



Figure 3 Real and Image sources in cloud



QUANTIFICATION AS A MEANS OF CONTROL OF TOXIC HAZARDS

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The recent EEC Directive on Major Accident Hazards is criticised for its approach to the control of highly toxic substances. The paper discusses the importance of dispersive energy as a determining factor and uses five exemplars to show that the levels of EEC control inventories are highly anomalous.

An alternative set of criteria are advanced (1) Only toxics contained in pressurised systems shall be controlled (2) The inventory of such substances shall be, typically, 10^8 LD₅₀s but with lower levels for persistent toxics.

THE PURPOSE OF THE PAPER

The purpose of the paper is to examine, in the light of such quantitative tests as are available, the criteria which have been put forward in recent years for the control of major toxic hazards.

There is strong public pressure to control these major toxic hazards as part of the general major hazards problem.

The response to this pressure, by national and supranational authorities, has entailed first a qualitative approach, the identification of toxic agents, and then a quantitative approach, the establishment of control inventories. Where such inventories are exceeded at any given site, responsibilities, over and above that which normally devolves upon the occupiers of an installation which processes toxic substances, will then be imposed on them.

The discussion of the details of this extra responsibility would be outside of the scope of this paper. In the main it will take the form of stringent hazard and risk surveys and the establishment of appropriate managerial controls. This will be coupled with a high degree of state supervision.

Such measures are likely to be expensive both to industry and to the state and should be implemented only in situations of true major hazard. Reducing the level of the control inventory will increase the cost of the exercise and the law of diminishing returns will apply. To treat every chemical works as a major hazard would be to dissipate the resources which ought to be devoted to really serious problems.

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Thus the inventories ascribed to the different substances should realistically reflect the relative dangers, to public and employees, of the substances.

I propose, therefore, to examine a number of toxic agents in the light of such quantitative data as are available, to reach a judgement as to whether levels of inventory, currently proposed, are realistic and soundly based.

INTRODUCTION

I have written this paper in the first person to emphasise the fact that many of the views in it are my personal opinions. I have to express these personal views because I am writing in a field in which, in certain areas, there is a lack of general agreement.

The subject matter of my paper does not include any discussion of substances which poison by radioactivity.

The discussion is concerned only with acute initiating events, i.e. events which will normally have run their course in an hour or so. These acute events are the "major accident" hazards I shall refer to later. That the paper deals only with acute events is not in any way to argue that chronic toxic problems which affect the working environment or which give rise to atmospheric pollution are unimportant. Their control, however, is based on techniques which differ widely from those used for the control of acute hazards.

I shall use the term "hazard" to mean a physical situation with a potential for harm to life or limb or damage to property.

I shall use the term "risk" to denote probability. "Risk", unqualified, means the probability of the potential of a major hazard being realised at any given level of harm. "Societal risk" means the probability of any social group sustaining a given level of fatalities. "Individual risk" means the probability of an individual, living in a specified place, receiving fatal injury.

The units of risk are expressed as a number of events per annum in each case.

THE DRAFT DIRECTIVE

The EEC Draft Directive on "The major accident hazards of certain industrial activities" (1) is currently (October 1981) in suspense because of failure to agree on Article 9 which requires one Member State to notify another Member State of hazards on its territory which may affect the citizens of the other Member State. It is expected that once agreement is reached on Article 9 the Directive will then be adopted.*

Once adopted it would lay upon the Member States the duty to enact legislation which would enforce, taking account of differing national circumstances and pre-existing legislation in the Member State, the provisions of the Directive.

It is not possible for me to spell out the implications of the whole

* Agreement was reached in December 1981.

Directive in this paper; such a spelling out could occupy a whole conference.

Suffice it to say that the Draft Directive, which has many resemblances to the UK Draft Notification and Survey Regulations, (2) lists or defines certain substances, and specifies certain inventories.

If the inventories of these substances on a given site exceeds a certain level there would lie with the occupier of that site the duty to comply with certain procedures. These again, and speaking very broadly, would correspond with the "survey" requirements of Ref. 2 and are fairly onerous.

