THEORY

WAREHOUSE FIRE (WHFIRE)

DATE: December 2023

This document describes the theory of the Warehouse Fire Model. This model calculates the composition and flow rates of the combustion products released to the atmosphere in the event of a warehouse fire.

No.	Date	Reason for Issue	Prepared by	Verified by	Approved by
1	15 April 2002	Draft	Winslow	HW	
2	4 October 2002	6.2 version	Witlox	DRW	
3	August 2008	6.54 version	Witlox		
4	March 2011	6.7 version	Witlox		
5	October 2017	8.0 version	Witlox		
6	May2021	Apply new template	D.Vatier		

Date: December 2023

Prepared by: Digital Solutions at DNV

ABSTRACT

The model is based on a subset of the risk-analysis methodology adopted in a TNO report by Molag and Blow-Bruggeman. The model calculates the average chemical structure of all pesticides stored in the warehouse. Assuming complete combustion, mass emission factors relative to the burned pesticide of NO2, SO2 and halides (HCl, HBr and HF) representing the toxic combustion products, are derived. The burning rate of the pesticide is calculated according to the building ventilation characteristics, the oxygen requirement of the stored pesticide and the type and performance of the fire mitigation system. The release rate of each toxic combustion product is then the product of the burning rate and the emission factor. The release velocity of the toxic combustion products is also calculated and a release temperature is assumed completing the information necessary to describe the discharge source term for input to a dispersion model. The release rates of unburned highly toxic substances and equivalent 2,3,7,8-trichlorodibenzodioxin in the effluent are calculated empirically.

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1. INTRODUCTION

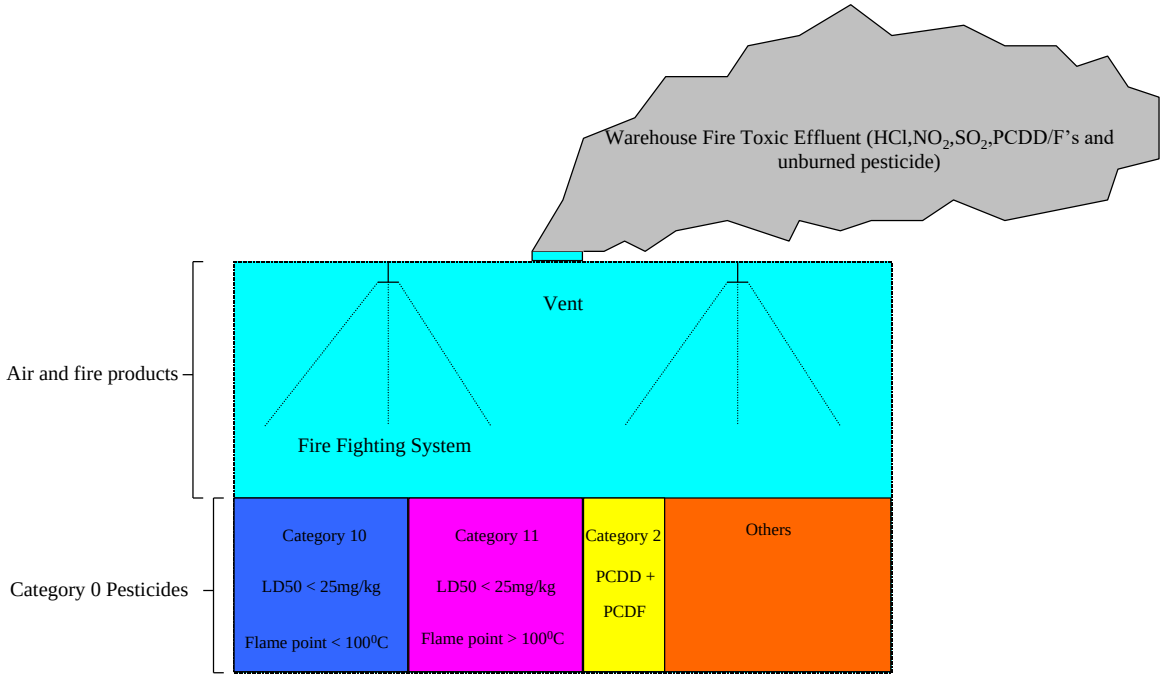
The combustion of flammable pesticides will usually result in the emission of toxic substances into the atmosphere. These substances may emanate from the combustion process itself or from the release of unburned toxic material. The threat of inhalation to people in the vicinity of the storage buildings containing hazardous substances has made it necessary to quantify the risk.

The current document describes the theory of The Warehouse Fire Model as incorporated in the consequence modelling package Phast and the quantitative risk assessment software package Safeti (with Dutch version called SAFETI-NL). The model is based on section 6 of the TNO report by M.Molag and J.M. Blow-Bruggeman[i] written for the Ministry of VROM of the Netherlands which deals with a risk analysis approach in the event of a fire from stored pesticides. The source code, originally written by VROM, was handed over to DNV in 1993. The code was subsequently incorporated into SAFETI 3.31 in the form of a DOS program called FIREDF[ii,iii]. An enhanced Windows version of the model was integrated into PHAST/SAFETI 6.2. Further enhancements associated with the upgrade of the Dutch guideline from CPR-15 guideline[v] to the PGS-15 guideline[iv] were applied to Phast (Risk) and SAFETI-NL 6.54. The interface was further updated for version 8.0 of Phast, Safeti and Safeti-NL.

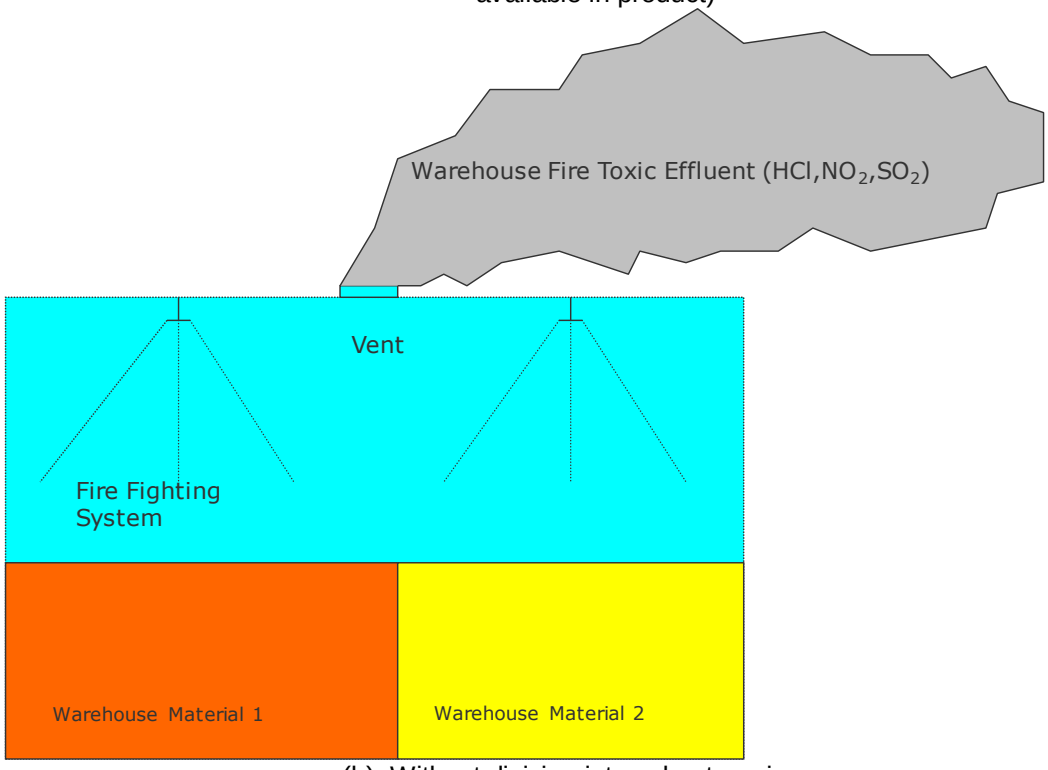
Figure 1 includes a schematic diagram illustrating the pesticides stored in the warehouse and the combustion products released from the warehouse to the atmosphere. The model calculates the emission rates of the toxic combustion products $S0_2$, NO_2 and halides (HCl, HBr and HF) from warehouse fires. The calculations are based on component composition, the oxygen requirement of the stored pesticide, the building ventilation and the fire-fighting equipment. The release velocity and temperature of the toxic combustion products are also given by the model. Further, it calculates from empirical data, the release rates of unburned highly toxic compounds (with LD_{50} for rats <25mg/kg [1]) and hazardous polychlorodibenzo-p-dioxins (PCDD's) and polychlorodibenzofurans (PCDF's). **Please note that from Version 8.0 it has been decided for simplification to report no longer in the product (Phast, Safeti) the latter release rates and the division of the pesticides in subcategories as indicated in** Figure 1**. Thus the latter data are available in the WHFRE spreadsheet only.**

The release rates, velocity and temperature of the toxic combustion products can serve as the discharge source-term for input to a dispersion model which in conjunction with toxicity data, population data and frequency of release can be used to quantify the risk to the surrounding population.

[1] The LD_{50} is the dose expressed as mass toxic substance per mass of test subject which is lethal for 50% of test subjects.



(a) With division into subcategories (available in WHFIRE spreadsheet only, division into categories not available in product)



(b) Without division into subcategories

Figure 1. Release of toxic combustion products following fire from pesticides stored in warehouse[2]

[2] Note that categories 2,10 and 11 are not mutually exclusive, ie. a pesticide in category 2 could also occur in category 10 or 11

2. MATHEMATICAL MODEL

2.1 Composition of stored materials

Pesticides are stored in the form of powders, liquids or solutions and may be packaged in drums, tanks or bags. The model distinguishes between active substance which comprises the pure hazardous pesticide chemical and inactive substance which includes the inert formulations in powders, non-hazardous solvents and packaging material.

2.1.1 Pesticide categories

As illustrated in Figure 1, the model categorises the pesticide materials in terms of their specific risk to the surrounding population. All considered materials fall into the total category:

- **0:** Materials that form toxic combustion products

Further, three subsets of the total category are defined in the model:

- **10:** Highly toxic materials with LD_{50} for rats of less than 25mg/kg and flash point of less than 100°C
- **11:** Highly toxic materials with LD_{50} for rats of less than 25mg/kg and flash point of more than 100°C
- **2:** Potential PCDD and PCDF generating compounds (see definition in section 2.2.1)

A few example permutations are that: highly toxic materials with a low flash point fall into categories 0 and 10. PCDD/F formers fall into categories 0 and 2. Highly toxic materials with a high flash point that are potential PCDD/F formers fall into categories 0,11 and 2 and materials that are neither highly toxic nor potential PCDD/F formers but form toxic products when combusted, fall into category 0 only.

2.1.2 Pesticide structural formula

If the content of the warehouse is known, the model calculates the average structural formula from the active stored pesticides. Otherwise it assumes a default value for the average structural formula. Active pesticide made up of a combination of the chemical elements C,H,O, N,S,P,Cl, F,Br,I, Mn,Zn and Sn are considered in the risk analysis.

Case of known warehouse content

For each element i within each category x an average number of atoms in the structural formula is calculated,

$$\bar{n}_{i,x} = \frac{\sum_{c=1}^{c_{\max,x}} n_{(i,c,x)} \frac{m_{c,x}}{M_{W,c,x}}}{\sum_{c=1}^{c_{\max,x}} \frac{m_{c,x}}{M_{W,c,x}}} \qquad (1)$$

where:

$\bar{n}_{i,x}$ = average number of atoms for element *i* in the average structural formula of category *x* materials

$n_{(i,c,x)}$ = number of atoms of element *i* in pesticide component *c* of category *x*

$c_{\max,x}$ = number of pesticide components in category *x*

$m_{(c,x)}$ = active mass of pesticide component *c* in category *x* (kg/kmol)

$M_{W,c,x}$ = molecular weight of pesticide component *c* in category *x* (kg)

This gives rise to an average structural formula for each category in the following format:

$$C_{\bar{n}_{C,x}} H_{\bar{n}_{H,x}} O_{\bar{n}_{O,x}} N_{\bar{n}_{N,x}} S_{\bar{n}_{S,x}} P_{\bar{n}_{P,x}} Cl_{\bar{n}_{Cl,x}} F_{\bar{n}_{F,x}} Br_{\bar{n}_{Br,x}} I_{\bar{n}_{I,x}} Mn_{\bar{n}_{Mn,x}} Zn_{\bar{n}_{Zn,x}} Sn_{\bar{n}_{Sn,x}}$$

The average molecular weight for each category can then be calculated as follows:

$$\overline{M}_{W,x} = \frac{\sum_{c=1}^{c_{\max,x}} m_{(c,x)}}{\sum_{c=1}^{c_{\max,x}} \frac{m_{c,x}}{M_{W,c,x}}} \qquad (2)$$

where[3]:

$\overline{M}_{W,x}$ = Molecular weight of the average structure of pesticide in category *x* (kg/kmol)

Case of unknown warehouse content (default values)

The default value for the average structural formula of active pesticide stored is chosen as follows[4]:

$$C_{3.6}H_{5.3}O_{0.4}N_{0.9}S_{1.3}P_{0.01}Cl_{0.8}F_{0.0}Br_{0.0}I_{0.0}Mn_{0.08}Zn_{0.01}Sn_{0.01}$$

2.2 Materials released during pesticide fire

The hazardous material released as effluent from the combustion of pesticides can comprise both toxic combustion products and unburned toxic storage materials. Figure 1 shows a schematic diagram of the toxic effluent from a pesticide fire.

2.2.1 Toxic combustion products

The composition of toxic combustion products resulting from pesticide fires is currently not fully understood[1]. A more accurate understanding could be provided by large-scale or micro-scale combustion experiments on specific chemicals of interest at a considerable cost. This model gives a methodology to predict the composition of toxic combustion products. The vast majority of the toxic combustion product results from complete combustion of the pesticide, while a relatively small portion of PCDD's and PCDF's is also generated. These are handled separately in the model, and are further described below.

Complete combustion products

The nature of the combustion products is dependent on the chemical formulae of the stored chemicals. Only pesticides constituting a combination of the elements C, H, O, F, Cl, Br, I, N, S, P, Mn, Zn and Sn are considered by the model. Complete combustion is assumed and the following products are assumed to be generated: CO_2, H_2O, HF, HCl, HBr, I_2, NO_2, N_2, SO_2, P_2O_5, MnO_2, ZnO and SnO_2. The general combustion reaction can be expressed as follows:

$$C_{\bar{n}_{C,x}} H_{\bar{n}_{H,x}} O_{\bar{n}_{O,x}} N_{\bar{n}_{N,x}} S_{\bar{n}_{S,x}} P_{\bar{n}_{P,x}} Cl_{\bar{n}_{Cl,x}} F_{\bar{n}_{F,x}} Br_{\bar{n}_{Br,x}} I_{\bar{n}_{I,x}} Mn_{\bar{n}_{Mn,x}} Zn_{\bar{n}_{Zn,x}} Sn_{\bar{n}_{Sn,x}} +$$

[3] The model also allows a user-specified pesticide molecular weight, which should be larger than the mole weight based on the specified atoms for C, H, O, N, S, P, Cl, F, Br, I, Mn, Zn and Sn. Thus this allows for additional atoms being present in the molecule, which are not assumed to contribute to additional combustion (oxygen requirement).

