Journal of Hazardous Materials, 31 (1992) 135–153
Elsevier Science Publishers B.V., Amsterdam

On the management of severe chemical accidents DECARA: A computer code for consequence analysis in chemical installations. Case study: Ammonia plant

Ioannis A. Papazoglou[a], Michalis Christou[b], Zoe Nivolianitou[a] and Olga Aneziris[c]

[a]*Institute of Nuclear Technology-Radiation Protection, National Center for Scientific Research "Demokritos", P.O. Box 60288, 153 10 Aghia Paraskevi, Athens (Greece)*
[b]*Department of Electrical Engineering, National Technical University of Athens, 42, Patission Str., Athens (Greece)*
[c]*Department of Chemical Engineering, National Technical University of Athens, 42, Patission Str., Athens (Greece)*

(Received January 21, 1991; accepted in revised form March 9, 1992)

Abstract

A computer package is presented for the integrated risk assessment of accidental releases of hazardous substances. DECARA provides an integrated risk analysis including source-term strength evaluation, estimation of the hazardous cloud dispersion and quantification of health impacts. Multiple accidents, each with a certain probability of occurrence can be handled. Dispersion of heavier as well as lighter-than-air gases released instantaneously or continuously, can be simulated. Time-varying release rates are possible. Uncertainty analysis can be performed including both parameter and modelling uncertainty. The code calculates the unconditional fatality probability at any point around the site of release. Isorisk curves or maximum individual risk versus distance from the source can be generated. The computer package is portable and available for running in personal computers

1. Introduction

This paper presents a computer package for the integrated risk assessment of accidental releases of hazardous substances. The name of the code is DECARA and it provides an integrated risk analysis including source-term strength evaluation, estimation of the hazardous cloud dispersion and quantification of health impacts.

The severe industrial accidents of recent years (Bhopal, Mexico City, San-

Correspondence to: I.A. Papazoglou, Institute of Nuclear Technology-Radiation Protection, National Center for Scientific Research "Demokritos", P.O. Box 60288, 153 10 Aghia Paraskevi, Athens, Greece.

0304-3894/92/$05.00

doz etc.) have led to a growing awareness on the part of both public authorities and plant owners of the severe risks associated with the operation of chemical installations. Decision-making on the safe design and operation of such installations can be substantially supported and improved by quantified risk assessment (QRA) [1,2]. On the other hand, the quantification of risk associated with the release of a toxic substance contained in a chemical installation has become a prerequisite for efficient emergency planning aimed at the mitigation of the consequences to the adjacent population of such releases.

The need for a tool to cope with consequence modelling problems has been evident since the late 1970s. This has led to a variety of packages dealing with the dispersion of lighter-than-air and heavier-than-air gases of a potentially hazardous nature (e.g. toxic or flammable) which are also commercially available (DENZ, CRUNCH, WHAZAN, ZZB, EFFECTS [3–8]).

Their applicability in integrated QRA is limited, however, because they lack one or more of the following:

(a) capability for integrated risk analysis, including source-term strength evaluation, estimation and dispersion of the hazardous cloud, and quantification of the unconditional fatality probability at any point around the site of a release;

(b) calculation of isorisk curves;

(c) capability of handling releases with time-varying emission rates;

(d) capability of handling multiple accident scenarios;

(e) capability of accepting an emergency response plan module;

(f) capability for an uncertainty analysis both in parameters and in physical models.

All these features are included in the DECARA code (DEmokritos Consequence Assessment of Released Ammonia) which has been tested using ammonia as "the hazardous substance". Owing to the modularized structure of the code other toxic substances can also be described, provided that the values of their physical properties are supplied to the model.

2. DECARA, a tool for integrated risk assessment

The structure of the computer code DECARA follows the procedural steps for integrated risk assessment as they are reported by Papazoglou et al. [9,10]. In particular, it starts from the point where a system analysis has determined the failure modes of the installation and the associated frequencies of occurrence, and proceeds with the major procedural steps of *assessment of plant damage states*, *assessment of ammonia release categories*, *assessment of consequences* and *integration of the results* into quantitative risk indices. The specific risk assessment tasks that have been computerized are:

(1) Establishment of plant damage states.

(2) Calculation of ammonia outflow rates and conditions.

(3) Calculation of evaporation rates in case of liquid release.
(4) Establishment of weather conditions.
(5) Description of the surrounding topography.
(6) Calculation of ammonia dispersion.
(7) Assessment of doses.
(8) Consequence calculation through a dose–response model.
(9) Integration of results.

There are nine modules in the code surrounding to these nine tasks. The specific physical submodels used in the code are relatively simple; taken from the open literature, they are described in the Appendix. Their complexity is determined by the computer-time and computer-storage requirements and by the degree of uncertainty that characterizes an integrated risk assessment.

2.1 Plant damage state module

A plant damage state defines the physical damage to the installation and the conditions of the hazardous material at the moment of the damage to the extent that the conditional probability of obtaining a particular release category is uniquely determined. In the case of ammonia a plant damage state is defined in terms of the type of installation, the size and location of the break, and the phase of the released ammonia. DECARA can handle refrigerated ammonia at atmospheric pressure stored in a tank or circulated through a pipe. Figure 1 schematically depicts the different plant damage states that can be handled by DECARA. For a refrigerated storage tank of given dimensions the amount of the ammonia present at the time of the accident is established through the height of the liquid phase. Next, it is determined (by the user) whether the break results in liquid or gaseous release. The size of the break is determined through its equivalent diameter. The height of the ammonia in the tank and the size of the break can be either deterministically defined or treated as random variables in order to quantify potential uncertainties about their value. Similar alternatives exist for pipe breaks.

For atmospheric pathways, a *release category* uniquely characterizes the atmospheric dispersion of the toxic substance and consists of the rate at which a gaseous substance leaves the site of the accident, the physical behaviour of the vapour (lighter or heavier than air) and the meteorological conditions.

In DECARA the release categories are defined from the plant damage state, the magnitude and the time behaviour of the outflow, the evaporation of liquid ammonia and the weather conditions. Figure 1 depicts the logic of DECARA for release category creation implemented through the plant damage state module and the following three modules.

