Spill behaviour using REACTPOOL
Part III. Results for accidental releases of phosphorus trichloride (PCl$_3$) and oxychloride (POCl$_3$) and general discussion

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Abstract

Phosphorus trichloride and oxychloride are aggressive materials, widely used in the process industries. On escape to the atmosphere they create toxic clouds that may cause serious damage to people and to the environment. When spilled onto the ground they create liquid pools that can boil, evaporate or even solidify. The main feature of the pool behaviour is the exothermic reaction of these chemicals with water, which is complicated and depends heavily on the amount of water available for reaction, and as result of which the pool has changing composition and properties. The purpose of this paper is to describe the dangers involved in cases of accidental releases of phosphorus trichloride and oxychloride, to report their properties, referring to toxicity data and major accidents. The spill behaviour of phosphorus trichloride and oxychloride has been incorporated into REACTPOOL [R.F. Kapias, C. Griffiths, J. Haz. Mater.]. Model results indicate that the pool behaviour is strongly affected by the amount of water available for reaction. Surface roughness and wind speed, also have a strong effect on the results. Although there are no experimental data for model validation, it is shown that REACTPOOL gives useful insights into the behaviour of such spills. The paper concludes with a discussion comparing the behaviour for several water reactive chemicals to which REACTPOOL has been applied. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Spill behaviour; REACTPOOL; Phosphorus trichloride; Phosphorus oxychloride

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1. Introduction

Phosphorus trichloride (PCl_3) and phosphorus oxychloride ($POCl_3$) are aggressive materials whose major hazard potential comes from the clouds of hydrogen chloride and phosphorus compounds produced when they escape from containment and are exposed to moisture. The potential to cause harm to people and the environment is recognised in various pieces of national and international legislation on major hazards [1–6].

There are no published attempts to model the behaviour of spills of PCl_3 and $POCl_3$. In addition, no experiments have been reported on their release behaviour. Some tests have been conducted to examine certain types of aqueous foams in suppressing vapours and fumes generated from spills of PCl_3 and $POCl_3$. These tests showed that only certain types of foam are effective in mitigating such spills [7].

Reports of accidental releases that have occurred give an indication of the behaviour of such spillages, but the level of detail given in such reports is very limited.

PCl_3 and $POCl_3$ are usually stored and transported in their liquid form and therefore on spillage to the atmosphere they create liquid pools, usually on land. The main feature of the pool is the exothermic reaction with water. The stoichiometry, kinetics and thermodynamics of this reaction depend on the amount of water available for reaction [8–10]. The energy produced by the reaction increases the temperature of the pool and thus increases the vapour evolution rate. The composition of the pool depends on the products of the reaction with water. Usually the pool will contain PCl_3 or $POCl_3$ liquid, phosphoric acid (H_3PO_4) and/or phosphorous acid (H_3PO_3) [8,9]. In some cases solid particles of red phosphorus may be generated when PCl_3 is spilled. Depending on the water availability HCl gas or HCl in aqueous solution will be generated. When there is excess water, HCl aqueous solution will always be formed. The amount of solvation depends on the quantity of water available. The pool properties will change continuously as the hydrolysis reaction proceeds. There are three sources of water available for reaction; free ground water, substrate water and atmospheric moisture.

PCl_3 and $POCl_3$ spills have been modelled using REACTPOOL [11]; see also [10,12–14]. Model results indicate that the pool behaviour is governed mainly by the amount of water available for reaction. PCl_3 or $POCl_3$ and HCl vapour or gas will be evolved from the pool. PCl_3 (or $POCl_3$) vapour will react with atmospheric moisture yielding HCl and phosphorus oxides. Aerosol particles may also be formed. The generated cloud will initially contain PCl_3 (or $POCl_3$), HCl and phosphorus oxides. The dispersion behaviour will be complicated since there will be numerous chemical and physical interactions taking place in the cloud. The fact that it is possible for the initial cloud to be denser than air complicates its behaviour even further.

2. Main properties and uses

PCl_3 is a clear, volatile liquid with a pungent, irritating odour. It is produced commercially by direct reaction 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 phosphorous acid [15,16].

Table 1
Properties of PCl_3 and $POCl_3$ [8,15,16]

Property	PCl_3	$POCl_3$
Molecular weight (kg kmol^{-1})	137.33	153.33
Freezing point (K)	181	274.3
Boiling point (K)	349	380.5
Critical temperature (K)	563	603
Liquid density (kg m^{-3}) at 25°C	1567	1640
Vapour pressure (atm) at 25°C	0.158	0.042
Liquid viscosity (cP) at 25°C	0.62	1
Liquid heat capacity (kJ kg^{-1} °C^{-1}) at 25°C	0.883	0.912
Liquid heat of formation (kJ mol^{-1}) at 25°C	−311.29	−601.66

In the USA, which is the main manufacturing country, the total capacity of PCl_3 units is 359,000 tonnes per year and demand increases about 5% per year (demand in 1998 was 210,000 tonnes) [17].

$POCl_3$ is a white to yellow, volatile liquid with a pungent, musty odour. It is produced by direct oxidation of PCl_3 with oxygen. About 75–80% of $POCl_3$ manufacture is estimated to be used in the manufacture of phosphate esters for plasticizers, flame retardants, hydraulic fluids and other applications [15,16]. In the USA, the total capacity is 44,000 tonnes per year. The demand in 1998 was about 35,000 tonnes and future growth is estimated at about 1% per year [18]. The main properties of PCl_3 and $POCl_3$ are shown in Table 1, and further details are given in Appendix A.

3. Toxicity and accidents

In respect of their human toxicity, both substances are described as neurotoxicants and respiratory toxicants. In addition, PCl_3 is described as a cardiovascular or blood toxicant and as a gastrointestinal or liver toxicant, and $POCl_3$ as a skin or sense organ toxicant [19,20]. The Threshold Limit Value (TLV) is reported to be 0.2 ppm or 1.1 mg m^{-3} for PCl_3 [21], and 0.1 ppm or 0.63 mg m^{-3} for $POCl_3$ [19].

Generally, the health effects of PCl_3 and $POCl_3$ to humans and animals are quite similar; they are more severe for $POCl_3$, since it is more toxic. Both substances are characterised as causing phosphorus poisoning. The most important manifestation of chronic phosphorus poisoning is osteomyelitis of the jaw bones ("phossy jaw"), most frequently of the mandible and less often of the maxilla, which commonly begins as a dental disturbance [21].

3.1. Human toxicity

Overall, inhalation, ingestion or contact (skin, eyes) with PCl_3 vapour, dust or liquid may cause severe injuries, burns or even death. In respect of short-term exposure it is a severe irritant of the eyes, mucous membranes, and skin and may produce severe burns. Inhalation of the vapour may also produce severe burns. It may produce severe breathing difficulties, which may be delayed as much as a day in onset. On contact with the eyes it

may cause severe burns with permanent eye damage. Swallowing PCl_3 may produce burns of the mouth, throat and stomach [22].

In respect of long-term exposures PCl_3 causes coughing, bronchitis, eye irritation, pneumonia and conjuctivitis. At lower chronic exposure levels asthma-like syndromes may develop followed by a chronic chemical pneumonitis [22].

The estimated fatal dose of PCl_3 is 1 g (or 1 ml) and the corrosive effect is complete destruction of skin or mucous membrane [23,24].

The irritant effects of PCl_3 result primarily from the action of HCl and acids of phosphorus, formed with water. Generally, inhalation could be expected to cause injury in humans ranging from mild bronchial spasm to severe pulmonary oedema or even death. The onset of severe respiratory symptoms may be delayed for 2–6 h, and after moderate exposure the onset may not occur until 12–24 h later [22].

Exposure to the vapour of $POCl_3$ may cause irritation of the eyes, dizziness, headache, weakness, anorexia, nausea, vomiting, chest pain, cough, dyspnea, bronchitis, bronchopneumonia, pulmonary oedema and nephritis. Both chronic and acute cases of occupational intoxication have been recorded [21,22]. Exposure at high levels may result in death. The onset of some of these effects may be delayed. All the above effects correspond to short-term exposures [21].

In respect of long-term exposures, it has been recorded that those constantly or frequently exposed to very small doses of $POCl_3$ vapour may suffer chronic poisoning which manifests itself in the form of pulmonary irritation, coughing and asthma [25].

3.2. Animal toxicity

Test with animals showed that PCl_3 caused dystrophic changes in internal organs, especially in kidneys, liver and the nervous system. Exposures of cats and guinea pigs showed that at concentrations below 0.7 ppm for 6 h, only slight effects were demonstrated. At concentration levels in the range 2–4 ppm for 1 h no severe symptoms were produced. However, serious effects were demonstrated for concentration in the range 50–90 ppm for 1 h. PCl_3 effects for these species were 5–10 times more severe compared to HCl effects [22,26].

Other tests showed that cats exposed to 2–4 ppm of PCl_3 vapour for 6 h showed no respiratory difficulty. At 23–90 ppm for 6 h, however, effects were severe [27].

In rats, the LC50 is 104 ppm for 4 h and the oral LD50 is 550 mg kg^{-1}; at autopsy, the chief finding was nephrosis; pulmonary damage was negligible. In guinea pigs, the LC50 is 0.28 mg m^{-3} for 4 h [22].

No detailed studies have been conducted on animal toxicity to $POCl_3$. It is reported that in rats the LC50 is 48 ppm for 4 h, and in guinea pigs the LC50 is 52 ppm for 4 h [22].

