VERIFICATION

POOL VAPORISATION

DATE: December 2023

This document describes the verification of the DNV model for the pool spreading and evaporation of liquid pools onto either land or water. It corresponds to the model as implemented into the DNV software package PHAST 6.0.

The document includes the results of a review of the PVAP model and a comparison of the PVAP model against the SRD/HSE model GASP.

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ABSTRACT

The pool model PVAP may either be run as a standalone model or may be called during the dispersion calculations following rainout. The PVAP theory was reviewed by David Webber. In addition PVAP results were compared against the SRD/HSE model GASP for a range of scenarios with the aim of testing the various sub-modules. The results and recommendations obtained by David Webber are as follows:

Pool spreading

1. The TNO pool-spreading model on land adopted in PVAP may give the right qualitative behaviour in case of an appropriate choice for the minimum pool thickness h_{min}. An improved formula for the minimum thickness may be considered, e.g. in terms of liquid viscosity etc. PVAP does not allow a zero minimum depth, while GASP recommends a zero minimum depth unless puddles are expected to form. As a result an improved formulation may be considered which does not need a minimum thickness.

2. The 'tuned' model of Dodge adopted in PVAP for spreading on water may not scale properly, particularly because an inappropriate force balance is used.

3. In the long term both above models could be replaced by logic in the GASP pool-spreading model, whick involves the solution of two first-order differential equations (spread rate, force balance) instead of one (spread rate).

Pool vaporisation

1. Unlike GASP, PVAP applies a non-unified treatment for evaporation and boiling. This may result in less smooth results.

2. For a boiling pool on land, the PVAP formula by Shaw and Briscoe for heat flow for conduction Q_{cond} is heuristic, and could be considered to be replaced by the improved GASP correlation introduced by Webber and Jones (1987). However the conduction models are very similar.

3. For an evaporating pool on land, the PVAP formula by McKay and Matsugu for heat flow from evaporation Q_{evap} is dimensionally not sound, and could be considered to be replaced by the more sound and well-validated GASP correlation by Brighton. The GASP correlation leads to significantly less evaporation on land.

4. For an evaporating pool on water, the PVAP formula by Dodge seems to be plausible for including the wind-speed dependent aerodynamic roughness length of the surface but it uses the dimensionally unsound correlation on land. It could be further compared with GASP formulation by Brighton. Note however that the PVAP evaporation rate is usually less than the dissolution rate.

5. No problems have been found for the following existing PVAP sub-models:

   - Boiling on water, although ice formation may be discounted and model for ice formation is complicated
   - The formula by Fleischer for heat convection on land or water
   - The formula for radiation
   - Dissolution on water, although it may be more complicated than necessary
   - Reaction of ammonia pool with water

Table of contents

1. REVIEW OF THE MODEL PVAP

1.1 Introduction

This is a peer review of the PVAP theory manual, as included in the current UDM Technical Reference Manual. Its objective is to identify the good points and possible shortcomings of the model described - hereinafter referred to as "the model" - in the PVAP theory manual - hereinafter "the document".

The model has many similarities to the model "GASP" which I constructed for HSE in the 1980's while at AEA Technology (then UKAEA Safety and Reliability Directorate). I don't think that a great deal has happened in this particular field since that model was completed, except for a new model possibly still under construction at CERC, to which I have no access. (Last time I checked in detail was in 1995 before reviewing the subject at a CCPS workshop in New Orleans.) This review will therefore, of its very nature, make strong reference to the work I did earlier. As it is not intended for publication, I'll acknowledge that it forms a personal opinion (supported of course by the arguments and references) and use the first person singular throughout. The references will be to papers cited in the document and to my own earlier work on the subject - of which a bibliography is appended.

1.2 Overall structure

1.2.1 Integral models

The model is an integral model. Integral models with equations of the form

$$\frac{dr}{dt} = \ldots \qquad \frac{dM}{dt} = \ldots \qquad \frac{dT}{dt} = \ldots.$$

representing the evolution of a pool of radius r, mass M, and temperature T are known to work quite well (although it is not obvious *a priori* that a single representative temperature is adequate for an extended pool). The model GASP is of this form and validates quite well against data - e.g. Webber and Jones 1987.

The model under study is of this form except that in some cases the spreading equation is given by prescribing r(t). This causes me some uneasiness on quite general grounds, and this is discussed below within this "overall structure" section, before coming on to specific sub-models. (In some cases the temperature is fairly constant and this simplifies the temperature equation - but this may be physically reasonable in those cases, and so further discussion of this is postponed to the section on the appropriate sub-model.)

1.2.2 Coupling of spreading and vaporisation

The coupling of the spreading and vaporisation components is, to first order, fairly simple. The mass equation can be written

$$\frac{dM}{dt} = JA$$

where A is the top area of the pool and J is the average local vaporisation rate (in kg/m^2/s). J is expected to be only weakly dependent on the pool area and so the total mass vaporisation rate is expected to be proportional to the pool area or to r^2. It is therefore desirable to get a good prediction for the radius.

The spreading rate can also depend on the depth (and hence on J via M). This is probably most important for boiling cryogens, where the pool mass may initially decrease very rapidly, and especially for cryogens spilt on water - as water recirculating beneath the cold pool can provide a very ready source of heat to vaporise the pool.

1.2.3 Some general comments on scaling

Pool spread and evaporation is a very good example of a process where many time and distance scales are important in the different sub-processes. As emphasised by the EC Model Evaluation Group, it is important to show that each sub-model has a sound physical basis to ensure that it scales correctly - both in absolute terms and relative to the other sub-models. Most validation studies are carried out on small scale experiments; most predictions are made for much larger scales, and so understanding the scaling properties of each sub-model is important. Furthermore it is clear from the above that the overall vaporisation rate is equally sensitive to predictions of the local vaporisation rate J and to the predicted pool size A - and so we need to understand both equally well.

Quite generally, a particular difficulty is caused by the use of correlations (sometimes unavoidable) with no particular "understanding" of phenomena. Every effort must be made in this case to ensure that they are used in circumstances similar to those in which they were derived and that they are not extrapolated beyond the range where they were derived. Dimensionally unsound correlations pose a particular problem in this regard.

1.2.4 The form of the spreading equations

Let me come back to my concern over having a form r(t) instead of a differential for dr/dt=.... Some explanation is in order.

Consider for the moment the motion of a rigid body. Since Isaac Newton, we have considered this classically in terms of forces and acceleration. For gravity driven, resisted motion, we expect something of the form

$$m\frac{d^2r}{dt^2} = F_{gravity} - F_{resistance}$$

What often happens is that the accelerating phase lasts only a short time after which there is an approximate balance of forces or

$$0 \approx F_{gravity} - F_{resistance}$$

Now the resistance force usually depends on the velocity dr/dt, and so this approximate equation can be manipulated into the form

$$\frac{dr}{dt} = \ldots$$

Note that this is not valid at early time, but if that is not the period of most interest, then this doesn't matter.

Fluids are a bit more complicated, but the same principles may hold when the period where acceleration is important is limited, and the fluid rapidly comes to a state where its overall motion is controlled by a balance of body forces.

Our ability to write a first order equation therefore hangs on our understanding of the forces as a function of velocity - for example resistance forces proportional to the square of velocity. Going one step further and writing r(t)=... effectively means we are anticipating the solution of this equation. And that solution depends on the other coupled differential equations in the system - in this case for example the dM/dt equation. And so writing r(t)=... prejudges the solutions of all the other relevant equations, rather than coupling them. This concern has been expressed more specifically in footnote (v) on p5 of the document but merits consideration, I believe, on very general grounds

1.2.5 Summary of overall structure

The overall structure of the model is therefore fine. But simplifying the spreading equation to the form r(t)=... may not be a good idea - on quite general considerations.

1.3 Sub-models

Having discussed the overall structure it remains to discuss the individual sub-model. These are

- gravity spreading on land
- gravity spreading on water
- vaporisation

- heat transfer

The first two on this list are the subject of a very confused literature, with even usually respectable sources getting in a hopeless mess, and so I'll sort it out with a long preamble before even starting to comment on the model in question.

1.4 Preamble to gravity spreading

1.4.1 Introduction

Gravity spreading models in the literature are a mess, and cannot be relied upon. Spreading on land and water are often horribly confused. Before going on to discuss this and the consequences for the model in question, let me briefly quote the most easily understood, reasonable model for a pool spreading on water.

1.4.2 The gravity-front resistance regime for spreading on water

This balances a gravity driving force (per unit perimeter) of order $g(\rho_w-\rho)h^2$ with a resistance force, owing to the need to displace more water ahead of the front, of order $h\rho_w(dr/dt)^2$. This balance results in an equation of the form

$$\frac{dr}{dt} = K\sqrt{g'h}$$

where $g' = g(\rho_w-\rho)/\rho_w$ and K is a constant. It is not valid in the early stages where acceleration (inertia) is important, nor in the later stages where the pool becomes thin enough that shear effects over the whole area of the pool start to dominate the resistance. But it is a reasonable approximation for a period.

An instantaneous, non-volatile release provides us with a suitable thought experiment. In this case the volume $V=\pi r^2 h$ is constant and the spreading behaves as

$$r^2 = r_0^2 \quad + \quad 2K\sqrt{\frac{g'V}{\pi}}\, t$$

or $r \sim \sqrt{t}$.

(**Aside:** This model is practically identical with a simple box model of a heavy gas cloud resisted by the ambient air. The $r \sim \sqrt{t}$ behaviour is extremely well observed in the overhead photographs of the Thorney island trials.)

1.4.3 Misconceptions of the gravity-inertia regime

Both Shaw and Briscoe and Dodge et al credit J Fay with deriving the above formula from a balance of gravity and inertia. It is safe to say that this is nonsense. Gravity balancing inertia is F = ma - it accelerates things. In the above solution the velocity goes as $dr/dt \sim 1/\sqrt{t}$ - that is to say it decelerates. This can only be due to a resistive force (and the derivation above is the simplest).

It is worth reproducing the erroneous argument. (I'll drop the constant $(\rho_w-\rho)$ for now, for reasons which will become apparent.) The argument, converted to cylindrical symmetry, goes that the gravity force is of order $g\rho h^2\ (2\pi r)$ and the acceleration term is $\rho V d^2r/dt^2$. This is heuristic but plausible, as is the subsequent argument that $d^2r/dt^2 \sim r/t^2$ (*but caveat emptor*). Put this all together with $V=\pi r^2 h$ and Bob's your uncle:

$$r^2 = \sqrt{\frac{2gV}{\pi}}\, t$$

However, as we have noted it is very easy to differentiate (the square root of) this (twice) to find

$$\frac{d^2r}{dt^2} = \frac{-1}{4}\left[\frac{2gV}{\pi}\right]^{1/4} t^{-3/2}$$

Interestingly r/t^2 has the same power law behaviour but the opposite sign, rather invalidating the original assumption. How did our original positive acceleration hypothesis suddenly turn into this deceleration? It is the $d^2r/dt^2 \sim r/t^2$ conjecture which is at fault. Let's do some proper (but not very difficult) mathematics, and look more closely at the differential equation omitting this guess.

$$\rho V \frac{d^2 r}{dt^2} = g\rho h^2 (2\pi r)$$

First use the volume relation to manipulate it into the form

$$\frac{d^2 r}{dt^2} = \frac{2gV}{\pi} r^{-3}$$

If, instead of making guesses, we just solve this equation (a radical approach!) we get quite a different answer. Using the standard method for such problems we multiply both sides by dr/dt and integrate to obtain

$$\frac{1}{2}\left[\frac{dr}{dt}\right]^2 = E - \frac{gV}{\pi} r^{-2} \qquad \equiv E - gh$$

The constant of integration E, is crucial - without it there is no real solution. This is an energy conservation law (kinetic = total - potential) obtained by the standard method. The kinetic is the half the velocity squared, the potential is gh and the integration constant E is the conserved total energy. We can now take the square root and integrate this to find

$$r^2 = \frac{gV}{\pi E} + 2E t^2$$

The pool starts from rest at t=0 and accelerates radially until r~t, an asymptote along which all the initial potential energy has been converted to kinetic. Exact, inviscid self-similar solutions of the shallow water equations with just this asymptotic behaviour have been constructed by Webber and Brighton (1986), using the energy conserving boundary condition h=0.

This is not the way real pools behave of course as we have neglected resistance, but it is the right answer for the energy conserving gravity-inertia regime. Despite the elegant simplicity of the true solution, the idea that an equation of the form

$$\frac{dr}{dt} \sim \sqrt{gh}$$

somehow corresponds to a pure gravity-inertia regime is one of the most widely propagated pieces of nonsense you are ever likely to meet. It is distressing to see how so many people came to this erroneous conclusion.

1.4.4 The problem

For spreading on water it might be entirely academic whether this last equation corresponds to gravity-inertia or gravity-front resistance. In any event, it is probably much better than the actual gravity-inertia equation, just because it does model the front resistance.

The problem with confusing the regimes comes when one considers spreading on land. If one accepts that this is a front resisted model, then one is not tempted to use it for spreading on land where there is no displaced water (and air is too thin to provide any significant resistance). However if one believes it to be an inertia-gravity model, then one is immediately tempted to use it as a model of spreading on land.

Shaw and Briscoe do just this and even retain the density difference factor. (What Shaw and Briscoe regard ρ_w as meaning in this case is far from clear). Other, more recent papers have taken this idea up - one, submitted to J. Haz. Materials a few years ago, argued that this formula expressed conservation of energy, completely oblivious to the fact that both kinetic and potential energy are decreasing monotonically.

Nor is the source of the resistive term clear: water and treacle spread and decelerate at the same rate according to this formula - and so can have nothing to do with laminar viscous flow.

What does one expect for real liquids spreading on land? Initially there might be a short period of acceleration, but thereafter the resistance forces will be dominated by friction with the ground causing laminar and turbulent shear flow. This force acts on the whole under-surface of the pool and scales quite differently from the water resistance force acting around the edge. As the pool becomes large in area and very shallow these forces become much larger resulting in a much slower spread than r~√t (typically $r \sim t^{2/7}$ and $r \sim t^{1/8}$ for instantaneously released pools in the turbulent and laminar gravity-resistance regimes respectively).

1.4.5 The solution

This problem with models like Shaw and Briscoe's (in particular Shaw and Briscoe's) was one of the things I set out to fix when I embarked upon the development of GASP in the mid-1980s (with the collaboration of Steve Jones and Phil Brighton at SRD). I believed then, and I believe now, that the only way to get an integral model in which one can have real confidence was to step back and include inertia, the driving force, and all the resistance terms in a pair of first order equations broadly of the form:

$$\frac{dr}{dt} = u$$

$$\frac{du}{dt} = F_{gravity} - F_{restance}$$

The details are given by Webber and Jones (1987) in the Boston conference paper, and by Webber and Brighton (1986) in the "Heavy Gas and Risk Assessment III" conference paper. Various resistance terms are included and allowance is made for the radial motion of water immediately beneath a floating pool. It is slightly more complicated than these equations, but only slightly. I don't believe that anyone has come up with anything better, and if asked to model this flow again, I'd do exactly the same thing - except that with the knowledge I have gained since I would explain both the problem and the solution better. I hope the above does at least the first part of this.

