

Assessment of Toxic Risks from Warehouse Fires

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This paper describes a method of assessment of toxic risks from warehouse fires. Such assessments will allow operators of enclosed stores containing toxic materials to judge the level of risk to nearby populations in the event of fire. This analysis is important both in developing mitigation strategies and in demonstrating that risks have been reduced as low as is reasonably possible. The production of risk assessments covering toxic fire fume can be required as a duty under Health & Safety at Work and COMAH regulations but there has been little available in the literature to guide the work.

This paper draws on the (often painful) experiences of operators, consultants and regulators over a period of more than 25 years to develop methods that are appropriately reliable but straightforward enough to be applied without excessive effort/expense. The method described aims for simplicity and transparency, even if the price for this is that the method uses assumptions that have to be made that introduce a level of conservatism.

Keywords (warehouse, toxicity, fumes, source term, dispersion)

Disclaimer

This paper and the work it describes were funded by the UK Health and Safety Executive (HSE). Its contents, including any opinions assumptions and/or conclusions expressed, are those of the authors alone and do not necessarily reflect HSE policy.

Introduction

This report describes a method for the assessment of acute risks from fumes during fires at chemical warehouses. The assessment of warehouse fires is potentially a very complex task because of the wide range of chemical and physical processes that occur and because key variables such as the site of ignition are not normally known in advance; so that the total number of fire scenarios is very large. The assessment has to be simplified: a small number of scenarios have to be chosen to reasonably but conservatively represent the whole. The method aims for simplicity and transparency, even if the price for this is that duty holders adopt the assumptions made to introduce a level of conservatism or can substitute their own. The assessment is modular and if the user finds that the method is appropriate apart from simplifying assumptions made in one stage then it is possible to substitute a more detailed analysis that reflects their actual circumstances.

The method deals with airborne risks to people, who live or work close to the site, during a 30 minute period in the early stages of a fire. It is assumed that after this period those affected by the smoke plume will have been able to escape or will have been helped to evacuate. The method does not deal with environmental risks associated with airborne releases or any other type of environmental risk e.g. from fire water run-off. The method does not cover risks associated with the mixing of incompatible materials in the course of a fire (e.g. cyanides and acids, hypochlorites and acids) or risks from explosions during warehouse fires.

This method may assist duty holders and their risk practitioners that carry out risk assessments of fire fume for chemical warehouses where these assessments are required.

The method comprises the following 10 modules:

- Module 1: Screening Test – a simple conservative method for low risk sites
- Module 2: Organising and presenting inventory data
- Module 3: Calculating convective heat flow and toxic mass flow
- Module 4: Dispersion calculation
- Module 5: Source terms for warehouses without planned ventilation in the event of fire
- Module 6: Source terms for nitrate stores
- Module 7: Source terms for chlorine producers
- Module 8: Warehouse with high proportions of heteroatoms (Cl, P or S)
- Module 9: Linking the results of dose calculations to harm
- Module 10: Incident frequency analysis

These approach taken in these modules is described in this paper.

MODULE 1: Screening Test

The purpose of this initial module is to provide the simplest possible screening calculation to determine whether the risk of death or injury from inhalation risks from the dispersal of stored toxic materials are in fact significant or whether fires can be regarded as similar to warehouses that do not store such chemicals. The following inputs are required:

1. The warehouse width W (m) and wind speed U (m/s)
2. The total acutely toxic mass M_{toxic} (kg). This is the total mass of products classified for acute human toxicity (inhalation or ingestion¹) as Category 1, Category 2, Category 3 or Category 4 in the Classification, Labelling and Packaging (CLP) Regulations [European Chemicals Agency].
3. The category of the most acutely toxic stored product in the CLP regulations (inhalation or ingestion).

With conservative assumptions about: the timing of involvement of the toxic; the proportion of material seeded into the fire plume “ f ”, buoyancy of smoke etc., a toxic index can be derived as follows - see Table 1 for values of ATE(mg/l).

$$\text{Toxic Index} = \frac{0.59}{U \times W^2} \cdot f \cdot \frac{M_{\text{toxic}}(\text{kg})}{1800(\text{s})} \cdot \frac{1000}{\text{ATE}(\text{mg/l})} \cdot \frac{1}{2} \quad \text{For screening } U \text{ should be assumed to be } 10 \text{ m/s and } f \text{ to be } 0.1$$

Table 1 : Values for Acute Toxic Estimate ATE (LC₅₀ – 4 hour) to be used in screening

Highest classification for acute toxicity Category 4 (Hazard Statement H332, H302)	1 mg/l
Highest classification for acute toxicity Category 3 (Hazard Statement H331, H301)	0.5 mg/l
Highest classification for acute toxicity Category 2 (Hazard Statement H330/2, H300/2)	0.05 mg/l
Highest classification for acute toxicity Category 1 (Hazard Statement H330/1, H300/1)	Lowest value of ATE (LC ₅₀ – 4 hours)

If the warehouse contains products classified as Category 1 for toxicity and values of LC₅₀ are not given in the MSDS then LC₅₀ can be estimated from a quoted LD₅₀ as follows [Fairhurst and Turner]

$$\text{LC}_{50} \text{ 4hour (mg/l)} = 0.014 \times \text{LD}_{50}(\text{mg/kg})$$

If the toxic index is less than unity there is almost no chance that a SLOTT (**Specified Level of Toxicity**) dose will be accumulated even by those very close to the warehouse. A SLOTT dose corresponds to [HSE]:

- Severe distress to almost everyone in the area;
- Substantial fraction of exposed population requiring medical attention;
- Some people seriously injured, requiring prolonged treatment;
- Highly susceptible people possibly being killed (of order 1% of a typical population)

Given the highly conservative nature of this simplified assessment (e.g. it is based on the assumption that there will be no plume lift-off) any warehouse with a toxic index less than 1 (and with planned vent area in the event of fire in excess of 20 m²) will be low risk and will not require further detailed analysis because of dispersal of stored toxics. Note other types of analysis might still be required for example:

1. The production of toxic combustion or decomposition products e.g. HCl, NO₂, Cl₂. This kind of assessment is covered in Modules 7 and 8.
2. Analysis of the environmental impact of fire water run off or other environmental risks.
3. Warehouses with less than 20 m² of planned fire ventilation will require additional analysis for emissions from ventilation controlled fires (Module 5).

