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An effective mitigation system for chlorine release from storage facilities: An IoT based practical approach using physical barriers

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Abstract
Most of the existing toxic gas mitigation techniques have difficulty in practical implementation. More effective mitigation methods are required for handling hazardous gas releases in Chemical Process Industries (CPIs). One of the most hazardous chemicals is chlorine, an integral part of almost all chemical industries, especially chlor-alkali. This study examined a possible accidental spill of liquid chlorine from a chlorine storage area. Computational Fluid Dynamics, Process Hazard Analysis Software Tool (PHAST), and Probit analysis were combined to develop the overall effect and vulnerability models. The dispersion of chlorine vapors at wind speeds of 2, 3, and 4 m/s was analyzed, and the corresponding threat zones were plotted. Many public establishments of extreme vulnerability were located inside the threat zones. Offsite emergency planning guidelines are necessary for such conditions. Based on the results of the consequence analysis, a practical and cost-efficient IoT (Internet of Things) based mitigation system using physical barriers is proposed. The proposed mitigation system accounts for entrapment, continuous removal, and safe handling of the chlorine vapor from the release area. The proposed mitigation system can be implemented in all CPIs dealing with the production and storage of toxic gases. The outcome of this study can contribute to the development of Emergency Response Planning (ERP) guidelines for chlorine release.

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1. INTRODUCTION

The present civilization is highly dependent on chemical and petrochemical industries directly or indirectly for daily needs. Over the past decades, there has been a steep increase in the count of new process industries. Accidents related to process industries have also increased proportionately, leading to widespread apprehension and distress. Eventually, researchers and industrial experts have focused more on process safety and risk management to tackle this expanding issue in the industry. Several accidents in the process industries have turned out to be massive disasters (Hakkinen, 2005; Hendershot, 2009; Khan and Abbasi, 1999; Labib, 2014). The Bhopal gas tragedy is the deadliest industrial disaster to date in the history of humankind (Bisarya and Puri, 2005). More than five thousand people died from inhaling the toxic methyl isocyanate gas accidentally released from the Union Carbide India Limited factory. However, the Bhopal incident improved safety practices in chemical process industries (Murphy et al., 2014). It is evident from previous accident cases that toxic gas release has the most lethal impact among the significant accidents occurring in Chemical Process Industries (CPIs). One of the most widely used toxic chemicals in process industries is chlorine, a yellow gas at room temperature. Chlorine is listed as an extremely hazardous chemical by the United States Environmental Protection Agency (EPA), defined in part 355 of the U.S. federal code of regulations (EPA, 2016). It is one of the toxic industrial chemicals of most significant concern, with a hazard index value of 500 and an Immediately Dangerous to Life and Health (IDLH) concentration of 10 ppm.

Chlorine is not a purpose-designed chemical warfare agent; nevertheless, it was used in World War 1 at Ypres, Belgium, due to its extreme lethality (Toxic Industrial Chemicals, 2002). Major chlorine release accidents in process industries have occurred during the transportation and transfer of liquid chlorine in pressure vessels (Buckley et al., 2012; Marco et al., 1998; National Transportation Safety Board, 2006; U.S. Chemical Safety and Hazard Investigation Board, 2003). Chlorine, being heavier than air, shows a dense gas dispersion pattern when released. Though chlorine is a dense gas, considerable wind speed can spread the accidental chlorine release over a large area in a short duration (Britter and McQuaid, 1988; Soman et al., 2012). A series of large-scale release experiments titled Jack Rabbit II was conducted to fill the critical knowledge gaps for accidental or intentional chlorine release (Nicholson et al., 2017). The tests developed more insights on modeling data for release source, atmospheric transport and dispersion, hazard and risk, and consequence assessment related to chlorine. Hanna et al. (2008) compared six widely used dense gas dispersion models for accidental chlorine release, including proprietary models Process Hazard Analysis Software Tool (PHAST) and TRACE.

This study aimed to perform the consequence analysis of the accidental leakage of chlorine from a storage pressure vessel and prepare an effective mitigation plan. The study considered a spontaneous leakage scenario of liquefied chlorine from a storage pressure vessel in a chlorine manufacturing plant. When an accidental release occurs from a chlorine storage pressure vessel, a significant amount of liquid chlorine vaporizes instantly due to its low boiling point. The remaining liquid chlorine gets collected in the surrounding dike and forms a pool (Gant et al., 2018) and subsequent pool evaporation occurs. The dike is a concrete structure and is provided to contain whole chlorine in the tank when released. For developing a proper Emergency Response Plan (ERP), it is critical to assess the extent of dispersion of chlorine vapors. The spreading area has to be considerably reduced to decrease the impact of chlorine release. Therefore, an adequate mitigation plan that also substantially minimizes the extent of the threat zones must be developed. Simultaneously, the mitigation plan should also account for the continuous removal of chlorine vapor from the release area. Different technologies like bunding, foam, gas absorption by water spray curtains, and steam curtains are used to mitigate chlorine release (Dimbour et al., 2003; Engelhardt, 2002; Weber, 2006). Aqueous sodium thiosulphate solution can readily reduce elemental chlorine to chloride anions (Mukherjee et al., 2018). The presently available mitigation methods have practical limitations, mainly when implemented in a large domain. This study proposes a simple and cost-efficient mitigation system with a high degree of effectiveness using Reinforced Poly Tetra Fluro Ethylene (RPTFE) curtains as a physical barrier. The proposed mitigation system can be conveniently installed on existing chlorine storage facilities without further alterations in the present piping and instrumentation setup.

2. MATERIALS AND METHODS

Accidental leakage of liquid chlorine from a chlorine storage pressure vessel (CPV) within a chlorine production plant was addressed here. The capacity of the chlorine storage pressure vessel is 50 tonnes. A portion of the liquid instantly flashes upon accidental release, and the rest is contained in a dike, resulting in a chlorine pool. The Unified Dispersion Model (UDM) was chosen to analyze the spread of gaseous chlorine and the ERPG areas by PHAST software (Pandya et al., 2012). The mass flow rate of chlorine vapor from the dike containment was calculated by a Computational Fluid Dynamics (CFD) software, ANSYS FLUENT (Wang et al., 2020). Probit analysis (James, 2014) was used to evaluate the impact of the release on the people. A mitigation system was suggested based on industrial-grade RPTFE curtains to contain and remove chlorine vapors. The flowchart of this study is shown in Figure 1.