1.5 Gravity spreading on land

1.5.1 The model

The model adopted by DNV for gravity spreading on land is

$$\frac{dr}{dt} = \sqrt{2g(h-h_m)}$$

where h is the pool depth and h_m is a minimum depth at which spreading is arrested.

Consider first the possibility $h_m=0$. This is just the model discussed at length in the previous section, and I have argued that it is completely wrong, despite its ubiquity. It cannot accurately model flow resisted by ground friction: it will predict too slow an initial spread and much too rapid a spread in the later stages. How important this is, is difficult to assess. Cryogens boil faster if they spread faster (getting access to heat from uncooled ground) so this may significantly underestimate the initial boil off rate and have a longer tail. But this will all be tied up with the release mechanism too.

However the case $h_m>0$ will probably be better. There are two new effects here: first the flow is arrested completely when it reaches this minimum depth, and second the flow decelerates markedly as it approaches this depth. If we look again at a non-volatile instantaneous release of volume V, then the solution of this equation is

$$r^2 = r_m^2\left[1 - \left(\frac{t}{t_m} - 1\right)^2\right]$$

where $r_m = \sqrt{V/\pi h_m}$ is the final radius and t_m is a time scale given by $\sqrt{r_m/2gh_m}$. I have chosen the origin of time to be the virtual point where r=0 and the solution is valid for $0<t< t_m$. This starts with r~√t while $h \gg h_m$ but slows down faster as h becomes of order h_m.

With the right choice of h_m it *may* give a reasonable approximate spreading law, but in reality the depth at which it stops spreading will depend on the ability of the ground to hold the liquid in puddles, and the rate of approach to this will depend on the viscosity of the liquid. (Again, this model predicts that treacle and water spread at the same rate - but presumably one isn't assessing treacle hazards too often. But what range of viscosities will the model be used for?)

The model's attribution of different values of h_m to different material substrates may be improved. Hard soil may be flat like a cricket pitch or otherwise - like a frozen ploughed field. The puddle holding ability of these surfaces would be quite different. (NB I *do* associate the minimum depth with a "puddle holding ability" rather than a capillary depth associated with surface tension, as surface tension effects are usually destroyed by dirty - i.e. real - surfaces.)

1.5.2 Conclusion

This model is wrong. But it gives the right qualitative behaviour and it is very difficult to see how wrong it is in the circumstances in which it will be used. The model is certainly very simple. In some circumstances it may be too simple - but some testing would be needed to assess this. In the meantime I would advise against using it with zero minimum depth or with liquids significantly more viscous than those for which any validation studies have been done. I don't know how to choose the best value of h_m. In the long term I'd replace it with the Webber et al model - but then of course that is exactly what I did do.

If one takes this route, there is one numerical problem which needs care: the resistance terms go as 1/h (turbulent shear flow) and $1/h^2$ (laminar lubrication theory flow). This results in very large resistance terms as the pool becomes thin and, in the numerical solution, one has to be wary of hitting h=0 or overshooting to find h<0.

1.6 Gravity spreading on water

1.6.1 The model

For spreading on water the model of Dodge et al is adopted. The mistake in guessing d^2r/dt^2 is propagated. I have argued above that the general procedure of adopting a model of the form r(t)=... is unsafe. The error in estimating the inertia term merely serves to highlight the problem. Of course Dodge et al have in fact estimated a front resistance term but this was by good luck rather than good judgement, and it leaves me rather distrustful of their whole approach.

Having said that, their gravity-viscous regime looks similar to that of the GASP model in effect (but the miss out the possibility of turbulent shear resistance). I am not sure what to make of the sudden increase in spreading rate (at least in the power law) due to surface tension. Invoking this for spills on a rough sea - or even in harbour- does not feel very relevant, but I'd need to think for quite a long time about that, and it probably doesn't have a very large effect as volatile pools, when they become that thin, will just evaporate.

Importantly, although it identifies them wrongly, this approach does highlight the fact that there will be different regimes of flow - something missing from the model of spreading on land. I don't believe all the approximations they make, but it would be very difficult to know how bad they were without extensive testing. My worry is that there is enough freedom to tune the model to Dodge et al's data, but that if the regimes are not correctly identified and modelled, than it won't scale properly. I share the worry expressed in DNV footnote (v) that it will not work for volatile pools (especially cryogens) but simply substituting M(t) for M(0) is just a wild guess at an improvement (although it may indeed be a practical improvement in the short term). It would need testing.

Again in the longer term, if effort is available, I'd do what I did before - use the model of Webber et al. The same numerical caution should be exercised as in the case of spreading on land. One of the advantages of this, is that you don't have to program explicit changes from one regime to another. The equations have been designed to make it happen smoothly and automatically.

1.7 Pool vaporisation

1.7.1 Overall model

The overall vaporisation model adopted is of the form

$$\frac{dT}{dt} = \frac{Q_{in} - Q_{evap}}{M.C_L}$$

where the input heat flux Q_{in} is accounted for in a sum of contributions. The evaporation rate is related to the heat Q_{evap} extracted and the heat of vaporisation:

$$E_{vap} = \frac{Q_{evap}}{\Delta H_v}$$

If the liquid is well below its boiling point then one expects the evaporation rate to be controlled by the dynamics of the atmosphere above the pool; if the liquid is boiling, then it is controlled by the heat supply.

In the former case the model of McKay and Matsugu is adopted (in a slightly modified form) for Q_{evap}; in the latter the approximation $Q_{evap} = Q_{in}$ is adopted.

This overall structure is physically sound and any debate is likely to be over the form of the sub-models used, and at what point the transition takes place between the "boiling" (heat input controlled) and "evaporation" (atmosphere controlled) modes of vaporisation.

1.7.2 Evaporation and boiling

Mathematical properties of the model

Before looking in detail at the sub-models, it is interesting to note that the transition from boiling to evaporation is implicit in the model equations used. In fact it is in the logarithmic term of Equation 55 of the document which implies that $Q_{evap} \rightarrow \infty$ as $T \rightarrow T_{boil}$. We used this model in the code GASP and simply solved the differential equation. (I say "simply" but that's not quite the case.)

What happens (mathematically) if you do this? For any given heat input there is an equilibrium temperature T_e where $Q_{evap}(T_e) = Q_{in}$ and $dT/dt=0$.

If the liquid is at this equilibrium temperature it will stay at it. (If we maintain constant heat input for the moment, then the equilibrium is stable: if $T>T_e$ then $dT/dt<0$ and if $T<T_e$ then $dT/dt>0$.)

"Boiling"

For large heat input Q_{in}, the equilibrium point will be, by definition, at a large value Q_{evap} - that is to say with T_e only slightly (sometimes very slightly indeed) below T_{boil} as defined by the singularity in the evaporation model. This is what we expect for cryogen spills, and is to all intents and purposes boiling, well modelled by simply taking $Q_{evap} \approx Q_{in}$.

However, as the surroundings cool and the pool remains effectively at its boiling point, then Q_{in} will decrease and the equilibrium $Q_{evap} \approx Q_{in}$ will only be a quasi-steady one. Because as $Q_{evap}(T)$ decreases, T must decrease, albeit only very slowly while we are close to T_{boil} where $Q_{evap}(T)$ is very steep. Therefore dT/dt is small (and negative) rather than zero. Nevertheless, the temperature *will* drop. And ultimately it will surely drop far enough that the heat input rate will no longer be so large as to exactly balance Q_{evap}. At this stage the atmosphere will start to have a say in the evaporation rate. This is the point where Q_{evap} and Q_{in} have both dropped far enough to be of the same order as dT/dt. One expects a transition from boiling to evaporation - particularly in the case of bunded cryogen spills.

"Evaporation"

For small heat input the equilibrium point will be at a smaller value of Q_{evap} - that is to say with the equilibrium temperature $T_e \ll T_{boil}$. This is what one expects in the case of spills of non-cryogenic substances. They will start at a temperature well below the boiling point and (unless there is a sudden source of heat) will stay well away from boiling. The temperature equation gives T(t) and one can calculate $Q_{evap}(t)$. This is my understanding of what is done in the model for non-cryogens. This is quite appropriate.

Unified evaporation and boiling

As noted above, the singularity in $Q_{evap}(T)$ means that one can treat all case like the evaporation model and boiling comes out "automatically". Solving the full temperature equation above removes any difficulty of deciding whether to use a boiling or evaporation model. It also copes automatically with "intermediate" substances like Butane which boil close to ambient temperature. These are great advantages.

However, I do not recommend this approach without reservation. Having tried to program it quite innocently I ran into enormous numerical difficulties. After quite a bit of analysis (see "Evaporation and boiling of liquid pools - a unified treatment" - Webber 1989) I finally understood exactly why that was and solved the problem. The full temperature equation leads to an enormously "stiff" numerical problem when high heat transfers are involved. (In fact it is the stiffest I have ever encountered with a ratio of time scales of the order of 10^{20} as explained in the cited work.)

If one can simply distinguish a boiling regime and evaporation regime as is done in the model under consideration, then all of this numerical problem is avoided (and the code runs much faster). The equations are well enough behaved if one stays far enough away from the boiling point.

The non-unified treatment

The problem with the non-unified treatment is what happens to initially boiling pools as the ground cools. A bunded LNG spill is a case in point. If the model has $Q_{evap} = Q_{in}$ then it is a good estimate of the vaporisation rate but one has no handle on the small dT/dt. It isn't clear from the document whether a change in pool temperature is modelled or not in this circumstance. If not then the pool will go on "boiling" forever - but more slowly as time goes on. This would effectively be ignoring the role of the atmosphere in determining the vaporisation rate and would appear to be an underestimate in the later stages, when the heat supply has largely diminished.

If one can estimate the pool temperature from the ground temperature and then estimate $Q_{evap}(T)$ from this an switch to the evaporation model when it drops below Q_{in} then this may be an improved model without the numerical difficulties of solving the solving the full temperature equation.

1.7.3 Boiling on land

The model adopts formulae given by Shaw and Briscoe for the conducted heat flux. Shaw and Briscoe's derivation is an extremely heuristic adaptation of formulae given by Carslaw and Jaeger in an attempt to generalise to the case where a pool is spreading, and as such I distrust it. Because of this, I have given a more rigorous treatment ("Heat conduction under a spreading pool" Webber 1987) in which the correct result, given Shaw and Briscoe's physical assumptions is shown to be

$$Q_{cond}(t) = -\frac{K\phi(t)A(t)}{\sqrt{\pi\alpha t}} - \frac{K}{\sqrt{4\pi\alpha}}\int_0^t dt'(t-t')^{-3/2}\left[\phi(t)A(t) - \phi(t')A(t')\right]$$

where $\phi(t) = T(t) - T_0$ with T_0 being the initial ground temperature. (This is also quoted by Webber and Jones 1987 but I think there's a misprint there.) This equation is true under the assumption of vertical conduction and perfect thermal contact at the surface for any pool which spreads monotonically outwards with area A(t) and temperature changing in any way. (That is to say when the spreading is such that ground once covered by the pool is never exposed again.) The cited work also includes results for imperfect thermal contact where a heat transfer coefficient at the surface is required.

This form is no more complicated to use in a computer program and is therefore recommended. But it is also worth noting that it should reduce to the same form for a bunded pool at constant temperature, and that the conducted heat flux is only usually the dominant effect for cryogenic spills, and so the difference may only be important for spreading cryogens.

In passing it is worth noting that some authors have considered film (Leidenfrost) boiling. The model under consideration makes no mention of it. I believe it is right to discount it as the evidence seems to indicate that it only happens on cleanly polished surfaces with high conductivity - more often found inside vessels than outside where spills are likely to occur.

1.7.4 Evaporation on land

The model adopts the correlation of McKay and Matsugu modified by a factor to allow for higher vapour pressures. The correlation is not dimensionally sound having wind speed to the power 0.78 and radius to the power 1.89. I therefore regard it as extremely suspect indeed and great care must be taken that it is not used outside the region where it has been fitted to data. Unfortunately, even using it for a different substance does this. Extrapolating from the O(1m) scale experiments of McKay and Matsugu to industrial scale with unreliable power laws is also extremely dangerous. The coefficient 2.1 at the front has implicit dimensionality and therefore must depend on something with dimensions - the substance properties are a prime candidate. To be sure that all the relevant physical phenomena have been accounted for one needs a model. Without full scale data on the behaviour of a very wide range of substances in different atmospheric conditions, there is really no way to gain confidence in this model.

This was exactly the problem faced by Brighton (1985) who has given a more scientific treatment, which comes up with a dimensionally understandable form for the evaporation rate which validates well against a range of data. I feel a lot more comfortable with it and recommend it very strongly.

1.7.5 Boiling on water

Ice formation is considered. As far as I am aware (and I'd put it even more strongly than the discussion in the document) there is no evidence for ice formation under pools except in very small scale experiments in shallow trays. (I have said this frequently at conferences and no-one has ever contradicted me or made me aware of such a phenomenon.) I would therefore be tempted discount ice formation.

The heat transfer model (no ice) in this case looks fine. Circulation of water under the pool makes it difficult to do anything better than an empirical heat transfer coefficient, and I know of no attempts to calculate this for industrial spills on water, or studies of how it might vary from rivers to harbours to the sea (where circulation properties might be rather different in principle).

In view of the unlikelihood of ice formation, the ice model looks complicated.

1.7.6 Evaporation on water

On both land and water, the evaporation term Q_{evap} models the rate at which the atmosphere can take away material from the surface of the pool. As the vapour disperses in the atmosphere it vaporises at the pool surface in order to maintain a concentration just sufficient to provide the correct partial pressure for liquid-vapour equilibrium at the surface. Calculating Q_{evap} is therefore purely an atmospheric advection-diffusion problem. This is acknowledged in the model which produces a dimensionally sound equation (eq. 71) following Dodge et al.

Broadly speaking, the model of Dodge et al for evaporation of a pool on water does attempt to derive the effects on the atmospheric flow of waves being whipped up by the wind - effectively a case of the aerodynamic roughness length of the surface being dependent upon wind speed, and looks very plausible. But otherwise the evaporation is by exactly the same mechanism as pertains on land, and my main initial surprise is why the dimensionally unsound correlation on land is used, when a similar analysis in that case would result in a more understandable formula as here.

Brighton, by the way, adopts exactly the same approach on land and water but regards the roughness length on water as effectively a universal constant which is deemed to allow for the existence of waves. It would be interesting to compare the two approaches.