2.2 Outflow module

For a given plant damage state, the user can determine the time behaviour of the ammonia outflow, i.e. whether it is an instantaneous release, a contin-

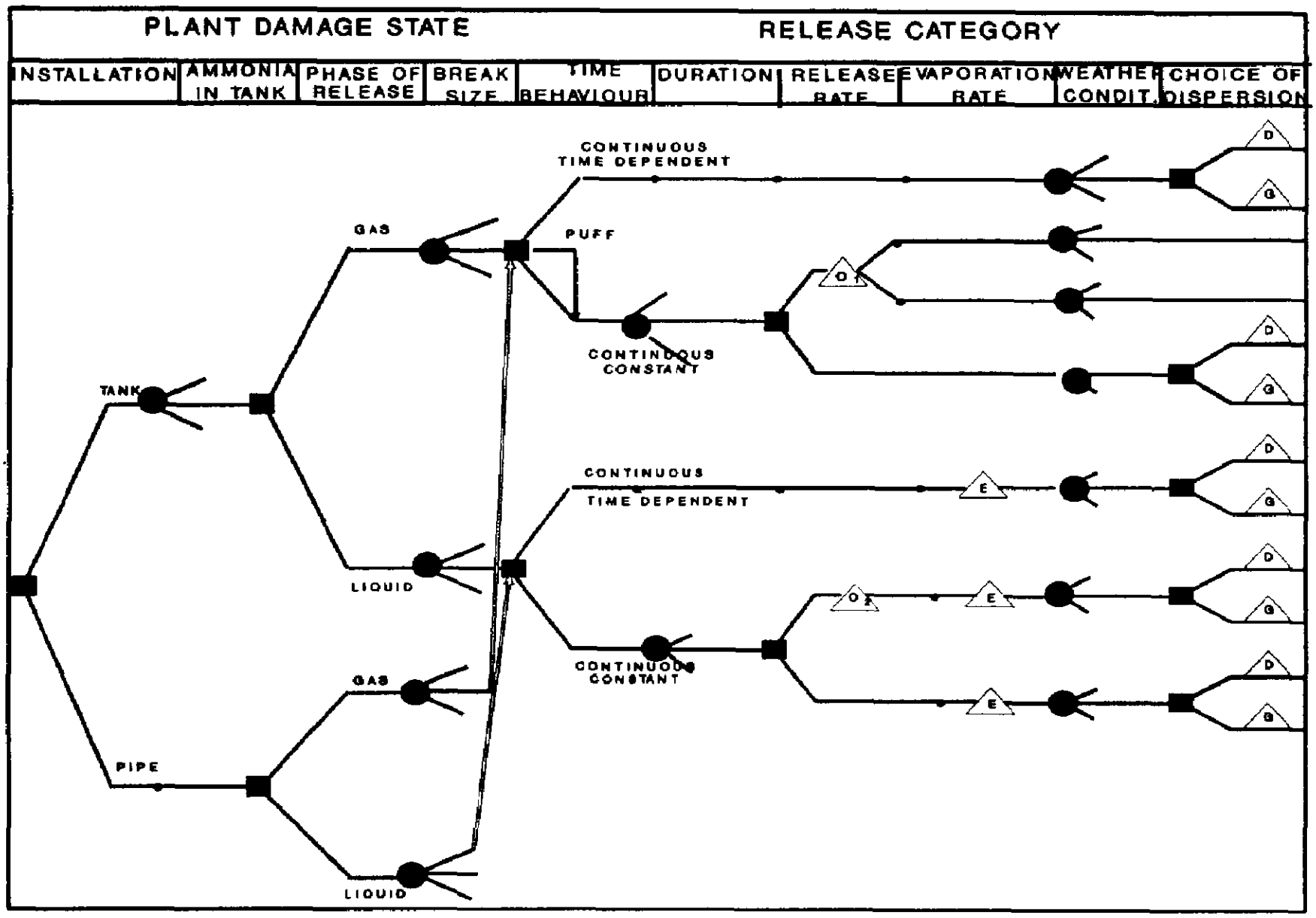

Fig. 1. Plant damage state handled by DECARA.

uous release at a constant rate or whether it is a continuous release with a time dependent rate. The magnitude and time behaviour of the outflow are determined by the user. In the case of continuous releases at a constant rate, the user has the option of having the rate calculated by either a *liquid outflow* model or a *vapour outflow* model (see Fig. 1). The duration of the release (if it is continuous at a constant rate) can be either determined by the user or treated as a random variable to quantify corresponding uncertainties. Instantaneous releases are treated as continuous and of a very short duration.

2.3 Evaporation module

In case of liquid ammonia outflow, a *spreading pool* and *evaporation* model calculates the evaporation rate of ammonia providing the necessary input to the atmospheric dispersion models.

2.4 Weather module

This module simulates the stochastic variability of the weather conditions, i.e. stability, wind speed, wind direction and ambient temperature. Once selected they are assumed constant for the duration of the accident. The weather

conditions can be correlated among themselves as well as with other parameters (e.g. amount of ammonia in the tank if the latter exhibits a seasonal dependability).

At this point (see also Fig. 1) the user can determine on the basis of the choices made so far whether a buoyant gas or a heavier-than-air gas dispersion model is applicable. If, in the case of gaseous release from a tank, the size of the break is treated as a random variable, the choice of a Gauss versus Dense dispersion model is made internally on the basis of the following criterion [14]. If the break is such that the resulting outflow is subcritical then a dense model is used, otherwise a Gauss model is used.

Collectively these four modules establish the release categories. A schematic interrelation of the remaining five models is given in Fig. 2.

2.5 Topography module

Owing to the fact that the dispersion models employed in the present version of DECARA are box models assuming a "flat terrain", the area around the site of the installation is divided into a grid by n_1 radial annuli and n_2 angular sectors. All consequence calculations are performed at the midpoints of the grid cells. The size of the grid (n_1, n_2) depends on the available computer memory.

2.6 Dispersion module

This module calculates the atmospheric dispersion of the released ammonia receiving as input the released vapour rate and the meteorological conditions. The module in its present form contains models for atmospheric dispersion of gases that are either buoyant or heavier than air. The release is continuous and can be time dependent. For each time step, each spatial point in the grid is

