The relationship between risk of death and risk of dangerous dose for toxic substances

A.P. Franks *, P.J. Harper, M. Bilo

Major Hazards Assessment Unit (MHAU), Health & Safety Executive, St Anne's House, Stanley Precinct, Bootle, Merseyside L20 3RA, United Kingdom

Abstract

The relationship between risk of dangerous dose or worse and risk of 'death' (expressed as LD50 or worse, or LD95 or worse) has been studied for acutely toxic substances using the Health & Safety Executive's (HSE) Risk Assessment Tool, RISKAT. The analysis was carried out for chlorine, ammonia, hydrogen fluoride and sulphur dioxide, at a range of major hazard sites. Consistent relationships, of the form $y = x^a/b$, were found between individual risk of dangerous dose or worse and individual risk of 'death'. These were $y = x^{1.11}/2.59$ for LD50 and $y = x^{1.23}/5.62$ for LD95, where y is the risk of 'death' and x is the risk of dangerous dose or worse. It is thought that the form of this relationship arises from the way hazard ranges vary with distance and the way in which large releases of toxic material tend to have lower frequencies of occurrence than smaller releases. The existence of a consistent relationship between different substances is thought to be due to the way in which HSE selects the toxicological data it uses and the fact that all of the substances studied have a similar mechanism of toxic action.

Keywords: Major Hazards; Quantitative Risk Assessment; Toxicity; Risk Criteria

1. Introduction

In the UK, the Health & Safety Executive (HSE) is the authority responsible for giving advice to local planning authorities (LPAs) concerning the safety implications of land-use planning in the vicinity of major hazard sites. In this context, Quantitative Risk Assessment (QRA) is an important technique used to inform the judgements made about the advisability or otherwise of land-use planning proposals. The use of QRA by the

---

* Corresponding author. Telephone: 0151 951 4193 Fax: 0151 951 3824.

HSE to consider toxic hazards at fixed installations is relatively well established, whilst use of the technique to consider risks from pipelines and flammables hazards is less advanced and is currently under development.

The criteria used by the HSE in formulating advice in the land-use planning context have been published in a discussion document [1] (which is currently under review). At the time that this document was produced, the majority of the experience gained by the HSE in the application of QRA was in relation to toxic hazards, especially chlorine. The document is therefore somewhat biased towards consideration of toxic hazards. Furthermore, risks from pipelines carrying hazardous materials were specifically excluded from the scope of the document.

This paper represents part of the work undertaken by the Major Hazards Assessment Unit (MHAU) of the HSE to further develop QRA methodology for pipelines and fixed installations handling flammable materials. As part of this work it may also prove necessary to develop new risk criteria for land-use planning purposes appropriate to such installations.

2. UK strategy for control of major hazards

The activity of the HSE in giving land-use planning advice forms part of an overall strategy for the control of major hazards in the UK.

This strategy evolved from concerns first expressed in 1967 by the Chief Inspector of Factories [2] through the deliberations of the Robens Committee, published in a report in 1972 [3], and the three highly influential reports published by the Advisory Committee on Major Hazards (ACMH) [4–6]. The ACMH recommended a three-pronged approach to dealing with the problem of major hazards, which forms the basis of the legislative framework in place today:

IDENTIFICATION: Implemented through the Notification of Installations Handling Hazardous Substances (NIHHS) Regulations, 1982 [7].

ASSESSMENT AND CONTROL: Implemented through the Control of Industrial Major Accident Hazards (CIMAH) Regulations [8], first introduced in 1984. The CIMAH Regulations represent the passing into UK law of the so-called Seveso Directive [9]. This European Directive has recently undergone an extensive review, leading to the proposal of a new Directive for the control of major hazards [10].

MITIGATION: Implemented through land-use planning controls (as embodied in the Planning (Hazardous Substances) or P(HS) Regulations 1992 [11] and Department of the Environment Circular 11/92 [12]) and the emergency planning requirements of the CIMAH Regulations.

With regard to the third aspect of this strategy, HSE act as a statutory consultee in order to give land-use planning advice to local authorities concerning developments proposed in the vicinity of installations to which these regulations apply.

Under the 'consents' regulations, HSE has a dual role as a statutory consultee. Firstly, it is consulted on all applications for hazardous substances consent. Secondly, where consent has been granted, it is consulted on proposals for developments in the vicinity of the hazardous installation.

3. Quantitative risk assessment for major hazards

The use of QRA by the HSE in relation to Major Hazards has been described in detail by others [1,13–15]. Essentially, the computerised QRA tool RISKAT is used to calculate the likelihood of individuals at locations around a major hazard site receiving a dangerous dose or greater from a series of user-specified releases with associated event frequencies.

The Major Hazards Assessment Unit (MHAU) uses QRA for:

1. setting consultation distances for NIHHS, CIMAH and 'Consents' major hazard sites. Applications to the local authority for planning permission for developments of land falling within the consultation distance are then sent by the local authority to the HSE for consultation;
2. providing advice to LPAs on the siting of new major hazard sites or on the development of land within the consultation distances of existing sites;
3. assisting with the identification of reasonably practicable risk reduction measures.

The scope of MHAU's QRAs is limited to that implicit in the CIMAH or P(HS) Regulations. Thus the assessments are only concerned with those events that have the potential to present a risk to those off site, but smaller events which could escalate into such events are also considered. However, substances not covered by these regulations or present in quantities less than the threshold quantity are normally excluded from the assessment.

The procedures adopted by HSE for estimating risk levels, and, in particular the RISKAT procedure, are described elsewhere [14,16,17] and are similar to those described by CCPS [18]. Increasingly QRA is used, though currently most flammable hazards are assessed by a consequence analysis. Parameters such as the distance to 1000 thermal dose units (tdu, i.e. $(kw\,m^{-2})^{4/3}$ s—representing about a 1% chance of fatality for a typical population)—or 500 tdu for vulnerable populations such as the occupants of an old people's home are used. In the case of blast overpressure the corresponding distances are those to 140 and 70 mbar, respectively.

As previously mentioned, in the case of toxic hazards the risk of receiving a dangerous dose *or worse* is estimated and assessed against published criteria [1].

4. The dangerous dose concept

The definition of and derivation of the so-called dangerous doses (or dangerous toxic loads, DTLs) used by MHAU in its QRAs has been described previously [19]. The approach used is a pragmatic one, representing, it is believed, the best that can be achieved under the usual prevailing circumstances of sparse data, with little or no information on human effects. The Specified Level of Toxicity (SLOT) appropriate to land-use planning considerations, resulting from exposure to a DTL, has been defined as one where there is:

1. Severe distress to almost everyone in the area
2. A substantial fraction of the exposed population requiring medical attention
3. Some people being seriously injured, requiring prolonged treatment
4. Highly susceptible people possibly being killed.

The choice of this SLOT represents a degree of compromise. For land-use planning purposes a SLOT based solely on lethality may not be stringent enough in that no account would be taken of serious but non-lethal effects, which may be of significant concern (such as serious, permanent injury or disfigurement). On the other hand, use of a SLOT based on only a low level of non-lethal effects could be too stringent, especially for accidental releases occurring only very rarely. The SLOT defined above therefore contains elements of serious injury as well as lethality (albeit at a low level).

The land-use planning SLOT has generally been taken to correspond to 1–5% lethality in the exposed population. The level of lethality varies within this range from substance to substance, since different substances produce different non-lethal effects with different degrees of seriousness.

In order to set the DTL for a substance under consideration, a critical assessment is made of the available toxicological data. Typically, this data search will result in the selection of an animal model (usually the most sensitive species and strain) represented by an LC50 (the concentration estimated to give rise to 50% lethality in the exposed population, at a stated duration of exposure) and associated duration of exposure. Probit analysis [20] is then applied to the data set selected to derive the lower exposure concentration estimated to give the lower lethality level required for the SLOT (1–5%).

In many cases, experimental observations suggest that the function relating exposure time and concentration has the form:

$$c^n \cdot t = A \tag{1}$$

Where A is a constant termed the Dangerous Toxic Load (DTL). Further analysis of the selected data is then performed in order to determine the appropriate value of n in Eq. (1).

HSE have performed this analysis for a range of substances and the results are available in published reports [21–27].

The above represents a simplified explanation (for the sake of brevity) of the way in which DTLs are defined. A more detailed account is given in the references supplied.

Within the RISKAT tool, the toxicity of the material under assessment is described by the values of A and n from Eq. (1).

