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AMMONIA
AS A MARINE FUEL
– Bunkering, Safety and Release Simulations

Maritime Energy & Sustainable Development (MESD)
Centre of Excellence (CoE)

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– Bunkering, Safety and Release Simulations

This study is conducted by the Maritime Energy & Sustainable Development (MESD) Centre of Excellence and has received research funding from the Singapore Maritime Institute (SMI).

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Executive Summary

Global warming is linked strongly to increased greenhouse gas (GHG) concentration in the earth's atmosphere. The maritime cluster plays a critical role in reducing GHG emissions by replacing fuels of fossil origin with low-carbon or carbon-free alternatives. As a carbon-free fuel, anhydrous ammonia has received much attention recently due to its established production technology, distribution infrastructure, and satisfactory energy density as a marine fuel.

As one of the largest bunkering ports in the world, Singapore will foresee opportunities arising from adopting alternative marine fuels, and the bunkering of ammonia can be one of the candidates. Currently, there is no established ammonia bunkering infrastructure or guidelines in Singapore. The other essential part - the safety study around the operational or accidental release during the ammonia bunkering process, is still awaiting a comprehensive investigation. Ammonia bunkering deserves a timely study in Singapore to prepare for its potential adoption in the future. The study led by MESD, together with ASTI, ABS and industry partners, aims to provide a timely report to the marine community that includes ammonia production and supply, hypothetical ammonia bunkering process, and impact analysis of ammonia release from various scenarios. The study started in September 2020 and concluded in September 2021, aiming at audiences ranging from port operators, bunker suppliers, ship owners and port authorities to other relevant stakeholders considering ammonia as the next generation low carbon fuel.

The ammonia value chain includes production, storage, transportation/distribution, bunkering and onboard energy conversion. Ammonia can be produced from fossil-based feedstock or renewables by the Haber Bosch process or electrochemical process. Given that 80% of global ammonia production is consumed as fertiliser and only 1% is spared for energy-related use, ammonia production capacity has to be upscaled to meet the rising energy demand. Meanwhile, the development of green ammonia plants with cost reduction will play a decisive role in entering the marine community, where business continuity must be achieved along with GHG emissions reduction from the future perspective. When ammonia attracts more recognition from the maritime industry, the entire value chain shall be developed to suit the needs of various types of vessels and bunkering configurations. Although ammonia bunkering standards and guidelines are not established yet, there have been increasing discussions and studies on ammonia bunkering in recent years. Examples include the work on provisional guidelines for ammonia fuelled ships and bunkering operations being developed by the International Association of Classification Societies (IACS).

The ammonia bunkering process shall be designed based on the fact that anhydrous ammonia is an ambient saturated liquid. Unlike normal ambient liquid fuels such as diesel or residual oil, ammonia relies on refrigeration or pressurisation to maintain the liquid phase. The operating temperature to store and transfer ammonia is from -33°C to ambient temperature (25°C), corresponding to a pressure range from 1 to 10 bar. Boil-off gas (BOG) can be generated at constant pressure by the addition of heat to saturated liquid and involves significant enthalpy change. In contrast, flash gas is generated when saturated liquid undergoes a reduction in pressure with no associated enthalpy change. This study proposes 33 ammonia bunkering configurations generated from the combination of 4 main bunkering supply modes (truck-to-ship, ship-to-ship, shore/terminal-pipeline-to-ship and cassette bunkering), 3 bunker receiving modes and 3 storage conditions (fully refrigerated, semi-refrigerated or non-refrigerated tanks). The study also presents hypothetical processes for ammonia bunker transfer under different storage conditions consisting of 8 main steps, namely 1) initial precooling, 2) bunker hose connecting, 3) 1st inerting, 4) purging, 5) transferring, 6) stripping, 7) 2nd inerting and 8) bunker hose disconnecting. The precooling process is not required if the bunker transfers from a non-refrigerated tank to a non-refrigerated tank. Similar to conventional marine fuel bunkering, the quality of ammonia bunker shall be regulated when anti-corrosion or combustion-supporting agents are added.

After comparing the threshold concentrations of ammonia to induce fire or harm to personnel, we conclude that its toxicity is of the utmost concern during ammonia bunkering. This study takes reference from the well-established AEGL (Acute Exposure Guideline Level) limits to gauge the toxic impact on humans during an ammonia release. Based on literature review and consultation with industry partners, leakage from the rupture of connecting hoses or pull-away incidents is one of the most common likely causes of the loss of containment for ammonia bunkering. When a catastrophic hose rupture happens, ammonia will release rapidly into the environment, causing danger to the personnel in the surroundings. The safety analysis carried out in this study is focused on the release of ammonia from the hose rupture scenario. Due to the limit of the study, there is no physical set-up for actual ammonia release and monitoring. The release of ammonia is studied by simulating the dispersion pattern using the simulation software PHAST (Process Hazard Analysis Software Tool) to predict the corresponding consequences of the release. Simulations are performed for various bunkering modes: shore-to-ship, truck-to-ship, ship-to-ship and simultaneous operations (SIMOPS), which include four loss-of-containment scenarios. The 3% lethality footprint is used as an indicator.

- *Scenario A Shore-to-Ship bunkering:* A total of 17,040 kg of ammonia is released in 1 min from the refrigerated storage with a rainout rate of more than 80%. The 3% lethality footprints reach a maximum downwind distance of 370 m during the day and 400 m at night.

- *Scenario B Truck-to-Ship bunkering:* 198 kg of ammonia is released in 1 min from the pressurised storage condition, with no rainout, and the vapour cloud forms a puff right after the end of the release. The ammonia cloud concentration falls below the AEGL-2 level by about 4 min during the day and 7 min at night. Although the maximum cloud footprint has reached approximately 800 m, the 3% lethality footprint is less than 100 m from the source of release for both day and night conditions.

- *Scenario C Ship-to-Ship bunkering:* A total of 17,040 kg of ammonia is released in 1 min with a rainout rate of approximately 80%, of which approximately 60% of this rainout will eventually dissolve in seawater. The 3% lethality footprints reached a maximum distance of about 1.3 km during the day and 700 m at night. The maximum cloud and lethality footprints are significantly larger during the day than at night.

- *Scenario D SIMOPS:* 17,040 kg of ammonia is released in 1 min. The dispersion pattern of ammonia over the sea is the same as that in scenario C. For the dispersion of ammonia over land, the 3% lethality footprints reached a maximum distance of 310 m during the day and 340 m at night.

A preliminary review of mitigation measures was conducted at the end of the study. Water curtains, absorbent spray, and membrane separation are commonly considered by other industries where there is a potential ammonia leak. However, these technologies have not found ways to meet the requirement of future ammonia bunkering operations. It is expected that various types of mitigation measures can be applied together to enhance performance. Further studies with physical validation are indispensable, as this is the decisive way to provide quantitative and qualitative proof of the mentioned mitigation measures. In Singapore, effective mitigation measures will help overcome challenges encountered during ammonia bunkering under land and sea space scarcity.

Table of Content

List of Tables

List of Figures

List of Abbreviations and Definitions

ACGIH	American Conference of Governmental Industrial Hygienist
AEGL	Acute Exposure Guideline Level
APR	Air Purification Respirator
ASSPU	Sudong Special Purpose Anchorage
ASTM	American Society for Testing and Materials
BDN	Bunker Delivery Note
BLEVE	Boiling Liquid Expanding Vapour Explosions
BOG	Boil-Off Gas
CAPEX	Capital Expenditure
CCS	Carbon Capture and Storage
CFD	Computational Fluid Dynamics
CI	Compression Ignition
CLP	Classification, Labelling and Packaging of Substances and Mixtures
COP	Coefficient of Performance
DME	Dimethyl Ether
DPM	Discrete Phase Model
EOR	Enhanced Oil Recovery
ERS	Emergency Release System
ESD	Emergency Shut Down
EU	European Union
FAME	Fatty Acids Methyl Esters
FHSBF	Floating Hydrocarbon Storage and Bunker Facility
FR	Fully Refrigerated
FSU	Floating Storage Unit
GHG	Greenhouse Gas
GHS	Globally Harmonised System of Classification and Labelling of Chemicals
HDRD	Hydrogenation-derived Renewable Diesel
HFO	Heavy Fuel Oil
HSE	Health and Safety Executive
HVO	Hydrotreated Vegetable Oil
IACS	International Association of Classification Societies
IBC	International Code for the Construction and Equipment of Ships carrying Dangerous Chemicals in Bulk
IDLH	Immediately Dangerous to Life or Health Concentrations
IGC	International Code of the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk
IGF	International Code of Safety for Ships using Gases or other Low-flashpoint Fuels
IMO	International Maritime Organization
ISO	International Organization for Standardization
KwR	Kilowatt of Refrigeration
LFL	Lower Flammability Limit
LHV	Lower Heating Value
LNG	Liquefied Natural Gas
LPG	Liquefied Petroleum Gas
LSFO	Low Sulphur Fuel Oil

MDO	Marine Diesel Oil
MFM	Mass Flow Meter
MGO	Marine Gas Oil
MPA	Maritime and Port Authority of Singapore
NEA	National Environment Agency
NFPA	National Fire Protection Association
NIH	National Institute of Health
NIOSH	National Institute for Occupational Safety and Health
NPSH	Net Positive Suction Head
NR	Non-Refrigerated
OSHA	Occupational Safety and Health Administration
PELS	Permissible Exposure Limits
PERC	Powered Emergency Release Coupling
PFP	power-to-fuel-to-power
PHAST	Process Hazard Analysis Software Tool
PM	Particulate Matter
PPE	Personal Protective Equipment
ppm	parts per million
PRD	Pressure Relief Devices
PTS	Pipeline-to-Ship
QCDC	Quick Connect-Disconnect Couplings
QRA	Quantitative Risk Assessment
RORO	Roll-on/roll-off
RPE	Respiratory Protection Equipment
SCBA	Self-Contained Breathing Apparatus
SCC	Stress Corrosion Cracking
SCR	Selective Catalytic Reduction
SI	Spark Ignition
SIMOPS	Simultaneous Operations
SOEC	Solid Oxide Electrolysis Cell
SR	Semi-Refrigerated
SS 648	Singapore Standard Code of Practice for Bunker Mass Flow Metering
STEL	Short-term Exposure Limits
STS	Ship-to-Ship
TEU	Twenty-foot Equivalent Unit
TR	Ton of Refrigeration
TR 56	TR 56 : 2020 Technical Reference for LNG Bunkering
TTS	Truck-to-Ship
TWA	Time-weighted Average
UDM	Unified Dispersion Model
UN	United Nations
VLCC	Very Large Crude Carrier

Molecular Formula	Definition
$BaCl_2$	Barium Chloride
$CaCl_2$	Calcium Chloride
CH_4	Methane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
H_2	Hydrogen Molecule
H_2O	Water
H_2S	Hydrogen Sulfide
$MgCl_2$	Magnesium Chloride
N_2	Nitrogen
N_2O	Nitrous Oxide
NH_3	Ammonia
NO_x	Nitrogen Oxides
O_2	Oxygen Molecule
SO_x	Sulphur Oxides

Chapter 1

Introduction

Maritime transportation is key to international trade and the global economy, where approximately 80% of global trade by volume is carried by sea [1]. Carbon dioxide (CO_2) is one of the key greenhouse gases that contribute to the warming of the earth and causes adverse climate change. CO_2 emissions from international shipping in 2019 were estimated to be 2% of global energy-related CO_2 emissions [2]. Recognising its important role in climate change, International Maritime Organization (IMO) adopted the IMO's structured plan, colloquially known as IMO 2050, in April 2018. It sets a target to reduce the total annual shipping GHG emissions by at least 50% by 2050 compared with 2008 while simultaneously pursuing efforts to phase them out entirely [3].

To achieve this aggressive GHG reduction target, replacing the primary energy source from the current fossil-based carbonaceous fuel with alternatives that have low or zero life cycle GHG emissions will be the most effective solution. Such alternatives include fuels fully derived from atmospheric carbon, such as those originating from biomass or renewable energy that contain carbon of atmospheric origin and give net-zero life cycle carbon emission in an acceptable time scale. Examples of such fuel include esters, hydrocarbons, alcohols and methane produced from biomass and renewable energies. Alternatively, a renewable fuel that does not contain any carbon can remove the warming potential from carbon dioxide. Renewable hydrogen, ammonia and any carbon-free derivatives fall under this category.

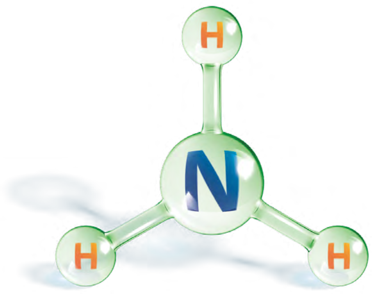
1.1 Properties of Ammonia

1.1.1 Physical Properties

Anhydrous ammonia is a clear and colourless gas at standard temperature and pressure conditions. It has a boiling point of -33°C at 1 atmospheric pressure and freezes at -78°C. Liquid anhydrous ammonia is lighter than water, with a specific gravity of 0.619 (water = 1). Liquid ammonia will expand 766 times when it changes from a liquid to a gaseous state. Anhydrous ammonia gas is lighter than air, with a specific gravity of 0.588 (air = 1). Hence, it will eventually rise in the air after being released into the environment. Ammonia has a distinct pungent odour, making it easy to detect and an important safety feature. The odour detection threshold for ammonia is around 5 parts per million (ppm) of air.

1.1.2 Chemical Properties

One ammonia molecule comprises 1 nitrogen atom and 3 hydrogen atoms, with the chemical formula NH_3 and a molecular weight of 17.03 g/mol. Anhydrous ammonia is essentially pure ammonia (>99% purity) without water, although 0.2% to 0.5% of water is usually added as an inhibitor to prevent stress corrosion cracking in high tensile-strength steel used to fabricate ammonia storage tanks [4].



