AN OUTREACH PROGRAM of the
PLANNING AND MANAGEMENT DIVISION of the
U.S. ENVIRONMENTAL PROTECTION AGENCY, REGION 1.

A Perspective on the Prevention, Prediction and Response Aspects of Major Chemical Accidents

January 7, 1990

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This document provides basic information for use by the public, emergency planners, fire chiefs, plant managers and process operators, and state and local government employees. Additional copies, and a companion four-hour, audio-visual module for presentation to interested public groups are available from Region 1 on request.

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January 7, 1990

Dear Reader:

*Attached is a guidance document on the three key points of major chemical accident concerns - **Prevention, Prediction, and Response.***

The information which is presented is believed by the author to be consistent with the teachings of the agencies and organizations which have jurisdiction or special competency in the subject area. It is intended to be of help to people in enhancing public safety. However, it is not presented as a statement of mandatory safety engineering. And no assurance is made that a particular action or control, if implemented, will prevent a future chemical accident.

The U.S. Environmental Protection Agency, and the U.S. department of Labor - OSHA have primary jurisdiction respectively for community and occupational safety. The U.S. Coast Guard has jurisdiction in matters involving navigable waters. And , it provides support services to federal, state and local authorities. If you have questions, members of these agencies will be pleased to be of service to you. Key EPA and OSHA personnel in Region I (New England States) whom you can contact directly for particular information are:

The U.S. Environmental Protection Agency (EPA)

SARA Title 111: Reporting, Inventories, and Technical Program Information
Thomas D' Avanzo (617) 565-4502

Chemical Safety Auditing - Ray Dinardo (617) 860-4385

The U.S. D.O.L - OSHA

Technical and Compliance - Occupational Health and Safety Standards -
Dr. Ronald Ratney (617) 565-7164. Fred Mallaby, CIH (617) 565-7164

The U.S. Coast Guard Strike Team, Atlantic Area, Commanding Officer: LCDR. G. A. Wiltshire has a 24-hour emergency service: (205) 694-6601.

*If you need additional information, or have questions about this document, please contact Norman Beddows, Regional Industrial Hygienist and Safety Manager, **EPA-Region 1, Planning and Management Division (617) 565-3388.***

ACKNOWLEDGMENT

A Perspective on the
Prevention, Prediction and Response
Aspects of Major Chemical Accidents

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Abstract

This document is presented in support of an outreach program of the U.S. Environmental Protection Agency, Region 1, under the 1986 Right To Know Act (EPRA).

It provides basic information for use by local emergency planners, fire chiefs, chemical plant managers and personnel, chemical safety auditors, state and local government employees and the public. This information will serve as a basis for discussion between the public and chemical facility managers to promote harmony in potentially contentious situations. And, it will serve as a basis for developing protocols for chemical safety auditing of many of the operations which comprise the highly variable chemical industry.

A background is provided in standards, regulations, motivation and policies. This complements information provided by the federal National Response Team, chaired by the U.S. Environmental Protection Agency. Chemical hazards are discussed. Aspects of prevention, prediction and response for major chemical accidents are presented.

For prevention: hazard analysis techniques are described, and matters of experience and guidance are discussed, especially in context with information provided in the 1989 U.S. Environmental Protection Agency's publication "CHEMICAL ACCIDENT PREVENTION BULLETIN." Also, certain engineering and administrative controls for safety are identified and described.

For prediction: hazard identification is described, and an explanation is given of how potential exposures and health and safety risks can be evaluated. Also, explanations and examples of the use of computer software for developing emergency prediction information are provided.

For emergency response: acute exposure risks are identified. Means of personal protection are discussed. Also, certain suppression and containment techniques are explained.

INTRODUCTION

Concern over the safety of manufacturing, transporting and using extremely hazardous chemicals is worldwide. Bhopal[1], Seveso[2], the Rhine River Spill[3], and other environmental catastrophes have made this so. Nationally, there is an increased awareness and concern. A great many people in the United States think that a major chemical accident will happen domestically in the next fifty years[4]. At the local level, many communities in which explosive or toxic chemicals are made or handled are fearful. Large residential areas and institutions have been established in some communities around chemical plants and tanks, which preceded them.

The U.S. Environmental Protection Agency (EPA) has been one of the principle agencies to date in developing policies and programs for preventing and mitigating major chemical accidents (involving either (i) **extremely hazardous substances** or (ii) **hazardous sustances**, as defined at Parts 101 (14) and 355 of Title 40, and section 1910.1200(c) of Title 29, of the Code of Federal Regulations). Other agencies who have primary responsibilities are the Department of Transportation, the Department of Labor - OSHA, and the U.S. Coastguard. In 1985, the U.S. Environmental Protection Agency introduced comprehensive accident prevention and emergency preparedness programs for use in the private and public sectors to protect the public. And the Superfund Amendment Reauthorization Act (SARA) of 1986 provided for community involvement in accident prevention, and prescribed programs for emergency

planning and notification. The relevant SARA programs are rather technical. However, dialogue between all the parties which EPA and OSHA promotes will off-set this.

The American Institute of Chemical Engineers, the Center for Chemical Process Safety, The World Bank, the chemical industry itself, and numerous technical societies[5] also support the private and public sectors in their efforts for chemical safety. Even so, some of the public believe that not enough is being done to protect them against potentially catastrophic effects from major chemical accidents. Evidently some of the public believe that some involuntary risks are substantially greater than levels reported by the governments' or the industrys' experts. Most people understand that there are inherent hazards in producing, using or transporting chemicals. Most people agree that the public's safety must be fully maintained. Few would agree, however, on a level of balance needed to achieve both optimal safety and economic viability in a chemical industry. Also, some people want the government to regulate the design and operation of chemical plants, in the same way that the Nuclear Regulatory Commission regulates design, construction, quality assurance and operation in the nuclear power generation industry[6]. The chemical industries resist this viewpoint. The U.S. Environmental Protection Agency evidently is not intent on regulating the **design or operation** of chemical plants and processes[7]. Rather, it seeks to have industries comply voluntarily with the highest standards for safety.

Federal and state agencies promote the use of the best practical technology, compliance with stringent standards and recommendations[8], and mutual cooperation of plant managers, emergency planners and the public. They ensure that local officials, fire fighters, and citizens have access to detailed information on chemical hazards. They have provided the risk-bearers and the local officials a real role in emergency prevention. Specifically, the U.S. Environmental Protection Agency requires facilities to undertake emergency planning, and be involved with state and local officials in emergency planning when an **extremely hazardous substance equal to or in excess of its threshold planning quantity** is present [**40 CFR 355.30(a)**]. The agency itself has broad police powers aimed at preventing and mitigating accidents.

The U.S. DOL - OSHA exerts an influence on chemical plant design and operation by enforcing specific standards and regulations, and, in the final analysis, by requiring the employer to provide work and workplaces for the employees which are free of recognizable hazards.

Complete regulation of the design of chemical processes would be very difficult. The industry is highly diversified in the chemicals which it uses and manufactures, and in the kinds of processes and equipment which it employs. No one set of safety criteria applies to even a single operation, and no sets of criteria apply as a basis for identifying all of the chemicals and processes which could be of concern. There are literally hundreds of relevant, mostly specification-oriented safety standards, codes and guidelines for the industry.

Performance-oriented standards also exist. The latter type has special value for highly variable process operations. Several national technical societies provide research support for safety. Some standards and groups are shown in Table 1.

STANDARDS, CODES, GUIDELINES & ORGANIZATIONS

National Fire Protection Association (NFPA)
NFPA 30 - Flammable & Combustible Liquids
NFPA 58/59/59A - Liquid petroleum; new designs
American Petroleum Institute (API)
API 650 - tanks welded steel
API 520/521 - design, construction, systems
API 526 - flanges, safety/relief valves
API Guidelines publication # 7580: Lessons learnt
API Recommended Practice # 1112: DOT response; emergencies.
API 2000 - venting low pressure storage tanks
American National Standards Institute (ANSI)
ANSI-B 31.3 - piping, chemical plant
ANSI.B 16.9 - overpressure design/piping
American Society Mechanical Engineers - Guidelines and Standards
American Institute of Chemical Engineers - Guidelines and Standards.
The Occupational Safety and Health Administration (OSHA) - The General Duty Clause: employers to provide safe workplaces, at 29 CFR.1910.5(a)(1).
The Emergency response rule, at 29 CFR Part 1910.120.

Table 1. Some Standards, Codes, Guidelines And Organizations

Motivation and Policies

Most managers in the domestic chemical industries are very committed to providing the highest achievable level of safety. They are morally motivated. The industries themselves are strongly motivated to provide maximal safety. They are so persuaded by the potential for criminal citation, the possible imposition of jail sentences on executives, and the great financial liability which

exists with a major chemical accident. However, to some extent, some plants are de-motivated by the low economic viability of some processes, and by frequent turn-over in executive management. In some plants, an emphasis on minimizing costs of investment and operations without due regard to the required level of engineered safety is evident.

Optimal safety in the chemical process industry may not be achieved through regulation alone. The highest level of chemical safety is likely to be attained only by industry, government and the public working openly together. Much can be achieved. Government could provide consultative services to the industry. Chemical safety audits, separate from enforcement actions, could be offered without plant managers fearing a threat of a first-instance sanction. The public could become more informed on chemical safety matters and more generally realize that great economic loss can arise by unwarranted pressure on chemical manufacturers, users or transporters. The industries might more openly advocate their programs for public safety, and ensure that their management systems are appropriate. Companies must make sure that efforts to minimize costs of investment and operations are not translated into implementing only minimal safety programs. Requiring only minimal safeguards, and minimal investment in equipment, real estate, and labor, without regard to the potential for a catastrophic accident, because a process or plant is mature or has a poor profitability, is quite unacceptable. The total resources of a company - not merely the short-term cash flow picture of a profit and loss center - must be available when **first** needed to achieve safety.

The managers of chemical industry and the heads of the agencies which are primarily involved should ensure that their senior staffs include experts in plant layout for safety; process and unit operations safety; and safety engineering. And, persons will be needed who will deal authentically with the concerns of the public.

Chemical Hazards

Airborne concentration and exposure duration are the key factors of potential acute health hazard with most chemical exposures. The most common concern of route of exposure is inhalation. Dermal exposure is another important concern - about a quarter of the known extremely hazardous substances show dermal toxicity. Airborne concentration is the primary factor of fire or explosion hazard with a flammable gas, vapor or mist. Pressure and temperature, of course, greatly affect both the potential for detonation with any given system, and the destructive energy of a gaseous release in an accident.

