VERIFICATION AND VALIDATION

# CONSEQUENCE MODELS FOR ACCIDENTAL RELEASES OF TOXIC OR FLAMMABLE CHEMICALS TO THE ATMOSPHERE

DATE: December 2023

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# ABSTRACT

Consequence modelling software for accidental releases of flammable or toxic chemicals to the atmosphere includes discharge modelling, atmospheric dispersion modelling and evaluation of flammable and toxic effects:

- First discharge calculations are carried out to set release characteristics for the hazardous chemical (including depressurisation to ambient). Scenarios which may be modelled includes releases from vessels (leaks or catastrophic ruptures), short pipes or long pipes. Releases considered include releases of sub-cooled liquid, superheated liquid or vapour; un-pressurised or pressurised releases; and continuous, time-varying or instantaneous releases.

- Secondly dispersion calculations are carried out to determine the concentrations of the hazardous chemical when the cloud travels in the downwind direction. This includes modelling jet, heavy-gas and passive dispersion regimes, and transitions between them. In the case of a two-phase release, liquid droplet modelling is required to calculate liquid rainout, subsequent pool formation/spreading and re-evaporation from the pool back to the cloud. For heavy-gas releases, effects of crosswind and downwind gravity spreading are present, while for short duration and time-varying releases effects of along-wind diffusion are relevant.. For pressurised instantaneous releases an initial phase of energetic expansion of the cloud occurs. Also, effects of indoor mixing (for indoor releases) and building wakes can be accounted for.

- Finally, toxic or flammable calculations are carried out. For flammables, ignition may lead to rising fireballs (instantaneous releases), jet fires possibly impinging on the ground (pressurised flammable releases), pool fires (after rainout) and vapour cloud fires or explosions. Radiation calculations are carried out for fires, while overpressure calculations are carried out for explosions. For each event, the probability of death is determined using toxic or flammable probit functions.

Testing of the software should ideally include for each consequence model “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 these consequence models.

Reference is made to the literature for the availability of experimental data. Thus, an extensive experimental database has been developed including experimental data for validation for the above models and scenarios, where many different chemicals are considered (including water, LNG, propane, butane, ethylene, ammonia, $CO_2$, hydrogen, chlorine, HF etc.). The above verification and validation is illustrated by means of application to the latest consequence models in the hazard assessment package Phast and the risk analysis package Safeti.

**Keywords:** consequence modelling, model validation, hazard identification and risk analysis

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# 1 INTRODUCTION

Consequence and risk assessments for the releases of hazardous materials are often produced using integrated software packages which seek to model a sequence of events and outcomes from the original loss of containment through to downwind flammable and toxic effects on human populations. Establishing overall confidence in these assessments requires that each stage in the calculations is accurately modelled. This paper presents such an overview, based on relevant published material.

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.

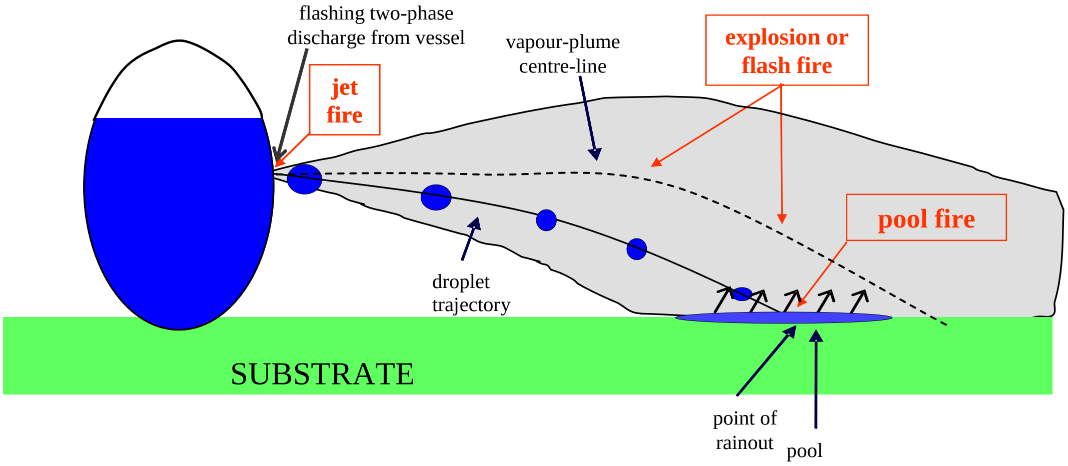


**Figure 1.** **Continuous two-phase release of flammable material with rainout**

To ensure the quality of consequence-modelling software thorough testing is paramount. This is ideally carried out by means of the following consecutive 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. Good agreement provides a justification for the simplified assumptions made to derive the mathematical model.

3. Sensitivity analysis. This involves carrying out many 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.

This paper includes a brief overview of the "verification" and "validation" of consequence models for accidental releases of toxic or flammable chemicals to the atmosphere. 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 SAFETI. The Phast results presented in this paper largely correspond to results from the latest Phast version 8.0, which is scheduled to be released in the final quarter of 2017.

A 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.

Sections 2, 3 and 4 describe the verification and validation for discharge modelling, dispersion and pool modelling, and flammable effects modelling, respectively. The experimental results quoted in the current paper are independent of the empirical basis of the model for the discharge, dispersion and pool models. The flammable models in Phast are largely semi-empirical models available in the public domain, and some degree of fitting may have been conducted against experimental data.

# 2 DISCHARGE

For releases of hazardous materials, a wide range of scenarios can occur including instantaneous releases (catastrophic vessel rupture), 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.

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 subsequent dispersion calculations.

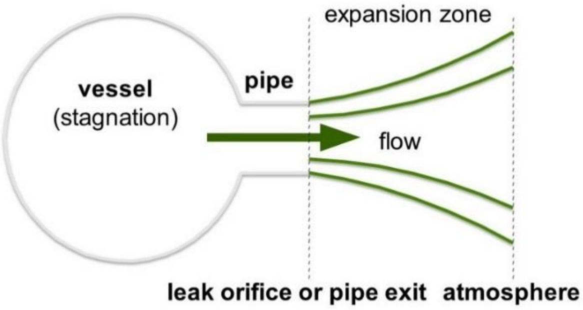


**Figure 2. Expansion from stagnation to orifice and from orifice to ambient conditions**

In literature, numerous discharge models can be found. Key literature including description of discharge models and experimental data include Perry’s handbook (Green and Perry, 2007), the DIERS project manual (Fisher et al., 1992), CCPS QRA guidelines (CCPS, 2000), Sections 15.1-15.9 in Mannan (2012), Chapter 2 in the TNO Yellow Book (TNO, 2005), and Britter et al. (2011). The authors 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.

<u>Verification and validation of mass flow rate</u>

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. HYSYS or PROII). The Phast time-varying discharge model TVDI (Stene et al., 2014) has been verified using Bernoulli for a time-varying release of water from a cylindrical vessel against an analytical solution (Figure 3), and it has been verified against an analytical solution for a time-varying release of an ideal gas from a vessel.