A toxic index greater than 1 **does not** necessarily mean that a warehouse represents a significant toxic risk from dispersal of stored materials but additional analysis based on the individual circumstances will be needed in the assessment.

MODULE 2: Organising and presenting inventory data

The purpose of this module is to gather and present information on the amounts and toxicity of various products and the proportion that might be dispersed by a fire. If the inventory is complex this may be the most difficult part of the assessment.

¹This is potentially a significantly conservative approach because the only significant route in the context of warehouse fires is inhalation. Some products have been shown by testing to be more toxic by the ingestion route than by inhalation. In other cases inhalation risks are dismissed in SDSs on the ground that the product (e.g. a biocide formulated as a granule) cannot be inhaled in normal use. In some case (e.g. sintered metal pellets) there is no potential for inhalation under fire conditions but in general the physical form of the product may change radically in fire conditions: it is appropriate to assume as a general rule that high oral toxic implies high inhalation toxic unless there is specific toxicological evidence to the contrary.

DISCOUNTING PRODUCTS: Toxic materials that are not combustible and are stored in non-combustible packaging will not contribute to fumes if they are:

- segregated horizontally from combustible materials by a distance of more than 3 m (racked storage > 2 levels) or 2 m (ground level storage) and
- isolated from burning pools caused by leakage from other goods in a large fire.

The latter conditions will normally **not** be satisfied if the warehouse also contains significant stocks of combustible liquids in plastic IBCs and drums.

DISPERSAL FRACTIONS: The proportion of stored various types products that could be dispersed by a fire (=“f”) has to be estimated. Appendix 1 gives guidance on this: the recommended proportion of a stored toxic that is dispersed varies between 0.1% and 10%. The dispersible mass DM_i of a particular toxic material is simply the total mass M_i multiplied by f .

ACCOUNTING FOR PRODUCT TOXICITY: This can be done using the classification of products in the CLP (Classification, Labelling and Packaging) regulations. The simplest and most conservative method involves assuming that the toxicity of a substance is the upper limit of its toxicity category in CLP. The 4-hour LC50s assumed here are taken from Table 1. New definitions of harm level (SLOT=injuries and SLOD=deaths) are required that are based on CLP data rather than HSE A values [HSE]. The following definitions are used to ensure that the new values are as similar as possible to the HSE definitions:

New definitions of SLOT (exposure causing injury)

$$SLOTconc\left(\frac{mg}{l}\right) = \frac{LC_{50}(30min)}{4} \quad or \quad SLOTconc\left(\frac{mg}{l}\right) = \frac{LC_{50}(4\ hour)}{4} \times 8 \quad [Eqn\ 1]$$

New definitions of SLOD (exposure causing death)

$$SLODconc\left(\frac{mg}{l}\right) = LC_{50}(30min) \quad or \quad SLODconc\left(\frac{mg}{l}\right) = LC_{50}(30min) \times 8 \quad [Eqn\ 2]$$

To deal with a complex inventory the masses of all toxic products should be adjusted so that they can be treated as if they were all a **representative CAT4 substance** with $LC_{50}(4\ hour) = 1\ mg/l$.

- The SLOT concentration for this representative substance is 2 mg/l. To determine the range at which a SLOT dose is accumulated in 30 minutes a dispersion calculation is needed to identify where the concentration falls to 2 mg/l (equivalent to $2 \times 10^{-3}\ kg/m^3$).
- The SLOD concentration for this representative substance is 8 mg/l. To determine the range at which a SLOD dose is accumulated in 30 minutes a dispersion calculation is needed to identify where the concentration falls to 8 mg/l (equivalent to $8 \times 10^{-3}\ kg/m^3$).

The total mass of the representative substance released by the fire is calculated (from the dispersible masses of various categories of product DM_i) as follows:

$$\text{Contribution from Category 4 products} = \sum_i DM(Cat4)$$

$$\text{Contribution from Category 3 products} = 2 \sum_i DM(Cat3)$$

$$\text{Contribution from Category 2 products} = 20 \sum_i DM(Cat2)$$

$$\text{Contribution from Category 1 products} = \sum_i \left[\frac{DM_i(Cat1)}{(LC_{50})_i} \right]$$

To calculate the mass of representative toxic released from a part of the warehouse the sums are carried out over products in that area.