[4] The average molecular formula for the pesticide storage is based on the 25 best sold pesticides in the Netherlands in 1987 according to the report "Individueel- en groepsrisico opslag bestrijdingsmiddelen voor verschillende brandbestrijdingssystemen" prepared by the Dutch Ministry of VROM.

$$[\bar{n}_{C,x} + \frac{\bar{n}_{H,x} - (\bar{n}_{Cl,x} + \bar{n}_{Br,x} + \bar{n}_{F,x})}{4} + \bar{n}_{S,x} + \bar{n}_{Mn,x} + 0.35\,\bar{n}_{N,x} + \bar{n}_{Sn,x} + \frac{5\bar{n}_{P,x}}{4} + \frac{\bar{n}_{Zn,x}}{2} - \frac{\bar{n}_{O,x}}{2}]O_2$$

$$\longrightarrow \quad \bar{n}_{C,x}\,CO_2 + \frac{\bar{n}_{H,x} - (\bar{n}_{Cl,x} + \bar{n}_{Br,x} + \bar{n}_{F,x})}{2}\,H_2O + \bar{n}_{Cl,x}\,HCl + \bar{n}_{Br,x}\,HBr +$$

$$\bar{n}_{F,x}\,HF + 0.35\,\bar{n}_{N,x}\,NO_2 + \bar{n}_{S,x}\,SO_2 + \bar{n}_{Mn,x}\,MnO_2 + \bar{n}_{Sn,x}\,SnO_2 + \bar{n}_{Zn,x}\,ZnO$$

$$+ \frac{\bar{n}_{P,x}}{2}\,P_2O_5 + \frac{\bar{n}_{I,x}}{2}\,I_2 + \frac{0.65\bar{n}_{N,x}}{2}\,N_2$$

The following assumptions have been made in the derivation of the above combustion reaction:

1. NO_2 is considered representative of both other possible NO_x compounds and HCN due to its similar toxicity to these compounds. According to CPR-15[v], it is assumed that the conversion fraction of the atom N in the burned pesticide to NO_2 is 0.35 while the remainder is converted into N_2. This factor has been reduced in PGS-15[iv] from 0.35 to 0.1.
2. It is assumed that all Cl, Br, F, I,P, Mn, Zn, Sn and S atoms in the burned pesticide are converted into HCl, HBr, HF, I_2, P_2O_5, MnO_2, ZnO, SnO_2 and SO_2 respectively.
3. It is assumed that there are more Hydrogen atoms than the sum of Cl, Br, and F.[5]

Due to the low toxicity of I_2, P_2O_5, MnO_2, ZnO and SnO_2 and N_2, the risk from these compounds in comparison with the other combustion products is considered to be negligible and they are subsequently ignored in the combustion effluent. Thus the only combustion products (besides the PCDD/PCDF generators) considered in the risk analysis are HCl, HBr, HF, NO_2 and SO_2. Because F and Br are found in much smaller quantities in pesticides than Cl and because the toxicity of HF and HBr is in the same order of magnitude as HCl, the emission rates of HF and HBr are added to that of HCl in the current approach.

PCDD's and PCDF's

PCDD's and PCDF's can form in the burning of polychloro-phenols and polychloro-aromatics. As a guide, compounds with one aromatic structure and at least two chlorine atoms on the benzene ring are considered to be potential PCDD/PCDF generators. Due to the fact that combustion of these compounds can form many different types of PCDD's and PCDF's with largely varying toxicity, the products are measured in terms of equivalent 2,3,7,8-trichlorodibenzodioxin (TEQ). This is a conservative approach as TEQ is the most toxic of these dioxins. The literature[1] states that between 1 and 10mg of TEQ per kg of burned polychlorophenols and polychloro aromatics is formed. For the risk analysis (section 3.3.3 of TNO report 90-424[1]) the most conservative estimate of 10mg of TEQ formed per kg burned PCDD/PCDF generators is used.[6]

2.2.2 Unburned toxic material

Air born powders or evaporated liquid may escape to the atmosphere without being burned due to inefficiency of the combustion process. Only highly toxic chemicals with LD_{50} for rats of less than 25mg/kg are considered relevant. Section 3.3.2 of the risk analysis methodology[1] gives the percentage of highly toxic material that is released unburned to the atmosphere[7]:

- A maximum of 10% of highly toxic material stored with a flash point of less than 100^0C (category 1.0). In the current model the worst-case value of 10% is assumed.
- A maximum of between 1-2% for compounds stored with a flash point of higher than 100^0C. In the current model the worst-case value of 2% is assumed.

[5] The current code checks that this assumption is true and if it is not valid the coefficient of H_2O is set to zero to avoid a negative contribution to the oxygen requirement. If this occurs the program gives a warning.

[6] Note that with this approach the same portion of burned pesticide (category 2) can be assumed to form complete combustion products and PCDD/PCDF's. Due to the fact that such a small portion is converted to PCDD/PCDF's there will be negligible error in the mass balance.

[7] ERROR. A similar mass conservation error occurs as in footnote 6, as 100% conversion is assumed for complete combustion of highly toxic material. The magnitude of this error will depend on the relative magnitude of the highly toxic material in the stored pesticide.

2.3 Fire development

The development of the fire and its effect on the surrounding population is dependent on the building ventilation and the type and performance of the fire mitigation system. These factors impact the fire surface area (and therefore the burning rate) and the fire duration.

2.3.1 Ventilation

The storage volume can be ventilated by natural or forced ventilation and is usually described by the ventilation factor which is measured in the number of building air changes per hour. The ventilation determines the amount of air (and therefore oxygen) that is available for the fire and therefore affects the rate of combustion. The number of air changes per hour ranges between 0 and 4 according to section 6.1 of TNO report 90-424[1]. The released products rise in the storage volume and leave the building through the ventilation ducts and openings, assumed to be at the top of the building.

2.3.2 Fire effect mitigation system

Guidelines for prediction of fire characteristics are given in TNO-report 90-424[1] and are summarised in Appendix A. The report categorises seven types of fire mitigation system and specifies fire duration, surface area and probability of occurring depending on the performance of the mitigation system.

Recommended revised guidelines are given in CPR-15[v] where twelve types of fire mitigation system are categorised. These are summarised in Appendix B. Depending on the performance of the system and the probability of the ventilation openings being open or closed, the fire surface area, duration and probability of occurring can be derived.

The above CPR-15 guideline has now been superseded by the PGS-15 guideline. This guideline is described in Appendix C.1.

2.3.3 Fire surface area

The size of the fire surface area depends on the amount of oxygen fed to the fire as well as the performance of the fire-fighting system. A poorly working system will allow the fire to achieve a larger surface area than a highly effective system. Thus the fire surface area ultimately depends on the probability of the fire mitigation system working at a certain performance level.

2.3.4 Fire duration

The fire duration depends on the circumstances surrounding the fire as well as the applied fire mitigation steps. The fire duration is the time required to extinguish the fire unless the maximum duration is reached. The maximum duration is limited to 30min which according to CPR-15[v]is considered to be the maximum time before plume rise takes place after which the fire effluent is buoyant and poses no toxic threat to the surrounding population.

2.4 Burn rate

The burn rate depends on the amount of oxygen available and the surface area of the flammable pesticide in contact with the oxygen. The influence of packaging material and solvents (whether they burn with the pesticide or remain inert) on the actual burning rate of the active material cannot be quantified with current knowledge. Therefore according to CPR-15[v] it is assumed that these inactive substances burn at the same rate as the active substances. We consider two scenarios in the risk analysis for calculation of the total burning rate (active and inactive):

2.4.1 Surface-area limited fire

If the air flow rate through the building is large enough to ensure that excess oxygen is available after combustion, then we term the fire "surface area limited". The standard maximum reaction rate given by CPR-15[v] where the fire is not limited by the oxygen supply is 0.025 kg/(s.m^2).

Therefore for a fire of surface area A (m^2) the maximum burn rate B_{max} (kg/s) is given by:

$$B_{\max} = 0.025A \quad (3)$$

In case of the storage of ADR Class 3 materials (flammable liquids) a modified maximum burn rate is applied as defined by Equation (19).

2.4.2 Oxygen-limited fire

When the flow rate of oxygen to the fire limits the combustion reaction rate to less than $B_{\max}$ then we term the fire "oxygen limited". The total amount of oxygen available for the fire is the sum of that initially in the building volume and the oxygen provided by the ventilation during the fire duration. By mass balance the rate of oxygen available to the fire can be expressed as[8]:

$$\dot{N}_{(O_2)} = \frac{y_{O_2}^{air}(1 + t_{fire}F)V}{\nu_{air} \times t_{fire}} \quad (4)$$

where:

$\dot{N}_{(O_2)}$ = rate of oxygen available to the fire (kmol/s)

F = ventilation factor (air changes per second)

V = volume of warehouse (m^3)

$y_{O_2}^{air}$ = mole fraction of O_2 in air

ν_{air} = molar volume of air (m^3/kmol)

t_{fire} = fire duration (s)

In order to calculate the oxygen requirement of the inactive material it is assumed that the structural formula of the inactive material is the same as that of the active material in line with the assumption in section 2.4 above. The total burning rate for an oxygen limited fire can then be given by[9]:

$$B_x = \frac{\dot{N}_{(O_2),x} \times \overline{M}_{W,x}}{\overline{n}_{o_{2,x}}} \quad (5)$$

where:

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[8] The TNO report 90-424 uses values of :

(a) $y_{O_2}^{air}$ =0.2: PHAST/SAFETI uses the more accurate value of $y_{O_2}^{air}$ =0.21

(b) ν_{air} =24m^3/kmol: this corresponds to a air molar volume at an assumed warehouse temperature of 20C: ν_{air} = 22.4*293.15/273.15

(c) t_{fire} =1800s: a more general value of fire duration is more appropriate. PHAST/SAFETI uses the duration input by the user (default from Table 3)

[9] ERROR in TNO report. The burn rate in the TNO report 90-424 incorrectly calculates the burn rates for categories 10,11 and 2 by multiplying the category 0 burn rate with the ratio of the number of moles oxygen required for complete combustion ($\overline{n}_{o_{2,x}} / \overline{n}_{o_{2,0}}$). PHAST/SAFETI 6.2 uses equation (5)

$\bar{n}_{o_{2,x}}$ = the number of moles of oxygen required to give complete combustion of one mole of the average pesticide structure of category *x* (see Section 2.1)

B_x = burning rate of the pure pesticide category *x* material (kg/s); this includes the burning rate of the packaging material etc.

$\dot{N}_{(O_2),x}$ = rate of oxygen available to the fire (kmol/s) for category *x*

$\dot{N}_{(O_2),x}$ is calculated using the oxygen requirement for category *x* relative to the total:

$$\dot{N}_{(O_2),x} = \dot{N}_{(O_2)} \left[\frac{\bar{n}_{o_2,x} \dfrac{m_x}{z_{act.x} \bar{M}_{W,x}}}{\bar{n}_{o_2,o} \dfrac{m_o}{z_{act.o} \bar{M}_{W,o}}} \right] \quad (6)$$

where m_x is the total active mass of category *x* (kg)

In the above equation the term between brackets […] represents the mole fraction of category x requirement relative to category 0: its enumerator represents the total moles of oxygen requirement (active and inactive) for category x, while the denominator represents the total moles of oxygen requirement for category 0.
If the burn rate calculated in this way is higher than the maximum burn rate (B_{max}) then there is excess oxygen available and the maximum burn rate should be used: $B_o = \min(B_o, B_{max})$.

Burn rate as function of fire duration

Above it is simplistically assumed that the burn rate B_o is constant along the entire fire duration t_{fire} while for increased fire duration this constant value is smaller. Using Equations (4), (5), (6) it can be derived that the burn rate B_o as function of fire duration t_{fire} is given by

$$B_o = \min \left\{ B_{\max} , \frac{y_{O_2}^{air} (1 + t_{fire} F) V \bar{M}_{W,o}}{\nu_{air} t_{fire} \bar{n}_{o_{2,0}}} \right\} \quad (7)$$

Figure 2 plots the value of this burn rate B_o as function of the fire duration. For very large fire durations the burn rate approaches B_∞,

$$B_\infty = \min \left\{ B_{\max} , \frac{y_{O_2}^{air} F \; V \bar{M}_{W,o}}{\nu_{air} \bar{n}_{o_{2,o}}} \right\} \quad (8)$$

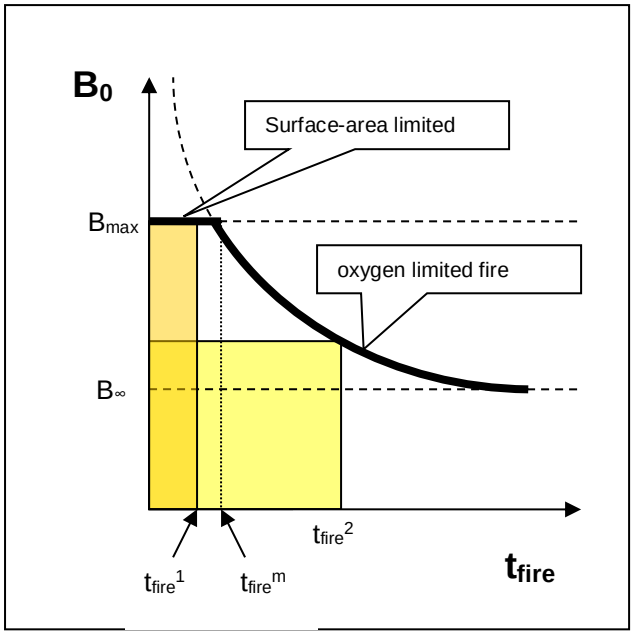


Figure 2. Burn rate B_o (kg/s) as function of fire duration t_{dur} (s)

In case $B_{max} \leq B_\infty$, the fire will be always surface-area limited with $B_o = B_{max}$ and the maximum fire duration equals $t_{fire}^{max} = m_0 / (z_{act,o} B_{max})$.

In case of $B_{max} > B_\infty$, let t_{fire}^{m} be the fire duration at which B_o reduces to B_{max}, i.e. the fire duration at which the fire switches from a surface-area limited fire to an oxygen-limited fire. From Equation (7) it follows that

$$t_{fire}^{\ m} = \left\{ \frac{B_{\max} \nu_{air} \bar{n}_{o_{2,x}}}{y_{O_2}^{air} V \bar{M}_{W,x}} - F \right\}^{-1} \qquad (9)$$

If the fire duration $t_{fire} \leq t_{fire}^{m}$, the maximum burn rate B_{max} is applied and the fire is surface-limited. For fire duration $t_{fire} \geq t_{fire}^{m}$, the burn rate is applied according to the formula for an oxygen-limited fire. The burn rate B_o decreases with increasing t_{fire} approaching the constant value B_∞ for $t_{fire} \rightarrow \infty$.

