



REACTPOOL: A new model for accidental releases of water reactive chemicals

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REACTPOOL: A new model for accidental releases of water reactive chemicals

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All chemicals that react violently with water or in contact with water liberate toxic gas are included in the list of substances covered by the majority of the international legislation on major hazards. This category includes a large number of chemicals that are used widely in the process industries. In two previous research reports, a new theoretical model that describes accidental spills of sulphur trioxide and oleum, which are substances with very complex behaviour that belong to this category, was described. It reports both the pool and the cloud behaviour. In the work reported here, the pool model was modified in a generic form in order to include other water reactive chemicals. REACTPOOL is a new model that can be used for both instantaneous and continuous liquid releases under a wide range of input parameters (steady or varying). It can be used for all liquids irrespective of their volatility/reactivity and it also describes pools consisting of more than one liquid that can have changing composition and properties. The behaviour of five different water reactive chemicals has been investigated using REACTPOOL. Namely they are: phosphorus trichloride, phosphorus oxychloride, chlorosulphonic acid, silicon tetrachloride and acetyl chloride.

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1) INTRODUCTION

Most existing pool models deal with pools that either boil or evaporate and which consist of one component with constant composition and properties. Some models can deal with multi-component pools of constant composition. Although this description is adequate for many chemicals, it cannot satisfactorily describe aggressive and reactive chemicals e.g. water reactive substances. Furthermore the possibility of solidification is widely ignored in most models. REACTPOOL is a new model that can describe all liquids and can be used for chemicals with extremely complicated behaviour such as water reactive substances [3, 4, 5, 6, 7].

Water reactive chemicals are generally aggressive materials with complicated properties. The hazardous nature of these substances is recognised in various items of legislation relating to industrial safety. Under the new Seveso II EU Directive, all substances that attract the risk phrases R14 "reacts violently with water" (including R14/15) or R29 "in contact with water, liberates toxic gas" are described as major hazards and are included in the list of chemicals covered by this Directive [8], which was implemented in the UK as the COMAH Regulations in 1999 [9].

The toxicity and the effects of water reactive materials on humans and on the environment are highly variable, depending not only on their properties, but also on the properties of their products on reaction with water or the atmosphere or the substrate.

In cases where these substances are stored, transported or used in their liquid form, spillage will create a liquid pool, usually on land (in most cases they are transported by road or rail tankers). The spreading liquid will react with any free water lying on the ground and will also extract any water present in the substrate. Depending on its properties it may absorb atmospheric moisture. It may also react with compounds present in the substrate. The reaction with water is usually highly exothermic, providing the pool with energy, raising the liquid temperature and its vapour pressure and thus increasing the vapour evolution rate. Depending on the pool temperature and the boiling and freezing points of the liquid, the pool may boil or evaporate or even solidify. The products of the reaction may be directly evolved (in cases where a product is generated in its gas phase) or be present in the pool in liquid form and thence evaporate. Hydrolysis products formed in the pool may be soluble or insoluble in the liquid pool. If insoluble they can either be suspended in the liquid or settle onto the bottom of the pool forming a film.

The core of REACTPOOL is based on the model developed for accidental releases of SO_3 and oleum [1; see also 10, 11, 12, 13]. These substances have very complicated behaviour, since they usually create a liquid pool with changing composition and properties and may boil or evaporate or even solidify depending on the conditions. Water is supplied to the pool from three sources: the ground, the atmosphere and the substrate. They also react with some substrate compounds. The pool behaviour is governed mainly by the amount of water available for reaction.

REACTPOOL consists of the core model, which is identical for all substances and describes general features of the pool behaviour (spreading, evaporation or boiling or solidification, energy and mass balances). The core is a generalised version of that used for SO_3 and oleum spills, modified to account for substances that react with water in a different way than SO_3 and oleum. For each of the incorporated substances an individual module has been developed that describes the properties of the substance and its products on reaction with water, and other individual features.

It should be noted that REACTPOOL can be used for any chemical irrespective of its affinity for water.

A particular difficulty is that data on properties of many water reactive chemicals and their reaction with water are not well established. Furthermore, there are almost no experimental data on their source behaviour.

2) WATER REACTIVE CHEMICALS

2.1) Identification

An extensive literature review has been conducted to identify water reactive chemicals of significance in major hazards. The main ones have been categorised as follows [14,15, 16, 17]:

- Inorganic acid halides, such as POX_3 , SOX_2 , SO_2X_2
- Organic halides, such as CH_3COX , CH_2COX .
- Sulphonic acids, such as HSO_3X
- Halides of non-metals (mainly phosphorus-halogen, silicon-halogen and boron-halogen compounds), such as PX_3 , SX_2 , PX_5 , SiX_4
- A number of silanes, such as HX_3Si , $\text{CH}_3\text{X}_3\text{Si}$
- Non-metal oxides, such SO_3 and oleum (mainly sulphur and phosphorus oxides)
- Anhydrous metal halides, such as AlX_3 , TiX_4 , ZrX_4 , SnX_4
- Radioactive materials, such as UF_6 .

Most of the identified substances contain a halogen bond in their structure. The majority of water reactive chemicals are in the liquid phase at ambient conditions (AlX_3 , PX_5 and UF_6 are solids and fluorosilanes are vapours).

Some of the water reactive chemicals that are commonly used in the process industries are: titanium tetrachloride (TiCl_4), sulphur trioxide (SO_3) and oleums, phosphorus trichloride (PCl_3), phosphorus oxychloride (POCl_3), silicon tetrachloride (SiCl_4), trichlorosilane (HCl_3Si), methyltrichlorosilane ($\text{CH}_3\text{Cl}_3\text{Si}$), chlorosulphonic acid (HSO_3Cl), boron trichloride (BCl_3), thionyl chloride (SOCl_2), acetyl chloride (CH_3COCl). Water reactive chemicals that exist in their solid or vapour phase at ambient conditions may also create a liquid pool on spillage following reaction with water.

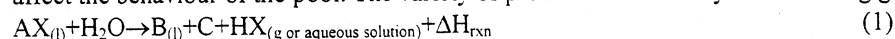
The Major Accident Hazards Bureau (MAHB) of the European Commission Joint Research Centre has published guidance documents for implementing Seveso II [18]. Table 1 shows how water reactive chemicals have been characterised and included in Seveso II [18]. The third column in Table 1 shows the qualifying quantities (tonnes) for the application of articles 6 and 7 of Seveso II (requirement for notification and major accident prevention policy). The fourth column indicates the qualifying quantities (tonnes) for application of article 9 (requirement to produce safety reports) [1, 14]. In this table RVW indicates that the chemical reacts violently with water, LTG shows that in contact with water it liberates toxic gas and HF that it is highly flammable. It should be noted that highly dangerous water reactive substances like PCl_3 , POCl_3 and AlCl_3 are not included in these guidance notes.

Table 1
Water reactive chemicals under Seveso II [8, 18]

Substance	Categorised as	Qualifying quantity (tonnes) for articles 6 and 7	Qualifying quantity (tonnes) for article 9
Sulphur dichloride	Named	1	1
Sulphur trioxide	Named	15	15
Acetyl chloride	RVW	100	500
Alkali ethoxides	RVW	100	500
Alkali methoxides	RVW	100	500
Chlorosulphonic acid	RVW	100	500
Disulphur dichloride	RVW	100	500
Lithium	RVW	100	500
Morpholyne-4-carbonyl chloride	RVW	100	500
Oleum	RVW	100	500
Phosphorus tribromide	RVW	100	500
Potassium	RVW	100	500
Potassium mufluorobis(triethylaluminum)	RVW	100	500
Propionyl chloride	RVW	100	500
Silicon tetrachloride	RVW	100	500
Sodium	RVW	100	500
Sulphur tetrachloride	RVW	100	500
Sulphuryl chloride	RVW	100	500
Thionyl chloride	RVW	100	500
Titanium tetrachloride	RVW	100	500
Tosyl isocyanate	RVW	100	500
Trichloro(methyl)silane	RVW	100	500
3,5-dichloro-2,4-difluorobenzoyl fluoride	LTG	50	200
Phosphorus pentasulphide	LTG	50	200
Trichlorosilane	HF	50	200

2.2) Reaction with water

The reactions of these chemicals with water are highly variable. The reaction products strongly affect the behaviour of the pool. The variety of products is shown by the following general reaction:



where AX is the water reactive chemical that contains a halogen X bond

B is a possible liquid product

C is a possible product (soluble or insoluble that may appear as a solid)

HX is the acid generated

ΔH_{rxn} is the heat of hydrolysis

In cases where at least one of the hydrolysis products is liquid (e.g. B), the pool will contain at least two liquids AX and B. The pool composition and properties will not be constant as AX continuously reacts with water producing B.

When a product C is formed, it could either be soluble or insoluble in the liquid. In the latter case, the solid particles may either settle or be suspended in the pool depending on the pool features and

the characteristics of the solids such as their size distribution and density. In cases of a soluble hydrolysis product and if the pool is not saturated all the pool characteristics change continuously. A new procedure has been developed to account for these changes as the SO₃/oleum model did not account for such phenomena since no C hydrolysis products were involved.

In all cases, when the water reactive chemical contains a halogen bond, acid HX will be formed. The phase of this acid is strongly determined by the amount of water available for reaction. If water is in excess a liquid aqueous solution of this acid is usually generated. If water reactive chemical AX is in excess, HX will be directly evolved to the atmosphere as a gaseous product. The following is a brief description of hydrolysis reactions of the most commonly used water reactive substances. Most of these reactions are rapid, complete and exothermic.

2.2.1) PCl₃ (phosphorus trichloride) hydrolysis

Reaction of PCl₃ with water in the liquid phase is quite complicated and depends strongly on the amount of water available. Two cases are encountered [19, 20]:

When {molesH₂O/molesPCl₃} ≥ 3:



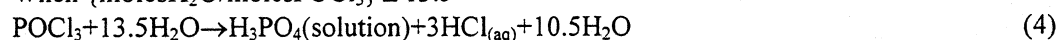
When {molesH₂O/molesPCl₃} < 3:



2.2.2) POCl₃ (phosphorus oxychloride) hydrolysis

Liquid phase hydrolysis of POCl₃ is not well defined in the literature. Three different cases are encountered depending on the availability of water [20]:

When {molesH₂O/molesPOCl₃} ≥ 13.5



When {13.5 > molesH₂O/molesPOCl₃} ≥ 3.5



When {molesH₂O/molesPOCl₃} < 3.5



2.2.3) SiCl₄ (silicon tetrachloride) hydrolysis

The rapid and highly exothermic reaction of SiCl₄ with water is described by the following overall equation [21]:



2.2.4) Hydrolysis of silanes

Most of the silanes are highly susceptible to hydrolysis. The driving force behind these reactions is the energy gain that accompanies the change from Si-X to Si-O. The reactivity of the Si-X bond in comparable silanes increases along the series: Si-F << Si-Cl < Si-Br < Si-I. The rate of hydrolysis decreases along the series: SiCl₄ > RSiCl₃ >> R₂SiCl > R₃SiCl, and it also decreases with increasing complexity of molecule R. The products of the hydrolysis reaction depend strongly on the amount

of water available for reaction and on the silane structure. Some possible products are silanols, polysiloxanes, siloxanes etc. In all cases, hydrogen halides will be generated [21].

2.2.5) SOCl₂ (thionyl chloride) hydrolysis

Thionyl chloride is hydrolysed rapidly and completely by water [22]:



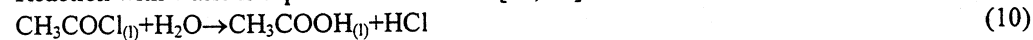
2.2.6) HSO₃Cl (chlorosulphonic acid) hydrolysis

This substance reacts violently with water [23]:



2.2.7) CH₃COCl (acetyl chloride) hydrolysis

Reaction with water is rapid and exothermic [22, 23]:



2.2.8) BCl₃ (boron trichloride) hydrolysis

The hydrolysis reaction is described by the following equation [22, 23]:



2.2.9) TiCl₄ (titanium tetrachloride) hydrolysis

Although this chemical is used widely in the process industries and has been involved in a number of major accidents, there are almost no data in the literature on its liquid phase reaction with water. Some sources report that it is soluble in cold water and decomposes in hot water to titanium dioxide solid particles and HCl gas; some others report that it rapidly reacts with water under any conditions.

2.2.10) SCl₂ (sulphur dichloride) hydrolysis

SCl₂ is an unstable compound that is readily dissociated (circa 16%) at room temperature to disulphur dichloride S₂Cl₂ and Cl₂. The only information on its hydrolysis reaction is that it decomposes rapidly and completely on treatment with water, forming HCl, thiosulphate and polythionic acids [22, 23]. Unfortunately there are no further data on its reaction with water.

2.2.11) S₂Cl₂ (disulphur dichloride) hydrolysis

S₂Cl₂ reacts only slowly with water at room temperature. On heating the reaction rate increases explosively. On hydrolysis elemental sulphur, thiosulphate, polythionic acids, HCl and SO₂ are formed [22, 23]. No data on the kinetics of this reaction and its dependence on temperature could be found.

With the exception of the hydrolysis reactions of PCl₃, HSO₃Cl, CH₃COCl and SiCl₄, the above reactions are not well defined theoretically or experimentally tested.

2.3 Survey of accidents involving spillages of water reactive chemicals

A survey of accidents that occurred in the USA between January 1990 and November 1999 was conducted and its results are summarised in Table 2. With the exception of aluminum chloride, the rest of the chemicals listed in Table 2 are in liquid form at ambient conditions.

It should be noted that the fourth column in Table 2 corresponds to accidents where injuries or evacuations or deaths were reported and are described here as "hazardous incidents". The main sources of information reported in Table 2 were found in the databases of the National Response Centre (NRC) [24] (covering years 1990- November 1999) and the Office of Hazardous Materials (OHM) (covering years 1993-1999) [25]. The NRC is a USA federal contact point for reporting oil and chemical spills and the OHM is part of the USA Department of Transportation of Research and Special Programs Administration. It is used by shippers and carriers for notifying incidents occurring during the transportation of hazardous materials. Some data were also found from the ARIP database of the Environmental Protection Agency (EPA) [26], and the EPA Toxic Releases Inventory (TRI), searchable from the TOXNET database (covering years 1995-1997) [27].

In some accident reports, data on number of people evacuated, number of injuries etc., were not known. Thus, it is probable that the number of incidents that involve evacuations or injuries is higher than indicated in Table 2. The table shows that there were more than 85 accidents per year in the USA alone involving spillages of these substances, and more than five of them involve evacuation and/or injuries. Two deaths were reported in a silicon tetrachloride accident that occurred in 1998 [28]. Titanium tetrachloride [29] and phosphorus oxychloride [30] were also reported to have caused fatal accidents (in Europe).

Table 2
Accidents that involved spills of water reactive chemicals that occurred in the USA during January 1990-November 1999 [24, 25, 26, 27].

Chemical	Number of incidents	Number of hazardous incidents	Number of injuries	Number of deaths
TiCl₄	473	13	13	-
SO₃	206	14	59	-
Oleums	70	4	4	-
AlCl₃	23	1	1	-
PCl₃	18	3	8	-
BCl₃	16	2	-	-
CH₃Cl₃Si	16	2	6	-
POCl₃	14	5	144	-
SOCl₂	12	2	17	-
HSO₃Cl	11	1	2	-
SiCl₄	8	4	7	2
S₂Cl₂	7	-	-	-
SCl₂	5	-	-	-
SiHCl₃	4	3	158	-
BBr₃	4	-	-	-
CH₃COCl	2	1	-	-
TOTAL	889	55	419	2

3) REACTPOOL MODEL DESCRIPTION

Phenomena taken into account are depicted in Figure 1.

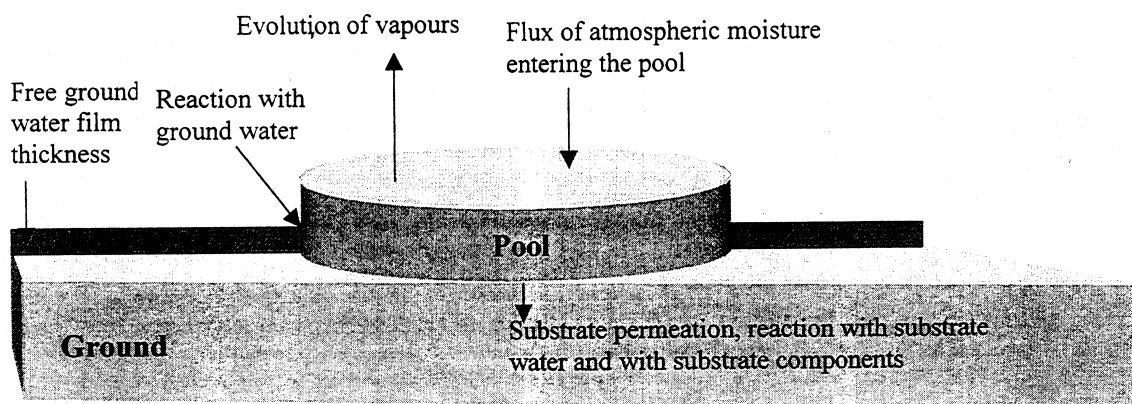


Figure 1

Phenomena taken into account in the modelling procedure (some dimensions are exaggerated)

3.1) Core of the modelling procedure

The core of the model is identical for all substances and describes phenomena such pool spreading, vapour evolution, mass and energy balances, reaction with water etc. It consists of different sub-models that describe different features of the behaviour of the liquids.

3.1.1) Pool spreading

The spreading behaviour of the pool is described by differential equations that are based on the principles of mass, momentum and energy conservation [31, 32]. In cases of instantaneous spills, spreading equations (2.1.1.1)-(2.1.1.3) in reference 1 are used to calculate the pool radius. For continuous spills equations (2.1.2.1)-(2.1.2.8) in reference 1 are used. In both cases, the pool spreads until it reaches a minimum layer thickness (h_{\min}); it then shrinks as the volume decreases due to evaporation and the pool depth remains constant at h_{\min} [1].

Many of the available pool models that describe the spreading behaviour by algorithms that make use of the minimum layer thickness on a surface, disregard the significance of variations of this parameter, setting it at a constant value for any type of surface.

Overall, the minimum layer thickness has a very strong effect on the pool radius. When the pool depth h , reaches the value of the minimum layer thickness (h_{\min}), spreading ceases, unless the rate of mass entering the pool is higher than the mass efflux, in which case spreading continues at $h=h_{\min}$. The mass entry rate is the sum of the spill rate plus the mass rate of addition from other sources (e.g. addition of water). The mass efflux rate is the mass evolution rate plus the mass rate of any other possible loss (e.g. production of solids that are insoluble in the liquid; see also Appendix A).

The value of h_{\min} is determined by the physical surface roughness (this term is used to distinguish it from the aerodynamic roughness length, z_o). It is suggested that a minimum value of 5 mm should be applied in cases of extremely smooth surfaces. For rougher surfaces, the value can be as large as a few centimetres [31]. Unfortunately, there is no experimentally based correlation that relates the value of the minimum layer thickness with the physical surface roughness.

In order to incorporate some reasonable relationship between h_{\min} and surface characteristics, the following correlation has been adopted; this parameterises the value of h_{\min} (m) as function of the aerodynamic surface roughness length z_o (m):

For $z_o \leq 0.0001$ m, $h_{\min} = 0.005$ m

For $z_o > 0.0001$ m and $z_o \leq 0.1$ m, $h_{\min} = 0.005 + \frac{z_o}{0.0001} 5 \times 10^{-6}$

For $z_o > 0.1$ m and $z_o \leq 1$ m, $h_{\min} = 0.01 + \frac{z_o}{0.1} 10^{-3}$ (12)

For $z_o > 1$ m and $z_o \leq 10$ m, $h_{\min} = 0.02 + \frac{z_o}{1} 3 \times 10^{-2}$

For $z_o > 10$ m, $h_{\min} = 0.05$ m

The above correlation assumes that the value of h_{\min} is within range 5 mm and 5 cm.