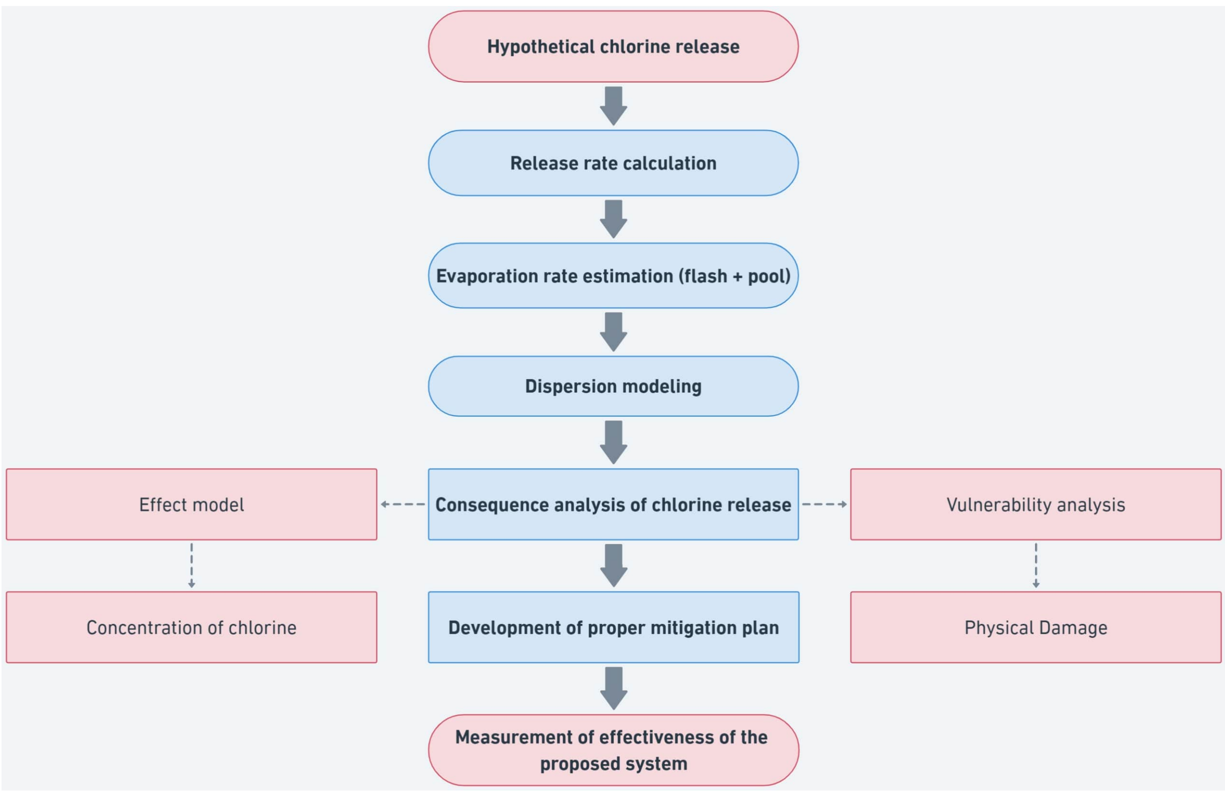

Figure 1. Methodology of the process.

3. HYPOTHETICAL RELEASE SCENARIO

The storage tank from which the hypothetical release occurs is a cylindrical pressure vessel capable of handling fifty tonnes. The storage pressure vessel is considered to be located at a central chlorine manufacturing facility in Kochi, South India, involved in the production, storage, and transportation of liquid chlorine. The density of liquid chlorine is 1473 kg/m^3, and its boiling point is 239 K at atmospheric pressure. In the storage facility, chlorine is stored in tanks as a superheated liquid at ambient temperature and an approximate pressure of about 5 bar. Liquid chlorine is transferred out of the tank by applying a pressure of 10 bar. It is assumed that the pipe joint connecting the tank and the sight glass ruptures during chlorine transfer from the storage tank. Forty tonnes of liquid chlorine will be released due to the rupture. The estimated duration of release is approximately 24 minutes. The release rate of liquid chlorine from the rupture point was calculated using Eq. (1) (Cameron and Raman, 2005). The release of pressurized liquid chlorine would lead to a two-phase jet release. A portion of the superheated jet flashes to form chlorine vapor. The fraction of the liquid flashed was calculated with Eq. (2) (Mannan, 2005). Tiny droplets of liquid chlorine also get entrained in the vapor to form an aerosol. The total airborne quantity due to flash vaporization and aerosol formation was calculated with Eq. (3) (Mannan, 2005).

$$W = C_d f(l)\sqrt{P_1} \times A_o \quad \text{(kg/s)} \tag{1}$$

The mass fraction of the liquid flashed (Φ) is given by,

$$\Phi = 1 - \exp\left[-\frac{C_p}{\Delta H_v}(T_1 - T_2)\right] \tag{2}$$

The fraction of the liquid entrained (e) in the vapor is typically taken as (Φ), and the total airborne quantity (M_v) is given by,

$$M_v = (\Phi + e)W \tag{3}$$

Larger droplets rain out and get collected in the dike of dimension 50 × 4 × 1 m forming a pool. The depth of the chlorine pool formed in the dike was calculated as 0.18 m. The chlorine pool also starts evaporating, and the vapor gets dispersed into the atmosphere until an equilibrium is reached. The pool evaporation also contributes to the total airborne quantity. Hence, the total airborne quantity of the release scenario is the sum of chlorine concentration from flash vaporization, aerosol formation, and pool evaporation. The schematic drawing of the storage area with the dike is shown in Figure 2. The ambient temperature of the location is 24–34 °C. Also, the typical wind direction in the locality is from the northwest (weatheronline.in).

4. CONSEQUENCE ASSESSMENT

The magnitude of the physical effects triggered by chlorine release and the damage caused are considered. The dispersion model analyses the chlorine spread area and quantifies the chlorine concentration at different levels. The vulnerability of the accidental release is expressed as the probability of death at the corresponding chlorine dose levels. Probit analysis is used to examine the impact of chlorine release and its potential harm.

4.1. Evaporation from the pool

The liquid chlorine in the pool evaporates due to the change in the thermodynamic equilibrium and sharp pressure decrease. The evaporation rate of liquid chlorine from the pool is required for calculating the total airborne quantity. CFD simulations were used to estimate the evaporation rate of chlorine from the dike pool. The following criteria were considered for modeling the chlorine pool evaporation:

- chlorine is evenly distributed throughout the layers,
- the top portion of the chlorine pool is stationary throughout the process,
- ambient humidity effects are negligible.

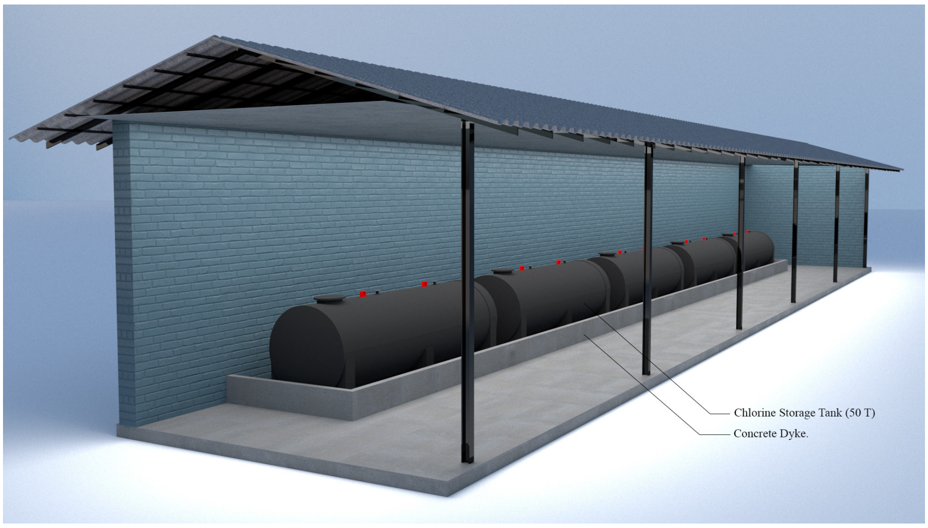

Figure 2. Schematic drawing of the storage area with dike.

The heat conduction from the dike floor takes place in an upward direction and is assumed to be perpendicular to the wind direction. The side walls are assumed to be adiabatic; therefore, the sidewall's heat flux is taken as zero. A 2D geometry domain of size 50 × 1 m was used to simulate the vaporization from the tank. The geometry was discretized using structural quadrilateral elements. The total number of elements was 160000, and the time step used in this study was 0.01 seconds.

Numerical simulations were done using the CFD software ANSYS FLUENT, based on a finite volume-method solver. The governing equations were solved by using the pressure-based incompressible flow solver. The k-epsilon standard model accounted for the turbulence effects, and the standard wall function was given for the near-wall treatment. The Volume of Fluid model [VOF] and the level set methods were used to consider the effects of evaporation. The total number of Eulerian phases was taken as three, and the volume fraction parameters were solved explicitly.

The governing equations can be considered as follows.

The energy balance equation is given by Eq. (4),

$$\frac{\partial(\rho E)}{\partial t} + \nabla\left(\vec{v}\left(\rho E + p\right)\right) = \nabla\left(k_{\text{eff}}\nabla T\right) + S_h \tag{4}$$

Where k_{eff} is the effective thermal conductivity. The first term on the right-hand side represents heat transfer due to conduction. S_h includes the heat of the chemical reaction.