At a more detailed level, some of the equations deriving the model do no look well throughout. As footnote (xv) points out constants like 0.01384 are presented with spurious accuracy and h_w, quoted as a dimensionless height, is in fact a frequency. (Actually Dodge et al make it clear that the constant 0.01384 is in fact 0.01384 seconds, which does give h_w the correct non-dimensionality, but they give no indication of what this time scale corresponds to physically.)

Formula (66) for the friction constant also looks over the top to me: it is a dimensionally unsound correlation (therefore containing no science) and a quick calculation (assuming a logarithmic wind profile) reveals that it means that the roughness length varies from about 1mm to about 2mm as the wind speed changes from zero to over 22.3 (sic) m/s. Of course from these formulae I can compute the roughness length to 3 significant figures for any given wind speed, and it worries me that Dodge et al did not realise that meteorology isn't really capable of this.

I would argue that 1mm to 2mm is not really a well-understood, important variation and that this model is not significantly different from assuming a constant roughness length. The computation of C_f is therefore largely as spurious as the "0.01384 seconds". Choosing z_0=1.5mm (say) would in fact be far more intuitively understandable than invoking an obscure metronome with exactly this period.

Correlations with Schmidt number, broadly of the form of the one presented, are a necessary ingredient in evaporation models like this (e.g. Brighton has something similar) and reflect our lack of understanding of what is going on in the viscous sublayer. In this case the obscure 0.01384s just complicates the recipe. It would be interesting to have a feel for how much the dimensionless coefficient Da* is predicted to vary in different conditions.

As a verification exercise it might be worthwhile programming the formula for Q_{evap} and comparing it with Brighton's. Also, as noted above, this approach (if done properly) is more scientific than the simple correlation for evaporation on land, and may be used to good effect there also.

1.7.7 Convection on land and water

It is difficult to assess the model here without going deep into the references, as it essentially boils down to a correlation between Nusselt number, Prandtl number and Reynolds number. But it is dimensionally sound. On the other hand the dimensions of the pool do enter (in a dimensionally sound, but perhaps not entirely intuitive, way) and therefore one should really test it at different scales. It may be that this sub-model will not dominate the overall heat transfer in too many circumstances: one possibility where it might do so is in bunded cryogenic spills after the ground has cooled enough to make the conducted flux small.

It is also worth noting that Brighton (1985) has looked at the effect on the convected heat flux of the pool being close to the boiling point. The factors which lead to the logarithmic singularity in the mass transfer rate, lead to a zero in the heat transfer rate. Effectively violent boiling prevents any convected heat from getting down into the pool. But as this usually happens when the heat transfer is vastly dominated by conduction anyway, it probably isn't important.

1.7.8 Radiation

I have no difficulties with the radiation heat transfer model adopted, save to say that it might be worth checking the sensitivity to emissivity and the possibility of reflection at the surface. This sub-model *is* needed - in some British Gas Experiments on butane pools I seem to remember they measured the radiative contribution and it was a significant part of the total heat flux. (But that work may not have been published and may therefore be to some extent confidential - so please don't quote me on it.)

1.7.9 Dissolution in water

This is done in a similar way to evaporation on water. I have not seen any other models for dissolution and therefore do not have any further comments on how it should be done better. However it seems clear that the rate of dissolving will be related to turbulence profiles in the water and therefore that the idea having a unique and accurate model valid for different rivers, estuaries, harbours, and the open sea may not be tenable. Therefore the model may be more complicated than necessary.

1.8 On validation and further developments

1.8.1 Validation

The validation steps involving spreading only, vaporisation only, and then both together are well thought-out.

I could argue that Figure 1 gives some support to my contention that spreading on land starts out faster than in this model and then slows down more, but the results aren't bad. The open question is whether the discrepancy would grow at larger scales.

Figure 2 confirms the classical result for a bunded cryogen. The improvements suggested here would make no difference to this particular case, but would affect spreading cryogens.

The other figures are more complicated. The fact that Butane has been addressed is interesting. It boils close to zero Celsius and as such is intermediate between less volatile liquids and cryogens. I should have thought it might prove one of the more difficult cases, depending on the ambient temperature, for a model which separates boiling and evaporation models.

The main difficulties with validation in general are (a) that data tend to be taken at small scales and (b) that some of the available data has already been used in prescribing the model. In the recommendations below I suggest a code comparison exercise as an added validation which can test the scaling - if only against another model.

1.8.2 Further developments

The document is right to suggest that one of the most important problems in using the predictions of pool models is having a dispersion model which can handle a time-dependent source. In fact the release rate and area will both in general be time dependent. HGSYSTEM may be the only "simple" model which comes close.

Multi-component liquids are less difficult - especially if you can assume ideal mixtures (Raoult's law) or if the non-ideality of the mixing is known.

1.9 Conclusions and recommendations

1.9.1 Conclusions

My main conclusions from reviewing this model, are the following:

- ☐ The model has a good overall structure.
- ☐ The results will depend on the complex interplay of the different sub-models.
- ☐ Different sub-models will be most prominent in different circumstances.
- ☐ All the sub-models appear qualitatively reasonable is as far as they can be assessed.
- ☐ Almost all the sub-models could be improved.

At this point I should emphasise that many of the improvements proposed here are based on my own work and that of Philip Brighton, but that there is a good reason for this. In the 1980's while I worked at SRD, we spent a long time with the identified shortcomings of SRD's exiting model, that of Shaw and Briscoe (which this model also refers to) putting them right. Philip produced what I still believe to be *the* seminal work on pool evaporation and convective heat transfer, while I worked on the spreading and heat conduction models. Our objective was to gain a proper scientific understanding of the phenomena, relying as little as possible on ill-understood correlations, and put this together in an integral model of the sort discussed here. The result was GASP. With what I've learned since, I'd still do most of it the same, except that I'd explain it and document it better. I might also look for a way around the stiffness of the unified vaporisation/boiling model but with faster computers, even that might not be necessary. But in any event, most of the sub-models used, complete with the reasoning behind them, are published (albeit sometimes in obscure places) and are therefore available for consideration. (Hence the bibliography.)

But to continue:

- ☐ In most cases it is unclear how big a difference using an improved sub-model will make, and therefore, mindful of the expense of doing this, I would suggest a programme of testing as below, in order to help identify the most cost-effective way of increasing confidence in the code.

1.9.2 Recommendations

First it is often useful for computer programs such as this to be able to output a wide variety of variable as they involve in time - more than are strictly needed by the hazard analyst. Examples in this case include the various contributions to the heat flux. This allows one to identify the most important phenomena in any given run of the code.

Assuming the code can do this, and that it has been compared with enough representative small scale experimental data, it would be interesting, and I believe cost-effective, to do a code comparison exercise modelling larger scale spills of different kinds and comparing the results with those of GASP. The objective would be to identify cases here they are giving significantly different predictions (if any) and to find out which sub-models are responsible for that difference. One could then focus on whether an improved sub-model in that area would be worthwhile (or of course whether it is a shortcoming of GASP). Agreement might lend confidence to both models.

GASP was written at SRD for HSE and has not been changed in a decade or more. It may be that HSE would regard a comparison exercise as timely. It would help them assess safety cases prepared with either code and such a model comparison is within the recommendations also of the EC Model Evaluation Group - which were produced long after GASP was written and which HSE support.

2. COMPARISON OF PVAP AGAINST THE POOL MODEL GASP

2.1 Introduction

Following the theory review of the PVAP model described in the previous chapter, this chapter describes the comparison of the PVAP model against the HSE/SRD pool spreading/evaporation model GASP. The accompanying data files (Excel spread sheets incorporating full PVAP runs as well as output from GASP) and the GASP output files themselves contain the detailed information. This report draws attention to the conclusions.

It should be emphasised that the runs chosen are not intended to model any specific accidents, but rather are chosen for their ability to focus as much as possible on individual sub-models, in order to facilitate scientific conclusions.

The original plan was to use hexane as a slowly vaporising substance but I couldn't find it in PVAP's data base and so acrylonitrile was used instead. Methane was used to model LNG throughout.

2.2 Spreading on land

The spreading tests were conducted first by running PVAP and then setting GASP's initial conditions to match as closely as possible. Water was chosen as the liquid in question as evaporation is negligible (it was switched off in GASP) and one can focus on the differences in the spreading model. Instantaneous releases of 1kg and 10te were chosen to give a large span of scales.

2.2.1 Run spread01

This is a 1kg release with a minimum depth set of 1cm in each case. In PVAP this was the default minimum depth for the ground considered. In GASP this parameter corresponds to the ground's ability to hold in puddles 0.01 m^3 of liquid per square metre of ground; it is not a default value, but rather the analyst is asked to consider the terrain in question.

The results show a very slightly different spreading pattern - which is not surprising in such a small release where starting and end conditions have both been matched exactly. The result from GASP with no minimum depth shows that the assumption of the minimum depth effectively determines the spreading behaviour almost in its entirety.

See figure 1.

2.2.2 Run spread10

A contrasting spreading case is provided by 10te of water spreading on ground where no minimum depth is supported.

Alert 1: A hitherto apparently undocumented feature of PVAP is that if you set a zero minimum depth, then this will be overridden by a hard-wired 1cm minimum depth. The results presented here were therefore obtained by setting a very small but non-zero minimum depth.

Alert 2: PVAP appears to behave reasonably until the radius reaches 160m after which some very odd results are obtained.

GASP and PVAP behave entirely differently, for reasons already analysed. GASP's results reflect the transition to laminar (lubrication theory) flow as the pool becomes shallow and will depend strongly on the viscosity of the liquid. PVAP's result is an ad-hoc spreading law used by Shaw and Briscoe for spreading on land.

See figure 2

2.2.3 Run spread 11

It is interesting to consider the larger 10te release but retaining the 1cm minimum depth as PVAP is more likely to be run with this configuration.

PVAP rapidly hits the minimum depth and stays there - with an apparent discontinuity which possibly hints at a less than rigorous numerical solution of the differential equations. (In the case of PVAP the pool is in fact evaporating at this point and it is not entirely clear how the program is handling this - although it does get smaller in radius at the constant minimum depth.)

GASP's approach to the minimum depth is very much slower owing to a transition to laminar flow - although it does get there eventually.

In contrast with the small scale releases then, the different spreading laws of the two programs do make a significant difference here.

See figure 3.

2.3 Boiling in a bund on land

2.3.1 Run boil01

A small (1kg) release was done into a small bund. We'll not discuss it in detail here as most of the conclusions are the same as in other runs.

2.3.2 Run boil11

This run consists of a 10te instantaneous release of LNG into a bunded area - with a 5m bund radius. The release temperature was takes and 111K - just below the boiling point. Note that a "user-defined" surface was used in PVAP to facilitate explicit matching of the ground conductivity and thermal diffusivity in PVAP and GASP.

The bund is rapidly encountered as seen in **fig 4** after which spreading stops. The time taken is 0.5s or 1s depending on which program you look at but this is only a small contribution to the overall vaporisation time. PVAP predicts the greater vaporisation rate as shown in **fig 5**.

But both programs can output enough information to give some hope of finding out why. The conducted and total heat fluxes into the pool look broadly similar in the two codes - **figs 6,7** and it is clear that the heat input is dominated by conduction. There is a cusp in each model at the point where the pool reaches the bund, after which the ground under the pool cools and the pool reaches no fresh warm ground and the heat input drops.

The heat of vaporisation in the two models is very different corresponding to different vaporisation rates. (**Fig 8**) This is because of the differences in the boiling/evaporation models. GASP solves the full temperature equation throughout the history of the pool and has no difference between "boiling" and "evaporation" but rather has limits of vaporisation controlled by heat input and by atmospheric transport, with a smooth transition from one regime to the other. In PVAP the transition from the boiling model (heat controlled) to the evaporation model (atmosphere controlled) occurs between 1.21s and 1.27s - shortly after the bund has been encountered and shortly after the temperature reaches 112K. In the final stages of PVAP the slightly higher vaporisation rate predicted by the evaporation model causes the temperature to drop more rapidly than in GASP in which it appears that the vaporisation is heat-input controlled for much longer. (**Figs 9,10**). In PVAP it appears that the temperature stays up at the boiling point only for as long as the vaporisation rate is less than the heat input rate. When the ground cools sufficiently to reverse this, then the pool temperature drops rapidly.

As explained in the PVAP theory manual, the heat of vaporisation shows a logarithmic singularity if the pool temperature becomes close to the boiling temperature, i.e. if the saturated vapour pressure becomes close to the ambient pressure. As a result a cut-off of the saturated vapour pressure is applied in PVAP to eliminate this singularity.[1] This plateau is required due to an artefact in the model which switches between boiling and evaporation. If the code can get into a mode where it is evaporating and is close to the boiling point, then there may be a maximum evaporation rate defined by the evaporation rate at boiling point. The logarithmic singularity in the evaporation rate model should actually prevent this and permit any evaporation rate below the boiling point, but the results will depend on how that is handled close to the boiling point[2]. (This was a key pint in the development of GASP which handles the singularity correctly and solves the full temperature equation always - although it took a lot of heartache to get it to that point.)

It might be interesting to study the precise balances in more detail here because, in effect, it looks like a significant difference in the models. Although it is worth pointing out that the wind speed here has been chosen deliberately very low

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[1] This paragraph has been added to explain the reason of the plateau.

[2] My understanding of the logic of PVAP (private communication A.Holt) is:

1) If the pool is boiling the evaporation rate is calculated from the heat of conduction, convection, radiation, solution and from the spill itself
2) If the pool is evaporating the evaporation rate is calculated from the heat of evaporation only
3) At each time step the change in pool temperature is calculated from the net heat flux whereby Qnet= Qcond+Qconv+Qrad+Qleak+Qsol-Qevap. If the pool is already at the boiling point and the change in temp is >=0 then the pool is boiling. Otherwise the pool is evaporating.

in order to emphasise heat-dominated vaporisation, and that different conclusions may be obtainable with different atmospheric conditions.

2.4 Spreading on water

To compare spreading on water the first task was to identify a substance which floats and is relatively non-volatile so that mass changes due to evaporation will be negligible and the spreading models can be compared in isolation. Also the substance must be in both the GASP and DNV databases. The best candidate found was acrylonitrile, which boils around 350K and is 20% or so lighter than water.

Unfortunately it is not entirely non-volatile and it also tends to dissolve (in PVAP - GASP does not model dissolution). An attempt was made to switch off evaporation in PVAP by setting zero wind speed but this causes the program to fail. It appears that dissolution can't be switched off.