5. The risk of dangerous dose or worse

As indicated earlier, the output of a QRA performed by MHAU is a 'map' of the individual risk of receiving a dangerous dose (DTL) *or worse* around a major hazard site. A given release of toxic substance may result in some of the exposed population just receiving a DTL. These are likely to be those people relatively further away from the source of the release. However, people closer to the release source may receive a significantly greater toxic load from the same release. Therefore the individual risks calculated in the QRA using, for example, the RISKAT tool, are not simply the individual risks of receiving a dangerous dose, but are the individual risks of receiving a dangerous dose *or worse*. In establishing criteria for land-use planning purposes, it is important to consider the magnitude of the 'or worse' proportion of the risk of dangerous dose or worse to a person.

The document describing the currently used risk criteria [1] gives some indication of the expected size of this 'or worse' element. The document states that a 1 chance per million per year (cpm) individual risk of dangerous dose or worse would be expected to include approximately a 1/3 cpm individual risk of death. This figure arose from a consideration of the QRA experience that had been gained by MHAU up to that date, which was principally with regard to toxic hazards, chlorine in particular.

If a situation arose where the 'or worse' element of the risk of dangerous dose or worse was greater than that assumed by the document, then the suitability of the criteria for use in that situation would have to be questioned. It has been observed, for example, in risk assessments for flammable gas pipelines that, over a significant range from the pipeline, the risk of dangerous dose or worse is almost entirely composed of risk of death. This may also be the case around some fixed installations handling flammable materials. This difference arises from the rate at which the hazardous effect falls off with distance, which is gradual for toxic releases and considerably steeper for thermal events. In crude terms, in a thermal event an individual either receives a large thermal 'dose' or is unaffected whereas with a toxic release serious effects may persist to a much greater distance, without giving rise to fatalities.

This being the case, the question now arises as to what criteria would be appropriate for land-use planning considerations around installations presenting thermal hazards. As a first step towards deriving these criteria, an investigation was carried out within MHAU into the relationship between the risk of dangerous dose or worse and the risk of death for a range of toxic substances. It is hoped that an understanding of this relationship for toxic hazards and comparison with the relationship between the risk of dangerous dose or worse and risk of death for thermal radiation hazards will help to inform any revised criteria that may be established.

6. Analysis

A total of nine risk assessments was chosen for analysis, representing a range of substances and installations. The details are given in Table 1 below. In summary, there

Table 1
Risk assessments used in analysis

Substance	Description
Chlorine (1)	Small bulk storage, frequent road tanker deliveries
Chlorine (2)	Bulk chlorine with vessels in building, water treatment
Chlorine (3)	Chlorine process plant
Chlorine (4)	'Standard' bulk chlorine installation
Ammonia (1)	Refrigerated and pressurised ammonia storage
Ammonia (2)	Pressurised liquefied ammonia storage
Hydrogen fluoride (1)	70% HF in plastic tanks
Hydrogen fluoride (2)	HF alkylation unit
Sulphur dioxide	Sulphur dioxide process plant

were four chlorine assessments, two ammonia assessments, two hydrogen fluoride assessments and one sulphur dioxide assessment.

The program RISKAT uses the concept of DTL (or, as it is commonly called, dangerous dose) as described earlier. The program can be used to investigate the risk of receiving any particular dose level by adjusting the '*A*' value in RISKAT (from Eq. (1)) to reflect that dose level. These dose-specific *A* values (corresponding to LD50 or LD95) were determined for each of the substances in Table 1 by the use of probits. The values were then inserted as the *A* values in the appropriate RISKAT files. RISKAT was then re-run for each case and the results compared with the originals.

Probits are normally expressed, for toxics, as:

$$P = a + b \cdot \ln(C^n t)$$

or, substituting Eq. (1):

$$P = a + b \cdot \ln(A)$$

By inputting the probit constant for 50% or 95% lethality (5 and 6.64, respectively) into this equation, the appropriate *A* value can be determined if values of *a* and *b* are known. These can be taken from probit functions for the substances in Table 1.

The HSE DTLs for these substances have been obtained from probit equations derived from the data given by the references [28–31] indicated in Table 2. Table 2 also gives details of a number of other probit equations found in the literature. The analysis

Table 2
Summary of probit equation data

Substance	Probit	a	b	n	LC50 (ppm)	LC01 (ppm)	Ratio LC50:LC01	Ref.
Chlorine	Withers & Lees 85	-8.29	0.92	2	250	70	3.5	[32]
	ten Berge 86	-19.05	1.1	3.5	195	107	1.8	[33]
	ten Berge 83	-5.04	0.5	2.75	429	79	5.4	[34]
	Zwart & Woutersen 92	-23.76	2.78	1.04	793	354	2.2	[35]
	ACDS 92	-4.4	0.52	2.75	208	41	5.1	[36]
	van Heemst 90	-10.1	1.11	1.65	484	136	3.6	[37]
	Schlagbauer & Henschler	-13.86	1.45	2	124	56	2.2	[28]
Ammonia	IChemE 86	-35.9	1.85	2	11525	6140	1.9	[38]
	ten Berge 86	-49.54	2.3	2.02	23252	14083	1.7	[33]
	Canvey 78	-51.42	2.21	2.75	3187	2170	1.5	[39]
	ACDS 92	-12.2	0.8	2	8504	1983	4.3	[36]
	Silver & McGrath	-41.86	2.26	2	5859	3497	1.7	[29]
HF	Mudan 89	-48.33	4.85	1	1972	1220	1.6	[40]
	USCG 80	-25.87	3.35	1	330	165	2	[41]
	ten Berge 86	-7.61	0.7	1.94	1636	301	5.4	[33]
	TNO 92	-7.61	0.7	1.94	1836	331	5.5	[42]
	Wohlslagel et al.	-38.99	4.43	1	678	401	1.7	[30]
SO$_2$	USCG 80	-15.67	2.1	1	627	207	3	[41]
	TNO 92	-23.8	1.14	3.7	368	212	1.7	[42]
	Bitron & Aharonson	-33.94	1.19	4	1484	911	1.6	[31]
	Bitron & Aharonson	-16.64	1.19	2	1569	592	2.7	[31]

was only performed for a single sulphur dioxide site since there is some concern over the validity of the probit used. The HSE probit is based on data by Bitron and Aharonson [31] and a linear regression was performed on the LC50 concentration/exposure-time data. This suggested a value for n of 4, although it is noted that this is based on only three data points. The current HSE DTL for sulphur dioxide is based on an n value of 2. Using this value, a probit of the following form can be determined:

$$P = -16.635 + 1.194 \cdot \ln(C^2 t)$$

To retain consistency with the DTL, this form of the probit was used in the analysis. Again, this probit is presented in Table 2. The probit based on an n value of 4 is also given for information.

It should be noted that several of the published probits listed in Table 2 are derived from the pooling of lethality data from different species in different experiments for varying exposure times—a methodology fundamentally different to that employed by HSE.

7. Results

7.1. Risk of LD50

Fig. 1 shows plots of risk of LD50 or worse against risk of dangerous dose or worse for chlorine, ammonia, hydrogen fluoride and sulphur dioxide. With the exception of sulphur dioxide, the data for the various assessments lie close together. Regression analysis of the complete data set gives a reasonably good fit to the function:

$$\text{Risk of LD50} = (\text{Risk of Dangerous Dose})^{1.12}/2.97 \tag{2}$$

R-squared value: 0.925725

It should be noted that the R-squared value refers to a linear regression analysis of the logarithmic version of Eq. (2). The R-squared values quoted below have been obtained in a similar way. This regression line is also shown in Fig. 1 (Regression 1).

Regression analysis of the data excluding that for sulphur dioxide gives a good fit to the function:

$$\text{Risk of LD50} = (\text{Risk of Dangerous Dose})^{1.11}/2.59 \tag{3}$$

R-squared value: 0.950281

This regression line is also shown in Fig. 1 (Regression 2).

