

PREDICTING THE CONSEQUENCES OF SHORT-TERM EXPOSURE TO HIGH CONCENTRATIONS OF GASEOUS AMMONIA

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Summary

This paper is an abbreviated version of a recent report [1] in Danish, prepared by OC Consulting Engineers and Planners A/S. The full length report has been submitted to the Danish National Agency for Environmental Protection (Miljøstyrelsen) as a proposed method for assessing the consequences to humans of the accidental release of gaseous ammonia.

Previously, much work has been done to predict the effects of long term occupational exposure to low concentrations of many different chemical substances and to the determination of threshold limit values (TLV's). Literature on short term exposure to high concentrations of toxic gases which could result from accidental releases is relatively sparse.

In preparing this paper a large number of reports of incidents involving the accidental release of ammonia were studied. These reports together with the probit equations proposed by Withers et al [2] allow the definition of a set of concentrations which are expected to cause relatively well defined toxic effects in humans.

To test the validity of the proposed method, it has been used to predict the consequences of the two relatively well documented ammonia accidents at Potchefstroom, South Africa (1973) and at Houston, Texas, U.S.A. (1976). The results were compared with the reports in Ammonia Plant Safety [3], and NTSB [4] of the two incidents. The proposed method gives reasonable although somewhat conservative estimates of what actually happened.

1. Definition of the problem

1.1 Risk assessment

Risk assessment is a technique which aims at identifying all the accidents which could occur on an industrial site, investigating the possible causes of these accidents and predicting their consequences.

The results of risk assessments should be used to decrease the likelihood of accidents, reduce the consequences of accidents which are not prevented and to prepare emergency plans.

Previously risk assessments have often concentrated on carrying out detailed statistical calculations to predict how often a particular type of accident

may be expected (e.g. once in a million years). This way of presenting a risk assessment is currently losing favour in Denmark as it is not easily understood by members of the public or the press and is not a particularly constructive way of preventing accidents.

An assessment of the consequences of a release of toxic gas might typically comprise the following steps:

1. Identification of the accident scenario and release type.
2. Calculation of the rate of release of the toxic substance and the rate at which the cloud is formed.
3. Calculation of cloud dispersion, based on a series of possible weather conditions (wind speeds and atmospheric stability categories) and estimation of the concentration versus time relationship.
4. Prediction of the toxic effect on human beings who remain within the cloud (nailed to a post).
5. Prediction of the toxic effects on people who escape by going indoors or running away.

This paper deals only with step 4.

1.2 Requirements of the toxicity model

It is necessary to distinguish between two different types of toxic cloud.

Continuous releases, or releases of long duration give rise to clouds of the plume type. Concentrations at various distances from the point of release are often assumed to be independent of time. This means that the toxic effects to a stationary observer in the cloud depend on the concentration and the length of time he spends in the cloud.

Instantaneous releases, or releases of short duration give rise to clouds of the puff type. A stationary observer will experience a concentration which rises to a maximum and subsequently falls back to zero. The toxic effects must be determined using an integral function of the concentration–time relationship.

It is also necessary to define the effects which the model is intended to predict. This is usually an irreversible effect, such as permanent disability or death. The model should provide realistic estimates rather than conservative ones. The estimates may then be interpreted with the desired level of conservatism.

2. Qualitative description of the toxicity of ammonia

2.1 Introduction

At standard temperature and pressure ammonia is a colourless gas with a pungent odour. It is extremely soluble in water, producing mildly caustic ammonium hydroxide solution.

The odour threshold is low (approx. 5 ppm)* compared with the level at

*ppm (parts per million) is a measure of concentration based on volume.

which acute harmful effects arise (approx. 5000 ppm). This gives ammonia excellent warning properties.

Due to its solubility, ammonia attacks wet tissue, i.e. the eyes and the mucous membranes of the respiratory system. Damage to the cornea may produce blindness. Bronchial spasm or oedema of the lungs may produce death within a few minutes. If death does not ensue, lung damage may increase the risk of lung infection. Permanent respiratory disability has been observed. Skin damage has been observed where victims have been splashed with liquid ammonia or concentrated ammonia solutions or exposed to extremely high concentrations of gaseous ammonia.

2.2 Study of case histories

A number of case histories have been studied. References [3–9] include case histories of a large number of ammonia accidents. Withers et al. [2] have made a study of 15 separate reports given by NIOSH [5] of acute accidental exposure to ammonia involving 81 casualties, most of whom recovered fully. The following permanent or chronic effects were observed among those who did not fully recover: 16 died, 9 had evidence of chronic residual lung damage, 7 had residual visual impairment, 1 had chronic skin lesions, and 1 had post-burn scarring of the skin.

