

VERIFICATION AND VALIDATION OF CONSEQUENCE AND RISK MODELS FOR ACCIDENTAL RELEASES OF HAZARDOUS CHEMICALS TO THE ATMOSPHERE

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ABSTRACT

This paper considers the “verification” and “validation” of consequence and risk models for accidental releases of toxic or flammable chemicals to the atmosphere. These models typically include a “physical description” of the phenomenon (e.g. cloud moving with the wind with air entraining into the cloud because of turbulence, etc.), a formulation of the corresponding “mathematical model”, an “algorithm” for solution of the above mathematical model, and “implementation” of this algorithm into code.

Testing of the resulting software program should ideally include “verification” that the code correctly solves the mathematical model (i.e. that the calculated variables are a correct solution of the equations), “validation” against experimental data to show how closely the mathematical model agrees with the experimental results, and a “sensitivity analysis” including a large number of input parameter variations to ensure overall robustness of the code, and to understand the effect of parameter variations on the model predictions.

The current paper includes an overview on how the above verification and validation could be carried out for discharge, atmospheric dispersion (including pools), flammable effects (e.g. pool fires, jet fires, explosions), and risk modelling. A wide range of release scenarios is considered including sub-cooled liquid releases, superheated liquid releases, vapour releases, un-pressurised and pressurised releases, and a wide range of hazardous chemicals is considered (e.g. water, LNG, propane, ammonia, HF etc). Reference is made to the literature for the availability of experimental data and the verification and validation is illustrated by means of application to the consequence models in the hazard assessment package Phast and the risk analysis package Phast Risk (formerly known as SAFETI).

1. INTRODUCTION

Typical release scenarios involve liquid, two-phase or gas releases from vessel or pipe work attached to vessels. Consequence modelling first involves discharge modelling. Secondly a cloud forms which moves in the downwind direction, and atmospheric dispersion calculations are carried out to calculate the cloud concentrations. In case of two-phase releases rainout may occur, and pool formation/spreading and re-evaporation needs to be modelled. For flammable materials modelling is required of jet fires or fireballs in case of immediate ignition, pool fires in case of ignition of a pool formed following rainout, and explosions or vapour cloud fires (flash fires) in case of delayed ignition; Figure 1 illustrates the example case of a continuous release with rainout.

To ensure the quality of consequence-modelling software thorough testing is paramount. This is ideally carried out by means of the following subsequent phases:

1. Verification that the code correctly solves the mathematical model, i.e. that the calculated variables are a correct solution of the equations. In case of a ‘simple’ mathematical model (e.g. not using differential equations but non-linear equations for unknown variables only), it can often be directly verified by insertion of the solved variables (calculated from the code) in the original equations, and checking that the equations are indeed satisfied. This is usually most expediently done by writing a ‘verification’ Excel spreadsheet in parallel with the code. In case of a more complex model expressed by a number of differential equations, the model can sometimes be solved analytically for some specific cases. Verification then consists of checking that the analytical solution is identical to the

numerical solution. For a more general case, the more complex model can no longer be solved analytically. The only way of verifying the model is by comparing it with another model that solves the same (type of) equations.

2. **Validation** against experimental data. After, as shown above, the code has been verified to correctly solve the mathematical model, validation against experimental data will show how closely the mathematical model agrees with the experimental results. This provides a justification for the simplified assumptions made to derive the mathematical model.
3. **Sensitivity analysis**. This involves carrying out a large number of input parameter variations (e.g. hole diameter, ambient temperature, etc.) for a number of base cases (e.g. continuous vertical methane jet release, instantaneous ground-level propane un-pressurised release, etc.). Its purpose is to ensure overall robustness of the code, and to understand the effect of parameter variations on the model predictions.

