

Risk assessment of ammonia bunkering operations: Perspectives on different release scales

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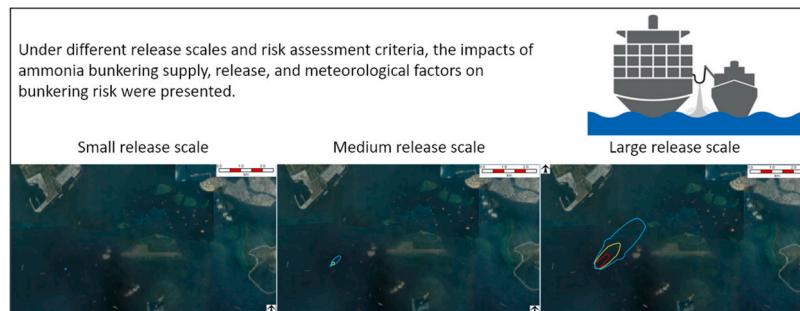
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HIGHLIGHTS

- Ammonia bunkering operational risk is assessed.
- Wind speed is the most important factor for small and medium release consequences.
- Hose diameter is the most significant factor for large release consequences.
- Larger lethality footprint changes more significantly from medium to large releases.

GRAPHICAL ABSTRACT



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ABSTRACT

Ammonia is an alternative marine fuel to reduce greenhouse gas emissions. Conducting studies on ammonia bunkering risk is essential as ammonia is toxic and corrosive to humans and the environment. This study aims to assess the ammonia bunkering operational risk from the perspectives of small, medium and large release scales. Scaling releases from small to medium results in more changes in cloud footprints at lower gas concentrations. Conversely, transitioning from medium to large releases causes more changes in cloud footprints at higher gas concentrations and lethality footprints with higher values. Moreover, this study performs a sensitivity analysis on ammonia bunkering supply, release, and meteorological factors. Wind speed is the most significant factor in small and medium releases, while hose diameter is the most significant factor in large releases. Under the given inputs, a 50% change in wind speed can have up to 100% change in the 1100 ppm maximum cloud footprint for small releases and a 663% change for medium releases. Similarly, a 50% change in hose diameter can result in a 1689% change in the 1100 ppm maximum cloud footprint for large releases. The research provides valuable insights into analysing ammonia bunkering operational risk considering different risk assessment criteria.

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1. Introduction

Emissions from shipping and related activities are part of the sources of pollutants and greenhouse gases. The International Maritime Organization (IMO) has adopted a revised strategy aimed at reducing greenhouse gas (GHG) emissions from international shipping. The objective is to achieve a minimum of a 20% reduction in total annual GHG emissions by 2030, a 70% reduction by 2040, and net-zero GHG emissions by 2050 compared to the 2008 baseline level [31]. In order to incentivise carbon intensity reduction within the maritime industry, shipping companies are required to procure carbon permits, initially covering a minimum of 40% of emissions in 2024, with this percentage rising to 70% in 2025 and eventually reaching 100% in 2026 [25]. It is crucial to transit from fossil-based marine fuels to low-carbon or carbon-free alternative fuels, such as methanol, biofuel, ammonia and hydrogen [2].

Among these alternative marine fuels, ammonia is a promising fuel that emits no CO₂ emission during combustion. Considering its lifecycle, green ammonia exhibits relatively low carbon emissions, particularly when it is produced from green electricity via the water electrolysis process [57]. Concerning the ammonia bunker supply chain, it is worth noting that ammonia production, storage and transportation have reached a well-developed stage, considering its extensive use in the fertiliser industry for several decades [38]. Furthermore, the development of ammonia-fuelled marine engines and fuel cells is currently underway at a pre-commercialisation stage [18,53,61]. Ammonia bunkering operations play a vital role in linking upstream supply and downstream consumption in the ammonia bunker supply chain [67]. However, limited literature exists on ammonia bunkering, particularly from the safety and risk perspective.

Ammonia, in its saturated liquid form, can exist under pressure, refrigeration, or both. It is characterised by lower flammability than hydrocarbon fuels, such as liquefied natural gas (LNG) and methanol. However, the primary concern surrounding ammonia implementation lies in its toxicity rather than its flammability and potential for explosions [21]. Ammonia poses significant health risks at different acute exposure guideline levels (AEGLs), with harmful effects ranging from transient (AEGL-1, 30 ppm) to irreversible (AEGL-2, 160 ppm), and potentially life-threatening or fatal (AEGL-3, 1100 ppm) within one hour [60]. Notably, past incidents in the United States have reported 16 fatalities over the last two decades, mainly attributed to the rupture of ammonia nurse tanks [13]. Similarly, China witnessed 82 ammonia refrigeration-related accidents between 2010 and 2020, resulting in 189 fatalities and 1081 injuries, all caused by ammonia refrigeration pipeline ruptures [37]. Fishing vessels, where ammonia is used for refrigeration, are the primary locations for ammonia release and dispersion accidents over water [46]. These incidents led to personnel fatalities and damage to the vessel's hull and machinery. Subsequently, any disruptions in bunkering operations at a port could directly impact cargo delivery, affecting regional activities [69]. It is critical to assess the consequences of ammonia release and establish safety zones during bunkering operations to mitigate operational risks. Thus, there is a pressing need for knowledge development to enhance the understanding of ammonia bunkering operational risk.

Regarding ammonia operational risk studies, the existing literature primarily focuses on ammonia safety for land-based applications [23,3,47]. Limited studies specifically address ammonia operational risk in the context of bunkering and marine operations. Cheliotis et al. [10] and Duong et al. [21] have conducted a review of the safety of ammonia-fuelled fuel cells and ammonia bunkering operations in the maritime industry, respectively. Fan et al. [26] conducted a risk assessment of ship-to-ship ammonia bunkering operations using a Bayesian network and concluded that ammonia toxicity contributed the most to the operational risk compared to flammability. Ng et al. [46] simulated accidental ammonia releases under different bunkering operation conditions in Singapore, providing insights into the 3%

lethality footprints of ammonia dispersion over land and seawater during both day and night time. However, it is still unclear how sensitive each factor is in influencing the operational risk of ammonia bunkering at small, medium, and large release scales, as well as how the operational risk of ammonia bunkering varies under different risk assessment criteria. Therefore, researching the impact of ammonia release in the marine environment and the corresponding risk assessment specific to bunkering operations is crucial.

This paper aims to evaluate the operational risk associated with accidental ammonia release during ammonia bunkering operations from the perspectives of small, medium and large release scales. A case study is conducted on ammonia release incidents during ship-to-ship bunkering operations at the port of Singapore. Moreover, a comprehensive what-if analysis is conducted to explore various release scenarios, considering bunkering supply factors, such as storage pressure, temperature, flow rate, hose length and diameter. Additionally, release factors, including release duration, elevation and direction, along with meteorological factors (wind speed, ambient temperature, sea surface temperature, relative humidity, Pasquill stability, and solar radiation flux), are discussed. Regarding techniques, a wide range of atmospheric models exists for particle dispersion, such as Box models, Gaussian models, Lagrangian/ Eulerian models, computational fluid dynamics (CFD) models, and models which include aerosol dynamics [30]. Given the extensive utilisation of the Gaussian model in chemical dispersion modelling, this study adopts the Gaussian dispersion model to compare the consequences of ammonia release.

This paper represents the pioneering effort in the literature to perform a sensitivity analysis encompassing various bunkering supply, release, and meteorological factors, while considering different release scales (small, medium, and large releases) and employing distinct risk assessment criteria (maximum cloud footprints and lethality footprints). The innovative aspect of this study lies in its ability to identify the most influential factor for each release scale, thereby making an original and valuable contribution to the field of ammonia bunkering risk research. The findings of this study present significant implications for bunker suppliers, ship owners, port operators and policymakers.

The remaining sections of this paper are organised as follows. Section 2 introduces a comprehensive literature review regarding the ammonia safety study for marine applications. It also summarises the factors that influence ammonia release and dispersion processes. Section 3 describes the research methodology for this study, including defining the research scope. Section 4 presents a case study illustrating accidental ammonia release consequences during ship-to-ship bunkering operations at the port of Singapore. Furthermore, a sensitivity analysis is conducted in this section. Section 5 discussed the key factors influencing ammonia bunkering operational risk and the implications of this study. Finally, in Section 6, the study concludes by summarising its contributions to the field.

2. Literature review on ammonia safety study for marine applications

2.1. Methods for evaluation of ammonia release consequences

Table 1 summarises the studies on the consequence analysis of ammonia release in water and marine-based applications. These studies have extensively addressed ammonia toxicity, flammability and corrosion hazards, providing valuable insights into risk categories and key contributing factors. Chen et al. [12] have extensively explored the risks associated with ammonia safety, encompassing pressure, fire, poisoning, and corrosion, while also summarising the existing regulations governing ammonia's use as chemical cargo, refrigerant in fishing vessels, and reducing agent for Selective Catalytic Reduction systems in marine diesel engines. When ammonia is used as a marine fuel, toxicity emerges as a major concern rather than its flammability [21]. Ammonia is flammable at concentrations of about 15% to 28% by volume in the air

Table 1

Summary of literature on the consequence analysis of ammonia release in water and marine-based applications.

Category	Reference	Research scope	Method / Tool	Key factors in quantitative risk assessment
Journal paper and conference paper	Raj and Reid [52]	Release in the lab, swimming pool and lake	Field experiment	Release scale and location, water temperature
	Raj [50]	Instantaneous, semi-continuous and continuous release on land and water	Field experiment	Radius of spread, evaporation rate, remaining liquid volume
	Quinn et al. [49]	Release in the coastal area	Field experiment	dry deposition flux, deposition velocity, particle radius, rainwater concentration
	Dharmavaram et al. [16]	Release from a semi-refrigerated barge	HACS-R model	Wind speed, orifice size
	Havens et al. [29]	Release in the bay	Numerical circulation model, LPDM, simulation	Wind speed, wind direction, gusts
	Ayvali et al. [4]	Ammonia as a marine fuel	Review	NA
	Cheliotis et al. [10]	Safety of ammonia fuel cell	Review	NA
	Crolius et al. [13]	Safety of ammonia as a marine fuel	Review	NA
	Fan et al. [26]	Release during ammonia ship-to-ship bunkering	Bayesian networks, ETA	Failure rate, wind speed, temperature, humidity, Pasquill class
	Triviza et al. [59]	Fuel cell safety	Hazard identification (HAZID), fault-tree analysis (FTA) and failure modes, effects, and criticality analysis (FMECA)	Bunkering specifications
	Chang et al. [9]	Ammonia leakage monitor system and sensor detector	Field experiment	NA
	Chen et al. [12]	Ammonia safety and protective measures	Review	Pressure, fire, poisoning, corrosion risks
	Pomonis et al. [48]	Release in marine engine room	CFD	Release condition
	Yadav and Jeong [66]	Release in marine engine room	CFD	Release condition
	Dharmavaram et al. [17]	Release on concrete and in water	Field experiment	Storage pressure and temperature, release duration, release rate, wind speed
	Duong et al. [21]	Safety assessment of ammonia bunkering operations	Review	NA
	Ng et al. [46]	Release during ammonia ship-to-ship bunkering	PHAST	Storage pressure and temperature, release duration, transfer flow rate, release height, release direction, dispersion surface
	Chen et al. [11]	Release in seawater and its impact on the nitrogen biogeochemical cycle	Review	NA
Report	Raj et al. [51]	Release in the lab, swimming pool and lake	Field experiment	Release scale and location, water temperature
	LR [35]	Release in the tank	CFD	Storage pressure, temperature, hose size, leak rate, release duration
	DNV [19]	Release during ammonia truck-to-ship and ship-to-ship bunkering	PHAST, HAZID	Storage pressure, temperature, flow rate, release frequency, hose diameter, release location, orifice size, release rate, release frequency
	DNV [20]	Release during ammonia ship-to-ship bunkering	PHAST	Storage pressure, temperature, flow rate, hose diameter
	Dawson et al. [15]	Release in seawater and environmental assessment	PHAST	Release frequency, orifice size, storage pressure and temperature, Pasquill stability, wind speed, ambient temperature, water temperature, humidity, solar radiation
	Laursen et al. [24]	Design of ammonia fuelled vessels	HAZID	Release type, risk profile
	LR [36]	Risk assessment of ammonia fuelled vessel	PHAST, event tree analysis	Leak detection, isolation, ignition probability, leak size and duration, boundary of leak space
	Yang et al. [68]	Release during ammonia truck-to-ship, ship-to-ship bunkering and shore pipeline-to-ship bunkering	PHAST	Bunkering mode and location, bunkering supply conditions, release conditions, meteorological factors

Source: Compiled by authors. (NA: not applicable)

[26]. When mixed with lubricating oil, its flammable concentration range will be larger.

