THEORY

TOXICS CALCULATIONS

DATE: December 2023

Following concentration calculations, the model TXCS calculates the toxic dose, the probit number, the probability of death, the integrated probability of death and the exposure duration of an observer to finite concentrations of a dispersing cloud.

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ABSTRACT

Following concentration calculations, the model TXCS calculates the toxic dose, the probit number, the probability of death, the integrated probability of death and the exposure duration of an observer to finite concentrations of a dispersing cloud.

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1 INTRODUCTION

TXCS calculates and returns the following toxic properties for a user defined height and user defined offset in the crosswind direction:

1. The toxic dose,
2. The probit number
3. The probability of death and
4. The integrated probability of death
5. The exposure duration/time of an observer to finite concentrations of a dispersing cloud[1]

In the case where the release material is a mixture, the dose and probit number can be calculated[2] for each individual component in the mixture.

With the exception of the model employed in simulating exposure duration, TXCS receives as input the processed UDM data. .

The indoor concentration, indoor dose, resulting probits and indoor probability & its integral are calculated by the indoor dose model. This model gives the user the additional capability of understanding the effects of toxic releases on population residing indoors.

As of version 8.61 there is an additional option to apply a concentration threshold for fatality as well as the integrated dose. This is to support regulatory requirements.

From version 8.80, an option i.e., the "Threshold Dose Effect" modelling, is available for modelling "fatality" or impact zones based on threshold doses derived from any of the ERPG/STEL/IDLH pure component concentrations. For mixtures of toxic components, two mixing rules are supported: "additive" and "non-interactive", for determining the effective threshold dose impact zone or fatality.

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[1] These calculations are only conducted along the centreline trajectory of the dispersing cloud. However, the algorithm is designed to handle the exposure time calculation for an observer at any position in space.

[2] To obtain the individual mixture component dose, probits etc the user must select toxic calculation method 3

2 OUTDOOR TOXIC LOAD, PROBIT AND PROBABILITY OF DEATH

2.1 Probability of death

2.1.1 Probability based on Probit Formula

The probability of death, p_{death}, for a given component i at a given position is calculated from a "Probit number", $P(i)$, within the maths library (routine PROBL)[3] as

$$p_{Death}(i) = \frac{1}{2}\left\{1 + \text{erf}\left[\frac{P(i) - 5}{\sqrt{2}}\right]\right\}$$

(1)

If a mixture has been released[2] the overall probability of death is {1- the product of surviving each material in turn} :

$$p_{Death} = 1 - \prod_{All\ components,\ c}\left(1 - p_{Death}(i)\right)$$

(2)

i.e. it is assumed that the probability of survival is the product of the probability of survival of each of the materials in turn; each material will kill independently of the others.

The inverse of this function is obtained by PROBIT using a binary sectioning method.

2.1.2 Concentration Threshold

This concept is introduced to represent the possibility that an intial exposure to a high enough concentration will be sufficient to incapacitate a person so they cannot escape. The user inputs are a concentration and a minimum lethality. If the local outdoor concentration exceeds this threshold then the overall probability of death becomes the maximum of this value and the value calculated from the probit formula or dangerous toxic load.

2.2 Probit number

The "Probit number" for a given component is calculated from the "Toxic load" (dose), $L_{Toxic}(i)$, (within TXCSPD) as

$$P(i) = T_A(i) + T_B(i)\ln L_{Toxic}(i)$$

(3)

where $T_A(i)$ and $T_B(i)$ are probit numbers A and B for material(i).

2.3 Toxic load

The "Toxic load" is calculated from the concentration of the material, C, at the given position. In case of a single-segment continuous cloud, the concentration does not vary with time (before QI transition), and the toxic load is given by

$$L_{Toxic}(i) = t_{exp} \times (f_i C)^{T_N(i)}$$

(4)

where t_{exp} is the exposure time to the material, f_i is the fraction of the toxic component(s) in the mixture and $T_N(i)$ is the probit number N for component i.

Otherwise the toxic load is evaluated by means of integration over time

$$L_{Toxic}(i) = \int_o^T \left[f_i C(t)\right]^{T_N(i)} dt$$

(5)

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[3] This function should be moved from MATH to TXCS

2.4 Integrated probability of death

The integrated probability of death at a given downwind position and height, PI, is found by integrating the probability of death in the crosswind direction:

$$PI = 2\int_0^\infty P_{Death} \, dy \qquad (6)$$

As will be discussed later, the integral will be carried out discretely by setting up a grid which extends out to a point where the probability of death is at the minimum. At a given downwind position the grid spacing in the crosswind direction is constant and the probability of death at each individual grid square will also be constant:

$$PI(x) = y(x) \times \left(2\sum_{y=1}^Y P_{Death}(x, y) + P_{Death}(x,0)\right) \qquad (7)$$

where

y(x) = Grid spacing in the crosswind direction at the given downwind position
Y = Crosswind grid position where the probability of death is at the minimum

<u>Unit conversion</u>

The Toxicity coefficients are stored in the properties database in assuming that concentrations are measured in parts per million (1 ppm = 0.000001) and durations are measured in minutes (1 minute = 60 seconds).

According to Equations (4) and (3), the probit number for a single-segment continuous cloud is calculated as:

$$P = T_A + T_B \ln t_{exp} C^{T_N} \qquad (8)$$

Hence, to get the correct probit number, we must convert the concentration from mole fraction to ppm and the time to from seconds to minutes:

$$
\begin{aligned}
P &= T_A + T_B \ln \frac{t_{exp}}{60}\left(1000000 \times C\right)^{T_N} \\
&= T_A + T_B \ln t_{exp} - T_B \ln 60 + T_B T_N \ln 1000000 + T_B T_N \ln C \\
&= T_A - T_B \ln 60 + T_B T_N \ln 1000000 + T_B \ln t_{exp} C^{T_N}
\end{aligned} \qquad (9)
$$

This transformation can most easily be effected if we convert the parameter T_A as soon as we take it out of the database and use $T'_A = T_A - T_B \ln 60 + T_B T_N \ln 1000000$ so that the probit number is then calculated as $P = T'_A + T_B \ln t C^{T_N}$ with the concentration and time now in standard units.