Anhydrous ammonia is an alkali and is very soluble in water, with an equilibrium solubility of 34% (w/w) at 20°C due to the polar nature of the ammonia molecule. The solubility of ammonia decreases with increasing temperature. The dissolution of ammonia in water results in the release of a large amount of heat in an exothermic process. The heat generated will cause rapid boiling and vaporisation of liquid ammonia. When ammonia is spilt onto any water surface, the amount of ammonia that can dissolve will depend on (i) the rate and extent of vaporisation; (ii) the extent of ice formation when water loses heat rapidly to the boiling and vaporisation of ammonia; (iii) the amount of heat generated from ammonia dissolution in water; (iv) the reactions of ammonia with impurities in water; and (v) the solubility of ammonia at that temperature. Based on observations from past incidents, only approximately 5% to 10% of ammonia may be able to remain dissolved in the water in some cases.

Ammonia, especially in the presence of moisture, reacts with and corrodes copper, zinc, and their alloys. However, iron, steel, aluminium, certain rubbers and plastics, and specific non-ferrous alloys are resistant to ammonia. They can be used for fabricating anhydrous ammonia containers, fittings and piping [4] [5]. More recommendations are presented in Chapter 3.

Ammonia does not exhibit stability or biofouling issues during storage as it is a stable compound toxic to living organisms. As ammonia is not a greenhouse gas, the operational leakages that occur during production, processing and transportation do not contribute to a rise in GHG emissions. In comparison, methane, a GHG, may leak from components in the natural gas systems such as the compressors, valves, pumps, flanges, gauges and pipe connectors, or from bleed-off valves and vents of pressurised storage tanks. It is estimated to produce a global warming potential of 28 over using a 100-year scale [6].

1.1.3 Classification of Ammonia

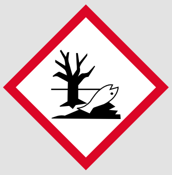
Ammonia is classified as Class 2 (Gases) and Division 2.3 (toxic gases) based on the UN Recommendations on the Transport of Dangerous Goods. It is assigned a UN code of 1005. Based on Regulation (EC) No.1272/2008 on Classification, Labelling and Packaging of Substances and Mixtures [CLP Regulations], ammonia falls under the hazards classes presented in Table 1.1[7] [8] [9]. The CLP Regulation is aligned with existing EU legislation to the United Nations Globally Harmonised System of Classification and Labelling of Chemicals (GHS). Ammonia is given a National Fire Protection Association (NFPA) health hazard rating of 3 and a fire hazard rating of 1.

GHS/CLP Hazard Classification


GHS06


GHS05


GHS04


GHS09

Signal word: Danger

Hazard statements
H221 Flammable gas
H280 Contains gas under pressure; may explode if heated
H314 Causes severe skin burns and eye damage
H331 Toxic if inhaled
H400 Very toxic to aquatic life with long-lasting effects

NFPA Rating

Health	3	Can cause serious/ permanent injury
Flammability	1	Must be preheated before ignition can occur
Instability	0	Normally stable, even under fire conditions
Special	-	-

Table 1.1 Hazards classes of ammonia

1.1.4 Flammability and Explosivity

Anhydrous ammonia is generally not considered a highly flammable product because of its high ignition temperature of 651°C. It is given an NFPA rating of 1 (slightly) for flammability, indicating that the materials must be preheated before ignition can occur. Ammonia vapour is flammable at high concentrations (15% to 28% by volume in air). It is unlikely that such high concentrations will occur except in confined spaces or the proximity of large spills. However, the presence of oil or other combustible material will increase the risk of fire hazards [10]. Anhydrous ammonia becomes unstable at 450°C to 500°C and dissociates into hydrogen and nitrogen.

In case liquid ammonia is stored in a pressurised vessel as a saturated liquid, boiling liquid expanding vapour explosions (BLEVEs) can occur [11] when the pressure vessel fails or when there is an external fire source. If the pressurised vessel fails, the saturated liquid ammonia will be exposed to atmospheric pressure and begin to boil violently and rapidly expand into vapour [12]. Ammonia can deflagrate if released in an enclosed space with a source of ignition present [13].

The flammability property of ammonia is compared with other marine fuels and is presented in Table 1.2. Although the flammability range of ammonia is wide, the auto-ignition temperature and minimum ignition energy are very high. Kondo had developed an RF index to assess the fire and explosion hazard of a flammable substance based on the upper and lower flammability limits and the heat of combustion of the fuels. It represents the total expectancy of fire or explosion hazards, where a higher RF index number indicates higher fire and explosion hazards. The RF index for ammonia is much lower than other fuels and is only 1.7% of the RF index for hydrogen [14].

Fuel	Ignition Energy (mJ)	Auto Ignition Temperature (°C)	Flashpoint (°C)	Flammability Limits (Vol%)	GHS	RF Index
Ammonia at -33°C	680	630	N.A.	15 to 28	2	6.8
Hydrogen at -253°C	0.011 / 0.017	560	N.A.	4 to 75	1	399.5
LNG at -162°C	0.28	537	-187	5 to 15	1	36.6
LPG (propane, butane)	0.25 / 0.26	287 to 537	-104, -155	1.9 to 10	1	52.2
Methanol	0.14	470	12	6 to 50	2	26.2
Ethanol	0.65	400	12	3.1 to 27.7	3	37.6
Dimethyl ether	0.29	350	-80	3 to 26.7	1	52.4

Data compiled from: INCHEM database, NIH database, NIOSH database, Shell Safety Data Sheets, [9], [15], [16], [17]

Table 1.2 Flammability properties of fuels

1.1.5 Toxicology Exposure and Health Impacts

Ammonia is not a cumulative poison, and repeated exposure will not produce additive or chronic effects on the human body. However, anhydrous ammonia is very soluble in water. Ammonia forms ammonium hydroxide and produces heat once it contacts moist surfaces. The corrosive and exothermic properties can immediately damage the eyes, skin, and mucous membranes of the oral cavity and respiratory tract [16]. Ammonia has an NFPA rating of 3 for health, indicating that short exposure above a certain threshold concentration may cause serious temporary or permanent injury. Regulatory short-term exposure limits (STEL) of up to 15 mins and time-weighted average (TWA) over 8 hours are established by the respective national workplace health and safety authorities to manage the exposure of ammonia to the workers during normal daily operations at their workplace (as shown in Table 1.3).

Authorities or Organisations	STEL 15 mins	TWA 8 hours
US Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELS) from 29 CFR 1910.1000 [18]	-	50 ppm
California Cal/OSHA Permissible Exposure Limits (PELS) from 29 CFR 1910.1000 [18]	35 ppm	25 ppm
EU Indicative Exposure Limit Values in Directives 91/322/EEC, 2000/39/EC, 2006/15/EC, 2009/161/EU (12 2009) [19]	50 ppm	20 ppm
UK Health and Safety Executive (HSE) EH40/2005 Workplace exposure limits [20]	35 ppm	25 ppm
Singapore Workplace Safety and Health (General Provisions) Regulations [21]	35 ppm	25 ppm
National Institute for Occupational Safety and Health (NIOSH) (guidelines only)	35 ppm	25 ppm
American Conference of Governmental Industrial Hygienist (ACGIH) (guidelines only), IDLH for ammonia: 300 ppm	35 ppm	25 ppm

Table 1.3 Guidelines and regulatory limits for ammonia exposure

Exposure guidelines are used by emergency planners and responders worldwide as guidance in dealing with the accidental release of chemicals into the environment. Acute Exposure Guideline Levels (AEGL) are developed by the US National Advisory Committee for Hazardous Substances. They represent the threshold exposure limits (exposure levels below which adverse health effects are not likely) for the general public, including susceptible individuals such as infants, children, elderly persons with asthma, and other illnesses. AEGLs consider both ammonia concentration and exposure time. Three levels, AEGL-1, AEGL-2, and AEGL-3, are developed for each of the five exposure times and are distinguished by varying degrees of severity of toxic effects, as presented in Table 1.4 [22].

Guidelines	10 min	30 min	1 h	4 h	8 h
AEGL-1	30 ppm	30 ppm	30 ppm	30 ppm	30 ppm
AEGL-2	220 ppm	220 ppm	160 ppm	110 ppm	110 ppm
AEGL-3	2,700 ppm	1,600 ppm	1,100 ppm	550 ppm	390 ppm
Level 1	Notable discomfort, irritation, or certain asymptomatic non-sensory effects. Effects are not disabling and are transient and reversible upon cessation of exposure.				
Level 2	Irreversible or other serious, long-lasting adverse health effects of an impaired ability to escape.				
Level 3	Life-threatening health effects or death.				

Table 1.4 AEGLs for emergency response

It shall be noted that AEGLs are conservative, and quantitative exposure estimates of acute lethality of ammonia in humans are not well documented. For example, a concentration of more than 5,000 ppm is reported to be “rapidly fatal” to humans [15]. However, an ammonia release case in South Africa in 1973 shows that 33,737 ppm was a 5-min zero mortality value [23].

As ammonia is a toxic chemical, proper safety precautions and procedures shall be observed and closely adhered to. The chemical industry adopted and followed such precautions and procedures when handling ammonia for years. Additional detection and protection system may need to be installed onboard ammonia-fuelled vessels, adding to the weight and space required.

1.1.6 Ammonia Properties as a Marine Fuel

Ammonia can be used directly in combustion engines to generate electricity or indirectly as hydrogen carriers for fuel cell applications. Ammonia can be easily cracked into nitrogen and hydrogen and has a high hydrogen density as it is highly hydrogenated, containing 17.2 wt% of hydrogen. Liquified ammonia has a higher volumetric hydrogen density (120 kg H_2/m^3 at -33°C, 1 atmospheric pressure) than liquid hydrogen (71 kg H_2/m^3 at -253°C) [4], making it a more efficient hydrogen carrier than hydrogen itself. A comparison of key marine fuel properties of ammonia with other fuels is tabulated in Table 1.5.

Ammonia is the only alternative carbon-free fuel besides hydrogen. Compared to carbon-based alternatives, ammonia feedstocks are unlimited as only air and water are needed as preliminary sources. It is easier, more efficient and cheaper to capture nitrogen (79% N_2 in the air) than carbon (0.04% CO_2 in air) from the air. Nitrogen from direct nitrogen capture is priced at US$0.0424/kg compared to US$0.20 to US$0.50/kg for direct carbon dioxide capture [4]. Ammonia is reported to have the highest power-to-fuel-to-power (PFP) index of 35%, followed by methane and methanol at 27% [24]. PFP is the ratio of the available output energy from a fuel's conversion process to its energy consumption in production.

Ammonia is an electrofuel that can be produced with hydrogen obtained from the electrolysis of water powered by renewable energy such as wind, solar, tidal and hydro [25] [26]. Electrofuels help to stabilise the energy grid by enabling the storage of excess variable renewable energies produced and releasing and utilising the energy when renewable generation output is low. The energy captured in electrofuels can also be distributed to areas where renewable energy sources cannot be harnessed.

Ammonia has a higher volumetric energy density (12.7 MJ/L) than liquid hydrogen (8.5 MJ/L). Ammonia can easily be condensed into liquid at relatively low pressures and high temperatures (-33°C at 1 atmospheric pressure or 25°C at 10 bar absolute pressure), thus making it easier and cheaper to transport than hydrogen. Hydrogen can be liquefied at -253°C into a light liquid with a specific gravity of 0.071 or highly compressed into a gas at 700 to 1,000 bar. The storage volume for ammonia (at -33°C, 1 atmospheric pressure) is approximately 50% smaller than that for hydrogen [27].

The combustion of ammonia in internal combustion engines dates to at least the Second World War, when ammonia was used to fuel buses in Belgium [28]. Although ammonia has a relatively low calorific value, low cetane number and low flame speed, many recent studies have shown that ammonia can be used in both spark-ignited and compression ignition engines with a pilot fuel injection of diesel or other high-cetane fuels or hydrogen to speed up the combustion. Trans-oceanic marine engines with large displacement volumes and operating at a constant low speed with high loads (supercharged) are favourable for ammonia combustion [29]. Dual-fuel marine engines fuelled by alternative fuels like LPG already exist. Since ammonia has similar physical properties as LPG, experience from these engines could help accelerate the adoption of ammonia for marine engines. Dual-fuel trans-oceanic engines that use both high energy density marine fuels such as LPG and ammonia have the advantage of greater combustion control to achieve the desired power output, efficiency and emissions [30] [31] [32] [33] [34] [35]. MAN Energy Solutions is currently modifying the existing 2-stroke LPG engine to use ammonia as a fuel with expected efficiency of more than 50% [36]. The 2-stroke ammonia engine will be commercially available by 2024, and MAN Energy Solutions will introduce a retrofit package to gradually rebuild existing maritime vessels by 2025 [27]. A list of ammonia development in the maritime industry is presented in Chapter 2.

Combustion of ammonia will eliminate the emission of carbon dioxide and pollutants SO_X, CO and particulate matter (PM). There is no carbon dioxide emission as ammonia is carbon-free. There will also be no carbon monoxide and particulate emissions comprising carcinogenic soot or unburnt carbon related to incomplete combustion of carbon-based fuels such as oil, coal and biomass.

Although the nitrogen content in ammonia may result in NO_x emissions, this is the case for all combustion processes, as combustion takes place in the air, which contains 79% of nitrogen. The power industry has extensive experience controlling NO_x emissions, such as using SCR (selective catalytic reduction) catalyst [27], where ammonia is used as a reduction agent to convert NO_x to N_2. However, N_2O emission from fuel nitrogen may be an issue that requires further studies. Combustion tuning or catalysts may be able to control or limit the generation of nitrous oxide.