If the dispersal fraction for all the products is assumed to be a constant f , then the total mass of the representative toxic from an area can be calculated from the masses of Category 4, Category 3 Category 2 and Category 1 products as follows

$$M_{toxic} = f \times \left[M(Cat4) + 2M(Cat3) + 20M(Cat2) + \sum_i \frac{M_i(Cat1)}{(LC_{50})_i} \right]$$

An example inventory from an agrochemicals store is shown in Table 2

Table 2: Calculation of equivalent dispersible masses

Product	Total Holding	Dispersible mass	Adjustment factor	Equivalent dispersible mass ²
H330/H300-Cat1 substances	None	None	-	0
H330/H300-Cat2 substances	15,200 kg	1,520 kg	20	30,400 kg
H331/H301-Cat3 Substances	47,500 kg	4,750 kg	2	9,500 kg
H332/302-Cat4 Substances	87,100 kg	8,710 kg	1	8,710 kg
Total				48,610 kg

Assessing how much of the toxic inventory is involved whilst people are exposed to fume

The user of the method will have to decide what proportion of the toxic inventory is released during the 30 minute period when smoke affects those nearby - the fire is assumed to take 3 hours to burn all of the warehouse contents. There are several options:

- (Most conservative assumption) All the toxic inventory is involved in the 30 minute period. If all of the toxics are in one small area of the warehouse this assumption is realistic, but it will be very conservative if the inventory is spread out all over the warehouse. The conservative assumption that all toxic materials are involved in a 30 minute period could be the default if very little information about stock locations is available. If this assumption is made it is appropriate to reduce the incident frequency by a factor of 6 because only a proportion of fires will involve toxics at the critical time (Module 10)
- (Least conservative assumption) One sixth of the inventory is consumed in the crucial 30 minute period. This is only reasonable if the toxic inventory can be relied on to be very uniformly spread over the warehouse. In this case all fires will release toxics during the times when people could be exposed and the incident frequency is simply the fire frequency.
- (Most realistic assumption but requires most work/information) The proportion of the total inventory (between 16.6% and 100%) consumed in 30 minutes is estimated for a reasonable worst case, based on what is known about the toxicity of different products and where they are stored. If storage and locations are very variable this option may not be available. Some appropriate adjustment of fire frequency can be made depending on how likely it is that toxics will be involved at the critical time when people may be exposed to smoke.

MODULE 3 - Calculation of convective heat flow from the fire and toxic mass flow

Assumptions:

1. The fire consumes all of the combustible contents of the warehouse in a period of 3 hours. The total mass of material consumed is M_{comb} (tonnes). Normally only a proportion of this will be classified as toxic.
2. The amount of combustible material (kg) consumed in the 1800 s period when people are exposed to smoke is assumed to be $M_{comb} / 6$.
3. The output from Module 2 was an estimate of dispersible amounts of a representative toxic material. The assessment should assume that the mass of dispersed toxic material DM_{toxic} in the 1800 s period is the worst case i.e. the maximum dispersible amount of representative toxic material stored in a circular area with a total combustible content of $M_{comb}/6$. This allows for the possibility that people will be exposed to smoke during the time when the fire is active in the area containing the most significant dispersible toxic inventory.

$$\text{The toxic release rate is } \dot{M}_{toxic} = \frac{DM_{toxic}(kg)}{1800(s)} \quad [\text{Eqn 3}]$$

4. The convective heat flow Q (MW) in the fire plume associated with combustion of the warehouse contents is:

$$Q(MW) = \frac{M_{comb}(kg)}{3 \times 3600(s)} \times H_c(MJ/kg) \times E \quad [\text{Eqn 4}]$$

H_c is the effective heat of combustion – assumed to be 20 MJ/kg. E is an efficiency - assumed to be 0.5

The relatively low value of E is conservative and allows for loss of heat from the combustion products to the environment (by radiation), to the building fabric by (radiation and convection) and the loss of some unburned material.

² Equivalent mass of a Cat 4 representative substance (30 min SLOT concentration for Cat 4 is 2×10^{-3} kg/m³).

MODULE 4 – Dispersion calculations

This module deals with the fume dispersion calculations that are required. It is assumed that the concentration of toxic material at ground level in fumes from the warehouse fire is a function of :

1. The mass release rate of toxic \dot{M}_{toxic}
2. The heat release Q (in MW) - the buoyancy number B determines the extent to which the hot plume lifts off. U is the wind speed. W is the building width.

$$B = \frac{26.7 \cdot Q(MW)}{U^3 \cdot W} \quad [\text{Eqn 5}]^3$$

3. The distance downstream R – it is assumed that the width (and length) of the warehouse are larger than the height and that the warehouse width is the appropriate source length-scale to use in calculations of downstream decay in concentration.

The dispersion modelling code ADMS [CERC] has been used to determine downstream concentrations for a range of fire sizes from 12.5 MW to 1600 MW in a warehouse 25 m x 75 m x 10 m (high). The fumes issue from a central circular area of the warehouse roof. The source diameter is equal to the building width (Figure 1). Repeat calculations with the building long axis perpendicular to the wind gave fairly similar results but confirmed that the geometry shown was the worst case. Wind speeds between 2 m/s and 20 m/s have been investigated. Buoyancy numbers varied between 0.002 and 200.

