Proceedings of the 35th European Safety and Reliability & the 33rd Society for Risk Analysis Europe Conference
Edited by Eirik Bjorheim Abrahamsen, Terje Aven, Frederic Bouder, Roger Flage, Marja Ylönen

Published by Research Publishing, Singapore.
doi: 10.3850/978-981-94-3281-3_ESREL-SRA-E2025-P7638-cd

Partition ratio evaluation for safety risk management of liquid ammonia spills to seawater

Ailo Aasen

Department of Gas Technology, SINTEF Energy Research, Norway. ailo.aasen@sintef.no

Yannick Jooss

Department of Gas Technology, SINTEF Energy Research, Norway. yannick.jooss@sintef.no

Hans L Skarsvåg

Department of Gas Technology, SINTEF Energy Research, Norway. hans.skarsvag@sintef.no

Marta Bucelli (*)

Department of Gas Technology, SINTEF Energy Research, Norway. marta.bucelli@sintef.no

Refrigerated liquid ammonia at atmospheric pressure is considered the safest transport and storage mode. In recent years, ammonia has gained attention as an alternative fuel to abate carbon emissions from the shipping fleet. Its implementation and use on the waterways imply some careful adjustments of technical systems and handling procedures on board to ensure, first and foremost, the safety of the public and the crew in case of accidental spill. Ammonia is toxic for humans, but it is also a threat to the marine environment, potentially killing fish by direct contact and by stimulating algae production leading to localized oxygen scarcity. On-board systems and procedures should therefore be thoughtfully engineered to minimize the risks to humans and the environment due to accidental ammonia releases. A complete and detailed understanding of the physical behavior of ammonia releases is therefore of paramount importance to ensure adequate design. This work presents a case study considering an emergency situation on a ship vessel caused by a large release of liquid ammonia to the sea. Accurate thermodynamics of the ammonia-water system are used to calculate the ratio of dissolution and evaporation (partition ratio) following a spill on water. The partition ratio calculation is based on the best available models in literature. The work discusses the sources of uncertainties in the modelling of accurate thermophysical behaviors of ammonia-water interactions. Finally, we discuss how accurate thermodynamic models might serve the design of safety systems and procedures to safeguard both crews and marine life and prevent unnecessary over-conservatism.

Keywords: Ammonia, alternative fuels, risk management, maritime safety, source term modelling.

1. Introduction

Anhydrous ammonia is an alternative fuel which can aid in decarbonizing offshore shipping and industry and act as a global energy carrier for hydrogen transport (DNV, 2022). Ammonia is considered and tested for use as fuel in internal combustion engines for ship propulsion or for power generation on offshore installations. In both cases, ammonia is used on the waterways or in their proximity. The implementation of ammonia for the decarbonization of both shipping and offshore power generation will increase both the number of transfer operations, the amount, and the stakeholders involved. Today, a limited number of bunkering and transfers is carried out per year. Each operation is performed by dedicated crews at specialized industrial sites. While used as a fertilizer for decades, accidents leading to severe injuries and deaths have been reported (ARIA, 2007). These events have resulted in injuries and fatalities due to the toxicity and flammability of ammonia. The potential large-scale implementation of ammonia on the waterways and its handling by different users introduce emerging risks and potentially stricter requirements. The International Code of Safety for Ships Using Gases or Other Low-flashpoint Fuels (IGF) code is presently being updated, and interim guidelines have been published Dec 2024 to account for the safety related properties of ammonia. Table 1 shows the concentrations at which ammonia can lead to severe effects (and/or death) on humans and marine life. Furthermore, ammonia also acts as a fertilizer in seawater, stimulating algae production and therefore limiting the oxygen available to fish and other marine animals (NIOSH, 1994).

Table 1 Health risks of ammonia at varying concentrations for humans and fish.

Effect	Concentration
Immediately Dangerous to Life or Health (IDLH) concentration	300 ppm (NIOSH, 1994)
Fatal for humans	5000 – 10 000 ppm (NIOSH, 1994)
Threat to marine life	Above 1700 mg/L (pH above 11) (ECHA, n.d.)
Fatal for fish (rainbow trout)	0.75-3.4 mg/L (Thurston and Russo, 1983)

In an emergency, releasing the ammonia under water is a potential safety measure. Experience from past experiments (Little, 1974) suggests that the behavior of liquid ammonia (LNH_3) when released under (and over) water is still unclear, in particular the partition ratio, i.e. the fraction of ammonia dissolved in water. This leads to concerns related to 1) the quantification of the amount of ammonia vaporized, bubbling from underwater and dispersing in air, representing a threat to human, and 2) the assessment of the ammonia left underwater representing a threat to marine life. A detailed and representative quantification of the partition ratio of ammonia into seawater can support the management of safety risks arising from the implementation on large-scale.

