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DECISION MAKING IN HAZARDOUS MATERIALS TRANSPORTATION*

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Summary

There are presently countless methods of risk analysis/risk assessment to make effective judgments of the safety of the movement of particular cargoes. Two tools to determine the hazard presented by a large quantity of hazardous materials are the "Equivalent Safety Concept" developed by Danahy and Gathy and the "Population Vulnerability Model" developed by Enviro Control, Inc. The Equivalent Safety Concept is a noncomputer technique that develops indexes for cargo hazard, for vessel design, and port safety. These are used to assist in a judgmental decision of authorization of vessel transit. The Population Vulnerability Model is a computer simulation of a cargo spill integrated with census data. The damage to life and property are calculated using the census data and the cargo properties to determine the number of deaths and injuries to personnel and dollar loss from the cargo release. The results and relative hazards calculated using these techniques are compared and analyzed.

Introduction

Safe movement of hazardous commodities by the marine mode is not a local problem but an international problem which impacts on every nation. National administrations have the responsibility of protecting their ports and waterways, and are interested in comprehensive, yet practical tools to be used for decision making concerning vessel and cargo movement.

The transportation and movement of hazardous materials are not possible without exposing the public at large to a certain degree of risk which is determined by the properties of the commodity and the method of its carriage. To minimize this risk, governments have created regulatory bodies charged with the responsibility of ensuring that cargo movement is performed in a safe manner. To accomplish this, each regulatory body must perform certain

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evaluations. Currently these are entirely judgmental. Decision makers develop requirements including such features as cargo containment system design, cargo segregation, allowable traffic routes, transit times, and in certain cases, prohibition against movement of the commodity.

Unfortunately, two individuals with access to the same information may develop widely varying requirements, and this is demonstrated by comparing the requirements imposed by different administrations for carriage of the same commodity. The recent work completed at IMCO in the development of the Chemical Code, the Liquefied Gas Code, and the Carriage of Dangerous Goods Code has done much to standardize the treatment given to various commodities. Many of the IMCO regulations, however, still remain based on judgment.

In theory all administrations should determine minimum requirements for moving hazardous materials safely. Any decisions reached are based on many factors, the primary ones being the port and its specific characteristics; the vessel, its design, size, maneuverability, and personnel; and the products being transported. The Coast Guard is the United States' primary maritime transportation regulatory agency and as such is responsible for ensuring safe operations in water transportation of hazardous materials.

In Title I of the Ports and Waterways Safety Act of 1972 the Coast Guard is charged as follows :

> "... In determining the need for, and the substances of any rule or regulation or the exercise of other authority hereunder the Secretary shall, among other things, consider —
> (1) the scope and degree of the hazards ..."

Historically the Coast Guard has performed the required evaluations by considering the many factors relating to the hazards of products. In many cases it was an intuitive feeling following the pattern: "I know chlorine is hazardous, so extra precautions are needed". The decisions were generally reasonable and defendable, but as new products with widely varying hazards were being moved, a more refined system of balancing requirements to product hazard was needed.

An increasingly popular tool is risk analysis. Risk analysis is a method of quantifying the likelihood and extent of damage presented by an activity. It not only involves the estimation of the expected loss over the course of a time period, but also has the objective of preparing a loss spectrum with appropriate probabilities. A method of risk determination which has been proposed for directly determining whether a ship may or may not enter a port is the Equivalent Safety Concept (ESC). The concept inherent in the ESC is not, in a sense, novel. The U.S. Coast Guard Captain of the Port (COTP) performs such an evaluation, either implicitly or explicitly, in his day-to-day performance of duty. All that the ESC does is to provide a systematic framework for the COTP within which to perform these evaluations. A more involved technique which is being developed under contract for the Coast Guard is the Population

Vulnerability Model (PVM). It is being developed as a step on the way to producing a complete risk analysis system to achieve a capability for evaluating the cost to society for a given cargo release. While both the PVM and ESC are useful by themselves, they are, in a long-term view, merely steps along the way in the development of a complete risk analysis system.

