



Assessment of the effectiveness of downward water sprays for mitigating gaseous chlorine releases in partially confined spaces

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Received 28 January 2002; received in revised form 12 July 2002; accepted 12 July 2002

Abstract

Water sprays are sometimes used as a means of mitigating accidental releases of chlorine gas. This paper gives results of a series of small-scale experimental field tests on the mitigation of chlorine gaseous releases (about 1 kg/min) by various downward water sprays. The releases were from a cylinder of liquefied chlorine located in a storage shed. The shed could be configured to simulate confined and semi-confined installations used at public swimming pools. The water sprays were located in the shed. During these tests, different types of spray nozzles and storage configurations were tested under various atmospheric conditions, in order to select the best water spray. It was shown that the best chlorine downstream concentration reduction (factor 3–5 at 10 m) was achieved with a flat fan water spray for the semi-confined configuration. Poor absorption in water was observed (<1%). The highest absorption (roughly 5%) was obtained with a fog water spray for the confined configuration. This is expected since chlorine is a low soluble gas. It has been evidenced for the confined configuration, that even if reduction of concentration has been observed (factor 2), downstream concentration remains very high (>10,000 ppm), and above critical level of toxicity. Consequently, the use of water sprays in this case without additives to promote absorption seems to be inefficient. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Mitigation; Chlorine; Downward water sprays; Storage sheds; Field tests

1. Introduction

Accidental releases of hazardous gases during transportation, or from fixed storage installations, can give rise to toxic and/or flammable vapor clouds, constituting serious risks

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to both people and property [1]. Though safety in industrial operations and process has improved since major chemical hazards (e.g. Bhopal in India, 1984), further research in the development of reliable mitigation devices is still needed. The problem of controlling such accidental leaks is often made worse by the fact that many hazardous gases of interest like chlorine, are heavier than air due to their high molecular weight, and lead to dense clouds [2]. The mixing and dispersion of such dense gases are often lower than those of passive ones [3].

This study focused on the safety of chlorine cylinders (bottles) at public swimming pools for water disinfection. The cylinders (bottles) of liquefied chlorine are usually stored in semi-confined sheds (open on one side). A loss of containment accident may present a serious chemical hazard [4,5] considering the high toxicity of chlorine. Accidental releases may occur during the replacement of spent bottles or as a result of equipment failures (flange, pipe, valve or seal). Although releases in confined or partially confined spaces, can be mitigated by standard pollution-control systems [6,7], they are technically and economically unviable for small storage installations. Today, there is no recommendation in France for the development of mitigation devices for the safety of users of small chlorine storage sheds at public swimming pools, hence the interest in this mitigation study adopting water sprays as a means of mitigating releases from such installations.

The dispersion/dilution ability of water sprays has been investigated in previous works [7–16]. Other authors [17,18] investigated this capability in the case of enclosed or partially enclosed spaces, but under ideal laboratory conditions.

Water sprays improve the rate of dilution and dispersion of heavy gases releases in gaseous phase, by acting as a technological barrier with subsequent effects (obstacle, mechanical dilution by air, absorption in water, and warming by water). Absorption of gas in water by liquid spraying can be very effective [10,16,19,20] for soluble gases (e.g. HF, NH₃). For less soluble gases, such as chlorine, the use of alkaline additives is needed to promote the mass-transfer from the gaseous phase to the liquid one [10]. This solution set some technical and economical problems, such as early corrosion and water contamination [7,10], and was not studied in a first approach. The principal mechanism involved in the dilution/dispersion enhancement is the air entrainment, i.e. the induced air movement resulting from the momentum transfer between the droplets of the water spray and the ambient air. Air entrainment by water sprays is well documented [10,11,21–27]. Nevertheless, few experimental field tests on mitigation of chlorine releases by water sprays have been carried out [28,29], owing to the cost of this kind of study.

Although the mitigation capability of water sprays have been recognized for some cases and under ideal conditions, it is difficult to demonstrate their effectiveness in real emergency operations. In order to provide definitive answers for chlorine storage installations at swimming pools, a study was carried out. The purpose of the work was to achieve a quantitative assessment of the ability of different downward water sprays to mitigate small releases of gaseous chlorine escaping from a storage shed. The reduction of chlorine ground-level concentrations in the near downstream field was considered. In the first part of this paper, the performance appraisal of different downward water sprays is described in the case of a semi-confined shed configuration. The second part illustrates the reduction of chlorine concentrations by water spraying for a confined shed. This study is sponsored jointly by the French Ministry of Environment and the manufacturers and users of chlorine.