The Directive foresees three main major accident hazards. (I shall call these "major hazards" below as this is the term that is well understood in the UK), the major hazards of fire, explosion and toxic release. In this paper I shall deal, in detail, with major toxic hazards and not with the major hazards of fire and explosion.

It may be said with confidence that the concept of "Major Hazards" originated in the UK and that it arrived on the EEC scene as a consequence of the Seveso incident in 1976.

MAJOR HAZARDS IN THE UNITED KINGDOM

I do not propose to set out this history in detail but a number of stages in the development of the control of Major Hazards in the UK may be noted.

The first of these was the Department of the Environment Circular 1/72 (3) which was issued to guide local planning authorities. It defined a Major Hazard as follows, in Paragraph 5, "A major hazard is defined for present purposes as a situation where, if any incident occurred, there might be substantial loss of life or serious injury outside the confines of the work-place". (My underlining, VCM.)

Paragraph 5 goes on to say candidly, "Because of the fortunate lack of experience of major hazards in this country, the preparation of this list (the list of substances and their inventories annexed, VCM) called for some arbitrary assumption to be made about the materials likely to be concerned and the quantities of them which would constitute a major hazard". (These are listed, in part, in Table 1.) The Circular required Local Planning Authorities (LPAs) to consult the Factory Inspectorate (now the Health and Safety Executive, the HSE) about developments which involved major hazard sites. The Circular did not, however, tell LPAs how they could discover the sites which had on them the substances listed and in quantities in excess of the inventories shown. (This, incidentally, is a matter which at the time of writing is still not resolved. There is no statutory basis at present, though there may be soon, for LPAs or HSE to determine these facts.)

In my view one of the principal objects of quantification of hazards is to eliminate, so far as is possible, the arbitrary nature of the assumptions which had, perforce, to be made in 1972 in order to take the initial steps towards the setting up of planning controls over the establishment of major hazards sites or the intensification of hazards or such sites, or of developments in the neighbourhood of such sites.

I believe that quantification has developed considerably in the interim and has, on the whole, confirmed the soundness of Circular 1/72. But, as I shall show later, I believe that there are many grounds for regarding the inclusion of certain substances or of certain inventories, in the EEC Draft

Directive as being both arbitrary and unjustified.

The UK Major Hazards Committee (the ACMH) established in 1975 in the aftermath of the Flixborough Inquiry, drew up its own list (4) and established its own set of inventories as a basis for the Notification and Survey Regulations which have, in October 1981, yet to become law in the UK. These were established to provide:

a set of substances with their appropriate inventories (which I shall refer to from now on as "sub ventories") which would trigger off formal notification procedures and assist the HSE in carrying out their duty to advise local planning authorities;

a set of sub ventories (actually the substances as in the notification procedures but with ten times the inventory) to enable HSE to require formal proof that the occupiers of the site are sufficiently aware of their hazards and can demonstrate that they have adequate means of dealing with them.

These three sets of sub ventories are listed in Table 1 along with the Draft EEC sub ventories. The ACMH went further than Circular 1/72 and advised in its Second Report (4) that there should be two further categories of toxic substances at levels which were defined as follows:-

- (a) Toxic liquids or gases likely to be lethal to man in quantities less than one milligramme.
- (b) Toxic solids likely to be lethal to man in quantities less than one milligramme other than those which are and which will be maintained at ambient temperature and atmospheric pressure.

The notification level for these was set at 100 grammes and the survey level at 1 kilogramme.

THE DRAFT EEC APPROACH TO HIGHLY TOXIC SUBSTANCES

The EEC has gone further than the ACMH approach in:-

- (1) Drawing up an extensive list of more than one hundred highly toxic substances with inventories ranging from 1 kilogramme upwards.
- (2) Drawing up a set of criteria for very toxic substances based upon LD₅₀ or LC₅₀ (i.e. the lethal dose or concentration capable of killing 50% of a given animal population) for oral administration or inhalation in rats or for cutaneous administration in rats or rabbits.

