Risk Assessment of Ammonia Fueled Ships

Consequences on Human Health of Ammonia Releases from Damaged Fuel Storage Tanks

Masia, Benedetta; Yang, Ming; Cozzani, Valerio

DOI
10.1021/acs.chas.4c00044

Publication date
2024

Document Version
Final published version

Published in
ACS Chemical Health and Safety

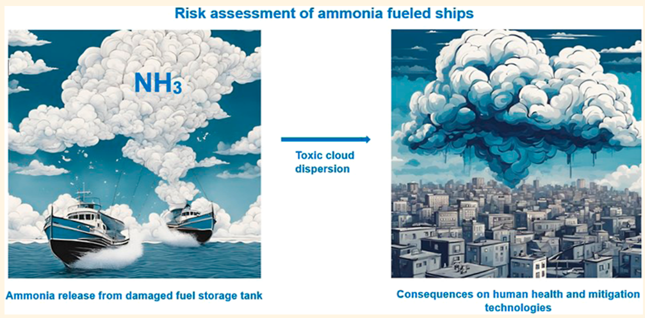
ACS CHEMICAL HEALTH & SAFETY

pubs.acs.org/acschas Article

Risk Assessment of Ammonia Fueled Ships: Consequences on Human Health of Ammonia Releases from Damaged Fuel Storage Tanks

Benedetta Masia, Ming Yang,* and Valerio Cozzani

Cite This: https://doi.org/10.1021/acs.chas.4c00044 Read Online



ABSTRACT: Ammonia is a promising fuel for decarbonizing the shipping industry, but its safety compared to traditional maritime fossil fuels remains questionable. As more projects explore ammonia-fueled vessels, safety concerns, particularly the acute toxicity and risks of ammonia release, are paramount. This research focused on the effects of accidental ammonia releases during ship-to-ship collisions, affecting ammonia tank integrity. We examined various release scenarios, considering factors like tank types and locations, breach sizes and positions, weather conditions, and dispersion patterns, using PHAST software for modeling. Results indicated that semipressurized tanks pose greater health risks on human health than fully refrigerated ones. Underwater releases are less hazardous, as a significant amount of ammonia dissolves before surfacing. Mitigation efforts, such as water curtains and containment basins, were evaluated for their effectiveness in minimizing the impact of ammonia releases. These measures significantly reduce risks to nearby populations but are less effective for crew safety onboard. This underscores the challenge of ensuring onboard safety in ammonia-fueled vessels, highlighting the need for innovative and effective safety design.

KEYWORDS: *ammonia toxicity, ammonia-fueled vessel, mitigating measures, ammonia underwater releases, lethality footprints, probability of death*

1. INTRODUCTION

Ammonia serves as a crucial carrier of hydrogen and energy, instrumental in meeting the Paris Agreement's 2050 climate neutrality objective through its potential to significantly reduce greenhouse gas (GHG) emissions, owing to its lack of carbon. This underscores the International Maritime Organization's (IMO) dedication to fulfilling the Paris Agreement's aims. The IMO advocates for the adoption of low and zero-carbon fuels, positioning ammonia as a viable option for marine propulsion.[1,2] This study investigates the safety aspects of using ammonia in marine settings, in line with the IMO's goals to reduce GHG emissions from international shipping by at least 20% by 2030 and 70% by 2040, relative to 2008 figure.[3]

Ammonia offers several advantages as a fuel within the maritime transport sector, beyond its lack of CO_2 production upon oxidation. It is versatile, being applicable in various combustion engines and fuel cells. Additionally, its storage and transportation are relatively straightforward, and it is already produced on a large scale, mostly for fertilizer production. However, the current methods of ammonia production from fossil fuels (mostly from natural gas and coal) are associated with high GHG emissions, as the creation of green ammonia on a grand scale incurs significant operational expenses (approximately four times that of LNG).[4] Furthermore, ammonia high toxicity necessitates costly mitigation measures.[5,6] It is also important to consider that emissions from ammonia-powered engines could disrupt the global nitrogen cycle due to the release of NOx and N_2O.[7−10] Also consider that N_2O is a very powerful GHG. Depending on its emission rate during combustion, ammonia could have very different impacts on climate.[10] Despite these challenges, ammonia has the potential to significantly benefit environmental health when produced using renewable energy sources, offering a path to fully decarbonize the shipping industry.

The primary concerns about the use of ammonia as an energy carrier revolve around the field of safety: ammonia is extremely toxic, and it can affect both human and environmental health. Therefore, it is important to analyze the

Received: May 21, 2024
Revised: August 21, 2024
Accepted: August 28, 2024

consequences that an ammonia release from a ship could generate. On land, ammonia releases are known to be dramatic. For example, in 1992 the country of Senegal experienced one of the worst ammonia releases ever happened. Twenty-two tonnes of liquefied ammonia were released through a two-phase flow. A dense vapor cloud spread over a significant distance causing 129 fatalities and 1150 injuries resulted from the inhalation of ammonia at high concentrations.[11]

The main aim of this study is the assessment of the effects that a naval collision could generate on an ammonia fueled vessels. Clearly enough, collisions could cause severe damage to ammonia fuel storage tanks causing hazardous ammonia releases. However, there are multiple influencing factors on the estimation of such consequences: the type and location of the ammonia storage tanks, the location of the vessel itself and the stability class of the atmosphere at the exact release moment. There are several studies addressing onshore ammonia releases, but only a few addresses offshore releases. The present study focused on underwater—ammonia releases, also considering ammonia dissolution in water.

2. METHODOLOGY

The methodology applied is schematically summarized in the diagram shown in Figure 1. For the purpose of this study, first

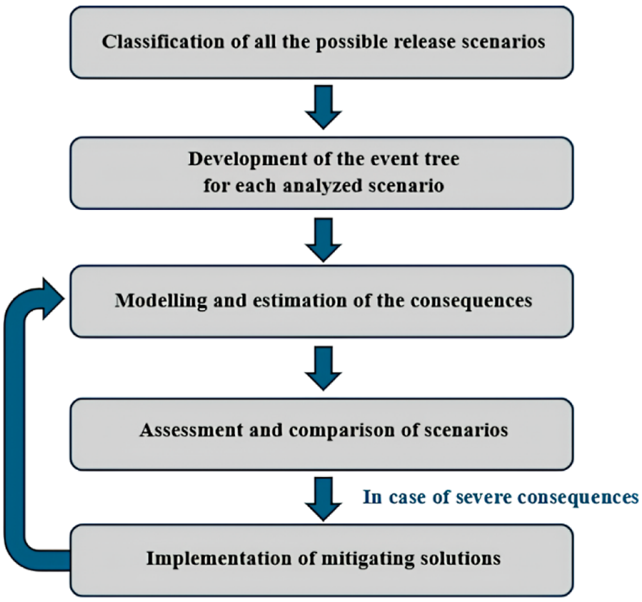


Figure 1. Flowchart of the procedure.

it was necessary to classify all the possible scenarios considering different types of tanks, positions of the tank on the vessel, hole sizes and hole positions on the tank itself. Second, event trees were produced for each scenario in order to consider all the possible accident outcomes. All scenarios were then modeled using the integral models included in the PHAST 8.4 software tool. The results obtained are then assessed with the aim to understand which is the worst-case scenario and which mitigating technologies could reduce the severity of consequences. As a final step, mitigating measures were implemented and the worst-case scenarios were remodeled to evaluate the efficiency of the technologies proposed.

In the context of ammonia-fueled ships, it is feasible to employ either fully refrigerated (FR) tanks (where ammonia is stored at −33.2 °C under atmospheric pressure) or semi-pressurized (SP) tanks (with ammonia stored at 10.4 °C and 6.2 bar) as fuel storage solutions.[12] It has been assumed that a handy-sized gas carrier would need approximately 2700 m^3 of ammonia to use as fuel for a journey of about 12,000 nautical miles. Regardless of the type, it has been assumed that the 2700 m^3 can be divided into three tanks, each containing a volume of around 1000 m^3 (the total energy content is approximately 12,000 GJ), with a diameter estimated to be 7 m and a length of 36 m.[13] Fuel storage tanks can be located both above and below the deck (inside the hull), determining two possible minimum release heights: respectively 15 and 3 m above seawater level. The location of the tanks is extremely important since it can lead to different scenarios. If the tank is located below the deck, inside the hull, there could be a specific rate of containment of the liquefied release. The degree of containment is important since, in case of release, an amount of ammonia may be constrained in the interhull of the ship, not dispersing into the air. Differently, if the tank is on the deck, there is no rate of containment and all the ammonia released will fall into the seawater.

Overall, four main cases were analyzed:

- SP fuel tank above deck,
- SP fuel tank below deck inside the hull,
- FR fuel tank above deck,
- FR fuel tank below deck inside the hull.

To explore a broad spectrum of potential outcomes, the assumption was made that a collision could lead to various forms of damage to the tanks. Specifically, in the case of ammonia tanks situated on the vessel deck, only a single release scenario was envisaged. Actually, the occurrence of a bow striking at such a height as to damage a deck-positioned tank on the impacted vessel is quite rare; thus, only a catastrophic rupture was deemed credible. A catastrophic rupture invariably leads to a complete loss of containment (LOC), with the release of ammonia into seawater, considered the most severe outcome. In fact, ammonia release forming a boiling pool on the water surface is more hazardous than the case of the release on a solid surface, such as steel. This is because the ammonia boil-off rate from a water surface pool is significantly higher, due to both the higher heat transfer coefficient and to the heat generated by the exothermic reaction of ammonia dissolving in water, which accelerates the vaporization of the ammonia more effectively than thermal conduction with solid ground. If ammonia forms a boiling pool entirely on the deck, the primary heat source for vaporization is the temperature difference between the pool ($T_{pool} = T_{nb}$) and the vessel's floor,[14] although heat transfer from air is also present. Thus, the heat transfer is assumed to be solely through conduction. The temperature of the ammonia boiling pool remains constant at −33 °C, whereas the temperature of the steel varies over time. Initially, the steel temperature equals that of the surrounding air. As the pool continues to boil, the metal surface cools down, reducing the contribution of heat transfer by conduction along with the boil-off rate. Over time, the heat transferred through conduction with steel decreases, while the heat transfer with water remains constant.

The case of ammonia fuel tanks below deck within the hull is different: it was interesting to investigate the consequences of releases from various hole sizes that could be generated by a

Table 1. Classification of all the Release Scenarios Considered

release scenario	tank type (FR or SP)	tank position	leak position vs water line	hole size	leak position vs ammonia level
A	fully refrigerated	on deck		catastrophic rupture	
B	fully refrigerated	inside hull	above WL	catastrophic rupture	
C	fully refrigerated	inside hull	above WL	250 mm	→below AL
D					→above AL
E	fully refrigerated	inside hull	above WL	750 mm	→below AL
F					→above AL
G	fully refrigerated	inside hull	below WL	catastrophic rupture	
H	fully refrigerated	inside hull	below WL	250 mm	→below AL
I					→above AL
J	fully refrigerated	inside hull	below WL	750 mm	→below AL
K					→above AL
L	femipressurized	on deck		catastrophic rupture	
M	semipressurized	inside hull	above WL	catastrophic rupture	
N	semipressurized	inside hull	above WL	250 mm	→below AL
O					→above AL
P	semipressurized	inside hull	above WL	750 mm	→below AL
Q					→above AL
R	semipressurized	inside hull	below WL	catastrophic rupture	
S	semipressurized	inside hull	below WL	250 mm	→below AL
T					→above AL
U	semipressurized	inside hull	below WL	750 mm	→Below AL
V					→above AL

collision on an ammonia tank. It is necessary to underline that the breach on the tank was assumed circular, even though it would have been more plausible to assume rectangular openings. There are various databases containing information about actual damages to the hull of the ship due to collisions;[15] but it is still a challenge to describe the relationship which correlates the size of the breach on the hull with that on fuel tanks. In view of the above considerations, assumptions on the hole sizes were made and only releases from the following equivalent hole diameters were analyzed:[16]

- 250 mm—maximum credible puncture hole,
- 750 mm—maximum credible hole from accidental events,[17]
- catastrophic rupture of the tank.

Another important aspect is the position of the hole in the tank. Indeed, this choice directly affects the ammonia mass outflow rate and can generate completely different outcomes. Two possibilities were analyzed:

- Release from the bottom of the tank (assumed at 0.5 m from the bottom); it means that there is a hydrostatic pressure induced by the volume of liquefied ammonia above the opening.
- Release from the head of the tank; it means that the breach is in the gaseous phase of the tank above the ammonia level (imagining the rate of fulfillment of 80%). The ammonia level is calculated to be at about 4.7 m; therefore, the hole above ammonia level was assumed to be at 5 m from the bottom of the tank.