Check for maximum fire duration

The total mass of burned pesticide equals $t_{fire}\ B_o$, e.g. for fire duration t_{fire}^2 it is given by the coloured area in Figure 2 (likewise for t_{fire}^1). For a given specified fire duration t_{fire}, the area of this coloured area should be smaller than the total mass in category 0, $m_o/z_{act,o}$. The maximum fire duration at which $m_o/z_{act,o}$ is reached (i.e. entire warehouse pesticides are burned) is given by t_{fire}^{max}

$$t_{fire}^{\ \max} = \frac{m_o}{z_{act,o} B_o} \qquad (10)$$

In case the specified fire duration t_{fire} is larger than t_{fire}^{max}, the fire duration t_{fire} will be reset to the maximum fire duration t_{fire}^{max}. Using $t_{fire} = t_{fire}^{max}$ and Equations (4), (5), (6) in Equation (10), leads to an equation for t_{fire}^{max}, with the following solution:

$$t_{fire}^{\ \max} = \frac{1}{F} \left\{ \frac{m_o \nu_{air} \bar{n}_{o_{2,x}}}{z_{act,o} y_{O_2}^{air} V \bar{M}_{W,x}} - 1 \right\} \qquad (11)$$

Thus the above fire duration is used as the modified value of t_{fire} in case all warehouse fire pesticides are burned for an oxygen-limited fire.

2.5 Emission rates

2.5.1 Combustion products HCl, NO_2 and SO_2

The total pesticide (category 0) is assumed to consist of 'pure' pesticide ('active' material) and the package material etc. It is assumed that the burning of the packaging material etc. does not result in the production of toxic burning products (no C, H, O, N, S, P, Cl, F, Br, I, Mn, Zn, S included in the structural formula of the packaging material).

The emission rates of the combustion products can be calculated from the product of their conversion fraction (mass combustion product per mass pesticide burned), and the burning rate of the active pesticide. The burning rate of the active pesticide is the total burning rate (as discussed in 2.4 above) multiplied by the active mass fraction:

$$\dot{m}_{prod} = \eta_{prod} B_0 z_{act,0} \qquad (12)$$

where:

prod	=	type of combustion product, *prod* = HCl, NO_2 or SO_2
$\dot{m}_{prod}$	=	release rate of combustion product (kg/s)
η_{prod}	=	mass conversion factor of combustion product (kg product/kg active pesticide burned)
$z_{act,0}$	=	average fraction of active material in the total pesticide (category 0)

The mass conversion factors of the combustion products (η_{prod}) can be expressed using the number of moles of Cl, F, Br, N and S per mol of pesticide (as per the combustion formula), their molecular weights, and their extent of conversion to HCl, HF, HBr, NO_2 and SO_2 (see Section 2.2.1)

In CPR-15 mass emission rates of HF and HBr were added to that of HCl, In PGS-15 this has been modified, i.e. molar emission rates of HF and HBR were added to that of HCl. This latter formulation has been included from version 6.7. Thus the adopted mass fractions HCl, NO_2 and SO_2 (kg / kg of active warehouse material) are as follows:

$$\eta_{HCl} = \frac{\bar{n}_{Cl,0} M_{W,HCl} + \bar{n}_{F,0} M_{W,HF} + \bar{n}_{Br,0} M_{W,HBr}}{\bar{M}_{W,0}} \text{ , } \textit{[CPR-15; before version 6.7]} \qquad (13)$$

$$\eta_{HCl} = \frac{\left[\bar{n}_{Cl,0} + \bar{n}_{F,0} + \bar{n}_{Br,0}\right] M_{W,HCl}}{\bar{M}_{W,0}} \text{ , } \qquad \textit{[PGS-15; from version 6.7]}$$

$$\eta_{NO_2} = \frac{0.35 \bar{n}_{N,0} M_{W,NO2}}{\bar{M}_{W,0}} \qquad (14)$$

$$\eta_{SO_2} = \frac{\bar{n}_{S,0} M_{W,SO2}}{\bar{M}_{W,0}} \qquad (15)$$

where $M_{W,HCl}$ = 36.458 kg/kmol, $M_{W,HF}$ = 20.008 kg/kmol, $M_{W,HBr}$ = 80.918 kg/kmol, $M_{W,NO2}$ = 46.01 kg/kmol, $M_{W,SO2}$ = 64.02 kg/kmol are the molecular weights of HCl,HF, HBr, NO_2, SO_2 respectively.

2.5.2 2,3,7,8-TCDD equivalent

The emission rate of TEQ is expressed as an empirical fraction of the PCDD/PCDF generating compounds (category 2) burned, using the empirical factor from Section 2.2.1 (10^{-5} kg of TEQ forms per kg of burned PCDD/PCDF):

$$\dot{m}_{TEQ} = 10^{-5} B_2 z_{act,2} \quad \textbf{(16)}$$

where:

$\dot{m}_{TEQ}$ = release rate of 2,3,7,8-TCDD equivalent (kg/s)

$z_{act,2}$ = average fraction of active material in category 2

2.5.3 Unburned highly toxic substances

The emission rates of unburned highly toxic materials are expressed as a mass fraction of the burn rates of the relevant category according to Section 2.2.2 (10% for category 10 and 2% for category 11). Thus the emission rates (kg/s) are[10]:

$$\dot{m}_{10} = 0.1 B_{10} z_{act,10} \quad \textbf{(17)}$$

where:

$\dot{m}_{10}$ = release rate of unburned active category 10 material (kg/s)

$z_{act,10}$ = average fraction of active material in category 10

$$\dot{m}_{11} = 0.02 B_{11} z_{act,11} \quad \textbf{(18)}$$

where:

$\dot{m}_{11}$ = release rate of unburned active category 11 material (kg/s)

$z_{act,11}$ = average fraction of active material in category 11

[10] According to TNO 90-424 (section 6.4 equation (6.9) and CPR-15 (section 4.2.4.3 equation (4.9)) the release rates of unburned category 10 and 11material is calculated by multiplying the fractions 0.1 and 0.02 for categories 10 and 11 respectively by the total active burn rate of highly toxic material ($B_{10} + B_{11}$). These equations are wrong according to the theory in the report sections above. Also it cannot be true because if only one of the categories 10 or 11 is present in the warehouse, an emission rate would still be calculated for the other category which is not even in the warehouse.

3. DISCHARGE SOURCE DATA FOR DISPERSION MODELLING

The model provides full information to create the discharge source term for subsequent input to a dispersion model for the toxic effluent mixture described in section 2.2.1 consisting of NO_2,SO_2 and HCl:

Release rate

The release rate is given by equation (7) in section 2.5.1.

Composition

The composition of the mixture can be calculated from the relative proportions of the sum of mass conversion factors η_{HCl} , η_{NO2} and η_{SO2} as calculated in section 2.5.1.

Release temperature

After combustion the effluent mixture is cooled by the walls of the warehouse and by the fire mitigation system (eg. H_2O or CO_2) to an unknown extent. Therefore the model assumes that the effluent mixture is released at the ambient temperature at the building height. Alternatively, the model also allows for a (larger) user-specified temperature

Release direction

The release direction is assumed to be vertical.

Release velocity

The velocity is calculated by assuming that the release emanates from the surface area of the storage at the building height. The mass release rate (kg/s) divided by the effluent density (based on the material composition and temperature above) gives the volumetric flow rate (m^3/s). This divided by the surface area of the storage would then give the release velocity (m/s).

The release rates of unburned category 10 and 11 material as well as category 2 material are also provided and could be used in the source term for the dispersion calculations, provided further assumptions of material composition representing the respective categories are made.

4. FUTURE DEVELOPMENTS

The following further improvements of the warehouse fire model can be considered for future implementation.

Modelling of excess air and non- toxic combustion products

The current model ignores the possibility of excess air and nitrogen remaining after removal of reacted oxygen being released to the atmosphere along with the toxic combustion products. This will effect the toxic dose calculated using results from the dispersion model. A simple attempt could be made by calculating the differences between the oxygen flow rate through the building and the oxygen supply rate required to maintain the burning rate in the case of surface area limited fires. The non-toxic combustion products (I_2, P_2O_5, MnO_2, ZnO and SnO_2 and N_2) are also ignored in the plume. These, along with the excess air would dilute the toxic products and Affect the toxic dose calculated with results from the dispersion model.

Extension to all DIPPR materials

The DIPPR materials database currently used by Phast (Risk) includes data of the stoichiometric amount of air required for complete combustion. This allows calculation of the number of moles of "combustion oxide" per mole of flammable material burned. Although this would lead to more accurate emission rate calculations, no information would be available for the composition of the "combustion oxide". The toxicity of the "combustion oxide" would have to be modelled separately before integration into the DNV products.

Final temperature of plume

Currently there is no calculation of the final temperature of the plume and the ambient temperature or a user-specified temperature is assumed for linkage with the unified dispersion model. A more accurate final temperature could be obtained by performing an energy balance in the warehouse taking into account heat of combustion of the pesticide, heat of vaporisation and sensible heat of liquids, heat transfer to the air and heat transfer to the fire extinguishing materials.

Combustion efficiency

A "combustion efficiency" (reaction extent) could be included for more accurate calculation of the relative proportions of combusted and unburned material in the fire effluent.

The modelling of the warehouse fire model and its GUI implementation could be fully aligned with the new RIVM version of the pool fire model POLF[vi]. This new version includes the modelling of excess air entrainment into the pool fire, the calculation of the plume temperature, and the combustion efficiency. The POLF thermodynamics could be e.g. applied to calculate the above final temperature of the plume. The extension to all DIPPR materials should also be carried out analogously. Also combustion efficiency is included in the pool fire model POLF.

APPENDICES

Appendix A Old guidance on fire development according to TNO report 90-424

This appendix summarises old guidelines on fire development according toTNO report 90-424[i]. Appendix B includes revised guidelines as given by the Dutch Government in Section 4.3 of CPR-15 [v].

A.1 Scenarios

Data for the prediction of fire surface area and duration are available for the following seven scenarios of fire mitigation taken from the TNO report 90-424[1].

1) Automatic sprinkler system (deluge)

2) Automatic gas extinguishing installation (eg. CO_2)

3) Automatic high expansion foam installation system (hi-ex)

4) Manual system operated by on-site fire fighting department using water deluge

5) Manual system operated by on-site fire fighting department using dry deluge

6) Manual system using smoke hatches[11]:

7) Manual system operated by local fire brigade

A.2 Fire surface area

Table 1 has been drawn up based on the probability structure of the above seven fire scenarios depending on the performance: works well, works adequately, works poorly, fails, fails (open room/hatches), fails (closed room/hatches). Note that the sum of the 'performance' probabilities equals 1 for each scenario.

Table 2 gives the fire surface areas relevant to these scenarios. According to the TNO-report 90-424[1] the maximum possible fire surface area is set at 300m^2. Also the report specifies that the fire surface area cannot be greater than the floor surface area of the storage building. Thus according to TNO-report 90-424[1] for an automatic sprinkler installation, the event where the mechanism fails has the lowest probability of occurring (0.01), but results in the worst scenario of the maximum surface area (300m^2). The report predicts that the event where an automatic gas extinguishing installation is in working order however (probability 0.99) restricts the fire to a surface area of 20m^2.

[11] If these are closed in the event of a fire they are able to restrict the supply of oxygen to the fire

Table 1. Probabilities for fire scenarios

Fire-Fighting System	Fire Scenario: Defined by Performance of System					
	Works Well	Works Adequately	Works Poorly	Fails	Fails (Closed Room/Hatches)	Fails (Open Room/Hatches)
Automatic System						
Deluge	0.45	0.44	0.1	0.01	-	-
Gas	0.99	-	-	-	0.005	0.005
Foam	0.45	0.44	0.1	-	0.005	0.005
Manual System operated by company fire brigade						
Deluge	0.35	0.45	0.1	0.1	-	-
Dry	0.4	-	0.1	0.5	-	-
Smoke Hatches	0.25	-	0.25	-	0.49	0.01
Action by local fire brigade						
No Automatic System, No company fire-brigade	-	-	-	1	-	-

Table 2. Default surface areas for fire scenarios (m^2)

Fire-Fighting System	Fire Scenario: Defined by Performance of System					
	Works Well	Works Adequately	Works Poorly	Fails	Fails (Closed Room/Hatches)	Fails (Open Room/Hatches)
Automatic System						
Deluge	20	50	100	300	-	-
Gas	20	-	-	-	300	300
Foam	20	50	100	-	300	300
Manual System operated by company fire brigade						
Deluge	20	50	100	300	-	-
Dry	50	-	100	300	-	-
Smoke Hatches	50	-	100	-	300	300
Action by local fire brigade						
No Automatic System, No company fire-brigade	-	-	-	300	-	-

A.3 Fire duration

Table 3 shows the relationship of fire scenario with fire duration as per the TNO-report[i].

Table 3. Default fire duration (min) for fire scenarios

Fire-Fighting System	Fire Scenario: Defined by Performance of System					
	Works Well	Works Adequately	Works Poorly	Fails	Fails (Closed Room/Hatches)	Fails (Open Room/Hatches)
Automatic System						
Deluge	30	30	30	20	-	-
Gas	5	-	-	-	30	30
Foam	15	15	15	-	30	20
Manual System operated by company fire brigade						
Deluge	30	30	30	30	-	-
Dry	30	-	30	30	-	-
Smoke Hatches	30	-	30	-	30	20
Action by local fire brigade						
No Automatic System, No company fire-brigade	-	-	-	30	-	-

Appendix B Old Revised guidance on fire development according to CPR-15

In Appendix A old guidelines on fire development according to TNO report 90-424[i] were given. In Appendix B.1 revised guidelines are summarised as given by the Dutch Government in Section 4.3 of CPR-15[v]. For further details the reader is referred to the latter document. In Appendix B.2 the recommended method is described for carrying out warehouse fire calculations in line with CPR-15 in SAFETI.

B.1 CPR-15 calculation of scenario frequencies and probabilities

The CPR-15 guidelines include a description of the scenarios to be taken into account including the calculation of the frequencies and probabilities for these scenarios. This can be summarised by the following consecutive steps:

1. Specify combination of **protection level and fire extinction system**. The thirteen different choices (numbered 1a, 1b, 2, 3, …., 12) are listed in Table 4. This table also includes a reference to the CPR-15 Table, including scenario details for the fire extinction system.

Table 4. CPR-15 protection levels and fire extinction systems

Protection level	Fire extinction system	CPR-15 table
1 – Automatic system	1a – Sprinkler in storage racks	4.2
	1b – Sprinkler not in storage racks	4.2
	2 – Deluge	4.3
	3- Gas	4.4
	5 – Hi-ex	4.6
	9 – Hi-ex with inside air	4.10
1 – Company fire brigade	6 – Manual deluge	4.7
	7 - Dry	4.8
	8 – Smoke hatches	4.9
1 – Local fire brigade	4 – Dry deluge	4.5
2 – Local fire brigade	10 – Mobilisation within 6 minutes	4.11
	11 – Mobilisation within 15 minutes	4.12
3 – Local fire brigade	12	4.13

2. Specify **frequency** of warehouse fire (default $8.8*10^{-4}$ for protection levels 1,2 and default $1.8*10^{-4}$ for protection level 3). See Section 4.3.3 in CPR-15 for further details.