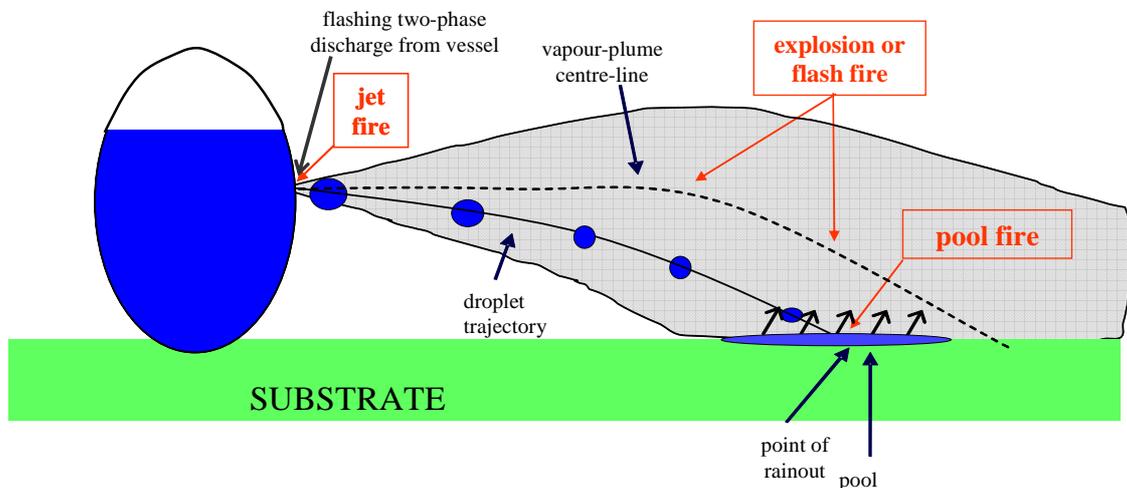


Figure 1. Continuous two-phase release of flammable material with rainout

This paper includes a brief overview of the “verification” and “validation” of consequence and risk models for accidental releases of toxic or flammable chemicals to the atmosphere. A limited number of key scenarios are considered, while reference is made to key papers for details. Reference is made to the literature for the availability of experimental data. The verification and validation is illustrated by means of application to the consequence models in the hazard assessment package Phast and the risk analysis package Phast Risk (formerly known as SAFETI).

Sections 2, 3 and 4 describe the verification and validation for discharge modelling, dispersion and pool modelling, and flammable effects modelling, respectively. Finally Section 5 includes a brief description on verification for risk modelling.

2. DISCHARGE

For releases of hazardous materials a wide range of scenarios can occur including instantaneous releases (catastrophic vessel rupture), and continuous and time-varying releases (leak from vessel, short pipe or long pipe). The stored material could be a sub-cooled liquid, a (flashing) superheated liquid, or a gas. As shown in Figure 2, the discharge model calculates both the expansion from the initial storage conditions to the orifice conditions, as well as the subsequent expansion from orifice conditions to atmospheric

conditions. For superheated liquid releases, liquid break-up into droplets occurs along the expansion zone. It is typically assumed that the length of the expansion zone is very small with negligible air entrainment.

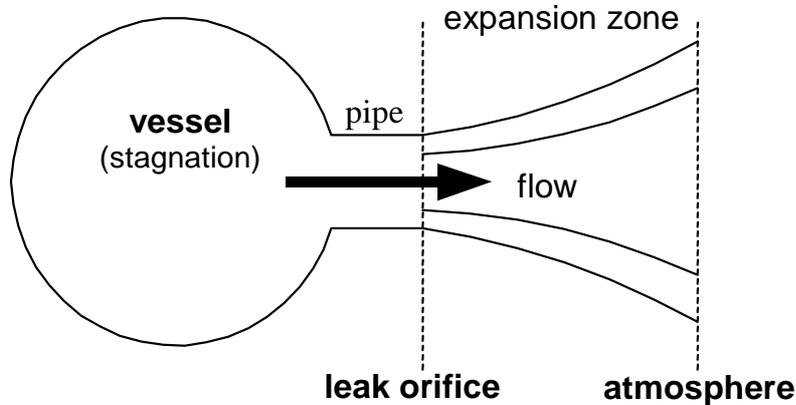


Figure 2. Expansion from stagnation to orifice and from orifice to ambient conditions

Key output data of the discharge model are flow rate, orifice data [velocity, liquid fraction] and post-expansion data [velocity, liquid fraction, initial droplet size (distribution)]. The post-expansion data are the starting point (“source term”) of the subsequent dispersion calculations.

