

Development of a model for Spills of Liquids On Porous Surfaces (SLOPS)

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The Defence Science and Technology Laboratory (Dstl) are required to provide hazard predictions to support planning, operations and post-incident analysis in the event of adversary use of Chemical, Biological, Radiological and Nuclear (CBRN) materials. In order to do this, they require a pool spreading and evaporation model to provide source terms for use with existing dispersion models. However, few existing pool spreading models consider the effects of ground porosity. Existing models of chemical spills tend to assume that the pool spreads over an impermeable surface and the persistence of the pool depends only on the presence of liquid on the surface.

The SLOPS model has been developed as an operational model for Dstl through collaborative work with scientists at the Health and Safety Executive (HSE). It is designed so that it can be used during an incident to quickly estimate the vaporisation of a liquid spill for input to a dispersion model. The SLOPS tool simulates liquid spreading over flat ground, the infiltration of liquid into the porous surface and evaporation from the pool during and after spreading. In order to create a quick-running operational tool, SLOPS is pre-populated with data for a range of substrates and chemicals, meaning data demands and response times are minimised.

The SLOPS model combines the well-established pool spreading and vaporisation model used in GASP (Webber, 1990) with the Green-Ampt model for infiltration (Green and Ampt, 1911). The subsurface evaporation model is an adaptation of models used in water resources engineering, in this case applied to chemical spills, to provide a simplified model of the complex evaporation processes after the pool has completely permeated into the substrate. The coupling of these models applied to non-water substances has not been found in the literature and offers unique insights into the initial evolution of a chemical hazard following release onto porous ground.

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Keywords: Chemical spills, porous surfaces, infiltration, model development, liquid spill model, Green-Ampt, GASP

Introduction

The Defence Science and Technology Laboratory (Dstl) are required to provide hazard predictions to support planning, operations and post-incident analysis in the event of adversary use of Chemical, Biological, Radiological and Nuclear (CBRN) materials. To do this they employ a range of hazard prediction tools, including atmospheric dispersion models. Dstl require a pool spreading and evaporation model to provide source terms for use with existing dispersion models. These models are used to predict aspects of the dispersing cloud such as size, concentration and persistence under various weather conditions. However, few existing pool spreading models consider the effects of ground porosity but instead assume that the pool spreads over an impermeable surface and the persistence of the pool depends only on the presence of liquid on the surface.

Liquid spills can infiltrate into the ground during spreading and remain there long after the pool expansion ceases and after the above surface liquid has evaporated. In terms of liquid pool sizes and consequent dispersing vapour cloud sizes, the assumption that the surface is impermeable is often a cautious estimate since the experimental data that exists for these cases has shown that the liquid does not travel as far over permeable surfaces (Ruddle, 1986; Belore et al., 1986). However, ignoring permeation could potentially underestimate the persistence of the hazard, particularly in cases where the liquid remains present for long durations, eg. a number of days. This is particularly important to emergency responders for setting exclusions zones and defining when it is safe for the workforce or the public to re-enter an area. Equally, overestimating the airborne hazard can lead to costly and inconvenient evacuations of unnecessarily large areas.

This paper presents a new source term model for spills of liquid on porous surfaces (SLOPS). The SLOPS model has been developed as an operational model for Dstl through collaborative work with scientists at the Health and Safety Executive (HSE). It is designed so that it can rapidly provide estimates of the vaporisation of a liquid spill for input to a dispersion model in order to be of use in operational time-frames (i.e. minutes). The SLOPS tool simulates liquid spreading over flat ground, the infiltration of liquid into the porous surface and evaporation from the pool during and after spreading.

Pool formation and spread has been studied in various contexts at scales from a cup of liquid on a pavement (Simmons et al., 2004) to dam breaks (Morris, 2000). In this study it is assumed that the formation of the pool can be classed as either instantaneous or steady continuous. For an instantaneous release, the liquid is initially assumed to be contained and quiescent and collapses under gravity when released and forms a pool. For a continuous release, the pool will continue to expand due to the addition of fresh material. Examples are sudden and total loss of containment from a storage vessel, or pipe failure (at ambient pressure), respectively.

There are many relevant factors that can affect pool spread. The properties of the liquid are important, e.g. viscosity and surface tension, and its interaction with the environment, which potentially results in evaporation, boiling and chemical reactions. The permeability of the ground results in loss of mass from the above surface pool and can cause multi-phase effects such as bubbles, which can affect the above surface pool spread and infiltration (Ruddle, 1986). Ground roughness, topography and obstructions have a significant effect on pool size and distribution.

Infiltration and subsurface flow are complex three-dimensional processes by which surface liquid passes into a substrate and flows beneath the surface. Flows over porous media and infiltration have been the focus of research in agriculture (e.g. Green and Ampt, 1911), fuel storage or transport (e.g. Moorhouse and Carpenter 1986) and handling of toxics (e.g. Parker and Nally, 2012), among other fields. The amount of liquid, or liquid head, above the ground affects infiltration and subsurface flow. As for above surface pool spreading, the properties of the infiltrating liquid are important, affecting the rate of infiltration and subsurface transport. Cryogenic liquids may cause freezing of water and other subsurface liquids and, depending on the substance, the presence of water or other liquids within the ground can cause chemical reactions, or simply affect available pore space.