Various methods employed to assess the potential consequences of ammonia release encompass simulation, numerical analysis and field experiments. Simulation, in particular, is widely utilised for evaluating ammonia release risks and involves techniques such as CFD (such as Ansys Fluent, Star CCM+, FLACS simulation tools), Bayesian networks, event tree analysis (ETA), ALOHA and PHAST simulation tools [26,46, 48,66,68]. These simulations consider a multitude of factors that can influence the outcomes of accidental ammonia release, including wind speed, temperature, humidity, Pasquill class, storage pressure and temperature, release duration, transfer flow rate, release height, release direction, and dispersion surface [26,46,68]. The uncertainties of the

information required in the quantitative risk assessment (QRA) can significantly influence the consequences [3,47].

In terms of mathematical models of plume and puff dispersion, there are three main types: Gaussian dispersion model, Lagrangian particle dispersion model (LPDM) and Eulerian dispersion model. Gaussian dispersion model applied in PHAST simulation tool does not resolve the flow between buildings. LPDM can be applied in the SCIPUFF (Second-order Closure Integrated PUFF) model, PMSS (Parallel Micro-Swift Micro-Spray) and QUIC 3D models, and it resolves the flow diagnostically or empirically, although not dynamically resolving the flow between buildings. For example, a coastal prediction system comprising a numerical circulation model and LPDM was applied to analyse the ammonia release into Tampa Bay in the United States in 2007 [29].

Eulerian model can be applied in CFD, LES (large eddy simulation), and LBM (lattice Boltzmann methods), and it can fully resolve the flow between buildings. Moreover, the HACS-R model was further refined to enhance accuracy by considering ammonia's boiling and rapid evaporation when released into water [16]. Additionally, the dispersion of a concentrated ammonia plume was simulated using the TRACETM dense gas dispersion model. The research findings revealed that only 30% of the released ammonia from the barge would disperse into the air, while the remaining 70% would dissolve in the water [16]. The rapid spreading and dissolution of ammonia in water significantly impact the amount of ammonia vaporised, even in situations involving intense boiling.

In addition to the simulation and numerical methods, researchers have conducted field experiments to assess the consequence of ammonia release on solid ground and in water. In the 1970 s, the US Coast Guard's Office of Research and Development conducted a program on the release of hazardous materials in water, and field experiments included ammonia spills in laboratories, swimming pools, and natural lakes [5, 50–52]. Subsequently, the Desert Tortoise test series and FLADIS ammonia trials were conducted in the 1980 s and 1990 s to assess the pressurised ammonia release and dispersion over land [17]. INERIS tested pressurised ammonia release on a large scale and compared the test results with atmospheric dispersion models [6]. Furthermore, the US Department of Homeland Security conducted ammonia release over land in the Jack Rabbit I project in 2010 and plans to conduct the Jack Rabbit III project to investigate ammonia release consequences further [41]. In addition, Dharmavaram et al. [17] carried out ammonia field experiments at the Det Norske Veritas (DNV) Spadeadam site in Northern England. However, there is currently a lack of experiments specifically focused on ammonia release into the seawater during ammonia bunkering operations.

2.2. Comparison of the behaviour of ammonia dispersion over land and water

Ammonia has been safely transported and stored worldwide for almost a century with standards, codes of practice and protocols to ensure safe handling. When liquid ammonia is released and spreads over land, this process occurs in two phases, and the density of the resulting ammonia cloud changes as it interacts with its surroundings [34]. For example, the density of ammonia at the boiling point of -33°C is about 0.9 kg/m^3 , and it is less than the density of dry air at 20°C , which is 1.2 kg/m^3 [33]. When released, a fraction of the ammonia will vapourise and aerosolise into the atmosphere, forming the ammonia cloud. The remaining portion will precipitate and accumulate as a liquid pool on the surface. If ammonia is released on land and the surface is relatively impermeable, the ammonia in the pool will continue to absorb heat from the surroundings and evaporate into the atmosphere [32]. However, if the surface is porous, a portion of the ammonia will penetrate into the ground.

It is worth noting that ammonia release from a pressurised container is more dangerous because of the ammonia-air dense gas mixture [34]. The dense gas is a mixture of ammonia liquid droplets, ammonia vapour, condensed water vapour droplets and air, with an ammonia concentration of at least 20,000 ppm [13]. If the percentage of the total mass of airborne ammonia initially in the liquid phase is between 16% and 20%, the ammonia cloud will be denser than air at low dilution [33]. Hence, ammonia clouds cannot be moved by buoyancy but can be moved by wind currents, making them dissipate more slowly.

When ammonia is used as a marine fuel, it presents greater complexities than its use as a cargo, requiring a comprehensive legal framework to safeguard human life, infrastructure and environmental protection measures [13]. When ammonia is released over a water surface, the portion on the water surface will continue to absorb heat from its surroundings and evaporate into the atmosphere. Concurrently, the other portion will dissolve into the water, depending on the

solubility constant of ammonia at the pool's temperature. The hazard of ammonia release in water depends on several factors, including the source strength of the vapour, the size of the ammonia pool, and the temporal behaviour of the released ammonia liquid [50]. In contrast to the diffusion of ammonia on land, the ammonia pool on the water surface undergoes a more intricate interplay of processes, including dissolution, partition (ice formation), and chemical reactions with seawater.

2.3. Research gaps and novelty

There are several research gaps in ammonia safety studies for marine applications. First, when ammonia is released on the water surface and in the water column, it exhibits distinct behaviours and undergoes more complex dispersion and dissolution processes compared to its dispersion over land. Hence, conducting more research on the consequence modelling of ammonia release on water is essential.

Second, ammonia bunkering operations would be more frequent than loading/offloading operations in a bunkering port, indirectly increasing the likelihood of ammonia release. Classification societies, such as DNV, ABS and Lloyd's Register (LR), have published ammonia safety study reports regarding the release consequence evaluation during bunkering operations [15,19,20,24,35,36]. These reports focused on the scenario analysis of ammonia releases and presented the consequences of release. However, to the best of our knowledge, no published literature addresses the sensitivity value of each factor in influencing the operational risk associated with ammonia bunkering across small, medium and large release scales. From the regulatory point of view, maritime stakeholders shall know the effect of these bunkering supply, release and meteorological parameters on the hazardous/ safety/ monitoring zones.

Moreover, there is a notable absence of comparisons regarding operational risks associated with different criteria of maximum cloud footprints and lethality footprints. Further research is needed in this area to fill these gaps in knowledge and provide a comprehensive assessment of the risks involved in ammonia bunkering operations. The innovation of this study is to find out how the bunkering supply, release and meteorological conditions influence the ammonia bunkering operational risk. The research findings would contribute to developing mitigation strategies for accidental ammonia releases during bunkering operations.

3. Methodology

According to Rausand [54], risk assessment involves the integration of risk analysis and risk evaluation. Fig. 1 illustrates the framework of the proposed methodology. The risk assessment of ammonia bunkering operations involves six steps in this study.

3.1. Step 1: identify loss of containment and select the failure event

Considering that ammonia bunkering has not been carried out at the current stage, this study analyses the loss of containment by taking the current bunkering operations and ammonia handling process as references. Leaks and ruptures in the bunker hoses are the most likely causes of containment loss [46]. The complete hose assembly system is the weakest point in the bunkering operations due to the high probability of human errors during the connection and disconnection of bunker hoses from the manifold [1]. Since bunker hoses are handled in a dynamic work environment, they represent the most vulnerable component in bunkering operations. According to the analysis conducted by the European Gas Pipeline Incident Data Group on gas pipelines, the most frequent failures arise from external interference (such as digging, piling, and groundworks), followed by corrosion and construction/material defects [22]. Additionally, ship-to-ship bunkering operation is the most employed bunkering mode based on current bunkering operation experience [26]. Hence, this study concentrates on the risk

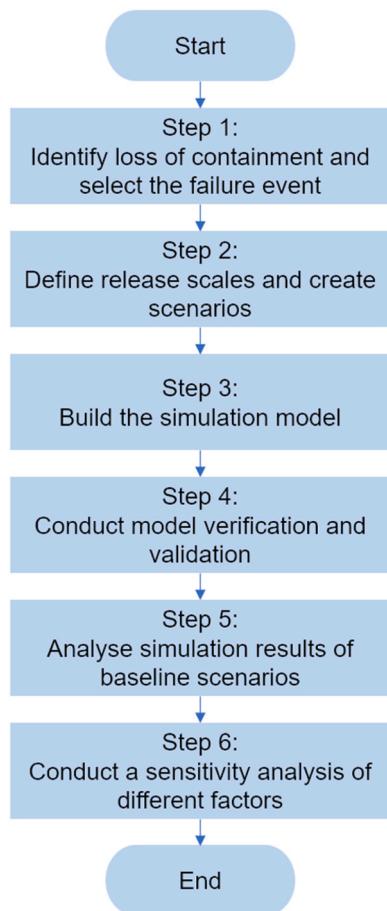


Fig. 1. Framework of the proposed methodology.
Source: Authors.

assessment of accidental ammonia releases from the manifold and bunker hose during ship-to-ship ammonia bunkering operations.

3.2. Step 2: define release scales and create scenarios

Based on interviews with experts from ammonia producers and the ammonia safety research institute, we have determined that releases can be classified as small, medium, or large, corresponding to 1%, 10%, and 100% of the hose diameter. Notably, a large release indicates a complete hose rupture. We conducted a comprehensive literature review to create the model inputs and identified critical factors. These factors are categorised into three main groups: bunkering supply conditions (including storage pressure and temperature condition, flow rate, hose length, and diameter), release conditions (comprising release duration, elevation, and direction), and meteorological conditions (including wind speed, ambient temperature, sea surface temperature, relative humidity, Pasquill stability, and solar radiation flux).

