Ocean Engineering 314 (2024) 119753

Contents lists available at ScienceDirect

Ocean Engineering

journal homepage: www.elsevier.com/locate/oceaneng

Research paper

Towards risk-informed design and operation of ammonia-powered ships: Critical aspects and prospective solutions

Rustam Abubakirov [a,**], Ming Yang [a,*], Giordano Emrys Scarponi [b], Valeria Casson Moreno [c], Genserik Reniers [a,d,e]

[a] Safety and Security Science Section, Faculty of Technology, Policy and Management, TU Delft, 2628 BX, Delft, the Netherlands
[b] LISES - Laboratory of Industrial Safety and Environmental Sustainability, DICAM - Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, via Terracini 28, 40131, Bologna, Italy
[c] Department of Civil and Industrial Engineering – University of Pisa, Largo Lucio Lazzarino n.2, 56126, Pisa, Italy
[d] Faculty of Applied Economics, Antwerp Research Group on Safety and Security (ARGoSS), Universiteit Antwerpen, 2000, Antwerp, Belgium
[e] CEDON, KU Leuven, 1000, Brussels, Belgium

ARTICLE INFO

Keywords:
Maritime safety
Decarbonization
Ammonia
Toxic risk
Human-machine interaction

ABSTRACT

Ammonia is a promising fuel for marine propulsion and generation, yet its acute toxicity and associated safety challenges necessitate careful consideration. Current regulations recognize the hazards of ammonia, introducing numerous technical safety measures in response. However, the effectiveness of these measures in ensuring acceptable risk levels for future vessels remains to be fully assessed. This study estimates the risk level onboard ammonia-powered ships, identifying the aspects with the largest and controllable influence on it. Three hypothetical concepts of ammonia fuel supply were developed in this study on an example tanker vessel and analyzed using the quantitative risk assessment (QRA) methodology. The obtained risk profiles were evaluated against the risks by an equivalent liquefied natural gas-fueled system, serving as a benchmark. The results demonstrate that ammonia-fueled ships exhibit individual risk levels for engineering crew with periodic duties in fuel preparation rooms (FPR), or similar compartments, which are 1–1.5 orders of magnitude higher than those observed for a conventional gas-fueled alternative. An analogous increase has been noted for the public potentially present onboard or in proximity. The study underscores the importance of managing human-machine interactions, enhancing the reliability of supply systems, and managing the systems' complexity to mitigate risks in FPRs. Regarding public safety, the analysis highlights new risk mechanisms introduced by ammonia and examines how storage conditions affect exposure levels. By offering a detailed QRA framework, this research contributes to the development of effective risk management strategies for ammonia-powered ships.

List of abbreviations

AEGL	Acute Exposure Guideline Level
BOG	Boil-off Gas
ESD	Emergency Shutdown System
FB	Fireball
FF	Flash Fire
FG	Flammable Gas
FMECA	Failure Mode, Effects, and Criticality Analysis
FPR	Fuel Preparation Room
FSA	Formal Safety Assessment
FVT	Fuel Valve Train

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IDLH	Immediately Dangerous to Life or Health
IGF	International Code of Safety for Ships using Gases or other Low-flashpoint Fuels
IMO	International Maritime Organization
IR	Individual Risk
JF	Jet Fire
LFL	Lower Flammability Limit
LNG	Liquefied Natural Gas
LOC	Loss of Containment
LSIR	Location-specific Individual Risk
MS	Machinery Space

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* Corresponding author.
** Corresponding author.
E-mail addresses: R.Abubakirov@tudelft.nl (R. Abubakirov), M.Yang-1@tudelft.nl (M. Yang).

https://doi.org/10.1016/j.oceaneng.2024.119753
Received 27 May 2024; Received in revised form 25 July 2024; Accepted 7 November 2024
Available online 18 November 2024

(*continued*)

PF	Pool Fire
PFD	Process Flow Diagram
POFD	Probability of Failure on Demand
PPE	Personal Protective Equipment
QRA	Quantitative Risk Assessment
SIL	Safety Integrity Level
T&FG	Toxic and Flammable Gas
TCS	Tank Connection Space
TD	Toxic Dispersion
TG	Toxic Gas
VCE	Vapor Cloud Explosion

1. Introduction

Ammonia has captured considerable attention in the maritime industry reflected in concrete developments in its introduction as fuel (MAN Energy Solutions, 2020; MPA Singapore, 2024; Wärtsilä, 2023). By storage conditions, it resembles common propane, it has adequate energy density, the molecule itself is carbon-free, and it can be sustainably produced (The Royal Society, 2020). These properties make ammonia valuable in the scope of the industry's decarbonization goals (IMO, 2018a). However, such potential comes with a unique challenge – ammonia is the first acutely toxic gas to be used as fuel. This prompts for a comprehensive revision of safety onboard, addressing new and old hazards related to fuel storage, supply, and consumer systems. Given these systems' diverse and increasingly complex design, identifying key aspects affecting the ships' safety performance becomes a primary concern.

At the time of writing this article, the most comprehensive guidelines on the safety of ammonia-fueled ships are represented by the rules from classification societies, which within the present work will be referred to collectively (American Bureau of Shipping, 2023; Bureau Veritas, 2022; DNV, 2023). The rules fully acknowledge the hazards of ammonia and address them by prescribing a series of technical safety measures in response. These measures are mainly presented by the approaches of double containment for potential leak sources, segregation of hazardous equipment, and mitigation of consequences following an accidental release. Many of the measures are not new to the maritime industry as these can be traced back to the IGF Code or preceding regulatory provisions for the use of low-flashpoint fuels, i.e., primarily liquefied natural gas (LNG) (IMO, 2016a, 2016b, 2009). In a retrospective view, the development of these engineering approaches coincides with LNG's well-proven safety record (Eliopoulou et al., 2016; Vanem et al., 2008).

However, there is limited evidence on the effectiveness of the proposed measures against ammonia toxicity. Ammonia and hydrocarbon fuels possess a drastically different set of hazardous properties. For comparison, ammonia is rapidly fatal at concentrations above 2700 ppm in the air, as defined by Acute Exposure Guideline Level 3 (AEGL-3), while methane's lower flammability limit (LFL) is an order of magnitude higher, at 50,000 ppm (Green and Southard, 2019; National Research Council, 2008). Note that the hazardous consequences for the former are also independent of ignition. In this light, demonstrating true safety level equivalence between novel (alternative) and conventional system designs, which is an essential logic in the maritime safety philosophy, does not involve predefined answers (Hamann and Peschmann, 2013). Solutions that provide an acceptable safety level for LNG will not necessarily be effective for ammonia. Meanwhile, when safety requirements for ammonia exceed those for LNG, a transparent illustration of the merits of the additional measures is naturally expected. In this context, a robust safety analysis would establish and systemically analyze the relationships between the systems' design and operational variables, with or without mitigation, to a consolidated metric indicative of the future safety level of a novel technology. Such analysis can be performed by adopting a quantitative risk-based framework.

Risk-based approaches are not novel to the maritime industry. IMO formally encodes these as Formal Safety Assessment (FSA) to support decision-making in regulation, thus providing a tool for its goal-based framework (Hamann and Peschmann, 2013; IMO, 2018b). Exemplary applications of risk-based approaches in ship design can be found in the series of publications under the SAFEDOR project concluded by Breinholt et al. (2012) or in the works with a specific focus on damaged ship stability by Papanikolaou et al. (2013). Concerning the chemical hazards, the proliferation of risk modeling coincides with the more widespread adoption of LNG, with many works being topic dedicated to third-party risk assessment in port areas due to strict risk acceptability limits in those (Jeong et al., 2020; Marroni et al., 2023; Xie et al., 2022). Meanwhile, quantitative publications on the onboard safety of LNG-fueled ships are scarce. Notable ones include Davies and Fort's (2013) release frequency analysis and an FPR explosion risk modeling by Jeong et al. (2017).

Concerning ammonia, the amount of literature on its safety does not match the rapid progress of the technology. Similar to LNG, recent years have seen an increasing number of risk assessments for ammonia bunkering (DNV, 2021; Fan et al., 2022; Jeong et al., 2020). The onboard safety has been addressed by de Vries (2019) through a qualitative risk assessment and by Trivyza et al. (2021) through a failure modes, effects, and criticality analysis (FMECA) of fuel storage and supply systems. While these methods are recognized tools for early-stage risk analysis in the industry, it is important to acknowledge that their outcomes often carry a significant degree of subjectivity, depending on the reviewers' background and unstated assumptions. Therefore, a recent study by Lloyd's Register Maritime Decarbonization Hub (LR MDH) and Mærsk Mc-Kinney Møller Center for Zero Carbon Shipping (MMMCZCS) (2023a) holds prominence as it first addresses ammonia safety onboard by applying the formal QRA methodology (Franks and Graugaard, 2022). QRA is a consolidated and proven method in chemical process industries onshore that, with relevant adaptations to the maritime context, can provide reliable data-supported insights into future risks onboard. The authors emphasize the value of the mentioned study but also urge a more consistent application of the methodology along with the principles for inherently safer design (Davies, 2022).

The present work aims to determine and analyze the impact of ammonia fuel system design choices on the risk level onboard, thereby outlining the system's safety-critical aspects. Ammonia offers great flexibility across storage, supply, and consumer technologies, e.g., allowing for various storage states and operational strategies. Such considerations are located high in the hierarchy of controls and, in theory, should have a larger influence on risk onboard than mitigative barriers, crew training, or personal protective equipment (PPE), which are substantially emphasized in the existing regulations and literature. The objective is to characterize a risk contribution hierarchy among various design and operational choices, thus enabling a more justified allocation of risk control measures in the future. Given the IGF code's central role in the emerging regulatory framework for ammonia and following the logic of alternative design, the study adopts a comparative approach, where the risks associated with ammonia systems are compared against that of a conventional technology – LNG. Section 2 introduces four fuel storage and supply concepts employed for the analysis. Section 3 provides an overview of the formal QRA methodology followed in the work. In general, this methodology complies with the "Purple Book", Uijt de Haag and Ale (1999), and its update by RIVM (2009), an established standard in chemical process industries. Section 4 presents the results of the QRA model, outlining the critical aspects and conditions for the safe use of ammonia as fuel. Section 5 concludes the study with final remarks.

2. Fuel storage and supply concepts

2.1. Basis of design

An Aframax-sized tanker has been selected as the reference vessel for this study as they, along with larger ocean-going vessels, represent a key market for alternative fuel developments (Atchison, 2022; Prevljak, 2022). Three ammonia concepts (A-I, A-II, and A-III) and a reference LNG system have been introduced and sized to provide equivalent nominal power and travel range without refueling. Fig. 1 provides a schematic illustration of this framework. Given a 16 MW engine and its overall efficiency of 50%, the energy input from the primary fuel has been set to 32 MJ/s for all concepts. Storage options have been assigned arbitrarily and estimated based on a 600-h autonomous trip a tanker is expected to travel.