In the literature numerous discharge models can be found. Key literature including description of discharge models and experimental data include Perry’s handbook¹, the DIERS project manual², CCPS QRA guidelines³, Sections 15.1-15.9 in Lees⁴, and Chapter 2 in the TNO Yellow Book⁵. The author did not find an up-to-date published overview of key experiments (benchmark tests for discharge models; input data and experimental results), in conjunction with a systematic evaluation of discharge models.

Key verification tests include comparison of the model against well-established analytical flow-rate equations for incompressible liquid (Bernoulli equation) and ideal gases. In addition verification could be considered between different discharge models and verification against results from process simulators (e.g. HYSIS or PROII)

Key validation tests include sub-cooled and saturated pipe and orifice releases of water (Sozzi and Sutherland⁶, Uchida and Narai⁷), and also data for hydrocarbon releases.

A detailed verification and validation has recently been carried out for the Phast discharge model for releases from vessels and/or short pipes including amongst others the above cases. Figure 3 illustrates the comparison for the Phast 6.53 model against sub-cooled water jets. The Phast long pipeline model has been validated for propane two-phase releases (Isle of Grain experiments^{8,9})

Detailed validation of droplet modelling for two-phase releases was carried out by Witlox et. al.¹⁰ using a range of droplet-size correlations accounting for both mechanical and flashing break-up of the droplets. This includes validation of initial droplet size against recently published experiments [STEP experiments (flashing propane jets), experiments by the Von Karman Institute (flashing R134-A jets), and water and butane experiments carried out by Ecole des Mines and INERIS]. It also includes validation of the rainout against the CCPS experiments (flashing jets of water, CFC-11, chlorine, cyclohexane, monomethylamine).

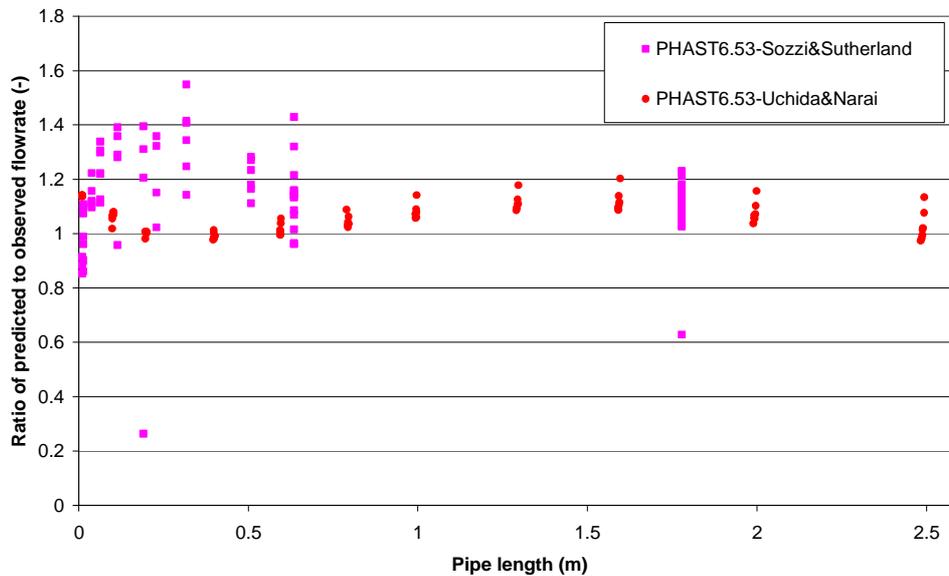


Figure 3. Phast 6.53 validation of flow rate for sub-cooled water release

3. DISPERSION AND POOL SPREADING/EVAPORATION

For dispersion modelling a very wide range of scenarios can be considered. Distinction can be made between momentum (un-pressurised or pressurised releases), time-dependency (steady-state, finite-duration, instantaneous or time-varying dispersion), buoyancy (buoyant rising cloud, passive dispersion or heavy-gas-dispersion), thermodynamic behaviour (isothermal or cold or hot plume, vapour or liquid or solid or multiple-phase, reactions or no reactions), ground effects (soil or water, flat terrain with uniform surface roughness, variable surface roughness, non-flat terrain, obstacles), and ambient conditions (e.g. stable, neutral or unstable conditions).