3.3. Accidents

Numerous incidents have occurred involving spillages of PCl_3 and $POCl_3$. In the period 1990–1999 there were about two reported accidents per year in the USA involving each of these substances [11]. This survey also shows that $POCl_3$ and PCl_3 incidents are amongst those likely to involve evacuations and/or injuries. Some of the most serious accidents reported are summarised in Table 2 [28–31].

Table 2
Accidents that involved spillages of PCl_3 and $POCl_3$ [28–31]

Year	Country	Products	Deaths	Injuries	Evacuated	Mass spilled (lbs)
1984	USA	PCl_3	–	125	–	–
1986	USA	$POCl_3$	–	125	–	–
1987	USA	$POCl_3$	–	14	16000	–
1988	USA	$PCl_3 + POCl_3$	–	3	–	$18 + 1645$
1990	USA	$POCl_3 + HCl$	–	46	1000	$8412 + 6000$
1990	USA	PCl_3	–	1	–	2200
1991	USA	$POCl_3$	–	1	9	–
1993	USA	$POCl_3 + SiCl_4$	–	1	90	–

Unfortunately there are no detailed reports of any of the accidents that involved spills of PCl_3 and $POCl_3$, most of which took place in the USA.

4. Reaction with water

PCl_3 and $POCl_3$ react with water exothermically. Unfortunately, data on kinetics and thermodynamics of these reactions are not very well established. For the hydrolysis reaction of $POCl_3$, there are no data in the literature. Information supplied from industry clarified some features of these hydrolysis reactions [9]. In cases of accidental spills, water will be supplied to the pool from the ground, the substrate and the atmosphere. Although there are no data on pools of PCl_3 and $POCl_3$ absorbing atmospheric moisture, it is expected that atmospheric water will enter the pool, in view of the high affinity of these substances for water. The amount of water available for reaction is the principal parameter determining the nature of the products and thermochemistry of these reactions.

4.1. Reaction of PCl_3 with water

Much of the basic research into the behaviour of PCl_3 and water was carried out more than 100 years ago. In spite of its age, it still provides some useful background. A brief review is given below. A thorough literature review of the PCl_3–water reaction can also be found elsewhere [8].

Mellor [32] describes the chemical properties of PCl_3 determined by early experimental work conducted between 1810 and 1928, including the reaction with water. Davy [33] noted a rise in temperature and the gradual formation of hydrochloric acid and phosphorus acid when water reacted with PCl_3 and suggested that 3 mol of water were required per mole of PCl_3

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl \tag{1}$$

For excess PCl_3 conditions, Kraut [34] observed the formation of some red phosphorus and phosphoric acid. He suggested that initially phosphorous acid was formed which then reacted with PCl_3

$$PCl_3 + 4H_3PO_3 \rightarrow 3H_3PO_4 + 3HCl + 2P \tag{2}$$
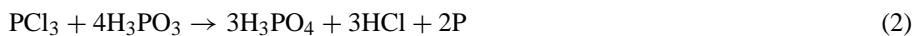
Overall, 12 mol of water were required per 5 mol of PCl_3 as indicated by the suggested total reaction

$$5PCl_3 + 12H_2O \rightarrow 3H_3PO_4 + 3HCl + 2P \tag{3}$$
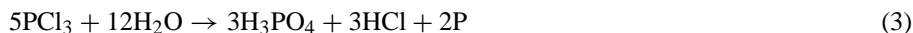
Geuther [35] reported that phosphorus separation only occurred with impure PCl_3 contaminated with arsenic chloride. He proposed further intermediate reactions for the excess PCl_3 case involving the formation of phosphine

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3 \tag{4}$$

$$PCl_3 + PH_3 \rightarrow 2P + 3HCl \tag{5}$$
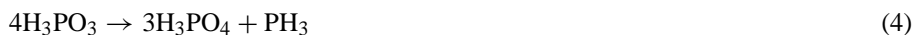
The overall reaction is still represented by Eq. (3). Besson [36] found that some phosphorus oxychloride is formed in excess PCl_3 conditions.

Carrara and Zoppelari [37] conducted a series of experiments to determine the reaction rate of some sulphur and phosphorus compounds with water. They assumed that water and PCl_3 reacted according to Eq. (1) and suggested the following rate for the hydrolysis:

$$\left(\frac{1}{t}\right) \log \left[\frac{A}{A-x}\right] = ACO = 3 \times 10^{-4} \, \text{min}^{-1} \tag{6}$$

where t (min) is time, O (cm^2) is the wet surface area, x (kg) is the quantity of reagent reacted, A (kg) is the total quantity of decomposable liquid and C (kg^{-1} cm^{-2} min^{-1}) is a constant. Although they do not state the value of A used in their experiments, subsequent analysis suggests that it was 10 kg [8]. These experiments were carried out at 5°C and were reported to be very energetic. However, this is inconsistent with the data and the final equation presented which estimates that only a small quantity of PCl_3 reacted in 70 min. This rate equation is of doubtful reliability.

Sidwig [38] discussed the nature of the water–trichloride reaction and suggested that the oxygen atom in a water molecule would attach itself to the lone pair of electrons on the phosphorus atom and a hydrogen and chlorine atom would then react to form HCl. This would be repeated until all chlorine atoms were displaced from the phosphorus.

Mitchell [39] observed that when PCl_3 reacts with water, the solution initially produced had much stronger reducing properties than after several hours and suggested the intermediate formation of an oxychloride, such as $P(OH)_2Cl$. He also reported a slight smell of phosphine which became more pronounced at much higher temperatures.

Hydrolysis of PCl_3 in the vapour phase was investigated by Hudson [40]. He detected no reaction between PCl_3 and water vapour and suggested that the pyramidal structure of PCl_3 and the lone pair of electrons prevented co-ordination occurring with water molecules. In solution, however, the intimate contact between the molecules allows reaction.

A literature review by Melhem and Reid [8] of phosphorus trichloride supports the reactions provided above. It also provides useful information on the possible reaction products. Phosphorous acid can exist in two tautomeric forms $HP(O)(OH)_2$ and $P(OH)_3$. Melhem and Reid suggest that it will predominantly be in the $HP(O)(OH)_2$ form. Phosphorous acid decomposes when heated yielding phosphoric acid and phosphine in the absence of water, and phosphoric acid and hydrogen when water is present. The equations for thermal

decomposition are

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3 \tag{7}$$

$$H_3PO_3 + H_2O \rightarrow H_3PO_4 + H_2 \tag{8}$$

These decompositions are reported to be fairly rapid at temperatures of about 250–275°C with (7) occurring at temperatures above 180°C. The decomposition reaction (7) may account for the observation of Mitchell [38] that some phosphine was detected and supports the reaction mechanisms proposed by Davy [33] and Geuther [35] in cases of excess water and excess PCl_3 respectively (Eqs. (1), (4) and (5), respectively).

In recent years there have been few publications on the PCl_3–water reaction. Schnockel and Schunk [41,42] reported the partial hydrolysis of gaseous PCl_3 to $POCl_3$ at high temperatures and also produced molecular phosphoric acid at very high temperatures.

Melhem and Reid [8] also report on some small-scale experiments on the hydrolysis characteristics. Their work is probably the most comprehensive investigation of the liquid phase reaction of PCl_3 and water. A total of 21 small-scale experiments were conducted, including both closed and open test cells. The water to PCl_3 molar ratio was varied from 1 to 25. In some tests water was added gradually. Most of the tests corresponded to excess water or balanced conditions, compared to the excess PCl_3 cases. In some tests HCl solution was added instead of water. It was found that when in contact, water and PCl_3 form two liquid layers with a reaction occurring at the interface. The impact of the interface surface area, layer depth, and stirring on the reaction rate was investigated experimentally. A reaction rate model that fitted the measured data was presented. For their study reaction (1) was assumed to occur. The reaction rate was reported as follows:

$$\frac{dN}{dt} = 8D^2 [H_2O]^2 [PCl_3]^{1/3} \exp\left(-\frac{3500}{T}\right)$$

where D (in.) is the diameter of the circular PCl_3/H_2O interfacial surface area, T (K) is the system temperature and $[H_2O]$, $[PCl_3]$ are the overall concentrations in kmol m^{-3}.

The main observations from these experiments are listed below.

- The reaction between water and PCl_3 begins immediately, with no delay.
- There is a delay in the evolution of gas from the reacting mixture as HCl produced by the reaction enters into solution in unreacted water.
- The gas evolved includes PCl_3 vapour.
- When HCl is added rather than water, the maximum temperature achieved is less (maximum approximately 75°C compared to 100°C) and the reaction appears to proceed more slowly.
- From the stoichiometric or balanced case ($H_2O/PCl_3 = 3$ mol), three stages were apparent following the addition of water. Firstly, a rapid temperature rise and little loss of vapour is observed as the reaction proceeds and all HCl enters into solution. Then the temperature falls due to further dilution with water, and PCl_3 vapour is evolved. Finally the temperature rises again and only HCl is liberated.
- The gas evolution rate per unit reactor cross-sectional area is dependent on the reactor size.

- No phosphine odour is detected during the experiments.
- The rate of gas evolution appears to be less for the excess PCl_3 cases, for both water and HCl addition scenarios.
- In the gradual addition cases, the rate of gas evolution suggests that the water reacts immediately and there is no opportunity for accumulation to occur.