The properties of the substrate and its heterogeneity are important factors impacting on capillary action and the movement of liquid in the subsurface (Or et al., 2013). The interaction between the spilled liquid and particulate or granular substrates, e.g. sand or gravel, can result in moveable beds and erosion (Ruddle and Widdowson, 1985). Whether a liquid is hydrophobic or hydrophilic and the wettability of the substrate are also relevant (Or et al., 2013). ‘Boundary’ features such as the ground water level or an impermeable layer might also need to be considered.

Evaporation is the process by which mass is lost from the liquid pool from above (pool evaporation) and eventually below (subsurface evaporation) the ground surface. Pool evaporation has been reasonably well investigated, in particular by the chemical storage industries including for cryogenic liquids (e.g. MacKay and Matsugu, 1973; Brighton, 1985; Bubbico and Mazzarotta, 2016).

When all the liquid is predicted to have permeated into the substrate then there is no longer any surface pool spreading, but evaporation may continue. There is extensive research into subsurface evaporation in the context of water resources engineering. Therefore, the bulk of the research to date focusses on water. For water in bare soil it is generally accepted to be a two-stage process (e.g. Or et al., 2013), although the transition between stages is not well understood. The first stage, Stage 1, is where moisture is available at, or is readily transported to, near the soil surface. In this stage, the evaporation is controlled by the surface evaporation which is governed by the surface and air temperature, insolation and wind. The second stage, Stage 2, is where the hydraulic transport of subsurface liquid to the soil surface is unable to supply water at the surface evaporation rate and the evaporation is controlled by subsurface water transport. The transition from Stage 1 to 2 is governed by the readily evaporable water (REW) available (Allen et al., 2005). Stage 2 is bounded by a zero flux plane, estimated experimentally to be between about 0.1 – 0.2 m, below which gravity dominates and flow is downward (Brutsaert, 2014).

The properties of the liquid have a significant effect on evaporation. Atmospheric conditions such as wind speed, surface roughness length and solar radiation as well as the temperature of the ground will affect both the pool evaporation and subsurface evaporation. Day and night cycles will also affect the evaporation rates. The type of substrate and its heterogeneity will affect subsurface evaporation with experimental data suggesting that the evaporation rate is higher for heterogeneous substrates. Conversely, properties such as lower wettability of the substrate can reduce evaporation rates (Or et al., 2013).

Models for the physical processes discussed above are fairly well developed and applied in their individual fields of study but rarely combined into one model. The many factors associated with the processes mean that they are frequently complex and it is not a simple task to interface existing models together, e.g. coupling pool spreading to subsurface flow.

For pool spreading, the shallow water equations (essentially neglecting vertical motion) are most frequently used and either reduced further to one-dimensional integral models (Webber, 1990) or solved as one or two-dimensional shallow water models (Linden et al., 1999; Webber et al., 2009; Keller and Simmons, 2005).

Most infiltration and subsurface flow models are derived from the Darcy equation, which is often either extended to the Richards equation (Richards, 1931) to account for unsaturated flow, or simplified depending on the application. A popular simplification is the one-dimensional downward penetrating sharp front model of Green and Ampt (1911), for which an analytical solution can be derived. The model requires few inputs (hydraulic conductivity, effective porosity and suction head) which can be obtained from experimental data for specific substrates but are commonly referenced to Rawls et al. (1983). Dedicated subsurface flow models are three-dimensional, multi-phase and multi-component, for example the EPA model STOMP (White and Oostrom, 2006).

For pool evaporation, MacKay and Matsugu (1973) is a commonly used empirical model, but Brighton (1985) questioned the validity of this correlation when applied at larger scales and proposed an alternative model. Both approaches have been adopted to model evaporation in various pool spreading models (e.g. Webber (1990); Keller and Simmons, 2005; Fabbri et al., 2017).

Subsurface evaporation models are mostly empirical with experimental datasets providing the evaporation rates for the staged process. In the first stage, when it is assumed that capillary action can maintain a wetted surface, the evaporation rate is still dominated by the atmospheric conditions and can be approximated using pool evaporation models. There are similarity solutions for the second stage (Brutsaert, 2014) and data for the REW (Allen et al., 2005) providing the switching point between the two stages. There do not appear to be any continuous models for the complete subsurface evaporation process.

In their review, Simmons and Keller (2003) conclude that a two-dimensional shallow water model is ideal for non-aqueous phase liquids (NAPLs), coupled to a multi-phase, multi-component subsurface flow model. However, they also acknowledge that the coupling is complicated and is much simpler with models such as Green-Ampt. They find only one model that includes spreading and infiltration (Hussein et al., 2002). However, there are other models available. For example, Belore and McBean (1986), LPOOL (Woodward, 1990), LSMS (Linden et al., 1999) and, more recently, STAWaRS (Tickle et al,

2014). As mentioned previously, no examples could be found of models for spreading, infiltrating pools that include subsurface evaporation once the above surface pool has evaporated.