3.3. Step 3: build the simulation model

The modelling of ammonia release consequences comprises two essential steps: discharge modelling and dispersion modelling. The discharge modelling phase involves determining the time and distance required for ammonia to transition from storage pressure to atmospheric pressure. The calculations in this stage consider the combined amount of emitted ammonia and its physical state during the discharge, employing the energy balance equation as the basis for these computations (Eq. 1) [8].

$$\dot{m} = C_D \times A \times P_1 \sqrt{\frac{2G_C}{R_g} \times \frac{M}{T_1} \times \frac{K}{K-1} \left[\left(\frac{P_2}{P_1} \right)^{\frac{2}{K}} - \left(\frac{P_2}{P_1} \right)^{\frac{K-1}{K}} \right]} \quad (1)$$

Where,

- \dot{m} is discharge rate (kg/s)
- C_D is discharge coefficient
- A is slot area (m^2)
- P_1 is the ammonia pressure after exit (kPa)
- P_2 is the ammonia pressure before exit (kPa)
- G_C is the gravity constant ($N s^2/kg m$)
- R_g is ammonia gas coefficient ($Pa m^3/mole K$)
- M is the ammonia molecular weight of the gas (kg/mol)
- T_1 is ammonia temperature before exit (K)
- K is the ratio of specific heat capacity under constant pressure to constant volume

The dispersion process initiates once the pressure of the released ammonia reaches the atmospheric pressure threshold. The Gaussian model is widely used for chemical dispersion modelling [63]. In this model, it is assumed that there is a continuous point source emission, and it characterises the concentration distribution of the released substance perpendicular to the direction of the wind as a Gaussian normal function [8]. In this study, Eq. 2 presents the Gaussian model used to depict the distribution of ammonia concentration.

$$C(x, y, z) = \frac{Q}{2\pi u \sigma_y \sigma_z} \left[\exp \left(-\frac{y^2}{2\sigma_y^2} \right) \right] \left\{ \exp \left[\frac{-(z-H)^2}{\sigma_z^2} \right] + \exp \left[\frac{-(z+H)^2}{\sigma_z^2} \right] \right\} \quad (2)$$

Where,

- $C(x, y, z)$ is the time average contaminant concentration (g/m^3)
- Q is source emissions strength (g/s)
- u is the mean wind speed at the effective stack height (m/s)
- σ_y and σ_z are dispersion coefficients in the crosswind direction and vertical direction (m)
- y and z are horizontal distance and vertical distance from the centreline (m)
- H is effective stack height, which is the total value of stack height and plume rise

The simulation tool PHAST version 8.71 was used to conduct discharge and dispersion modelling for the two-phase ammonia release scenario. PHAST is a widely recognised and validated simulation tool in chemical process modelling and has been validated [42,64,65]. The Unified Dispersion Model (UDM) in PHAST simulates various dispersion phenomena, including initial turbulent expanding jets, dense spreading and turbulent mixing, slumping dense phases, buoyant elevated phases and passive dispersion. The simulation results generated by PHAST enable the prediction of the affected area and the vapour concentration at any specified distance.

However, the UDM model employed in PHAST has limitations, as it does not consider the height variations of the surrounding infrastructure, such as piers, moored ships and onshore facilities, which can influence ammonia dispersion [28]. Physical barriers can mitigate the spread of ammonia vapour in the atmosphere [39]. This study does not consider mitigation measures in consequence modelling and analysis. Therefore, the research work conducted in this study follows a worst-case approach for assessing the risk of accidental ammonia releases [7]. Moreover, this simulation study does not include the chemical reaction process between ammonia and water. As the research focus is the consequence of ammonia release for humans, this study does not evaluate the impact of released ammonia in seawater on aquatic life.

3.4. Step 4: conduct model verification and validation

Verification and validation of the simulation model are critical components of a simulation study. Model verification involves confirming the accurate implementation of assumptions in the computer program and ensuring that the model operates as expected [56]. In this study, the simulation model runs in sequence without interruptions and error messages. On the other hand, model validation aims to ensure that the model faithfully represents the real-world system [56]. As no ammonia-fuelled vessels are in operation, specific information on ammonia release during ammonia bunkering is not available to directly validate the PHAST simulation model. However, researchers from the UK's Health and Safety Executive (HSE), DNV, Syngenta, and DGA Maîtrise NRBC utilised the PHAST ammonia dispersion simulation models. They concluded that the simulation results aligned well with measured ammonia gas concentrations [41].

3.5. Step 5: analyse simulation results of baseline scenarios

This paper utilises baseline scenarios encompassing small, medium, and large ammonia releases, with orifice sizes equivalent to 1%, 10%, and 100% of the hose diameter. The remaining simulation inputs are held at constant values. To provide a quantitative assessment of the release consequences, this study employs maximum cloud footprints for various ammonia gas concentrations and lethality footprints after one-hour dispersion as risk assessment criteria.

The range of ammonia gas concentrations spans from 30 ppm to 1600 ppm, encompassing various levels of harmful effects, starting from transient effects (AEGL-1, 30 ppm) to irreversible impacts (AEGL-2, 160 ppm) and potentially life-threatening or fatal consequences (AEGL-3, 1100 ppm) within a one-hour timeframe [60]. It is worth noting that AEGL values denote threshold exposure limits for the general public and are subject to variations over time. The consequence analysis focuses on presenting the ammonia maximum cloud footprints at the height of 0 m (the level of seawater).

The lethality footprints presented in this study demonstrate the consequences of ammonia toxic hazards, considering both gas concentration and exposure duration. Using the probit calculation method in the PHAST tool, the study assesses the probability of lethality resulting from specific toxic exposures, providing a spectrum of lethality values ranging from 1% to 99%. The following sections provide comprehensive details on the lethality footprint values and their respective areas.

3.6. Step 6: conduct a sensitivity analysis of different factors

Sensitivity analysis plays a crucial role in gauging the model's responsiveness to variations in input parameters [55]. By investigating uncertainties, sensitivity analysis enhances the reliability of the model and helps identify the most critical exposure or risk factors, assisting in proposing mitigation measures [27]. The nominal range sensitivity method, also called local sensitivity analysis or threshold analysis, is applied to provide a comprehensive what-if analysis. The objective is to assess the sensitivity of factors related to bunkering supply, release and meteorological conditions. Nominal range sensitivity analysis explores how model outputs are affected when a single model input is systematically varied across its complete range of credible values, while all other inputs are held at their nominal or base-case values [14].

This study sets five values as simulation inputs for each factor and selects the middle value as the base value. The sensitivity is calculated by dividing the percentage change in output by the percentage change in input. For this sensitivity analysis, risk assessment criteria are the maximum cloud footprint at 1100 ppm after 1-hour dispersion and the 3% lethality footprint. The AEGL-3 for ammonia gas at 1100 ppm represents that individuals could experience severe health effects or life-threatening conditions after short-term exposure. These effects are meant to be an upper limit for short-term exposure, and exposure above

this level could result in significant health risks.

4. Case study

4.1. Problem set-up

Singapore, recognised as the largest bunkering port globally [43], holds promising potential to conduct ammonia bunkering operations in future. This paper selects the port of Singapore as the case study. As illustrated in the methodology section, the study specifically concentrates on accidental ammonia releases and dispersion over seawater during ship-to-ship bunkering operations.

Table 2 shows the simulation inputs for both baseline scenarios and sensitivity analysis, categorised into bunkering supply, release and meteorological conditions. In the baseline scenarios, the values of these factors are assumed based on the interview with ship operators of ammonia carriers, the Singapore Quantitative Risk Assessment Technical Guidance and the settings of environmental conditions in Ng et al. [46]. For example, a fully refrigerated storage condition for the baseline scenarios is chosen, with an atmospheric pressure and ammonia storage temperature of -33.5°C . The Guidelines for Quantitative Risk Assessment (QRA) suggested an isolation time of one minute for the release from an automatically operated shut-down system [58].

In the sensitivity analysis, each factor is individually assessed while maintaining all other parameters constant. The values of each factor vary between $\pm 25\%$ and $\pm 50\%$ for sensitivity analysis. The setting of these values shall consider the engineering design. For example, the flow rate for an 8-inch bunker hose can vary from 0 to $2200 \text{ m}^3/\text{h}$ [46]. $1000 \text{ m}^3/\text{h}$ flow rate is selected as the baseline scenarios with $\pm 25\%$ and $\pm 50\%$ ranges for sensitivity analysis. The Singapore Quantitative Risk Assessment Technical Guidance suggested five minutes for the release from a remotely operated shut-down system [45]. In addition, the setting of these meteorological conditions in sensitivity analysis considers the historical daytime data for Singapore [40]. The $\pm 12.5\%$ and $\pm 25\%$ variations are for ambient temperature, sea surface temperature and relative humidity. Furthermore, the setting of solar radiation flux varies between $\pm 10\%$ and $\pm 20\%$. This is due to the upper limit of solar radiation flux, 1.2 kW/m^2 , in the simulation tool.

4.2. Results of baseline scenarios

4.2.1. Different gas concentrations as criteria

In the baseline scenarios, this study examines accidental ammonia releases at small, medium, and large release scales with different criteria. **Fig. 2** shows the area of maximum cloud footprints for various ammonia gas concentrations, ranging from 30 ppm to 1600 ppm. The maximum cloud footprint areas significantly decrease after altering the risk assessment criteria for ammonia gas concentration from 30 ppm (AEGL-1) to 1100 ppm (AEGL-3). Specifically, for small releases, the area reduces from 395 to 23 m^2 ; for medium releases, it decreases from 77,168 to 847 m^2 ; and for large releases, it decreases from 2,791,360 to $171,135 \text{ m}^2$. The large release scale presents the worst-case scenario.

The simulation results reveal distinct behaviour between large and small/medium ammonia releases. Transitions from small to medium release scales result in more substantial changes in the footprint of lower gas concentrations. Conversely, shifts from medium to large release scales significantly impact the footprint of higher gas concentrations. For example, the AEGL-1 (30 ppm) cloud footprint will increase 195 times when transitioning from a small to medium orifice size and 36 times when transitioning from medium to large. However, the AEGL-3 (1100 ppm) cloud footprint will expand 60 times when moving from a small to a medium release and 157 times when shifting from a medium to a large release. This highlights the crucial role of release scale in the dispersion behaviour of ammonia gas concentrations.

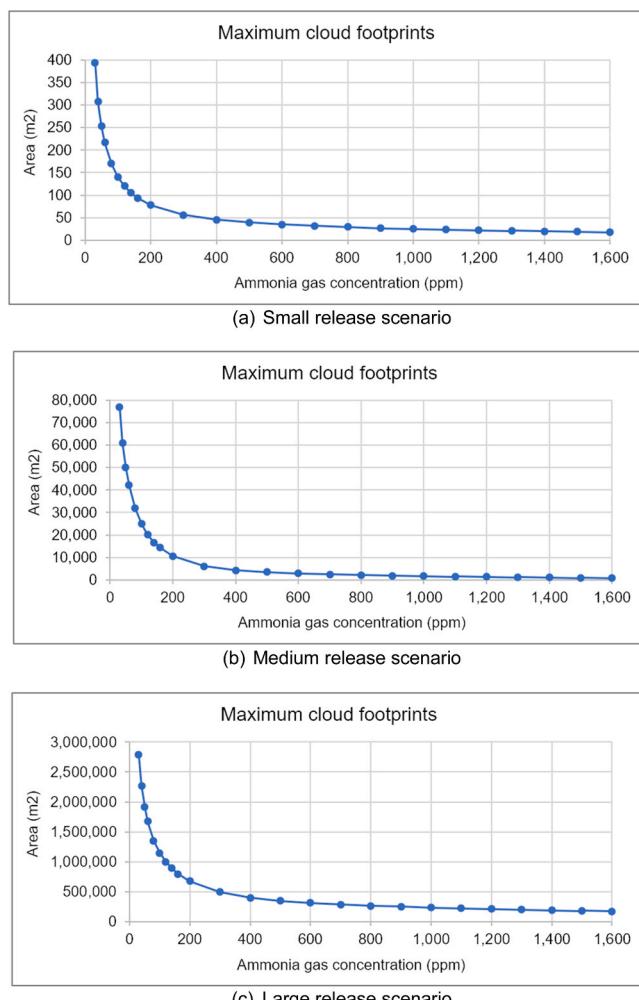
Table 2
Simulation inputs for ammonia release risk assessment.