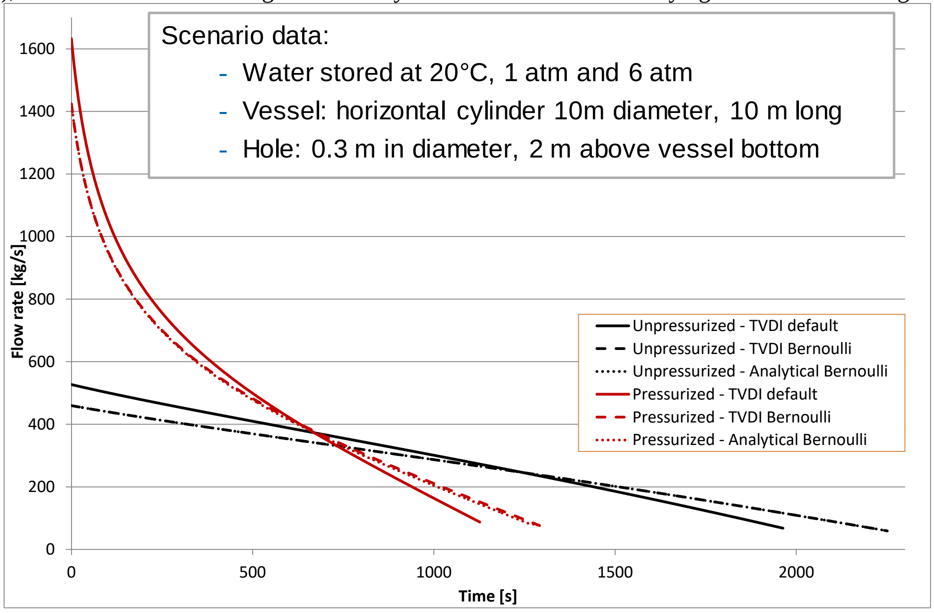


**Figure 3. Verification of time-varying discharge model TVDI for release of water from a vessel**

Key validation tests include sub-cooled and saturated pipe and orifice releases of water (Sozzi and Sutherland, 1975; Uchida and Nariai, 1966), and data for hydrocarbon releases. Figure 4 illustrates the comparison for the Phast steady-state (initial rate) discharge model against sub-cooled water jet experiments. The Phast time-varying discharge model has been validated against $CO_2$ releases (Witlox et al., 2014). The Phast time-varying long pipeline model has been validated for propane two-phase releases [Isle of Grain experiments (Cowley and Tam, 1988; Webber et al., 1999)].

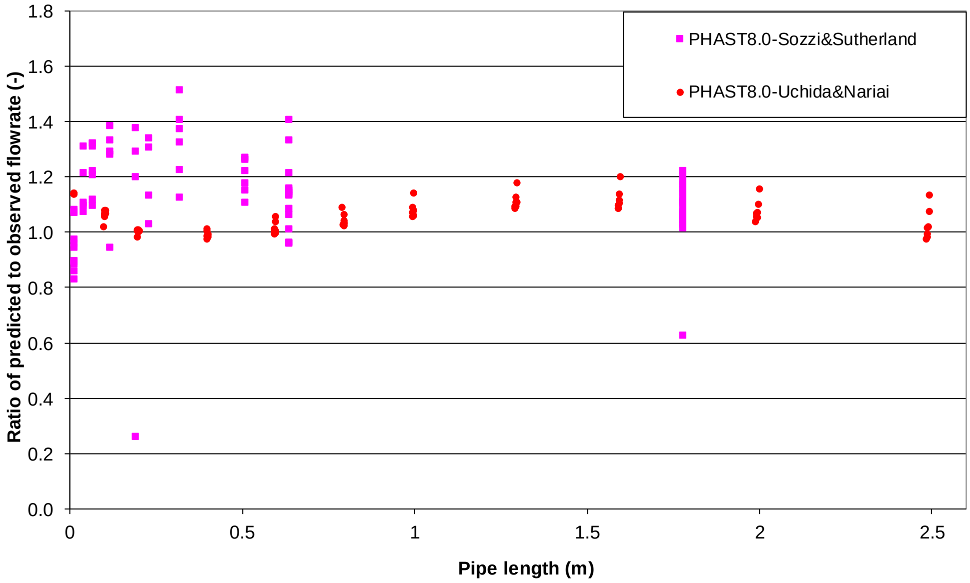


**Figure 4.** **Validation of Phast steady-state discharge model for sub-cooled water release**

Verification and validation of post-expansion data and rainout

Witlox et al. (2017) summarise the results of a literature review on atmospheric expansion modelling (Figure 2) and provide recommendations on selection of model equations to ensure a most accurate prediction for the near-field jet dispersion against available experimental data. The correctness of the numerical solution to the Phast atmospheric expansion model ATEX was verified analytically and the importance of non-ideal gas effects was investigated. For a wide range of experiments including both high-pressure gas releases [hydrogen; natural gas and ethylene (Birch et al., 1984; Birch et al, 1987)] and high-pressure two-phase releases (propane, ammonia, $CO_2$, HF) it was confirmed that the ATEX conservation-of-momentum option without a post-expansion velocity cap provides overall more accurate concentration predictions than the isentropic assumption.

Detailed validation of droplet and rainout modelling for two-phase releases was carried out by Witlox and Harper (2013) using a range of droplet-size correlations accounting for both mechanical and flashing break-up of droplets. This includes validation of initial droplet size for small-scale experiments by Cardiff University (water, cyclohexane, butane, propane and gasoline), the EU STEP experiments (flashing propane jets), experiments by the Belgium Von Karman Institute (flashing R134-A jets), and experiments carried out in France by Ecole des Mines and INERIS (water and butane). It also includes validation of the rainout against the CCPS experiments (flashing jets of water, CFC-11, chlorine, cyclohexane, monomethyl amine) Finally it included validation of flow rate, initial droplet size, rainout and temperature against HSL experiments (subcooled jets of water and xylene). Table 1 includes measured and predicted rainout for the HSL experiments using a range of methods for predicting rainout. It is seen that the default Phast 8.0 method (CCPS modified droplet size criterion) results in most accurate rainout predictions. This was also confirmed for the CCPS rainout flashing experiments.