Total Energy E is given by Eq. (5),

$$E = \frac{\sum\limits_{q=1}^{n} \alpha_q \rho_q E_q}{\sum\limits_{q=1}^{n} \alpha_q \rho_q} \tag{5}$$

The volume fraction (α) of any phase is calculated by Eq. (6) as follows for the q^{th} phase:

$$\frac{1}{\rho_q}\left[\frac{\partial\left(\alpha_q \rho_q\right)}{\partial t} + \nabla.\left(\alpha_q \rho_q \vec{v_q}\right)\right] = S_{\alpha_q} + \sum_{p=1}^{n}\left(\dot{m}_{pq} - \dot{m}_{qp}\right) \tag{6}$$

where, $\sum\limits_{q=1}^{n} \alpha_q = 1$, '$n$' is the total number of phases.

The velocity inlet and pressure outlet conditions are given at the inlet and outlet of the domain. Wind velocities of 2 m/s, 3 m/s, and 4 m/s are given at the inlet. The temperature of the liquid chlorine inside the pool is at its boiling point. All walls are assumed to be no-slip adiabatic. The "SIMPLE" scheme is used to solve the pressure velocity coupling, and all other terms are solved with second-order accuracy.

4.2. Dispersion model

The dispersion calculation provides an estimation of the area affected and also the expected average vapor concentration. The chlorine leakage occurs in three stages: dynamic dispersion, gravity dispersion, and atmospheric dispersion (Xin et al., 2021). PHAST UDM for continuous release is used for modeling chlorine dispersion and estimating Emergency Response Planning Guidelines (ERPG) levels. ERPGs represent varying levels of consequence in response to a chemical exposure of 1 hour in duration. The PHAST UDM can efficiently model the dispersion following an elevated two-phase pressurized release (Witlox et al., 1999a). It employs linked modules for jet, heavy, and passive two-phase dispersion, including possible droplet rainout, pool spreading, and re-evaporation. Table 1 lists the input variables taken into account for the PHAST simulation. A comparison of the threat zone area at 4 m/s was performed for 'very unstable' (A), 'moderately unstable' (B/C), and 'stable' (F) Pasquill stability conditions and is shown in Figure 3. The three factors that define atmospheric stability are solar radiation, night time sky over, and surface winds. Considering these factors of the area of study, the Pasquill stability class B/C was considered here as a conservative approach. The concentration C for continuous dispersion in UDM is given by Eq. (7) (Witlox et al., 1999b) as $C = C\left(x, y, \zeta\right)$.

$$C\left(x, y, \zeta\right) = C_o\left(x\right) F_v\left(\zeta\right) F_h(y) \tag{7}$$

where, $F_v\left(\zeta\right) = \exp^{\left\{-\left|\frac{\zeta}{R_z}\right|^n\right\}}$, $F_h\left(y\right) = \exp^{\left\{-\left|\frac{y}{R_y}\right|^m\right\}}$.

Table 1. Input variables for PHAST simulation.

Input variables	Value
Ambient temperature	303 K
Atmospheric Pasquill stability	B/C (Moderately unstable)
Pipe roughness	0.045 mm
Solar radiation flux	0.7 kW/m^2
Relative humidity	60%
Tank head above the discharge point	2 m

The above equation describes the exponential decay of the plume concentration in y and ζ in terms of the cross-wind and vertical dispersion coefficients $R_y(x)$, $R_z(x)$. Empirical correlations are adopted for the exponents m and n. The area of the cloud in the x-direction is obtained by double integrating $F_v\left(\zeta\right)$. $F_h\left(y\right)$ over the variables y and ζ.

4.3. Vulnerability model

4.3.1. PROBIT analysis

Probit analysis considers the concentration of a chemical and the duration of exposure according to toxic load and its associated death probability to the exposed population. The

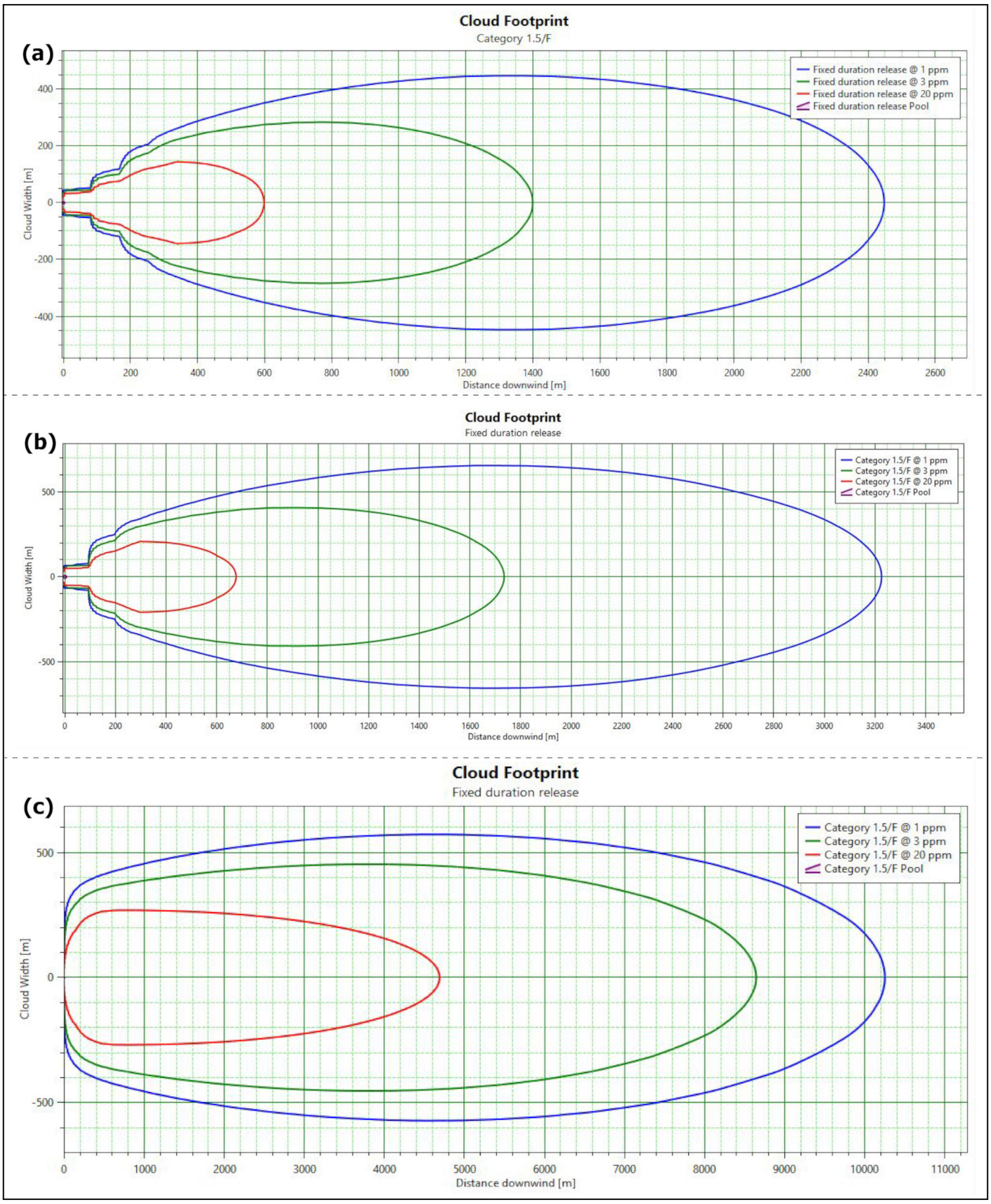

Figure 3. Threat zone area at Pasquill stability classes A (a), B/C (b) and F (c).

probit value can be estimated from Eq. (8). Once the probit score is calculated, the probability value can be read from the probit table. The probit table can transform any probit value into a corresponding probability.

The probit score Z is calculated by,

$$Z = X + Y \ln(\text{Dose}) \tag{8}$$

where, $\text{Dose} = \int C^m t \cdot \mathrm{d}t$.