Category	Factors	Values for the baseline scenarios	Values for sensitivity analysis
Bunkering supply condition	Storage pressure (temperature)	1 bar (-33.5°C)	3 bar (-9.1°C) 4.5 bar (1.3°C) 6 bar (9.4°C) 7.5 bar (16°C) 9 bar (21.6°C)
	Flow rate	1000 m^3/h	500 m^3/h 750 m^3/h 1000 m^3/h 1250 m^3/h 1500 m^3/h
	Bunker hose length	40 m	20 m 30 m 40 m 50 m 60 m
	Bunker hose diameter	8 in.	4 in. 6 in. 8 in. 10 in. 12 in.
	Number of release positions	1	1
	Release duration	1 min	2 min 3 min 4 min 5 min 6 min
	Release elevation above sea	15 m	7.5 m 11.25 m 15 m 18.75 m 22.5 m
	Release direction	0° (Horizontal)	45° 67.5° 90° (Vertical) 112.5° 135°
	Orifice size	Small release: 1% of hose diameter Medium release: 10% of hose diameter Large release: 100% of hose diameter	Small release: 1% of hose diameter Medium release: 10% of hose diameter Large release: 100% of hose diameter
	Dispersion surface	Seawater	Seawater
Meteorological condition	Wind speed	3 m/s	2 m/s 3 m/s 4 m/s 5 m/s 6 m/s
	Ambient temperature	33 °C	22.5 °C 26.25 °C 30 °C 33.75 °C 37.5 °C
	Sea surface temperature	30 °C	19.5 °C 22.75 °C 26 °C 29.25 °C 32.5 °C
	Relative humidity	0.7	0.525 0.6125 0.7 0.7875 0.875
	Pasquill stability	Class C	Class A Class B Class C

Table 2 (continued)

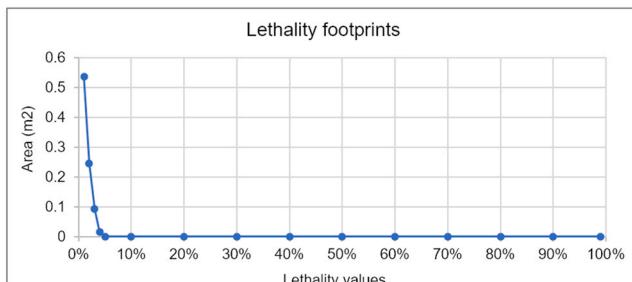
Category	Factors	Values for the baseline scenarios	Values for sensitivity analysis
	Solar radiation flux	1 kW/m^2	Class D Class E 0.8 kW/m^2 0.9 kW/m^2 1 kW/m^2 1.1 kW/m^2 1.2 kW/m^2

Source: Authors.

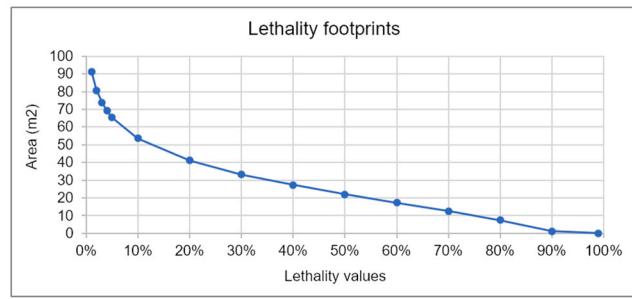
**Fig. 2.** The area of maximum cloud footprints of different concentrations in the baseline scenarios.

4.2.2. Different lethality footprints as criteria

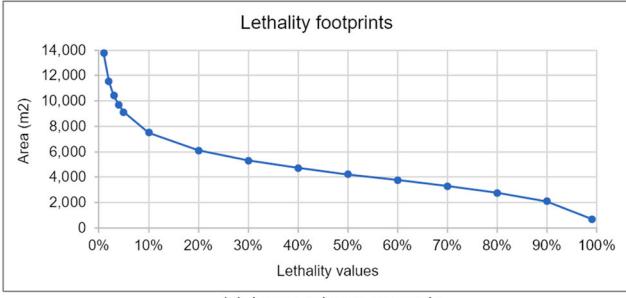
In the baseline scenarios, Fig. 3 presents the area of lethality footprints, ranging from 1% to 99% lethality values. The area decreases from 91 to 0 m^2 for medium release and decreases from 13,758 to 693 m^2 for large release. For small releases, the lethality footprint is negligible. Notably, this shift in release scale has a more pronounced impact on footprints with higher lethality values. For example, when the orifice size changes from medium to large, the 3% lethality footprint will increase by 141 times, and the 80% lethality footprint will expand by 372 times.



(a) Small release scenario



(b) Medium release scenario



(c) Large release scenario

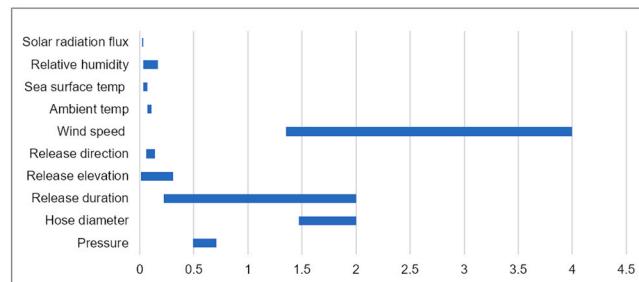
Fig. 3. The area of lethality footprints in the baseline scenarios.

4.3. Sensitivity analysis

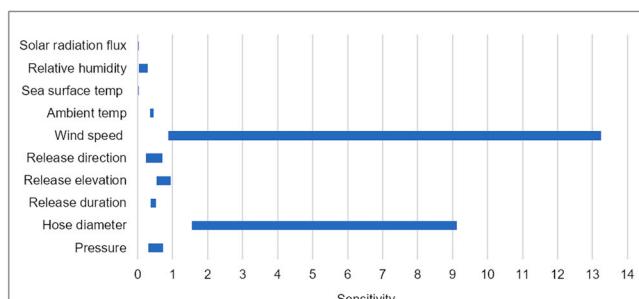
For each small, medium and large release scenario, this study conducts the sensitivity analysis to evaluate how the model is sensitive to the changes in different factors. These factors include storage pressure and temperature, flow rate, hose length, hose diameter, release duration, elevation, direction, wind speed, ambient temperature, sea surface temperature, relative humidity, Pasquill stability and solar radiation flux. For each factor, this study shows four sensitivity values. It is worth noting that the influence of different parameters varies in different ammonia release scales, and their sensitivities on 1100 ppm maximum cloud footprint and 3% lethality footprint also differ significantly.

4.3.1. Small release

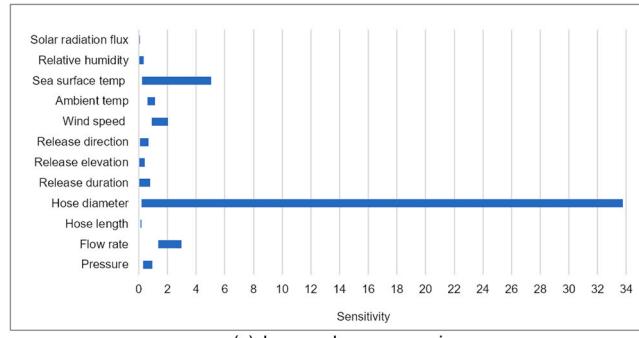
When the orifice size is 1% of the hose diameter, it is defined as a small release in this study. The sensitivities of different factors to 1100 ppm maximum cloud footprint are shown in Fig. 4. In small release scenarios, wind speed is the most significant factor based on its sensitivity of the area of 1100 ppm maximum cloud footprint. For instance, when the wind speed changes from 4 m/s to 5 m/s (25% changes in input), the area of 1100 ppm maximum cloud print would change from 17.24 m² to 0 (100% changes in output), and the sensitivity ratio would be 4. Similarly, under the given inputs, the sensitivity ratio of wind speed varies from 1.35 to 4, followed by the hose diameter with a sensitivity of 1.47 to 2.0, the release duration with a sensitivity of 0.22 to 2 and the pressure with a sensitivity of 0.49 to 0.71. The sensitivity of other factors is less than 0.5. The simulation results also show that flow



(a) Small release scenario



(b) Medium release scenario



(c) Large release scenario

Fig. 4. Sensitivities of different factors to 1100 ppm maximum cloud footprint.

rate and hose length do not influence the bunkering operational risk when only a small ammonia release exists. Furthermore, the simulation result shows that a 3% lethality footprint is considered negligible in small release scenarios in this study.

4.3.2. Medium release

When the orifice size is 10% of the hose diameter, it is defined as the medium release in this study. Similar to the small release scale, wind speed is the most significant factor for the medium release from the perspective of 1100 ppm maximum cloud footprint. The sensitivity ratio varies from 0.87 to 13.25 for wind speed, followed by the hose diameter, with a sensitivity of 1.54 to 9.12. For example, when wind speed is 4 m/s, a 50% reduction in wind speed results in a 663% change in the area of maximum cloud footprint of 1100 ppm. The sensitivity on 1100 ppm maximum cloud footprint is less than 1 for the other factors. As with small-scale releases, neither flow rate nor hose length influences operational risk during ammonia bunkering at a medium-scale release.

Furthermore, Fig. 5 shows the sensitivities of different factors to the 3% lethality footprint. Under the risk assessment criteria of the 3% lethality footprint, wind speed is still the most significant factor in medium release scales, with a sensitivity of 1.49 to 3.28, followed by the hose diameter, with a sensitivity of 1.33 to 1.57. For example, when wind speed is 4 m/s, a 50% reduction in wind speed results in a 152% change in the area of 3% lethality footprint.

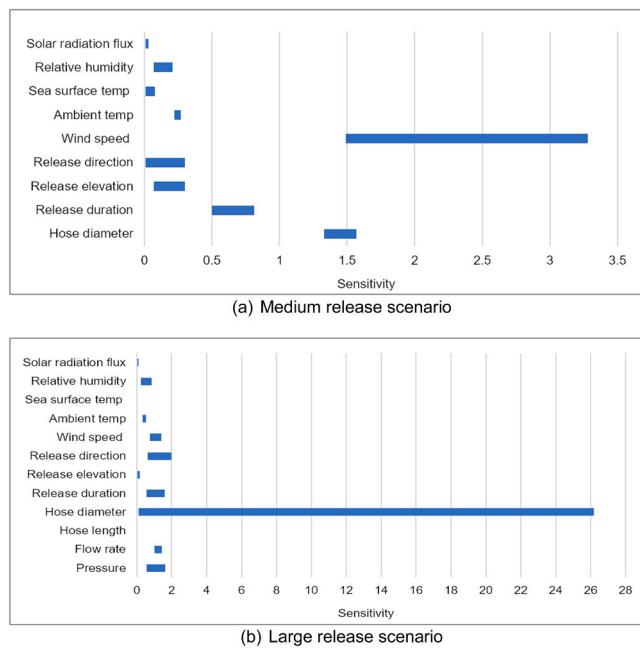


Fig. 5. Sensitivities of different factors to 3% lethality footprint.

4.3.3. Large release

Different from the small and medium releases, the large release represents the hose rupture scenario. Under the risk assessment criteria of 1100 ppm maximum cloud footprint, hose diameter is the most significant factor in large release scenarios with a sensitivity of 0.18 to 33.77, followed by the flow rate with a sensitivity of 1.35 to 2.99 and sea surface temperature with a sensitivity of 0.23 to 5.03. For instance, a 50% change in hose diameter can result in a 1689% change in the 1100 ppm maximum cloud footprint for large releases. In addition, the sensitivity of these four factors (hose diameter, flow rate, ambient

temperature and sea surface temperature) to the 1100 ppm maximum cloud footprint becomes more pronounced at larger release scales, in contrast to medium and small release scales.