2.4.1 Run water01

This run consists of a small (1kg) instantaneous release of acrylonitrile on water.As expected, the spreading laws look similar.[3]

See figures 11 and 12

2.4.2 Run water11

This run consists of a larger (10 te) instantaneous release of acrylonitrile on water. Again PVAP spreads somewhat faster than GASP in the early stages but then apparently hits a minimum depth and shrinks as it vaporises and dissolves. It is not entirely clear what this represents as the substrate is "deep open water". PVAP also predicts a significant decrease in volume due to dissolution - rather larger than the loss due to vaporisation in the low wind conditions which were chosen. In GASP we matched the wind conditions in an attempt to give the same vaporisation rate but could not match the dissolution.

(Even allowing for the simplicity of the dissolution model in PVAP, this seems to have highlighted a shortcoming in GASP as it would appear that there are conditions where dissolution is a more ready source of mass loss in the pool than vaporisation.)

See figures 13,14.

2.5 Evaporation in a bund on land

2.5.1 Run evap01

This run models 1kg of acrylonitrile (again chosen for its ready availability in both PVAP and GASP) in a small bund with a more typical 10m wind speed of 5.8m/s. PVAP predicts vaporisation at about twice the rate predicted by GASP which cools the pool more quickly than happens in GASP. This highlights differences in the vaporisation sub-model.

See figures 15,16

2.5.2 Run evap11

This run models 10te of acrylonitrile in a 5m radius bund. Differences in spreading to the bund are the same as in boil11; differences in evaporation are the same as in evap01.

See figures 17-19

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[3] CODE corrected. In the old 5.2 version of PVAP severe oscillations occurred for the volume (Figure 12).

2.6 Spreading and boiling simultaneously

2.6.1 Run sboill01

We return to methane on land in low wind speed but now remove the bund. Again the conductivity of the ground has been arranged to match in GASP and PVAP and a negligibly small minimum depth parameter has been used (as PVAP will not allow zero).

As expected, GASP's faster initial spread, allows the pool to come into contact with warmer ground faster, and enhances the boiling rate.

The conducted heat fluxes (W) are quite different but this is again probably entirely due to the differences in the spreading models.

This, combined with the different vaporisation models, means that the net heat fluxes bear only a qualitative resemblance. Nevertheless the effects of the falling conduction as the ground cools followed by the rising conduction as the pool finds warmer ground, followed again by falling conduction as the pool spread slows, are noticeable in both models.

See figures 20-24[4]

2.6.2 Run sboill11

Finally consider a 10te instantaneous unbunded methane release on land. This time we introduce a minimum depth again - the same in both models.

The spreading rates are different again (but this is concealed somewhat by the choice of logarithmic axis on the graph). However the graph does highlight a very different philosophy about the significance of the minimum depth concept. In GASP it is deemed to be puddle formation. This stops liquid from spreading, but does not prevent the depth from becoming smaller as the liquid later evaporates. Evaporation therefore does not involve radial shrinkage. In PVAP the minimum depth prevents vaporisation below this depth and thus the vaporisation drives radial shrinkage. This reduces the surface area and thence the vaporisation rate meaning that liquid hangs around for much longer. (GASP has a capillary model with a surface-tension minimum depth which acts in a similar way, but it is not recommended to set a 5cm capillary depth, and in any event it is not recommended that one should use this unless the surface is expected to be very flat and very clean. Therefore this was not used.)

PVAP switches from "boiling" to "evaporation" after about 1 second. However this does not immediately have an effect on the temperature - presumably because there is still a net heat input which will not allow the pool to drop below its boiling point. This only becomes negative after O(100s) and the pool then starts to cool very rapidly, as in earlier cases.

See figures 25-30

2.7 Some general conclusions

The above is a short summary of the results. More details can be found in the accompanying EXCEL files from PVAP, which also have the GASP results incorporated. Some of the more general conclusions are:

- The conduction models appear to be very similar.
- Evaporation on land is significantly faster in PVAP than in GASP
- Evaporation on water is less clear as it is less (in PVAP) than the dissolution rate.

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[4] CODE corrected. The old 5.2 version of PVAP became unstable after a while and oscillated wildly between evaporation and boiling modes.

- GASP doesn't model dissolution and the indications here are that it ought to.
- The spreading laws are very different in the two models.
- The spreading models can be brought more into line in *some* cases by choosing the same minimum depth. And in fact in PVAP the spreading is completely sensitive to the choice of minimum depth. PVAP will not allow a zero minimum depth, but it can be chosen very small to mimic flat ground. However I have argued that the PVAP model of spreading (in particular on land) is not a good one and it still seems to me that the minimum depth is a fudge factor whose choice totally dominates the spreading properties. This is fine for fitting experimental data but it removes all predictive power from the model. GASP on the other hand recommends a zero minimum depth unless you have reason to suspect that puddles will be formed, in which case this is estimated from the volume which can be held in puddles per square metre of ground; it is not dependent on the material of the ground where pitted concrete an furrowed soil may both in principle have the same result. It is also not dependent on the material properties. When flat ground is prescribed GASP's pool slows by means of turbulent shear flow based on skin friction followed by laminar (lubrication theory) flow as the pool becomes thin. It becomes much slower than in PVAP if the latter is used with a negligible minimum depth. It also depends on the viscosity of the liquid in a well-defined way. Finally the spreading rate *does* strongly affect the vaporisation rate in the case of cryogens.
- PVAP switches between evaporating and boiling modes and it isn't completely clear (to me) why it should be doing it exactly when it is. GASP solves the temperature equation unifying boiling and evaporation regimes. This is the largest single source of stiffness in the GASP equations and I thought earlier that it should be avoided - essentially as PVAP does. However having seen the output from the two codes, I have completely changed that opinion and believe that GASP's method is better: it gives smoother results, does not take any arbitrary decisions about evaporation or boiling, and did not take significantly longer to execute when the programs were run. (And GASP is a 16 bit implementation - a 32 bit version would be significantly faster.)
- The approach of testing the various sub-models individually is a very useful one. In comparing just with (say) data on volume-as-a-function-of-time for a spreading, boiling LNG pool, would give smooth curves concealing a wealth of complicated physics seen in the heat transfer graphs.

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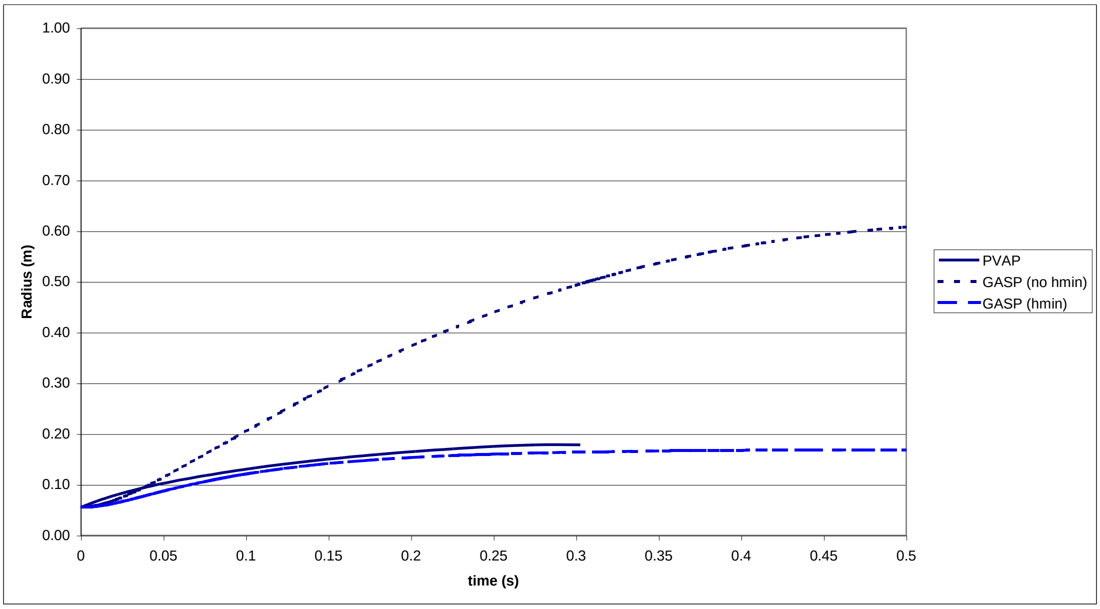

Figure 1. Case spread01. Spreading from a 1kg instantaneous release of water on ground giving a minimum depth of 1cm. The smooth ground GASP result is shown for comparison.

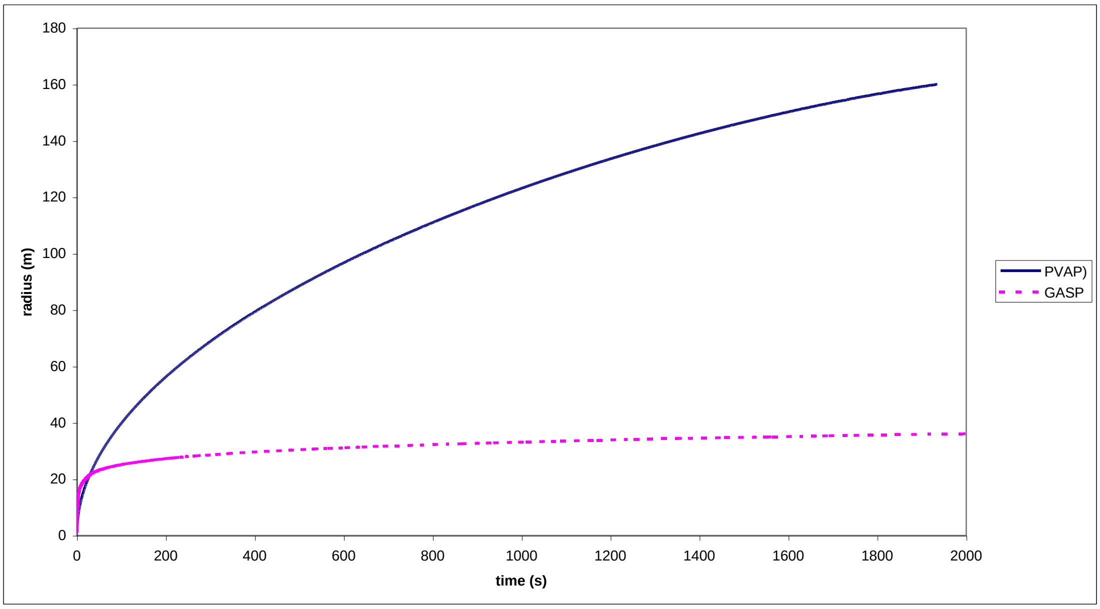

Figure 2. Case spread10. Spreading from a 10te instantaneous release of water on ground giving a negligible minimum depth.

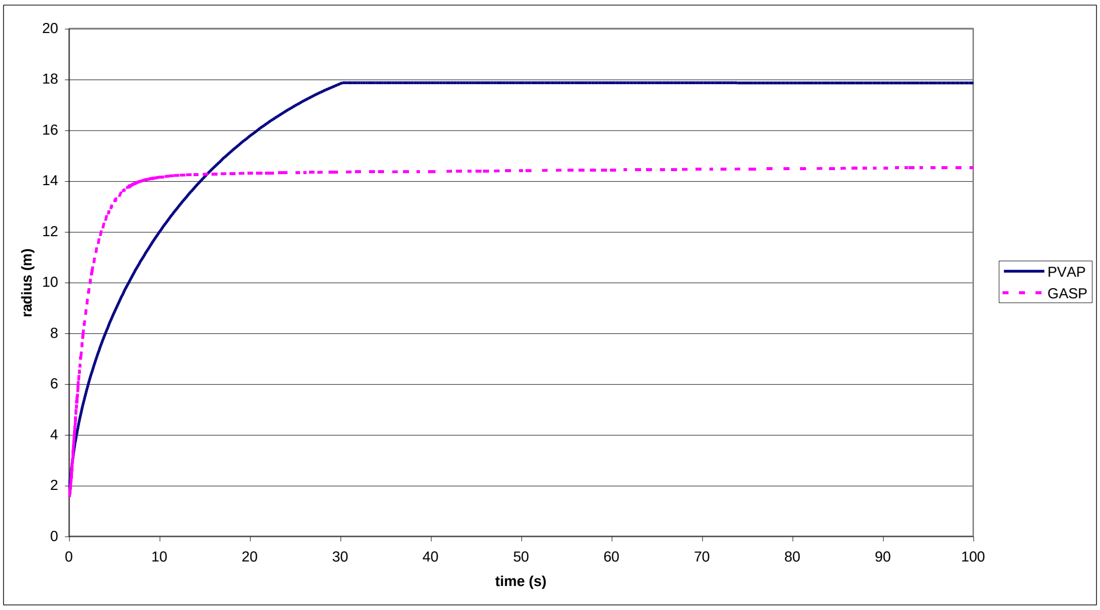

Figure 3. Case spread11. Spreading from a 10te instantaneous release of water on ground giving a minimum depth of 1cm.

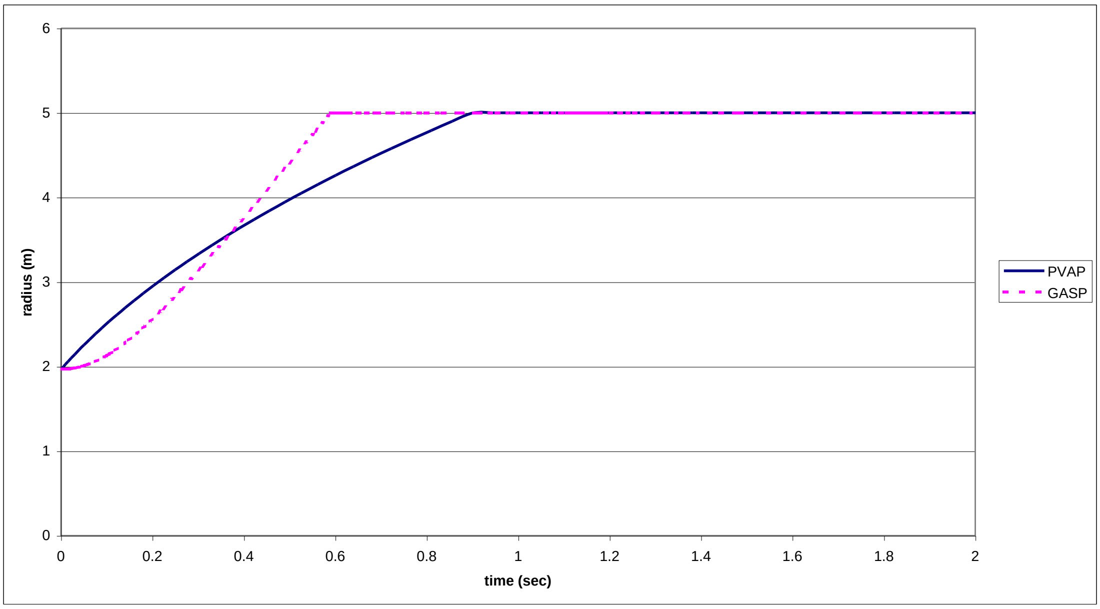

Figure 4. Case boil11. Spreading from a 10te instantaneous release of LNG in a 5m radius bund.