Based on results from animal studies, the values of regression coefficients X and Y are available. C represents the amount of the corresponding chemical (mg/m^3). The duration of exposure is expressed as 't' in minutes.

The probit constants (CCPS, 1999) for chlorine are listed in Table 2.

Table 2. Probit constants for chlorine.

Parameter	value
X	–8.29
Y	0.92
M	2

5. RESULTS OF CONSEQUENCE ASSESSMENT

5.1. Evaporation from the dike pool

CFD model was employed to simulate the vaporisation of liquid chlorine collected in the dike upon the unexpected leakage of 40 tonnes of chlorine from the storage pressure vessel. The boiling point of liquid chlorine at standard pressure conditions is 238 K. Liquefied chlorine has a latent heat of vaporization of 288.1 kJ/kg. The thermal conductivites of chlorine, air and the surrounding dike are 0.0089 W/mK, 0.0262 W/mK and 1.7 W/mK respectievely. The heat capacities of liquid chlorine and air is taken as 948 J/kgK, and 1006 J/kgK respectievely. The evaporation rates of chlorine vapor from the dike for wind velocities 2 m/s (a), 3 m/s (b), and 4 m/s (c) were calculated using the CFD software (Figure 4).

The evaporation rate of chlorine from the dike pool was observed to increase up to 80 seconds for all the wind velocities. The pattern of mass flow rate is highly fluctuating and non-uniform. The high fluctuation is due to the sudden increase in the evaporation rate of liquid chlorine. The results indicate a continuous variation in the temperature of the chlorine pool and, thereby, a non-uniform condition. In general, after 100 seconds, the evaporation rate decreases; after 300 seconds, the evaporation rate is almost uniform, and the system is seen to attain saturation. After reaching the saturation conditions for the concerned wind velocities, the evaporation rates from the pool are 2.65 kg/s, 3.46 kg/s, and 4.8 kg/s, respectively. The total airborne quantity (flash, aerosol, and pool evaporation) is used to estimate the suction rate needed for blowers in the proposed mitigation system.

5.2. Atmospheric dispersion of chlorine

The ERPG threat zones, estimated using the PHAST UDM, and their corresponding map view are illustrated in Figure 5. For the moderately unstable (B/C) atmospheric Pasquill stability condition considered here, chlorine may propagate to a range of 4 km from its release point, depending on the wind speed. The total chlorine in the tank is supposed to empty in 24 minutes. A significant amount of chlorine instantly vaporizes during this time, and the toxic cloud spreads to a large area. The instant vaporization of liquid chlorine mainly contributes to the vapor cloud formation at this stage. After the release duration of 24 minutes, the size of the vapor cloud diminishes as the cloud formation is now predominantly due to the pool evaporation alone.

As observed from the map view, the threat zones, i.e., the area vulnerable to chlorine release, is a densely populated municipal area. Also, the site has multiple facilities of extreme vulnerability, including dwellings, schools, health centres, civil stations, churches and temples. The region outlined in blue is the ERPG-1 level with chlorine vapor content in the air significant up to 1 ppm. The green outlined area shows ERPG-2 level where the amount of chlorine vapor is greater than 3 ppm. The area outlined in red indicates ERPG 3 zone with chlorine vapor concentration greater than its threshold value, 20 ppm.

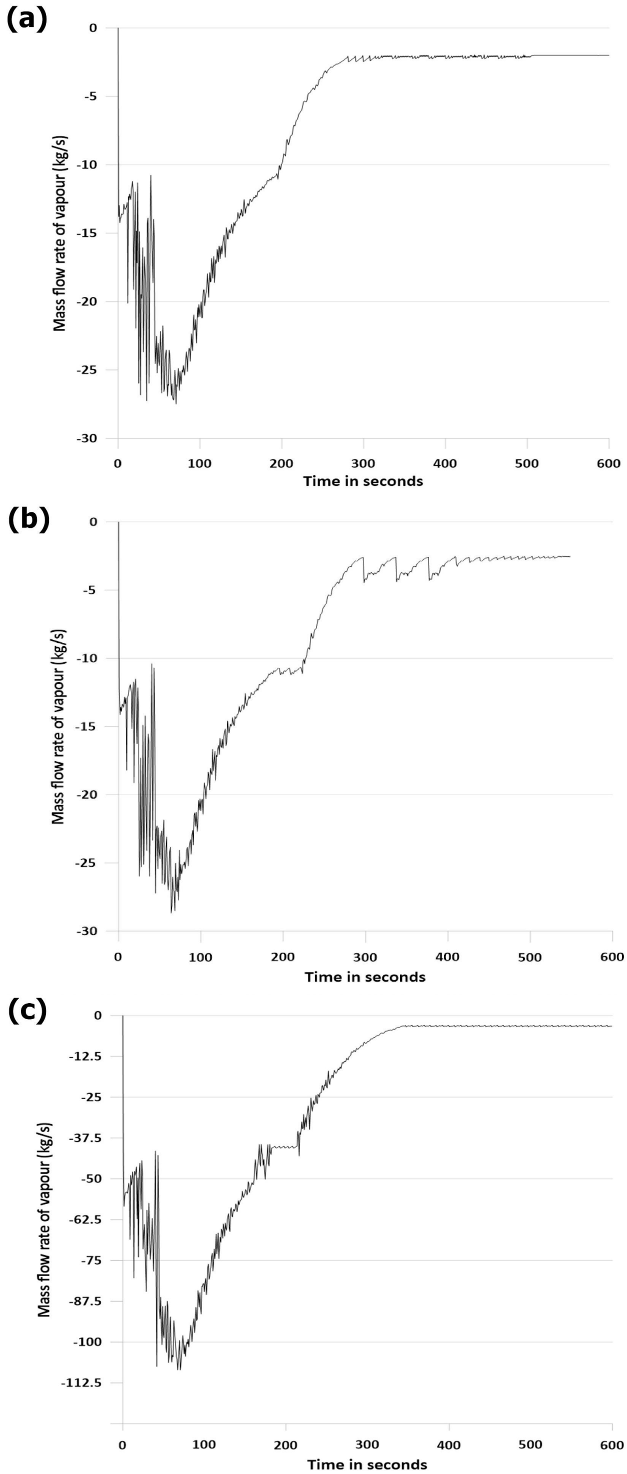

Figure 4. Evaporation rate from the pool at 2 (a), 3(b) and 4(c) m/s.