3. Specify likelihood P_{do} of doors being open. There are options of either automatic or manual closing doors. The default probability for the doors being open is P_{do} = 0.02 for automatic, and P_{do} = 0.1 for manual closing doors. The **ventilation rate** of 4 is used for closed doors and infinite for open doors. See end of Section 4.3.2 in CPR-15 for further details.

4. Specify range of scenarios. There are a number of fire scenarios, determined by a range of fire surface areas and whether the doors are open and closed (different ventilation rates). The precise range of fire scenarios and corresponding **fire surface areas**, **fire duration** and **probabilities** are set from the CPR-15 table corresponding to the type of fire extinction system (see above Table 4). Furthermore account for the following:

   4.1. The possible range of fire surface areas includes 20, 50, 100, 300, 900, 1500, 2500 m^2. The fire surface area must not be larger than the total warehouse storage surface area. Moreover the sum of the probabilities for all fire scenarios must be equal to one.[12] See also the second part of Section 4.3.2 in CPR-15.
   4.2. If the storage space is fireproof for time t_{proof}, then use fire duration t_{dur} = max {t_{dur} from table, t_{proof}}. After time of t_{proof} plume is assumed to lift off.[13]

[12] Use maximum fire surface area = warehouse surface area, with probability = sum of probabilities from table of all surface areas larger than warehouse surface area

[13] This is a modified suggestion from CPR-15. The original CPR-15 states: 'If storage space is fireproof for more than 20 minutes, increase fire duration to 30 minutes for areas > 300 m^2 and systems 1,2,4,11,12'

4.3. If ADR Class 3 materials stored in synthetics package without a floor partition, then a maximum storage surface area is applied dependent on the type of system (see first part of Section 4.3.2 in CPR-15 for further details):

4.3.1. system 1 - maximum storage surface area is 800m^2 with probability 0.005 P_{do} [14]

4.3.2. system 4 - maximum storage surface area is 100m^2

4.3.3. system 6 - maximum 600 m^2 with probability 0.05 P_{do}[14]

4.3.4. systems 7 - maximum 300 m^2 with probability 0.5 P_{do}[14]

4.3.5. systems 8 - maximum 300 m^2 with probability 0.5

4.3.6. system 10,11 - maximum 1500 m^2 with probability 0.06

[14] CPR-15 states a probability with missing term P_{do}, which appears to be an error

B.2 CPR-15 method for SAFETI 6.53 warehouse fire calculations

The previous section described the determination of the scenarios and corresponding surface area, fire duration, and scenario probability. Fore each of these scenarios calculations are to be carried out in SAFETI. This includes WHFIRE warehouse fire calculations to evaluate the composition and amount of HCl/SO_2/NO_2 mixture released from the building, and subsequent dispersion calculations (using the building wake model). The results of toxicity calculations and the fire scenario probabilities are subsequently used as input to the SAFETI risk calculations.

Further details on the recommended method for carrying out the SAFETI 6.53 calculations are described in further detail below.

1. Open new study

2. “Materials” tab: insert a pesticide for each pesticide material present in the warehouse and specify its individual structural formula

3. “Models” tab: create two models. The first model is used for modelling those scenarios with door closed (ventilation rate of 4), while the second model is used for those scenarios with doors open (infinite ventilation rate):
   3.1. “pesticide” tab: specify stored mass and active mass fraction for each material stored in the warehouse
   3.2. “building” tab, tick “roof/lee release”, specify building data (use building angle = 0, and choose building width W identical to building length L such that B*L equals the actual building surface area), choose ventilation rate of 4 for case of open doors and do not specify ventilation rate for closed doors (by default infinite rate is used)
   3.3. “risk” tab, you do not need to supply a frequency here in case you supply scenario frequencies

4. The user needs to generate a table as for the above example. He can do this as follows using the guidance from Appendix B.1.
   4.1. Identify combination of protection level and fire extinction system (see Table 4)
   4.2. Specify frequency of warehouse fire
   4.3. Set likelihood P_{do} of doors being open
   4.4. Identify scenarios and set fire surface, fire duration and probability for each scenario (Table 4 lists the CPR-15 Table corresponding to each fire extinction system, in which these data can be found).

5. Specify scenarios in line with above

Appendix C New revised guidance on fire development according to PGS-15

In Appendix B.1 guidelines were summarised as given by the Dutch Government in Section 4.3 of CPR-15[v]. In Appendix C.1 further revised guidelines are summarised according to the PGS-15 guidance[iv]. For further details the reader is referred to the latter document. Appendix C.2 describes the method for warehouse fire calculations in Phast (Risk) and SAFETI-NL. Appendix C.3 includes SAFETI-NL verification using the example in the PGS-15 guidelines.

C.1 PGS-15 calculation of scenario frequencies and probabilities

PGS-15 protection levels and fire-fighting systems

Protection level	PGS15 System no.#	Fire-fighting system (label)	CPR-15 table	Total fire freq. (/year)	ADR Class 3 max. surface (m2)	probability of infinite ventilation rate P_{do}
1 – Automatic system	1.1a	1.1a. Automatic sprinkler system	4.2	8.8E-4	800	standard
	1.1b	1.1b. Automatic in rack sprinkler system	4.2	8.8E-4	800	standard
	1.2	1.2. Automatic deluge system	4.3	8.8E-4	2500	standard
	1.3	1.3. Automatic inerting gas system	4.4	8.8E-4	2500	P_{do}=0.005
	1.5	1.5 Automatic Hi-ex foam system with outside air	4.6	8.8E-4	2500	P_{do}=1
	1.6	1.6 Automatic Hi-ex foam system with inside air	4.10	8.8E-4	2500	standard
1 – Company fire brigade	1.7	1.7 Company fire brigade with manual deluge system	4.7	8.8E-4	600	standard
	1.8	1.8 Company fire brigade only	4.9	8.8E-4	300	P_{do}=1
	1.9	1.9 Manual deluge system with water supply by the company fire brigade	4.8	8.8E-4	300	Standard
1 – Local fire brigade	1.10	1.10 Manual deluge system with water supply by the local fire brigade	4.5	8.8E-4	100	standard
2 – Fire detection and company or local fire brigade	2.1a	2.1a. Fire brigade – mobilisation < 6 minutes ADR class 3 stored in synthetic packaging	4.11	8.8E-4	800	P_{do}=1
	2.1b	2.1b. Fire brigade – mobilisation < 6 minutes ADR class 3 not stored in synthetic packaging or no ADR class 3	4.11	8.8E-4	1500 / 2500##	P_{do}=1
	2.2a	2.2a. Fire brigade – mobilisation < 15 minutes ADR class 3 stored in synthetic packaging	4.12	8.8E-4	800	P_{do}=1
	2.2b	2.2b. Fire brigade – mobilisation < 15 minutes ADR class 3 not stored in synthetic packaging or no ADR class 3	4.12	8.8E-4	1500 / 2500##	P_{do}=1
3 – Local fire brigade and preventive measurements only	3.1	3.1 Local fire brigade – preventive measurements only	4.13	1.8E-4	2500	P_{do}=1

Notes ad table:

#: System 1.4 **not** in warehouse model! (no lethal effects by plume rise)

##: Maximum surface area for storage of ADR class 3 not stored in synthetic packaging (2.1b and 2.2b) is 1500 m^2; no ADR class 3 is 2500 m^2. Since the maximum fire surface area to be considered is 900 m^2, this has no consequences**.** Since the GUI can include only one entry value, the entry value of 1500m^2 is chosen.

List of fire scenarios for PGS-15 systems

1.1a. Automatic sprinkler system

Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
20	*1800*	*0.45*	*1800*	*0.45*
50	*1800*	*0.44*	*1800*	*0.44*
100	*1800*	*0.1*	*1800*	*0.1*
300	*1800*	*0.01*	*1800*	*0.005*
900			*1800*	*0.005*

1.1b. Automatic in rack sprinkler system

Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
20	*1800*	*0.63*	*1800*	*0.63*
50	*1800*	*0.26*	*1800*	*0.26*
100	*1800*	*0.1*	*1800*	*0.1*
300	*1800*	*0.01*	*1800*	*0.005*
900			*1800*	*0.005*

1.2. Automatic deluge system

Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
20	*1800*	*0.63*	*1800*	*0.63*
50	*1800*	*0.26*	*1800*	*0.26*
100	*1800*	*0.1*	*1800*	*0.1*
300	*1800*	*0.01*	*1800*	*0.005*
900			*1800*	*0.005*

1.3. Automatic inerting gas system

This system does not use the standard P_{do} but P_{do}=0.005.

Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
20	*300*	*0.99/0.995 ≈0.995*		
300	*1800*	*0.005/0.995 ≈0.005*		
900			*1800*	*1*

1.5 Automatic Hi-ex foam system with outside air

P_{do}=1

Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
20			*600*	*0.89*
50			*600*	*0.09*
100			*600*	*0.01*
300			*1800*	*0.005*
900			*1800*	*0.005*

1.6 Automatic Hi-ex foam system with inside air

Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
20	*600*	*0.89*	*1800*	*0.89*
50	*600*	*0.09*	*1800*	*0.09*
100	*600*	*0.01*	*1800*	*0.01*
300	*1800*	*0.01*	*1800*	*0.005*
900			*1800*	*0.005*

1.7 Company fire brigade with manual deluge system

Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
20	*1800*	*0.35*	*1800*	*0.35*
50	*1800*	*0.45*	*1800*	*0.45*
100	*1800*	*0.1*	*1800*	*0.1*
300	*1800*	*0.1*	*1800*	*0.05*
900			*1800*	*0.05*

1.8 Company fire brigade only

$P_{do}=1$

Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
50			*1800*	*0.2*
100			*1800*	*0.3*
300			*1800*	*0.28*
900			*1800*	*0.22*

1.9 Manual deluge system with water supply by the company fire brigade

Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
50	*1800*	*0.2*	*1800*	*0.2*
100	*1800*	*0.3*	*1800*	*0.3*
300	*1800*	*0.5*	*1800*	*0.25*
900			*1800*	*0.25*

1.10 Manual deluge system with water supply by the local fire brigade

Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
300	*1800*	*1*	*1800*	*0.6*
500			*1800*	*0.4*

2.1a. Fire brigade – mobilisation < 6 minutes ADR class 3 stored in synthetic packaging

P_{do}=1

Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
300			*1800*	*0.72*
800			*1800*	*0.28*

2.1b. Fire brigade – mobilisation < 6 minutes ADR class 3 not stored in synthetic packaging or no ADR class 3

P_{do}=1

Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
50			*1800*	*0.2*
100			*1800*	*0.3*
300			*1800*	*0.28*
900			*1800*	*0.22*

2.2b. Fire brigade – mobilisation < 15 minutes ADR class 3 not stored in synthetic packaging or no ADR class 3

P_{do}=1

Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
300			*1800*	*0.78*
900			*1800*	*0.22*

2.2a. Fire brigade – mobilisation < 15 minutes ADR class 3 stored in synthetic packaging

P_{do}=1

Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
300			*1800*	*0.55*
800			*1800*	*0.45*

3.1 Local fire brigade – preventive measurements only

P_{do}=1

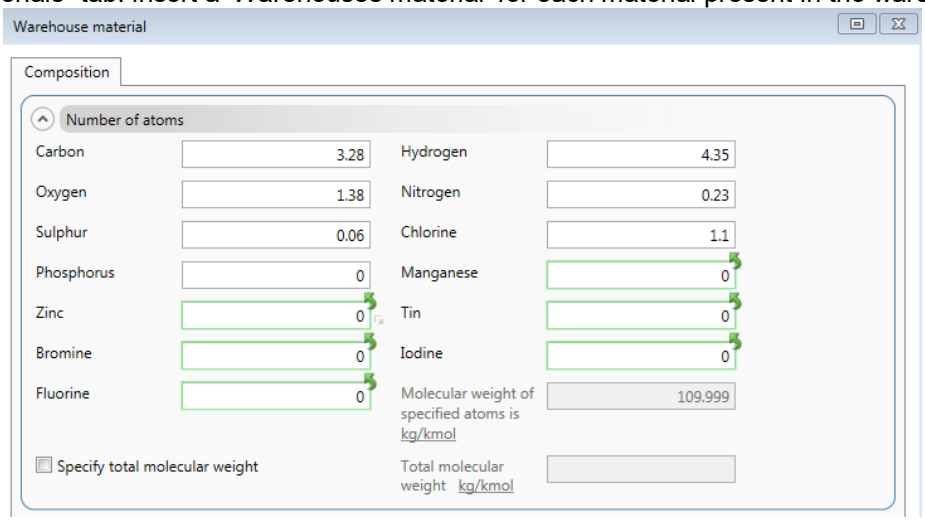
Fire surface area (m^2)	*Doors closed*		*Doors open*	
	Fire duration (s)	*Probability presuming doors closed (fraction)*	*Fire duration (s)*	*Probability presuming doors open (fraction)*
300			*1800*	*0.78*
900			*1800*	*0.22*

C.2 Method for Safeti and SAFETI-NL 8.0 warehouse fire calculations

The subsequent steps for the new 8.0 version are as follows:

1. Open new study

2. “Materials” tab: insert a ‘Warehouses material’ for each material present in the warehouse

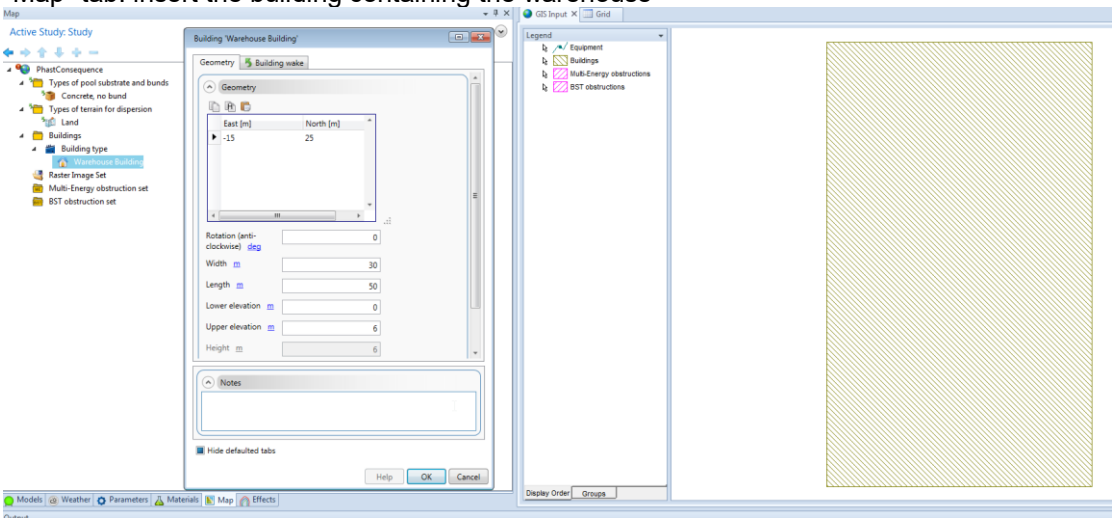


2.1. Specify its individual structural formula in “Warehouse material” tab:

2.1.1. The number of atoms of C, H, O, N, S, Cl, F, Br should always be specified. Combustion reactions will be included for all those atoms specified. Oxygen requirement will account only for those combustion reactions for which atoms are specified in the individual structural formula (see theory described earlier in this report for details, e.g. MnO only included if Mn is specified).