As risk tools develop, the Coast Guard will be better able to make judgmental decisions to prevent or minimize the effects of cargo releases. For example, Vessel Traffic Systems (VTS) are designed to prevent collisions in crowded waterways, similar to Air Traffic Control Systems controlling aircraft at airports. A risk analysis technique can be useful in making such decisions as to where an expensive VTS should be located. If a new facility to handle an especially hazardous product is to be located in a particular COTP's area of responsibility, he must determine what special restrictions should be imposed on the facility, on vessels carrying the product, and on other traffic near the facility. Both the PVM and ESC have the potential of quantitatively or semiquantitatively predicting the change in safety produced by a specific COTP requirement. The PVM and the ESC are both in a developmental stage.

Equivalent Safety Concept

The Equivalent Safety Concept (ESC) [1] was developed by Danahy and Gathy as a tool for decision making by Coast Guard personnel. It is used to determine the relative risks and hazards associated with vessels carrying hazardous materials in waterways under Coast Guard jurisdiction. The ESC assigns a hazard rating to the cargoes being shipped, the Cargo Index (CI), based on the physical, chemical, and toxicological properties of the commodity. Similarly, a rating of relative safety is determined for the vessel transporting the cargo, the Vessel Index (VI). The VI is based on the physical characteristics of the vessel; the safer the vessel, for example, more maneuverability, double skins, or smaller cargo tanks, the higher is the Vessel Index. By dividing the Vessel Index by the Cargo Index, a Transportation Index (TI) can be established. The lower the Transportation Index the greater is the hazard presented to the people and structures adjacent to the waterway.

In a similar manner a Port Safety Index (PSI) can be established for each port. The PSI varies as a result of changing conditions in the port, including traffic density, weather conditions, channel bends, and traffic crossings. By comparing the Transportation Index with the Port Safety Index the local authorities are in a position to make a quantitative judgment on the relative hazard of a particular vessel movement and therefore whether it should be permitted.

The Cargo Index (CI) is a quasi-scientific method for determining the relative hazard of any cargo to be transported; the higher the numerical value the greater is the relative hazard. The value is determined by the cargo's physical, chemical, and toxicological properties. The formula presented by Danahy et al. is:

$$\mathrm{CI} = 10\,K_1\left[\left(\frac{\rho_{\mathrm{vapor}}}{\rho_{\mathrm{air}}}\right)\left(\frac{T_{\mathrm{amb}}}{T_{\mathrm{BP}}}\right)\left(\frac{1}{\mathrm{TLV}}\right)\right]^{1/2} \quad \text{(toxic cargoes)}$$

$$\mathrm{CI} = \frac{K_1K_2}{2}\left[\left(\frac{\mathrm{UFL}-\mathrm{LFL}}{\mathrm{LFL}}\right)\left(\frac{\rho_{\mathrm{vapor}}}{\rho_{\mathrm{air}}}\right)\left(\frac{T_{\mathrm{amb}}}{T_{\mathrm{BP}}}\right)\right]^{1/2} \quad \text{(flammable cargoes)}$$

where $K_1 = 3\,(1 - \exp(-P_{\mathrm{V}}/90))$; $K_2 = 0.1\,(10 + \exp(300/T_{\mathrm{AI}}))$; P_{V} = vapor pressure at 300K (kPa); $\rho_{\mathrm{vapor}}/\rho_{\mathrm{air}}$ = specific gravity of vapor relative to air; T_{AI} = auto-ignition temperature (°C); T_{amb} = ambient temperature, arbitrarily set at 280 K; T_{BP} = boiling point of product (K); TLV = Threshold Limit Value in parts per million by volume, as established by the American Conference of Governmental and Industrial Hygienists; UFL = Upper Flammable Limit (vol. %); and LFL = Lower Flammable Limit (vol. %).

Using these formulae, a determination of the hazard presented by various cargoes can be calculated. For those chemicals that are both flammable and toxic, two CI's are prepared, and the higher one only is used in the ESC. Table 1 summarizes the relative hazard ratings of several chemicals.