Dividing the reports into two groups to distinguish between injury from exposure to gaseous ammonia and injury from other kinds of exposure to ammonia (e.g. splashes of aqueous ammonia or liquid ammonia to the eyes or skin), a clearer picture is built up. Of 60 persons exposed to gaseous ammonia, only one case of permanent eye injury is reported. This victim also suffered residual lung damage. Unfortunately, the concentrations were not known in any of the cases.

From examination of the case histories, a number of general conclusions may be drawn: Firstly, serious injury to human beings was limited to a region within a few hundred meters from the point of release, see Markham [10], and Baldock [11]. Secondly, the most serious hazard from exposure to gaseous ammonia has been damage to the respiratory system. Thirdly, survivors who are later shown to suffer permanent lung damage are in a very serious condition immediately after the accident and require intensive hospital care for several weeks. There is reason to believe that they would have died without this care.

2.3 Definition of irreversible effect

Persons who are directly sprayed or splashed with liquid ammonia or a strong aqueous solution of ammonia may suffer very serious injuries but the effects are limited to the immediate vicinity of the release. Gaseous ammonia, however, may form a cloud which spreads over a large area and affects many people. From a risk assessment viewpoint, the toxic effects of gaseous ammonia are

thus the most relevant and are the only ones considered here. Examination of the case histories leads to the conclusions that

- emphasis should be placed on injury to the respiratory system by exposure to gaseous ammonia,
- survivors who later suffer permanent lung damage would probably have died without prompt medical treatment.

Literature values for lethal concentrations to human beings are based on animal experiments, and as laboratory animals do not receive veterinary care after exposure, it is reasonable to define the lethal toxicity as the critical irreversible effect. This seems a valid simplification as identification of this effect is easy and reliable and animal experiments are generally directed towards producing this effect. Interpretation of the experimental results is thus made easier.

3. Quantitative description of the toxicity of ammonia

3.1 Probit analysis

Probit analysis is a well-known technique for expressing the lethal effects of chemical substances in terms of concentration and exposure time. As it is based on a statistical distribution, estimation of the parameters defining this distribution requires a large volume of experimental data. Such data are obviously not available for human beings and the parameters must be extrapolated from animal data.

The probit or probability unit is a random variable with a mean of 5 and a variance of 1. It may be converted to a percentage by means of a simple conversion table, giving e.g. LC_{50} equivalent to probit 5.00 or LC_{20} equivalent to probit 4.16.

The highly complex problems of extrapolating animal data to human beings have been treated by Withers et al. [2]. Estimation of the parameters in the probit equation is based on the work of Ten Berge, a contributor to Withers et al.'s report [2]. It is found that for human beings

$$LC_{50, 30 \text{ min.}} = 11,500 \text{ ppm}$$

and the probit equation will have the form

$$\text{Probit} = 1.85 \ln D - 35.9 \quad (1)$$

with the dose term D given by

$$D = \int_0^t C^2 dt,$$

where C is concentration in ppm, t is exposure time in minutes, and LC_{50} (lethal concentration) is the concentration at which 50% of an exposed population would die.

An exposure time of 30 min is often referred to in the literature. This has no particular significance as the probit function allows any combination of concentration and exposure time to be calculated.

The probit function is unlikely to be valid, however, for exposure times of less than 5 min. In addition to this, there is little data to support the use of the probit function where exposure times exceed 60 min.

3.2 Effects of short-term exposure

The spectrum of effects of the exposure of healthy adults to ammonia may be divided arbitrarily into the three categories given below.

3.2.1 Mild effects

Exposure to concentrations lower than 5000 ppm for a few minutes.

Symptoms: restricted to the eyes and upper respiratory tract, smarting sensation in the eyes and mouth, pain when swallowing, marked hoarseness and tightness of the throat, slight cough.

Signs: reddening of the conjunctivae, lips, mouth and tongue with swelling of the eyelids and oedema of the throat. No clinical signs of lung involvement.

Consequences: spontaneous recovery without pulmonary complications ensuing.

3.2.2 Moderate effects

Exposure to concentrations in the range 5,000 to 10,000 ppm for a few minutes.

In this category there is evidence of the progression of effects deeper into the respiratory tract with involvement of the bronchi and bronchioles.

Symptoms: exaggeration of the symptoms described under mild effects. Feeling of tightness in the chest, difficulty in swallowing, sometimes complete loss of voice. Cough with copious sputum, sometimes bloodstained.