7.2. Risk of LD95

Similarly, Fig. 2 shows a plot of risk of LD95 or worse against risk of DTL for the various substances. Again, the data points from different assessments lie on approximately the same curve, although there is visibly more 'scatter' in the data than in the LD50 cases. Regression analysis of the complete data set gives:

$$\text{Risk of LD95} = (\text{Risk of Dangerous Dose})^{1.21}/6.22 \tag{4}$$
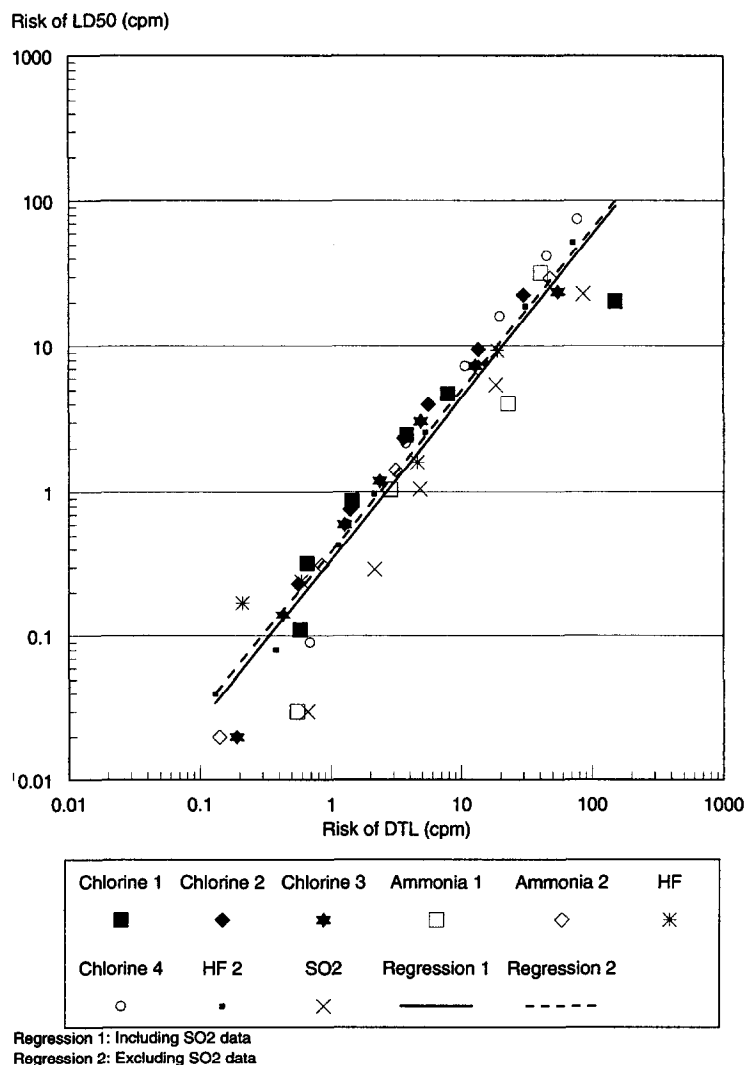
Risk of LD50 (cpm)

Fig. 1. Risk of LD50 versus risk of dangerous dose.

R-squared value: 0.847313
This regression line is also shown in Fig. 2 (Regression 1).
Excluding the sulphur dioxide data and repeating the analysis gives:

$$\text{Risk of LD95} = (\text{Risk of Dangerous Dose})^{1.23}/5.62 \tag{5}$$

R-squared value: 0.884198
This regression line is also shown in Fig. 2 (Regression 2).
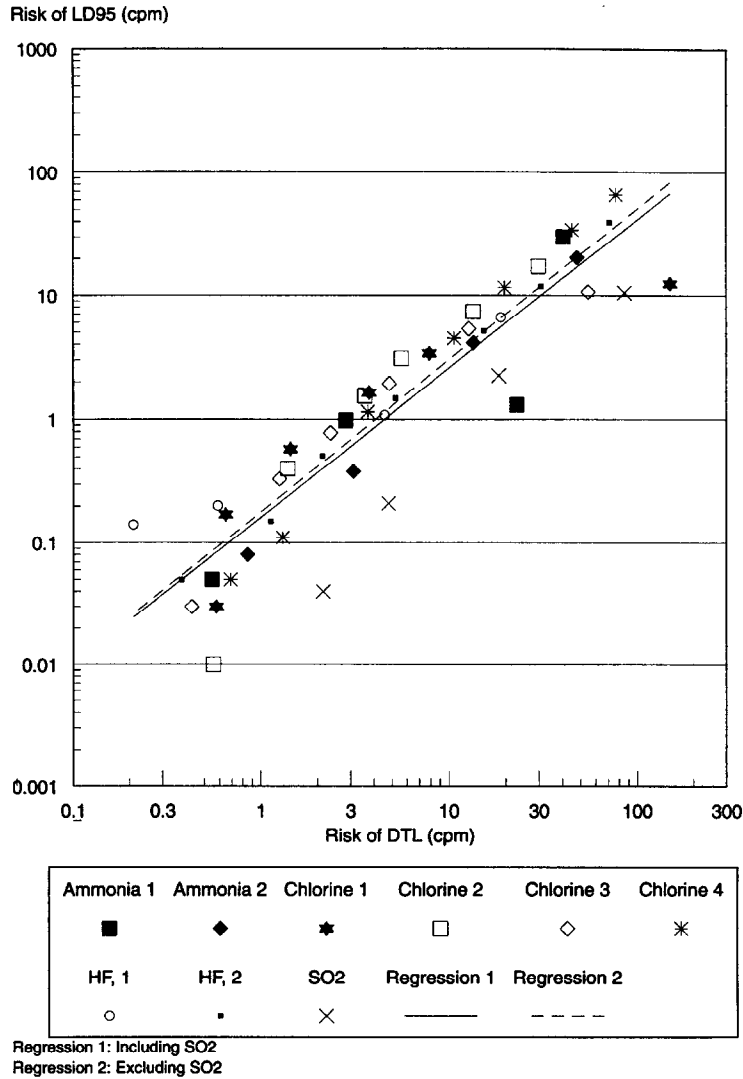The lower correlation coefficient values obtained reflect the increased scatter observed.

Fig. 2. Risk of LD95 versus risk of DTL.

7.3. Risks using different probits

Chlorine assessment 2 was repeated using three further probit equations, those of the ACDS study [36], ten Berge (1983) [34] and Zwart and Woutersen [35], to establish both the DTL and LD50. The results are displayed in Fig. 3, together with those obtained earlier using the probit from this study to establish the DTL and LD50. The data appear to fall on two curves—an upper curve on which data using the probit from this study and the Zwart and Woutersen probit lie and a lower curve corresponding to the ACDS probit and ten Berge (1983) results.

Risk of LD50 (cpm)
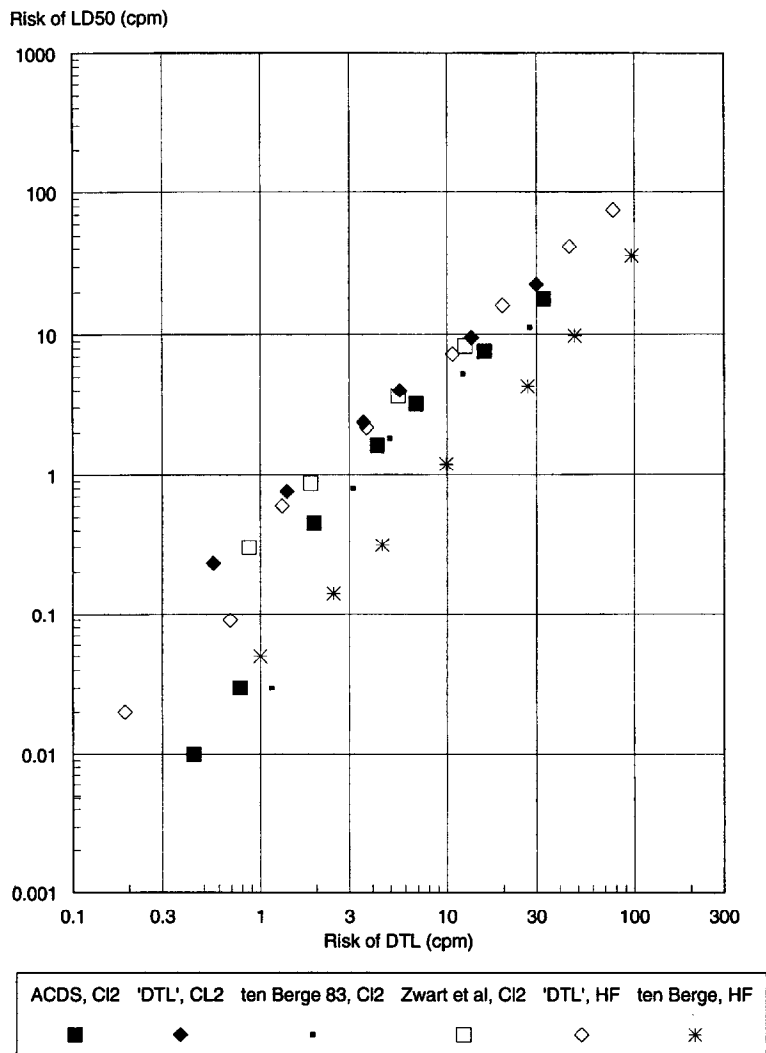
Fig. 3. Comparison of results for different probits for chlorine and hydrogen fluoride.