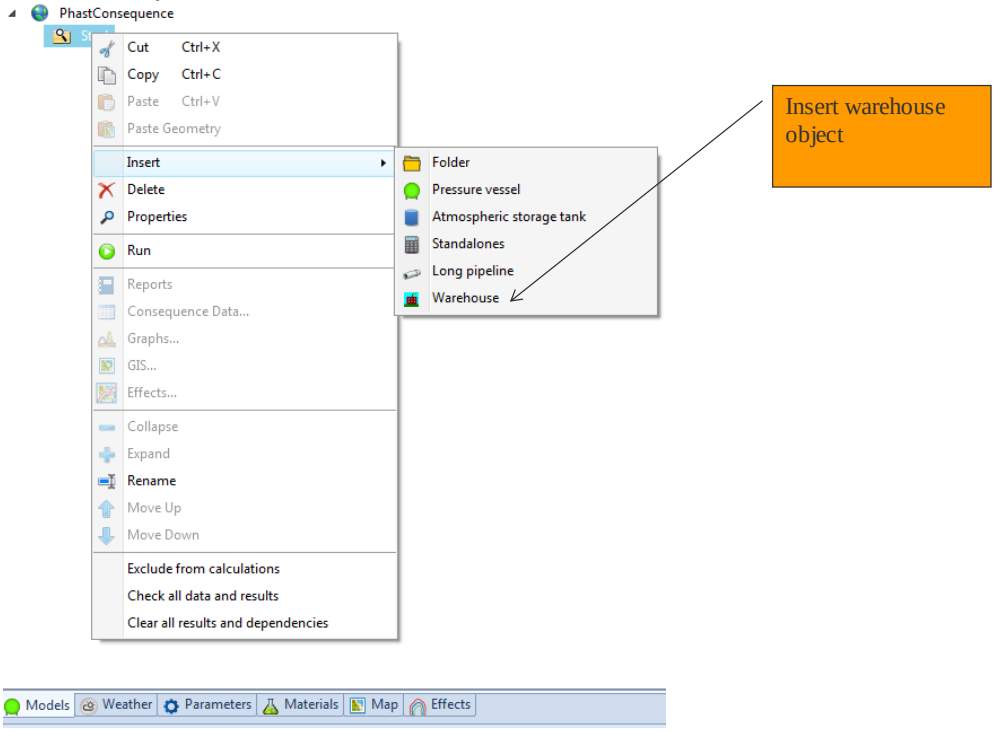
2.1.2. In case not all atoms are specified in the individual structural formula, the molecular weight for the pesticide should be user-specified. The specified molecular weight M_W needs to be larger than those based on the atoms already specified in the structural formula.

3. “Map” tab: insert the building containing the warehouse

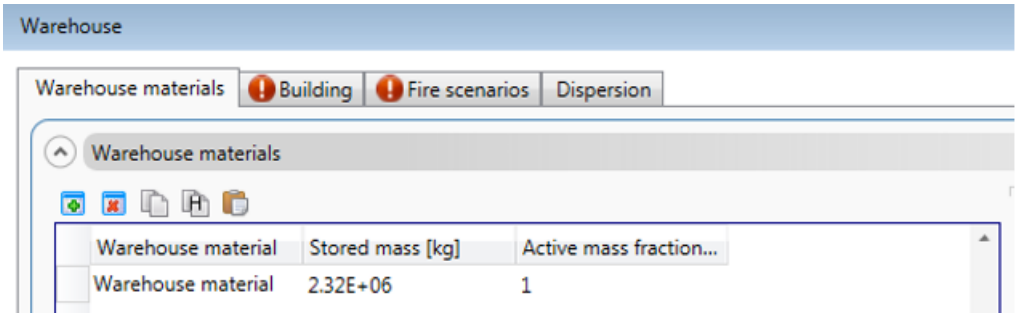


4. “Models” tab: create warehouse fire model

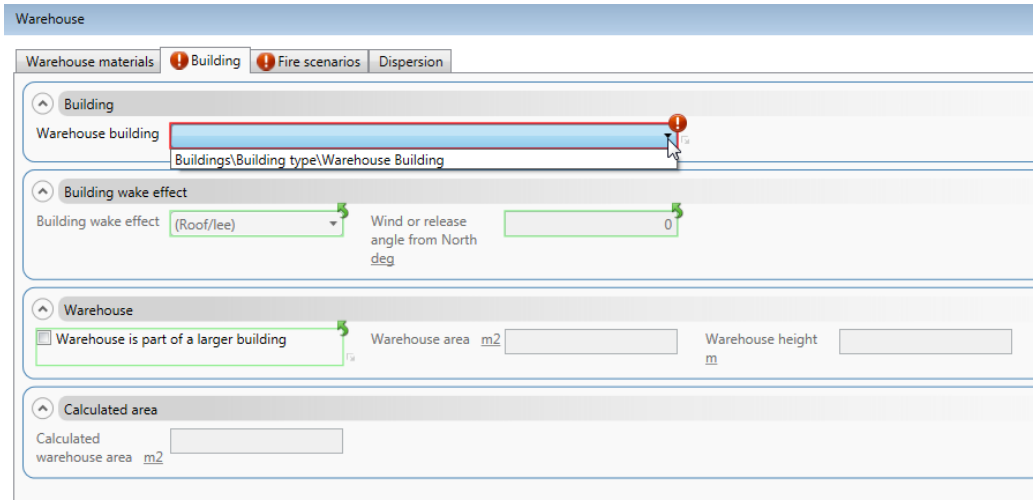
4.1. insert warehouse object



4.2. “Warehouse Materials” tab: specify stored mass and active mass fraction for each material stored in the warehouse

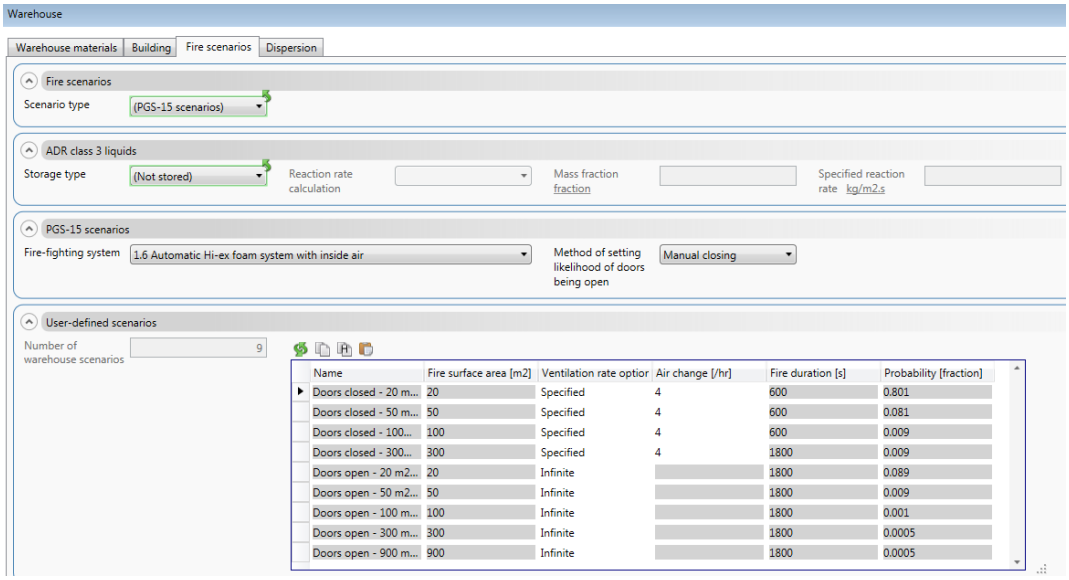


4.3. “Building” tab:



- Specify whether building wake effects (roof/lee release model) need to be accounted for
- (input in Phast only) specify angle between wind direction and North axis. This angle is not required in Safeti and Safeti-NL. Risk calculations currently do not allow consequence calculated to depend on the wind direction, and therefore in Safeti and Safeti-NL a rectangular building with width W and building length L is replaced with an equivalent square building with the same building surface area while applying a building angle θ_{BWM} =0
- Tick-box whether warehouse forms part of a larger building. If this tick-box is ticked, the user needs to specify the following additional data: surface area A_{wh} and height H_{wh} of warehouse. The upper limit for input of A_{wh} will be 2500m^2 (added general warehouse fire parameter). Moreover the following conditions must be satisfied: warehouse surface area $A_{wh} \leq$ overall building surface area BL, and warehouse height $H_{wh} \leq$ overall building height H. If tick-box not ticked, LW$\leq$2500m^2.

4.4. "Fire scenarios" tab. This tab defines the fire scenarios to be applied. The user defines whether to generate fire scenarios according to standard PGS-15 scenarios or he needs to define "user-defined scenarios" himself:



4.4.1. In case the user selects to "use PGS-15 scenarios", he needs to specify the following data:

- The type of fire-fighting system; see Appendix C.1 (system number 1.1a, 1.1b, 1.2, 1.3, 1.5, 1.6, 1.7, 1.8, 1.9, 1.10, 2.1a, 2.1b, 2.2a, 2.2b or 3.1)

- Method of setting likelihood of doors being open using either manual closing doors or automatically closing doors. For some fire-fighting systems this method is not used and this field is greyed out. In this case the likelihood of infinite ventilation rate is set for the fire-fighting system as defined in the warehouse fire parameters (not available to the non-admin user).

- Storage type, i.e. whether ADR Class 3 materials (synthetics or in other packaging) are stored in warehouse. In case of ADR Class 3 materials stored in synthetics packaging, the maximum storage area depends on the type of fire extinction system and is obtained from the "Warehouse fire parameters" (hidden to non-admin SAFTEI-NL user). In case ADR Class 3 materials are not stored, the standard maximum reaction rate given by CPR-15[v] (where the fire is not limited by the oxygen supply) is used: R_{st} = 0.025 kg/(s.m^2). Otherwise the maximum reaction rate R is either determined from a user-specified reaction rate R_{user}, R = R_{user}, or from a user-specified mass-fraction of ADR Class 3 materials, η_{ADR3}:

$$R = (1-\eta_{ADR3})R_{st} + \eta_{ADR3}R_{ADR3} \qquad (19)$$

Here R_{ADR3} = 0.1 kg/(s.m^2) is the maximum reaction rate for ADR Class 3 materials.

4.4.2. In case the user selects to use “user-defined scenarios”, he needs to define himself the data for each scenario. The data for each scenario are all contained in one row of the table:

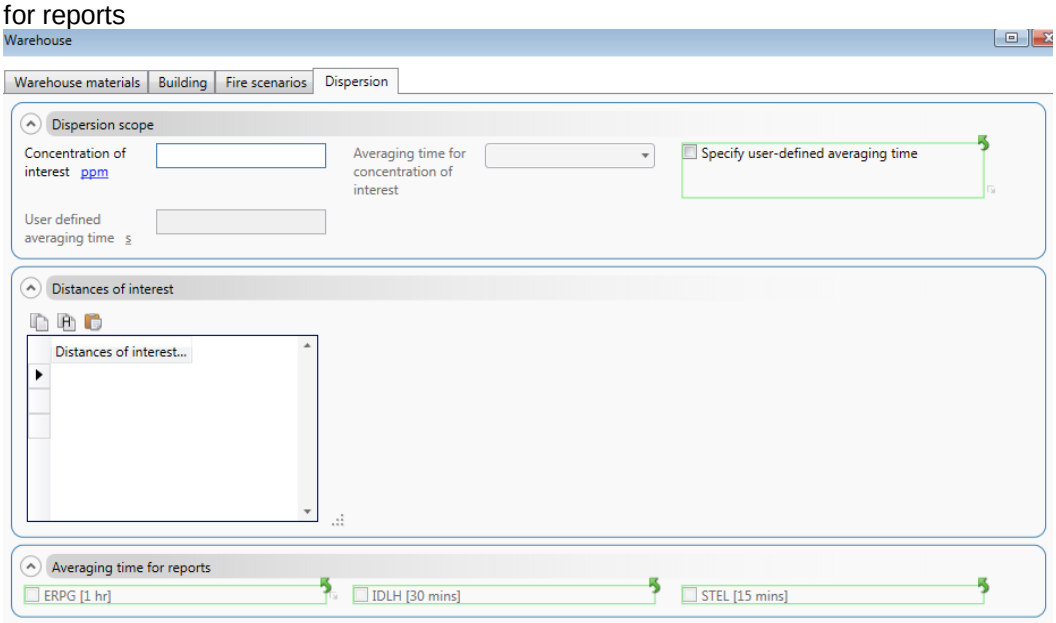
- The first column contains the name of the “scenario”
- The second column contains the fire surface area (must be >0 and ≤ the warehouse surface area A_{wh})
- The third column specifies whether ventilation rate needs to be specified. An infinite ventilation rate (“doors open”) is presumed if the ventilation rate is not specified. Otherwise, the ventilation rate (air changes/air; must be >0) needs to be specified in the fourth column.
- The fifth column is the fire duration (must be >0)
- The sixth column contains the relative probability (fraction). The sum over all rows must be 1. If this is not the case, the numbers will be renormalized such that their sum is 1.

In case the user selects “user-defined”, the “scenario definition” input data above are greyed out (not used) [15]. In this case the user also needs to specify the total warehouse fire frequency (default $8.8x10^{-4}$/year) in the “Risk” tab.

After the user has entered the data above and selects ‘OK’, the GUI will automatically generate the scenarios underneath the warehouse fire model (by invoking the WHFIRE entry point WHFSCE for defining the scenarios).

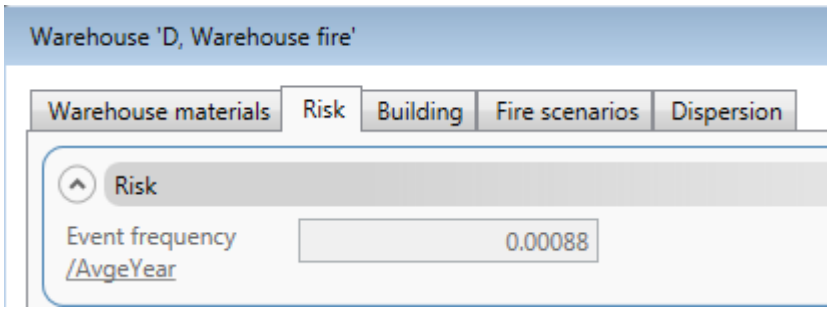
In case the tick-box “use PGS-15 scenarios” is ticked and in case the user wishes to modify the PGS-15 scenario, the user must first accept the input data (by selecting ‘OK’), re-edit the “warehouse fire” object and subsequently select the option “user-defined scenarios”. The user-defined data applied by default will correspond to the PGS-15 table appropriate with the protection level and fire extinction system. Thus this includes data for all (open-door and closed-door) fire scenarios including the total warehouse fire frequency. The user would subsequently be able to add or modify the fire scenarios.