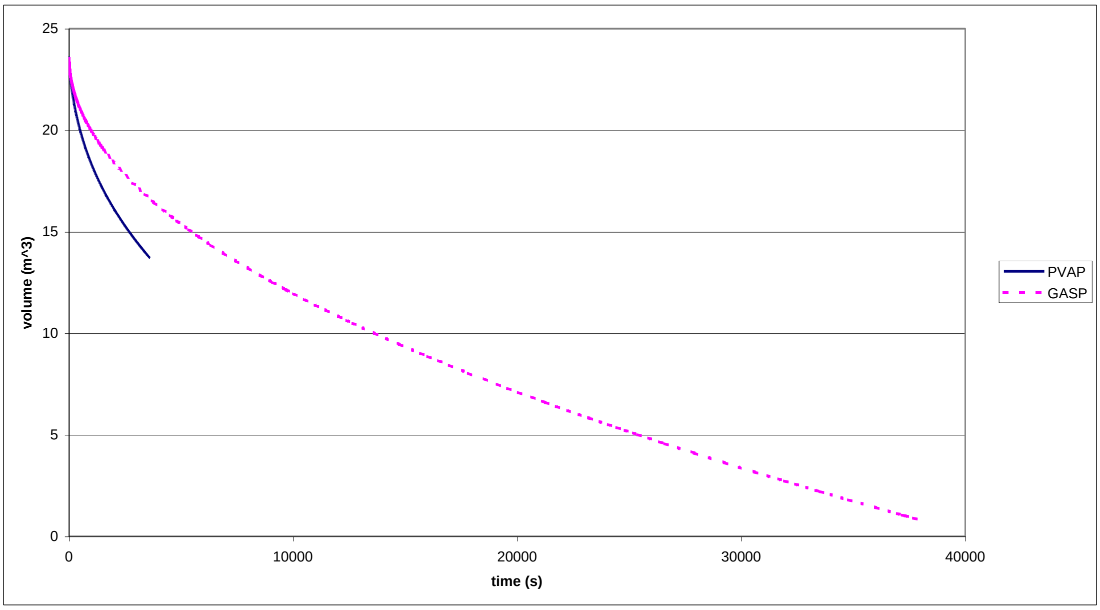

Figure 5. Case boil11. Vaporisation from a 10te instantaneous release of LNG in a 5m radius bund. The graph shows the volume of liquid left in the pool.

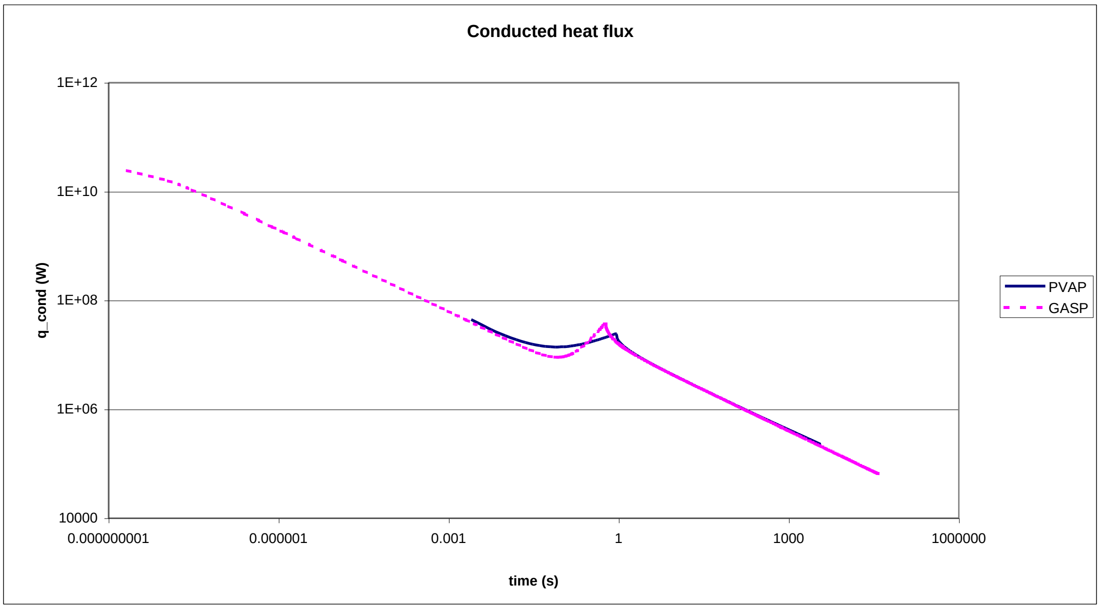

Figure 6. Case boil11. Heat conducted into a 10te instantaneous release of LNG in a 5m radius bund.

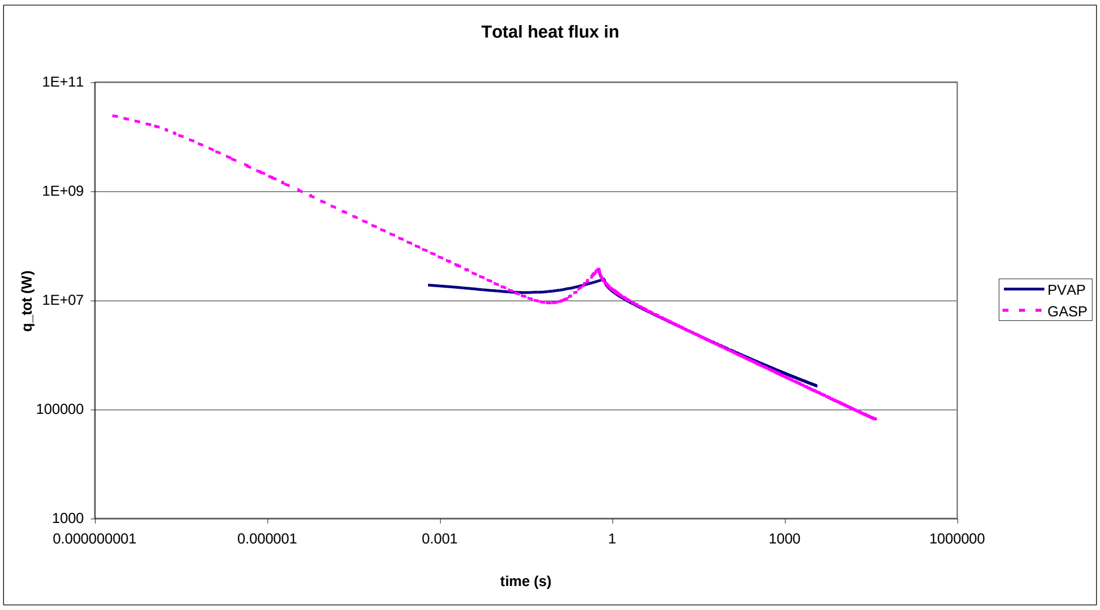

Figure 7. Case boil11. Total heat transfer into a 10te instantaneous release of LNG in a 5m radius bund. This does not include the heat of vaporisation.

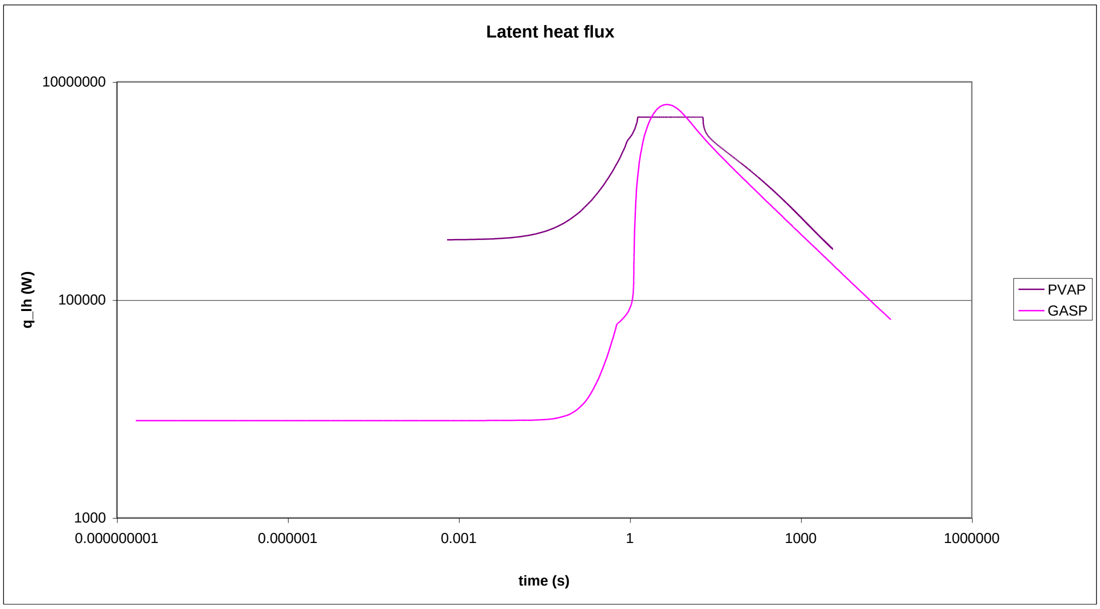

Figure 8. Case boil11. The rate at which heat of vaporisation is extracted from the pool.

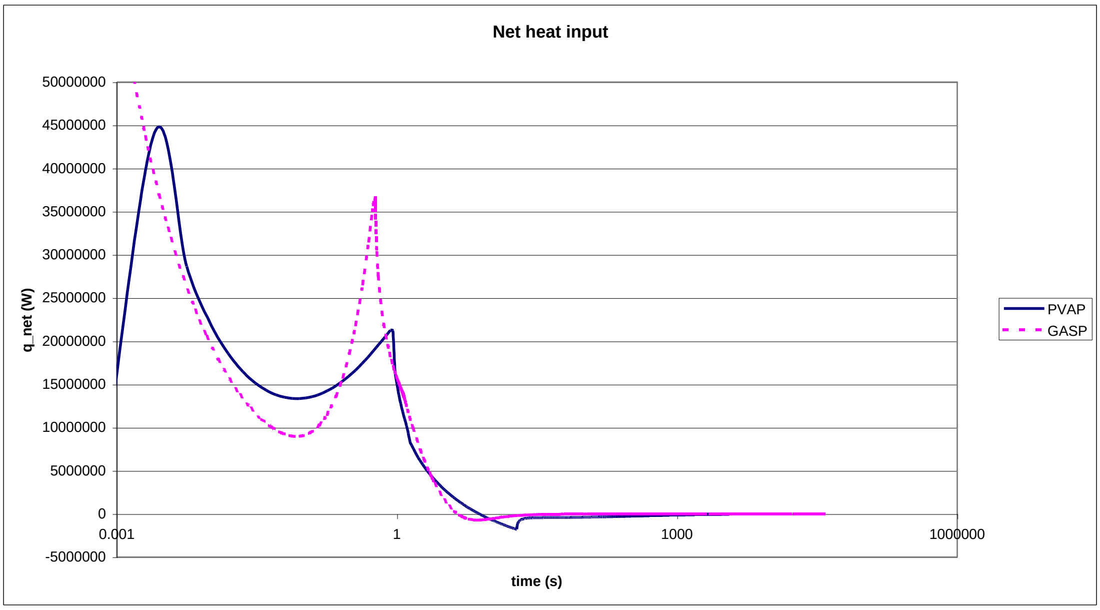

Figure 9. Case boil11. The net heat input (heat in minus heat of vaporisation) to the pool.

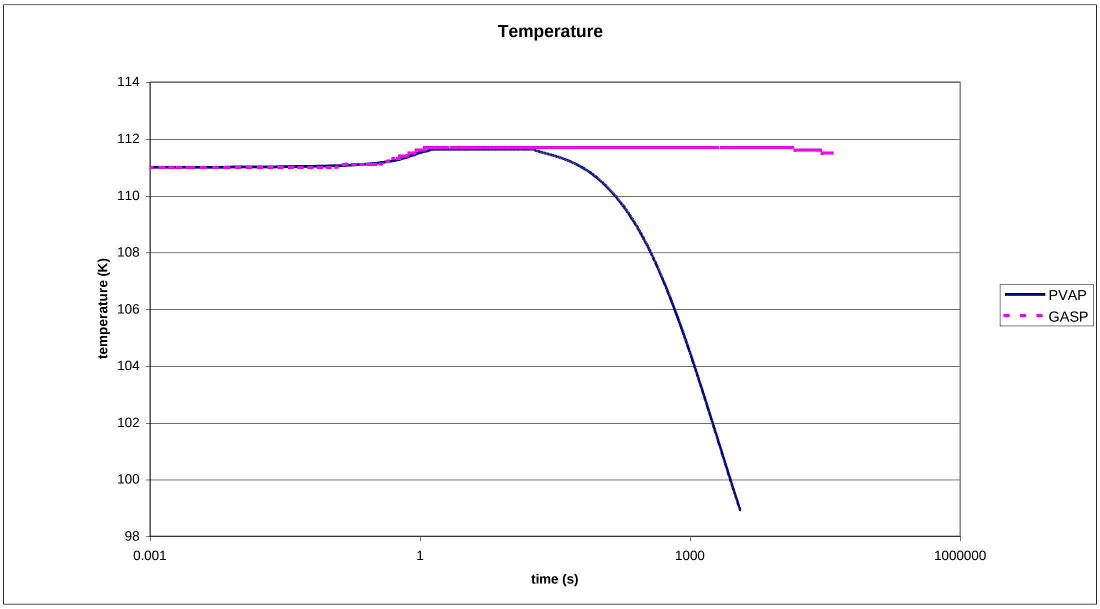

Figure 10. Case boil11. The pool temperature.

