# Assessment of Toxic Risks from Warehouse Fires

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Why is the assessment of fume risks from chemical warehouses important ?

1. It is a legal responsibility under COMAH

2. It can motivate and guide improvements … fire precautions, segregation, stock reorganisation ...

3. It can support a “Let Burn” policy where this is appropriate.

**History of regulation**

1984 Control of Industrial Major Accident Hazards (**CIMAH**) Regulations implemented the European Communities "Seveso" Directive

1992 Extension of CIMAH Regulations to cover sites that simply stored toxic materials i.e. chemical warehouses.

1999 Current COMAH Regulations also apply to chemical warehouses

Sandoz Fire - 1st November 1986

COMAH Regulations

SCHEDULE 4

PART 1: PURPOSE OF SAFETY REPORTS

**….2.** demonstrating that major accident hazards have been identified and that the necessary measures have been taken to prevent such accidents and to limit their consequences for persons and the environment;

PART 2: MINIMUM INFORMATION

**….4**. assessment of the extent and severity of the consequences of identified major accidents;

Could there be toxic risks from fumes (in principle)?

Simple (worst case) assumptions

- Dangerous dose for paraquat — $7 \times 10^{-5}$ kg/$m^3$
- Mass of active in warehouse — 500,000 kg
- Maximum volume of “fatal” cloud — $7.1 \times 10^{9}$ $m^3$

If such a cloud were 1 kilometre wide and 100 m high it would stretch for 71 kilometres.

Excessively conservative. More realistic modelling is required.

Important issues in warehouse fire risk assessment:

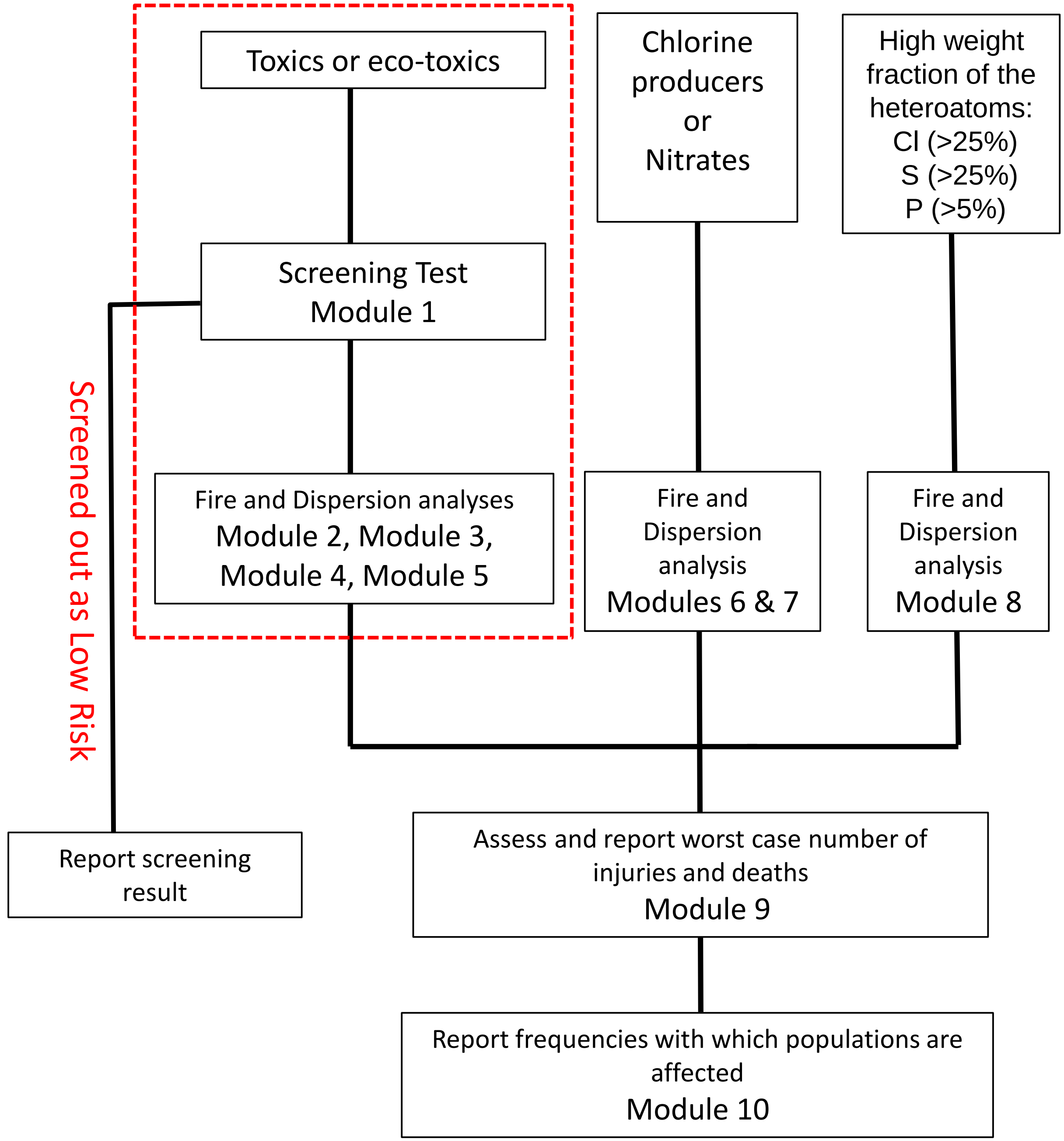
- Frequency
- Timing of fire growth/Structural response
- Toxic release rate
- Buoyancy of fumes
- Dispersion
- Toxic effects
- Representing a large complex inventory