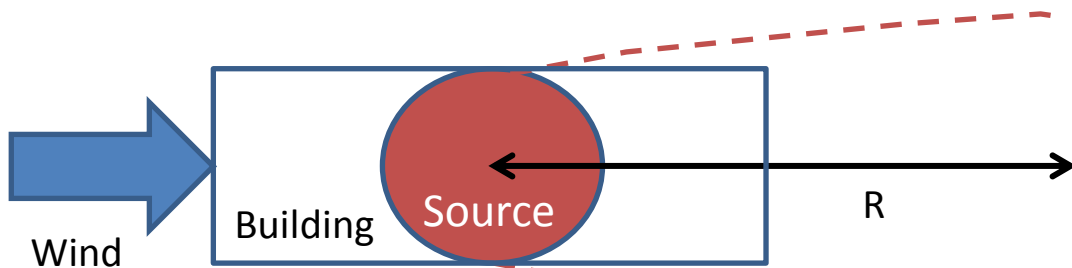


Figure 1: Geometry used in dispersion analyses

For buoyancy numbers in the range of interest (B= 0.001 to 4) the dependence of concentration on buoyancy and distance downstream can be separated and dispersion results can be represented by the following equation:

$$C = 0.17 \cdot \frac{\dot{M}_{toxic}}{U \cdot W^2} \cdot \left(\frac{W}{R}\right)^{1.2} \cdot 10^{-(0.7 \log_{10} B + 0.12 (\log_{10} B)^2)} \quad [\text{Eqn 6}]$$

C is the concentration (kg/m³), \dot{M}_{toxic} is the rate of release of toxic material (kg/s), W is the warehouse width (m)

R (m) is the distance downstream from the centre of the warehouse (W/R < 0.4), U is the wind speed (m/s) use 10 or 15 m/s, B is the buoyancy number. The quantity $Conc / \left(\frac{\dot{M}_{toxic}}{U \cdot W^2}\right)$ is referred to as the *dimensionless concentration*. The fit between Eqn 6 and the results of the ADMS calculations is shown in Figure 2.

³ Note: some analysts have defined B with an additional factor of 1/π

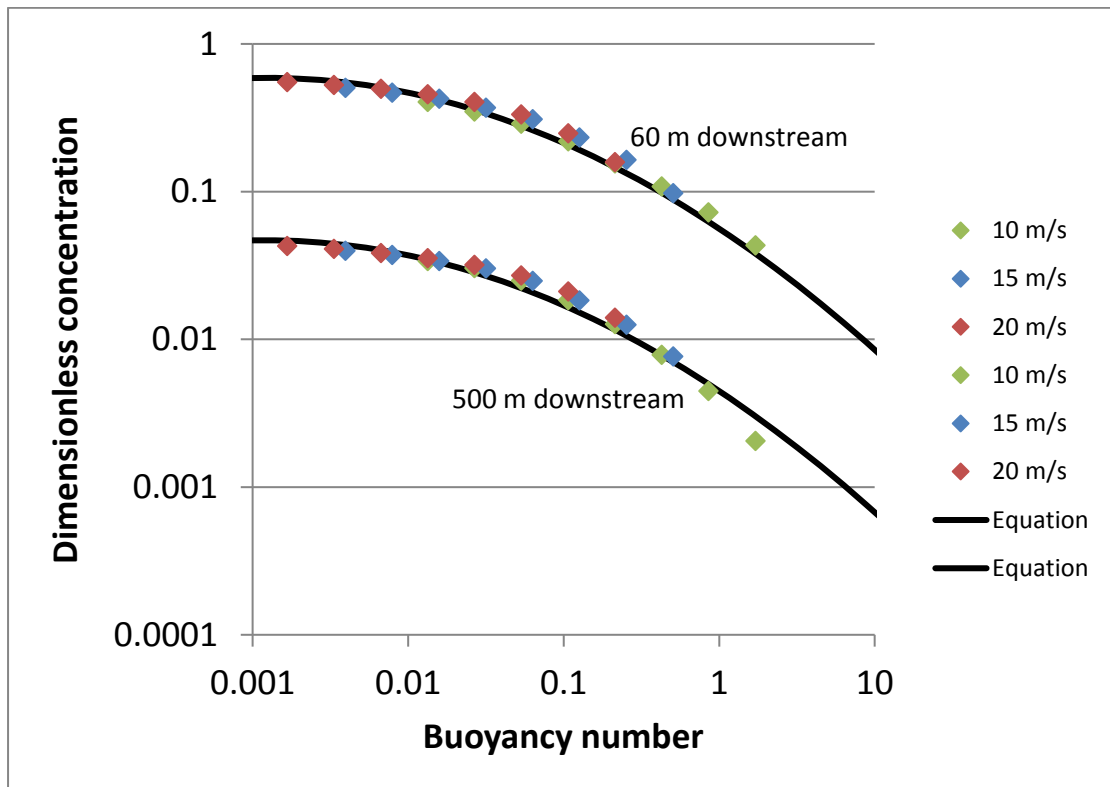


Figure 2: Prediction of dimensionless concentration as a function for buoyancy number for two distances downstream.

In the context of dispersion of fume from warehouse fires it is appropriate to make the following assumptions:

1. The area where the dose or concentration exceeds a given level (e.g. SLOT or SLOD dose) is an **ellipse**.
2. Figure Figure 3
3. The maximum width of the plume can be estimated from the maximum range according to Eqn 7

$$\text{Maximum width} = 0.75 (\text{Maximum range})^{0.75} \quad [\text{Eqn 7}]$$

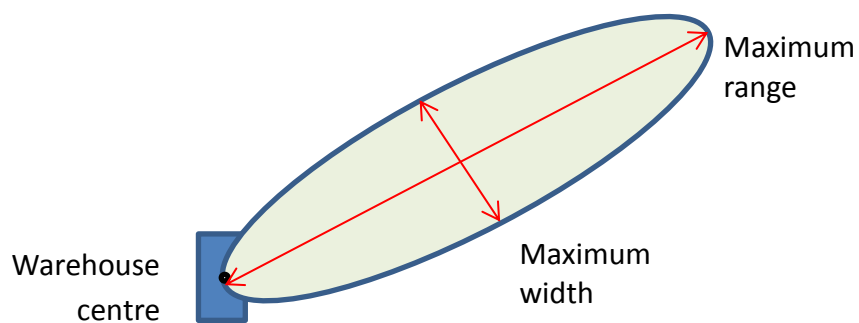


Figure 3: SLOT or SLOD plume shape and dimensions

MODULE 5 – Ventilation controlled fire (with no external combustion of fume)