Signs: distress, increase in pulse and respiration rates. Marked swelling of the eyelids with spasm and lacrimation. Moderate oedema of the oro-pharynx with burning of the mucous membranes and resultant stripping of the epithelium to reveal dark red glazed patches. Examination of the chest reveals diminished air entry with the presence of moist sounds.

Consequences: fatalities due to obstruction of airways or complications such as lung infection cannot be ruled out.

3.2.3 Severe effects

Exposure to concentration in excess of 10,000 ppm for a few minutes.

Symptoms: Symptoms of oro-pharynx and eyes similar to those described under moderate effects. Persistent cough with copious frothy sputum.

Signs: shock, restlessness and obvious distress. Rapid pulse of poor volume.

Cyanosis and great difficulty in breathing. Generalized moist sounds in the chest.

Consequences: death as a result of asphyxiation may be expected. Survivors may die later as a result of complications, such as lung infections.

3.3. *Vulnerable members of the population*

So far the problem has been limited to defining the effect of toxic gas on healthy adults. A significant proportion of the population, however, is more vulnerable. The principal categories of vulnerable people are children, old people, and people with respiratory or heart disorders. The approach used by Withers and Lees [12] and by Eisenberg [13] has been used here to derive a probit equation for the lethal toxicity of ammonia to the vulnerable section of the population. The probit equation has the following form

$$\text{Probit} = 3.04 \ln D - 59.1 \quad (2)$$

$$\text{with } D = \int_0^t C^2 dt,$$

where C is concentration in ppm and t is exposure time in minutes.

3.4 *Effects of short-term exposure on vulnerable members of the population*

A cautious and somewhat arbitrary interpretation of the derived probit equation for the vulnerable section of the population gives the following:

Mild effects: exposure to concentrations lower than 2,500 ppm for a few minutes.

Moderate effects: exposure to concentrations in the range of 2,500–5,000 ppm for a few minutes.

Severe effects: exposure to concentrations in excess of 5,000 ppm for a few minutes.

3.5 *Emergency planning*

If an accidental release of ammonia cannot be brought under control rapidly, emergency plans must be set in operation to ensure that the population at risk is either protected, or removed from the area and those already affected are rescued and given the necessary medical treatment. The concentration level at which emergency plans should be set in operation (Public Emergency Limit or PEL) is an important element in these plans.

Markham [10] discusses voluntary exposure to gaseous ammonia and lists the following typical effects (Table 1).

Other sources referred to by NIOSH [5] state that concentrations in the range of 1,000–2,000 ppm are safe for short periods.

According to the Journal of the Kansas Medical Society [14], the Chemical Manufacturers' Association (U.S.A.) recommends that persons who have been

TABLE 1

Typical effects of gaseous ammonia to humans

Concentration (ppm)	Exposure time (min)	Effect
72	5	Some irritation
330	30	Concentration tolerated
600	1-3	Eyes streaming within 30 s
1,000	1-3	Eyes streaming instantly, vision impaired but not lost. Breathing intolerable to most participants after the time of exposure
1,500	1-3	Instant reaction was to get out of the atmosphere

exposed to a concentration of ammonia of above 1,200 ppm for more than half an hour without respiratory protection should be assumed to be in danger. 1,200 ppm would therefore appear to be a reasonable Public Emergency Limit (PEL) value.

4. The effect of simple precautions

4.1 *Running away from the gas cloud*

As mentioned before, ammonia has excellent warning properties. The assumption that an observer would stand still in a cloud with a very pungent odour is unrealistic. Examination of case histories also indicates that many people have saved themselves by escaping from the cloud.

Quantification however, is very difficult, and although, under most circumstances, a number of people certainly would be able to escape, the effect of this has not been taken into account. This introduces a margin of safety into the calculations.

4.2 *Going indoors*

The effect of going into a closed building is well documented. By closing doors and windows and stopping mechanical ventilation, indoor concentrations an order of magnitude lower than outdoor concentrations are achieved. If the risk assessment being carried out is not particularly concerned with individual risk, the effect of going indoors should not be included in the calculations. It should be noted, however, that persons who go or remain indoors have a very good change of survival. Often, breathing through a damp cloth will increase the chances of survival even more.

5. Validation of the model

5.1 Introduction

The model described is based on theoretical work and data extrapolated from experiments on laboratory animals. In contrast with many other toxic chemicals, however, there is a relative wealth of data on the toxic effects of ammonia on human beings. Ammonia has been used in industry on a large scale for about 50 years, and although standards in the industry are generally high, a number of serious accidents have occurred. A study of these accidents provides an important contribution to the understanding of ammonia hazards, as theoretically calculated effects may be compared with the observations made after accidents.