3.1.2) Availability of water

The amount of water available for reaction is determined by estimating the amount available from each source. In all cases, water reactive chemicals will encounter free ground water and will also extract substrate water. Most will also absorb atmospheric moisture. All these sources are modelled according to section 2.2 in reference 1.

3.1.3) Reaction with the substrate

Water reactive materials are usually highly aggressive and can react with some of the components of any type of substrate e.g. in the case of a concrete surface on which SO_3 /oleum or chlorosulphonic acid is spilled H_2SO_4 reacts exothermically with calcium hydroxide [33]). These possible reactions are modelled according to section 2.2.3 in reference 1.

3.1.4) Energy balance

An energy balance that takes into account all the significant energy sources is implemented to calculate the pool temperature in each time step. This energy balance expands some ideas previously reported [34] by incorporating energy sources that are significant for water reactive chemicals. The following sources are taken into account for evaporation (see section 2.5 in reference 1):

- Energy of reaction with water
- Evaporation energy
- Energy of addition
- Net solar radiation
- Long-wave radiation from the atmosphere
- Long-wave radiation emitted by the pool
- Sensible energy transfer between the ground and the pool
- Conduction of heat from the ground
- Heat of reaction between chemical and substrate

The energy balance is modified for boiling or solidification as shown in sections 2.7 and 2.8 in reference 1.

3.1.5) Evaporation model

In cases where the pool temperature is within the range set by the boiling and freezing points, the pool evaporation rate is calculated by Brighton's model [35]. This analytic model takes into account effects of surface roughness, friction velocity of the airflow and high vapour pressure on the mass transfer process (for details see section 2.6 in reference 1).

3.1.6) Boiling

In cases where the heat balance is such that the pool boils, its temperature is set equal to the boiling point and any excess heat is used in the vaporisation process. The possible boiling point difference between successive time steps is taken into account in a modified energy balance (compared to that one shown in section 3.1.4; for details see section 2.6 in reference 1).

3.1.7) Solidification

In cases where the heat balance is such that the pool temperature falls to the freezing point, the pool solidifies. Depending on whether spreading has ceased two cases are encountered; solidification before and after spreading ceases. The former case is the most complicated one as there would be a newly spilled liquid pool on top of a solid phase and between these two layers there would be a temperature difference. The free solid area will sublime (see section 2.8 in reference 1).

Detailed descriptions of the above sub-models can be found elsewhere [1]. In this report, the main modifications and additions to the SO_3 /oleum model are described in detail. Some modifications are listed in Appendix A. Reaction of the chemical with water has been incorporated into the core model in a general form, that accounts for all the scenarios that are described in sections 3.2-3.4. Three different cases are encountered depending on whether liquid or solid or gas products are formed.

3.2) Liquid hydrolysis product

When at least one liquid is formed from the hydrolysis reaction, the liquid pool will contain at least two liquids; water reactive chemical AX and liquid product B. As the reaction of the chemical with water proceeds, chemical AX will continuously yield B. Therefore, the liquid composition and properties will change. All the pool properties are assumed to be dependent on the mole fractions of

the liquids present [36, 37]. For example, density will be given by the following:

$$\rho_l = X_{AX} * \rho_{AX} + X_B * \rho_B \quad (13)$$

where ρ_l (kg m^{-3}) is the density of the mixture of liquids in the pool, ρ_{AX} (kg m^{-3}) is the density of water reactive chemical AX and ρ_B (kg m^{-3}) is the density of product B. X_{AX} and X_B are the mole fractions of components AX and B respectively.

Apart from AX (which is usually volatile), liquid B may also evolve from the pool depending on its volatility and the pool temperature. Assuming ideal solution, the vapour pressure of each liquid will be given from Raoult's law. The vapour pressure of product B, P_B (atm) will be:

$$P_B = X_B P_B^O \quad (14)$$

where P_B^O (atm) is the vapour pressure of the pure component B.

The rest of the pool properties are calculated according to equation 13. If more than one liquid product is present, the pool will contain more than two components and its properties are then calculated accordingly to the above.

3.3) Solid hydrolysis product

Two different cases are encountered, depending on whether the solid product of the hydrolysis reaction is soluble or insoluble in the pool liquid.

3.3.1) Soluble hydrolysis product

When the solid product of the hydrolysis reaction 2.2.1 is soluble in the spilled liquid the following phenomena take place:

- Boiling point elevation
- Freezing point depression
- Vapour pressure reduction

In addition, if the pool is not saturated its density, viscosity, specific heat and thermal conductivity change continuously as long as the concentration of the soluble product C changes. These changes depend on the quantity of product C present in the liquid medium. They are calculated as functions of the molar fractions of the liquid and product C according to equation 2. As the pool spreads the quantity of product C increases. Depending on the amount present in the pool and other characteristics, the pool may reach its saturation point. From this point and onwards any excess will be precipitated. This scenario is investigated in section 3.4.1

The boiling point of a dilute solution of a non-volatile, non-dissociating solute is elevated compared to that of the pure solvent. For an ideal solution (a solution that follows Raoult's Law), the boiling point elevation ΔT_b is given by the following relationship [38]:

$$\Delta T_b = E_b m \quad (15)$$

where m is the molality and E_b is the ebullioscopic constant, a characteristic property of the solvent which can be calculated from the following equation [38]:

$$E_b = \frac{RT_b^2 M}{\Delta H_{vap}} \quad (16)$$

where R is the molar gas constant, M is the molar mass of the solvent and ΔH_{vap} is the molar enthalpy of vaporisation of the solvent.

The freezing point of a dilute solution of a non-volatile, non-dissociating solute is depressed compared to that of the pure solvent. If the solution is ideal, the absolute freezing point depression is expressed as [36]:

$$\Delta T_f = E_f m \quad (17)$$

where E_f is the cryoscopic constant given from [38]:

$$E_f = \frac{RT_f^2 M}{\Delta H_{fus}} \quad (18)$$

where ΔH_{vap} is the molar enthalpy of fusion of the solvent.

The vapour pressure reduction ΔP for an ideal solution of a non-volatile solute is given by the following equation [36, 37]:

$$\Delta P = P_1^o x_2 \quad (19)$$

where P_1^o is the vapour pressure of the solvent and x_2 is the molar fraction of the solute.

3.3.2) Insoluble hydrolysis product

Depending on the turbulence and thus the mixing in the pool and on the particle size distribution and density of the solid, the insoluble particles could either settle on the bottom of the pool or be suspended in the liquid pool.

In cases where there is a lack of turbulence inside the pool, the solid particles may settle on the bottom of the pool forming a film. The solid film that is formed may change the rate of heat conduction from the ground. In these cases the equation that gives the overall heat transfer coefficient U_{grd} ($\text{kJ m}^{-2} \text{h}^{-1} \text{K}^{-1}$) (equation 2.5.12 in reference 1) should be modified to include the resistance of heat transfer due to the presence of the solid film:

$$U_{grd} = \frac{1}{\frac{1}{h_{grd}} + \frac{1}{h_{liq}} + \frac{1}{h_{solids}}} \quad (20)$$

where h_{liq} ($\text{kJ m}^{-2} \text{h}^{-1} \text{K}^{-1}$) is the heat transfer coefficient that accounts for the thermal resistance between the ground surface and the lower pool surface, h_{grd} ($\text{kJ m}^{-2} \text{h}^{-1} \text{K}^{-1}$) is the heat transfer coefficient of the ground and h_{solids} ($\text{kJ m}^{-2} \text{h}^{-1} \text{K}^{-1}$) is the heat transfer coefficient of the solid film, given from the following equation [36]:

$$h_{solids} = \frac{k_{solids}}{d_f} \quad (21)$$

where k_{solids} ($\text{kJ m}^{-2} \text{h}^{-1} \text{K}^{-1}$) is the thermal conductivity of the solid particles and d_f (m) is the depth of the film. Assuming uniform distribution of the solid particles on the bottom of the pool:

$$d_f = \frac{V_{solids}}{A} = \frac{M_{solids}}{\rho_{solids} \pi A} \quad (22)$$

where M_{solids} (kg) is the mass of the solid particles, ρ_{solids} (kg m^{-3}) is the density of the solid and A (m^2) is the pool area.

If the particles are settled, the liquid pool properties will not be affected by their presence. If the pool is turbulent the particles will be mixed throughout the liquid. Boiling will usually ensure that particles are suspended, affecting the liquid properties. All the pool properties change continuously

as more particles are generated, until the liquid becomes saturated. The pool density ρ (kg m^{-3}) will be given from the following relationship:

$$\rho = \frac{M_p}{V_p} = \frac{M_l + M_{\text{solids}}}{\frac{M_l}{\rho_l} + \frac{M_{\text{solids}}}{\rho_{\text{solids}}}} \quad (23)$$

where M_p (kg) and V_p (m^3) are the mass and volume of the pool and M_l (kg) and ρ_l (kg m^{-3}) are the mass and density of the liquid phase in the pool.

The specific heat C_p ($\text{kJ kg}^{-1} \text{K}^{-1}$) of the pool will be:

$$C_p = \frac{M_{\text{solids}}}{M_p} C_{ps} + \frac{M_l}{M_p} C_{pl} \quad (24)$$

For spherical particles at low concentrations, the relative viscosity μ_p/μ_l (where μ_p ($\text{kg m}^{-1} \text{s}^{-1}$) is the viscosity of the pool and μ_l ($\text{kg m}^{-1} \text{s}^{-1}$) is the viscosity of the liquid) is related to the volume fraction ϕ of the particles according to the following equation [39]:

$$\frac{\mu_p}{\mu_l} = 1 + 2.5\phi \quad (13)$$

The volume fraction of the solid particles in a liquid pool is calculated as follows [39]:

$$\phi = \frac{\frac{M_{\text{solids}}}{\rho_{\text{solids}}}}{\frac{M_{\text{solids}}}{\rho_{\text{solids}}} + \frac{M_l}{\rho_l}} \quad (14)$$

This description is strictly valid under conditions of infinite dilution where only single particle/medium interactions are important.

All the rest of the pool properties are calculated according to equation 2.

3.4) Gas or vapour hydrolysis product

In cases where product HX of reaction (1) is in its gas (or vapour) phase, it will evolve directly to the atmosphere. Depending on halogen X, toxic gases like HCl and HF may be produced. HX is produced in its gas phase usually when there is an excess of water reactive chemical AX. When water is in excess an aqueous solution of liquid HX is formed and is part of the liquid pool (see section 3.2). In cases of accidental releases, it is quite unlikely that there will be an excess of water. Thus, it is assumed that the majority of the cases involve the direct generation of HX gas.

4) CALCULATION PROCEDURE – INPUTS AND OUTPUTS

A simplified algorithm of the modelling procedure is depicted in Figure 2. Modelling calculations are performed at small time increments. The user first selects which water reactive chemical is spilled. The code responds by loading its characteristics from the individual module. Every time step, δt (s), is split into three steps: the spill, the reaction and the evolution steps.

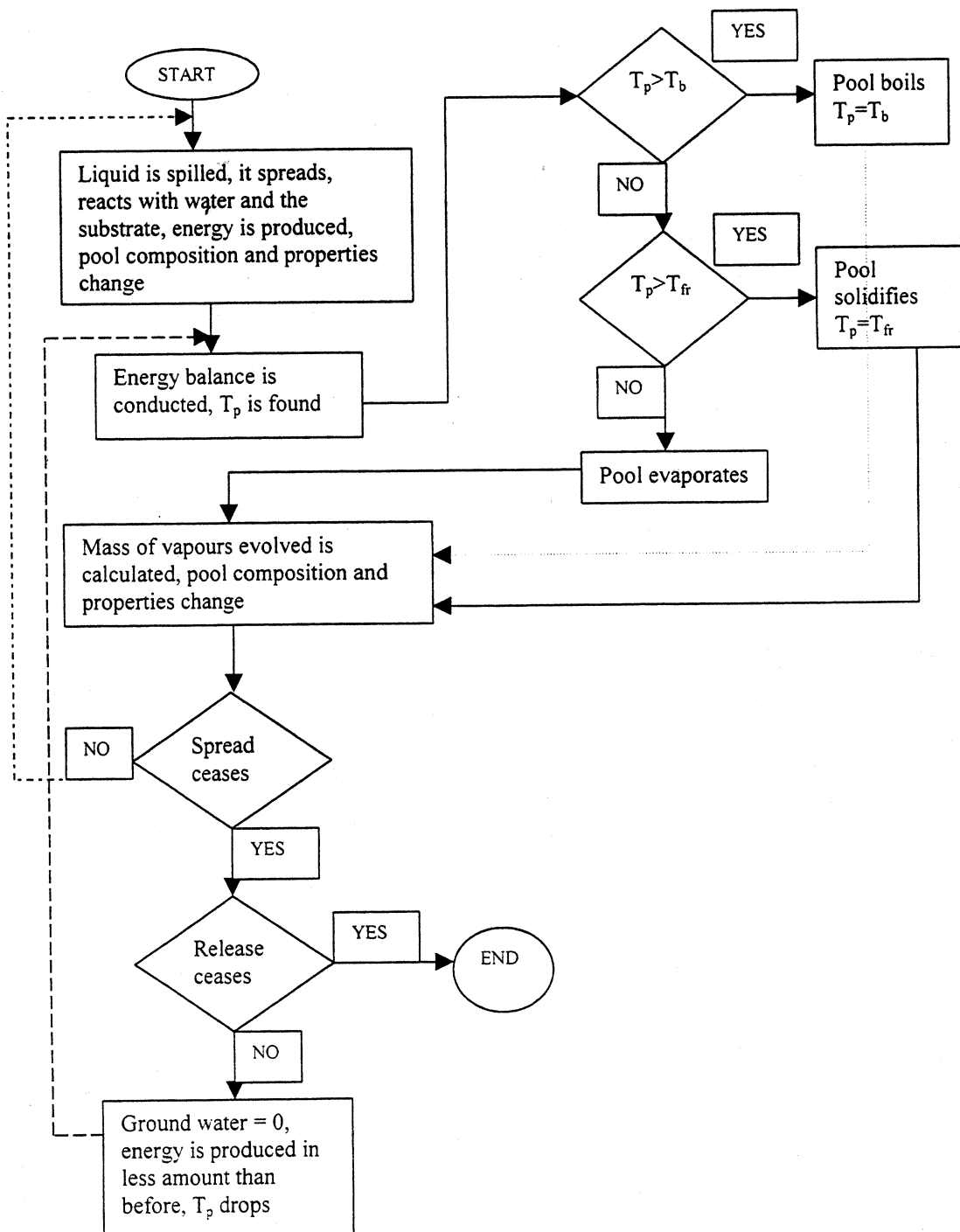


Figure 2
Logical representation of the algorithm of the modelling procedure

4.1) Spill

At the beginning of the time step the total quantity of liquid in the pool will be:

$$M_p = M_r + \delta t M' \quad (15)$$

The pool may consist of one or more liquid phases and it also may contain soluble solids or insoluble suspended particles. All the properties of the liquid (density, freezing point, boiling point, heat capacity etc.) are calculated. The pool radius R (m) is calculated by solving the spreading equations. For an instantaneous release, equation 2.1.1.1 of reference 1 is solved and for a continuous release, equation 2.1.2.1. The method followed to solve these equations is the fourth-order Runge-Kutta method, using a time increment of 0.01 s. After calculating the pool radius, the depth, h (m), and the surface area of the pool, A (m²), are calculated.

4.2) Reaction

Descriptions of this step requires the following questions to be answered for each water reactive chemical:

- Does the water reactive chemical absorb atmospheric moisture?
- Do any of the liquids react with components of substrates like concrete, asphalt or soil?
- Are solid particles produced?

If the answer to the above is positive, descriptions of the above phenomena have to be provided. In view of lack of any relevant data, it is assumed that if the pool absorbs atmospheric moisture, then the amount absorbed can be estimated in a way similar to that used to describe SO₃ and oleum pools (see Appendix A) [1]. In all cases, the pool will encounter free ground water while spreading and it will also extract substrate water, so that there will be at least two sources of water available for reaction.

The total mass of water available for reaction is calculated (equations 2.2.1.1, 2.2.2.9, 2.2.3.11 in reference 1). If water is in excess, the mass of water that reacts will be equal to the amount required to consume all the quantity of the water reactive chemical. The heat of reaction is then calculated. At this stage the composition of the pool may change again (in cases where liquid, or soluble solid or insoluble suspended solid is generated). As a result of the composition changes the properties of the pool will change and they are recalculated. The values of all energy terms are found from the relevant equation (see section 2.5 in reference 1). The temperature of the pool is calculated by the trial and error method because there are several interrelated parameters that are dependent on the pool temperature.

4.3) Evolution

If the temperature is below the boiling point and above the freezing point the pool will evaporate and the amount evolved is calculated using Brighton's model [35]. If the pool boils, the amount evolved is calculated using equation 68 of reference 3. In both these cases and if the pool contains more than one liquid (e.g. water reactive chemical AX and product B), liquid B may also evolve depending on its volatility and the pool temperature. In the case of solidification of the pool the procedure depends on whether solidification occurs before or after the spill ceases. The equations given in sections 2.8.1 and 2.8.2 of reference 1, respectively, are solved and the quantity of water reactive chemical sublimed, is calculated. At the end of the time step, the composition of the pool changes again and all the properties of the pool are recalculated. If solidification has occurred the

possibility of melting is checked. When the spill ceases, the pool stops spreading, and water will only be available from the atmosphere (in cases where the substance absorbs atmospheric moisture) and from the substrate. These calculation steps are repeated until either the whole quantity of water reactive chemical has been evolved, or the episode is terminated by emergency action intervention.

4.4) Model inputs

REACTPOOL has been provided with a user-friendly interface and all the necessary help and information on the spill behaviour. The model inputs are:

- Substance spilled: there is a list of chemicals that have been incorporated into the model. Modules for additional chemicals are readily added.
- Type of spill: the user should define whether it is a continuous or instantaneous spill.
- Amount spilled in cases of instantaneous release (kg).
- Spill rate in cases of continuous releases (kg s^{-1}).
- Type of surface: whether it is concrete, or asphalt or soil of different types (see Appendix A).
- Wind speed at a reference height of 10m (m s^{-1}).
- Roughness length of the substrate (m): this parameter determines the value of the minimum layer thickness as shown in equation 12.
- Location of the accident: defined by the longitude and latitude (degrees).
- Time of the accident (hours) and day number of the year that the accident occurred.
- Free ground water film thickness (m): free ground water is assumed to be present as a film and the average value of the film depth is used to estimate the amount of free ground water available for reaction. For wet ground conditions the value of this parameter should be higher than 0.002m [29].
- Atmospheric relative humidity (%).
- Spill duration (s): for continuous releases it is the time at which the spill terminates. For instantaneous releases the value of this parameter is set equal to 10s.
- Release duration (s): this is the time at which the pool ceases to release material to the atmosphere.
- Maximum pool radius (m): this parameter accounts for the presence of confinement.
- Air temperature (K) and release temperature (K): in many cases these two temperatures will be equal.
- Cloud cover factor (tenths): this parameter is equal to 10 for total cloud cover and 0 for a clear sunny day.

It should be noted that the input parameters can either be steady or varying. In cases of varying input parameters the user defines the time varying function.