According to an industrial source [9] hydrolysis of PCl_3 in excess water proceeds as follows:

$$PCl_3 + 3H_2O \rightarrow H_3PO_{3(aq)} + 3HCl_{(aq)} \tag{9}$$

The heat of hydrolysis into a large excess of H_2O (i.e. all the HCl solvated) will be $-286.9 \, kJ \, mol^{-1} \, PCl_3$.

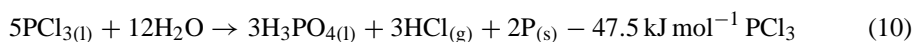### 4.2. Expected reaction of PCl_3 and water in cases of accidental spills

The literature reviewed suggests that under stoichiometric or excess water conditions the reaction between PCl_3 and water will follow Eq. (1) with 3 mol of HCl forming for every mole of PCl_3 consumed. The heat of this reaction was calculated by Melhem and Reid [8] to be $-64.6 \, kJ \, gmol^{-1} \, PCl_3$ if HCl forms as a gas and $-289.2 \, kJ \, gmol^{-1} \, PCl_3$ if aqueous HCl forms. The latter case is considerably more exothermic due to the high HCl heat of solution.

In cases where PCl_3 is in excess, the overall reaction is described by Eq. (3). The heat of this reaction is $-47.5 \, kJ \, gmol^{-1} \, PCl_3$ and $-272.1 \, kJ \, gmol^{-1} \, PCl_3$ for the gaseous and aqueous cases, respectively.
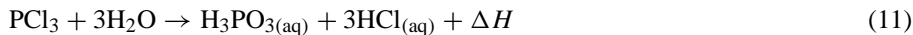
Reaction (1) will take place only when the molar ratio of water to PCl_3 is greater than or equal to 3, i.e. for every kg of PCl_3 there should be at least about 0.393 kg of water. REACTPOOL model results indicate that it is extremely unlikely that there will be excess water even under conditions of high ground water availability (this is usually the main water source; see Section 7).

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. It is expected that HCl will be directly evolved to the atmosphere in its gaseous phase unless there is excess water to allow the HCl to enter into solution.

Overall, the reaction expected to take place in cases of excess PCl_3 is

$$5PCl_{3(l)} + 12H_2O \rightarrow 3H_3PO_{4(l)} + 3HCl_{(g)} + 2P_{(s)} - 47.5 \, kJ \, mol^{-1} \, PCl_3 \tag{10}$$

In cases of excess water

$$PCl_3 + 3H_2O \rightarrow H_3PO_{3(aq)} + 3HCl_{(aq)} + \Delta H \tag{11}$$

where the amount of energy produced is dependent on the amount of water solvated by HCl.

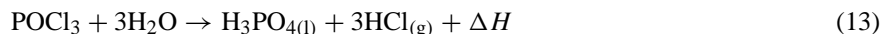### 4.3. Reaction of $POCl_3$ with water

Unfortunately there are no reported data on the liquid phase reaction of $POCl_3$ with water. The only source of information found, came from one of the major manufacturers of $POCl_3$ [9]. According to this source three different cases are encountered:

1. POCl$_3$ is added to sufficient water to give 36% HCl

$$POCl_3 + 13.5H_2O \rightarrow H_3PO_{4(s)} + 3HCl_{(aq)} + 10.5H_2O + \Delta H \qquad (12)$$
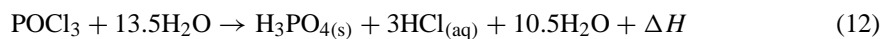
$\Delta H = -286.19 \, kJ \, mol^{-1} \, POCl_3$

2. Just enough water is added to POCl$_3$ to give HCl gas

$$POCl_3 + 3H_2O \rightarrow H_3PO_{4(l)} + 3HCl_{(g)} + \Delta H \qquad (13)$$

$\Delta H = -89.54 \, kJ \, mol^{-1} \, POCl_3$

3. Only a very small amount of water is added to POCl$_3$

$$2POCl_3 + H_2O \rightarrow P_2O_3Cl_4 + 2HCl + \Delta H \qquad (14)$$

$\Delta H = +0.0484 \, kJ \, mol^{-1} \, POCl_3$

4.4. Expected reaction of POCl$_3$ with water in cases of accidental spills

Reaction (12) will take place only if the molar fraction of water to POCl$_3$ is greater than or equal to 13.5, i.e. every kg of POCl$_3$ requires about 1.585 kg of water. As shown in Section 7 this is unlikely to occur in an accidental spill on land, since very large amounts of water are required. Reaction (13) will occur only when the molar fraction of water to POCl$_3$ is lower than 13.5 and higher than or equal to 3.5, i.e. for every kg of POCl$_3$ there should be less than 1.585 kg but more than 0.352 kg of water. Reaction (14) will take place only when the mass fraction of water to POCl$_3$ is less than 0.352. It should be noted that P$_2$O$_3$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. Unfortunately, due to the lack of data reaction (14) 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 (13) takes place.

5. Behaviour on release

PCl$_3$ and POCl$_3$ are usually stored and transported (by rail or road tankers) in their liquid form and therefore on spillage they will create liquid pools, usually on land. In cases where water is in excess, reaction with water will be complete and there will be no PCl$_3$ or POCl$_3$ left in the pool. In these cases the pool will contain the liquid products of the hydrolysis reactions and possibly solid particles. However, these scenarios are very unlikely to occur because of the large amount of water required, so that reaction of these substances on spillage is likely to occur in most cases under excess PCl$_3$ or POCl$_3$ conditions.

5.1. Pool behaviour of PCl$_3$ spills

On escape from containment PCl$_3$ will create a liquid pool, which can either boil or evaporate. There is no possibility of solidification. There is no indication in the literature of possible reactions of PCl$_3$ or any other hydrolysis products with compounds of any type of substrate. Two different cases are encountered depending on the amount of water available for reaction.

5.1.1. Excess water or balanced cases

As shown in Section 5.2, in these cases reaction (1) occurs and there should be at least 0.393 kg of water for every kg of PCl_3. Liquid H_3PO_3 and HCl will be generated possibly in the form of aqueous solutions. The amount of solvation of these two liquids is determined by the amount of excess water. The pool will contain H_3PO_3 and HCl and its composition and properties will be constant, as every mole of PCl_3 will form 1 mol of H_3PO_3 and 3 mol of HCl, i.e. the pool will contain 75% HCl and 25% H_3PO_3 on a molar basis. The hydrolysis is highly exothermic providing the pool with energy, raising both the temperature and the vapour evolution rates. HCl vapour will be evolved due to its high volatility. The amount of H_3PO_3 evolved is negligible due to its extremely low volatility. The heat of reaction depends on the amount of water available. Overall, excess water conditions are very unlikely to be encountered unless there is a large external source of water.

5.1.2. Excess PCl_3 cases

In Section 5.2 it is shown that reaction (3) will take place in this case and for every kg of PCl_3 less than 0.393 kg of water is required. Liquid H_3PO_4 will be generated from this reaction. The pool composition and properties will not be constant as PCl_3 continuously reacts with water forming H_3PO_4. Solid particles of red phosphorus will also be formed. Unfortunately there are no data on the solubility of these particles in a liquid medium that is a mixture of PCl_3 and H_3PO_4. HCl gas will be generated from the reaction and it will directly evolve to the atmosphere. Reaction with water is exothermic and PCl_3 vapour will also evolve; the amount of H_3PO_4 vapour evolved is negligible in view of its extremely low volatility at the temperatures expected to be encountered in cases of accidental spills.

5.2. Pool behaviour of $POCl_3$ spills

When $POCl_3$ is spilled onto the ground, it will create a liquid pool that can either boil (when there is high availability of water) or evaporate or even solidify (when there is low availability of water). There is no indication in the literature of possible reactions of $POCl_3$ or any other hydrolysis products with compounds of any type of substrate. Two different cases are encountered depending on the amount of water available for reaction.

5.2.1. Excess water or balanced cases

As shown in Section 5.4, in these cases reaction (12) occurs and there should be at least 1.585 kg of water for every kg of $POCl_3$ spilled. H_3PO_4 and HCl liquids will be formed and may exist as aqueous solutions. The pool composition and properties will be constant. The amount of solvation and the heat of hydrolysis depend on the amount of water in excess. Reaction with water is highly exothermic and HCl vapour will be evolved.

5.2.2. Excess $POCl_3$ cases

When there is less than 1.585 kg of water per kg of $POCl_3$ reaction (13) is assumed to occur. As mentioned in Section 5.4, reaction (14) may also occur under low availability of water, but since this reaction is not well defined, reaction (13) is assumed to take place in all these cases. H_3PO_4 liquid is produced and the pool properties and composition will

continuously change as the hydrolysis reaction proceeds. HCl gas will be directly evolved as a reaction product. The reaction with water is exothermic, raising the pool temperature, resulting in the evolution of $POCl_3$ vapour.

It should be noted that for both PCl_3 and $POCl_3$ spills, both cases (water excess and chemical excess) may be encountered, making the pool behaviour even more complicated, as more components will be present. This could occur for example if the free ground water film thickness is varying from one place to another in the spill area.