One last consideration for tanks inside the hull concerned the position of the breach compared to the seawater line. An additional distinction, which can lead to completely different scenarios, was made: both ammonia releases above water level and underwater were considered. Table 1 shows all the scenarios that were modeled using the PHAST 8.4 software applying all the assumptions discussed.

Since one of the main aims of this study is to understand how atmospheric and environmental conditions can influence the consequences of a release, all the release scenarios were modeled varying two parameters:

- Weather conditions (typical for Rotterdam). The aim was to compare the consequence of a release occurring during the day and at night. It was of interest to evaluate the influence of weather stability and wind speed. Day and night were modeled assuming the parameters listed in Table 2.

Table 2. Comparison between Day and Night Atmospheric Conditions

	day (5D)	night (1.5F)
air temperature	12 °C	8 °C
water temperature	10 °C	10 °C
humidity	80%	90%
solar radiation flux	0.25 kW/m^2	0
Pasquill stability class	D	F
wind speed	5 m/s	1.5 m/s

Location of the release—dispersion surface. The scenarios were modeled considering the cloud dispersion both on seawater and land. The land, hypothetically represented by the Port of Rotterdam, was modeled with a high surface roughness (3 m), while the open sea was characterized by 0.2 m of roughness. The land hypothetically represents the port of Rotterdam, around which it is imagined that the population resides. These two locations are also different by the number of people that could be impacted by the consequences of the accident scenario. The main interest was to analyze the influence of surface roughness on the dispersion of the ammonia toxic cloud.

In the modeling of above water scenarios, PHAST 8.4 is capable of accounting the fraction of ammonia dissolving in

https://doi.org/10.1021/acs.chas.4c00044
ACS Chem. Health Saf. XXXX, XXX, XXX−XXX

water from the pool and calculating the heat released through this exothermic reaction.[18] Additionally, PHAST considers this heat contribution either into the pool vaporization or the heating of the toxic cloud. This is particularly useful since the mass of ammonia dissolving is generally high and not negligible as well as the heat produced by the ammonia dissolution in water. Release scenarios from semi pressurized tanks are generally modeled as flash clouds or flashing jets, while those from refrigerated tanks are generally described as time varying liquid discharges. The only assumptions made is that for scenarios C and E it is possible to consider that 20% of the liquefied ammonia discharged is constrained inside the hull.

It should be remarked that PHAST cannot simulate underwater scenarios. Thus, specific assumptions were introduced to determine an amount of toxic substance reaching the water surface and dispersing.[19,20] When an ammonia tank is damaged underwater, depending on the relative pressure, it is necessary to consider that instead of an ammonia outflow, there could be a water inflow inside the tank. It would be extremely interesting to determine how the pressure inside the tank changes, considering that the reaction of dissolution determines an increase of temperature and pressure inside the tank, which could even explode. However, the analysis of this scenario is beyond the scope of the work.

The key assumptions introduced to model the underwater release scenarios are discussed below.

2.1. Scenario G. A hypothetical catastrophic rupture of a FR tank inside the hull below the water level causes the underwater release of the whole amount of liquefied ammonia stored. It is necessary to consider both the reaction of dissolution of ammonia with water and the vaporization of the remaining liquid part. In particular, it is assumed that 70% of the total amount released dissolves. This is a typical value suggested in the literature for the evaluation of ammonia dissolution in water. The remaining 30% represents the quantity of ammonia vaporized underwater. Nevertheless, 10% of the vaporized ammonia consists of bubbles that can dissolve in water before reaching the surface. The amount of ammonia vapors that reach the water surface creates a toxic cloud, whose consequences need to be estimated through the PHAST software. The assumption of immediate underwater ignition was neglected since ammonia is more reactive with water. The reaction of dissolution reduces the availability of free ammonia molecules that could participate in combustion reactions.

2.2. Scenarios H and J. In these scenarios, the hull space due to the collision is quickly filled with water, as well as the storage tank. The seawater inflows inside the atmospheric tank through the hole because the pressure inside the FR tank is lower than the hydrostatic pressure of the seawater outside. When water enters the tank, it reacts with ammonia with an exothermic reaction. This heat source induces the vaporization of ammonia. The main assumption is that the reaction between ammonia and water proceeds completely inside the tank. The generation of bubbles and vapors inside the tank leads to an increase of pressure. The increase of pressure may enlarge the hole, but it is unlikely that this would affect the equivalent diameter of release, since the tank is normally capable of withstanding 8 bar internal pressure. When the pressure becomes higher than the hydrostatic external pressure, an outflow of gaseous ammonia starts. However, since the hole is located at the bottom of the tank (0.5 m), it is possible that ammonia vapors remain in the head of the tank and that the outflow is mainly caused by ammonia dissolved in water. Since it is expected that an underwater release of ammonia dissolved in water takes place, it was assumed that only 10% of the total ammonia stored vaporizes and reaches the surface, neglecting the possible bubble dissolution.

2.3. Scenarios I and K. In these scenarios, the seawater inflows inside the tank because the pressure inside the tank is lower than the hydrostatic pressure outside. When water enters the tank, it reacts with ammonia with an exothermic reaction. This heat source induces the vaporization of ammonia. The generation of bubbles and vapors inside the tank leads to an increase of pressure. When the pressure becomes higher than the hydrostatic external pressure, an outflow of ammonia starts. Again, if the tank resists the increase of pressure, there is an outflow of ammonia through a jet. If the tank fails, a catastrophic rupture may occur, and these scenarios become identical to scenario G. In i of a jet, the outflow of ammonia can be assumed mainly due to bubbles since the hole is on the head of the tank. Basically, the only difference with scenarios H and J is that the hole is located in the head of the tank (5 m). Therefore, it is expected that a higher fraction of vaporized ammonia can outflow and reach the surface. The value assumed is 20%.

2.4. Scenario R. When an underwater release takes place from a semi pressurized tank, the pressure inside the tank is higher than the hydrostatic pressure. Thus, ammonia outflow is always expected. In this scenario, an underwater flash occurs since there is a catastrophic rupture of the tank. It is necessary to consider that a fraction of ammonia immediately flashes and surfaces leaving the water, a fraction dissolves in water and the remaining vaporizes thanks to the heat of dissolution generated by the reaction. The fraction flashed is assumed equal to the one of the corresponding scenarios above water level (M). The fractions of liquid ammonia dissolved and bubbles dissolving while rising are assumed equal to those of scenarios from FR tanks, respectively 0.7 and 0.1.

2.5. Scenarios S, T, U, V. These scenarios are all described by underwater flashing jets with different amounts of ammonia vapor depending on the location and size of the breach on the tank. Indeed, the pressure inside the tank (6 bar) is higher than the hydrostatic pressure of the seawater. Thus, it was always assumed to be an ammonia outflow and not a water inflow. The only difference with scenario R is that the release is continuous and not instantaneous. Therefore, the values assumed for the fraction of ammonia flashed and dissolved are expected to be different. The following assumptions were made:

- Scenario S: the fraction flashed was chosen equal to 60% of the total mass stored in the tank. This value was chosen lower than that of the corresponding case above water level (scenario N). Actually, when the release is above water, the total amount of mass flashed considers also the fraction vaporized during the fall, from the vessel into the water, which is not present in this case.
- Scenario U: the percentage chosen to identify the flash is 50%, specifically lower than case S since the hole in scenario U is bigger. Actually, it is expected to notice a higher fraction of vaporization in those scenarios characterized by smaller hole dimensions.
- Scenarios T and V: these scenarios are characterized by a hole in the tank above ammonia level. The fraction of ammonia flashed was assumed equal to the one of the

https://doi.org/10.1021/acs.chas.4c00044
ACS Chem. Health Saf. XXXX, XXX, XXX−XXX

corresponding scenarios above water. It is expected that, after an immediate ammonia release determined by the pressure drop, a water inflow begins. The reaction of dissolution is imagined completely conducted inside the tank; the assumption is that 80% of the remaining mass inside the tank dissolves, as for scenario I.

3. UNMITIGATED CONSEQUENCE OF THE ABOVE-WATER RELEASE SCENARIOS

3.1. General Considerations. Pool formation on water: influence of release height, weather conditions and dispersion surface on the initial mass of the boiling pool.

A first consideration regards the amount of ammonia forming the boiling pool on the water surface. The main hypothesis behind the catastrophic rupture of a FR tank is that the whole ammonia stored in the tank (680,000 kg) is discharged into the sea and creates a boiling pool. The PHAST software starts the modeling of the boiling pool considering an initial ammonia mass of 640,000 kg approximately. This implies that a fraction of liquefied ammonia vaporizes before reaching the water surface. The release height of 15 m above seawater level implies that ammonia falls for 15 m before reaching the water. It may be assumed that a small percentage of liquefied ammonia vaporizes (~6%) thanks to the heat provided by the contact with air. Sometimes the fall is shorter since the release height is only 3 m above sea level (a.s.l.) and, consequently, the amount of ammonia vaporized while falling is assumed to be lower (~4%). This consideration is also valid when the catastrophic rupture regards SP tank. It is more difficult to evaluate the percentage vaporized during the fall since it is mixed with the volume of ammonia flashed. In several scenarios it is possible to observe a difference in the amount of ammonia vaporized during the fall between day and night, and consequently a different amount of initial mass of the boiling pool on water. This may be explained since during the day, the air has a higher temperature, and the atmospheric conditions are generally more turbulent. These factors lead to a higher ammonia vaporization rate during the drop from the vessel in daily hours. This phenomenon is more evident in the case of continuous discharge rather than in the case of catastrophic rupture. For example, it may be considered scenario N (dispersion over water): during the day there is no pool formation since the whole amount released flashes and vaporizes during the fall, while during the night a rained-out pool is formed.

One last consideration regards the influence of the dispersion surface on the mass vaporized during the fall. This influence is particularly evident in scenarios of continuous releases from SP tanks (scenario N or P). In particular, it is noticeable that the mass forming the rained-out pools is much higher when the dispersion occurs on land. It is expected that the ammonia mass flashed does not vary with the dispersion surface since it is only a function of the storage properties inside the tank. Consequently, the different mass vaporized during the fall is the explanation behind the different mass of the pools. It is worth nothing that the formation of an aerosol during the fall is not considered. This results that the greater the roughness, the lower the mass vaporized during the fall. The presence of buildings on land contributes to the wind shadow effect: basically, the wind is partially reduced and the droplets of ammonia falling from the vessel are less induced to their vaporization. Overall, the rained-out pools contain more ammonia when the dispersion surface is the land since the vaporization during the fall is partly discouraged. The consequences tend to be more severe when there is a higher portion of ammonia vaporized; therefore, it is preferable to notice a higher mass of ammonia forming a pool. The wind shadow effect on land can be a positive phenomenon for the toxic cloud dispersion. Indeed, structures provide a buffer against wind, reducing its speed, and allowing more time for the ammonia cloud to warm up. When the ammonia cloud is heated up, it tends to disperse more vertically, reducing the effects of its toxicity on the population.

3.2. Pool Vaporization and Solution Rates: Weather Influence. Weather conditions have a strong influence on the ammonia dissolution and vaporization rate. In particular, it is possible to compare the intensity of vaporization and dissolution during day and night. Table 3 collects data obtained from scenario A (chosen as example) modeled considering dispersion over water; similar results were obtained for most of the cases.

Table 3. Data from Scenario A: Dispersion over Seawater

	mass vaporized [kg]	mass dissolved [kg]	maximum mass vaporization rate [kg/s]	maximum solution rate [kg/s]	time for the pool to extinguish [s]
day (5D)	240,000 (37%)	405,000 (63%)	2350	4700	190
night (1.5F)	330,000 (51%)	315,000 (49%)	1500	1600	400

Both ammonia mass vaporization rate and solution rate in water are higher during the day (5D). This explains why during the night (1.5F) the pool on water takes almost double the time to completely dissolve/vaporize. The day is characterized by higher wind speed, air temperature, radiation flux and turbulence; all these factors favor the vaporization. Even though the mass vaporization rate is higher during the day, the total amount of ammonia vaporized tends to be higher during the night. This is because during the day the solution rate itself is higher than the mass vaporization rate, and a higher amount of ammonia rapidly dissolves into the seawater. The fact that the maximum solution rate is higher during the day could be explained considering that the high wind speed promotes the mixing of ammonia and water. This turbulence, typical of the day could be a favorable factor for the increase of ammonia solubility and could explain why the solution rate is lower during the night, which is not characterized by so much wind. Moreover, typically the concentration of ammonia in air is higher during the day, inducing a higher ammonia partial pressure. This could represent a driving force for ammonia to dissolve in water until equilibrium is reached. Further studies could be helpful to explain why the solution rate is higher during the day, considering that the same water temperature has been considered for day and night, thus the variation is not related to the variation of solubility with temperature. Overall, it is possible to notice that the total ammonia mass vaporized tends to be higher during the night.