| **Experiment – input data (release height = 1m)** | | | | **% rainout measured** | **% rainout predicted (UDM rainout methods)** | | | **% rainout predicted (simple correlations)** | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **chemical** | **nozzle (mm)** | **stagnation pressure (barg)** | **temperature (°C)** | | **CCPS original /modified** | **JIPIII + parcels** | **Melhem** | **Kletz** | **Lautkaski** | **Devaull** |
| Water | 2.5 | 5.0 | 7 | 98.4 | 98.5 / 99.5 | 99.9 | - | 100 | 60 | 81.7 |
| | | 9.5 | 7 | 96.3 | 98.1 / 98.7 | 99.8 | - | 100 | 60 | 81.7 |
| | 5 | 4.8 | 7 | 99.0 | 98.7 / 99.5 | 99.9 | - | 100 | 60 | 81.7 |
| Xylene | 2.5 | 4.2 | 11 | 96.8 | 96.7 | 99.5 | 99.3 | 100 | 60 | 29.2 |
| | | 8.0 | 11 | 91.4 | 90.8 | 98.9 | 98.0 | 100 | 60 | 29.2 |
| | | 10.3 | 11 | 90.4 | 86.7 | 98.6 | 97.1 | 100 | 60 | 29.2 |
| | | 15.8 | 11 | 82.1 | 75.1 | 97.7 | 94.0 | 100 | 60 | 29.2 |
| | 5 | 4.0 | 11 | 94.3* | 97.2 | 99.7 | 99.3 | 100 | 60 | 29.2 |
| | | 7.7 | 11 | 89.9 | 93.1 | 99.5 | 98.3 | 100 | 60 | 29.2 |
| | | 8.5 | 2 | 95.3 | 95.2 | 99.7 | 98.8 | 100 | 60 | 25.6 |
| | | 13.1 | 5 | 85.2* | 88.8 | 99.4 | 97.2 | 100 | 60 | 26.7 |

**Table 1.** **Measured and predicted rainout for HSL experiments**
[*experiment for which a significant amount of rainout was not captured]

# 3 DISPERSION AND POOL SPREADING/EVAPORATION

For dispersion modelling a very wide range of scenarios can be considered. These can be characterised on the basis of 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 book (TNO, 2005), Sections 15.11-15.54 in Mannan (2012), and the CCPS dispersion guidelines (CCPS, 1996). Key experiments (benchmark tests for dispersion; input data and experimental results) have been stored in the MDA database by Hanna et al. (1993) 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 SMEDIS (Daish et al., 1999). The SMEDIS project has also produced a protocol for evaluating heavy gas dispersion models, which has also more recently been adapted for application to LNG (PHMSA database; Ivings et al., 2007).

Model verification and validation for dispersion models is illustrated below for the Phast dispersion model UDM (Witlox and Holt, 1999; Witlox, Harper and Fernandez, 2017). This is an integral model, which can account for all the above type of releases except for effects of obstacles, variable surface roughness and non-flat terrain. The verification and validation for the UDM can be summarised as follows [see Witlox, Harper and Fernandez (2017) for full details and a detailed list of references]:

## 3.1 Near-field dispersion

- Continuous releases (jet and near-field passive dispersion). For an elevated horizontal continuous jet (of air), the UDM numerical results have been verified against an analytical solution based on the near-field jet entrainment correlation. For vertical jets very good agreement has been obtained against both the “Pratte and Baines” and “Briggs” plume rise correlations.

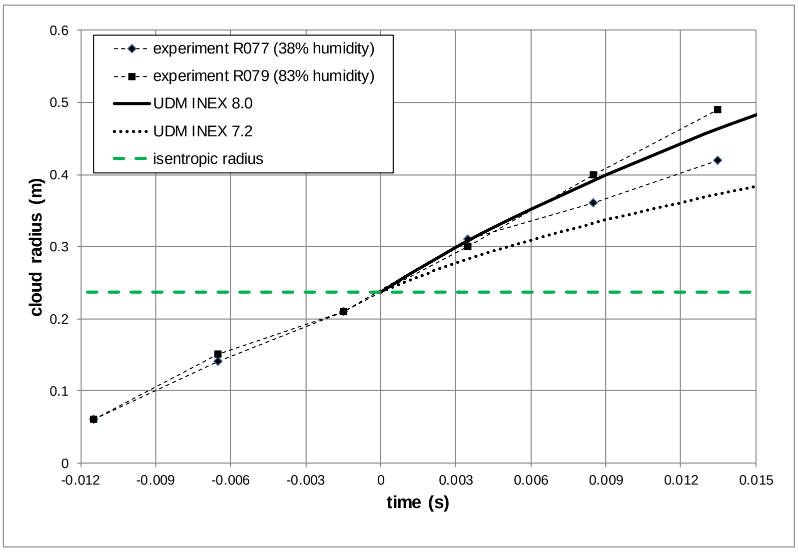


**Figure 5.** **Validation of dispersion submodel INEX against Schmidli experiment**
[1 litre vessel with 100% Freon-12 fill, temperature 22C, elevation 0.62m]

- Pressurised instantaneous releases. The UDM model contains a separate sub-model INEX to model the initial dispersion phase of energetic instantaneous expansion following a catastrophic vessel rupture; see Witlox, Harper and Webber (2017) for full details. For ground-level vapor or two-phase releases the correctness of the numerical predictions is confirmed against an analytical solution. The model has been validated against previously published experimental data (Maurer et al., 1977; Pettitt, 1990; Schmidli, 1993) for pressurized releases with and without rainout (nitrogen, Freon 11, Freon 12, propane and butane). For two-phase releases the new model predicts an increased amount of rainout, which is more in line with the experimental data. Figure 5 includes an example of validation against a Freon 12 experiment by Schmidli. The visible aerosol cloud radius slightly increases with humidity, while the effect of humidity on concentrations (and therefore INEX predictions) is insignificant. Thus in this context there is a need for experimental data including concentration measurements rather than measuring a somewhat arbitrary visible cloud radius.

## 3.2 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 McQuaid (1976), and it was also validated against the HTAG wind tunnel experiments (Petersen and Ratcliff, 1988). The Phast UDM model assumes large-scale 3D atmospheric dispersion, and therefore a modified version of the UDM was used to enable this numerical verification and validation for 2D dispersion or wind-tunnel conditions. Finally, the UDM model was verified against the HGSYSTEM model HEGADAS.

## 3.3 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.

## 3.4 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 thermodynamics module also allows for more rigorous multi-component modelling (Witlox et al., 2006). 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 experiments by Schotte (1987). In the case of pressurised CO2 storage, solid CO2 may form upon depressurisation to ambient pressure and this is accounted for in the thermodynamics model for mixing the CO2 with the ambient air (Witlox, Harper and Oke, 2009).

## 3.5 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 form 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 Webber (2010) 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, ethane, ethylene, propane, butane, pentane, hexane, cyclo-hexane, toluene, ammonia, nitrogen, water, Freon-11)].

For multi-component mixtures, the PVAP model was verified against the HGSYSTEM pool model LPOOL and validated against hydrocarbon mixtures (Fernandez et al., 2012); see Figure 6 for validation against an LNG mixture experiment by Burgess et al. (1972).