The State of the Draft Directive

In its current form the Draft has an Annex III which lists 178 different substances, or in a few cases, classes of substances, with inventories ranging from 1 kilogramme to 50,000 tonnes and in mainly random order without regard to whether they are flammable, explosive, reactive, corrosive, carcinogenic or toxic or whether they are gases, liquids or solids.

Table 1 suggests some very rough degree of correspondence between ACMH survey levels and EEC Annex III levels, the most serious discrepancies being those of hydrogen cyanide and for sulphur dioxide. However, as I shall show later, these anomalies are slight when contrasted with the anomalies

presented by the highly toxic substances category.

THE QUESTION OF A VECTOR

There are some who, for one reason or another, seek to make the public's flesh creep with an announcement that a piece of x, the size of an orange, contains enough toxic material to poison the entire population of London, (or the United Kingdom, or the world).

Such statements are, however, largely meaningless as they afford no insight as to how the material is expected to gain entry into the bodies of so many millions of people. In short, there is no disclosure of the vector which will take the poison to the person.

To take an actual example, a dose of about 150 milligrams of chlorine has a 50/50 chance of killing an adult. Thus one tonne of chlorine can, theoretically, kill 3.5 million people. If we accept that in the gas attack at Ypres to be discussed later 1 tonne of chlorine killed 30 people it follows that 10⁵ fatal doses were released for every fatality at Ypres. (Much the same was true of bullets in that war.)

This argument aside, toxic substances need "dispersive energy" to get them to their victims. In liquefied or compressed toxic gases this dispersive energy is present as internal energy. In refrigerated gases it is put in, if they are spilled, as heat taken up from the surroundings. In liquids at ambient temperature, when this is below their atmospheric pressure boiling point, the energy may be present as potential energy, that is they flow to find their own level, or it may be pressure energy say from a pump and this may form jets.

With solids the dispersive energy is virtually zero and they are only dangerous if propelled, when in a state of sub-division, by a fluid possessed of adequate dispersive energy. This can happen, of course, when a reactor explodes or suffers a run-away exotherm involving a release through a vent.

We may, perhaps, classify toxics roughly in their order of magnitude of dispersive energy as follows:-

| | |
|---|-----------|
| Gases liquefied under pressure | (Highest) |
| Compressed gases | |
| Gases stored as refrigerated liquids | |
| Liquids under pressure | |
| Liquids at ambient temperature and pressure | |
| Solids | (Lowest) |

For equal toxicity this will represent the order of danger. In particular we should expect that liquefied gases would be far more dangerous than solids.

A CHOICE OF EXEMPLARS

I propose to choose a number of substances for which there is some degree of quantitative evidence as to the inventory level at which they would become major hazards which, as expressed in the Terms of Reference of the ACMH, "have the potential to present major hazards to employees, or to the public or the environment"

The exemplars I have chosen are chlorine, ammonia, arsenic, bis (2 chloroethyl) sulphide (mustard gas) and 2, 3, 7, 8 Tetrachloro di benzo p

dioxin (TCDD, Dioxin). I have chosen them because there is a relatively large amount of information about them. Tables 1 and 2 give certain basic data.

TABLE 1 - Comparison of Threshold Inventories for some Toxic Substances.

| Substance | Circular 1/72 | ACMH "Notifiable" | ACMH "Survey" | EEC Annex III |
|-------------------|------------------|----------------------|------------------|------------------|
| Phosgene | 5 | 2 | 20 | 20 |
| Chlorine | 25 | 10 | 100 | 50 |
| Acrylonitrile | 50 | 20 | 200 | 200 |
| Sulphur Dioxide | 50 | 20 | 200 | 1000 |
| Hydrogen Cyanide | 50 | 20 | 200 | 20 |
| Bromine | 100 | 40 | 400 | 500 |
| Ammonia | 250 | 100 | 1000 | 500 |
| Carbon Disulphide | Not listed | 20 | 200 | 200 |

The quantities given are either tons or tonnes; the difference between a ton and a tonne is too small to be significant here.