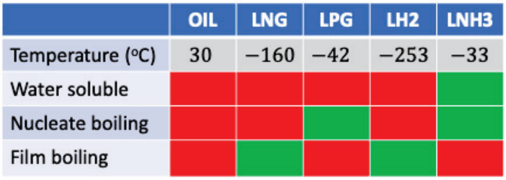
This paper presents the state of the art for experimental data and models for ammonia spills on seawater. Relevant aspects include the partition ratio, but also aspects such as the possibility of aerosol generation or underwater explosions. We also discuss knowledge gaps and their implications for risk management.

2. State of the art of ammonia-water interaction and their implications on safety risk management

Storing and handling ammonia as a refrigerated liquid (-33 °C) at atmospheric pressure is considered safer than pressurized storage (DNV-GL, 2021). The reason is that the rupture of a pressurized ammonia vessel immediately forms a cold, heavy and toxic fog. A refrigerated ammonia release on land will generally result in a liquid pool, and the resultant boil-off vapor will be buoyant and hence less dangerous (Skarsvåg et al., 2024).

The behavior of refrigerated liquid ammonia on a body of water is less understood. In terms of solubility and boiling regime, it differs from other energy carriers (Table 2) such as oil, Liquefied Natural Gas (LNG), Liquid Hydrogen (LH_2). The most similar energy carrier is Liquefied Pressurized Gas (LPG), which like LNH_3 causes nucleate boiling when spilled into water. However, unlike LPG, LNH_3 is highly soluble in water (with an exothermic reaction) and generates large amounts of vapor upon mixing. Although the temperature difference indicates that liquid ammonia should be characterized as nucleate boiling on water, it is due to its solubility perhaps more accurate to label the boiling dissolution-enhanced nucleate boiling. In contrast, LPG does not dissolve into water. This causes ice formation for LPG spills, whereas the heat released when mixing NH_3 into water, combined with the resultant freezing point depression, will inhibit ice formation. In fact, mixing LNH_3 with seawater is exothermic and can yield mixture temperatures upwards of 50 ℃ (Little, 1974).

Table 2 Physical characteristics of spills of common energy carriers. Temperature listed correspond to boiling points at atmospheric pressure.



	OIL	LNG	LPG	LH2	LNH3
Temperature (°C)	30	−160	−42	−253	−33
Water soluble	🟥	🟥	🟥	🟥	🟩
Nucleate boiling	🟥	🟥	🟩	🟥	🟩
Film boiling	🟥	🟩	🟥	🟩	🟥

2.1. Experiments and availability of data

Most knowledge for accidental liquid spills to sea has been developed for current energy carriers, such as LNG and oil. Experimental data of LNH_3 spills on and into water are sparse. Such release scenarios are challenging to characterize in detail, particularly for LNH_3, with added complexity posed by the simultaneous dissolution reaction, evaporation, and mixing.

To de-risk transport of refrigerated NH_3 on waterways, the United States Coast Guard commissioned tests of LNH_3 spills on and into water (Little, 1974). Controlled spills were conducted at laboratory intermediate and large scale, with released amounts between 0.75 L and 180 L. The spill rate, spill angle, water temperature, water salinity, containment of the spill region, air flow and water flow were varied during the tests. The parameters were varied one at a time, while keeping the others constant. Generally, the LNH_3 was spilled continuously, but in addition also a series of quasi-instantaneous spills was conducted.

The partition ratio was measured by concentration measurements in water and air after the spill. Evaporation was optically observed only in a small region around the spill. A thin layer of aqueous NH_3 spread horizontally along the surface. The influence of the varied parameters on the partition ratio is visualized in Figure 1. Even at similar conditions, the measured partition ratios varied considerably between experiments, with results ranging from 43% to 95%. Within the scatter, only limited influence of the varied parameters was identified. This led to the conclusion that the process is thermodynamically controlled, and largely insensitive to the mixing dynamics. However, this was not examined systematically, and realistic surface impact scenarios were not explored. Pressurized underwater spills led to increased partition ratios, which suggests an influence of mixing. This can have an impact also for surface spills with large downward momentum where the LNH_3 penetrates deeply below the water surface.

