irritation tests, the exposure is for a 24 or 48-hour period using an open or covered patch, and the degree and type of irritation is determined. The albino guinea pig is most often used, and a series of tests involving nine applications over a period of three weeks is utilized. The material is applied to the abraded skin or by intradermal injection. After a two weeks' rest period, a final challenge application is made, and any marked increase in reaction is noted.

Eye Irritant: For eye irritation, a drop of the liquid or solid in liquid suspension is placed in the eye (without washing) of an albino rabbit, and observed at various intervals ranging from one hour up to a maximum of seven days.

RADIATION

Alpha Exposure (Symbol α): Alpha particles may be ejected spontaneously from the nuclei of some radioactive elements. It is identical to a helium nucleus. It has low penetrating power and short range. The most energetic alpha particle will generally fail to penetrate the skin. Danger occurs when matter containing alpha-emitting radionuclides is introduced into the lungs or intestinal tract.

Beta Exposure (Symbol β): Beta particles are electrons, positive or negative, emitted during radioactive disintegration. They are less ionizing and more penetrating than the alpha particles. At lower energy levels, the effects will approximate very closely that of X-irradiation. Beta particles may be effectively shielded by lead, copper, iron, aluminum, glass, concrete, plastic, or water. Reactions are similar to thermal burns of varying degrees, depending on the dosage.

Gamma Exposures (Symbol γ): Gamma rays are a quantum of electromagnetic radiation emitted by a nucleus, having energies usually between 10 kev and 10 mev. They are more penetrating than alpha or beta particles. The most effective material for gamma shielding is lead. Iron, steel and high density concrete may also be used but require greater thicknesses to obtain the same gamma reduction factor.

Neutron Exposures: A neutron is a particle of 0 charge and mass number 1. Neutrons may be shielded by use of such materials as hydrogenous cement, water and paraffin.

Measuring Devices: Several types of measuring devices have been developed:

a. The Geiger counter: Very efficient beta counter and detects a small fraction of gamma radiation.

b. The Ionization Chamber: Principally for gamma radiation but may be designed to detect alpha, beta and gamma radiations.

c. Photographic film may be used to detect alpha, beta and gamma radiations. These radiations will affect photographic film in proportion to the intensity and duration of the exposure.

d. Pocket dosimeters are available based on the principle of a tiny electroscope with ranges up to 100r.

Source: A. Spiegelman. Hazard Survey of the Chemical and Allied Industries, Technical Survey #3, American Insurance Association, 1968.

APPENDIX V

Prediction of Contaminant Concentrations Resulting from Accidental Spillages in Navigable Streams

The U. S. Geological Survey, using fluorescent dyes, has made numerous tests simulating the movement of soluble contaminants in rivers and streams. A typical measurement consists of injecting a slug of dye into a flowing stream and measuring the dye-cloud concentration with time as it passes selected downstream points. Thus the rate or time of travel of a solute may be accurately measured.

Because of longitudinal dispersion, the solute cloud elongates and concentrations decrease as it progresses downstream. The magnitude of the observed time-concentration curve is affected (1) directly by the quantity of solute injected; (2) inversely by absorption and decay; and (3) inversely by the discharge at the site since it is a dilutant. A fourth factor, longitudinal dispersion, determines both the shape and the magnitude of the time-concentration curve. On larger navigable streams, dispersion tends to show less variation from one river to the next.

An analysis of data for numerous time-of-travel tests indicates that, for a wide variety of streams, a single curve can be used to relate the maximum probable unit concentration to the elapsed traveltime sufficiently to allow the approximate prediction of maximum probable contaminant concentrations. Unit concentration, C_u, may be defined as the concentration produced in a discharge of one cubic foot per second (cfs) due to the spillage of 1 pound of conservative contaminant. Figure 1 shows the maximum unit concentrations versus lapsed time as measured on a variety of streams in the United States. For clarity, only the highest set of data for 20 time-of-travel measurements on the Missouri River has been shown. It is suggested that the solid line serve as the uppermost limit or maximum concentration relationship which might be expected. Although the lines defined by observed data have a slope of approximately -0.6, for practical and