For toxicity, the relationship of concentration and duration of exposure, and the potential for toxic lethality are not the same for all extremely hazardous chemicals. As an example, the impact of methyl isocyanate (MIC) increases rapidly as the exposure time increases, even when the initial, short-term exposure is without apparent effect; whereas the toxicity of chlorine or ammonia does not disproportionately increase with increasing duration of exposure. For these two chemicals, the initial dose is the significant determinant of severity of effect. The influence of duration of (inhalation)

exposure on response, regarding a serious hazard with a gas or vapor, may be evaluated using the ratio of the 10 minute and the 30 minute median lethal concentrations (LC50s) from animal studies, when these data are known. As an example, MIC exhibits a 10 minute, LC50, and a 30 minute LC50, respectively, of approximately 600 and 100 parts per million (ppm) - a 6:1 ratio. However, chlorine exhibits a 10 minute LC50, and 30 minute LC50, respectively, of approximately 450 ppm, and 250 ppm - a 2:1 ratio. Comparisons can be made in other ways. Table 2 provides data.

CHEMICAL [Extreme Hazard]	IDLH [ppm]	LC50/10' [ppm]	LC50/30' [ppm]	BPt °C	Ht.VAP* KJ/KG
PHOSGENE	2	72	24	8	253
BROMINE	10	651	376	59	194
HYDROGEN FLUORIDE	20	992	331	19	1562
CHLORINE	25	433	250	-34	288
HYDROGEN CYANIDE	60	597	277	26	935
HYDROGEN SULPHIDE	300	550	441	-62	550
SULPHUR DIOXIDE	100	1882	627	-10	1882
HYDROGEN CHLORIDE	100	5555	1850	-84	443
AMMONIA	500	20,000	11540	10	1374

LC50/10' = Median Lethal Concentration, 10 minutes, animal studies.
Source: PROCEEDINGS: 1987 SYMPOSIUM ON PREVENTING MAJOR CHEMICAL ACCIDENTS, American Institute of Chemical Engineers.

Table 2. Some Toxicological and Physical Property Data.

ASPECTS OF PREVENTION

Hazard Analysis and Chemical Safety Auditing

The diversity and complexity of the chemical industry and its processes are so great that even the use of the most comprehensive line-by-line check lists (such as the thousands-of-line sized lists used in the petroleum industry in conjunction with other analytical schemes) is not fully adequate for hazard analysis. Systematic evaluations involving consideration of potential inter-related, contributing events are also needed. These types of evaluations should be conducted by a team of specialists, for the maximum benefit. People with experience in the particular chemical plant or process in case should be part of every team. A systems-approach coupled with specific expertise is the preferred basis for making a chemical safety audit. In California and New Jersey, this is mandatory and analytical methods are prescribed. At times, chemical safety auditing calls for the skills of a safety consultant or the prime contractor who has special knowledge of the particular process. They will work with the in-house engineers and specialists.

Formal analytical techniques are now used throughout the chemical and petroleum industries to prevent losses and solve problems. No one technique is the universal method of choice. A hazard analysis technique which is very beneficial when used at the conceptual stage of a project, might not provide the information necessary to identify and correct an existing problem. The technique to use in a particular situation needs to be carefully selected.

Safety engineering techniques - Hazard Inventory, Risk Analysis, Fault Tree Analysis, Event Tree Analysis, Hazard and Operability Studies (HAZOPS), and Failure Modes And Effects Analysis (FMEA) are described briefly here.

Hazard Inventory. This technique[8] is applicable to both the design and operation of a chemical plant. It involves identifying and classifying risks in terms of (a) the types and qualities of toxic and hazardous chemicals which are stored or used, (b) the storage and handling conditions or practices employed, and (c) the engineering and management systems involved. The recording of physical spacing is important. Distances should be set aside for safety assurance. Typically, a 200 foot spacing around hazardous operations is used to enhance safety and make mitigation of liquid releases easier. Dikes are used to contain liquid spills and subsequent dispersion when either flammable materials are stored in any way in the plant, or potentially interactive factors of hazard exist -such as a spill of flammable liquid spreading under a storage tank of hydrogen cyanide.

No special format for record-keeping is required or specified for hazard inventory. The technique is useful for making improvements in plant lay-out, process control, and risk management. It is a requirement for conducting a comprehensive safety audit. Lastly, an inventory of **extremely hazardous substances** in **reportable quantities (RQ)** is mandatory under SARA Title 111.

Risk Analysis. This is a technique[9] for characterizing risks which is especially useful in designing plants; siting plants; and changing processes. It helps coordinators to plan for emergencies. It is used throughout the chemical and petroleum industries. Risk analysis involves three basic steps: (a) identifying failure cases and modes; (b) assessing the respective consequences of the identified failures **(in the case of a detonation risk with a chemical accident, the destructive energy and impact effects at distances may be expressed as an equivalent amount of TNT explosive)**; and (c) estimating the respective probabilities of the failures. These factors are considered together for each event in assessing impact. Identifying failure cases involves knowing the inventories of toxic or hazardous chemicals, and carefully considering process flows, piping, control instrumentation, and modes of operation. Check-lists and "What If" evaluations are used for this purpose. After characterizing events, a grid of risk classes (low, medium, high) is made, as a record of the analysis.

Assessing the consequences of a failure in the above scheme involves classifying the possible outcome of an accident in terms of human health and safety (and ecology and community welfare). For this, modeling releases for toxic or fire/explosive impacts is very useful. In modeling, assessment is based on plausible worst-case scenarios. Also, potential exposures are assumed, and the issue is whether or not the concentrations **and** the durations of exposure at various locations would be sufficient to cause serious, acute (or chronic) health hazards. Also, fire risks are assessed. In making a risk analysis for a chemical plant, information on frequency of failure is needed. Histories of

physical plant equipment, system and operator failures are useful for this purpose. In many chemical plants, a data base already exists in the maintenance department, which may be used for this purpose. The technique is limited in usefulness when data of failure or accident rates are scant or incomplete, or when the models used for evaluating exposures are inaccurate or otherwise limited. Risk analysis can be of great value in designing and siting new plants, and in operating existing ones. As a yardstick of risk, one "standard" for acceptable (major accident) risk is one in a million/year - - 10^{-6}/year. Systems reliability studies of complex processes are especially important to designers. Several techniques exist for use in design work and safety management, and may have preferred applications. These include Fault Tree analysis, and Event Tree Analysis. These techniques are used extensively in the chemical industry, and are briefly described here.

Fault Tree Analysis. This technique[10], involves identifying and defining modes of failure called "**top events**." Two examples of top events are the release of a toxic gas from a rupture in a pressure vessel; and the thermal runaway of a chemical reaction in a vessel.

For each top event, precedent events and combinations of precedents which lead directly to the failure are identified. A "tree" diagram of causes and effect is developed. The diagram shows (a) causation, and (b) estimates of the associated frequencies of occurrences. In this way, the contributory causes and the direct cause of a failure or accident are found, and required preventative

actions are identified. A feature of fault tree analysis is the use of **AND** and **OR** gates to express logical cause and effect relationships. Rules for construction exist. A safety analyst **and** individuals who have knowledge and experience of the type of plant and process involved are needed to perform the analysis.

Event Tree Analysis. This is another systems reliability technique[11]. The "event tree" is similar in format to the "fault tree", except that "**bottom events**" are first identified. Thereafter, the possible outcomes from these bottom events are stated, and a series of "gate" questions, with **YES** and **NO** strings (with assigned probabilities) are employed. This technique allows human error and other factors to be shown in relationship to consequences.

Figures 1a and 1b illustrate typical branches of the "Fault Tree", and the "Event Tree", respectively (without the estimates).

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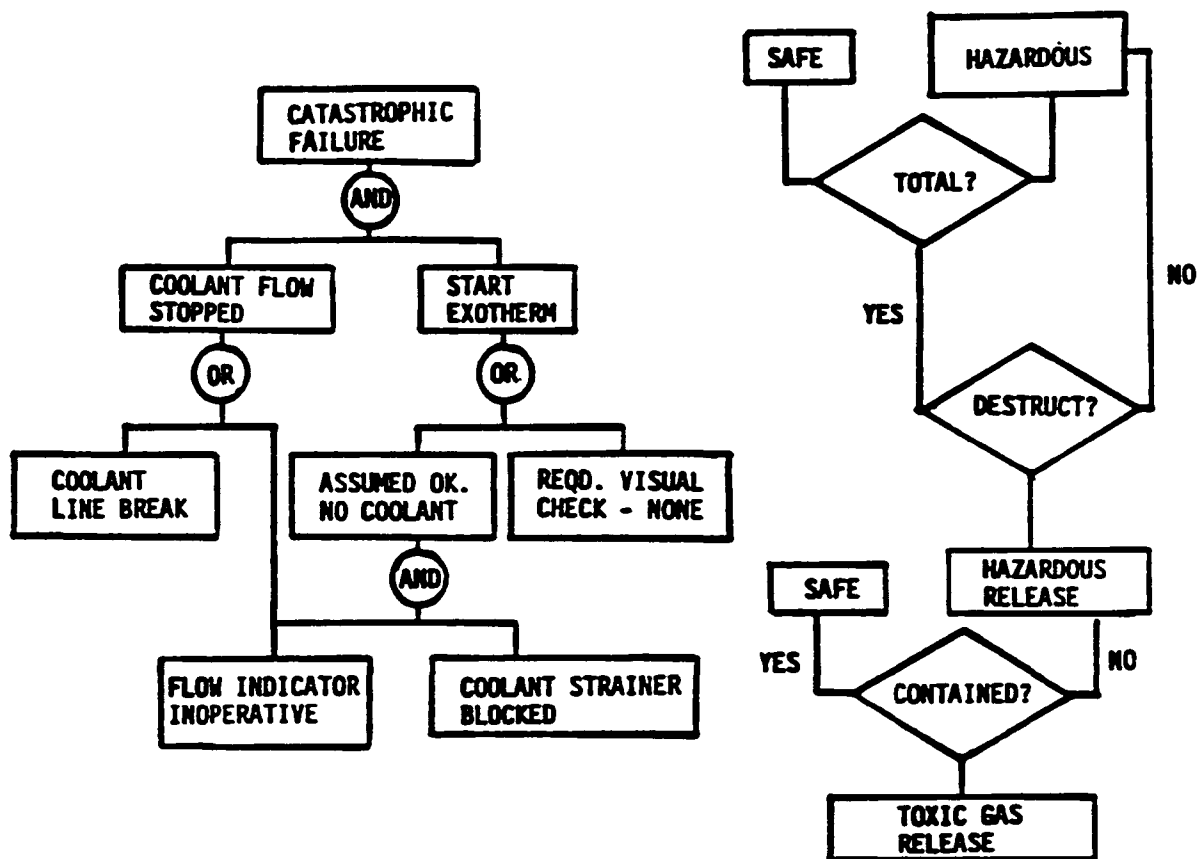
Figure 1a: Fault Tree Form   Figure 1b: Event Tree Form

Hazard and Operability Studies - HAZOPS. This is a technique[12] which involves the systematic identification and evaluation of possible routes to failure in a system. It provides a basis for conducting a thorough safety evaluation of a new plant design, making recommendations for major improvements to proposed or existing processes, and developing reliability and risk analyses. It is used extensively in the chemical and petroleum industries at the design stage for risk identification and problem resolution.   HAZOPS uses a study-team approach to address sets of potential problems and produce alternative

solutions. The technique is labor-intensive. Typically, several hundreds of man-days will be expended in studying piping and instrumentation for a new plant, before anything is ordered.