A similar conversion as the above is applied for the more general toxic load in terms of time-dependent concentration C, i.e. using Equation (5) instead of Equation (4).

2.5 Dangerous Toxic Load[i]

An alternate to the probit relationships, discussed in the sections above, is the concept of a dangerous toxic load. Two levels of dangerous toxic load can be considered.

- Specified level of toxicity (SLOT) – This approximately equates to the toxic load which would give rise to 1 % fatality and is defined by the HSE as

  - A level causing severe distress to almost everyone in the area
  - A substantial fraction of the exposed population requiring medical attention
  - Some people seriously injury requiring prolonged treatment
  - Highly susceptible people possibly being killed

- Significant likelihood of death (SLOD) – This equates to the toxic load which would give rise to a likely fatality of 50 %.

For the purpose of risk assessment and determining the probability of death, we will only consider the SLOD value and make the simplifying assumption that the probability of death for toxic loads greater than the SLOD value will be 1, whilst the probability of death for toxic loads less than the SLOD value will be 0:

$$P_{Death} = 1.0, \ L_{Toxic} \geq SLOD;$$
$$P_{Death} = 0, \ L_{Toxic} \prec SLOD \qquad \text{(1a)}$$

The HSE state that "….This approximation results from the assumption that those people inside the SLOD contour who do not die (due to factors such as physiology, fitness level etc) will be balanced by an approximately equal number outside the SLOD contour who do not die …."[ii]

In the implementation of the dangerous toxic load the material probit values A and B are overwritten such that B is chosen to be an appropriately large value of 1E6. Assuming that a probit value of 10 will give a probability of death of 1, the toxic B value is then:

$$A = 10 - B \ln(L_{Toxic})$$

2.6 Threshold Dose Effect Modelling

This concept is similar to the toxic load (section 2.3) and dangerous toxic load (section 2.5) logic. Here, the user inputs are a concentration (ERPG/STEL/IDLH), reference duration ($t_{exp,ref}$) and for indoor threshold dose effect calculations, an air change rate as well as tail time (see section 3).

The reference threshold dose ($L_{Toxic,ref}(i)$) for any toxic component (i) is determined from equation (4) with $t_{exp,ref} = t_{exp}$ and $L_{Toxic,ref}(i) = L_{Toxic}(i)$.

For materials comprising a single toxic component, if the local outdoor/indoor toxic dose for the toxic component exceeds $L_{Toxic,ref}(i)$ then the overall probability of death will be 1.

For mixtures of toxic components, two mixing rules are supported: the more conservative "additive" as well as the "non-interactive" mixing rules. These mixing rules are applied in determining the effective threshold dose as a result of contributions from each toxic material resulting in fatality.

With the "non-interactive" mixing rule, the components in the mixtures have different modes of actions (different toxic effects) and do not interact. The overall probability of death is 1 for cases where $L_{Toxic,ref}(i)$ is exceeded for any of the toxic constituents and zero otherwise (see equations (10) and (11)).

$$p_{Death} = 1, \qquad \max_{i=1,N} \left[\frac{L_{Toxic}(i)}{L_{Toxic,ref}(i)} \right] \geq 1 \qquad \text{(10)}$$

$$p_{Death} = 0, \qquad \max_{i=1,N} \left[\frac{L_{Toxic}(i)}{L_{Toxic,ref}(i)} \right] < 1 \qquad \text{(11)}$$

Where $L_{Toxic}(i)$ is calculated from equation (4) or (5), for outdoor exposure and equation (18) for indoor exposure.

With the "additive" mixing rule, the components in the mixtures have similar modes of actions (similar toxic effects) and the effective dose is assumed to be the sum of the dose contributions from each toxic component relative to its threshold dose ($L_{Toxic,ref}(i)$). In this case, the overall probability of death is 1 for cases where the sum of individual component lethalities based on "non-interaction" is greater or equal to 1 and zero otherwise (see equations (12) and (13)). The "additive" mixing rule is conservatively applied by default to mixtures of toxic components unless otherwise specified.

$$p_{Death} = 1, \sum_{i=1}^{N} \left(\frac{L_{Toxic}(i)}{L_{Toxic,ref}(i)} \right) \geq 1 \qquad \text{(12)}$$

$$p_{Death} = 0, \sum_{i=1}^{N} \left(\frac{L_{Toxic}(i)}{L_{Toxic,ref}(i)} \right) < 1 \qquad \text{(13)}$$

3 INDOOR CALCULATIONS

The adopted model for indoor concentration corresponds to the model by Bellamy et. al.[iii]. The response of population to toxic concentrations is also discussed in this reference, but this is not used in the current TXCS model. The model of Bellamy et al. has been enhanced by allowing for the scenario where the population will exit the building at a specified time interval, t_T, after the outdoor concentration begins to fall. This time interval is referred to as the 'tail-time'. This scenario allows the population to 'realise/be informed' that the outside environment is less harmful than the indoor.

3.1 Indoor concentration

3.1.1 Mathematical model

The indoor concentration, C_{in} (kg/m³) is related to the outdoor concentration, C_{out}, by

$$\frac{dC_{in}}{dt} = \frac{C_{out} - C_{in}}{\tau} \tag{14}$$

Here τ (s) is dependent on the ventilation rate r (air changes within building per second) by r = 1/τ. Thus it is representative of the time required for exchange of air inside the building with the outside.

3.1.2 Numerical solution

For a given segment, the outdoor concentration, $C_{out}=C_{out}(\underline{x},t)$, at a given location, $\underline{x}$, and time (within the segment) is obtained from the concentration profiles.

Case of continuous dispersion (constant outdoor concentration) [4]
It is assumed that this outdoor concentration remains constant during the segment duration for continuous releases[5]. If the indoor concentration has the value C_I at $t = 0$, then the above equation may be solved analytically to give:

$$C_{in}(t) = C_{out} + \left(C_I - C_{out}\right)\exp\left(-t/\tau\right) \tag{15}$$

It should be noted that in this context $t = 0$ corresponds to the time at which the downwind edge of the cloud arrives at the building (i.e. arrives at the location $\underline{x}$).