Types	Fuel / Alternative Fuel	Properties		Energy Content		Combustion Emissions					Feedstock	Feedstock Availability	Storage	
		Chemical Structure	Physical State	Specific Energy MJ/kg	Energy Density MJ/L	CO_2	SO_x	NO_x	PM	CO			Storage Condition	Net Storage Volume[1] m^3
Carbon Free	Ammonia (liquid -33°C)	NH_3	Saturated liquid	18.9	12.7	×	×	●	×	×	Fossil, water, air	High	-33°C at 1 atm. pressure; 25°C at 10 bar absolute pressure	3,070
	Hydrogen (liquid -253°C)	H_2	Boiling liquid	120	8.5	×	×	●	×	×	Fossil, water, biomass	High	-253°C at 1 atm. pressure; 25°C at 350 to 700 bar	4,590
Marine Fuel	HFO RMG380	~ C_{20} to ≥ C_{50}	Liquid	39.5	39	●	●	●	●	●	Crude oil	High	Atmospheric	1,000
	LSFO	~ C_{20} to ≥ C_{50}	Liquid	39.5	39	●	◉	●	●	●	Crude oil	High	Atmospheric	1,000
	MDO	~ C_8 to C_{21}	Liquid	42.6	36.0	●	◉	●	●	●	Crude oil	High	Atmospheric	1,080
Low Carbon	LNG at -162°C	CH_4	Boiling liquid	48.6	20.8	◉	○	◉	○	○	Natural gas	High	-162°C	1,875
	LPG (propane and butane)	C_3H_8 C_4H_{10}	Saturated liquid	46.6	23.6	◉	◉	●	○	○	Natural gas	High	5 to 15 bar	1,650
	Methanol	CH_3OH	Liquid	20.0	16.2	◉	○	◉	○	○	Natural gas, biomass	High	Atmospheric	2,410
	Ethanol	CH_3CH_2OH	Liquid	27.0	21.2	◉	○	◉	○	○	Biomass	Low	Atmospheric	1,835
	DME (dimethyl ether)	CH_3OCH_3	Saturated liquid	28.9	19.2	◉	○	●	○	○	Fossil, biomass	Low	5 to 15 bar	2,030
Biogenic	FAME	C_{12} to C_{22} fatty acids esters	Liquid	36 to 38	32 to 34	◉	○	●	◉	◉	biomass	High	Atmospheric	1,180
	HVO/HDRD	~ C_8 to C_{21}	Liquid	43 to 44	32 to 34	◉	○	◉	◉	◉	biomass	High	Atmospheric	1,180

● Similar to baseline (Heavy Fuel Oil – RMG 380)	◉ Lower than baseline
○ Negligible or below detection limit	× Absolute zero emission

Table 1.5 Comparison of fuel properties of ammonia with conventional and alternative fuels[2]

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[1] Required storage volume is computed based on the energy density of respective fuels, not considering additional insulation, tank type or auxiliary systems required.

[2] Data compiled from multiple sources [37], [38], [39], [40], [41]

1.2 Research Gaps, Objectives and Methodology

As a new bunker fuel, provisions and guidelines need to be established to ensure a safe and operationally feasible ammonia bunkering process. However, current technological maturity is still low, and the production of green ammonia is expensive. In addition, the lack of bunkering infrastructure and process poses a barrier to adopting ammonia as an alternative marine fuel.

1.2.1 Research Gaps

Availability: Ammonia production technology from low carbon feedstock is still in its infancy stage. As a major gap in the ammonia value chain, the development is expected to keep up with future demand.

Ammonia Bunkering Infrastructure: Without bunkering infrastructure, shipbuilding companies and ship owners may not commit to building and operating ammonia-fuelled ships. The current ports that can handle ammonia are only for on-loading or off-loading purposes. Ammonia bunkering infrastructure such as port with dockside bunkering and special-purpose ship that performs ship-to-ship ammonia bunkering is currently unavailable.

Energy Converter Technology: There is a need for further development in the technology for internal combustion engines, furnaces/boilers and fuel cells that are dedicated to using ammonia. Due to the low flammability, high ignition energy and slow frame velocity of ammonia, there are still challenges to adopting ammonia as the main fuel for the marine industry.

Ammonia Bunkering Safety: As ammonia has been widely used on land for various chemical industries, safety analysis for ammonia handling, storage and transportation on land has been carried out comprehensively and extensively. However, as sea-borne transportation of ammonia is only limited to on-loading and off-loading at limited terminals and ports, there is limited safety study done for the marine industry.

1.2.2 Objectives

The objectives of this study are to provide an overview of ammonia supply and to carry out an ammonia bunkering safety study, which includes several selected scenarios in Singapore, using a proposed hypothetical ammonia bunkering process and simulation method to demonstrate the impacts of an ammonia release.

1.2.3 Methodology

Extensive information was extracted from literature and databases. Industry partners were consulted to provide LNG, and LPG bunkering information and shore-based ammonia handling, transportation, loading and off-loading experience. Simulation was done by PHAST software to assess the spatial extent of the consequences of accidental ammonia release for various bunkering scenarios.

Chapter
1

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Chapter
2

Ammonia Production and Supply

2.1 Ammonia Production

2.1.1 Overview

Ammonia has been produced and transported worldwide for over a century. 80% of global ammonia production is consumed as fertiliser [1]. Ammonia is also used for refrigeration, chemical, mining, and power generation [1]. Global ammonia production was 185 million tonnes in 2020, which has increased by 25 times in 70 years [2] [3]. As shown in Figure 2.1, global ammonia production is correlated to the world population [2] [3] [4]. It is estimated that nitrogen fertilisers are responsible for feeding 48% of the world's population, and the lives of around half of humanity are made possible by Haber-Bosch nitrogen [5]. It is assumed that 1 tonne of ammonia is responsible for the food supply of around 20 people per year.

The current ammonia production capacity is insufficient to meet the new demand for ammonia as a marine fuel in the maritime industry. Based on the consumption of an 8,000 TEU container ship travelling at 21 knots, approximately 150 tonnes of HFO are required per day [6]. In comparison, 326 tonnes of ammonia per day or 97,800 tonnes per year (300 operating days per year) are required based on the equivalent energy density of the fuels (LHV of HFO is 40.4 MJ/kg, and liquid ammonia is 18.6 MJ/kg [7]). The 8,000 TEU ammonia-fuelled container ship would consume the same quantity of ammonia as the food production for 2 million people per year (Figure 2.2). This new demand for ammonia as a marine fuel will lead to competition with the existing fertiliser market. As such, ammonia production capacity shall be increased proportionally to meet the new demand for energy use.

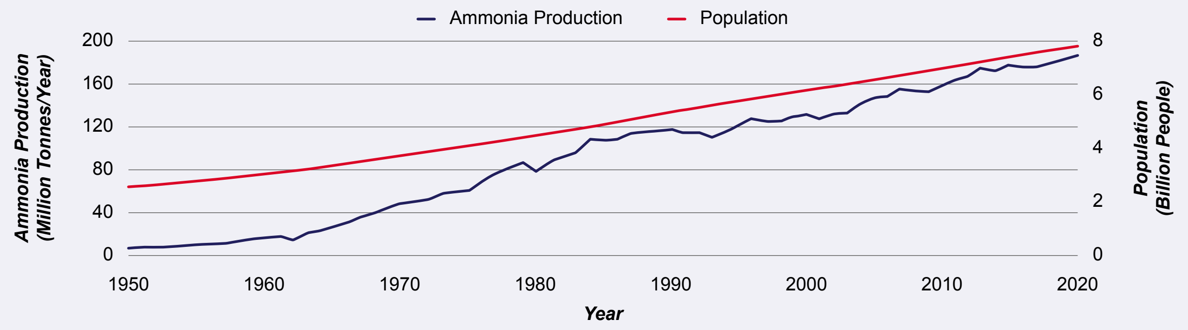

Figure 2.1 Global ammonia production and world population

Figure 2.2 Ammonia bunker consumption and food supply

Ammonia is also required for bioenergy and biofuel production, contributing 10% and 1.5% of the global energy requirement, respectively [5]. Population growth, food supply improvements, and biomass use to provide energy will lead to a further increase in the demand for nitrogen [5] and a greater ammonia demand.

The increased use of ammonia will release more reactive nitrogen into the environment, affecting the global nitrogen cycle and the ecological system. Reactive nitrogen is readily converted into life-supporting protein, causing oxygen depletion in fresh waters by eutrophication. These effects can be mitigated through intervention strategies focusing on reducing the reactive nitrogen or converting it back to atmospheric dinitrogen [5].

2.1.2 Ammonia Synthesis

Ammonia is one of the most synthesised industrial chemicals in the world [8]. Hydrogen as a feedstock is mainly produced using hydrocarbons or carbohydrates as feedstock from the low-cost steam reforming process [9]. Hydrogen is also produced commercially through water electrolysis, accounting for 3.9% of the world's hydrogen production [9]. In addition to steam reforming and electrolysis, other hydrogen production methods include biomass gasification, the photolysis of water by sunlight, and the partial oxidation of hydrocarbons. Gasification and partial oxidation are less efficient than steam reforming, and the photolysis method is not commercially available [1]. Nitrogen is produced from air by cryogenic fractional distillation of liquid air, pressure swing adsorption and polymeric membrane separation technology [10]. Cryogenic fractional distillation of liquid air is the most used method for industrial-scale production [10].

Currently, 90% of the world's ammonia is produced through the Haber Bosch process developed by Fritz Haber and Carl Bosch in 1909 [8]. It is an energy-intensive process, requiring a temperature of 450°C to 500°C, a pressure of up to 200 bar, and an iron-based catalyst [11]. Ammonia can also be produced by electrolytic synthesis involving liquid electrolytes, molten salts, composite membranes and solid-state electrolytes [4]. The energy consumption for electrochemical processing is about 20% lower than the Haber Bosch process [12]. However, the main drawback of the electrochemical process is the low productivity, which is unsuitable for large-scale production. As an improvement, Solid Oxide Electrolysis Cell (SOEC), combined with steam electrolysis, is more efficient than classical electrolysis [13]. As shown in Figure 2.3, the waste heat generated is used to produce steam [13]. However, SOEC has not yet reached the commercial scale, although it is believed to have the most potential in the future. For the time being, the Haber Bosch process is still the mainstream industrial process to produce ammonia.

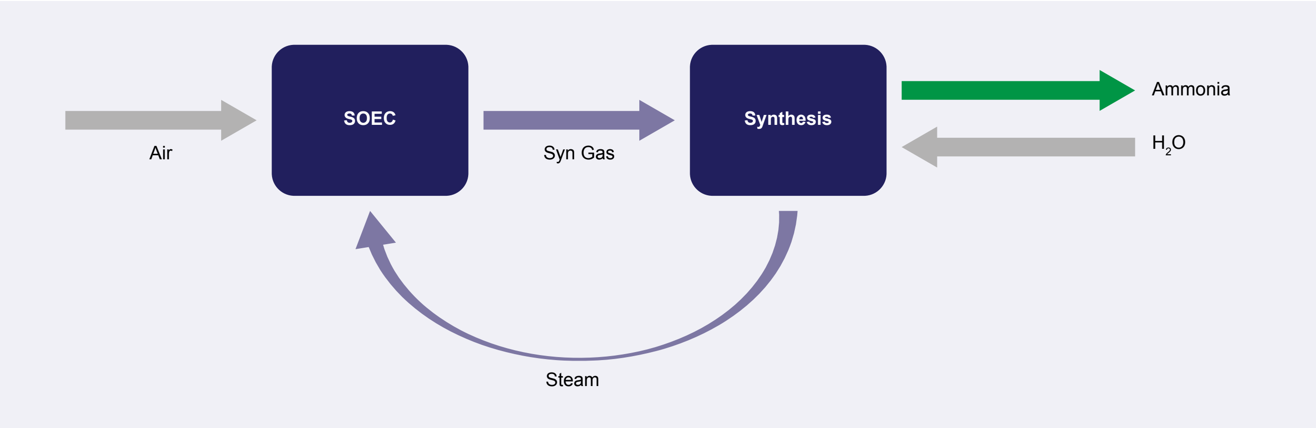

Figure 2.3 Synergy between SOEC and fuel synthesis

The ammonia industry has informally adopted a colour scheme to describe the carbon intensity of ammonia produced from different pathways and feedstocks (Figure 2.4). Several processes, including pre-treatment, conversion and synthesis, are required when converting primary energy into ammonia.

- *Brown ammonia* (conventional ammonia) is produced from common feedstocks, including natural gas, coal and fuel oil, which account for 72%, 22% and 4% of total ammonia production, respectively [8]. The production process includes gasification, water gas shift reaction, acid gas removal, methanation, Haber Bosch or electrochemical synthesis.
- *Blue ammonia* production is similar to brown ammonia. Still, the carbon capture and storage (CCS) or enhanced oil recovery (EOR) process is added to prevent the carbon emission generated by the process.
- *Turquoise ammonia* production involves using renewable electricity to convert natural gas into carbon black and hydrogen via methane pyrolysis, and the carbon black is retained. In contrast, hydrogen is sent for ammonia production.
- *Green ammonia* (renewable or sustainable ammonia) is produced entirely from water and air with renewable electricity. The production process of turquoise and green ammonia does not emit nitrogen oxides, sulphur oxides, or CO_2.