2. Experimental section

2.1. Procedure

Basically, the principle of the small-scale experimental field tests carried out, was to release chlorine from a storage shed, and to measure its concentration downstream with and without a water spray operating between the gas source and the points of measurement. Firstly, a natural dispersion test without water sprays operating was realized, in order to have a reference for the tests carried out during the second stage with different downward water sprays operating. Prior to each test, the storage shed was rotated to its correct orientation, i.e. open side in the downstream wind direction, and the gas sensors network suitably deployed (Fig. 1). The test was started once the wind speed and particularly wind direction became roughly steady. The photo-ionization gas detectors (PIDs) and weather monitor data logger, video recorder, and the timer were all started simultaneously with the gaseous release. When operating, the water spray was turned on once the release started. The bubblers sensors were remotely switched on, thirty seconds after the beginning of the release. Gas supply, water spray, video recorder and data loggers were all turned off together, after a release period of about 4 min. Tests conditions are summarized in Table 1.

2.2. Field test site

The experiments were carried out on a field test site located in the Gard department (France). It consists of a flat rectangular area (roughly 20,000 m²), sandy and barren

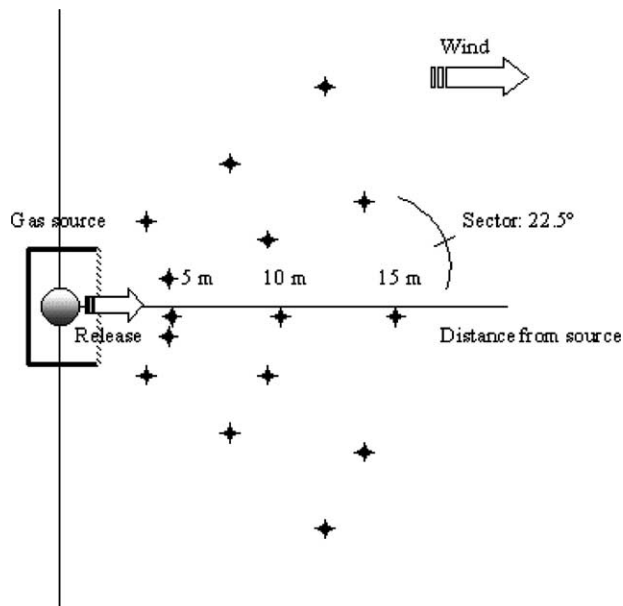


Fig. 1. Gas sensors network and storage shed position.

Table 1
Experimental conditions for the releases of gaseous chlorine

Source rate required (kg/min)	1
Duration of release (min)	4
Storage vapor pressure of the liquefied chlorine bottle (bar)	10
Total capacity of the bottle (kg)	24
Discharge orifice diameter (mm)	4
Discharge pressure imposed (bar)	1
Water supply pressure (bar)	5
Duration of bubblers sampling (min)	3.5

(no grass), and the surface roughness length, z_0 was estimated as being of 0.001 m [32]. In such a field test approach, the atmospheric conditions are not controlled (variations in wind speed and direction).

2.3. Storage shed

Releases from enclosed spaces have been carried out with an experimental storage shed made of Plexiglass® panels and aluminum framework. In this shed of 2 m × 1.25 m × 2 m, the 2 m × 1.25 m side could be fully open or closed by means of a door, achieving two storage configurations. For the confined configuration (Fig. 2A), the shed, considered virtually airtight, was fitted with an inside spray header, and a border spray header (Fig. 2B) was used for the semi-confined one (see subsequent sections). The semi-confined configuration (shed open on one side) simulates the case of semi-confined storage sheds at public swimming pools. The water pressure supply could be monitored by a pressure gauge placed at the water inlet pipe.

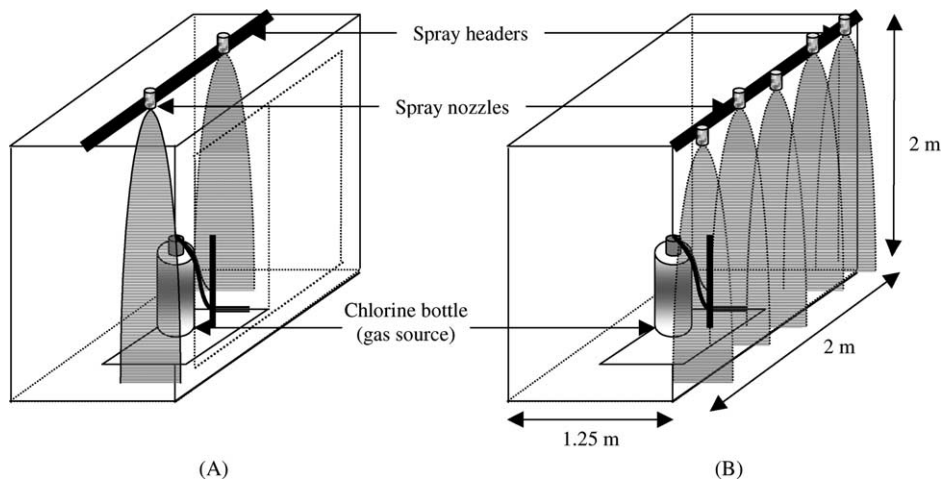


Fig. 2. Storage shed configurations with the spray headers. (A) Confined configuration with the inside spray header. (B) Semi-confined configuration with the border spray header.