Case of instantaneous dispersion (time-varying outdoor concentration)

For an instantaneous release, the differential equation for the indoor concentration may be written in discrete form using a central differencing method:

$$\left(\frac{1}{\delta t} + \frac{1}{2\tau}\right)C_{in}(t + \delta t) = \left(\frac{1}{2\tau}\right)(C_{out}(t + \delta t) + C_{out}(t)) + \left(\frac{1}{\delta t} - \frac{1}{2\tau}\right)C_{in}(t) \tag{16}$$

This discrete form of the equation may be solved for $C_{in}(t+\delta t)$. However, when $\dfrac{\delta t}{\tau} > 2$ this may lead to unphysical (-ve) values for $C_{in}(t+\delta t)$, in which case the following 1st order implicit scheme is employed to :

$$\left(\frac{1}{\delta t} + \frac{1}{\tau}\right)C_{in}(t + \delta t) = \left(\frac{1}{\tau}\right)C_{out}(t + \delta t) + \left(\frac{1}{\delta t}\right)C_{in}(t) \tag{17}$$

Thus, the indoor concentration may be obtained from the outdoor concentration.

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[4] The building location should ideally be taken as the most appropriate position at which the pollutant flows into the building (so the most correct value of the outdoor concentration will be adopted).

[5] For a finite-duration continuous release (single-segment) equation (15) is applicable during the period at which the cloud passes along $\underline{x}$ and at times before the QI transition. After the segment has passed (i.e. at the arrival time of the next segment) the start time is reset to 0 and the outdoor concentration is chosen to correspond to the next segment (note that possibly overlap or hole may occur). Instantaneous logic is used after QI transition. Finally note that $C_I=0$ for the first segment.

3.2 Indoor toxic load, probit & probability of death

The indoor toxic load, $L^{in}_{Toxic}(i)$ for component i is computed from the indoor concentration, C_i in exactly the same manner as the outdoor toxic load is computed from the outdoor concentration.

$$L^{in}_{Toxic}(i) = \int_o^T \left[f_i C_{in}(t) \right]^{T_N(i)} dt \tag{18}$$

Here T is the exposure time. Thus, once the indoor concentration has been computed, in theory the indoor dose, indoor probit, indoor probability of death and indoor probability of death integral may be derived.
For a continuous segment, $C_{in}(t)$ is computed from equation (11). Thus, this expression is substituted in equation (14).

$$L^{in}_{Toxic}(i) = \int_o^T \left[f_i \left(C_{out} + (C_I - C_{out}) \exp\left({-t}/{\tau} \right) \right) \right]^{T_N(i)} dt \tag{19}$$

$T_N(i)$ is not necessarily an integer and so the derived expression may not necessarily be integrated analytically. The integral is evaluated numerically employing an algorithm based upon Simpson's rule.
For an instantaneous segment C_{in} and its corresponding dose integral are evaluated numerically.

Tail-time (t_T)
Once the cloud passes and the outdoor concentration has started to fall, the indoor concentration will decay. After a specified time period given by the tail time, t_T, following the start of decline in the outdoor concentration during the final cloud segment (at time t_d), the population will move outdoor. Let's call this time $t_{move} = t_d + t_T$, the total time it takes for the indoor population to move outdoors measured from the time of arrival of the cloud to the building. Thus from this point no more toxic dose will be experienced by the population indoors. (Note that the outdoor concentration does not have to reach zero, it has to begin to decrease.) Hence, the upper time limit, T, in equations (14 & 15) is given by

$$T = \min\left(t_d + t_T, t_{exp} \right) \tag{20}$$

The time at which the outdoor concentration starts to decline, t_d, is estimated as the time when the outdoor concentration, [6]evaluated along the cloud centreline, has dropped 95% from its maximum value.

If the population remains indoors after the outdoor concentration has dropped below the minimum, i.e. $t_{move} > t_{end}$, where t_{end} is the time for the outdoor cloud to leave the building, there will be an additional indoor exposure for a time given by

$$t^{in}_{exp} = \left(t_{move} - t_{end} \right) \tag{21}$$

During this period the outdoor concentration is zero and the indoor concentration is given by

$$C_{in}(t) = C_{IE} \exp\left({-t}/{\tau} \right) \tag{22}$$

Where C_{IE} is the indoor concentration value at the end of the exposure time (i.e. when C_{out} becomes 0). Substituting the expression in equation (18) into equation (14) & integrating, gives the following expression for the contribution to the indoor dose:

$$L^{in}_{Toxic}(i) = (f_i C_{IE})^{T_n(i)} \frac{\tau}{T_n(i)} \left(1 - \exp\left(- {T_n(i)\, t^{in}_{exp}}/{\tau} \right) \right) \tag{23}$$

Thus this contribution may be evaluated analytically.

If, on the other hand, the population moves outdoors before the outdoor concentration has dropped below the minimum, i.e. $t_{end} > t_{move}$, there will be an additional exposure to the toxic cloud outdoors for a time given by:

$$t^{out}_{exp} = \left(t_{end} - t_{move} \right) \tag{24}$$

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[6] SAFETI-NL 8.0: The decay time, t_d is evaluated based on cloud centreline concentrations. Note that: the cloud centreline concentration versus time profile employed in t_d evaluation is computed over the actual (off-centreline) duration of the passing cloud (at any given location, $\underline{x}$). For instantaneous releases with rainout, the off-centreline approach (pre SAFETI-NL 8.0) for estimating t_d was found to result in inconsistent (orders of magnitude step-jumps in) t_d predictions at fixed downwind but increasing crosswind distances. The step increases in predicted t_d resulted in over-prediction of time taken by indoor populations to move outside. For other types of releases, both t_d estimation approaches give very similar results.

This final contribution to the toxic load is evaluated from equation (5), using t_{move} and t_{end} as the limits of the integral.