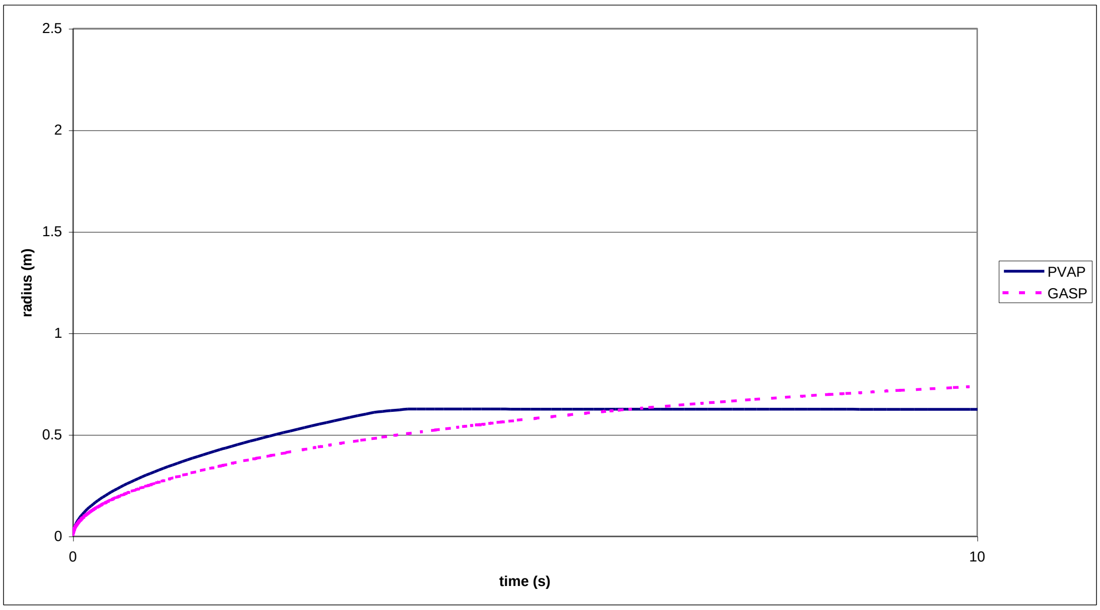

Figure 11: **Case water01.** An instantaneously released 1kg acrilonitrile pool spreading on water

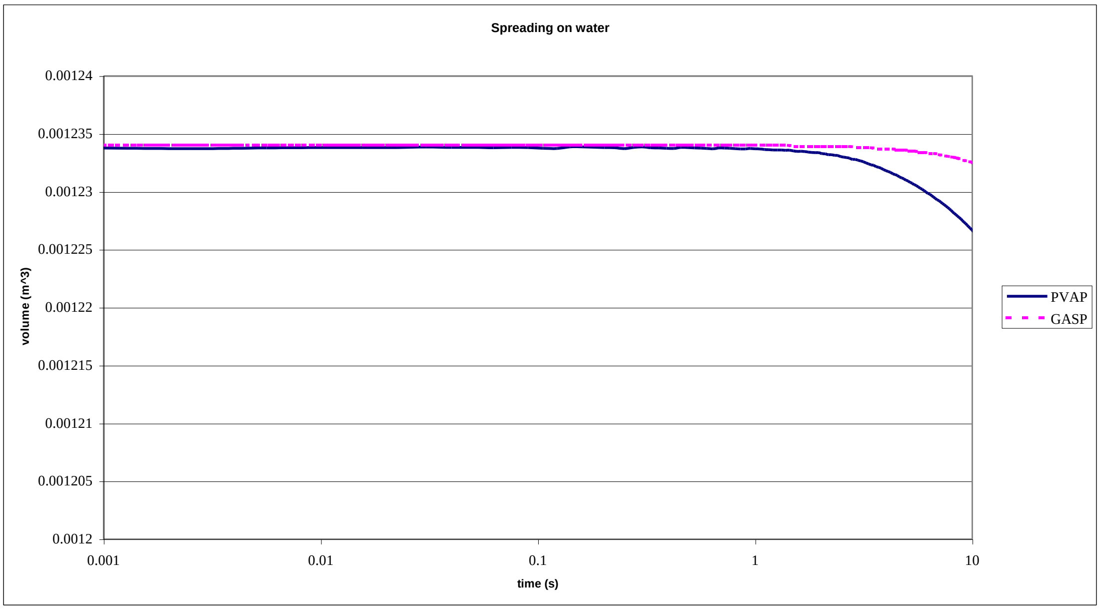

Figure 12: **Case water01.** An instantaneously released 1kg acrilonitrile pool spreading on water

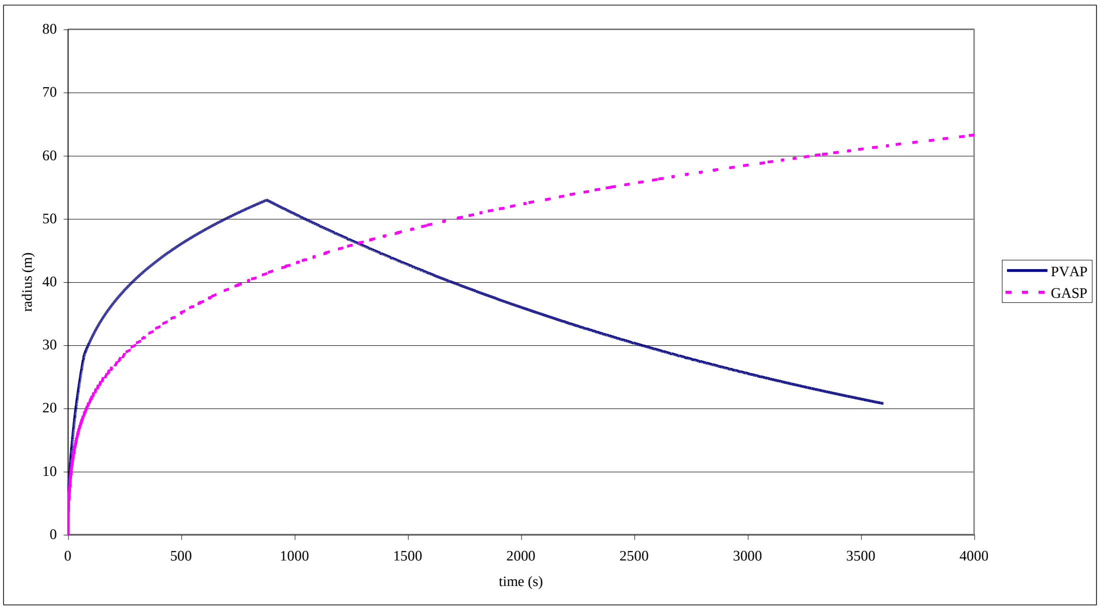

Figure 13: Case water11. An instantaneously released 1kg acrilonitrile pool spreading on water. The difference between models may largely be due to a minimum depth in PVAP which GASP doesn't have for spreading on water.

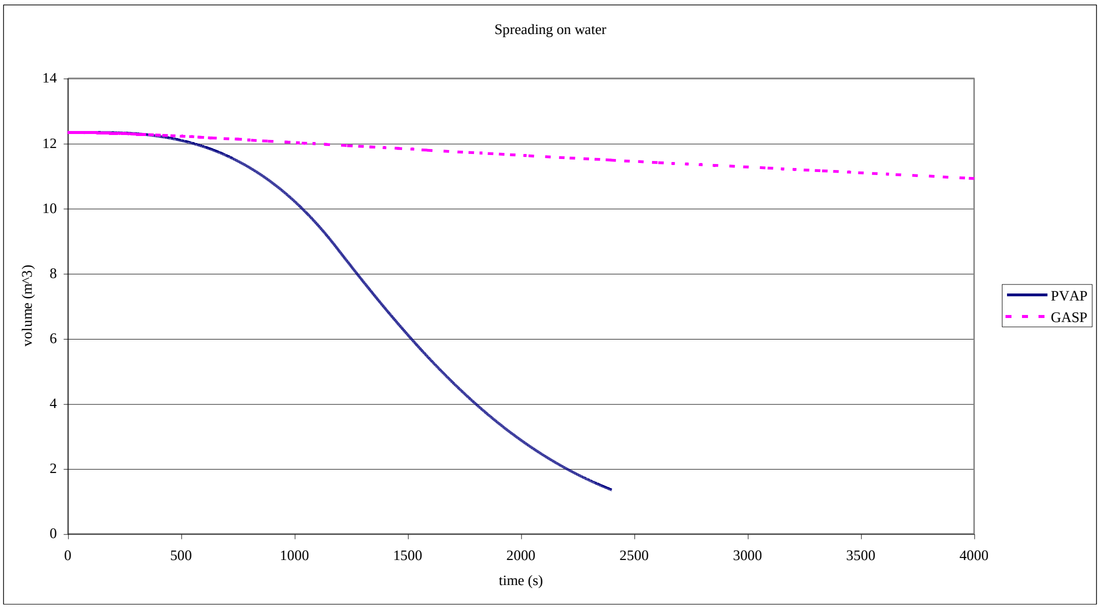

Figure 14: Case water11. An instantaneously released 1kg acrilonitrile pool spreading on water. The differences between models may be largely dissolution which GASP doesn't model.

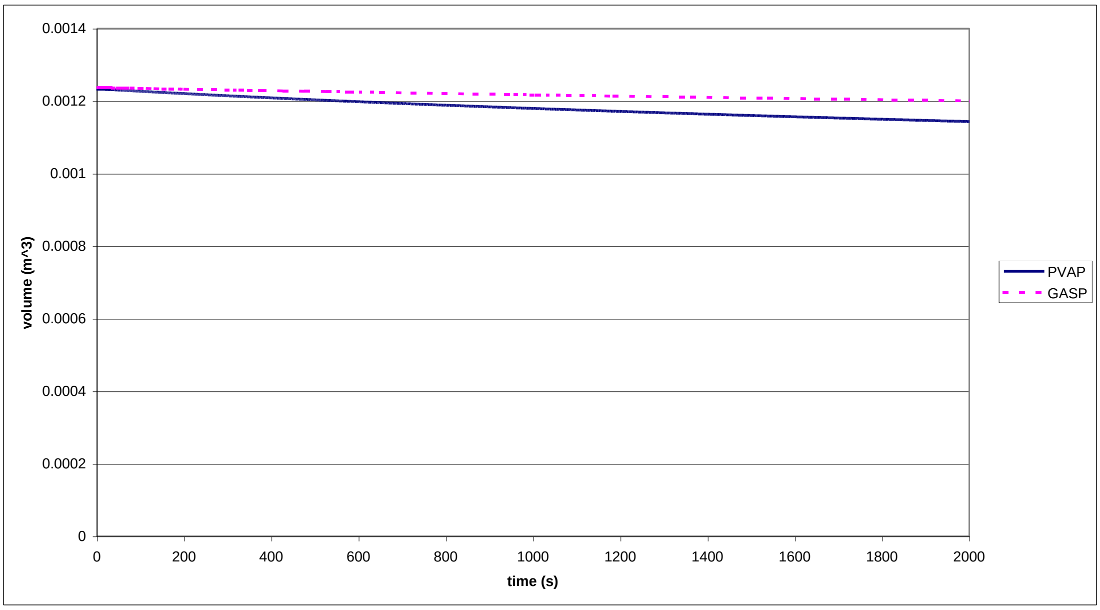

Figure 15: **Case evap01.** A finite volume of acrylonitrile evaporating in a bund. GASP predicts about half the evaporation rate of PVAP.

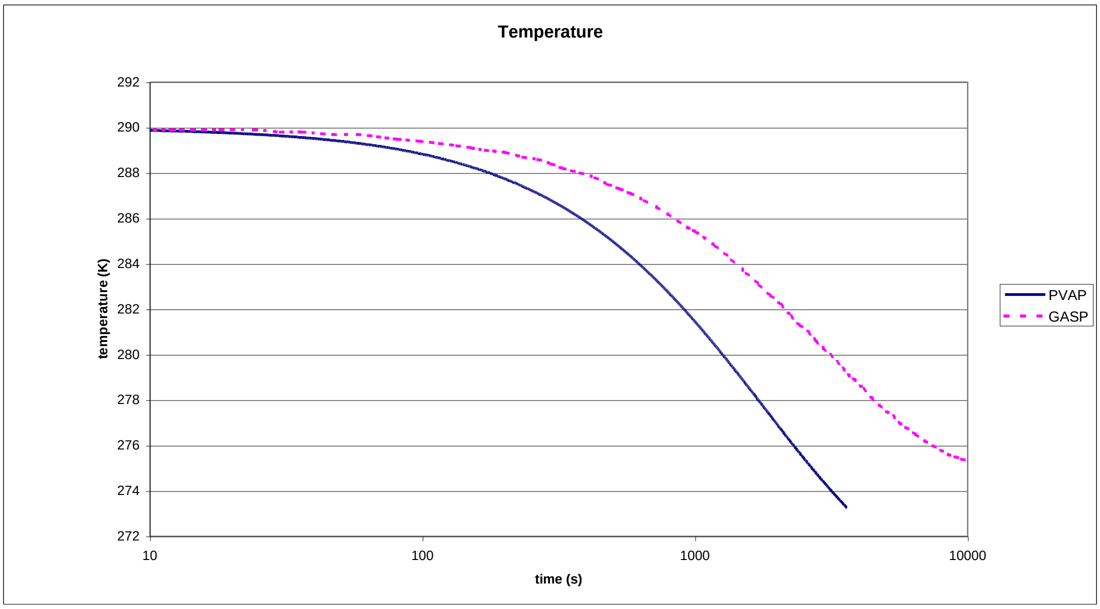

Figure 16: **Case evap01.** A finite volume of acrylonitrile evaporating in a bund. GASP predicts a slower temperature drop than PVAP

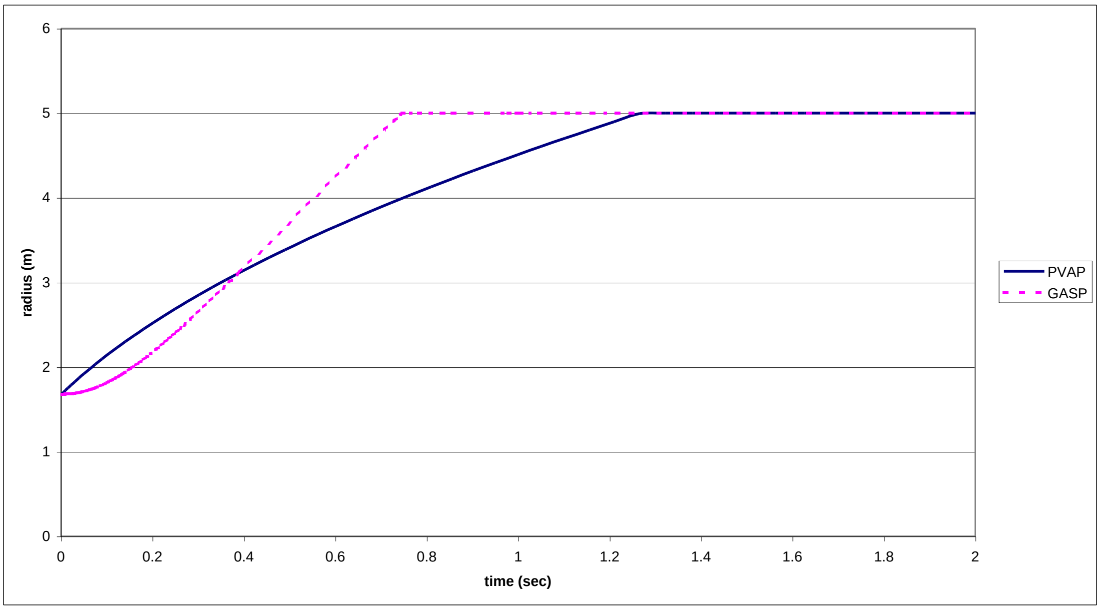

Figure 17: Case evap11. A larger volume of acrylonitrile evaporating in a bund.