Calculations which predict the theoretical consequences of two major accidents have been carried out using the probit function and the concentration levels proposed in this paper. The results were compared with the effects described in the published accident reports. The gas dispersion calculations were carried out using the commercially available WHAZAN program package [15].

Attempts were made to ensure that the data input corresponded as closely as possible to the real situation. A detailed description of the input data for the two calculations is given in the Appendix.

5.2 Gas dispersion

The density of ammonia relative to air is 0.59.

Gaseous ammonia released at the same temperature and pressure as the surrounding air would therefore behave as a buoyant release and be dispersed primarily by atmospheric diffusion and wind turbulence.

In industry, however, most ammonia is stored in liquid form, in one of the following three ways:

- Fully refrigerated ammonia, maintained at its atmospheric boiling point (-33°C) and at, or very close to atmospheric pressure;
- Pressurized ammonia stored at ambient temperature. The pressure is equal to the saturated vapour pressure of ammonia at this temperature;
- Semi-refrigerated ammonia. As for pressurized ammonia, but if the ambient temperature rises above a preset limit, cooling systems are employed to hold the ammonia temperature below this limit.

A liquid release from any such storage facility will produce very powerful cooling effects as the latent heat of vaporization is transferred from the surrounding air to the liquified ammonia. A dense cloud containing ammonia and air will usually be the result. Dense clouds give more serious consequences than buoyant clouds.

The initial phase of dense cloud dispersion is dominated by a gravity slumping phase. Gradually, as more air and heat mix into the cloud, atmospheric

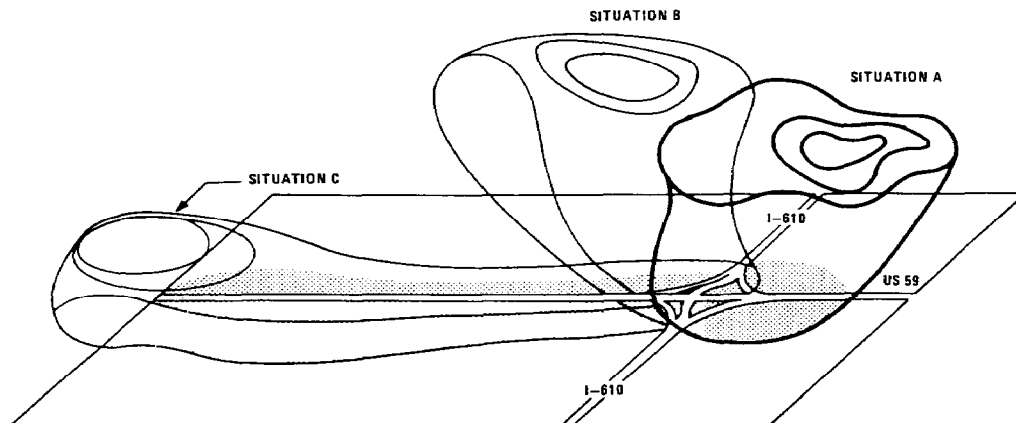


Fig. 1. Artist's concept of the spread of ammonia under three different meteorological situations. Source: City of Houston, Air Pollution Control, Accident Report, 1976 [8].

diffusion and wind turbulence effects take over and the density of the cloud becomes neutral (i.e. equal to that of the surrounding air).

In all types of gas dispersion, the wind-turbulence effects are a very important factor and they vary widely with differing wind speeds and Pasquill atmospheric stability categories. Figure 1 (which is taken from NTSB [4]) shows how gas dispersion can vary under three different meteorological conditions (Situations A, B and C).

5.3 The Houston accident

Five people were killed and 178 injured by the release of 17.2 tonnes of pressurized, anhydrous ammonia following the crash of a tank-semitrailer in a highway accident, NTSB [4]. The visible cloud extended approx. 1,150 m downwind with a maximum width of approx. 550 m, see Fig. 2. Photographs of the cloud are reproduced in NTSB [4]. All of the fatalities and permanent disabling injuries involved victims who were within approx. 70 m of the release point. It should be noted that dispersion corresponded to Situation A in Fig. 1. Figure 2 shows the positions of the victims.