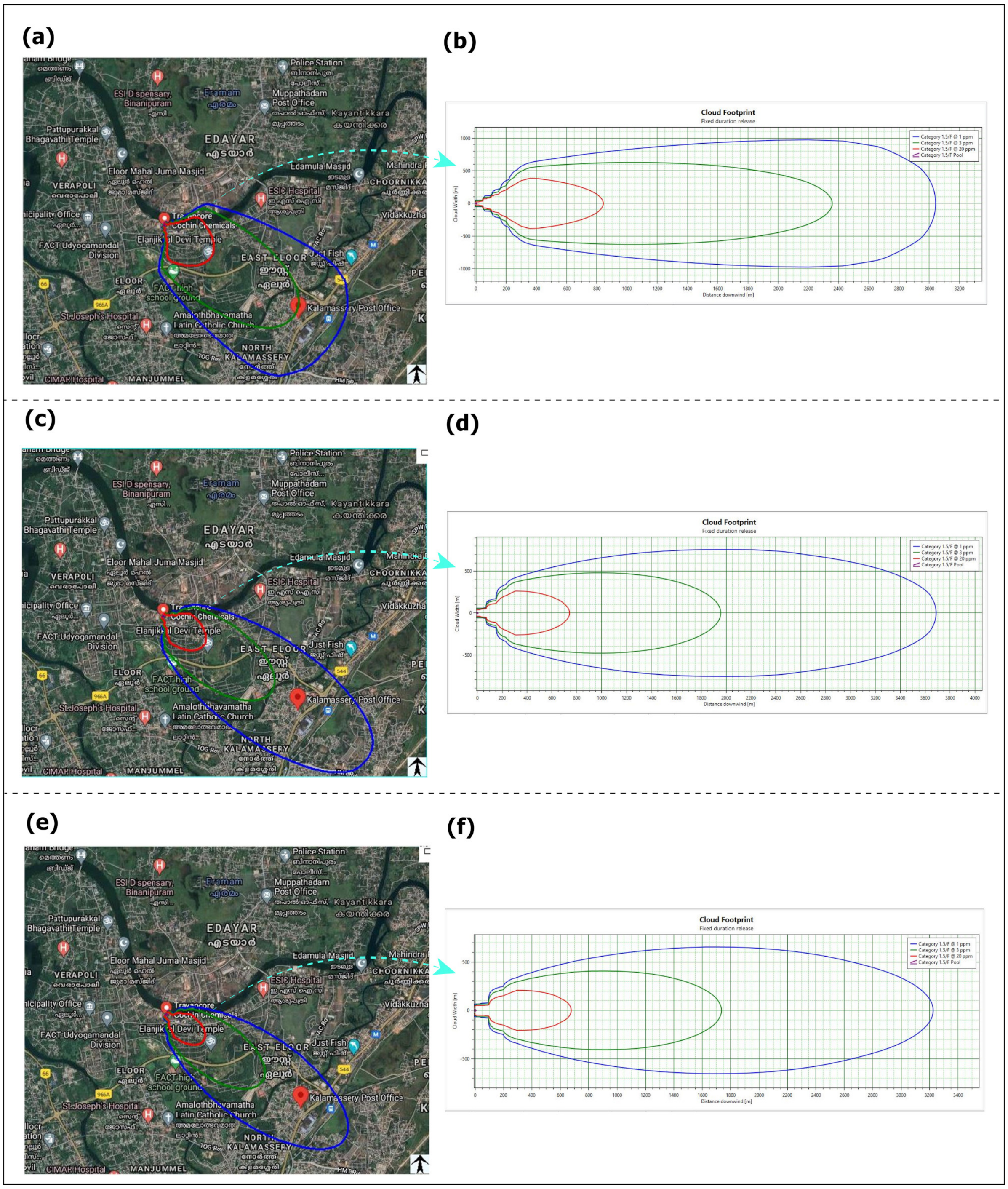

Figure 5. Threat zone area and corresponding map view at 2, 3 and 4 m/s.

5.3. Vulnerability assessment

The likelihood of fatality due to the chlorine leakage was analyzed using the probit study. *Probit study* is an empirical analysis based on the toxic property of a substance, its atmospheric dosage, and the duration spent in contact with the chemical.

Figures 6 show the chances of fatality in the ERPG levels at various wind speeds. The probit analysis shows that the fatality likelihood is significant to a distance of 0.7 km from the release point. The total population of Eloor municipality is 154,245, according to the 2011 India census (Census of India, 2011). The ERPG zones can be considered high-risk areas, as people inhabiting these areas may develop acute health problems due to the toxic effects of chlorine. Therefore, adequate mitigation systems should be installed to prevent or reduce the harmful effects of chlorine release. The mitigation strategy should reduce the vapor cloud area, thereby reducing mortality.

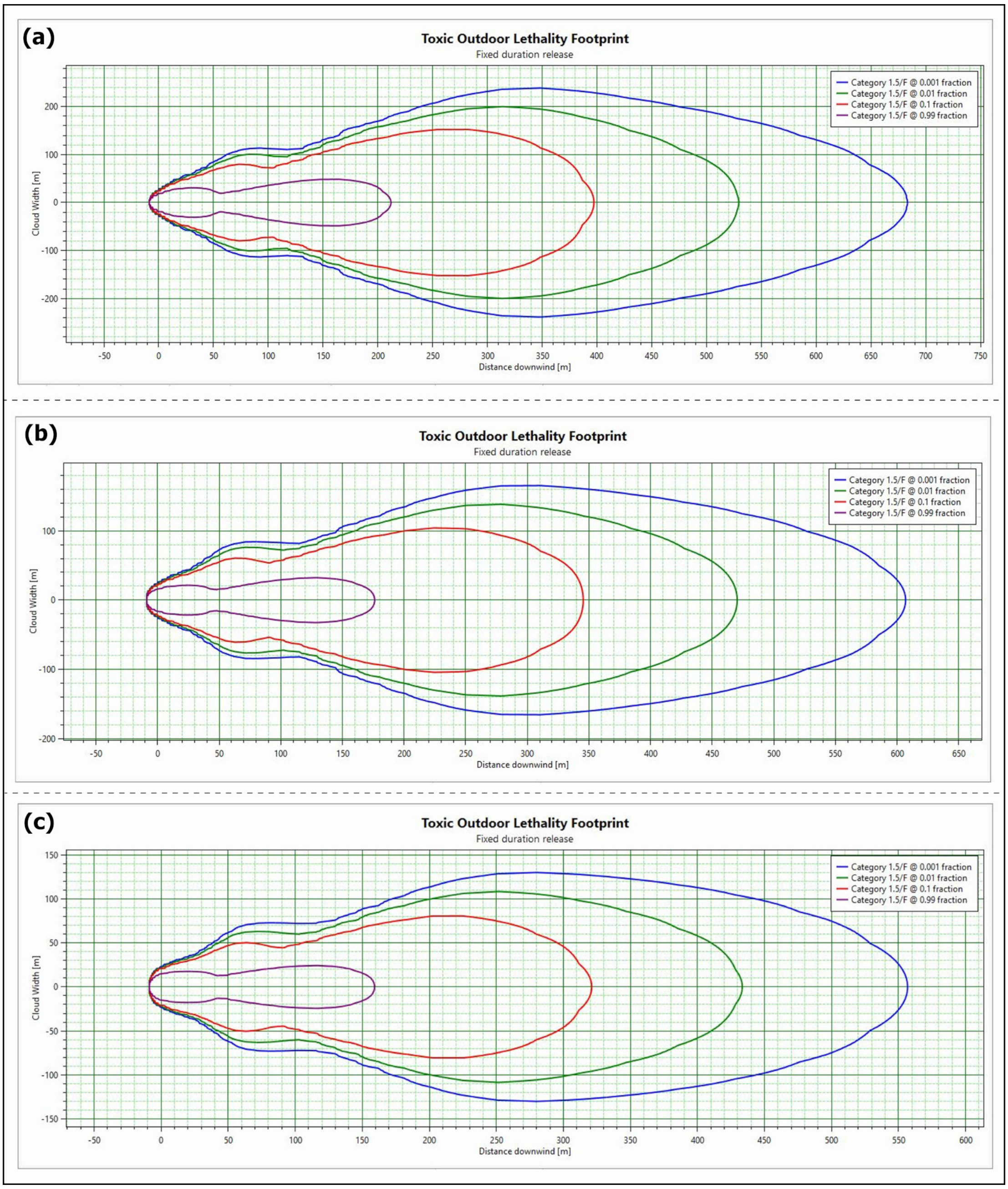

Figure 6. Lethality foot prints at 2 (a), 3 (b) and 4 (c) m/s.

6. PROPOSED MITIGATION MODEL

The proposed mitigation model for the chlorine storage area is shown in Figure 7. To reduce the area of the threat zone, the leaked chlorine vapor should be contained at a very early stage. Also, the evaporation rate of liquid chlorine from the dike pool must be reduced. The heat transfer from the pool mainly occurs in two ways: conduction from the dike area and convection from the surrounding air. Covering the existing dike area with materials with poor thermal conductivity reduces the pool evaporation rate by conduction. Poly Tetra Fluoro Ethylene (PTFE) is one such material, as it has almost six times lower thermal conductivity than concrete. It has a thermal conductivity of 0.25 W/mK and is suitable for liquid chlorine handling. It is proposed that the existing floor be provided with a PTFE lining with a thickness of 10 mm.