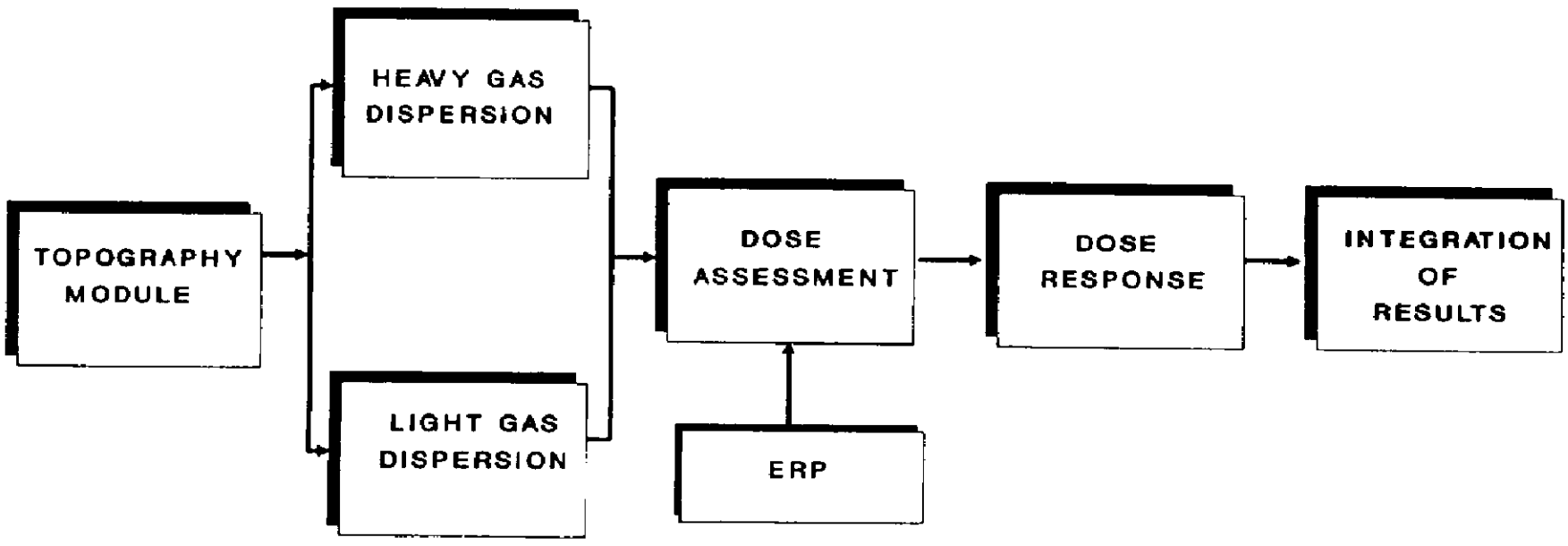

Fig. 2. Modules used in DECARA. Consequence assessment on integration of results.

assigned a concentration of ammonia resulting from the calculated shape, position and concentration of the cloud during this time step.

2.7 Dose module

The dose to an individual is calculated as a function of time at each grid point given the results of the dispersion module and the results of the emergency response plan. An *emergency response plan* refers to all protective actions aiming at limiting the exposure of individuals to the released toxic substance. In its present form the code does not contain an explicit model for emergency response. It rather assumes that an individual will be exposed to the ammonia cloud for a predetermined period of time.

2.8 Dose–response module

The dose–response model calculates the fatality probability for an individual receiving the dose calculated by the dose module.

2.9 Risk assessment module

This module integrates the partial results of each module into a quantitative risk index as follows. Let i be an index over all possible accident scenarios ($i=1,...,I$), and f_i the frequency of occurrence of each scenario (e.g. per year of installation operation).

The number of possible scenarios and their corresponding frequencies are determined by the user. In the case of ammonia storage several accidents resulting in ammonia release are possible as, for example, a tank rupture owing to overpressure or a pipebreak between the loading ship and the tank. DECARA is run for each scenario separately.

For each accident scenario, the first four modules generate a number of ammonia release categories, each specifying the duration and the rate of ammonia vapour release, whether it behaves as a lighter or heavier-than-air gas, and the weather conditions. Let w be an index over all possible release categories ($w=1,...,N$) and k_{iw} the probability of obtaining release category w given the occurrence of accident scenario i.

The conditional probabilities k_{iw} are indirectly estimated in DECARA through a Monte Carlo simulation based in the Latin Hypercube Sampling (LHS) scheme [19]. According to this approach, a sample of N release categories, conditional on an accident scenario i, are generated, consisting of a random sample of all parameters affecting the release category, that are treated as random variables (see Fig. 1). Each element of the sample determines a release category, after possible calculations by the outflow and/or evaporation models, with probability of occurrence equal to $1/N$.

The topography module provides a grid of points characterized by their polar coordinates (r,ϕ). The dispersion model calculates the concentration

$c(r,\phi,t|w,i)$ for each spatial point (r,ϕ) at each instant of time (t), conditional on a specific release category (w) and a specific accident scenario (i). The dose model calculates from $c(r,\phi,t|w,i)$ the dose of an individual at each spatial point, $d(r,\phi|w,i)$, again conditional on a specific release category (w) and an accident scenario (i). The dose response model calculates from $d(r,\phi|w,i)$ the probability of an individual fatality at each point (r,ϕ), $R(r,\phi|w,i)$, conditional on a specific release category (w) and an accident scenario (i).

Finally, the integration module calculates the unconditional on the release category individual risk at a point (r,ϕ), $R(r,\phi|i)$, according to:

$$R(r,\phi|i)=\sum_{w}R(r,\phi|w,i)k_{iw} \tag{1}$$

$R(r,\phi|i)$ is the probability of an individual fatality at the point (r,ϕ) as a result of an accident of type i per year of installation operation.

To obtain the integrated risk, the unconditional individual risk must be averaged over all possible accident scenarios, that is:

$$R(r,\phi)=\sum_{i}R_i(r,\phi)f_i \tag{2}$$

An isorisk curve can be derived from:

$$R(r,\phi)=\text{constant} \tag{3}$$

where the constant is the required level of risk characterizing the isorisk curve. It should also be noted that the individual risk can be obtained as a function of the distance from the origin of the release according to

$$R(r)=\max_{\phi}\{R(r,\phi)\} \tag{3'}$$

where the risk at distance r is set equal to the maximum risk over all directions.

3. Use of DECARA in the probabilistic safety analysis of an ammonia storage plant

DECARA is a tool for integrated risk assessment. To that end it has been used in the probabilistic safety analysis of an ammonia storage plant [10]. To demonstrate its use some of the results of this analysis are presented here.

Ammonia is stored in a refrigerated tank which is periodically loaded from a ship via a pipeline. A break in the aerial section of the pipe was treated according to the following assumptions. The break will result in the release of liquid ammonia at the unloading rate of the ship for a period of time. The released ammonia forms a spreading pool of refrigerated liquid which evaporates as a result of heat transfer from the soil and is dispersed as a heavier-than-air gas (see Fig. 1).