Very poorly ventilated warehouses can emit large quantities of chemicals that have been vaporised but not combusted. If the level of venting is particularly low these materials may be too cool to burn as they mix with fresh air on exiting the warehouse. An assessment of this type of fume production is appropriate for all warehouses that do not have a minimum level of planned roof-level ventilation in the event of fire. Roof venting can be achieved using permanently open vents, fire louvres linked to detection or skylights made from PVC, polycarbonate or other material with a low melting point. The minimum ventilation level assumed to guarantee afterburning is a (fully) open area of 20 m². Individual vents should be distributed along the length of the warehouse. The ideal design for a toxic warehouse would include low-melt skylights covering at least 10% of roof area.

Assumptions made in analysis of ventilation controlled fires with no external afterburning:

1. If the open area of roof vents is greater than the specified level (20 m²) then partially mixed air and fuel vapours (flames) will extend to roof level; igniting the fuel rich vapours exiting at roof level and efficiently destroying vaporised toxic materials. Calculation of the risks associated with these emissions is then not necessary.
2. Toxic materials that are not combustible and are stored in non-combustible packaging will not be involved in a ventilation controlled fire. Toxic materials that are stored as aqueous suspension or solutions will not contribute however they are packaged. Toxic materials that cannot enter the vapour phase, without thermal decomposition to much less toxic materials, will not contribute to the release.
3. The maximum rate of fuel combustion in a ventilation controlled fire that might be sustained without triggering external flaming is 2 kg/s. The maximum rate of fuel vaporisation (without combustion) is twice the rate of combustion i.e. 4 kg/s. Hence the total amount of material combusted or vaporised in 1800s is about (2 kg/s + 4 kg/s) x 1800 s = 10.8 tonnes.
4. The area where vaporisation occurs during the ventilation controlled fire is localised in the smallest possible circular area i.e. an area containing 10.8 tonnes of goods. The toxic inventory of the worst case area in the warehouse is assumed - consistent with the constraint that the area should contain 10.8 tonnes of goods.
5. The toxic material and any associated combustible packaging or solvent (and any other goods in the area identified) are consumed at the same rate. If the 10.8 tonnes of goods in the chosen area contains (w/w): 30% toxic material, 20% packaging material and solvents and 50% other goods then the total release rate of toxic material is 0.3 x 4 kg/s = 1.2 kg/s.
6. The total convective heat associated with the release (allowing for heat losses) is assumed to be 10 MW.
7. The probability that toxic materials are involved at the time smoke affects people is roughly the (mass) ratio of toxic to total goods stored.

The specification of the minimum ventilation to trigger external combustion of fuel rich fumes is highly uncertain. The value of 20 m² given above is based on an assumed analogy between the height of flames above a source of fuel and extent of the reaction zone where an oxygen inflow burns during mixing with a fuel rich atmosphere within the warehouse. Alternative analyses may be possible if the relative locations of vents, stored materials etc. are known.

MODULE 6: Decomposition of nitrates (e.g. ammonium nitrate, sodium nitrate)

These materials should not be stored in conditions where they may mix with combustible materials in the event of fire. The possibility of melting and flow of either combustibles and nitrates (or both) should be considered. If a store contains nitrates and toxics the method below can be used to assess the risks associated with self-sustaining decomposition of the nitrates. An analysis of toxic risks, in the event of conventional fire may also be needed.

If no data for decomposition in the specific storage conditions is available then it should be assumed that NO₂ and heat production during decomposition will occur at the following rates:

Storage of nitrates in a building without significant fire load (other than in-use pallets):

- NO₂ production = 20 g/s per tonne nitrate (in the largest stack⁴)
- Heat release (including losses to the building) = 37 kW per tonne (in the largest stack)

Storage of nitrates in a building with a significant fire load:

- NO₂ production = 20 g/s per tonne nitrate (total in warehouse)
- Heat release (including losses to the building) = 37 kW per tonne (total in warehouse)

The HSE SLOT concentration (30 minute exposure) for nitrogen dioxide is 56.7 ppm or 1.12 x 10⁻⁴ kg/m³, (15 °C, 1000 mbar)

The HSE SLOD concentration (30 minute exposure) for nitrogen dioxide is 145 ppm or 2.85 x 10⁻⁴ kg/m³.

MODULE 7: Decomposition of chlorine producers

These materials (e.g. swimming pool chemicals, solid hypochlorites, chlorocyanuric acids and salts) should not be stored in conditions where they may mix with combustible materials in the event of fire. The possibility of melting and flow of combustibles should be considered. If a store contains chlorine producers and toxics the method below can be used to assess the risks associated with production of chlorine. An analysis of toxic risks in the event of conventional fire may also be needed. If no data for decomposition in the specific storage conditions is available then it should be assumed that Cl₂ and heat production during decomposition will occur at the following rates:

Storage of chlorine producers in a building without significant fire load (other than in-use pallets):

- Cl₂ production = 50 g/s per (in the largest stack)
- Heat release (including losses tonne chlorine producer to the building) = 150 kW per tonne (in the largest stack)

Storage of chlorine producers in a building with a significant fire load:

- Cl₂ production = 50 g/s per tonne chlorine producer (total in warehouse)

⁴ It is assumed that the stack separation is sufficient to prevent spread of the decomposition reaction between stacks.