4.5) Model outputs

The model outputs appear both as a result report and in the form of graphic displays. The result report shows the average values of the pool features in three regimes: in the spreading period, in the period after spreading ceases and for the total release duration. Graphs of the pool characteristics as function of time show the changing characteristics of the pool. The time dependent model outputs are:

- Pool radius (m)

- Pool temperature (K)
- Pool composition (in cases where two or more liquids are present)
- For each species released to the atmosphere, the amount of vapour evolved (kg) and the vapour evolution rate (kg s^{-1})
- Boiling and freezing points (K)

Other outputs are:

- Spreading duration (s)
- Total release duration (s)

5) POOLS OF PCl_3 , POCl_3 , HSO_3Cl , SiCl_4 and CH_3COCl

Five water reactive chemicals have already been incorporated into REACTPOOL (apart from SO_3 and oleums). Namely they are: phosphorus trichloride, phosphorus oxychloride, chlorosulphonic acid, silicon tetrachloride and acetyl chloride. The properties of these chemicals and of their hydrolysis products were parameterised as functions of temperature and are listed in Appendix B.

5.1) PCl_3 spills

PCl_3 is a clear, volatile liquid with a pungent, irritating odour. It is produced commercially by direct union of elemental phosphorus with chloride. Crude PCl_3 is then purified by distillation. Its main uses are as a pesticide intermediate and in the production of plastics, elastomer additives and in the production of POCl_3 and phosphorus acid [22, 23].

On escape to the atmosphere it creates liquid pools on land. The main feature of the pool behaviour is the reaction of PCl_3 with water. The reviewed literature suggests that under stoichiometric or excess water conditions the reaction between PCl_3 and water will follow equation 2. Three moles of HCl will be formed for every mole of PCl_3 [19]. The heat of this reaction was calculated by Melhem and Reid to be $-64.6 \text{ kJ/gmolePCl}_3$ if HCl forms as a gas, and $-289.2 \text{ kJ/gmolePCl}_3$ if aqueous HCl forms [19]. The latter case is considerably more exothermic due to the high HCl heat of solution.

In cases of excess PCl_3 , the overall reaction is described by equation 3. The heat of this reaction is $-47.5 \text{ kJ/gmolePCl}_3$ and $-272.1 \text{ kJ/gmolePCl}_3$ for the gaseous and aqueous cases respectively. Apart from HCl , H_3PO_4 liquid will also be formed. The pool will contain two liquids: PCl_3 and H_3PO_4 and its composition and properties will continuously change. Solid particles of red phosphorus will also be formed. These particles are assumed to be insoluble in the liquid medium and they deposit onto the bottom of the pool forming a film that alters conduction of heat from the ground (see section 3.3).

Reaction 2 will take place only when the molar ratio of water to PCl_3 is greater or equal to 3, i.e. for every kg of PCl_3 0.393 kg of water are required. In these cases H_3PO_3 as an aqueous solution will also be formed and be present in the pool. REACTPOOL model results indicate that it is extremely unlikely that there will be water excess even under very high ground water availability (it is usually the main water source; see section 6).

In cases of accidental spills water will be added gradually, and in these cases it has been suggested that reaction with water is instantaneous and there is no opportunity for accumulation [19]. It is expected that HCl will be directly evolved to the atmosphere in its gaseous phase unless there

excess is water that will allow HCl to enter into solution.

The generated cloud will initially contain PCl_3 vapour and HCl gas (H_3PO_3 and H_3PO_4 evolution rates are negligible in view of their extremely low volatility).

5.2) POCl_3 spills

POCl_3 is a white to yellow, volatile liquid with a pungent, musty odour. It is produced by direct oxidation of PCl_3 with oxygen. About 75 to 80% of POCl_3 manufacture is estimated to be used in the manufacture of phosphate esters for plasticizers, flame retardants, hydraulic fluids and other applications [22, 23].

Unfortunately, there are very limited data on the hydrolysis reaction of POCl_3 . The only source of information came from one of the manufacturers [20]. Reaction 4 ($\Delta H = -286.19 \text{ kJ/mol POCl}_3$ when 36% of HCl solution is produced) will take place only if the molar fraction of water to POCl_3 is greater or equal to 13.5, i.e. every kg of POCl_3 requires about 1.585 kg of water. This is almost impossible to occur in cases of accidental spills, since very large amounts of water are required. Reaction 5 ($\Delta H = -89.54 \text{ kJ/mol POCl}_3$) will occur only when the molar fraction of water to POCl_3 is lower than 13.5 and higher or equal to 3.5, i.e. for every kg of POCl_3 there should be less than 1.585 kg and more than 0.352 kg of water. Reaction 6 ($\Delta H = +0.0484 \text{ kJ/mol POCl}_3$) will take place only when the mass fraction of water to POCl_3 is less than 0.352. It should be noted that $\text{P}_2\text{O}_3\text{Cl}_4$ is a complex compound and no information could be found on its nature and properties. It is expected that it will further react with water forming phosphorous acids [20]. Unfortunately, due to the lack of data reaction 6 cannot be adequately described. Therefore it is assumed that in all cases where the molar fraction of water to POCl_3 is below 10.5, reaction 5 takes place.

On escape to the atmosphere POCl_3 creates a liquid pool with changing composition and properties. In most cases reaction 5 will take place and the pool will contain POCl_3 and H_3PO_4 liquids. HCl gas will be directly evolved as a hydrolysis product. The liquid pool may either boil or evaporate or even solidify.

The generated cloud will initially contain POCl_3 vapour and HCl gas.

5.3) HSO_3Cl spills

HSO_3Cl contains equimolar quantities of HCl and SO_3 . It is often referred in the literature as chlorosulphuric acid or simply CSA. It resembles sulphur trioxide in its behaviour and properties, although it is generally described as less toxic than SO_3 . HSO_3Cl is a colourless, mobile, extremely reactive liquid with pungent odour. It fumes very strongly in air and has been used as a military smoke-generating agent. Its main uses are in organic synthesis as a sulphating, sulphonating or chlorosulphonating agent. Its applications are principally as an intermediate in the production of synthetic detergents, drugs and dyestuffs. It is preferred in some applications because it is a strong sulphonating agent but less destructive than SO_3 . It is non-flammable, but it may cause ignition by contact with combustible materials [22, 23].

On escape from containment it creates liquid pools, usually on land. It is highly hygroscopic and reacts readily and exothermically with any available water. The pool will contain H_2SO_4 and HSO_3Cl or excess water, and its composition and properties will continuously change as HSO_3Cl

reacts with water generating H_2SO_4 liquid and HCl gas, according to equation 7 ($\Delta H = -1115 \text{ kJ/kg}$ of reacted water). It may boil or evaporate depending on the conditions and mainly on the amount of water available for reaction (there is no possibility of solidification). H_2SO_4 will also attack concrete or asphalt surfaces and will react with some of their compounds [33].

The generated cloud will initially contain HCl gas, HSO_3Cl and small quantities of H_2SO_4 vapours. HSO_3Cl will continuously react with atmospheric moisture yielding H_2SO_4 and HCl vapour and gas respectively. At a certain point all its quantity will be consumed. H_2SO_4 and HSO_3Cl vapour will also interact with atmospheric moisture yielding aerosols. Some of the amount of vapour and aerosol will be deposited on the ground due to gravitational settling and other deposition effects. In many cases the generated cloud will initially be denser than air. Only after some distance downwind, allowing adequate dilution with air, will it become passive. Overall, the behaviour of the generated cloud is too complex as it will initially contain three components in different phases (vapours and aerosols). Even after some distance downwind, it will contain HCl gas and H_2SO_4 aerosol. Its behaviour resembles the behaviour of clouds generated from spills of SO_3 and oleum with the additional complexity that a third component, HCl is involved.

5.4) SiCl_4 spills

SiCl_4 is a colourless, clear, mobile, fuming liquid with suffocating odour. Its main industrial use is in the production of semiconductors, silica fume and other silicon compounds. It has also been used as a warfare agent [22, 23].

On escape from containment it creates liquid pools that solely contain SiCl_4 liquid. The hydrolysis reaction occurs according to equation 9 ($\Delta H = -4050 \text{ kJ/kg}$ of reacted water) [21]. Orthosilicic acid solid particles are assumed to be insoluble in liquid SiCl_4 . In cases where the pool and other characteristics are such that insoluble settled particles are formed, the pool composition and properties will be constant. In all cases the pool will either boil or evaporate; there is no possibility of solidification due to the extremely low freezing point of silicon tetrachloride (204.3K).

Apart from HCl that is directly evolved from the hydrolysis reaction, SiCl_4 will also evolve in view of its high volatility. The generated cloud will initially contain SiCl_4 and HCl vapours. SiCl_4 will react with atmospheric moisture yielding HCl and orthosilicic acid solid in a similar way to the liquid phase hydrolysis reaction. Overall, the behaviour of the generated cloud is extremely complicated due to all the phenomena expected to take place. The fact that it is very possible for the generated cloud to be initially denser than air adds to this complexity.

5.5) CH_3COCl spills

Acetyl chloride is a colourless, mobile liquid with a pungent odour. It is used on a large scale as a catalyst and its main applications are in qualitative organic analysis, in the synthesis of pharmaceuticals, grease and dyes and in the preparation of industrial acetic derivatives [22, 23]. It reacts violently with water according to equation 10 ($\Delta H = -5000 \text{ kJ per kg reacted } \text{H}_2\text{O}$).

The pool composition and properties are not constant; the pool contains CH_3COCl and CH_3COOH . HCl gas is directly liberated to the atmosphere in its gaseous phase. Both CH_3COCl and CH_3COOH are evolved from the pool (CH_3COOH always in smaller amounts than the chloride due to its lower vapour pressure). The pool may boil (b.p. $\text{CH}_3\text{COCl} = 325 \text{ K}$, b.p. $\text{CH}_3\text{COOH} = 391 \text{ K}$) or evaporate or

even solidify after spreading ceases (m.p. CH_3COCl = 160 K, m.p. CH_3COOH = 290 K).

The generated cloud will contain CH_3COCl and CH_3COOH vapour and HCl gas. Its behaviour will be very complicated as many interactions and processes are expected to take place (vapour phase hydrolysis of CH_3COCl , aerosols generation etc.)

6) REACTPOOL MODEL RESULTS

Overall, the pool behaviour of water reactive chemicals is strongly affected by the amount of water available for reaction. The main water source is usually the free ground water. The surface roughness and the wind speed also have strong effects on the results. The rest of the input parameters have weaker effects.

A large number of release scenarios was examined. The ones presented in the following sections were judged to be the most representative and appropriate for each case. It should be noted that all investigated spills are continuous. Instantaneous spills have a very similar behaviour. The values of the release scenario input parameters are shown in Table 4. It should be noted that parameters given a single value in this table remained constant in all investigated scenarios. These parameters do not have a significant effect on the results.

Table 4
Values of the release scenario input parameters

Spill rate and duration = 16 kg s^{-1} for 600 s
Maximum duration of release to the atmosphere = 1800 s
Maximum pool radius = 50 m
Type of substrate = concrete
Free water film thickness on the ground, w_g = 0.0005 m, 0.0015 m, 0.003 m, 0.005 m
Surface roughness length, z_o = 0.1m, 0.0001m, 1 m
Wind speed at 10 m, U_{10} = 5 m s^{-1} , 2 m s^{-1} , 10 m s^{-1}
Air temperature = Release temperature = 288 K
Atmospheric radiation factor = 0.84
Cloud cover factor = 7
Relative humidity = 70%
Location = North England, UK (latitude = 54° , longitude = 2°)
Time step used in the calculations = 0.01 s

6.1) Water supply to the pool

The percentage contribution of each of the three water sources to the total water usage for PCl_3 and POCl_3 pools is shown in Figure 3. This figure shows that in most cases free ground water is the dominant water source (70-98%) and its contribution increases with increasing film ground water thickness. Atmospheric water is usually the second most important water source (2-30%) and its contribution increases with decreasing amount of free ground water. Concrete water is usually the least significant source and its contribution increases with decreasing free ground water film thickness. HSO_3Cl , SiCl_4 and CH_3COCl have similar behaviour as to the percentage water supply to

the pool.

It should be noted that although atmospheric moisture and concrete water are not the dominant water sources, they are the only sources of water available for reaction for the after spreading period and thus, they have a strong effect on the pool behaviour in this period.

6.2) Effect of free ground water film thickness on the amount of vapours evolved

As shown in section 6.1, the main water source into the pool is the free water lying on the ground. The effect of this parameter to the total amounts of vapour and gas evolved for the total release duration (1800 s) is shown in Figure 4. This figure shows that the amounts evolved to the atmosphere significantly increase with increasing free ground water film thickness.

Additionally, the amount of solid particles of red phosphorus and orthosilicic acid produced in cases of PCl_3 and SiCl_4 spills respectively, also increases with increasing free ground water film thickness.

The pool behaviour in the spreading period is different compared to the one after spreading ceases. Average vapour evolution rates are much higher in the spreading period as shown in Figure 5 (spills of PCl_3 and POCl_3), compared to the average vapour evolution rates in the after spreading period as shown in Figure 6 (spills of PCl_3 and POCl_3).

6.3) Pool temperature profiles for different values of free ground water film thickness

Pools generated from accidental spills of water reactive chemicals will have temperatures changing with time. Figure 7 shows that the pool temperature increases with increasing values of free ground water film thickness. Temperatures higher than 450 K and 500 K are encountered during the early spreading stages under high values of w_g , for PCl_3 and POCl_3 spills respectively. Pool temperature drops just after pool spreading ceases, since free ground water is no longer encountered. All types of pools boil under high ground water availability ($w_g > 0.0015\text{m}$). They usually boil in the early stages of spreading when the surface area of the pool is still small. It has been found that only POCl_3 and CH_3COCl pools may solidify under extremely low values of w_g ($< 0.0001\text{m}$) and only after spreading ceases. It should be noted that the boiling and freezing points of the pool are not constant. In all cases (except of SiCl_4 pools) the pool boiling and freezing points are higher compared to the ones of the pure water reactive liquids. This is due to the fact that the secondary liquids produced from the hydrolysis reactions have higher boiling and freezing points and therefore elevate the pool boiling and freezing point (see Appendix B).

6.4) Pool radius profiles for different values of free ground water film thickness

As expected, the pool radius increases with decreasing values of free ground water film thickness as shown in Figure 8. As shown in section 6.2, increasing values of w_g correspond to increasing vapour evolution rates and therefore lower amounts of liquid present in the pool. Pool radius continuously increases during the spreading period (which is usually only slightly longer than the spill duration) and it reaches its maximum value just after the spill duration of 600 s; then it slowly shrinks.

6.5) Pool composition profiles for different values of free ground water film thickness

With the exception of SiCl_4 pools, pools of PCl_3 , POCl_3 , HSO_3Cl and CH_3COCl are a mixture of two liquids and their composition and properties change continuously as water reactive chemical continuously reacts with water yielding a secondary liquid.

The mass percentage of water reactive chemical in the pool decreases with increasing w_g , as indicated in Figure 9 (for PCl_3 and POCl_3 spills), since more secondary liquid is produced at higher values of w_g and additionally there is more water reactive chemical evolved to the atmosphere.

6.6) Effect of surface roughness length on the amount of vapour evolved

The surface roughness length, z_o , is the parameter that determines the value of the minimum layer thickness h_{\min} and therefore strongly affects the pool radius and the surface area of evolution [2]. Figure 10 shows that increasing values of roughness length, result in decreasing amounts of vapours evolved. This occurs since higher values of roughness length correspond to higher values of h_{\min} and therefore smaller pool radius and surface areas and lower vapour evolution rates. Generally, although the effect of the surface roughness length z_o is quite strong, it is weaker than the effect of the free ground water film thickness.

6.7) Effect of wind speed on the amount of vapour evolved

The wind speed at a reference height of 10m, U_{10} (m s^{-1}) has a relatively strong effect on the amount of vapours of the water reactive chemical evolved as shown in Figure 11. Increasing wind speed increases their amount evolved. However, the wind speed does not have a significant effect on the amount of HCl evolved, since this is directly evolved as a hydrolysis reaction product and is primarily affected by the amount of water available for reaction.

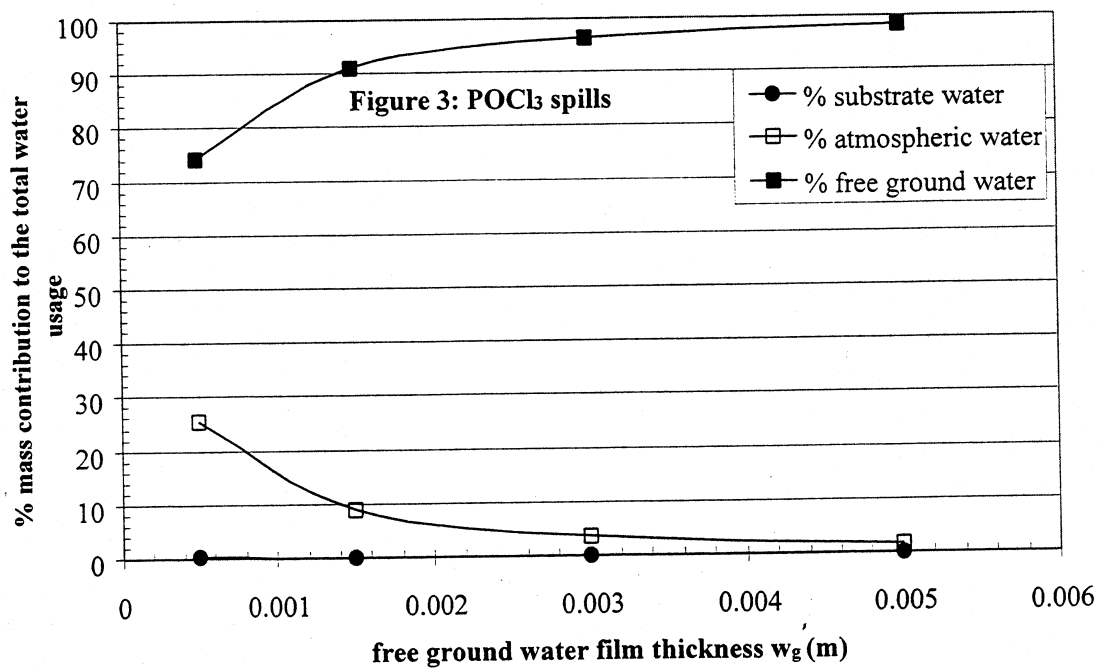
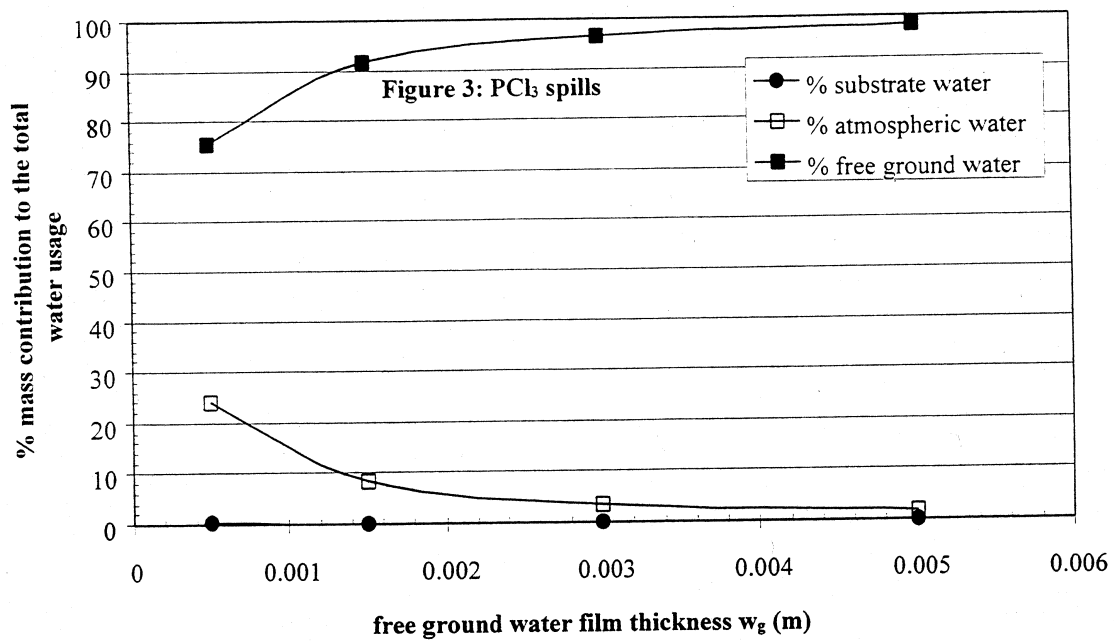