It should, however, be noted that if the last segment is continuous, T, in equations (14 & 15) is t_{exp} since the outdoor concentration is constant for the whole segment and therefore the tail time does not commence until the end of the segment, i.e. $t_d = t_{exp}$. The additional contributions to the indoor dose due to the decay of the indoor concentration, as discussed above, will therefore be accounted for over the entire tail time.

The indoor probits, probability of death and probability integral are computed from the indoor toxic load in exactly the same way as for the outdoors. See equations (1,2,3 & 6).

# 4 AVERAGING-TIME EFFECTS FOR TOXIC RELEASES

4.1 Introduction

The release of toxic chemicals into the atmosphere results in the dispersion of a toxic cloud in the downwind direction. The variation in time of the concentration will depend on both the release characteristics (continuous, finite-duration, instantaneous or time-varying release) and the effects of wind meander. The effects of wind meander are included by the selection of an appropriate averaging time. The selection of the averaging time should be appropriate for the calculation of the toxic effect for an 'average' human, who is located at a fixed position ($\underline{x}$, $\underline{y}$, $\underline{z}$) and observes a concentration $C(\underline{x}$, y, z, t), (ppm), as function of time t.

In the PHAST/SAFETI dispersion models UDM (outdoor dispersion) and BWM (building-wake dispersion), the averaging time t_{av} for toxics is currently selected by default equal to 600 seconds. The logic in the UDM for passive dispersion coefficients and its choice of averaging times is fully consistent with that adopted by HGSYSTEM (HEGADAS)[iv,v], SLAB[vi] and the old TNO yellow book[vii]. However, the CCPS guidelines (1996)[viii] and EPA's "guide for Performing hazard assessment" (1995)[ix] state that the averaging time should always be less or equal to the exposure time, since toxicological relations may not be valid for periods of zero concentrations. EPA (1991)[x] recommends that $(t_{av})_{meander} = \min(t_{haz}, t_{rel})$, with t_{rel} the release duration and t_{haz} the averaging time associated with the hazard assessed. However for fully transient effects, it suggests to use $t_{av} = t_{haz}$ only. No further justification is given, and also no clear definition of t_{haz} is provided[7].

As a result, an additional option is implemented in which allows the selection of the averaging time equal to the exposure time. This section describes the calculation of toxic effects using both the existing PHAST/SAFETI logic as well as the added option. The formulation reported in this section has been discussed with a range of toxicologists.[xi]

4.2 Effect of wind meander on concentrations: averaging-time effects

For this purpose, it is important to distinguish between the 'instantaneous' concentration $C_{ins}(\underline{x}$, y, z, t), and the averaged concentration $C(\underline{x}$, y, z, t). The concentration $C(\underline{x}$, y, z, t) is the concentration including effects of wind-meander (with averaging time t_{av}); see Figure 1.
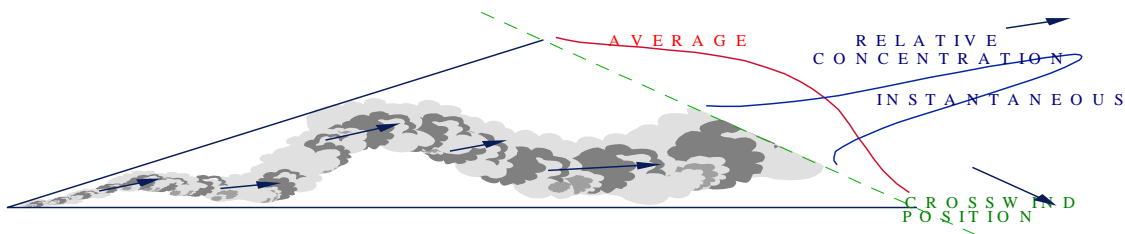
Figure 1. Effect of wind meander on concentration profile
At a given downwind distance the figure shows both the un-averaged crosswind concentration profile (instantaneous concentration C_{ins}) as well as the averaged concentration C

The effects of wind meander are only included following the transition to passive dispersion, and is not taken into account for the initial jet and/or heavy-gas phase. In the case of pure passive dispersion this means that:

$$C(\underline{x}, y, z, t) = \left(\frac{t_{av}^{ins}}{t_{av}} \right)^{0.2} C_{ins}(\underline{x}, y, z, t) \tag{25}$$

Here C_{ins} is the instantaneous, un-averaged concentration and $t_{av}^{ins} = 18.75s$. Note that the default assumption for toxic compounds is $t_{av} = t_{av}^{tox} = 600$ seconds, and therefore $C(\underline{x}$, y, z, t) = 0.5 $C_{ins}(\underline{x}$, y, z, t), i.e. the 10-minutes averaged concentration is half of the un-averaged concentration. See the UDM theory manual for further details.

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[7] This is presumably the time for which the point experiences above LFL concentrations for flammables and above toxic concentration for toxics?

As a result of the above, the toxic load evaluated in equation (5) becomes:[8,9]

$$L_{\text{Toxic}}(i) = \int_o^T \left[f_i C(\underline{x}, y, z, t) \right]^{T_N} dt = \int_o^T \left[f_i \left(\frac{t_{av}^{ins}}{t_{av}} \right)^{0.2} C_{ins}(\underline{x}, y, z, t) \right]^{T_N} dt$$

(26)

Where T_N is the probit number N for component i.

Equation (26) defines the effect of averaging time on the probability of death, probit and toxic load calculations as described in section 2.

Note: for the evaluation of the probability of death for a mixture, PHAST/SAFETI currently allows for three options, i.e. (A) a user-specified mixture probit, (B) a probit based on the most toxic chemical, and (C) a probit based on a calculated mixture probit. See the literature for further details on the joint toxic action of chemical mixtures[xii,xiii].

A. User-specified mixture probit

For this case the user needs to specify the probit coefficients A, B, N for the given mixture. Subsequently the mixture probit, toxic load and probability of death are calculated as described in Section 2 with usage of the total mixture concentration.

This method is recommended to be chosen if the user has sufficiently accurate know-how of the probit coefficients A, B, N of the mixture.