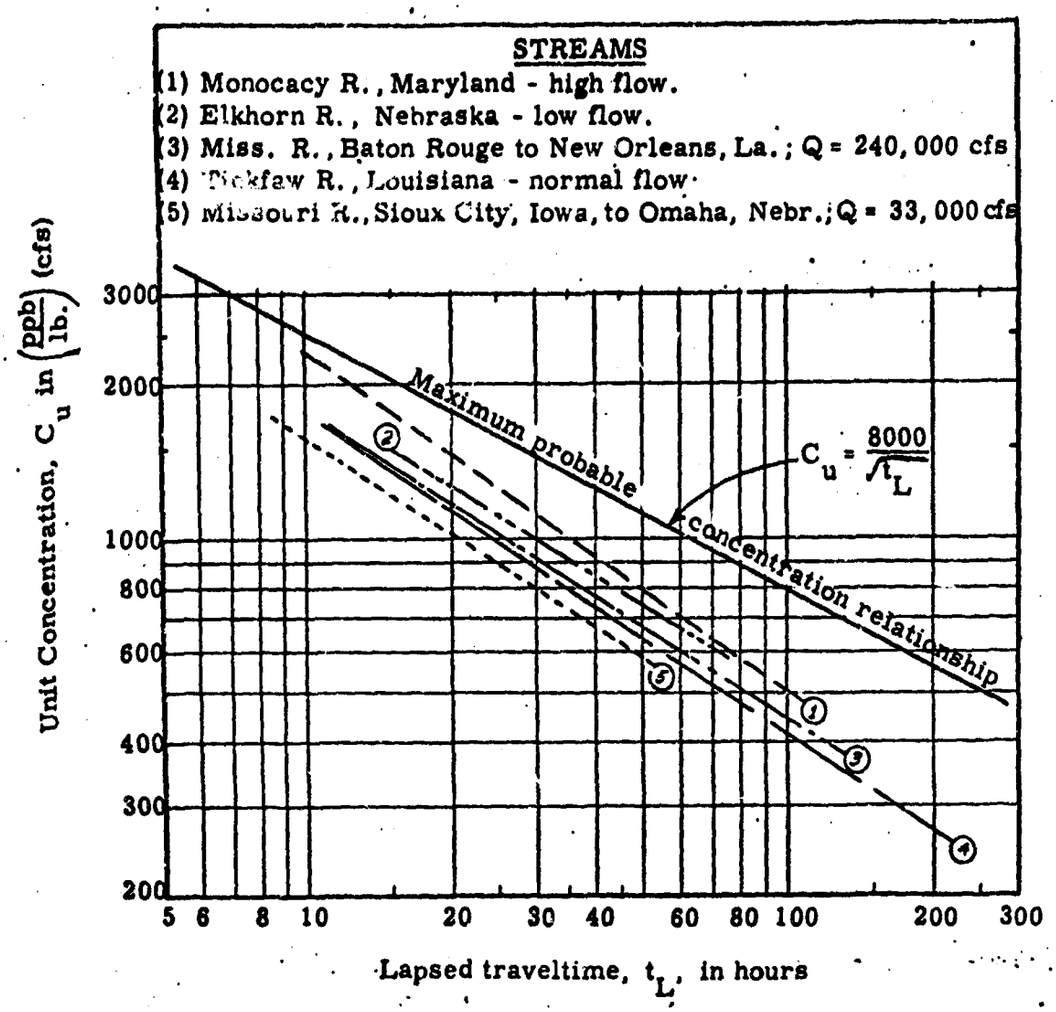


Figure 1.--General relationships for various streams showing attenuation of maximum concentration with traveltime to be expected from spillage of a conservative contaminant for similar conditions of discharge and dispersion.

theoretical reasons the maximum probable concentration line has been given a slope of -0.5.

Evidence indicates that once lateral dispersion is complete, similar reduction in maximum concentrations as defined by Figure 1, page 64, may occur in tide-affected rivers and estuaries. Unfortunately, tidal discharge and time-of-travel data are limited. As a rule, many days may be required for complete lateral dispersion of a contaminant spilled in an estuary, and initially much greater concentrations than predicted by Figure 1 would probably exist.

The data used in defining the curves of Figure 1 are for solutes. Oils or other non-soluble contaminants would not disperse in the same manner, and concentrations would probably be greater than those defined for solutes.

Use of Figure 1 requires the independent determination of the traveltime of the contaminant from the point of spillage to the water user downstream. The best time-of-travel data will come from actual tests such as presented by Stewart,[40] and Bowie and Petri.[39] In the absence of such information, stream velocities may be estimated from discharge measurements made by the U.S. Geological Survey or the U.S. Corps of Engineers. For the normal range of flows on the Missouri River from Sioux City, Iowa, to St. Louis, Mo., the Mississippi River from St. Louis to Cairo, Ill., and the Mississippi River from Baton Rouge to New Orleans, La., the velocities range from 2 to 4 mph, 2 to 3 mph, and 1 to 2 mph, respectively. In the absence of data, a high estimate of velocity for computing the lapsed time will usually be best, as this allows the least time for dispersion to take place. Figure 1 will yield the safest estimate.

Using lapsed time, Figure 1 provides a unit concentration value. The maximum probable concentration likely to exist at the location in question can then be computed as

$$C_{max} \text{ (micrograms/l or ppb)} = C_u \times \frac{W \text{ (pounds of contaminant spilled)}}{Q \text{ (river discharge in cfs)}}$$

or, using the equation of the solid line of Figure 1

$$C_{max} = \frac{8000}{t_L} \times \frac{W}{Q}$$

Example: A barge containing 10,000 lbs. of chemical X is accidentally ruptured on the Missouri River at Jefferson City, Missouri, when the river has a discharge of approximately 50,000 cfs. (At that rate in the Missouri, a total travel time of 111 hours will exist between Jefferson City and St. Louis, Missouri).

What will be the maximum probable concentration at St. Louis, Missouri?

Answer: Using equation (2)

$$C_{max} = \frac{8000}{\sqrt{111}} \times \frac{10,000}{50,000} = 152 \text{ ppb}$$

APPENDIX VI

The following terms are defined in DOD 4145.27M (see ref. 19) for purposes of clarity:

Explosion: A chemical reaction of any chemical compound or mechanical mixture which, when initiated, undergoes a very rapid combustion or decomposition releasing large volumes of highly heated gases which exert pressures on the surrounding medium. Also, a mechanical reaction in which failure of the container causes the sudden release of pressure from within a pressure vessel; for example, pressure rupture of a steam boiler. Depending on the rate of energy release, an explosion can be categorized as a deflagration, a detonation, or a pressure rupture.

Deflagration: A rapid chemical reaction in which the output of heat is sufficient to enable the reaction to proceed and be accelerated without input of heat from another source. Deflagration is a surface phenomenon with the reaction products flowing away from the unreacted material along the surface at subsonic velocity. The effect of a true deflagration under confinement is an explosion. Confinement of the reaction increases pressure, rate of reaction and temperature, and may cause transition into a detonation.

Detonation. A violent chemical reaction within a chemical compound or mechanical mixture evolving heat and pressures. A detonation, in contradistinction to deflagration, is the reaction which proceeds through the reacted material toward the unreacted material at supersonic velocity. The result of the chemical reaction is exertion of extremely high pressures on the surrounding medium forming a propagating shock wave which is originally of supersonic velocity. A detonation, when the material is located on or near the surface of the ground, is normally characterized by a crater.

APPENDIX VII

Incidents Available for Distance Quantity Relationship Studies

July 17, 1968 - Abingdon, Virginia

A semi-trailer fuel tank truck and a locomotive of a 60 car N&W freight train collided at a grade crossing in the center of the business district. There was a severe fire and an apparent explosion. (Under investigation by the National Transportation Safety Board.)

August 1, 1961 - Creve Coeur, Marquette Heights, North Pekin, and Bartonville - suburbs of Peoria, Illinois.

At 12:15 a.m., a barge carrying 600 tons of anhydrous ammonia suffered a rupture in the 4-inch discharge hose above the dock. A heavy cloud of vapor formed immediately and eventually covered an area of 12 square miles. The high pressure flow continued until the ammonia compressor at the terminal was shut down at about 12:30 a.m. Between 2:00 a.m. and 2:30 a.m. the electric power controlling the air compressor of the barge tank valves was cut off. About 350 tons of liquid anhydrous ammonia were lost. The winds were southeasterly, 5 to 6 knots, and shifted to southerly by 6:00 a.m. The temperature ranged from 74°F to 75°F and the relative humidity remained about 90%. Approximately 13,000 people were evacuated from the four towns without accident or injury. About 40 persons received treatment in local hospitals. The terminal crew was hampered in its emergency control efforts by a lack of adequate protective clothing and oxygen masks. Foliage was severely damaged in the area blanketed by the vapor and "tons" of fish were killed in the river. (TASK SILENCE, "The Post-Midnight Alarm and Evacuation of Four Communities Affected by an Ammonia Gas Release," Frank M. Steadman, Editor, Project

Summit. The University of Pennsylvania Institute for Cooperative Research, Philadelphia, Pennsylvania, 17 September 1962).