- Heat release (including losses to the building) = 150 kW per tonne (total in warehouse)

MODULE 8: Warehouses containing high weight proportions of hetero-atoms Cl, S and P

The assessment of weight proportions P_{Cl} , P_S , and P_P of the hetero-atoms Cl, S and P should be carried out in the worst case circular area containing approximately 1/6th of the combustible content in the warehouse. The substances listed in Table 3 should *not* be counted in determining proportions of hetero-atoms:

Table 3: Type of substances that will *not* produce acid gases in fires

Chlorine containing compounds	Sulphur containing compounds	Phosphorus containing compounds
Metal chlorides	Metal sulphates	Metal phosphates/polyphosphates
Aqueous suspensions	Aqueous suspensions	Aqueous suspensions
Any other material that will not release HCl in severe fires.	Any other material that will not release SO ₂ in severe fires.	Any other material that will not release P ₄ O ₁₀ in severe fires.

Calculations are normally appropriate to assess the potential effects of acid gases, if the weight proportions of hetero-atoms are greater than the following limits: Cl > 25% w/w, S > 25% w/w and P > 5% w/w.

In most circumstances hetero-atoms at or just above the specified levels will not lead to SLOT doses of acid gases but there may be concentrations above the IDLH⁵ levels that could be of significance in emergency planning.

The rates of production of acid gases and heat (allowing for losses) to be assumed are shown in Table 4 – the total combustible mass in the warehouse is M_{comb} (kg). Note: the rates of heat release of compounds with very high proportions of Cl, S and P are assumed to be less than normal combustibles - i.e. those with low hetero-atom content.

Dispersion calculations can be carried out using the method described in Module 4. Results of dispersion calculations can be interpreted using data in Table 5.

	HCl	SO ₂	P ₄ O ₁₀
Mass release rate (kg/s)	$M_{HCl} = P_{Cl} \frac{M_{comb}}{10800} \cdot \frac{36.5}{35.5}$	$M_{SO_2} = P_{SO_2} \frac{M_{comb}}{10800} \frac{64}{32}$	$M_{P_4O_{10}} = P_{P_2O_5} \frac{M_{comb}}{10800} \cdot \frac{284}{124}$
Heat release rate (MW)	$Q_{HCl} = \frac{M_{comb}}{10800} \cdot 5$	$Q_{SO_2} = \frac{M_{comb}}{10800} \cdot 5$	$Q_{P_2O_4} = \frac{M_{comb}}{10800} \cdot 5$

Table 4: Mass release rate for acid gases and net heat release rates

Table 5: Levels of harm associated with combustion products

	HCl	SO ₂	P ₄ O ₁₀
MW	36.5	64	284
ASLOT ⁶	2.37 x 10 ⁴ ppm.min	4.65 x 10 ⁶ ppm ² .min	600 ppm.min
ASLOD	7.65 x 10 ⁴ ppm.min	7.45 x 10 ⁷ ppm ² .min	2400 ppm.min
n	1	2	1
SLOT conc (30 min)	790 ppm (1.2 x 10 ⁻³ kg/m ³)	394 ppm (1.1 x 10 ⁻³ kg/m ³)	20 ppm (2.4 x 10 ⁻⁴ kg/m ³)

⁵ IDLH = Immediate Danger to Life and Health [NIOSH]

⁶ ASLOT, ASLOD and n are the toxicity parameters defining HSE SLOT and SLOD dose fractions;

Fraction of SLOT dose = $\frac{1}{ASLOT} conc(ppm)^n \cdot \Delta t(min)$, Fraction of SLOD dose = $\frac{1}{ASLOD} conc(ppm)^n \cdot \Delta t(min)$,

SLOD conc (30 min)	2550 ppm ($3.9 \times 10^{-3} \text{ kg/m}^3$)	1576 ppm ($4.3 \times 10^{-3} \text{ kg/m}^3$)	80 ppm ($9.6 \times 10^{-4} \text{ kg/m}^3$)
IDLH	50 ppm ($7.7 \times 10^{-5} \text{ kg/m}^3$)	100 ppm ($2.7 \times 10^{-4} \text{ kg/m}^3$)	8 ppm ($9.6 \times 10^{-5} \text{ kg/m}^3$)

Example: A warehouse with dimensions 30 x 80 x 8 m contains 1,500 tonnes of combustible goods, a proportion of which are heavily chlorinated substances. In the area where storage of these materials is concentrated there are 250 tonnes of combustible goods that contain 35% molecular chlorine by weight.

The proportion of chlorine w/w is above the limit (25%) where an assessment is appropriate. From Table 4 the mass release of HCl and heat are 83 kg/s and 1150 MW. The analysis shows SLOD concentrations are not reached even in high winds but in the worst conditions IDLH levels extend to about 500m. The substantial difference in ranges to SLOD and IDLH arises because of the strong irritant effect of HCl at relatively low concentrations. The assessment suggests that a large fire is not likely to directly cause serious permanent injuries but that a large area downwind will be seriously affected by acid gases in the case of high winds and will have to be evacuated urgently.

For warehouses with significant proportions of more than one heteroatom separate calculations of fractional concentrations of all the gases are required for the IDLH, SLOD and (possibly) SLOD levels. These fractional concentrations should be added at each distance. In some cases there may be areas of a warehouse that contain both significant amounts of dispersible toxic material and a high proportion of heteroatoms. In this case the reduced rates of heat release specified in Table 4 should (conservatively) be used. Separate calculations of fractional concentrations of the acid gases and dispersed toxic are required for the IDLH, SLOD and (possibly) SLOD levels. These fractional concentrations should be added.