Experimental datasets which provide suitable data for validating models of spreading evaporating pools over porous surfaces are scarce. Belore and McBean (1986) measured pool size and permeation depth for water and ‘doped’ water (increased viscosity), spilled onto plywood and turf over loosely packed soil. Both two and three dimensional tests were undertaken with liquid released continuously into the centre of the domains via a slot (2D) or a hole (3D) and a range of flow rates. The scale of the two dimensional releases was 10 m x 0.4 m and the three dimensional releases were 3 m square. The data has been used for model validation purposes previously by Woodward (1990) so it should be suitable for future validation work.

There are other experimental datasets available for spills onto porous surfaces, but they are not suitable for validating the present model. Simmons et al. (2004) and Simmons and Keller (2005) present a set of small scale experiments for a range of different liquid spills on concrete and other surfaces but they are all on sloping ground and the model developed here assumes flat ground. Ruddle and Widdowson (1985) and Ruddle (1986) carried out a series of experiments in a 10 m channel instantaneously releasing water over painted surface, corrugated plastic, two different sizes of shot and gravel with both moveable and fixed beds. The work provides some nice videos of infiltration into porous beds but the data are not suitable for model validation here. Moorhouse and Carpenter (1986) performed experiments with LNG spilled onto concrete and soil but this has the added complexity of a cryogenic liquid, for which the current model is not applicable.

In the following sections of this paper, an overview of the SLOPS model is provided and a discussion of verification and validation efforts. The paper concludes with potential future directions for the model.

SLOPS model development

SLOPS models the spreading and evaporation of non-boiling volatile liquids spilt onto porous ground. The time varying output from SLOPS is intended to act as a source term model to provide input for modelling subsequent dispersion of the evaporated vapour. The ground surface is assumed to be horizontal, but may include a bund and/or uniform undulations that restrict the pool spread. Either instantaneous or steady continuous spills can be modelled. The main features of the model are shown schematically in Figure 1 and elaborated further in this section.

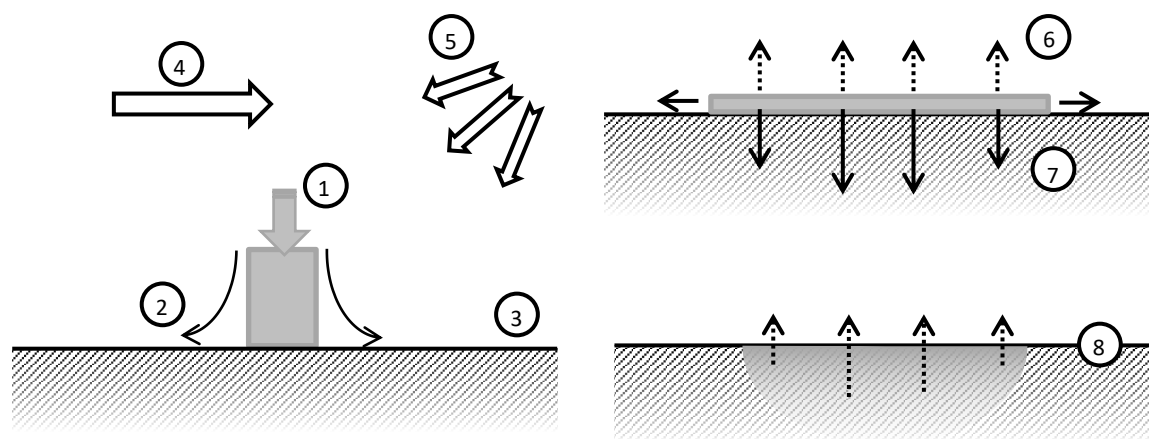


Figure 1 Schematic showing the main features of the SLOPS model. (1) Instantaneous or steady continuous discharge, (2) Pool spreading, (3) Horizontal surface with uniform undulations restricting pool spread, (4) Atmospheric conditions, (5) Solar effects, (6) Surface liquid evaporation, (7) Infiltration into the porous substrate, (8) Sub-surface evaporation.

SLOPS is based on the well-established model GASP¹, which is a 1D axisymmetric integral model for pool spreading and vaporisation over impermeable horizontal surfaces. GASP is based on the original works of Webber (1990), which implements the evaporation model of Brighton (1985). This is also the basis for the EU model ADAM (Fabbri et al., 2017) and the TNO Yellow Book (Van den Bosch and Weterings, 2005). GASP has been evaluated by HSE (Webber et al., 2010) and is subject to ongoing validation, both within and outside of HSE, as experimental data becomes available (Webber and Jones, 1987; Webber, 1991; Batt, 2014; Fabbri et al., 2018; Ulumuddin et al., 2018).

The model consists of a number of coupled ordinary differential and algebraic equations describing the evolution of the pool over time. The differential equations of the model have the form:

¹ Gas Accumulation over Spreading Pools <https://www.esrtechnology.com/index.php/services/safety-and-risk-management/managing-safety-and-risk/consequence-analysis/2-uncategorised/226-gasp> Accessed on 16th January 2020

$$\begin{aligned}
\frac{dR}{dt} &= \dots \\
\frac{dU}{dt} &= \dots \\
\frac{dV}{dt} &= \dots \\
\frac{dT}{dt} &= \dots
\end{aligned}
\tag{1}$$

where R is the radius of the pool, U is the radial velocity at the edge of the pool, V is the volume of the pool, T is the temperature of the pool. R , U , V and T are denoted as “primary” variables. The model is specified by defining the right-hand sides of the equations in (1) in terms of “secondary” variables derived from the primary ones. In general, the secondary variables are algebraic functions of the primary variables. Exceptions are heat conduction into the pool and infiltration into the porous substrate – these are expressed as integrals over time. This results in a system of integro-differential equations. The mathematical equations for GASP are presented in full by Webber (1990) and are not reproduced here.