3.3. Dispersion of Ammonia: Heavy Gas Dispersion. Studying the height of the cloud while dispersing after the release from FR tanks, it is possible to demonstrate that ammonia disperses as a heavy gas when the cloud is mainly produced by a boiling pool on the water surface. Actually, as the models and past experiments suggest, the boiling pool vaporizes absorbing heat provided by the surroundings. This leads also to the condensation of water vapors and could determine the cool down of the remaining liquid. The low temperatures and the possible presence of water or ammonia droplets determine a heavy dispersion of the cloud. What's more important, it is well-known that ammonia reacts with water, and it is possible to imagine that the reaction could happen also between ammonia vapors and water present in the air. This reaction could possibly form a mist of ammonium hydroxide, which is heavier than dry ammonia gas. This could be an additional explanation behind the heavy gas dispersion of ammonia. PHAST confirms that there is no elevation of the cloud from the ground. It is possible to demonstrate that also the dispersion of a cloud generated from the catastrophic rupture of a SP tank proceeds like heavy gas dispersion. It is necessary to remark that the same result has been achieved across all the scenarios. Basically, also in this case ammonia disperses like a heavy gas and the cloud is always attached to the ground. The cloud in this case is formed through a flash. Liquid ammonia rapidly vaporizes due to the pressure drop leading to a cooling effect of the cloud. The cloud results colder and heavier than air and, while dispersing, it can also lead to the condensation of some water vapors, which make the cloud even heavier. The heavy gas dispersion turns into a passive dispersion only in a few scenarios characterized by a hole in the gaseous phase of the tank. Scenarios D, F, O and Q are characterized by a low ammonia mass released, mainly made of ammonia vapors without droplets. Therefore, the heating of these clouds is favored. The cloud dispersion in all the other above water scenarios evolves as a heavy gas cloud at ground level. This increases the severity of the potential consequences of ammonia releases.

3.4. Influence of the Height of Release. The accident scenarios are modeled considering mainly two release heights: 15 and 3 m above seawater level. This parameter has a strong influence on the severity of consequences. Among all those analyzed, there are some scenarios that are comparable, since they are characterized by the same amount of ammonia released and release time, while they only differ in the release height: A−B and L−M. Data about the lethality footprint (0.1% ammonia concentration is considered) is collected in the below Table 4 in order to facilitate comparisons. The decision to evaluate the lethality footprint at 0.1% arises from the highly toxic nature of ammonia. Its colorless and pungent odor pose significant challenges in effectively mitigating the consequences of an ammonia release. The concentration limit used is the immediately dangerous to life or health (IDLH) level, this value for ammonia is equal to 300 ppm. Exposure to ammonia must be limited to permissible limits to guarantee the safety of the staff on the ammonia fueled ships and of the population living in the vicinity of the release site. If the ammonia concentration is above certain thresholds, even though for short exposure times, it may cause serious reversible and not injuries. At low concentration ammonia can irritate eyes and skin, while at high concentration ammonia is a threat for human life.

Table 4. Collection of Data—Lethality Footprint 0.1%

scenario: dispersion surface + release height	lethality footprint 0.1% day (5D) [m^2]	lethality footprint 0.1% night (1.5F) [m^2]
A: on water, 15 m	7.68×10^5	8.24×10^5
A: on land, 15 m	3.8×10^5	1.79×10^6
B: on water, 3 m	7.64×10^5	6.64×10^5
B: on land, 3 m	3.93×10^5	1.79×10^6
L: on water, 15 m	8.24×10^6	1.15×10^7
L: on land, 15 m	6.5×10^5	2×10^6
M: on water, 3 m	3.77×10^6	5.31×10^6
M: on land, 3 m	4.82×10^5	1.22×10^6

The lethality footprints tend to be larger during the night. As previously explained, the ammonia solution rate is so high during the day that ammonia tends to dissolve instead of vaporizing. Differently, during the night the solution rate is lower, and the total mass of ammonia vaporized is higher. Consequently, during the night there is a higher amount of ammonia dispersing in air, causing broader lethality footprints. Regarding the influence of the release height, it results that the lethality footprints for release heights of 15 m are larger than those at 3 m, irrespective of the type of tank, dispersion surface or weather conditions. This is mainly because of the following facts:

- When the release height is lower, the rained-out fraction is higher, and a lower quantity of ammonia is released into the atmosphere. Actually, a lower amount of ammonia vaporizes during the fall since the drop distance (from the vessel to seawater) is smaller.
- When the release height is higher, ammonia has more time to mix with air; while descending, ammonia concentration is more and more diluted. A higher release height induces a potential threat to a broader region while a lower release height can create a cloud with higher concentrations but less dispersing. Actually, a release close to the ground can be easily blocked by obstacles determining a smaller impact area. On the other side, a higher release can bypass many obstacles allowing the cloud to disperse further before descending.
- When the release height is lower, the cloud of ammonia vaporized during the flash or during the fall is closer to the dispersion surface. For example, since a high amount of heat is generated from the reaction of ammonia and water, if the cloud is closer to the surface, it gains more heat and tends to become lighter and disperse more vertically. This vertical dispersion results in a smaller lethality footprint for scenarios B and M, since the toxicity height of interest is 1.5 m for humans.

It is possible to conclude that an increase in release height is correlated with a broader dispersion area of the cloud, determining a larger lethality footprint 0.1%. A wider lethality footprint does not always imply a higher probability of death (PoD), but in these cases, it is confirmed that scenario A and L have higher PODs than scenario B and M. Actually, A and L are characterized by a higher percentage of total ammonia vaporized due to the higher distance of the falling from the vessel into the sea.

A final consideration regards the fact that the difference between scenarios L and M is more pronounced than that between scenarios A and B. This means that the release height has a stronger influence when the release is from SP tanks. Actually, the total mass vaporized from scenarios A and B is almost the same (slightly higher for scenario A), while there is a significant difference in the amount vaporized between scenarios L and M. In particular, the main difference is the quantity of ammonia vaporized during the fall or from the droplets. This is marginally higher in scenario L. The main

https://doi.org/10.1021/acs.chas.4c00044
ACS Chem. Health Saf. XXXX, XXX, XXX−XXX

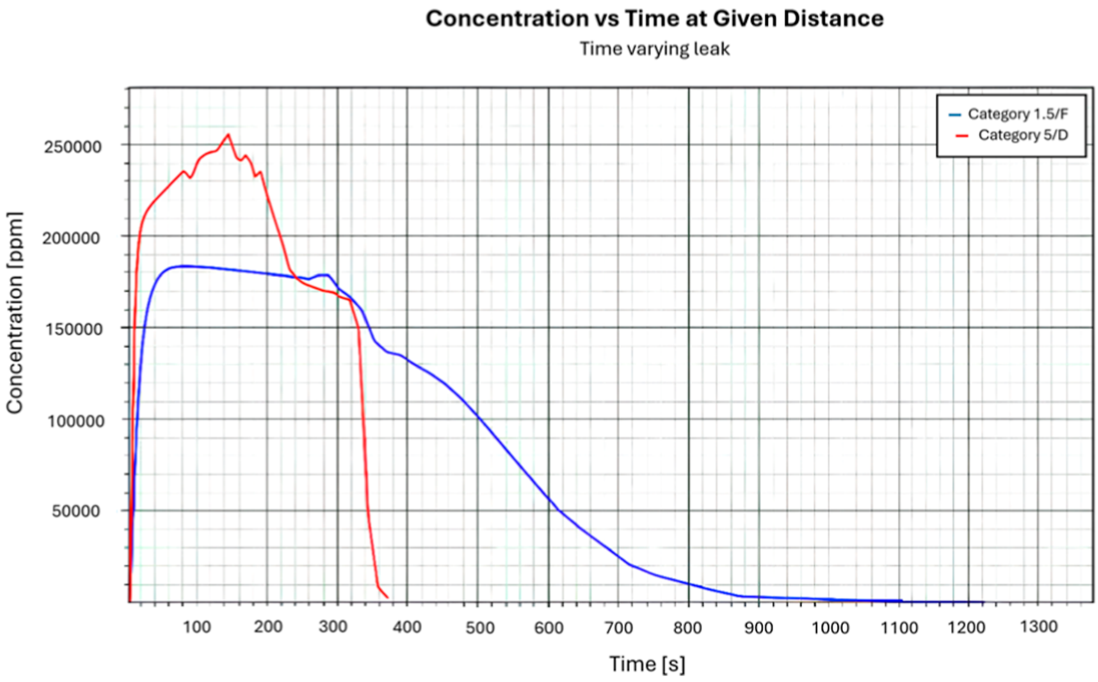


Figure 2. Concentration vs time dispersion on land—scenario E.

reason could be that when a catastrophic rupture regards a SP tank, an aerosol with a high percentage of droplets is formed. These droplets have more time to vaporize when the release is from 15 m (a.s.l.). On the other hand, if the catastrophic rupture is from a FR tank, vaporization regards only the rained-out pool which is falling. The release height has a stronger impact on the vaporization of droplets stuck in the aerosol than on the rained-out pool falling, since it is easier to heat small droplets than a liquefied ammonia pool with greater dimensions.

3.5. Dispersion on Land. The PoD at any distance from the release source tends to be always higher during the night when the dispersion of the toxic cloud occurs over land. This is due to the sum of different contributions: first, most scenarios are characterized by a higher total mass of ammonia vaporized during the night, due to the lower ammonia solution rate. Only a few scenarios are described by a higher percentage of ammonia vaporized during the day. The PoD is still higher during the night since the high wind speed and turbulence, typical of the day (5D), helps the dispersion and dilution of the cloud. Actually, when the dispersion is on land, the contribution of the high surface roughness (3 m) becomes more evident: the presence of obstacles like buildings and structures blocks the spreading of the cloud, leading to areas of higher concentration. Favorable conditions for dispersion occurring during the day, such as increased wind speed and vertical mixing, encourage the decrease of toxic concentrations over long distances. On the other hand, the high atmospheric stability during the night limits the spread and dispersion of the toxic cloud. Basically, ammonia vapors are stuck in a stable boundary layer, which can trap pollutants close to the ground. What's more, the presence of buildings can obstruct wind flows and create areas where air is stagnant, allowing for the accumulation of toxic substances. Therefore, the stable weather of the night combined with the elevated surface roughness and the low wind speed explains why the PoD is higher during the night if the cloud disperses over land, even for those few scenarios with a total mass of ammonia vaporized higher. Even though it has not been taken into account in the modeling, it is important to highlight that during the night not only the physics of the ammonia release but also the difficulty in seeing the dispersion might affect the human response, increasing the risk.

Scenario E represents an interesting example: ammonia concentration in air can be higher during the day in the vicinity of the release source. However, at higher distances from the source, the toxic concentration dilutes thanks to the favorable daily weather conditions (Figure 2). On the other hand, during the night the ammonia concentration tends to be higher due to the combination of high atmospheric stability, lower wind speed and wind shadow effect. Overall, when the dispersion occurs on land, the PoD is higher during the night in the whole range of distances from the release point. This consideration is valid for the whole range of scenarios from SP and FR tanks.