B. Probit based on most-toxic chemical

For this case the probit coefficients A, B, N corresponding to the most toxic chemical are adopted. The concentration used is the sum of the concentrations of all toxic components in the mixture. The most toxic component is defined prior to the dispersion calculations as that which has the lowest concentration that gives rise to 50% fatality for an exposure time of 1800 seconds.[10]

This method is recommended if the toxic effects resulting from one component of the released mixture are expected always to be significantly larger than the toxic effects resulting from the other components.

C. Calculated mixture probit

For this case it is considered that each component in the mixture kills independently. Therefore the probit of the mixture is calculated as the product of all the mixture component's probit numbers. Component's probit numbers are calculated as described in section 2 (see equations (1) and (2)).

4.3   Evaluation of averaging time for toxics releases

4.3.1   Default logic

For toxic releases, the user can apply the following choices for selection of averaging time:

1.   Default toxic averaging time: $t_{av} = t_{av}^{tox} = 600s$

2.   Averaging time corresponding to guidelines:
      2.1.   STEL – short term exposure limit: 900s
      2.2.   IDLH – immediate dangerous to life and health: 1800s
      2.3.   ERPG – emergency response planning guideline: 3600s

Toxicological relations are normally based on at least 10 minutes duration, and therefore usage of probit functions for lower durations than 10 minutes may result in less accurate results. Usage of 10 minutes instead of 1 hour averaging time results in a relative small difference in concentrations. According to toxicologists[xi], this difference is much smaller than the

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[8] The Toxicity coefficients are stored in the properties database assuming that concentrations are measured in parts per million (1 ppm = 0.000001 mole fraction) and durations are measured in minutes (1 minute = 60 seconds). Internally in PHAST concentrations are expressed in terms of mole fraction and time in seconds. A conversion is therefore carried out in order to obtain the correct Probit. . The data stored for chlorine in the property database are A = -3.419, B = 0.5, N = 2.75.

[9] in this equation t=0 corresponds to the arrival time (first time at which concentration become positive, and t=T corresponds to the departure time (after which concentration is zero). Note there appears to be no cut-off value of T; the value of T may be longer than the release duration (maximum PHAST value of 1 hour) because of along-wind diffusion.

[10] A possible improvement of this is to carry out this more precisely during the dispersion calculations, using the actual toxic load based on the actual concentration and the actual exposure time at the given location. This means that different chemicals may be most toxic at different locations.

expected inaccuracy of the toxicity based on the probit function. As a result the current default value of 10 minutes averaging times for toxic releases seems to be reasonable and this is also the choice most commonly applied in the literature (see also Chapter 6 in CCPS Guidelines[viii]) and in commercially available software.

4.3.2   Toxic effect driven by concentration

However for some toxic chemicals, the mode of toxic action is driven by concentration (large value of concentrations) and does not depend on the actual duration at which the concentration is achieved. The probit function exponent N would be typically much larger than 1. For these toxic chemicals, time averaging would not be appropriate, and therefore usage of the instantaneous time t_{av}^{ins}=18.75s is recommended.

4.3.3   Toxic effect driven by absorbed dose

For other toxic chemicals, the mode of action of the toxic compound is driven by absorbed dose (small value of probit function coefficient N, i.e. close to 1). For these chemicals the averaging time should correspond to the time duration at which the dose is achieved, i.e. the 'exposure time' t_{exp}. Use of an averaging time larger than the exposure time, could lead to the usage of too low (averaged) concentrations in the evaluation of the toxic load in the probit function.

For an exposure time larger than the maximum averaging time t_{av}^{max} = 3600 seconds, the adopted averaging time would be t_{av}^{max}. For an exposure time less than the instantaneous averaging time t_{av}^{ins}=18.75s, the adopted averaging time would be t_{av}^{ins}.[11] Otherwise the adopted averaging time would be equal to the exposure time. Thus the averaging time is given by the formula below:

$$t_{av}(\underline{x}, y, z) \; = \; \max \left\{ t_{av}^{\;ins}, \min \left(t_{\exp}(\underline{x}, y, z), t_{av}^{\;tox} \right) \right\} \qquad (\textbf{27})$$

In the above equation, the exposure time and therefore the averaging time is a function of the position ($\underline{x}$, y, z). In the current PHAST dispersion models (UDM and BWM), the received exposure time would be a function of the centre-line cloud distance and height only (x, z), i.e. it does not depend on the distance from the centre-line[12]. Moreover the calculation of the exposure time is chosen to be based on the un-averaged cloud (i.e. using t_{av}^{ins}).

The option of averaging time = exposure time, is only available when the exposure time can be calculated, i.e. if the concentration at a given centre/line downwind distance and height is known as a function of time. Thus this option is not available for the finite-duration correction, which does not supply concentration as a function of time.[13]

4.3.4   Evaluation of exposure time

In the EPA guidelines[x, ix] the exposure time is defined as the time period for which hazard exists but no clear definition is given. Following discussion with toxicologists[xi], the most appropriate definition of the exposure time [if mode of action of the toxic compound is driven by absorbed dose] would be dose based, i.e. the time for which a certain given fraction of the totally received toxic load L_{Toxic} is achieved. It was suggested to choose the time between which a fraction $f = 0.05$ and $(1-f) = 0.95$ is achieved, i.e. between 5% and 95% of the toxic load.

In case of intermittent concentration, the exposure time would not include the periods, for which the concentration is less than a cut-off concentration c_{tox}^{min} (mole fraction). Based on discussions with toxicologists[xi], a zero cut-off concentration is chosen as default, i.e. $c_{tox}^{min} = 0$. It is strongly recommended not to change this value.

Thus PHAST adopts the following additional parameters for exposure time calculations:

1.   cut-off fraction f of toxic load (default $f = 0.05$); exposure time is time between which fraction f and fraction $(1-f)$ of toxic load is achieved (ignoring periods with concentration below c_{tox}^{min})
2.   cut-off concentration c_{tox}^{min} (mole fraction); default $c_{tox}^{min} = 0$

Example of evaluation of exposure time: two subsequent clouds

The above evaluation of averaging time is illustrated in the figure below, in the case where the observer experiences two subsequent clouds.