This accident scenario is associated, therefore, with release categories which

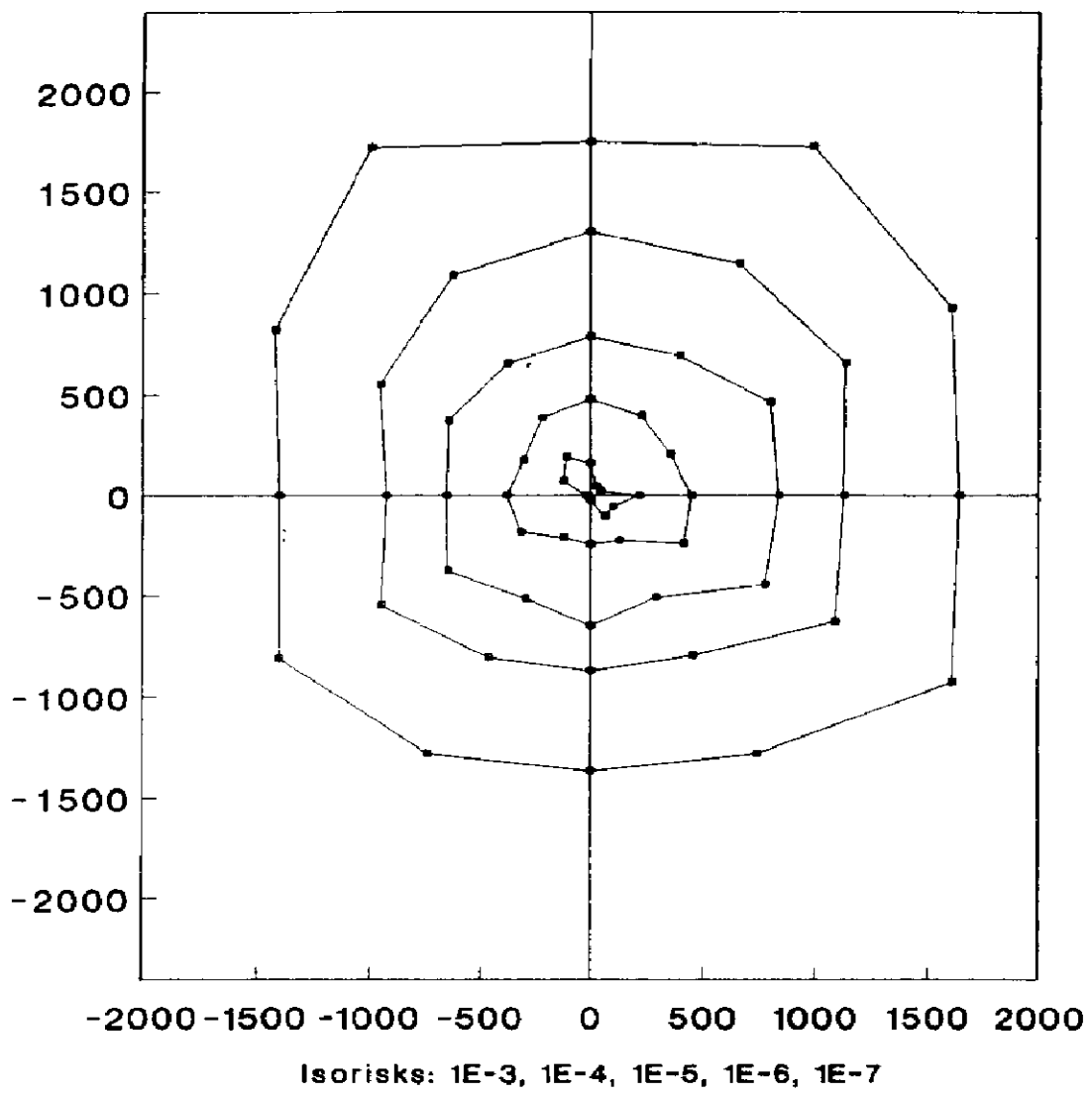

Fig. 3. Ship-to-tank pipe failure: unconditional isorisk curves.

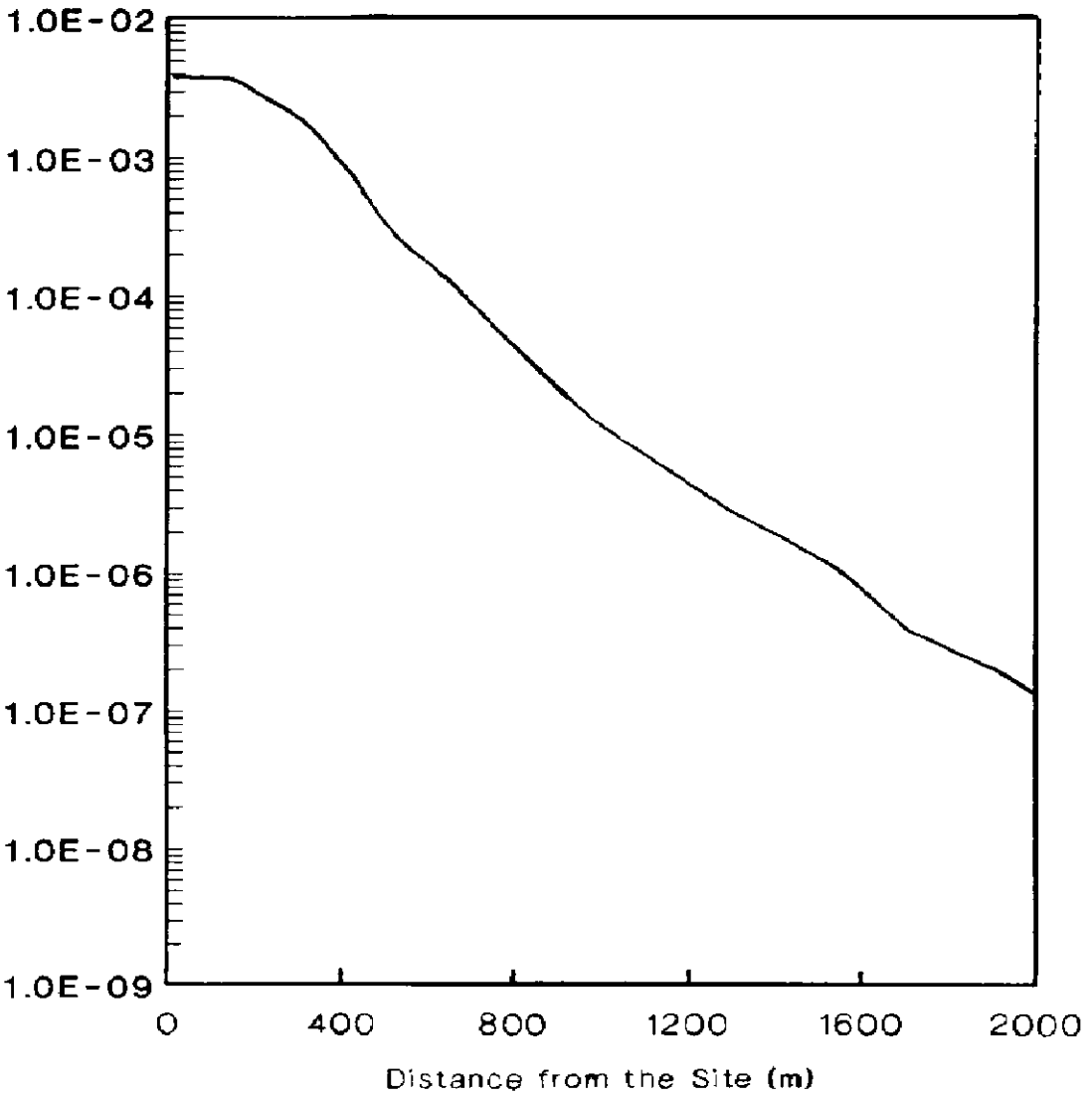

Fig. 4. Ship-to-tank pipe failure: unconditional risk vs. distance.