Almost all of these are complex problems and there is very little technical guidance available.

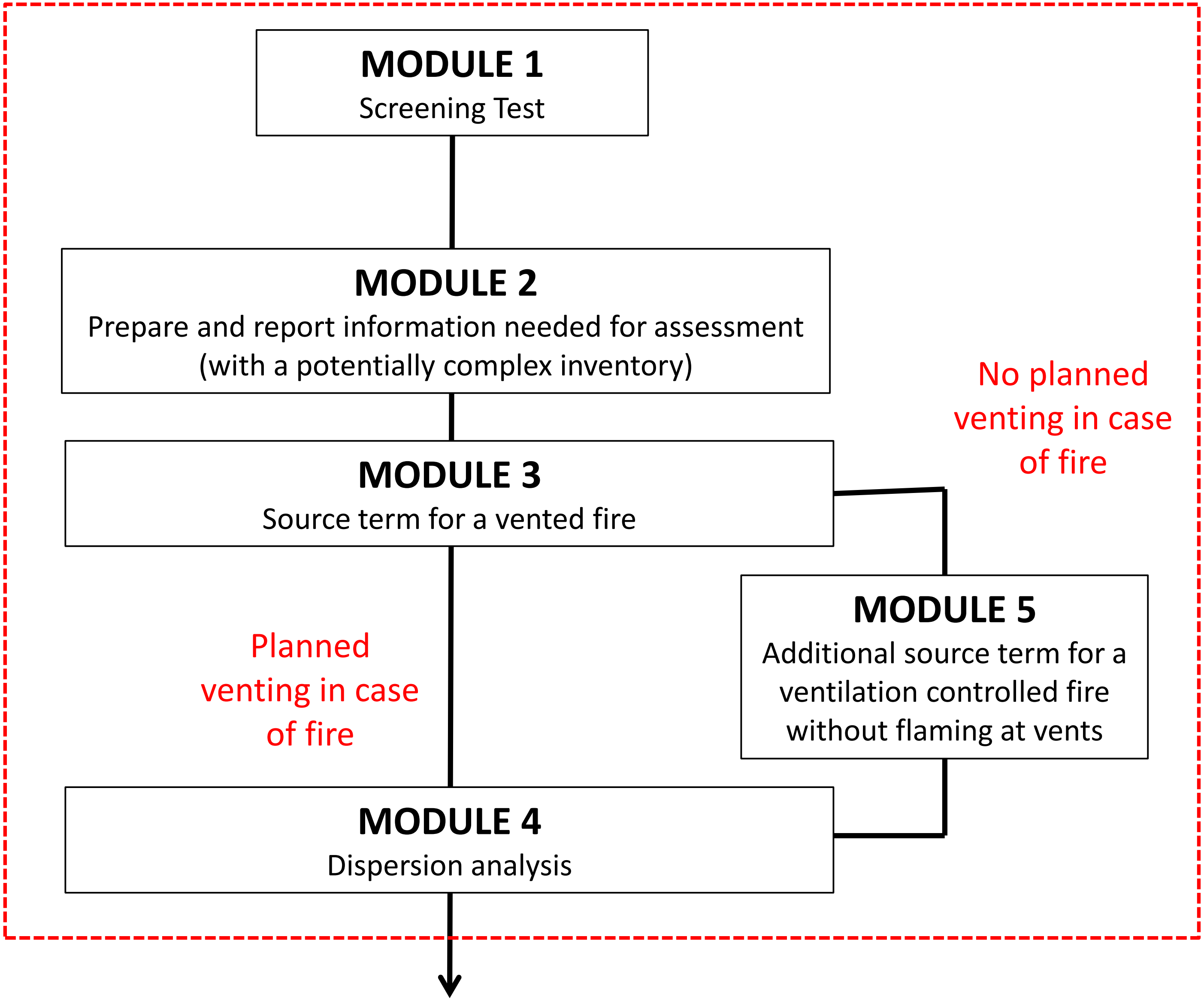
Ventilation controlled fire no external flaming