MODULE 9: Linking the results of dose calculations to harm

The source term and dispersion analyses in Modules 3 and 4 yield maximum ranges to SLOD concentrations (for 30 minute exposure). Module 4 also describes how the overall (elliptical) plume shapes can be simply estimated from the maximum ranges. The effects of these plumes can be determined by superimposing the SLOD contour on maps showing local populations. Research suggests the number of people within the SLOD dose contour is a reasonable estimate of the number of people that might be injured by a major incident [Franks et al].

The analyses in Modules 3 and 4 will also determine if there is a (much smaller) area where SLOD doses might be accumulated. SLOD stands for Significant Likelihood of Death and SLOD concentrations roughly correspond to an LC₅₀ for a 30 minute exposure. For a roughly evenly distributed population, Research also suggests the number of people inside the SLOD concentration contour is a reasonable estimate of the potential number of fatalities. This approximation results from the assumption that those people inside the SLOD contour who do not die (due to factors such as physiology, fitness levels, etc.) will be balanced by an approximately equal number outside the SLOD contour who do die, again due to factors such as physiology, state of health etc.

If the analysis shows that SLOD and/or SLOD doses can be accumulated, the assessment should include;

- estimates of the number of injuries and deaths in the worst-case weather conditions. (these may be illustrated by a map showing the SLOD/SLOD contours and surrounding populations)
- an assessment of the frequency with which populations might be affected (see Module 10).

MODULE 10: Frequency analysis

The overall frequency of serious fires in all types of warehouses in the UK can be determined from Fire and Rescue Service statistics: the total number is large and relatively stable year on year. A number of studies over the last 30 years have compared the rate of fires with estimates of the total population of warehouses. In all cases the conclusion has been that the rate of serious fires (causing widespread structural damage to the roof) is around 0.01 per annum for each warehouse i.e. on average warehouses are seriously damaged by fire every 100 years. Unfortunately the contents of burned warehouses were not routinely recorded by fire crews, so it is not possible to determine the frequency of fires in, for example, chemical warehouses. It is likely that standards of security and ignition control in chemical warehouses are higher than average and relevant research would support estimates of warehouse serious fire frequency of around 3×10^{-3} per annum. Any substantially lower values used in safety reports should be justified in detail.

A reduction in frequency may be applied if toxics are only stored in a small area of the warehouse (see Module 2). This reflects the fact that people are only exposed to smoke for a small fraction of the total fire duration and toxics may not be involved at this stage. The frequency with which persons are likely to be exposed to fumes from a major fire in a given warehouse is also generally much less than the fire frequency because the wind has to be blowing in a particular range of directions and with a minimum strength.

The probability that the wind speed will be 5, 10 or 15 m/s depends on the location. Approximate but reasonable average (inland) values for this frequency assessment are shown in Table 6.

Table 6: Wind speed probabilities (inland sites)

Wind speed (m/s)	5	10	15
Probability	0.5	0.1	0.03

For a typical UK wind rose the maximum wind frequency in the prevailing direction is about twice that which would be expected if the wind blew in all directions with equal probability

The probability that someone near a site will be exposed to a SLOT or SLOD dose also depends on their distance from the site relative to the maximum range of the plume. If the person is very close to the site the probability they will be affected is high and this probability declines to zero if they are at the maximum range of the plume. The approximate variation of this probability as a function of the ratio $R = \text{Distance to target} / \text{Maximum plume range}$, for a uniform wind rose, is shown in Table 7.

Table 7: Probability of exposure $p = \frac{1}{\pi} \arctan \left[\frac{0.46}{R} \cdot (R - R^2)^{\frac{1}{2}} \right]$

Ratio R (Target distance/Maximum plume range)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Probability of exposure	0.300	0.236	0.194	0.163	0.137	0.114	0.093	0.071	0.048

Discussion

Warehouse fires are amongst the most common and destructive events to affect chemical storage sites worldwide; sometimes large quantities of toxic and high toxic materials are destroyed. However, the authors know of no offsite fatalities linked to such events and it must be the case that this would only occur in unusual circumstances i.e. a particularly toxic inventory, unfavourable weather, high population density etc. The purpose of warehouse fire assessment is to identify such high risk cases and generally to direct efforts to reduce risk. Such mitigation measures include: providing planned ventilation in the event of fire; separating toxic materials from combustible goods where possible (materials that are both Toxic and Flammable should be treated as Flammable) and storing dispersible toxics at ground level.

There are many examples of chemical warehouses fires that have caused major environmental damage through contaminated firewater run-off. One use of fire plume toxicity assessment is to support “let burn” decisions in planning for and dealing with large fires.