5.3. Behaviour of clouds generated from spills of PCl₃ and POCl₃

Clouds (or plumes) generated from accidental spills of PCl_3 or $POCl_3$ will initially contain two vapours or gases: PCl_3 or $POCl_3$ and HCl. Both PCl_3 and $POCl_3$ will interact with atmospheric moisture yielding a number of possible products such as HCl and phosphorus oxides. Literature data on these processes are limited and not well defined (some references are reported in Section 5.1 [40–42]). HCl will also interact with atmospheric moisture, forming aerosols. Generally, the cloud behaviour is expected to be similar to that resulting from SO_3 and oleum spills [43,44].

6. Pool behaviour and incorporation into REACTPOOL — model results

Details of the modelling procedure in REACTPOOL are given elsewhere [11]. In order to incorporate PCl_3 and $POCl_3$ all of their properties, and the properties of their possible products on reaction with water, have been parameterised as functions of temperature, as listed in Appendix A. All cases have been incorporated (excess water or balanced and excess PCl_3 or $POCl_3$). In cases of PCl_3 spills solid particles of red phosphorus are usually formed. These particles may be soluble or insoluble in the liquid medium and when insoluble may be suspended or settle on the bottom of the pool. It has been assumed that particles of red phosphorus are insoluble. In cases where the pool boils it has been assumed that particles remain suspended in the pool, affecting its properties [11]. If the pool is more quiescent the particles are expected to settle on the bottom of the pool forming a film that alters the conduction of heat from the ground. Model results indicate that the major part of the pool behaviour is characterised by evaporation rather than boiling, and therefore solid particles of red phosphorus will settle on the bottom of the pool (see Section 8).

In view of the lack of any relevant data on the amount of atmospheric moisture absorbed by the liquid in the pool, this is estimated by the same procedure followed in the model for SO_3 and oleum spills [11].

7. REACTPOOL model results

The model results show that, overall, the pool behaviour is strongly affected by the amount of water available for reaction. The main water source is usually the free ground water. In all cases investigated reaction with water occurred under excess PCl_3 or $POCl_3$ conditions. The surface roughness and the wind speed also have a strong effect on the results. The rest

Table 3
Values of the release scenario input parameters

Spill rate ($kg\,s^{-1}$) for 600 s	16
Maximum duration of release to the atmosphere (s)	1800
Maximum pool radius (m)	50
Type of substrate	Concrete
Free water film thickness on the ground, w_g (m)	0.0005, 0.0015, 0.003, 0.005
Surface roughness length[a], z_0 (m)	0.1, 0.01, 0.001, 0.0001
Wind speed at 10 m, U_{10} ($m\,s^{-1}$)	5, 2, 10
Air and release temperature (K)	288
Atmospheric radiation factor	0.84
Cloud cover factor	7
Relative humidity (%)	70
Location	North England, UK (latitude $= 54°$, longitude $= 2°$)
Time and day	09.00 h and 298 (25 October)
Time step used in the calculations (s)	0.01

[a] The corresponding values for h_{min} are 1 cm, 8.5 mm, 7 mm, 5 mm, respectively.

of the input parameters have a weaker effect. POCl$_3$ pools may solidify after spreading ceases under conditions of extremely low availability of water; there is no possibility of solidification for PCl$_3$ spills.

The results of a large number of different release scenarios were 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 3. It should be noted that parameters given a single value in this table were kept constant in all scenarios. These parameters do not have a significant effect on the results.

Figs. 1–9 show the results for the above scenarios. These show the behaviour of the main pool properties and the vapour evolution rates.

8. Effects of different parameters on the pool behaviour of water reactive chemicals

In this section a discussion of REACTPOOL results for accidental releases of chlorosulphonic acid (HSO$_3$Cl) [45], silicon tetrachloride (SiCl$_4$) [46], phosphorus trichloride (PCl$_3$) and oxychloride (POCl$_3$), sulphur trioxide (SO$_3$) and oleums [47] is presented, drawing attention to the similarities and differences in the pool behaviour of these chemicals. The results shown in the following comparison tables correspond to scenarios with the same values of all input parameters for all chemicals presented.

8.1. Water supply to the pool

The percentage contribution of each of the three water sources to the total water usage for HSO$_3$Cl, SiCl$_4$, PCl$_3$ and POCl$_3$ pools is shown in Fig. 1 of Parts I, II and III of this series of papers. These figures show that in most cases free ground water is the dominant
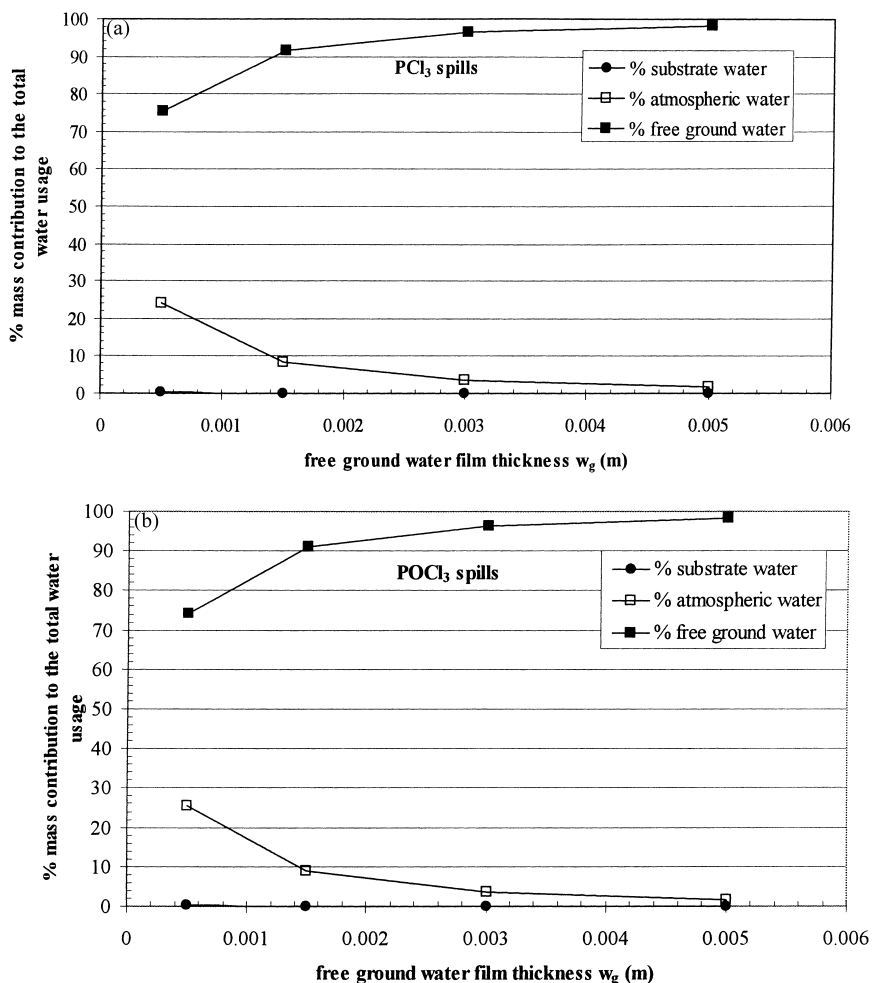
Fig. 1. Percentage supply of the three water sources to the total amount of water provided for reaction for spills of $16 \, \text{kg s}^{-1}$ for $600 \, \text{s}$ of (a) PCl_3 and (b) $POCl_3$ ($z_0 = 0.1 \, \text{m}$, $U_{10} = 5 \, \text{ms}^{-1}$).

water source (usually 70–98%) and its contribution increases with increasing free ground water film thickness. Atmospheric water is usually the second most important water source (usually 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. Table 4 shows the differences in values of the percentage contribution of the three water sources into the pools of different water reactive chemicals, at $w_g = 0.0005 \, \text{m}$.

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 after the spreading has ceased, and thus, they have a strong effect on the pool behaviour in this period.
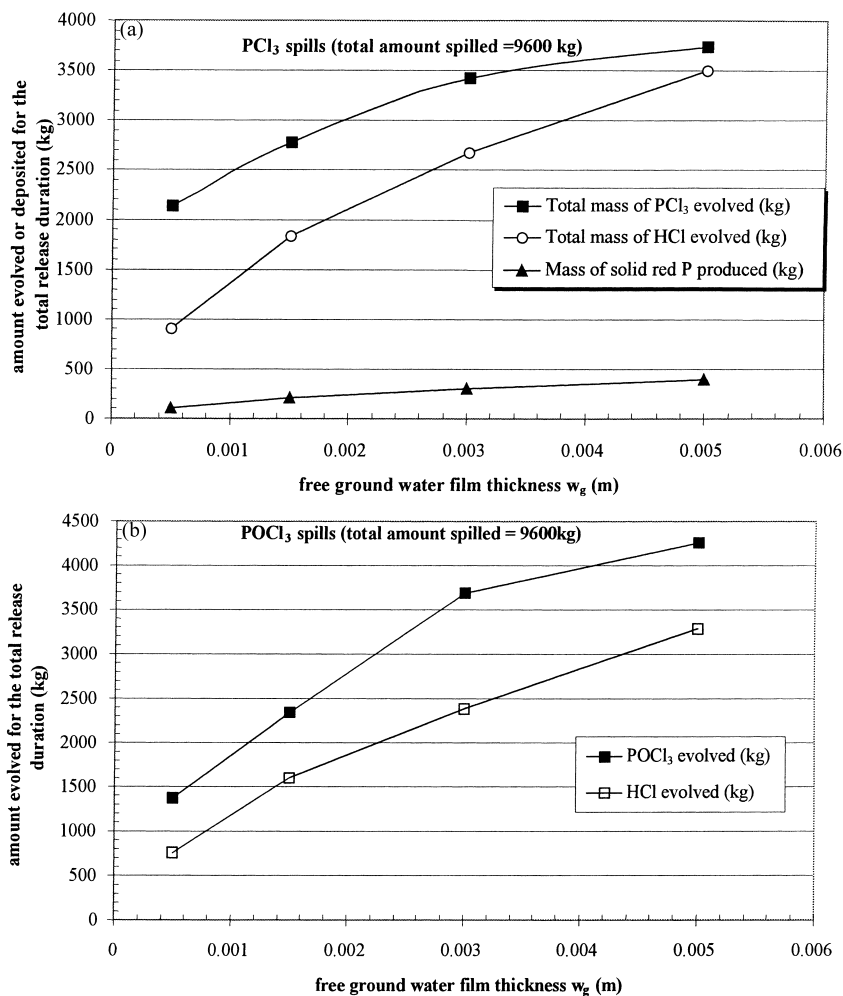
Fig. 2. Effect of free water film thickness on the amount of vapour evolved to the atmosphere for spills of $16\,\text{kg\,s}^{-1}$ for 600 s of (a) PCl_3 and (b) $POCl_3$ ($z_0 = 0.1\,\text{m}$, $U_{10} = 5\,\text{ms}^{-1}$).