4.5. “Dispersion” tab: specify concentrations and distances of interest, and averaging times to be adopted for reports



4.6. “Risk” tab. For user-defined scenarios, you can specify the total warehouse fire frequency here (sum of all scenario frequencies). For PGS-15 scenarios the input value cannot be modified.

[15] The storage type is also available in the case of a user-defined scenarios in order to enable a user-specific reaction rate and the specification of ADR Class 3 liquids. Currently for user-defined scenarios always the standard maximum reaction rate for surface-area limited fire is applied (as defined by the parameters; default 0.025kg/s/m^2)



5. Run warehouse fire model.

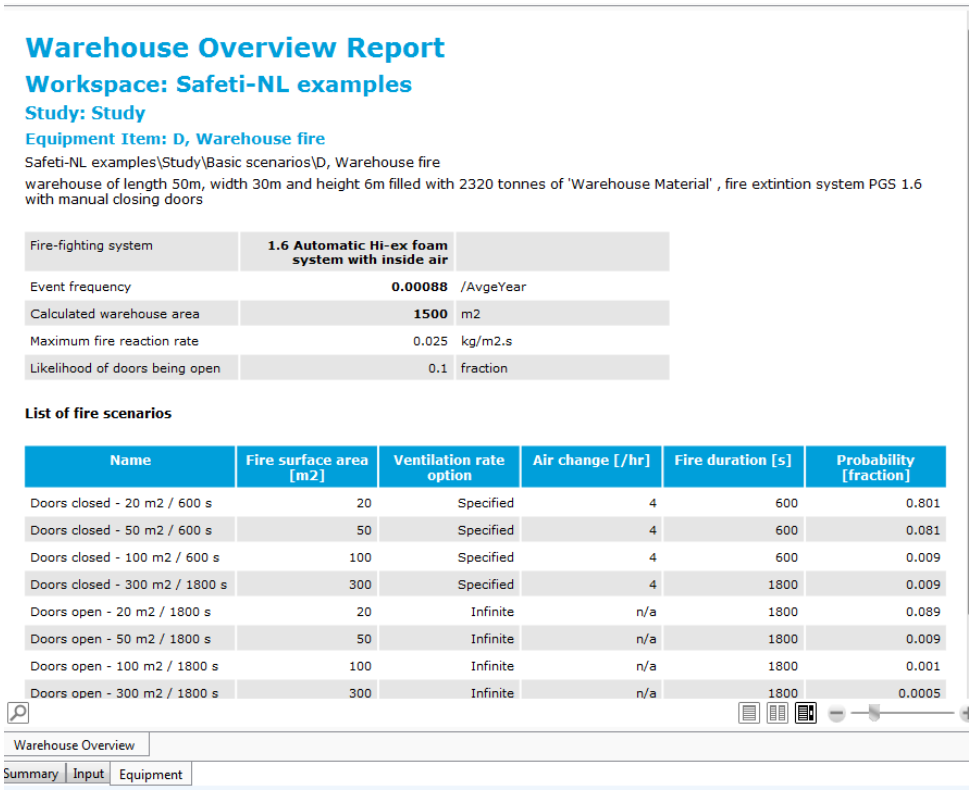
   This would carry out a run of the WHFIRE model for each of the scenarios.

6. View reports of warehouse fire model

   6.1. Overview report. This provides the following data:

   - Fire-fighting system
   - Total warehouse fire frequency (per year)
   - Warehouse surface area (m^2)
   - Maximum reaction rate for surface-area limited fire ($kg/s/m^2$)
   - Likelihood of doors being open (%) [not defined for a user-defined scenario]
   - Complete list of the fires scenarios, including scenario name, fire surface area, ventilation rate, fire duration, and probability (fraction)

   For example an overview report for fire-fighting system 1.6 looks as follows:



Warehouse Overview Report

Workspace: Safeti-NL examples

Study: Study

Equipment Item: D, Warehouse fire

Safeti-NL examples\Study\Basic scenarios\D, Warehouse fire

warehouse of length 50m, width 30m and height 6m filled with 2320 tonnes of 'Warehouse Material' , fire extintion system PGS 1.6 with manual closing doors

Fire-fighting system	**1.6 Automatic Hi-ex foam system with inside air**	
Event frequency	**0.00088**	/AvgeYear
Calculated warehouse area	**1500**	m2
Maximum fire reaction rate	0.025	kg/m2.s
Likelihood of doors being open	0.1	fraction

List of fire scenarios

Name	Fire surface area [m2]	Ventilation rate option	Air change [/hr]	Fire duration [s]	Probability [fraction]
Doors closed - 20 m2 / 600 s	20	Specified	4	600	0.801
Doors closed - 50 m2 / 600 s	50	Specified	4	600	0.081
Doors closed - 100 m2 / 600 s	100	Specified	4	600	0.009
Doors closed - 300 m2 / 1800 s	300	Specified	4	1800	0.009
Doors open - 20 m2 / 1800 s	20	Infinite	n/a	1800	0.089
Doors open - 50 m2 / 1800 s	50	Infinite	n/a	1800	0.009
Doors open - 100 m2 / 1800 s	100	Infinite	n/a	1800	0.001
Doors open - 300 m2 / 1800 s	300	Infinite	n/a	1800	0.0005

   6.2. Individual reports for each fire scenario, containing results of WHFIRE calculations

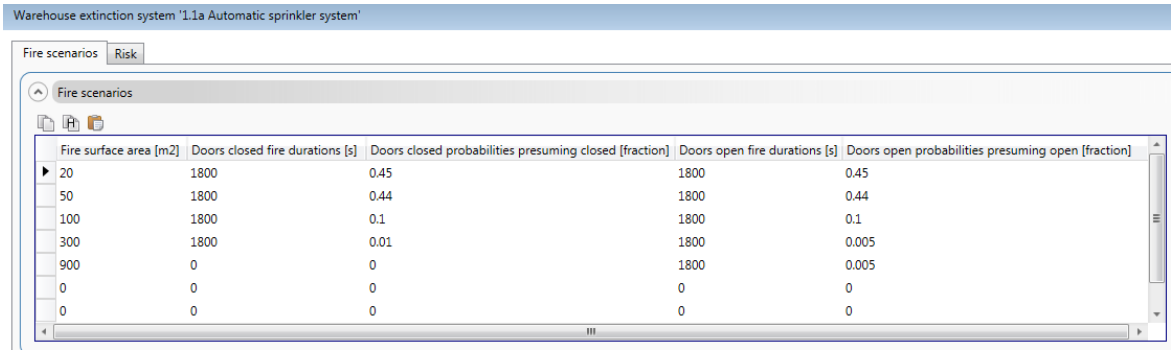
Parameters available via Admin mode

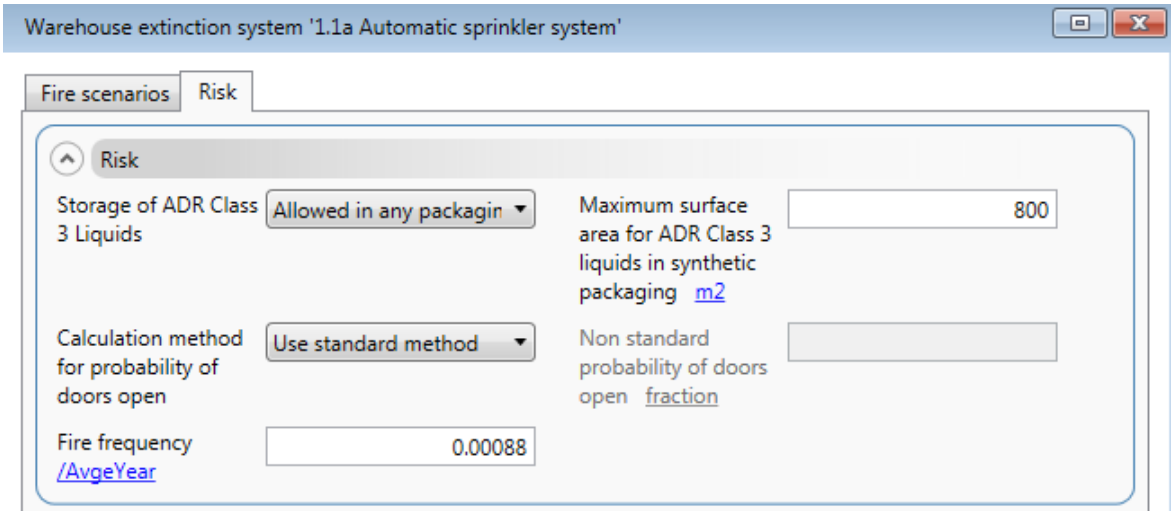
In admin mode the user would have access to the following parameters (hidden to the SAFETI-NL non-admin user) via the “Warehouse fire parameters” tab *(added tab)*. This would include the following:

- “Children” underneath the “Warehouse fire parameters” tab for each fire extinction system including the corresponding PGS-15 tables; see Appendix C.1 for details. Each “child” (fire extinction system) would include the following parameters:

  - Fire frequency for fire extinction system
  - Maximum surface area in case of storage of ADR Class 3 materials in synthetic packaging.
  - Calculation method for probability of doors open , $P_{do.}$
  - Parameters for duration and probability (percentage or fraction) for fire surfaces 20, 50, 100, 300, 900, 1500, 2500 m^2 and for both cases of doors open and doors closed. The sum of all probabilities fractions should be 1.

  For example the tab pages for fire extinction system 1.1a (automatic sprinkler system not in storage racks) look as follows:



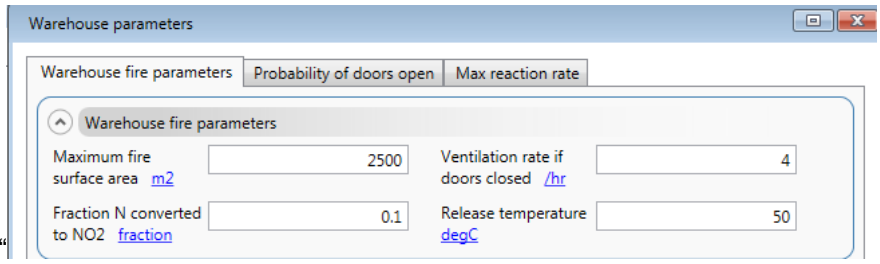


There is the possibility by the Admin user to generate “children” in addition to the above set of “children”. This would allow adding data for new fire fighting systems.

- general warehouse parameter tabs including

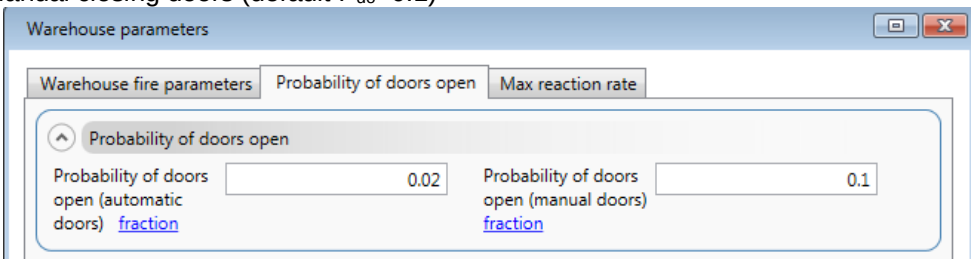
  - “Warehouse Fire parameters”
    - upper limit for warehouse fire surface area (default 2500m^2)
    - ventilation rate for doors open (default 4 air changes / hour)
    - conversion rate of N to NO_2 (default 0.35; see WHFIRE theory manual for details)

- temperature to be adopted for release temperature: tick-box either “ambient” temperature (6.51/6.53 default), or specified temperature (6.54 default with value of 50C)

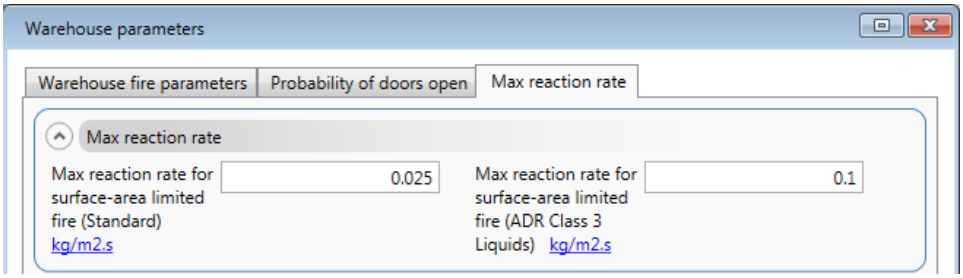


“

- probability of doors open” tab
  - automatic doors (default P_{do}=0.02)
  - manual closing doors (default P_{do}=0.1)



- ”maximum reaction rate” tab defining maximum reaction rate for surface-area limited fire
  - standard rate, R_{st}
  - case of storage of ADR Class 3 materials, R_{ADR3}



C.3 Example and WHFIRE verification against CPR-15

The example given below corresponds to the example described in Section 4.5 in CPR-15. This example was reproduced using the PHAST/SAFETI implementation of WHFIRE, and it was confirmed that the results agreed with those reported in CPR-15.

Problem description

1. Material data for pesticides in warehouse are as follows:

   1.1. The following eleven materials are stored in the warehouse (including amount in metric tonnes): aniline (200te), chloroform (320te), ethylene glycol (250te), phenol (200te), furfural (100te), hexandiol (185te), formic acid (140te), salicydic acid (320te), sulfurylchloride (200te), ethene tetrachloride (305te). Thus the total stored mass is 2320 metric tonnes, and according to Equation (1), the average structural formula is $C_{3.28}H_{4.35}O_{1.38}N_{0.23}S_{0.06}Cl_{1.1}$
   1.2. None of the above materials are highly toxic. No ADR Class 3 materials (flammable liquids) are stored.
   1.3. The storage involves technically pure materials, meaning 100% active material.

2. Building data. The building length, width and height are L_b=50m, W_b = 30m, H_b=6m. The building angle is taken to be zero degrees (wind parallel to building-length axis)

3. Manual closed doors are adopted

4. Fire system. An automatic “Hi-ex with inside air” fire fighting system is applied (PGS system 1.6).

5. The annual fire frequency = $8.8 * 10^{-4}$

Definition of SAFETI input data / scenarios according to CPR-15

1. Building data
   - An equivalent square building of $(L_bW_b)^{1/2}$=38.7299m is adopted. Thus the building length, width and height are L_b=38.7299m, W_b = 38.7299m, H_b=6m. Thus the fire storage area is A_b = 50*30 = 1500m^2.
   - According to the above CPR-15 guideline, the ventilation rate is 4 in case the doors are closed and infinite in case the doors are open.