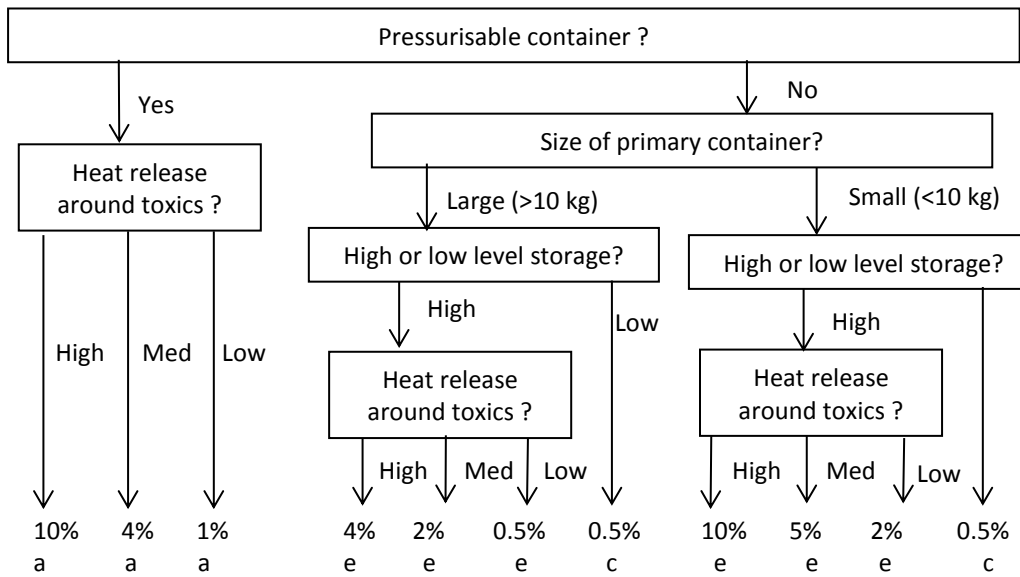
This method should be of interest to warehouse trade associations and other bodies. The authors would be willing to discuss its use should such bodies wish to adopt this method.

References

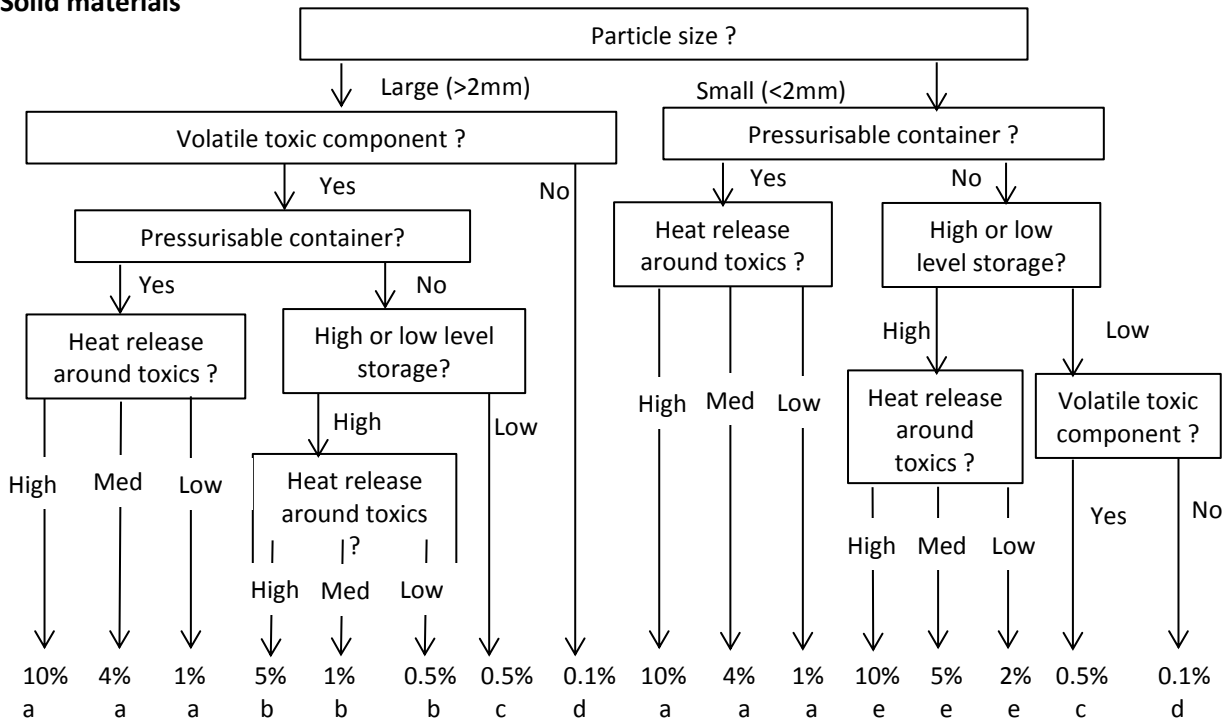
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Appendix 1 – Suggested dispersal fractions

Liquid materials



Solid materials



Notes on dispersal mechanisms:

- a - dispersal of toxic vapour or particulates during failure of pressurised container
- b - vaporisation of toxic materials in upper intermittent sections of the flames
- c - vaporisation of toxic materials around margins of a large fire
- d - no obvious mechanism
- e - uplift of droplets/particulates produced during the fire engulfment of commodities at high level

Definitions

Volatile toxic component : A toxic component that can be vaporised at ambient pressure without thermal decomposition.

Pressurisable container : A container that can develop an over pressure of at least 1 bar during heating e.g. a steel tight-head drum or steel IBC.

Non-pressurisable container : A container that cannot develop an over pressure of 1 bar during heating e.g. a plastic bottle, plastic drum or plastic IBC.

High level storage: Pallets stored on racks at two or more levels or stacked more than two pallets high.

Low level storage: Pallets stored on the ground or stacked no more than two pallets high

Heat release is judged on the estimated average combustible content of pallets within 3 m of the product (horizontal distance).

High heat release rate around toxics: Combustible content >100 kg per pallet

Medium heat release rate around toxics: Combustible content <100 kg and >20 kg per pallet

Low heat release rate around toxics: Combustible content <20 kg per pallet

If there is a sufficient stock of combustible liquids in plastic containers to cover the floor of the warehouse to a depth of 10 mm, then the heat release rate should be considered high everywhere: unless there are bunds, drains etc. designed to control the rapid loss of liquid. More information on IBCs can be found at www.hse.gov.uk/research/rrhtm/rr564.htm