TABLE 2 - Basic Data on the Exemplars

| Substance | ACMH survey inventory | EEC Annex III inventory | State in normal industrial practice | Toxicity LD ₅₀ (mg/kg) | TLV (mg/m ³) |
|----------------|--------------------------|----------------------------|---|---|-----------------------------|
| Ammonia | 1000 tonnes | 500 tonnes | Liquefied gas | 350 Oral, Rat | 18 |
| Chlorine | 100 tonnes | 50 tonnes | Liquefied gas | 2* | 3 |
| Arsenic Oxides | | 100 - 500 Kg | Solid | 8 - 55 Oral, Rat | 0.05 |
| Mustard Gas | | 1 Kg | Liquid or solid | 9 skin, Rat 92 skin, Mouse 20 skin, Dog | |
| Dioxin** | | 1 Kg | Solid | 0.14 Oral, Mouse 0.022 Rat 0.115 Rabbit | |

* Deduced from LC₅₀ (lethal concentration when inhaled)

** LD₅₀ values for dioxin vary greatly with animal species being very much lower for small animals.

The values for toxicity quoted by the literature vary very greatly. Those quoted here are mainly from the NIOSH Registry. (5)

Animal Tests and Industrial Conditions

Animal tests are, of course, conducted on animals which are unable to take avoiding action, and there are wide differences in the significance to be attached to the data. For many substances only the oral route is significant, thus unless the victims ingest the toxic material, injury is not likely to ensue. For an acute event therefore speedy evacuation may successfully prevent harm from occurring.

The same is not true of toxic gases where, unless respiratory protection is available, injury is certain for anyone caught in a gas cloud.

Certain liquids, or even solids, lie somewhere between, in that injury may ensue by contact with the skin. Generally danger will diminish from gas to liquid and from liquid to solid.

I propose now to look at the exemplars in detail, starting with chlorine as the gas on which most data are available.

Chlorine

The properties of chlorine are fairly well known. It is a green gas, about 2.5 times as dense as air and when breathed in sufficient concentration this leads to immediate respiratory distress. Its TLV is 1.0 ppm by volume. Concentrations of 35 - 50 ppm breathed for 1 hour are expected to kill most people exposed and 1000 ppm will kill in seconds.

Chlorine is handled in industry as a liquefied gas. If containment be lost and liquid be spilled some 25 - 30% of this liquid will immediately evaporate and form a gas cloud. This cloud will travel with the wind being a heavy cloud initially but it will eventually become dilute by turbulent mixing until, at some distance down stream, perhaps a kilometre from the point of release, it will be harmless. The residual pool of liquid, at its atmospheric boiling point of - 34°C, will then evaporate at a rate determined by the rate of intake of heat from the surroundings and by the rate with which it mixes with air at the surface of the liquid.

Because of the large scale on which it is manufactured (about 30×10^6 tonnes per annum world wide) and its evident toxic properties, chlorine escapes have been made the subject of intense study. I would not hesitate to say that it is the most heavily studied toxic gas.

In addition it was used extensively as a poison gas in World War 1. For example, the April 1915 gas attack at Ypres, which took the undefended allied troops completely by surprise, is worthy of study. Here 168 tonnes of chlorine killed about 5,000 men, though it must be said that everything favoured high casualties. (I have discussed this more fully in my paper "How lethal are explosions and toxic escapes".(6) I recommend that more detailed study be given to First World War historical data.

Studies have been conducted on the amount of gas likely to arise from a spillage of any given magnitude; the theoretical adiabatic flashing fraction (TAFF) being about the only figure which can be calculated with accuracy. Even here it is almost impossible to determine how much additional immediate vaporisation occurs from contact with the relatively hot surroundings and how much contribution there is from spray or froth. Some authorities favour doubling the TAFF value for actual clouds.

A further stage is to calculate how the cloud develops and here a notable development has been the recognition of the density term. Previous models, such as the Pamela Bryant Model (7), which were based on neutral buoyancy, have now been discarded for the initial dense phase.

A recent review by McQuaid (8) summarises present approaches. In addition, trials at Porton Down UK have provided means for checking models against actuality.