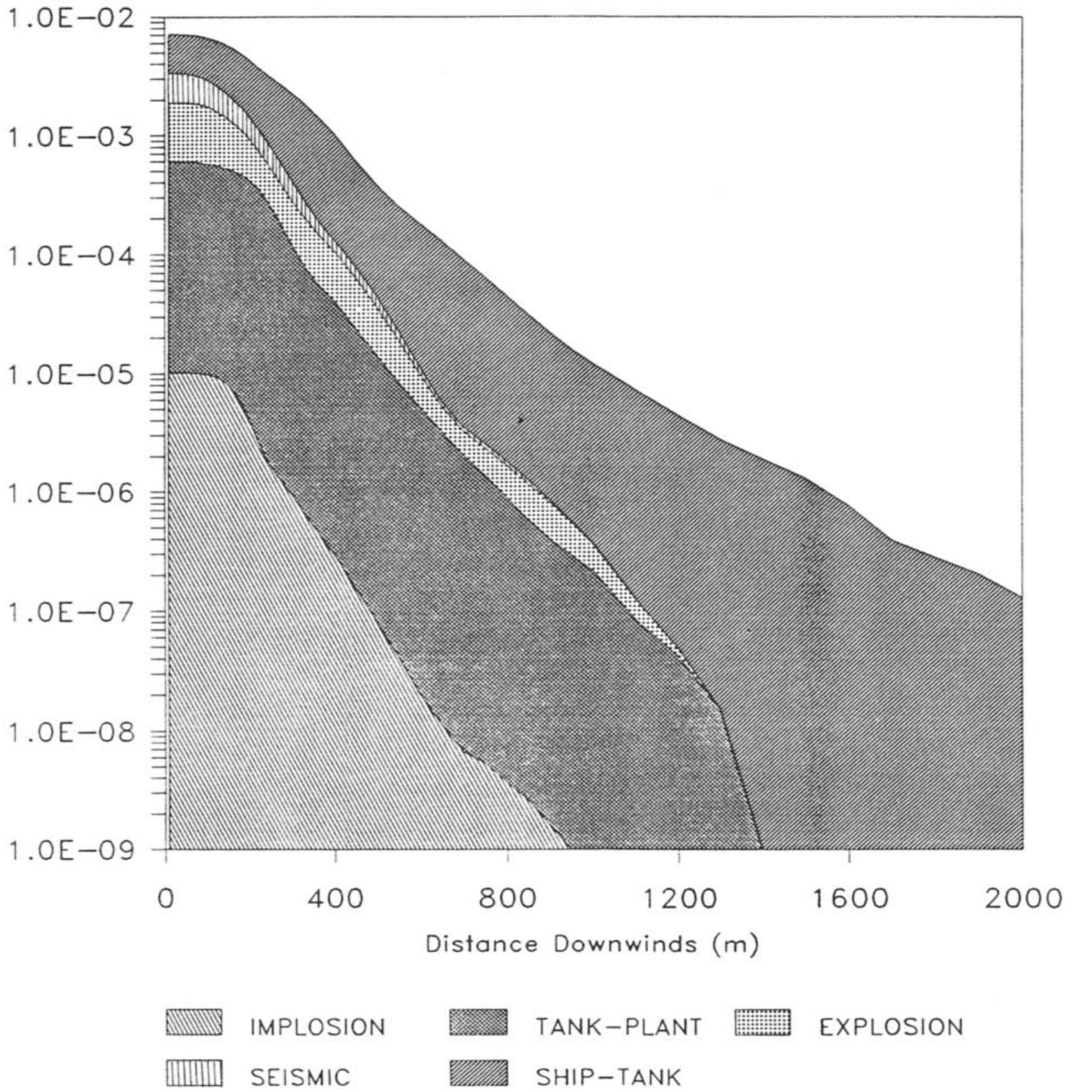

Fig. 5. Maximum individual (total) risk.

are characterized by a single dispersion model, but with variable weather conditions and varying amounts of ammonia released. The latter is the case because the release rate is constant, but the duration of the release is, in general, a random variable depending on the time that it will take for the release to be sensed and to stop the ship's pumps. The duration of the release has been assumed to be uniformly distributed between 5 and 20 minutes.

Significant dependence on weather conditions has been also observed. Air temperature, weather stability category and wind speed directly affect the

evaporation rate and the dispersion rate of ammonia. Furthermore, the wind speed direction affects the expected concentration at each point surrounding the site of installation. All these parameters exhibit a stochastic variability, not only in the values that they take, but also on the possible combinations of these values (correlations). A worst-case approach would consist in considering the combination of the worst possible values and assume these constant over all possible accidents. A realistic approach was, however, followed in this case, in that the stochastic variation of weather conditions along with the existing correlations were explicitly modelled in the consequence assessment.

Figure 3 presents isorisk curves for various levels of risk conditional on the fact that the ship-tank pipebreak has been realized, while Fig. 4 gives the individual risk as a function of the radial distance, again conditional on this accident scenario.

Corresponding results have been obtained for four other accident scenarios and integrated according to eq. (2). The maximum individual risk as a function of the distance r from the installation is given in Fig. 5.

4. Software characteristics

DECARA is a computer code written in FORTRAN (Lahey Compiler) for MS-DOS systems. The running of the code, as far as memory requirements are considered, is flexible and it depends on the size of the application and the accuracy of the results. Main parameters that affect the memory requirements are the density of the grid, the size of the weather sample and the number of time steps for the slumping period of the heavy-cloud dispersion model. A realistic application (as the one described above) assumes the following:

- Site mesh: 100 intervals $\times$ 12 sectors
- Size of release category sample: 100
- Time steps: 10000

and requires 420 kbyte of memory. For a more complicated application the 640 K memory of a simple computer is not sufficient and extended memory is required.

5. Conclusions

The computer code DECARA has been used in the quantitative risk assessment of an ammonia storage plant. This application highlighted the following merits of the code:

1. It offers the capability for an integrated risk analysis including source-term strength evaluation, estimation and dispersion of the hazardous cloud, and quantification of the unconditional fatality probability at any point around the site of a release.
2. It can obtain isorisk curves.

3. It can handle releases with time-varying emission rates.
4. In self-contained calculations it can evaluate the risk to which an individual is exposed by the application of the appropriate emergency planning scheme.
5. It can treat uncertainties in both the physical modelling of a release category and the weather conditions.
6. It can describe the dispersion of both heavier and lighter-than-air gases.

A major advantage of DECARA is its modularized structure, which permits for easy expansion of the code. Future versions of DECARA will allow (among others) for the evaluation of risk caused by multiple sources and not just one emission point as it is in its present form.