TABLE 1

ESC relative hazard ratings, CI

Commodity	Basic hazard (Toxic or Flammable)	CI
Phosgene	T	150.0
Chlorine	T	51.0
Acrolein	T	42.6
Hydrogen chloride	T	19.7
Allyl chloride	T	18.2
Ethyleneimine	T	16.7
Ethylene oxide	F	12.7
Methyl bromide	T	12.55
Carbon disulfide	F	11.4
Dimethylamine	T	10.9
Hydrogen fluoride	T	10.2
Ethyl ether	F	7.95
Acetaldehyde	F	6.2
Ethylene	F	5.63
Ammonia (anhydrous)	T	4.96
Vinyl chloride	F	4.6
Butadiene	F	4.5
Propylene	F	4.4
Methyl chloride	T	4.24
Butane	F	4.0
Propane	F	3.74
Carbon tetrachloride	T	3.37
Methane	F	2.69
Benzene	T	2.08
Acrylonitrile	T	1.3

The Vessel Index (VI) is a calculation of the relative ability of a vessel to contain the cargo and minimize or avoid damage. It was developed by identifying and grouping vessel characteristics considered to have an important influence on vessel safety such that:

$$\text{VI} = K\left(\frac{F_1}{F_2 F_3}\right)$$

K is a scaling constant for relating the Indexes. F_1 is the grouping of variables contributing to resisting the release of cargo in the event of an accident. F_2 represents the potential for damage if cargo is released. F_3 is the grouping of variables influencing the likelihood of causing an accident.

The determination of these parameters is still in the developmental stage; however, as an initial estimation the following relationships were recommended by Danahy et al. :

$$F_1 = f_\text{B} + f_\text{L} + f_\text{P} + f_\text{T} + f_\text{S}$$

where f_B = double bottom = 2; f_L = center tank location = 3; f_P = pressure vessel tank = 1.5; f_T = tank strength = MAWP/P_V; and f_S = vessel stability (Type I = 5, Type II = 2).

$$F_2 = f_\text{C} = \text{capacity factor} = \left[\frac{\Delta c}{s} + \Delta t\right]^{2/3} /100$$

where Δc = total cargo capacity (m^3); s = number of cargo tanks; and Δt = largest cargo tank capacity (m^3).

$$F_3 = f_\text{R} + f_\text{LB} + f_\text{E} + f_\text{N} - f_\text{A}$$

where f_R = turning factor = $\sqrt{\text{length (m)}/100}$; f_LB = lead barge factor = 2; f_E= exposed barge factor = 1; f_N = tow size factor = $\sqrt{\text{number of barges}}$; and f_A = acceleration factor = $\sqrt{10\ \text{SHP/vessel displacement (tons)}}$;

The vessel index is not a fixed number but varies with the location of cargo stowage and quantity of hazardous cargo on board. By varying these parameters the vessel owner could establish the VI for the vessel to increase or decrease it as necessary.

The Port Safety Index (PSI) is calculated by considering two sets of influencing variables. Those characteristics of the port and waterway which contribute to the occurrence of a marine accident are considered in the determination of the first set. The second set is composed of those characteristics on the shore which indicate the degree of damage expected for an assumed release of cargo. The calculation is performed using the following equations:

$$\text{PSI} = TS_1S_2 \times 10^{-5}$$

$$S_1 = \left\{3\left[\frac{1}{V} + \frac{100}{W} + \frac{500}{R} + \frac{10}{d} + \frac{n^3}{3} + \frac{V_\text{k}^2}{15}\sin\theta\right]\right\}^{1/2}$$

$$S_2 = \left[\frac{4P_1 + 2P_2 + P_3 + P_4}{2000}\right] + A + C$$

where V = unobstructed line of sight (m); W = channel width (m); R = channel radius of turn (m); d = distance from side of channel to solid obstruction (m); n = number of channel junctions and river crossings; V_k = maximum water current (knots); θ = angle of current measured from channel axis; T = traffic density (tonne/month); P_1, P_2, P_3 = population densities (fixed) (people/km^2) measured at different distances from the waterway; P_4 = population density (mobile) (vehicles/km^2); A = public/commercial activities within 3 km (people/km^2); and C = industrial activities within 3 km (people/km^2).

By dividing the Vessel Index by the Cargo Index a quantification of the overall hazard presented by the ship and its cargo is developed.

TI = VI/CI

This overall quantity is called the Transportation Index, TI. By comparing the TI to the PSI a decision can be made concerning the need for additional control on the cargo movement. If the TI is greater than the PSI the cargo movement can be considered relatively safe and the vessel movement can proceed without special considerations. However, if the TI approaches or is less than the PSI, additional controls and close attention to the vessel movement are necessary. Some controls to be considered include Coast Guard escort, commercial tug escort, safety zone demarcation, and one way traffic.