2.4. Water supply and water sprays

In order to study the mitigation performance for both storage configurations, two downward nozzle spray headers, fixed at the top of the shed at a height of 2 m above the ground, were used. Both were 2 m long and 32 mm in diameter, and were constructed from rigid plastic water tubing (PVC). For the confined configuration, the inside header had only two outlets 1 m apart. The border header used for the semi-confined configuration, had outlets at intervals of 20 cm apart, which could be plugged if not used. Water flow rates were not directly measured, but were derived from the spray nozzles characteristics. Chlorine has a low solubility (7.37 g/l at 20 °C), so little absorption in water could be expected, particularly for the semi-confined configuration. To verify this, samples of the sprayed water were collected in vessels for subsequent analysis and for both configurations.

2.5. Water spray nozzles

During the tests, different types of spray nozzles were used: flat fan, full cone, hollow cone and fog (Table 2). All these standard spray nozzles (Lechler) are mainly characterized by spray pattern, droplet size distribution, initial droplet velocity, and nozzle flow number (F). The latter represents the water consumption of a nozzle considering its water flow rate (Q_w) for a given water supply pressure (P_w). The expression is: $F = Q_w/P_w^{1/2}$.

2.6. Gas source

Cylinders (bottles) of liquefied chlorine (B20, Air Liquide), pressurized at 10 bar and fitted with a dip pipe to achieve a steady gaseous release, were used as a gas source for the experiments carried out. Typically, the releases were from a cylinder located in the storage

Table 2
Spray nozzles main characteristics^a

Spray pattern	Nozzle types			
	Flat fan	Full cone	Hollow cone	Fog
Number of nozzles	10	2	2	2
Interval space (cm)	20	60	60	100
Diameter of spray ^b (m)	1.6	1.4	1.4	1.5
Spray angle (°)	90	90	90	130
Water supply pressure (10 ⁵ Pa)	5	5	5	5
Initial droplet velocity (m/s)	21	15.5	3.5	37.7
Sauter mean diameter ^c (μm)	409.8	514.4	425.2	190
Water flow rate per nozzle (10 ⁻⁴ m ³ /s)	0.7	3.3	3.3	4.7
Total water flow rate per meter of spray header (10 ⁻⁴ m ³ /(s m))	3.3	3.3	3.3	4.7
F^d (10 ⁻⁷ m ³ /(s Pa ^{1/2}))	0.9	4.7	4.7	6.7

^a For a water supply pressure of 5×10^5 Pa.

^b At a height of 0.8 m from the nozzle.

^c D_{32} : diameter of a drop whose ratio of volume to surface area is equal to that of the complete spray sample.

^d F : nozzle flow number.

shed, and gaseous chlorine was released horizontally through a flexible pipe at 40 cm above the ground. The release flow rate was monitored by mean of a pressure gauge regulator maintained at 1 bar, in order to reach a steady source rate of about 1 kg/min. The mean gas flow rate over the duration of the release was derived by weighing the bottle before and after each release.

2.7. Gas sensors locations

A circular measurement network with the shed at the center of the circle was used throughout the experiments. This enables experiments to be made for any wind direction by rotating the shed. Gas sensors were located in the downstream wind direction (Fig. 1) at 10 cm above the ground on arcs of 5, 10 and 15 m and on axes of 22.5° of sector each. Chlorine concentrations were measured till 15 m, in order to assess the dilution ability of the water sprays in the near downstream field of the source.

2.7.1. Bubbler gas sensors

About 30 bubbler sensors were used throughout the tests. The basic principle is to trap selectively the compound of interest to be measured in a solution that will be analyzed later. The samples were taken horizontally at about 10 cm above the ground. The air/chlorine mixture was pumped at 1.5 l/min through 150 ml of sodium hydroxide solution (0.1 M). Chlorine concentration was inferred from detecting the hypochlorite anion formed by UV spectrophotometry (291.5 nm). This trapping method was effective up to 95%, with an accuracy of 15% [33].

2.7.2. Photo-ionization gas detectors (PID)

Continuous measurements of chlorine concentration were realized during the experiments, by means of PIDs (Mini RAE 2000-RAE Systems). During the experiments, these devices were fitted out with a 11.7 eV discharge lamp to ionize chlorine. In the full-scale range (0–10,000 ppm), these sensors have a resolution of 1 ppm, a response time (t_{90}) of 2 s, and a measurement accuracy of $\pm 20\%$ of reading. Samples were taken horizontally at about 10 cm above the ground.

2.8. Weather monitor

The wind speed and direction were measured throughout each test at a height of 10 m, with an anemometer (Young-05106) connected to a weather monitor central (Young-26700) for data logging. Other relevant meteorological data were simultaneously measured: temperature, relative humidity, and barometric pressure.