January 31, 1961 - New Roads and Morganza, Louisiana

Seventeen freight cars were derailed and a tank car containing 30 tons of liquid chlorine was punctured at 8:15 a.m. A slight wind from the east spread the chlorine gas over an area at least six and one-half miles long and three miles wide. The chlorine gas had dispersed from the scene of the accident by about 10:30 a.m., but was still reported present two hours later at the western end of the affected area. The residue at the accident site was neutralized with caustic soda and soda ash. About 2,000 people were involved. Seventy-five persons were treated at the local hospital and one of them, a child, died. Another 75 persons were treated by doctors outside the hospital. A large number of farm animals were killed and many other animals were affected in various ways. Crops and other types of foliage were severely damaged. (ARMED SERVICES TECHNICAL INFORMATION AGENCY, AD 269681, TASK SIROCCO, "Community Reaction to an Accidental Chlorine Exposure," by Louis Segaloff, University of Pennsylvania Institute for Cooperative Research, 15 November 1961.)

July 1968 - Rockport, Massachusetts

A cloud of about 400 gallons of liquid propane leaked from a ruptured (I.C.) delivery hose (at rate of 3 gpm). Initially the wind was calm, the temperature was 45° to 50°F, and the weather was fair. Visual observations of the cloud suggested it was not over four feet above the ground, but this was actually moisture. No ignition occurred. ("Liquid Propane Leak." Fire Journal. 62:24-25, July, 1968.)

July 25, 1962 - Berlin, New York

The failure of a cargo tank of a tractor tank semi-trailer unit resulted in the sudden and complete release of about 6,875 gallons of

LP-Gas. The gas-air mixture covered an area of about 207,000 square feet (or 4.75 acres) and averaged about 80 feet in height. The wind was reported as "light." Ignition occurred from an undetermined source, and extensively damaged eight dwellings, a church, a large garage, 4 smaller garages, 3 large barns and 11 vehicles. Poor welding practices possibly contributed to the tank failure. Other possible causes of failure were severe dynamic stresses or impacts, and an internal 150-psi pressure from the cargo. (Walls, W. L. "LP-Gas Tank Truck Accident and Fire, Berlin, New York." National Fire Protection Association Quarterly, Q 57-1, pp. 2-8, July 1963.)

November 30, 1962 - Cornwall, Ontario

A tank car developed a leak and 30 tons or approximately 4,000 gallons of chlorine drained onto a railway siding during a period of approximately one hour. This evaporated in about 2 1/2 hours. A light easterly wind carried chlorine fog into residential areas. Eighty-nine homes were evacuated, and 26 persons were hospitalized, most for only a short time. Chlorine fog spread over a square mile, or 30-block section, and the odor of chlorine was detected for a distance of 15 miles.

June 27, 1968 - Scandia, Kansas

Approximately 8,000 to 11,000 gallons of anhydrous ammonia were accidentally released when a small trailer rolled off an 18" loading platform, breaking or disconnecting the connection from a 2-inch pipe. One observer described a "mushroom cloud one-half mile high." Total discharge time was 60 to 75 minutes. No wind measurements were made at Scandia, but residents reported "very calm" conditions. Weather Bureau records at Concordia (15 miles from Scandia) indicate the following conditions at the time of the accident: temperatures of 62° to 74°F; wind direction of 250° to

190°; and wind speed of 8 to 10 m.p.h. Evacuation of the town prevented serious massive exposures. Damage to plants occurred as far as 2 miles away; some odor was detected 6 miles away (ammonia odor is reported detectable at 5 p.p.m.). Another observer states that fumes were noted in one location 4 miles from the plant. Various degrees of "burning" were observed 2-3 miles north and east of the area. One field, 100 acres of silage feed, was damaged approximately 2 miles from the scene.

February 27, 1968 - Hagerstown, Maryland

A propane carrier with 8,300 gallons of liquid propane was struck at the pump by a locomotive. The tank and tractor rolled over on their sides, entangling the trailer jacks and under carriage. Three thousand five hundred to 4,000 gallons of propane were released at the scene over a period of 14 hours. Leaking propane was controlled by ice which formed at the ruptured valve. The ice formed due to the refrigeration of the expanding gas, to water fog applied by the responding fire service, and to a temperature of 18°F during the night and early morning. Wind was chiefly out of the northwest at approximately 5-6 m.p.h., changing to northeast occasionally. Humidity was not measured but was believed to be low. Gas vapor was largely dissipated within a 60-foot area by water fog. An irregular area at the center of the city, which approximated 2,400 by 3,000 feet, was evacuated. The incident was monitored by five two-man teams with combustible gas indicators. No ignition occurred.

APPENDIX VIII

Background Data for Use in Estimating Hazard Potential

Jacobs and Buckley describe missile dispersal from an exploding vessel which included a 60 ton fragment hurled 1,200 feet. A steel 4 feet by 10 feet by 5/8 inch steel fragment from an ethylene oxide tank car at Litchfield, Illinois traveled nearly 3/4 of a mile. A mathematical model for estimating fragment risks of explosives has been formulated and programmed for electronic data processing.[65] Substances such as ethylene oxide and nitromethane, which are known to detonate, but for which existing test procedures are not completely definitive, raise doubt as to the assurance for evaluating the stability of new and relatively unknown substances. Propargyl bromide[66] and n-propyl nitrate are examples of other high-energy compounds being shipped commercially in quantity. Knowledge and experience is limited and imperfect in evaluation of hazard potential for such substances. For substances with high potential energy, or with known instability under emergency conditions, one suggested approach is to extend the "fire" or "stability" rating (as presently applied in the National Fire Protection Association 704-M and the NRC Committee on Hazardous Materials evaluation systems) to include two additional considerations: monopropellant burning, and detonation energy. Substances in commerce which exhibit these properties to various degrees include:

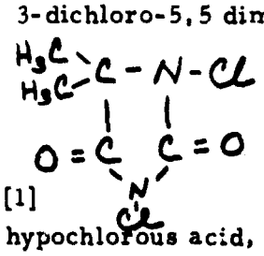
ethylene oxide
nitromethane
n-propyl nitrate
propargyl halides (bromide and chloride)
allene
other triple-bond molecules
di- and tri-nitro aromatic molecules
diborane
ammonium nitrate and AN-FO mixtures
conventional explosives
methyl ethyl ketone peroxides and certain other peroxides

It may be prudent to apply caution with these and with other high-energy substances until more complete and adequate tests are available. An index of hazardous chemical criteria recommended by the American Insurance Association, New York, is given in Appendix IV. The American Society for Testing and Materials E-27 Committee on Hazard Potential of Chemicals is considering this problem.[67,68,69,70] Test criteria for binary mixtures resulting in hazardous reactions are being developed by The Dow Chemical Company under contract to the Committee on Hazardous Materials.