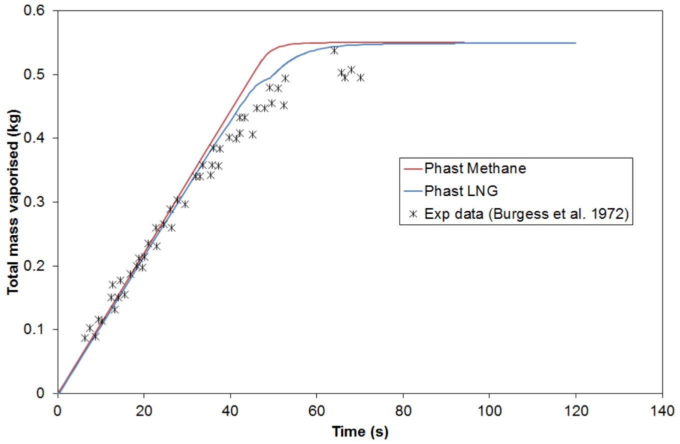
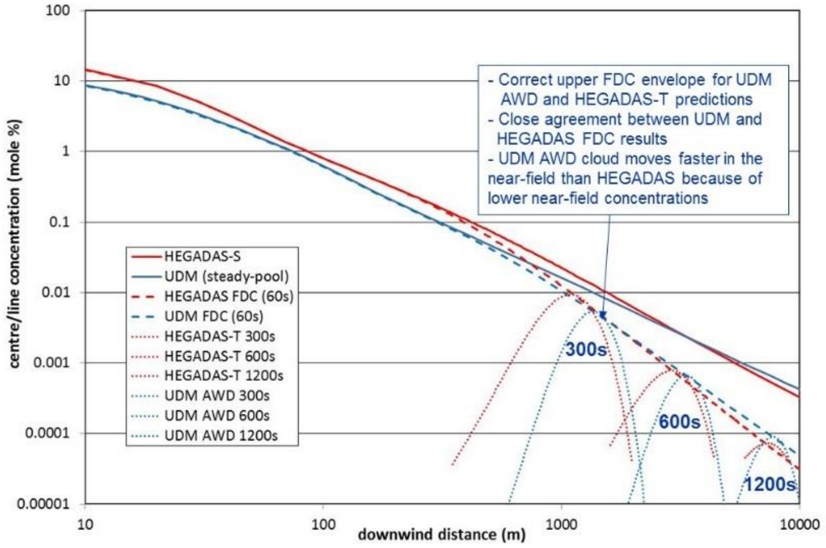


**Figure 6.** PVAP validation against LNG mixture experiment

## 3.6 Finite-duration and time-varying releases

For finite duration releases, the UDM "Finite-duration-correction" (FDC) 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.

A new version of the Phast dispersion model UDM was developed to more accurately simulate time-varying effects resulting from a pressure drop in a vessel or pipe and/or from a time-varying pool (following rainout or from direct spill). This model accounts for effects of along-wind-diffusion (due to ambient turbulence) resulting in reduced far-field concentrations. In addition, it accounts for effects of gravity spreading (both in crosswind and downwind directions) resulting in modified near-field concentrations in case of heavy-gas low-momentum releases at low wind speed. This new model has been tested for an elevated release from a long pipeline without rainout (including HGSYSTEM verification; Witlox et al., 2015), and it has also been tested for cases with rainout. Additionally, it was verified against the time-varying HGSYSTEM model HEGADAS-T for the case of dispersion from a pool (Figure 7), and it has been validated against the Kit Fox experiments (20-second releases of $CO_2$ from a ground-level area source during both neutral and stable conditions; see Figure 8); see Witlox and Harper (2014) for details.



- Correct upper FDC envelope for UDM AWD and HEGADAS-T predictions
- Close agreement between UDM and HEGADAS FDC results
- UDM AWD cloud moves faster in the near-field than HEGADAS because of lower near-field concentrations

**Figure 7.** UDM verification against HEGADAS for 60s spill of butane (pool on water with bund radius 10m; dispersion over land)

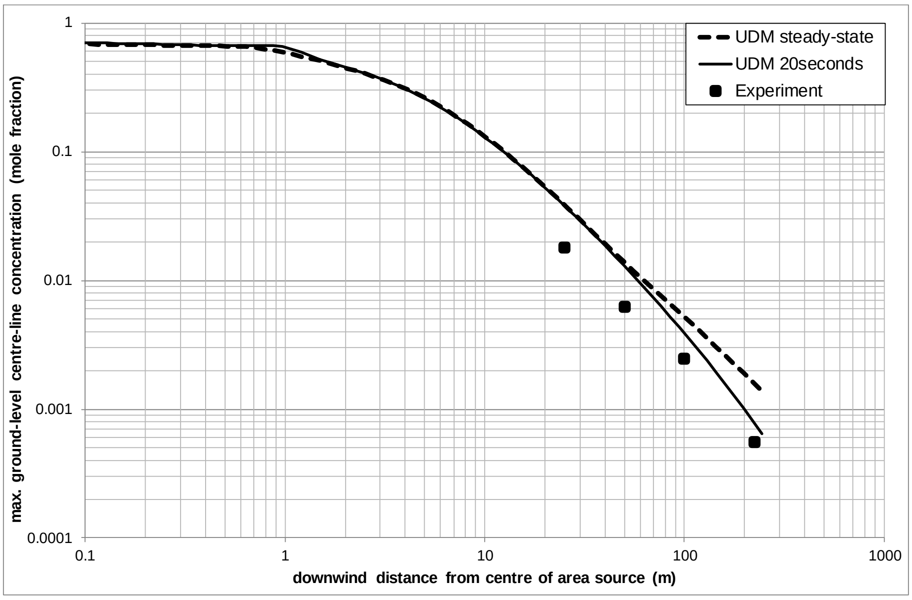


**Figure 8. UDM validation for Kit Fox experiment KF0706 (20 second release)**

The above summarises 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, REDIPHEM and PHMSA 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)
- CO2PIPETRANS - BP and Shell [$CO_2$ jets; cold steady-state and time-varying (liquid storage) or hot supercritical time-varying (dense vapour storage)]
- Goldfish (continuous elevated two-phase HF jet)
- Thorney Island (instantaneous un-pressurised ground-level release of Freon-12)
- Maplin Sands, Burro and Coyote (continuous evaporation of LNG from pool)
- Kit Fox (continuous and finite-duration heavy-gas dispersion of $CO_2$ from area source)