The basic procedure in a HAZOPS is to ask certain guide-words during the course of scrutinizing many possible operating conditions and deviations. This identifies possible causes of potential accidents. **What if** questions using guide-words are asked. For example, "what if more temperature occurred"; "what if reverse flow occurred"; "what if more pressure arose"; "what if more time elapsed in a self-heat situation." The words **more, reverse** and similar descriptors are used in this way to explore potential upsets whose consequences are to be evaluated.

Failure Modes and Effects Analysis (FMEA). This is a simple, widely-used technique[13], similar to HAZOPS. It is used to systematically identify possible failure modes and inter-related factors. It involves the use of first-principles and engineering experience in looking at components separately, and identifying possible ways of failure.

Information on Experience and Guidance

Personal experience in chemical processing, knowledge of the proximate and contributory causes of past accidents and near-misses, and knowledge of design and the principles of hazard analysis are indispensable for managing an accident prevention program. A historical perspective is also indispensable.

Some points on these matters are discussed here. And findings are reported from a 1989 study by the U.S. Environmental Protection Agency · of why chemical accidents happen.

Chemical Accident and Release Information

The U.S. Environmental Protection Agency's Chemical Accident Prevention Bulletin (July 1989, OSWER-89-008-1) provides information on why chemical accidents occur. The bulletin focuses on reports of accidents, and a database, developed under Title III requirements. This information is intended to provide local emergency planning committees with the means of holding useful dialogs with local facilities on accident prevention and investigation. The Accidental Release Information Program (ARIP) findings are:

● "The most frequently released chemicals in the ARIP database have been chlorine, methyl chloride, ammonia, sulfuric acid, and sodium hydroxide--all large-volume industrial chemicals.

● Most of the releases occurred at facilities that manufacture chemicals or other products.

● Although accidents commonly have more than one cause, the most commonly cited causes are equipment failure and operator error.

● About a quarter of the releases were from storage vessels, and a similar number from piping and process vessels. Valves and other equipment contributed to a smaller fraction of releases.

● Most releases occurred during routine processing of chemicals; loading, unloading, and maintenance played a lesser, but significant role."

Remarks On Storage Tank Accidents

Storage vessel accidents feature in about a quarter of the (SARA) reported accidental releases; releases of one hundred to one thousand or more gallons are most often involved. Some of the more common causes of failure involved are mechanical impact; embrittlement; delamination; and internal development of a vacumm - "sucking in." Incorrect selection or fabrication of construction material can lead to failure. Plasticized polymers continuously exposed in use to leaching agents, such as sodium hydroxide, are prime candidates for impact or cyclical stress failure. A blockage of a vent at the time of emptying can cause an internal vacumm, and lead to collapse.

Safety Design and Operation Criteria for Tanks and Storage re: Extremely Hazardous Substances.

Criteria for evaluating storage tank and related activities include the following:

● a roof over a tank and bunded area (weather protection)

● impervious, sloping, non-reactive, low heat-tranfer base support

● vertical concrete (higher than flood plain height) walls for containment

● strong barriers to guard against impact from trucks

● a drainless, insulated sump tank (200 gallon ?) for lesser spill containment, equipped with: a pump or air lift for rainwater; a non-return flap valve; and a vent leading to an absorption or a destruction unit

● tank pipework connections and pumps above the tank top

● remote-operated, Teflon seat-ball valves, and internal plug valves.

NOTE: IN SOME SAFETY DESIGNS, A BOTTOM VALVE IS PRECLUDED.

- pressure and temperature, multiple sensors

- a piping flow control system to prevent the simultaneous feeding and discharge of the tank

- no sharing of vent pipes for any system component

- no dead volume space in valve, loop, vent or pipe places

- mimimal inventory, balanced against risks involved in material loading and transfer

- wind-indicators (windsock), strategically placed

- physical separation from potential harm (such as from a fire from a spill, affecting another vessel), and from critical plant structures and boundaries

- dedicated fire fighting equipment, dedicated personal protective equipment, and means of access for accident mitigation

- formal standard operating procedures covering such points as (i) material-handling, (ii) trained personnel only allowed as operators, (iii) the correct selection, use, and maintenance and storage of personal protective equipment, and (iv) the proper handling and storage of transfer lines and equipment - transfer lines must never be left on the ground, dirt will get on the connection surfaces. A raised open-grid metal trough should should be used for storage.

Other general aspects of safeguarding tanks and associated equipment are mentioned elsewhere. As a final comment here, the use of rail-cars as a permanent in-process inventory storage facility for an extremely hazardous substance without the safeguards mentioned is not prudent.

Figure 2 shows some possible features of construction for storage tank safety.
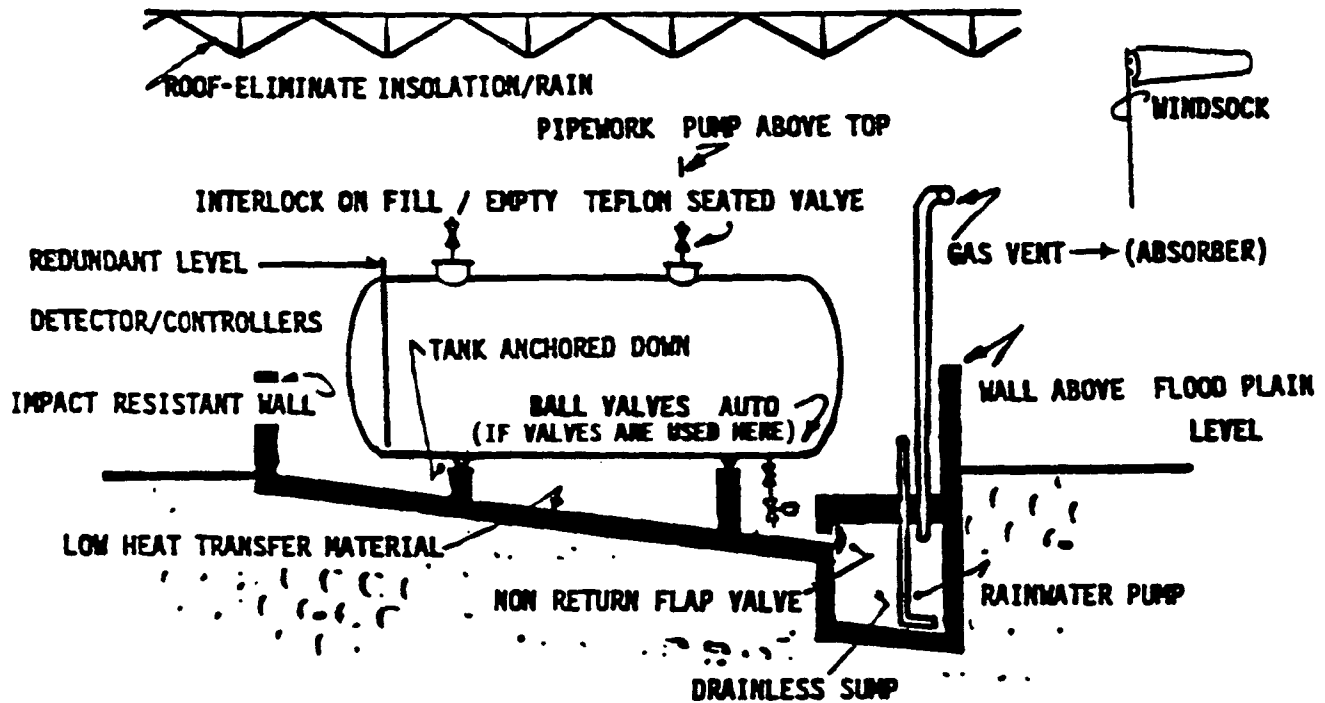
Figure 2. Safety Design features for Storage Tanks

Remarks On Pressure Vessel Accidents

Pressure vessels are extensively used in chemical processing; they are involved in many major accidents. Over-pressurization and inadequate pressure relief capability are causes. However, these are not the dominant ones. More common causes involve failure of the non-pressurized parts of the system because of corrosion, wear, impact, or human error in the design or operational stages. Other common causes include exotherms in stagnant pools of reactive

material in dead spaces, and loss of coolant in a reactor self-heat failure (the latter point is illustrated in Figure 1a). Some general aspects of safeguarding reactor vessels and associated equipment are mentioned later.

Controls For Process Safety

Potential areas of future accidents in existing plants are aging facilities, reduced investments in equipment and maintenance, a reduction in the availability of skilled operators and maintenance personnel, and a thin-sprea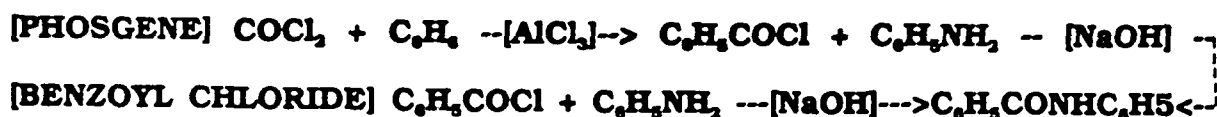ding of the available cadre of skilled process operators and chemical safety engineers. At the time of start-up of a new plant or process, experienced or skilled personnel may be in short supply, limitations can be severe. This is a vulnerable time when the value of incorporated **engineered** control is often demonstrated. Safety depends on the use of engineered controls as least as much as on operator-skill.