References

1 Health and Safety Executive, Quantified Risk Assessment: Its Impact to Decision Making, HMSO, London, 1989.
2 Health and Safety Executive, Risk Criteria in Land-use Planning in the Vicinity of Major Industrial Hazards, HMSO, London, 1989.
3 L.S. Fryer and G.D. Kaiser, DENZ: A Computer Program for the Calculation of the Dispersion of Dense Toxic or Explosive Gases in the Atmosphere, SRD Report R152, UKAEA, Safety and Reliability Directorate, Warrington, 1979.
4 S.F. Jagger, Development of CRUNCH: A Dispersion Model for Continuous Releases of a Denser-than-air Vapour into the Atmosphere, SRD Report R229, UKAEA, Safety and Reliability Directorate, Warrington, 1983.
5 WHAZAN Computer Code, User's Guide and Theory Manual, Technica, London, 1988.
6 I.C. Ziomas, C.S. Zerefos and A.F. Bais, Design of a system for real time modeling of the dispersion of hazardous gas releases in industrial plants, J. Loss Prev. Process Ind., 2 (1989) 194–199.
7 A.F. Bais, C.S. Zerefos and I.C. Ziomass, Accidental releases from storage installations, J. Loss Prev. Process Ind., 2 (1989) 155–160.
8 EFFECTS, The TNO Software Package for PC's for Calculation of the Physical Effects of the Escape of Hazardous Material, (TNO), Netherlands Organisation for Applied Scientific Research, Apeldoorn, The Netherlands, 1990.
9 I.A. Papazoglou, Z. Nivolianitou, O. Aneziris and M. Christou, Probabilistic safety analysis in chemical installations, J. Loss Prev. Process Ind., 5(3) (1992) in press.
10 I.A. Papazoglou, Z. Nivolianitou, O. Aneziris and M. Christou, Probabilistic Safety Analysis in Chemical Installations, DEMO-90/14 report, Athens, November 1990.
11 Vapour Cloud Source Dispersion Models, AIChE, Center for Chemical Process Safety, NY, 1989.
12 Methods for Calculation of the Physical Effects of the Escape of Dangerous Materials (Liquids and Gases), Netherlands Organisation for Applied Scientific Research, (TNO) Report, The Hague, 1980.
13 S.R. Hanna and P.J. Drivas, Guidelines for Use of Cloud Dispersion Models, AIChE, New York, NY, 1987.
14 G.D. Kaiser, A review of models for predicting the dispersion of ammonia in the atmosphere, plant/operation progress, 8(1) (1989) 58–64.
15 Portable Computer System for Use in Toxic Gas Emergencies, Air Source Branch, Ontario Ministry of Environment, Toronto, Report ISBN 07743-8932-X, Nov. 1983.

16 C.J. Wheatley, B. Cabrol, R.J. Carpenter, S.F. Jagger, G. Nussey, R.P. Cleaver, R.D. Fitzpatrick and A.J. Byrne, Comparison and Test of Models for Atmospheric Dispersion of Continuous Releases of Chlorine, SRD Report R 438, UKAEA, Safety and Reliability Directorate, Warrington, July 1988.
17 S.F. Jagger, The Application of the Computer Code DENZ, SRD Report R277, Safety and Reliability Directorate, Warrington, 1985.
18 R.M.J. Withers, The Lethal Toxicity of Ammonia. A Report to the MHAP, I Chem E North Branch Papers 1986, No. 1, I Chem E Manchester, 1986.
19 R.L. Iman and M.J. Shortencarier, A FORTRAN 77 Program for the Generation of Latin Hypercube Random Samples, NUREG/CR-3624, SAND-2365, Sandia National Laboratories, Albuquerque, NM, 1984.

Appendix

Physical models in DECARA

A1. Outflow models

The *liquid outflow* model is based on the Bernoulli equation which estimates the initial release rate. This model is used for liquid outflows for both pipe-breaks and tank breaks [11].

$$\dot{m}_g = c_F A \rho \{2(P - P_a)/\rho + g(h_o - h_{out})\}^{1/2} \tag{A.1}$$

where $\dot{m}_g$ is the liquid release rate (kg s^{-1}), c_f is the discharge coefficient (in DECARA $c_f = 0.6$), A is the cross-section of outflow opening (m^2), P is the pressure in the tank or pipe (Pa), P_a is the atmospheric pressure (Pa), ρ is liquid density (kg m^{-3}), g is gravity acceleration (m s^{-2}), h_0 is the liquid level in the tank (m) and h_{out} is the liquid level at the outflow opening (m).

The *vapour outflow* model is based on the model presented in the "Yellow book" by TNO [12]. The gas outflow rate is given from the following equation:

$$\dot{m}_g = y_o c_F A_o \{[2/(\gamma+1)]^{(\gamma+1)/(\gamma-1)} P_{ro}/(8314\, T_{ro}/M)^{0.5}\}^{0.5} \tag{A.2}$$

where $\dot{m}_g$ is the vapour release rate (kg s^{-1}), c_f is the discharge coefficient (in DECARA $c_f = 0.6$), A_o is the cross-section of the outflow opening (m^2), $\gamma = c_p/c_V$ is the ratio of specific heats at constant pressure and volume, P_{ro} is the pressure in the rank or pipe (Pa), P_a is the atmospheric pressure (Pa), and T_{ro} is the temperature in tank (K).

The parameter $y_o = 1$, if the flow is critical or

$$y_o = (P_a/P_{ro})^{(1/\gamma)}\{1 - (P_a/P_{ro})^{(\gamma-1)/\gamma}\}\{2/(\gamma-1) \times [(\gamma+1)/2]^{(\gamma+1)/(\gamma-1)}\}^{0.5} \tag{A.3}$$

if the flow is subcritical. The flow is critical if the following condition is satisfied:

$$P_a/P_{ro} < [2/(\gamma+1)]^{(\gamma/(\gamma-1))} \tag{A.4}$$

Otherwise the flow is subcritical.

A2. Spreading pool and evaporation model

The spread of liquid ammonia, the formation of a pool and the evaporation of ammonia are modelled according to [5,12]. Firstly, it is assumed that the liquid at any instant forms a pool of circular platform and of uniform height. This pool will spread under gravity until it reaches any enclosing bound wall. The pool radius is given by [5]:

$$r = (t/y)^{3/4} \tag{A.5}$$

where t is the time after the initiation of the release, and

$$y = (9\pi D_L/32g\dot{m}_g)^{1/3} \tag{A.6}$$

where r is the radius of the pool (m), D_L is the density of liquid ammonia (kg m^{-3}) and $\dot{m}_g$ is the release rate of liquid ammonia (kg s^{-1}).

Secondly, as far as the evaporating mass is concerned, it is assumed that the dominant mechanism for the phenomenon is heat transfer through the ground (due to conduction). Therefore, the evaporation rate is calculated from the equation [5]:

$$dm/dt = \pi r^2 k(T_A - T_B)(H_{VAP} t^{1/2}) \tag{A.7}$$

where r is the radius of the pool (m), T_A is the atmospheric temperature (K), T_B is the boiling point of ammonia (K), H_{VAP} is the heat of evaporation (kJ kg^{-1}) and k has the value 6.68 10^5 for an average soil.

The evaporation of the liquid ammonia results in a continuous release into the atmosphere, which forms a plume.

A3. The dispersion models used in DECARA

DECARA has two dispersion models for lighter-than-air and heavier-than-air releases.

A3.1 Dispersion model for buoyant cloud

If the cloud formed after the release is lighter-than-air the dispersion is buoyant from the beginning and the ammonia concentration is normally (Gauss) distributed within the plume. The ground concentration is determined from [13]:

$$C(x,y) = \{\dot{m}_g/(\pi U \sigma_y \sigma_z)\}\exp\{-y^2/(2\sigma_y^2)\} \tag{A.8}$$

where: $\dot{m}_g$ is the vapour release rate (kg s^{-1}), x is the coordinate in the wind direction, y the coordinate in the direction vertical to the wind direction, U is the wind speed (m s^{-1}), and σ_y, σ_z are the dispersion coefficients in the y, z directions.

for any point (x,y) downwind. The dispersion coefficients σ_y, σ_z depend on the distance x, as well as on the weather stability class and the roughness of the ground [14].