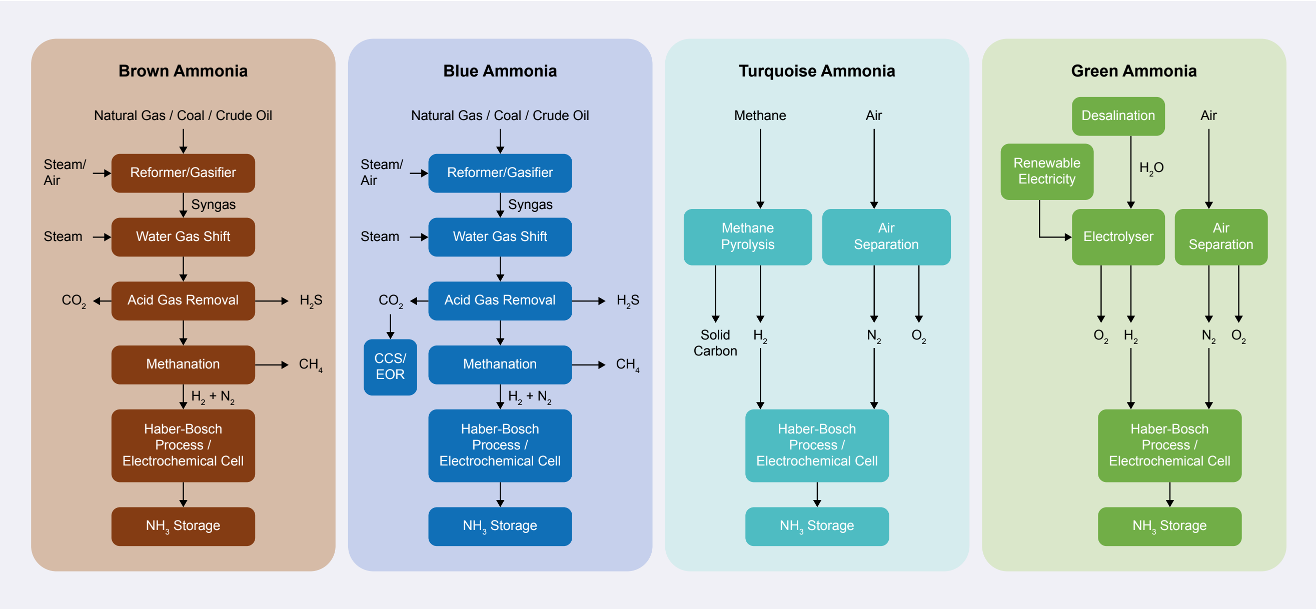

Figure 2.4 Ammonia production routes

Current trends for ammonia synthesis are to decarbonise and electrify the process [14]. The electricity from renewable sources such as solar, wind and biomass could be the main driver. At the same time, the improvements in catalysts could further decrease the operating temperature and pressure, achieving higher overall efficiency [14].

2.1.3 Green Ammonia Developments

Currently, green ammonia is produced on a small scale. The green hydrogen produced from renewable electricity is the key component for green ammonia production. Ammonia can be produced at the hydrogen production plant, and the only additional material is nitrogen which is abundant in air and can be easily separated. The most established ways of producing green hydrogen are water electrolysis and biogas reforming [15]. Biomass-based hydrogen production is an alternative to electrolysis-based hydrogen for small-scale ammonia synthesis if the biomass feedstock is sufficient.

Table 2.1 summarises the global initiatives and R&D projects for green ammonia production. Solar, wind and hydroelectricity are the main sources of energy inputs. Several countries such as Australia, Chile and Saudi Arabia recently announced their interests in investing in green ammonia projects. Countries with wind and solar resources near large reservoirs or sea could have great potential. Once the listed green ammonia plants go into full-scale operation, the annual production capacity will exceed 20 million tonnes.

Press Release	Country	Plant Location	Main Developers	Annual Capacity (tonnes)	Energy Source	Ref.
2019	Chile	Mejillones	ENAEX, ENGIE	18,000	Solar	[16]
2020	New Zealand	Kapuni	Ballance-Agri, Nutrients, Hiringa Energy	5,000	Wind	[17]
2020	Saudi Arabia	Red Sea Coast	Air Products, ACWA Power, NEOM	1,200,000	Solar, wind	[18]
2020	Scotland	Orkney	Eneus Energy	4,015	Wind	[19]
2020	Denmark	Western Jutland	Haldor Topsoe, Vestas	5,000	Solar, wind	[20]
2020	Norway	Porsgrunn	Yara, NEL Hydrogen	500,000	Hydro	[21]
2020	Australia	Tasmania Bell Bay	Origin Energy	420,000	Hydro	[22]
2021	Australia	Pilbara	Yara, ENGIE	850,000	Solar	[23]
2021	Morocco	Rabat	Fusion Fuel, Consolidated Contractors Group S.A.L.	183,000	Solar	[24]
2021	United Arab Emirates	Abu Dhabi	Abu Dhabi Ports, Helios Industry	200,000	Solar	[25]
2021	Bolivia	Oruro	H2 Bolivia S.A., the Government of Oruro	500,000	Solar	[26]
2021	Mauritania	In the north	CWP Global	10,000,000	Solar, wind	[27]
2021	Chile	Magallanes	Total Eren	4,400,000	Wind	[28]
2022	Malaysia	Bintulu	Samsung Engineering, Lotte Chemical, POSCO, Sarawak Economic Development Corporation	630,000	Renewable energy	[29]
2022	Spain	Aragon	Copenhagen Infrastructure Partners, Fertiberia, Vestas, Enagás, Naturgy	200,000	Solar, wind	[30]
2022	Norway	Southwestern coast	Hy2gen, Trafigura and Copenhagen Infrastructure Partners	219,000	Hydro	[31]
2022	Oman	Duqm	Scatec, ACME Group	1,200,000	Solar	[32]
2022	Egypt	Ain Sokhna	Scatec, Egyptian government entities	3,000,000	Solar, wind	[33]
2022	Canada	Quebec	Trammo, Teal Corporation	800,000	Hydro	[34]

Table 2.1 List of green ammonia development projects

2.1.4 Ammonia Production Cost

The costs of ammonia production, storage and distribution vary according to the production pathways and locations. The average production cost of brown ammonia is 340 USD/t [35], while the storage and distribution cost for transporting ammonia from south Australia to Singapore is 60 USD/t [35]. The ammonia fuel cost is 400 USD/t in total. A case study conducted for the Emma Maersk sailing at 22 knots showed that a carbon tax of 127 USD/tCO_2e is required to equalise an ammonia-fuelled vessel's total life cycle costs [36].

The key cost components for ammonia production cost are capital investment cost and operational cost. The capital investment cost of a green ammonia plant comprises the cost of equipment for hydrogen production, nitrogen production, ammonia synthesis and storage. The capital cost of the electrolyser accounts for about half to two-thirds of the capital investment [35]. Hence, reducing the electrolyser investment cost will make green ammonia more cost-competitive. For capital investment cost, the size of ammonia plant is an important factor due to economies of scale [35]. For conventional natural gas-based ammonia plants, the capital intensity cost ranges from 1,000 to 1,300 USD/t/year based on the average data obtained from 2015 to 2020 [37]. The range depends on the location and year of construction. Currently, all the green ammonia plants in operation are small-scale because the capacity of the wind and solar power plants is insufficient to support a large-scale standard Haber-Bosch ammonia plant [37]. The capital intensity of green ammonia plant investment is about 1,750 to 2,200 USD/t/year based on the average data obtained from 2015 to 2020 [37].

Operational cost is approximately 2% to 5% of capital expenditure per year [35]. Hydrogen production cost is the key cost driver in ammonia production. Brown hydrogen produced from methane steam reforming costs between 956 and 1,794 USD/t [35]. Blue hydrogen production cost is between 1,477 and 2,427 USD/t while green hydrogen production costs range from below 1,630 USD/t to above 4,079 USD/t [35]. The price of green hydrogen will fall with the development of more cost-efficient equipment and a reduction in renewable energy [38].

2.2 Ammonia Storage and Distribution

2.2.1 Ammonia Trade

Currently, the ammonia trade supply chain is well established. Ammonia is shipped as bulk cargo on ammonia carriers, accounting for the 3rd largest seaborne trade in liquefied gases market, after LNG and LPG [39]. The largest ammonia exporting country in 2020 is Saudi Arabia, and the top 10 ammonia exporting countries account for about 85% of total ammonia exports, as shown in Figure 2.5 [40].

There were about 170 ammonia terminals worldwide in 2020, and the geographical distribution is shown in Figure 2.6 [41]. Ammonia terminals are located separately from the production plants. The major bunkering ports (indicated as red dots in Figure 2.6) include Singapore, Fujairah, Rotterdam and Panama. They are located close to the existing ammonia terminals, which have the potential to supply ammonia bunkers on a large scale. Vopak terminal on Jurong Island is the only ammonia terminal in Singapore, and it only has an ammonia storage capacity of 10,000 m^3. Given the low volumetric density of ammonia and the high volume of bunkering activities in Singapore, one could foresee a substantial increase in the ammonia storage capacity in Singapore is required.

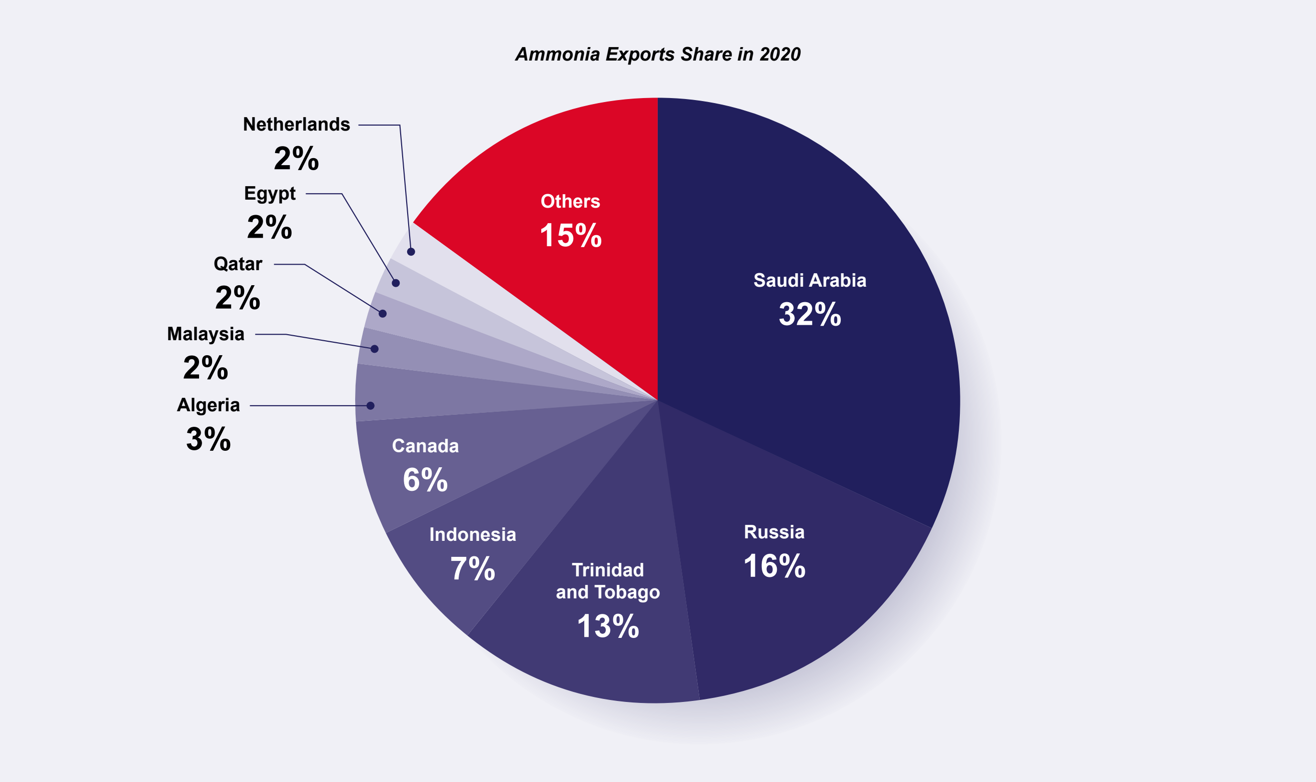

Figure 2.5 Ammonia exports in 2020

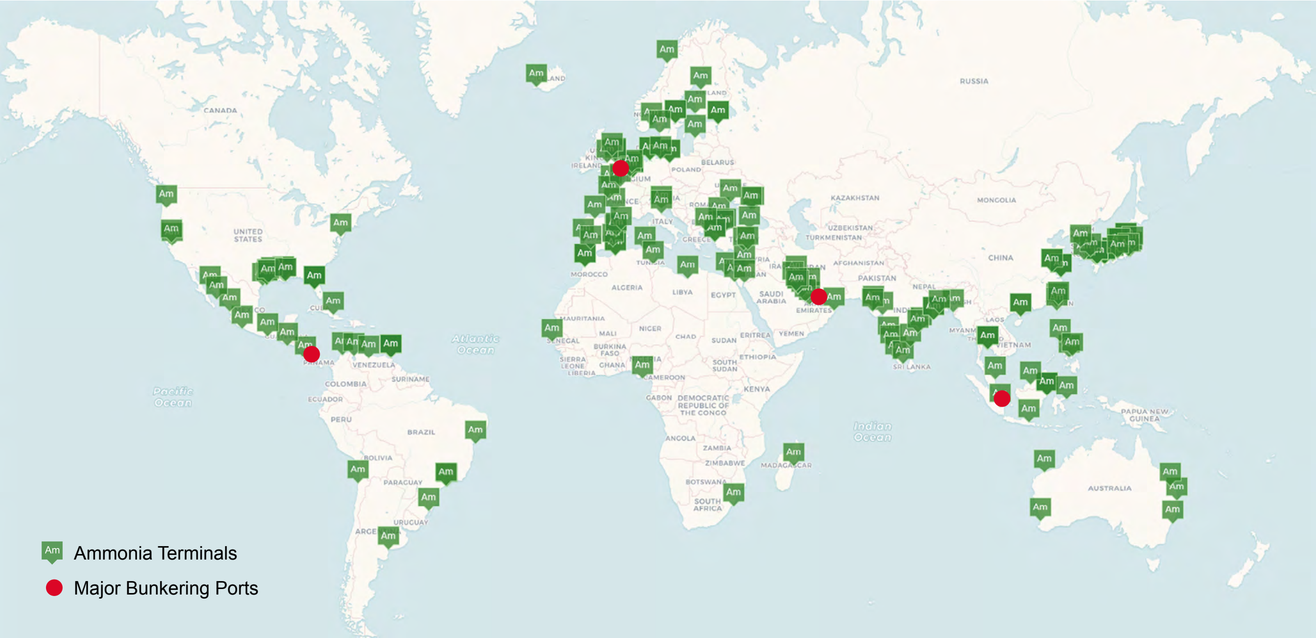

Figure 2.6 Ammonia terminals distribution and major bunkering ports in 2020

2.2.2 Storage Tanks and Materials

Ammonia is in a gaseous state at ambient temperature and pressure. It is normal to transport liquid ammonia by compression, refrigeration, or a combination of both to ensure cost-effective transportation. Currently, three types of storage tanks are used to contain liquid ammonia at different operating pressure and temperature. These include a fully refrigerated (FR) tank (at -33°C) at atmospheric pressure, semi-refrigerated (SR) tank and a non-refrigerated (NR) tank at ambient temperature. NR and SR tanks are used to store smaller quantities of ammonia. The SR tank allows heat gain from the surroundings. The resultant boil-off must be managed by providing suitable thermal insulation and refrigeration [42]. The advantage of NR storage is that no additional energy is required to keep ammonia in a liquid phase. Although the operational cost of the NR tank is minimal compared to SR and FR tanks, it has the highest CAPEX. One tonne of carbon steel can fabricate a 45-tonnes FR tank compared to a 2.8-tonnes thick-wall NR tank [35].