Table 4
Percentage contribution of the three water sources for pools of different water reactive chemicals at $w_g = 0.0005\,\text{m}$

	Free ground water (%)	Atmospheric water (%)	Concrete water (%)
SO_3	49	50	1
Oleum (20%)	95	4	1
PCl_3	76	23	1
$POCl_3$	73	26	1
$SiCl_4$	80	19	1
HSO_3Cl	81	18	1
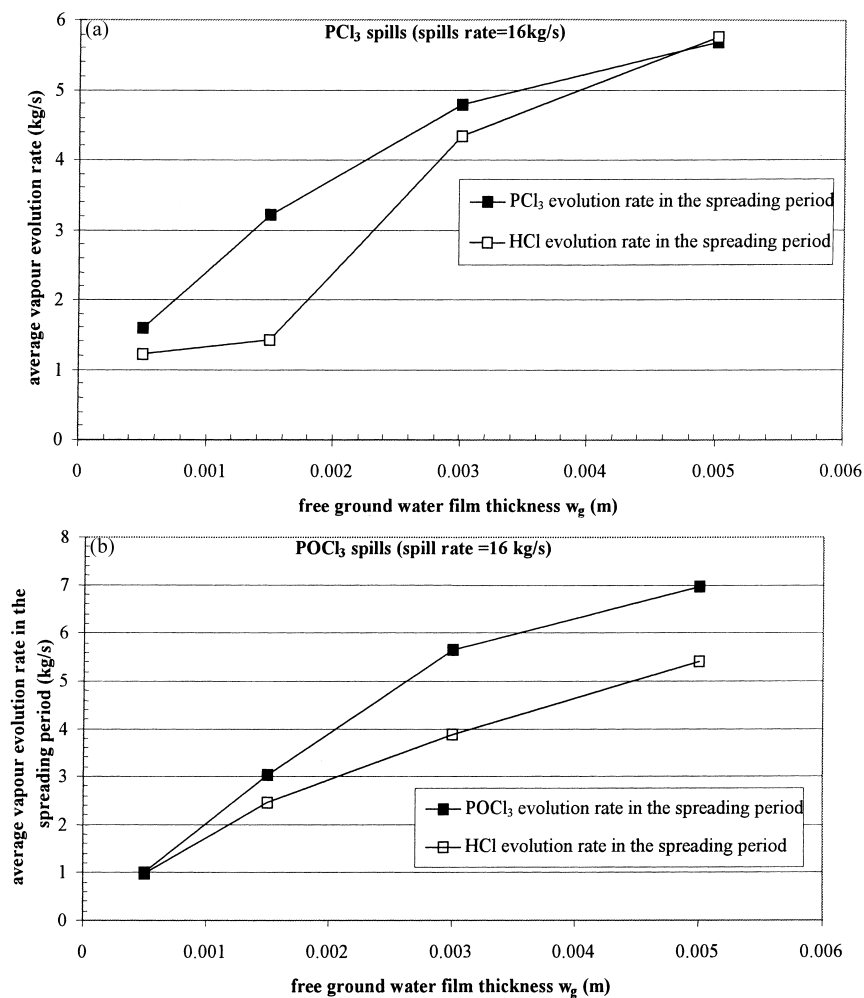
Fig. 3. Effect of free water film thickness on the vapour evolution rates in the spreading period for spills of $16\,kg\,s^{-1}$ for 600 s of (a) PCl_3 and (b) $POCl_3$ ($z_0 = 0.1\,m$, $U_{10} = 5\,ms^{-1}$).

8.2. Effect of free ground water film thickness on the amount of vapours evolved

As shown in Section 8.1, the main source of water entering the pool is the free water lying on the ground. The effect of this parameter on the total amounts of vapours and gases evolved for the total release duration (1800 s) is shown in Fig. 2 of Parts I, II and III. These figures show that the amounts of the water reactive chemicals and HCl evolved increase significantly with increasing free ground water film thickness. For example, a change of 100% in the value of free ground water film thickness results in a 75% change of the amount of PCl_3 or $POCl_3$ and HCl vapour evolved.
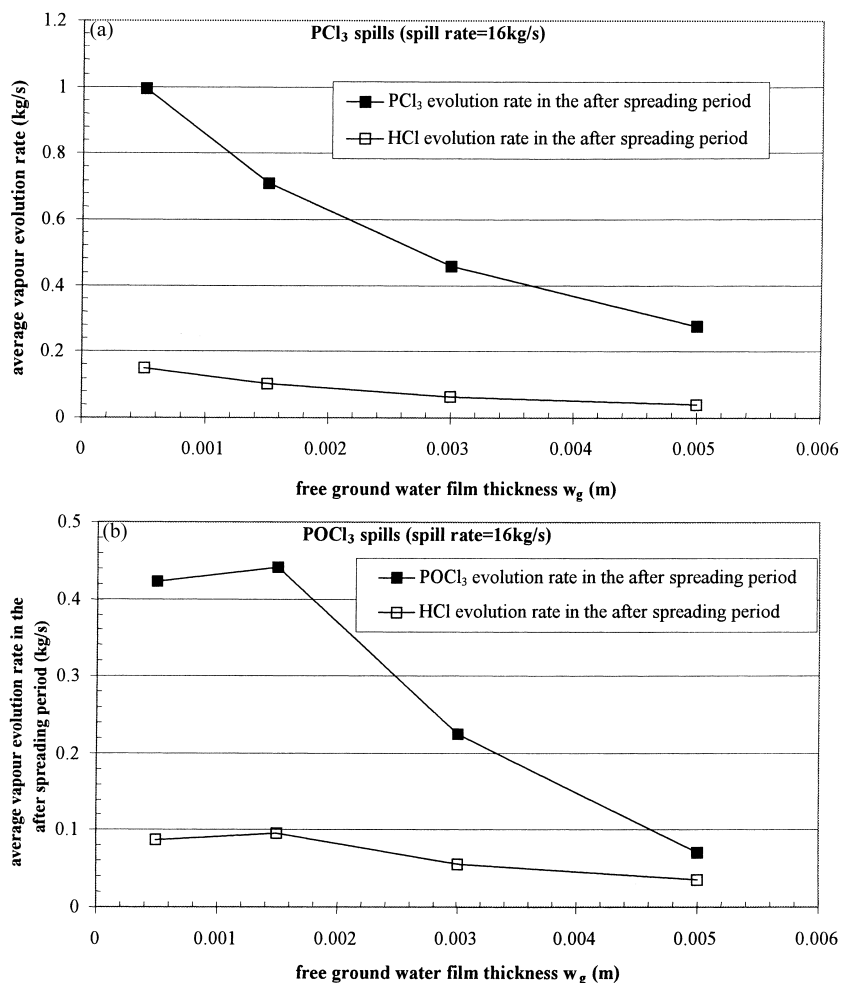
Fig. 4. Effect of free water film thickness on the vapour evolution rates in the after spreading period for spills of $16\,kg\,s^{-1}$ for $600\,s$ of (a) PCl_3 and (b) $POCl_3$ ($z_0 = 0.1\,m$, $U_{10} = 5\,ms^{-1}$).

Additionally, the amount of solid particles of red phosphorus produced in cases of PCl_3 spills, also increases with increasing free ground water film thickness. It should be noted though, that in all cases, the amount of red phosphorus produced is not very high. This is due to the stoichiometry of reaction (3) that suggests that for every 12 mol of reacted H_2O, only 2 mol of red phosphorus are generated. Generally, the free ground water film thickness (w_g) is the parameter that most strongly affects the pool behaviour of any water reactive chemical.