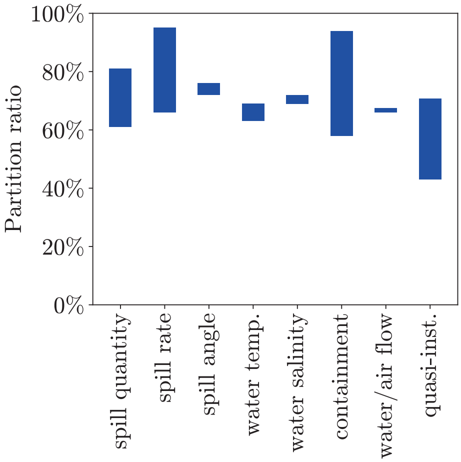


Figure 1 Range of partition ratios observed by (Little, 1974) by varying different parameters.

More recently the so-called red squirrel ammonia field experiments investigated spills of pressurized and refrigerated NH_3 on both dry land and onto a water surface (Dharmavaram et al., 2023). Partition ratios of above 50% were observed for spills on water. A short-duration vapor release was observed, followed by very low vaporization rates from the water pool the LNH_3 was spilled on. The focus of this study was primarily on tracking and modelling the dispersion in air, rather than a detailed analysis of the interaction between refrigerated NH_3 and water.

In addition, several initiatives, such as the Jack Rabbit program ("https://www.uvu.edu/es/jack-rabbit/," n.d.) and the ARISE JIP (https://www.arise-partnership.org/), investigate very large experimental spills of chlorine and ammonia both on land and to sea. For releases on land, they found that for both chlorine and ammonia the observed hold-up time of the cloud that forms increases linearly with $1/u^3$, where u is the wind velocity.

2.2. Available modelling tools

The state-of-the-art model for predicting the partition ratio of liquid ammonia spills is the Raj-Reid model (Raj and Reid, 1978), and originates from the US Coast Guard research program in the 1970s (Raj et al., 1974). This is a thermodynamic model based on energy balance and equilibrium thermodynamics of ammonia and pure water. The model assumes a hypothetical process where an initially pure LNH_3 pool mixes with incremental additions of liquid water (Figure 2). One adds an infinitesimal amount of water to the pool, allows the mixture to equilibrate adiabatically, and removes the vapor puff. Thermodynamics dictates that vapor production stops after the NH_3 in the (initially pure LNH_3) pool is sufficiently diluted with water. The fraction of the NH_3 remaining in the pool equals the predicted partition ratio.

From the nature of the model, it follows that predictions from the Raj-Reid model are independent of factors such as wind condition, spill scenario (impact velocity, angle, rate and quantity), and depth (for subsea releases). The model accounts for water temperature, where a weak dependence is found, (Figure 3); comparing with the experimental results (Figure 1) it seems to accurately reproduce this variability.

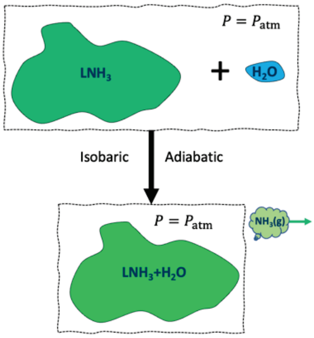


Figure 2 Illustration of the hypothetical mixing process assumed by Raj and Reid. Small amounts of water are incrementally mixed into an LNH_3 pool, and the vapor puff is continually removed.

The merit of the Raj-Reid model is its simplicity and that it approximately predicts the magnitude of the partition ratio and its general dependence on temperature. Beyond this, it lacks predictive power, and is not conservative in any direction. Raj and Reid stated that their model "gives the upper bound for the partition coefficient, i.e. a lower bound for the amount of vapor liberated in a spill." However, this is not true for subsea spills; in fact, for sufficiently deep subsea spills the partition ratio will be 100%, since all ammonia will dissolve before reaching the surface. Moreover, a spill that is spread thinly across a large water surface, should have lower partition ratios, with more ammonia entering the air. This case may occur for small spills if the released ammonia has a large horizontal momentum.

Other variations of thermodynamic models are conceivable, such as assuming small incremental additions of LNH3 into a pool of water. The drawback is that the partition ratio will then depend on the amount of water, and for a sufficiently large pool of water all LNH3 will dissolve (partition ratio 100%). Moreover, any thermodynamic model of this form does not account for extraneous factors such as penetration depth of spills, or wind and water flow patterns. But with a better understanding of how mixing process is affected by the extraneous factors, one may be able to piece together several such thermodynamic processes into a more realistic overall model.