In the literature numerous text books and articles on dispersion can be found. Key literature including description of models and experimental data include Chapter 4 in the TNO yellow book⁵, Sections 15.11-15.54 in Lees⁴, and the CCPS dispersion guidelines¹¹. Key experiments (benchmark tests for dispersion; input data and experimental results) have been stored in the MDA database by Hanna et al.¹² in conjunction with comparison and validation of a wide range of models. Likewise data are stored in the REDIPHEM database partly as part of the EU project SMEDIS¹³. The SMEDIS project has also produced a protocol for evaluating heavy gas dispersion models, which has also recently been proposed for application to LNG¹⁴.

Model verification and validation for dispersion models is illustrated below for the Phast dispersion model UDM^{15,16}. This is an integral model, which can account for all the above type of releases except for effects of obstacles and non-flat terrain. The verification and validation for the UDM can be summarised as follows (see the UDM Technical Reference Manual¹⁶ for full details and a detailed list of references):

1. Jet and near-field passive dispersion. For an elevated horizontal continuous jet (of air), the UDM numerical results are shown to be identical to the results obtained by an analytical solution. For vertical jets very good agreement has been obtained against both the “Pratte and Baines” and “Briggs” plume rise correlations.
2. Heavy-gas dispersion. The UDM numerical results are shown to be in identical agreement against an analytical solution for a 2-D isothermal ground-level plume. The UDM has been validated against the

set of three 2-D wind-tunnel experiments of McQuaid¹⁷. The new formulation has also been validated against the HTAG¹⁸ wind tunnel experiments. Furthermore the UDM model was verified against the HGSYSTEM model HEGADAS.

3. Far-field passive dispersion. For purely (far-field) passive continuous dispersion, the UDM numerical results are shown to be in close agreement with the vertical and crosswind dispersion coefficients and concentrations obtained from the commonly adopted analytical Gaussian passive dispersion formula. The same agreement has been obtained for the case of purely (far-field) passive instantaneous dispersion, while assuming along-wind spreading equal to cross-wind spreading in the analytical profile.
4. Finite-duration releases. The UDM “Finite-duration-correction” module has been verified against the HGSYSTEM/SLAB steady-state results, and shown to lead to finite-duration corrections virtually identical to the latter programs. Furthermore excellent agreement was obtained using this module for validation against the Kit Fox experiments (20-second releases of CO₂ during both neutral and stable conditions; see Figure 4).
5. Thermodynamics. The UDM dispersion model invokes the thermodynamics module while solving the dispersion equations in the downwind direction. This module describes the mixing of the released component with moist air, and may take into account water-vapour and heat transfer from the substrate to the cloud. The module calculates the phase distribution [component (vapour, liquid), water (vapour, liquid, ice)], vapour and liquid cloud temperature, and cloud density. Thus separate water (liquid or ice) and component (liquid) aerosols may form. The liquid component in the aerosol is considered to consist of spherical droplets and additional droplet equations may be solved to determine the droplet trajectories, droplet mass and droplet temperature. Rainout of the liquid component occurs if the droplet size is sufficiently large. The UDM homogeneous equilibrium model has been verified for both single-component and multi-component materials against the HEGADAS model. The UDM HF thermodynamics model (including effects of aqueous fog formation and polymerisation) was validated against the experiment by Schotte¹⁹.
6. Pool spreading/evaporation. If the droplet reaches the ground, rainout occurs, i.e. removal of the liquid component from the cloud. This produces a liquid pool which spreads and vaporises (see Figure 1). Vapour is added back into the cloud and allowance is made for this additional vapour flow to vary with time. The UDM source term model PVAP calculates the spreading and vapour flow rate from the pool. Different models are adopted depending whether the spill is on land or water, and whether it is an instantaneous or a continuous release. The pool spreads until it reaches a bund or a minimum pool thickness. The pool may either boil or evaporate while simultaneously spreading. For spills on land, the model takes into account heat conduction from the ground, ambient convection from the air, radiation and vapour diffusion. These are usually the main mechanisms for boiling and evaporation. Solution and possible reaction of the liquid in water are also included for spills on water, these being important for some chemicals. These effects are modelled numerically, maintaining mass and heat balances for both boiling and evaporating pools. This allows the pool temperature to vary as heat is either absorbed by the liquid or lost during evaporation.