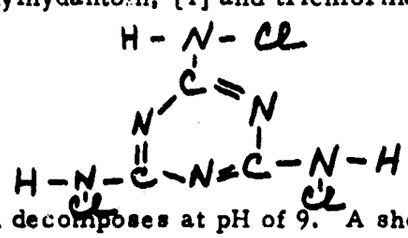
Certain molecular configurations, recognized as possessing special so-called explosophoric atom groupings, include:

C≡C group, present in acetylene derivatives
N-X group, in halogen compounds of nitrogen
N=N group, in salts of fulminic acid or fulminates
N=O group, in nitrates and nitro compounds
O-O group, in peroxides and ozonides
O-Cl group, in chlorates and perchlorates

Halogen-containing compounds, from which the halogen is easily released, should be suspect as unstable.[71] Examples of these molecules with high-halogen content which have caused fires or release of toxic gases during transportation or storage include calcium hypochlorite, $Ca(OCl)_2$, frequently referred to as HTH,[72] and certain dichlor organics such as halazone, 1, 3-dichloro-5, 5 dimethylhydantoin, [1] and trichlormelamine (TCM) [2].



[1]



[2]

[1] releases hypochlorous acid, and decomposes at pH of 9. A short-term limit of 0.5 mg/m^3 for 15 minutes has been established by the Pennsylvania

Department of Health due to extreme irritation from dusts of this substance (1969).

Even small amounts of some substances as a contaminant may have a significant effect on other substances during shipment. Small percentages of moisture and impurities may initiate an exothermic decomposition which may ignite other substances or cause a violent uncontrolled reaction. For example, acrolein will react violently with caustic, and ethyl alcohol reacts vigorously with nitric acid. For a more complete study or index of chemical reactivity, reference should be made to the "Tentative Guide to the Compatibility of Chemicals," September 17, 1969, prepared by the NRC Committee on Hazardous Materials, and to other references, such as National Fire Protection Association guides 49-M, 491-M, 325-M, and 704-M.

Ammonium nitrate-sulfur mixtures have been studied for detonation potential,[73] as have ammonium nitrate-fuel oil mixtures.[74] Rocket boosters of very large size and high energy potential are now being transported by water. The panel has made no assessment of the potential hazards of such systems.[75]

The spontaneous heating of substances such as wool, ammonium nitrate, and solutions of organic peroxides, as well as the size of the critical mass of these and similar materials, can also be important factors in storage and transportation.[76] The panel has not explored these aspects in detail.

APPENDIX IX

Emergency Assistance from Chemical Suppliers

The following telephone numbers have been established by chemical suppliers for assistance and advice on emergencies which may occur during the handling, shipping, or use of their products. They are believed to be accurate and working numbers as of April 23, 1970.

AMERICAN CYNAMID

201/835-3100 - Wayne, New Jersey

DOW

517/636-4400 - Midland, Michigan. (The Texas Division of Dow has emergency number 713/238-2011. Ask for Plant Protection.)

DuPONT

302/774-7500 - Product Information Center, Wilmington, Delaware

HOOKER

716/285-6655 - Niagara Falls, New York

MONSANTO

314/OX4-1000 - St. Louis, Missouri, or the nearest Monsanto Plant

UNION CARBIDE

304/744-3487 - Chemical Distribution Group (HELP)

212/LL4-4785 - Dr. C. Dernehl, New York

Alternate call: 412/327-1020 - Dr. C. P. Carpenter, Pittsburgh, Pennsylvania

NATIONAL AGRICULTURAL CHEMICALS ASSOCIATION

513/961-4300 - Pesticide Safety Team Network

NATIONAL DISTILLERS & CHEMICAL CORPORATION

513/761-5653 (day) - Mr. L. Strohl, Cincinnati, Ohio

513/777-2539 (night) - in case of no response, call 217/253-3311, Tuscola, Illinois and ask for Mr. K. J. Patton

WYANDOTTE

313/282-3300 - Wyandotte, Michigan
504/348-3231 -- Baton Rouge, Louisiana
715/887-4000 - Port Edwards, Wisconsin

REFERENCES

(1) Two levels of possible nuclear occurrences have been envisaged in a nuclear drydock shipyard (a) the Nuclear Incident and (b) the Nuclear Accident (which results in a Public Hazard). Emergency safety plans have been developed for both incidents. See:
Oliver, T. A. "Accident Problems in Nuclear Drydock." The Annals of Occupational Hygiene (London). No. 2, 11:159, April 1968.
The planning which can be incorporated into shipment of hazardous materials is illustrated in:
Ernest, F. A., and R. Maker. "Shipment of a Large Liquid Source-A Case History." American Institute of Chemical Engineers Meeting, Boston, December 1964. (Nuclear Science Abstract 7560-CONF-641201-2).
See also:
J. M. Morgan, Jr., J. W. Knapp, and J. T. Thompson, A Study of the Possible Consequences and Costs of Accidents in the Transportation of High Level Radioactive Materials. (UC-70, Atomic Energy Commission NYO-9772, Washington, D.C., 1961).

(2) F. F. Leimkuhler, M. J. Karson, and M. T. Thompson, Statistical Analysis of the Frequency and Severity of Accidents to Potential Highway Carriers of Highly Radioactive Material, (Atomic Energy Commission NYO-9771, Washington, D.C., July 1961).

(3) Jensen, Arne. "Safety at Sea Problems." Accident Analysis and Prevention. 1:1-7, August 6, 1968.

(4) Wells, R. R., Blecker, H. G., and McDonald, B. L., Estimating the Dangers Presented to Ports and Waterways from Marine Transportation of Hazardous Cargoes: An Analytical Model, 12 December 1969, to be published, U.S. Coast Guard, Washington, D.C.