3. Results and discussion

The purpose of this study was to assess the effectiveness of downward water sprays. An assessment method could be the dilution ratio (DR) approach, based on the concentration reduction achieved by water sprays [7,9,21]. In this work, the DR at a given downstream

Table 3
Principal data gathered during the chlorine release tests

Test no.	Type	Parameters					
		$Q_{\text{gas}}^{\text{a}}$ (kg/min)	U^{b} (m/s)	θ^{c} (°)	T^{d} (°C)	Rh ^e (%)	PSC ^f
Semi-confined configuration							
2.1	Natural dispersion	0.9	2.0	185	18.1	47	A/B
2.2	Hollow cone spray	0.7	3.8	222	14.1	60	B/C
2.3	Full cone spray	0.7	1.8	231	24.1	33	A/B
3.1	Natural dispersion	1.3	0.6	188	11.1	82	B
3.2	Flat fan spray	1.2	0.9	157	11.8	83	B
3.3	Fog spray	1.2	1.9	218	12.1	85	B
4.1	Natural dispersion	0.8	0.2	12	13.7	90	B
4.2	Flat fan spray	0.7	0.3	345	14.2	85	B
Confined configuration							
3.4	Natural dispersion	1	0.2	169	13.4	70	B
3.5	Fog spray	0.8	0.2	179	17.8	72	B
3.6	Flat fan spray	0.8	1.7	176	15.4	71	B

^a Mean gas flow rate over the duration of the release.

^b Mean horizontal wind speed at 10 m.

^c Mean wind direction: direction from which the wind is coming (measured clockwise from north in degrees).

^d Ambient temperature.

^e Relative humidity.

^f Pasquill–Turner stability category.

point is the ratio of chlorine concentration measured in the absence of water spray (natural dispersion), to that measured with water spray operating for similar atmospheric conditions. In these calculations, chlorine concentrations were normalized to a gas flow rate of 1 kg/min, since the experimental gas flow rates were very similar and about 1 kg/min. Liquid samples of sprayed water containing chlorine as ClO^- form were analyzed by end point titration with sodium thiosulphate. The percentage of chlorine absorption in water was calculated by making the ratio of the amount of dissolved chlorine to the amount released during the test. The pH of the sprayed water was also measured, before and after contacting the chlorine cloud. The principal data collected during the tests are presented in Table 3.

3.1. Semi-confined storage configuration

3.1.1. Concentrations and atmospheric conditions

The ground-level concentrations measured in the axis of the cloud at various distances downstream from the gas source are presented in Table 4 for both the natural dispersion and water sprays tests. The concentrations decayed with the distance from the gas source, as shown in Fig. 3. Concentrations decrease slightly with distance for the flat fan water spray test, as discussed later. For the three natural dispersion tests, the concentrations measured exhibit differences with the lowest values obtained for the test no. 2.1. The most likely explanation is that the atmospheric conditions differences between the tests have caused different clouds behaviors, by acting on their dispersion.

Table 4

Concentrations in the axis of the cloud downstream from the gas source (semi-confined configuration)^a

Test no.	Type	$Q_{\text{gas}}^{\text{b}}$ (kg/min)	U^{c} (m/s)	Concentrations (ppm)		
				5 m	10 m	15 m
2.1	Natural dispersion	0.9	2.0	225	25	5
2.2	Hollow cone spray	0.7	3.8	290	20	20
2.3	Full cone spray	0.7	1.8	190	10	5
3.1	Natural dispersion	1.3	0.6	1860	280	100
3.2	Flat fan spray	1.2	0.9	790	155	35
3.3	Fog spray	1.2	1.9	1505	355	230
4.1	Natural dispersion	0.8	0.2	9800	8120	2750
4.2	Flat fan spray	0.7	0.3	2155	1700	930

^a Time averaged over the duration of sampling.^b Mean gas flow rate over the duration of the release.^c Mean horizontal wind speed at 10 m.

Particularly, at the small gas flow rates used, the cloud would soon become passive at the highest wind speeds. In low wind speed conditions like those of test no. 4.1 (0.2 m/s), the cloud exhibited a typical wide lateral spreading. Conversely for test no. 2.1 with higher wind speed (2 m/s), the cloud width was smaller and it spread over a great distance downwind. Another important parameter to consider is the influence of wind direction, as wind meander can affect the observed concentration. Fig. 4 shows an example of two concentration time recordings, with and without water sprays operating (test nos. 3.2 and 3.1, respectively). The concentrations are lower (factor 3) when the flat fan water spray was operating. Both recordings present concentration fluctuations, as a result of changes in wind direction. Indeed, in low wind speeds conditions (e.g. test no. 4.1), variations in wind direction up to $\pm 20^\circ$ were observed. This is expected, since changes in wind direction can greatly change