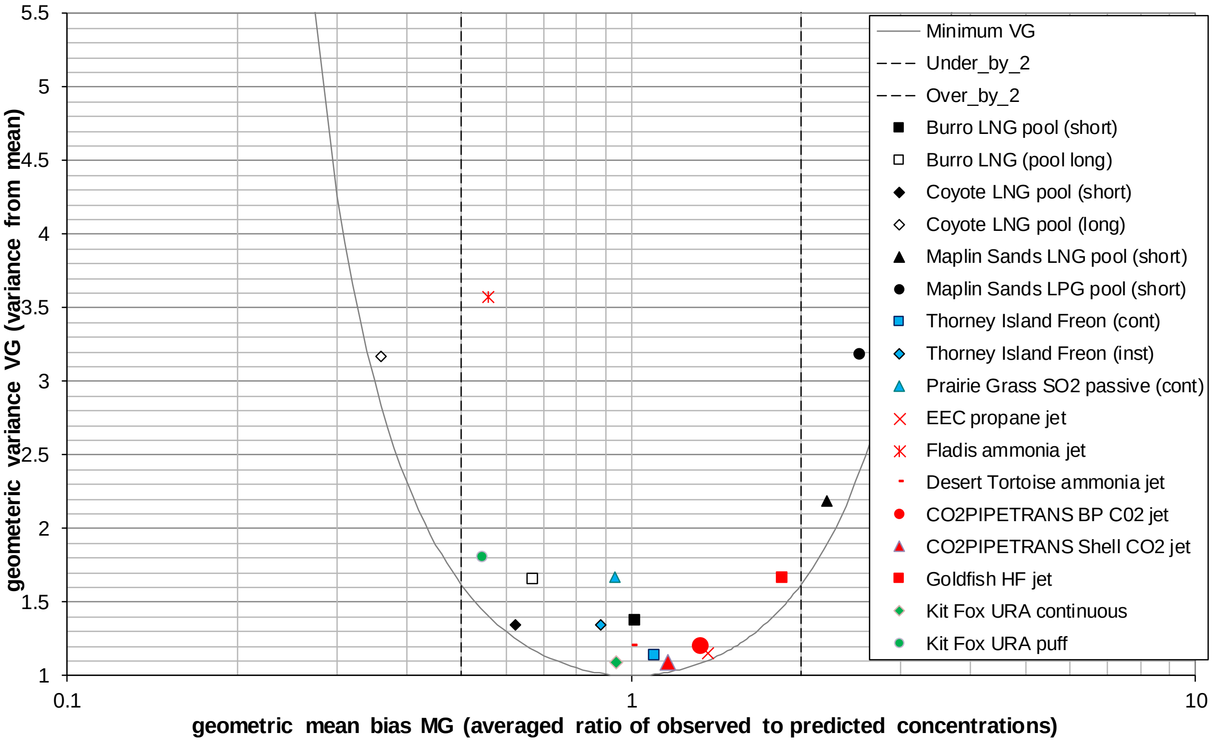


**Figure 9. Summary MG and VG values for centreline concentration (UDM 8.0)**

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. (1993) were used to calculate the geometric mean bias MGF (under or over-prediction of mean) and mean variance VG (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. For each experimental data set, Figure 9 shows summary MG and VG values for the peak centre-line concentrations using the new UDM 8.0 model (including along-wind diffusion and along-wind gravity effects) as well as for the Kit Fox the FDC model. Pool experiments are indicated by black makers applying either 'short' averaging times (applying maximum concentration) or 'long' averaging times (applying averaged concentration over given time-averaging window). Pressurised two-phase releases are indicated by red markers. Thus the overall performance of the UDM in predicting both peak centreline concentration and cloud widths was found to be good for the above experiments, except perhaps for the under-prediction for the Maplin Sands experiments. The results were found to be overall better or close to results from an earlier UDM 6.7 version, which was approved in case of LNG releases for USA LNG regulatory purposes (Witlox et al., 2012).

The overall UDM model was also verified by means of comparison against other models for three US chlorine accidents involving elevated two-phase chlorine jet releases. This is illustrated by Figure 10 for the case of the Graniteville accident; see Hanna et al. (2007) for full details.

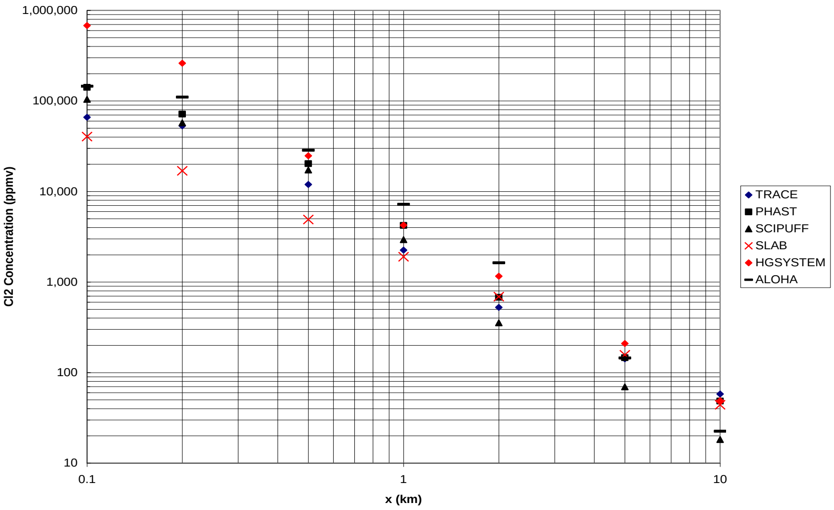


**Figure 10.** **UDM (Phast) verification against other models for Graniteville Chlorine accident**

# 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). 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 book (TNO, 2005), Sections 16-17 in Mannan (2012) and the CCPS guidelines (CCPS, 1994).

## 4.1 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 12.

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.

Fireball models can be distinguished between static models (fixed fireball location during fireball duration) and more advanced dynamic models (rising fireball accounting for lift-off). These models can easily be verified by simple hand calculations or Excel spreadsheets. The dynamic fireball model from Martinsen and Marx (1999) has been implemented in Phast 8.0, and has been shown to lead to improved predictions for experiments by HSE (propane) and GL (butane); see e.g. Figure 11. See Oke and Witlox (2017) for further details of Phast fireball model validation and a detailed literature review on fireball models.