PVAP was verified by David Webber against the SRD/HSE model GASP for a range of scenarios with the aim of testing the various sub-modules, and overall good agreement was obtained. The PVAP spreading logic was first validated against experimental data for spreading of non-volatile materials. Subsequently the PVAP evaporation logic was validated against experimental data in confined areas where spreading does not take place. Finally comparisons were made for simultaneously spreading and vaporising pools. The above validation was carried out for both spills on water and land, and a wide range of materials was included [LNG, propane, butane, pentane, hexane, cyclo-hexane, toluene, ammonia, nitrogen, water, Freon-11]).

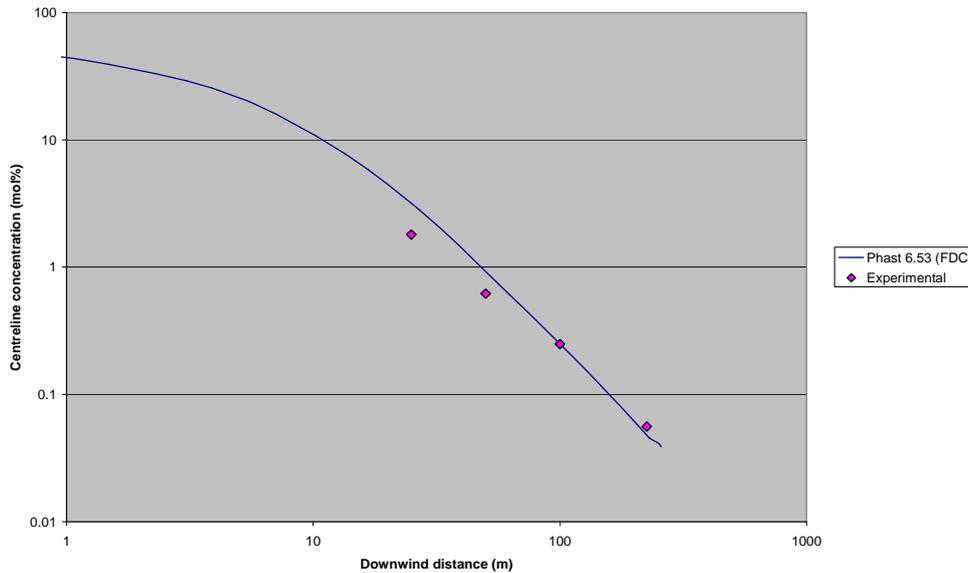


Figure 4. UDM results for Kit Fox experiment KF0706 (20 second release)

The above covers the verification and the validation for the individual UDM modules. The validation of the overall model was carried out against large-scale field experiments selected from the MDA and REDIPHEM databases, including the following:

- Prairie Grass (continuous passive dispersion of sulphur dioxide).
- Desert Tortoise and FLADIS (continuous elevated two-phase ammonia jet)
- EEC (continuous elevated two-phase propane jet)
- Goldfish (continuous elevated two-phase HF jet)
- Maplin Sands, Burro and Coyote (continuous evaporation of LNG from pool)
- Thorney Island (instantaneous un-pressurised ground-level release of Freon-12)
- Kit Fox (continuous and finite-duration heavy-gas dispersion of CO₂ from area source)

Each of the above experimental sets was statistically evaluated to determine the accuracy and precision of the UDM predictions with the observed data. Formulas adopted by Hanna et al.¹² were used to calculate the geometric mean bias (under or over-prediction of mean) and mean variance (scatter from observed data) for each validation run. This was carried out for centre-line concentrations, cloud widths, and (for the SMEDIS experiments) also off centre-line concentrations. The overall performance of the UDM in predicting both peak centreline concentration and cloud widths was found to be good for the above experiments.