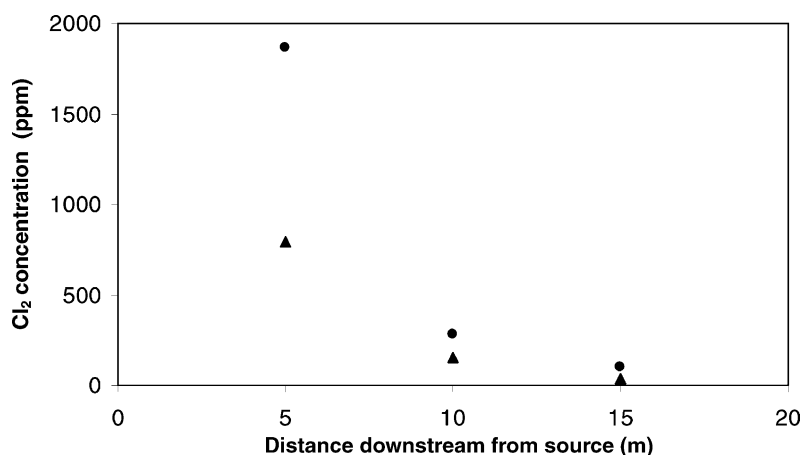


Fig. 3. Variation of chlorine ground level concentration with distance downstream from source for the natural dispersion test no. 3.1 (●), and the flat fan water spray test no. 3.2 (▲).

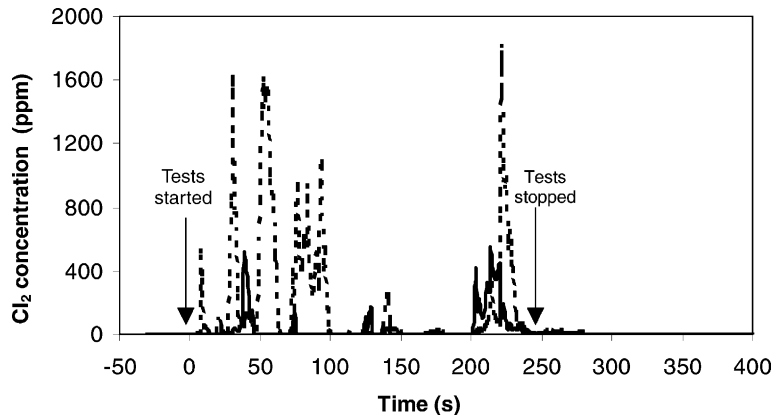


Fig. 4. Concentration time histories obtained during two continuous chlorine releases: one performed without water spray being activated (dotted line), and the other with flat fan spray operating (solid line).

the chlorine concentration measured at a given downstream point, because the cloud could be moved away from the sensor concerned. Therefore, the concentration variability between the tests could be partly attributed to changes in wind speed and wind direction. In addition to the level of concentration, relative humidity may have an influence on cloud behavior too, particularly on its appearance. Visual observations suggest that the visibility of the cloud is partly dependent upon the humidity level of the atmosphere. If we consider the test no. 2.1 for instance, the narrow cloud was hardly visible, which might result from the mean relative humidity level in the atmosphere during the release (47%). In contrast, for the test no. 4.1 as a result of the higher level of humidity (90%), the release had the characteristic appearance of a crawling wide and dense yellow cloud. The ground-level concentrations seem to be higher for the atmospheric conditions previously mentioned, i.e. low wind speeds and high levels of humidity.

3.1.2. Dilution ability of the water sprays tested

The dilution ability of the different downward water sprays tested has been assessed by using the DR approach [7]. In this work, the DR at a given downstream point is the ratio of chlorine concentration in absence of water spray, to that measured with water spray operating for very similar gas flow rates and atmospheric conditions. The DR-values are given in Table 5, for three downstream distances: 5, 10, and 15 m. Considering the average DR-values (average for the three downstream distances), the results exhibit poor values for hollow cone and fog water sprays. Virtually, no concentration reduction was observed for these water sprays in the semi-confined configuration. The lowest average DR-values observed for the hollow cone water spray ($DR = 0.7$), and for the fog water spray ($DR = 0.9$), could result from the variability in atmospheric conditions, particularly in wind speed and direction. A very slight concentration reduction seems to be achieved when full cone water spray was operating. The highest concentration reduction was observed for the flat fan water spray (test nos. 3.2 and 4.2), with average DR-values of 2.3 and 4.1, respectively. Moodie [9], Moore and Rees [21] reported in their studies that the effectiveness of dilution

Table 5
Concentration reduction achieved by the water sprays for semi-confined configuration (DR)

Test no.	Type	DR			
		5 m	10 m	15 m	Average ^a
2.2	Hollow cone spray	0.8	0.8	0.4	0.7
2.3	Full cone spray	1.1	2.5	1.0	1.5
3.2	Flat fan spray	2.2	2.8	2.0	2.3
3.3	Fog spray	1.4	0.9	0.4	0.9
4.2	Flat fan spray	4.5	4.8	2.9	4.1

^a Average of DR-values for the three downstream distances.

is higher in low wind speeds conditions, which can explain the better dilution achieved by the flat fan water spray in test no. 4.2 compared to 3.2. The dilution ability of the flat fan water spray is well illustrated in Fig. 3 for the test no. 3.2, as the 5 m downstream peak concentration was about 800 ppm, whilst about 1800 for the natural dispersion test. These results seem to suggest that, the flat fan water spray performed better than the other sprays for the semi-confined configuration. The better performances of flat fan water sprays have been previously mentioned by Moodie [9] for unconfined releases. It seems that for releases from semi-enclosed spaces like storage sheds, the results tend to be similar.