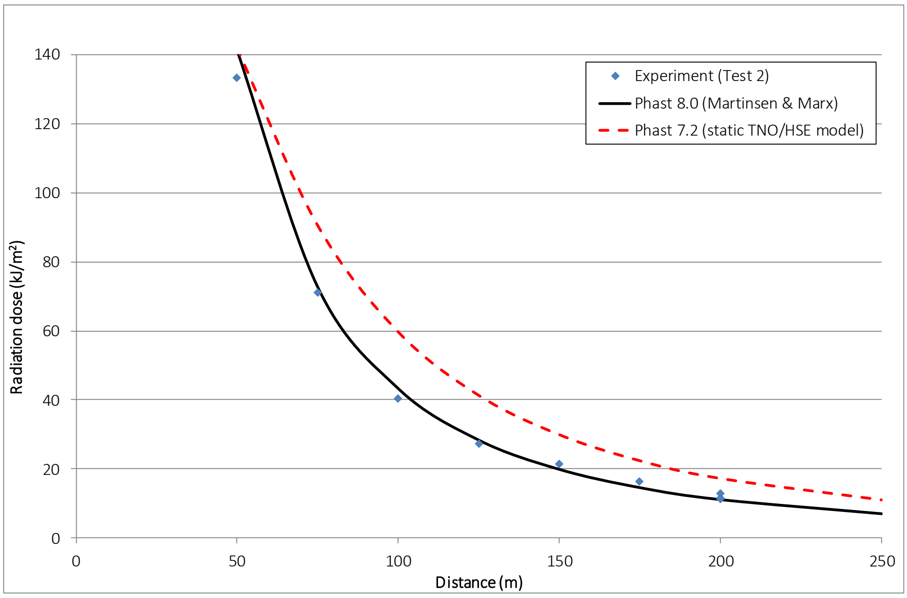


**Figure 11.** **Radiation dose predictions for butane fireball experiment by Johnson (GL)**

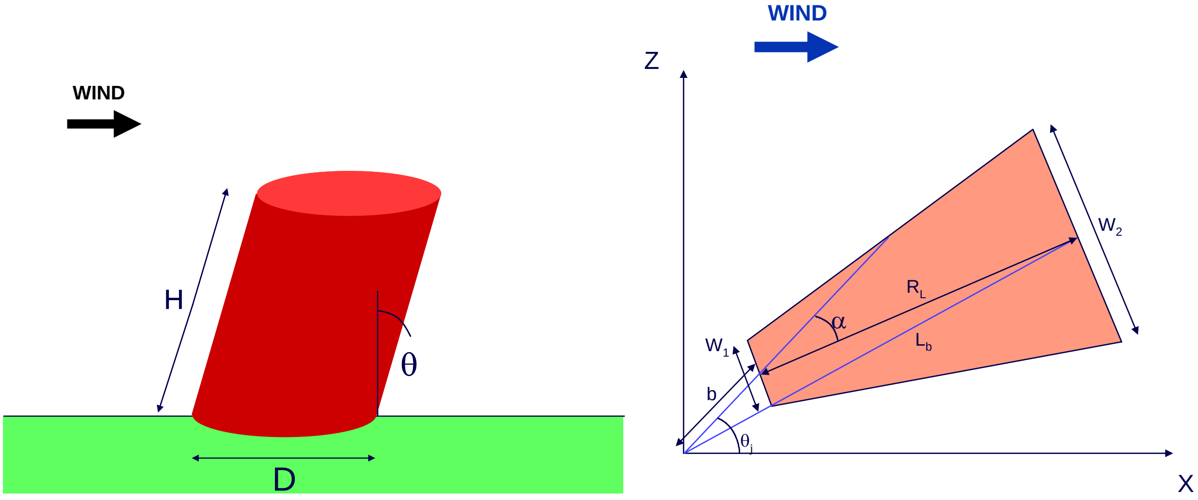


Figure 12. Geometry for pool fire (tilted cylinder) and jet fire (cone)

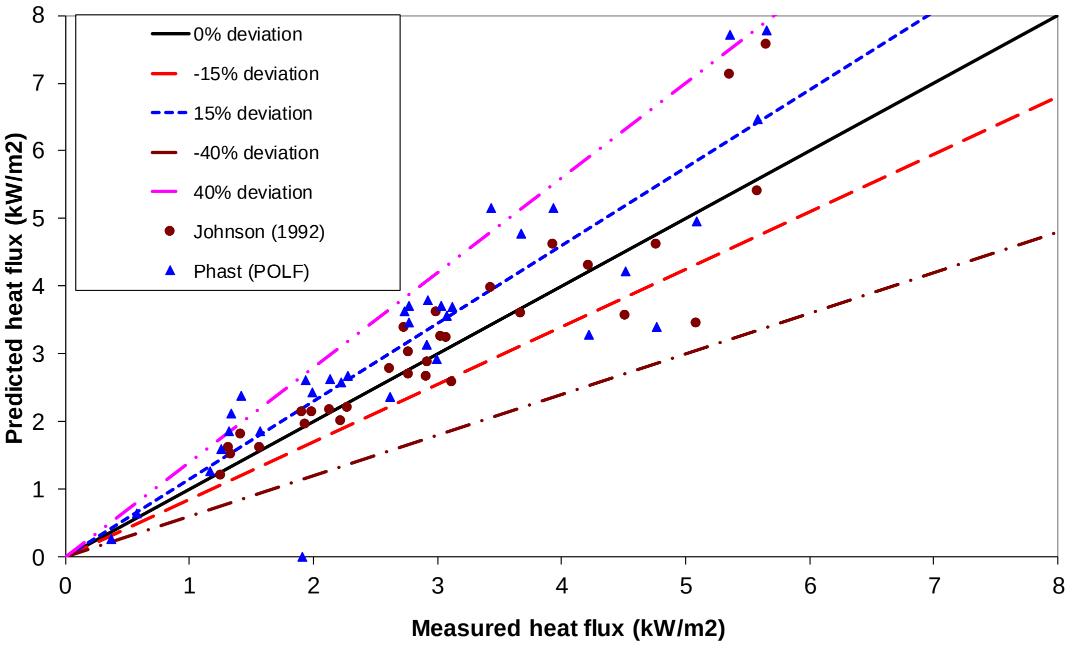
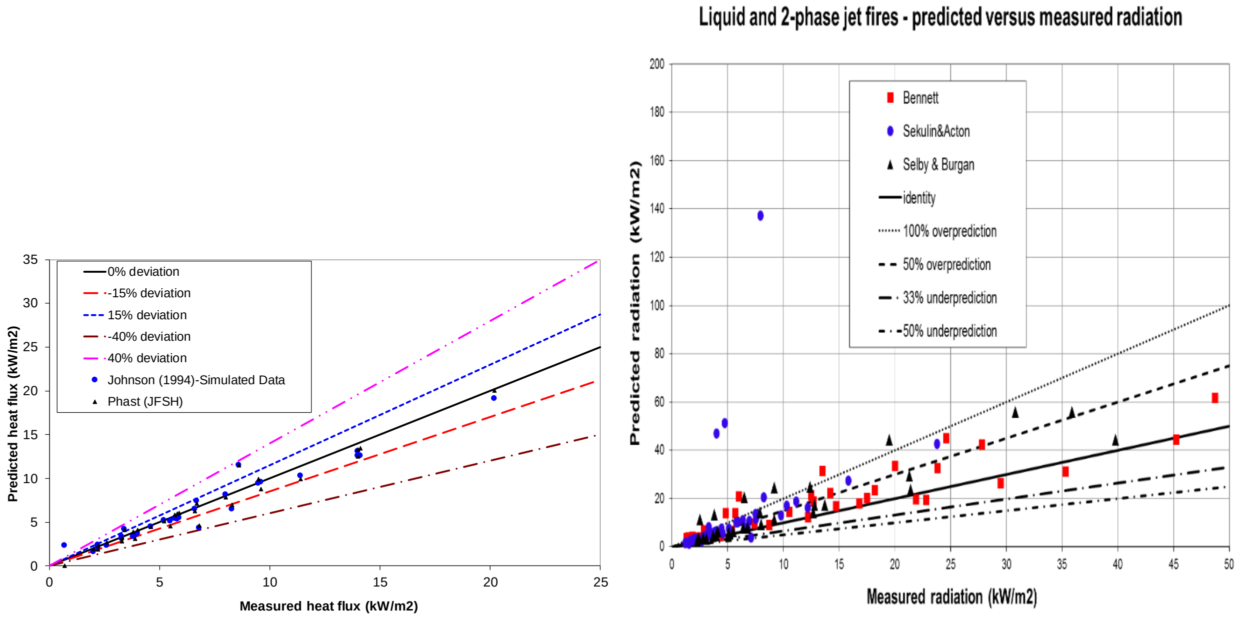


Figure 13. Predicted against measured incident radiation at different observer positions and orientations using Phast and Johnson pool fire models



(a) Johnson natural gas experiments (b) liquid and two-phase releases

**Figure 14.** **Predicted against measured incident radiation at different observer positions and orientations**

The Phast pool fire model has been validated against data for LNG pool fires (Johnson, 1992); see Figure 13 which also includes verification against model predictions by Johnson (1992). Furthermore, it has been validated against the Montoir LNG tests (Nedelka et al., 1990) and hexane tests (Lois and Swithenbank, 1979).