4. FLAMMABLE EFFECTS

This section deals with the verification and validation of flammable effect models (fireballs, pool fires, jet fires and explosions, vapour cloud fires). Furthermore the most-established empirical models are considered only. Key literature including description of these models and experimental data include Chapters 5-6 of the TNO yellow book⁵, Sections 16-17 in Lees⁴ and the CCPS guidelines²⁰.

Fireballs, jet fires and pool fires

Empirical models for these fires include empirical correlations describing the fire geometry (most commonly a sphere for a fireball, a tilted cylinder for pool fire, and a cone for the jet fire) and the surface emissive power (radiation per unit of area emitted from the fire surface area); see Figure 5.

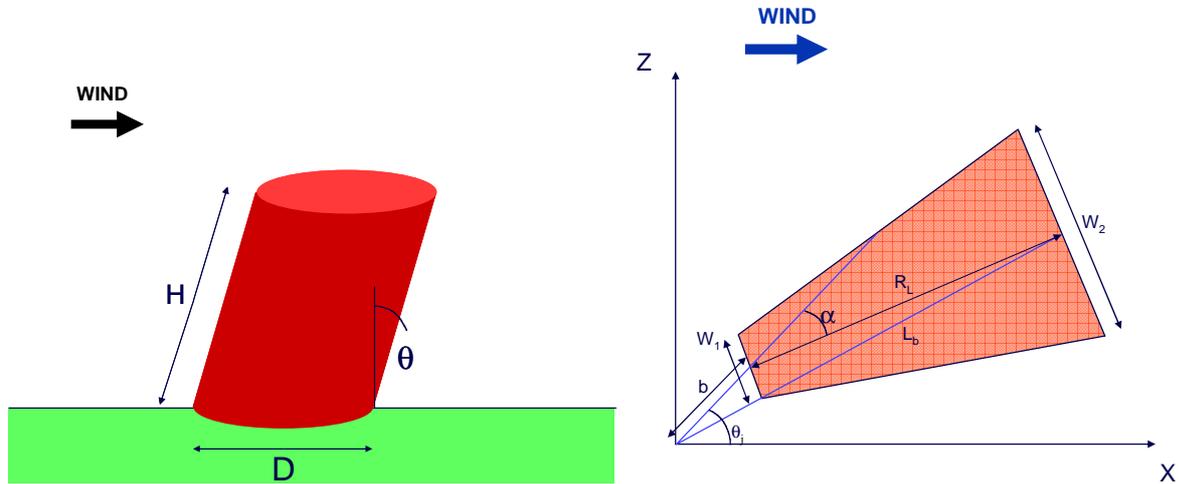


Figure 5. Geometry for pool fire (tilted cylinder) and jet fire (cone)

The radiation intensity (W/m^2) for an observer with given position and orientation is set as the product of the surface emissive power and the view factor. The view factor including the effects of atmospheric absorption is derived by means of integration over the flame surface. In Phast this integration is carried out numerically, while other models adopt analytical expressions for specific fire geometries.

The fireball model from Martinsen and Marx²¹ is based on extensive literature, detailed tests and also allows for lift-off. More simplistic models are included in the above general references. The latter models can easily be verified by simple hand calculations.

The Phast pool fire model has been validated against data for LNG pool fires²²; see Figure 6 which also includes verification against model predictions by Johnson²². Furthermore it has been validated against the Montoir LNG tests (Nedelka et al²³) and hexane tests (Lois and Swithenbank²⁴).