3.6. PoD: Surface Roughness Influence-Comparison Land Versus Water. There are some noticeable characteristics about the dispersion of a toxic cloud common to almost all the scenarios with FR and SP tanks. The dispersion surface is important since the roughness has a direct impact on the cloud dispersion. In particular, the port of Rotterdam was modeled considering a surface roughness of 3 m while the open seawater surface with 0.2 mm. From the results obtained and collected in the previous tables, it results that the PoD at a fixed distance tends to be always higher when the dispersion occurs over the seawater surface. This was an unexpected result since usually the concentration decreases slower over land due to the presence of buildings, which are obstacles to the dispersion. The dispersion on water, where there are no obstacles, typically lets the toxic concentration dilute easily. Against expectations, from the results obtained, it seems that the dispersion over land is more efficient than the one over water. An explanation could regard the fact that ammonia disperses like a heavy gas, and its dispersion is influenced both by wind speed and surface roughness. The cloud moves

https://doi.org/10.1021/acs.chas.4c00044
ACS Chem. Health Saf. XXXX, XXX, XXX−XXX

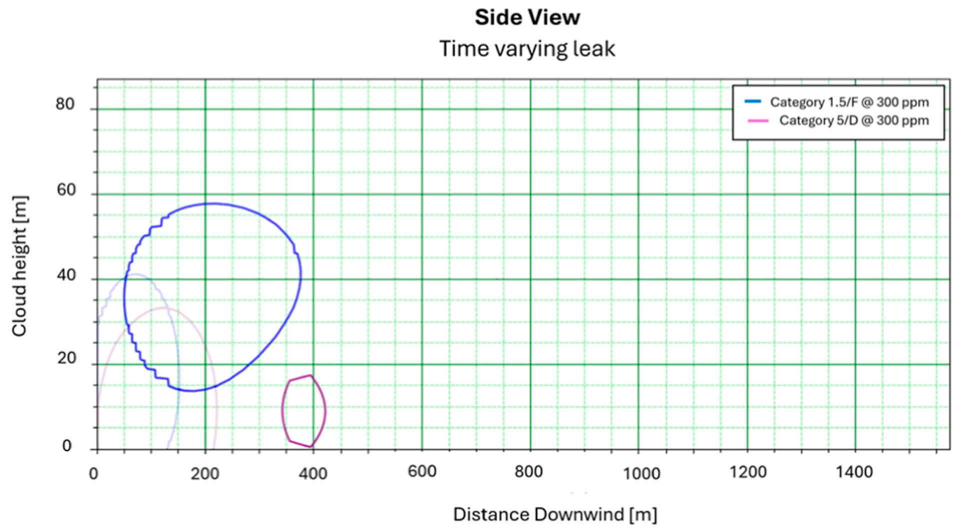


Figure 3. Cloud height in time and space—scenario F.

attached to the ground and the dispersion surface heats the plume/puff potentially turning the dispersion into a passive one. Basically, the land is characterized by a higher surface roughness, which can represent an obstacle to the wind for the wind shadow effect. For this reason, the cloud moving on the land is warmed up and tends to disperse more intensively in the vertical direction. The vertical dispersion is a favorable phenomenon since the height of interest for toxicity is 1.5 m, which represents the height at which humans breathe. The water surface has the potential to exchange more heat (since more heat is produced by the reaction of dissolution of ammonia in water), but it is completely exposed to the wind. Actually, the toxic clouds tend to have a broader impact area when over sea, determining, even at higher distances from the release point, a higher PoD. Indeed, when the wind is not obstructed, it leads to more horizontal dispersion, and this could explain the broader cloud footprint over water. What's more, seawater is characterized by limited changes in the temperature, and also this stability could contribute to the reduction of vertical mixing. Therefore, if the cloud disperses horizontally, the ammonia concentration tends to remain higher even at long distances, and people can be exposed for a longer time to the toxic concentration. Differently, if the cloud disperses vertically, it becomes less hazardous for human health since high concentrations tend to be at high elevation and the duration of exposure tends to be lower. The difference between the cloud maximum footprint extension is more evident during the day. This evidence suggests that the wind speed and in general weather conditions have a key role in the explanation of why the PoD is higher when the dispersion is over water.

3.7. Specific Considerations Regarding Scenarios Involving FR Tanks. *3.7.1. Comparison between Scenario D and F: Ammonia Gaseous Outflow—Breach above Ammonia Level.* Both scenarios D and F consider a hole that affects the tank above ammonia level. The only difference is the diameter of this opening. From these scenarios, it was expected to notice a discharge from the orifice equal to the boil-off rate of the ammonia inside the tank. However, the PHAST simulation considers that the pressure inside the tank decreases from 1.02 to 1.013 bar. This pressure drop determines a small vaporization of the ammonia stored inside. It was expected to notice, after this first phase, a constant discharge rate representing the boil-off rate of the remaining ammonia stored inside the tank and below the hole height. Differently, PHAST considers the discharge rate equal to 0 kg/s after the pressure inside the tank decreases until the atmospheric one. However, heat transfer through tank walls occurs, vaporizing ammonia at the atmospheric pressure. Thus, a boil-off gas was expected to be formed and discharged from the orifice. Heat transfer to ammonia is required to lead to the vaporization of the ammonia still inside the tank. The following assumptions were thus introduced:

- Since ammonia is stored inside the tank and the opening to the atmosphere is a hole, the contribution of air convection is considered low, as well as that of radiation.
- The FR tank has an insulation system. Therefore, a temperature increase is expected within the tank, but it would still require a considerable amount of time.

Therefore, it is possible to deduce that liquefied ammonia, still inside the tank after the collision, would require some time to start vaporizing since there are no immediate and important heat sources. For this reason, these scenarios can effectively be simplified considering that only the pressure drop caused by the hole determines a fixed rate of vaporization, which rapidly tends to zero. As previously mentioned, PHAST software does not consider the heat transfer to the cryogenic ammonia remaining inside the tank. This approximation can be acceptable, as the ammonia boil-off rate is low, easily mixing with air and dispersing.

Analyzing the consequences of the amount vaporized from the pressure drop for scenarios D and F, it results that there is no lethality footprint or PoD plotted if the dispersion occurs over seawater surface. However, if the dispersion occurs over the land, the PoD is higher, even though always lower than 0.2. What's more, if the dispersion over land occurs during the night the PoD is still 0, while if the dispersion occurs during the day the PoD can be up to 0.2. This can be explained by studying the dispersion height of the cloud. Since the mass of ammonia released in these scenarios is lower, the cloud formed tends to absorb more easily the heat provided by the dispersion surface and the surrounding. For this reason, in scenarios D and F the dispersion becomes a passive one, in particular during the night. Figure 3 shows that the nightly

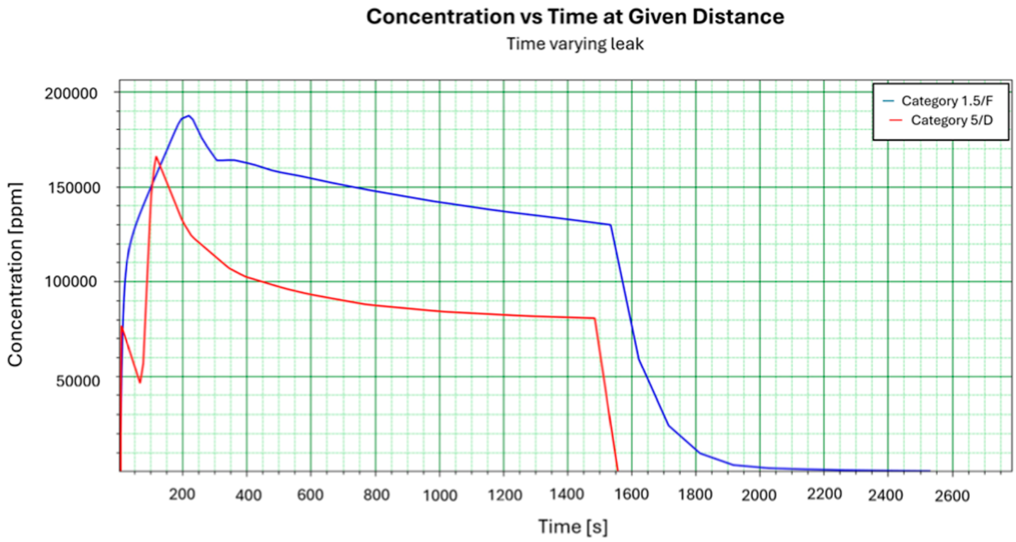


Figure 4. Scenario C dispersion on water—concentration vs time.

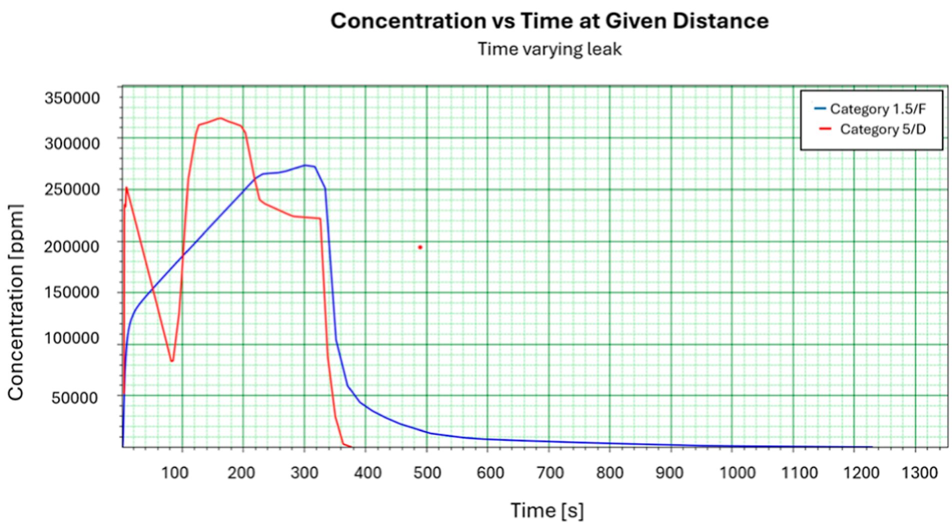


Figure 5. Scenario E dispersion on water—concentration vs time.

cloud is heated rapidly through the contact with ground and tends to rise higher into the atmosphere. The daily cloud remains heavy for longer, causing more problems to human health due to ammonia toxicity. This is the reason why the PoD is always higher during the day. The explanation behind this phenomenon is related to the lower wind speed characterizing the night: it lets the cloud be easily warmed up by the ground. Moreover, the heat exchanged with the water surface is sensibly higher (due to the exothermic dissolution of ammonia in water) and this leads to the formation of lighter clouds when the dispersion is over water. Solar radiation and air humidity can influence cloud dispersion as well. However, it is necessary to remark that these parameters can also influence the reaction of ammonia dissolution. For this reason, their contribution should be analyzed in more detail. Overall, scenarios D and F represent the best-case scenarios among all those from FR tanks.

3.7.2. Comparison between Scenario C and E: Ammonia Liquid Discharge—Breach below Ammonia Level, Influence of Hole Diameter. Scenarios C and E are both characterized by a hole below ammonia level in FR tank. In this case, there is a liquid discharge mainly determined by the hydraulic pressure of the liquid above the hole. The only difference between these two scenarios is the dimension of the hole since they are characterized by the same release height (3 m) and height of the hole on the tank (0.5 m).

In both these scenarios, the liquid discharge falls into the seawater, partly vaporizes, and partly dissolves. During the falling itself, a percentage of ammonia vaporizes and does not contribute to the formation of the pool. It is possible to notice that this quantity is much higher in the case of smaller holes on the tank. Actually, the liquid outflow from a smaller hole is characterized by a lower flow rate and a higher discharge time. The liquid is exposed to the atmosphere for a higher amount of time since it is released slower: this implies that the mass rained out is more when the hole has a diameter of 750 mm. The amount of ammonia dissolved into the water is higher when the scenario is characterized by a bigger hole. Actually, since the rained-out pool contains more mass, the pool radius is bigger and the surface contact between ammonia and water is higher. When the hole is 250 mm, since ammonia is released in smaller quantities but for a longer time, the pool is generally smaller and the solution rate lower. Therefore, the total amount of ammonia vaporized is higher when the release is

https://doi.org/10.1021/acs.chas.4c00044
ACS Chem. Health Saf. XXXX, XXX, XXX−XXX

from a small breach (considering a fixed discharge time). Consequently, comparing the trend of concentration versus time of the two scenarios, it is possible to notice that even though scenario E is characterized by a higher peak of maximum concentration, the time required to have the concentration below a fixed one is lower. Actually, the release time of scenario E is just 600 s while those of scenario C is 3600 s. Figures 4 and 5 show that the concentration requires more time to decrease under a certain limit if the hole is smaller (scenario C).

The higher total mass of ammonia vaporized in scenario C does not imply that the PoD is necessarily always higher for this scenario. Actually, the PoD for a potential victim located at an important distance from the release source is much higher for scenario C if the dispersion occurs over water during the night. But this is no longer true if the dispersion occurs on land and during the day. Scenarios C and E can both be considered as the worst-case scenarios; only after the definition of weather conditions, dispersion surfaces and distance of interest it is possible to understand which scenario has the more severe consequences.

3.7.3. Worst-Case Scenario among Releases from FR Tanks. To understand which is the worst-case scenario among those from the FR tank (in order to implement the correct mitigating measures), it is possible to compare the PoD and the lethality footprints 0.1% of scenarios A, C and E. Based on all the previously discussed considerations, it is evident that these three scenarios have more hazardous outcomes than all the others. Actually, A represents the catastrophic rupture from 15 m above seawater level, which is worse than the same scenario at 3 m (B), while C and E have the worst outcomes among all the continuous releases.