The present set of ammonia concepts aims to be representative of the broadest range of the power technologies foreseeable at the moment. These include ammonia–diesel technologies, utilizing a small amount of heavy fuel/diesel oil as a pilot or promoter to aid ammonia combustion, or ammonia–hydrogen configurations, using hydrogen produced onboard as a promoter. The current ammonia–diesel engines can be classified mainly into two types depending on the state of ammonia supply (MAN Energy Solutions, 2020; Wärtsilä, 2023). The first requires liquid ammonia to the injector, with the corresponding supply included in the study as the A-II concept, while the second requires low-pressure vapor, represented by A-III. Considering diesel's limited rate and hazardous properties, compared to ammonia or natural gas, the pilot diesel systems are omitted in the present analysis. Regarding ammonia–hydrogen configurations, these mark a more distant step in the technology development and have been addressed in the present study under the A-I concept, primarily inspired by the works of de Vries (2019) and de Vos (2020). Due to the complexity of ammonia cracking onboard and hydrogen's extreme flammability, the promoter fuel systems cannot be disregarded for the A-I. Concerning the reference LNG concept, a low-pressure supply system, as for Wärtsilä (2019) dual-fuel engines, has been selected.

The following sections specify the design of the selected concepts set.

2.2. Alternatives in storage

There are effectively two options for ammonia storage onboard the reference vessel.

- **Refrigerated**: liquid ammonia is stored close to its saturation at nearly atmospheric pressure inside IMO Type A, Type B, or membrane tanks with design pressures up to 0.7 barg maximum. This configuration needs a boil-off gas (BOG) management system through the supply to consumers or reliquefaction. The tanks are located within the hull by a specified distance from the ship sides and bottom to minimize the likelihood of a loss of containment as a result of collision, grounding, or other contacts (IMO, 2016a).
- **Semi-pressurized**: ammonia is a saturated liquid at any pressure above atmospheric and below 4–9 barg, depending on the design pressure of IMO Type C tanks used for such service. A BOG management system is also required for this option unless it is a fully-pressurized storage with the tank's design pressure above 18 barg, which is practical only for smaller volumes (DNV, 2023). Type C tanks offer flexibility in location and can be placed either within the hull or on the upper deck, subject to the minimal safety distance requirements specified by the IGF Code or analogous provisions (IMO, 2016a).

Fig. 2 presents a schematic layout of the storage with associated supply items. The study assumes refrigerated storage with a prismatic IMO Type A tank for concepts A-I and A-II and semi-pressurized storage with two identical IMO Type C tanks on the deck for concepts A-III and LNG. The total capacity of both options is approximated to 5000 m^3 with the storage conditions for further modeling set as displayed in Fig. 1. Note that the present selection is arbitrary, and other combinations of storage and supply system are possible.

2.3. Alternatives in supply

As illustrated in Fig. 2, the supply systems have been organized in two independent trains rated at 50% of the total consumption each. Existing safety provisions require the system elements to be allocated inside dedicated compartments (American Bureau of Shipping, 2023; Bureau Veritas, 2022; DNV, 2023). Referring to the concepts, this implies the presence of one or two tank connection spaces (TCS) from which the fuel is supplied to the FPRs. There, the fuel is conditioned to meet consumer requirements and directed to a machinery space (MS) and eventually to engines through fuel valve trains (FVT). Requirements for protection of supply piping vary between the rulesets, yet the present study assumes double (protected) piping anywhere within the machinery space and open decks. Fig. 3 presents simplified process flow

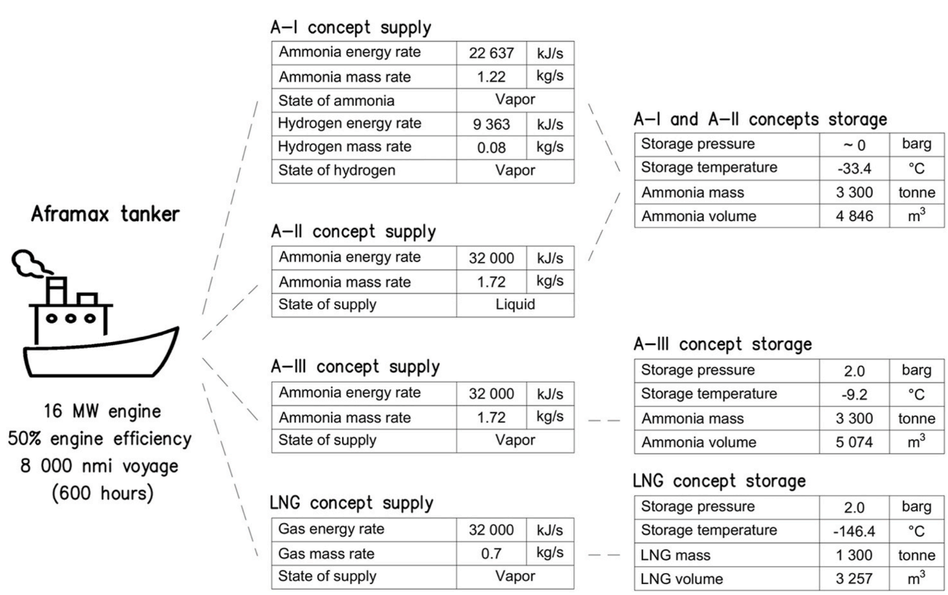

Fig. 1. Overview of four alternative fuel storage and supply concepts designed to provide a comparable service on the same vessel.

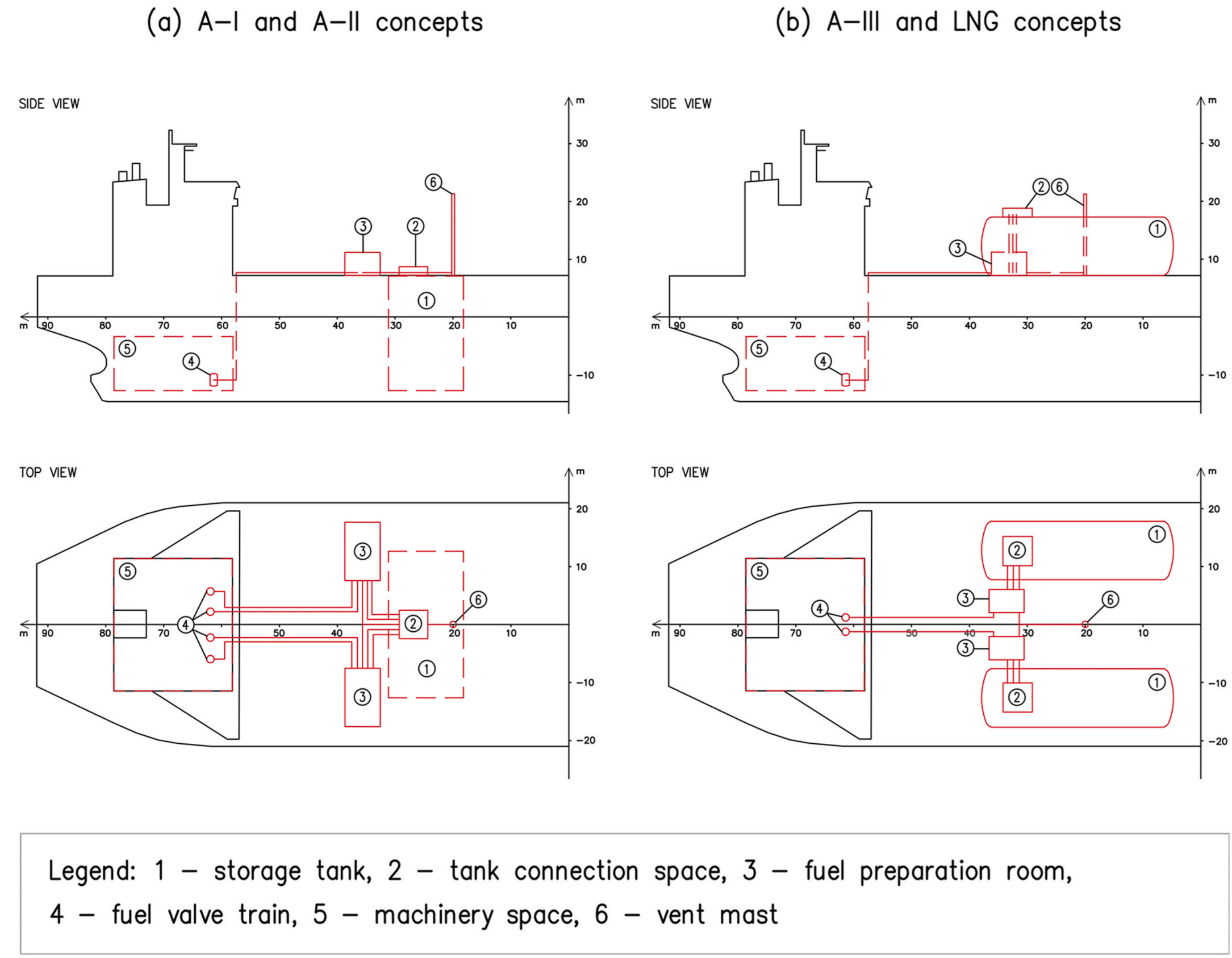

Fig. 2. Schematic layout of the fuel storage and supply system items onboard the reference vessel in two feasible configurations.

diagrams (PFD) of the supply concepts. The corresponding process parameters are provided in Appendix A. The concepts' working principles can be summarized as follows.

- **A-I.** Based on the work of de Vries (2019), this concept involves the supply of liquid ammonia to the FPR by a submersible pump, where it is vaporized and heated above its dew point. BOG from the tank (0.1% fuel vaporization rate per day) is compressed and combined with the main stream. Part of the ammonia is fed to the engine at a pressure of 7 barg before the FVT. Another part is partially cracked to 35–65 vol% hydrogen – ammonia mixture required for stable combustion and injected into the engine port (Zheng, 2020).
- **A-II.** This concept denotes the supply of liquid ammonia as for direct injection engines (MAN Energy Solutions, 2020). The overall system can be subdivided into low- and high-pressure parts. In the low-pressure part, liquid ammonia is fed to the FPR at 25 barg while the BOG undergoes a reliquefaction process. Then, the combined stream is pressurized to 80 barg by a high-pressure pump, heated to approximately 40 °C, and supplied to the engine. The configuration implies that some ammonia is recirculated back at a rate which varies with the engine load. For the present modeling, an ammonia return of 20% from the consumption has been adopted following the work of Lee et al. (2022).
- **A-III.** This concept represents fuel systems for engines with a port injection of ammonia (Wärtsilä, 2023). In principle, the concept is analogous to A-I, with cracking being excluded. The vaporized ammonia from a submersible pump and compressed BOG are combined, and the stream is supplied to the FVT at 7 barg, 60 °C and further to the engine.
- **LNG.** This concept is essentially the same as A-III and serves in combination with the same family of engines run on natural gas (Wärtsilä, 2019, 2023). The combined stream of vaporized LNG and compressed boil-off is supplied to the FVT at 7 barg, 20 °C and further to the engine.