The results of repeating HF assessment 2 (the alkylation unit) using the ten Berge probit [33] are also shown in Fig. 3, together with the earlier 'DTL' probit results.

8. Discussion

Throughout this section, 'risk of x' has been used to indicate 'calculated individual risk of x or worse', for brevity.

8.1. Risk of LD50 and Risk of LD95

The results obtained show that in the case of LD50, there is a good correlation between risk of LD50 and risk of DTL across a range of substances and types of site. In the case of LD95 a similar correlation exists, although it is not as good as that for LD50. The existence of these correlations poses a number of questions, particularly:
- Why does risk of death (LD50 or LD95) correlate to risk of DTL in this way (i.e., a function of the form $y = x^a/b$, see Eqs. (2)–(5))?
- Why should the results for different substances fall on the same curve?

The discussion below seeks to answer the first of these questions, using chlorine as an example:

8.1.1. Formulation of risk

At a given distance from the risk source, individual risk in given weather conditions may be expressed as:

$$\text{Risk at given distance} = \text{function}(\Sigma f_i \, p_w)$$

Where f_i are the event frequencies in the given weather conditions which contribute to the risk at this range (i.e., those with a long enough hazard range) and p_w is the probability of the weather category /wind-speed combination giving rise to a given hazard range. Note, therefore, that in RISKAT each event will give rise to four 'sub-events' corresponding to the four weather category/wind-speed combinations considered by the programme.

Hazard ranges for DTL are longer than those for LD50. Generally speaking, at a given distance there will, therefore, be fewer events contributing to the risk of LD50 than the risk of DTL. In the near field, however, nearly all events will contribute to both and therefore the two risk figures will converge, as is typically seen in risk-distance plots.

In seeking to explain the results obtained it will, therefore, be necessary to investigate hazard range relationships and event frequency relationships.

8.1.2. Hazard range relationships

Using the predictions of the dispersion code GASTAR [43] for a range of continuous and instantaneous chlorine releases, plots of hazard range versus release size (or rate) have been obtained (see Figs. 4–7). Again, plots of the type $y = x^a/b$ (where y is now the hazard range and x the release rate/size) are obtained, with very good correlations.

8.1.3. Frequency relationships

It is observed that, typically, small releases with low hazard ranges occur with a higher frequency than large releases with long hazard ranges. The next step of the investigation involved looking at this relationship in more detail by:
1. Taking a chlorine risk assessment and converting the various release rates to hazard ranges using the kinds of correlation derived in the 'hazard range relationships' section above (Section 8.1.2).
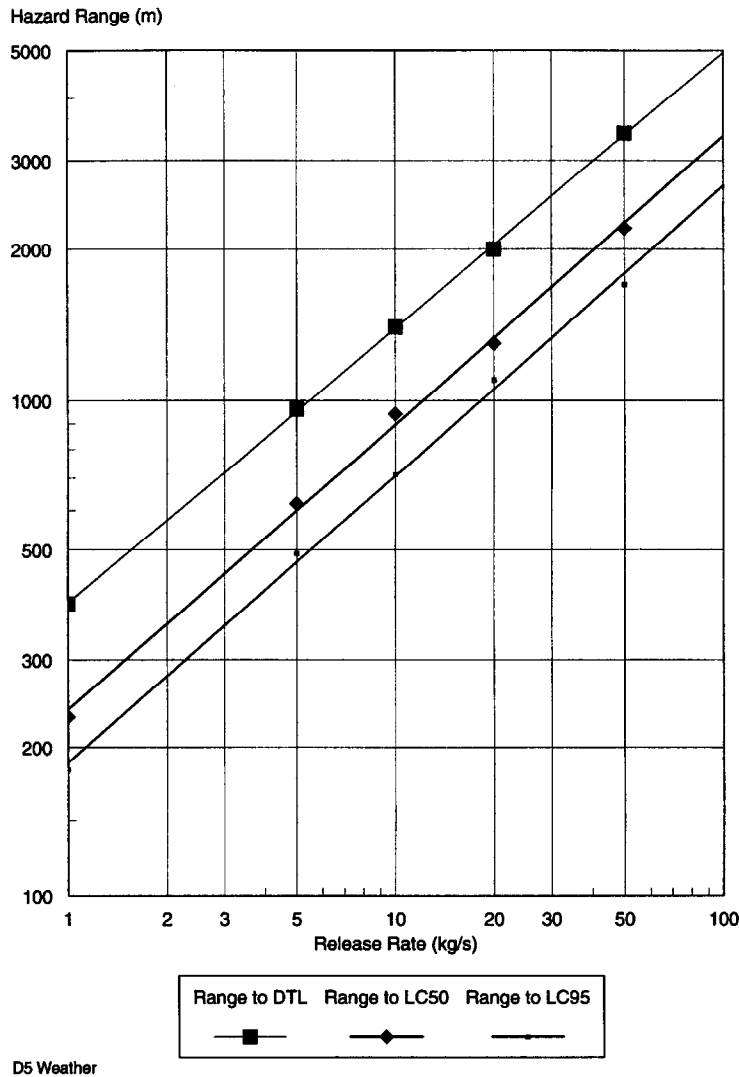
Hazard Range (m)

Fig. 4. Hazard ranges for chlorine 2-phase jets (D5 weather).

2. For a range of distances, calculating the sum of the $f_i p_w$ products that would contribute to the risk at that distance. To simplify the calculations only two weather categories, D5 and F2, were considered.

3. Plotting the 'cumulative frequencies' against range.

The results, for chlorine assessment 3, are shown in Fig. 8. Again, functions of the form $y = x^a/b$ may be fitted to the data, with reasonable correlation out to around 1000 m. The two regression lines obtained are also shown in Fig. 8.

8.1.4. Relationship between risk of LD50 or LD95 and Risk of dangerous dose

It is now possible to see why a $y = x^a/b$ relationship is obtained for risk of death against risk of dangerous dose.
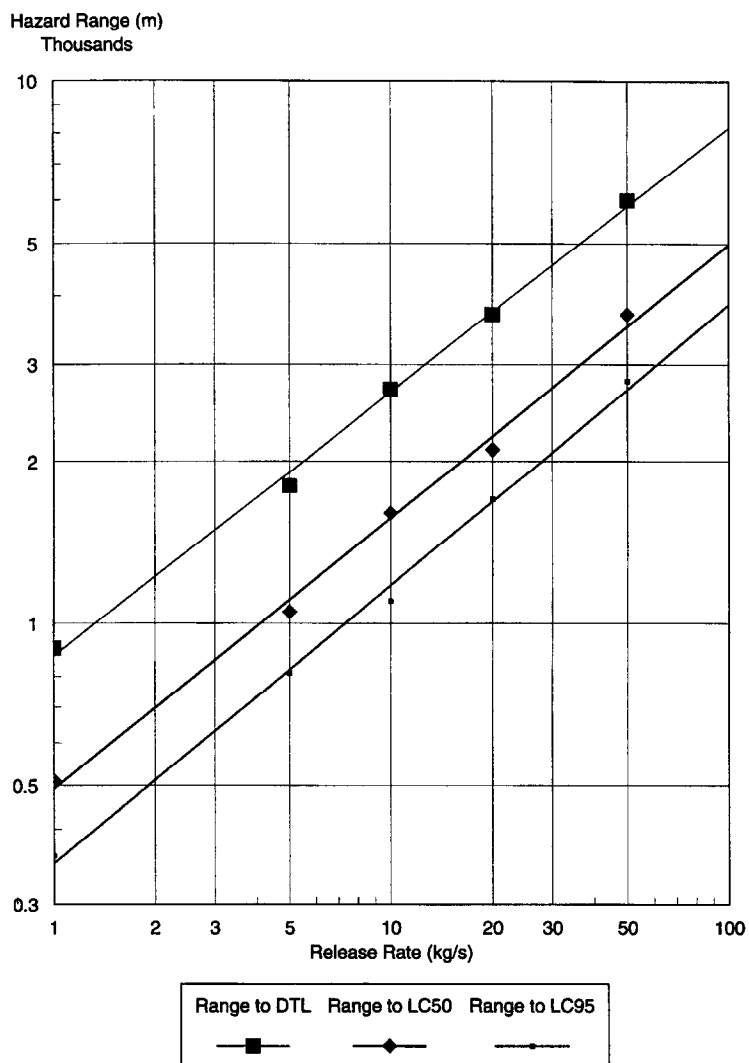
Hazard Range (m)
Thousands

Fig. 5. Hazard ranges for chlorine 2-phase jets (F2 weather).