A3.2 Dispersion model for heavy gas cloud

Ammonia vapours in some cases behave as a heavier-than-air gas. According to Kaiser [14] this may happen in a refrigerated ammonia tank if liquid escapes under large hydrostatic head pressure. In this case the jet can be fragmented and leave some droplets airborne.

The dense gas dispersion model is a simple box model which considers an infinitesimal slice of the following dimensions:

W = cloud semi-width (m)

H = cloud height (m)

dx = cloud depth (m)

This model takes into account the following basic processes:
- Formation of the cloud and initial entrainment of air.
- The slumping phase.
- Transition to passive dispersion phase.
- The passive dispersion period.

A3.2.1 Initial entrainment of air. The first phenomenon following the release of ammonia into the atmosphere is the entrainment of air into the cloud, owing to the temperature difference between the air and the released mass. In order to model this phenomenon, it is assumed that the mass of the entrained air (which may be humid) is sufficient for the evaporation of all the ammonia existing in droplet form [6,7,15], i.e.:

$$\dot{m}_a = (\delta L_g \dot{m}_g)/[C_{p_a}(T_a - T_g) + X_w L_w] \quad \text{(A.9)}$$

where $\dot{m}_a$ is the rate of entrained air (kg s^{-1}), $\dot{m}_g$ is the release rate (kg s^{-1}), δ is the fraction of liquid (in droplets) in the released mass (user defined), L_g is the latent evaporation heat of ammonia (kJ kg^{-1}), C_{p_a} is the specific heat of air (kJ kg^{-1} K^{-1}), T_a is the ambient temperature (K), T_g is the temperature of release (K), X_w is the mass mixing ratio of water vapour (water in air) (user defined), and L_w is the latent evaporation heat of water (kJ kg^{-1}).

A3.2.2 Slumping phase. After the air entrainment comes the slumping phase. The cloud goes through a gravitational slumping phase owing to its excess density. The ammonia is assumed to be uniformly distributed within the slice, which spreads laterally due to gravity effects. The spreading rate is then expressed by [16]:

$$dW/dt = K\{(\rho_{ga} - \rho_a) g H/\rho_a\}^{1/2} \quad \text{(A.10)}$$

where K is a constant (in DECARA $K=1$), ρ_{ga} is the density of the ammonia–air mixture (kg m^{-3}), ρ_a is the density of air (kg m^{-3}) and g is gravity accel-

eration ($=9.81\ \mathrm{m\ s^{-2}}$). Air is also entrained as the slice progresses downwind. Defining as:

$$m_a^* = m_a/\mathrm{d}x \tag{A.11}$$

the rate of air entrainment is determined from the following equation as a function of time and distance [3,4,16]:

$$\dot{m}_a^* = 2\rho_a(WU_T + HU_E) \tag{A.12}$$

where U_T is the top entrainment velocity ($\mathrm{m\ s^{-1}}$), and U_E is the edge entrainment velocity ($\mathrm{m\ s^{-1}}$).

The calculation of the top entrainment velocity is based on the density difference between the plume and the ambient air. This velocity is calculated according to [3,7,16] from:

$$U_T = K_1 U_L / R_i \tag{A.13}$$

$$U_L = K_2 U \tag{A.14}$$

$$R_i = (\rho_{ga} - \rho_a) g l / (\rho_a U_L^2) \tag{A.15}$$

$$l = 5.88 H^{0.48} \tag{A.16}$$

where U_L is the longitudinal turbulence velocity ($\mathrm{m\ s^{-1}}$), U is the windspeed at 10 m height ($\mathrm{m\ s^{-1}}$), l is the turbulence length scale (m), R_i is the Richardson number, K_1 is a constant with value 0.3 [7,16], K_2 is a constant, with values depending on the weather stability class (its value is 0.3 for Pasquill Classes A and B, 0.25 for Classes C and D and 0.16 for Classes E and F [7,16].

On the other hand the edge entrainment velocity is directly related to the plume spreading rate:

$$U_E = K_3 \mathrm{d}W/\mathrm{d}t \tag{A.17}$$

and K_3 is a constant with value 0.7 according to Bais et al. [7] and Wheatley et al. [16].

As the slice progresses downwind, its temperature increases, since it is heated from the ground and the air. The rate of increase of temperature is given by [17]:

$$\mathrm{d}T/\mathrm{d}t = \{\dot{m}_a^* C_{p_a}(T_a - T_{ga}) + 2WK_4(T_{ground} - T_{ga})^{4/3}\}/(C_{p_a} m_a^* + C_{p_g}\dot{m}_g/U) \tag{A.18}$$

where $\dot{m}_a^*$ is the rate of entrained air ($\mathrm{kg\ m^{-1}\ s^{-1}}$), $\dot{m}_g$ is the release rate of ammonia ($\mathrm{kg\ s^{-1}}$), T_a is the ambient temperature (K), T_{ga} is the temperature of the ammonia–air mixture (K), T_{ground} is the temperature of the ground (K), C_{p_a} is the specific heat of air ($\mathrm{kJ\ kg^{-1}\ K^{-1}}$), C_{p_g} is the specific heat of ammonia ($\mathrm{kJ\ kg^{-1}\ K^{-1}}$), U is the wind speed ($\mathrm{m\ s^{-1}}$), and K_4 is a constant with value 1.07 according to Fryer and Kaiser [3].

As a result of the increase in the temperature, the average density of the ammonia–air mixture within the slice changes as follows [7]:

$$\rho_{ga} = (m_a^* + \dot{m}_g/U)T_a/\{[m_a^*/\rho_a + \dot{m}_g/U\rho_g)]T\} \quad (A.19)$$

The height of the slice, and consequently the height of the plume at the corresponding point, is calculated from the volume of the slice:

$$H = (m_a^* + \dot{m}_g/U)/(2W\rho_{ga}) \quad (A.20)$$

Numerical solution of eqs. (A.10)–(A.20) provides the values of plume height and width at any requested point. Finally, the concentration of ammonia at any point within the slumping phase is determined from:

$$C = \dot{m}_g/(2WHU) \quad (A.21)$$

A3.2.3 Termination of the slumping phase. Because of air entrainment the ammonia plume is constantly diluted. After some time the gravity effects become less important and atmospheric turbulence becomes the dominant controlling factor in plume growth. The plume height then starts to increase slowly, indicating the termination of the slumping phase.

To determine the transition point from the slumping period to the passive dispersion phase, two independent criteria are used, following Jagger's suggestion [4]:

$$dW/dx \ll 2.14\, d\sigma_y/dx$$

or (A.22)

$$\rho_{ga} - \rho_a < 0.001 \text{ kg m}^{-3}$$

A3.2.4 Passive dispersion period. For the passive dispersion phase the model assumes Gaussian dispersion. The problem in the modelling of this period consists in matching a Gaussian distribution to the existing uniform distribution of the plume and its finite size.