(5) Evenett, N. B. "Problems Posed by the Trend Towards Specialized Vessels, and the Validity of Using Tonnages as a Basis of Rating." The Insurance Institute of London. Award paper of Cuthbert Heath

Centenary Award, 1968-1969. Because of the obvious relation to size of cargo, the following three paragraphs from Mr. Evenett's paper should be noted:

> Undoubtedly the cargoes carried in specialized vessels will sometimes present underwriters with a problem. Tankers are being purposebuilt for the carriage of chemicals, acids, solvents, asphalt, liquefied gases, sulphur and chlorine, to name but a few. Some of these have their own peculiar hazards, being volatile in nature. Previous experience of the bulk carriage of certain forms of refined petroleum which became highly volatile under wrongly applied pressures in loading and discharge will be recalled. This is the major, but by no means the only factor involving the hull underwriters. The possibility of breakdown in ancillary equipment, allowing the cargo to re-gasefy, or solidify, according to its nature must be envisaged, with the consequent difficulties in discharge. On a long voyage, there must be a possibility of the voyage being broken up short of destination, where there may be no suitable arrangements for discharge, no speedy means of on-forwarding the cargo and no local market for the cargo. This would adversely affect the adjustment of General Average against the hull underwriter.
>
> Increasing specialisation and increasing size mean increasing values. Passenger liners are still the front-runners as far as ship values are concerned, but at the present rate of progress the margin of difference between the luxury ship designed for the convenience of fare-paying passengers, and the electronically-operated, very possibly nuclear-powered high performance, pressurised cargo carrier of the future will dwindle to nothing, and the balance could well swing in the opposite direction. As there are likely to be more cargo carriers than passenger liners, a major problem for insurers is likely to be that of capacity. The tremendous monetary accumulation in hull, freight and cargo insurances could well present difficulties, and a collision could prove to be a catastrophe, in purely financial terms.
>
> As ships age, and become obsolete, they are bought by smaller operators, frequently outside the nationality for

which they have heretofore traded, generally for charter work. Such operators may have had no previous experience of the particular trade which they are about to enter, other than that it is lucrative, and the standard of management may well deteriorate. When this situation is reached with the complex ships now operating underwriters will face even greater problems.

(An interesting footnote to the above: British shipping underwriters announced on December 20, 1969, an increase in rates for ships over 50,000 tons gross. Three large tankers, with tonnages of 98,000; 100,500; and 207,000 sank during 1969. (New York Times, December 21, 1969).

(6) Starr, Chauncey. "An Overview of the Problems of Public Safety." Symposium on Public Safety-A Growing Factor in Modern Design. National Academy of Engineering Publication No. 1752, National Academy of Sciences Publication Office, 1970.

The general conclusions of this paper may be of interest:

> First, the indications are that the public is willing to accept 'voluntary' risks roughly 1000 times greater than 'involuntary' exposures. Second, the statistical risk set by disease appears to be a psychological yardstick for establishing the level of acceptability of other risks. Third, the acceptability of risk appears to be crudely proportional to the cube of the benefits (real or imagined). Fourth, the social acceptance of risk is directly influenced by public awareness of the benefits of an activity, as determined by advertising, usefulness, and the number of people participating. Fifth, in the application of these criteria to atomic power plant safety, it developed that an engineering design objective determined by the economic criteria resulted in a design target risk level about 200 times less than the present socially accepted risk for electric power.
>
> Perhaps of greatest interest is that this methodology for revealing existing social preferences and values may be a means of providing the social benefit vs. cost insight so necessary for judicious national decisions in new technological developments.

See also:

Starr, Chauncey. "Social Benefit Versus Technological Risk." Science. 165-1232-1238, September 19, 1969.

(7) Watson, R. R. "Quantity-Distance Criteria-A More Flexible Policy in Future?" Minutes of the 11th Annual Explosives Safety Seminar, Sheraton-Peabody Hotel, Memphis, Tennessee, September 9-10, 1969, conducted by the Armed Services Explosives Safety Board, Washington, D.C. Pages 109-140. (Ministry of Defence, United Kingdom).

(8) "Safety Distances for Explosives: The Degree of Damage to Houses Deemed to be an Acceptable Risk." Annex to Technical Memorandum, United Kingdom Directorate of Safety (Army), Department of Defence, 1969. The so-called Outside Safety Distance prescribed by the Explosives Safety and Transport Committee (U.K.) and by comparable agencies in other N.A.T.O. countries, defines and depicts acceptable and unacceptable blast damage.

(9) U.S. Departments of the Army, the Navy, and the Air Force. Responsibilities for Technical Escorts of Chemical Biological, and Etiological Agents: Storage and Shipment of Supplies and Equipment (AR 740-32, OPNAVINST 8070.1, AFR 136-4, MCO 4030.25). Washington, D.C., April 7, 1966.

U.S. Army Materiel Command. Headquarters. Safety, Chemical and Biological Accident and Incident Control (CBAIC) (AMC Regulation Number 385-22). Washington, D.C. 20315, September 28, 1967.

Fletcher, P. T. "Safety of Nuclear Ships in Port." Atom. No. 19, pp 10-16, 1958. (Nuclear Science Abstract 13:5504).

(10) 4,500,000 known chemicals (estimated by the American Chemical Society) of which 850,000 are listed by Chemical Abstracts. Organized information useful in hazard control is available as follows:

National Library of Medicine (estimated)	31,000 listings
National Poison Control Center (estimated)	40,000 trade names
NAS-NRC Advisory Center on Toxicology estimated listings (about 4000 of which are "chemicals")	50,000-60,000
National Safety Council Chemical Data Sheets	77*
Manufacturing Chemists Association Safety Data Sheets-- Cards 85; Water Information Cards 20.*	95*; Chem.
American Industrial Hygiene Association Hygiene Guides	160*
NAS Publication No. 1465-1970 Edition (Evaluation of the Hazards)	209 industrial chemicals
CG-388-1970 Edition (U.S. Coast Guard)	200 chemicals
Threshold Limit Values, American Conference of Governmental Industrial Hygienists	500 (approx.) (1969)
National Fire Protection Association	2,000 (approx.)

*Several additional in preparation.

Note: These numbers cannot be easily compared since treatment by different groups is not uniform, and mixtures are often considered instead of individual chemicals. Less than a thousand chemicals have been adequately evaluated for safety in the context of this report. Wide acceptance of books and other literature which present incomplete or easily misunderstood evaluations, further confuse the information problem. Even reputable sources are not always up-to-date, or completely accurate, and the latest information should be evaluated in perspective to check credibility.

(11) Effects of Chronic Exposure to Low Levels of Carbon Monoxide on Human Health, Behavior, and Performance. A report prepared by the Committee on Effects of Atmospheric Contaminants on Human Health and Welfare, National Academy of Sciences-National Academy of Engineering, Washington, D. C., 1969.

(12) Gillenwater, Lyhle, E. "Chemical Spills From Barge Accidents: A Concern of the State." Proceedings for the National Academy of Sciences-U. S. Coast Guard Advisory Committee on Hazardous Materials Conference on Barge Transportation of Chemicals (Charleston, West Virginia). pp 82-86, July 28-29, 1965.