Figure 3
 Percentage supply of the three water sources to the total amount of water provided for reaction for spills of 16 kg s^{-1} for 600s of PCl_3 and POCl_3 ($z_0=0.1\text{m}$, $U_{10}=5 \text{ ms}^{-1}$)

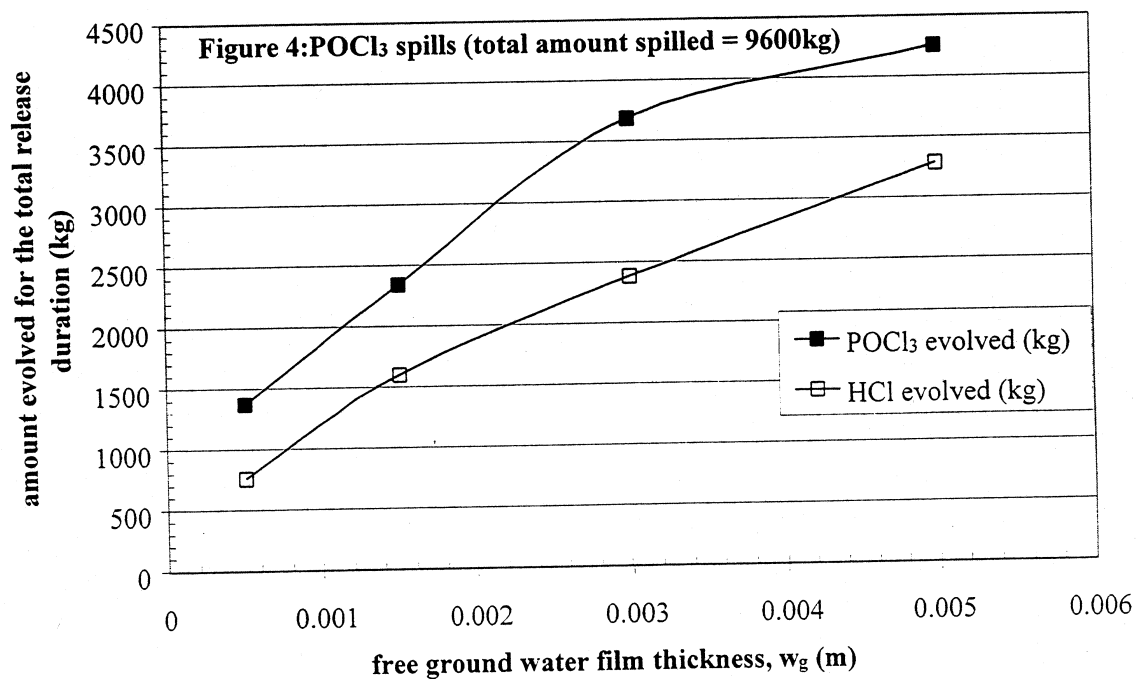
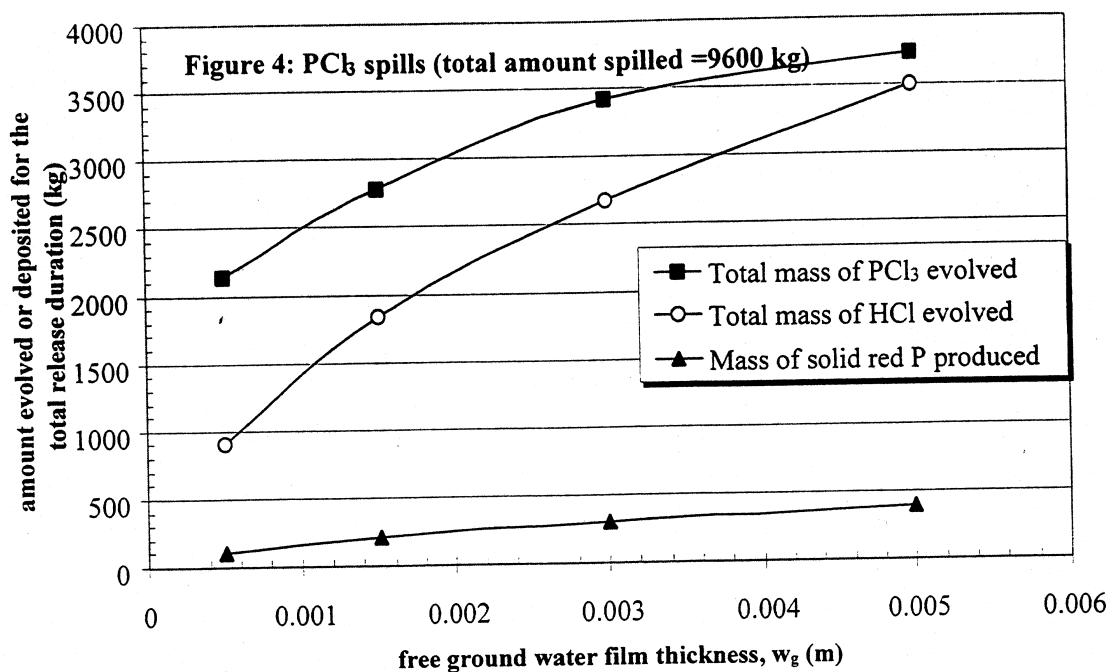


Figure 4
Effect of free water film thickness on the amount of vapour evolved to the atmosphere
for spills of 16 kg s^{-1} for 600 s of PCl_3 and POCl_3 ($z_0=0.1\text{m}$, $U_{10}=5 \text{ ms}^{-1}$)

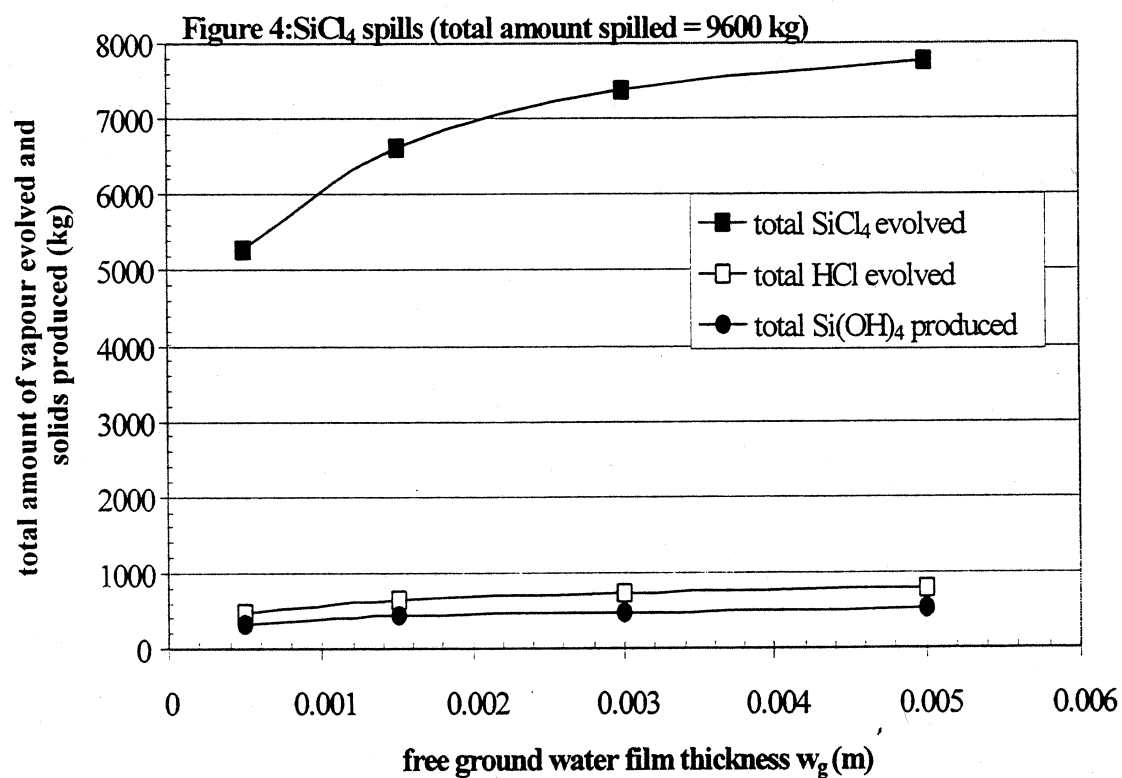
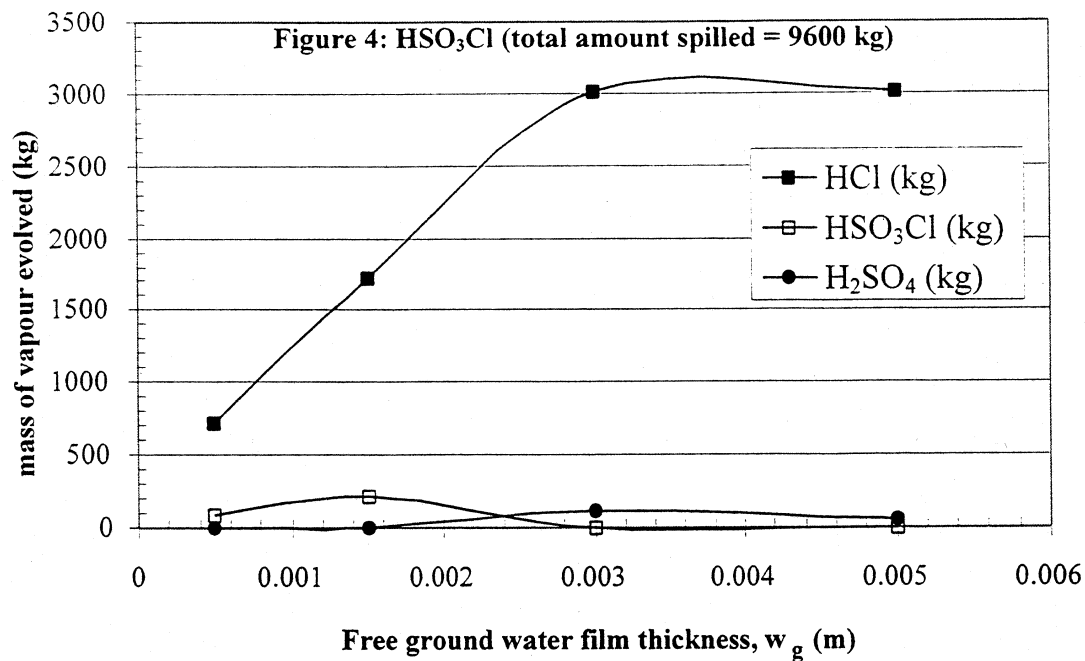


Figure 4
Effect of free water film thickness on the amount of vapours evolved to the atmosphere for spills of 16 kg s^{-1} for 600 s of HSO_3Cl and SiCl_4 ($z_0=0.1 \text{ m}$, $U_{10}=5 \text{ ms}^{-1}$)

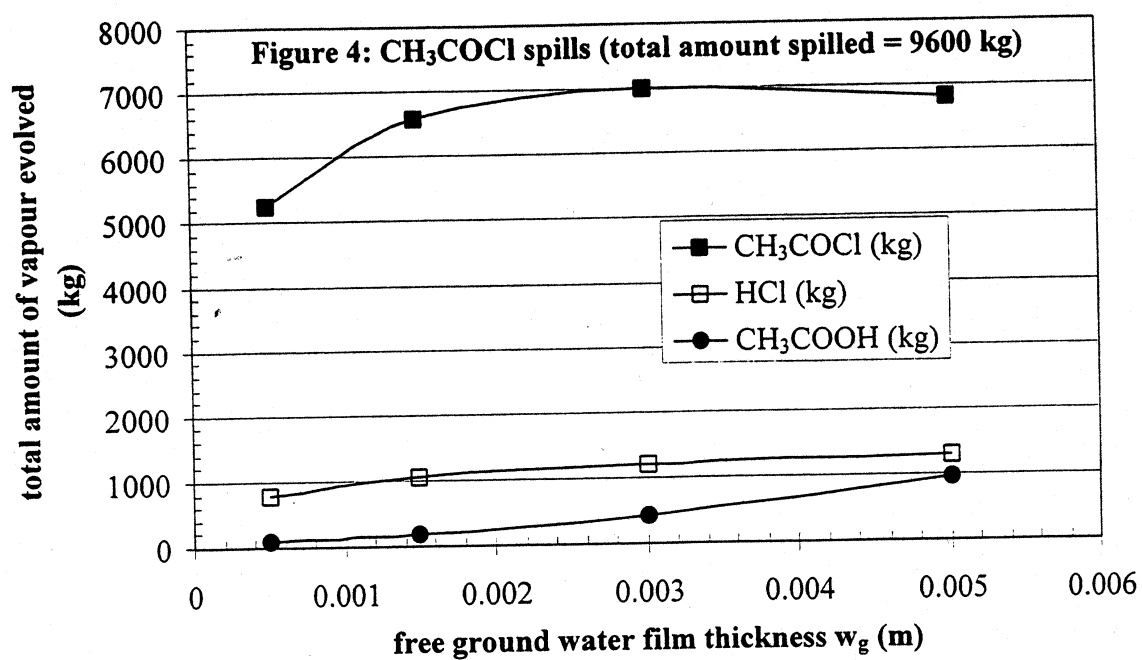


Figure 4
 Effect of free water film thickness on the amount of vapours evolved to the atmosphere
 for spills of 16 kg s^{-1} for 600 s of CH_3COCl ($z_0=0.1\text{m}$, $U_{10}=5 \text{ ms}^{-1}$)

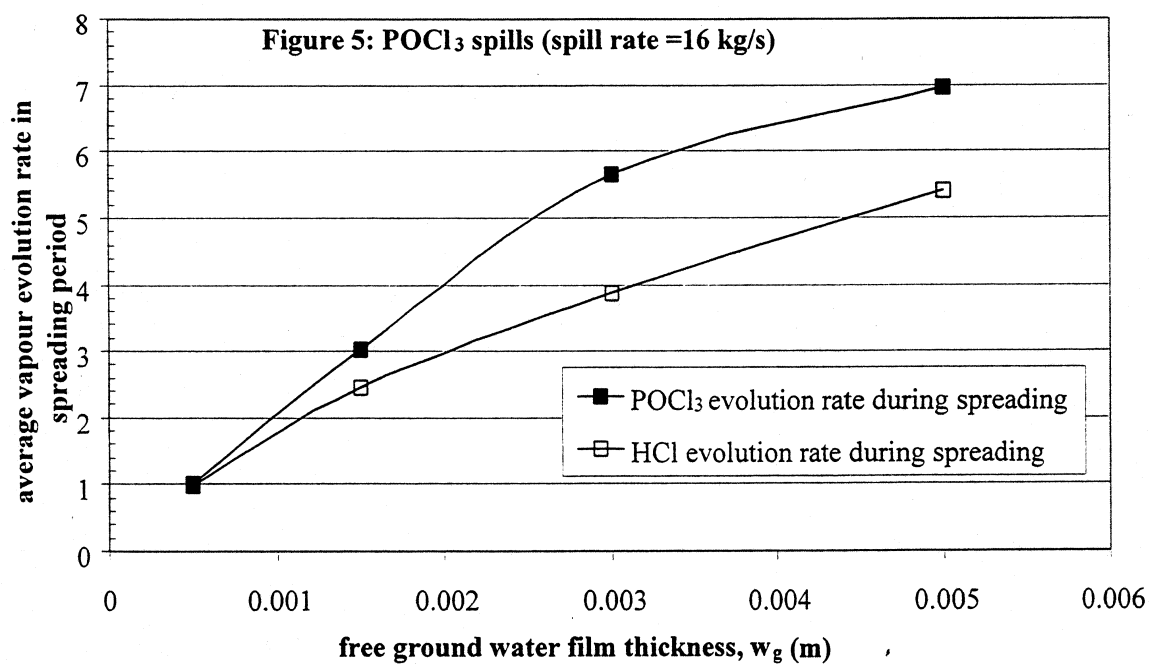
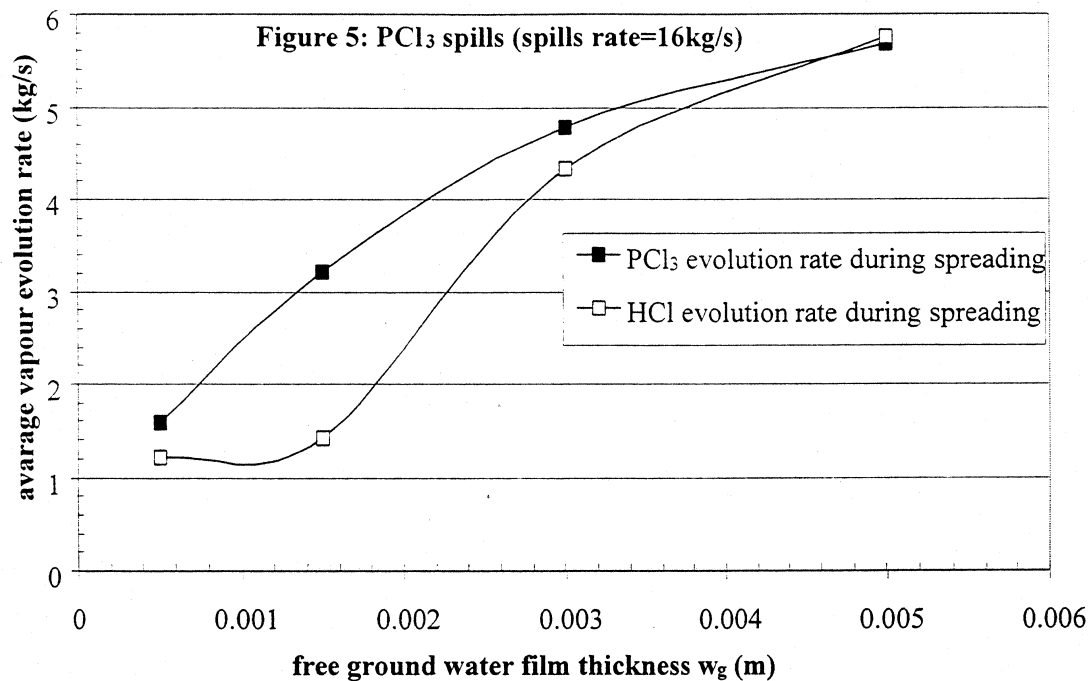


Figure 5
Effect of free water film thickness on the vapour evolution rates in the spreading period for spills of 16 kg s^{-1} for 600 s of PCl_3 and POCl_3 ($z_0=0.1\text{m}$, $U_{10}=5 \text{ ms}^{-1}$)