The Phast jet fire model has been validated against vertical natural-gas releases (Chamberlain²⁵), horizontal natural-gas and two-phase LPG releases (Bennett et al.²⁶), and horizontal liquid-phase crude oil releases (Selby and Burgan²⁷). It has also been verified against model predictions by Johnson²⁸ in the case of the horizontal natural-gas releases; see Figure 7.

Explosion

Fitzgerald²⁹ includes a detailed comparison of the TNO multi-energy (1988), Baker-Strehlow (1999) and CAM models (1999). This includes information of the latest versions of these models and comparison against experimental data (EMERGE experiments by TNO³⁰ and BFETS experiments by SCI³¹). Clear conclusions are provided indicating under which conditions which model is best on overpressure prediction. The latest available versions of the multi-energy (MULT) and Baker-Strehlow (BSEX) models have been implemented into Phast. They have been validated against the above EMERGE and BFETS experiments; see Figure 8 for the predictions of overpressure (as function of distance from the edge of the

congestion zone) for the case of the EMERGE 6 propane experiment (medium-scale 3D medium-congestion).

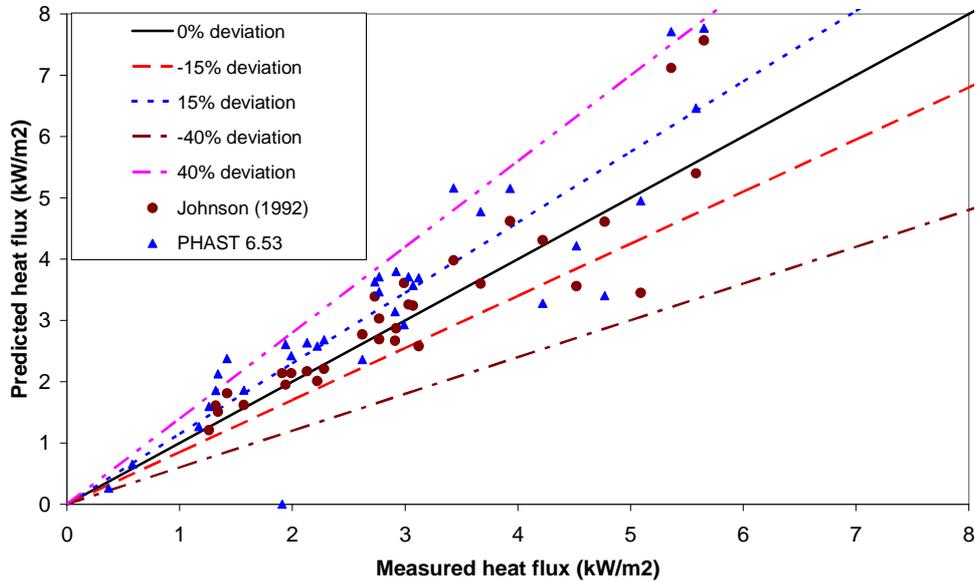


Figure 6. Predicted against measured incident radiation at different observer positions and orientations using the Phast 6.53 and Johnson pool fire models