6.1. IoT-enabled RPTFE dome

The accidental release must be contained promptly to prevent the rapid spread of the toxic chlorine gas. In the proposed mitigation system, accidental chlorine releases are contained through industrial-grade RPTFE curtains surrounding the dike area. Chlorine vapor spread is effectively localized using these curtains, made of PTFE sheets reinforced with carbon or graphite, providing high load capacity and corrosion resistance

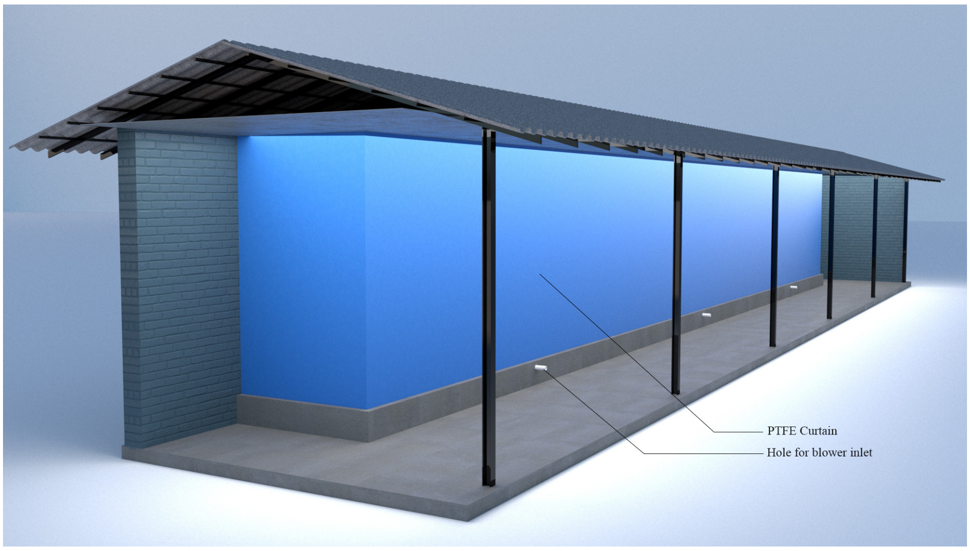

Figure 7. Proposed mitigation model.

(Lee et al., 2007). They are mounted on the roof ceiling of the dike area in order to ensure proper operation. The curtains are designed to fall from the top through guide rods, connecting the ceiling and the dike wall. Metal rings attached to the curtains facilitate their movement through guide rods. The accidental chlorine release will result in a high-velocity two-phase momentum jet. The guide rods, placed every 5 meters along the dike wall, provide structural rigidity to the PTFE dome.

An IoT (Internet of Things)-based approach is proposed to improve the functionality of the mitigation system. IoT refers to the network of interconnected devices, sensors, and systems that communicate and exchange data over the Internet. It allows for the integration of physical objects and digital technologies, enabling the collection, analysis, and sharing of data in real time. IoT has emerged as a transformative technology with applications in various fields, including chemical process systems. The IoT-enabled system provides real-time data, enabling operators and control systems to make informed decisions and respond promptly to potential hazards.

In the proposed mitigation system, IoT-enabled chlorine gas sensors are installed within the dike area, set to respond at the Immediately Dangerous to Life or Health (IDLH) concentration of 10 ppm. The IoT-enabled robust chlorine gas sensors like AQBot Cl2, TB200B-EC4-Cl2-50-01, SnO_2 nanowires (Van Dang et al., 2016) etc. can accurately measure low concentrations of chlorine at ppb (parts per billion) level in the ambient air. These sensors are capable of monitoring the chlorine emissions from the sources on a real-time basis, and can communicate over advanced communication protocols. As soon as a chlorine release occurs and the IDLH concentration is reached, the gas sensors detect the presence of chlorine gas, triggering an automatic operation of the RPTFE curtains to form a closed dome. Simultaneously, a safety alarm is activated, and the control room is instantly notified. The IoT system can establish an additional layer of safety communication by sending an SMS alert simultaneously to the registered mobile numbers of the local residents. By integrating a communication module into the IoT infrastructure, timely and relevant information can be disseminated to ensure the safety and well-being of the residents. The SMS notification would provide crucial information about the incident, such as the nature of the release, the wind speed and direction, safety instructions, and contact details for emergency services. This proactive approach enhances emergency response capabilities and promotes community awareness and preparedness. However, to prevent damage to the RPTFE dome, it is crucial to continuously transfer the trapped chlorine gas to the chlorine purge line.

IoT technology can be applied to automate the transfer of chlorine vapor from the closed dome using vacuum gas blowers. With a suction rate calculated based on the total airborne quantity of chlorine, these blowers extract the chlorine vapor from the dome. The inlets of the blowers are strategically placed inside the curtain dome through dedicated slots in the dike wall, which can be equipped with rubber bushes to remain closed when not in use. The airborne chlorine collected by the vacuum blowers is then transferred to scrubbing tanks containing caustic solution through the purge line. The caustic soda tanks are located at the sodium hypochlorite manufacturing plant. The chlorine vapors react with the caustic solution in the scrubbing tanks to form sodium hypochlorite. Sodium hypochlorite, also known as soda bleach, is a widely used and effective antibacterial agent.

The integration of IoT technology allows for the automation of various components within the system, including the operation of the RPTFE curtains, vacuum blowers, actuators, and inlet valves to the purge line. Real-time monitoring of system parameters, such as gas concentration, curtain deployment, blower operation, and chlorine transfer, can be achieved through IoT connectivity. Furthermore, the utilization of cloud-based platforms for data storage and processing enables remote access to system information, facilitating system optimization and performance evaluation. The Flowchart of the proposed mitigation model is shown in Figure 8.

6.2. Effectiveness of the proposed model

Comparisons between the ERPG levels generated by the accidental chlorine release and the prescribed mitigation system were performed. It was observed that the proposed mitigation system could considerably decrease the risk area. The comparison of the threat zone areas and the maximum distances of vapor spread before and after implementing the proposed methodology is shown in Table 3 and Table 4, respectievely. The results indicate that the area under the ERPG-1 zone is reduced from 4.8 km^2 to 0.9 km^2 for the wind speed of 2 m/s. So a roughly 80% reduction in the threat area can be achieved by implementing this modification. The threat zones of the release and their corresponding map view at 2, 3 and 4 m/s after implementing the proposed mitigation system are illustrated in Figure 9.

7. CONCLUSIONS

The study assessed the impact of the accidental leakage of liquid chlorine from a storage pressure vessel in a typical chlorine manufacturing facility. The study also proposed an effective mitigation system for the storage area. The consequence effect model estimated the ERPG regions from the

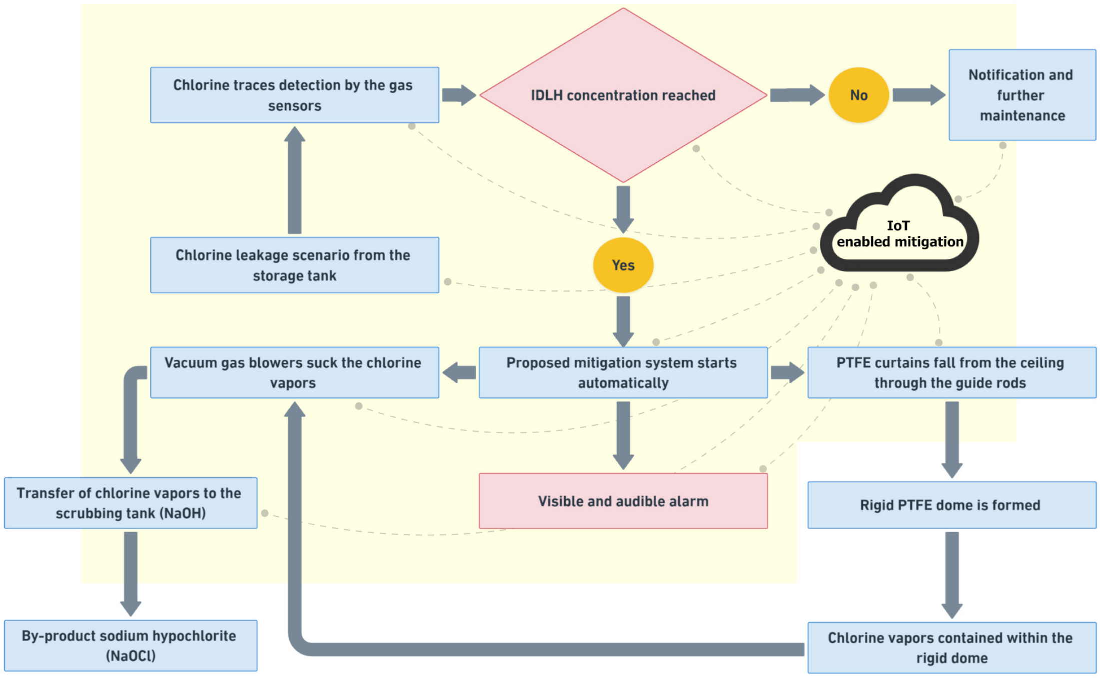

Figure 8. Flowchart of the proposed mitigation model.