Results in Table 5 relative to the effectiveness of the water sprays tested, can be discussed in terms of air entrainment. In many previous papers [11,22–25,30,31] air entrainment has been investigated for different spray configurations. Entrained air flow rate was inferred from McQuaid's entrainment relationship for conical sprays [11,12,30]. An air entrainment ratio (Q_a/Q_w), defined as the ratio of entrained air flow rate (Q_a) to sprayed water flow rate (Q_w), can be determined. The alternative approach proposed by Moore and Rees [21] for the particular case of flat fan water sprays was used. Results are given in Table 6. The highest values were achieved for the flat fan water spray, with a total entrained air flow rate ($Q_{a\text{ total}}$) of $6.6\text{ m}^3/\text{s}$, and a entrained air velocity of 4.8 m/s . These observations above tend to show that the flat fan water spray is the most effective water spray, for mitigating chlorine concentrations by mechanical dilution for semi-confined configuration.

Table 6
Theoretical air entrainment values relative to spray nozzles properties^a

Nozzle type	A^b (10^{-3} l/m^3)	$Q_{w\text{ total}}^c$ ($10^{-4}\text{ m}^3/\text{s}$)	$Q_{a\text{ total}}^d$ (m^3/s)	v_a^e (m/s)
Flat fan	1.7	6.6	6.6	4.8
Hollow cone	7.5	6.6	4.6	3.0
Full cone	7.5	6.6	4.6	3.0
Fog	9.4	9.5	5.7	3.2

^a For a water supply pressure of 5.10^5 Pa (see Table 2).

^b $A = (P_w^{1/2} F)/D^2$.

^c $Q_{w\text{ total}}$: total water flow rate by water spray.

^d $Q_{a\text{ total}}$: theoretical total entrained air flow rate by water spray.

^e v_a : theoretical entrained air velocity.

Table 7
Absorption of chlorine in sprayed water (semi-confined configuration)

	Nozzle type	
	Flat fan	Fog
Test no.	3.2	3.3
C _{Cl₂} (10 ⁻² g/l) ^a	7.76	6.87
Cl ₂ dissolved (%) ^b	0.3	0.3
pH	6.4	6.5

^a Chlorine concentration in sprayed water effluents.

^b Ratio of dissolved to released chlorine.

3.1.3. Absorption effectiveness

Partial or total removal of a pollutant from a toxic cloud can be achieved by absorption in water, contrary to mechanical dilution. This is well documented [16,19,20], particularly for high soluble gases, such as hydrogen fluoride or ammonia. Results shown in Table 7 for flat fan and fog water sprays only, are indicative of poor absorption of chlorine in water for the semi-confined configuration, as expected, considering its low solubility. For both sprays, the chlorine concentration in sprayed water effluents was about 7×10^{-2} g/l. The very slight percentage of chlorine absorption in water (<1%), was confirmed with low acidification of the sprayed water effluents. This can be ascribed to the fact that, mechanical dilution by air was promoted for the semi-confined configuration, and this was antagonistic to absorption.

When using sprays with coarse drops to promote mechanical dilution, mass-transfer is hampered by air entrainment. In contrast, to enhance contact time and interfacial area in order to promote absorption, water sprays with fine drop size are required [7]. An alternative to promote chlorine absorption in water could be the use of doped water sprays with alkaline additives (e.g. sodium hydroxide, alkali, potassium iodide), thus, enhancing mass-transfer by initiating chemical reactions [7,10]. Nonetheless, this costly solution may raise some technical problems, as corrosion, water contamination and additional chemical hazard. Better absorption might also be achieved by using a series of water sprays [17,29], at the expense of water consumption.

3.2. Confined storage configuration

3.2.1. Inside concentrations

For the confined configuration, only fog and flat fan water sprays were tested. Inside concentrations measured (15 cm height) with and without water sprays operating are presented in Table 8, with the corresponding DRs. The insides concentrations are higher in absence of water sprays. Visual observations during the test without water sprays operating, shown an interesting steady stratified cloud behavior, as two layers were observed (Fig. 5). The first one looking like a very dense yellow cloud nearly made of pure gaseous chlorine, has filled up till mid-height the volume of the storage shed after 2 min of release. The second layer, mainly made of air, took up the upper volume of the shed. An explanation could be that in absence of turbulences induced from either water sprays operation or atmospheric

Table 8
Concentrations inside the storage shed and corresponding dilution ratios (confined configuration)^a

Test no.	Type	Concentrations (ppm)	DR
3.4	Natural dispersion	26,050	
3.5	Fog spray	15,385	1.7
3.6	Flat fan spray	12,625	2.1

^a Time averaged over the duration of sampling.

conditions (i.e. calm environment), the chlorine release exhibited a very dense cloud behavior magnified by the confinement.