The TCS, FPR, and machinery spaces are compartments with a controlled environment. As stated in the classification rules, these must be equipped with independent ventilation systems providing 30 air changes per hour as a minimum (American Bureau of Shipping, 2023; Bureau Veritas, 2022; DNV, 2023). The compartments are also to be equipped with gas detectors, emergency shut-down (ESD), and various other mitigative barriers specific to an individual ruleset. Following DNV (2023) regarding the barriers, the study assumes a catastrophe (or emergency) ventilation system with a rate of at least 300 m^3/h per square meter of a deck, or 45 changes per hour, whichever is greater, activated by the detection of ammonia in the air. These specifications are important in further risk evaluation, and the sensitivity of the results

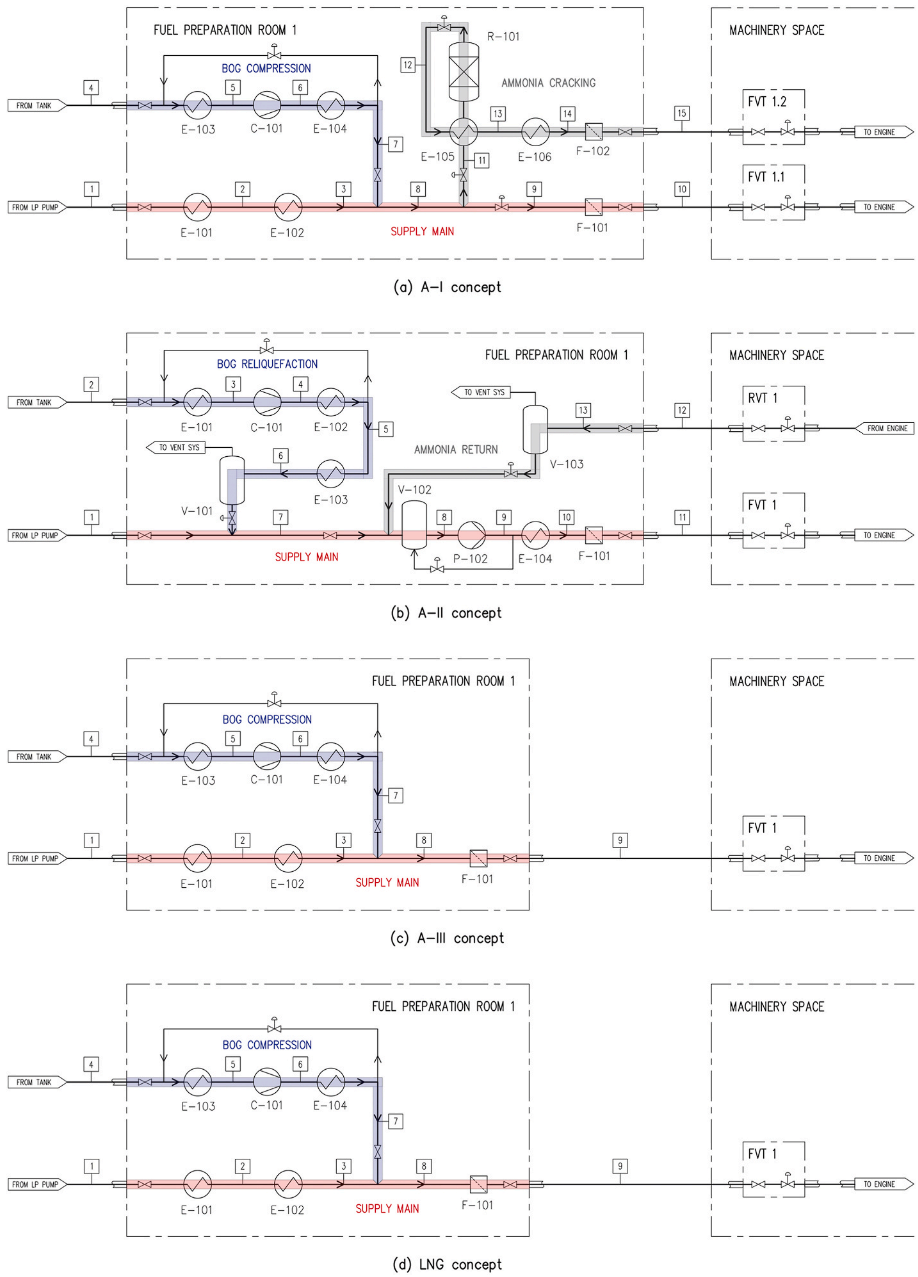

Fig. 3. Simplified process flow diagrams of the fuel supply concepts analyzed in the present study.

on these values will be discussed.

Note that the introduced concepts might not be optimal from economic or other perspectives. For instance, redundancy of the fuel supply and its arrangement in two trains would rather be a necessity for A-I or other ammonia concepts but not for LNG. Similarly, using BOG as fuel may not be the universal choice in practice. These and similar aspects, if deemed technically feasible and not contradicting applicable rules, were designed analogously across all concepts. The differences induced by more fundamental factors such as fuel composition, its state, or supply complexity on the risk level were the subject of investigation, and minimization of interference from indirect factors on the comparative study results was desirable.

3. Risk evaluation methodology

This section presents the employed risk evaluation methodology, which is based on the Dutch "Purple Book" QRA guideline and its update (RIVM, 2009; Uijt de Haag and Ale, 1999). The text highlights the core concepts and any modifications made to address the maritime specifics. Section 3.1 introduces the key quantities involved in the QRA, i.e., location-specific individual risk (LSIR) and individual risks (IR) for exposed population groups, Section 3.2 addresses LOC scenario definitions with their frequency, and Section 3.3 – scenario consequence analysis. A schematic flowchart of the methodology and the location of its elements within the context is illustrated in Fig. 4. The concepts presented in Section 2 serve as input to the procedure, which yields intermediate results in terms of LSIR distributions onboard. Upon introducing exposed population groups further in Section 4, the LSIR profiles allow calculation and assessment of the IRs, which are concluded by the identification of systems' safety-critical aspects and applicable mitigation solutions.

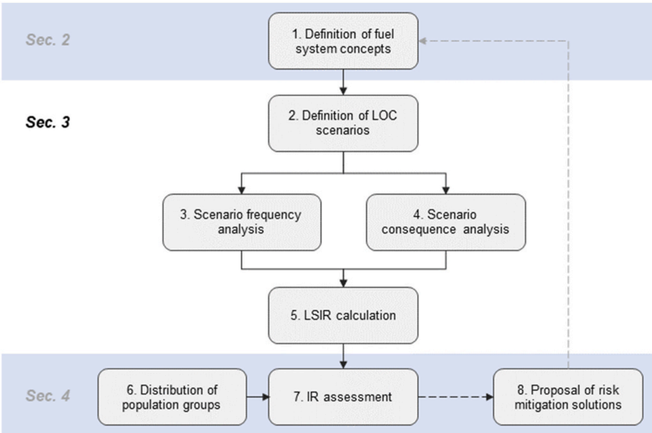

Fig. 4. Schematic flowchart of the employed QRA methodology.

3.1. Individual risk estimate

Individual risk imposed by elements of the fuel systems to population groups onboard and ashore is the key metric for the present safety assessment. With reference to HSE (2003), although a similar definition is present in IMO (2018b), the IR for a given population group with the size of n can be defined as:

$$IR = \theta \cdot \sum_i LSIR_i \cdot p_i \quad (1)$$

where $LSIR_i$ is a location-specific individual risk at location i, p_i is the probability of a (e.g., crew) member from the given population group to be present at location i during regular shifts taking a fraction θ of a year. The terms θ and p_i are specific to the population group, inferable from the manning profile of the operations, and will be discussed in Section 4.2 along with results. Meanwhile, the LSIR at i can be defined as:

$$LSIR_i = \sum_j P_{fat} \cdot P_{exp} \cdot P_{sc} \cdot \lambda_{LOC_j} \quad (2)$$

where.

- P_{fat} is the probability of fatality given exposure of an unprotected person continuously located at location i to the effects of loss of containment (LOC) event j. Hereafter, it will be shortly referred to as probability of fatality.
- P_{exp} is the probability of exposure of an unprotected person continuously located at location i to the effects of LOC event j. This will be shortly referred to as probability of exposure.
- P_{sc} is the probability of a hazardous scenario occurring following a LOC event j. P_{sc} are provided by event trees for each hazardous substance category and the LOC type as summarized in Appendix B. In general, P_{sc} is equal to the ignition probability for flammable events and 1 for toxic dispersion events.
- λ_{LOCj} is the frequency of a LOC event k per *ship*-year estimated by a scenario frequency analysis for the hazardous equipment onboard.

This formulation of LSIR has been adopted from the "Purple Book" with minor modifications (Uijt de Haag and Ale, 1999). There, the LSIR, as in Equation (2), is referred to as IR, but to standardize the terms with the ones used in IMO (2018b) and to avoid possible confusion, we will distinguish the location-specific terms. Secondly, for the onboard risk evaluation, the variations in the weather appear to be less significant than for chemical installations onshore because most of the supply equipment is located inside ship compartments. Therefore, a single representative weather class was chosen and applied throughout the calculations effectively setting its probability of occurrence to 1.

3.2. LOC scenario definitions and frequency analysis

Reference Manual Bevi Risk Assessments has been employed in this study as the main data source on the LOC scenarios and frequencies (RIVM, 2009). The choice of the data source was primarily governed by the level of detail available on the fuel system concepts, which corresponded to the level of a PFD. For this reason, among the two popular LOC data sources – the UK HSE Hydrocarbon Release Database (HCRD) and the Dutch Bevi Manual, the latter was more suitable for the purpose. The influence of data source choice to the risk assessment outcomes are discussed in DNV (2013) and Pasman (2011); and these will be revisited in Section 4.2.

Table 1 summarizes the values of adopted failure frequencies across the LOC scenario types inherent to the fuel system equipment. Given the similarity of damage mechanisms inherent to equipment onboard and onshore, concluded by an internal hazard identification analysis, the frequencies have been taken from RIVM (2009) as provided, except for double piping and fuel tanks. The double piping does not appear as a dedicated equipment category in any database; therefore, reduction factors reported by Davies and Fort (2013) were deemed credible and applied. Meanwhile, evaluation of the tank LOC frequency posed a more complex task.