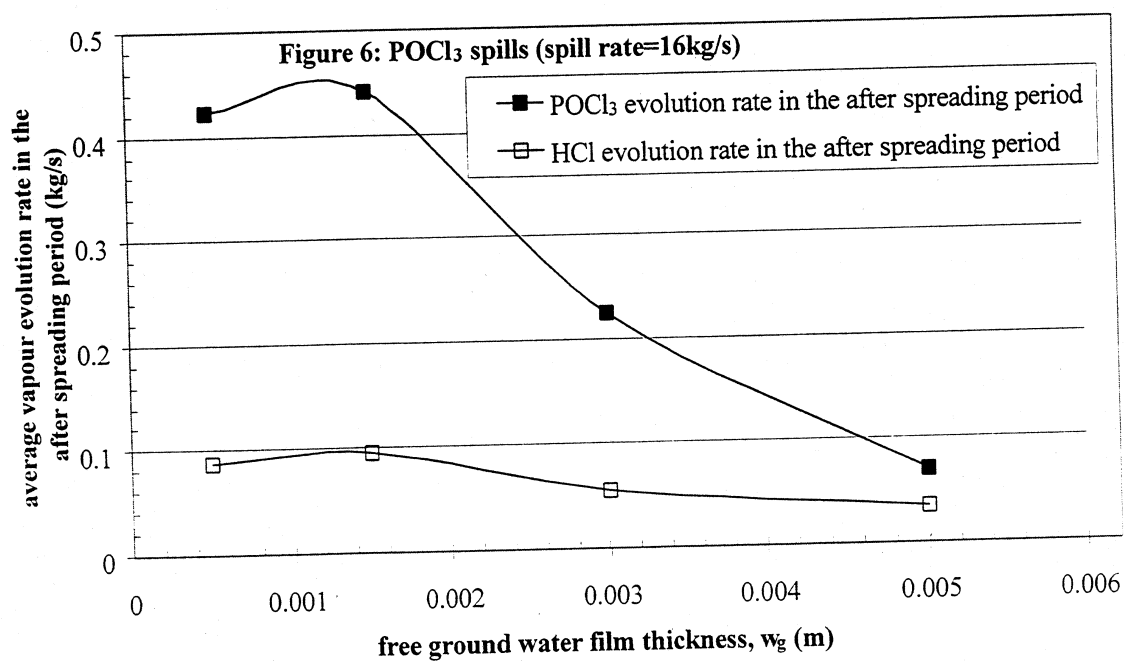
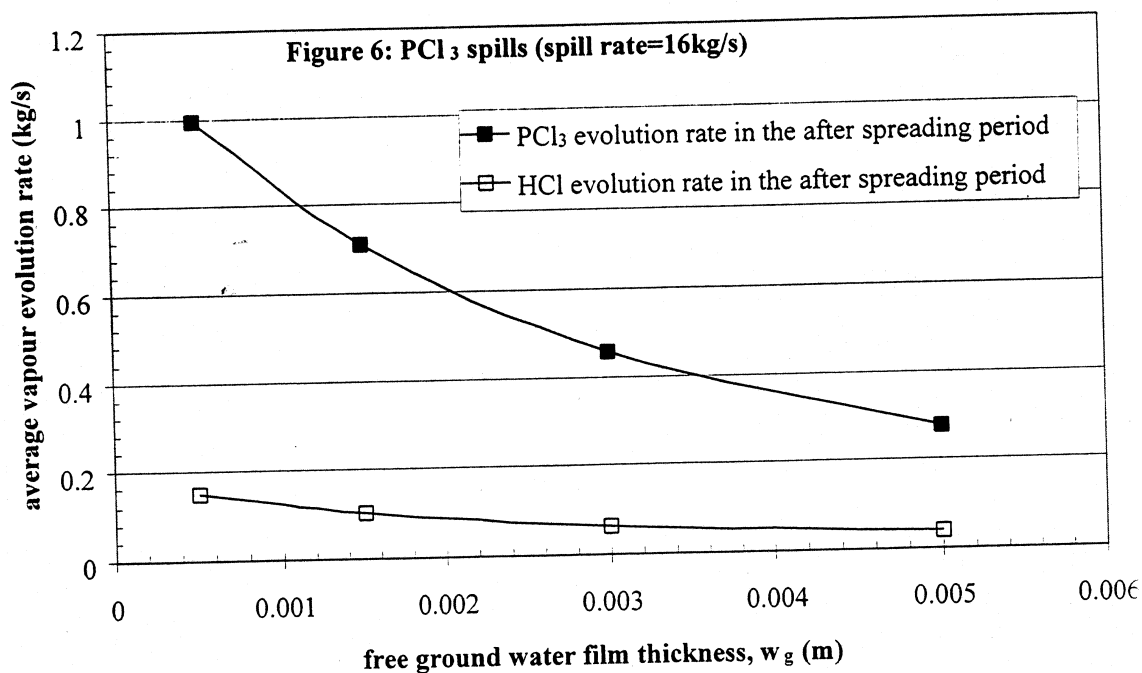


Figure 6
Effect of free water film thickness on the vapour evolution rates in the after spreading period for spills of 16 kg s^{-1} for 600 s of PCl_3 and POCl_3 ($z_0=0.1\text{m}$, $U_{10}=5 \text{ ms}^{-1}$)

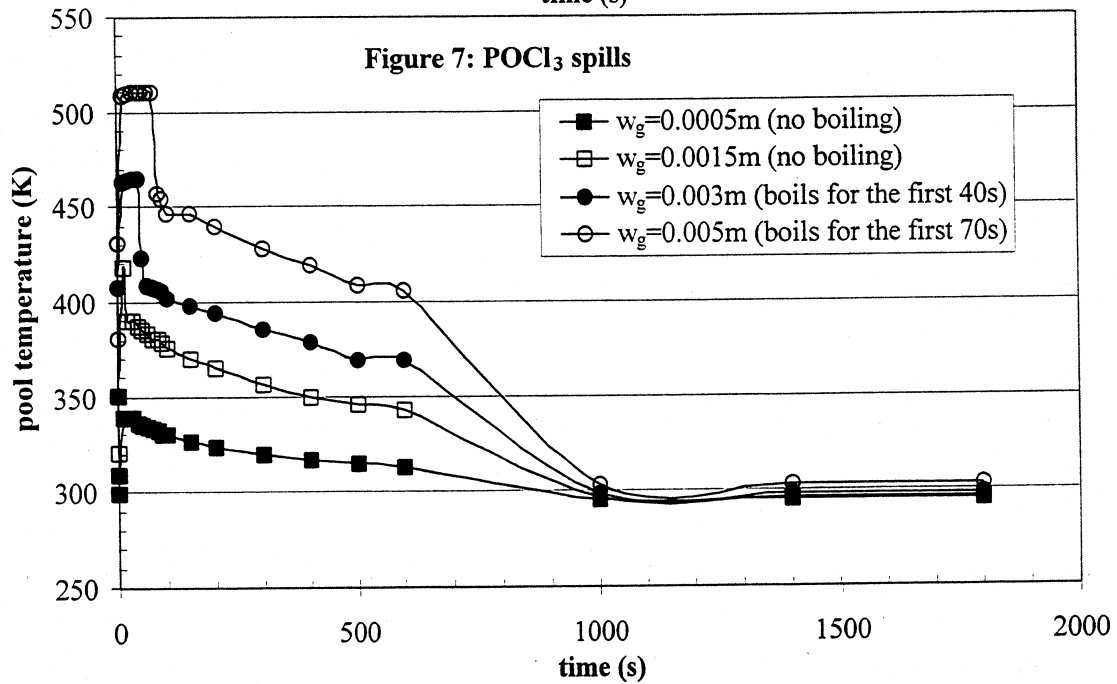
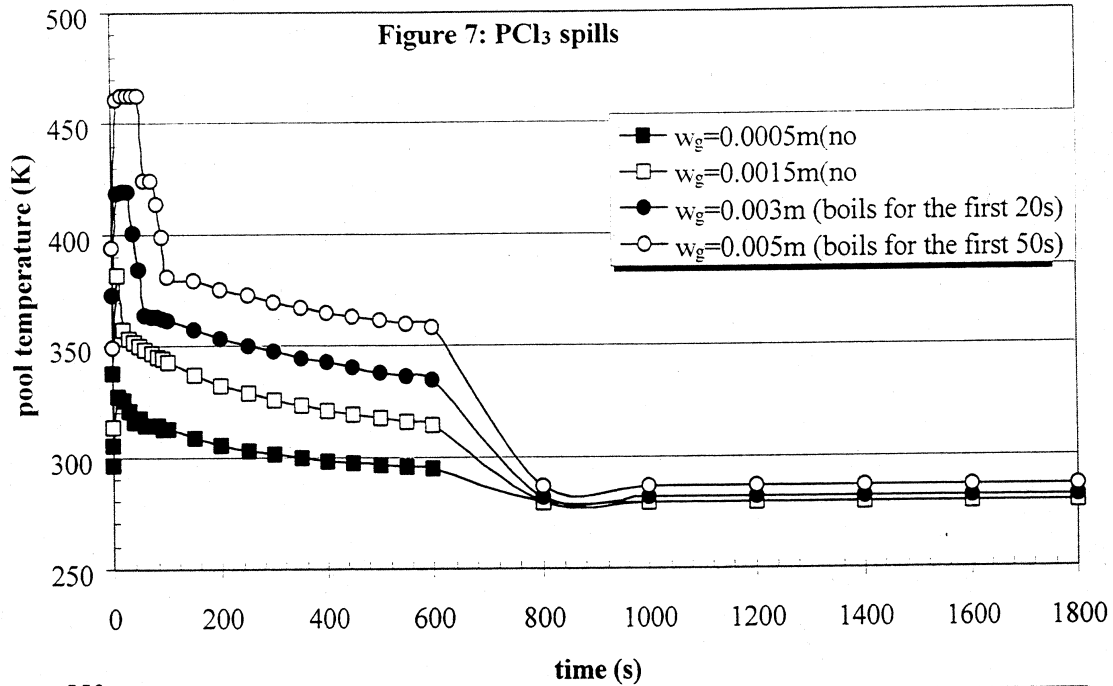


Figure 7

Pool temperature profiles under different values of w_g for spills of 16 kg s^{-1} for 600 s of PCl_3 and POCl_3 ($z_0=0.1 \text{ m}$, $U_{10}=5 \text{ m s}^{-1}$)

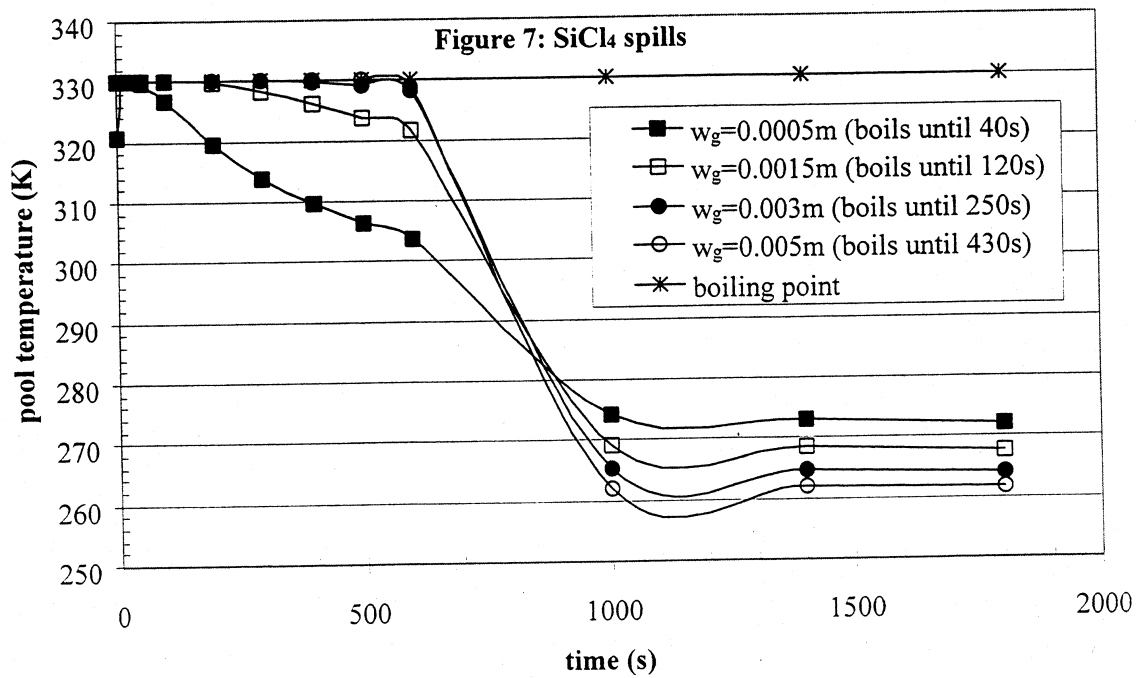
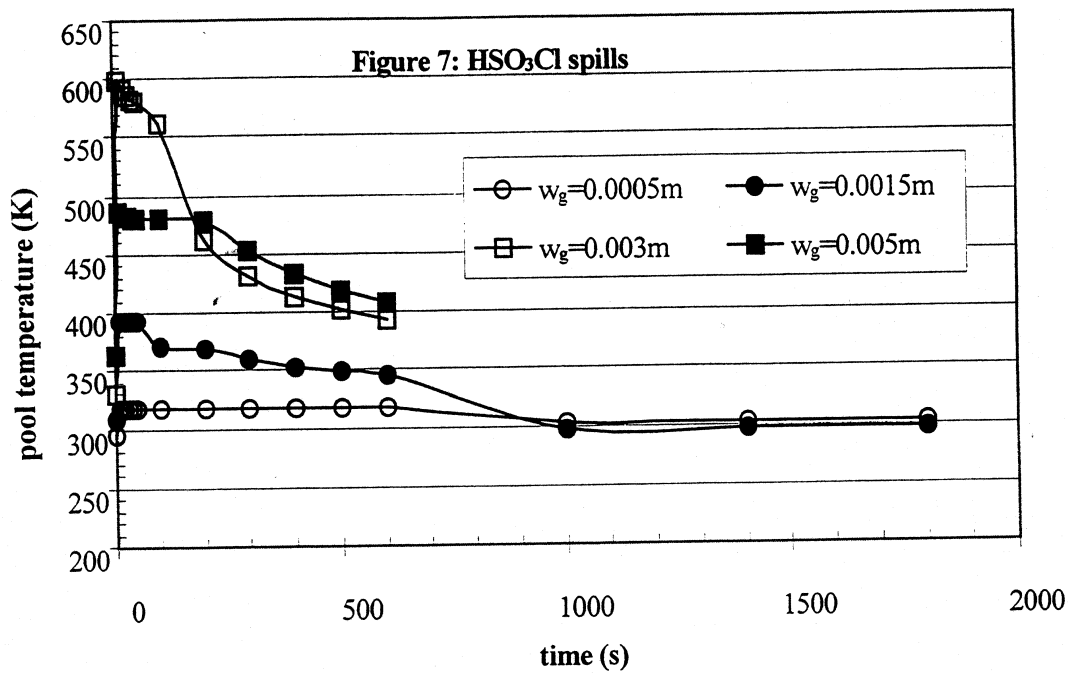


Figure 7

Pool temperature profiles under different values of w_g for spills of 16 kg s^{-1} for 600 s of HSO₃Cl and SiCl₄ ($z_0=0.1 \text{ m}$, $U_{10}=5 \text{ m s}^{-1}$)

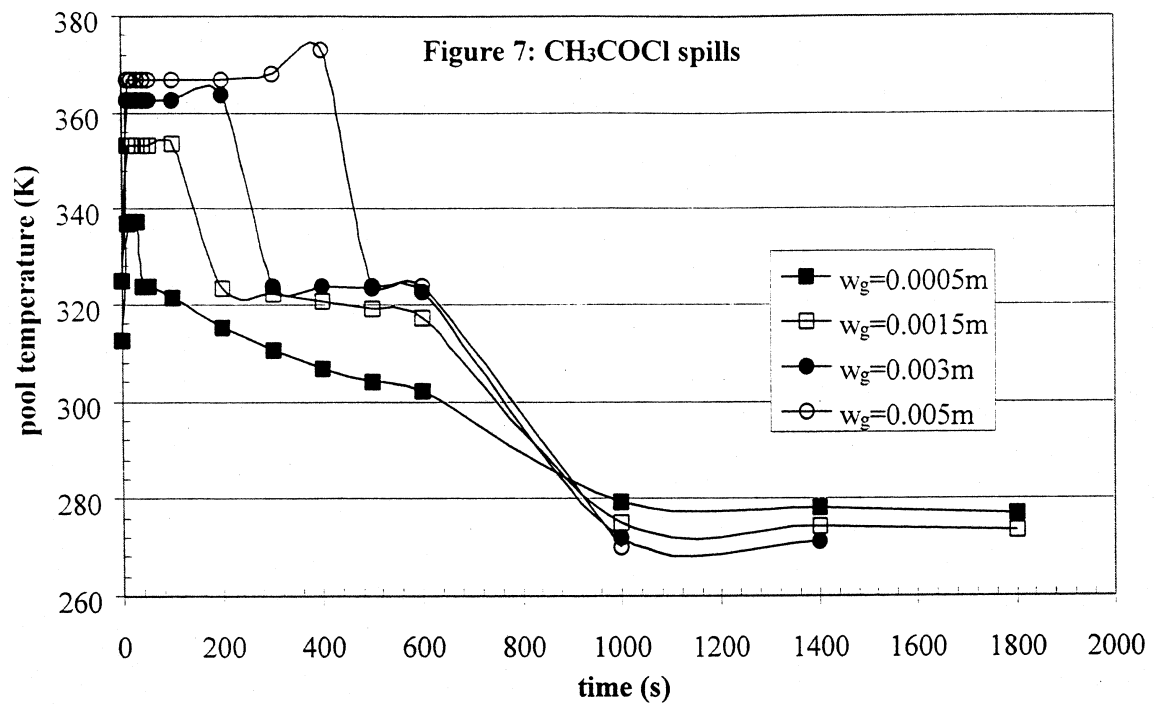


Figure 7

Pool temperature profiles under different values of w_g for spills of 16 kg s^{-1} for 600 s of CH_3COCl ($z_0=0.1 \text{ m}$, $U_{10}=5 \text{ m s}^{-1}$)