In sum, the Equivalent Safety Concept is a tool for evaluation of transportation risk in an easily usable form.

Population Vulnerability Model

The Population Vulnerability Model (PVM) [2,3] is a computerized risk analysis tool being developed for the Coast Guard by Enviro Control, Inc. It is not intended as an emergency response tool but as a planning tool. This tool not only calculates the travel of the released cargo and chemical reactions of a cargo spill, but it also calculates the effect the spilled products have on the surrounding population and property.

The process is divided into two phases, cargo spill analysis followed by the damage assessment analysis. First, in Phase I, the PVM analyzes the physical material; the products of reactions, if chemical reaction occurs; the thermal radiation levels, if combustion occurs; and the overpressures, if detonation occurs. This analysis is almost completely independent of spill site location and geometry. This computerized calculation follows closely the methodology developed for the Chemical Hazards Response Information System (CHRIS) and the Hazards Assessment Computer System (HACS), both of which were designed as emergency response tools. HACS is essentially a computerized CHRIS, and many of the PVM models are, with major or minor modifications, HACS models; some PVM models are entirely new.

Each spill analysis is composed of one or more models covering one step of a spill sequence. For example, for Liquefied Petroleum Gas spills from a ship's tank, one model computes the release rate, another the pool spread and evaporation rates, and yet another the vapor dispersion. These models are run sequentially with the output from one automatically becoming the input for the next. If at some time the vapor cloud is ignited, the cloud flash fire model is used; if the pool is ignited, the pool fire model is used. Finally, for chemicals known to undergo unconfined vapor phase detonations a detonation model is available. The user identifies the models to be used and physical data pertaining to the spill such as wind, tank size, shape, and location of tank penetration.

In Phase II, the effects on population and property are calculated. The resources at risk are taken from United States Census data and are presented in the form of census tracts; resources are assumed uniform throughout the census tract, and are represented as population data and property value data. People are harmed by toxic gases, by cloud and pool burning thermal radiation, and by overpressure, impact, and fragmentation from vapor cloud detonation. Structures are harmed by ignition, through thermal radiation from pool burning and vapor burning, as well as from the blast wave generated by vapor cloud detonation.

To determine the effects on people and structures probits were developed. These probits are statistical relationships for toxic, blast, and thermal radiation effects, relating the percentage of the resource affected to the level and duration of the damage mode involved. Appendix I describes the preparation and use of toxic probits. No allowance is made for the response of the population such as seeking shelter from a pool fire or the evacuation from an area threatened by a toxic gas cloud. To the extent that the population does respond to an accident, the number of casualties is overestimated by the PVM. This is compensated to some degree by the fact that no distinction is made between the high risk population (young, old, and infirm) and the normal risk population. The computer techniques used in the PVM performs calculations at intervals of two minutes of simulated time unless otherwise specified by the user. For each time interval the computer performs a Phase I analysis for the quantity and location of the released cargo, and the effects of the fire or detonation, if any. The computer calculates the vapor concentration, thermal radiation, or blast overpressure at the center of each census tract. When Phase I is entirely complete, Phase II of the PVM calculates the deaths, injuries, irritations, and property damage for each cell for each time interval. This completes a simulation.

Although the PVM is a numerical tool, and it appears very quantitative, there are still many judgmental factors. Judgment is involved in designing the accident scenarios and judgment is involved in interpreting the numerical results. Finally, whether the numerical losses mandate certain restrictions does require judgment on the part of the decision maker.

PVM test series

As a test of the capabilities of the PVM a series of simulations was run using anhydrous ammonia (NH_3), chlorine (Cl_2), hydrogen chloride (HCl), hydrogen fluoride (HF), Liquefied Natural Gas (LNG), and methyl bromide (CH_3Br). In order to have a common basis on which to compare results, only toxicity was considered for this series. By ignoring fire as a damage mode, the hazard of LNG, and to a lesser extent, that of NH_3, was reduced (Table 2).