The approaches for addressing ship tank integrity in the QRA vary substantially as there is an apparent lack of evidence-supported discourse behind. Tank LOC scenarios can be disregarded entirely, being conditioned on the unlikeliness of initiating events, or their frequencies can be approximated from similar equipment (Davies and Fort, 2013; DNV, 2021; Iannaccone et al., 2019). From the authors' perspective, the first should be discouraged as the low likelihood of a tank LOC (anywhere up to 10^{-5} per year) is leveraged by severe consequences, and the public is critically averse to high-consequence events. Thus, the present study follows the approximation approach. RIVM (2009) and the earlier "Purple Book" list the conditional probabilities of a tank's LOC given a ship collision for double-hull refrigerated and semi-pressurized gas carriers. These can be related to the present case with IMO Type A and Type C tanks, respectively, as both share the collision as a primary failure mode. Note that fuel tanks are greatly smaller than cargo tanks if used on the same vessel; therefore, a 1/10 factor was applied to the original values to represent the conditional probability of a collision impacting the zone of fuel tanks. The resultant values used in the present analysis are reported in Table 1.

3.3. Scenario consequence analysis

Estimation of the consequences following a LOC event involves modeling of source term and scenario physical effects. Section 3.3.1 introduces the source term models employed, which were common for all scenario types. Substantial differences are present in the effect estimation procedures for scenarios in open and confined spaces. These are discussed separately in Sections 3.3.2 and 3.3.3.

3.3.1. Source term modeling

Following an equipment's LOC, the outflow of a hazardous substance to the surrounding space, $Q_S(t)$, eventually governs the magnitude of scenario consequences. The present study assumes the time-dependence of the term, accounting for stringent leak isolation requirements to the fuel systems. Thus, the outflow has been set to continue at the initial rate Q_{S0} until the equipment is isolated at time t_I and decay exponentially after the isolation as follows:

$$Q_S(t) = \begin{cases} Q_{S0}, t < t_I \\ Q_{SI}(t), t \geq t_I \end{cases} \quad (3)$$

$$Q_{SI}(t) = Q_{S0}\ exp\left(\frac{-Q_{S0}(t - t_I)}{I}\right) \quad (4)$$

Table 1
Failure frequencies for the fuel system equipment (1/y). Blank fields: LOC is not applicable. Data source: RIVM (2009).

LOC type	IMO Type A tank	IMO Type C tank	Piping (Values per m of length)	Heat exchanger tube side	Heat exchanger shell side	Pressure vessel	Reactor vessel	Pump	Compressor
1 - Continuous release of 75 m^3 (Type A), 126 m^3 (Type C) in 1800 s	$1.5\bullet10^{-4}\bullet f_0$ Note 1	$1.2\bullet10^{-5}\bullet f_0$ Note 1							
2 - Continuous release of 20 m^3 (Type A), 32 m^3 (Type C) in 1800 s	$6\bullet10^{-4}\bullet f_0$ Note 1	$2.5\bullet10^{-3}\bullet f_0$ Note 1							
3 - Rupture in the pipe			DN < 75: $1\bullet10^{-6}$ [75; 150]: $3\bullet10^{-7}$ DN > 150: $1\bullet10^{-7}$ Note 2					$1\bullet10^{-4}$	$1\bullet10^{-4}$
4 - Leak with effective diameter of 10% of the nominal diameter, up to a maximum of 50 mm			DN < 75: $5\bullet10^{-6}$ [75; 150]: $2\bullet10^{-6}$ DN > 150: $5\bullet10^{-7}$ Note 2					$4.4\bullet10^{-3}$	$4.4\bullet10^{-3}$
5 - Rupture of 10 pipes at the same time				$1\bullet10^{-6}$					
6 - Instantaneous release of entire contents					$5\bullet10^{-5}$	$5\bullet10^{-7}$	$5\bullet10^{-6}$		
7 - Release of entire contents in 10 min in a continuous and constant stream					$5\bullet10^{-5}$	$5\bullet10^{-7}$	$5\bullet10^{-6}$		
8 - Continuous release of contents from a hole with an effective diameter of 10 mm					$1\bullet10^{-3}$	$1\bullet10^{-5}$	$1\bullet10^{-4}$		

Notes.
1. Provided as a conditional probability of LOC given impact. For this study, f_0 is adopted from Eliopoulou and Papanikolaou (2007) as $2.57\bullet10^{-3}$ per ship-year, which corresponds to the long-term collision frequency of Aframax tankers.
2. If double-walled piping is used, the frequency should be reduced by a factor of 10 for LOC3 and by a factor of 75 for LOC4 (Davies and Fort, 2013).

where I is the inventory of material contained inside equipment.

The models for calculation of the initial outflow rate, Q_{S0}, are well-established in the domain and were adopted from the "Yellow Book" (Van den Bosh and Weterings, 2005). Depending on process conditions and the state of contained material, the "Yellow Book" models for liquid outflow, gas outflow, and outflow of pressurized liquefied gas through holes were applied for the Q_{S0} calculations according to the LOC definitions of Table 1.

After the time interval t_I has passed, the leaking section is isolated, and it continues to depressurize through a hole at a reduced rate. t_I is a sum of the detection time, t_d, at which the ESD systems are activated, and ESD valves closure time, t_c. Referring to the QRA by DNV (2021), these have been taken as 60 and 30 s, respectively, thus yielding 90 s in total for t_I. ESD system's probability of failure on demand (POFD) was set to 0.01, the maximum for SIL 2 level detectors expected for ammonia operations (IEC, 2010).

Note that in case of a breach in the tank, instantaneous and fixed-duration releases (LOC #1, 2, 6, 7), time-dependence in the outflow rate does not apply. In these and in the case of ESD failure, Q_S was set to Q_{S0} for the entire release duration.

3.3.2. *Effects in open spaces*

Upon a release, considered substances form a toxic and/or flammable cloud that can potentially lead to a fatality following one of the hazardous scenarios indicated in event trees in Appendix B. For a given location, the scenario consequences are represented by a duplet ($P_{\exp}$, P_{fat}), where the former is linked to the geometry of a scenario footprint, e.g., the contours of a toxic cloud, while the latter is related to the exposure intensity. In open spaces, the listed parameters depend critically on the material's atmospheric dispersion characteristics and its interaction with the substrate.

In light of this, Unified Dispersion Model (UDM), as provided in DNV Phast version 8.4 package, has been selected as the main tool for consequence modeling for the effects on open spaces. UDM has proven to be reasonably accurate in predicting phenomena of interest for ammonia: rainout, pool formation, absorption into water, and dense cloud behavior, with the same being true for LNG releases (Witlox et al., 2013; Witlox and Harper, 2013). Using the package, physical effect intensity levels and associated footprints have been calculated for the QRA scenarios which assume the consequences on the weather deck. Table 2 summarizes the approaches and threshold values used.

All consequences, including for the tank's LOC, have been estimated at the height of 1 m above the weather deck, with the probability of fatality contours down to $P_{fat} = 0.001$ calculated for probit-based models. For vapor cloud explosions and flash fires, the "Purple Book" adopts threshold values. These values were taken as two boundaries with the P_{fat} set to decrease linearly with the distance between the two. Note that the "Purple Book" provides $P_{fat} = 0$ for flash fires anywhere beyond the LFL contour. To avoid discontinuities in the LSIR profile, the ½ LFL lower bound of fatality has been introduced in the present work. Eventually, the obtained contours have been plotted on the open deck

Table 2
Models and threshold values for the physical effect estimations adopted in the present study. Data source: Uijt de Haag and Ale (1999).

Hazardous scenario	$P_{fat} = 1$	$P_{fat} = 0$
Flash fire (FF)	LFL	½ LFL
Fireball (FB)	Probit model – heat radiation	
Jet fire (JF)	Probit model – heat radiation	
Pool fire (PF)	Probit model – heat radiation	
Vapor cloud explosion (VCE)	0.3 bar	0.1 bar
Toxic dispersion (TD)	Probit model – ammonia toxicity	

Note. LFL – lower flammability limit. LFL contour is recorded at the time of ignition.

layouts with the scenario rotation being applied throughout (Uijt de Haag and Ale, 1999).

3.3.3. Effects in confined spaces

Integral models like UDM have a limited utility in modeling of the consequences in ships' compartments due to the heavy obstruction, effects of confinement, and forced ventilation. The gas release, following atmospheric expansion and loss of momentum, will disperse in highly turbulent conditions leading to an extensive mixing with the air masses inside. Considering this, an assumption on uniform distribution of the gas within the compartment volume can be a simple yet useful proxy for the consequences inside (Lautkaski, 1997; Montoya et al., 2009; Shair and Heitner, 1974).

Assuming uniform gas distribution, the exposure zone will occupy an entire compartment area setting $P_{\exp}$ to 1 everywhere, and the consequences will be related to the average gas concentration C established at time t. Given the vapor source term Q_{SG}, defined as $Q_{SG} = f \bullet Q_S$, where f is the vapor mass fraction of Q_S once the released the material reaches atmospheric pressure, the room's volume V, and ventilation rate v, the relationship between the quantities is described by the first-order differential equation:

$$V\frac{dC}{dt} = Q_{SG} - vC \tag{7}$$

which has solution for concentration as follows:

$$C(t) = \left(C(t_0) + \int_{t_0}^{t} \frac{Q_{SG}}{V} e^{\frac{v\theta}{V}} d\theta \right) e^{-\frac{vt}{V}} \tag{8}$$

Equation (8) has been solved numerically accounting for time-dependence of the source term and ventilation rate. Note that from the start of a release to its detection, the systems operate in their normal mode with the standard ventilation. After gas detection at t_d, the emergency ventilation rate applies, as specified in Section 2.3, followed by leak isolation afterwards. The resulting concentration profile serves as input for the probit model for ammonia toxic dispersion scenarios yielding $P_{fat,s}$ – probability of fatality following the safeguards' successful activation. For each of the LOC modeled, there is a sub-scenario that the gas leak remains undetected with the system continuing operation in the normal mode. $P_{fat,f}$ is the corresponding probability of fatality given the ESD systems fail to activate. The P_{fat} is the weighted average of the two sub-scenarios:

$$P_{fat} = P_{fat,s} \cdot (1 - POFD) + P_{fat,f} \cdot POFD \tag{9}$$

Regarding flammable scenarios, the average concentration can be a valid indicator of the possibility of a confined explosion (FF and VCE combined) if the gas is buoyant and the leak is located close to the floor (Harris, 1983). This is the case for the systems analyzed. If the gas concentration exceeds LFL, and once ignited, this will lead to fatal consequences everywhere inside the room. Considering the arrangements of FPR, TCS, and to a lesser extent, MS, the confined explosions are expected to be vented through the roof or specialized arrangements; and therefore, no effects on the surroundings from an explosion inside were considered. Regarding jet fires, pool fires, and fireballs, these are less amenable to analytic approximations, and the same procedure for their physical effect estimations as in open spaces was applied with conservative adjustments. For example, if the flame was occupying more than 20% of a room's area, the probability of fatality and exposure both were rounded up to 1, to account for the temperature of combustion products and heat reflection from walls, which are not allowed for otherwise.