These results are consistent with expectations. Actually, it is difficult to find an absolute worst-case scenario since it is first necessary to choose the dispersion surface and the weather conditions of interest. However, it is necessary to specify that scenarios C and E are simulated in PHAST without incorporating the hypothesis of containment previously introduced. Given that the hole in these scenarios is located in the liquid phase at the tank's bottom, it is expected that a part of the liquefied ammonia, constituting the potential pool, is constrained inside the vessel hull. Hence, considering, for instance, that 20% of the ammonia rained out onto the water surface is confined within the hull, forming a boiling pool on the steel, it is possible to deduce that the results presented above could be partially different. Actually, the vaporization on the vessel floor is expected to be slower, but the 20% of ammonia constrained could entirely vaporize, while a portion of this volume would have dissolved in water. An interesting observation regards the fact that the positioning of the tanks inside the hull does not represent a mitigative solution. Actually, the scenarios of continuous release inside the hull could also determine more severe consequences than the catastrophic rupture on deck.

The estimation of worst-case scenarios actually depends on the aim of the project. The study of lethality footprints identifies as worst-case the scenario characterized by a widespread of the toxic cloud, which covers a large area, while the analysis of PoDs considers as worst-case the scenario characterized by the highest probability of lethal outcomes for the victim exposed to the hazardous release.

3.8. Specific Considerations Regarding Scenarios Involving SP Tanks. *3.8.1. Comparison between Scenario O and Q: Hole above Ammonia Level—Chocked Flow.* The only difference between scenarios O and Q is the dimension of the hole, which has a diameter of 250 mm in scenario O and 750 mm in scenario Q. In both the cases, the breach causes a flashing jet which is mainly formed by gaseous phase and some droplets. All the droplets vaporize during the fall without forming a rained-out pool. Basically, it results that from scenario O are released 80,000 kg in 3600 s and from Q 90,000 kg in 800 s. The maximum release time chosen was 3600 s: if scenario O had continued, a greater quantity would have been released since the driving force had not yet been exhausted. The jet, which is almost all ammonia vapor, escapes the hole with the so-called "chocked flow". Analyzing the consequences, it results that scenario Q is characterized by a higher peak of concentration but the concentration itself requires less time to decrease under a certain value. The ammonia release from scenario O continues for more than an hour. The cloud can reach longer distances from the release source. Consequently, it results that the PoD near the release source is higher for scenario O, characterized by a bigger hole, while the PoD at greater distances is higher for scenario Q, characterized by a smaller hole. It is difficult to determine which of the two scenarios has the worst consequences, since it depends on the distance analyzed. Nevertheless, it is possible to confirm that the case of breach above ammonia level has the least adverse outcomes among all the scenarios from SP tanks, as it was also noticed for scenarios D and F for FR tanks. Again, the main reason is that these clouds, containing a lower ammonia mass, are heated up by the dispersion surface more easily. It is interesting to remark that the clouds produced in scenarios O and Q (from SP tank) are heavier than those of the corresponding scenarios D and F (from FR tank) due to the possible presence of ammonia droplets in the flashing jet.

A final consideration concerns the amount of liquefied ammonia remaining inside the tank. This is at 10.4 °C at the atmospheric pressure, therefore it should behave as a boiling pool and vaporize. However, the PHAST software is not able to consider the boil-off rate of what remains inside the tank, as in the case of scenarios D and F. This approximation is still plausible since the boil-off rate is expected to be negligible. Indeed, the tank is usually insulated, and the hole is small enough to reduce the contribution of air convection.

3.8.2. Comparison between Scenario N and P: Hole below Ammonia Level—Flashing Jet. Both the scenarios N and P are characterized by a flashing jet at 0.5 m from the bottom of the tank. The release is a multiphase jet: a rain-out pool is formed on the water surface and an aerosol containing gaseous ammonia and liquid droplets leaves from the opening in the hull. For both the scenarios, the amount of ammonia rained-out is higher if the dispersion occurs during the night and on land. Actually, it is possible to imagine that a higher amount of heat is released from the water (thanks to the reaction of dissolution of ammonia) and this heat tends to increase the vaporization of the ammonia droplets contained in the two-phase jet, determining a higher mass to be vaporized. Moreover, the dispersion over land is characterized by a lower wind speed due to the wind shadow effect and this also limits vaporization. In both the N and P scenarios, 600,000 kg of ammonia are released but at a different release rate. Scenario N is characterized by a smaller hole and the release takes almost 2500 s, while the ammonia mass is released in just 270 s in scenario P. Since the release is slower, scenario N is characterized by a higher amount of ammonia vaporized; on

https://doi.org/10.1021/acs.chas.4c00044
ACS Chem. Health Saf. XXXX, XXX, XXX−XXX

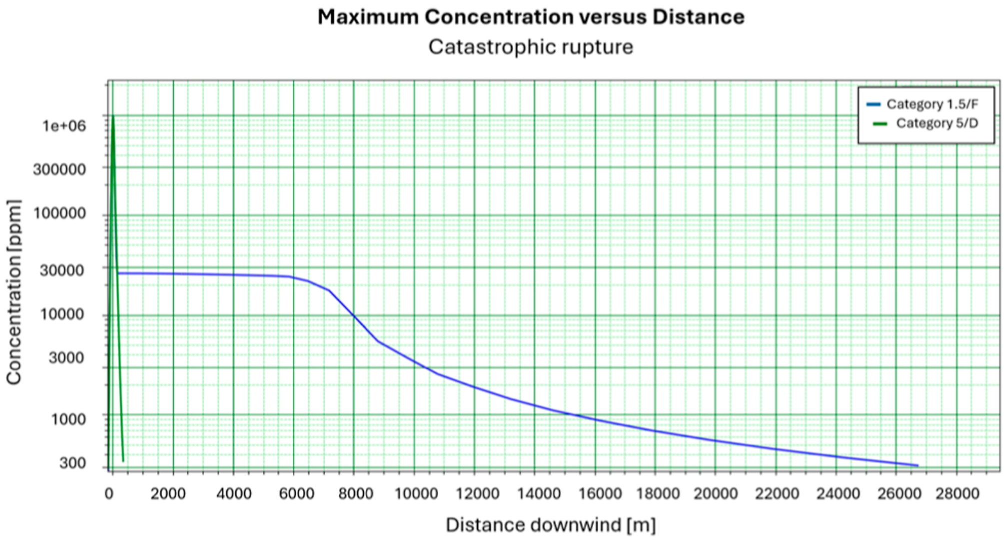


Figure 6. Concentration vs distance—scenario R (dispersion over water).

the other side P is described by more mass rained-out that forms a boiling pool on the seawater surface. The higher the mass rained out, the bigger the radius of the pool, the higher the contact surface between ammonia and water; this leads to the dissolution of a higher portion of ammonia. Therefore, scenario N is described by a higher mass of total ammonia vaporized.

The PoD is higher for scenario N if the dispersion occurs over water, while for scenario P if on land. This result is coherent with the results in the plots showing the area of the lethality footprints 0.1%: the lethality footprint is broader, in terms of surface area, for scenario N if the dispersion is over water and for P if over land. Scenario P is characterized by a higher peak of concentration, but since the release time is lower, the concentration requires less time to decrease. When the dispersion is on land, buildings create zones with high toxic concentrations since the wind is partially blocked by the structures. Differently, scenario N is characterized by lower ammonia concentrations, but the release time is longer. For this reason, the toxic cloud is formed and disperses for more time creating a larger lethality footprint. Overall, when the dispersion occurs on land, the peak of concentrations has a higher influence on the PoD, and this explains why scenario P results as the worst-case scenario. However, when the dispersion occurs on water, where there is no confinement for the cloud, a lower ammonia concentration but for longer exposure times can determine a higher number of fatalities. Actually, the wind favors a more horizontal dispersion, inducing the toxic cloud to spread over a broader area. Therefore, in the event of release over the water, scenario N results as the worst-case scenario. As in the case of scenarios from FR tanks, the determination of the worst-case scenario depends on the dispersion surface, weather conditions, and distance from the source chosen.

3.8.3. Worst-Case Scenario among Releases from SP Tanks. As concluded also for scenarios from FR tanks, there can be more than one worst-case scenario, since this depends on the dispersion surface and weather conditions considered. It is also expected that these conclusions differ if obtained from the analysis of PoD or lethality footprints. Lethality footprints show the geographic area characterized by the death of 0.1% of the population. They are particularly useful for the study of emergency plans and zoning. The PoD represents the likelihood of fatality under specific conditions of exposure, since it is calculated considering a specific position of the hypothetical victim, concentration of ammonia in air and exposure time. For these reasons, the PoDs are often used for a detailed risk assessment or sensitivity analysis. In this instance, as well it is not possible to conclude that positioning the tanks within the hull is safer. While it may be claimed that placing the tanks below the deck could be a mitigating solution in the event of a catastrophic rupture, the possibility that a hole in the tank is present makes this conclusion invalid. Actually, a continuous release from a tank within the hull could generate even worse outcomes, since the portion of ammonia vaporized tends to be higher. Therefore, it is not possible to identify a single worst-case scenario.

4. UNMITIGATED CONSEQUENCES OF THE UNDERWATER RELEASE SCENARIOS

Analyzing the outcomes from underwater releases presents significant challenges, due to the numerous assumptions underpinning the modeling of such scenarios. As detailed in the Methodology section, there is a notable lack of information on ammonia underwater releases, and the PHAST software lacks the capability to simulate conditions beneath water. The findings discussed in the following sections thus rely extensively on the assumptions introduced in the Methodology section. Future research should focus on verifying these assumptions to ensure the accuracy and reliability of the results.

4.1. Underwater Catastrophic Ruptures. Since both scenarios G and R have been modeled considering the amount of ammonia vaporized reaching the water surface, there is no difference between them. In fact, it is not important from which type of tank ammonia is released, since it has been directly considered that the total amount of gaseous ammonia forms the toxic cloud. For this reason, the PoD of scenario R is always higher, since it is the scenario characterized by a higher mass dispersing (226,620 kg scenario R vs 183,600 kg scenario G). The lethality footprint 0.1% covers a broader area when the release is modeled during the night, independently from the dispersion surface. During the day, characterized by higher wind speed and turbulence, the dispersion of the toxic cloud is

https://doi.org/10.1021/acs.chas.4c00044
ACS Chem. Health Saf. XXXX, XXX, XXX−XXX

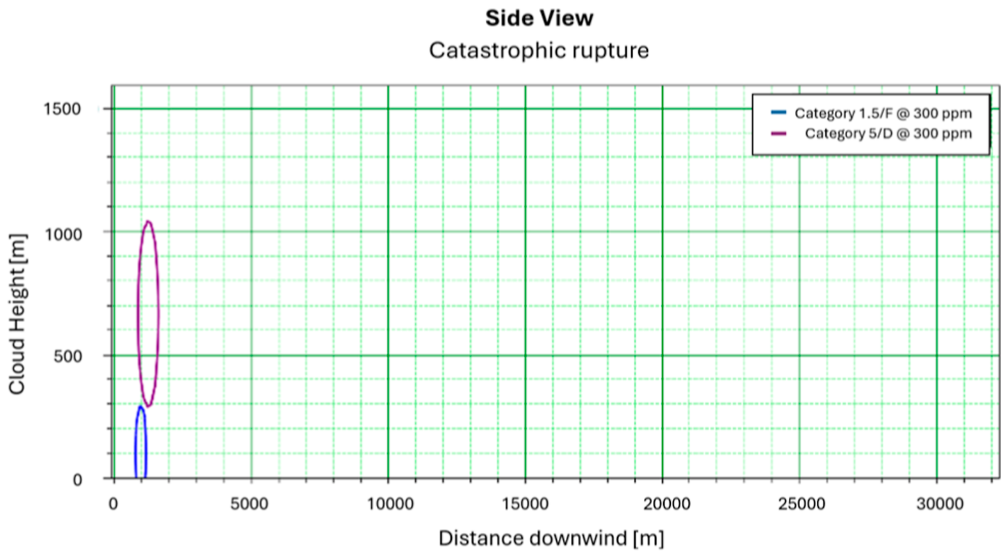


Figure 7. Scenario G—cloud height for the dispersion on water.