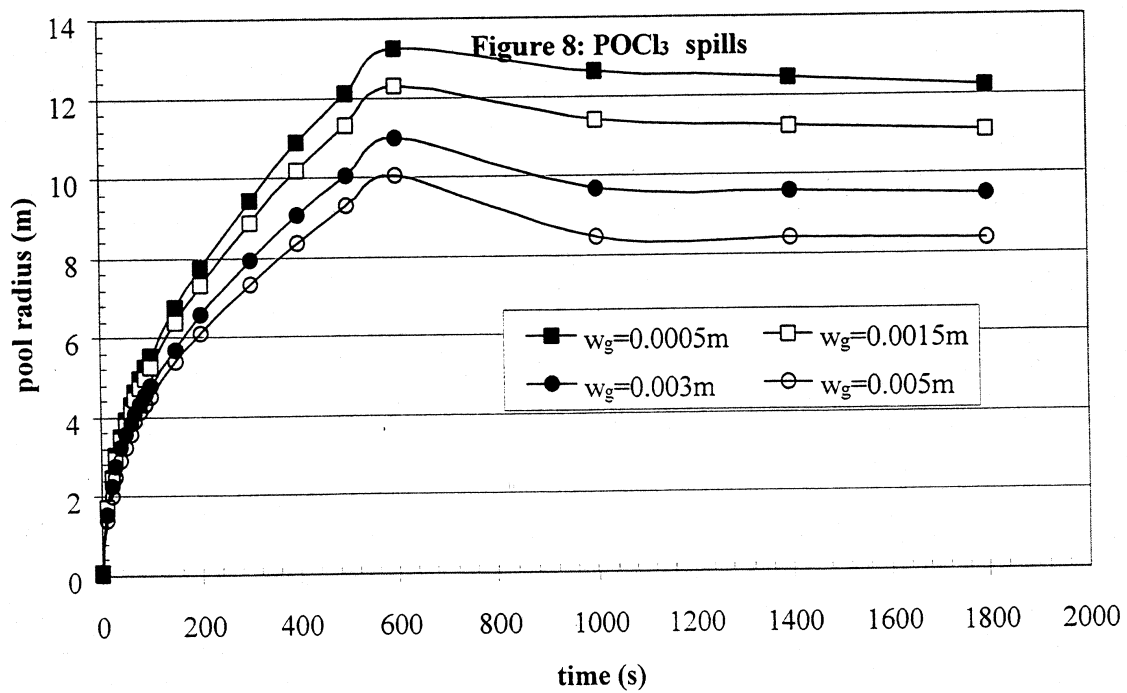
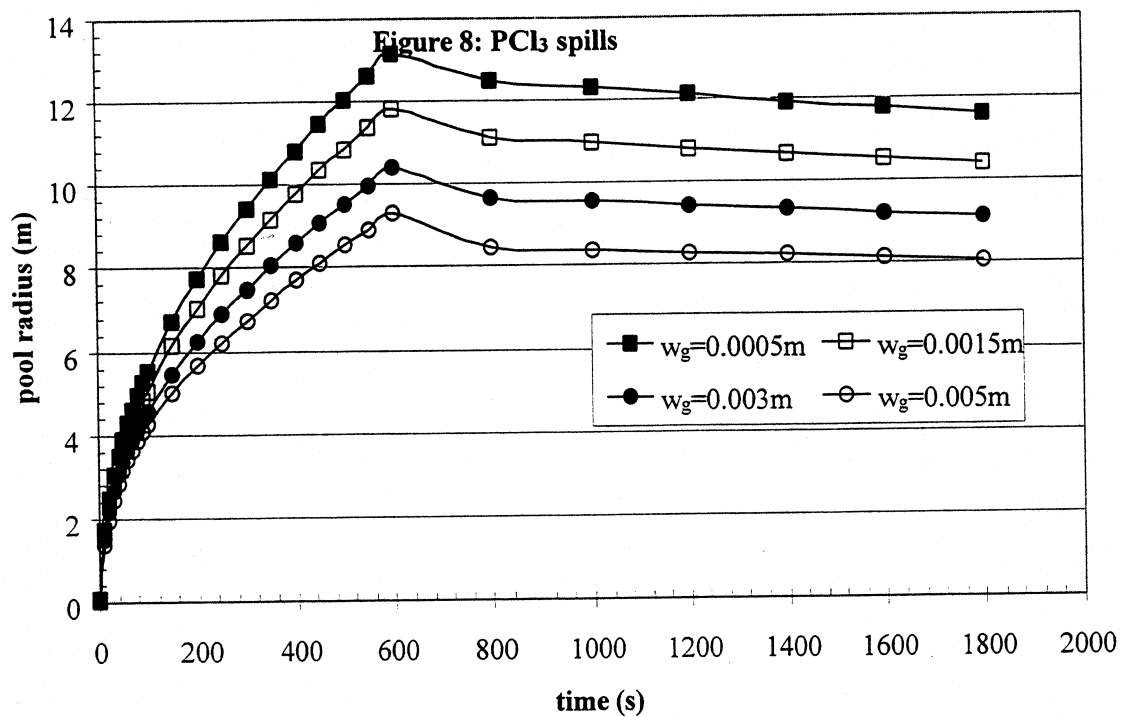


Figure 8
Pool radius profiles under different values of w_g for spills of 16 kg s^{-1} for 600 s of PCl_3 and POCl_3 ($z_0=0.1 \text{ m}$, $U_{10}=5 \text{ m s}^{-1}$)

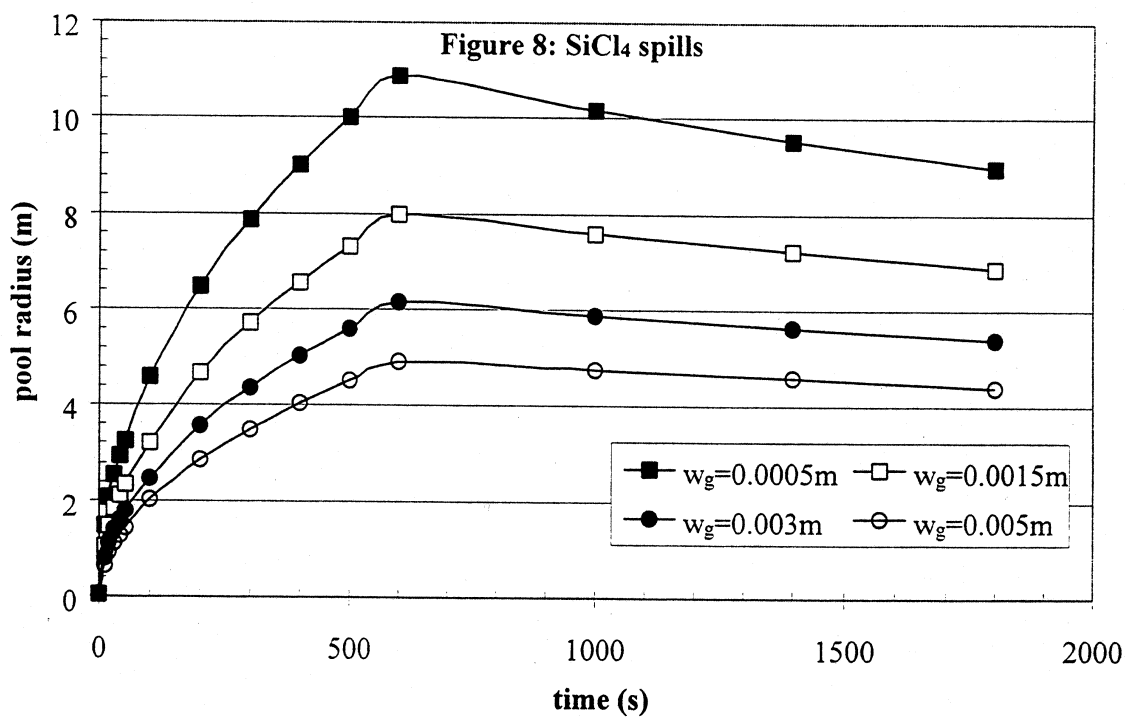
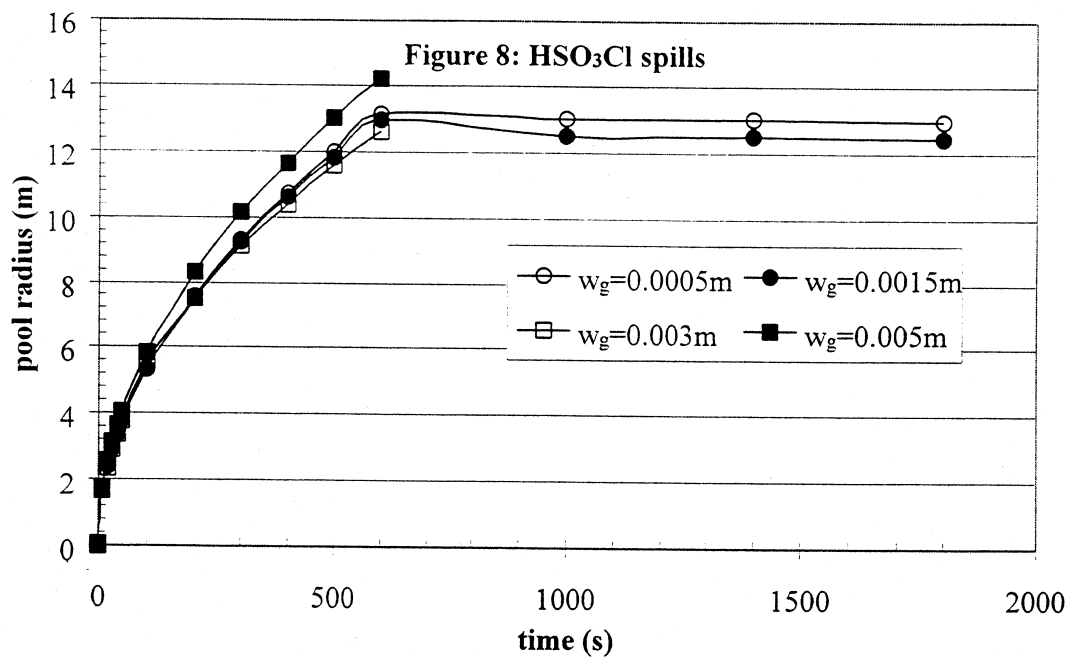


Figure 8
Pool radius profiles under different values of w_g for spills of 16 kg s⁻¹ for 600 s of HSO₃Cl and SiCl₄ ($z_0=0.1$ m, $U_{10}=5$ m s⁻¹)

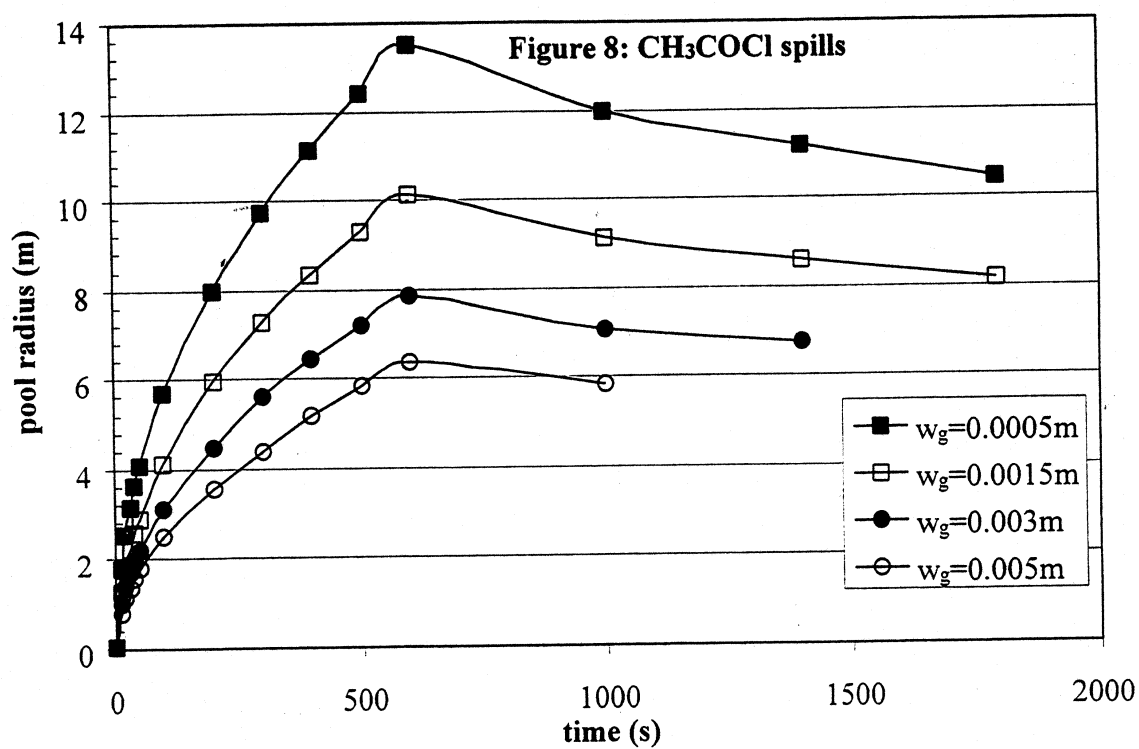


Figure 8
Pool radius profiles under different values of w_g for spills of 16 kg s^{-1} for 600 s of CH_3COCl ($z_0=0.1 \text{ m}$, $U_{10}=5 \text{ m s}^{-1}$)

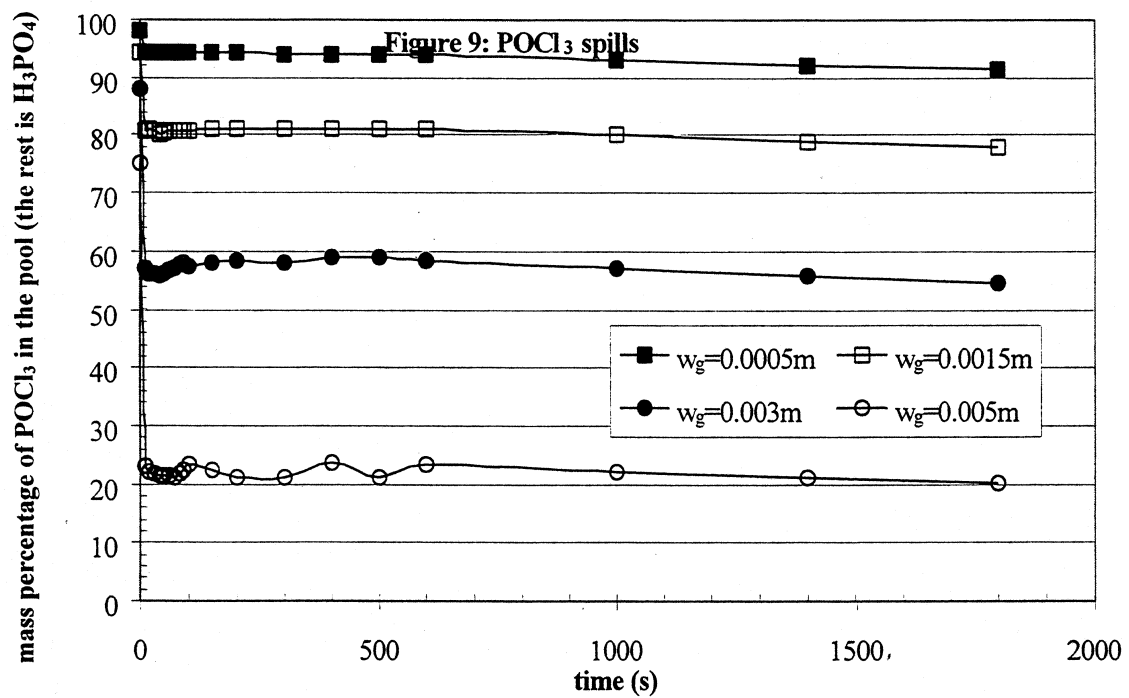
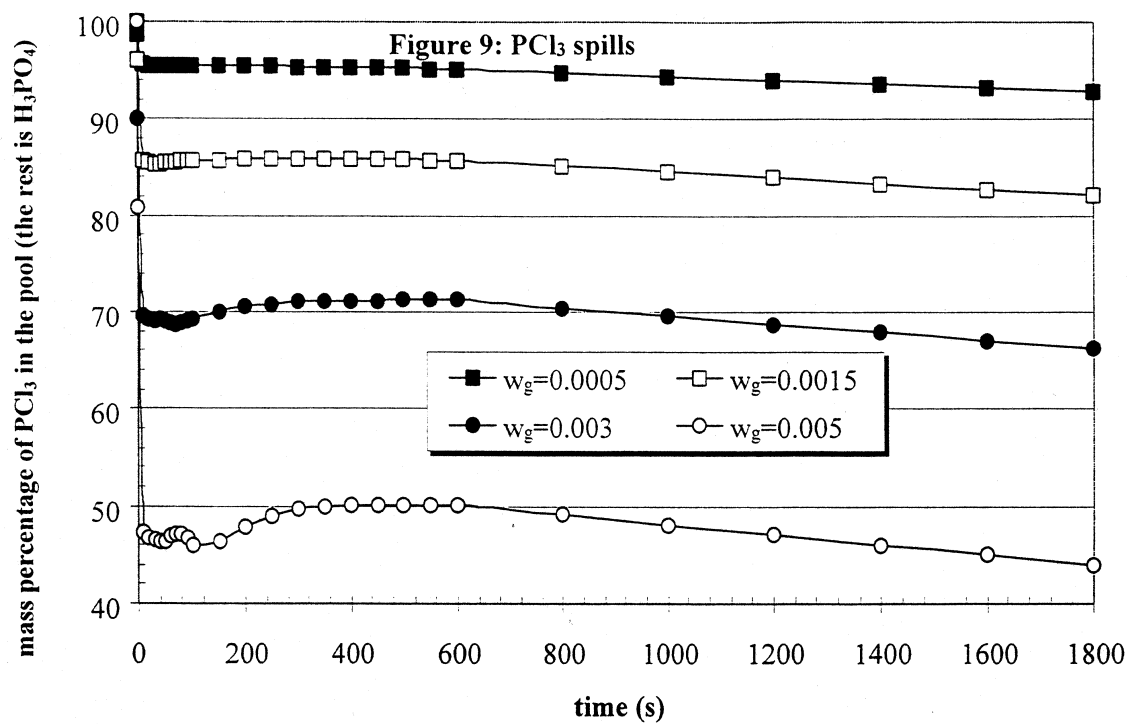


Figure 9
Pool composition profiles under different values of w_g for spills of 16 kg s^{-1} for 600 s of PCl_3 and POCl_3 ($z_0=0.1 \text{ m}$, $U_{10}=5 \text{ m s}^{-1}$)