The results of the QRA were summarized on the basis of LSIR iso-contours on the layouts. These iso-contours have been produced by superimposition of the LSIR contributions by each LOC event and the hazardous scenarios following it, according to the event trees, with subsequent *LSIR(x, y)* contour generation and Gaussian smoothing. The procedures have been performed in Jupyter Notebooks on Python 3. We express our genuine appreciation to the contributors of the open-source Python environment (Hunter, 2007; McKinney, 2010).

4. Results and discussion

4.1. Location-specific individual risk

Fig. 5 presents LSIR distributions for the four concepts. On open decks, the profiles indicate LSIR 1 m above the deck surface, and for compartments – LSIR inside. Fig. 6 summarizes the risk magnitudes at selected points in a more comparative format. D1 is a point on the weather deck far from supply elements, at a potential location of ventilation inlets to accommodation. D2 is a deck point close to supply elements, indicating the expected LSIR maximum in open spaces. The other two points represent the machinery space and fuel preparation rooms. The term *unmitigated* in Fig. 6 refers to the LSIR magnitudes for compartments if no leak isolation and emergency ventilation have been applied. Table 3 presents further a (mitigated) LSIR breakdown for the selected points by contributing equipment groups.

The entire discussion of the results as follows is organized in a comparative format, where the risks are compared between ammonia and the LNG reference and between ammonia concepts themselves. Thus, the "delta" of the risks and not their absolute magnitudes are key in the discussion. Besides the logic of alternative design described in the introductory section, the primary objective for this is to minimize the effects of methodological errors on derivable conclusions. QRA as a method involves many uncertainties, with the ones in failure frequencies being substantial. For example, if the UK HCRD data had been used, all LSIR and IRs reported in this work would have been up to two orders of magnitude higher (DNV, 2013; Pasman, 2011). And if the judgment relied on the absolute values of risks, the outcomes of such safety decision-making would be heavily affected by the uncertainties. Instead, referring to the "delta" of the risk relative to a currently accepted technology – LNG, designed and analyzed by the same methods, is deemed to be methodologically robust.

Thus, by assigning the risk level reference to the LNG concept, two distinct trends can be highlighted. In open spaces, ammonia concepts demonstrated LSIRs that are comparable to LNG. Meanwhile, the risk inside compartments for ammonia has been systematically higher regardless of system design or mitigation applied.

4.1.1. LSIR inside compartments

The higher LSIRs inside confined spaces are explainable by a combination of at least three factors. Firstly, more ammonia is required to deliver the same power to consumers than LNG or any other hydrocarbon fuel. Secondly, upon release, ammonia becomes shortly fatal at 2700 ppm (AEGL-3), whereas methane's LFL is 50,000 ppm. Lastly, disregarding asphyxiation scenarios, methane cloud needs to ignite to result in unwanted consequences; meanwhile, the consequences of ammonia releases are independent of ignition. The combined effect is clearly observable for systems with the same level of complexity (e.g., compare LSIRs between A-III and LNG concepts, which are identical except for material supplied). Also, note that LSIR differences between ammonia concepts are not as prominent as between ammonia and LNG, thus highlighting the inherently high consequences of ammonia leaks. Certainly, the provisioned mitigation for ammonia releases inside compartments appears more advanced than for LNG, yet these advancements fall short of providing adequate LSIR reductions. Fig. 6 presents two sets of results for compartments: mitigated (with gas detection and isolation within 90 s and emergency ventilation) and unmitigated (without everything mentioned, i.e., leak proceeds undetected and dissipated with normal ventilation). As indicated, the difference between the two ammonia concepts was approximately one order of magnitude. Inside MS, such difference reduces the gap but still leaves the risk significantly above that of any LNG scenario. Meanwhile,

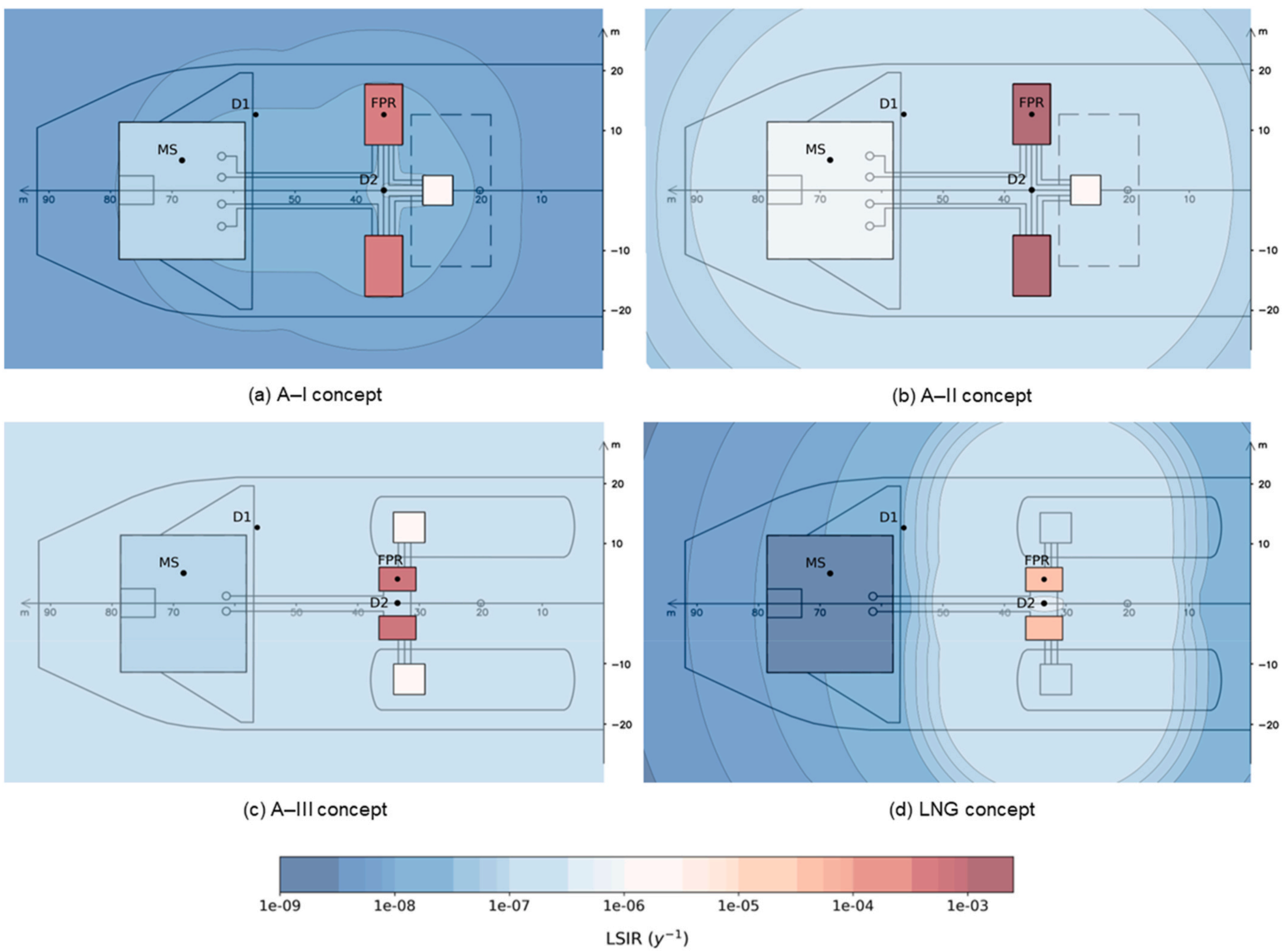

Fig. 5. Location-specific individual risk distribution onboard the analyzed concepts.

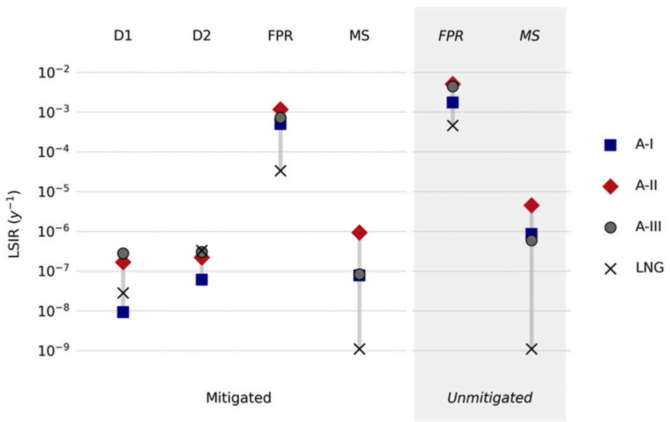

Fig. 6. Comparison of location-specific individual risks at the selected points across the concepts and mitigation scenarios.

inside FPR, the mitigated LSIR of ammonia concepts ranged from $5\cdot10^{-4}$ to $1\cdot10^{-3}$ per year, which at its lower bound equals the LSIR of unmitigated LNG. The judgment on the tolerance of the LSIRs is beyond the scope of the present work, as in practice, there is no single LNG technology, and respective reference risks vary. However, the perspective of operating ammonia FPRs as (un)safe as enclosed FPRs with single-walled LNG equipment with no detection and isolation would rather urge further improvements.

Reflecting on the limited effectiveness of the proposed mitigation, the issue roots not in the technical requirements for the systems, e.g., ventilation rates, but in the chosen mitigation strategy itself. Following a release, ammonia removal rate will tend to $v\cdot C$, as in Equation (7); and the ratio of immediately dangerous concentrations between natural gas and ammonia is $(50{,}000/2700) \approx 19$, although a lower concentration is advisable for the latter. To keep the $v\cdot C$ product constant, increasing the ventilation rate from 30 to 45 changes, thus reducing the ratio by only 1.5, or further within technical feasibility does not offer much potential, same as re-emphasizing rapid isolation yielding comparable gains in mass released. Ammonia risk management inside confined spaces requires alternative approaches.