Well ventilated external flames

# Structure of the proposed method



# Main modules for toxics



## Dealing with complex toxic inventories

You can use:

1. HSE “A” and “n” values
http://www.hse.gov.uk/chemicals/haztox.htm .

(Good for a small number of common single component chemicals)

Or

2. Classification data under CLP
https://echa.europa.eu/guidance-documents/guidance-on-clp

(More practical if there are a large number of mixtures e.g. agrochemicals.)

# $LC_{50}$ (4 hour) levels to be assumed in assessment

| | |
|---|---|
| Products classified acutely toxic<br>Category 4<br>(Hazards statement H332, H302) | 1 mg/l |
| Products classified acutely toxic<br>Category 3<br>(Hazards statement H331, H301) | 0.5 mg/l |
| Products classified acutely toxic<br>Category 2<br>(Hazards statement H330/2, H300) | 0.05 mg/l |
| Products classified acutely toxic<br>Category 1<br>(Hazards statement H330/1, H300) | $LC_{50}$ (4 hour) |

# How are $LC_{50}$ values used to define levels of harm?

An exposure time of 30 minutes is assumed

**Definition of SLOD (exposure causing death)**

$$SLODconc\left(\frac{mg}{l}\right) = LC_{50}(30min)$$

$$or \quad SLODconc\left(\frac{mg}{l}\right) = LC_{50}(4\ hour) \times 8$$

**Definition of SLOT (exposure causing injury)**

$$SLOTconc\left(\frac{mg}{l}\right) = \frac{LC_{50}(30min)}{4}$$

$$or \quad SLOTconc\left(\frac{mg}{l}\right) = \frac{LC_{50}(4\ hour)}{4} \times 8$$

# Reducing a complex inventory to an equivalent dispersible mass

| **Example agrochemicals warehouse**<br><br>Product | Total Holding (kg) | Dispersible mass (10% dispersal) (kg) | Adjustment factor | Class 4 Equivalent dispersible mass |
|---|---|---|---|---|
| H330/H300-Cat1 substances | None | None | - | 0 |
| H330/H300-Cat2 substances | 15,200 | 1,520 | 20 | 30,400 |
| H331/H301-Cat3 Substances | 47,500 | 4,750 kg | 2 | 9,500 |
| H332/302-Cat4 Substances | 87,100 | 8,710 kg | 1 | 8,710 |
| Total | | | | 48,610 |

## Assessment of the generation of heat and dispersal of toxic materials

There is always a complex risk balance between generation of heat, release of toxic materials and plume lift off.