The pool behaviour for the spreading period is different to that after spreading ceases. Average vapour evolution rates are much higher in the spreading period as shown in Fig. 3 of Parts II and III, compared to the average vapour evolution rates in the after spreading period as shown in Fig. 4 of Parts II and III.
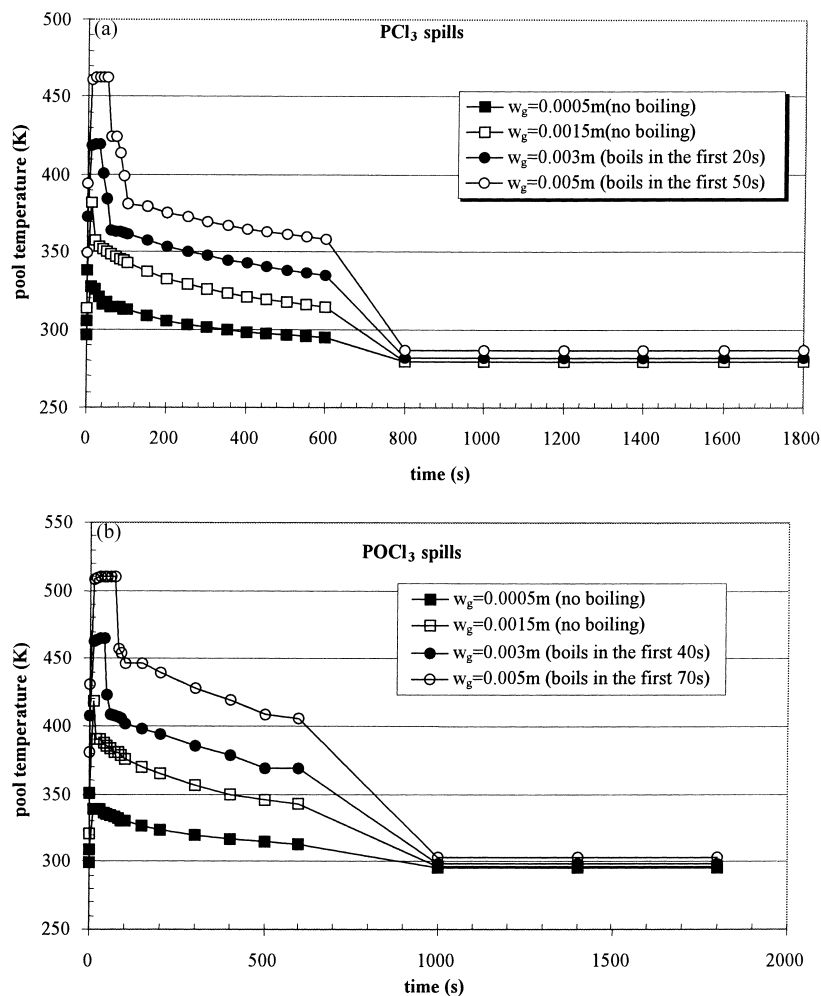
Fig. 5. Pool temperature profiles under different values of w_g for spills of $16\,\mathrm{kg\,s^{-1}}$ for $600\,\mathrm{s}$ of (a) PCl_3 and (b) $POCl_3$ ($z_0 = 0.1\,\mathrm{m}$, $U_{10} = 5\,\mathrm{m\,s^{-1}}$).

Table 5 compares the total amount of vapour evolved for the total release duration for spills of different water reactive chemicals at $w_g = 0.0015\,\mathrm{m}$. It should be noted that in this table the total amount of vapour evolved is the sum of all vapours and gases evolved. For example, in cases of PCl_3 and $POCl_3$ spills this amount corresponds to the mass of PCl_3 or $POCl_3$ and HCl evolved taken together.

8.3. Pool temperature profiles for different values of free ground water film thickness

Fig. 5 of Parts II and III and Fig. 3 of Part I, show the time dependence of the pool temperature; it generally increases with increasing values of free ground water film thickness.
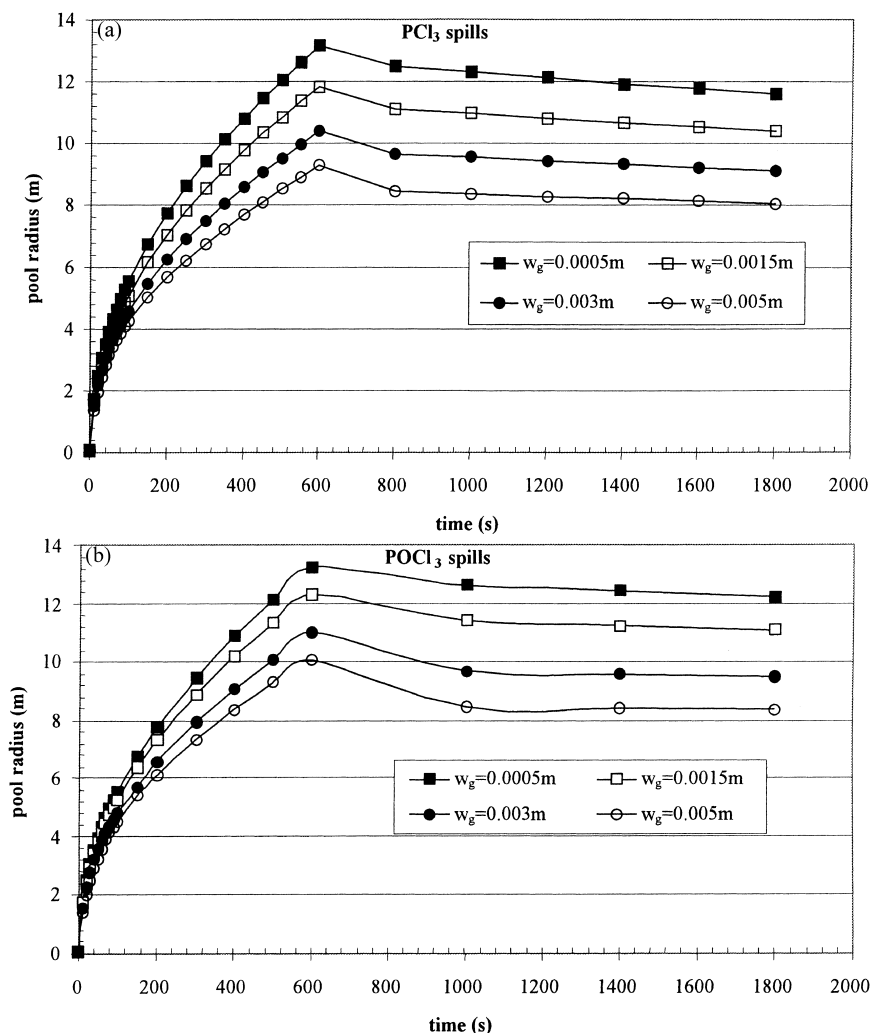
Fig. 6. Pool radius profiles under different values of w_g for spills of $16\,\mathrm{kg\,s^{-1}}$ for $600\,\mathrm{s}$ of (a) PCl_3 and (b) $POCl_3$ ($z_0 = 0.1\,\mathrm{m}$, $U_{10} = 5\,\mathrm{m\,s^{-1}}$).

Temperatures higher than 450 and 500 K are encountered during the early spreading stages under high values of w_g, for PCl_3 and $POCl_3$, respectively. Pool temperature drops just after pool spreading ceases, since free ground water is no longer encountered. Most of the water reactive chemical pools boil under high ground water availability ($w_g > 0.0015\,\mathrm{m}$), usually during the early stages of spreading while the surface area of the pool is still small. It has been found that only $POCl_3$ pools may solidify under extremely low values of w_g ($<0.0001\,\mathrm{m}$) and only after spreading ceases. It should be noted that the boiling and freezing points of the pools are not constant (except for $SiCl_4$ pools). In all cases the pool boiling and freezing points are higher than those of the pure water reactive liquid
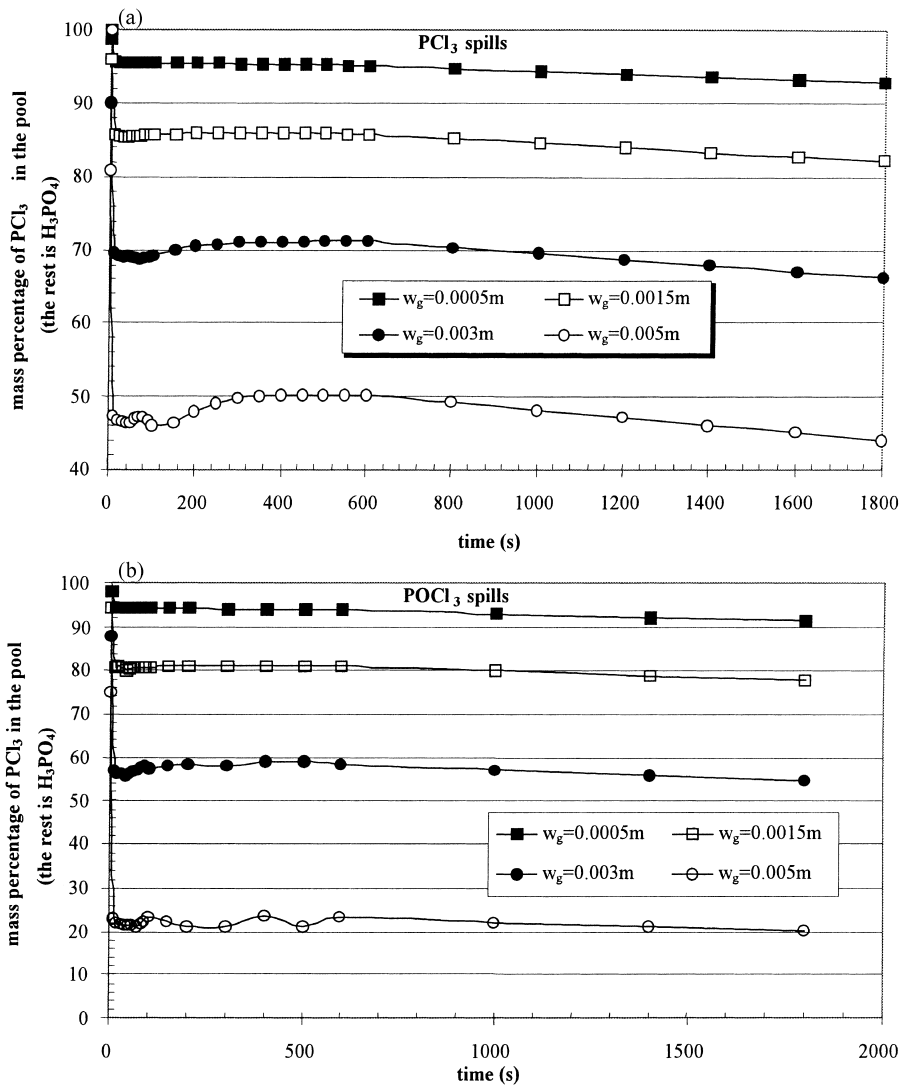
Fig. 7. Pool composition profiles under different values of w_g for spills of $16\,\mathrm{kg\,s^{-1}}$ for $600\,\mathrm{s}$ of (a) PCl_3 and (b) $POCl_3$ ($z_0 = 0.1\,\mathrm{m}$, $U_{10} = 5\,\mathrm{m\,s^{-1}}$).