At present, GASP does not model infiltration into porous terrain, subsurface flow or subsurface evaporation. Therefore, for infiltration SLOPS uses the popular Green-Ampt model and the two stage subsurface evaporation process is modelled using the surface vaporisation model of Brighton (1985) in Stage 1 and the diffusion similarity model of Brutsaert (2014) in Stage 2. The Stage 2 evaporation model is an adaptation of models used in water resources engineering, in this case applied to chemical spills, to provide a simplified model of the complex evaporation processes after the pool has completely permeated into the substrate. The coupling of these models applied to non-water substances has not been found in the literature and offers unique insights into the initial evolution of a chemical hazard following release onto porous ground.

The complete set of mathematical equations for SLOPS are presented in full in Batt and Tickle (2019).

Material Balance

The total volume, V_{total} of the liquid spill is given by

$$\frac{dV_{total}}{dt} = Q_{sorc} - \frac{q_{evap}}{\rho_L} A
\tag{2}$$

where

q_{evap} is the mass evaporation rate per unit area from the pool surface (as for GASP)

A is the top area of the pool

ρ_L is the liquid density

Q_{sorc} is the volumetric discharge rate into the pool and may be zero (an instantaneous release) in which case V_{total} is initially non-zero. Otherwise Q_{sorc} may be a specified function of time (for example $Q_{sorc} = \text{constant}$ for a fixed period and zero thereafter) and there may or may not be liquid in the pool initially.

Since the pool may seep into porous ground, it is useful to differentiate between the volume of the pool above the ground, V_{pool} , and the volume of liquid permeated below the ground, V_{sub} :

$$V_{total} = V_{pool} + V_{sub}
\tag{3}$$

The quantity of liquid permeated below the ground is given by

$$\frac{dV_{sub}}{dt} = Q_{sub}
\tag{4}$$

Where Q_{sub} is the volumetric infiltration rate of liquid into the porous substrate (specified below).

Evaporation

Evaporation from the above surface pool is modelled in SLOPS in the same way as in GASP. When all the liquid is predicted to have permeated into the substrate then there is no longer any surface pool spreading but evaporation continues. SLOPS models the post-spreading phase of evaporation as follows:

1. Evaporation continues at the same rate as for the wetted surface (like STAWaRS, Tickle et al., 2014).
2. After a delay, vaporisation decays according to empirical evidence from long-term (over days) drying of bare soils (based on Brutsaert, 2014).

The vaporisation decay model is based on the following:

- The existence of a subsurface zero-flux plane, at depth d_s above which there is upward flow of liquid by capillary action, below which there is downward liquid flow under gravity.
- Evaporation is assumed to continue at the full rate (Stage 1) until a time t_0 when the cumulative liquid mass evaporated from the substrate equals the liquid mass in the substrate down to depth d_{re} dependent via equation (7) on the substrate readily evaporable water depth, d_{rew} .
- Thereafter the vaporisation rate (Stage 2) is decayed according to the diffusion similarity solution given by Brutsaert (2014).

The diffusion similarity solution is

$$E = E_0 \sum_{n=1,2,\dots}^{\infty} \exp\left(-\frac{(2n-1)^2(t-t_0)}{\tau_s}\right) \quad (5)$$

where

E is the volumetric evaporation rate per unit area [$L T^{-1}$]

E_0 is a characteristic evaporation rate scale based on the weighted-mean soil diffusivity \bar{D} , the initial liquid content, which is assumed to be saturated, ϕ_{sa} and the depth d_s : $E_0 = 2\bar{D}\phi_{sa}/d_s$

τ_s is a characteristic timescale given by $\tau_s = 4d_s^2/(\pi^2\bar{D})$

d_s is the zero-flux depth, which is around 100-200 mm for the three studies considered in Brutsaert (2014). Here it is assumed that a value of 150 mm is representative. Hence E_0 and τ_s can be calculated from the equations above.

In the limit of small times $(t - t_0) \ll \tau_s$ equation (5) reduces to

$$E = \frac{1}{2}De_0[t - t_0]^{-1/2} \quad (6)$$

where De_0 is known as the desorptivity, which is related to \bar{D} and ϕ_{sa} (assuming initial saturation of the region by permeated liquid) with the expression $De_0 = 2\phi_{sa}(\bar{D}/\pi)^{1/2}$. For the three field trials analysed in Brutsaert (2014), all had $De_0 \approx 6 \text{ mm day}^{-1/2}$ and this is used here as a basis for estimating \bar{D} .

Initially, E given by equation (5) may exceed the evaporation rate from the wetted pool surface, in which case a cap is applied by the free surface pool rate, $q_{evap} = \min(q_{evap,pool}, \rho_L E)$.