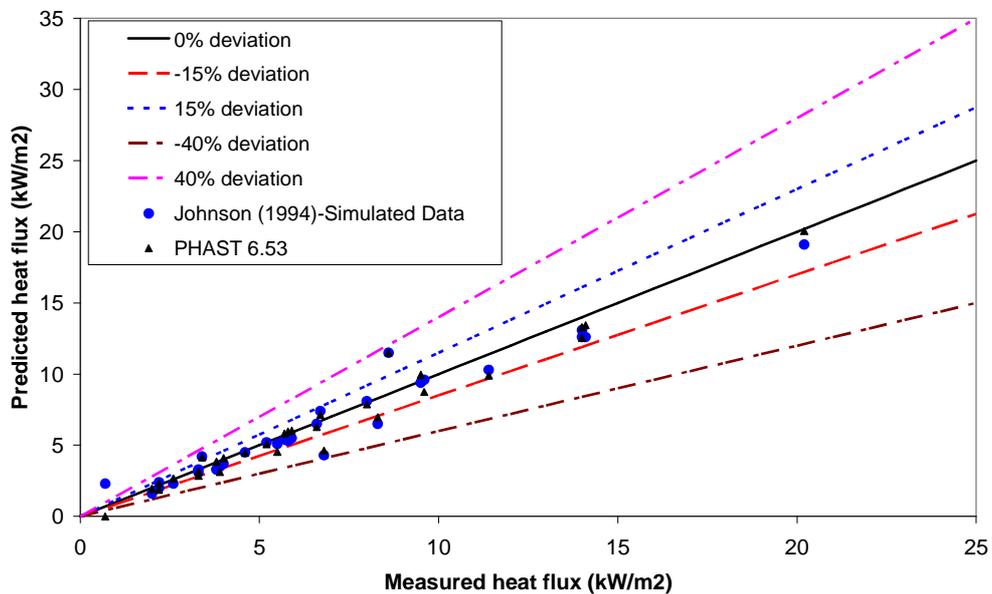


Figure 7. Predicted against measured incident radiation at different observer positions and orientations using the Phast 6.53 and Johnson jet fire models

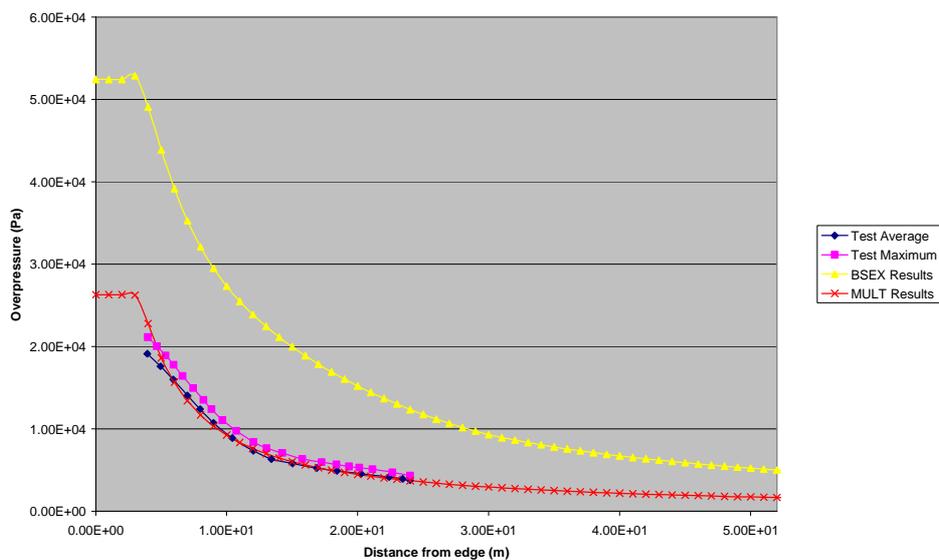


Figure 8. Validation of Phast models MULT and BSEX against EMERGE 6

5. RISK MODELLING

The above consequence calculations can be used to determine the probability of death for a given toxic or flammable event. For toxic events this is derived from the concentrations using toxic probit functions. For fires this is derived from the radiation using a flammable probit function, while for explosions it is set using the results for the overpressure calculations. See the Dutch Green Book (old English version³² and updated Dutch version³³) for details on verification and validation on this.

A failure event tree can now be generated including failure probabilities for all the above toxic and flammable events. Using this event tree, accident frequencies, weather and ignition source probabilities, the individual risk (annual probability of death for person at specific location) can now be calculated. Furthermore using population data the societal risk (risk to overall population) can be calculated.

The major risk tool for carrying out these calculations is DNV's tool Phast Risk with a Dutch-specific application called SAFETI-NL³⁴. The risk calculations in Phast Risk and SAFETI-NL have been extensively verified against analytical solutions and by other means in order to ensure that the theory has been implemented correctly for all possible types of combinations of flammable and toxic outcomes in conjunction with a wide range of ignition and population data.

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