(except for $SiCl_4$ pools). It should be noted that the pool temperature can reach the boiling point of the pure liquid without boiling, because of the presence of a liquid product, which elevates both the boiling and freezing points of the mixture (see Appendix A of Parts I and III).

Table 6 shows the pool temperature range and the pool boiling and solidification duration for spills of different water reactive chemicals under the same values of input parameters for two different cases ($w_g = 0.0015\,\mathrm{m}$ and $w_g = 0.003\,\mathrm{m}$).
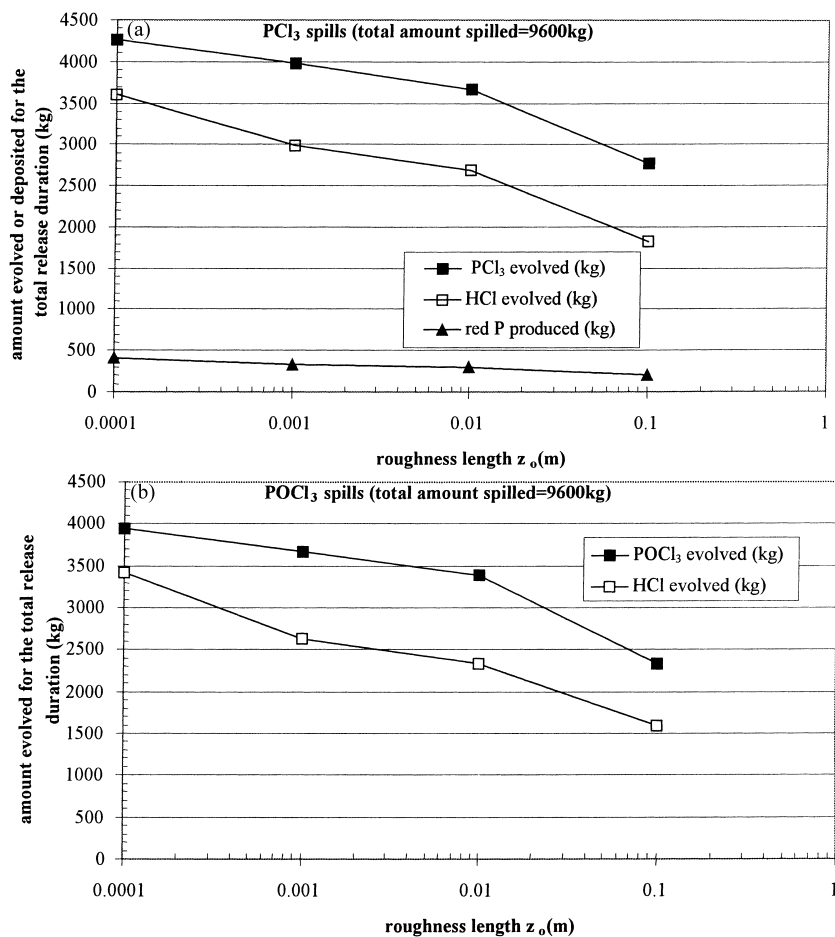
Fig. 8. Effect of surface roughness length on the amount of vapour evolved to the atmosphere for spills of $16 \, \mathrm{kg \, s^{-1}}$ for $600 \, \mathrm{s}$ of (a) PCl_3 and (b) $POCl_3$ ($w_g = 0.0015 \, \mathrm{m}$, $U_{10} = 5 \, \mathrm{ms^{-1}}$).

8.4. 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 Fig. 6 of Parts II and III and Fig. 4 of Part I. As indicated in Section 8.2, 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 slightly longer than the spill duration) and reaches its maximum just after the spill duration of $600 \, \mathrm{s}$; then it slowly shrinks.

8.5. Pool composition profiles for different values of free ground water film thickness

Pools generated from spills of HSO_3Cl, PCl_3 or $POCl_3$ are a mixture of two liquids: HSO_3Cl, PCl_3 or $POCl_3$ and H_2SO_4 or H_3PO_4. The mass percentage of PCl_3 or $POCl_3$ in
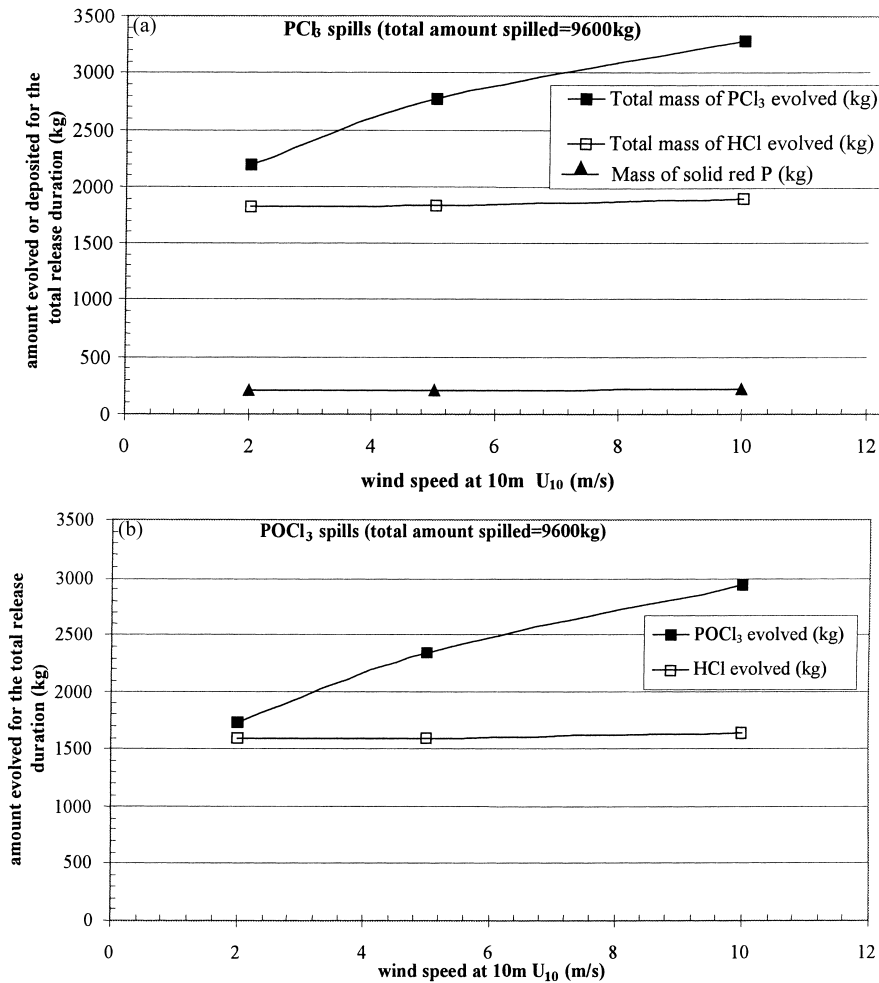
Fig. 9. Effect of wind speed on the amount of vapour evolved to the atmosphere for spills of $16\,\mathrm{kg\,s^{-1}}$ for $600\,\mathrm{s}$ of (a) PCl_3 and (b) $POCl_3$ ($w_g = 0.0015\,\mathrm{m}$, $z_0 = 0.1\,\mathrm{ms^{-1}}$).

the pool decreases with increasing w_g, as indicated in Fig. 7, since more H_3PO_4 is produced at higher water availability and at the same time there is more PCl_3 or $POCl_3$ evolved to the atmosphere. In this figure, it is also shown that the pool composition changes continuously with time.