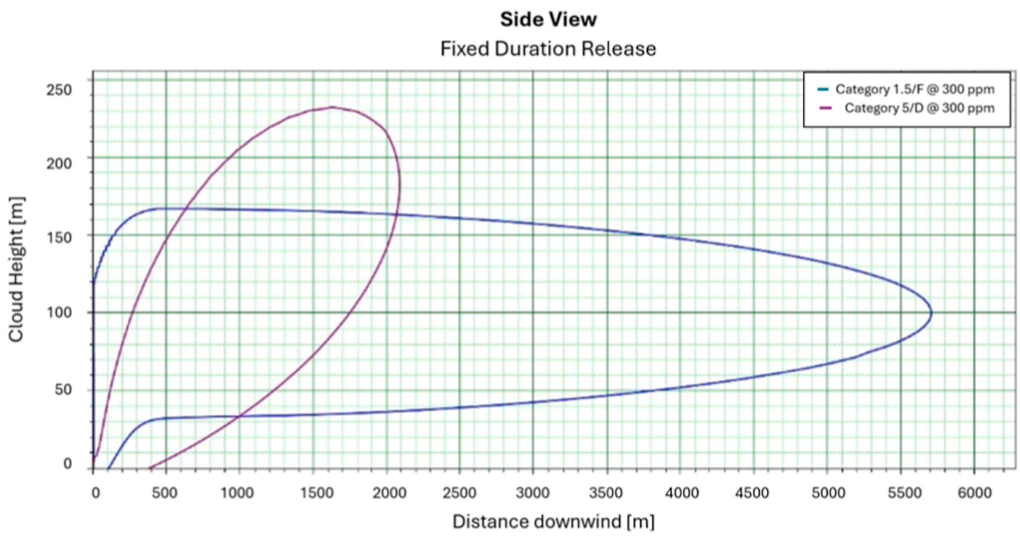


Figure 8. Scenario T—cloud height when the dispersion is on water.

enhanced, and the toxic concentration decreases rapidly under a fixed value, even for short distances from the release source. Differently, during the night the atmosphere is more stable and there is a lower wind speed: the cloud toxic concentration requires more distance to decrease under 300 ppm (IDLH value) as Figure 6 clearly shows. Moreover, it is possible to notice that the dispersion of the toxic cloud is always lighter during the day. An explanation could be related to the air humidity: during the night, the air humidity is higher, and ammonia tends to react with water generating ions. For this reason, the night cloud tends to be denser and to disperse attached to the ground for more time, determining more severe consequences (Figure 7).

The lethality footprint is always larger if the dispersion occurs at night, but some more interesting observations can be made. The lethality footprint 0.1% during the day is broader on land, while during the night is broader on water. When the dispersion occurs on land, it is necessary to consider a higher surface roughness, which tends to block the wind (wind shadow effect). The nocturnal cloud persists over short distances, lingering due to the absence of wind, making it easier to be heated upon contact with the ground. The lethality footprint 0.1% for the dispersion on land during the night is smaller than the corresponding one over water since the toxic cloud is more heated and tends to move more vertically. On the contrary, the cloud dispersing during the day determines a bigger lethality footprint over land than over water. Actually, even though the wind speed is lower over land (due to the presence of buildings), the cloud is not efficiently heated by the ground because the wind is not absent. In open sea, the cloud is easily diluted during the day due to the lower atmospheric stability and the horizontal dispersion provided by the wind.

Overall, scenario R has more severe outcomes than scenario G, but it is less hazardous than a catastrophic rupture above water level. Actually, a lower quantity of ammonia vapor is released in the atmosphere, since a large quantity of this toxic substance dissolves underwater. Of course, underwater scenarios generate more severe outcomes for the aquatic toxicity, but they are not the worst-case scenarios if human health is considered.

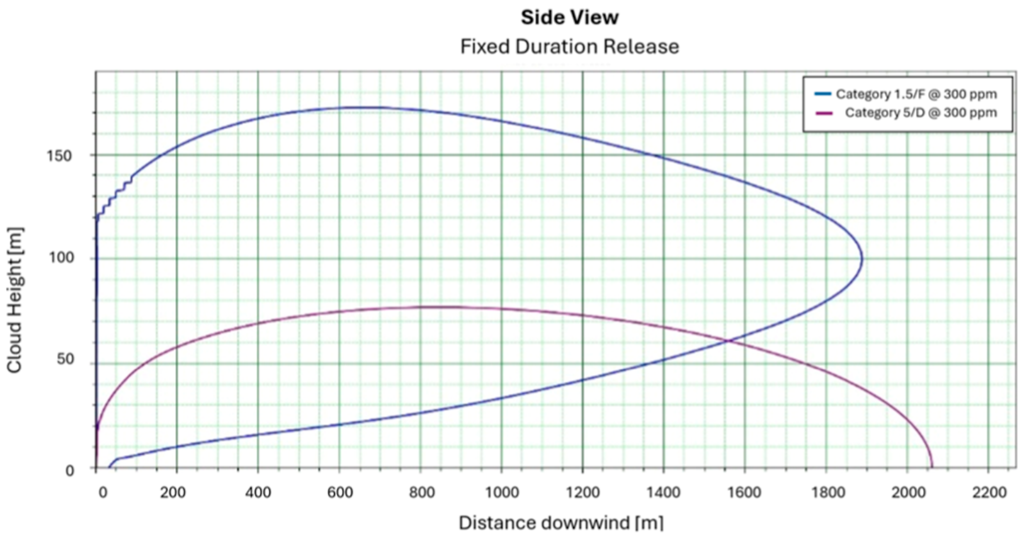


Figure 9. Scenario T—cloud height when the dispersion is on land.

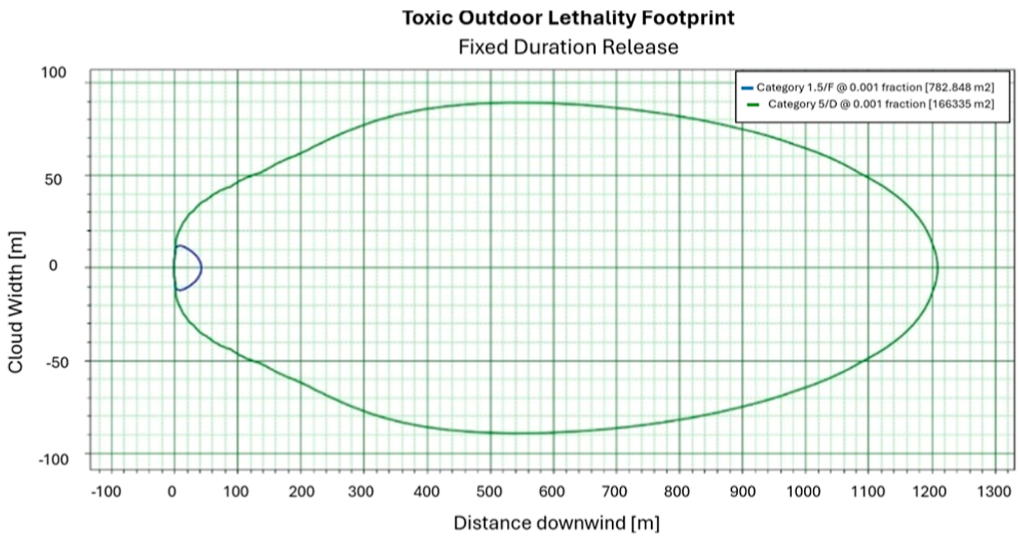


Figure 10. Scenario S—dispersion on land, lethality footprint 0.1%.

4.2. Underwater Continuous Releases—Influence of the Dispersion Surface. The dispersion surface impacts both the PoD and the lethality footprints 0.1% of the analyzed underwater scenarios. In particular, the dispersion surface has a direct impact on the type of dispersion of the ammonia toxic clouds. From the results obtained from the modeling on PHAST, it is possible to notice that when the dispersion occurs on water, the clouds tend to disperse more as a light gas cloud. Actually, water has the potential to exchange a higher amount of heat since the reaction of ammonia dissolution is strongly exothermic. For this reason, the clouds dispersing on water are warmed up by contact with the water surface and tend to disperse vertically more than the corresponding clouds on land. The following Figures 8 and 9 from scenario T show the difference between the cloud height when the dispersion occurs on water and land. The same consideration is valid for all the underwater release scenarios and is more evident when the comparison concerns the dispersion during the day.

4.3. Underwater Continuous Releases—Influence of Weather Conditions on the Cloud Dispersion. As for the scenarios modeled above water, it is possible to find a correlation between the PoD, the lethality footprint 0.1% and the weather conditions characterizing the release time. The PoD is always higher when the cloud disperses during the day, regardless of the type of tank or the hole size. Coherently, the lethality footprints 0.1% always covers a broader area of impact during the day independently from the dispersion surface. This consideration is valid for both the dispersion on land and water, but the reasons behind this result may be different. When the dispersion occurs on land, the lethality footprint during the day is particularly broader than that during the night, as clearly shown in Figure 10. The results in the figure concern the simulation of scenario S, but the same trend is observable across all the examined scenarios with dispersion over land.

The area covered by the lethality footprint 0.1% during the day is more than two hundred times larger than that occurring during the night. There is a specific explanation behind this behavior: the cloud during the night tends to disperse as a light gas, as previously explained. Its vertical movement determines lower concentrations at human height (1.5 m). On the other hand, the day cloud tends to disperse more heavily, since it is

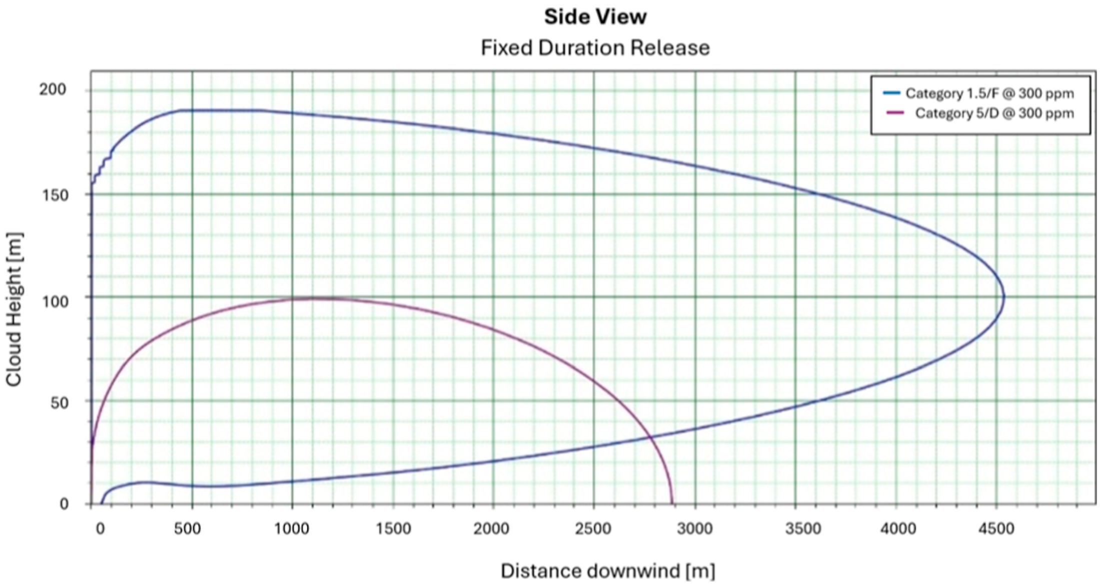


Figure 11. Cloud height of scenario S—dispersion on land.

less heated from the surface. Actually, the day is characterized by more wind, which is an obstacle to the conduction between the cloud and the ground. Figure 11 from scenario S shows the ammonia cloud that during the day spreads attached to the ground, while during the night it has an elevation of about 10 m.

When the dispersion occurs on water, the difference between the lethality footprints during the day and the night is not so marked. Both the clouds during the day and night tend to disperse more lightly thanks to the heat generated by the reaction of ammonia dissolution. The cloud formed during the day is heavier, but it does not disperse attached to the ground for distances so wide such as for the dispersion over land.

4.4. Underwater Continuous Releases—Influence of the Outflow Mass Rate. The outflow mass rate is both a function of the total mass released and of the release time. Both these values are strongly dependent on the assumptions previously discussed in the Methodology section. In particular, the release time chosen was 2000 s for scenarios with a 250 mm hole (H, I, S, T) and 200 s if the hole is 750 mm (J, K, U, V). The consequences are directly influenced by the mass rate. In particular, the higher the flow rate, the larger the lethality footprint 0.1%. Actually, when the mass rate is high, the dispersion surface has to heat up a higher quantity of ammonia released per unit of time. Consequently, the heat exchange tends to be limited and the cloud tends to disperse more heavily, increasing the PoD at ground level. Similarly, when the mass released per unit of time is lower, it is easier to warm it up and to make dispersion lighter. It is possible to conclude, for the reasons explained, that the worst-case scenario is U (mass rate = 1800 kg/s) and the best-case scenario is H (mass rate = 34 kg/s). Studying the heights of the clouds of these two scenarios, it is evident, especially during the night, that the cloud formed by a lower mass flow rate tends to disperse more like a light gas, reducing the severity of consequences of toxicity for humans.