However, the process is highly stochastic. Models have to have fed into them assumptions about atmospheric stability and wind speed and for any given community the direction of the wind at the time of release is of key importance.

In principle, however, it is now possible to calculate the concentration of chlorine at any given distance and its variation with time.

If we want, for any particular spot, to calculate the integral of concentration and time between limits of x seconds after release to y seconds after release, we will be involved in a chain calculation with a set of terms such as

$$+ [A][B]f[C](D)f[E](F)f[G](H)$$

where

- A = Source term (magnitude and rapidity of release of agent)
- B = Probability of a release of this magnitude and rapidity
- C = Speed of wind
- D = Probability that the wind will have this speed
- E = Atmospheric stability term
- F = Probability that this stability will obtain
- G = Wind direction
- H = Probability that wind will blow in this direction.

Even when these are evaluated there remain other terms such as the population density and the probability that the people affected can get indoors and seal themselves in etc., etc.

Unfortunately the final result cannot be more accurate than the accuracy with which any of the terms are known.

It is not surprising, therefore, to find very wide variations in the values obtained for societal and individual risk. (For an example of the end results of the use of these methods see the Canvey Report.(9))

However, with chlorine there is a good deal of historical evidence and this enables the end result of any such calculations to be compared with the Mortality Index concept I first developed in Ref. 6.

The ACMH Second Report (4) quoted a Mortality Index for chlorine of 0.33, i.e. 3 deaths per 10 tonnes spilled. This figure is much lower than

some theoretical predictions would lead us to expect. And it is made up almost entirely of employees, not the public.

A variant on the Mortality Index is to ask the question, "If the societal risk and individual risk as calculated for a given location are correct, what would be the implications on a world scale for the 1000 or so chlorine installations we know exist throughout the world?"

An individual risk of 1 in 10^6 years sounds low. But how many people in the world live within a kilometre of a major chlorine installation?

A 1 kilometre circle from a chlorine plant is about 3 sq. kilometres. Allowing that 2 of these are in the factory this leaves 1 sq. kilometre for housing. Accepting a density of 4,000 per sq. kilometre (the figure assumed for Canvey Island (9)) the number of public deaths per annum should be:

$$\text{No.} = P \times Cl_n \times I_R$$

$$\text{where } P = \text{population exposed} = 4 \times 10^3$$

$$Cl_n = \text{Number of major chlorine installations in the world} = 10^3$$

$$I_R = \text{individual risk} = 10^{-6}$$

This would suggest 4 members of the public would be killed per year from chlorine released from factories. I would think, looking at Table A in Ref. 4 that the figure is less than one (107 deaths from factory releases in 60 years, and probably 90% were employees, this is about 1 person in 6 years).

This line of argument would suggest that the individual risk is less than 1 in 10^6 years and is nearer 1 in 10^7 years.

Harris (10) has provided a graph which suggests that over recent years chlorine fatalities (including transport) average about 1 death per year for employees and public. However, the recent Mexico rail accident of 1st August 1981 which killed 17 will perturb this statistic.

Thus if we take chlorine as an exemplar we might expect the spillage of an EEC Annex III inventory of 50 tonnes to lead to about 15 fatalities with 1 - 2 being sustained by the general public. The risk of such an occurrence in a factory is very small, if we take all factory spillages, from 2 tonnes upwards there have only been 11 recorded in 64 years. (4) It is of interest that of the 11 cases of chlorine spillages in factories quoted in Ref. 4 only 1 involved a spillage greater than the EEC Annex III inventory.

Ammonia

Whereas Ref. 4 records 17 major chlorine leaks it records only 11 major ammonia leaks. Ammonia can be seen from Table 2 to have a toxicity only about 1/200 of chlorine. Though the formula NH_3 suggests that ammonia is much lighter than air, there is ample evidence that when anhydrous liquid ammonia is spilled it behaves initially as a dense gas. However, this dense gas behaviour is likely to be less persistent than is the case with chlorine.