TABLE 2

Predicted concentration contours. Houston accident (see Appendix)

Isopleth (ppm)	Approx. length (m)	Approx. max. width (m)
1,200	1,130	400
2,500	875	420
5,000	835	430
10,000	600	350

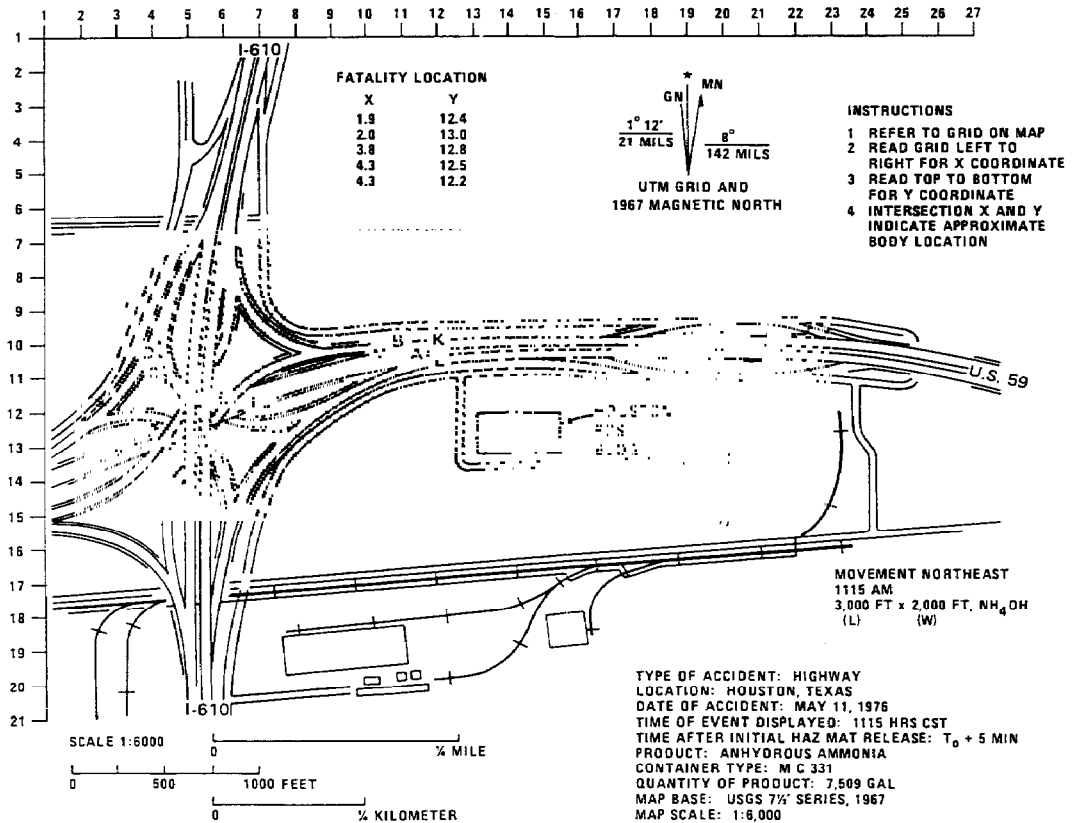


Fig. 2. Location of victims, when rescued, discussed in case histories.

The predicted concentration contours are shown in Table 2 and Fig. 3 (the apparent inconsistencies in maximum width are due to model inaccuracies). The distance to zero percent fatality calculated by means of the probit equation (eqn. 1) is approx. 200 m. Input to the calculations is shown in the Appendix.

The visible cloud was slightly larger than the calculated 1,200 ppm isopleth but direct comparison is difficult as the concentration at the edge of the visible cloud is not known. The 1,200 ppm isopleth gives a reasonably precise limit for the area in which victims were affected severely enough to need hospital treatment.

5.4 The Potchefstroom accident

Eighteen persons died and an unknown number were injured by the release of 38 tonnes of anhydrous ammonia following the sudden catastrophic failure of a pressurized storage tank, Ammonia Plant Safety [3]. Figure 4 shows the positions of the victims.

The visible cloud extended approx. 450 m downwind with a maximum width

of approx. 300 m. All of the fatalities involved victims within approx. 200 m of the release point.

The predicted concentration contours are shown in Table 3 and Fig. 5 (The apparent inconsistencies in maximum width are due to model inaccuracies.) The distance to zero percent fatality calculated by means of the probit equation (eqn. 1) is approx 450 m. Input to the calculations is shown in the Appendix.

In this case the calculation greatly overestimates the size of the cloud. This may be due to an error in the initial cloud size given in Ammonia Plant Safety [3]. the cloud size at Potchefstroom certainly seems small in comparison with the cloud at Houston where only about half as much ammonia was released.