A fully refrigerated tank is used for storing large quantities of ammonia. They are usually fabricated from carbon steel and are cylindrical with a flat bottom and slightly domed lids. FR tanks can be single-wall or double-wall, as shown in Figure 2.7 [43]. Single-wall tank is made of low-temperature carbon steel with external insulation [42]. The insulation must be air-tight to keep out moisture from the air, which could degrade the insulation by forming ice crystals. The double-wall tank has an inner wall of low-temperature grade carbon steel and an outer wall of normal carbon steel. The space in-between is filled with insulation materials. The double-wall tank can be designed with improved integrity, where both the inner and outer bottoms and walls are made of low-temperature carbon steel and are designed for full containment [42]. However, the CAPEX for a double-wall tank is higher than a single-wall tank, but the operational costs are lower [35].

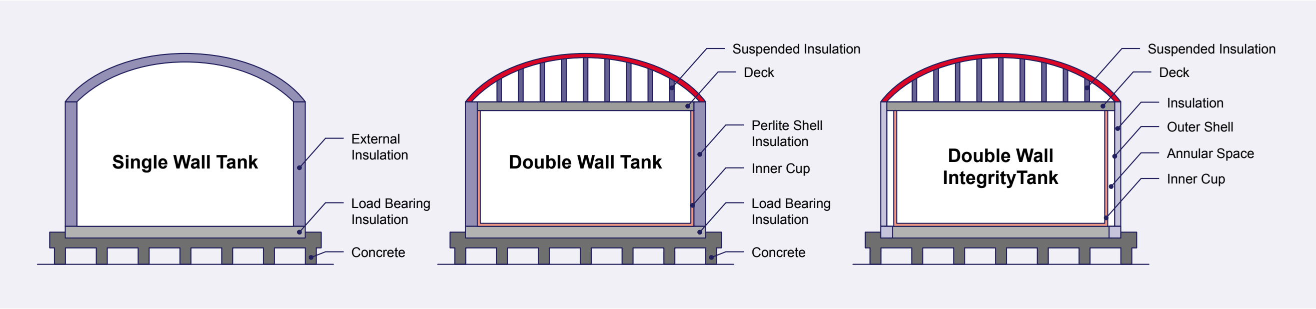

Figure 2.7 Refrigerated ammonia storage tank types

Ammonia is a corrosive substance. Thus, the storage tank, fuel supply system and engine parts should be made with compatible materials. Ammonia is incompatible with copper, zinc and their alloys [44]. The commonly used material for ammonia storage tanks is carbon steel, such as the American Society for Testing and Materials (ASTM) A537 Class II, ASTM A516 Grade 60N, and ASTM A516 Grade 70N. In addition, construction materials for ammonia handling must be resistant to low temperatures and stress corrosion cracking (SCC) [42]. The presence of oxygen (or air) and residual stresses combined with applied stress in and near the welds are the causes of SCC. It can lead to tank rupture, causing disastrous impacts on humans and the environment. Some measures to prevent SCC include using stainless steel equipment, performing nitrogen purging to remove oxygen (or air) and adding at least 0.2% water to ammonia [45]. The amount of water required depends on the oxygen concentration in ammonia. The higher the oxygen concentration, the more water is needed to inhibit SCC [46]. In addition, the use of high-yield strength steel should be avoided. The yield strength should not exceed 350 N/mm^2 [42].

Comprehensive regulations, standards and guidelines have been established over the years for ammonia storage, handling and transportation in the chemical, fertiliser and refrigeration industry. Ammonia is currently handled as a bulk commodity frequently loaded and unloaded from terminals to vessels and vessels to terminals. Regulations and procedures are well-established for the on-loading and off-loading process. However, there are no such regulations and procedures for ammonia bunkering in the maritime industry. There are several differences between the transfer of ammonia as a cargo and as a bunker. Recognising and understanding these differences is essential before establishing the regulations and standards for ammonia bunkering. Key differences such as transferring configurations, frequency, duration and operation procedures are identified and discussed in Chapter 3. Furthermore, it is worth noting that fuel specifications of ammonia to be used in marine combustion engines, boilers, or fuel cells are still undefined. ISO 8217 (Petroleum products - Fuels (class F) - Specifications of marine fuels) is widely used to specify the quality of petroleum fuels. Still, it does not provide specifications on alternative fuels, such as ammonia.

2.2.3 Distribution by Land and Sea Transport

Ammonia is almost invariably transported as a liquid on both land and sea. On land, the most flexible mode of transportation for short-distance distribution of ammonia is by nurse tanks (capacity of 3.78 to 5.48 m^3) within the agricultural area and tanker trucks (capacity of 11 to 25 m^3) via highway [45]. For long-distance distribution, ammonia is often transported in tank cars by railway (capacity of 50 to 110 m^3 per tank, 50 to 150 tanks per journey) and pipelines [35]. Ammonia expansion with temperature limits ammonia loading to 57% to 85% of the tank's volume [45]. The capacity of the pipeline depends on the pipeline diameter and length. The diameter of an ammonia pipeline ranges from 50 to 350 mm [45]. Pipelines can connect multiple ammonia-producing plants with multiple storage locations, which may be hundreds of miles apart. The main drawback of railway and pipeline distribution is the lack of flexibility.

In terms of ammonia sea transport, it is common to use LPG carriers to transport liquid ammonia. There are four types of independent tanks of gas carriers, namely type A IGC tank, type B IGC tank, type C IGC tank and membrane tank. Type A and type B tanks are fully refrigerated at atmospheric pressure, and an onboard refrigeration system is required. Type C tank can be pressurised up to 20 bar at ambient temperature or semi-pressurised at a lower temperature. Moreover, ammonia can be transported by barge for inland shipping. For example, a lot of ammonia is transported by barge on the Mississippi river each year [73].

2.3 Ammonia Demand by Maritime Sector

The maritime industry has recognised the potential usage of ammonia as an alternative marine fuel. International Association of Classification Societies, such as Lloyd's Register, DNV, ABS and Korea Register, are joining with shipbuilding companies and engine manufacturers to design ammonia-fuelled vessels. For example, DNV published "Ammonia as a marine fuel safety handbook" in 2021 to show how the ship arrangement is affected by the ammonia fuel installation and how to accommodate ammonia fuel in the different parts of the system [47]. ABS published the "Guide for ammonia-fuelled vessels" in 2021, which describes the requirement for the ship design and arrangement, fuel containment system, material and general pipe design, bunkering and fire safety, etc. [48]. Korea Register launched a "Report on ammonia-fuelled ships" in 2021 to provide a direction for safety regulations of ammonia-fuelled ships by studying ammonia characteristics [49].

As shown in Table 2.2, most ammonia projects in the maritime field are focused on designing ammonia-fuelled vessels starting from 2019 and beyond. These projects cover the common types of vessels, including tankers, gas carriers, bulk carriers, container ships, RORO cruise liners, and tugboats. In addition, there is growing interest in the ammonia-fuelled tanker design based on the project numbers. The ammonia carrier is identified as the first type of vessel to adopt ammonia as bunker fuel. In terms of vessel design and construction locations, most of them are located in Asia and Europe, such as China, South Korea, Japan, Norway, Finland and Denmark.

Although ammonia bunkering standards and guidelines are not developed yet, there are several discussions and projects on ammonia bunkering in the maritime industry. This study started in 2020 and was the first to conduct the ammonia bunkering and release simulation study in Singapore. Some organisations also conducted ammonia bunkering studies, such as ITOCHU Group, A. P. Moller - Maersk A/S and Global Centre for Maritime Decarbonisation [51] [52] [53] [54]. All these projects consider Singapore as a potential ammonia bunkering port. One of the reasons is that Singapore is the biggest bunkering port based on the current bunker sales volume. When ammonia is adopted as a marine fuel in future, the Singapore bunkering port will become an essential part of the entire ammonia bunker supply chain.

Category	Press Release	Location	Main Partners	Project Description	Ref.
Ammonia Bunkering	2020	Singapore	Nanyang Technological University, American Bureau of Shipping, Ammonia Safety and Training Institute, ExxonMobil, EPS, MAN Energy Solutions, Jurong Port, PSA International, Hoegh LNG	Ammonia as the marine fuel in Singapore – supply chain, bunker safety and potential issues	[50]
	2020	Singapore	Itochu group, Itochu Enex, Itochu Corporation, Vopak terminal	Memorandum of Understanding to study ammonia marine fuel supply chain in Singapore	[51] [52]
	2021	Singapore	A. P. Moller - Maersk A/S, Fleet Management Limited, Keppel Offshore & Marine, Maersk Mc-Kinney Moller Center for Zero Carbon Shipping, Sumitomo Corporation, Yara	Ammonia as marine fuel in Singapore	[53]
	2022	Singapore	Global Centre for Maritime Decarbonisation	Ammonia bunkering study	[54]
Bunker Tanker / Gas Carrier	2019	South Korea	MISC Berhad, Samsung Heavy Industries, Lloyd's Register, MAN Energy Solutions, Yara, Maritime and Port Authority of Singapore	The Castor Initiative: design an ammonia-fuelled tanker, establish the design, concepts and identify the regulatory requirements	[55] [56]
	2019	Finland	Wärtsilä, Aker Solutions, DFDS, Equinor, Grieg Star	Zeeds (Zero Emission Energy Distribution at Sea initiative): Onshore and offshore green NH_3 production and distribution	[57]
	2020	Japan	NYK Line, Japan Marine United Corporation, Nippon Kaiji Kyokai (ClassNK)	Ammonia fuelled ammonia gas carrier and ammonia floating storage and regasification barge	[58]
	2020	Norway	Grieg Edge, Wärtsilä	120 m long ammonia fuelled tanker with a cargo capacity of 7,500 m^3 of ammonia	[59]
	2020	South Korea	Hyundai Mipo Dockyard, Lloyd's Register, MAN Energy Solutions	50,000 DWT MR tanker design	[60]
	2021	China/ Greece	Avin International, China's New Times Shipbuilding	Suezmax series tanker	[61]
	2022	South Korea	Lloyd's Register, Samsung Heavy Industries, MISC Berhad	Ammonia fuelled very large crude carriers (VLCCs)	[62]

Table 2.2 List of ammonia-fuelled vessels and bunkering projects

Category	Press Release	Location	Main Partners	Project Description	Ref.
Bulk Carrier	2019	China	Shanghai Merchant Ship Design & Research Institute (SDARI), Lloyd's Register	180,000 tons bulk carrier design	[63]
	2020	Japan	Japan Shipping Zero Emission Project by industry consortium	80,000 DWT bulk carrier concept design	[64]
	2022	China	Shanghai Merchant Ship Design & Research Institute, China State Shipbuilding Corporation	Ammonia fuelled 7,000-unit capacity car carrier	[65]
Container Ship	2019	China	Dalian Shipbuilding Industry Co., Lloyd's Register, MAN Energy Solution	23,000 TEU ultra-large container ship concept design	[66]
	2019	China	American Bureau of Shipping, MAN Energy Solutions Shanghai Merchant Ship Design & Research Institute	2,700 TEU container ship design (Chittagongmax Container)	[67]
	2020	South Korea	Lloyd's Register, Daewoo Shipbuilding & Marine Engineering, MAN Energy Solutions	23,000 TEU ultra-large container ship design	[68]
Other Types of Vessels	2020	Norway	Colour Fantasy	The world's largest RORO cruise liner	[69]
	2020	Japan	NYK Line, IHI Power Systems Co., Ltd., Nippon Kaiji Kyokai (ClassNK)	Tugboat design	[70]
	2020	Denmark	Global Maritime Forum, Lauritzen-Kosan, Yara, Ørsted, Wartsila, MAN Energy Solutions, DNV, Danish Ship Finance, DNB, Fürstenberg Maritime Advisory	The construction of the world's first ammonia-powered deep-sea vessel	[71]
	2020	Norway	Ship FC Consortium, Equinor, Eidesvik Offshore, Wärtsilä, Prototech, Yara, FraunhoferIMM, SME Persee, The University of Strathclyde, National Centre for Scientific Research, Demokritis, North Sea Shipping, Capital-Executive Ship Management, Star Bulk Ship Management, Sustaina	Offshore vessel Viking Energy: 2 MW ammonia fuel cell to be retrofitted	[72]

Table 2.2 List of ammonia-fuelled vessels and bunkering projects (Cont'd)

Chapter
2

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Chapter
3

Ammonia Bunkering Operation

3.1 Bunkering Operation

Bunker is the fuel supplied to a vessel for its propulsion and/or machinery, and bunkering operation is the bunker delivery to the vessel [1]. Singapore is one of the world's largest and most important bunkering ports, with around 50 million tonnes of total bunker sales in 2021 [2]. The huge bunker sales volume in the past several years also indicates that Singapore plays an important role in the global bunkering industry. If ammonia is considered a candidate bunker fuel, the port of Singapore can be foreseen as one of the potential ammonia bunkering hubs.