Scaling for non-water liquids

The above analysis is for water in soil. To account for liquid properties differing from water the following rescaling is applied:

$$\begin{aligned} d_{re} &= d_{rew} \left(\frac{\rho_w}{\rho}\right) \left(\frac{\sigma}{\sigma_w}\right) \\ d_{sf} &= d_s \left(\frac{\rho_w}{\rho}\right) \left(\frac{\sigma}{\sigma_w}\right) \\ E_{0f} &= E_0 \left(\frac{P_v(T_{sub})}{P_{vw}(T_{sub})}\right) \left(\frac{\bar{D}}{\bar{D}_w}\right) \left(\frac{d_s}{d_{sf}}\right) \\ \tau_{sf} &= \tau_s \left(\frac{\nu_w}{\nu}\right) \left(\frac{\rho}{\rho_w}\right)^3 \left(\frac{\sigma_w}{\sigma}\right)^3 \\ h_{sf} &= h_{sw} \frac{\rho_w \sigma}{\rho \sigma_w} \end{aligned} \quad (7)$$

where ρ represents the density and σ the surface tension with subscript w denoting water properties and non-subscripted denoting the permeating spill liquid.

It is assumed that d_s and d_{re} scale in the same way as capillary depth in Keller and Simmons (2005). \bar{D} is assumed to scale directly with the binary diffusion coefficient in air. E_0 is assumed to scale directly with the substance vapour pressure, P_v , (evaluated at the substrate temperature), and with \bar{D} and d_s according to their definitions above.

h_{sf} is the suction head (matric potential) at the wetted front, to account for the ‘wicking’ effect in the porous medium and is used in modelling the substrate infiltration in the following sections. It is assumed to be related to that of water, h_{sw} , by following Keller and Simmons (2005).

Pool spreading

The overland pool spreading over rough ground is modelled following the rough land spreading model in GASP (Webber, 1990) and is not reproduced here. However, it is worth noting that spreading of the pool stops when the pool depth h falls below the puddle depth, h_{stag} . It is possible in the case of a continuous spill for spreading to (re)start when the pool depth h rises above the puddle depth, h_{stag} . Some implementations based on Webber (1990), e.g. Fabbri et al. (2017), assume that the pool depth cannot be less than a minimum value, h_{min} . In such implementations further reduction in the overland pool volume shrinks the area of the pool, whereas in Webber (1990) the overland pool depth can decrease to zero with the pool area constant (stagnant in puddles).

Substrate infiltration

Infiltration of liquid into a porous substrate is calculated using a one dimensional Green-Ampt infiltration model (Green and Ampt, 1911). The velocity of infiltration, w_c , at the spill centre is given by

$$w_c = \begin{cases} K_s \left[\frac{h + h_{sf}}{Z_{sc}} + 1 \right] & Z_{sc} < Z_{sc,max} \\ 0 & \text{otherwise} \end{cases} \quad (8)$$

$$\frac{dZ_{sc}}{dt} = \frac{1}{\phi_{sa}} w_c$$

K_s is the saturated hydraulic conductivity of the liquid in the substrate which is related to the substrate permeability, k_{perm} (units of area), by

$$K_s = \frac{k_{perm}g}{v_L} \quad (9)$$

Z_{sc} is the depth of permeation of the wetted front in the porous substrate at the pool centre

$Z_{sc,max}$ is the maximum permeation depth, at which point infiltration stops (horizontal transport in the substrate is neglected) – this may be used to represent the effect of an impermeable layer or water table

ϕ_{sa} is the volume of the void space that is available to be occupied by the infiltrated liquid per unit volume of the porous medium. The presence of water in the substrate reduces the void volume available for infiltration. ϕ_{sa} is related to the substrate porosity in dry conditions, ϕ_{sd} , and the initial effective saturation of the porous substrate, f_{sat} , ($0 \leq f_{sat} \leq 1$) with the expression $\phi_{sa} = \phi_{sd}[1 - f_{sat}]$.

The infiltration rate into the substrate is assumed to be reduced due to blocking effect of water in the substrate by including a multiplicative factor of $[1 - f_{sat}]$ on w_c in equation (8). There is a singularity in equation (8) when $Z_{sc} = 0$. However, this singularity is integrable and can be dealt with by standard numerical techniques.

Equation (8) is for permeation into the substrate at the centre of the pool. For a spreading pool, the outer parts will have been in contact with the substrate for a shorter time and hence the penetration depth in the outer parts will be less than at the centre. This is accounted for in an approximate way by assuming that the penetration depth, Z_s , at radius r and time t is equal to the penetration depth at the centre at the earlier time $t - t_{arrive}$ where t_{arrive} is the time of arrival of the edge of the pool at radius r , i.e.

$$Z_s(r, t) = Z_{sc}(t - t_{arrive}(r)) \quad (10)$$

Equation (10) neglects the effect of varying pool depth, h , as the pool spreads, but has the required qualitative behaviour of tending to zero at the edge of the spreading pool and tending to uniform penetration at large times after the pool has ceased spreading.