5. DISCUSSION ON UNIMITIGATED SCENARIOS

Comparing the PoD and the lethality footprints 0.1% of the worst-case scenarios, it is possible to deduce that accident scenarios from SP tanks determine more severe consequences than those from FR tanks. It is important to underline that the focus of this study is the assessment of the consequences of ammonia releases on human health and not on marine life. One could argue that, considering environmental consequences, releases from FR tanks could represent the worst-case scenarios since they are characterized by a higher mass of ammonia rained out. However, when considering only toxicity to humans, the SP tanks represent the greatest danger because of the sum of different contributions. First, a hole in an SP tank results in a higher quantity of vaporized ammonia, as the ammonia rapidly flashes due to the pressure difference between the tank's interior and exterior (5.2 bar gauge). Consequently, a smaller rained-out pool is formed and a lower volume of ammonia dissolves into the seawater. Overall, scenarios from SP tanks are characterized by higher toxic concentrations. Second, discharging jets from SP tanks tend to reach greater distances, since they are propelled by pressure: the PoD tends to be higher even at extremely high distances from the release source. Overall, the refrigerated storage of ammonia is most effective in reducing the severity of consequences in the event of an ammonia release due to a ship-to-ship collision. Therefore, it can be affirmed that opting for refrigerated storage tanks is the most effective design choice for reducing the outcomes of accidental ammonia releases.

Underwater releases are always less hazardous than those occurring above water, considering only the effects on human health. They are characterized by lower volumes of ammonia vaporized, since ammonia dissolution is clearly predominant when the release is underwater. Moreover, when ammonia reaches the surface, it has a temperature definitely higher than its normal boiling point, and the resulting cloud consists of ammonia vapors, without droplets. Ammonia bubbles, while rising, are warmed by the seawater, leading to a hotter cloud compared to those of above water releases. Consequently, hotter clouds have the tendency to disperse more lightly, resulting in lower concentration of toxic substance at human

https://doi.org/10.1021/acs.chas.4c00044
ACS Chem. Health Saf. XXXX, XXX, XXX−XXX

height. Furthermore, since underwater release clouds usually contain a lower ammonia mass, they are more easily warmed by the contact with the dispersion surface, leading to a passive dispersion just a few meters away from the release point. For all these reasons, considering as focus of this research the consequences on human health, it is possible to conclude that the outcomes are less severe if a collision determines an underwater—ammonia release. Actually, most ammonia dissolves underwater and the clouds generated have the tendency to be easily warmed up and disperse like light clouds.

6. MITIGATING MEASURES AND MITIGATED RESULTS

In order to reduce the severity of consequences, it is necessary to implement mitigating measures. Among the most used technologies for the mitigation of ammonia releases are water curtains and water mists. They are the most economic and efficient techniques to mitigate heavy gas clouds. Water curtains are efficient in absorbing ammonia because water droplets can capture and dissolve the ammonia gas, reducing its vapor pressure and concentration in the air. This process helps in lowering ammonia concentration levels exploiting the high solubility of ammonia in water (517 g/L at 20 °C). Water curtains have three specific effects:

- ammonia mass transfer by chemical absorption in water,
- mechanical dispersion of the cloud by air entrainment,[21]
- heat transfer due to temperature differences.

Overall, the toxic ammonia cloud is diluted and is induced to disperse lighter. Results reported in the literature show that water curtains can absorb up to 80% of the released ammonia: the upper limit is represented by ammonia equilibrium with water. The actual effectiveness depends on several different parameters concerning ammonia properties, atmospheric conditions, and characteristics of the water curtain itself. There are some aspects which can influence the efficiency of this system:

- Water mists or fine droplets guarantee a larger interfacial area and time of contact which increase ammonia dissolution.[22]
- The addition of acids convert ammonia into the less toxic ammonium ion. Also, the addition of inorganic salts or surfactants can strongly increase the efficiency of these barriers (up to 97%).[23]
- Nozzle spacing: if the nozzles are too distant, the cloud could pass through empty spaces.

Water curtains usually generate a vertical spray in both downward and upward operating mode. Upward curtains help the vertical dispersion of the cloud and usually lead to a higher ammonia reduction efficiency. The rate of this process is directly proportional to ammonia concentration, and from a kinetic aspect, ammonia absorption can be described in accordance with the kinetic reaction of pseudo first order. If pure water is used, it is possible to assume that 80% of the ammonia released is absorbed and to remodel on PHAST the mitigated worst-case scenarios to observe the reduction of the severity of consequences.

Moreover, in the specific case of release from the deck of the vessel, it is possible to assume the implementation of a physical barrier to contain liquefied ammonia. This idea could be useful, but it is necessary to consider that, even though ammonia has a small explosivity/flammability range, the presence of obstacles increases the probability of vapor cloud explosions. It is possible to assume that a physical barrier could prevent the falling from deck of a percentage of liquefied ammonia into the seawater, but the effects of this barrier on ignition hazard and explosivity should be verified. The implementation of a containment basin for the ammonia tanks on deck was thus assumed. In the case of FR tank, the advantages of containment are more evident since there is a higher liquefied ammonia outflow. Nevertheless, the worst-case scenarios are typically derived from SP tanks: ammonia liquefied outflow is propelled at a greater distance, resulting in a discharge into the sea generally higher than the volume contained within the basin. For SP tanks, it is possible to imagine that only 20% of the liquefied ammonia is really contained on the deck. In particular, scenario L and P, worst-case scenarios of this research, have been remodeled on PHAST with the implementation of mitigating measures. In the following the mitigated scenarios are discussed.

6.1. Scenario L: Consequences after the Implementation of Mitigating Measures. In the event of a catastrophic rupture of a SP tank on deck (15 m a.s.l.), the following assumptions are considered:

a water curtains implemented on deck can absorb 80% of the dense cloud formed by the amount of ammonia flashed. It is noticeable that the percentage of ammonia flashed in the unmitigated scenario is lower than the quantity of ammonia vaporized during the fall or from the pool on water surface. Water curtains do not have efficiency on the toxic vapors which have not been generated on the deck of the vessel. In this case, the optimal solution is to limit the amount of liquefied ammonia which falls from the vessel. Scenario L is described by 94,000 kg of flashed ammonia: 80% of this mass is absorbed through water curtains, the remaining percentage is warmed up by the contact with water and it is possible to imagine it will disperse lightly. Overall, thanks to the implementation of water curtains, ammonia flashed probably is irrelevant for the estimation of consequences.

b Containment basins on deck can reduce the amount of ammonia falling into the sea. This solution determines an important reduction in the amount of ammonia contributing to human lethality. Actually, it is possible to imagine that both the amounts of ammonia vaporizing during the fall and forming the pool are reduced by up to 20%. Considering the low vaporization rate of the pool on the ground (floor of the vessel), it is possible to neglect the quantity of ammonia vaporizing from the basin. Considering unmitigated data obtained for this scenario, 529,000 kg were considered to fall from the deck; considering a reduction of 20%, just 423,000 kg of liquefied ammonia are supposed to fall into the sea.

Approximatively, it is possible to remodel on PHAST scenario L, considering an atmospheric tank containing just 423,000 kg of liquefied ammonia falling from 15 m. Actually, the pressure has an influence on the amount of ammonia flashed; but, since it has already been discussed in the previous considerations, modeling the tank of scenario L like a SP one would be an error since PHAST would consider again the possibility of flash. As expected, the PoD after the implementation of mitigating measures results sensibly lower. Figure 12 shows the reduction of the toxic PoD after the

https://doi.org/10.1021/acs.chas.4c00044
ACS Chem. Health Saf. XXXX, XXX, XXX−XXX

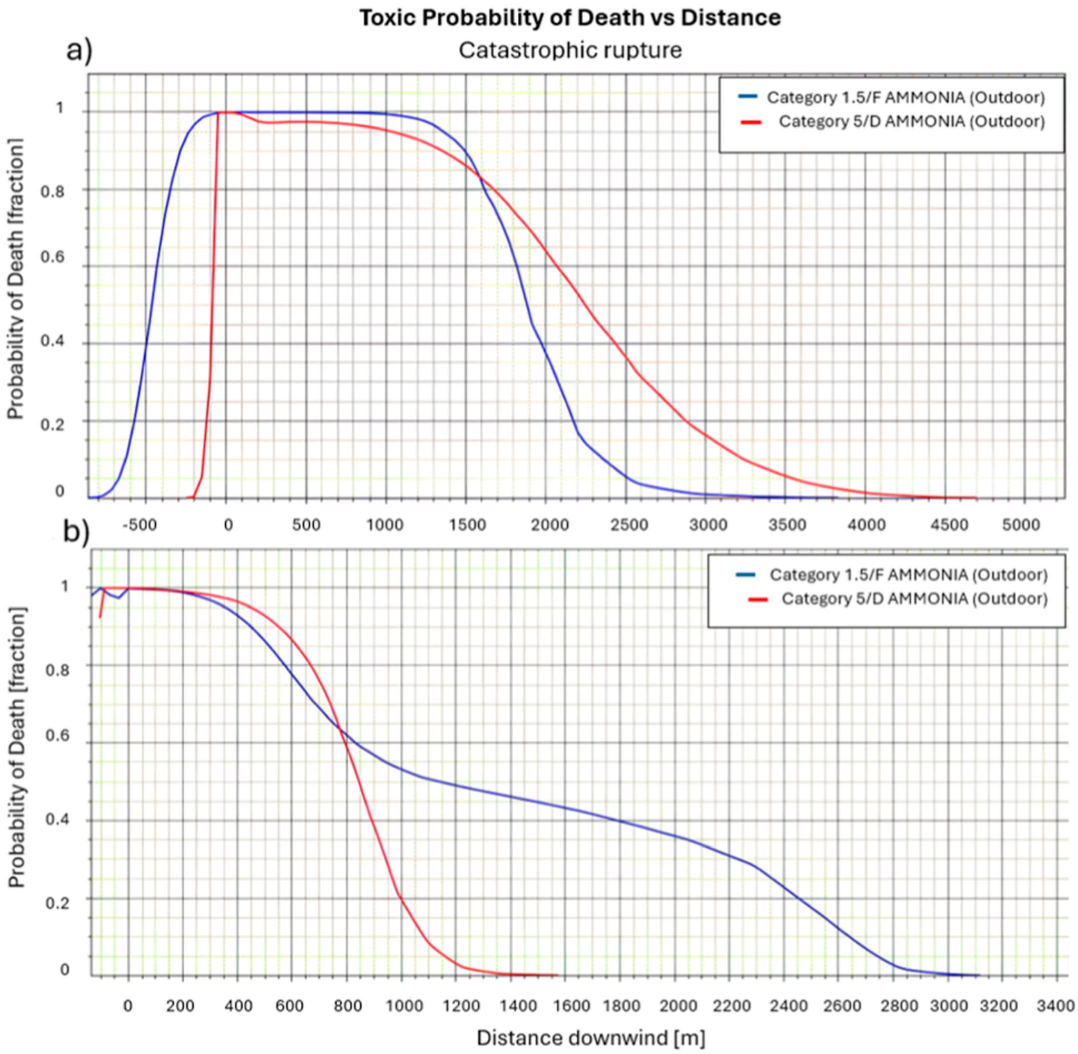


Figure 12. PoD—scenario L overwater unmitigated (a) and mitigated (b).

implementation of mitigating measures in the modeling of scenario L considering the overwater dispersion. Table 5 illustrates the percentage of reduction of the PoD at varying distances from the source after the implementation of the mitigating measures proposed.

It is evident that the implementation of mitigative measures proves effective in diminishing the PoD mainly at significant distances from the release source. However, since ammonia is extremely toxic, the PoD for the crew on the vessel (basically located at 0 m from the release source) is always 1. There is no way to reduce the PoD of onboard workers with these types of measures (even if it would be interesting to consider the efficiency of toxic isolation chambers or other personal protection equipment (PPE)). The mitigating measures proposed are efficient when the aim is to protect the population living in the vicinity of the release (vessel at the port). Actually, if the vessel is in the open sea, the effectiveness of water curtains is negligible, due to the absence of the population. In this case, the main concern would regard environmental impact of the release. The great advantage is evident in the event of a release at the port (the dispersion of the toxic cloud would occur over land involving population): it is necessary to reduce the distance downwind at which the PoD is still more than 0 to reduce the number of fatalities. Again, there is no possibility that water curtains and containment basins could mitigate the consequences for the onboard crew, but it is extremely important that the PoD at 500 m is reduced up to 100% over land. The PoD is generally lower over land as discussed in the previous chapters and it could be further reduced with these mitigative measures.