A high fire load increases plume lift-off and reduces effects at ground level…

But it tends to increase the efficiency with which toxic materials are dispersed.

# How is this balance reflected in the method?

## Heat generation

The fire consumes all of the combustible contents of the warehouse in a period of 3 hours.

## Plume Dispersion

The ground level concentrations fall off with increasing heat generation

## Dispersal of toxic materials

"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" … (definitions) ... "and isolated from burning pools caused by leakage from other goods in a large fire."

For low (non-zero) fire loads, low dispersal fractions also usually apply.

## On balance

Overall, a very low fire load warehouse is likely to be associated with a lower risk – if it is sensibly organised.

Dispersion is controlled by the buoyancy number

Heat

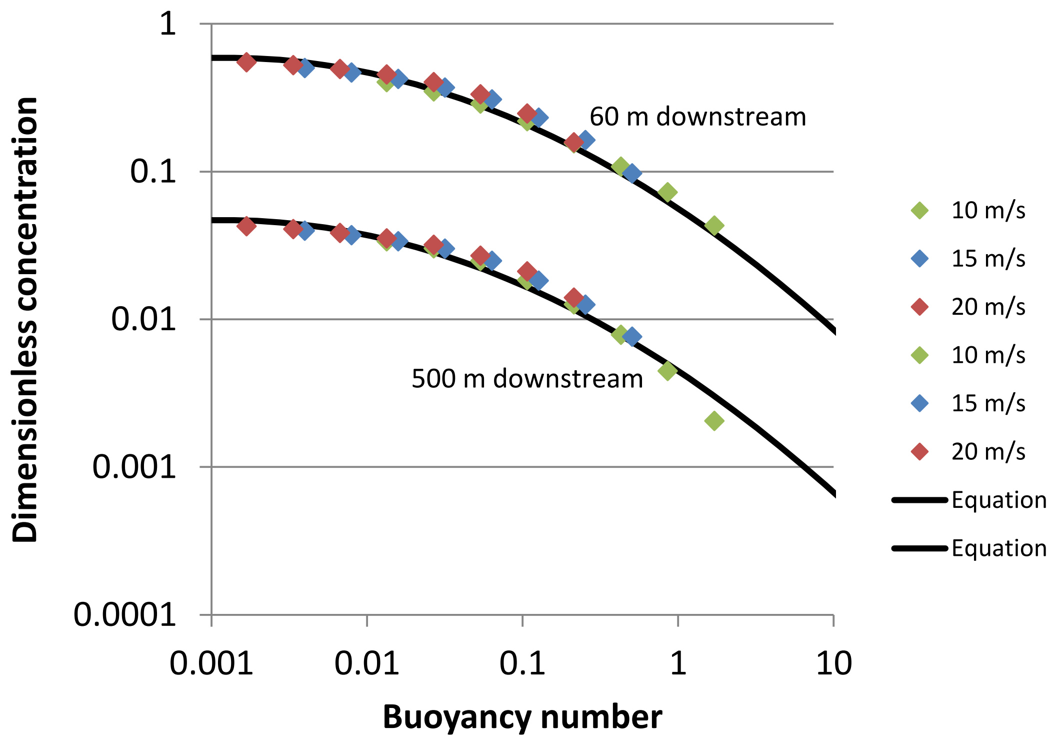
$$B = \frac{26.7\ .\ Q(MW)}{U^3\ .\ W}$$

Wind Size

A single equation is provided to calculate concentrations downwind

$$C = 0.17\ .\ \frac{\dot{M}_{toxic}}{U\ .\ W^2}\ .\ \left(\frac{W}{R}\right)^{1.2}\ .\ 10^{-(0.7 log_{10}B\ + 0.12\ (log_{10}B)^2)}$$