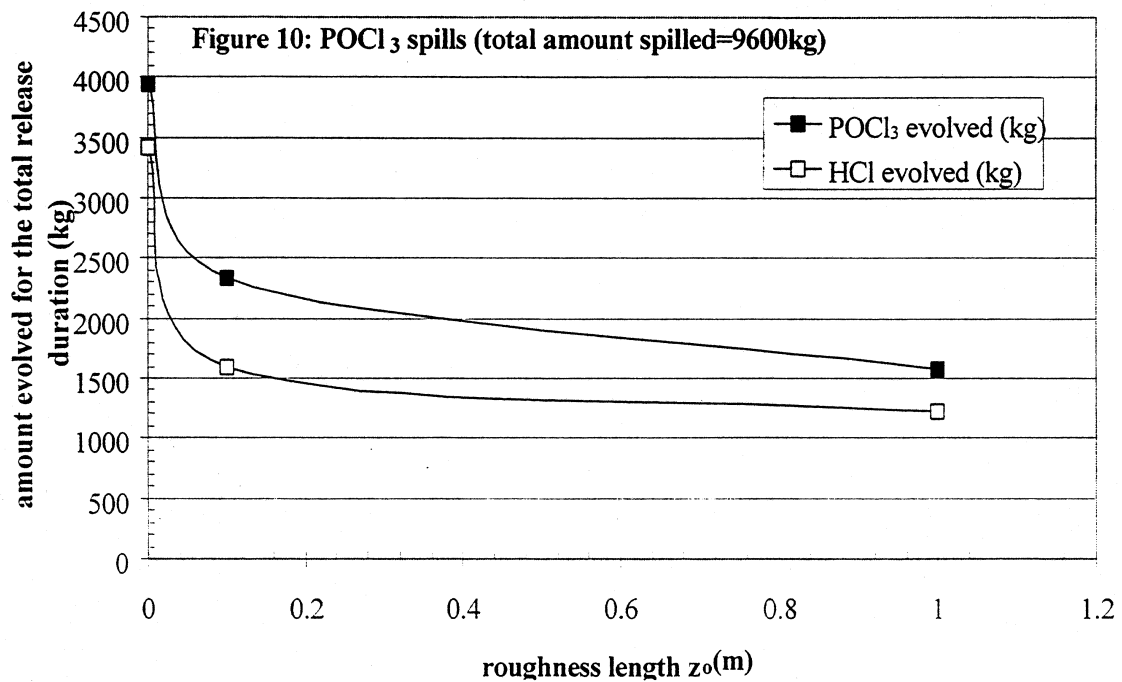
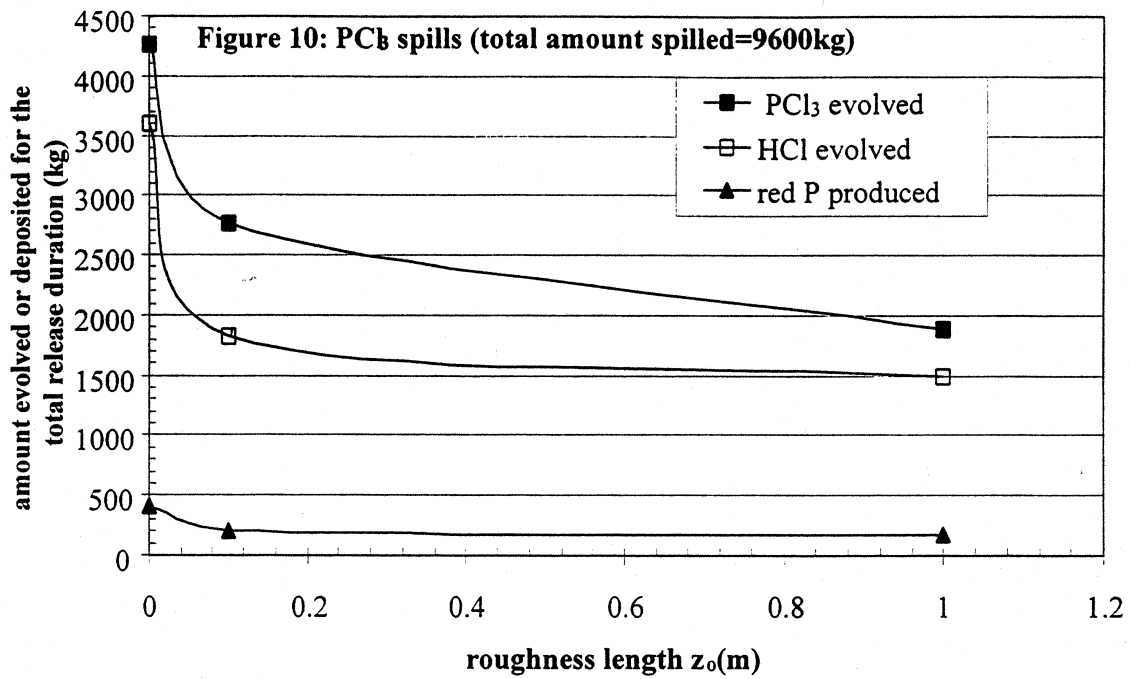


Figure 10
Effect of surface roughness length on the amount of vapours evolved to the atmosphere
for spills of 16 kg s^{-1} for 600 s of PCl_3 and POCl_3 ($w_g=0.0015 \text{ m}$, $U_{10}=5 \text{ m s}^{-1}$)

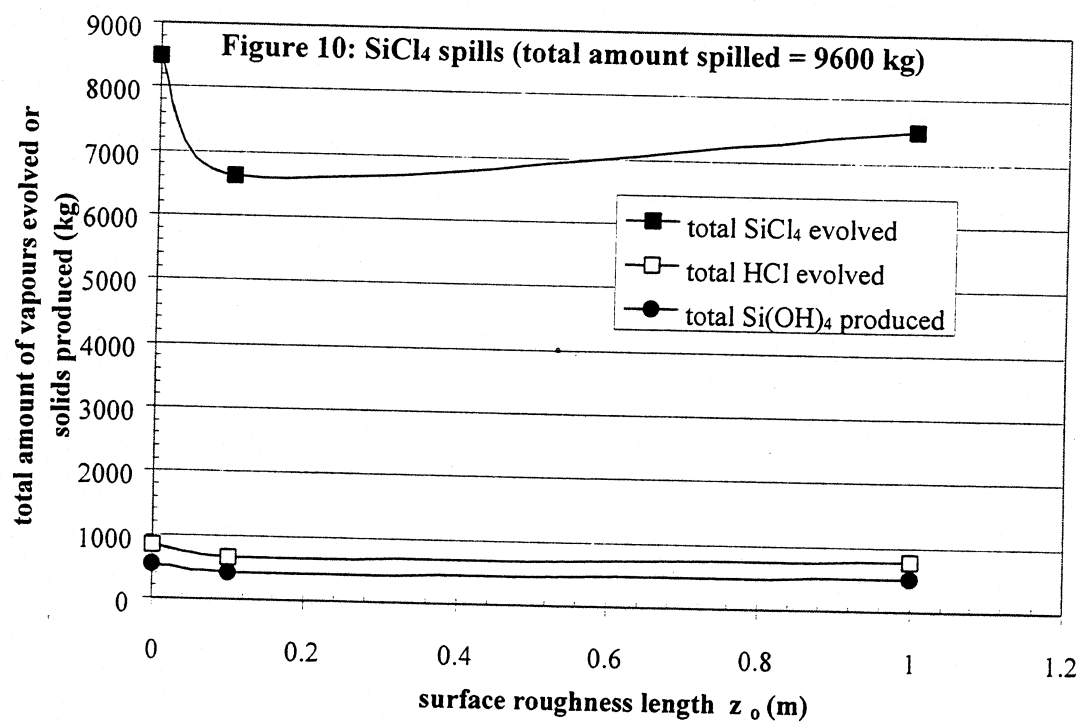
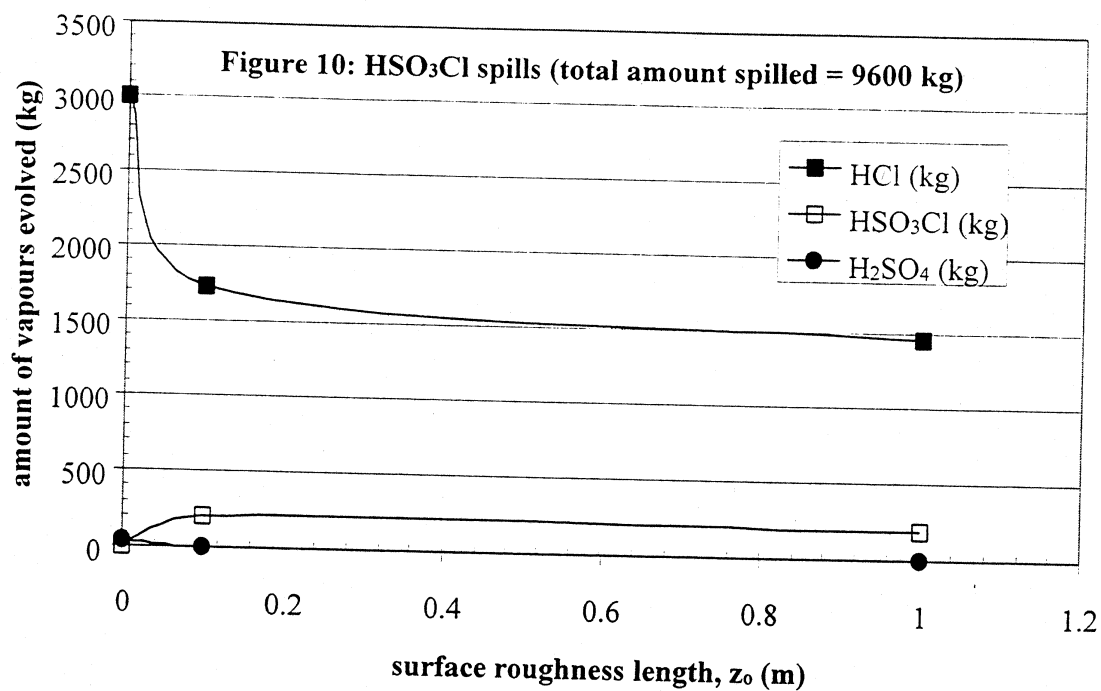


Figure 10
 Effect of surface roughness length on the amount of vapours evolved to the atmosphere
 for spills of 16 kg s^{-1} for 600 s of HSO₃Cl and SiCl₄ ($w_g=0.0015 \text{ m}$, $U_{10}=5 \text{ m s}^{-1}$)

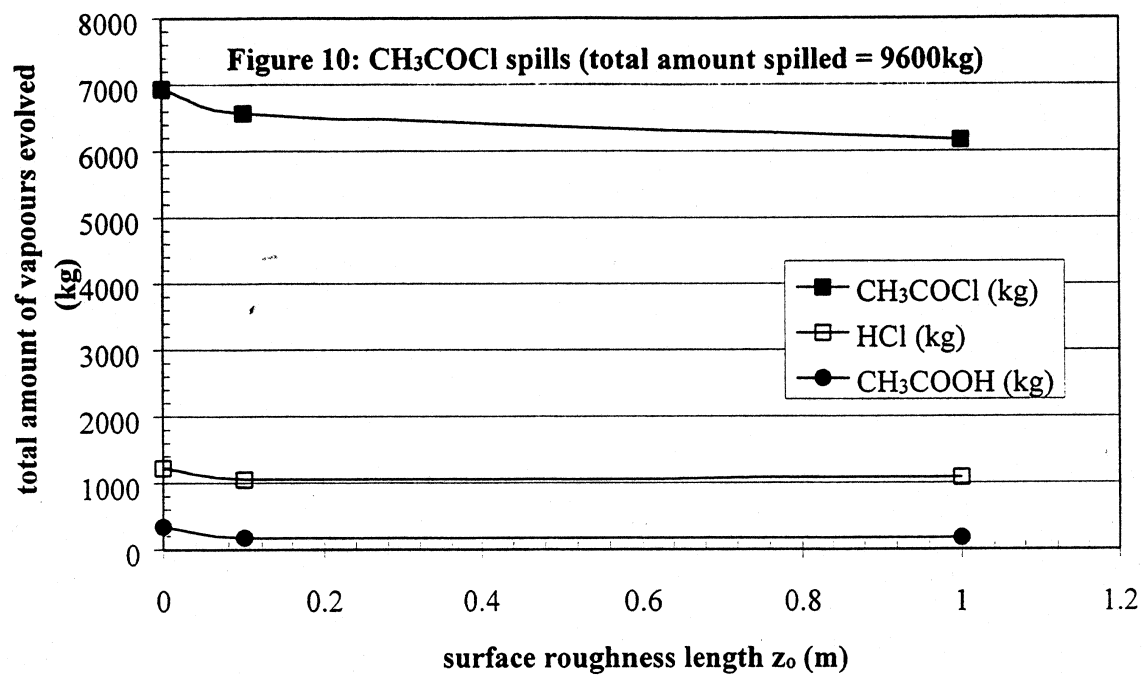


Figure 10
 Effect of surface roughness length on the amount of vapours evolved to the atmosphere
 for spills of 16 kg s^{-1} for 600 s of CH₃COCl ($w_g=0.0015 \text{ m}$, $U_{10}=5 \text{ m s}^{-1}$)

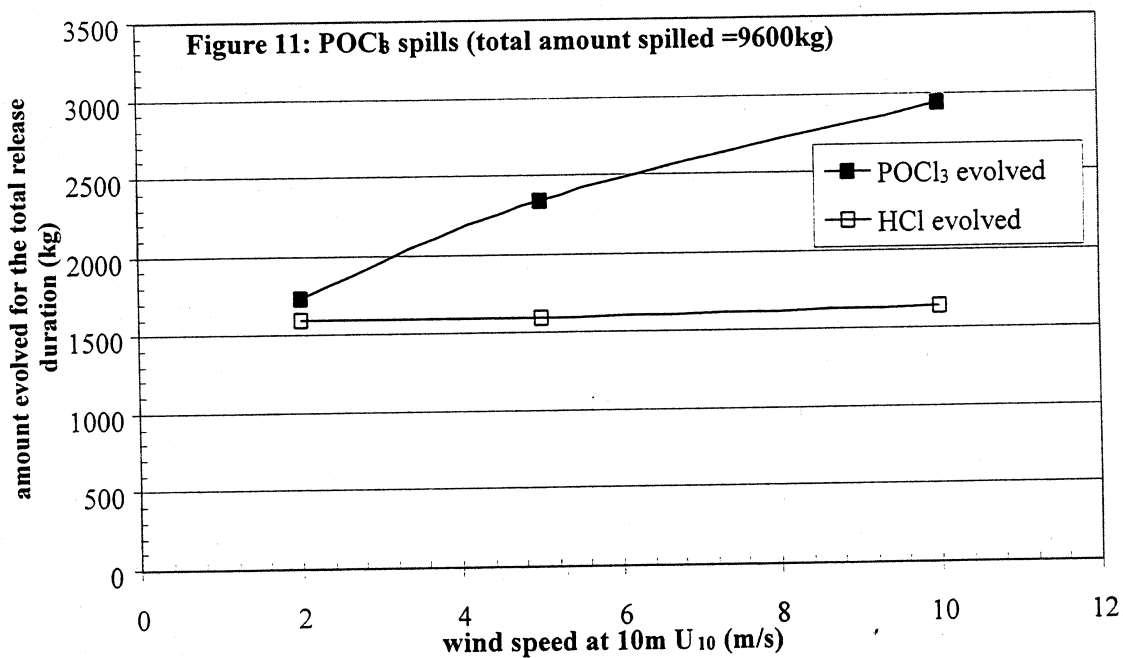
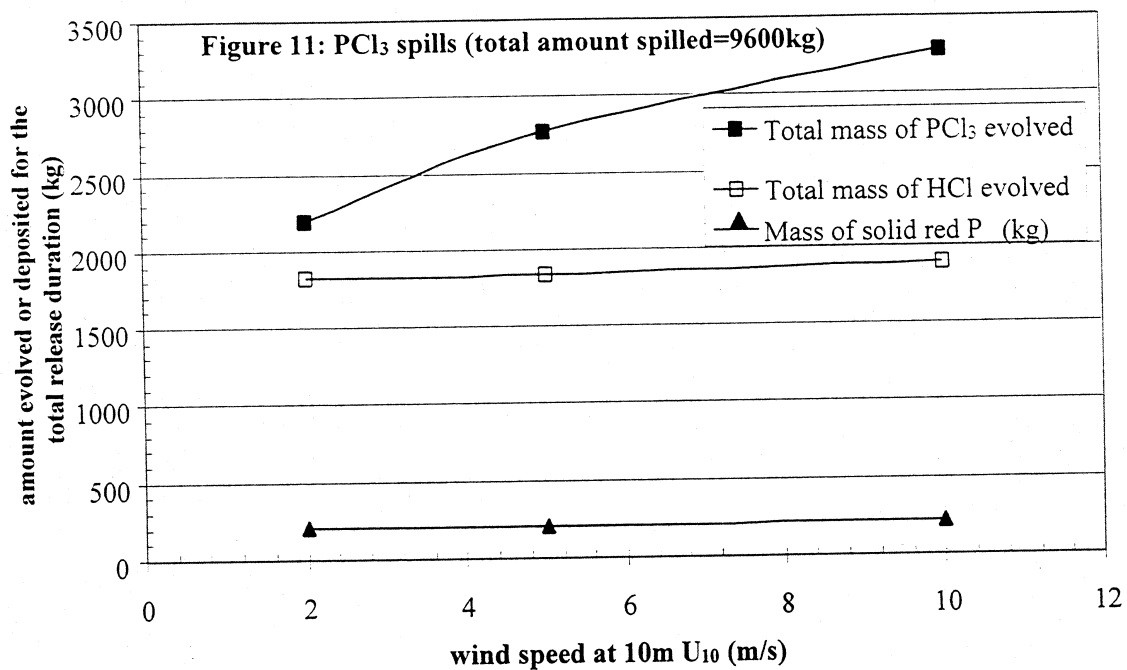


Figure 11
Effect of wind speed on the amount of vapours evolved to the atmosphere for spills of 16 kg s^{-1} for 600 s of PCl_3 and POCl_3 ($w_g=0.0015 \text{ m}$, $z_o=0.1 \text{ m}$)

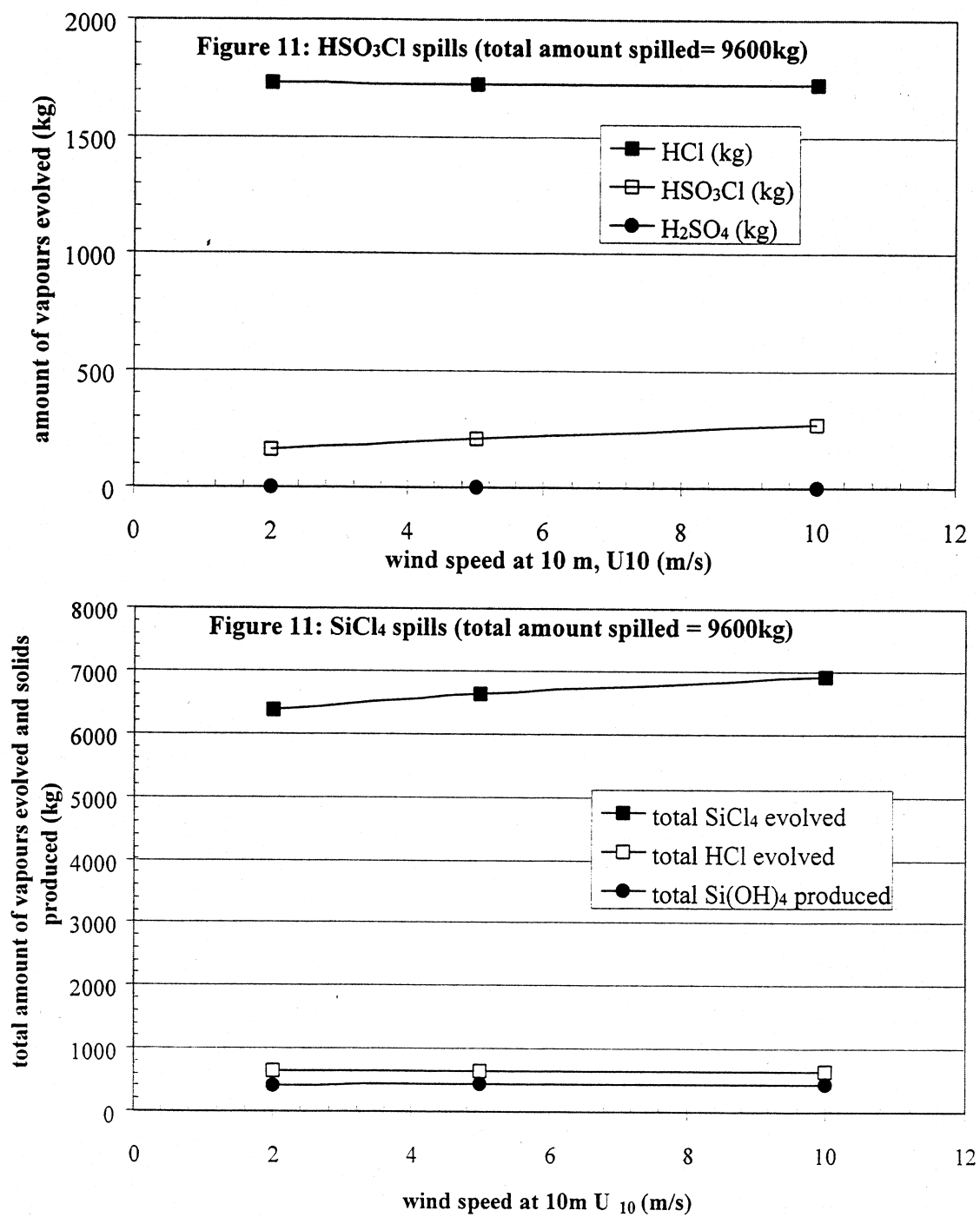


Figure 11
Effect of wind speed on the amount of vapours evolved to the atmosphere for spills of 16 kg s⁻¹ for 600 s of HSO₃Cl and SiCl₄ ($w_g=0.0015$ m, $z_0=0.1$ m)