Table 5. PoD % of Reduction after the Implementation of Mitigation Barriers

scenario L mitigated	% reduction in PoD at 50 m (%)	% reduction in PoD at 200 m (%)	% reduction in PoD at 500 m (%)	% reduction in PoD at 1000 m (%)
over water, day	0	0	15	79
over water, night	0	0	25	47
over land, day	0	39	100	
over land, night	0	5	83	100

6.2. Scenario P: Consequences after the Implementation of Mitigating Measures. Scenario P is characterized by a continuous release (3 m a.s.l.) from a hole in a SP tank located inside the hull of the vessel. In this case the amount of ammonia flashed is globally higher, but there is a continuous

https://doi.org/10.1021/acs.chas.4c00044
ACS Chem. Health Saf. XXXX, XXX, XXX−XXX

flashing jet lasting longer. The expectation is that water curtains are more efficient than in the previous case since they must treat a lower mass flow but for a longer time. It is assumed that 80% of ammonia is absorbed by water and the remaining part forming the toxic cloud is warmed enough to disperse lighter. Scenario P can be remodeled considering that the consequences of the amount flashed are completely mitigated thanks to the implementation of water curtains. The percentage of liquefied ammonia which falls from the vessel into the sea is partially reduced thanks to the assumed presence of a containment basin. Overall, scenario P can be represented by a continuous release from an atmospheric tank containing the remaining liquefied ammonia which is falling into the water (the quantity not flashed and not constrained inside the basin). In particular, the release is modeled as a time fixed one since, from the unmitigated scenario P, it is well-known the discharge time. Again, as explained in scenario L, there is no possibility to mitigate the consequences generated from ammonia fallen from the vessel. After the implementation of mitigating measures, it is interesting to estimate mainly the consequences generated from the percentage of ammonia fallen into the sea. The results regarding the reduction of the PoD after the implementation of mitigating measures at different distances from the release source are collected in Table 6.

Table 6. PoD—% of Reduction after the Implementation of Mitigating Barriers

scenario P mitigated	% reduction in PoD at 50 m (%)	% reduction in PoD at 200 m (%)	% reduction in PoD at 500 m (%)	% reduction in PoD at 1000 m (%)
over water, day	0	30	95	100
over water, night	0	60	95	100
over land, day	0	40	100	
over land, night	0	10	79	100

All the comments introduced for scenario L are still valid for scenario P: it is noticeable that mitigating measures can strongly reduce the PoD at significant distances from the source and this is particularly important when ammonia toxic cloud disperses on land involving population.

7. DISCUSSION ON MITIGATED SCENARIOS

The mitigating solutions considered (water curtains and containment basins) are not able to reduce the PoD for the onboard members of the crew. In order to reduce the PoD of onboard workers, it is necessary to think about the implementation of toxic isolation rooms and the use of PPE. As expected, the reduction in the PoD thanks to mitigating barriers is more evident in the event of a continuous release since water curtains absorb ammonia released with a lower mass flow rate. Actually, continuous releases lead to the flash of a higher quantity of liquefied ammonia; thanks to the low mass flow rate, water curtains can easily absorb and heat the toxic cloud.

Ship design plays a crucial role on preventive measures. The adoption of a double hull construction is a widespread practice aimed at safeguarding the tanks within the ship's hull. This design feature significantly enhances the ship resistance against leaks and spills, serving as a critical barrier that protects the internal tanks from external breaches. Furthermore, the International Code of Safety for Ships using Gases or other Low-flashpoint Fuels (IGF code) prescribes safety margins that dictate the minimum distance between the tanks and the ship sides. These guidelines are designed to reduce the risk of damage that could lead to a hazardous release, thereby bolstering the ship safety infrastructure.

It is observed that the majority of ship collisions, which pose a significant risk for hazardous releases, occur while ships are docked at ports. This insight leads to the proposition that additional safety measures could be beneficial, especially during these vulnerable times. The introduction of isolation chambers and PPE could offer layers of protection for crew members, particularly for those involved in port activities. Isolation chambers could serve as secure areas that prevent the spread of hazardous substances in the event of a release, while PPE would provide individual protection against exposure.

Exploring the implementation of such safety enhancements requires a comprehensive approach that considers the unique challenges and operations at ports. This could involve conducting risk assessments to identify potential hazards and determining the most effective placement and type of isolation chambers. Additionally, ensuring that all crew members are equipped with and trained in the use of appropriate PPE is essential. Such measures not only aim to minimize the immediate risks to crew members but also contribute to the overall safety culture within the maritime industry.

In summary, while it is impossible to completely eliminate the risk of hazardous releases on ships, adopting a proactive stance focused on the prevention and the minimization of exposure may significantly mitigate the potential consequences for the crew. By integrating robust ship design features, such as double hulls and adherence to safety guidelines, with targeted safety measures at ports, including isolation chambers and PPE, the maritime industry can enhance the protection of its most valuable asset—the crew.

8. CONCLUSIONS

This study investigates the outcomes and mitigation strategies for ammonia releases during ship-to-ship collisions involving ammonia-fueled vessels. It considers various storage configurations SP and FR tanks, located either inside the hull or on the deck, affecting the release scenarios and environmental impact. SP tanks, stored at 6 bar and 10 °C, differ from FR at 1.013 bar and −33.2 °C in their response to breaches. The study shows that deck-located tanks may undergo a total LOC upon collision, while those within the hull might only be punctured, offering different containment challenges.

This analysis highlights how storage conditions influence the nature of ammonia release—either as a boiling pool on water, producing a mix of vapor and liquid, or a flash release creating a toxic cloud. The potential damage to tanks largely depends on the colliding vessel bow shape. Considering various hole sizes and positions, results in different impacts on human health and environment.

This study, based on the results obtained from the integral models included in the PHAST software tool, shows that no single worst-case scenario is present when considering the variability of factors like release height, hole size, and weather conditions. However, releases from SP tanks generally result in more severe human health risks due to increased vaporization, while releases from FR tanks pose greater environmental risks through ammonia dissolution in water. Mitigation measures, including water curtains and containment basins, prove partially effective, reducing the death probability in the vicinity of the vessel, but do not significantly protect crew members on the vessel itself.

Finally, the design and location of ammonia storage on vessels greatly influences the severity of potential accidents. SP tanks pose higher risks to human health, suggesting the need for stringent mitigation strategies and protective measures for crew members. The study underscores the importance of considering both environmental and health impacts during the vessel design phase and recommends further research addressing the enhancement of onboard safety.

AUTHOR INFORMATION

Corresponding Author

Ming Yang − *Faculty of Technology, Policy and Management, Delft University of Technology, Delft 2600, The Netherlands;* orcid.org/0000-0002-6544-9226; Email: m.yang-1@tudelft.nl

Authors

Benedetta Masia − *LISES—Department of Civil, Chemical, Environmental, and Materials Engineering, University of Bologna, Bologna 40126, Italy*

Valerio Cozzani − *LISES—Department of Civil, Chemical, Environmental, and Materials Engineering, University of Bologna, Bologna 40126, Italy;* orcid.org/0000-0003-4680-535X

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.chas.4c00044

Author Contributions

CRediT: **Benedetta Masia** conceptualization, formal analysis, investigation, methodology, visualization, writing - original draft; **Ming Yang** conceptualization, investigation, methodology, project administration, resources, supervision, writing - review & editing; **Valerio Cozzani** funding acquisition, project administration, resources, supervision, writing - review & editing.

Notes

The authors declare no competing financial interest.

ABBREVIATIONS

GHG, green house gases; IMO, International Maritime Organization; LNG, light natural gas; T_{pool}, temperature of the pool; T_{nb}, normal boiling temperature; LOC, loss of containment; SP, semipressurized (tank); FR, fully refrigerated (tank); PoD, probability of death; IDLH, immediately dangerous to life and health; PPE, personal protective equipment

REFERENCES

(1) Machaj, K.; Kupecki, J.; Malecha, Z.; Morawski, A. W.; Skrzypkiewicz, M.; Stanclik, M.; Chorowski, M. Ammonia as a Potential Marine Fuel: A Review. *Energy Strategy Rev.* **2022**, *44*, 100926.

(2) IRENA. *A Pathway to Decarbonise the Shipping Sector by 2050*, 2021.

(3) IMO. *Reduction of GHG Emissions from Ships*, 2023 IMO STRATEGY Reduct, GHG Emissions SHIPS, 2023.

(4) Al-Aboosi, F. Y.; El-Halwagi, M. M.; Moore, M.; Nielsen, R. B. Renewable Ammonia as an Alternative Fuel for the Shipping Industry. *Curr. Opin. Chem. Eng.* **2021**, *31*, 100670.

(5) Ampah, J. D.; Yusuf, A. A.; Afrane, S.; Jin, C.; Liu, H. Reviewing Two Decades of Cleaner Alternative Marine Fuels: Towards IMO's Decarbonization of the Maritime Transport Sector. *J. Cleaner Prod.* **2021**, *320*, 128871.

(6) Kim, K.; Roh, G.; Kim, W.; Chun, K. A Preliminary Study on an Alternative Ship Propulsion System Fueled by Ammonia: Environmental and Economic Assessments. *J. Mar. Sci. Eng.* **2020**, *8* (3), 183.

(7) Wu, B.; Wang, Y.; Wang, D.; Feng, Y.; Jin, S. Generation Mechanism and Emission Characteristics of N2O and NO in Ammonia-Diesel Dual-Fuel Engine. *Energy* **2023**, *284*, 129291.

(8) Zero Carbon Shipping 03/2023. https://cms.zerocarbonshipping.com/media/uploads/documents/Ammonia-emissions-reduction-position-paper_v4.pdf (accessed Nov 4, 2023).

(9) Wolfram, P.; Kyle, P.; Zhang, X.; Gkantonas, S.; Smith, S. Using Ammonia as a Shipping Fuel Could Disturb the Nitrogen Cycle. *Nat. Energy* **2022**, *7* (12), 1112−1114.

(10) Bertagni, M. B.; Socolow, R. H.; Martirez, J. M. P.; Carter, E. A.; Greig, C.; Ju, Y.; Lieuwen, T.; Mueller, M. E.; Sundaresan, S.; Wang, R.; Zondlo, M. A.; Porporato, A. Minimizing the Impacts of the Ammonia Economy on the Nitrogen Cycle and Climate. *Proc. Natl. Acad. Sci. U.S.A.* **2023**, *120* (46), No. e2311728120.

(11) Dharmavaram, S.; Pattabathula, V. Learning from the Worst Ammonia Accident. *Chem. Eng. Prog.* **2023**, *119*, 47.

(12) IGF Code. https://www.register-iri.com/wp-content/uploads/MSC_Resolution_39195.pdf (accessed Sep 20, 2023).

(13) NoGAPS Design. https://cms.zerocarbonshipping.com/media/uploads/documents/Nordic-Green-Ammonia-Powered-Ship-NoGAPS_final.pdf (accessed Oct 22, 2022).

(14) Woodward, J. L.; Pitbaldo, R. M. *LNG Risk Based Safety*, 2010.

(15) Lützen, M. Ship Collision Damage, PhD Thesis, Technical University of Denmark, Department of Mechanical Engineering, 2001.

(16) Pitblado, R. M.; Baik, J.; Hughes, G. J.; Ferro, C.; Shaw, S. J. Consequences of Liquefied Natural Gas Marine Incidents. *Process Saf. Prog.* **2005**, *24* (2), 108−114.

(17) LNG Safety and Security Aspects. In *Handbook of Liquefied Natural Gas*; Mokhatab, S., Mak, J. Y., Valappil, J. V., Wood, D. A., Eds.; Elsevier, 2014; pp 359−435.

(18) DNV. PVAP Theory December 2023. https://myworkspace.dnv.com/download/public/phast/technical_documentation/04_pool_vaporization/PVAP%20Model%20Theory.pdf (accessed Jan 13, 2024).

(19) Qi, R.; Raj, P. K.; Mannan, M. S. Underwater LNG Release Test Findings: Experimental Data and Model Results. *J. Loss Prev. Process. Ind.* **2011**, *24* (4), 440−448.

(20) Zhang, Y.; Zhu, J.; Teng, L.; Song, C.; Li, Y. Experimental Research of LNG Accidental Underwater Release and Combustion Behavior. *J. Loss Prev. Process. Ind.* **2020**, *64*, 104036.

(21) Cheng, C.; Tan, W.; Liu, L. Numerical Simulation of Water Curtain Application for Ammonia Release Dispersion. *J. Loss Prev. Process. Ind.* **2014**, *30*, 105−112.

(22) Dandrieux, A.; Dusserre, G.; Ollivier, J.; Fournet, H. Effectiveness of Water Curtains to Protect Firemen in Case of an Accidental Release of Ammonia: Comparison of the Effectiveness for Two Different Release Rates of Ammonia. *J. Loss Prev. Process. Ind.* **2001**, *14* (5), 349−355.

(23) Hua, M.; Shen, X.; Zhang, J.; Pan, X. Protective Water Curtain Ammonia Absorption Efficiency Enhancement by Inorganic and Surfactant Additives. *Process Saf. Environ. Prot.* **2018**, *116*, 737−744.