Information about population distribution was taken from census data for an inland river port. A tank barge with a 300 ton cylindrical tank containing a refrigerated, liquefied gas at atmospheric pressure, was postulated as being moored at one bank of the river. A moderate wind was assumed to exist in a direction that would produce vapor cloud travel over several census tracts. A circular opening 5 cm in diameter was postulated below the liquid level in the tank. The spill duration for this series was arbitrarily chosen to be 30 min (with one exception) and with 2-min time intervals.

These results illustrate the weaknesses and strengths of the PVM. Clearly, there is a definite ordering of degree of damage from releases of these cargoes. Since LNG is virtually non-toxic (it is usually considered a simple suffocant), the fact that the PVM calculates neither injuries nor fatalities from toxic effects is reasonable. Similarly, since NH_3 is not as toxic as the remaining chemicals, the relatively few predicted fatalities are reasonable. As discussed in Appendix I, NH_3 has little potential for permanent injury. The large casualties predicted for HCl, HF, and Cl_2 appear to be more reasonable. Unfortunately all results from CH_3Br are incorrect due to an improperly prepared set of toxicity probits.

TABLE 2

PVM calculations*

Chemical	Predicted fatalties			Injuries		
	Sheltered	Unsheltered	Total	Sheltered	Unsheltered	Total
NH_3	54	173	227	0	0	0
Cl_2	10,686	13,416	24,102	327	2033	2360
Cl_2**	46,686	47,740	94,726	0	6576	6576
HCl	26,057	26,057	52,104	0	0	0
HF	26,026	26,051	52,077	1999	6554	8553
LNG	0	0	0	0	0	0
CH_3Br	27,928	30,407	58,335	0	0	0

*It must be emphasized that the test runs done with the Population Vulnerability Model assume a release. In actual practice safety requirements specified for the cargo containment system, the vessel, and the vessel transit are developed to preclude the possibility of such a release. This is done by requiring adherence to the applicable codes and by specifying such additional requirements as are necessary in the judgment of the Coast Guard and the local Coast Guard Captain of the Port.

**This run was for a simulated duration of 158 min rather than 30 min.

The number of casualties is strongly dependent on an a priori user supplied datum, the simulation duration. Note that the results for Cl_2 increase greatly when the duration increased from 30 min (the duration for all other cargoes) to 158 min. Examination of the concentration results indicates that the cloud continues to be hazardous as it travels downwind even at the 158-min mark. There is no capability within the PVM for determining a cut-off time during the calculation process; this cut-off time must be inputted a priori. Planned modifications to the PVM include a simulation duration-independent system for continuous spills. For instantaneous spills, or for spills with rapidly fluctuating release rates, a cut-off time will still be required. Since all vapor concentrations are calculated before the effects on population and property are calculated, any termination routine based on the damages to vulnerable resources will be difficult if not impossible to implement. Currently, therefore, the user must be aware of the possibility he may underestimate the danger from a release if the simulation is terminated too quickly.

The model used for determining downwind concentrations was adapted from classical air dispersion models. This model, which is widely accepted for air pollution predictions, does not include provisions for accounting for vapor density. In typical air pollution studies this may be of relatively minor importance because of the low concentrations; however, in case of a major spill the effects of vapor density become more pronounced and need to be taken into account.

Furthermore, there are some uncertainties as to the reasonableness of the rankings between HF, HCl, and Cl_2. Note that Cl_2 spill is less serious than the HCl or HF while most indications are that Cl_2 is more hazardous. To the best of our knowledge, the toxicity probits for these three chemicals are correct with the 50% lethality concentration for a 15-min exposure for Cl_2 being much lower than those for HCl and HF. Intuitively this should result in more predicted fatalities for Cl_2. Also, the vapor pressure and vapor density of HF are much lower than for Cl_2; because of this we would expect the losses from HCl and HF releases to be significantly less than a chlorine release.

Finally, the toxicity probits and the physical properties for HCl and HF fatalities are different, yet the simulations give nearly equal results. In the ESC the physical and toxicological properties of a cargo interact in a straightforward manner but for the PVM these properties interact in a very complex manner. These apparent discrepancies in the rankings may be either superficial or significant; more study of these results and 120 more simulations are planned. For the moment, the advantages in using the simpler ESC are clear.