The volumetric infiltration rate, Q_{sub} , is then given by evaluating the following integral over the pool area at each time step:

$$Q_{sub} = \int_0^{R(t)} w_c(t - t_{arrive}(r)) 2\pi r dr \quad (11)$$

Heat balance

The heat balance for the pool is written as:

$$MC_p \frac{dT}{dt} = A[q_H - q_{evap}\Delta H_{vap}] + Q_{sorc}\rho_L C_{pL}[T_{sorc} - T] + \frac{Q_{subc}}{\phi_{sa}}\rho_{sub}C_{psub}[T_{sub} - T] \quad (12)$$

MC_p is the thermal inertia of the liquid (above and below ground) including a contribution from the porous substrate in thermal contact with the liquid permeated into the ground:

$$MC_p = \rho_L V_{total} C_{pL} + \rho_{sub} Z_{sc} A C_{psub} \quad (13)$$

C_{pL} is the specific heat capacity of the liquid

C_{psub} is the specific heat capacity of the substrate material accounting for water content

ρ_{sub} is the density of the substrate material accounting for water content

Q_{subc} is given by $Q_{subc} = A dZ_{sc}/dt$

ΔH_{vap} is the heat of vaporisation

T_{sorc} is the source temperature

T_{sub} is the substrate temperature

The heat transfer q_H per unit area to the pool is the sum of heat conduction from the ground, q_{Hcond} convection from the atmosphere q_{Hconv} and thermal radiation q_{Hrad}

$$q_H = q_{Hcond} + q_{Hconv} + q_{Hrad}$$

q_{Hcond} and q_{Hconv} are calculated as in GASP. However, the radiative heat flux, q_{Hrad} from the atmosphere to the pool is taken to be constant in GASP. In SLOPS it is given by the sum of short wave and long wave components as in Fabbri et al. (2017):

$$\begin{aligned} q_{Hrad} &= q_{Hsw} + q_{Hlw} \\ q_{Hsw} &= C_{sol} [1 - 0.0071 C_L^2] [\sin(\chi_{sol}) - 0.1] \\ q_{Hlw} &= \epsilon_{pool} \sigma_{SB} [T_a^4 - T^4] \end{aligned} \quad (14)$$

where

C_{sol} is the solar constant (1111 W/m²)

C_L is the cloud cover in tenths (0 for clear and 10 for complete cover)

χ_{sol} is the solar elevation (rad) [calculated as a function of time according to Appendix 1 of Byrne et al. (1992)]

ϵ_{pool} is the surface emissivity of the pool (assumed to be 0.95)

σ_{SB} is the Stefan-Boltzmann constant (5.67×10^{-8} Wm⁻²K⁻⁴)

Significant assumptions and uncertainties

Several assumptions have been made in developing the SLOPS model in order to capture the important physics while retaining a fast-running operational model. It is important that these factors are understood when the model is used and when the model results are interpreted. If appropriate, sensitivity studies should be undertaken. The following are some of the known assumptions, limitations and uncertainties but this is not an exhaustive list.

Subsurface evaporation

The subsurface evaporation decay approach is very simplistic and its validity is uncertain, particularly in terms of application to fluids other than water, timescales less than a day, and for a wider set of substrates and ambient conditions than those considered in Brustaert (2014). The main merit is that its inclusion allows, albeit approximately, for longer persistence of liquid within the substrate when neglecting this may be a concern. However, if this aspect of the model is required for quantitative rather than qualitative purposes, then consideration should be given to how this simple approach might be improved and whether other aspects of the model also need modification to be applicable to longer times involved (e.g. variability of meteorological conditions over hours to days).

Substrate properties

The assumption of homogeneity is known to affect both infiltration and subsurface evaporation. In reality there is large variability in substrate properties, even for nominally the same substrate type. For example, there are many different types of concrete and substrate property value ranges can be very large. The values are also empirically determined. Consideration therefore needs to be given to obtaining appropriate values for the substrate of interest and ideally assessing the sensitivity of the model predictions to the values used.

Pool spreading

The model relies on the assumption of a circular pool and axisymmetric pool spreading. It also assumes homogeneous flat ground, which is not representative of many real locations. The puddle depth parameter is known to have a large impact on the final pool size but is an uncertain parameter that requires estimation for a given site.

Liquid infiltration

SLOPS uses a one dimensional infiltration model, which may be a poor approximation at large times. Also, the infiltration model was originally derived for water and has been extended to other substances. There is a precedent for this approach (Simmons and Keller, 2003), but the validity of it remains uncertain.

The effect of initial water saturation is only a void blockage in the model. In reality, the level of water content depends on the substrate. For example, sand is considered saturated at 15% void water content, while clay is saturated at 60% void water content (Observant, 2019). To model these effects would require a more complex subsurface flow model.

Pool evaporation

SLOPS is currently restricted to non-boiling, non-reacting liquids. The model is not applicable indoors due to the atmospheric model assumptions and there are currently no effects of non-neutral atmospheric conditions. The meteorology, which governs the evaporation rate, is currently assumed static, which is unlikely to be the case for long term spill durations (days).

SLOPS is not valid in nil or very low wind conditions because the assumed scaling with atmospheric friction velocity (Brighton, 1985) may no longer apply. Also, the model assumes that there is zero background concentration of the gas in air, which means that there is no effect of an overlying gas cloud on the pool evaporation.