Concerning the 3% lethality footprint, the most significant factor is hose diameter, exhibiting a sensitivity ranging from 0.1 to 26.17, followed by release direction, pressure, release duration, flow rate and wind speed. The sensitivity on 3% lethality footprint is less than 1 for the other factors. The simulation result indicates that each ammonia bunkering supply, release or meteorological factor performs differently on the cloud and lethality footprints.

5. Discussions and implications

5.1. The effects of small, medium and large releases

Fig. 6 and **Fig. 7** show the comparison of maximum cloud footprints (AEGL-1, AEGL-2 and AEGL-3) and the comparison of lethality footprints (3%, 10%, 50% and 99% lethality) in the baseline scenarios. Based on the simulation results of baseline scenarios, we find that the footprint of smaller gas concentrations changes more significantly with shifting from small to medium releases. Targeted mitigation strategies are necessary to address localised impacts effectively. This may involve implementing measures specific to the activities that are sources of smaller emissions. On the other hand, large releases require more comprehensive and robust approaches, such as emergency response plans and containment measures.

Moreover, shifts from medium to large release scales significantly affect the footprints with higher lethality values. Therefore, from the engineering design perspective, it is important to implement advanced active mitigation systems, such as automated shut-off valves, pressure relief devices, or containment strategies, to limit the release orifice size. It is also recommended to investigate and implement passive mitigation measures, such as installing barriers or structures that can limit the spread of hazardous substances and reduce the affected area.

The sensitivity analysis reveals that each factor exhibits varying performance depending on the release conditions. Each factor will be

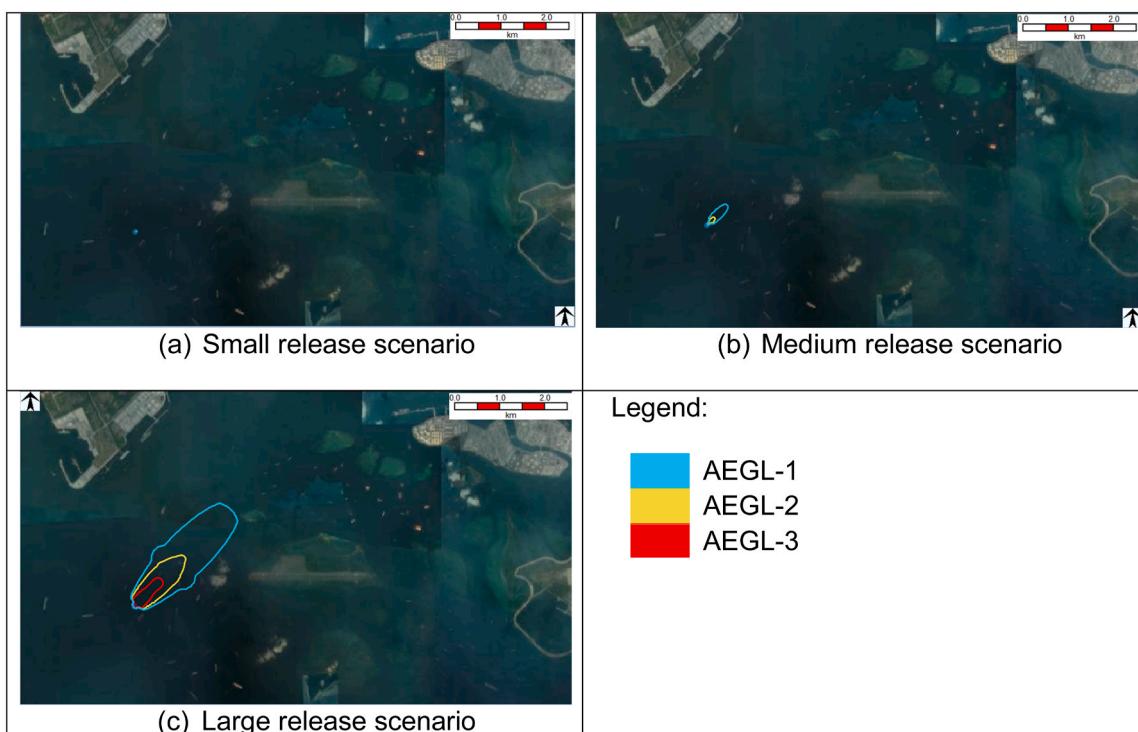


Fig. 6. Comparison of AEGL-1, AEGL-2 and AEGL-3 maximum cloud footprints in the baseline scenarios.

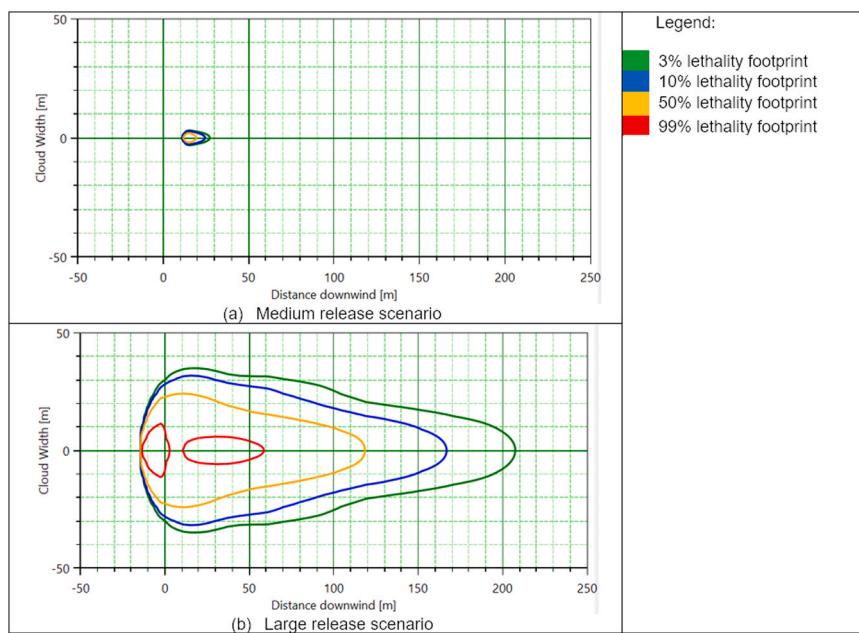


Fig. 7. Comparison of 3%, 10%, 50% and 99% lethality footprints in the baseline scenarios.

more sensitive to the 1100 ppm maximum cloud footprint when the release scale changes from small to large, except for release duration and wind speed (Fig. 4 and Fig. 5). Hence, from the operations perspective, when there is a small release during the bunkering operations, the crews should take mitigation measures to control the accident and avoid escalating the release scale.

Furthermore, policymakers shall consider the variable effects of different ammonia release scales when designing regulations and emission standards. Flexible and adaptive policies can ensure appropriate controls are applied to ammonia gas emissions of varying magnitudes, striking a balance between cost-effectiveness and environmental protection. The variable impact of ammonia release scales can have economic implications for affected industries, especially if stringent measures are needed to control larger releases.

5.2. Discussion on wind speed

The sensitivity analysis shows the change of ammonia release consequences when the wind speed is in the range of 2 to 5 m/s. Within the scope of small and medium releases, wind speed is the most significant factor influencing the consequence. Higher wind speed carries ammonia vapour over a greater distance during the initial dispersion process, such as within the first minute. However, for higher wind speed, the area encompassing the 1100 ppm maximum cloud footprint or the 3% lethality footprint becomes comparatively smaller after one hour of dispersion, as illustrated in Fig. 8. This phenomenon can be attributed to the rapid dispersion and dilution of ammonia vapour facilitated by higher wind speeds. Consequently, the duration of exposure to high concentrations is significantly reduced, resulting in a reduction in the lethality footprint.

One of the new findings is that wind speed is less sensitive to 1100 ppm maximum cloud footprint or 3% lethality footprint in large release scenario compared to medium release scenario. To illustrate, when the wind speed decreases from 4 m/s to 2 m/s, the area of the 1100 ppm maximum cloud footprint changes from 688 m² to 5,247 m² in the medium release scale, representing a significant 662.7% increase. In contrast, within the large release scale, the change moves from 168,068 m² to 340,107 m², reflecting a 102.4% increase. This difference can be attributed to the larger droplet size at large release scales. The condensation of water vapour on the surface of ammonia droplets has

thermal and dilution effects on the evaporation of ammonia [62]. Larger droplets have a smaller surface area relative to their volume, so wind speed has a relatively smaller sensitivity to their evaporation.

It is worth noting that strong winds, such as typhoons, can cause port disruption and economic loss [70]. The findings of this study underscore the importance of considering wind speed data when developing regulations and guidelines for the management of ammonia bunkering to improve public safety and minimise potential hazards. This new finding encourages a paradigm shift in research and practice, urges further exploration of the complex interplay between meteorological conditions and ammonia dispersion, and paves the way for more effective, data-driven approaches to reduce risk and protect human life.

5.3. Discussion on hose diameter and flow rate

When the hose diameter changes from 4 to 12 inch, the area of 1100 ppm maximum cloud footprint and 3% lethality footprint in small and medium release scales would be larger. Conversely, in large release scales, the coverage area experiences a reduction. This phenomenon is attributed to the increased dissolution of ammonia liquid droplets into the seawater and a diminished dispersion of ammonia gas within the atmosphere during large releases. The knowledge of how hose diameter influences ammonia bunkering operational risk can guide the planning and design of bunkering supply infrastructure.

In the case of large releases, hose diameter and flow rate play the most important role in reducing the 1100 ppm maximum cloud footprint and 3% lethality footprint. When the flow rate varies from 500 to 1,500 m³/h, the consequence of ammonia release would be severe, and the 3% lethality footprint would be larger. Yang and Lam [67] conducted a sensitivity analysis of bunkering supply and demand configurations and concluded that flow rate greatly influences ammonia bunkering service time. Another constraint of selecting bunker hose size and flow rate is the consideration of fluid dynamics, such as water hammer effects during ammonia transfer. According to interviews with experts in ammonia handling operations, ammonia flow velocity will probably be limited to 12 m/s due to possible cavitation in the swivel of the marine loading arms. Therefore, it is worth noting that a delicate balance exists between employing a lower flow rate to mitigate operational risks associated with ammonia bunkering and utilising a higher flow rate to enhance the bunkering efficiency.