2. Manual closed doors are adopted which according to the above CPR-15 guideline implies the probability of P_{do} = 0.1 that the doors are open.

3. Scenario data. The range of (10) scenarios [fire area/durations for both open and closed doors and corresponding probabilities] are now found from Table 4.10 (for system 9) in the CPR-15 guideline [see also Table 4.14/4.15]. Note that In comparison with PGS-15 system 1.6 this allows for an added fire area of 1500m^2 in case of doors open.

ventilation rate (air changes per hour)	*fire area (m2)*	*fire duration (min)*	*probability*	*frequency (annual)*
doors closed: 4	20	10	0.89(1-P_{do})=0.801	$7.0488*10^{-4}$
	50	10	0.09(1-P_{do})=0.081	$7.128*10^{-5}$
	100	10	0.01(1-P_{do})=0.009	$7.92*10^{-6}$
	300	30	0.01(1-P_{do})=0.009	$7.92*10^{-6}$
doors open: ∞	20	30	0.89P_{do}=0.089	$7.832*10^{-5}$
	50	30	0.09P_{do}=0.009	$7.92*10^{-6}$
	100	30	0.01P_{do}=0.001	$8.8*10^{-7}$

	300	30	$0.005P_{do}$=0.0005	$4.4*10^{-7}$
	900	30	$0.004P_{do}$=0.0004	$3.52*10^{-7}$
	1500	30	$0.001P_{do}$=0.0001	$8.8*10^{-8}$

4. The conversion rate of N to NO2 of 0.35 is adopted (non-default CPR-15 value, since PGS-15 value is 0.10)

WHFIRE consequence results (and their verification against values reported in CPR-15 report)

1. The HCl, SO_2, NO_2 mass fractions (values 0.842,0.08,0.078) in the modelled released HCl/SO_2/NO_2 plume were found to be identical to those reported in the CPR-15 guideline
2. The total burn rate and the HCl/SO_2/NO_2 release rate (kg/s) were both found to be identical to CPR-15 for each of the above 10 scenarios[16] (see tables 4.15 and 4.16 in CPR-15 guideline).

ventilation rate (air changes per hour)	*fire area (m2)*	*fire duration (min)*	*Burn rate (kg/s)*	*HCl/SO2/NO2 release rate (kg/s)*
doors closed: 4	20	30	0.5	0.22
	50	30	1.25	0.54
	100	30	2.50	1.08
	300	30	4.07	1.77
doors open: ∞	20	30	0.5	0.22
	50	30	1.25	0.54
	100	30	2.50	1.08
	300	30	7.50	3.25
	900	30	22.50	9.75
	1500	30	37.50	16.24

Phast Risk analysis

1. Open new study
2. “Materials” tab. Ideally 11 pesticide materials (for each of the materials in the new database) would be specified with the individual structural formulas, but these are not reported in CPR-15. Therefore a single ‘averaged’ pesticide material is used (called ‘CPR-15 Example’), with the averaged structural formula $C_{3.28}H_{4.35}O_{1.38}N_{0.23}S_{0.06}Cl_{1.1}$ as reported in CPR-15.
3. “Models” tab. First the PGS-15 fire-fighting system 1.6 is selected. Subsequency the thus-generated scenarios are edited (via user-defined scenario) to allow addition of the added fire area of 1500 m^2 in case of doors open.
4. Finally in admin mode the non-default CPR-15 N to NO2 conversion rate of 0.35 is applied.

[16] This is for one exception, i.e. for scenario doors closed with large area 300m^2, for which the fire was oxygen-area limited instead of surface-area limited. The WHFIRE (SAFETI value) for the burn rate was 4.07 kg/s which is slightly larger than the value of 3.88 kg/s reported in CPR-15. This is caused by using the more exact value of y_{O2}^{air} =0.21 instead of y_{O2}^{air} =0.20 [see footnote 8 and Equation (4) for details]

Appendix D Guidance on input and output data for WHFIRE model

D.1 Input data

A list of the input data is given in Figure 3. These data are split into the following categories:

1. Number of materials in warehouse

   This is number of materials in the warehouse, for which data need to be specified.

2. Materials method

   The user specifies a flag which takes the value 1 if default values are to be used in the calculation of the pesticide structural formula, or 2 if the user wishes to specify the structural formula for the pesticides himself.

3. Material data for each pesticide in warehouse

   A list of comma separated values is required for each input with the number of values corresponding to the number of materials in the warehouse, as specified above.

   3.1. Material total mass (incl. packaging material) (kg).This is the mass of active and inactive material.
   3.2. Material active mass fraction. This is the fraction of the total mass that is pure pesticide.
   3.3. flag: category 10 material (highly toxic with flash point <100C):1, or category 11(>100C):2, or not highly toxic:3. If the material is highly toxic with a flash point of less than 100^0C the item in the list corresponding to that material takes a value of 1. If the material is highly toxic with a flash point of greater than 100^0C the item in the list corresponding to that material takes a value of 2. If the material is not highly toxic the item in the list corresponding to that material takes a value of 3.
   3.4. flag:category 2 material (dioxin generator):1 or not:2. If the material is a PCDD/PCDF former(dioxin generator) then the item in the list corresponding to that material takes a value of 1, otherwise it takes a value of 2.
   3.5. If the user has specified a value of 2 for the above materials method it is necessary to specify the structural formula, otherwise if the user specified 1, then this set of input data is not necessary:
      3.5.1. C atom input array. The number of carbon atoms for each input pesticide is required
      3.5.2. O atom input array. The number of oxygen atoms for each input pesticide is required
      3.5.3. N atom input array. The number of nitrogen atoms for each input pesticide is required
      3.5.4. S atom input array. The number of sulphur atoms for each input pesticide is required
      3.5.5. Cl atom input array. The number of chlorine atoms for each input pesticide is required
      3.5.6. Br atom input array. The number of bromine atoms for each input pesticide is required
      3.5.7. F atom input array. The number of fluorine atoms for each input pesticide is required
      3.5.8. P atom input array. The number of phosphorus atoms for each input pesticide is required
      3.5.9. Mn atom input array. The number of manganese atoms for each input pesticide is required
      3.5.10. Sn atom input array. The number of tin atoms for each input pesticide is required
      3.5.11. Zn atom input array. The number of zinc atoms for each input pesticide is required
      3.5.12. I atom input array. The number of iodine atoms for each input pesticide is required.
   3.6. flag: 1 (derived molecular weight from specified atoms) or 2 (user-specified molecular weight)
   3.7. user-specified molecular weight (kg/kmol; only used if above flag = 2). This must be specified in case there are atoms present in the molecular in addition to the above. These additional atoms are not presumed to result in additional combustion (oxygen requirement). This user-specified molecular weight should be larger than the molecular weight derived from the above specified atoms.

4. Building (warehouse) data

   4.1. flag: ventilation factor infinite:1 or not:2. If there is ample ventilation (fire is surface area limited) then specify a value of 1 otherwise
   4.2. ventilation rate (=no.of air changes per second; not used for infinite ventilation factor) (s^{-1}).This is required if an input value of 2 was given for the above flag.

4.3. surface area of the storage(m^2). This is the floor/roof area of the warehouse storing the pesticides. Thus it should equal the product of the building length and the building width.
4.4. building height(m). This is the height of the warehouse storing the pesticides

5. Scenario data

5.1. fire surface area (m^2).Guidelines on this value are available in section 2.3 of this document.
5.2. fire duration (s). Guidelines on this value are available in section 2.3 of this document.

6. Ambient data

6.1. Temperature (K)

7. Parameters (values to be changed by expert users only):

7.1. data determining release temperature as used as starting temperature of the dispersion calculations: flag (1 – use specified temperature, 2 – use ambient temperature), and (in case flag=1) release temperature. The release temperature should not be selected smaller than the ambient temperature.
7.2. converion rate of N atoms to NO_2 atoms
7.3. maximum reaction rate for surface-area limited fires

	D	E	F	L	M	N
2	**Inputs**		**DNV MODEL WHFIRE (Warehouse Fire)**			
3	**Input**	**Description**	**Units**	**Limits**		**Default**
4	**Index**			**Lower**	**Upper**	
12	7	number of materials in warehouse		1	40	3
32	**Materials method**					
33	A	flag for input of pesticide structural formula: use defaults: 1 or user-defined:2		1	2	2
34	**Material data for each pesticide in warehouse**					
35	A	material total mass (incl. packaging material)	kg	0.1	1.00E+08	1E4,1E4,1E4
36	A	material active mass fraction		0	1	0.8,0.8,0.8
37	A	flag: category 10 material (highly toxic with flash point <100C):1, category 11 (highly toxic with flash point >100C):2, or not highly toxic:3		1	3	2,1,3
38	A	flag:category 2 material (dioxin generator):1 or not:2		1	2	2,1,2
39	A	number of C atoms (not used in case of Dutch defaults)		0	1000	18,12,12
40	A	number of H atoms (not used in case of Dutch defaults)		0	1000	20,8,21
41	A	number of O atoms (not used in case of Dutch defaults)		0	1000	4,1,3
42	A	number of N atoms (not used in case of Dutch defaults)		0	1000	2,0,2
43	A	number of S atoms (not used in case of Dutch defaults)		0	1000	1,0,1
44	A	number of Cl atoms (not used in case of Dutch defaults)		0	1000	0,6,0
45	A	number of Br atoms (not used in case of Dutch defaults)		0	1000	0,0,0
46	A	number of F atoms (not used in case of Dutch defaults)		0	1000	0,0,0
47	A	number of P atoms (not used in case of Dutch defaults)		0	1000	0,0,1
48	A	number of Mn atoms (not used in case of Dutch defaults)		0	1000	0,0,0
49	A	number of Sn atoms (not used in case of Dutch defaults)		0	1000	0,0,0
50	A	number of Zn atoms (not used in case of Dutch defaults)		0	1000	0,0,0
51	A	number of I atoms (not used in case of Dutch defaults)		0	1000	0,0,0
52	A	flag: mole weight specified: 1 or not: 2 (not used in case of Dutch defaults)		1	2	2,2,2
53	A	molecular weight (not used in case of Dutch defaults)		2	1.00E+08	2,2,2
54	**Building (warehouse) data**					
55	A	flag: ventilation factor infinite:1 or not:2		1	2	2
56	A	ventilation rate (=air changes per second; not used for infinite ventilation factor)	Hz	0	2.00E+02	0.001111111
57	A	surface area of the storage	m^2	0.001	2.50E+05	1500
58	A	storage area height	m	0.001	5.00E+02	10
59	**Scenario data**					
60	A	fire surface area	m^2	0.001	2.50E+05	300
61	A	fire duration	s	1	1.00E+05	1800
62	**Ambient Data**					
63	A	temperature	K	200	350	275
64		**PARAMETERS (values to be changed by expert users only)**				
65	A	release temperature flag: use input below (1) or ambient temperature (2)		1	2	2
66	A	release temperature	K	200	900	323.15
67	A	conversion rate of N atoms to NO2 atoms	fraction	0	1	0.35
68	A	maximum reaction rate for surface-area limited fires	kg/s/m2	1.00E-08	1	0.025

Figure 3. Input data to the warehouse fire model (WHFIRE)

D.2 Output data

A list of output data is given in Figure 4**.** These data are split into the following categories:

1. Storage categories. Data for the average pesticide representing the mixture of pesticides in the warehouse are output here.

   A) mass (including packaging material) (kg). The total mass of the average pesticide (active and inactive) is output here for each of the categories 0, 10, 11 and 2.
   B) active mass (excluding packaging material) (kg). The active mass of the average pesticide is output here for each of the categories 0, 10, 11 and 2.
   C) active mass fraction. The active mass fraction of the average pesticide is output here for each of the categories 0, 10, 11 and 2.
   D) active moles (kmol). The number of kmols of the active portion average pesticide is output here for each of the categories 0, 10, 11 and 2.
   E) average structural formula. The average molecular weight (kmol/kg) of the average pesticide and the number of atoms of C, H, O, N, S, Cl, Br, F, P, Mn, Sn, Zn, and I in the structural formula of the average pesticide is output here.

2. Combustion

   A) Moles of combustion products per mol completely combusted active pesticide. The number of moles of each combustion product formed after 1 mol of active average pesticide is combusted is output here. Results are given for each of the following combustion products: CO_2, H_2O, NO_2, SO_2, HCl, HBr, HF, P_2O_5, MnO_2, ZnO, SnO_2, I_2, N_2

   B) oxygen requirement for complete combustion (kmol)

      B.1) oxygen requirement category x. The amount (kmol) of oxygen required to completely combust the active portion of the average pesticide in category x where results are output for x = 0, 10, 11, 2.
      B.2) moles oxygen required per mol average pesticide category 0. The number of moles of oxygen required in the combustion reaction (see section 2.2.1) to react with 1 mol of active portion of the average pesticide of category 0.
      B.3) mass fraction of category 10 and 11 oxygen requirement relative to category 0. This is the sum of oxygen requirement category 10 and oxygen requirement category 11 (see B.1 above) divided by the oxygen requirement category 0).
      B.4) mass fraction of category 2 oxygen requirement relative to category 0. This is the oxygen requirement category 2 (see B.1 above) divided by the oxygen requirement category 0).

   C) emission

      C.1) mass toxic products (NO2, SO2, HCl/HBr/HF) per unit mass of burned cat.0 (kg). This is the sum of the masses (kg) of the HCl (which includes HCl, HBr and HF as discussed in section 2.2.1),NO_2 and SO_2 formed when 1kg of category 0 material (active and inactive) is combusted (although it is assumed that inactive material does not give rise to combustion products as discussed in section 2.5.1)
      C.2) mass unburned highly toxic material per unit mass of burned cat. 0. This is the mass (kg) of highly toxic material from the active portions of categories 10 and 11 that escapes unburned when 1kg of category 0 material (active and inactive) is combusted. It is assumed that inactive material does not give rise to unburned highly toxic material.
      C.3) mass other burned material (CO2, P205, Mn02, ZnO, SnO2, I2, N2) , per unit mass of burned cat. 0. This is the sum of the masses (kg) of the CO2, P205, Mn02, ZnO, SnO2, I2, N2 formed when 1kg of category 0 material (active and inactive) is combusted. It is assumed that inactive material does not give rise to these combustion products.

C.4) mass PCDD/PCDF generators (TEQ) (active category 2) per unit mass of burned cat. 0. This is the mass (kg) of equivalent 2,3,7,8-trichlorodibenzodioxin (TEQ) representing the hazardous polychlorodibenzo-p-dioxins (PCDD's) and polychlorodibenzofurans (PCDF's) formed when 1kg of category 0 material (active and inactive) is combusted.

C.5) mass fraction NO_2 in effluent mixture (NO_2,SO_2,HCl/HBr/HF).This is the mass fraction of NO_2 in the effluent mixture consisting of HCl (which includes HCl,HBr and HF as discussed in section 2.2.1),NO_2 and SO_2.