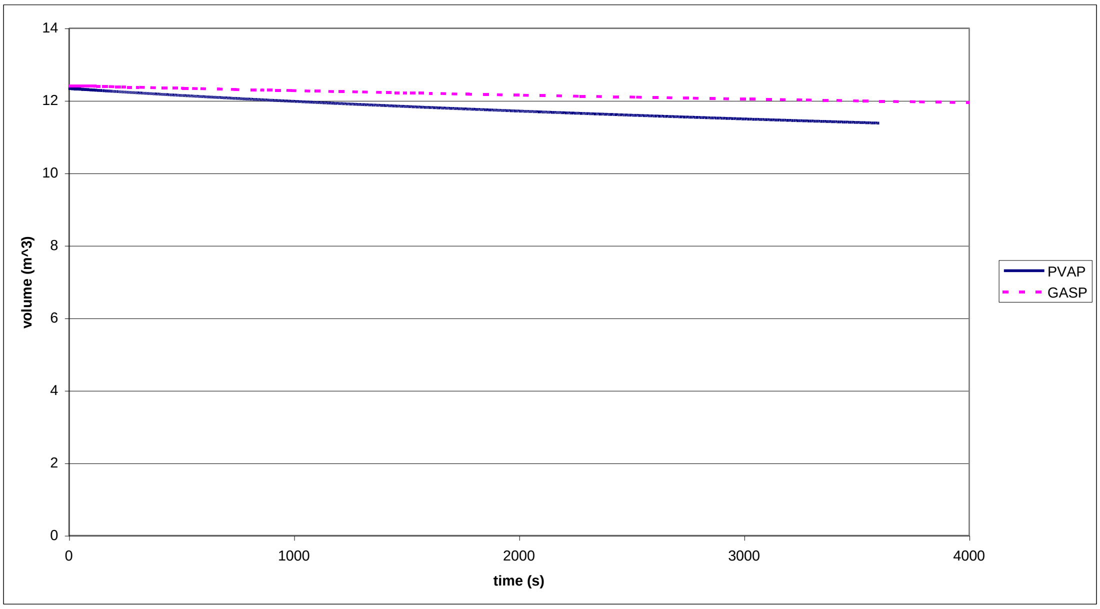

Figure 18: Case evap11. A larger volume of acrylonitrile evaporating in a bund.

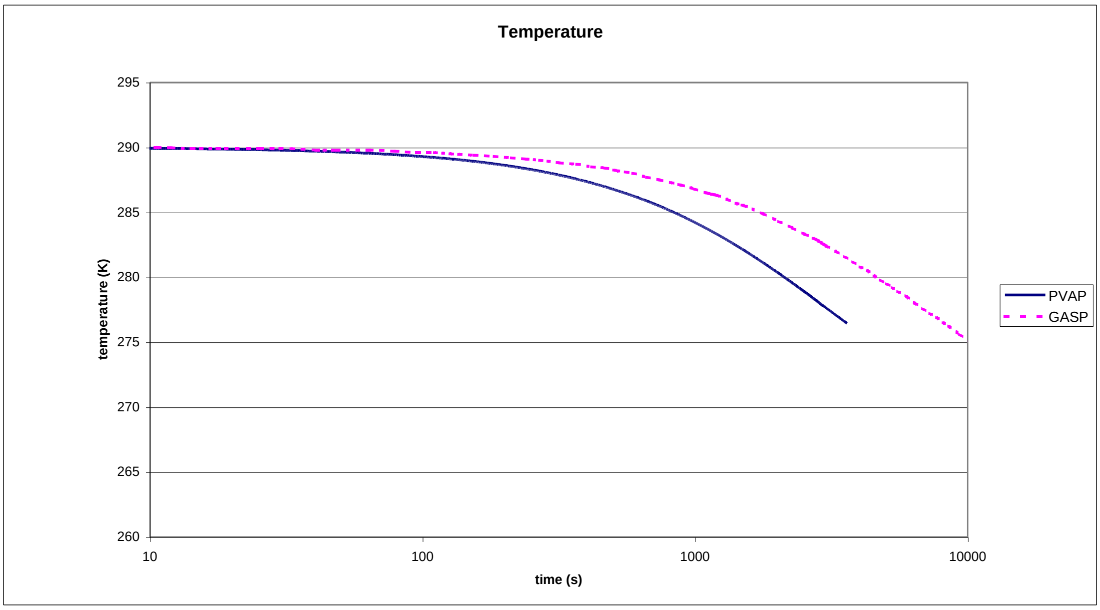

Figure 19: Case evap11. A larger volume of acrylonitrile evaporating in a bund.

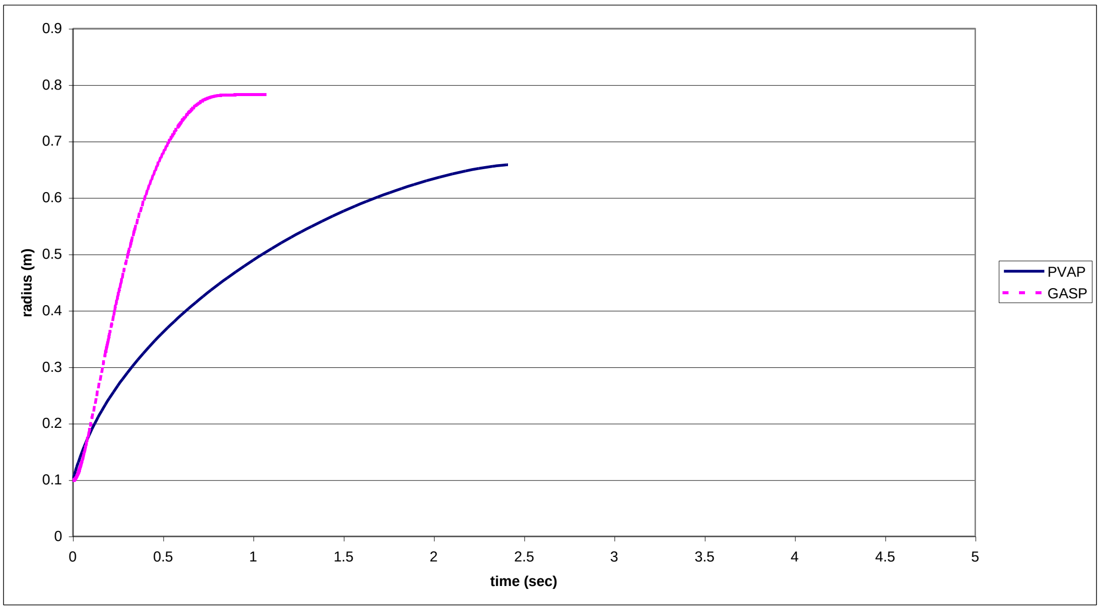

Figure 20: **Case sboil01.** A small unbunded methane release on flat ground.

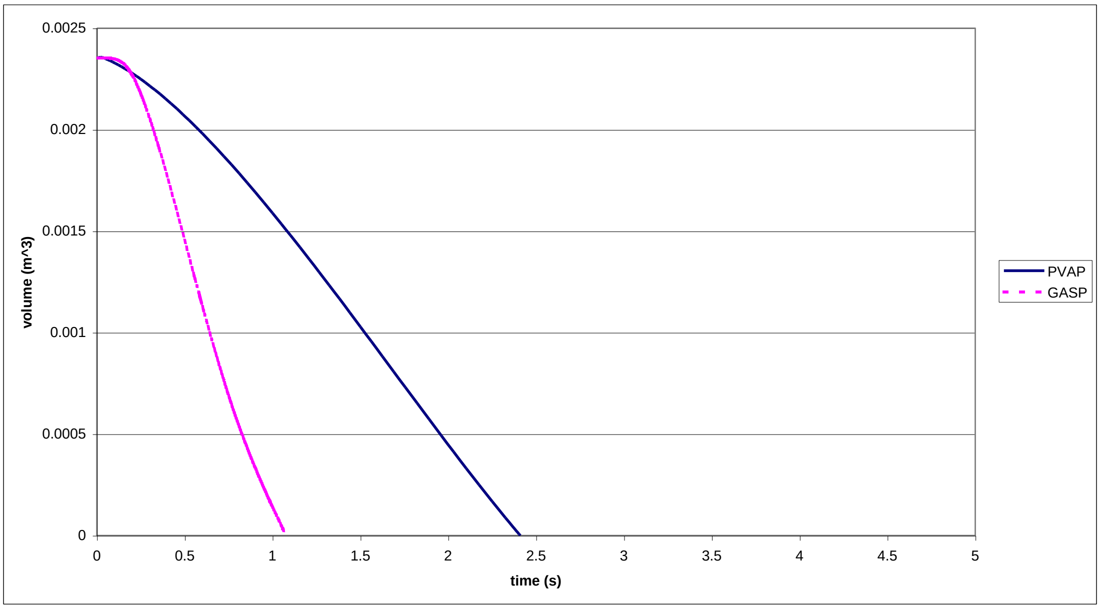

Figure 21: **Case sboil01.** A small unbunded methane release on flat ground.

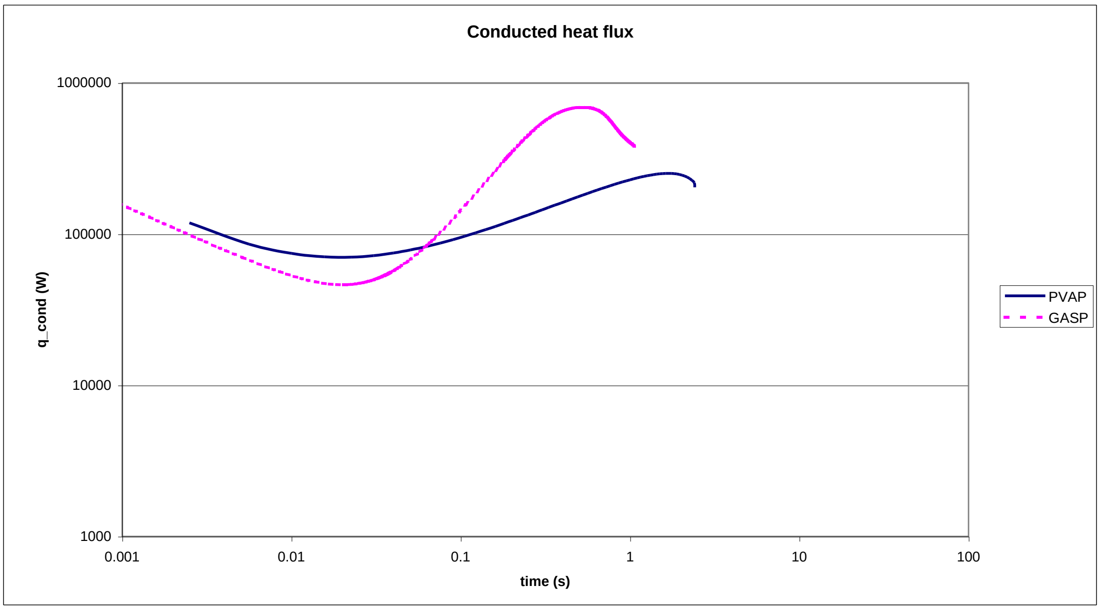

Figure 22: Case sboil01. A small unbunded methane release on flat ground.

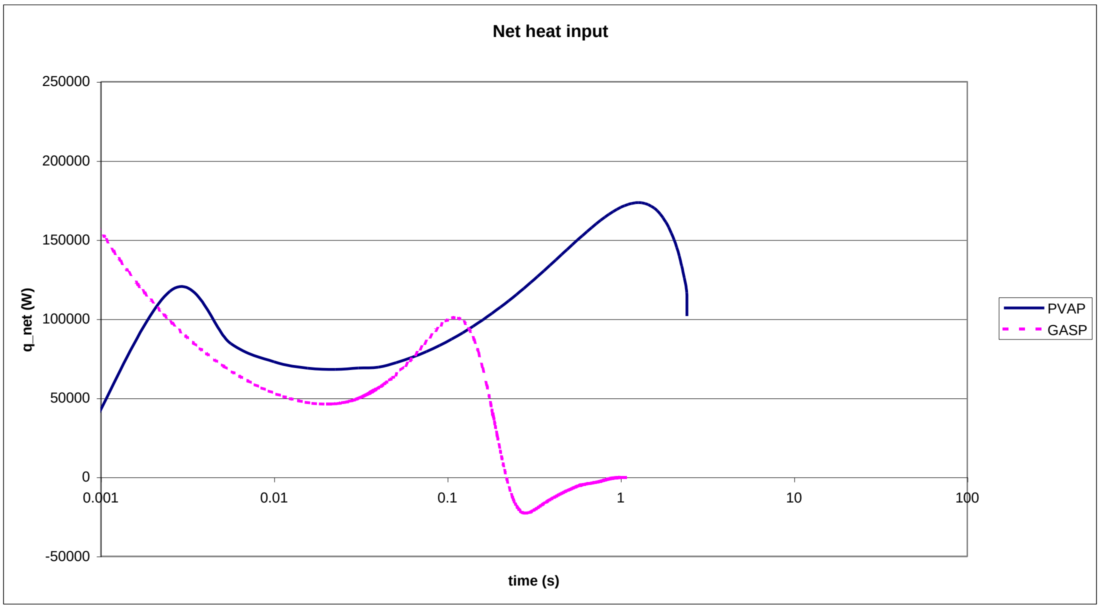

Figure 23: Case sboil01. A small unbunded methane release on flat ground.