The Phast jet fire model (Oke et al., 2017) has recently been modified to account for ground impingement. It has been validated against vertical natural-gas releases (Chamberlain, 1987), horizontal natural-gas and two-phase LPG releases (Bennett et al., 1991), horizontal two-phase butane releases (Sekulin and Acton, 1995) and horizontal liquid-phase crude oil releases (Selby and Burgan, 1998). It has also been verified against model predictions by Johnson et al. (1994) in the case of the horizontal natural-gas releases. See Figure 14 for validation predictions.

## 4.2 Explosion

Fitzgerald (2001) 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 TNO (EMERGE, 1998) and BFETS experiments by SCI (Selby and Burgan, 1998)). Clear conclusions are provided indicating under which conditions which model is best on overpressure prediction. Fitzgerald (2001) states that the overpressure predictions of the CAM and multi-energy models were found to be more accurate than the Baker-Strehlow model. CAM was found to be the most complex method to use. The Baker-Strehlow model predictions was quoted to have a high degree of confidence due to the lack of assumptions made in the comparisons and it is quoted to be the easiest of the three methods to apply. The Baker-Strehlow model has evolved through ongoing research and applications in hazard analysis, including an update to the blast curves in 1999 and new flame speed table in 2005, and the model is now usually referred as Baker-Strehlow-Tang model.

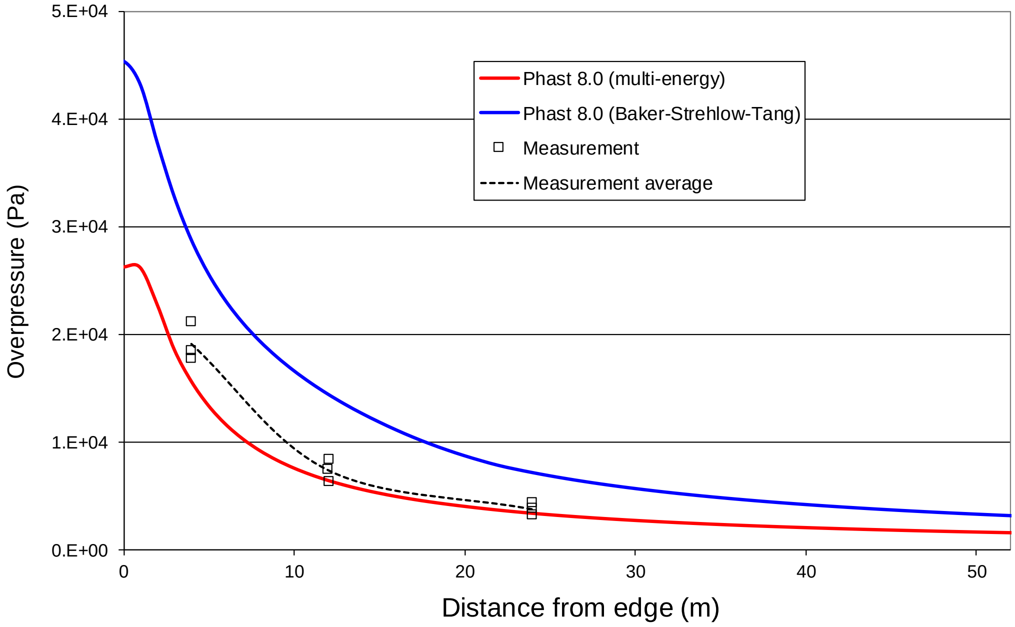


**Figure 15. Validation of Phast models MULT and BSEX against EMERGE 6**

The latest available versions of the multi-energy and Baker-Strehlow-Tang models have been implemented into Phast. They have been validated against the above EMERGE and BFETS experiments; see Figure 15 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).

# 5 EXPERIMENTAL DATABASE

In the previous sections, reference has been made to the literature for the availability of experimental data. Thus, an extensive experimental database has been developed including experimental data for validation for the above models and scenarios. This includes many different chemicals including water, LNG, propane, butane, ethylene, ammonia, CO2, hydrogen, chlorine, HF etc.

The overall validation of Phast 8.0 against experimental data is summarised by Table 2, Table 3 and Table 4, for successively discharge models, dispersion models (including rainout and pools) and flammable effects (fireballs, pool fires, jet fires and explosion):

- The first column of these tables includes the type of consequence model (including the name of the associated Phast model) and the second column the name of the chemical.
- The subsequent columns include references of experimental data for this chemical and consequence model. Here distinction is made between unpressurised or pressurised releases, continuous/time-varying or instantaneous releases, and vapour or liquid stagnation conditions.

Grey-coloured cells indicate cells for which model validation is not relevant or applicable, for example in Table 3, no pool modelling is required for vapour releases, since liquid pools may only form for liquid releases, and the discharge – leak scenario is not applicable for instantaneous releases. Experiments relevant for natural gas and LNG are marked as yellow coloured cells. Red-coloured text in the cells refer to experimental data for which Phast model validation has not yet been carried out.

References included in these tables partly refer to work carried out by the DNV droplet JIP and the DNV CO2PIPETRANS JIP; see Witlox and Harper (2013) and Witlox et al. (2014) for details on references.

For the explosion model, the release scenario involved a congested area where the area was filled with a uniform concentration of vapour, and therefore in Table 4 the reference for the explosion experiments are included at the bottom of the table (since the columns are not applicable).

| **MODEL** | **CHEMICAL** | **PRESSURISED RELEASE** | |
|---|---|---|---|
| | | **Continuous/time-varying** | |
| | | **Vapour** | **Liquid** |
| **Discharge -vessel orifice leak (DISC/TVDI)** | | | subcooled and superheated (Sozzi and Sutherland, 1975; Uchida and Nariai, 1966; DNV droplet JIP III - Cardiff), subcoolled (DNV Ndroplet JIP IV - HSL) |
| | **CO2** | supercritical (CO2PIPETRANS; BP/Shell; time-varying) | continous and time-varying (DNV JIP CO2PIPETRANS; BP/Shell/large-scale) |
| | **hydrogen** | Shell HSL | |
| | **NG/LNG** | | Shell (confidential - SpadeAdam), possibly future DNV GL JIP) |
| | **LPG/propane** | | subcooled (Bennett, 1991), DNV droplet JIP III - Cardiff |
| | **butane** | | Shell (Duree, 1995 - subcooled), INERIS (Touil, 2004), DNV Droplet JIP (Cardiff) |
| | **cyclohexane** | | DNV droplet JIP III - Cardiff |
| | **xylene** | | subcooled (Droplet JIP IV - HSL) |
| | **hycrocarbon mixture** | | **gasoline** (DNV droplet JIP III - Cardiff), **C1 to C4 mixtures** - time-varying (Szepanski, 1994; Haque et al., 1992) |
| **Discharge - short pipe FBR (DISC/TVDI)** | **water** | | subcooled and saturated (Sozzi and Sutherland, 1975; Uchida and Nariai, 1966) |
| | **LNG** | | |
| | **LPG** | | Bennett (1991), time-varying (Melhem&Fisher,1997) |
| **Discharge - long pipe (GSPP/PBRK)** | **C02** | | DNV JIP CO2PIPETRANS |
| | **Hydrogen** | Air Products (also crater effects; confidential) | |
| | **NG/LNG** | PIPESAFE Canada (Acton et al., 2000) | |
| | **LPG** | | Isle of Grain (BP/Shell; Cowley and Tam, 1988) |