Table 3. Reduction in the threat zone area by the proposed model.

ERPG threat zone	Wind velocity – 2 m/s		Wind velocity – 3 m/s		Wind velocity – 4 m/s	
	Without any mitigation system [km^2]	With the proposed mitigation system [km^2]	Without any mitigation system [km^2]	With the proposed mitigation system [km^2]	Without any mitigation system [km^2]	With the proposed mitigation system [km^2]
ERPG-1 (1 ppm)	4.80	0.90	4.30	0.84	3.30	1.2
ERPG-2 (3 ppm)	2.10	0.68	1.40	0.63	1.06	0.76
ERPG-3 (20 ppm)	0.36	0.26	0.23	0.19	0.20	0.15

Table 4. Reduction in the maximum distances of vapour spread by the proposed model.

Maximum threat zone distance	Wind velocity – 2 m/s		Wind velocity – 3 m/s		Wind velocity – 4 m/s	
	Without any mitigation system [km^2]	With the proposed mitigation system [km^2]	Without any mitigation system [km^2]	With the proposed mitigation system [km^2]	Without any mitigation system [km^2]	With the proposed mitigation system [km^2]
ERPG-1 (1 ppm)	3.05	0.92	3.69	1.27	3.22	1.58
ERPG-2 (3 ppm)	2.36	0.86	1.95	1.14	1.74	1.34
ERPG-3 (20 ppm)	0.85	0.70	0.74	0.70	0.67	0.64

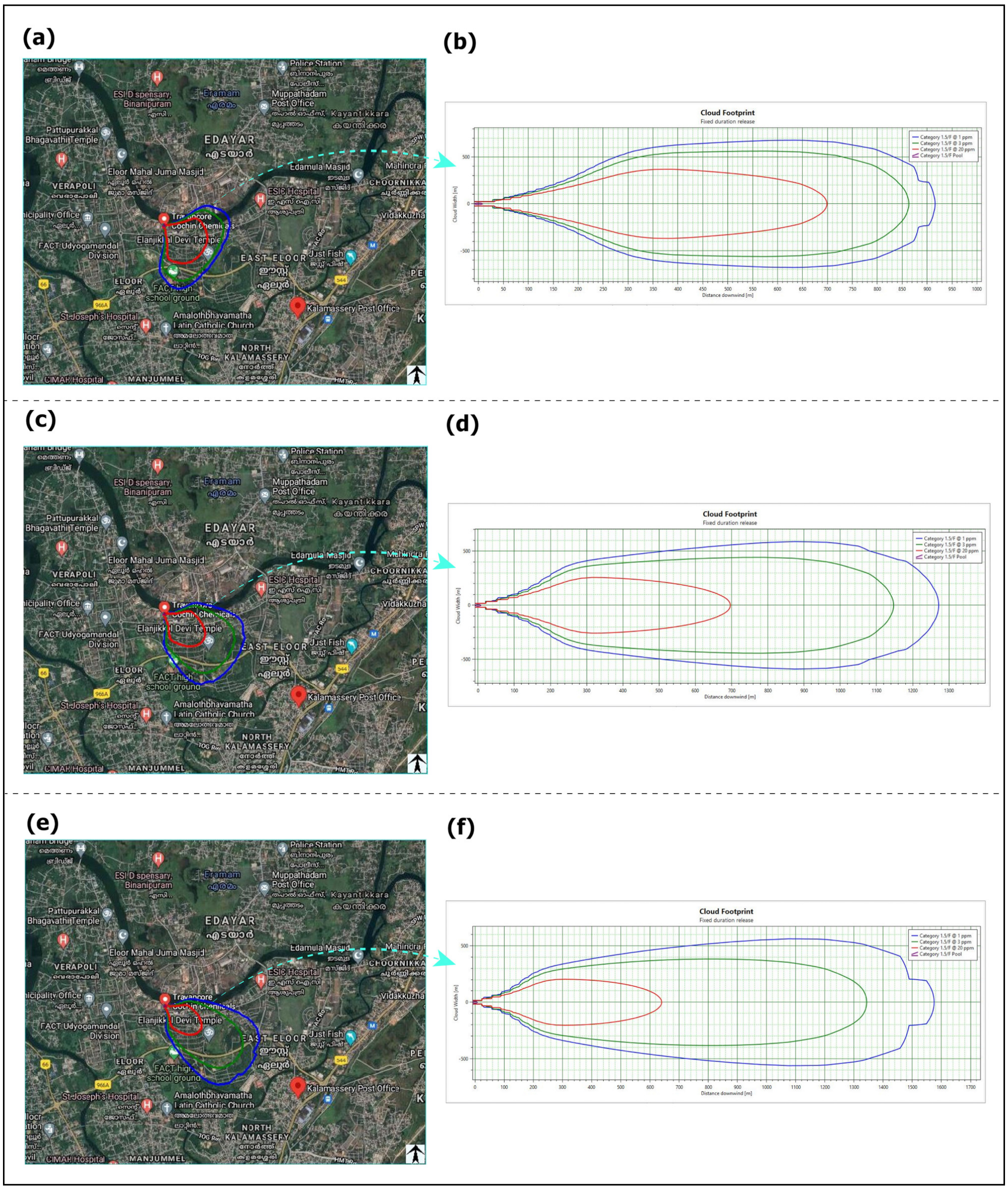

Figure 9. Threat zone area and the corresponding map view at 2, 3 & 4 m/s with the proposed mitigation system.

PHAST 8.0 by employing the UDM. The dispersion model also estimated the average chlorine vapor concentration inside the ERPG regions. The CFD pool evaporation model calculated the evaporation rate of liquid chlorine collected in the dike. The map view of the region under the threat zone was plotted using the GIS module of PHAST 8.0.

From the dispersion study, it is evident that the vapor cloud area decreases with increased wind speed. The shorter threat zone area at higher wind velocities occurs because the wind pushes the chlorine vapor cloud to disperse it forward in the downwind direction. The concentration of the cloud is diluted more readily at higher wind velocities. The maximum ERPG area in the dispersion study was observed at 2 m/s wind speed. The maximum distance from the point of release for the vapor cloud was noticed at 3 m/s wind speed. The chlorine vapor dose is more significant than its ERPG-1 level, up to 3.6 km for 3 m/s wind speed. The area's dense population will make the scenario more adverse, and it might turn into a deadly disaster.

The probability of deaths in the vicinity of the chemical plant due to the chlorine leakage scenario was calculated using the Probit study. According to the probit study, there is a significant risk of mortality in the downwind direction up to 0.2 km^2 from the chlorine leakage site. Though the lethal effect of the release is reduced beyond this area, people may suffer from other acute health issues due to prolonged exposure to chlorine vapor. However, the threat zone may be reduced by up to 80% of the existing setup by implementing the proposed mitigation system.