C.6) mass fraction SO_2 in effluent mixture (NO_2, SO_2, HCl/HBr/HF).This is the mass fraction of SO_2 in the effluent mixture consisting of HCl, NO_2 and SO_2.

C.7) mass fraction HCl/HF/HBr in effluent mixture (NO_2, SO_2, HCl/HBr/HF). This is the mass fraction of HCl (which includes HCl, HBr and HF as discussed in section 2.2.1) in the effluent mixture consisting of HCl ,HBr and HF.

D) oxygen flow rate and pesticide burn rates

D.1) oxygen flowrate available to the fire. This is the flow rate of oxygen $\dot{N}_{(O_2)}$ through the building (kmol/s) which would be available for combustion in the case of a fire.

D.2) molar burn rate assuming oxygen-limited fire (category 0). This is the burn rate (kmol/s) of total (active and inactive) category 0 pesticide calculated assuming the fire is oxygen limited (ie. is not limited at B_{max} as discussed in section 2.4)

D.3) Flag: (1) If fire is surface area limited or (2) if fire is ventilation limited. The molar burn rate from D.2 is converted to a mass burn rate and is compared with B_{max} . If it is less than B_{max} then the fire is ventilation limited and the flag gives a value of (2). If it is greater than B_{max} then the fire is surface area limited and the flag takes a value of (1) and (D.4) below takes a value of B_{max}

D.4) actual mass burning rate (category 0). This is either the burn rate calculated according to (D.3) above in the case of a ventilation limited fire or B_{max} in the case of a surface area limited fire.

D.5) fire duration (seconds). This equals the input fire duration (scenario data) t_{fire} in case t_{fire} is smaller than the time t_{fire}^{max} at which all warehouse material is burned. Otherwise it equals t_{fire}^{max}.

3. Release data

3.1 release temperature. This is the temperature (K) of the toxic effluent mixture as it is released to the atmosphere.

3.2 mass release rate of toxic combustion products (NO2,SO2,HCl/HBr/HF). This is the sum of the release rates (kg/s) of the components of the toxic effluent mixture consisting of NO_2, SO_2 and HCl (including HBr and HF).

3.3 mass release rate of unburned highly toxic material. This is the mass release rate (kg/s) of highly toxic material from the active portions of categories 10 and 11 that escapes unburned to the atmosphere during the warehouse fire.

3.4 mass release rate of PCDD/PCDF generating material (TEQ). This is the mass release rate (kg/s) of equivalent 2,3,7,8-trichlorodibenzodioxin (TEQ) representing the hazardous polychlorodibenzo-p-dioxins (PCDD's) and polychlorodibenzofurans (PCDF's)

	D	E	F	L	M	N
69	**Outputs**					
70	**Output**	**Description**	**Units**			
71	**Index**					
72		***ERROR STATUS***				***OK***
76	**Storage categories**					
77		**A) mass (including packaging material)**				
78	A	mass category 0 (total)	kg			30000.00
79	A	mass category 10 (LD50<25mg/kg, fl.point<100C)	kg			10000
80	A	mass category 11 (LD50<25mg/kg, fl.point>100C)	kg			10000
81	A	mass category 2 (PCDD,PCDF generators)	kg			10000
82		**B) active mass (excluding packaging material)**				
83	A	active mass category 0	kg			24000
84	A	active mass category 10	kg			8000
85	A	active mass category 11	kg			8000
86	A	active mass category 2	kg			8000.00
87		**C) active mass fraction**				
88	A	active mass fraction category 0	fraction			0.8
89	A	active mass fraction category 10	fraction			0.8
90	A	active mass fraction category 11	fraction			0.8
91	A	active mass fraction category 2	fraction			0.8
92		**D) active moles**				
93	A	active kmoles category 0	kmol			69.48666
94	A	active kmoles category 10	kmol			21.00377
95	A	active kmoles category 11	kmol			22.19633
96	A	active kmoles category 2	kmol			21.00377
97		**E) average structural formula**				
98	A	average molecular weight	kg/kmol			345.39
99	A	average atoms C				13.9166
100	A	average atoms H				16.75105
101	A	average atoms O				2.714892
102	A	average atoms N				1.395459
103	A	average atoms S				0.6977295
104	A	average atoms Cl				1.813623
105	A	average atoms Br				0
106	A	average atoms F				0
107	A	average atoms P				0.3782966
108	A	average atoms Mn				0
109	A	average atoms Sn				0
110	A	average atoms Zn				0
111	A	average atoms I				0

Figure 4 (a) Output of storage data

	D	E	F	L	M	N
70	**Output**	**Description**	**Units**			
71	**Index**					
72		***ERROR STATUS***				***OK***
112	**Combustion**					
113		**A) Mols of combustion products per mol completely combusted active pesticide**				
114	A	mol CO_2 per mol combusted pesticide	fraction			13.9166
115	A	mol H_2O per mol combusted pesticide	fraction			7.468714
116	A	mol NO_2 per mol combusted pesticide	fraction			0.4884106
117	A	mol SO_2 per mol combusted pesticide	fraction			0.6977295
118	A	mol HCl per mol combusted pesticide	fraction			1.813623
119	A	mol HBr per mol combusted pesticide	fraction			0
120	A	mol HF per mol combusted pesticide	fraction			0
121	A	mol P_2O_5 per mol combusted pesticide	fraction			0.1891483
122	A	mol MnO_2 per mol combusted pesticide	fraction			0
123	A	mol ZnO per mol combusted pesticide	fraction			0
124	A	mol SnO_2 per mol combusted pesticide	fraction			0
125	A	mol I_2 per mol combusted pesticide	fraction			0
126	A	mol N_2 per mol combusted pesticide	fraction			0.4535242
127		**B) oxygen requirement for complete combustion**				
128	A	amount oxygen required category 0	kmol			1247.461
129	A	amount oxygen required category 10	kmol			252.0453
130	A	amount oxygen required category 11	kmol			503.8566
131	A	amount oxygen required category 2	kmol			252.0453
132	A	moles oxygen required per mol average pesticide category 0	fraction			17.95252
133	A	mass fraction of category 10 and 11 oxygen requirement relative to category 0	fraction			0.6059525
134	A	mass fraction of category 2 oxygen requirement relative to category 0	fraction			0.2020467
135		**C) emission**				
136	A	mass toxic products (NO_2,SO_2,HCl/HBr/HF) per unit mass of burned cat.0	fraction			0.3087279
137	A	mass unburned highly toxic material (active categories 10 and 11) per unit mass of burned cat. 0	fraction			3.20E-02
138	A	mass other burned material (CO2,P205,Mn02,ZnO,SnO2,I2,N2) , per unit mass of burned cat. 0	fraction			1.82E+00
139	A	mass PCDD/PCDF generators (TEQ) (active category 2) per unit mass of burned cat. 0	fraction			2.67E-06
140	A	mass fraction NO_2 in effluent mixture (NO_2,SO_2,HCl/HBr/HF)	fraction			0.1685939
141	A	mass fraction SO_2 in effluent mixture (NO_2,SO_2,HCl/HBr/HF)	fraction			0.3353346
142	A	mass fraction HCl/HF/HBr in effluent mixture (NO_2,SO_2,HCl/HBr/HF)	fraction			0.4960715
143		**D) oxygen flow rate and pesticide burn rates**				
144	A	oxygen flowrate available to the fire	$kmol.s^{-1}$			0.21875
145	A	molar burn rate assuming oxygen-limited fire (category 0)	$kmol.s^{-1}$			1.22E-02
146	A	Flag: (1) If fire is surface area limited or (2) if fire is ventilation limited				2.00E+00
147	A	actual mass burning rate (category 0)	$kg.s^{-1}$			4.208549
148	A	fire duration (input fire duration reset if larger than maximum fire duration)	s			1800
149	**Release data**					
150	A	release temperature	K			275
151	A	mass release rate of toxic combustion products (NO2,SO2,HCl/HBr/HF)	$kg.s^{-1}$			1.299296
152	A	mass release rate of unburned highly toxic material	$kg.s^{-1}$			1.35E-01
153	A	mass release rate of PCDD/PCDF generating material (TEQ)	$kg.s^{-1}$			1.12E-05

(b) Output of combustion data and release data

Figure 4. Output data to the warehouse fire model (WHFIRE)

D.3 Detailed information on WHFIRE errors and warnings

Below information on errors/warnings/messages are given, which can currently be produced by the WHFIRE model.

Error messages

1 "%1%Real% moles of oxygen required per mole of pesticide - no combustion takes place"

This message occurs when it not possible for the material in the average structural formula to form one of the combustion products: NO2, SO2, CO2, P205, Mn02, ZnO, SnO2 by reaction with oxygen (for example in the case of 'pesticide' HCl).

2 "Fire surface area %1%Area% is larger than surface of the storage"

This message occurs when the fire surface area is greater than the surface area of the storage.

3 "No toxic effluent mixture containing at least one of NO2,SO2,HCl,HBr,HF will be produced"

A fatal error will occur if in the combustion of the average pesticide none of the products NO2,SO2,HCl,HBr,HF is formed because according to the model the effluent mixture will be none toxic.

5 "Specified mole weight smaller than mole weight %1%MolarMass% derived from pesticide atoms"

The user specifies the atoms for all chemical elements contributing to the combustion. This message occurs in case he specifies a molecular weight which is smaller than the molecular weight derived from the specified atoms. To avoid this message, he can either not specify the molecular weight (in case there are no other atoms present in the molecule) or he should specify a larger molecular weight (in case there are additional atoms present not contributing to the combustion).

6 "Specified release temperature smaller than ambient temperature %1%Temperature%"

The user must specify a release temperature (of the combustion products to the atmosphere; starting point of dispersion calculations), which is larger than the ambient temperature.

Data range checking: If the input data are out of range (see limits in spreadsheet MDE_TEST_WHFIRE.XLS) then one or more of the following fatal error messages will occur:

101 "Integer input array size %1%Integer% is out of range"
102 "Real input array size %1%Integer% is out of range"
103 "Real output array size %1%Integer% is out of range"
104 "Integer output array size %1%Integer% is out of range"
105 "Number of materials in the warehouse %1%Integer% is out of range"
106 "Dutch default flag %1%Integer% is out of range"
107 "Array element(s) of material masses %1%Mass% is out of range
108 "Array element(s) of material percentage active mass %1%Real% % is out of range"
109 "Array element(s) of material high toxic flags %1%Integer% is out of range"
110 "Array element(s) of material dioxin flags %1%Integer% is out of range"
111 "Array element(s) of material number of C atoms %1%Real% is out of range"
112 "Array element(s) of material number of H atoms %1%Real% is out of range"
113 "Array element(s) of material number of O atoms %1%Real% is out of range"
114 "Array element(s) of material number of N atoms %1%Real% is out of range"
115 "Array element(s) of material number of S atoms %1%Real% is out of range"
116 "Array element(s) of material number of Cl atoms %1%Real% is out of range"
117 "Array element(s) of material number of Br atoms %1%Real% is out of range"
118 "Array element(s) of material number of F atoms %1%Real% is out of range"
119 "Array element(s) of material number of P atoms %1%Real% is out of range"
120 "Array element(s) of material number of Mn atoms %1%Real% is out of range"
121 "Array element(s) of material number of Sn atoms %1%Real% is out of range"

122 "Array element(s) of material number of Zn atoms %1%Real% is out of range"
123 "Array element(s) of material number of I atoms %1%Real% is out of range"
123 "Array element(s) of material number of I atoms %1%Integer% is out of range"
124 "Flag: ventilation factor infinite:1 or not:2 %1%Integer% is out of range"
125 "Ventilation rate %1%Frequency% is out of range"
126 "Surface area of the storage %1%Area% is out of range"
127 "Building height %1%Length% is out of range"
128 "Fire surface area %1%Area% is out of range"
129 "Fire duration %1%Time% is out of range"
130 "Fire Temperature %1%Temperature% is out of range"
131 "Array element(s) of material release-temperature flags %1%Integer% is out of range"
132 "Array element(s) of material molecular weight %1%MolarMass% is out of range"
133 "Release-temperature flag %1%Integer% is out of range"
134 "Release temperature %1%Temperature% is out of range"
135 "Conversation rate %1%Real% of N to NO2 atoms is out of range"
136 "Maximum reaction speed %1%MassFlowPerUnitArea% is out of range"
201 "Sum %1%Real% of open-door scenario probabilities is not 1"
202 "Sum %1%Real% of closed-door scenario probabilities is not 1"

Warning messages

The following warning messages occur (depending on the material category) if the number of hydrogen atoms is less than the sum of the halogen atoms (Cl,Br,F) in the average structural formula of the category as in this case there is insufficient hydrogen to produce H_2O.

1001 "The number of hydrogen atoms %1%Real% is less than the sum of the halogen atoms (Cl,Br,F) in the average structural formula of category 0"
1002 "The number of hydrogen atoms %1%Real% is less than the sum of the halogen atoms (Cl,Br,F) in the average structural formula of category 10"
1003 "The number of hydrogen atoms %1%Real% is less than the sum of the halogen atoms (Cl,Br,F) in the average structural formula of category 11"
1004 "The number of hydrogen atoms %1%Real% is less than the sum of the halogen atoms (Cl,Br,F) in the average structural formula of category 2"

Messages

2001 "Specified fire duration reduced to time %1%Time% at which all warehouse materials are burned"

The above message is issued if the user specifies a fire duration t_{fire} which is larger than the time t_{fire}^{max} at which all warehouse pesticides are burned. In this case the fire duration t_{fire} is reduced to t_{fire}^{max}, where the value of t_{fire}^{max} is obtained as described in Section 2.4.2.

NOMENCLATURE

A	surface area of fire (m^2)
B	burn rate of pesticide including packaging material etc. (kg/s)
n	number of atoms
$\overline{n}$	number of atoms in the average structural formula
$\dot{N}_{(O_2)}$	molar flow rate of oxygen (kmol/s)
m	active mass of pesticide (kg)
$\dot{m}$	release rate material(kg/s)
M_W	molecular weight of individual pesticide (kg/kmol)
$\overline{M}_W$	molecular weight of average structural formula (kg/kmol)
t_{fire}	fire duration (s)
$y_{o_2}^{air}$	mole fraction of oxygen in air
z_{act}	average mass fraction of active material = ratio of burn rate of pure pesticide (excluding packaging material etc.) to burn rate of total pesticide (including packaging material etc.)
η_{prod}	mass conversion factor of combustion products (kg product/kg active pesticide burned)
v_{air}	molar volume of air (m^3/kmol)

<u>subscripts</u>

c	pesticide component comprising a combination of the elements C,H,O,N,S,P,Cl,Br,F,I,Sn,Mn,Zn
i	element (either C,H,O,N,S,P,Cl,Br,F,I,Sn,Mn,Zn)
prod	combustion product (HCl, NO_2 or SO_2)
x	material category: - 0: total - 10: LD_{50} < 25 mg/kg with flash point <100°C - 11: LD_{50} < 25 mg/kg with flash point >100°C - 2: PCDD+PCDF)

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