In contrast, when water sprays operated, no stratification was observed with a single yellowish volume of gaseous chlorine mixed with air primarily present in the storage shed. Considering the DR-values in Table 8, the concentration reduction seems not to be influenced by the type of water spray (roughly factor 2). It could result from the dilution of the chlorine amount released in a volume twice larger, owing to the turbulences induced by water sprays. The absorption effectiveness was investigated to make a comparison between the semi-confined configuration and the confined configuration.

3.2.2. Absorption effectiveness

A better percentage of chlorine absorption in water was obtained (Table 9) in comparison with the semi-confined configuration, with the highest value (5.1%) for the fog water spray. Indeed, higher level of concentration observed in consequence of confinement, with subsequent contact time enhancement, contributed to promote mass-transfer. The effect of this improved absorption was the high acidity of the sprayed water effluents after contacting chlorine, namely pH 2.0. The fog spray seems to perform better than the flat fan one,



Fig. 5. Steady stratified cloud behavior for the confined configuration.

Table 9
Absorption of chlorine in sprayed water (confined configuration)

	Nozzle type	
	Flat fan	Fog
Test no.	3.6	3.5
C_{Cl_2} (10^{-1} g/l) ^a	9.0	9.5
Cl_2 dissolved (%) ^b	3.8	5.1
pH	2.3	2.3

^a Chlorine concentration in sprayed water effluents.

^b Ratio of dissolved to released chlorine.

probably owing to its small droplet size (Table 2). Nonetheless, even if relative concentration reduction was observed either by mechanical dilution or by absorption, it must be emphasized that chlorine concentrations measured inside the storage shed are still very high (>10,000 ppm), about one thousand times greater than the IDLH (immediately dangerous to life or health) concentration for chlorine ($IDLH_{Cl_2} = 10$ ppm). Therefore, the use of alkaline additives seems to be necessary to improve absorption, and to lower chlorine concentrations under critical level of toxicity.

4. Conclusions

Accidental releases of hazardous gases can sometimes be controlled by using water sprays. In this paper, the scope was restricted to gaseous releases of chlorine from a cylinder of liquefied chlorine located in a storage shed, to simulate small installations used at public swimming pools. For the semi-confined configuration, the flat fan water spray was the most effective for mitigating chlorine gaseous releases from such installations. In the near downstream field (10 m), the ground-level concentrations reduction achieved by mechanical dilution was about a factor 3–5, when this water spray was operating. For the confined configuration, the concentrations were reduced by a factor 2, which could result from the dilution of the chlorine amount released in a volume twice larger. Better absorption was observed for the confined configuration, and it could be attributed to contact time enhancement and higher concentrations, which promoted mass-transfer. Although a high value was obtained for the fog water spray (5.1%), absorption remains still poor with the water sprays tested and for both storage configurations. Further experimental field tests are, therefore, needed to refine the quantitative assessment of the mitigation performances of the different water sprays tested. Nonetheless, these results and conclusions open ways for further research, particularly the use of chemical additives to promote absorption.

Acknowledgements

The authors would like to thank the chemical hazards squad of the Ales city fire department for their technical contributions to the experiments. They are grateful for financial support from the French Ministry of Environment.