(13) Juillerat, E. E. "Turmoil in the Valley." Fire Journal. No. 1, 63:9-18, January 1969.

(14) Yutzy, Daniel. "Priorities in Community Response." American Behavioral Scientist. No. 3, 13:344-353, January-February, 1970.

(15) "Assault on Fogs." Science News. No. 9, 96:165-167, August 30, 1969.

(16) National Science Foundation. Weather Modification (NSF 69-18). Tenth Annual Report, 1968. Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402. See also Fleagle, Robert C., Editor, Weather Modification. Science and Public Policy - University Washington Press, 147 pp, 1970.

(17) Ewing, Ann. "Doing Something About Weather." Science News. No. 9, Vol. 4, November 1968.

(18) The American Table of Distances. Pamphlet No. 2. Institute of Makers of Explosives, 420 Lexington Avenue, New York, N. Y. 10017, June 5, 1964. It should be noted that these tables were not intended for use in transportation, but for the storage of bulk mass-detonating explosives.

(19) Department of Defense. DOD Ammunition and Explosives Safety Standards (DOD 4145.27). Washington, D.C., March 1969.

(20) The Study of Missiles Resulting from Accidental Explosions: A Manual for Investigators (Atomic Energy Commission Safety and Fire Protection Bulletin 10). Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402, March 1966.

(21a) An Indepth Report of a Systems Study of Oil Spill Cleanup Procedures, Dillingham Environmental Co., LaJolla, Calif., 330 pages in 2 volumes, July 1970, available from American Petroleum Institute, Washington, D.C. See also: More Weapons for Oil Spills, pages 40-42, Chemical Engineering, July 13, 1970.

(21) Special Study Reports on Tanker Oil Spillage and Remedies. Research Coordination Bureau. Science and Technology Agency, March 1969. (Japanese). English-language translation available from Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia 22151.

(22) Barclay - Smith, P., ed. Oil Pollution of the Sea. British Advisory Committee on Oil Pollution of the Sea, London, 1969. (Proceedings of the International Conference on Oil Pollution of the Sea, Rome, Italy, October 1968).

(23) Corcoran, E. F., and D. B. Seba. "Surface Slicks as Concentrators of Pesticides in the Marine Environment." Pesticides Monitoring Journal. No. 3, 3:190-193, 1969.

(24) Johnson, Oliver W. "Spread of Burning Oil." In "Water on Oil Fires." Quarterly-National Fire Protection Association. No. 2, 55:141-146, October 1961.

(25) Sliepcevich, C. M., and J. R. Welker. "The Burning Rates of Liquid Fuels." Prepared for National Research Council Committee on Hazardous Materials, Cargo Containment Panel, February 1970.

(26) U.S. Department of the Interior. Bureau of Mines. Safety Research Center. Hazards of LNG Spillage in Marine Transportation (Final Report S-4105). Coast Guard Contract No. MIPR-Z-70099-9-92317. Pittsburgh, Pennsylvania 15213, January 1970.

(27) Sliepcevich, C. M. et al. "LNG Spills: To Burn or Not to Burn!" Presented at the Distribution Conference Operating Section, American Gas Association, Inc., Philadelphia, Pennsylvania, May 12-15, 1969.

(28) Ball, W. L., and Clyde McKinley. "Special Considerations in Safe Transport of Cryogenic Fluids." Presented at the Symposium on Safety in the Transportation of Hazardous Materials, American Institute of Chemical Engineers, Sixty-Second Annual Meeting, Washington, D. C., November 16-20, 1969.

(29) Neill, Dewitt T. "Heat Transfer from an Uncontrolled Buoyant Diffusion Flame." PhD Dissertation, University of Oklahoma, 1968.

(30) Burgess, D. S., J. Grumer, and A. Strasser. "Diffusive Burning of Liquid Fuels in Open Trays." Fire Research. No. 3, 3:177-192, 1961.

(31) Spalding, D. B. "The Burning Rate of Liquid Fuels from Open Trays by Natural Convection." Fire Research, Abstracts and Reviews. No. 3, 4:236-238, September 1962.

(32) "Some Observations on Pool Burning." pp 50-67; "Burning Rates of Liquid Fuels in Large and Small Open Trays." pp 68-75; "Tests on Combustion Velocity of Liquid Fuels and Temperature Distribution in Flames and Beneath the Surface of the Burning Liquid." pp 76-92. International Symposium on the Use of Models in Fire Research. National Academy of Sciences-National Research Council (Publication 786), Washington, D.C., 1961.

(33) Bader, B. C. "Heat Transfer in Liquid Hydrocarbon Fuel Fires." Nuclear Engineering Part XIV (Symposium Series No. 56, American Institute of Chemical Engineers). 61:78-90, 1965.

(34) Howerton, A.E. "Estimating the Area Affected by a Chlorine Release." Loss Prevention, a CEP Technical Manual, prepared by Editors of Chemical Engineering Progress, American Institute of Chemical Engineers. 3:48-53, 1969.

(35) Brinkley, S. R. "Determination of Explosion Yields." Loss Prevention, a CEP Technical Manual, prepared by Editors of Chemical Engineering Progress, American Institute of Chemical Engineers. 3:79-82, 1969.

(36) Florida Engineering and Industrial Experiment Station. Technical Papers 346 & 347. No. 3, 20 March 1966.

(37) Brown, A. B. "Observations of Fragment and Masses from Various Types of Structures." Minutes of the 11th Annual Explosives Safety Seminar, Sheraton-Peabody Hotel, Memphis, Tennessee, September 9-10, 1969, conducted by the Armed Services Explosives Safety Board, Washington, D.C. 1:341-348.

(38) Brasie, W. C., and D. W. Simpson. "Guidelines for Estimating Damage from Chemical Explosions." Symposium, Loss Prevention in the Process Industries, American Institute of Chemical Engineers (Preprint 21A). St. Louis, Missouri, February 18-21, 1968. (A re-calculation of data suggests the energy factor for hydrogen is about 1%).

(39) Bowie, J. E. and L. R. Petri. "Travel of Solutes in Lower Missouri River." U.S. Geological Survey Hydrological Inv. Atlas (HA-332). 1969.

(40) Stewart, R. M. "Time of Travel of Solutes in Mississippi River from Baton Rouge to New Orleans, La." U.S. Geological Survey Hydrological Inv. Atlas (HA-260). 1967.