Comparison of mortality indices shows that the M_T for ammonia is only 0.02/0.30 i.e. 1/15 of that of chlorine which is about an order of magnitude worse than we should expect from the ratio of their toxicities. The ACMH and EEC inventories for ammonia as related to chlorine, i.e. at about 10 of

NH_3 to 1 of Cl_2 , appears to relate more closely to the M_T ratio than to the toxicity ratio. It should be remembered that this relates only to ammonia liquefied under pressure. Refrigerated ammonia at, or around atmospheric pressure, is much less dangerous.

In my view, because of the very narrow data base for the other gases listed by the ACMH, the most fruitful course will be to study chlorine and ammonia releases and to attempt to relate the other gases to them by comparing toxicity, TAFF and cloud buoyancy.

Arsenic Oxides

Table 2 shows arsenic oxides to be appreciably less toxic than chlorine and, taking into account the consideration that arsenic oxides are solids whereas chlorine is a liquefied gas, we would expect that arsenic oxides be regarded as much less dangerous than chlorine and merit a much higher inventory than for chlorine. What the table shows is that the EEC Annex III regards arsenic oxides to be 100 to 500 times as dangerous as chlorine! But how does this accord with historical experience?

There was a spillage at Manfredonia, Italy, on 26th September 1976. Here effectively 10 tonnes of arsenic oxides and 18 tonnes of potassium oxide were released in an incident in which a scrubber column in an ammonia synthesis plant, working at 26 bars, burst (see Ref. 11).

Alkaline arsenic compounds were discharged over an area of 10 sq. kilometres. There were no human fatalities. Of 200 persons examined 30 cases of slight arsenic poisoning were noted. Only 5 were employees; 120 employees were present on the site at the time of the explosion.

There were some 700 large farm animals in the region, none of which suffered permanent harm. Some 1,500 chickens and rabbits were slaughtered. The incident cost over $\pounds 1 \times 10^6$ to clean up.

In my opinion this single historical example, involving 10 tonnes of arsenic compounds, does not, in any way, justify an Annex III inventory of 100 - 500 kilograms.

It will be noted that the vector was a gas mixture initially at a pressure of 27 bars.

Mustard Gas

The toxicity of mustard gas, bis (2 chloro ethyl) sulphide, can be seen from Table 2 to be less than that of chlorine when administered through the skin and to correspond roughly with that of arsenic oxides.

When administered through the skin it raises painful blisters. It was extensively used in World War 1 because of its persistence (it is relatively involatile) and it had a high ratio of non-fatally injured to fatally injured. A valuable source of information on the toxic effects of war gases is Prentice (12) and Table 3 is derived from this reference.

What this table shows, though its conclusions must be treated with caution as the data can hardly be very accurate, is that mustard gas, whatever its military virtues in denying territory to an enemy, was far less lethal than chlorine, phosgene or chlorine/phosgene mixtures. (The mortality for phosgene is appreciably lower than would be expected from laboratory

studies. I attribute this to its low value of TAFF which is virtually zero in winter and thus there is only a weak vector.)

This information, which represents the most extensive data we possess, would seem to justify a higher level of inventory than for chlorine. Instead Annex III gives an inventory of 1 kilogram for mustard gas, thus rating it as 5×10^4 times as dangerous as chlorine. Nothing in the historical experience gives the slightest justification for this rating.

Dioxin

The 1976 Seveso incident, which is very fully reported in Ref. 11 and summarised in Ref. 13, involved the release, after a run-away reaction, of about 2 - 3 kilograms of dioxin (2, 3, 7, 8 Tetra chloro dibenzo p dioxin or TCDD).

This incident is widely regarded as having been chiefly responsible for producing the EEC Draft Directive as a result of public pressure in Italy.

The vector in this case was several tonnes of phenolic and other organic vapours which were vented after a run-away reaction.

There were no fatalities and, so it is claimed, no foetal damage. (14) However it led to the deaths, namely as the result of slaughter, of many farm animals, including 80,000 poultry.