No separate dispersion model needed



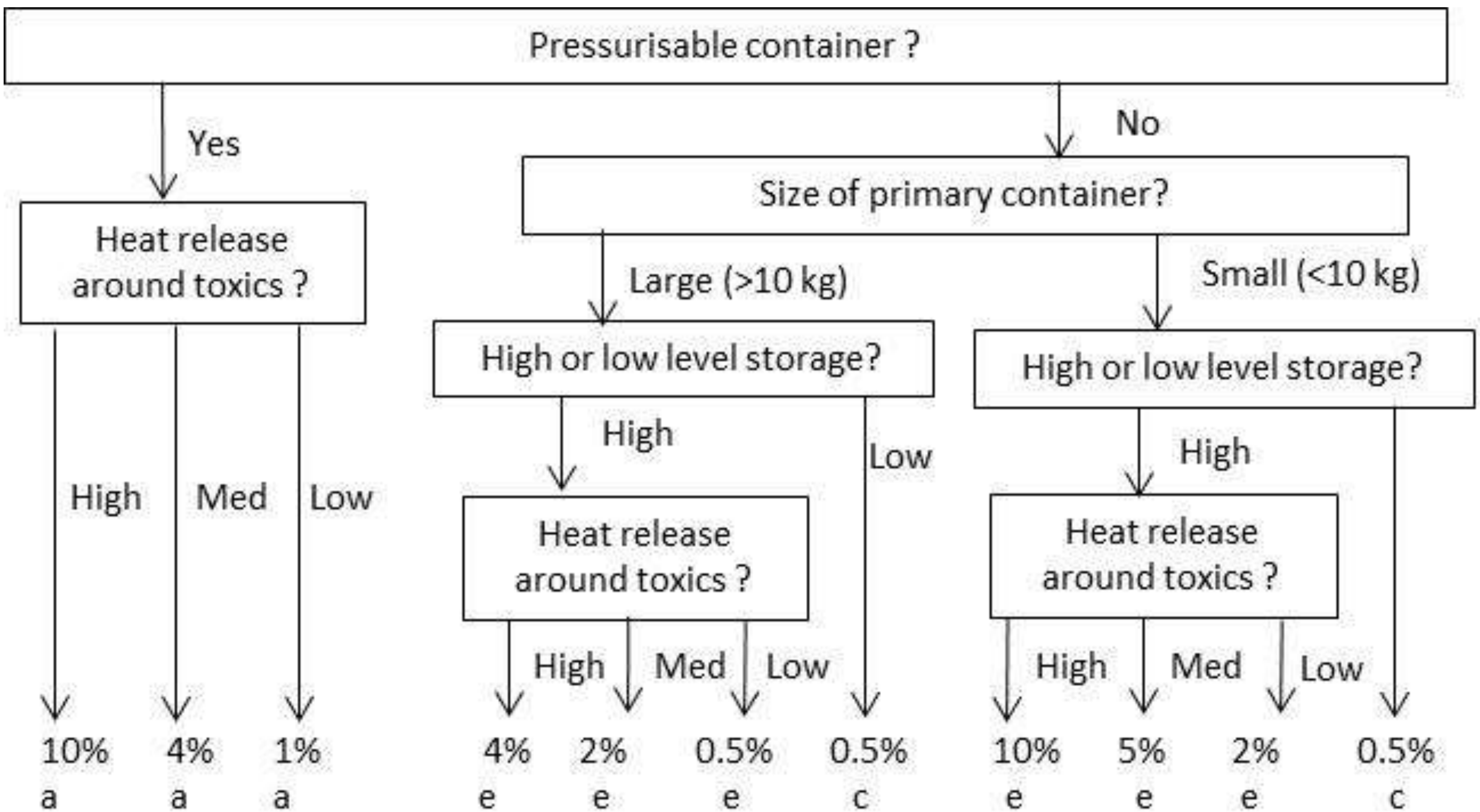
# Plume seeding (release) fractions

| Factors increasing risk | Factors reducing risk |
|---|---|
| High level storage | Ground level storage |
| Small package sizes | Large package sizes |
| Fine powders | Non dispersible materials |
| Pressurisable containers | Non-pressurisable containers |
| High thermal stability | Decomposition before boiling |
| Restricted ventilation[1] | Flammable toxic material |
| | Recirculation (in the warehouse)[2] |