To ensure that plants operate at the lowest risk, comprehensive engineering plans, together with safety programs, are needed. Both types of control must be considered in the design phase and the plant operation phase. At the conceptual engineering and design time, major efforts in process hazard analysis must be made. This includes studying any alternative chemistries and processes to make sure that the least hazardous reactants and conditions are used. On this point, the toxicity of a chemical may be greatly changed by a minor change to the molecule. Also, the vapor hazard with a process may be decreased by increasing reactant molecular weight. As an example, in a series

of (moderately) exothermic Friedel Craft/Schotten-Baumann reactions, the substitution of extremely hazardous phosgene (boiling point:8°C) by benzoyl chloride (boiling point:140°C) is sometimes possible, while still making the same desired product:

[PHOSGENE] COCl₂ + C₆H₆ --[AlCl₃]--> C₆H₅COCl + C₆H₅NH₂ -- [NaOH] ⌐
[BENZOYL CHLORIDE] C₆H₅COCl + C₆H₆NH₂ ---[NaOH]--->C₆H₅CONHC₆H5<--⌐

Other examples of risk reduction with **chemistry-process** changes are:

● mercury free dyemaking (replacing mercury catalysed AQ sulphonation, CIBA-GEIGY process)

● continuous polymerization of styrene in a closed system (rather than batch-processing in a vented pressure vessel, MONSANTO process)

● the use of a condenser on a vent on a pressure vessel charged with toxic reactants.

It must be said, however, that the oportunity to use alternative chemistries and processes is generally quite limited. Nevertheless, the point is worth reiterating that a formal procedure should be established to ensure that the senior managers are given information on options, so that they can properly manage the risks.

To minimize risks of fire and explosion, the design of new or modified chemical plants should require certain critical processes and facilities to be remote and

physically isolated from both each other and the plant boundary. Guidance on such safeguarding is provided in various API and NFPA codes. Also, local and state codes are useful (and applicable). Providing safety by distance is an effective way to control explosion risk. And physical isolation can be very effective in limiting the potential damage from spills of flammable or corrosive liquids. Invariably, using distance as a safety control entails greater first-costs for real estate, compared to using a close-packed (less safe) layout. Safety and net economy may have to be strongly argued during the cost-benefit reviews.

The point which may need making is that the cost of a major accident, however infrequent, is always very great. The Bhopal settlement cost a reported $470 millions!

Passive (Intrinsic) and Active (Extrinsic) Safeguards

To incorporate safety in new and existing facilities, one needs to employ both passive and active principles.

Passive principles are policies and plans, essentially. These include such matters as:

● requiring each plant to have Standard Review Plans, and Standard Safety Operating Plans. These plans would cover evaluation of potential accidents; dispersion prediction information; groundwater protection; safety assurance in new or changed processes, facilities or operations; mandatory periodic meetings

with local planners, interested citizens and media personnel who may be involved in public safety; safe working practices, including the "buddy" system with high hazard activities; and other points.

● requiring critical facilities to be located in remote locations and safeguarded by distance and diking, when appropriate.

● requiring design for mitigation of accidents.

● requiring experts to participate in the selection and sizing of pressure relief equipment and flame arrestors; in vessel and piping construction and material selection; and in decision-making on process automation-versus-manual control

● requiring a human factors engineer to participate in the concept and design stages of planned new construction

● requiring pre-processing system leak checks, and periodic, non-destructive testing of vessels and parts involved in any high hazard process

● requiring regular formal inspections of all process piping, flanges and gaskets, and instrumentation when they are part of, or service any high hazard process

● requiring the use of hard wired back-up for critical interlocks, and alarms on hazardous processes

● requiring multiple, and different types of, controls on hazardous processes (control redundancy)

● requiring electrical, coolant and other critical services, and tanks and equipment for extremely hazardous chemicals, to be physically protected against accidental impact or abrasion, and "backed - up" by emergency services.

- emphasizing that flash point and auto-ignition point are not constants, and that the dynamics (e.g., agitation) of the process can create risks

- requiring studies of potential rates of reaction and self-heat rates (in some studies of upsets, 1000°C/minute plus, instantaneous rates have been reported)

- requiring pilot plant scale-up studies for safety in new processes, and safety rules for each pilot plant

- requiring the preferential selection of reactants, processes and conditions which pose the least impact on the community in an accidental release.

- requiring feasible pressure relief systems to match plausible worst-case overpressurization/self-heat conditions

- requiring reactor vessels to be operated at the lowest feasible pressures and temperatures (a cubic foot of gas at 2000 psi and 20°C has about as much potential energy to do some harm as has a pound of TNT, even if the release modes are different!)

- having a firm policy of physically protecting tanks, gas lines, and critical valves and lines against impact by fork-lift and other types of trucks

- prohibiting any physical change or procedural change to any process and procedure, regardless of any percieved inutility, without the express permission of both the Manager of Engineering and the Manager of Safety. This prohibition would be conspicuously posted on the equipment.

Active principles are related to <u>operating or using</u> engineering and administrative controls. Such active safeguarding includes using:

● pressure relief devices. Most importantly, such devices need to be sized to match the pressure generated in a maximal self-heat case, when this is physically feasible

● rupture discs. The associated pipes and **support**-structure must be strong enough to absorb the potential rupture thrust force

● automated detector systems for critical process parameters

● back-up storage/liquid spill containment capacity (flexible tanks are available with capacities up to 100,000 gallons)

● a separator and a containment vessel. These would be installed in-line, after a rupture disc or relief valve

● inerting and explosion-venting of low pressure tanks used for storing flammable liquids at or above their respective flash points

● periodic acoustical-testing of critical fiberglass and metal tanks, vessels and parts

● dedicated fire-fighting, and personal protection equipment

● a multi-channel automated monitor/alarm system for leak detection, with all extremely hazardous chemical processes

● a back-up containment pressure vessel (properly-sized, larger than the primary reactor) for highly poisonous chemicals, such as phosgene or hydrogen cyanide

● positive-pressurization of (i) an on-site command center, and (ii) electrical controllers and devices in hazardous (DIVISIONS I and 2) locations

● a TFE-fluorocarbon valve seat with a valve in a high hazard system, to assure full closure of the valve

● a public communication procedure and system for emergency action, including public evacuation (on which the public must be well-informed before any accident occurs).

In using active safeguards, the design and equipment employed should be in accordance with the most recent and stringent regulations and standards. They should also meet the standards of the relevant guidance from competent authorities, such as insurers. It is noted that some consensual safety standards do not address or meet all of the needs for safety in some situations. And design should accommodate the plausible worst-case regarding self-heat, corrosion and wear, not the average cases. On the point of effective codes, safety standardization has made considerable progress in recent years. This has come from newer engineering design guidelines and process simulation with computerization. The American Institute of Chemical Engineers, the chemical safety design institutes, the American Society of Mechanical Engineers and the larger engineering companies have made major contributions in these areas.

Controlling Contributory Human Error

Many major chemical accident reports point to human error - error in operation or maintenance as the proximate cause. Accidents are often attributed to an operator's error, without due regard to the existence of other contributors, such as inadequate design or poor administration.

Controlling **all** contributory human error is important for safety. This involves such matters as:

- removing repetitive tasks from the operator's direct control. This involves automation using reliable appropriate sensors and controllers

- making a process tolerant of an operator error. For example, use maximum or minimum liquid level controllers; maximum temperature shut-offs; flow rate controllers, and (high-high/low-low) limit controllers

- simplifying vessel construction, piping, and operating features

- using valves and equipment with the better rating for use in severe chemical environments, whenever extremely hazardous substances are involved

- color-coding and labelling pipes, and labelling valves

- operating vent pipes to scrubbers under a slight negative pressure, with appropriate sensing and interlocking of critical functions, to control accidental releases (as might occur in starting up a process with an open vent valve)

- automating infrequent process-termination steps

- holding safety talks which include stressing the point that automation does not reduce the need for safety training. If anything, it makes the training of operators and maintenance personnel even more critical to safe operations.

- providing specific instruction and training to operators and maintenance personnel

- providing refresher training at least annually to operators and maintenance personnel, and first-responders - to whom standard 29 CFR 1910.120 applies

- not assuming that a trained and instructed operator will perform a task consistently and will not deviate from a standard operating procedure.

- involving operators and workers in chemical safety audits

- giving the operator control of a critical service. For example, the operator would have lock-out control of a (normally open) water-line on a process chiller.

- conducting mock exercises to assure a satisfactory response to an accidental spill, and test the (mandatory) spill prevention and counter measure plan.

Management, and Management Systems

Most managers throughout the chemical process industry are highly committed to the cause of safety and environmental protection. Many of them undergo continuing education, and participate in relevant technical meetings. However, some of the systems and practices that some managers employ do not indicate or reflect a high level of commitment.

Safety management systems, methods for assessing plans, and procedures for evaluating risks and auditing practices are an integral part of every successful management program for accident prevention. The importance that the management places on safety must be seen in the actions of the managers and staff. The general manager, the senior managers and their staffs need to be involved personally in meetings with employees, local officials, interested citizens, and local media personnel at appropriate times. The safety committee must meet at least monthly. Also, all process operations should be observed regularly to make sure that "short-cuts" have not been introduced. And managers must guard against accident risks from a decline in an operator's ability or fitness. Operators and shop stewards must appreciate this need.

ASPECTS OF PREDICTION

Hazard identification and modeling of atmospheric dispersion of extremely hazardous chemical releases underlie developing emergency prediction information. The acute health risk is determined from the acute exposure data, the kinds of end-points resulting from the exposures, and the probabilities of the exposures occurring.

Hazard Identification, and Hazard Determinants

Toxicity and physical properties are major determinants of acute health hazard. And boiling point, density and latent heat of vaporization underlie the vapor hazard from a release. Terrain and meteorology influence dispersion. Also, dispersion depends on the type of release, and the nature of the chemical itself. As an example of how a chemical property can influence dispersion, look at a denser-than-air gas release. Chlorine gas, which is about twice as dense as air, tends to follow the line of least resistance to travel, when it is undiluted. In reported cases of a major chlorine release, one frequently reads about chlorine moving down a valley.

Another example of the effect of a physical property on dispersion, is that of a liquid which has a specific heat lower that another liquid with a similar boiling point vaporizing relatively faster, with a similar heat input. On the preceding point, compare chlorine and ammonia:

CHLORINE: B.Pt: -34°C. Ht.Vap^n.: 288 kJ/kg.

AMMONIA: B.Pt: -33°C. Ht.Vap^n.: 1374 kJ/kg.

With other factors being equal, in some spill situations, ammonia will evaporate relatively slower than chlorine because of its greater heat of vaporization.