Ammonia accident

The United States has been fortunate in having few accidents in the water mode involving hazardous materials; it is said that no "innocent bystanders" have been killed in such accidents, although, unfortunately, some crewmembers and shoreside employees have. In 1977, at a small terminal on the Ohio River, there was a spill of anhydrous ammonia. This incident involved a barge carrying anhydrous ammonia liquefied under pressure. While offloading NH_3, a slit-like tear developed in a five-inch cargo hose. Approximately 32.6 m^3 of ammonia were released over a 42-min period.

Fortunately no fatalities were recorded but 33 people were hospitalized for varying periods of time. This situation was simulated to compare the simulation's results with the actual event. Of course this is only a partial test of the PVM but, due to the paucity of accidents, it is the best of those available.

To model this spill, data were taken from Coast Guard reports, including wind direction, wind speed, and weather condition. Due to the complexities of calculating flow through a torn cargo hose at a pressure of about 700 kPa, the release rate was assumed to be constant at about 0.78 m^3/min, permitting the "Venting Rate Model" to be bypassed. The average release rate is directly used in the model entitled "Simultaneous Spreading and Evaporation of a Cryogen on Water". The ability to bypass a model whose output is already known is a useful feature of the PVM; not only is it a significant savings in time and effort possible, but inaccuracies resulting from the execution of a superfluous model are avoided.

The vulnerable resources for use in the Phase II analysis simulating this spill were drawn from 1970 census data for the area in question. Due to the low population density the census tracts are larger in area than those used in the simulation series discussed earlier. These larger census tracts result in a coarser grid. However, the census data were not altered.

The PVM simulation estimated that 2,838 people were temporarily irritated and that there were no permanent injuries or fatal casualties. The lack of fatalities is in agreement with the accident, but the number of people experiencing irritation may appear high. Actually, the term temporary irritation refers to all types of non-permanent injuries. Undoubtedly many people not hospitalized were irritated, but only those that were hospitalized were reported. Finally, the prediction that there were no permanent injuries is due solely to the fact that, as discussed in Appendix I, permanent injuries are uncommon with ammonia.

The results of this simulation demonstrates that the PVM overestimates the harm done by such spills but is usable for hazard estimation. Many more tests are necessary before one can say that the PVM makes accurate predictions. Further simulations will be run as data from accidents become available. As is well known, detailed information about accidents is difficult to obtain.

ESC model refinements

Professor Peter J.F. Griffiths at the University of Wales Institute of Science and Technology has been involved in a hazardous cargo assessment project of Grangemouth, a port on the River Forth in Scotland. Beginning with the Cargo Index developed by Danahy et al., they have revised it to:

$$\mathrm{CI} = K_\mathrm{V} I_\mathrm{A} \left[\rho_\mathrm{V} \left(\frac{\mathrm{UFL} - \mathrm{LFL}}{\mathrm{LFL}}\right)\right]^{1/2} \quad \text{(flammable cargoes)}$$

and

$$\mathrm{CI} = \frac{K_\mathrm{V}}{\mathrm{TLV}} [\rho_\mathrm{V}]^{1/2} \quad \text{(toxic cargo)}$$

in which

$$K_\mathrm{V} = 1 - [1 - \exp(-P_\mathrm{V}/100)]$$

and

$$I_\mathrm{A} = \exp(100/T_\mathrm{AI})$$

where K_V = vaporization factor; ρ_V = vapor density relative to air; I_A = autoignition factor; TLV = Threshold Limit Value (ppm); P_V = vapor pressure (kPa); and T_AI = autoignition temperature (°C).

The overall Cargo Index is calculated by:

$$\mathrm{CI} = 2\ \mathrm{CI\ flammable} + 3\ \mathrm{CI\ toxic} + \mathrm{CI\ aquatic} + \mathrm{CI\ amenity}$$

Whereas Danahy used only the highest CI for hazard determination, Griffiths uses a summation of each of the factors affecting the Index. This recognizes the dual mechanism by which damage can be done. Since we are concerned with the capability of a cargo to cause loss of life, it seems unimportant as to how the death is caused, the only question being whether or not it indeed occurs. In Danahy's analysis a death by fire is the same as death by a toxic material. Griffiths also revised the inverse square root relationship of the TLV to an inverse relationship, as he felt the effect of concentration was overly diminished in the ESC.