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[11] Note that choosing an averaging time less than t_{av}^{ins}, would result in unrealistic large concentrations, and this is therefore not acceptable.

[12] Although strictly speaking for distances sufficiently far away from the centre-line, the cloud concentrations and therefore the exposure time is zero. However averaging time would not affect already zero concentrations.

[13] FUTURE. For FDC a simplistic approach of using release duration could be adopted, or via a simple formula for downwind-distance dependent exposure duration (based on downwind passive dispersion coefficient σ_x)
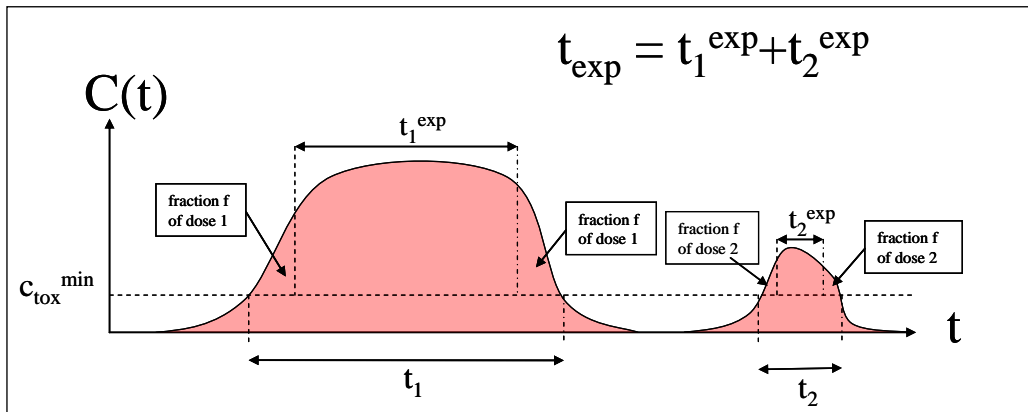
(a) Averaging time set as duration for which fraction (*1-2f*) of segment doses has been achieved
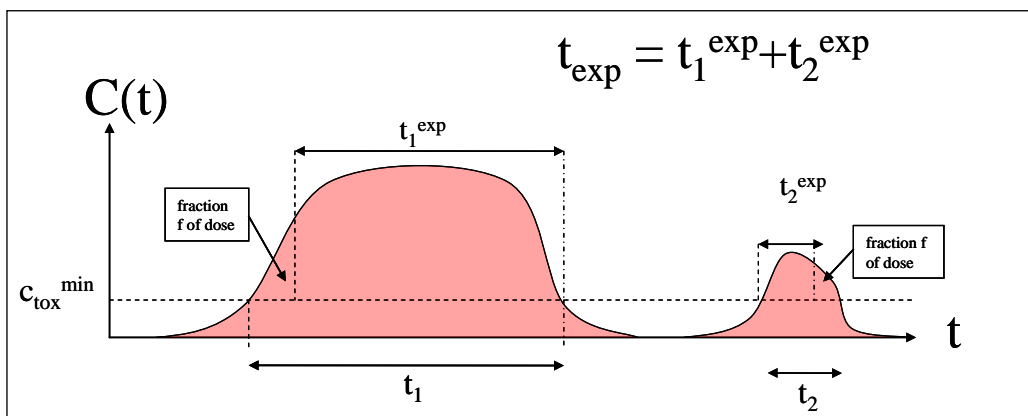
(b) Averaging time set as duration for which fraction (*1-2f*) of total dose has been achieved

Figure 2. Concentration C(t) at given location as function of time t; multiple clouds

In Figure 2 the following is adopted:

- The times t_1, t_2 refer to the duration at which the first and second segment experience concentrations above $c_{tox}{}^{min}$. The calculations of the toxic load L_1 (for segment 1) and the toxic load L_2 (for segment 2) are based on these durations.

- The times $t_1{}^{exp}$, $t_2{}^{exp}$ refer to the duration at which the fraction (*1-2f*) of the toxic load has been received. This may be done in two manners:

    a) Individually for each segment (see Figure 2a): fraction (*1-2f*) of loads L_1 and fraction (*1-2f*) of load L_2
    b) Referring to the total toxic load $L = L_1+L_2$ (see Figure 2b): fraction (*1-2f*) of the total load L. This approach has been selected for PHAST, since it can be more easily implemented.

- The total exposure duration equals the sum of the segment exposure times: $t_{exp} = t_1{}^{exp} + t_2{}^{exp}$.

- The adopted averaging time in the concentration evaluation (for the toxic load calculation)[14] will be set equal to $t_{av} = t_{exp} = t_1{}^{exp} + t_2{}^{exp}$.

The above evaluation of segment and total exposure time would be fully based on un-averaged (instantaneous) concentrations[15].

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[14]If both segments are treated truly independent, one could consider to adopt different averaging times for both segments for the final toxic load evaluation, i.e. the averaging time $t_{av} = t_1{}^{exp}$ would be adopted for the first segment, and $t_{av} = t_2{}^{exp}$ would be adopted for the second segment (with lower cut-off value of 18.75 seconds and upper cut-off value of 3600 seconds). The corresponding loads would be summed for the total toxic load effect. Note that this would make the overall algorithm even more difficult (with not only averaging time being a function of position, but also multiple averaging times at a given position). Moreover there would be an unrealistic discontinuity depending whether two segments are treated as one segment or two segments. Thus this approach is suggested not to be adopted.

[15] The exposure time as defined in method is actually a function of the averaging time t_{av} (since concentration C in toxic load depends on t_{av}). Some iterative procedure could be considered, to iterate until the 'correct' averaging/exposure time is achieved. However this type of accuracy may not be needed and it would be also CPU intensive. It is therefore not recommended at this stage.