Regarding terrain and meteorology, examples of relevant effects are:

● the sun immediately heating the ground-level air, causing turbulence and enhanced dispersion

● nighttime cooling and stratification of ground-level air, causing reduced turbulence and dispersion (nighttime releases frequently pose potentially serious impacts)

● structures and obstacles, such as tall buildings in city centers and trees in urban areas, creating a degree of meteorological ground roughness which provides enhanced air turbulence and relatively greater dispersion.

Methodology Underlying Prediction Information Software

Software products are commercially available[14] for modeling air releases for acute health risk analysis. At this time, there are about 40 models available for evaluating vapor cloud dispersions (the Center for Chemical Process Safety of the American Institute of Chemical Engineers published a guideline review of such models in 1987).

Underlying the methodology used with many such models is classification and quantification of:

● the release - as a continuous release; term release; area-term release, or area-continuous release

- the atmospheric stability - in terms of wind-speed, daytime sunlight, and nighttime clouds

- the terrain: city-terrain or standard-terrain.

Deposition rates and other factors also apply.

Commercial software products are usually based on the Gaussian Plume model[15]. This model is widely accepted and it is the work-horse for emergency prediction purposes. In some instances, sophisticated versions of the model are used which can factor into the dispersion estimate the effects of complex terrain, buoyancy, and the thermodynamic factors with the chemical release. In other cases, different dispersion models which are quite complex are used. Examples of such models are those used for modeling dispersion of isotopes, prescribed in the NRC Regulatory Guide #1.111.

Figure 3 shows typical (minimal) input for a simple and very useful model for predicting emergency information, with a generally acceptable level of precision, bearing in mind the limited accuracy existing for the dose-response picture for most of the chemicals of concern.
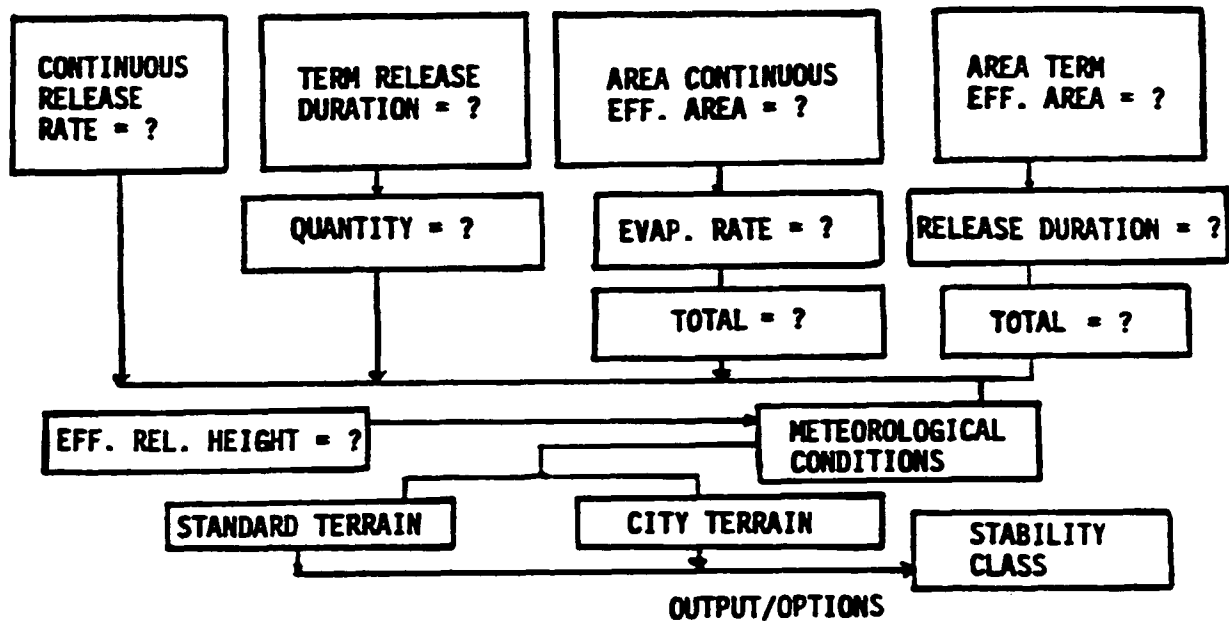
Figure 3. Input for Emergency Prediction Information

Typical Output of A Simple Model

The typical output of a simple emergency prediction information includes:

● optional monochrome or color screen display

● print-outs of concentrations at down-wind and cross-wind locations and distances (in units of miles or kilometers)

● receptor-height concentrations (in units of part per million-ppm, or milligram per cubic meter-mg/m^3)

● arrival times, in minutes or hours, of airborne concentrations distributions (plumes), downwind and cross-wind of the release.

● a summary of the program input; and

● sometimes, airborne concentrations expressed in terms of the "immediately dangerous to life or health" (IDLH) value, and/or the DOL. OSHA Permissible Exposure Limit(s) (PEL) or the ACGIH Threshold Limit Value(s) (TLV) for the chemical.

Figures 4 and 5 show the output obtained with one product[16] for a hypothetical release - a nighttime, ground-level, 5-minute release of 1000 pounds of phosgene from a ruptured tank. The wind speed is 1 mile per hour. The terrain is open level country (standard terrain). In this example, relevant concentrations are expressed in terms of: parts per million; the IDLH-value (phosgene: 2 parts per million); and the 8-hour, time weighted average, threshold limit value (0.1 part per million).
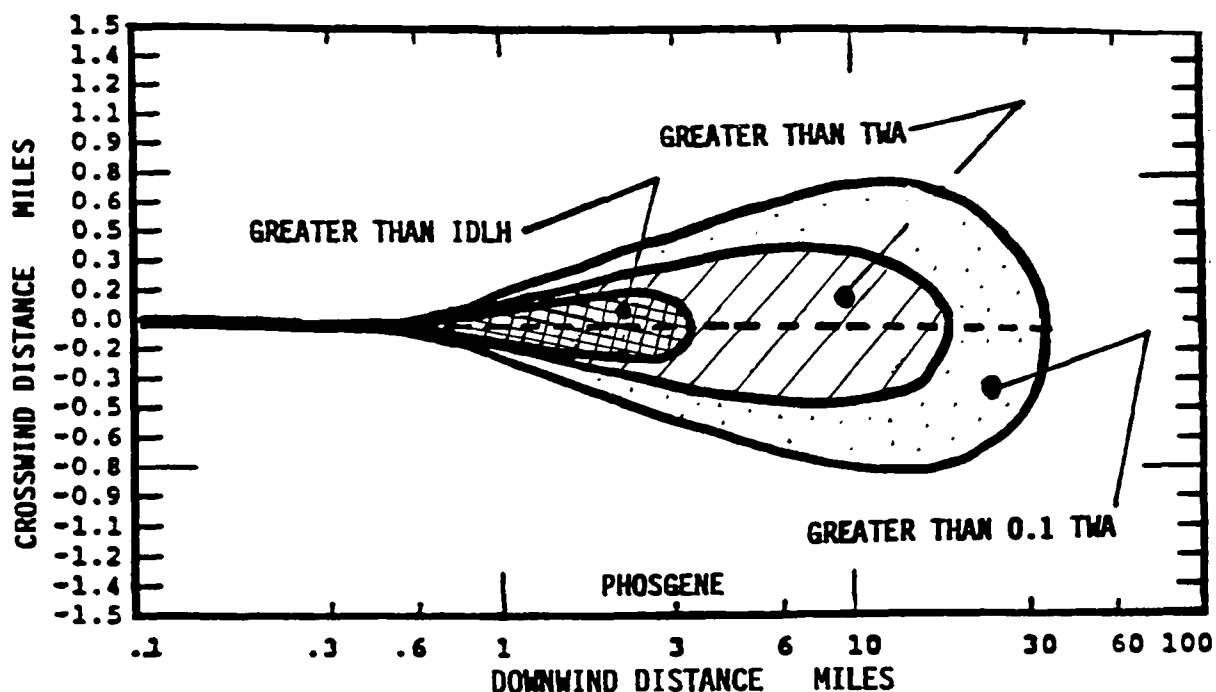

Figure 4. Down-Wind and Cross-Wind Concentrations

```
PHOSGENE      CAS Number: [75-44-5]
  TWA :    0.10 ppm   TWA :    0.40 mg/m^3
  IDLH :        2 ppm
    DOWNWIND              MAXIMUM CONCENTRATION        ARRIVAL TIME
    Distance-Mi            mg/m^3        ppm           hours:minutes
```

DOWNWIND Distance-Mi	MAXIMUM mg/m^3	CONCENTRATION ppm	ARRIVAL TIME hours:minutes
0.10	120000	30000	: 6
0.20	30000	7300	:12
0.30	13000	3200	:18
0.40	7100	1700	:24
0.50	4400	1100	:30
0.60	3000	740	:36
0.70	2200	530	:42
0.80	1600	400	:48
0.90	1300	310	:54
1.00	1000	250	1: 0
2.00	170	42	2: 0
4.00	16	3.9	4: 0
6.00	6.6	1.6	6: 0
8.00	3.4	0.83	8: 0
10.0	2.0	0.50	10: 0
20.0	0.42	0.10	20: 0

Figure 5. Arrival Times, Distances, and Concentrations

Precision of Predictive data

The predictive information obtained from current models is only approximate, but it is usually good enough to be very useful in decision-making for emergencies. With simple models, when dense gases are involved, over-prediction of airborne levels may occur because of the non-neutral buoyancy conditions. However, reportedly, for low levels below about five percent, the effect is usually minor and it conservatively influences the output. Comparative test data for establishing precision are not plentiful. A sufficient number of tests have been conducted by the federal government (in particular, the U.S. Department of Energy, in the mid-80's) and private organizations whose

reported results can be used to evaluate a simple model (which actually can be more useful in a real emergency than a less user-friendly, more sophisticated one because of a stop occurring with the use of the latter type model when data are unknown). As a general comment on precision, software vendors claim that agreement between actual and predicted data for releases of extremely hazardous chemicals is often about x3 - x5, either way. Reportedly, agreement is optimal when the region of concern is (i) outside of the immediate zone of the release, that is the area of concern is more than 250 feet away from the site of release, and (ii) lies in level, open terrain.

Specific performance and comparative test data for the commercially available products are available from the suppliers.

Using Predictive Information, and Exposure Guidelines

When emergency data and prediction information on a release have been obtained, the next step is to compare them to the known or assessed, relevant immediately dangerous to life or health (IDLH) level[17]. This is done to establish the zone of vulnerability.