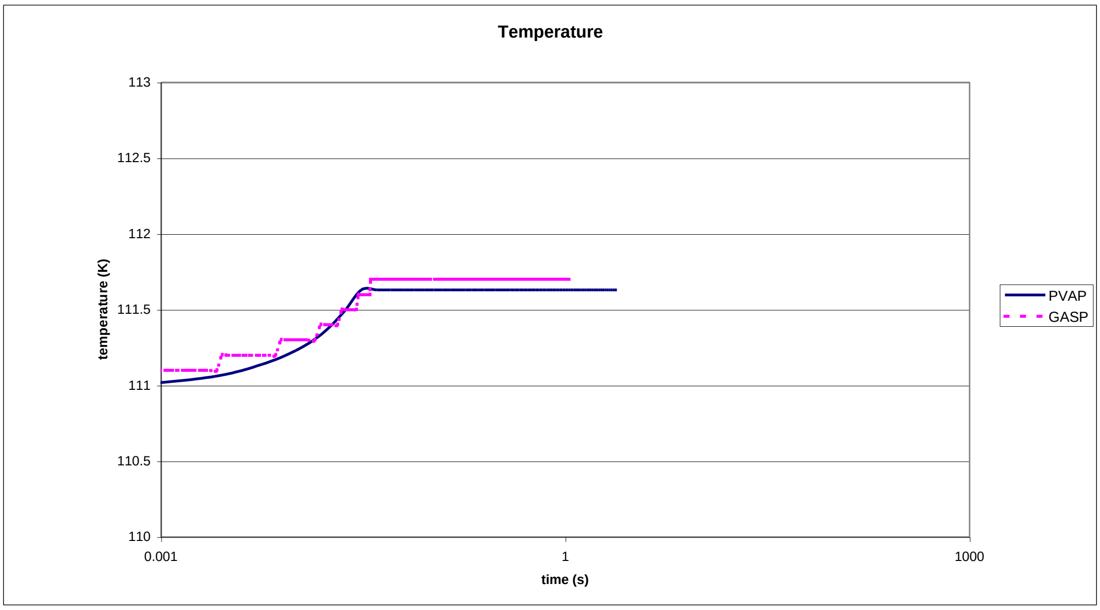

Figure 24: Case sboil01. A small unbunded methane release on flat ground.

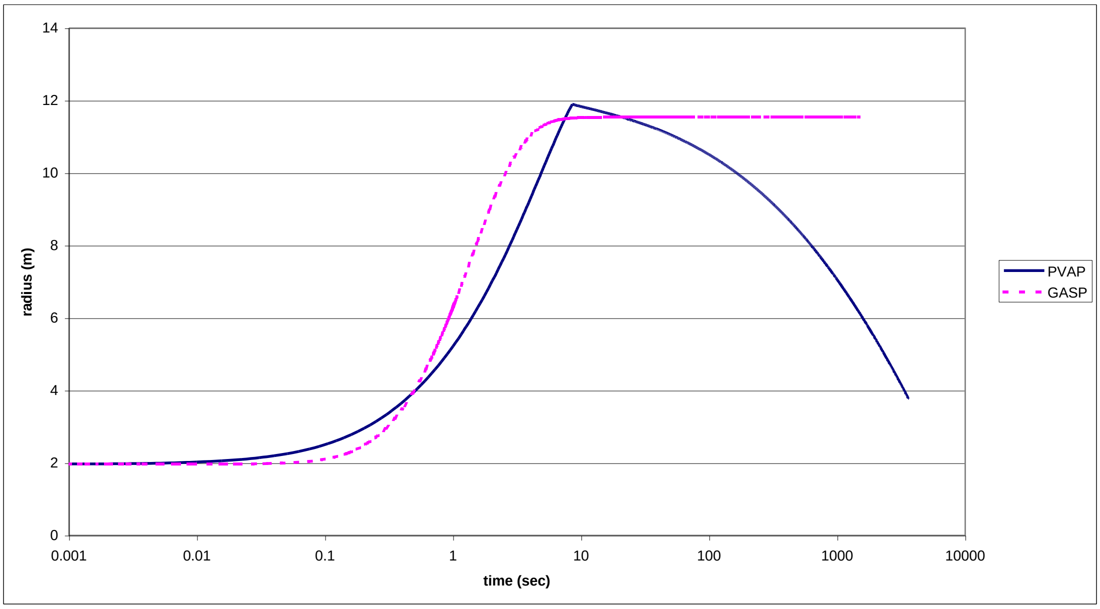

Figure 25: Case sboil11. A large unbunded methane release on ground supporting a minimum depth.

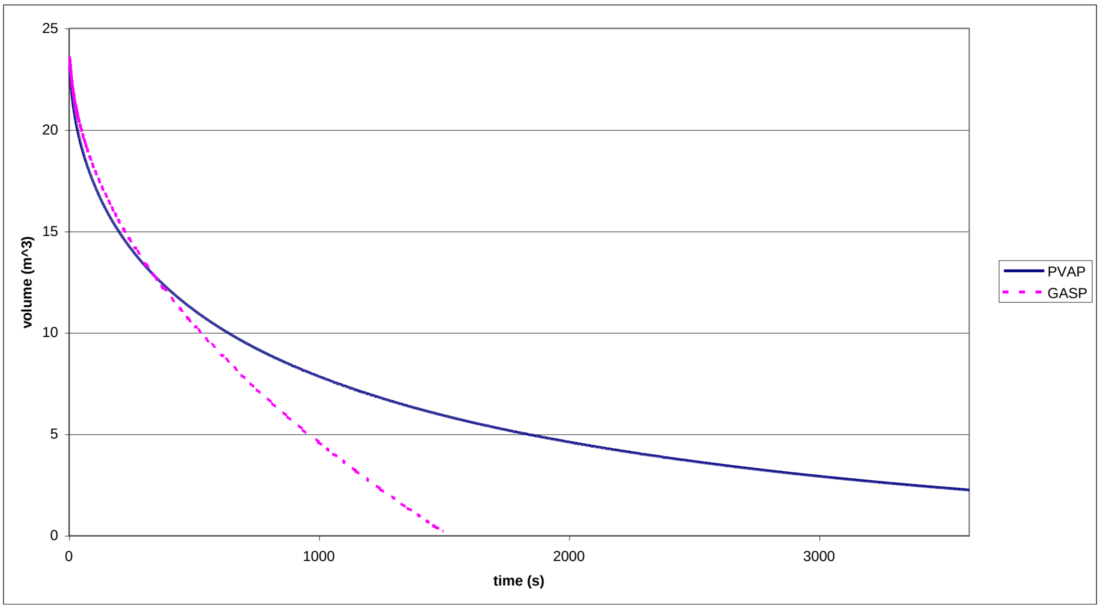

Figure 26: Case sboil11. A large unbunded methane release on ground supporting a minimum depth.

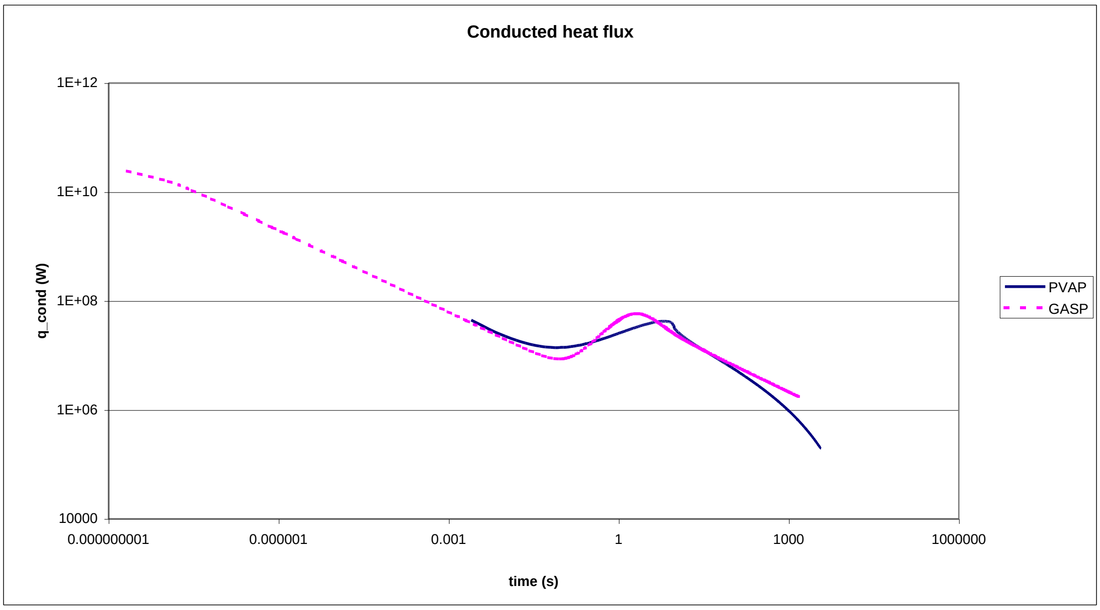

Figure 27: Case sboil11. A large unbunded methane release on ground supporting a minimum depth.

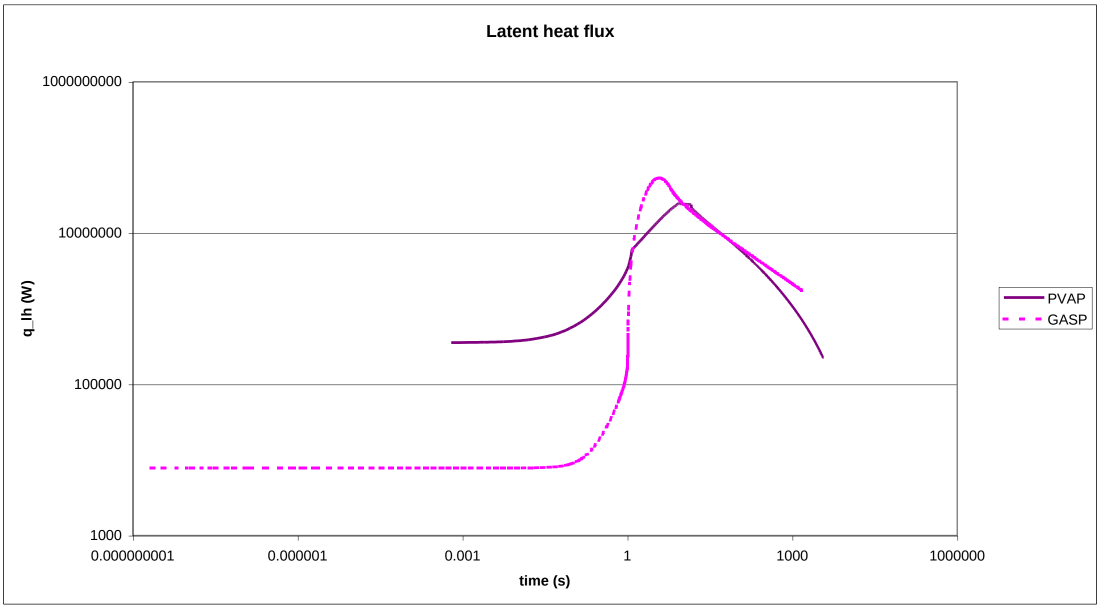

Figure 28: Case sboil11. A large unbunded methane release on ground supporting a minimum depth.

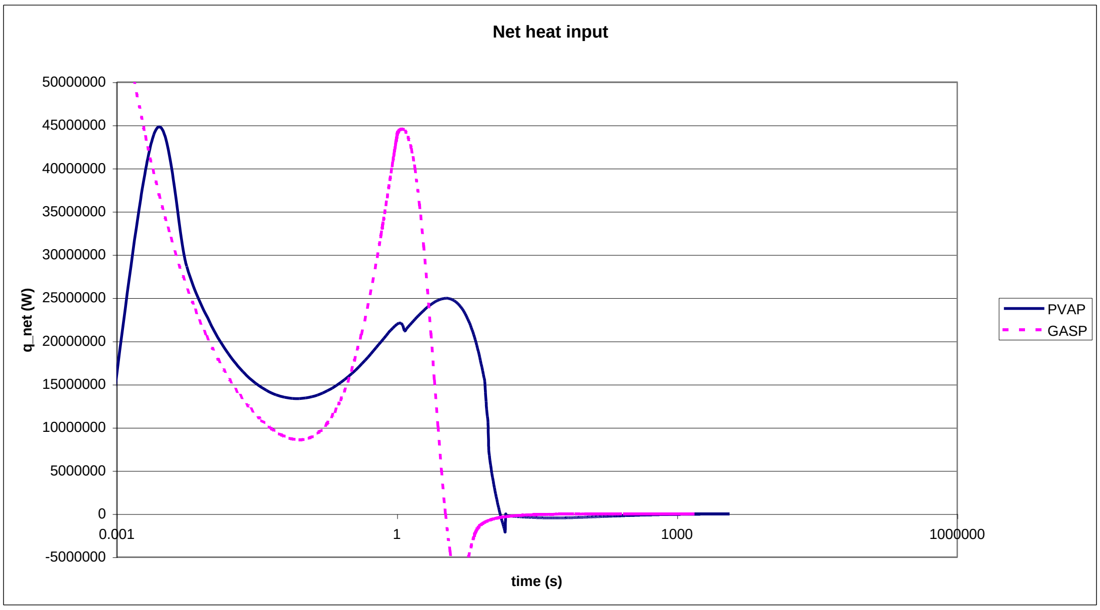

Figure 29: Case sboil11. A large unbunded methane release on ground supporting a minimum depth.

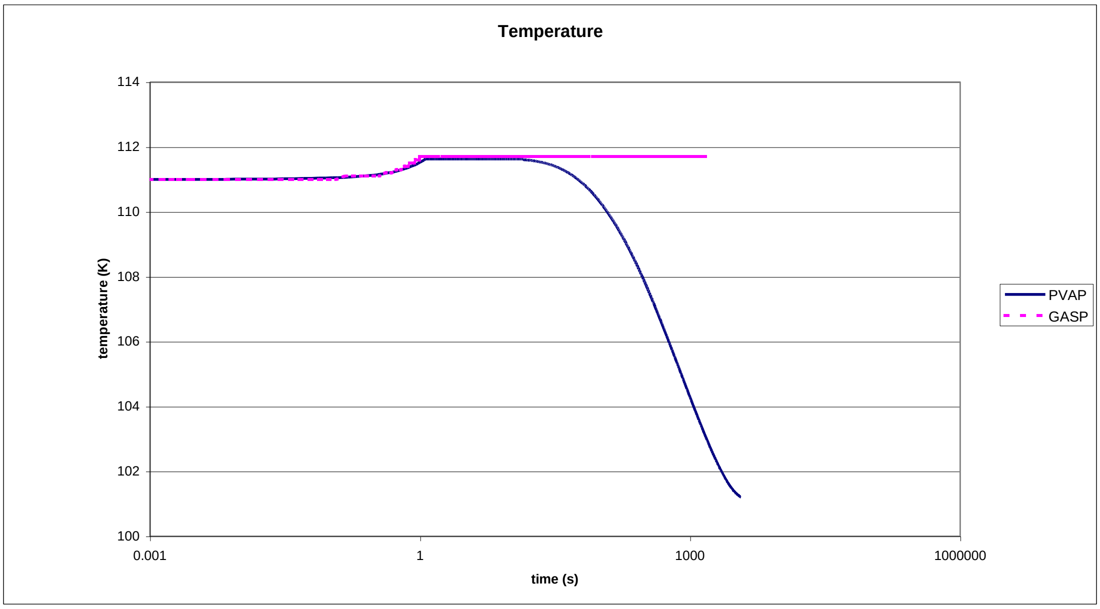

Figure 30: Case sboil11. A large unbunded methane release on ground supporting a minimum depth.

SPREADSHEETS

Figures 1 – 30 – PVAP_GASP_COMP.XLS

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