(41) Wilson, F., Jr. "Time-of-Travel Measurements and Other Applications of Dye Tracing." Water Resources Division, U.S. Geological Survey, Washington, D.C. Prepared for presentation at the 14th General Assembly, International Union of Geodesy and Geophysics, Berne, Switzerland, September 27 - October 7, 1967.

(42) Daily River Forecast. Available from the local River District Office of the U.S. Weather Bureau. For additional information concerning specific rivers covered by this service, contact the Environmental Science Services Administration, Washington, D.C.

(43) Elliott, W. P. and M. L. Barad. "Operational Prediction of Diffusion Downwind from Line Sources." Air Force Survey in Geophysics (No. 156). Meteorology Laboratory Project 7655, Air Force Cambridge Research Laboratories, Office of Aerospace

Research, U.S.A.F., A.V.C.R.L.-64-163. March 1964, 56 pages. AD-441-351.

(44) Recommended Guide for the Prediction of the Dispersion of Airborne Effluents. Sponsored by A.S.M.E. Committee on Air Pollution Control, Maynard Smith, ed. Brookhaven National Laboratory. First Edition May 1968, 85 pages. American Society of Mechanical Engineers, 345 E. 47th Street, New York, N.Y. 10017. (This publication is primarily for stack discharges resulting in plumes, but Chapter I, "Meteorological Fundamentals," and Chapter II, "Behavior of Airborne Effluents," have application to the releases from transportation as well.)

(45) See also Turner, D. Bruce. Workbook of Atmospheric Dispersion Estimates. Environmental Health Series, Air Pollution, Public Health Service (Publication No. 999-AP-26). U.S. Department of Health, Education and Welfare, Cincinnati, Ohio. Revised 1969.

(46) Military Chemistry and Chemical Agents. Department of the Army Technical Manual 3-215; Department of the Air Force Technical Manual 355-7; Washington, D.C., December 1963.

(47) Brown, J. M. Probing the Law and Beyond: A Quest for Public Protection from Hazardous Product Catastrophes. (Staff Discussion Paper 402). Program of Policy Studies in Science and Technology, The George Washington University, Washington, D. C. 20006.

(48) Evaluation of the Hazard of Bulk Water Transportation of Industrial Chemicals - 1970 Revision. National Academy of Sciences, Committee on Hazardous Materials, Washington, D. C. 20418.

(49) "Material Safety Data Sheet: Requirements for Reporting Hazardous Materials, Safety and Health Regulations for Ship Repairing, Shipbuilding, Shipbreaking." Federal Register. No. 1, 35:10-13, January 1, 1970.

(50) Study and Analysis of Identification and Marking Systems for Intermodal Containers. (Contract # DOT-OS-A9-020). Systems Analysis and Research Corporation, Cambridge, Massachusetts. Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia 22151. Clearinghouse Number PB-185-141.

(51) U. S. Coast Guard. Chemical Data Guide for Bulk Shipment by Water - 1970 Edition. (CG-388). U. S. Government Printing Office, Washington, D. C. 20202.

(52) H. R. 15631, "A Bill to Incorporate the National River Academy of the United States." (Hon. Bill Alexander, Ark.), Congressional Record, No. 15, 116, February 5, 1970.

(53) See Chapter 5, "Optimum Traffic Flow, Congestion and Design in a Waterway System: Determination by Simulation," in Inland Waterway Transportation: Studies in Public and Private Management and Investment Decisions. Resources for the Future, Inc., 1755 Massachusetts Avenue, N. W., Washington, D. C. 20036

(54) Tentative Guide to Compatibility of Chemicals. Approved September 17, 1969 by the NRC Committee on Hazardous Materials, and submitted to the U. S. Coast Guard Headquarters, Washington, D. C.

(55) Fawcett, Howard H. "The Literature of Chemical Safety - 1969 Edition." Presented at the Middle Atlantic Regional Meeting, American Chemical Society, Washington, D. C., February 13, 1969. (Unpublished).

(56) Federal Communications Commission Rules and Regulations. Part 83, Section 83.358. Rules specify safety frequencies:

2003 Kc (Great Lakes)

2638 Kc (All areas)

2738 Kc (All areas except Great Lakes and Gulf of Mexico)

2830 Kc (Gulf of Mexico only)

(57) "A Study of Uniform Reporting System for All Modes of Transportation in Reporting Incidents and Accidents Involving the Shipment of Hazardous Materials." (Recommendations, Item 3, Page 14). The National Transportation Safety Board, Washington, D.C. 20591, March 21, 1969.

(58) Smoot, George F., and James F. Blakey. Systems for Monitoring and Digitally Recording Water-Quality Parameters. U.S. Department of the Interior, Geological Survey, Water Resources Division, Washington, D. C., August 1966.

(59) "American National Standard Practices for Respiratory Protection." (ANSI Z88.2-1969). American National Standards Institute, Inc., 1430 Broadway, New York, New York 10018, 1969.

(60) McCann, Robert B. "A Survey of Naval Architects and Consulting Engineers, Ship Operators and Shipbuilders on a Fire Fighting Capability for Tugboats." (Student Research Paper #47). Fire Protection Curriculum College of Engineering, University of Maryland, College Park, Maryland. May 25, 1966, 42 pages.

(61) Howells, G. P., T. J. Kneipe, and M. Eisenbud. "Water Quality in Industrial Areas: Profile of a River." Environmental Science & Technology. No. 1, 4:26-35, January 1970.

(62) Wilson, J. E. and W. E. Forrest. "Potomac River Time-of-Travel Measurements." Reprinted from Symposium on Diffusion in Oceans and Fresh Waters, Lamont Geological Observatory, Palisades, New York. 1964. 18 pages.

(63) Wilson, J., E. D. Cobb and N. Kyotsukwra. "Movement of a Solute in the Potomac River Estuary at Washington, D.C. at Low Inflow Conditions." (Geological Survey Circular 529B). U.S. Department of the Interior, Washington, D.C. 1969.

(64) Ketchum, B.H. "Eutrophication of Estuaries," pages 197-209; Carpenter, J. H., D. W. Pritchard, and R. C. Whaley. "Observations of Eutrophication and Nutrient Cycles in Some Coastal Plain Estuaries," pages 210-221. In Eutrophication: Causes, Consequences, Correctives. Proceedings of A Symposium at University of Wisconsin, Madison, Wisconsin, June 11-15, 1967. Printing and Publishing Office, National Academy of Sciences, Washington, D. C. 20418. Published 1969.

(65) Ahlers, E. B. "Fragment Hazard Study." Minutes of the 11th Annual Explosives Safety Seminar, Sheraton-Peabody Hotel, Memphis, Tennessee, September 9-10, 1969, conducted by the Armed Services Explosives Safety Board, Washington, D. C. Pages 81-107.