In practice, the zone will be set-up using either a fractional value of one-fifth or one-tenth of the IDLH, depending of the judgment of the responsible coordinator. When an IDLH value is unknown, ten times (or somewhat greater) the threshold limit value[18] (TLV) for the chemical, if it is known, may be useful (and conservative) as an approximation of the IDLH level (others have proposed

using a x500 factor, this could be too great in some cases, in the view of the writer). The selection of such a factor requires informed judgment.

ASPECTS OF RESPONSE TO RELEASES

Despite the best of preventative planning, major chemical accidents happen, and mitigation plans must be developed beforehand. In the plan must be requirements for well-trained response personnel and appropriate equipment being immediately available, and procedures for in-plant and community communications being in place. Specific federal (OSHA and EPA) regulations apply to each one of these points.

In planning for mitigation, one needs to identify potential hazards, and evaluate potential exposures and durations of exposures. A plausible worst-case scenario is to be used when accurate information is missing. With regard to hazards, when a flammable liquid or gas is released, a fire may result within a matter of minutes when the vapor or mist concentration is above the relevant lower flammable limit (LFL) [the more familiar concern in this regard is a major accidental release of light hydrocarbons or LPG, which is to be dreaded]. Static electricity and other sources for initiating a fire must be presumed to exist in all such releases. The primary safeguard in such a case is rapid evacuation. Apart from the risk of fire, exposures involving inhalation of toxic substances and dermal uptake of such substances must be presumed to arise, unless

information to the contrary is known. Initially, in responding to a release of a toxic chemical, maximal risk is to be presumed to exist, and maximal personal protection is presumed to be needed. Thus, a self contained breathing apparatus, in the pressure demand mode, together with a fully encapsulating suit, will be used by each responder. Only after hazards have been properly assessed can any lower level of protection be employed.

Large-scale releases of many chemicals can present serious health hazards through inhalation at distances which are several miles downwind of the site of the release, even though there is no accompanying fire hazard. This could require either rapid evacuation or the public staying indoors with the windows closed, depending on the risk.

When a ground-level release of a volatile, toxic chemical occurs, the responders who are close to the release are the ones who first face imminent danger, regardless of their compass location. In the case of a ground-level release of a denser-than-air liquid, the spill can move initially against the wind direction. First-responders must be thoroughly trained and instructed in handling releases. People at the work site can be exposed within minutes of the start of the release. And the local community - people who are down-wind by several miles may become seriously exposed within the hour or thereabouts, depending on the wind speed, the magnitude of the release, and other factors. Communities farther away may be exposed to serious or non-serious conditions within a few hours. The point is that dangerous exposures can confront

employees, workers and people in the nearby communities within minutes of the start of a major chemical accident. Everyone must be instantly alerted and told what to do. They must be informed in advance what the public alarm is, and what they must do when the alarm is given (that is, evacuate, stay indoors, listen to a radio station, obey officials, et cetera). It must be realized that in some grave accidents, people who are more than ten miles from the release may experience a serious harm or a major nuisance within a few hours of the start of the release.

To safeguard people who might be affected in a major chemical accident, a contingency plan must be in place. The plan must be thoroughly understood **and** practiced by those who are required to take corrective action, and by the people who will be affected. It must cover or require, amongst other things:

- a company-fire department-citizens plan for emergency alert, evacuation, and other safety needs
- engineered containment, and provision of needed equipment, such as a pump and a flexible (instant) storage tank
- assurance of the immediate availability of trained personnel
- assurance of the immediate availability of personal protection. At least six sets of either Level A or Level B protection will be required, depending on the hazards involved
- administrative procedures to inform the public, to be in place.

Personal Protection

Personal protection for first-responders and those involved in cleanup efforts must be selected on the basis of the route of entry, and the toxicity of the chemical of concern. Protection against a chemical which poses potentially serious inhalation and dermal (including eye) hazards, such as liquid chlorine (first degree hazard), would require the use of a self-contained breathing apparatus (SCBA), and a fully encapsulating suit: Level A in U.S. EPA terminology[19]. In the case of a serious inhalation hazard only, a self-contained breathing apparatus, with suitable body covering (Level B protection) would be required.


NOTE: A distinction may be made between going into a normally safe area and undertaking a potentially hazardous activity, such as transfering hydrogen cyanide from a rail car, and entering a site wherein a release of an extremely hazardous substance has occurred, with respect to respiratory protection prcedures and equipment for use. This topic, and the requirements for a respiratory protection program are too extensive to be discussed here. Specific regulations under OSHA and EPA must be consulted, and the provisions applied, before a first response is implemented. Detailed information on respiratory protection and related matters is given in the Niosh Publication, #85.115; the OSHA standards at 29 CFR. 1910.134, and 1910.120; and the EPA standard at 40 CFR 311 - which extends application of the OSHA standard to state and local agencies.

Containment, and Suppression of Vaporization

Physical containment and reduction of vaporization of liquid are needed to mitigate a release. A concrete berm and catchments need to be constructed. Other requirements include:

● reduction of the spill surface area (to control vaporization)

● reduction of heat transfer to any pool of a liquid of low specific heat (for vaporization control). Use lightweight or thermally insulated concrete.

● provision of sunshade (for controlling temperature and pressure increases in containers, and to reduce vaporization rate)

● assurance that the floor of the containment structure does not dangerously absorb or react with the spilled material. Asphalt should not be used below a tank containing a strong oxidant

● assurance that drainage is provided for collection (via a sump), and that storm and sewer drains are not contaminated

● physical shielding of structures against wind, to reduce dispersion

● the use of reactive materials to absorb or neutralize a chemical, provided that this can be done **without** excessive, rapid energy (heat) liberation. For example, sand might be used under a hydrofluoric acid tank, for neutralization of minor spills. The stoichiometry is favorable:

$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$$
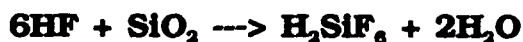
Foam For Vapor Containment and Fire Hazard Control

The vaporization rate of a pool of flammable and non-flammable liquid can be reduced in some situations using foam. Fire risks from petroleum spills are commonly controlled using foam. This basically involves keeping air away from the liquid surface.

Foam application to an outdoor pool of a toxic chemical can be effective in reducing the effects of insolation and air flow on the dispersion rate. Also, foam can be useful in some cases in controlling the movement of the associated air plume. However, the application of foam to a spill can also cause dispersion, especially when the liquid has a low specific heat, relative to the foam. Using foam to control exposures or contain a spill with an extremely toxic, highly volatile liquid is of questionable value. Using a foam for an **indoor** release of an extremely hazardous, very volatile liquid -as might occur in a laboratory accident - is not correct. Blanketing the spill with foam would make the problem worse. Foam application, collapse and reapplication would add heat to the pool, and increase the pool area. This would increase the vaporization rate and cause the indoor concentration to increase.

When foam is planned to be used in a response to a major chemical accident, consideration must be given to:

● the compatibility of the foam with the chemical

● the foam expansion factor [EF] - the volume of foam divided by the volume of water used to make the foam.

[Note foam characteristics, by EF, are:

EF=10, heavy and wet; EF=100, firm; and EF=200, light and mobile].

● the drainage of the foam (the amount of water from the collapse of a volume of foam). More water can add heat to the pool.

Most importantly, the advantages of using a foam - suppression of the concentration immediately above the pool of the spill, and reduction in the effects of insolation and wind dispersion - must be weighed against providing a heat gain to the pool being covered, thus increasing the vaporization rate.

Water Used For Dispersion or Containment

Reducing acute hazards from a release of a water-soluble, toxic liquid or a toxic chemical which readily hydrolyses, such as titanium tetrachloride, can be achieved with water. A water spray can be effective in dispersing a release of a combustible or flammable liquid, and in holding concentrations below the lower flammable limit [for most flammable liquids, this limit lies in the range of about 0.7 (7000 ppm) to about 5 percent (50,000 parts per million)].

Spraying is usually done using a high flow/fine (fog) spray nozzle. Application is made from downstream, when this can be achieved without risk. When envelopment in a cloud of a flammable vapor or a toxic chemical is likely, application is made from upstream.

Containment of a plume of a low solubility, denser-than-air vapor or gas, such as chlorine, can be effectively achieved using a water spray. Also, the movement of a toxic plume can be controlled in this way.

A water spray should not be applied to any large mass of an alkaline earth carbide or an alkali metal. In the latter cases, acetylene and hydrogen, respectively, would evolve and create a fire hazard. However, water can be sprayed on a reactive, toxic, inorganic halide, such as boron trifluoride, phosphurous trichloride, tin tetrachloride, and titanium tetrachloride, to reduce dispersion; acid vapors which are themselves toxic will of course be created.

A pool of immiscible, non-reactive liquid which is denser than water can be contained using a water blanket. This effectively controls vaporization and facilitates recovery or neutralization. Spills of carbon disulfide and liquid bromine can be handled in this manner.

Other Containment, and Control Measures

Sand, sulphate powder, granular powder, and certain polymeric powders can be used to contain spills. The underlying principle of using a solid sorbent is to reduce the liquid surface area, and, consequently, the rate of vaporization. The density of the bulk of the solid material which is to be used should be less than the density of the spilled liquid. The powder must not react violently with the liquid. It must be fine enough to provide a thick cover.

Chemical neutralization, physical barriers, the use of fans, the use of plugs and patches and ignition are other containment and control measures. These are mentioned briefly here:

● neutralization of an acid spill can be achieved using soda ash

● neutralization and solidification of some acid or caustic spills can be achieved using commercially available products

● an impervious cover placed over a volatile liquid spill can effectively reduce vaporization

● fans can be used to disperse vapors from a flammable liquid spill so that the lower flammable level is not reached. Use totally enclosed, fan cooled (TEFC) motors with the proper NFPA 30 class-division-group rating

● a plug or a patch can be used to stop a leak from a vessel (these remedies have been pioneered by the Chlorine Institute)

● a quick-setting adhesive, or magnetic clamps, with a gasket and cover arrangement can be used to contain some leaks

● ignition may be used to minimize the escape of a release of a flammable vapor or toxic gas, such as hydrogen cyanide or hydrogen sulphide. However, ignition (as distinct from high temperature incineration) is not useful for controlling a toxic gas release when its concentration is lower than its lower flammability limit, at which time the concentrations could still be potentially lethal. Also, the use of ignition is counter-indicated for chemicals whose oxidation products are toxic. For example, chlorine-containing hydrocarbons produce phosgene when they are burned in the open.

Administrative Efforts For Safety and Public Assurance

An ounce of prevention is worth a pound of cure. This is especially true in safety management. Managers need to make sure that new plant or projects involving major changes are bid to exacting safety specifications. The bidder will offer generally sound safety engineering, but some bidders do not always have all of the expertise needed for safety assurance. Also, they will offer whatever is deemed competitive.