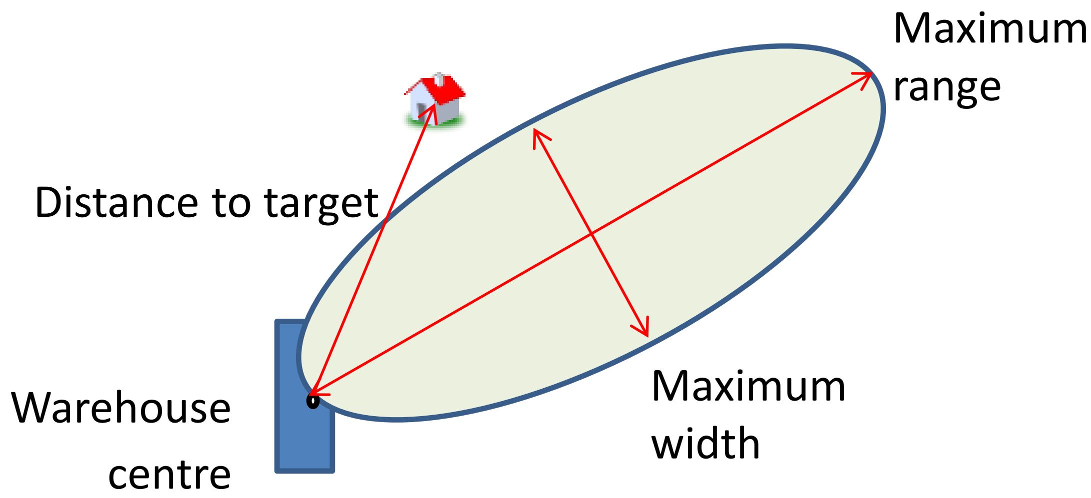
[1]For volatile (and combustible) toxic materials – e.g. pesticides

[2]For non-volatile , incombustible toxic materials – e.g. heavy metal powders

# Liquid products



# Calculating plume shape and probability of exposure




Maximum width (m) = 0.75 (Maximum range - m)$^{0.75}$

R = Distance to target / Maximum plume range

Probability of exposure $p = 1/\pi \;.\; \arctan 0.46\, R \;.\; (R-R^2)^{1/2}$

| 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 (uniform wind rose) | 0.300 | 0.236 | 0.194 | 0.163 | 0.137 | 0.114 | 0.093 | 0.071 | 0.048 |

# Wind speed probabilities (inland sites)

| Wind Speed (m/s) | Probability |
|---|---|
| 5 | 0.5 |
| 10 | 0.1 |
| 15 | 0.03 |

# Example wind direction data (London) – Prevailing wind is SW

| Wind direction | Probability (relative to a uniform wind rose) |
|---|---|
| W | 1.95 |
| SSW | 1.58 |
| WSW | 1.31 |
| WNW | 0.951 |
| NW | 0.804 |
| NNW | 0.634 |
| N | 0.756 |
| NNE | 0.756 |
| NE | 0.707 |
| ENE | 0.853 |
| E | 0.682 |
| ESE | 0.609 |
| SE | 0.560 |
| SSE | 0.707 |
| SSW | 1.26 |
| S | 1.85 |

# Incident history – harm to people

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 and storing dispersible toxics at ground level.

## Incident history – harm to the environment

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.

## The future

This method has been more fully documented (with numerous examples) than is possible at Hazards 29. The method may 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 or develop the method.