If:

$$y = x^a / b$$

and

$$y' = x^{a'} / b'$$

Where y = 'cumulative frequency' for dangerous dose
y' = 'cumulative frequency' for death
x = distance
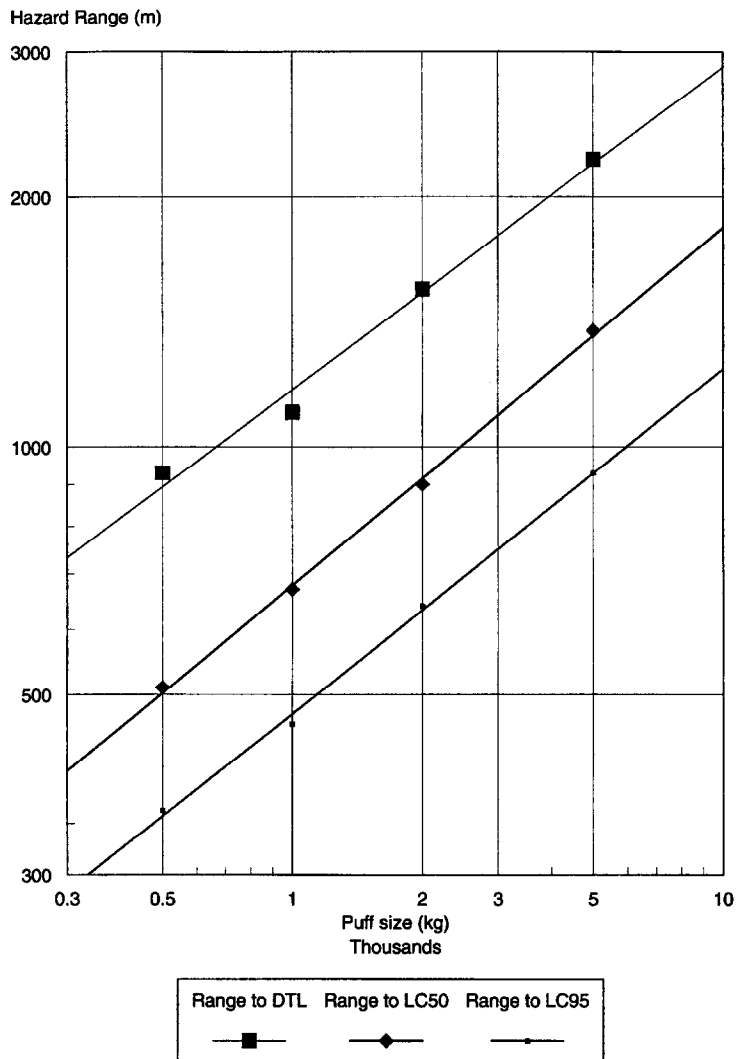
Hazard Range (m)

Fig. 6. Hazard ranges for chlorine puff releases (D5 weather).

then it is relatively simple to show that:

$$y = (y')^A / B$$

With

$$A = (a/d)$$

$$B = \{b'^{(a/d)}/b\}^{-1}$$

Which is a function of the desired form and remembering that risk is represented by y.
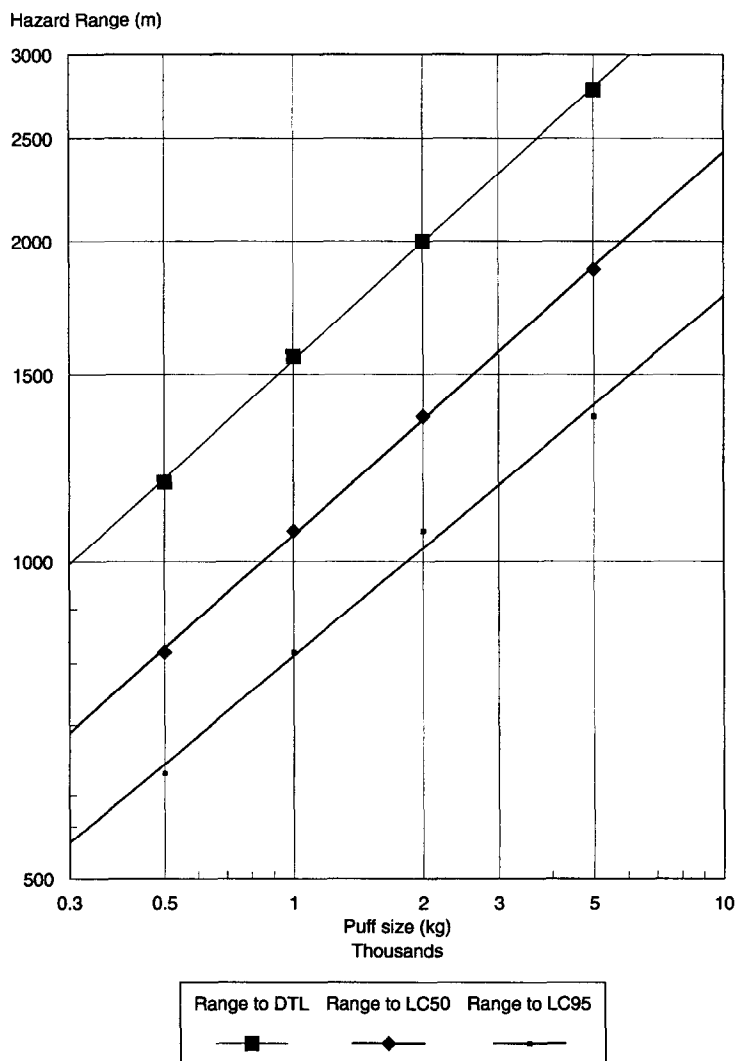
Hazard Range (m)

Fig. 7. Hazard ranges for chlorine puff releases (F2 weather).

From these initial investigations it appears that the $y = x^a/b$ relationship between risk of death and risk of dangerous dose arises from the way in which hazard range varies with release size (DTL hazard ranges being longer than LD50 hazard ranges) and the way in which the 'cumulative frequency' of events contributing to risk at a given distance varies with range (which in turn arises from the fact that, typically, small releases occur more often than big ones). Similar arguments apply to risks of receiving an LD95.

Deviations from this relationship may be explained in terms of features specific to a risk assessment. In the example chosen, for instance (see Fig. 8), the release scenarios

Chlorine Assessment 3
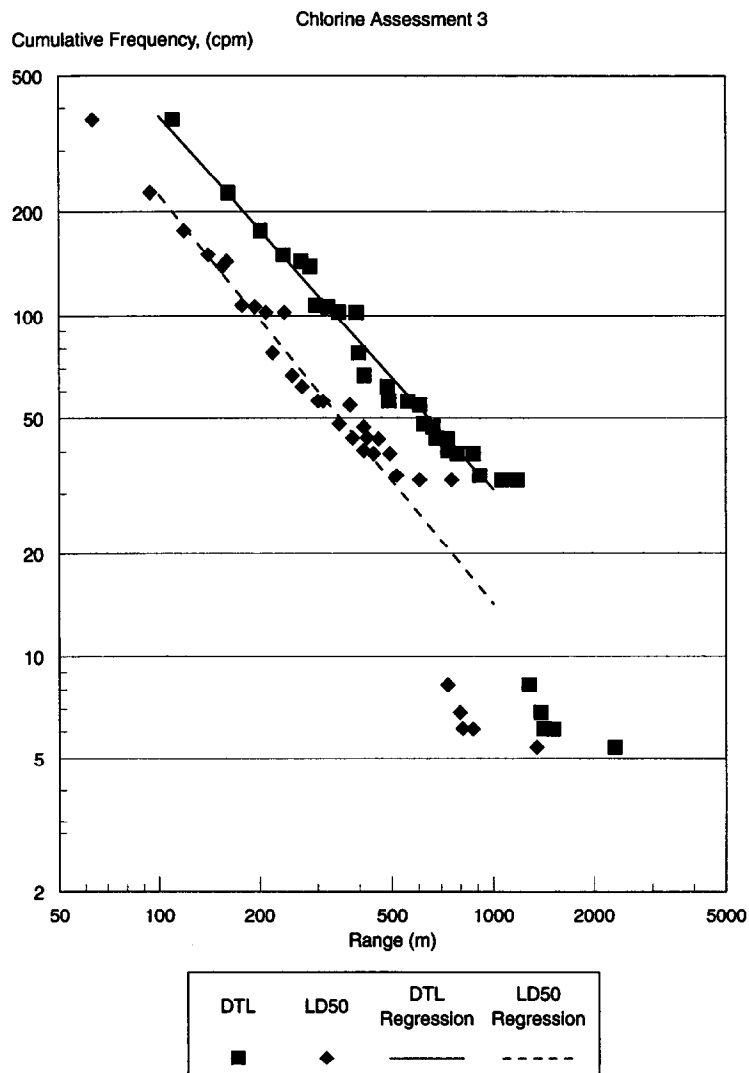
Cumulative Frequency, (cpm)