Training and instruction of personnel needs to be ongoing. Refresher safety training in specific operations and standard safety operation procedures (SSOPs) are essential for safety. Automation is not a substitute for trained workers; equipment is only as good as the people who use it.

Responses to emergencies must usually be made within minutes to avert a catastrophe. In some situations, it is unrealistic to expect a timely response from a local organization; the distances might be too great, for example. In these situations, the only practical thing to do is to use specially trained plant personnel as first-responders. If this is undertaken, the management must assure the safety of the responders. They must comply with the relevant provisions of the OSHA Emergency Response rule, at 29 CFR Part 1910.120.

An important but uncommon aspect of risk management is the (radical?) policy of assuming certain reactors, vessels and components to be potentially unsafe, rather than safe, at a certain point (3/4 ?) in their currently expected maximal

useful life, and requiring reliability assurance from a designated manager. As an example, in the case of a reflux condenser which has operated in a chemically and physically hostile environment for, say, 12 years, one would assume it to be potentially unsafe, because of internal corrosion and stress cracks, and require it to be thoroughly examined and tested, regardless of any code test done a few years earlier.

A comprehensive (but easily read) plan for alerting the community and starting an evacuation, when necessary, must be in place and well-understood by the employees, the fire department officers, and the public. Such a plan should be developed with input from local safety officials, and neighbors.

As a parting comment, for a facility or chemical plant to be, and be seen as, a good neighbor, the plant administrators must make sure that they promptly and authentically respond to all of the concerns of the community.

N.A.B

January 7, 1990.

* * *

References and End Notes

1. Bhopal, India. 1984 methyl isocyanate released, due to water ingress, uncontrolled self-heat, and tank rupture. More than 2000 deaths initially reported.

2. Seveso, Italy. 1976 toxic gas release forced major evacuation. Long term effect of major dioxin release, major concern.

3. 1987 release of many chemicals from Sandoz company. Major contamination of the Rhine with mercury and organics. No fatalities; chronic health effects major concern.

4. A poll taken in 1986 by Roper Associates.

5. The American Institute of Chemical Engineers,the American Society of Mechanical Engineers are dominant in this area.

6. Regulations at Title 10, the Code of Federal Regulations.

7. Statement of Mr. Lee Thomas, former EPA Administrator. February 3, 1987, Washington, Int. Symposium on Preventing Major Chemical Accidents.

8. Standards and recommendations from the National Consensus standards groups and technical societies listed (5).

9. Risk analysis, for more description see ISGRA, Risk Analysis in the Process Industries, 1985 Report. Institution of Chemical Engineers, London.

10/11/13 Techniques. There is extensive descriptive material on these topics. For literature and reprints, consult the National Safety Council, Chicago, Illinois 93120, 527.4800.

12. Hazops key words: see The (1977) Guide, same topic, of the Chemical Industries Association. London, Eng.

13. The Center of Chemical Process Safety is particularly active in this area. It is group within the American Institute of Chemical Engineers.

14. Many products are offered. A review of (40) vapor cloud dispersion models is available from the Center for Chemical Process Safety -(212-705-7657). The EpiCode software from Homann Associates, Fremont, CA, and the Cameo 2 Software from the National safety Council are two easy-to-use products for Public Hygiene work.

15. The model is described in EPA Guide, OAQPS Guideline on Air Quality MODELS, EPA REPORT 450-78-028.

16. Epicode and (extensive) library. Homann Associates, 39831 San Moreno, CT. Fremont, CA 94539 (415) 490-6379.

17. IDLH is not consistently defined in the regulations of the relevant agencies. Herein, it means the concentration at which a serious harm is likely to arise within a matter of minutes with a continuing exposure. The official definition given in the Mine Safety and Health Administration Standard at 30 CFR. Part 11.3 is preferred by the writer for the purpose of response, discribed herein.

18. TLV trademark term for threshold limit values established by the American Conference of Governmental Industrial Hygienists.

19. See "EPA - OCCUPATIONAL HEALTH AND SAFETY MANUAL, #1440."

APPENDIX

EPIcode™ ALGORITHMS

COORDINATE SYSTEM

In the **EPIcode** system, we have placed the coordinate origin ($x = 0$, $y = 0$, $z = 0$) at ground level, *beneath* the point at which the chemical substance is released. The x axis is the *downwind* axis, extending horizontally with the ground in the average wind direction. The y axis is the *crosswind* axis, perpendicular to the downwind axis, also extending horizontally. The altitude axis (z axis) extends vertically. A plume travels along, or parallel to, the downwind axis. The figure below illustrates the **EPIcode** coordinate system.
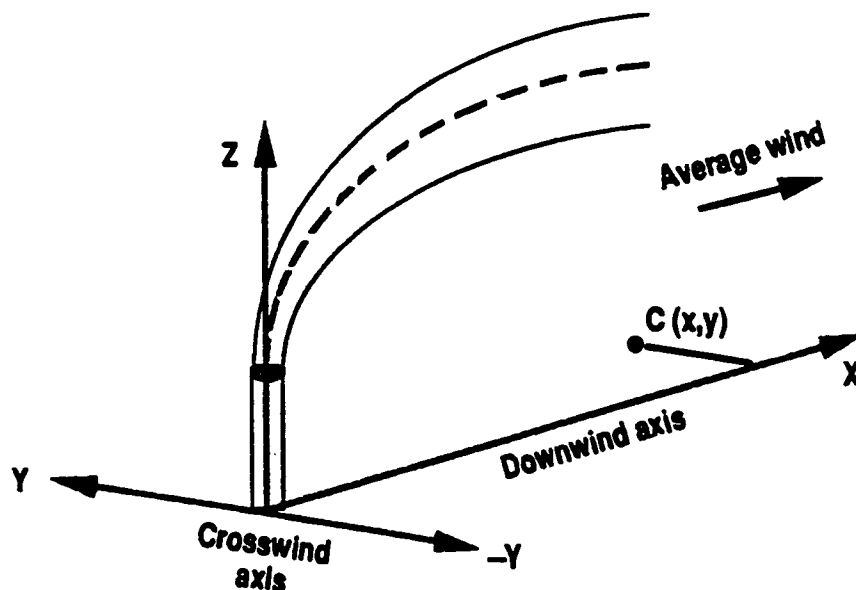
BASIC EQUATION

The origin of the Gaussian model is found in work by Sutton (1932), Pasquill (1961, 1974), and Gifford (1961, 1968). Additional background and supplemental information on the Gaussian model can be found in Turner (1969) and Hanna et al. (1982).

We use the following Gaussian model equations to determine the concentration for a gas or an aerosol (particles less than approximately 20 μm in diameter).

Continuous Phase:

$$C(x,y,z,H) = \frac{Q}{2\pi\sigma_y\sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\left\{\exp\left[-\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right] + \right.$$

$$\left. \exp\left[-\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right]\right\}$$

Puff Phase:

$$C(x,y,z,H) = \frac{Q_T}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\left\{\exp\left[-\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right] + \right.$$

$$\left. \exp\left[-\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right]\right\}$$

The "puff" equation is used for an instantaneous term release, and the "continuous" equation is used for a continuous release. For a non-instantaneous term release (e.g., 0.5 min., 120 min., etc.) **EPIcode** automatically selects the appropriate equation. This selection process is based upon the plume length (release duration × wind speed) relative to the σ_x at the specific downwind location being considered. We assume that $\sigma_x = \sigma_y$. For a term release when the plume length is less than σ_x, the plume diffusion process is more accurately characterized by the Puff equation. The Continuous equation is used whenever the plume length is greater than or equal to $2\sigma_x$. For plume lengths between σ_x and $2\sigma_x$, a combination of both equations is used.

If the Inversion Layer option is in effect, and σ_z exceeds the inversion height L, the following equations are used.

Continuous Phase, σ_z > L:

$$C(x,y,z,H) = \frac{Q}{\sqrt{2\pi}\,\sigma_y L\, u} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]$$

Puff Phase, σ_z > L:

$$C(x,y,z,H) = \frac{Q_T}{2\pi\sigma_x\sigma_y L} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]$$

where C = atmospheric concentration (ppm, mg/m³)
     Q = source term (g/s, m³/s, etc.),
       or for a term release
     Q = Q_T/release duration (g/s, etc.)
     Q_T = total release (g, m³, etc.)
     H = effective height of chemical substance release
     x = downwind distance (m)
     y = crosswind distance (m)
     z = vertical axis distance (m)
     σ_x = standard deviation of the concentration
       distribution in the downwind axis direction
       (x axis, meters) $\sigma_x = \sigma_y$.
     σ_y = standard deviation of the concentration
       distribution in the crosswind direction
       (y axis, meters)
     σ_z = standard deviation of the concentration
       distribution in the vertical direction
       (z axis, meters)
     u = average wind speed at the effective release
       height (m/s, mph)
     L = inversion layer height (m).

An upwind virtual point source, which results in an initial σ_y equal to the effective radius of the area source, is used to model an area release.

The values of σ_y and σ_z are representative of a sampling time of ten minutes. Concentrations directly downwind from a source decrease with sampling time primarily because of a larger σ_y due to increased meander of wind direction. For sampling times greater than ten minutes, and less than the total release time for term releases, the following equation can be used to predict the sampling results (Turner, 1969):

$$C_s = C\left(\frac{10}{t_s}\right)^{0.2}$$

where C_s = the concentration averaged over t_s minutes.

For example, you run an air sampler for one hour (60 min) at a particular downwind location. The EPIcode estimate at this location is 25 mg/m^3. However, the one-hour average concentration expected from the previous equation is:

$$C_s = 25\,\text{mg/m}^3\left(\frac{10\,\text{min}}{60\,\text{min}}\right)^{0.2} = 17\,\text{mg/m}^3$$

EFFECTIVE RELEASE HEIGHT

The actual plume height may not be the physical release height, e.g., the stack height. Plume rise can occur because of the velocity of a stack emission, and the temperature differential between the stack effluent and the surrounding air. The rise of the plume results in an increase in the release height, as shown in the figure at the top of the next page.