Verification and validation

Model verification tests formed part of testing SLOPS alongside a series of additional tests with scenarios designed to represent inputs that might be used in the model in practice as well as indicating model sensitivity. The testing undertaken is reported in Batt and Tickle (2019). An example of the general effect of including porosity in the model on vaporisation rate and pool radius, compared with an impermeable surface, is shown in Figure 2. The model predictions behave qualitatively as might be expected. The vaporisation rate is highest for a liquid pool on an impermeable surface because a larger pool forms. The liquid persists for approximately twice as long for a spill on a gravel surface as for a spill on an impermeable surface.

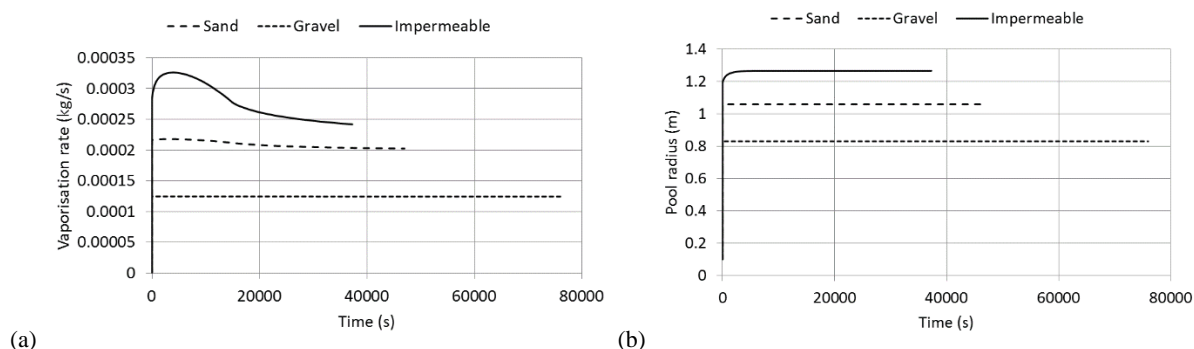


Figure 2 (a) Vaporisation rate for an instantaneous release of water onto an impermeable substrate, sand and gravel. (b) Pool radius for an instantaneous release of water onto an impermeable substrate, sand and gravel

SLOPS has been verified against GASP for heat conduction, convection, pool surface vaporisation and over ground spreading for both continuous and instantaneous releases (Batt and Tickle, 2019). Comparisons were made with analytic solutions of the Green-Ampt model in order to verify the implementation of the infiltration model in SLOPS. Two cases are considered here, for which there are analytic solutions given in Appendix A of Simmons and Keller (2005):

1. The liquid head above the surface is approximately constant
2. The liquid head declines due to the infiltration into the ground

Figure 3a shows a comparison between SLOPS predicted permeation depth and the analytic solution for Case 1. Figure 3b shows a comparison between SLOPS predicted pool depth and the analytic solution for Case 2.

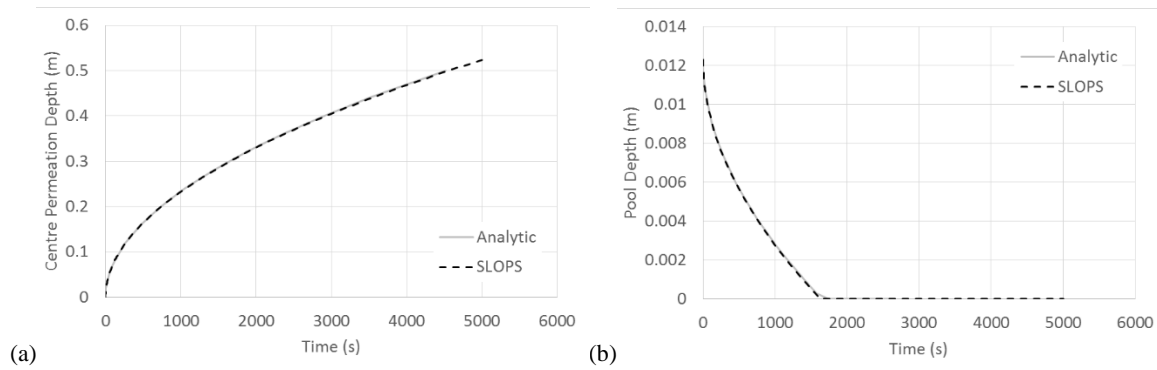


Figure 3 (a) Substrate permeation depth for the constant head approximation. (b) Pool depth for the declining head approximation. The grey line (analytic solution) lies underneath the black dashed line (SLOPS prediction) in both images.

The above comparisons are for a non-spreading pool. In the case of a spreading pool, the permeation depth varies with radius and time. SLOPS uses a simplifying assumption for this and integrates the infiltration over the pool area to calculate the resultant volume infiltration rate at any given time. A useful consistency check is to compare the predicted infiltration depth at a given time with calculated volume of infiltrated liquid at that time – an example is given in Figure 4a. At 200 s the predicted infiltration volume is approximately 1.085 m³ which, accounting for the available pore space, corresponds to an average permeation depth of approximately 0.007 m – this is in qualitative agreement with the subsurface profile shape shown in Figure 4a.