Model comparisons

The PVM is essentially deterministic; for a given set of circumstances it calculates the consequences. The ESC is probabilistic since the likelihood of an event is an important factor in the final answer. For a complete analysis of risk both the consequences and the probabilities are important. A major difference between the two models is that the PVM deals with the cargo and the port area, ignoring the ship except for the mathematical description of the cargo tank. The ESC involves the ship, the cargo, and the port area. Since the ECS is probabilistic, the degree of safety inherent in the design of the ship is an important factor absent in the PVM.

The PVM provides an excellent tool for evaluating the Cargo Index of the ESC. The former is a highly complex computerized tool as compared to the simple, straightforward approach of the Danahy model. If equal size spills are assumed for specified cargoes in the PVM the ranking of the cargo based on predicted deaths and injuries can be compared to the relative hazard ratings of Danahy's Cargo Index and Griffith's Cargo Index. In addition, the detailed analysis done in the PVM to determine the toxicological effects of selected substances provides the data base Danahy recommended for further refinement of the Cargo Index (CI). In his original model Danahy used TLV as a relative measure of toxic hazard.

A TLV is established for long-term continuous workplace exposure and not the one-time high-level exposure associated with an accident. It is based on toxicological testing but the actual value is established by a consensus of governmental and industrial hygienists. It is established at a low level so that there are no noticeable effects of the exposure. Danahy noted that the LC_{50} or some other toxicity standard would be preferable if sufficiently reliable data for this determination were available. The probits of the PVM can be used to provide a more accurate evaluation of relative hazard. The values we selected in our evaluation were 50% lethality with a 15-min exposure. The 15-min exposure was selected because this is a realistic time for people exposed to the vapor cloud to respond and, if possible, evacuate the affected area. With these changes we propose the Cargo Index be calculated as:

$$\mathrm{CI} = \frac{1}{C^*}\left[1 - \exp\left(-P_{\mathrm{V}}/100\right)\right]\left(\frac{\rho_{\mathrm{vapor}}}{\rho_{\mathrm{air}}}\right)\left(\frac{T_{\mathrm{amb}}}{T_{\mathrm{BP}}}\right)$$

where C^* is the concentration in parts per million by volume calculated for 50% lethality with a 15-min exposure using the toxicity probit of the PVM.

Table 3 summarizes the predictions of the PVM and the ESC. As can be seen, the primary effect of our revised CI calculation is a much higher rating for Cl_2. Unfortunately, as discussed earlier, the results of the Population Vulnerability Model do not appear as credible as expected. We are continuing the development effort by reviewing the results and investigating the apparent inconsistencies of the results.

The simplicity and direct approach by which the Danahy and our modified formulae were developed make them still the most promising method for risk analysis, especially in the short term. Since the equations were developed

TABLE 3

Relative toxic effects of cargoes

	Danahy CI	PVM predicted fatalities	Revised CI
Cl_2	10.3	106.	407.
HCl	4.0	230.	8.1
HF	2.1	229.	4.3
CH_3Br	2.5	259.*	2.2
NH_3	1.00	1.00	1.00

*Calculations were performed using an incorrect probit.

using factors considered controlling in the damage-producing mechanism the results are easily defendable. We are grateful there have been no major accidents involving these cargoes to bear out the relative ratings of our calculations.

In conclusion, we are in the developmental stages of both a relatively simple, straightforward method of risk balancing in the Equivalent Safety Concept (ESC) and a much more complex computerized model for determining the effects of hazardous materials release. By the continual updating and revision of the factors used in determining the Port Safety Index (PSI), the Vessel Index (VI), and the Cargo Index (CI), the ESC will become a valuable tool for use of governmental bodies. Similarly, the Population Vulnerability Model (PVM) with changes and improvements will provide more detailed and location-specific information on which to base operational requirements. Initial test runs with the PVM indicate several important problems. More work is needed before much confidence can be placed in this tool. For the immediate future, then, the ESC is more promising.

Appendix I: toxicity probits

The toxicity of the various cargoes is of the utmost importance but relating fragmentary data on dosage and response in man and animals to a percent of the population harmed is difficult. One way is to construct a probit, a statistical artifact, used to relate concentration and exposure time to a value of damage or injury. The probit is of the form:

$$\mathrm{Pr} = a + b \ln X$$

The values for a and b and the form of the function X are derived from experimental dosage-response data. This probit is a Gaussian distributed random variable with a mean of 5 and a variance of 1. The percent of population affected is related to the cumulative Gaussian distribution with, for example, 50% of the population affected when the value of the probit is 5.0.