Note that the present QRA results indicate LSIR inside FPRs being orders of magnitude greater than that of MS regardless of a specific concept or fuel; and there are two reasons for that. Firstly, FPRs accommodate more supply items, including rotating equipment, e.g., high-pressure pumps and/or BOG compressors, and hydrogen production systems, if present. These processes and equipment contribute largely to the leak frequencies and the total LSIR, as evidenced by Table 3. Concerning rotating equipment, seals and flanges around are natural leak sources there; meanwhile, ammonia cracking assumed heat optimization with the placement of toxic and/or flammable material streams at both sides of an exchanger. Secondly, machinery spaces for ocean-going vessels tend to accommodate all main and auxiliary systems in one room, thus reflecting in the rooms' substantial volume. Gases accumulate within larger volumes slower; and this fact, added to the lower number of leak sources and the application of double piping inside MS, explains the difference between the two compartments. However, consider that the observed behavior might be different for smaller or subdivided MS.

4.1.2. LSIR in open spaces

As indicated in Figs. 5 and 6, LSIRs in open spaces onboard are within one order of magnitude between any concept, which can be interpreted as comparable. This relatively minor variance is chiefly due to the effects of atmospheric dispersion and an identical set of leak sources on decks. Relative to LNG, LSIRs for A-II and A-III were generally higher, whereas A-I demonstrated consistently lower risks. To address the causes of such behavior, it is necessary to separate LSIRs imposed by the tanks from those by supply piping. Table 3 shows that such LSIRs in open spaces onboard are equally influenced by the type of storage and the state of ammonia transported between the compartments. Observations regarding these two components are detailed below.

Fuel storage in the semi-pressurized form results in considerably larger risks in open areas: LSIRs by the Tank in Table 3 are 4–48 times higher for the A-III and LNG concepts than the others. The higher consequences of pressurized releases are directly linked to material flashing and the formation of gas clouds of high concentrations above the toxicity threshold for ammonia and LFL for natural gas. In contrast, refrigerated/subcooled materials need to "find" heat first, e.g., from the water below, to result in the majority of unwanted consequences. This, in combination with the assigned LOC frequencies, which were approximately three times higher for the semi-pressurized storage, yields the LSIR differences reported. Additionally, while ammonia and LNG in the same storage impose LSIRs that are comparable in magnitude near the tanks, ammonia releases tend to create larger exposure zones. Such distinction is clear between the concepts A-III and LNG. In practice, this will lead to a larger number of people being affected by the accidental ammonia releases.

Similarly, supply of ammonia from a tank to the engine as a pressurized liquid is a less preferred mode from a safety perspective, and the effect of this aspect on the LSIRs onboard can be as strong as storage conditions. For example, comparing LSIRs between concepts A-I and A-II, which effectively differ in the fuel supply from FPR to MS, shows significant distinctions in the LSIR distribution. Concept A-I assumes a superheated vapor in supply piping, and A-II – pressurized liquid. Overall, the preferred mode of ammonia transport over the longer distances onboard is either superheated vapor or liquid below −33 °C. Once in the two-phase region, the leak consequences become sensibly more severe, and temperature changes within this region have a limited impact on the risk. This is evident when comparing LSIRs by piping between A-II and A-III. The former assumes transport from FPR to MS at 40 °C, 80 bar versus −9 °C, 8 bar from the tank to FPR of the latter, with both segments being the primary risk drivers in respective categories.

Table 3
The LSIR values and their source contributions at the selected points.

Point	A–I		A–II		A–III		LNG	
D1	9.29e-09		1.68e-07		2.79e-07		2.82e-08	
Tank	6.60e-09	71%	6.60e-09	4%	2.03e-07	73%	2.82e-08	100%
Piping	2.69e-09	29%	1.61e-07	96%	7.60e-08	27%	0	0%
D2	***6.05e-08***		***2.20e-07***		***3.03e-07***		***3.28e-07***	
Tank	6.60e-09	11%	6.60e-09	3%	2.03e-07	67%	3.18e-07	97%
Piping	5.39e-08	89%	2.13e-07	97%	1.01e-07	33%	1.04e-08	3%
FPR	***5.01e-04***		***1.17e-03***		***7.23e-04***		***3.36e-05***	
Supply main	1.19e-05	2%	1.04e-03	89%	2.48e-05	3%	2.63e-06	8%
BOG comp./rel.	1.07e-04	21%	1.18e-04	10%	6.98e-04	97%	3.10e-05	92%
Cracking/return	3.82e-04	76%	1.04e-05	1%	N/A		N/A	
MS	***7.80e-08***		***9.34e-07***		***8.26e-08***		***1.10e-09***	

4.2. Individual risk for population groups onboard

The introduction of ammonia leads to many changes in location-specific risks. However, the changes are not equal in the effect imposed on the individual risk to crew members or the public ashore. To distinguish the critical ones, it is necessary to add who will be affected, the number of individuals affected, and how likely the individuals will be exposed to the risks in practice, as stated by Equation (1). Considering that the IR is the weighted sum of LSIRs in open spaces, supply compartments, and the superstructure block/accommodation for any population group onboard, it can be discretized among the selected points in the following way:

$$IR = \theta \cdot \sum_i LSIR_i \cdot p_i \propto LSIR_{D1} \cdot p_{D1} + LSIR_{D2} \cdot p_{D2} + LSIR_{MS} \cdot p_{MS} +$$

$$+ LSIR_{FPR} \cdot p_{FPR} + \alpha \cdot LSIR_{D1} \cdot (1 - p_{D1} - p_{D2} - p_{MS} - p_{FPR}) \quad (10)$$

where the $\alpha \cdot LSIR_{D1}$ term denotes the LSIR inside accommodation, which is a fraction of the LSIR immediately outside, i.e., at D1 (Uijt de Haag and Ale, 1999). Thus, $\alpha < 1$.

The crew aboard a tanker can be classified into three general groups: stewards, deck crew, and engineering crew, each comprising n individuals. Adopting a simplified view, the following work allocations and exposure probabilities can be expected during a day onboard.

1. Stewards ($n < 5$). Practically all time is spent inside accommodation and other rooms unrelated to ammonia supply. Thus, $p_{D1} = p_{D2} = p_{MS} = p_{FPR} = 0$.
2. Deck crew ($n < 20$). The work time (12 h) is spent either on open decks or in spaces with unlimited access to them, e.g., bridge. This can be approximated as $p_{D1} = p_{D2} = 0.25$.
3. Engineering crew ($n < 10$). Half of the work time is spent inside MS with a short (10-min) task inside FPR per day; another half is spent in open spaces or similar. This can be considered as $p_{MS} = 0.243$, $p_{D1} = p_{D2} = 0.125$, $p_{FPR} = 0.007$.

Table 4 presents the calculations and resultant individual risks experienced by the population groups during the work hours. The reported values of IR for stewards correspond to the IR maximum expected for this group and are equal to the IR maxima experienced by everyone during the remaining 12 h off shift. This follows from α being less than 1. Note that there are always one or two *LSIR·p* terms accounting for the absolute majority inside the total IR sum and determining its order of magnitude. These terms are highlighted with color. Such dependencies enable the derivation of valuable insights into the criticality of different design and operational aspects.

Reflecting on the results in Table 4 and the earlier discussion on LSIR trends for ammonia and LNG, the following conclusions can be drawn on the state of IRs.

1. Stewards: the IR imposed by ammonia fuel systems on this population group is comparable (within one order of magnitude) to that posed by existing LNG technologies. Since LNG-related risks are tolerable and low for this and similar groups in practice, it would be reasonable to expect the same to be true for ammonia, regardless of the storage conditions. For stewards, Equation (10) reduces to $IR \propto \alpha \cdot LSIR_{D1}$, and even in the limiting case of $\alpha = 1$, i.e., the accommodation provides no protection, the conclusion remains valid. However, as noted in Section 4.1.2, accidents with ammonia will tend to impact more people. Therefore, the statement above is valid only if the population onboard does not exceed conventional 20–30 people for a tanker or similar merchant vessel. Otherwise, e.g., in the case of an ammonia-powered cruise ship ($n > 1000$), the additional risks by ammonia tanks might not be tolerable/acceptable from a societal risk perspective.
2. Deck crew: analogously to the case above, tolerable and low IR is expected for the group of the assumed size. In this case, $IR \propto LSIR_{D1} \cdot p_{D1} + LSIR_{D2} \cdot p_{D2}$, and given the similarity of LSIRs on open decks between the fuels, no altered conclusion is possible regardless of the exact values of p_{D1} and p_{D2}.
3. Engineering crew: the entire IR dependence for this group reduces to $IR \propto LSIR_{FPR} \cdot p_{FPR}$, i.e., to the risks associated with a 10-min daily task inside FPR; and such dependence will remain valid down to the hundredths of the assumed time. Since the crew IRs for all ammonia concepts are considerably higher than for the LNG, where fire/explosion risks in confined spaces are already a point of concern, the potential of arriving at the intolerable IRs for engineering crew of ammonia-powered ships is significant. A challenge of this situation is that, unlike the risks in open spaces, no solution mandated by the current regulations that allows effective mitigation of ammonia risks in confined spaces has been identified (see Section 4.1.1). In this light, it is noteworthy that no scenario with the general public exposed to FPR risks can be foreseen.

Thus, the risk profile of ammonia-fueled ship operations is distinguishable by elevated risk for the engineering personnel potentially present in FPRs and for the public onboard or nearby. The acceptance of future technology will critically depend on the risk mitigation effectiveness in these two cases. Regarding FPRs, the results suggest that mitigation through technical barriers alone is not sufficient, thereby prompting the investigation of alternative control possibilities over the IR. Concerning public safety, the use of ammonia affects larger population groups, with the factors influencing the extent of such exposure requiring further elaboration.

4.3. Critical aspects and prospective solutions

Based on the aforementioned dependences of risks in the present QRA model, we identify four aspects that provide significant opportunities for control and enhancement of safety performance of ammonia-powered ships. The aspects (i) to (iii) below are related to the risks in

Table 4
Calculations and final values of the IR induced by fuel storage and supply elements for population groups onboard.

Group		A–I		A–II		A–III		LNG	
Point	*p*	*LSIR*	*LSIR*p*	*LSIR*	*LSIR*p*	*LSIR*	*LSIR*p*	*LSIR*	*LSIR*p*
D1	0.50	9.3e-09	4.6e-09	1.7e-07	8.4e-08	2.8e-07	1.4e-07	2.8e-08	1.4e-08
IR $_{stewards}$			**4.6e-09**		**8.4e-08**		**1.4e-07**		**1.4e-08**
D1	0.25	9.3e-09	2.3e-09	1.7e-07	4.2e-08	2.8e-07	7.0e-08	2.8e-08	7.0e-09
D2	0.25	6.1e-08	1.5e-08	2.2e-07	5.5e-08	3.0e-07	7.6e-08	3.3e-07	8.2e-08
IR $_{deck}$			**1.7e-08**		**9.7e-08**		**1.5e-07**		**8.9e-08**
D1	0.125	9.3e-09	1.2e-09	1.7e-07	2.1e-08	2.8e-07	3.5e-08	2.8e-08	3.5e-09
D2	0.125	6.1e-08	7.6e-09	2.2e-07	2.7e-08	3.0e-07	3.8e-08	3.3e-07	4.1e-08
MS	0.243	7.8e-08	1.9e-08	9.3e-07	2.3e-07	8.3e-08	2.0e-08	1.1e-09	2.7e-10
FPR	0.007	5.0e-04	3.5e-06	1.2e-03	8.2e-06	7.2e-04	5.1e-06	3.4e-05	2.4e-07
IR $_{engineering}$			**3.5e-06**		**8.5e-06**		**5.2e-06**		**2.8e-07**

FPRs, (iv) – to ammonia tanks and public safety.