8.6. Effect of surface roughness length on the amount of vapour evolved

The surface roughness length z_0 strongly affects the behaviour in two ways. Small values of z_0 imply small values of the minimum layer thickness h_{min} and therefore z_0 has an indirect effect on the pool radius and the surface area of evolution. Additionally, it also

Table 5
Comparison of behaviour of pools from spills of $16\,kg\,s^{-1}$ for $600\,s$ of SO_3, 65% oleum, 20% oleum, PCl_3, $POCl_3$, $SiCl_4$ and HSO_3Cl^a

Material spilled	Total amount of vapour evolved (kg)
$SiCl_4$	7300
SO_3	6800
PCl_3	4400
$POCl_3$	4000
Oleum (65%)	3000
HSO_3Cl	2000
Oleum (20%)	200

[a] Total amount spilled $= 9600\,kg$; $w_g = 0.0015\,m$.

enhances the friction velocity u^* and the evaporation flux from the pool surface. Fig. 8 of Part III, Fig. 7 of Part II and Fig. 5 of Part I, show that increasing values of roughness length result in decreasing total amounts of vapours evolved. This occurs since higher values of roughness length are associated with 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_0 is quite strong, it is weaker than the effect of the free ground water film thickness.

8.7. Effect of wind speed on the amount of vapour evolved

The wind speed at a reference height of $10\,m$, U_{10} ($m\,s^{-1}$), has a relatively strong effect on the amount of vapour evolved as shown in Fig. 9 of Part III, Fig. 8 of Part II and Fig. 6 of Part I. Increasing wind speed increases the amount evolved. However, the wind speed does not have a significant effect on the amount of HCl evolved, since HCl originates from

Table 6
Pool temperature range and pool boiling and solidification duration for spills of different water reactive chemicals[a]

	Temperature range (K)	Boiling duration (s)	Solidification duration (s)
$w_g = 0.0015\,m$			
PCl_3	280–340	None	None
$POCl_3$	295–420	None	None
$SiCl_4$	270–330	0–120	None
HSO_3Cl	295–390	None	None
SO_3	270–345	0–80	602–1800
Oleum (20%)	350–420	None	None
$w_g = 0.003\,m$			
PCl_3	285–420	0–20	None
$POCl_3$	300–470	0–40	None
$SiCl_4$	265–330	0–250	None
HSO_3Cl	390–600	0–30	None
SO_3	320–390	0–200	None
Oleum (20%)	350–420	None	None

[a] Values for SO_3/oleum are recalculated for these w_g values, which were not included in [47].

a hydrolysis reaction and its evolution rate is primarily affected by the amount of water available for reaction.

8.8. Solid particles of red phosphorus for spills of PCl$_3$

Model results indicate that relatively small quantities of solid particles of red phosphorus will be formed. Even under very high water availability ($w_g = 0.005$ m), the mass of phosphorus produced (about 400 kg) is less than 5% of the total amount of PCl$_3$ spilled (9600 kg). It has been assumed that these particles are insoluble and settle onto the bottom of the pool. Their only influence on the pool behaviour is that they form a film that changes the heat conduction from the ground. In the previous it was shown that in most cases the generated pool evaporates for the major part of the release duration. In an evaporating pool, there will not be adequate turbulence and mixing in the liquid to keep the particles suspended. Therefore, it is assumed that these particles will settle. Model sensitivity to the assumption that particles will be soluble or insoluble in the liquid in the pool has been checked and it was shown that in all cases model results change less than 2%. This can be attributed to the small amounts of particles produced compared to the amounts of PCl$_3$ and H$_3$PO$_4$ present in the pool.

9. Conclusions and general discussion

Water reactive chemicals are generally important substances in the field of major hazards. They are used widely in the process industries and have been involved in many hazardous incidents. REACTPOOL is the implementation of a new model that describes the pool behaviour of such spills.

A number of different release scenarios for different water reactive chemicals were investigated and the main conclusions and observations extracted are the following.

- The pool behaviour of water reactive chemicals is mainly affected by the amount of free ground water available for reaction. Increasing the amount of free ground water results in decreasing the pool radius, increasing pool temperature and increasing vapour evolution rates.
- The surface roughness length and the wind speed also a relatively significant effect on the results. Increasing roughness length and wind speed results in increasing vapour evolution rates.
- The generated pool is usually a mixture of two or more liquids and has changing composition and properties (spills of HSO$_3$Cl, PCl$_3$, POCl$_3$, SO$_3$, oleums). In some cases however, the liquid pool will contain only the water reactive chemical (SiCl$_4$ spills).
- The pool may boil or evaporate or even solidify. It usually boils under high availability of water and usually during the early spreading stages. Solidification occurs only for spills of SO$_3$, oleum and POCl$_3$ under low availability of water and in most cases in the period after spreading ceases.
- The hydrolysis reaction of water reactive chemicals may produce solid particles (SiCl$_4$ and PCl$_3$ spills).

- PCl_3 or $POCl_3$ and HCl vapour and gas will evolve to the atmosphere. HCl gas is directly evolved from the hydrolysis reaction.
- The main source of water is usually the free ground water.

Generally, REACTPOOL gives useful insights into the behaviour of such spills. It is very easy to use and calculation times were very satisfactory. A sensitivity analysis of model results to some of the assumptions used, was presented in a previous publication [47]. In the same paper it is shown that usually the main energy inputs and outputs to the pool are the heat of reaction, the heat of evaporation (or generally evolution) and the heat of addition.

All the results reported in this series of papers correspond to continuous spills of water reactive chemicals. Instantaneous spills generally behave in a similar way. Results for instantaneous spills of SO_3 and oleum are given in the earlier paper [47].

The pool model results show that clouds generated from spills of water reactive substances will initially contain more than one vapour or/and gas. Numerous chemical and physical interactions will take place. Such clouds are expected to be initially denser than air and only after some distance downwind will they become passive and chemically inactive. Overall, clouds of water reactive chemicals will resemble in some aspects the SO_3/oleum clouds [43]. As shown in the case of SO_3/oleum clouds the initial processes and interactions could be very crucial, since they strongly affect the cloud characteristics in all regimes. Therefore, ignoring them will result in misrepresentation of the cloud behaviour and will possibly lead to significant modelling errors. Future investigation should be aimed at the development of a general thermodynamic model that will adequately and inclusively describe the processes that occur in such clouds. This model could then be incorporated into an existing atmospheric dispersion code, extending its scope to include the dispersion behaviour of water reactive chemicals.

The main difficulty in the modelling procedure is the lack of experimental data on the release behaviour of such releases. Properties and hydrolysis reactions of some water reactive chemicals are not well defined in the literature. It is strongly recommended that experiments should be carried out to provide the necessary data for model validation and further improvement.

Acknowledgements

Appendix A

Various sources were used to identify the properties of PCl_3, $POCl_3$, H_3PO_4 and red P [8,9,15,16,48].

Properties of PCl_3:

- molecular weight, $MW = 137.33 \, \text{kg} \, \text{kmol}^{-1}$;
- boiling point, $bp = 349 \, \text{K}$;

- freezing point, fp = 181 K;
- liquid density, ρ (kg m^{-3}) (T (K)): $\rho = 1617 - (2(T - 273))$;
- heat capacity, C_p (kJ kg^{-1} K^{-1}): $C_p = (177.03 - 0.46599T)/\text{MW}$;
- viscosity, μ (cP): $\mu = 3.737 \exp(-0.006T)$;
- thermal conductivity, k (kW m^{-1} K^{-1}): $k = 0.1839 - 0.00011322\,T$;
- vapour pressure, P (atm): $\log P = [7.6645 - (1657.3/T)]/760$;
- heat of vaporisation, H (kJ kg^{-1}): $H = (-0.0908T + 85.261)\,4.184$;
- Schmidt number, Sc (estimated according to reference [48]) = 1.782;
- critical temperature, T_c (K) = 563;
- critical volume, V_c (cm^3 mol^{-1}) = 260;
- heat of formation (liquid), H_{vl} (kJ mol^{-1}) = −311.29;
- heat of formation (gas), H_{vg} (kJ mol^{-1}) = −306.27;
- latent heat of fusion, H_s (kJ mol^{-1}) = 5.39.

Properties of POCl$_3$:

- molecular weight, MW = 153.33 kg kmol^{-1};
- boiling point, bp = 380.55 K;
- freezing point, fp = 274.3 K;
- liquid density, ρ (kg m^{-3}) (T (K)): $\rho = 1676 - (0.8(T - 283))$;
- heat capacity, C_p (kJ kg K^{-1}): $C_p = (194.16 - 0.4768T)/\text{MW}$;
- viscosity, μ (cP): $\log \mu = 9.4372 - (1042.1/T)$;
- thermal conductivity, k (kW m^{-1} K^{-1}): $k = 0.1892 - 0.0000651\,T$;
- vapour pressure, P (atm): $\log P = [7.734 - (1846/T)]/760$;
- heat of vaporisation, H (kJ kg^{-1}): $H = (-0.0926T + 87.639)\,4.184$;
- Schmidt number, Sc (estimated according to reference [48]) = 1.82;
- critical temperature, T_c (K) = 602.1;
- heat of formation (liquid), H_{vl} (kJ mol^{-1}) = −601.7;
- heat of formation (gas), H_{vg} (kJ mol^{-1}) = −561.9;
- latent heat of fusion, H_s (kJ mol^{-1}) = 13.1.

Properties of H$_3$PO$_4$:

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

- molecular weight, MW = 98 kg kmol^{-1};
- boiling point, bp = 533 K;
- freezing point, fp = 294 K;
- liquid density, ρ (kg m^{-3}) = 1675;
- heat capacity, C_p (kJ kg K^{-1}) = 1.083;
- heat of formation (liquid), H_{vl} (kJ mol^{-1}) = −1271.6;
- heat of formation (solid), H_{vs} (kJ mol^{-1}) = −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 listed below:

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

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