This effective increase in release height leads to lower concentrations at the ground level. If you are not able to visually estimate or calculate the effective release height, we recommend you use the actual physical release height (i.e., the height of the stack)—or use zero height for a ground-level release. This will always yield conservative estimates.
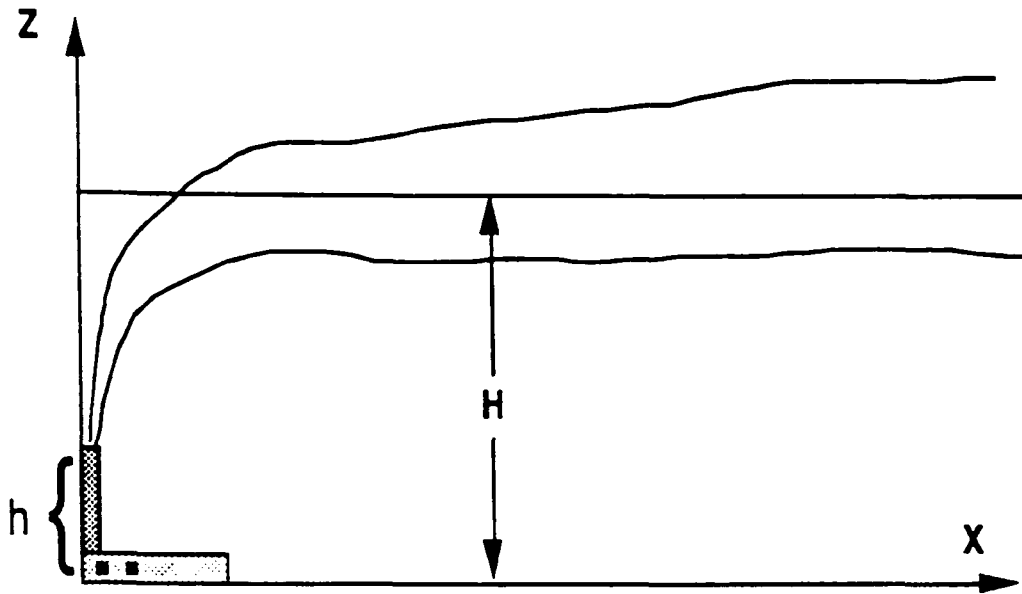
If the release is from a stack, and you know additional information on the stack discharge velocity, temperature, and stack diameter (i.e., if you are designing a new stack for a building), **EPI**code can automatically calculate the effective release height. This can also be applied to an area release if the effective release radius is less than fifty meters.

Select Calculate PLUME RISE by typing PR from the release height prompt. **EPI**code calculates both the momentum plume rise (Briggs, 1969) and the buoyant plume rise (Briggs, 1975) and chooses the greater of the two results. The recommended methodologies in the above two references are strictly followed.

STABILITY CLASSIFICATION

Meteorologists distinguish several states of the atmospheric surface layer: unstable, neutral, and stable. These categories refer to how a parcel of air would react when it is displaced adiabatically in the vertical direction. The **EPI**code model offers two ways to select the atmospheric stability category.

For users who are not familiar with the different stability classifications commonly used in meteorology, EPIcode will select the appropriate stability classification with informa- tion you provide from direct observations. Or, a user can directly select and force a particular stability classification.

The simplified method requires selection of the solar insola- tion factor and ground wind speed (at a 2 meter height). EPIcode then automatically determines the atmospheric stability category from the matrix given in Table 1. This table contains criteria for the six stability classes, which are based on five categories of surface wind speeds and four categories of solar insolation. This scheme is widely used in meteorology and is accepted for stability class estimation.

Table 1. Meteorological conditions used to define the Atmospheric Stability Categories, A-F, used in EPIcode.

	Sun conditions		
Ground wind speed (m/s)	High in sky	Low in sky or cloudy	Nighttime
<2	A	B	F
2-3	A	C	E
3-4	B	C	D
4-6	C	D	D
>6	C	D	D

Pasquill Stability Types:
   A: Extremely Unstable   D: Neutral
   B: Moderately Unstable   E:Slightly Stable
   C: Slightly Unstable   F: Moderately Stable

The user may also select the stability class, A-F, directly from the table. In addition to these six stability classes, EPIcode also allows you to enter W for the worst-case scenario. If W is selected, EPIcode uses *all* stability classes to determine the downwind concentration, then chooses only the class resulting in the highest contaminant concen- tration for the particular ground-level location. For

documentation purposes the displayed output indicates which stability class gave rise to the worst case at each downwind location.

DETERMINATION OF σ_y AND σ_z

The standard deviations of the crosswind and vertical concentrations from the basic equation are σ_y and σ_z, respectively.

Once the atmospheric stability category has been determined, EPIcode uses the equations given in Table 2 to estimate σ_y and σ_z for two terrain types—Standard and City. The City terrain factor accounts for the increased plume dispersion from crowded structures and the heat retention characteristics of urban surfaces, such as asphalt and concrete. The City terrain factor will estimate lower concentrations than the Standard factor, due to the increased dispersion from large urban structures and materials. Choosing Standard terrain will give the most conservative estimates.

Table 2. Equations used to determine σ_y and σ_z. This methodology is derived from Briggs, 1973.

Pasquill type	σ_y (m)	σ_z (m)
	Open Country	
A	$0.22x(1 + 0.0001x)^{-1/2}$	$0.20x$
B	$0.16x(1 + 0.0001x)^{-1/2}$	$0.12x$
C	$0.11x(1 + 0.0001x)^{-1/2}$	$0.08x(1 + 0.0002x)^{-1/2}$
D	$0.08x(1 + 0.0001x)^{-1/2}$	$0.06x(1 + 0.0015x)^{-1/2}$
E	$0.06x(1 + 0.0001x)^{-1/2}$	$0.03x(1 + 0.0003x)^{-1}$
F	$0.04x(1 + 0.0001x)^{-1/2}$	$0.016x(1 + 0.0003x)^{-1}$
	City	
A-B	$0.32x(1 + 0.0004x)^{-1/2}$	$0.24x(1 + 0.001x)^{1/2}$
C	$0.22x(1 + 0.0004x)^{-1/2}$	$0.20x$
D	$0.16x(1 + 0.0004x)^{-1/2}$	$0.14x(1 + 0.0003x)^{-1/2}$
E-F	$0.11x(1 + 0.0004x)^{-1/2}$	$0.08x(1 + 0.00015x)^{-1/2}$

x = downwind distance, m

For brief (puff) releases of less than ten minutes, the experimental data indicate that that σ_y and σ_z are smaller by about a factor of two (Slade, 1968). **EPIcode** automatically uses the following algorithms to determine the short-term standard deviations, σ_y' and σ_z'. These values replace the σ_y and σ_z in the basic Gaussian equation.

The new σ_y' and σ_z' are a factor of two smaller than σ_y and σ_z for release durations less than or equal to one minute. For durations between one and ten minutes, the factor is linearly interpolated, as shown below.

Release Duration, t

(min)	σ_y'	σ_z'
t > 10	σ_y	σ_z
1 ≤ t ≤ 10	$\sigma_y/(-0.11t + 2.11)$	$\sigma_z/(-0.11t + 2.11)$
t < 1	$\sigma_y/2$	$\sigma_z/2$

In a term release and for plume travel times [distance/u(H)] longer than 10,000 seconds, the "continuous" plume σs are more characteristic of the observed diffusion process. For long plume travel times, only continuous-plume σs are used. The transition between puff and continuous σs begins at plume travel times of 1000 seconds and is complete by 10,000 seconds.

Wind Speed Variation with Height

The wind speed a user inputs to **EPIcode** is the estimate for a height of two meters. However, the Gaussian plume equation requires the wind speed at height H, the effective release height. **EPIcode** automatically uses the following power-law formula to determine the wind speed for all effective heights greater than two meters.

$$u(H) = u(2)\left[\frac{H}{2}\right]^P$$

where u(2) = surface wind speed (m/s) at 2 meters height.
       H = effective release height (m).
       P = factor from Table 3.

Table 3. Exponential factor used by EPIcode for calculating wind speed variation with height (from Irwin (1979).

	Stability Class					
	A	B	C	D	E	F
City	0.15	0.15	0.20	0.25	0.40	0.60
Standard terrain	0.07	0.07	0.10	0.15	0.35	0.55

PLUME DEPLETION

Very small particles and gases or vapors are deposited on surfaces as a result of turbulent diffusion and Brownian motion. Chemical reactions, impaction, and other biological, chemical, and physical processes combine to keep the released substance at ground level. As this material deposits on the ground, the plume above becomes depleted. EPIcode uses a source-depletion algorithm to adjust the air concentration in the plume to account for this removal of material.

The source term in EPIcode is allowed to decrease with downwind distance. The code accomplishes this by multiplying the original source term by a source-depletion factor, DF(x). The evaluation of this depletion factor has been described by Van der Hoven (in Slade, 1968).

The equation used in EPIcode is:

$$DF(x) = \left[\exp \int_0^x \frac{1}{\sigma_z(x) \exp\left[\frac{1}{2}\left(\frac{H}{\sigma_z(x)}\right)^2\right]} \, dx \right]^{-\frac{v}{u}\sqrt{\frac{2}{\pi}}}$$

where:

DF(x)   =   Depletion factor.

x   =   Downwind distance.

v   =   Deposition velocity. The deposition velocity
is empirically defined as the ratio of the ob-
served deposition rate (e.g., $mg/m^2 \cdot s$) and
the observed air concentration near the
ground surface (e.g., mg/m^3).

u   =   Average ground level (2 m) wind speed.

H   =   Effective release height of chemical.

σ_z (x)   =   Standard deviation of the air concentration
distribution in the vertical direction (z axis)
for either Standard or City terrain, as
applicable.

The default values for the deposition velocities used in
EPIcode are:

Physical form of substance	v (cm/s)
Solid	1
Gas/vapor	0.1
Unknown	0.1

These default values can be changed by the user if more
applicable information is available (e.g., increased deposi-
tion due to chemical reactivity, etc.).

ACCURACY

The many uncertainties associated with the variables in the Gaussian model, such as fluctuations in the meteorological conditions, or type of terrain, result in a degree of imprecision in the calculated ground level concentrations. If inappropriate meteorological data, source term assumptions, effective stack height, etc., are input into the program, large errors are possible in the **EPI**code estimates. Given accurate input assumptions, the standard deviation of the ground concentration as calculated by **EPI**code is thought to be approximately a factor of five. In other words, 68% of the time (i.e., the percentage of observations within ±1 standard deviation, assuming a Gaussian distribution) the calculated ground-level concentration will be within a factor of 5.

Other percentages can be inferred from the Gaussian distribution. If C is the calculated ground-level concentration, this means that 50% of the time the true concentration should lie between C/3 and 3C; and 80% of the time between C/8 and 8C. For example, if the calculated value were 300 ppm, at least half of the time you would expect the true value to lie between 100 ppm and 900 ppm.