Naturally, a more comprehensive model would include accurate submodels for the heat, mass and momentum transfer mechanisms – in other words, a computational fluid mechanics (CFD) model. The challenges and promise CFD will be discussed in Section 5.

2.3. Safety risk management

According to ISO 31000:2018, the risk management framework is defined as in the process presented in Figure 4.

The development of specific and detailed thermophysical models supported by experimental data could contribute to and support the risk management process for ammonia used as a ship fuel, and limit (if not avoid) over-conservatism. The models and data could support the risk analysis by providing more detailed consequence models for risk analysis, as well as supporting the risk treatment phase.

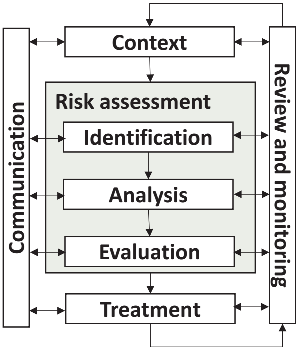


Figure 3 Risk management framework (ISO, 2018).

3. Case Study

This study considers the bunkering of an ammonia fueled ship where ammonia is stored on board as a saturated refrigerated liquid at ambient pressure and -33 °C. The operation consists of three main units, as follows: on-board storage of ammonia, transfer equipment (hose), and onshore storage of ammonia at the terminal. It is assumed that the liquid ammonia is transferred by a sub-merged pump from the onshore storage tank to the ship storage tank. A preliminary hazard identification for the liquid ammonia transfer is carried out to identify potential failures and their causes and consequences. For each defined hazard, a set of representative loss of containment (LOC) scenarios is defined based on the quantitative risk analysis guidelines (RIVM, 2005). For each LOC scenario, the release rates are calculated depending on the release phase conditions (in this case: liquid single-phase or flashing liquid releases). Finally, reference accident scenarios are defined and considered further in the study. It should be noted that this study considers only the release scenarios that can result in spills of refrigerated liquid ammonia to sea. Releases of toxic (gaseous) material from the pressure relief systems and safety valves are not addressed further in this work. Such releases shall always go to a safe location and not be a threat to people and are supposed to be a part of the safety system.

The equipment identified as most critical is the transfer hose carrying liquid ammonia from the onshore ammonia terminal storage tank to the ship tank. Specifically, the connection point between the hose and the ship tank is addressed as the most critical for spills of liquid ammonia to sea. A summary of the reference accident scenarios for the hose, including the calculated release rates considered, is provided in Table 3 below.

Table 3 Reference accident scenarios for the transfer of liquid ammonia (at boiling point) with a flexible hose.

Type	Diameter (mm)	Rate
Full-bore	150	350 m^3/h
Small	15	25 m^3/h

4. Results

We have used the Raj-Reid model to estimate partition ratios (Table 4) for the reference accident scenarios. We calculated the thermodynamic properties using the highly accurate reference equation of state for the ammonia-water mixture available through REFPROP V10 (Huber et al., 2022).

The temperature-dependence of the predicted partition ratio is weak, and for simplicity we therefore assumed a fixed water temperature of 10 °C. The model predicts a partition ratio of 73%, meaning that 27% of the vapor will release to the atmosphere as gaseous ammonia (GNH_3). The high release rate to air seen in Table 4 is because the gaseous ammonia has ~ 770 times higher volume than the refrigerated liquid.

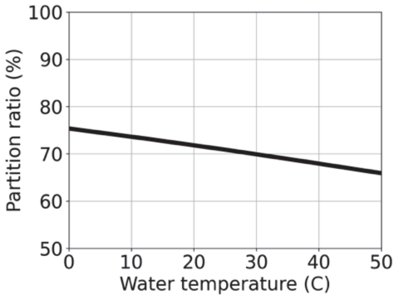


Figure 4 Temperature dependence of the partition ratio in the Raj-Reid model.

Once the partition ratio has been determined, a typical dispersion study would proceed with conventional CFD models for dispersion of the ammonia in air and, if needed, in water.

Table 4 Rates of liquid ammonia dissolved to sea, and gaseous ammonia released to air.