733 people had to leave their homes semipermanently and the use of land for ordinary husbandry was forbidden for a time to some 27,000 people. Though 477 people were burned by contact with contaminated surfaces only 34 of these were subsequently found to be suffering from chloracne, the characteristic symptom of exposure to dioxin. On the other hand a number of persons were found to have contracted chloracne in some degree without a previous history of burns. Only a small proportion were severe cases. However, chloracne is only one symptom and other internal disorders usually accompany it.

Extensive, and so it would appear, inconclusive investigations were conducted into foetal deaths, abortions and malformations and also into the general death rate. (11)

The area affected most severely was about 3.5 sq. kilometres in extent and the general cost of the disaster was about £70 million (1976).

It may be noted that dioxin is characterised by high thermal stability (up to 800°C) and great persistence in soil. Soil samples initially showed mean values of up to $580 \mu\text{g}/\text{m}^2$. The "half life" of dioxin in the soil was found to be 2 - 3 years though the literature had suggested about one year.

The Report (11) contains information on some 13 cases prior to 1976 in which factory workers were exposed to dioxin, 9 were acute events, 5 were cases of occupational exposure. Over 500 persons were affected by unstated or unknown quantities of dioxin and it seems possible that 3 people have died from occupational exposure. (15)

A major follow up of the Nitro, West Virginia 8/3/49 explosion which affected 282 employees, of whom 121 contracted chloracne, provided no evidence for long term ill effects. (16)

TABLE 3

| Agent | No. of battles in which used | Tonnage | Killed | Non-lethal Injury | Mortality Index M_I | Non-lethal Casualty Index NLCI |
|-------------------------------|------------------------------------|---------|--------|----------------------|-----------------------------|---|
| Chlorine | 7 | 1,209 | 7,312 | 25,483 | ca 8 | ca 24 |
| Phosgene | 4 | 828 | 2,227 | 9,568 | ca 2.5 | ca 12 |
| Chlorine/ Phosgene Mixture | 23 | 2,835 | 16,946 | 56,801 | circa 6 | ca 20 |
| Mustard Gas | 8 | 10,002 | 1,342 | 57,548 | circa 0.15 | ca 5.75 |

Holmstedt (15) has concluded, "Based upon the many human accidental exposures, it is fair to assume that TCDD has a low acute toxicity to man compared to certain animal species, e.g. the guinea pig." (Ref. 11 shows considerable variations (2 orders of magnitude) between one animal and another.)

The Translation of the Official Report (11) has 81 pages of references to dioxin, totalling between 650 and 700. Virtually all of these are scientific, i.e. are related to the chemistry of dioxin or are toxicological, medical, veterinary or biological studies.

There are virtually no engineering studies. None of the case studies I have seen, apart from some studies of Seveso, make any attempt to estimate the quantity of dioxin released in the particular incident. I have estimated in Ref. 13 that the quantity involved could not have been less than 0.25 kilograms. Cattabeni et al (17) estimate that between 0.45 and 3 kilograms were released.

All of this makes quantification difficult. And even if we know more about the quantities released what conclusions could we come to? If a major hazard be measured by potential fatalities the proposed level for dioxin of 1 kilogram appears well below the level which could cause multiple fatalities. If measured in financial terms Seveso cost £30 - 50 million per kilogram. This figure is perhaps only an order of magnitude less than the damage index of U_{235} ! And, in other ways, dioxin resembles radioactive fall out, both in relation to the small quantities necessary to produce adverse symptoms, and the persistence of the phenomenon.

CONTROL BY MEANS OF THE "NUMBER OF FATAL DOSES" CONCEPT

An alternative method of controlling high toxic substances would be to retain the listing of inventories of the common toxics manufactured in bulk such as chlorine, ammonia etc. and to add a general provision that any pressure system, which upon loss of containment may release as vapour, aerosol, fume or smoke a quantity of toxic material equivalent to, or exceeding, X unit LD_{50} doses, shall be subject to the same requirements as the common toxics. The number of LD_{50} s should take account of the various constituents which would make up a cloud and also take account of fault conditions such as occurred at Seveso.