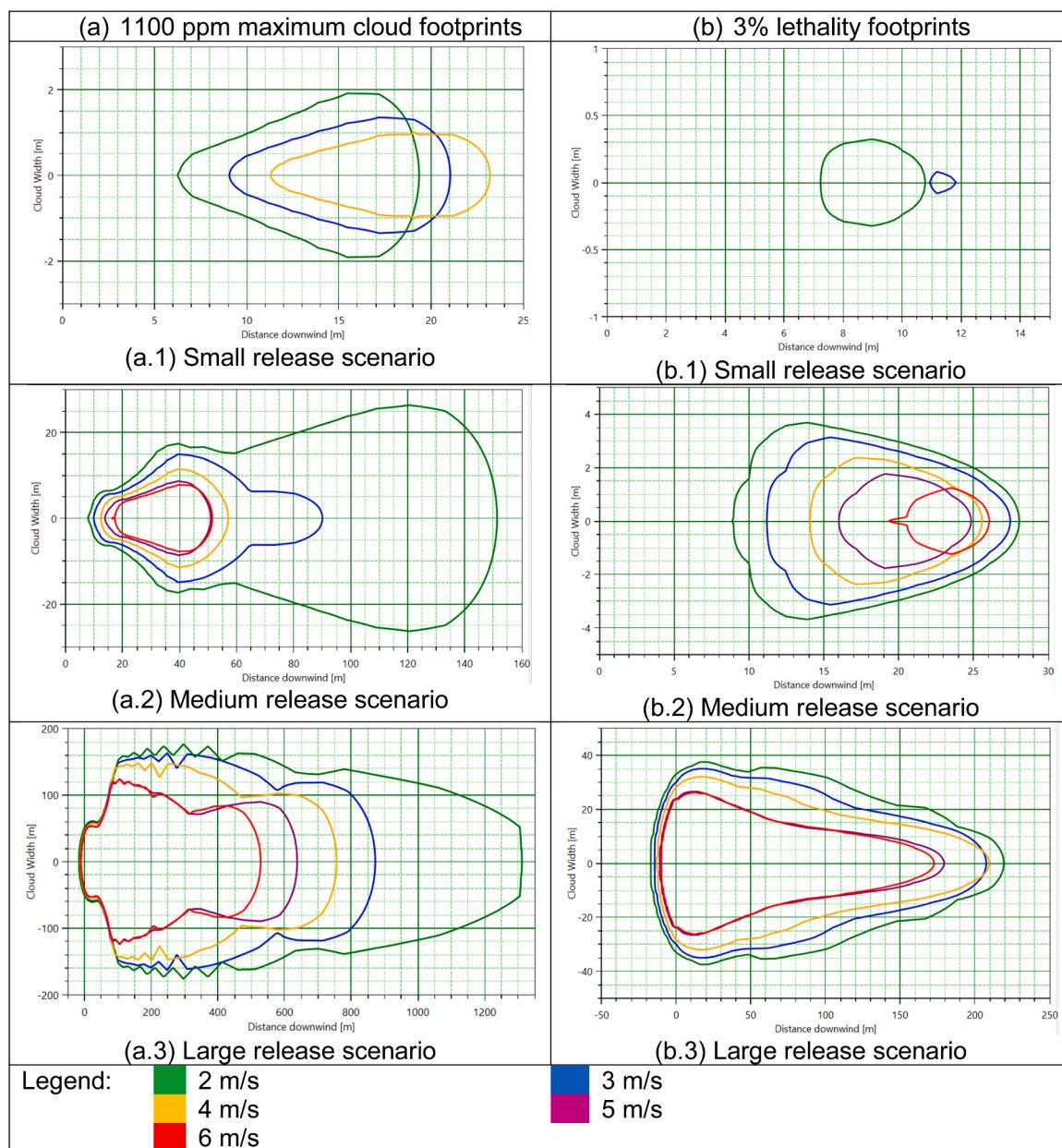


Fig. 8. The effect of wind speed on the 1100 ppm maximum cloud footprint and 3% lethality footprint.

5.4. Discussion on ambient temperature and sea surface temperature

Fig. 9 shows the effect of air and sea surface temperature on the 1100 ppm maximum cloud footprint in large release scenarios. The higher the ambient temperature, the larger the 1100 ppm maximum cloud footprint. As ambient temperature increases, ammonia vapour spreads around more easily instead of rising. In contrast, higher sea surface temperature leads to a smaller 1100 ppm maximum cloud footprint. This is because the higher the sea surface temperature, the higher the ammonia vapour rises into the atmosphere.

Another finding is that when the difference between the air and sea surface temperatures becomes larger, the area of the 1100 ppm maximum cloud footprint will become larger. For example, when the ambient temperature is 22.5 °C, 30 °C and 37.5 °C and the sea surface temperature is 30 °C, the 1100 ppm maximum cloud footprint is 162,817 m², 204,111 m² and 234,234 m² in large release scenarios, respectively. This finding has implications for the risk assessment associated with ammonia bunkering across different ports. Since water

has a higher heat capacity, its temperature changes more gradually than air. Notably, in certain tropical and equatorial regions like Singapore, the seawater temperature commonly exceeds that of the air. Consequently, it becomes imperative to tailor safety considerations in policy decisions based on the specific climatic conditions of individual ports.

5.5. Discussion on Pasquill stability

This paper did not calculate the sensitivity ratio of Pasquill stability, because the variations in Pasquill stability in this study are not expressed numerically, but rather represented by different classes. Pasquill stability also depends on other meteorological factors, such as solar radiation and wind speed. Pasquill stability has the greatest impact on the 1100 ppm maximum cloud footprint in the medium release scale compared to that in small and large release scales, as presented in Fig. 10. However, with a shift from Class C to Class E Pasquill stability, the 3% lethality footprint decreases by 25.37% in medium release and 2.72% in large release.

As Pasquill stability shifts from unstable (Class A Pasquill stability) to

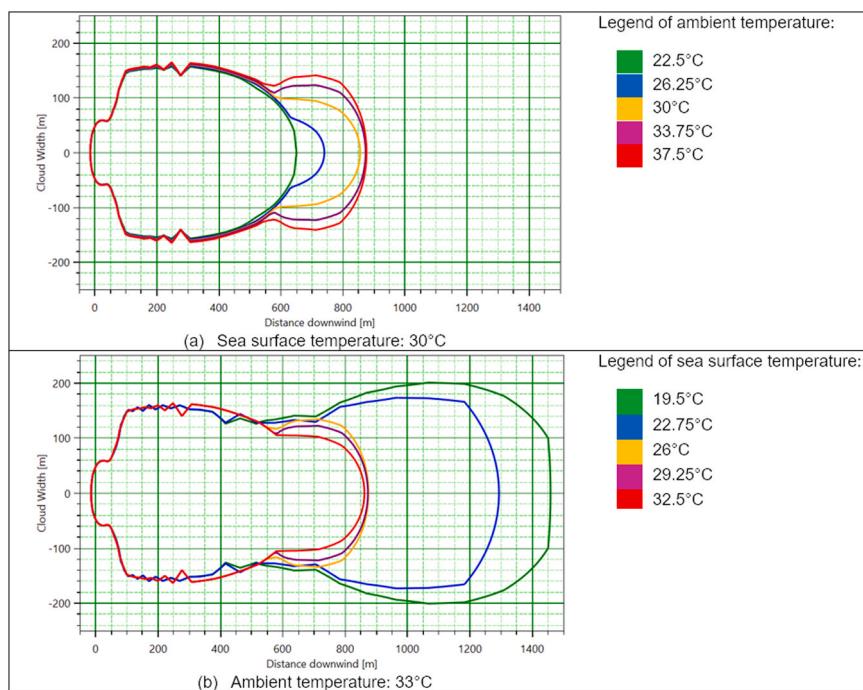


Fig. 9. The effect of air temperature and sea surface temperature on the 1100 ppm maximum cloud footprint in large release scenarios.

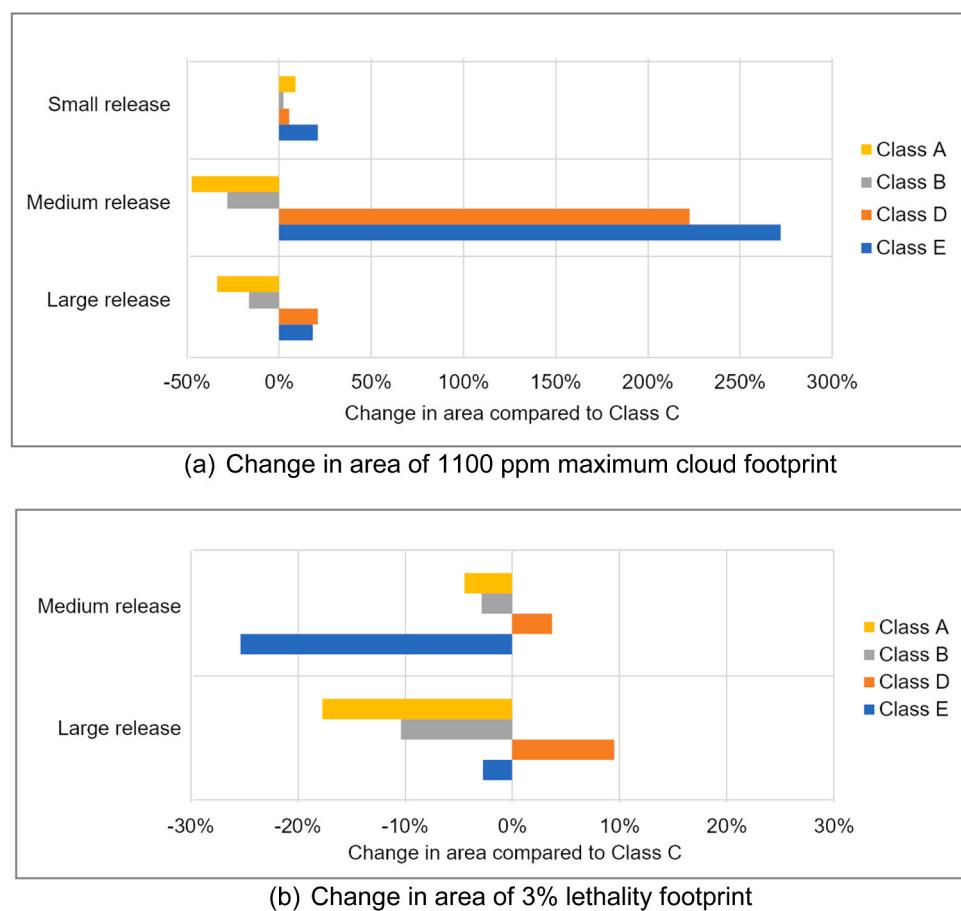


Fig. 10. Variations in 1100 ppm maximum cloud footprint and 3% lethality footprint compared to Class C Pasquill stability.

stable (Class E Pasquill stability), the area of the maximum cloud footprint at 1100 ppm will expand. For example, when transitioning to Class E Pasquill stability, the area of 1100 ppm maximum cloud footprint increases by 21%, compared to its observation under the condition of Class C Pasquill stability. This phenomenon can be explained because the dispersion of an ammonia cloud extends over a broader expanse when the atmosphere is more stable. Vertical mixing is hindered during such periods, and exchanges between different atmospheric layers are constrained. Ammonia, confined at a specific altitude, faces limitations in mingling and dilution with the surrounding air. Consequently, it becomes transported over longer distances downwind. Therefore, the more stable the atmosphere, the farther ammonia disperses.

5.6. Implications for ammonia bunkering in different bunkering ports

According to the estimated ammonia release rates reported by the Health and Safety Executive in the UK, it was assumed that there was a total of 3.1 ammonia releases for every 100,000 movements of ammonia carriers [13]. When ammonia is used as a marine fuel, much more ammonia will be transported by sea. The heightened activities related to ammonia loading and bunkering operations pose an increased risk of ammonia release. This heightened risk has significant implications for port operations, particularly for bunkering ports. For instance, there were 100,807 vessel arrivals at the port of Singapore in 2022 [44]. If all these vessels conduct ammonia bunkering operations or carry ammonia as cargo/bunker in Singapore, it may result in three cases of ammonia release annually. Consequently, it becomes imperative for bunkering ports to establish and enforce stringent policy requirements to ensure the safety of ammonia bunkering operations.

Furthermore, different bunkering ports shall make their policy decisions while considering the specific meteorological conditions, including wind speed, ambient temperature, and sea surface temperature. For example, the ammonia cloud footprint is relatively smaller when sea surface temperatures are higher than ambient temperatures in Singapore. However, dispersion phenomena may differ for ports with a lower probability of sea surface temperature surpassing air temperature. Based on the insights and implications derived from this study, future research can focus on quantitatively assessing ammonia bunkering operational risks across diverse bunkering ports.