<u>Cases for evaluation of exposure time</u>

The above definition of exposure time results in consistent predictions between continuous, finite-duration, instantaneous and time-varying releases:

1. If the observer <u>x</u> only observes a continuous cloud with release duration t_{dur}, the exposure time equals $t_{exp} = (1\text{-}2f)^*t_{dur}$ = 0.9 t_{dur}[16]. For a finite-duration continuous release, this exposure time will be observed for all downwind distances before the quasi-instantaneous (QI) transition, and before the point of rainout.

2. For instantaneous clouds, the exposure time will typically increase because of along-wind diffusion in the downwind direction. Similarly this will also apply for continuous finite-duration releases after the QI transition.

3. Currently along-wind diffusion effects are not included for time-varying releases and dispersion after rainout. This may result in considerable under prediction of exposure times, and over-prediction of concentrations, although doses [=exposure time * concentration] are expected to be more reasonable. Thus predicted toxic effects are expected to be more reasonable if the probit-function exponent N≈1, but otherwise predicted toxic effects will be less accurate.

4.3.5   Algorithm in case of averaging time equal to exposure time
The algorithm for setting averaging concentrations and averaged widths, in case of averaging time equal to exposure time, is as follows:

1. First carry out a run of the dispersion model with no time-averaging (t_{av} = t_{av}^{ins} = 18.75s) to determine the un-averaged cloud, i.e. the un-averaged concentration as function of time and location.

2. Determine from the above un-averaged results the exposure time t_{exp} as function of downwind distance and height (x, z)[17].

   2.1. Set toxic load L_{toxic} from Equation (5) assuming unaveraged concentrations
   2.2. Set times at $t_{min}(x)$, $t_{max}(x)$ which fraction f and (1-f) of toxic load is achieved
   2.3. If concentrations all > c_{min} between t_{min} and t_{max} then t_{exp} = t_{max}-t_{min} otherwise ignore all time periods with concentration less than c_{min}

3. If all exposure times are smaller than 18.75s, always use the above un-averaged results. If all exposure times are larger than 3600s, apply t_{av} =3600s[18]. Otherwise apply an algorithm accounting for the averaging time being a function of the distance along the centre-line:

   3.1. Recommended method for PHAST (single UDM core run): process and re-organize UDM data via RECP and subsequently employ Cld_Txcs to determine for each downwind distance the appropriate averaging time t_{av}(<u>x</u>), and to set the averaged concentration and averaged cloud width accordingly.

   3.2. Proposed method for future work (multiple UDM runs):

      3.2.1. Run UDM for a range of averaging times, e.g. for 18.75, 37.5, 75, 150, 300, 600s, 1500s, 3600s or 18.75, 60, 180, 600, 1500, 3600s.
      3.2.2. Determine UDM appropriate averaging-time adjusted values (UDM post-processing) via interpolation of the above data. Let concentration c_1 be the calculated concentration at averaging time t_1 and c_2 the calculated concentration at averaging time t_2, then for averaging time $t_1 < t_{av} < t_2$, the concentration c at t_{av} is set as follows (exact interpolation for purely passive):

(28)

$$\ln(c) = \ln(c_1) + \frac{\ln\left(\frac{t_{av}}{t_1}\right)}{\ln\left(\frac{t_2}{t_1}\right)} \ln\left(\left(\frac{c_2}{c_1}\right)\right)$$

The same type of interpolation applies for the crosswind width.

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[16] In reality along-wind diffusion would take place at the cloud edges resulting in increased exposure time, but this is currently ignored prior to the QI transition.

[17] Here exposure time is set as indicated in the current section using the UDM post-processor models

[18] t_{av}=3600s is applied via a single UDM run after PHAST6.5, and using RPRO for PHAST6.5