General Bunkering Modes and Procedures

There are three main bunkering modes for conventional marine fuel (Figure 3.1), namely ship-to-ship bunkering (STS), truck-to-ship bunkering (TTS) and shore/terminal pipeline-to-ship bunkering (PTS) [3]. Ship-to-ship bunkering is the most common method of delivering marine fuel to ships. Bunker barge can be a simple floating structure of tanks with a pumping system and pipelines on board. After the bunker barge is moored alongside the receiving vessel, a flexible hose connects from the barge to the bunker manifold of the receiving vessel to start the bunkering operation. Sounding or mass flow metering is the common method to measure the bunker quantity. Truck-to-ship bunkering is the most common way to deliver small quantities of bunker and is usually for bunkering distillate fuels. In this case, the receiving vessel is usually harbour craft. The trucks are equipped with hoses on racks and engine-driven pumps on board. For truck-to-ship bunkering, bunker quantity is measured by gauging tank contents using a gauging stick, flow meter or by weighing bridge. For shore/terminal pipeline-to-ship bunkering, the terminal pipeline and pumping system are designed to allow internal fuel transfers for batch blending and delivery to receiving vessel.

Ship-to-ship bunkering

Ship-to-ship bunkering with cargo handling (SIMOPS)

Truck-to-ship bunkering

Figure 3.1 Different bunkering modes for conventional marine fuel carried out in Singapore

Simultaneous operations (SIMOPS) refer to situations where more than one operation or activity runs parallel to the bunkering process on land, water or the vessels involved [4]. Additional hazards may be introduced during SIMOPS, and the resultant combined hazards need to be assessed, discussed and agreed upon during the pre-delivery meeting. Proper control measures must be implemented and monitored during the bunkering operations [5]. SIMOPS is commonly carried out in Singapore to shorten the port call. With the adoption of ammonia as a marine fuel, SIMOPS bunkering shall remain "business as usual". Therefore, a SIMOPS-related study needs to be included, and the impact of ammonia leakage during terminal operations shall be fully addressed.

The bunkering operation consists of three processes: pre-delivery, during delivery, and post-delivery. In the pre-delivery process, the representatives of the bunker supplier, shipowner/operator and bunker surveyor conduct a pre-delivery meeting to prepare the required documentation, such as the bunker requisition form, bunkering pre-delivery safety checklist, mass flow metering system seals checklist and meter reading record form. Upon completion, they will connect the bunker hose, inspect the sampling equipment and take custody transfer samples at the manifold of the supply vessel. The delivery process starts from commencing pumping to recording meter totaliser readings at the end of the transfer. The representatives must ensure that the agreed pumping rate is adhered to by the bunker vessel, and all stoppages and the associated reasons are recorded. They will then prepare to strip and carry out line cleaning of bunker hose. When the bunker quantity is fulfilled, the cargo officer will stop metering. In the post-delivery process, the representatives must complete and sign off the required documents, such as bunker metering tickets and bunker delivery notes (BDN).

LNG Bunkering

Liquefied Natural Gas (LNG) mainly consists of methane (CH_4) with a typical concentration of 70% to 99% by mass [6], along with a few percent of ethane and a trace amount of propane and butane [7]. LNG is stored at atmospheric pressure at a temperature of around -163°C. Due to its flammability, additional safety requirements are needed. LNG bunkering requires specialised infrastructure for supply, storage and bunkering operations.

There are five steps in the LNG bunkering process. 1) Pre-bunkering. The operation includes mooring and pre-cooling preparations, safeguards, and authorisation. 2) Leak test, grounding and purging/inerting are conducted before hose connection. 3) LNG is transferred under supervision and monitoring. 4) After completing the transfer, draining/stripping and purging/inerting are conducted. 5) Disconnect the hose and complete the documentation [7]. The inert gas facility can be on both the bunker supply side and the bunker receiving side. A vapour return line is highly recommended for LNG ship-to-ship bunkering with an atmospheric tank; however, it is generally not possible for LNG truck-to-ship bunkering. The basic bunkering principle, procedure and requirements of LNG bunkering can be extended to that of ammonia.

LPG Bunkering

Liquefied Petroleum Gas (LPG) is defined as a mixture of propane and butane in liquid form [9]. Under ambient conditions, propane is in the gaseous phase and has a boiling point of -42°C. Butane has two boiling points at -0.5°C and -12°C for n-butane and isobutane, respectively. LPG can be stored in fully refrigerated (-50°C at ambient pressure), semi-refrigerated (-10°C at 4 to 8 bar pressure) and fully pressurised (at 17 bar, corresponding to the vapour pressure of propane at 45°C) tanks in steel spheres or cylindrical tank. Compared to marine fuel oil and LNG, the boiling point of LPG is the closest to ammonia. Ammonia storage condition is similar to LPG. As such, LPG carriers are also designed to carry ammonia.

There are several possible combinations of LPG bunkering with fully refrigerated tanks, semi-refrigerated tanks and fully pressurised tanks. When both the supply and receiving tanks are fully pressurised, a vapour return system is required to transfer the gas back into the bunker supply tank to prevent excessive pressure build-up in the receiving tank. This configuration is the most common and cost-effective LPG bunkering option because an LPG carrier can be used as the LPG bunker vessel without major modifications [10]. If the supply tank is fully pressurised and the receiving tank is semi-refrigerated, the pressure must be reduced by lowering the temperature in a liquefaction plant [9]. A vapour return system with a compressor is needed for the bunker vessel to prevent the build-up of vapour pressure in the receiving tank. When both the supply and receiving tank are semi-refrigerated, the vapour return system and modifications of the re-liquefaction plant in receiving vessel are required [9]. Suppose the bunker supply tank is semi-refrigerated and the receiving tank is fully pressurised. In that case, a heater and booster pump are required for the bunker vessel to avoid rollover conditions and cause a sudden rise in the pressure. In this case, a vapour return system is recommended because the vapour pressure in the receiving tank can be too high for the bunker supply tank.

3.2 Ammonia Transfer Operations

3.2.1 Thermodynamic Properties of Ammonia

Anhydrous ammonia is transported and transferred as a saturated liquid. Hence, it is important to understand its thermodynamic properties when developing an ammonia bunkering procedure. Figure 3.2 shows the R717 ammonia pressure enthalpy chart [13]. The saturated liquid curve indicates 100% liquid at boiling point, and the saturated vapour line indicates 100% gas at boiling point. The horizontal distance between the two saturation lines measures the latent heat of evaporation. The evaporation process travels horizontally from the saturated liquid line through the dryness fraction zone to the saturated vapour line as heat is added, which may occur at a constant temperature and pressure. Saturated liquid ammonia at a temperature of -33°C and 0.1 Mpa is indicated as point E in Figure 3.2. When heat is added at constant pressure, a phase change occurs as it moves horizontally to the right from point E to point K. In this case, when the added heat from the surroundings enters the -33°C liquid ammonia tank through the insulation, the resulting evaporated gas at point K is known as “Boil Off Gas” (BOG). Phase change can also occur if the pressure is reduced without adding heat. Saturated liquid ammonia at a temperature of 36°C and 1.39 MPa is indicated as Point A in Figure 3.2. When pressure is reduced, a phase change occurs as it moves vertically down from Point A to Point B into the dryness fraction zone, with about 23% of the mass flow, instantaneously evaporating as “flash gas”.

The transfer of anhydrous liquid ammonia usually takes place at atmospheric pressure. Chemical-resistant centrifugal pumps are used for pumping saturated liquid ammonia to prevent cavitation. When transferring ammonia liquid from one atmospheric pressure tank to another, the height from the surface of the liquid in the origin tank to the centrifugal pump suction port is known as the “net positive suction head” (NPSH). Maintaining the correct NPSH according to the pump performance curve requirements when pumping a saturated liquid is important to ensure no flash gas bubbles are formed to cause cavitation. At the suction end of the pump, the ammonia condition will be very close to the saturation line at slightly elevated pressure due to the NPSH requirement, which is indicated as point F in the sub-cooled liquid zone in Figure 3.2. At the discharge end of the pump, ammonia exists as a sub-cooled liquid, as indicated by Point G in Figure 3.2. Due to the increase in pressure, ammonia will remain as a sub-cooled liquid through the insulated pipe until it enters the receiving tank.

The different storage conditions for liquid ammonia will result in multiple bunkering configurations. Fully refrigerated (FR) tanks are insulated tanks operating at a temperature of -33°C and slightly above atmospheric pressure (Point E). Semi refrigerated (SR) tanks are insulated pressurised tanks operating at a temperature of -10°C to 4°C [14] and a pressure of 3 to 5 bar (Point H to Point J). Non-refrigerated (NR) tanks are uninsulated pressure tanks operating at ambient temperature and pressure of 8 to 14 bar (Point C to Point A), usually with a design pressure of up to 21 bar. In Singapore, ammonia bunkering will take place in tropical weather conditions where temperatures range from 19°C to 37°C, as shown in Figure 3.3 [15].

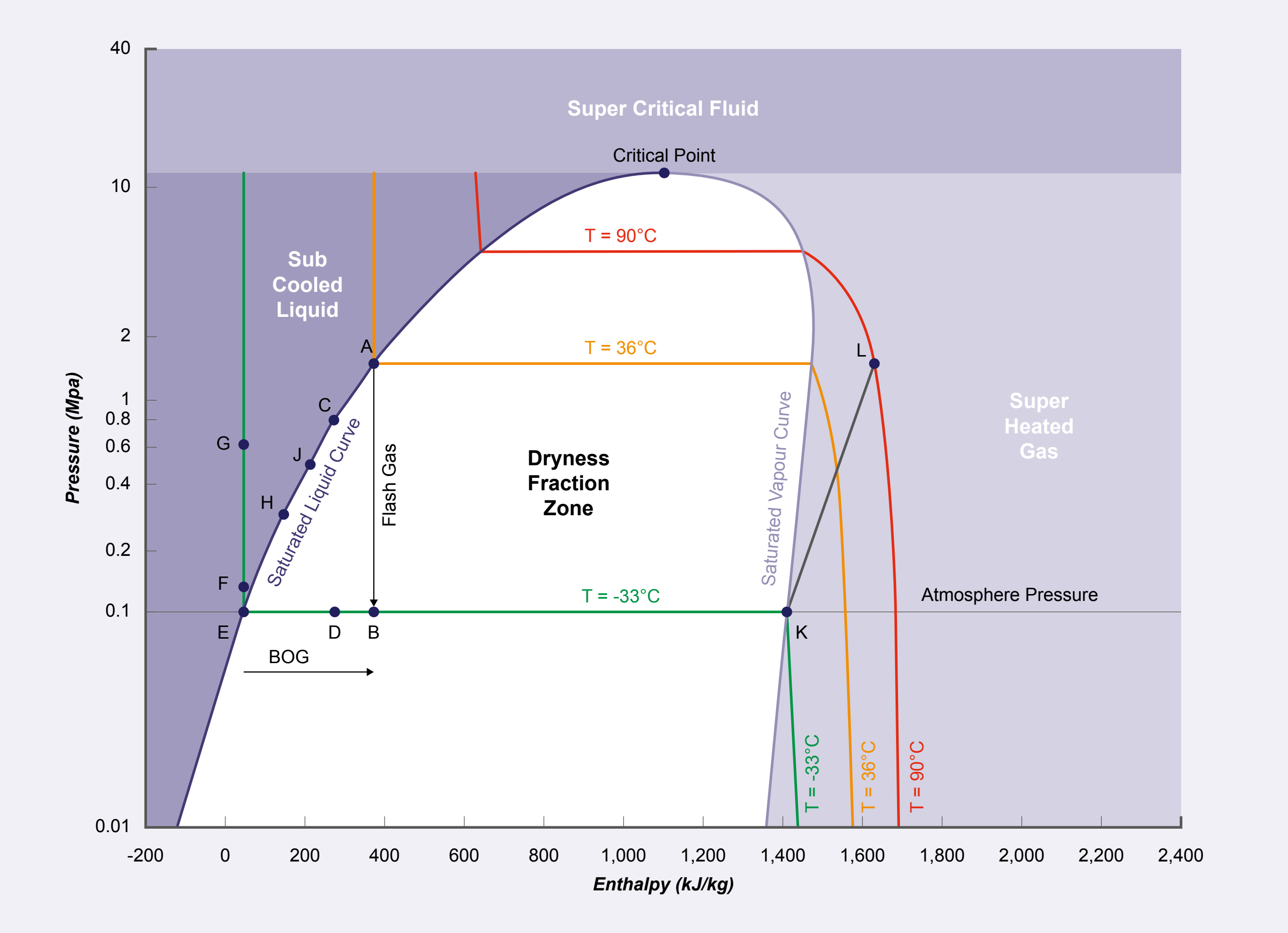


Figure 3.2 Ammonia pressure enthalpy chart

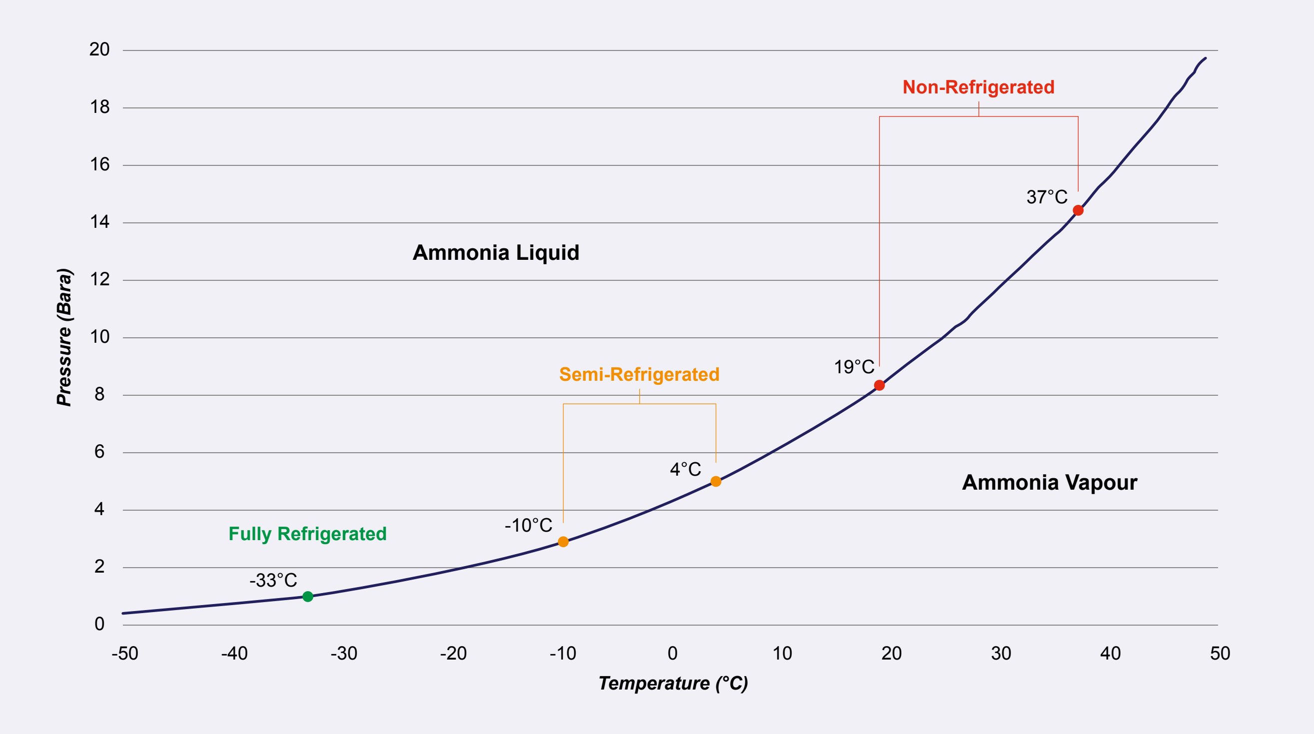


Figure 3.3 Ammonia vapour pressure at gas-liquid equilibrium (boiling point)