Type	**LNH_3 (dissolved)**	**GNH_3 (to air)**
Full-bore	256 m^3/h	26 800 m^3/h
Small	18 m^3/h	1 910 m^3/h

5. Discussion

5.1. Gaps and needs for ammonia release modelling

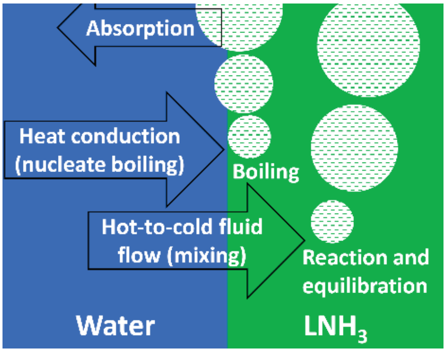


Figure 5 Illustration of key physical interactions between an LNH_3 spill and water.

A key outstanding requirement to safe use of ammonia is accurate dispersion modeling, needed to establish toxicity zones. Although the partition ratio is a key input to dispersion models, there are other aspects important to such risk analyses.

Little et al. (Little, 1974) laid out four unresolved questions for ammonia spills at sea:

- What is the amount of aerosol generated above a surface spill, and how does it relate to the mode of spill (instant, continuous) and the rise of the vapor cloud?
- Why is there a rapidly rising vapor cloud for spills on water, while for land-based spills one often sees ground-hugging fogs?
- What are the mechanisms, if any, that can cause underwater explosions in the case of instantaneous large subsea releases of LNH_3?
- What are the scaling laws governing the maximum radius of the boiling zone as a function of the size of the spill?

There is currently a lack of both experimental results, physical understanding, and modeling tools that address these questions. This is not surprising considering the complex physics of the mixing process (Figure 5). One poorly understood aspect is the formation and impact of ammonia-water fog on dispersion characteristics, which only recently has been studied for land-based spills (Skarsvåg et al., 2024). One of the key unknowns when scaling up the use of LNH_3 as an energy carrier is the influence of the *size* of the spill. One of the aims of the *SafeAm* project ("SafeAm – Increased safety of ammonia handling for maritime operations," 2024) is to develop such a model, and publish it in a freely available, open-source manner.

A full description of the dissolution and evaporation process can potentially be done in a multiphase CFD framework. This would require detailed sub-models that account for the local heat transfer, dissolution and relaxation towards the two-phase equilibrium. This is very challenging, since the real process involves multiple length scales, from bubbles governed by surface tension to buoyancy forces acting on the scale of the entire mixing zone, and furthermore, due to the very different time scales involved from rapid equilibration to the slower large-scale mixing.

SafeAm will also address the possibility of subsea explosions, which Little et al. describe as follows: *"Small-scale experiments on the release of LNH3 and other cryogens under water have determined that there is a possibility of pressure* *explosions occurring underwater. The physical aspects of such explosions are not fully understood at this time…"* A key outstanding question is whether such pressure peaks are due to a nucleation event or simply a fast, vapor-generating equilibrium process.

5.2. Need for more experimental data

While previous experiments give an approximate value for the partition ratio, the detailed mechanisms governing the dissolution and evaporation of refrigerated LNH_3 are not yet well described. Spills can occur in many ways and thus with a wide range of release rates, quantities and boundary conditions. To develop scalable thermophysical models, it is critical to increase the understanding of the governing mechanisms. In addition, a systematic investigation of the influence of turbulent mixing is required. These models can then be applied to accidental spills onto water as well as to scenarios when LNH_3 is spilled subsea as a safety measure.

Since a dependency on the spill size is expected, spills at both lab scale and larger spills at representative scale must be studied to validate models and further improve our understanding.

5.3 Risk management perspective

The design of safety systems and the implementation of emergency procedures for handling liquid ammonia spills shall be optimized to minimize their impact on people and crews, the environment and marine life for a scale-up of ammonia as an alternative ship fuel or energy carrier.

Methods for risk analysis and advanced techniques able to include more detailed thermodynamics into the risk pictures are needed. This will improve the overall risk management process.

The calculation of more precise mass transfer and evaporation rates to evaluate a credible partition ratio in different conditions of pH, spill rate and quantity, penetration depth, wind and water flow, salinity, and temperature (as explained above) will support the development, implementation and execution of emergency preparedness measures. Furthermore, it will also influence the choice of a safety strategy that limits the excessive conservatism associated with the quantity of ammonia dissolved in water and the volume released into air. Different safety measures for the near field and far field could be defined considering both the safety of crews, personnel and the general public as well as environmental protection.