(i) ***Crew presence in FPR.*** The individual risk for the engineering crew is proportional to $LSIR_{FPR} \cdot p_{FPR}$, and while the $LSIR_{FPR}$ is challenging to reduce by technical barriers, a considerable minimization of p_{FPR} is feasible. In practice, this would involve moving the human-machine interface for as many engineering operations from FPRs to a safer location, e.g., by establishing remote monitoring of the processes through CCTVs and sensors instead of visual inspections on site. These measures are listed in LR MDH and MMMCZCS (2023a, 2023b), and while we fully concur with the recommendations drawn on this aspect, the significance of control over human interactions is deemed to be left largely undervalued. As illustrated in Section 4.1.1, acting on ventilation rate or isolation times would yield rather marginal reductions in toxic release consequences, probabilities of fatality, $LSIR_{FPR}$, and eventually IR. Conversely, the IR is directly proportional to the time spent in FPR, and if on-site routine inspections and testing constitute the bulk of cumulative time spent there, performing these operations remotely will lead to reductions in the IR's order of magnitude. Certainly, the proposed steps will not make FPRs a safer space. Nevertheless, the consequences of toxic gas leaks are primarily dangerous to humans, and provided a well-designed vent system, their effects are limited to a room where it happens. Therefore, there is a rationale to keep the human and FPRs apart.

(ii) ***Supply system reliability.*** Enhancing system reliability addresses other reasons for a human to be present in FPR. These would still be required for some inspections, testing, planned and corrective maintenance. The idea behind this measure is to reduce the frequency of the remaining human-hardware interactions through a more reliable and autonomous fuel system design. For the engineering crew, $IR \propto LSIR_{FPR} \cdot p_{FPR} = p_{fc} \cdot \lambda_{LOC} \cdot p_{FPR}$, where p_{fc} is a general probability of fatal conditions establishing after an LOC in FPR, lumping exposure and scenario development, and λ_{LOC} is a total LOC frequency there. Enhancing system reliability has a synergetic effect on IR both through λ_{LOC} and p_{FPR}. Firstly, higher component reliability correlates positively with its integrity, thus demonstrating lower λ_{LOC}. Secondly, a high-reliability process requires fewer physical interactions for the reasons above, thus, lower p_{FPR} as well. In practice, reliability issues mainly concern the systems' flow control and rotating equipment, the latter of which is the leading risk driver inside FPRs, according to Table 3. The existing market offers multiple prospective solutions for these units through the application of advanced materials, seals, or seal-less designs, and future ammonia operations would largely benefit from them. Even the RIVM (2009) manual distinguishes canned pumps from sealed ones with a difference of 1–2 orders of magnitude in λ_{LOC} alone. Improving system reliability yields not only lower IRs onboard but also more predictable and consistent operations, which are advantageous from many other perspectives.

(iii) ***Supply system complexity.*** Elaborating further on human-hardware interaction, a shorter interface between the two, achievable through simpler fuel systems, reflects positively on safety. For example, the concepts A-I and A-III are similar in fuel supply processes, except the former adds the production of hydrogen; and with all else being equal, the A-I will call for more monitoring and interventions for successful operation. Analogously to the reliability aspect, system complexity affects λ_{LOC} and p_{FPR} in the proportionality $IR \propto p_{fc} \cdot \lambda_{LOC} \cdot p_{FPR}$. Simpler processes involve less equipment, fewer connections, fewer leak sources, and thus lower leak frequency. A simpler process requires fewer interactions as well. The key in this strategy is to ensure that the reductions in λ_{LOC} and/or p_{FPR} are not compensated by worsening consequences, p_{fc}. Such negative feedback has been observed for the A-I and A-III pair, where A-III, a simpler process in FPR, had on average higher consequences and LSIR than A-I (see Table 3). The compartment volume has been the cause for that: it is logical to allow smaller rooms for A-III due to its simplicity and size since the volume in a ship is precious. However, gases accumulate in smaller volumes faster; thus, a balance between the two factors must be preserved. Addressing the practical realization of the complexity aspect, simpler ammonia-diesel configurations are preferable over the others. Otherwise, the increase in complexity must be counterbalanced by solutions in (i), (ii), and other measures where practicable.

(iv) ***Fuel storage type.*** A leak from an ammonia tank is the largest single scenario influencing risk to the public, which can be passengers or 3rd parties ashore, e.g., residents near ports or waterways. Risk tolerability and/or acceptability limits are typically the strictest for these groups, at least one order of magnitude lower than for the crew (IMO, 2018b; Vrijling et al., 2005). Since ammonia effects have a higher chance of reaching the public in case of an accident, the significance of safe fuel storage for ammonia increases. While skipping the probabilistic aspects of storage safety, where more explicit links between the tank design, its location, and barriers to its integrity must be established, there is a straightforward relationship in consequences: lower storage temperature leads to lower consequences. Ammonia has a larger fatal exposure zone for the same energy stored than any conventional hydrocarbon fuel; and increasing the temperature will expand this zone, putting more people at risk. Such a temperature-dependence is primarily governed through the amount of ammonia discharged from a tank following a LOC and the size of a dense cloud immediately produced upon ammonia flashing. Besides that, ammonia carries a characteristic property – odor. Although concentrations below 300 ppm are not considered immediately dangerous to life or health (IDLH), the public's exposure even to 5 ppm will trigger consequences of psychosocial character: nuisance, discontent, and potentially panic (Ludwig et al., 1994; Makarovsky et al., 2008). These lead to the ramifications and risks to an operator's reputation and, for the same reasons, introduce a security risk component. Solutions that minimize all the risks combine low-temperature storage and high-integrity tanks.

To summarize the role of the listed aspects in safety management, these can be presented on an F-N curve, which indicates the societal risk by operations. When considering the curve for conventional oil or gas tanker operations, as presented in IMO (2018b), the introduction of ammonia will graphically be reflected by the substitution of risks associated with hydrocarbon fuels with the new ones inherent to ammonia. Based on the developed QRA model, the present analysis identifies two areas concerning specific population groups where this substitution results in significant changes. These are conceptually represented in Fig. 7 by A and B. In A, the change is expected due to the increased risk magnitudes for the engineering crew, and as the access to FPRs is restricted only for this small group of people onboard, this area will naturally be limited on the horizontal axis. In area B, the change is primarily driven by the increase of hazardous zones around ammonia tanks, which will expose more persons beyond existing crews, potentially including the public ashore. The aim of minimizing crew presence in FPRs, enhancing supply system reliability, and reducing its complexity is the mitigation of the new risk in A. The main role of ammonia storage temperature reduction is minimizing the risk arising in B. Given the additive nature of risks, the listed solutions should not be considered as a substitute of any kind to the applicable design rules, operational practices, or even the choice of PPE (ASTI, 2023; LR MDH and MMMCZCS, 2023b). Instead, these should be considered in combination with the other available risk control options while aiming for a more optimal and justified allocation of those. What distinguishes the

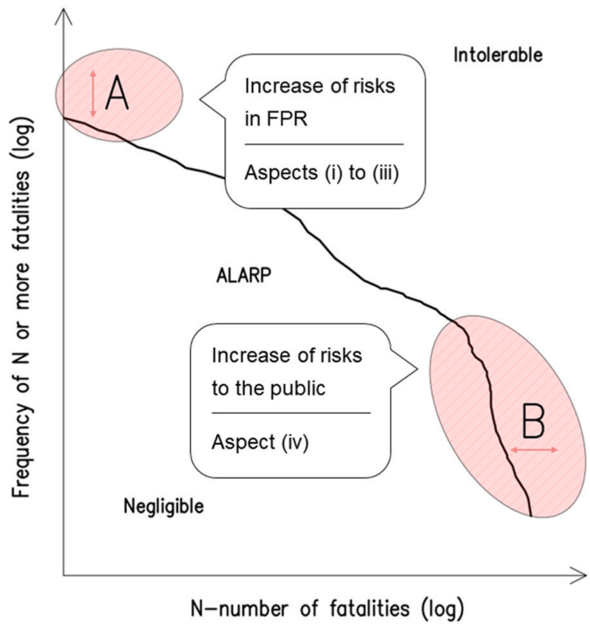

Fig. 7. An F-N curve of conventional tanker ship operations, adapted from IMO (2018b), with an indication of the increased risk areas due to ammonia use. Based on our analysis, the listed aspects have the largest influence and control potential for the risk in the corresponding two zones.

identified opportunities from others is a unique combination of their high influence on risk and the feasibility of implementation in practice.

This study has limitations that must be considered along with the results. Firstly, the study has been demonstrated through an example of a single ocean-going tanker vessel, which affects the generalizability of recommendations drawn. Although the mentioned classification rules do not discriminate between vessel types and the trends summarized in Fig. 7 are driven primarily by the general physicochemical properties of ammonia, the magnitudes of the risk increments will depend significantly on the specifics of individual projects. For example, the volume of compartments greatly influences the risk inside. Therefore, a careful analysis must be performed before applying the recommendations to smaller coastal vessels or other substantially distinct vessel types. Secondly, the employed comparative analysis assumed a similarity between existing reference LNG-fueled operations and future ammonia-based ones. This assumption has a range of implications, ranging from the integrity of fuel supply equipment remaining unchanged to more complex factors such as comparable sailing frequencies of the ships. Lastly, this work solely addresses the human safety risks associated with the use of ammonia, i.e., only fatality risks associated with acute exposure. Such scope excludes environmental or any other risks both in water and atmosphere, like releases of ammonia below IDLH or its incomplete combustion resulting in the formation of NO_x/N_2O and affecting local air quality and greenhouse gas emission levels. All these factors are viewed as essential considerations in evaluating ammonia as fuel beyond the safety issues listed.

5. Conclusions

This study presents an analysis of safety risks associated with the use of ammonia as a fuel by employing the QRA methodology. Through a comparative lens, the paper examines the risks inherent to the three distinct ammonia fuel system concepts, varying in design and operational parameters, against those posed by a conventional LNG system serving an equivalent function. By analyzing variations in the concepts' LSIR and IR, along with the factors influencing these risks, safety-critical aspects of ammonia-powered ship design and operations have been identified.