The adoption of these criteria would obviate the need to compile and update long lists of highly toxic substances, it would take account of the vast range of values for LD_{50} and it would accord with the spirit of self regulation as it would lay upon the occupier the duty to ascertain LD_{50} values for material in process or likely to arise under fault conditions. It would also satisfy the condition that a vector is a prime necessity.

As a basis for discussion I would suggest that X should have a value of 10^6 .

The present EEC inventories, expressed as numbers of LD_{50} s are set out in Table 4.

* LD_{50} is the index of toxicity. It is the dose, expressed as milligrams per kilogram of body weight which will kill 50% of an exposed population. Thus a unit LD_{50} is the dose in mg. which would kill 50% of a population of animals each weighing 1 kg. and with a susceptibility equal to that of the animal species on which the LD_{50} value had been determined.

TABLE 4 -

| Substance | No. of unit LD_{50} s in inventory |
|----------------|--------------------------------------|
| Ammonia | 1.4×10^9 |
| Chlorine | 2.5×10^{10} |
| Arsenic Oxides | 2×10^6 to 6×10^7 |
| Mustard Gas | 10^4 to 10^5 |
| Dioxin | 7×10^6 to 5×10^7 |

GENERAL CONCLUSIONS

The quantification of major hazards is a science which is still in its infancy.

Some theoretical studies have been conducted, mainly around chlorine, and these, combined with experimental work currently in progress may produce, in the fairly near future, fairly reliable models for predicting the development of clouds under varying conditions of wind speed and atmospheric stability. The risks so deduced, for any given community, are expressible only in statistical terms and must show considerable variance.

But the population behaviour term is not deducible from dispersion models, and has to be quantified separately. In open country it may be possible to make a theoretical appraisal but it is much more difficult to assess it in a built-up area where houses provide a fair degree of protection.

Against all this is the yardstick of historical experience, expressed as the mortality index. Generals learned in the First World War that poison gases were not a wonder weapon and that, tonne for tonne, chlorine and phosgene were not all that superior to high explosive as a means of killing people. I would advocate deeper study of the experiences of the First World War as a means of quantifying the likely effects of the common toxic gases.

I believe that the inventory levels for chlorine and ammonia (and other common toxic gases made on a large scale) as worked out by the ACMH and the EEC make approximate common sense; they correspond to fatality levels in the 10 to 50 region of which perhaps 1 - 5 would occur among the public.

I do not believe that the level of inventory quoted for mustard or arsenic compounds makes any sense at all.

I advocate that, in general, the control of highly toxic substances would best be accomplished by requiring special controls of pressurised systems containing more than unit 10^8 LD_{50} s.

However, in view of the special problems associated with dioxin,

especially its persistence, the figure might be set, for this substance, at a lower level of 10^7 LD₅₀s or even of 10^6 LD₅₀s. The way could be left open for other substances to be similarly treated as special cases where persistent widespread contamination may be demonstrated as a likely consequence of uncontrolled release.

SYMBOLS USED

- Cl_n = number of chlorine installations in the world.
 I_R = individual risk expressed as probability of suffering death in unit time (10^{-6} years).
 LD_{50} = Dose which kills 50% of exposed population (mg/kg)
 M_I = mortality index (Tonnes⁻¹)
 NLC_I = non lethal casualty index (Tonnes⁻¹)
 P = number of population exposed

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INTRODUCTION

The effects of explosions at a distance are those due to shock waves in air, the ground or in water. In respect of major hazards the region of principal interest is the field somewhat remote from the origin. It is not proposed therefore to deal in this paper with effects such as cratering and damage caused in the immediate vicinity of the explosion.

First, propagation of shock waves in air, the ground and in water will be considered. In respect of propagation in air in particular there is considerable difference between that from a condensed explosive and that from a large unconfined cloud; these will be considered separately.

Second, the interactions of shocks with structures will be outlined; to define the loading to which a structure may be subjected, and the consequences.

SHOCK WAVES IN AIR

A shock wave in air, whatever its initial structure, tends to transform itself into the simple form known as an ideal shock wave. This follows from the properties of air as a compressible gas, regardless of the source the front of a pressure disturbance steepens as it travels through the air, a process known as 'steepening-up'.

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