While it is true that people's response to toxic chemicals is related to such factors as age, sex, health, and weight, a single probit for all individuals is the most feasible approach. The form of the function X is, generally,

$$X_1(c,t) = \int c^n t^m \, \mathrm{d}t$$

In most cases the approximation

$$c^n t^m \, \mathrm{d}t = \sum_j c_j{}^n t_j{}^{m+1}$$

is valid. Often, only dose is important, so $n = 1$, $m = 0$, and $X = (ct)$. This simple rule is obeyed by HCl, HF, and CH_3Br. For NH_3 and Cl_2, m has the value of 2.75. Carbon tetrachloride (CCl_4) is an example of a chemical with m less than 0; here

$$X(c,t) = \sum_j c_j t_j^{1/2}$$

For each cargo separate functions are required for fatalities, injuries, and irritations, with probits for fatalities and injuries, and concentration thresholds for irritations. The effects of "injury" are permanent, but those of "irritation" are only temporary, the effects disappearing after the vapor cloud passes away. For NH_3 and HCl the general human response is such that the individual either entirely recovers or he dies, so that no permanent injury probit is required. These probits are affected by whether the individual is sheltered or unsheltered, that is, whether he is indoors or outdoors. For lack of better information, the PVM places half the population inside and half outside. As an approximation the PVM assumes that the product (ct) is the same for indoor populations as for outdoor population; detailed calculations as well as limited experimental data support this approximation. The indoor concentration is calculated stepwise from the outdoor concentration using the air change rate of the structure; the previous indoor concentration, and the present outdoor concentration. The air change rate is the number of times per hour that the air is completely changed within a structure. This rate varies, under average conditions, from 0.3 to 2.0 changes per hour, depending on the type of structure. Since it would be impractical to calculate different change rates for each building, an average is calculated as a function of wind speed and temperature difference between the inside and the outside. The probits used for indoor exposure are the same as those used for outdoor exposure; for substances for which dosage is important, that is, for which X has the form (ct), those indoors are as safe as those outdoors. Both CH_3Br and HCl are of this form. For those substances for which X has the form $(c^n t)$, where n is greater than 1, those indoors are significantly safer than those outdoors. The irritation thresholds are based on the concept that above a certain concentration irritation occurs, the irritation including lachrymation, breathing difficulties, and odor. Since human response is so variable, this threshold is deliberately set low, and all exposed to this threshold concentration are considered irritated.

For the PVM test series the toxic lethality probits equation is of the form:

$$\Pr = a + b \ln c t^y$$

(see Table A1).

TABLE A1

Constants for the toxic lethality probit equation

Chemical	*a*	*b*	*y*
Acrolein	−9.93	2.05	1.00
Ammonia	−30.57	3.82	0.36
Carbon tetrachloride	−11.19	1.006	0.50
Chlorine	−17.10	4.65	0.36
Hydrogen chloride	−21.76	2.65	1.00
Hydrogen fluoride	−25.87	3.35	1.00
Methyl bromide	−55.53	5.16	1.00
Phosgene	−19.27	3.69	1.00

Appendix II: Properties of chemicals used for comparisons

TABLE A2

	Vapor pressure at 300 K (kPa)	Boiling point (K)	Density vapor/air	TLV (ppm)	C^*
Acrolein	60.3	326.	1.94	0.10	97.0
Acrylonitrile	15.2	351.	1.83	20.	
Allyl chloride	51.2	318.	2.6	1.	
Ammonia	1069.	240.	.59	25.	4174.
Benzene	13.8	353.	2.77	10.	
Carbon tetrachloride	17.2	350.	5.3	10.	21.66
Chlorine	816,	239.	2.49	1.	43.4
Dimethylamine	221.	280.	1.65	10.	
Ethylenimine	29.4	329.	1.5	0.5	
Hydrogen chloride	4964.	168.	1.3	5.	1620.
Hydrogen fluoride	117.	293.	.71	3.	666.
Methyl bromide	231.	277.	3.27	15.	8288.
Methyl chloride	607.	249.	1.8	100.	
Phosgene	196.	281.	3.4	0.1	47.9

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