Table 2. List of experiments for discharge model validation

| MODEL | CHEMICAL | UNPRESSURISED RELEASE | | | | PRESSURISED RELEASE | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Continuous /time-varying | | Instantaneous | | Continuous /time-varying | | Instantaneous | |
| | | Vapour | Liquid | Vapour | Liquid | Vapour | Liquid | Vapour | Liquid |
| Dispersion (UDM) | CO2 | McQuaid windtunnel line source, Kit Fox cont./20s area source | | | | supercritical (CO2PIPETRANS; BP/Shell; time-varying) | continous and time-varying (CO2PIPETRANS; BP/Shell; large-scale/long-pipe) | | |
| | Ammonia | | | | | | Desert Tortoise, FLADIS | | |
| | Chlorine | | | | | | UTAH Jack Rabbitt (2015,2016) - data will be made available but issues of ground impingement/obstacles; validation by HSE using Phast 7.11; preliminary validation DNV GL using pre 8.0 version | | |
| | Propane/LPG | | Maplin Sands (on water) | | | | EEC | | Schmidli (1993) |
| | HF | | | | | | Goldfish | | |
| | NG/LNG (methane) | | Maplin Sands, Burro, Coyote (on water) | | | BG Birch et al. (1984) | Shell (confidential - SpadeAdam), possibly future DNV GL JIP) | | |
| | Hydrogen | | | | | Shell HSL | | | |
| | Others | Prairie Grass **SO2** (passive), Thorney/Island **Freon/Nitrogen mixture** | | **Freon/Nitrogen mixture** (Thorney Island) | | **Ethylene** (BG: Birch et al., 1984) | | **nitrogen** (Landis, 1994) | **propylene** (Maurer, 1977), **R-11** (Pettitt, 1990), R-12, butane (Schmidli, 1993) |
| | | | | | | | | | |
| Initial droplet size ATEX) | LNG | | | | | | | | |
| | several | | | | | | JIP (Cardiff **cyclohexane/water/gasoline/butane/propane**; HSL **xylene/water**), INERIS **butane, VKI R134-A**, STEP **propane**, HSL **propane**, Ecole de Mines **water**) | | Pettitt (**Freon**), Schmidli (**propane**) |
| Rainout (UDM) | LNG (methane) | | | | | | Shell (confidential - SpadeAdam), possibly future DNV GL JIP) | | |
| | several | | | | | | JIP-IV subcooled releases (**water, xylene**), CCPS superheated releases (**CFC-11, chlorine, cyclohexane, MMA,water**), 2-phase large-scale superheated releases with little/no rainout (**ammonia, propane, HF**) | | Schmidli (**Freon 12, propane**) |
| Pool spreading/evaporation (PVAP) | water | | Belore&McBean (spread - plywood) | | | | | | |
| | LNG (methane) | | Moorhouse&Carpenter (soil/concrete), Burro (water), MKOPSC | | Reid&Wang (soil/concrete - bund), Burea of mines (water - bund) | | | | |
| | ammonia | | Raj&Reid (on water - reaction) | | Raj&Reid (on water - reaction), Norman&Dowel (insulated surface -bund) | | | | |
| | Others | | Dodge (**pentane/octane**,spr.water), Reid&Smith (**propane** on water with bund) | | Dodge (**pentane/octane**,spr.water), Burea of Mines (**nitrogen** on water - bund), Reijnhart&Rose (**toluene, pentane** on insulated surface; bund), Norman and Dowell (**acrylnitrile, ethyleneoxide, butane, propylene, carbondisulfide**; bund - insulated surface), Okamoto (**hydrocarbon mixtures**; bund - insulated surface); Habid (**ethanol/cyclohexane**; bund - insulated surface); Kawamura&McKay (toluene, hexane, pentane, cyclohexane, R-11; sand - bund), Reid&Smith (**ethane, propane, butane, ethylene** on water with bund) | | | | |

**Table 3.** List of experiments for validation of dispersion models (including rainout and pools)

| MODEL | CHEMICAL | UNPRESSURISED RELEASE | | | | PRESSURISED RELEASE | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Continuous /time-varying | | Instantaneous | | Continuous /time-varying | | Instantaneous | |
| | | Vapour | Liquid | Vapour | Liquid | Vapour | Liquid | Vapour | Liquid |
| Fireball (TVFM; Martinsen&Marx) | propane | | | | | | | | Shell (Johnson et al., 1991), HSL/BG (Roberts et al. .2000) |
| | hydrogen | | | | | | | | Air Products (not documented) |
| | butane | | | | | | | | Shell (Johnson et al., 1991) |
| | NG/LNG | | | | | | | | |
| Pool fire (POLF) | LNG | | Shell (bund; Johnson, 1992), GdF Montoir (bund; Nedelka, 1889), Sandia | | | | | | |
| | Hexane | | bund (Lois&Swithenback, 1979) | | | | | | |
| Jet fire (JFSH) | NG/LNG | | | | | Shell (Chamberlain, 1987; vertical), Shell (Johnson, 1994; Bennett et. al., 1991; horizontal) | | | |
| | hydrogen | | | | | Air Products (not yet included in jet fire validation documentation) | | | |
| | LPG | | | | | | CEC project AA Shell/BG (Bennett et al.. 1991) | | |
| | butane | | | | | | CEC project JIVE (Sekulin&Acton, 1995) | | |
| | crude oil | | | | | | SCI (Selby&Burgan, 1996) | | |
| | | | | | | | | | |
| Explosion (MULT, BST) | | **methane, propane** (EMERGE - TNO), **methane** (BFETS - SCI), **ethylene** (Shell Deer Park accident) | | | | | | | |

**Table 4.** List of experiments for validation of flammable effect models

# 6 SUMMARY AND CONCLUSIONS

An overview has been provided of verification and validation of consequence models, including discharge models, dispersion and pool spreading/evaporation models, and flammable effect models. An extensive range of release scenarios is considered. The verification and validation has been illustrated by means of application to the Phast consequence modelling package (version 8.0). An extensive experimental database has been developed including experimental data for validation for the above models and scenarios, where many different chemicals are considered (including water, LNG, propane, butane, ethylene, ammonia, CO2, hydrogen, chlorine, HF etc.).

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