TABLE 3

Predicted concentration contours, Potchefstroom accident (see Appendix)

Isopleth (ppm)	Approx. length (m)	Approx. max. width (m)
1,200	2,670	680
2,500	1,400	650
5,000	910	640
10,000	730	660

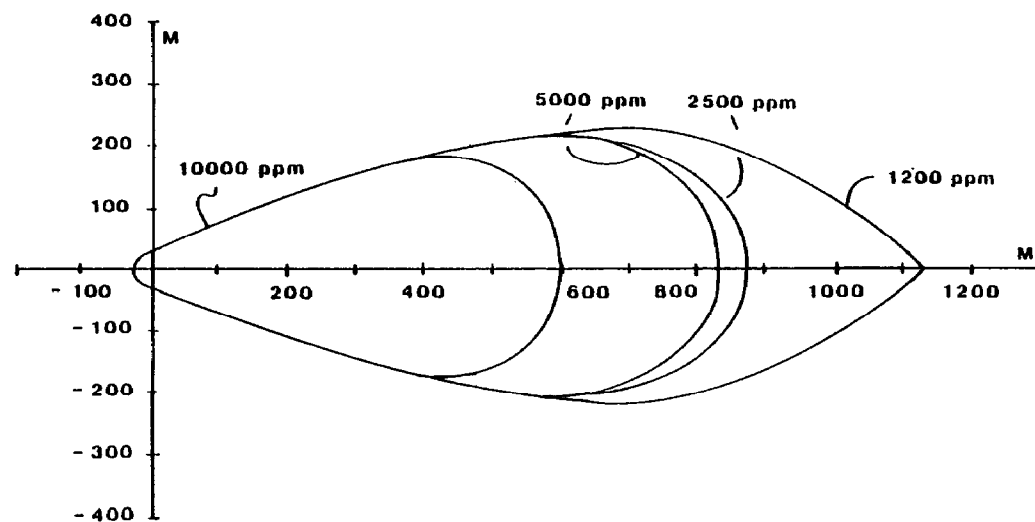


Fig. 3. Houston ammonia accident WHAZAN; predicted concentration isopleths.

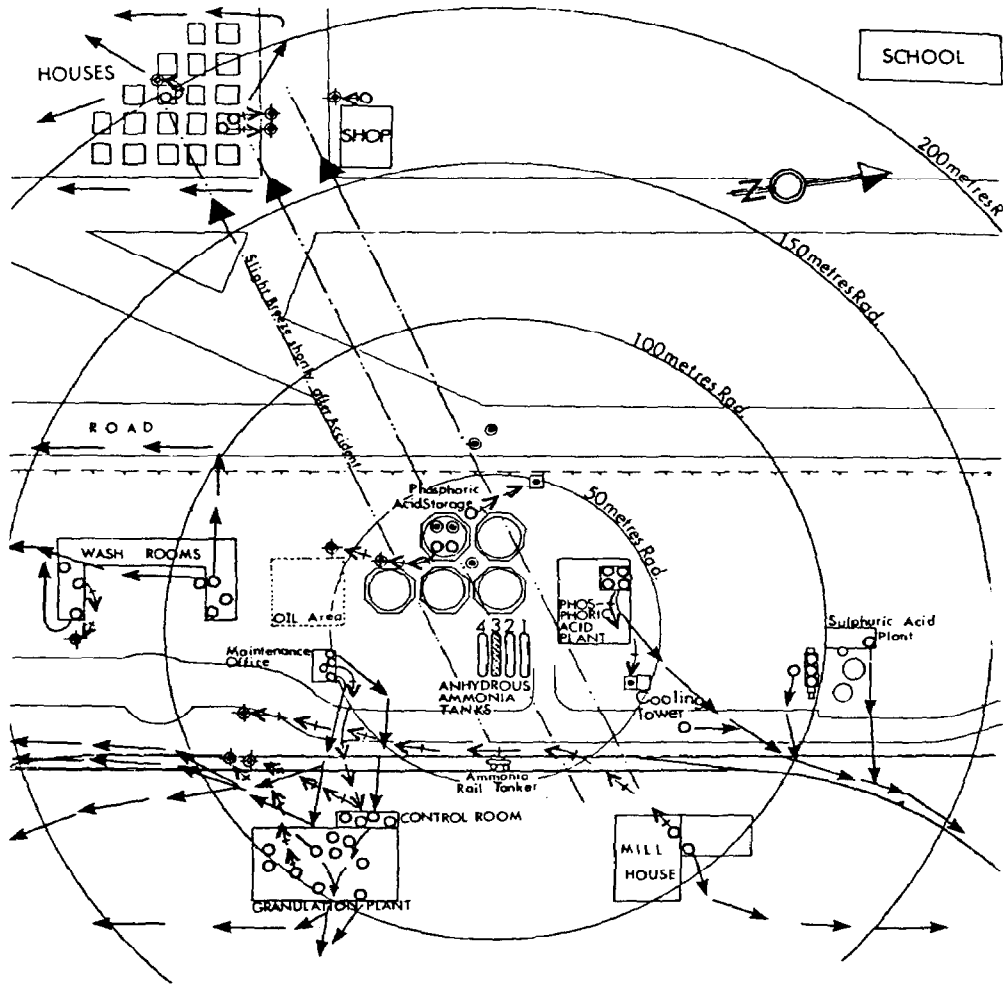


Fig. 4. General layout of Potchefstroom plant.