SYMBOLS

A_o	area of the opening, m^2
C_d	coefficient of discharge (≈ 0.61)
C_p	specific heat of liquid, kJ/(kg·K)
P_1	upstream pressure, Pa
T_1	storage temperature, K
T_2	normal boiling point, K
ΔH_v	latent heat at boiling point, kJ/kg
W	total release rate, kg/s
$f(l)$	flow correction function, based on length

REFERENCES

Bisarya R.K., Puri S., 2005. The Bhopal gas tragedy – A perspective. *J. Loss Prev. Process Ind.*, 18, 209–212. DOI: 10.1016/j.jlp.2005.07.006.

Britter R.E., McQuaid J., 1988. *Workbook on the dispersion of dense gases*. HSE Contract Report No 17/1988. UK Health and Safety Executive.

Buckley R.L., Hunter C.H., Werth D.W., Whiteside M.T., Chen K.-F., Mazzola C.A., 2012. A case study of chlorine transport and fate following a large accidental release. *Atmos. Environ.*, 62,184–198. DOI: 10.1016/j.atmosenv.2012.08.025.

Cameron I.T., Raman R., 2005. *Process systems risk management*. 1st edition, Vol 6., Elsevier Academic Press, 205–207.

CCPS, 1999. Guidelines for chemical process quantitative risk analysis. Center for Chemical Process Safety, John Wiley & Sons.

Census of India, 2011. Kerala Part XII-B Series-33 District Census Handbook Ernakulam Village and Town Wise Primary Census Abstract (PCA). Directorate of Census Operations Kerala, 516.

Dimbour J.P., Dandrieux A., Gilbert D., Dusserre G., 2003. The use of water sprays for mitigating chlorine gaseous releases escaping from a storage shed. *J. Loss Prev. Process Ind.*, 16, 259–269. DOI: 10.1016/S0950-4230(03)00038-X.

Engelhardt D.F., 2002. *Chlorine absorption on falling drops and transfer to water curtains*.

Gant S., Weil J., Delle Monache L., McKenna B., Garcia M.M., Tickle G., Tucker H., Stewart J., Kelsey A., McGillivray A., Batt R., Witlox H., Wardman M., 2018. Dense gas dispersion model development and testing for the Jack Rabbit II phase 1 chlorine release experiments. *Atmos. Environ.*, 192, 218–240. DOI: 10.1016/j.atmosenv.2018.08.009.

Hakkinen P.J, 2005. Seveso disaster, and the seveso and seveso II directives, In: Wexler P (Ed.), *Encyclopedia of Toxicology* (Second Edition), 1–4. DOI: 10.1016/B0-12-369400-0/10011-0.

Hanna S., Dharmavaram S., Zhang J., Sykes I., Witlox H., Khajehnajafi S., Koslan K., 2008. Comparison of six widely-used dense gas dispersion models for three actual railcar accidents, In: Borrego C., Miranda A.I. (Eds.), *Air pollution modeling and its application XIX*. NATO Science for Peace and Security Series Series C: Environmental Security. Springer, Dordrecht. DOI: 10.1007/978-1-4020-8453-9_49.

Hendershot D., 2009. Remembering Flixborough. *J. Chem. Health Saf.*, 16, 46–47. DOI: 10.1016/j.jchas.2009.03.006.

James M.D., 2014. Simplified methods of using probit analysis in consequence modeling. *AIChE Spring Meeting and Global Congress on Process Safety*, New Orleans, LA, 31 March 2014. Availabe at: https://www.aiche.org/conferences/videos/conference-presentations/simplified-methods-using-probit-analysis-consequence-modeling.

Khan F.I., Abbasi S.A., 1999. Major accidents in process industries and an analysis of causes and consequences. *J. Loss Prev. Process Ind.*, 12, 361–378. DOI: 10.1016/S0950-4230(98)00062-X.

Labib A., 2014. Chapter 7 – Chernobyl Disaster, In: Labib A. (Ed.), *Learning from Failures*. Butterworth-Heinemann, 97–106. DOI: 10.1016/b978-0-12-416727-8.00007-2.

Lee J.-Y., Lim D.-P., Lim D.-S., 2007. Tribological behavior of PTFE nanocomposite films reinforced with carbon nanoparticles. *Composites, Part B*, 38, 810–816. DOI: 10.1016/j.compositesb.2006.12.006.

Mannan S., 2005. Lees' loss prevention in the process industries. Vol 1., 857–858. DOI: 10.1016/B978-0-7506-7555-0.X5081-6.

Marco E., Peña J.A., Santamarìa J., 1998. The chlorine release at Flix (Spain) on January 21st 1996: a case study. *J. Loss Prev. Process Ind.*, 11, 153–160. DOI: 10.1016/S0950-4230(97)00014-4.

Mukherjee S., Dharmavaram S., Jaskolka S., 2018. Effectiveness of water sprays in mitigating toxic releases. *Proc. Safety Prog.*, 37, 256–262. DOI: 10.1002/prs.11948.

Murphy J.F., Hendershot D., Berger S., Summers A.E., Wiley R.J., 2014. Bhopal revisited. *Proc. Safety Prog.*, 33, 310–313. DOI: 10.1002/prs.11716.

National Transportation Safety Board, 2006. Collision of Union Pacific Railroad Train MHOTU-23 With BNSF Railway Company Train MEAP-TUL-126-D with subsequent derailment and hazardous materials release, Macdona, Texas, June 28, 2004. Railroad Accident Report NTSB/RAR-06/03. Washington, DC.

Nicholson D., Lian N., Hedrick A., Schmidt E., 2017. Final test report for Jack Rabbit (Jr) II. ATEC Project No. 2015-DT-DPG-SNIMT-F9735. WDTC Document No. WDTC-SPD-FTR-001.

Pandya N., Gabas N., Marsden E., 2012. Sensitivity analysis of Phast's atmospheric dispersion model for three toxic materials (nitric oxide, ammonia, chlorine). *J. Loss Prev. Process Ind.*, 25, 20–32. DOI: 10.1016/j.jlp.2011.06.015.

Soman A.p.R., Sundararaj G., Devadasan S.R., 2012. Consequence assessment of chlorine release. *Proc. Safety Prog.*, 31, 145–147. DOI: 10.1002/prs.11479.

Toxic industrial chemicals, 2002. *BMJ Military Health*, 148, 371–376.

U.S Environmental Protection Agency, 2016. Code of Federal Regulations, PART 355 – Emergency planning and notification, 449–468. Available at: https://www.govinfo.gov/content/pkg/ CFR-2016-title40-vol30/pdf/CFR-2016-title40-vol30-part355.pdf.

U.S. Chemical Safety and Hazard Investigation Board, 2003. DPC Enterprises Festus Chlorine Release. REPORT NO. 2002-04-I-MO, 99. Available at: https://www.csb.gov/dpc-enterprises-festus-chlorine-release.

Van Dang T., Duc Hoa N., Van Duy N., Van Hieu N., 2016. Chlorine gas sensing performance of on-chip grown ZnO, WO_3, and SnO_2 nanowire sensors. *ACS Appl. Mater. Interfaces*, 8, 4828–4837. DOI: 10.1021/acsami.5b08638.

Wang J., Yu X., Zong R., 2020. A dynamic approach for evaluating the consequences of toxic gas dispersion in the chemical plants using CFD and evacuation modelling. *J. Loss Prev. Process Ind.*, 65, 104156. DOI: 10.1016/j.jlp.2020.104156.

Weber M., 2006. Some safety aspects on the design of sparger systems for the oxidation of organic liquids. *Process Safety Prog.*, 25, 326–330. DOI: 10.1002/prs.10143.

Witlox H.W.M., Holt A., 1999a. *A unified model for jet, heavy and passive dispersion including droplet rainout and re-evaporation*. Center for Chemical Process Safety Conference 1999.

Witlox H.W.M., Holt A., 1999b. *Unified dispersion model – Technical reference manual*. UDM Version 6.0, June 1999, Det Norske Veritas, London.

Xin B., Yu J., Dang W., Wan L., 2021. Dynamic characteristics of chlorine dispersion process and quantitative risk assessment of pollution hazard. *Environ. Sci. Pollut. Res.*, 28, 46161–46175. DOI: 10.1007/s11356-020-11864-z.