Fig. 8. Cumulative frequency versus hazard range for chlorine assessment 3.

fall into two categories—smaller releases occurring within a building and giving hazard ranges in the near- or mid-field and larger indoor releases or those which occur outside, giving rise to relatively long hazard ranges. This is reflected in the 'step' in the data seen in Fig. 8.

The proposed explanation may be tested by carrying out RISKAT runs to obtain risks of LD50 and risks of DTL for a hypothetical chlorine installation where the release rates and frequencies follow perfectly the kind of relationships described above. That is, the release rates follow a logarithmic progression (0.1, 1, 10, etc., $kg\,s^{-1}$) and with a logarithmic variation in release frequencies (i.e., the frequency of a $0.1\,kg\,s^{-1}$ release is
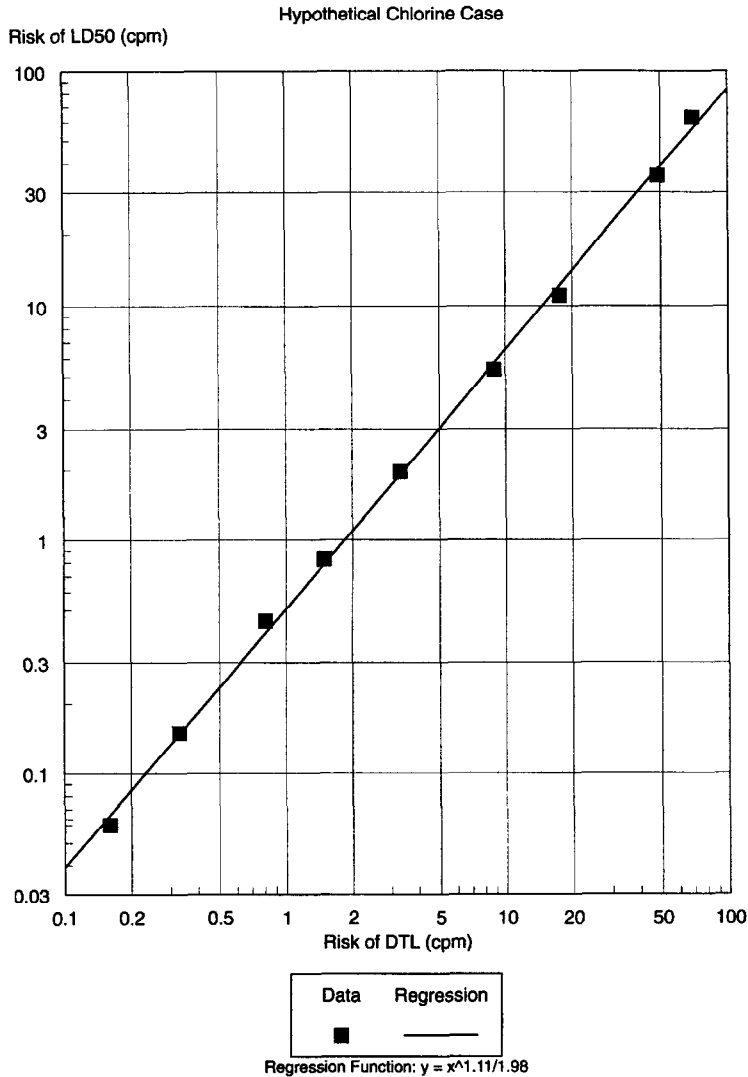
Hypothetical Chlorine Case

Fig. 9. Risk of LD50 versus risk of DTL for hypothetical chlorine case.

ten times that for a $1\,\mathrm{kg\,s}^{-1}$ release); and similarly for puff releases. According to the arguments above, the risk of LD50 or LD95 against risk of DTL plot should follow a $y = x^a/b$ type function almost perfectly. Indeed, this was found to be the case, as Figs. 9 and 10 illustrate. Regression analysis of these data gives:

$$\text{Risk of LD50} = (\text{Risk of Dangerous Dose})^{1.11}/1.98$$

R-squared value: 0.998725and:

$$\text{Risk of LD95} = (\text{Risk of Dangerous Dose})^{1.17}/3.16$$

R-squared value: 0.99682

Hypothetical Chlorine Case

Risk of LD95 (cpm)

Risk of DTL (cpm)

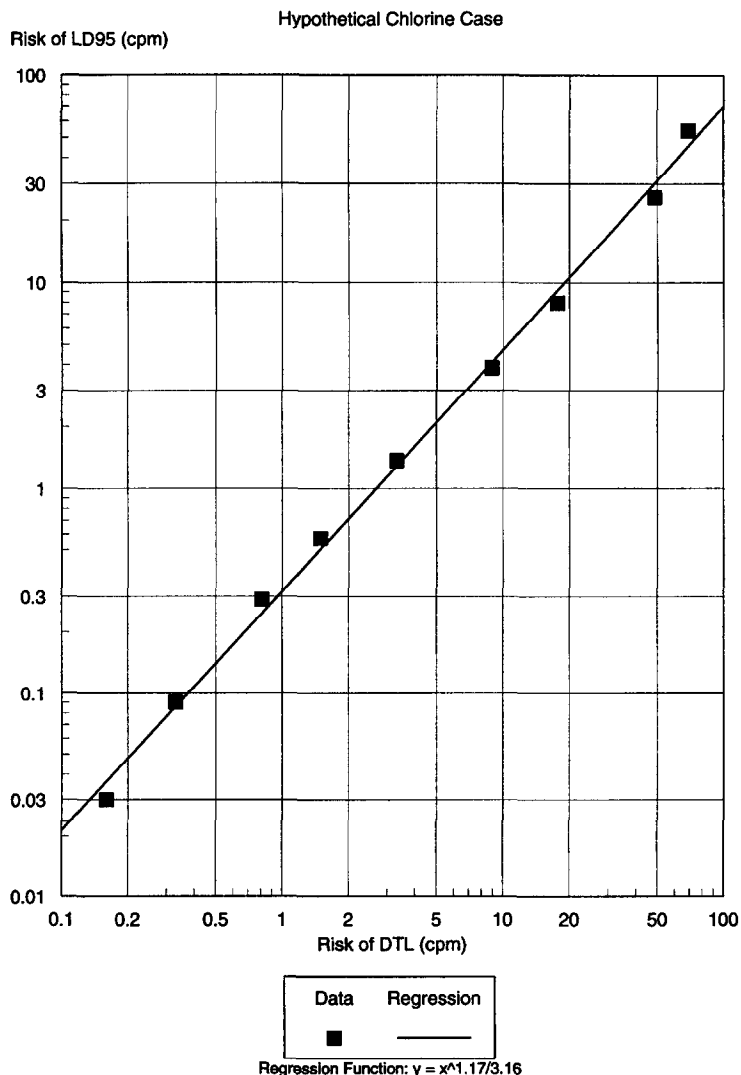| Data	Regression
■	———

Regression Function: y = x^1.17/3.16

Fig. 10. Risk of LD95 versus risk of DTL for hypothetical chlorine case.

An interesting result is now obtained if these lines from the hypothetical case are plotted with the 'real' data obtained earlier (see Figs. 11 and 12). It can be seen that the 'hypothetical' lines pass through much of the data, for both LD50 and LD95. The lines also lie above the lines obtained from the regression analyses of the data sets.