References

- [1] J. Casal, H. Montiel, E. Planas-Chuchi, J.A. Vilchez, J. Guamis, J. Sans, Information on the risks of chemical accidents to the civil population. The experience of Bay Llobregat, *J. Loss Prev. Process Ind.* 10 (1997) 169–178.
- [2] J. Havens, Review of dense gas dispersion field experiments control, *J. Loss Prev. Process Ind.* 5 (1992) 28–41.
- [3] R.P. Koopman, D.L. Ermak, S.T. Chan, A review of recent field tests and mathematical modelling of atmospheric dispersion of large spills of denser-than-air gases, *Atmos. Environ.* 23 (1989) 731–745.
- [4] W.J. Decker, Chlorine poisoning at the swimming pool revisited: anatomy of two minidisasters, *Vet. Hum. Toxicol.* 30 (1988) 584–585.
- [5] T.T. Martinez, C. Long, Exposition risk from swimming pool chlorinators and review of chlorine toxicity, *Clin. Toxicol.* 33 (1995) 349–354.
- [6] V.M. Fthenakis, P.D. Moskowitz, R.D. Sproull, Control of accidental releases of hydrogen selenide and hydrogen sulphide in the manufacture of photovoltaic cells: a feasibility study, *J. Loss Prev. Process Ind.* 1 (1988) 206–212.
- [7] V.M. Fthenakis, The feasibility of controlling unconfined releases of toxic gases by liquid spraying, *Chem. Eng. Commun.* 83 (1989) 173–189.
- [8] K. Moodie, Experimental assessment of full-scale water spray barriers for dispersing dense gases, in: *Proceedings of the Symposium of the Institution of Chemical Engineers, Manchester*, vol. 5, 1981, pp. 5.1–5.13.
- [9] K. Moodie, The use of water spray barriers to disperse spills of heavy gases, *Plant Operat. Prog.* 4 (1985) 234–241.
- [10] J.M. Buchlin, Mitigation of problem clouds, *J. Loss Prev. Process Ind.* 7 (1994) 167–174.
- [11] J. McQuaid, Air entrainment into bounded axisymmetric sprays, *Proc. Inst. Mech. Eng.* 189 (1975) 197–202.
- [12] J. McQuaid, The design of water-spray barriers for chemical plants, in: *Proceedings of the 2nd International Symposium on Loss Prevention and Safety Promotion in the Process Industries, Heidelberg*, 1977.
- [13] L.A. Eggleston, W.R. Herrera, M.D. Pish, Water spray to reduce vapor cloud, in: *Proceedings of the AIChE Loss Prevention Symposium*, vol. 10, Missouri, 1976, pp. 31–42.
- [14] J.W. Watts, Effects of water spray on unconfined flammable gas, in: *Proceedings of the AIChE Loss Prevention Symposium*, vol. 10, Missouri, 1976, pp. 48–54.
- [15] P.H. Rothe, J.A. Block, Aerodynamic behavior of liquid sprays, *Int. J. Multiphase Flow* 3 (1977) 263–272.
- [16] K.W. Schatz, R.P. Koopman, Water spray mitigation of hydrofluoric acid releases, *J. Loss Prev. Process Ind.* 3 (1990) 222–233.
- [17] J.M. Smith, M. Van Doorn, Water sprays in confined applications: mixing and release from enclosed spaces, in: *Proceedings of the Symposium of the Institution of Chemical Engineers*, vol. 5, Manchester, 1981, pp. 2.1–2.13.
- [18] P.F. Linden, S.F. Jagger, J.M. Redondo, R.E. Britter, K. Moodie, The effect of a water spray barrier on a tunnel fire, Report of the Institution of Mechanical Engineers, C438/013-IMechE, 1992, pp. 59–64.
- [19] D.N. Blewitt, J.F. Yohn, R.P. Koopman, T.C. Brown, W.J. Hague, Effectiveness of water sprays on mitigating anhydrous hydrofluoric acid releases, in: *Proceedings of the AIChE International Conference on Vapor Cloud Modeling*, New York, 1987, pp. 155–180.
- [20] V.M. Fthenakis, Water-spray systems for mitigating accidental indoor releases of water-soluble gases, *J. Loss Prev. Process Ind.* 14 (2001) 205–211.
- [21] P.A.C. Moore, W.D. Rees, Forced dispersion of gases by water and steam, in: *Proceedings of the Symposium of the Institution of Chemical Engineers*, vol. 5, Manchester, 1981, pp. 4.1–4.14.
- [22] F.G.S. Benatt, P. Eisenklam, Gaseous entrainment into axisymmetric liquid sprays, *J. Inst. Fuel* 42 (1969) 309–315.
- [23] F.E.J. Briffa, N. Dombrowski, Entrainment of air into a liquid spray, *AIChE J.* 12 (1966) 708–717.
- [24] D.J. Rasbash, G.W.V. Stark, Some engineering properties of sprays, *Chem. Eng.* 40 (1962) A83.
- [25] G. Heskestad, H.C. Kung, N.F. Todtenkopf, Air entrainment into water sprays and spray curtains, in: *Proceedings of the ASME Winter Annual Meeting*, 76-WA/FE-40, 1976, pp. 2–12.
- [26] J.M. Buchlin, Aerodynamic behavior of liquid spray—experimental procedure (Part II), VKI Report no. 168, 1979.

- [27] J.M. Buchlin, Aerodynamic behavior of liquid spray—design methods (Part I), VKI Report no. 171, 1980.
- [28] J.R. Thomerson, D.E. Billings, Chlorine vapor suppression tests DOE Nevada test site, Report of DOE in association with Dow Chemical Company, 1990.
- [29] C.H. Buschman, Experiments on the dispersion of heavy gases and abatement of chlorine clouds, in: Proceedings of the 4th International Symposium on Transport of Hazardous Cargoes by Sea and in Land Waterways, Jacksonville, 1975, pp. 475–488.
- [30] J. McQuaid, The design of water-sprays barriers ventilators, *J. Occup. Accid.* 1 (1976) 9–19.
- [31] J. McQuaid, K. Moodie, The scope for reduction of the hazards of flammable or toxic gas plumes, *J. Occup. Accid.* 5 (1983) 135–141.
- [32] R.I. Harris, N.C. Helliwell, J.S. Hopkins, T.V. Lawson, A. Mc Pherson, Characteristics of Wind Speed in the Lower Layers of the Atmosphere Near the Ground: Strong Winds (Neutral Atmosphere), Engineering Sciences Data Unit publication, Item no. 72026, 1972.
- [33] A. Dandrieux, G. Dusserre, J. Ollivier, Small scale field experiments of chlorine dispersion, *J. Loss Prev. Process Ind.* 15 (2002) 5–10.