3.2.2 Ammonia Refrigeration System

In the fertiliser industry, the ammonia transfer process has been carried out for decades worldwide. Transfers from FR tank to FR tank, including ship-to-shore, shore-to-ship and ship-to-ship operations (shown in Figure 3.4), are usually carried out at a transfer rate of 250 to 1,500 tonnes per hour [16] without generating flash gas. Figure 3.5 shows the transfer from the NR tank to the FR tank, such as from a road tanker to an FR terminal tank. The transfer rate is around 5 to 20 tonnes per hour, which is limited by the refrigeration system's capacity to cope with the flash gas release rate [16]. The temperature should be stable during ammonia transfer. Hence, a heat exchanger is needed to transfer liquid ammonia from a low-temperature tank to a high-temperature one. Similarly, a cooler is needed when transferring ammonia from a high-temperature tank to a low-temperature tank.

Atmospheric pressure terminal storage tanks are fully insulated with at least 30 cm of insulation. Liquid ammonia is stored at a temperature of -33°C, and any heat gain through the insulation from the surroundings will cause a small amount of the liquid to vaporise into gas as boil-of gas (BOG). For FR and SR tanks, if the inbound temperatures do not meet the requirement of the receiving terminal tank, the BOG management system must run until the required temperatures are achieved. BOG system will compress the ammonia vapour to liquefy it and return it to the storage tank to maintain a safe storage pressure. Sometimes, the condensed liquid may be sold off as high-purity distilled liquid of technical grade quality. In the cases of moving vapour and increasing pressure, two-stage refrigeration compressors are used for refrigerated ammonia storage, while a single-stage refrigeration compressor is used for semi-refrigerated storage [14].

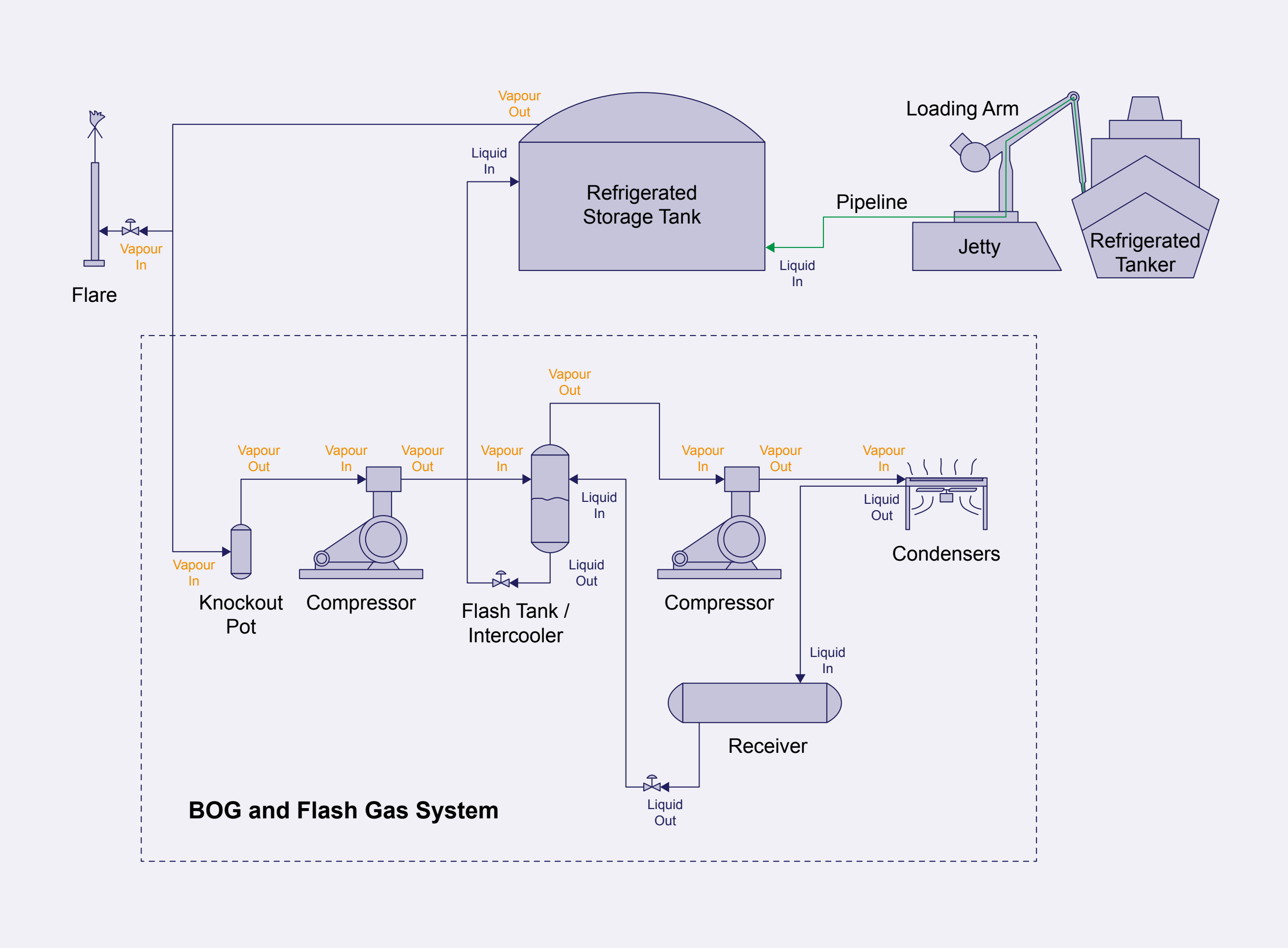


Figure 3.4 Ammonia cold inbound

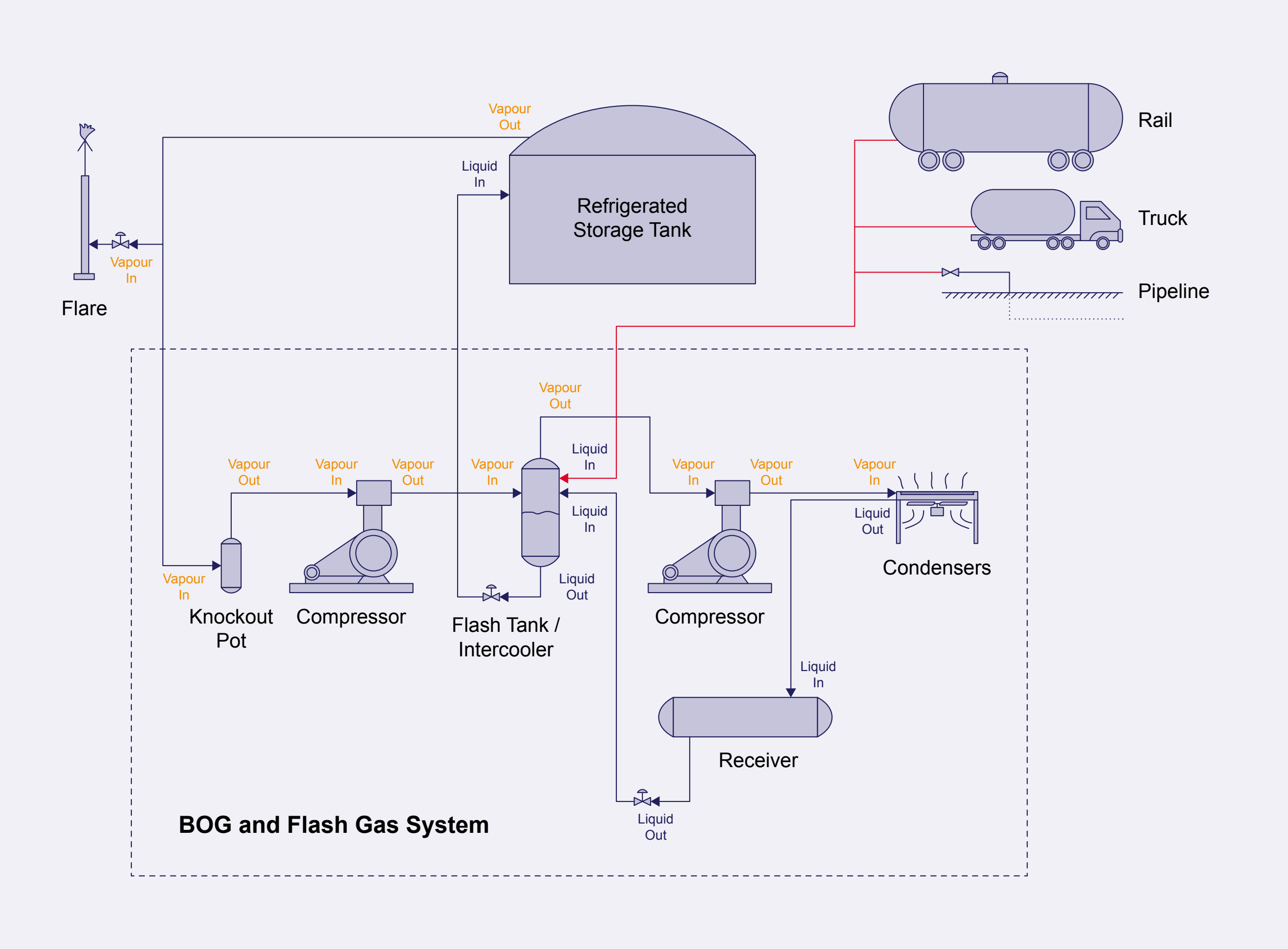


Figure 3.5 Ammonia warm inbound

Figure 3.4 and Figure 3.5 present the process flow of the BOG management system. When saturated vapour passes from the storage tank to the first compressor, the vapour is compressed from less than 7 kpag to 200 to 400 kpag [16]. A knockout pot protects the compressors from damage caused by the incoming liquid. Hot vapour from the first compressor is cooled in the flash tank in preparation for the next compression. The vapour is near its saturation temperature when entering the second compressor. The vapour is further compressed from 200 to 400 kpag to a condensing pressure of 1,030 to 1,550 kpag [16]. Condensers are used to remove the total heat rejected by the system to condense the gas into a liquid, where it drains by gravity into the receiver. Liquid ammonia is then transferred from the receiver to the flash tank for an intermediate flash on its way back to the storage tank. Finally, liquid ammonia at intermediate pressure is transferred from the flash tank to the storage tank. A flare gas system is installed to combust the ammonia vapour released through pressure control within the storage system.

3.2.3 Energy Consumption During Ammonia Transfer

Flash Gas Energy Consumption

The volume of flash gas generated can be calculated and is presented in the following example. The ammonia liquid in the NR tank is at 36°C and 14 bara (Point A in Figure 3.2). When it arrives in the FR tank at 1 bara (point B in Figure 3.2), it has a dryness fraction of 0.23 [13]. As a result, 23% of the total mass flow will immediately vaporise as flash gas (Point K in Figure 3.2), while the remaining 77% of the mass flow remains as a liquid at a temperature of -33°C (Point E in Figure 3.2).

If the transfer rate is 20 tonnes per hour during truck-to-ship bunkering, 4.6 tonnes per hour of flash gas will be generated. The 4.6 tonnes per hour equates to 5,171 m^3 per hour of flash gas at 1 bara based on the specific volume of ammonia vapour being 1.1242 m^3/kg. To re-liquefy this flash gas, a large refrigeration system is required to compress the gas back up to 14 bara (Point K to L in Figure 3.2) and feed it into the condensers to liquefy it (Point A in Figure 3.2). The mass flow of flash gas at Point K is 4,600 kg/h, and the volume flow is 5,171 m^3/h. The gas is compressed from point K to point L in an oil-injected ammonia compressor. The discharge temperature is kept below 100°C by the injected oil cooling during the compression process. The power consumption required to run this size refrigeration system will be in the order of 700 kW.

BOG Energy Consumption

BOG is generated during FR ammonia storage and transport due to heat transmission through the insulated surface areas of the tanks. The required energy to handle the BOG management system is calculated in the following example. It is assumed that there are three tanks in the 20,000 tonnes ammonia carrier with a total surface area of 10,000 m^2 based on the tank dimensions. It is assumed that the tanks are covered with 0.3 m of insulation (e.g., Dow Styrofoam) with a heat transfer coefficient of 0.2 w/m^2K [17]. It should be noted that the insulation will deteriorate with age.