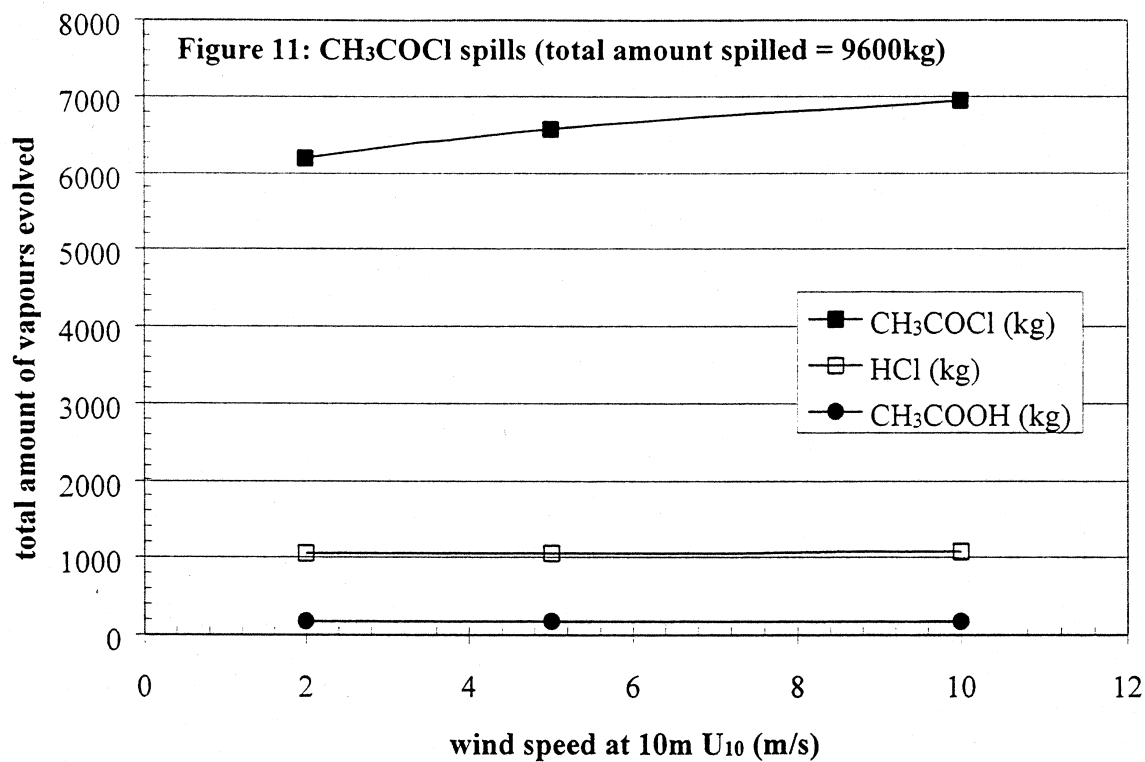


Figure 11
Effect of wind speed on the amount of vapours evolved to the atmosphere for spills of 16 kg s⁻¹ for 600 s of CH₃COCl ($w_g=0.0015$ m, $z_0=0.1$ m)

7) CLOUDS GENERATED FROM SPILLS OF WATER REACTIVE CHEMICALS

In many cases, clouds generated from accidental spills of water reactive chemicals will contain more than species. The water reactive vapour usually interacts with the atmospheric moisture present, yielding either secondary vapour or aerosols or both, which may further interact with moisture. It has become common practice to model the dispersion of these chemicals in a simplified way, ignoring these reactions, or assuming that they are effectively complete at the instant of release from the pool into the atmosphere. In some cases, it has been assumed that in spite of these reactions, the generated cloud will behave as a passive one from its outset. As it has been shown in the case of SO_3 and oleum spills, there is not usually enough atmospheric moisture above the pool for complete and instantaneous reaction. The generated cloud is usually denser than air, with several chemical and physical interactions taking place [2; see also 40, 41, 42].

It is expected that accidental spills of water reactive chemicals will result in the generation of a cloud with complex behaviour with several processes occurring in it. Whether it will initially be denser than air or passive is a function of many parameters such as the vapour evolution rates from the pool, the wind speed, the atmospheric stability etc. It can be expected that in many cases the cloud would be similar to that generated from spillage of SO_3 /oleum. It is clear that each one of these chemicals should be treated individually in respect of its spillage and dispersion behaviour.

8) CONCLUSIONS – DISCUSSION- RECOMMENDATIONS

Water reactive chemicals are important substances in the field of major hazards and are included in many items of international legislation. A number of major accidents have occurred that involved spillages of these materials. Some of these incidents have caused fatalities and serious injuries.

None of the existing source models was judged to be satisfactory in describing the pool behaviour of accidental spills of water reactive substances. REACTPOOL is a new model that describes the pool behaviour of water reactive chemicals in a realistic way. It can incorporate any water reactive chemical and it can also be used for spills of non-reactive substances. Substances that have already been incorporated into the model are: sulphur trioxide and oleums, phosphorus trichloride, phosphorus oxychloride, silicon tetrachloride, chlorosulphonic acid and acetyl chloride. The code is designed to facilitate the addition of further substances. Overall, REACTPOOL is very well behaved and its main advantages are:

- It describes the pool behaviour of water reactive chemicals in a realistic way taking into account the significant processes and interactions that occur in the liquid phase.
- Although the pool behaviour can be very complicated, calculation times are very satisfactory (usually less than 10 min on a Pentium II).
- It can be used for either instantaneous or continuous liquid spills, under a wide range of input parameters (steady or varying).
- The programme is very easy to use, having a user-friendly interface and providing all the necessary help and information on the release behaviour.
- It can also be used for any liquids irrespective of its reactivity and volatility.

Model results indicate that the pool behaviour is principally affected by the way that the reaction of the chemical with water occurs, and by the amount of water available for reaction. Surface roughness and wind speed, also have significant effects. The pool behaviour for the spreading

period is different to that after spreading. The pool temperature is higher for the spreading period, and so are the vapour evolution rates since during this period there is more water available for reaction (free ground water is only available during the spreading period).

The main difficulty in the modelling procedure is that properties and reactions of water reactive chemicals are not very well defined in the literature. Furthermore, although there are numerous accidents occurring every year, there are no experimental data on their release behaviour. Further improvement and validation of the model depends on the availability of these data.

Running the programme for different substances revealed the significance of their individual properties and features. It is concluded that this model constitutes a substantial advance in the modelling of clouds generated from spills of water reactive chemicals, where (except for modelling of HF spills) much of the current practice has been based on excessive use of simplifying assumptions. Future investigation will be aimed at the development of a dispersion model for water reactive chemicals that will include thermodynamic descriptions of possible interactions that occur in such clouds. It should be noted that the main focus of such a project should be the development of the thermodynamic model since there are numerous sophisticated dispersion models that can adequately describe the rest of the cloud characteristics.

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APPENDIX A

Changes in REACTPOOL

The changes that occurred in the core model of REACTPOOL compared to the SO₃/oleum model are listed here.

Mass balances

The mass of water reactive chemical M_{AX} (kg) in the pool at each time step is:

$$M_{AX} = (M_{AX})_{\text{spilled}} - (M_{AX})_{\text{reacted}} - (M_{AX})_{\text{evolved}}$$

The mass of liquid B M_B (kg) possibly produced by reaction 1 is:

$$M_B = (M_B)_{\text{generated}} - (M_B)_{\text{evolved}}$$

At each time step there may be solid particles and excess water present in the liquid pool.

Spreading equations

In spreading equation (8) of reference 3, for continuous spills, term S₁ (kg) represents the total mass loss of the pool, and is given from the following equation:

$$S_1 = (M_w)_{\text{reacted}} - (M_{AX})_{\text{evolved}} - (B)_{\text{evolved}} - (HX_g)_{\text{evolved}} - (C_s)_{\text{settled}}$$

where (M_w)_{reacted} (kg) is the cumulative mass of reacted water (HX_g)_{evolved} (kg) is the cumulative amount of gas or vapour HX evolved directly to the atmosphere and (C_s)_{settled} (kg) is the cumulative amount of particles settled on the bottom of the pool.

Atmospheric water

The flux of moisture entering the pool is modelled in a simple way assuming that all moisture content of the air from a height equal to the roughness length, up to a height H' (m) above the roughness length of the surface enters the pool. In reference 1 it has been assumed that:

$$H' = \frac{R}{30} \frac{p}{100}$$

where p is the % free SO₃ in the liquid. In the current approach this equation has been modified:

$$H' = \frac{R}{30} \frac{M_{AX}}{M_p}$$

In other words if only water reactive chemical is present in the liquid, H' will be equal to R/30.

Different types of surface

The following surfaces have been incorporated into the code:

- Concrete
- Asphalt
- Soil (sandy,dry)
- Soil (moist,8% water,sandy)
- Soil (average)

The user can choose any of these five types of substrate and the characteristics and properties (thermal conductivity, porosity, density etc.) of each type are automatically loaded in the code. For each water reactive chemical an investigation should be conducted for identifying and describing possible reactions with any components of these five types of substrate.

APPENDIX B

Properties of water reactive chemicals and their hydrolysis products

Various sources were used to identify the properties of PCl_3 , POCl_3 , H_3PO_4 and red P [22, 23, 43, 44].

Properties of liquid PCl_3

- Molecular weight, $\text{MW} = 137.33 \text{ g mol}^{-1}$
- Boiling point, $\text{bp} = 349 \text{ K}$
- Freezing point, $\text{fp} = 181 \text{ K}$
- Liquid density, $\rho \text{ (kg m}^{-3}\text{) (T (K))}: \rho = 1617 - (2(T - 273))$
- Heat capacity, $C_p \text{ (kJ kg}^{-1} \text{ K}^{-1}\text{)}: C_p = (177.073 - 0.46599T) / \text{MW}$
- Viscosity, $\mu \text{ (cP)}: \mu = (3.737 \exp(-0.006T))$
- Thermal conductivity, $k \text{ (kW m}^{-1} \text{ K}^{-1}\text{)}: k = 0.1839 - 0.00011322T$
- Vapour pressure, $P \text{ (atm)}: \log P = (7.6645 - \frac{1657.3}{T}) / 760$
- Heat of vaporisation, $H \text{ (kJ kg}^{-1}\text{)}: H = 4.184(-0.0908T + 85.261)$
- Schmidt number, $\text{Sc (estimated according to reference [44])} = 1.782$
- Critical temperature, $T_c \text{ (K)} = 563$
- Critical volume, $V_c \text{ (cm}^3 \text{ mol}^{-1}\text{)} = 260$
- Heat of formation (liq), $H_{\text{el}} \text{ (kJ mol}^{-1}\text{)} = -311.29$
- Heat of formation (gas), $H_{\text{vg}} \text{ (kJ mol}^{-1}\text{)} = -306.27$
- Latent heat of fusion, $H_s \text{ (kJ mol}^{-1}\text{)} = 5.39$

Properties of liquid H_3PO_4

Phosphoric acid properties are usually reported in its solution form. Only the properties of interest in the modelling procedure are reported here.

- Molecular weight, $\text{MW} = 98 \text{ g mol}^{-1}$
- Boiling point, $\text{bp} = 533 \text{ K}$

- Freezing point, $fp = 294 \text{ K}$
- Liquid density, $\rho \text{ (kg m}^{-3}\text{)} = 1675$
- Heat capacity, $C_p \text{ (kJ kg}^{-1} \text{ K}^{-1}\text{)} = 1.083$
- Heat of formation (liq), $H_{vl} \text{ (kJ mol}^{-1}\text{)} = -1271.6$
- Heat of formation (solid), $H_{vs} \text{ (kJ mol}^{-1}\text{)} = -1284.4$

Properties of red P

Properties of red phosphorus are not well established. It is generally reported that they are intermediate between those of the white and black forms. The ones of interest here are reported below:

- Molecular weight, $MW = 31 \text{ g mol}^{-1}$
- Density, $\rho \text{ (kg m}^{-3}\text{)} = 2160$
- Heat capacity, $C_p \text{ (kJ kg}^{-1} \text{ K}^{-1}\text{)} = 0.684$
- Thermal conductivity, $k \text{ (kW m}^{-1} \text{ K}^{-1}\text{)} = 0.639$ (no data were found on red phosphorus so an intermediate value between those of white and black was chosen).

Properties of liquid POCl_3

- Molecular weight, $MW = 153.33 \text{ g mol}^{-1}$
- Boiling point, $bp = 380.55 \text{ K}$
- Freezing point, $fp = 274.3 \text{ K}$
- Liquid density, $\rho \text{ (kg m}^{-3}\text{)} (T \text{ (K))}: \rho = 1676 - (0.8(T - 283))$
- Heat capacity, $C_p \text{ (kJ kg}^{-1} \text{ K}^{-1}\text{)}: C_p = (194.16 - 0.4768T) / MW$
- Viscosity, $\mu \text{ (cP)}: \log \mu = 9.4372 - \frac{1042.1}{T}$
- Thermal conductivity, $k \text{ (kW m}^{-1} \text{ K}^{-1}\text{)}: k = 0.1892 - 0.0000651T$
- Vapour pressure, $P \text{ (atm)}: \log P = (7.734 - \frac{1846}{T}) / 760$
- Heat of vaporisation, $H \text{ (kJ kg}^{-1}\text{)}: H = 4.184(-0.0926T + 87.639)$
- Schmidt number, Sc (estimated according to reference [44]) = 1.82
- Critical temperature, $T_c \text{ (K)} = 602.1$
- Heat of formation (liq), $H_{vl} \text{ (kJ mol}^{-1}\text{)} = -601.7$
- Heat of formation (gas), $H_{vg} \text{ (kJ mol}^{-1}\text{)} = -561.9$
- Latent heat of fusion, $H_s \text{ (kJ mol}^{-1}\text{)} = 13.1$

Properties of liquid HSO_3Cl

- Molecular weight, $MW = 116.525 \text{ g mol}^{-1}$
- Boiling point, $bp = 428 \text{ K}$
- Freezing point, $fp = 193 \text{ K}$
- Liquid density, $\rho \text{ (kg m}^{-3}\text{)} (T \text{ (K))}: \rho = 596.72 \times 0.2852 \left(-1 - \frac{T}{700} \right)^{0.28571}$
- Heat capacity, $C_p \text{ (kJ kg}^{-1} \text{ K}^{-1}\text{)}: C_p = 1.204 + 1.402 \times 10^{-4} T - 2.887 \times 10^{-6} T^2$

- Viscosity, μ (cP): $\log \mu = -0.5472 + \frac{126.93}{T} + 1.0574 \times 10^{-3} T - 3.6166 \times 10^{-6} T^2$
- Thermal conductivity, k (kW m⁻¹ K⁻¹):
 $k = 0.208 \times 10^{-3} - 1.1086 \times 10^{-7} T - 1.6832 \times 10^{-10} T^2$
- Vapour pressure, P (mm Hg):
 $\log P = -5.604 - \frac{2760.4}{T} + 8.4466 \log T - 2.2029 \times 10^{-2} T + 1.1699 \times 10^{-5} T^2$
- Heat of vaporisation, H (kJ kg⁻¹): $H = 528.3 \left(1 - \frac{T}{700}\right)^{0.443}$
- Schmidt number, Sc (estimated according to reference [44]) = 1.64
- Critical temperature, T_c (K) = 700
- Critical volume, V_c (cm³ mol⁻¹) = 195

Properties of H₂SO₄ are not reported since they are readily available in most chemistry handbooks.

Properties of liquid SiCl₄

- Molecular weight, MW = 169.9 g mol⁻¹
- Boiling point, bp = 330.2 K
- Freezing point, fp = 204.3 K
- Liquid density, ρ (kg m⁻³) (T (K)): $\rho = 521.16 \times 0.26416 \left(-1 - \frac{T}{507}\right)^{0.2815}$
- Heat capacity, C_p (kJ kg⁻¹ K⁻¹):
 $C_p = 1.00164 - 1.00214 \times 10^{-3} T - 2.40288 \times 10^{-6} T^2 + 1.08366 \times 10^{-8} T^3$
- Viscosity, μ (cP): $\log \mu = 14.917 - \frac{1635.3}{T} - 4.2676 \times 10^{-2} T + 3.3228 \times 10^{-5} T^2$
- Thermal conductivity, k (kW m⁻¹ K⁻¹):
 $k = 0.0151 \times 10^{-3} - 8.0951 \times 10^{-8} T - 2.9387 \times 10^{-10} T^2$
- Vapour pressure, P (atm):
 $\log P = 25.5694 - \frac{2391.1}{T} - 7.3965 \log T - 9.3193 \times 10^{-10} T + 2.7569 \times 10^{-6} T^2$
- Heat of vaporisation, H (kJ kg⁻¹): $H = 254.44 \left(1 - \frac{T}{507}\right)^{0.383}$
- Schmidt number, Sc (estimated according to reference [42]) = 1.974
- Critical temperature, T_c (K) = 507
- Critical volume, V_c (cm³ mol⁻¹) = 326
- Latent heat of fusion, H_s (kJ kg⁻¹) = 45.069

Properties of Si(OH)₄

- Molecular weight, MW = 96.1 g mol⁻¹

- Density, ρ (kg m^{-3}) = 2185 (varies from 2150 to 2220)
- Heat capacity, C_p ($\text{kJ kg}^{-1} \text{K}^{-1}$): $C_p = 0.04124 + 2.75 \times 10^{-3} T - 0.161 \times 10^{-5} T^2$
- Thermal conductivity, k ($\text{kW m}^{-1} \text{K}^{-1}$) = 0.00133 (for SiO_2 particles).

Properties of liquid CH_3COCl

- Molecular weight, MW = 78.5 g mol^{-1}
- Boiling point, bp = 325 K
- Freezing point, fp = 160 K
- Liquid density, ρ (kg m^{-3}) (T (K)): $\rho = 1527.5 - 1.4333T$
- Heat capacity, C_p ($\text{kJ kg}^{-1} \text{K}^{-1}$): $C_p = 1.493$
- Viscosity, μ (cP): $\mu = 0.1245 - 0.0003T$
- Thermal conductivity, k ($\text{kW m}^{-1} \text{K}^{-1}$): $k = 0.5688$
- Vapour pressure, P (atm): $\log P = 0.9869(3.96568 - \frac{1062.867}{T - 55.531})$
- Heat of vaporisation, H (kJ kg^{-1}): $H = 365$
- Schmidt number, Sc (estimated according to reference [42]) = 1.477
- Critical temperature, T_c (K) = 508
- Critical volume, V_c ($\text{cm}^3 \text{mol}^{-1}$) = 196

Properties of CH_3COOH

- Molecular weight, MW = 60 g mol^{-1}
- Boiling point, bp = 391 K
- Freezing point, fp = 290 K
- Liquid density, ρ (kg m^{-3}) (T (K)): $\rho = 1504.4 - 1.4969T$
- Heat capacity, C_p ($\text{kJ kg}^{-1} \text{K}^{-1}$): $C_p = 2.031$
- Viscosity, μ (cP): $\mu = 0.6556 - 0.0018T$
- Vapour pressure, P (atm): $\log P = 0.9869(4.68206 - \frac{1642.54}{T - 39.764})$
- Heat of vaporisation, H (kJ kg^{-1}): $H = 395$