6. Conclusions and way forward

The scale-up of ammonia use necessitates accurate physical models to support risk management. A spill of refrigerated ammonia at sea results in a violent and complex mixing process. The Raj-Reid model for partition ratios is a simple thermodynamic model that yields a ballpark estimate for how much ammonia partitions to the sea, and how much ends in the air. Unfortunately, it has limited predictive power, and we illustrated how this model gives identical partition ratios in two very different case studies. There is currently a lack of modeling tools that account for the influence of dynamic effects such as spill size, rate and depth.

An important, outstanding problem is therefore to develop computational fluid dynamics models that account for dynamic effects. This requires accurate submodels based on an increased understanding of the physical mass, heat, and momentum transfer mechanisms that occur in the mixing process.

To ensure reliability, such models must be validated against experiments. It is crucial that such experiments cover various scales since the behavior of spills, including its partition ratio, depend on the spilled amount. Small spills will mix faster with water and can be studied in more detail than large spills. Large spills, however, are crucial to understand for risk analysis. With ongoing research projects for both small spills (SafeAm) and large spills (ARISE), the coming years hold the promise to considerably increase our understanding of ammonia spills at sea.

Acknowledgement

The work presented in this article was supported by the SafeAm project, funded by the Research Council of Norway (project no. 344210) and industrial partners. The authors wish to thank Ole Kristian Sommersel, Sandra Hennie Nilsen, and Marthe Solaas for feedback. Views and opinions expressed are those of the authors only and do not necessarily reflect those of the Research Council nor the industrial partners.

References

ARIA, 2007. Rupture of a cryogenic ammonia tank in a fertilizer production plant. La référence du retour d'expérience sur accidents technologiques. URL https://www.aria.developpement-durable.gouv.fr/fiche_detaillee/717_en/?lang=en (accessed 12.13.24).

Dharmavaram, S., Carroll, M.J., Lutostansky, E.M., McCormack, D., Chester, A., Allason, D., 2023. Red Squirrel Tests: Air Products' ammonia field experiments. Process Safety Progress 42, 481–498. https://doi.org/10.1002/prs.12454

DNV, 2022. Maritime Forecast to 2050. Energy Transition Outlook.

DNV-GL, 2021. Ammonia as a Marine Fuel - Safety Handbook.

ECHA, n.d. Ammonia, anhydrous. Substance Info-Card of the European Chemical Agency [WWW Document]. URL https://echa.europa.eu/substance-information/-/substanceinfo/100.028.760 (accessed 12.10.22).

https://www.uvu.edu/es/jack-rabbit/ [WWW Document], n.d.

Huber, M.L., Lemmon, E.W., Bell, I.H., McLinden, M.O., 2022. The NIST REFPROP Database for Highly Accurate Properties of Industrially Important Fluids. Ind. Eng. Chem. Res. 61, 15449–15472. https://doi.org/10.1021/acs.iecr.2c01427

ISO, 2018. Risk Management - Guidelines, ISO 31000:2018.

Little, A.D., 1974. Prediction of Hazards of Spills of Anhydrous Ammonia on Water. Prepared for US Coast Guard. NTIS - National Technical Information Service.

NIOSH, 1994. Ammonia - Immediately Dangerous to Life or Health (IDLH) Concentrations from the National Institute for Occupational Safety and Health. [WWW Document]. URL https://www.cdc.gov/niosh/idlh/7664417.html (accessed 12.10.22).

Raj, P.K., Hagopian, J., Kalelkar, A.S., 1974. Prediction of Hazards of Spills of Anhydrous Ammonia on Water. US Defence Technical Information Center.

Raj, P.P.K., Reid, R.C., 1978. Fate of liquid ammonia spilled onto water. Environ. Sci. Technol. 12, 1422–1425. https://doi.org/10.1021/es60148a008

RIVM, 2005. Guideline for quantitative risk assessment "Purple book" CPR18E, Publication Series on Dangerous Substances (PGS 3).

SafeAm – Increased safety of ammonia handling for maritime operations [WWW Document], 2024. . SINTEF. URL https://www.sintef.no/en/projects/2023/safeam__increased_safety_of_ammonia_handling_for_maritime_operations/ (accessed 11.27.24).

Skarsvåg, H.L., Fyhn, E.H., Aasen, A., 2024. Influence of ammonia-water fog formation on ammonia dispersion from a liquid spill. Journal of Loss Prevention in the Process Industries 92, 105446. https://doi.org/10.1016/j.jlp.2024.105446

Thurston, R.V., Russo, R.C., 1983. Acute Toxicity of Ammonia to Rainbow Trout. American Fisheries Society 112, 696–704.