This relative location of the 'hypothetical' and regression lines is to be expected when it is considered that the scatter in the real data will tend to be in the downward direction and hence will pull downwards any line based on a regression analysis of the data. The downward trend in the scatter is due to the fact that the risk of LD50 or LD95 can never be higher than the risk of DTL.

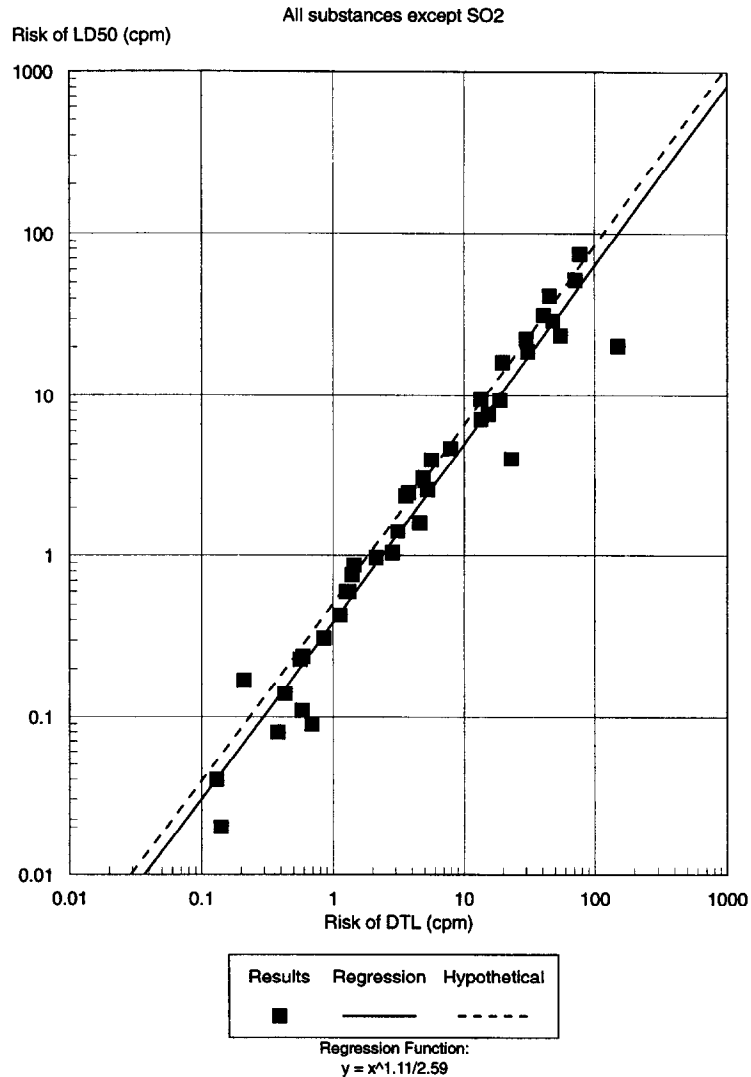**Risk of LD50 (cpm)**

All substances except SO2

Fig. 11. Risk of LD50 versus risk of DTL for all substances except sulphur dioxide.

It appears, therefore, that in answer to the first of the questions posed above, 'Why does risk of death (LD50 or LD95) correlate to risk of DTL in this way (i.e., a function of the form $y = x^a/b$)?', the response is that the relationship arises out of the way in which hazard range varies as a function of release size and how the frequency of an event varies with release size.

The second question, 'Why should the results for different substances fall on the same curve?', now needs to be addressed:
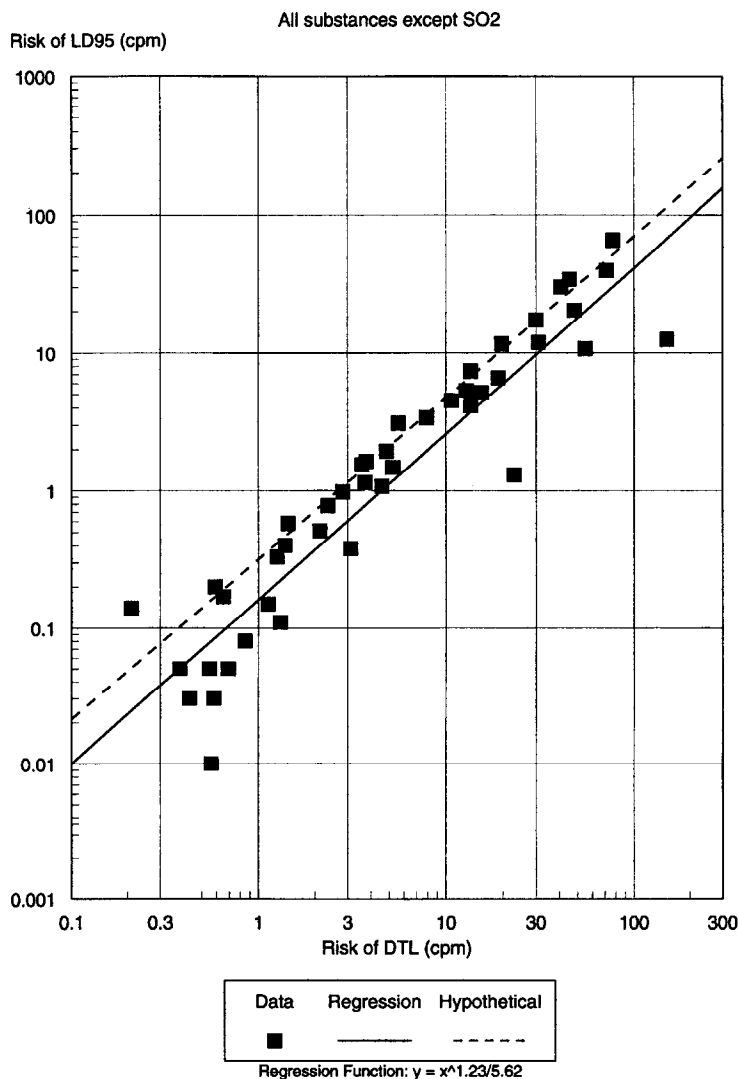
All substances except SO2

Risk of LD95 (cpm)

Risk of DTL (cpm)

Data	Regression	Hypothetical
■	——————	– – – – –

Regression Function: y = x^1.23/5.62

Fig. 12. Risk of LD95 versus risk of DTL for all substances except sulphur dioxide.

8.1.5. Variation of probit equation

On considering the analyses from a toxicological viewpoint a number of features emerges worthy of further discussion. The approach to the derivation of toxic loads (DTLs) in relation to Major Hazards used by HSE for toxic substances has been described above. A fundamental emphasis of this approach is the identification and use of data from a single study, preferably from human experience but most usually from an animal study in the most sensitive species, as is the case with the substances considered in the current analysis. It is important to bear this approach in mind when considering the outcome of the current analysis.

The similarity in the relationship between risk of DTL and risk of LD50 or LD95 for the different substances can be partly explained by the reasons given above but it is also noted that the substances under consideration have largely a similar mechanism of action (i.e. irritancy to the respiratory tract and lungs) and therefore a similarity in the relationships between risk of LD50 and risk of DTL may not be unexpected.

If one considers the ratios of LC50 to LC01 as derived from the single inhalation study data used in the derivation of the DTL for the substances in question, a fairly close range emerges of ~ 1.7–2.7 (see Table 2). This relatively small variation is perhaps to be expected since the data (i.e. LC50, LC01) used reflect the approach adopted of using only data from single studies to develop a position. Indeed, the observed similarity in these ratios has been remarked upon previously [19]. When the analysis introduces other probits which have generally been derived from pooled data, with some exceptions, from various studies and/or species then it can be seen that the variation in the LC50:LC01 ratio (where both the LC50 and LC01 have been calculated using the probit in question) is more marked, reflecting the increased variability that would be predicted from using such heterogeneous data sets. This is also reflected by the larger spread one observes in the relationship of risk of receiving an LD50 compared to that of receiving the DTL (e.g. see Fig. 3) when using probits derived in such a way. Overall, therefore, the use of a single data set as advocated in reference [19] provides a more consistent and apparently robust approach when performing the type of analysis considered here.

A final point worth considering relates to the use of LC95 compared to the DTL. It is noted that there is more scatter in such data (e.g. see Fig. 2 compared to Fig. 1) and the variation in the ratio LC95:LC01 was found to be greater. This is perhaps to be expected since an LC value is a statistically derived estimate of lethality and the LC95 lying near the outer bounds of the data set (with the need to extrapolate) will be subject to greater uncertainty and thus variation. In contrast since the LC50 lies at the statistical midpoint of the data-set, is subject to less uncertainty. This would suggest that the use of LC95 would result in more variability, as is observed.