If T is used to indicate the transition point, the critical dispersion parameters σ_y and σ_z are calculated according to [3,16]:

$$\sigma_y^T = W_T/2.14, \quad \sigma_z^T = H_T/2.14 \quad (A.23)$$

After that, for any distance downwind, x, the Gaussian dispersion coefficients can be easily modified in a manner similar to that described by Fryer and Kaiser [3,16]:

$$[\sigma_y'(x)]^2 = [\sigma_y^T]^2 + [\sigma_y(x - x_T)]^2$$
$$[\sigma_z'(x)]^2 = [\sigma_z^T]^2 + [\sigma_z(x - x_T)]^2 \quad (A.24)$$

The ground level ammonia concentration at the point (x, y) in the passive period is calculated by:

$$C = \dot{m}_g(\pi U \sigma'_y \sigma'_z)\exp\{-y^2/(2\sigma'^2_y)\} \quad \text{(A.25)}$$

A4. Dose assessment model

The Dose model calculates the dose of an individual at each spatial point $\mathrm{d}(r,\phi|w,i)$ conditional on a specific release category (w) according to:

$$\mathrm{d(r,\phi|w,i)} = \int_0^{t_0} [c(r,\phi|w,i)^N \mathrm{d}t \quad \text{(A.26)}$$

where $c(r,\phi|w,i)$ is the concentration of ammonia at point (r,ϕ) (in ppm) and N is a user supplied constant.

A5. Dose–response model

The toxic effects of the exposure of an individual to an ammonia cloud are assessed with the help of a selected dose–response model. The model giving the probability of death of an individual (P_o) exposed to a toxic substance and used in DECARA is as follows [5]:

$$R(r,\phi|w,i) = P_o = 0.5\ (1+\mathrm{erf}(P-5)/1.4142) \quad \text{(A.27)}$$

where erf is the error function and P is the "probit" value of the toxic substance given by

$$P = A + B\ln\{\mathrm{d}(r,\phi|w,i)\} \quad \text{(A.28)}$$

where $\mathrm{d}(r,\phi|w,i)$ is the dose received by the individual and A, B are parameters depending on the substance. For ammonia these parameters have the following values [18]:

$A = -35.9$, and $B = 1.85$.

A6. Limited evaluation of DECARA

In order to evaluate DECARA against a known package calculating also the consequences of toxic releases, certain benchmark calculations have been performed between DECARA and WHAZAN [5] regarding heavy-gas/prolonged release models. The results are expressed as probability of individual fatality versus the distance from the source of the release for a given release and given weather conditions. Since identical dose–response models have been implemented in both models any differences in the results are caused by differences in the dispersion models.

The assumptions made for the benchmark calculations were the following:

- Release rate: 20 kg s^{-1}

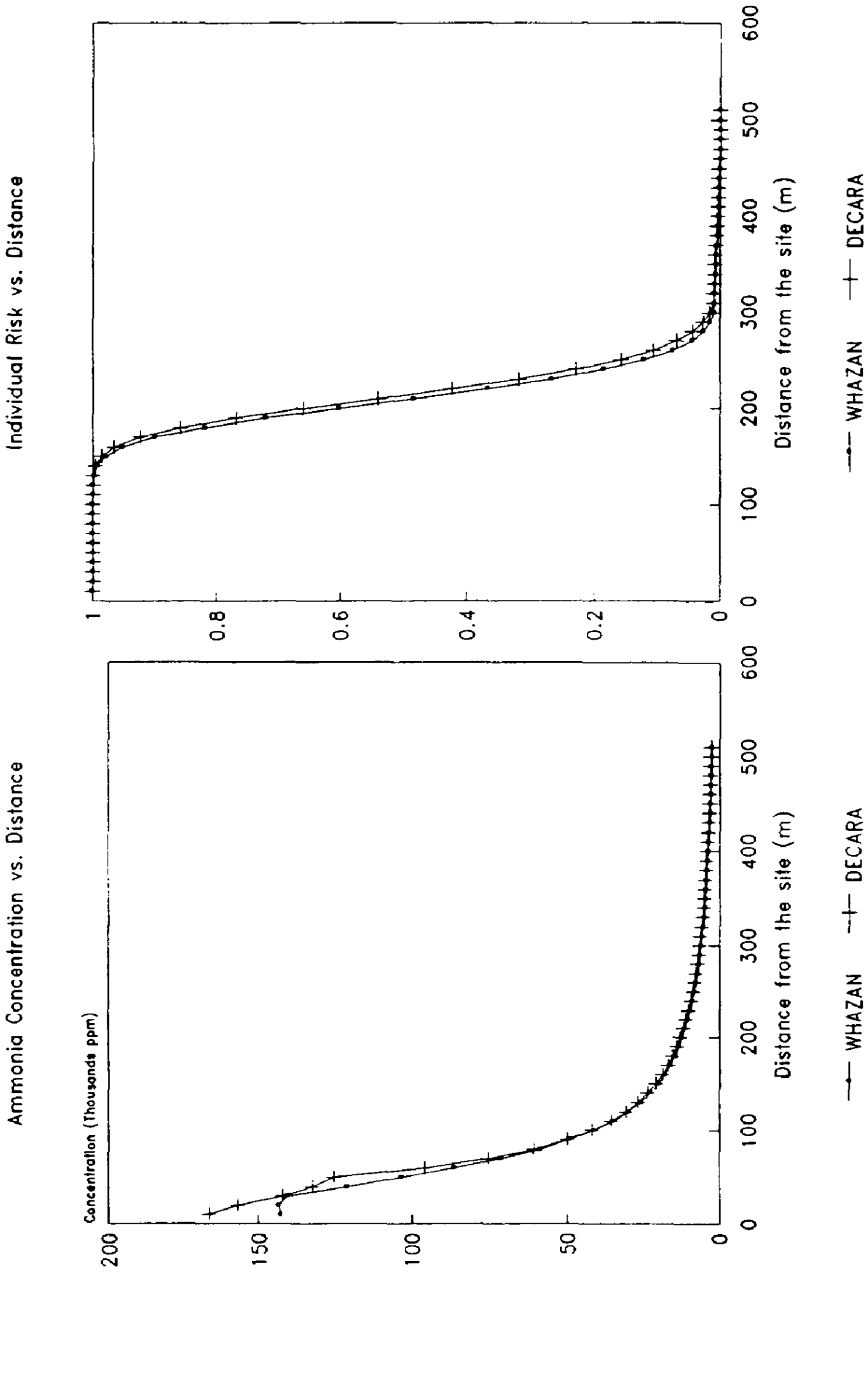

Fig. 6. Comparison between WHAZAN and DECARA (wind speed: 4 m s^{-1}),

- Release duration: 30 min
- Release temperature: 244 K (−29°C)
- Ambient temperature: 293 K (20°C)
- Ambient humidity: 70%
- Weather stability class (Pasquill): D

In addition, three different calculations were performed for three wind speeds, namely, 1.45, 4 and 8 m s^{-1}. The results of one case (4 m s^{-1}) are shown in Fig. 6.

The analysis of the whole set and the comparison of the results indicates a very good agreement between the two models. A slight difference in the predicted risk is due to the inherent features of each model and the algorithm for the solution of the differential equations. Under this perspective, DECARA slightly underestimates the risk with respect to WHAZAN.

The results of our test indicate that the differences between the two models are minor and insignificant for all practical purposes of consequence prediction.