Our findings indicate that the safety profiles of ammonia-powered ships are marked by an elevated IR for two population groups: for engineering crew with duties in FPRs and for the public potentially present either onboard or in proximity. Regarding ammonia FPRs, the increase of IR by 1–1.5 orders of magnitude relative to the reference LNG level has been observed for all ammonia concepts under consideration. Low acute toxicity concentrations of ammonia compared to the LFL of natural gas, independence of the toxic effects from the ignition, and the larger inventories of ammonia available in the rooms were the main contributing factors. Meanwhile, the application of technical mitigation strategies listed in the current rulesets was insufficient for achieving LSIRs comparable to those of hydrocarbon fuels. In this light, we have outlined strong and controllable dependences of the crew IR on the exposure duration, reliability, and complexity of the fuel supply system. The analysis indicates that minimizing crew presence in the compartment through the management of human-machine interactions, ensuring the choice of high-reliability components, and preference for simpler systems offer sensible opportunities to reduce risk for the engineering crew. For the public, the increased risk is attributed to the larger impact zones of accidental ammonia releases, thereby affecting individuals currently not exposed to chemical hazards by conventional ships. The risk increase for this group depends significantly on the distance from the vessel, which is negligibly small close to the storage tanks and increases with the distance due to the larger hazardous footprints of toxic clouds compared to the flammable ones. Key mitigation strategies for the case include lowering storage temperatures and opting for high-integrity tanks.

The main advantage of the demonstrated QRA framework in maritime safety analysis is its ability to enhance transparency in safety decision-making, providing a clear and traceable rationale behind recommendations drawn. Although prone to uncertainties, the framework facilitates communication of risk levels among diverse maritime safety stakeholders. QRA serves as a tool for ship designers, builders, operators, and owners to assess compliance of prescriptive requirements relative to their declared goals and apply more independent, risk-informed decision-making for the assets they are ultimately responsible for. Certainly, the application of QRA itself is time and cost-consuming, yet its requirement arises only when significant changes to the systems are made. As ammonia and other alternative fuels gain broader commercial use, the insights and best practices established through the practice will be codified into the industry's prescriptive regulatory framework. The application of QRA allows passing through this introduction phase in a more controllable manner.

CRediT authorship contribution statement

Rustam Abubakirov: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Ming Yang:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Giordano Emrys Scarponi:** Writing – review & editing, Supervision, Resources, Methodology, Conceptualization. **Valeria Casson Moreno:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Genserik Reniers:** Writing – review & editing, Supervision.

Declaration of competing interest

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

Acknowledgments

This publication is supported by the AmmoniaDrive project (project 14267) which is financed by the Netherlands Organisation for Scientific Research (NWO).

Appendix A

This appendix reports stream data (Tables A1 – A4) on operating conditions of the fuel supply system concepts analyzed in the present study. Each concept has been sized to supply 32 MJ/s of energy equivalent from the tank. Selection and working principles for the concepts are discussed in Section 2. Hazardous material (hazmat) classes have been assigned for the streams based on Uijt de Haag and Ale (1999). The hazmat classes are abbreviated as FG – flammable gas, TG – toxic gas, T&FG – toxic and flammable gas, and L. – liquefied.

Table A1
Stream data for the concept A-I (Fig. 3a).

Stream	Units	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Pressure	barg	8.3	8.1	7.9	0.1	−0.1	8.1	7.9	7.9	7.9	7.0	7.9	7.5	7.3	7.1	7.0
Temperature	°C	−33	22	61	−33	−28	207	61	61	61	60	61	630	229	60	60
Ammonia flow	kg/s	0.822	0.822	0.822	0.038	0.038	0.038	0.038	0.860	0.469	0.469	0.391	0.164	0.164	0.164	0.164
Hydrogen flow	kg/s	0	0	0	0	0	0	0	0	0	0	0	0.040	0.040	0.040	0.040
Nitrogen flow	kg/s	0	0	0	0	0	0	0	0	0	0	0	0.187	0.187	0.187	0.187
Total flow	kg/s	0.822	0.822	0.822	0.038	0.038	0.038	0.038	0.860	0.469	0.469	0.391	0.391	0.391	0.391	0.391
Hazmat class		L.TG	TG	TG	TG	TG	TG	TG	TG	TG	TG	TG	T&FG	T&FG	T&FG	T&FG

Table A2
Stream data for the concept A-II (Fig. 3b).

Stream	Units	1	2	3	4	5	6	7	8	9	10	11	12	13
Pressure	barg	25.0	0.1	−0.1	24.8	24.6	24.4	24.4	24.4	80.3	80.1	80.0	30.0	30.0
Temperature	°C	−33	−33	−28	336	59	58	−28	−14	−13	40	40	50	50
Ammonia flow	kg/s	0.822	0.038	0.038	0.038	0.038	0.038	0.860	1.032	1.032	1.032	1.032	0.172	0.172
Hazmat class		L.TG	TG	TG	TG	TG	L.TG	L.TG	L.TG	L.TG	L.TG	L.TG	L.TG	L.TG

Table A3
Stream data for the concept A-III (Fig. 3c).

Stream	Units	1	2	3	4	5	6	7	8	9
Pressure	barg	7.5	7.3	7.1	2.0	1.8	7.3	7.1	7.1	7.0
Temperature	°C	−9	22	60	−9	0	104	71	60	60
Ammonia flow	kg/s	0.841	0.841	0.841	0.019	0.019	0.019	0.019	0.860	0.860
Hazmat class		L.TG	TG	TG	TG	TG	TG	TG	TG	TG

Table A4
Stream data for the LNG concept (Fig. 3d).

Stream	Units	1	2	3	4	5	6	7	8	9
Pressure	barg	7.5	7.3	7.1	2.0	1.8	7.3	7.1	7.1	7.0
Temperature	°C	−146	−128	20	−146	−126	−67	20	20	20
Methane flow	kg/s	0.333	0.333	0.333	0.007	0.007	0.007	0.007	0.340	0.340
Hazmat class		L.FG	FG	FG	FG	FG	FG	FG	FG	FG

Appendix B

Event tree diagrams presented in Figure B1 specify the probabilities of hazardous scenarios, P_{sc}, following a LOC event. These are utilized in the QRA model through Equation (2). The applicability of the event trees is determined by the hazmat classes reported in Appendix A and the character of a LOC defined in Table 1. The key parameters in the event tree diagrams: probabilities of direct and delayed ignition, P_{dir} and P_{del}, respectively, and fraction of explosion, F_{exp}, have been adopted from Uijt de Haag and Ale (1999). The listed values were applied to scenarios both in confined and open spaces, including F_{exp}, as a significant level of obstruction by the storage tanks and pipe racks on the weather deck does not allow excluding explosion possibility in any of the cases.

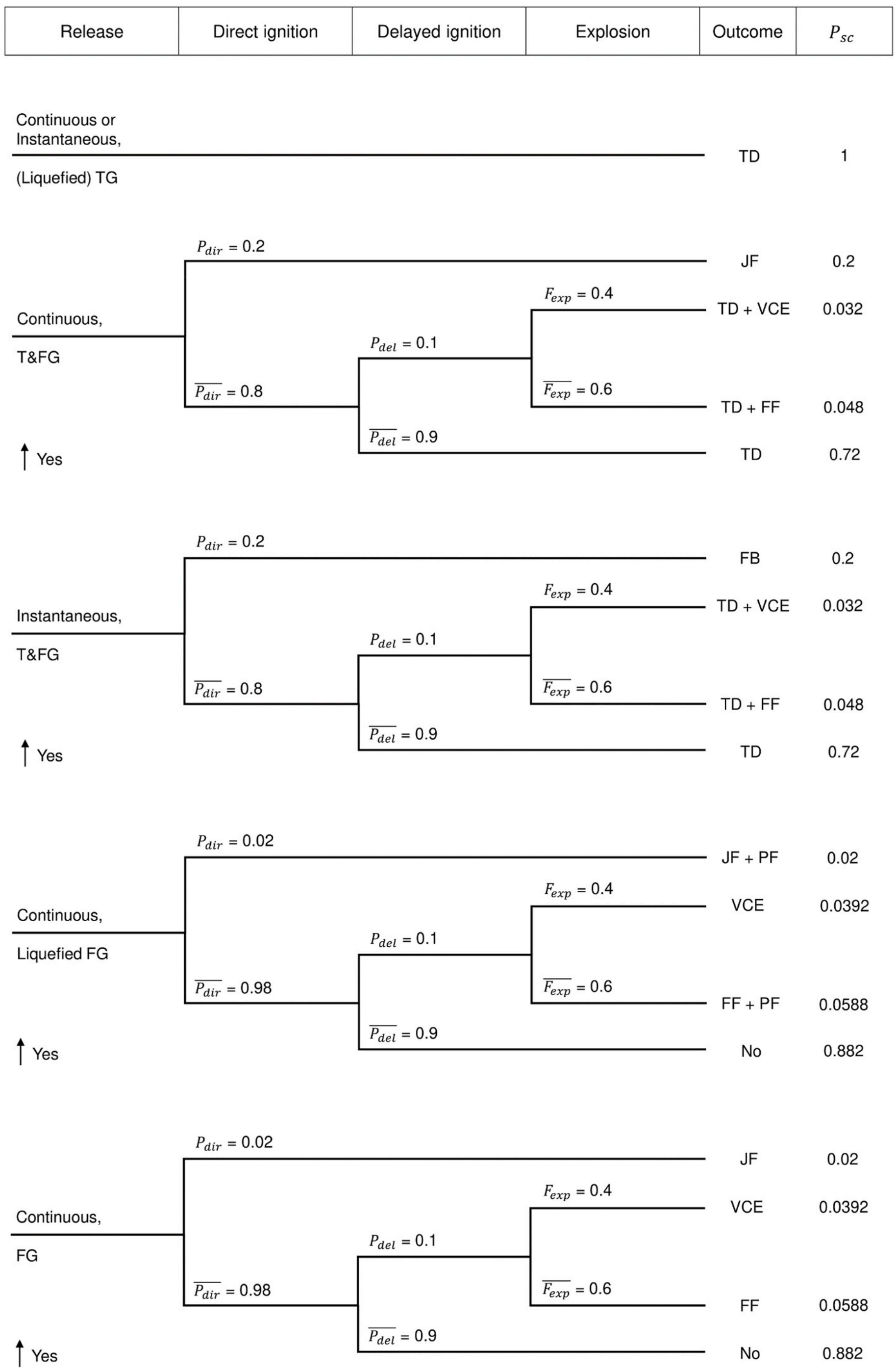

Fig. B1. Event tree diagrams with probabilities of the hazardous scenarios by release classes adopted in the present study.

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