6. Conclusions

This study investigates the ammonia bunkering operational risk across various scales of accidental ammonia release. The Port of Singapore is chosen as a representative case to illustrate the risks involved in ammonia bunkering at a bunkering port. The research provides valuable insights into how varying each ammonia bunkering supply, release, and meteorological factor affects the risk of ammonia bunkering. The simulation results show that:

1. Increasing the release scale from small to medium results in more significant changes in the cloud footprint at lower gas concentrations. While transitioning from medium to large release scale leads to greater changes in the cloud footprint at higher gas concentrations and lethality footprints with higher values.
2. Under the risk assessment criteria of 1100 ppm maximum cloud footprint, wind speed emerges as the most influential factor for both small and medium release scales, exhibiting sensitivities of up to 4 and 13.25, respectively.
3. In the case of large release scales, hose diameter emerges as the most important factor, exhibiting a sensitivity of 33.77 to 1100 ppm maximum cloud footprint and a sensitivity of 26.17 to the 3% lethality footprint.

This study fills the gap in the area of how sensitive each factor is in influencing the operational risk of ammonia bunkering under small,

medium, and large release scales and how the ammonia bunkering operational risk varies under different risk assessment criteria. It makes contributions to the domain of ammonia as a marine fuel, benefiting both scientific understanding and practical applications. Firstly, it enriches the existing literature by filling gaps in ammonia bunkering safety within the maritime sector. Notably, this study is the first to explore the combined impact of various factors related to ammonia bunkering supply, release, and meteorological conditions on bunkering risk while considering different release scales. Furthermore, the risk assessment process developed in this research can be extended to investigate the hazards of other types of alternative fuels, such as biofuel and methanol. Additionally, its applicability extends beyond ammonia release from the bunker hose to other risk events, including storage tank rupture.

This study also provides valuable practical recommendations that hold significant relevance for stakeholders in the maritime and transportation sectors. For instance, the insights and discussions concerning the risk associated with ammonia bunkering can serve as valuable references for bunker suppliers when making decisions regarding bunkering supply configurations. The study emphasises the significance of wind speed and hose diameter in ammonia bunkering operational risk. Furthermore, it provides crucial insights for government and port operators, enabling them to make policy adjustments, such as setting limits on ammonia bunkering operations based on wind speed considerations.

There are a few limitations in this study. Firstly, the risk assessment does not take into account the potential risks associated with ammonia corrosion, pool fire, jet fire and explosion. The release scenarios proposed in this study only consider one-point release, while multiple points of release during ammonia bunkering may occur. Moreover, flows between buildings and ship superstructure are not considered when calculating the consequences of various release scenarios, which may not fully capture the complete picture. The sensitivity analysis is a local sensitivity analysis with a fixed value range, and the range is assumed based on the engineering design and meteorological conditions in Singapore. However, the bunkering supply, release and meteorological factors would have random uncertainties.

Future research could address these limitations by conducting a more detailed analysis of the uncertainties associated with the selected factors, considering the distribution of changes in each factor. Special attention may be given to refining the model by incorporating the CFD simulation method to account for near-field dispersion simulation. Furthermore, in order to validate the simulation work, conducting field experiments on ammonia release over seawater becomes essential in the future. With increased experience in ammonia bunkering simulation and experiments, obtaining more accurate estimations of ammonia bunkering operational risk will be possible. It is crucial to emphasise that simulation results are based on the assumption that no mitigation measures are implemented. Therefore, in future studies, incorporating mitigation measures would contribute to a better understanding of ammonia bunkering operational risks.

Environmental implication

Ammonia toxicity and corrosiveness are major concerns when used as a marine fuel. Ammonia can pose a significant risk to humans, as it can rapidly release toxic fumes, causing severe chemical burns upon contact with skin or eyes. Its toxicity to the marine environment raises additional concerns when bunkering operations are regularly conducted in the terminal or anchorage area. This paper assessed ammonia bunkering operational risk from the perspectives of small, medium and large release scales. It shows the impacts of bunkering supply, release, and meteorological factors on release consequences while considering release scales and employing distinct risk assessment criteria.

CRediT authorship contribution statement

Yang Mengyao: Formal analysis, Investigation, Methodology, Visualization, Writing – original draft. **Lam Jasmine Siu Lee:** Conceptualization, Funding acquisition, Methodology, Resources, Supervision, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

- [1] Akyuz, E., Celik, M., Akgun, I., Cicek, K., 2018. Prediction of human error probabilities in a critical marine engineering operation on-board chemical tanker ship: the case of ship bunkering. *Saf Sci* 110, 102–109. <https://doi.org/10.1016/j.ssci.2018.08.002>.
- [2] Al-Enazi, A., Okonkwo, E.C., Bicer, Y., Al-Ansari, T., 2021. A review of cleaner alternative fuels for maritime transportation. *Energy Rep* 7, 1962–1985. <https://doi.org/10.1016/j.egyr.2021.03.036>.
- [3] Amendola, A., Contini, S., Ziomas, I., 1992. Uncertainties in chemical risk assessment: results of a European benchmark exercise. *J Hazard Mater* 29 (3), 347–363. [https://doi.org/10.1016/0304-3894\(92\)85041-X](https://doi.org/10.1016/0304-3894(92)85041-X).
- [4] Ayvali, T., Tsang, S.E., Van Vrijaldenhoven, T., 2021. The position of ammonia in decarbonising maritime industry: an overview and perspectives: part ii: costs, safety and environmental performance and the future prospects for ammonia in shipping. *Johns Matthey Technol Rev* 65 (2), 291–300. <https://doi.org/10.1595/205651321X16127941688787>.
- [5] Benson, T.H., Sinclair, J.R., 1982. US coast guard research and development program for hazardous chemical discharge response. *J Hazard Mater* 6 (3), 267–276. [https://doi.org/10.1016/0304-3894\(82\)80015-0](https://doi.org/10.1016/0304-3894(82)80015-0).
- [6] Bouet, R., Duplantier, S., Salvi, O., 2005. Ammonia large scale atmospheric dispersion experiments in industrial configurations. *J Loss Prev Process Ind* 18 (4–6), 512–519. <https://doi.org/10.1016/j.jlp.2005.07.016>.
- [7] Carter, D.A., Hirst, I.L., 2000. Worst case' methodology for the initial assessment of societal risk from proposed major accident installations. *J Hazard Mater* 71 (1–3), 117–128. [https://doi.org/10.1016/S0304-3894\(99\)00075-8](https://doi.org/10.1016/S0304-3894(99)00075-8).
- [8] Casal, J., 2018. Atmospheric dispersion of toxic or flammable clouds. In: Casal, J. (Ed.), Evaluation of the effects and consequences of major accidents in industrial plants, 2nd ed... Elsevier, pp. 269–330. <https://doi.org/10.1016/c2016-0-00740-4>.
- [9] Chang, J., Zhu, C., Wang, Z., Wang, Y., Li, C., Hu, Q., et al., 2022. A full-set and self-powered ammonia leakage monitor system based on CNTs-PPy and triboelectric nanogenerator for zero-carbon vessels. *Nano Energy* 98, 107271. <https://doi.org/10.1016/j.nanoen.2022.107271>.
- [10] Cheliotis, M., Boulougouris, E., Trivya, N.I., Theotokatos, G., Livanos, G., Mantalos, G., et al., 2021. Review on the safe use of ammonia fuel cells in the maritime industry. *Energies* 14 (11), 3023. <https://doi.org/10.3390/en14113023>.
- [11] Chen, M., Jiang, S., Han, A., Yang, M., Tkalich, P., Liu, M., 2024. Bunkering for change: knowledge preparedness on the environmental aspect of ammonia as a marine fuel. *Sci Total Environ* 907, 167677. <https://doi.org/10.1016/j.scitotenv.2023.167677>.
- [12] Chen, Y., Pu, J., Xu, X., Mei, X., 2022. Research on safety risks analysis and protective measures of ammonia as marine fuel. *Proc 2022 7th Int Conf Power Renew Energy (ICPRE)* 766–771. <https://doi.org/10.1109/ICPRE5555.2022.9960531>.
- [13] Crolius, S., Pugh, D., Morris, S., Velera-Medina, A., 2021. Safety Aspects. In: Velera-Medina, A., Banares-Alcantara, R. (Eds.), Techno-Economic Challenges of Green Ammonia as an Energy Vector. Elsevier, pp. 221–257. <https://doi.org/10.1016/B978-0-12-820560-0-00010-2>.
- [14] Cullen, A.C., Frey, H.C., 1999. Probabilistic techniques in exposure assessment: a handbook for dealing with variability and uncertainty in models and inputs. Springer Science & Business.
- [15] Dawson, L., Ware, J., Vest, L., 2022. Ammonia at sea: Studying the potential impact of ammonia as a shipping fuel on marine ecosystems. Environment Defense Fund, Ricardo PLC and Lloyd's Register.
- [16] Dharmavaram, S., Tilton, J.N., Gardner, R.J., 1994. Fate and transport of ammonia spilled from a barge. *J Hazard Mater* 37 (3), 475–487. [https://doi.org/10.1016/0304-3894\(93\)E0099-N](https://doi.org/10.1016/0304-3894(93)E0099-N).
- [17] Dharmavaram, S., Carroll, M.J., Lutostansky, E.M., McCormack, D., Chester, A., Allason, D., 2023. Red squirrel tests: air products' ammonia field experiments. *Process Saf Prog* 42, 481–498. <https://doi.org/10.1002/prs.12454>.
- [18] Dimitriou, P., Javaid, R., 2020. A review of ammonia as a compression ignition engine fuel. *Int J Hydrog Energy* 45 (11), 7098–7118. <https://doi.org/10.1016/j.ijhydene.2019.12.209>.
- [19] DNV. Ammonia bunkering of passenger vessel - Concept quantitative risk assessment. 2021.
- [20] DNV. External safety study - bunkering of alternative marine fuel for seagoing vessels. 2021.
- [21] Duong, P.A., Ryu, B.R., Song, M.K., Nguyen, H.V., Nam, D., Kang, H., 2023. Safety assessment of the ammonia bunkering process in the maritime sector: a review. *Energies* 16 (10), 4019. <https://doi.org/10.3390/en16104019>.
- [22] EGIG. Gas pipeline incident, 11th Report of the European Gas Pipeline Incident Data Group (EGIG) (period 1970 – 2019); 2020.
- [23] Fabbri, L., Contini, S., 2009. Benchmarking on the evaluation of major accident-related risk assessment. *J Hazard Mater* 162 (2–3), 1465–1476. <https://doi.org/10.1016/j.jhazmat.2008.06.071>.
- [24] Laursen, R., Barcarolo, D., Patel, H., Dowling, M., Penfold, M., Faber, J., et al., 2022. Potential of Ammonia as Fuel in Shipping. European Maritime Safety Agency.
- [25] European Council and Council of the European Union. Fit for 55': Council and Parliament reach provisional deal on EU emissions trading system and the Social Climate Fund. 2022. <https://www.consilium.europa.eu/en/press/press-releases/2022/12/18/fit-for-55-council-and-parliament-reach-provisional-deal-on-eu-emissions-trading-system-and-the-social-climate-fund/#:~:text=The%20Council%20and%20Parliament%20agreed%20to%20include%20maritime%20shipping%20emissions,2025%20and%20100%25%20for%202026>. [Accessed on 30 December 2022].
- [26] Fan, H., Enshaei, H., Jayasinghe, S.G., Tan, S.H., Zhang, C., 2021. Quantitative risk assessment for ammonia ship-to-ship bunkering based on Bayesian network. *Process Saf Prog* 41 (2), 395–410. <https://doi.org/10.1002/prs.12326>.
- [27] Frey, H.C., Patil, S.R., 2002. Identification and review of sensitivity analysis methods. *Risk Anal* 22 (3), 553–578. <https://doi.org/10.1111/0272-4332.00039>.
- [28] Gerbec, M., Vidmar, P., Pio, G., Salzano, E., 2021. A comparison of dispersion models for the LNG dispersion at port of Koper, Slovenia. *Saf Sci* 144, 105467. <https://doi.org/10.1016/j.ssci.2021.105467>.
- [29] Havens, H., Luther, M.E., Meyers, S.D., 2009. A coastal prediction system as an event response tool: Particle tracking simulation of an anhydrous ammonia spill in Tampa Bay. *Mar Pollut Bull* 58 (8), 1202–1209. <https://doi.org/10.1016/j.marpolbul.2009.03.012>.
- [30] Holmes, N.S., Morawska, L., 2006. A review of dispersion modelling and its application to the dispersion of particles: An overview of different dispersion models available. *Atmos Environ* 40 (30), 5902–5928. <https://doi.org/10.1016/j.atmosenv.2006.06.003>.
- [31] IMO, 2023. International Maritime Organization (IMO) adopts revised strategy to reduce greenhouse gas emissions from international shipping. International Maritime Organization, London, UK. <https://www.imo.org/en/MediaCentre/PressBriefings/pages/Revised-GHG-reduction-strategy-for-global-shipping-adopted.aspx>. Accessed on 30 July 2023.
- [32] Kaiser, G.D., 1989. A review of models for predicting the dispersion of ammonia in the atmosphere. *Plant/Oper Prog* 8 (1), 58–64. <https://doi.org/10.1002/prsb.720080115>.
- [33] Kaiser, G.D., Griffiths, R.F., 1982. The accidental release of anhydrous ammonia to the atmosphere: a systematic study of factors influencing cloud density and dispersion. *J Air Pollut Control Assoc* 32 (1), 66–71. <https://doi.org/10.1080/00224740.1982.10465371>.
- [34] Kaiser, G.D., Walker, B.C., 1978. Releases of anhydrous ammonia from pressurised containers - the importance of denser-than-air mixtures. *Atmos Environ* 12 (12), 2289–2300. [https://doi.org/10.1016/0004-9681\(78\)90269-X](https://doi.org/10.1016/0004-9681(78)90269-X).
- [35] LR, 2020. Hydrogen and Ammonia Infrastructure Safety and Risk Information and Guidance. Lloyd's Register.
- [36] LR, 2022. Quantitative Risk Assessment of Ammonia-fuelled Vessels. Lloyd's Register.
- [37] Luo, C., Zhao, Y., Xu, K., 2022. Study on the regularity of ammonia-related refrigeration accidents in China from 2010 to 2020. *Int J Environ Res Public Health* 19 (14), 8230. <https://doi.org/10.3390/ijerph19148230>.
- [38] MacFarlane, D.R., Cherepanov, P.V., Choi, J., Suryanto, B.H., Hodgetts, R.Y., Bakker, J.M., et al., 2020. A roadmap to the ammonia economy. *Joule* 4 (6), 1186–1205. <https://doi.org/10.1016/j.joule.2020.04.004>.
- [39] Mastellone, M.L., Ponte, M., Arena, U., 2003. Design of mitigation systems for indoor and outdoor ammonia releases. *J Loss Prev Process Ind* 16 (2), 93–101. [https://doi.org/10.1016/S0950-4230\(02\)00116-X](https://doi.org/10.1016/S0950-4230(02)00116-X).
- [40] Meteorological Service Singapore. Historical Daily Records. 2023. <http://www.weather.gov.sg/climate-historical-daily/>. [Accessed on 12 May 2023].
- [41] McGillivray, A., Harper, M., Hart, F., Puttick, S., Ibrahim, A., Verdier, L., Gant, S., Hetherington, R., Tucker, F., PHAST modelling of the Desert Tortoise and FLADIS ammonia trials for the Jack Rabbit III model inter-comparison exercise [Paper presentation]. 21st International Conference on Harmonisation within