5 CONCENTRATION AND RISK BASED TOXIC MODELLING

The criteria for halting the dispersion modelling impacts on the toxic calculations. If the criteria selected is "Mixed basis" or "Distance based" the edges of the toxic cloud are determined on the basis of the minimum probability of death, with a hard low limit set to the lethality calculated from the dispersion stopping concentration and an exposure time equal to the maximum release duration. The toxic probability of death vs distance plot will show a variable lethality along the downwind direction.
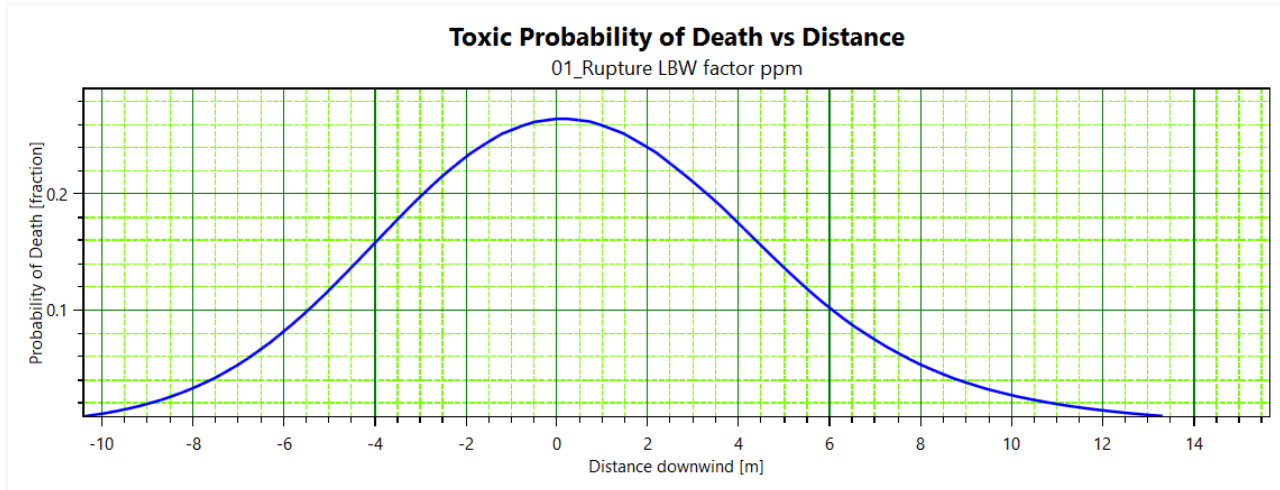
If, on the other hand, the criteria selected is "Concentration and Risk based" the model will require the user to provide a concentration of interest and will produce toxic results with 100% lethality inside the maximum dispersion footprint and 0% lethality outside it. The toxic probability of death transect will show a flat profile.
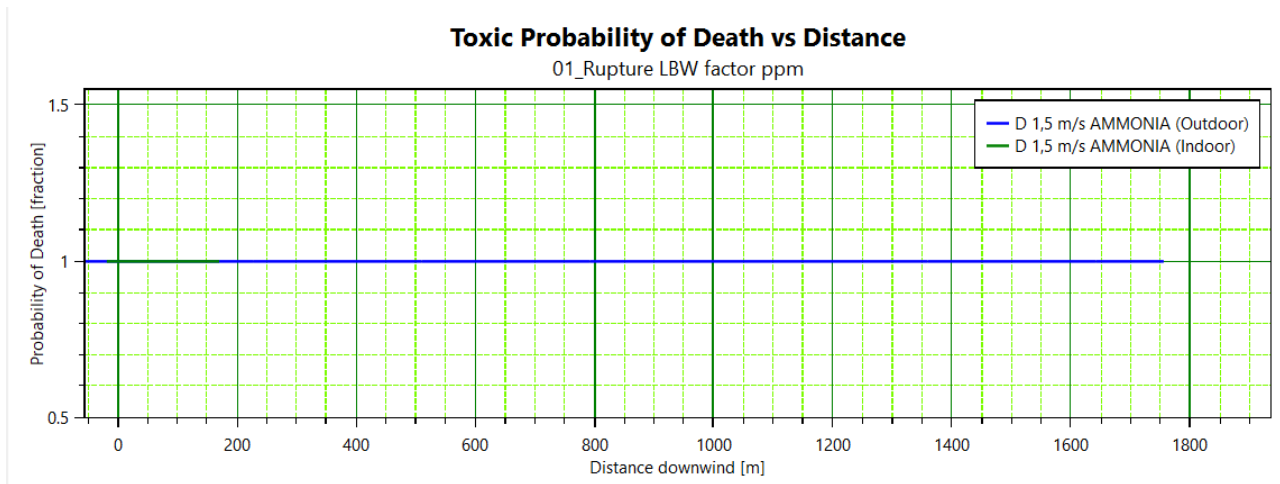
The modelling of toxic effect zones is done applying the "Concentration and Risk based" criteria to the effect level concentrations selected, regardless of the general setting of the dispersion halting criteria. The effect zone modelling uses the toxic averaging time.

6 VERIFICATION

Indoor dose
For a single segment continuous (outdoor) release the indoor concentration may be derived analytical and is given in equation **(11)**. For substances that have an integer value for the probit number, T_N, the indoor dose may be computed from equation **(15)**. The probit number and probability of fatality can then be derived from the indoor dose. These analytical values for indoor dose, probit & fatality provide a check on the implementation of the model within the program for correctness and accuracy.

Averaging time for toxic releases: exposure time = averaging time
See TXCS_OBSV_Testing.doc for details of model verification.

7 SENSITIVITY ANALYSIS

Indoor dose
Testing is to be performed for a range of building exchange rates, *r*. For the limits *r = 0*, no exchange with indoors, to *r = ∞*, immediate exposure to outdoors.

Averaging time for toxic releases: exposure time = averaging time
See TXCS_OBSV_Testing.doc for details of model sensitivity analysis.

8 LIMITATIONS AND FUTURE DEVELOPMENTS

This section covers recommendations for further work.

Averaging time for toxic releases: exposure time = averaging time

The following discusses the current limitations and future improvements to the "exposure time = averaging time" model.

Multiple UDM runs (elimination of concept of core-averaging time)

Following elimination of the usage of the concept of core averaging time in the UDM, more accurate concentration calculations can be carried out by adopting the actual averaging time in the UDM simulations. In the case of averaging time = exposure time, this would necessitate multiple UDM runs (see Section 4.3.5 for further details).

Usage of actual instead of mean concentrations in toxic load evaluation

The time-dependent effects taken into account by the UDM are effects resulting from time-dependent effects of the release (finite-duration, instantaneous or time-varying) or those resulting from rainout (time-dependent pool evaporation).

The UDM predicts a mean concentration including time-averaging to account for wind meander. Thus it does not take into account time-dependent effects resulting from wind meander and/or turbulent concentration fluctuations around the mean.

In the evaluation of the toxic load [see Equation (5)] one should strictly speaking adopt the actual concentrations. Usage of a time-averaged mean concentration would be only appropriate for the probit-function exponent $N \approx 1$. However, for N significantly larger than 1, the large values of the concentration would contribute more than the smaller values, and therefore usage of time-averaged concentration values could result in too low values of the toxic load.

Improved modelling of averaging-time effects
Dave Wilson (1995)[xiv] states that the factor $(t_{av}/t_{av}^{ins})^{0.2}$ in the formula for the passive crosswind dispersion coefficient is incorrect (t_{av} = averaging time, t_{av}^{ins} = equivalent instantaneous value of averaging time), since it does not account properly for source size (duration t_{dur}) and plume travel time t_{trav}:

i. t_{trav} = 60s, t_{dur} = 600s → large increase of time-exposure averaged plume width
ii. t_{trav} = 6000s, t_{dur} = 600s → small effect on plume spread

He proposes a new model, but with several unresolved issues (as such, this model is not practically applicable at this stage).

NOMENCLATURE

f	fraction of component
i	number of component in released toxics mixture
p_{death}	probability of death (-)
P	probit number (-)
PI	integrated probability of death
L_{Toxic}	toxic load, s
x	horizontal downwind distance, m
y	crosswind distance, m
r	building exchange rate, s^{-1}
t	time, s
t_d	time at which outdoor concentration begins to decline, s
t_{exp}	exposure time, s
t_T	tail time, s
z	vertical height, m
τ	building exchange timescale, s
δt	incremental timestep, s

Subscripts

in	indoor
out	outdoor
I	indoor at t=0

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