○ Positions where people were working or present at the time of the accident.

→ → Routes followed by people who escaped.

--- Routes followed by people who died.

□ Positions of people who were found dead.

⊕ Positions where people who tried to escape, were found injured and who subsequently died.

⊙ Positions, where people who could not escape, were found injured and who subsequently died.

..... Approximate direction of slight breeze that sprang up shortly after the accident.

▨ Tank 3, the West End of which failed.

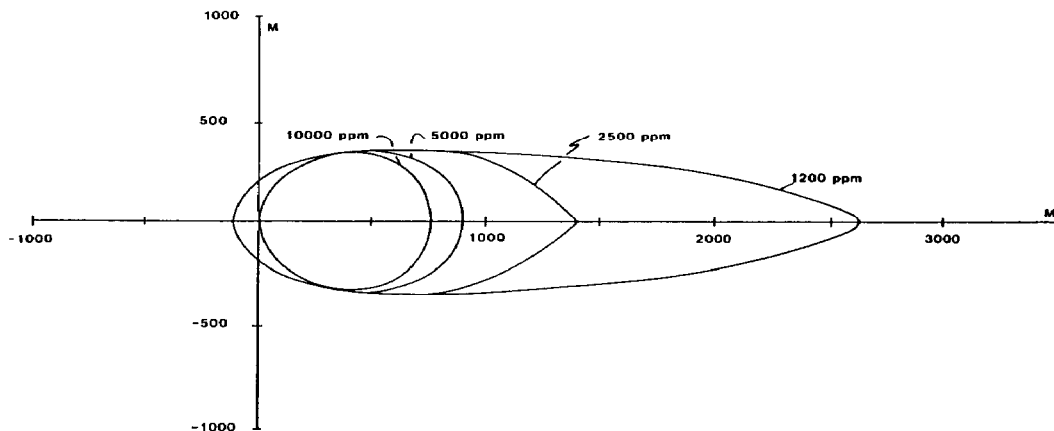


Fig. 5. Potchefstroom Ammonia accident WHAZAN; predicted concentration isopleths.

6. Discussion

Many objections can be raised to the mathematical modelling of the toxic effects of accidental releases of hazardous materials but, unfortunately, no alternative approach exists. Each of the steps mentioned in Section 1.1 carries its own level of uncertainty and this uncertainty is multiplied when the results of one step are used as input to the next. Often conservative assumptions are made at an early stage and these can lead to an extremely pessimistic estimate of the expected consequences. This is not particularly helpful to emergency planners who need more realistic ideas of the consequences to be expected, in order to prepare operable contingency plans.

Objections to the particular approach employed in this paper can also be raised. These objections may include the following:

- Dispersion models determine average concentrations, but in reality concentrations are continuously fluctuating. The approximation used to replace the integral in the dose term (eqns. 1 and 2) may therefore not be valid.
- In order to determine the 0% fatality value, the probit equation was extrapolated beyond its limits of validity.
- Great care needs to be taken when attempting to derive meaningful toxic response data from the results of animal experiments. The extrapolation of such data to humans also involves great uncertainty.
- Information on real accidents is relatively sparse.

7. Conclusions

Gas dispersion calculated by means of the WHAZAN dense cloud model (version 1.3) provides a fairly realistic estimate of the area of the cloud.

The areas in which deaths and permanent injuries actually occurred at Houston and Potchefstroom were relatively small compared with the calculated predictions.

At Houston the maximum distance at which death or permanent injury was observed was 8.5 times less than the calculated distance to the 10,000 ppm isopleth and 3 times less than the calculated distance to 0% fatality (probit method).

At Potchefstroom the maximum distance at which fatalities* were observed was 3.5 times less than the calculated distance to 10,000 ppm and 2.5 times less than the calculated distance to 0% fatality (probit method). The following table compares the results obtained by the model with the maximum distance from the source at which deaths were observed, using 2 criteria; the calculated distance to the 10,000 ppm isopleth and the calculated distance to 0% fatality.