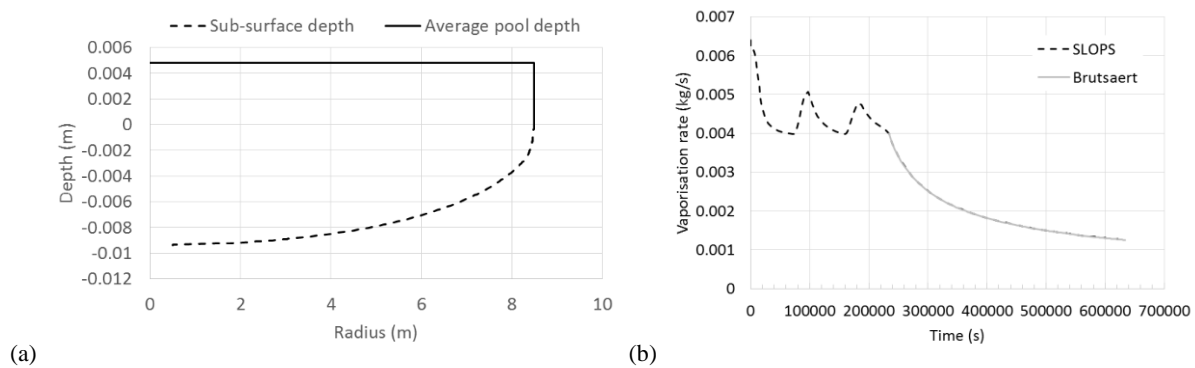


Figure 4 (a) Depth profile at 200s of a spreading pool with infiltration. (b) Vaporisation rate test, at later times, the dashed SLOPS line is obscured by the grey line of the Brutsaert model.

In Figure 4b the vaporisation rate predicted by SLOPS is compared with a spreadsheet calculation of the Brutsaert drying model using the same parameters. Initially, there is a liquid pool above the surface, contained within a bund, which vaporises as per Brighton (1985). Once the pool has completely permeated into the substrate, the vaporisation rate continues using the Brighton model, diurnal oscillations in the vaporisation rate can be observed in Figure 4b. Eventually, the REW depth is reached and the Brutsaert evaporation model takes over. Figure 4b show that there is good agreement where the SLOPS model has transitioned to using this model.

The verification test results show good agreement between SLOPS predictions and other independently coded models, correlations or analytic solutions. The results suggest that, at least for the features covered by the tests, the model equations are coded and solved correctly.

There are very few suitable validation datasets available for this sort of model. The pool spreading and vaporisation components of SLOPS compared well with the GASP model during verification. Therefore, indirect validation can be achieved by referring to existing validation of GASP (Webber and Jones, 1987; Webber, 1991). Similarly, indirect validation for the pool evaporation and infiltration models of SLOPS was achieved by relying on existing validation of the Brighton model and Green-Ampt models (Brighton, 1985; Simmons and Keller, 2005).

A more direct validation of the SLOPS model would be preferred and for this good quality validation datasets are required. In future work, the Belore and McBean (1986) experiments will be analysed in an effort to obtain suitable measurement data and undertake a model comparison exercise.

Future work

The subsurface evaporation model in SLOPS is a relatively novel implementation and there is some uncertainty in the model predictions. This aspect of the model would benefit from further research and testing. In particular, the infiltration and the subsurface evaporation models in SLOPS are both based on research where water is the substance of interest. Additional work and experiments are required in order to validate the adjustments applied to extend the models to substances other than water.

The dataset of Belore and McBean (1986) may provide suitable validation data for future work but additional experiments of liquid spills on different substrates are required, ideally including measurements of evaporation and persistence. Detailed measurements of the hydraulic and thermal properties of the substrate should also be taken in order to reduce uncertainty in these parameters in future model validation exercises.

There are several other aspects of the model that would benefit from further work. At present the model assumes fixed meteorology, which is not realistic, particularly for pools that persist for a number of days. The impact of this should be assessed and the model could be developed to accommodate time varying meteorology. Further tests of the model sensitivity to different substrate properties should be undertaken. The current values may not be the most accurate representation of the substrate of interest.

SLOPS has significant potential for expansion to provide source terms for a wider range of scenarios, while still providing an operational model. The model could be extended for reactive substances, for example, by adopting some of the physics from HSE's model STAWaRS (Tickle et al, 2014). It could also be extended to cryogenic liquids, for example, by implementing more of the physics from GASP (Webber, 1990).

Conclusions

A new model, SLOPS, has been presented for spills of liquids on porous surfaces. The model is based on the well-established pool spreading and vaporisation model, GASP, with extensions for infiltration and subsurface evaporation. The infiltration model implemented follows the widely used and well-understood approach of Green-Ampt. The subsurface evaporation model is an adaptation of water resources engineering knowledge applied to chemical spills to provide a simplified model of complex evaporation processes after the pool has completely permeated into the substrate. The coupling of pool spreading and vaporisation, infiltration and subsurface evaporation, for non-water substances, has not been found in any existing models.

SLOPS has been verified against analytical solutions and through comparison with GASP. A series of additional tests have been carried out which provide confidence that the model is performing as expected for ranges of values. Validation to date has been achieved indirectly by relying on comparison with other models that have been validated elsewhere.

SLOPS has been developed as an operational model for Dstl providing source terms for liquid spills on porous surfaces and, in particular, liquid persistence. Further validation of the model would provide greater confidence in the model predictions and provide potential for the further development of the approach allowing application to a wider range of scenarios.

Disclaimer

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