- Atmospheric Dispersion Modelling for Regulatory Purposes, Aveiro, Portugal.2022, September 27–30.
- [42] Mousavi, J., Parvini, M., 2016. A sensitivity analysis of parameters affecting the hydrogen release and dispersion using ANOVA method. *Int J Hydron Energy* 41 (9), 5188–5201. <https://doi.org/10.1016/j.ijhydene.2016.01.042>.
- [43] MPA. Bunkering Services Providers. Maritime and Port Authority of Singapore, Singapore; 2023. (<https://www.mpa.gov.sg/port-marine-ops/marine-services/bunkering/bunkering-service-providers>). [Accessed on 15 May 2023].
- [44] MPA. Maritime Performance. Maritime and Port Authority of Singapore, Singapore; 2023. (<https://www.mpa.gov.sg/who-we-are/newsroom-resources/research-and-statistics/port-statistics>). [Accessed on 30 November 2023].
- [45] National Environment Agency. National Environment Agency Development Control Singapore QRA Technical Guidance. Singapore. 2016. (<https://publicat.iereeksgevaarlijkestoffen.nl/documents/81474/1664357417-pgs3-1999-v0-1-quantitative-risk-assessment.pdf>). [Accessed on 20 March 2023].
- [46] Ng, C.K.L., Liu, M., Lam, J.S.L., Yang, M., 2023. Accidental release of ammonia during ammonia bunkering: dispersion behaviour under the influence of operational and weather conditions in Singapore. *J Hazard Mater* 452, 131281. <https://doi.org/10.1016/j.jhazmat.2023.131281>.
- [47] Papazoglou, I.A., Christou, M., Nivolianitou, Z., Aneziris, O., 1992. On the management of severe chemical accidents DECARA: a computer code for consequence analysis in chemical installations. Case study: Ammonia plant. *J Hazard Mater* 31 (2), 135–153. [https://doi.org/10.1016/0304-3894\(92\)85002-I](https://doi.org/10.1016/0304-3894(92)85002-I).
- [48] Pomonis, T., Jeong, B., Kuo, C., 2022. Engine room fire safety evaluation of ammonia as marine fuel. *J Int Marit Saf Environ Aff Shipp* 6 (1), 67–90. <https://doi.org/10.1080/25725084.2021.2015867>.
- [49] Quinn, P.K., Charlson, R.J., Bates, T.S., 1988. Simultaneous observations of ammonia in the atmosphere and ocean. *Nature* 335 (6188), 336–338. <https://doi.org/10.1038/335336a0>.
- [50] Raj, P.K., 1981. Models for cryogenic liquid spill behavior on land and water. *J Hazard Mater* 5 (1-2), 111–130. [https://doi.org/10.1016/0304-3894\(81\)85009-1](https://doi.org/10.1016/0304-3894(81)85009-1).
- [51] Raj, P.K., Hagopian, J., Kalekar, A.S., 1974. Prediction of hazards of spills of anhydrous ammonia on water. Arthur D. Little Incorporated.
- [52] Raj, P.P., Reid, R.C., 1978. Fate of liquid ammonia spilled onto water. *Environ Sci Technol* 12 (13), 1422–1425. <https://doi.org/10.1021/es60148a008>.
- [53] Rathore, S.S., Biswas, S., Fini, D., Kulkarni, A.P., Giddey, S., 2021. Direct ammonia solid-oxide fuel cells: a review of progress and prospects. *Int J Hydron Energy* 46 (71), 35365–35384. <https://doi.org/10.1016/j.ijhydene.2021.08.092>.
- [54] Rausand, M., 2013. Risk assessment: theory, methods, and applications. John Wiley & Sons.
- [55] Saltelli, A., Ratto, M., Tarantola, S., Campolongo, F., 2006. Sensitivity analysis practices: strategies for model-based inference. *Reliab Eng Syst Saf* 91 (10-11), 1109–1125. <https://doi.org/10.1016/j.ress.2005.11.014>.
- [56] Sargent, R.G., 2010. Verification and validation of simulation models. Proceedings of the 2010 winter simulation conference. IEEE, pp. 166–183. <https://doi.org/10.1109/WSC.2010.5679166>.
- [57] Seddiek, I.S., Ammar, N.R., 2023. Technical and eco-environmental analysis of blue/green ammonia-fueled RO/RO ships. *Transp Res Part D: Transp Environ* 114, 103547. <https://doi.org/10.1016/j.trd.2022.103547>.
- [58] Stoffen, P.G. Guidelines for quantitative risk assessment. Ministerie van Volkshuisvesting Ruimtelijke Ordening en Milieu, CPR 18E; 2005.
- [59] Trivza, N.L., Cheliotis, M., Boulougouris, E., Theotokatos, G., 2021. Safety and reliability analysis of an ammonia-powered fuel-cell system. *Safety* 7 (4), 80. <https://doi.org/10.3390/safety7040080>.
- [60] US EPA, 2022. Access Acute Exposure Guideline Levels (AEGLs) Values. US Environmental Protection Agency. (<https://www.epa.gov/aegl/access-acute-exposure-guideline-levels-aegls-values#chemicals>).
- [61] Valera-Medina, A., Xiao, H., Owen-Jones, M., David, W.I., Bowen, P.J., 2018. Ammonia for power. *Prog Energy Combust Sci* 69, 63–102. <https://doi.org/10.1016/j.pecs.2018.07.001>.
- [62] Vesala, T., Kukkonen, J., 1992. A model for binary droplet evaporation and condensation, and its application for ammonia droplets in humid air. *Atmos Environ Part A Gen Top* 26 (9), 1573–1581. [https://doi.org/10.1016/0960-1686\(92\)90057-R](https://doi.org/10.1016/0960-1686(92)90057-R).
- [63] Wang, B., Chen, B., Zhao, J., 2015. The real-time estimation of hazardous gas dispersion by the integration of gas detectors, neural network and gas dispersion models. *J Hazard Mater* 300, 433–442. <https://doi.org/10.1016/j.jhazmat.2015.07.028>.
- [64] Witlox, H.W., Fernandez, M., Harper, M., Stene, J., 2017. Modelling and validation of atmospheric expansion and near-field dispersion for pressurised vapour or two-phase releases. *J Loss Prev Process Ind* 48, 331–344. <https://doi.org/10.1016/j.jlp.2017.05.005>.
- [65] Witlox, H.W., Fernández, M., Harper, M., Oke, A., Stene, J., Xu, Y., 2018. Verification and validation of Phast consequence models for accidental releases of toxic or flammable chemicals to the atmosphere. *J Loss Prev Process Ind* 55, 457–470. <https://doi.org/10.1016/j.jlp.2018.07.014>.
- [66] Yadav, A., Jeong, B., 2022. Safety evaluation of using ammonia as marine fuel by analysing gas dispersion in a ship engine room using CFD. *J Int Marit Saf Environ Aff Shipp* 6 (2-3), 99–116. <https://doi.org/10.1080/25725084.2022.2083295>.
- [67] Yang, M., Lam, J.S.L., 2023. Operational and economic evaluation of ammonia bunkering–Bunkering supply chain perspective. *Transp Res Part D: Transp Environ* 117, 103666. <https://doi.org/10.1016/j.trd.2023.103666>.
- [68] Yang, M., Ng, C.K.L., Liu, M., 2022. Ammonia as a marine fuel - bunkering, safety and release simulations. Maritime Energy and Sustainable Development Centre of Excellence. Nanyang Technological University..
- [69] Zhang, Y., Lam, J.S.L., 2016. Estimating economic losses of industry clusters due to port disruptions. *Transp Res Part A: Policy Pract* 91, 17–33. <https://doi.org/10.1016/j.tra.2016.05.017>.
- [70] Zhang, Y., Wei, K., Shen, Z., Bai, X., Lu, X., Soares, C.G., 2020. Economic impact of typhoon-induced wind disasters on port operations: a case study of ports in China. *Int J Disaster Risk Reduct* 50, 101719. <https://doi.org/10.1016/j.ijdr.2020.101719>.