It is therefore proposed that the similarity of the risk of LD50 against risk of DTL relationships observed for the different substances arises from the consistent way in which the toxicity data used have been selected and the similarity in toxic action of the substances under consideration.

9. Conclusions

Correlations have been shown to exist between risk of LD50 or LD95 and risk of dangerous dose which holds for a range of toxic substances and types of site. The correlations are:

$$\text{Risk of LD50} = \left(\text{Risk of DTL}\right)^{1.11}/2.59$$

and:

$$\text{Risk of LD95} = \left(\text{Risk of DTL}\right)^{1.23}/5.62$$

The form of the correlations is due to the way in which hazard range varies with release size and the way in which release frequency varies with release size. The coincidence of the curves for different substances is due, it is thought, to the method of selection of the toxicity data used and the similarity in toxic action of the these substances.

10. Further work

It is intended to repeat analyses of this type for other toxic substances, particularly those with a different mode of toxic action to those considered here (such as acrylonitrile). It is also intended to investigate further the relationship between risk of 'death' and risk of 'dangerous dose' or worse for thermal radiation and blast overpressure.

Acknowledgements

The views presented in this paper are those of the authors and do not necessarily represent those of the HSE.

References

[1] Health and Safety Executive, Risk Criteria for Land-use Planning in the Vicinity of Major Industrial Hazards, HMSO, London, 1989.

[2] HM Chief Inspector of Factories, Annual Report, HMSO, London, 1967.

[3] Lord Robens (chrmn), Safety and Health at Work, Cmnd 5034, HMSO, London, 1972.

[4] Health and Safety Commission, Advisory Committee on Major Hazards: First Report, HMSO, London, 1976.

[5] Health and Safety Commission, Advisory Committee on Major Hazards: Second Report, HMSO, London, 1979.

[6] Health and Safety Commission, Advisory Committee on Major Hazards: Third Report, HMSO, London, 1984.

[7] Health and Safety Executive, The Notification of Installations Handling Hazardous Substances Regulations 1982, SI 1982/1357, HMSO, London, 1982.

[8] Health and Safety Executive, Control of Industrial Major Accident Hazard Regulations 1984, SI 1984/1902. Amended 1988 (SI 1988/1982), 1990 (SI 1990/2325) and 1994 (SI 1994/118) HMSO, London.

[9] CEC, European Community Directive on the Major Hazards of Certain Industrial Activities, 82/501/EC, Off. J. Eur. Community, L230 (1982).

[10] EC, Proposal for a Council Directive on the Control of Major Accident Hazards Involving Dangerous Substances (COMAH). Off. J. Eur. Communities, 37 No. C106, (1994) 4–21. Council document 5542/94.

[11] Department of Environment, Planning (Hazardous Substances) Regulations, HMSO, London, 1992.

[12] Department of Environment, Planning Control for Hazardous Substances, Circular 11/92, HMSO, London, 1992.

[13] C. Nussey, Uncertainty in risk assessment, Proc. 4th Euredata Conf., Venice, March 1993.

[14] C. Nussey, M. Pantony and R. Smallwood, Health and Safety Executive's risk assessment tool, RISKAT, Trans. I. Chem. E., 71 Part B (1993) 29–40.

[15] C. Nussey, D.A. Carter and K. Cassidy, The application of consequence models in risk assessment: a regulator's view, Int. Conf. Mitigating the Consequences of Accidental Releases of Hazardous Materials, Sept. 1995, New Orleans, AIChE.

[16] D.A. Carter, D.M. Deaves and S.R. Porter, Reducing the risks from major toxic gas hazards, Proc. 8th Int. Symp. Loss Prevention and Safety Promotion in the Process Industries, June 1995, Antwerp.

[17] S. Porter, Risk mitigation in land-use planning, Proc. Conf. and Workshop on Modelling and Mitigation of the Consequences of Accidental Releases, New Orleans, 1991, pp 463–482, AIChE.

[18] Centre for Chemical Process Safety, Guidelines for Chemical Process QRA, 1989, AIChE.

[19] S. Fairhurst and R.M. Turner, Toxicological assessments in relation to major hazards, J. Hazard. Mater., 33 (1993) 215–227.

[20] D.J. Finney, Probit Analysis, Cambridge University Press, Cambridge, 1977.

[21] R.M. Turner and S. Fairhurst, Toxicology of Substances in Relation to Major Hazards: Acrylonitrile, HMSO, London, 1989.

[22] R.M. Turner and S. Fairhurst, Toxicology of Substances in Relation to Major Hazards: Chlorine, HMSO, London, 1990.

[23] M.P. Payne, J. Delic and R.M. Turner, Toxicology of Substances in Relation to Major Hazards: Ammonia, HMSO, London, 1990.

[24] R.M. Turner and S. Fairhurst, Toxicology of Substances in Relation to Major Hazards: Hydrogen Fluoride, HMSO, London, 1990.

[25] R.M. Turner and S. Fairhurst, Toxicology of Substances in Relation to Major Hazards: Hydrogen Sulphide, HMSO, London, 1990.

[26] R.M. Turner and S. Fairhurst, Toxicology of Substances in Relation to Major Hazards: Sulphuric Acid Mist', HMSO, London, 1992.

[27] M. Meldrum, Toxicology of Substances in Relation to Major Hazards: Nitrogen Dioxide, HMSO, London, 1992.

[28] M. Schlagbauer and D. Henschler, The toxicity of chlorine and bromine with single or repeated inhalation, Int. Arch. Gewerbepathol. Gewerbehyg., 23 (1967) 91–98.

[29] S.D. Silver and F.P. McGrath, A comparison of acute toxicities of ethylene imine and ammonia to mice, J. Ind. Hyg. Toxicol., 30 (1948) 7–9.

[30] J. Wohlslagel, L.C. Dipasquale and E.H. Vernot, Toxicity of solid rocket motor exhaust: effects of HCl, HF and alumina on rodents, J. Combust. Toxicol., 3 (1976) 61–70.

[31] M.D. Bitron and E.F. Aharonson, Delayed mortality of mice following acute doses of CH_2O, SO_2, Cl_2 and Br_2, J. Am. Ind. Hyg. Ass., 39(2) (1978) 129–138.

[32] R.M.J. Withers and F.P. Lees, The assessment of major hazards. The lethal toxicity of chlorine. Part 2, Model of toxicity to man, J. Hazard. Mater., 12 (1985) 283–302.

[33] W.F. ten Berge, A. Zwart and L.M. Appelman, Concentration–time mortality response relationship of irritant and systemically acting vapours and gases, J. Hazard. Mater., 13 (1986) 301–309.

[34] W.F. ten Berge and M. Vis van Heemst, Validity and accuracy of commonly used toxicity assessment models in risk analysis, 4th Int. Symp. Loss Prevention, Harrogate, 1983.

[35] A. Zwart and R.A. Woutersen, Acute inhalation toxicity of chlorine in rats and mice: time–concentration mortality relationships and effects on respiration, J. Hazard. Mater., 19 (1988) 195–208.

[36] HSC Advisory Committee on Dangerous Substances, Major Hazards Aspects of the Transport of Dangerous Substances, HMSO, London, 1992.

[37] M. Vis van Heemst, Estimating chlorine toxicity under emergency conditions, Chlorine Safety Seminar, Brussels, November 14–15, 1990.

[38] R.M.J. Withers, The lethal toxicity of ammonia—a report to the MHAP, IChemE N.W. Branch Papers, 1986 No 1, Manchester, January 1986.

[39] HSE, Canvey—An investigation of Potential Hazards from Operations in the Canvey Island/Thurrock Area, HMSO, London, 1978.

[40] K. Mudan, The use of toxicity data in quantitative risk assessment of HF alkylation units, AIChE Summer National Meeting, August 1989.
[41] W.W. Perry and W.J. Articola, Study to Modify the Vulnerability Model of the Risk Management System, CG-D-22-80, US Coast Guard, Washington DC, 1980.
[42] TNO, Methods for Determination of Possible Damage to People and Objects Resulting from the Release of Hazardous Materials, CPR 16E, Voorburg, December 1989.
[43] Reference Manual for GASTAR (GASeous Transport from Accidental Releases), Cambridge Environmental Research Consultants Ltd., Cambridge, England, 1996.