(66) Forshey, D. R., Cooper, J.C., Martindell, G. H., and Kuchta, J. M. "Potential Hazards of Propargyl Halides and Allene." Fire Technology. 5:100-111, 1969.

(67) "Tentative Method of Test for Drop-Weight Sensitivity of Liquid Monopropellants" (ASTM Designation: D 2540-66 T). Issued 1966.

(68) "Tentative Method of Test for Critical Diameter and Detonation Velocity of Liquid Monopropellants" (ASTM Designation: D 2541-66T). Issued 1966.

(69) "Tentative Method of Test for Shock Sensitivity of Liquid Monopropellants by the Card-Gap Test" (ASTM Designation: D 2539-66T). Issued 1966. American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania. Book of ASTM Standards, Part 18, copyrighted 1967. Subcommittee 3 of E-27 Committee has compiled a bibliography on Impact Testing (October 28, 1968, Memorandum of C. M. Mason, Secretary).

(70) Van Dolah, R. H. "Shock Sensitivity and Its Evaluation," Chapter 20, pp. 319-329. In H. H. Fawcett and W. S. Wood, Eds. Safety and Accident Prevention in Chemical Operations. New York: Interscience, 1965.

(71) Chang, S. L. and G. Berg. "Chlormelamine and Iodized Chlormelamine Germicidal Rinse Formulations." U.S. Armed Forces Medical Journal. 1:33-34, January 1959.

(72) Lindeijer, E. W. "Possibilities of Explosion in Bleaching Powder: A Literature Review." Technological Laboratory of National Defence Research Organization, Rijswijk, Netherlands. (Distributed at the International Symposium on the Carriage of Dangerous Goods, Rotterdam, the Netherlands, May 27, 1968).

(73) Mason, Charles M., David R. Forshey, and Frank J. P. Perzak. "Fire Hazards of Ammonium Nitrate-Sulfur Systems." Journal of Agricultural Food Chemistry. No. 6, 15:954-966, November-December 1967.

(74) U.S. Department of the Interior. Bureau of Mines. Explosives Research Center. Sympathetic Detonation of Ammonium Nitrate and Ammonium Nitrate-Fuel Oil (R.I. 6746). 1966.

(75) "High Energy Propellants." 8th Explosives Safety Seminar, NASA Marshall Space Flight Center. Sponsored by the Armed Services Explosives Safety Board, Washington, D.C., August 9-11, 1966. Proceedings: Minutes of the Seminar, AD 801103, p. 20.

(76) Lee, P. R., "Safe Storage and Transportation of Some Potentially Hazardous Materials," J. App. Chem. (London), 19 December 1969, pp 345-351.

RESEARCH NEEDS OF CARGO SIZE LIMITATIONS PANEL

I. Short-time (Emergency) Guides for "Massive" Once-in-a-Life Exposures

This investigation is a key element in determining what area should be evacuated in the event of a gross release of a toxic gas or vapor in air. The Federal Air Pollution Administration and the NRC Advisory Committee on Toxicology are actively considering this requirement.

II. Rate of Underwater Release of Corrosive Gases from Cylinders and Other Containers

Although it is generally recognized that corrosive gases and vapors become more corrosive with water, no rates of deterioration of cylinders or tanks underwater have been located, other than recent Bureau of Mines investigations. The more general question arises as to the reaction of containers under water with other gases, such as sulfur dioxide, hydrogen chloride, hydrogen fluoride, phosgene, hydrogen sulfide, and ammonia, at depths associated with barge and ocean transport, and at temperatures encountered in rivers and ocean harbors. Corrosive liquids, such as acids, should be included in the underwater investigation.

III. Spillage of Flammable Liquids on Water

Although much attention has been directed lately to petroleum spills on water, there is a paucity of information on the spread, diffusion, dilution, and evaporation of chemicals under various conditions of temperatures, winds, and other variables. The relative solubility and dilution of chemicals due to wave action will doubtlessly be factors.

IV. Burning Rates on Water

Closely related to III (above) is the question of the size and duration of a fire which would result from the release of a large cargo. Limited data are available for gasoline and tanker oil spillages, but

are more difficult to obtain for other substances. This data would be especially important for dealing with spills and in congested waterways and locks.

V. Movement of Liquid Releases

Further generalizations or a model would be helpful in extending the existing stream-travel measurements taken by the U. S. Geological Survey into more useful form. These should be extended to include all navigable streams. Further investigations should include liquids and solids of various densities; a better understanding of tidal flow pollutions; basic data on leaks from damaged containers; and extent of the hazard associated with release of flammable and/or toxic liquids on water. Predictions can then be made for spread of the spill, as well as its travel and absorption by the bottom. Translated into practical terms, this would permit the Coast Guard to predict when a spill would reach a given location such as a city water-intake, a dam, or other sensitive location, and to alert downstream personnel.

VI. Analysis of Past Casualties

The Coast Guard is attempting a more complete analysis of past accidents to obtain probability factors of greater credibility. This should be of value to the whole committee.

VII. Completeness and Availability of Hazard Information

The panel recommends a review of existing information to insure that relevant data is complete and that needed hazard information on all cargoes being shipped is supplied to the Coast Guard.

The panel strongly endorses the concept of a National Hazard Information Control Center, along the lines which the Coast Guard has in advanced planning. Sufficient knowledge exists already to make such a system highly useful. The system will assist in pinpointing gaps or incompleteness in present knowledge.

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13. ABSTRACT

Cargo size has been studied in the context of water transport of bulk chemicals, many of which have been previously identified as hazardous if accidentally released.

The panel concludes no firm or arbitrary size limits presently exist or can be scientifically justified with the present information. However, larger shipments, with greater potential hazard to the public domain, demand greater attention to:

-- container integrity;
-- adequate pre-shipment hazard evaluation and control;
-- a higher level of technical monitoring, supervision, and escort;
-- a faster availability of emergency control information and procedures, and more complete two-way emergency reporting of near-misses, minor accidents, as well as casualties, with subsequent detailed analysis and feed-back, to protect the interests of the shipper, operating and emergency personnel, and the public.

Areas of incomplete knowledge and needed research have been delineated.

The existence of a practical mutual-assistance plan for prompt mobilization of all available facilities, manpower, and knowledge, backed by actual training and exercises in response, should be emphasized in appraising introduction of the larger cargoes into a port.

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Hazardous Materials						
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Contamination						
Accident						
Vapor Cloud						
Dispersion						
Tankers						
Cargo						
Pollution						

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