	10,000 ppm criterion	0% fatality criterion
Houston	8.5	3
Potchefstroom	3.5	2.5

Degree of overestimate.

It may be concluded that the distance to zero percent fatality provides a fairly realistic estimate of the limit of the high risk area.

For use in risk assessments it seems reasonable to conclude that the area covered by a toxic ammonia cloud may be represented by 4 isopleths at ground level:

- 10,000 ppm: Very high risk
- 5,000 ppm: High risk: very high risk to vulnerable members of the population
- 2,500 ppm: Some risk: high risk to vulnerable members of the population
- 1,200 ppm: Predicted limit of cloud for emergency planning purposes.

The area in which fatalities may be expected, may be calculated using the two probit equations, eqn. (1) for healthy adults and eqn. (2) for vulnerable members of the population.

This method makes no attempt to predict the actual number of deaths that may occur as a result of an accidental release of ammonia. The isopleths define

*Note that permanent injury was not mentioned in the Potchefstroom report.

the area within which people could be in danger if they were unable to do any of the following:

- escape from the area in time;
- go indoors, close windows and doors and switch off mechanical ventilation;
- use simple protective measures such as a wet cloth;
- obtain medical attention.

Experience shows that these measures contribute greatly to the saving of lives.

It must be remembered that the reasonable level of agreement between the predicted and observed consequences of the two accidents is by no means scientific proof of the validity of the model. The model overestimated the consequences of the accidents by factors of between 2.5 and 8.5. This is an improvement on some other predictions, based purely on concentration criteria, where the overestimate is far greater.

It should also be noted that in an emergency, many people will already be indoors. Weather conditions which hinder the rapid dispersion of a gas cloud are low wind speed and Pasquill categories E or F. Such conditions are most likely to occur at night. Advice to go or remain indoors and close doors and windows would often be more appropriate than large-scale evacuation.

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Appendix 1

Calculation of Houston Accident

WHAZAN Dense Cloud Model.

Option 2: Instantaneous release of flashing liquid.

WHAZAN	Data Input	
Mass Released (kg)	<1.000 - 1.00E+07> (None)	:17200
Temp. of Release (K)	<243.3 - 1.00E+03> (None)	:299
Dilution Factor	<.0 - 1.00E+04> (60.00)	:10
Radius (Zero for Rad=Hght.)	<.0 - 1.00E+03> (.0)	:
Rainout Factor	<.0 - 1.000> (.500)	:
Stayout Factor	<.0 - 1.000> (.0)	:
Are Data OK <Y or N> (Y) :		

WHAZAN	Data Input	
Wind Speed (m/s)	<1.00E-01 - 50.00> (3.000)	:4
Atmospheric Stability Category	<A - F> (D)	:B
Surface Roughness Parameter	<1.00E-02 - .400> (1.00E-01)	:.17
Ambient Temperature (K)	<200.0 - 400.0> (293.0)	:299
Ambient Humidity (%)	<.0 - 100.0> (80.00)	:
Print Step Size (m)	<1.000 - 100.0> (10.00)	:
Min. Conc. of Interest (ppm)	<1.00E-03 - 1.00E+05> (None)	:1200
Are Data OK <Y or N> (Y) :		

Calculation of Potchefstroom Accident

WHAZAN Dense Cloud Model.

Option 2: Instantaneous release of flashing liquid.

WHAZAN	Data Input	
Mass Released (kg)	<1.000 - 1.00E+07> (None)	:38000
Temp. of Release (K)	<243.3 - 1.00E03> (None)	:288
Dilution Factor	<.0 - 1.00E+04> (60.00)	:10
Radius (Zero for Rad=Hght.)	<.0 - 1.00E+03> (.0)	:
Rainout Factor	<.0 - 1.000> (.500)	:0
Stayout Factor	<.0 - 1.000> (.0)	:
Are Data OK <Y or N> (Y) :		

WHAZAN	Data Input	
Wind Speed (m/s)	<1.00E-01 - 50.00> (3.000)	:2
Atmospheric Stability Category	<A - F> (D)	:
Surface Roughness Parameter	<1.00E-02 - .400> (1.00E-01)	:.17
Ambient Temperature (K)	<200.0 - 400.0> (293.0)	:292
Ambient Humidity (%)	<.0 - 100.0> (80.00)	:35
Print Step Size (m)	<1.000 - 100.0> (10.00)	:
Min. Conc. of Interest (ppm)	<1.00E-03 - 1.00E+05> (None)	:1200
Are Data OK <Y or N> :		