Based on the First Law of Thermodynamics, the change in internal energy between any two equilibrium states (ΔE) is equal to the difference between the heat transfer into the system (Q) and work done by the system (W). In addition, based on the Second Law of Thermodynamics, the total entropy of an isolated system cannot decrease, and heat transfer occurs spontaneously from higher to lower temperature bodies. In this case, the heat flow into the tank via insulation is 126 kW when the temperature difference is 63 K. Additional energy is required for the BOG management system to maintain the temperature of the ammonia storage tank.

A safety factor shall be added to ensure that the refrigeration system can handle the additional load when a higher temperature liquid is loaded into the tank. When a safety factor of 1.5 is used in this calculation, the required refrigeration capacity is 189 kW. The overall Coefficient of Performance (COP) for the refrigeration system at this condition is approximately 1. Therefore, the power consumption to run the BOG component of the refrigeration system will be in the order of 190 kW.

To achieve 100% standby/backup, a refrigeration system for the ammonia tanker will require two 190 kW electric drive oil-injected screw compressors. In general, ammonia bunker vessels should be fitted with refrigeration systems capable of keeping the cargo at -33°C under all normal operating conditions and environment. The ammonia refrigeration systems on board the ships shall be designed with an appropriate safety factor to remove any sensible heat from the cargo before any transfer. The greater the safety factor, the more power is required.

Cargo Temperature Adjustment Before Unloading

During the transfer of ammonia cargo from an FR bunker tank to an FR receiving tank, precautions shall be taken to ensure that the cargo is precisely at the temperature required by the receiving tank. If the cargo temperature is higher, the onboard refrigeration system must be operated at a capacity over and above that of the BOG requirement to bring the cargo temperature down to the required value. The following example illustrates this process.

An FR ammonia carrier sets off on a voyage with 20,000 tonnes of anhydrous ammonia in the tanks at a temperature of -32°C and a pressure of 6.93 kpag (shown in Table 3.1 [13]). The destination is a shore-based terminal which operates at a temperature of -33°C and a pressure of 1.72 kpag [13]. When the vessel reaches its destination, it has to reduce the cargo temperature to -33°C using its onboard refrigeration system. The heat that must be removed from the cargo is 88.8 million kJ. In the case of removing this amount of heat in 24 hours, 1,028 KwR (kilowatt of refrigeration), equivalent to 292 TR (ton of refrigeration), is needed. Onboard refrigeration systems are required for FR ammonia carriers, not only for the BOG re-liquefaction but also to ensure the cargo is at the correct temperature before unloading.

Temperature (°C)	Pressure (kpag)	Enthalpy (kJ/kg)	Density (kg/m^3)
-33.33	0.00	48.76	682.0
-33.00	1.72	50.23	681.6
-32.50	4.28	52.45	680.9
-32.00	6.93	54.67	680.3

Table 3.1 Examples of ammonia temperature, pressure, enthalpy and density

Rollover Consideration

Although the probability is low, an FR bulk liquid ammonia tank may suffer a “rollover” phenomenon. Rollover occurs when a large portion of a warmer liquid rises from the bottom of the tank to the top, with a colder liquid at the top sinking to the bottom all of a sudden (shown in Figure 3.6). Ammonia vapour is released rapidly because of this spontaneous mixing of liquid ammonia with different densities in one storage tank. It occurs when a liquid body is stratified with a density inversion, which means a liquid layer just above its boiling point is covered by a cooler layer [18]. Rollover may result from pushing a huge quantity of slightly warmer liquid into the bottom of the tank. The lower warmer liquid density coupled with the potential formation of gas bubbles will drive the upward movement. The best way to minimise the risk of rollover is to ensure all ammonia fed into the tank is always within the temperature specification.

The other problem with transferring a huge quantity of slightly warmer liquid into an FR tank is that the BOG generated may overwhelm the tank’s re-liquefaction refrigeration system and cause a rise in the top pressure. In this case, relief vents on the top of the tank could be lifted [19]. As shown in Figure 3.6, when there is little vertical heat or mass transfer in the storage tank due to hydrostatic pressure, both liquid layers establish their convection currents. The upper cooler layer releases vapour and loses heat, increasing its density. The lower layer has a higher temperature due to the heat absorbed from the surroundings, so its density decreases. The lower warmer layer will roll over the cooler upper layer resulting in heat release, and a large volume of boil-off gas will be generated rapidly. As a result, the tank is overpressured, leading to the discharge of ammonia vapour through the relief valve, or in the worst case, causing structural damage to the tank.

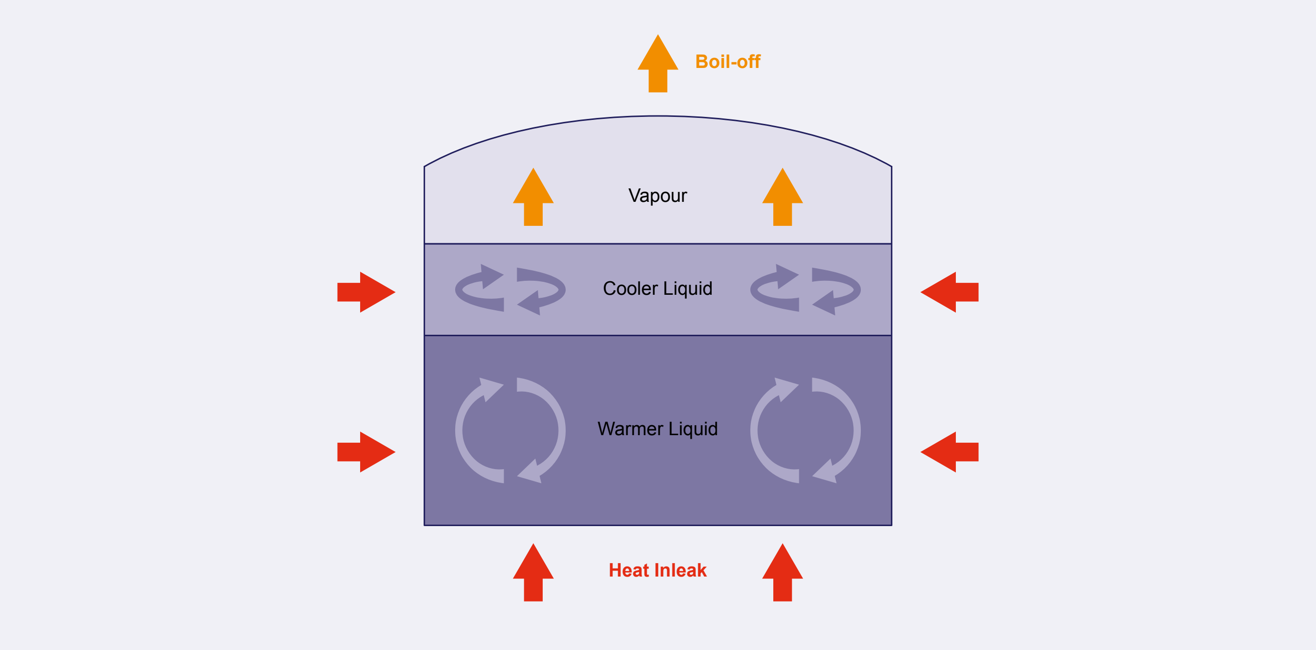


Figure 3.6 Different densities in an ammonia storage tank

3.3 Ammonia Bunkering Concept

3.3.1 Comparison of General Bunkering, Ammonia Loading and Ammonia Bunkering

Existing HFO/MGO, LNG and LPG bunkering operations and ammonia loading and unloading process are used to create the concept design of ammonia bunkering. However, these operations have some differences, as presented in Table 3.2 and Table 3.3. These differences will influence the concept design of ammonia bunkering.

	HFO/MGO Bunkering	LNG Bunkering	Ammonia Bunkering
Volume Needed*	1	1.9	3.1
Toxicity/Lethality Concern	Low	Low	High
Corrosion	No	No	Yes
Flammability Concern	Low	High	Low
Working Principle	Liquid	Saturated liquid	Saturated liquid
Cryogenic/Refrigerated Tank	No	Must	Optional
Filling Limit	No requirements	98% [6]	98%
Standards	SS 648 for Singapore	TR 56 for Singapore	IGF Code
Guideline & Procedure	In place	In place	Not established
Purging	No	Advisable	Advisable
Vapour Return	No	Optional	Preferably no
BOG Rate	No	High	Low

* Note: To deliver the same amount of energy based on LHV.

Table 3.2 Comparison of conventional marine fuel, LNG and ammonia bunkering

Bunker volume required to deliver the same amount of energy is different due to the different LHV of the fuels. LHV of residual fuel, LNG and ammonia is 39.5 MJ/kg, 20.8 MJ/kg and 12.69 MJ/kg, respectively [11]. Based on MPA port statistics 2020, an average of 1,200 tonnes of marine fuel is transacted per bunker call. For the same endurance, the quantity of ammonia shall be 3 times more.

Hazards class of ammonia is different. Ammonia is toxic and corrosive but less flammable than LNG.

Storage conditions. Ammonia and LNG are transported and handled as saturated liquid due to their low boiling point. At the same time, HFO/MGO is usually stored at ambient temperature as a sub-cooled liquid due to their high boiling point.

Filling limit for LNG and ammonia storage tanks is 98% [6] [20], while the *tank heel requirement* is about 5% to 10% for LNG and 4% for ammonia.

Regulations and guidelines. In Singapore, bunker suppliers and ship owners follow the SS 648 and TR 56 for conventional marine fuel and LNG bunkering. Requirements for ammonia bunkering may be covered under the provisions of the IGF Code in future. IGF Code requires all receiving vessel manifolds to be fitted with Quick Connect-Disconnect Couplings (QCDC), and bunker manifolds are to be inerted. After the transfer operation is completed, the manifold shall be purged by hot gas and inerted by N_2. The purging operation for LNG bunkering may be adopted for ammonia bunkering.

Vapour return line is not required for conventional marine fuel bunkering, while it is optional for LNG bunkering and ammonia loading. In this study, we assume there is no vapour return line for ammonia bunkering operation to simplify the bunkering process.

BOG management system is required for LNG bunkering and ammonia bunkering using a refrigerated tank. Daily sea shipping BOG rates of LNG and ammonia are 0.12% and 0.024% based on the same ship capacity [21]. BOG requirements depend on the temperature difference between the environment and the tank and the voyage duration [21]. Table 3.3 summarises the comparison of the ammonia loading and unloading process and ammonia bunkering operation.

	Ammonia as Cargo	**Ammonia as Bunker Fuel**
Guideline & Procedure	Well established	Not established
Specifications	Chemical or fertiliser	Fuel for ICE or fuel cell
Vapour Return Line	Equipped	Optional
BOG Management	Equipped	Optional
Tank Size & Flow Rate	Higher capacity, higher flow rate	Lower, with a broad range of capacity and flow rate
Operational Frequency	Low, limited to tankers	Very high, applies to various types of vessels
Operation Experience	Limited to industrial use	Not established
Operation Modes	Fewer combinations	Up to 33 combinations
Dispersion and Release Study	Limited to industrial sites	Little
Mitigation Measures	Mostly land-based applications	No

Table 3.3 Comparison of ammonia handling and ammonia bunkering

Regulations and guidelines. The guideline and procedure for ammonia handling as cargo is well established under the IGC Code. There is currently no guideline or procedure for ammonia bunkering, but the provisions will likely be covered under the IGF Code. The differences between these codes are discussed previously.

Ammonia quality requirements are different. When ammonia is used as cargo, all parties follow the chemical or industrial grade requirements, and there should be no deviation from the agreed specifications. The O_2/water ratio requirement for bunker fuel differs between bunker supply vessels and bunker receiving vessels. It is advisable to avoid installing a vapour return line in the bunkering system to prevent contamination from bunker vessels.

Receiving vessel's tank capacity is different. The cargo tank capacity of ammonia tankers is around 20,000 to 60,000 m^3, while the fuel tank capacity of bunker receiving vessels such as Panamax container ship is around 5,000 to 7,000 m^3.

Frequency of ammonia loading and unloading operation is much lower than that of ammonia bunkering because the ammonia bunker vessels supply ammonia to many different types of vessels daily. In contrast, ammonia cargo handling simply transfers it from one terminal to another via ammonia tankers.

Operating mode. For sea transport, ammonia handling operation is limited to ammonia carriers and terminal storage tanks. For ammonia bunkering, ammonia can be transferred in the refrigerated or pressurised condition via different modes, namely ship-to-ship, shore/pipeline-ship, truck-to-ship and cassette transfer.

Safety studies. Extensive dispersion studies on accidental ammonia release have been conducted for ammonia handling operations over the years. However, no such study has been done for ammonia bunkering.

3.3.2 Bunkering Modes and Configurations

Based on the current bunkering operation experience, there are four possible ammonia bunkering modes, namely truck-to-ship (TTS), ship-to-ship (STS), shore/terminal pipeline-to-ship (PTS) and cassette bunkering. The ammonia bunkering process would be cold inbound or warm inbound, which means ammonia can be transferred from an FR, SR or NR tank to an FR, SR or NR tank. There are 33 possible ammonia bunkering configurations shown in Table 3.4. The schematics of these bunkering modes are shown in Figure 3.7. However, some configurations will be excluded due to practical limitations.

Bunker Supply									**Cassette Bunkering**						**Receiving Vessel**
Truck			**Bunker Vessel**			**Terminal Pipeline**			**Shore**			**Bunker Vessel**			
FR	**SR**	**NR**	**FR**	**SR**	**NR**	**FR**	**SR**	**NR**	**FR**	**SR**	**NR**	**FR**	**SR**	**NR**	
1	4	7	10	13	16	19	22	25	28			31			**FR**
2	5	8	11	14	17	20	23	26		29			32		**SR**
3	6	9	12	15	18	21	24	27			30			33	**NR**

Table 3.4 Ammonia bunkering operation configurations

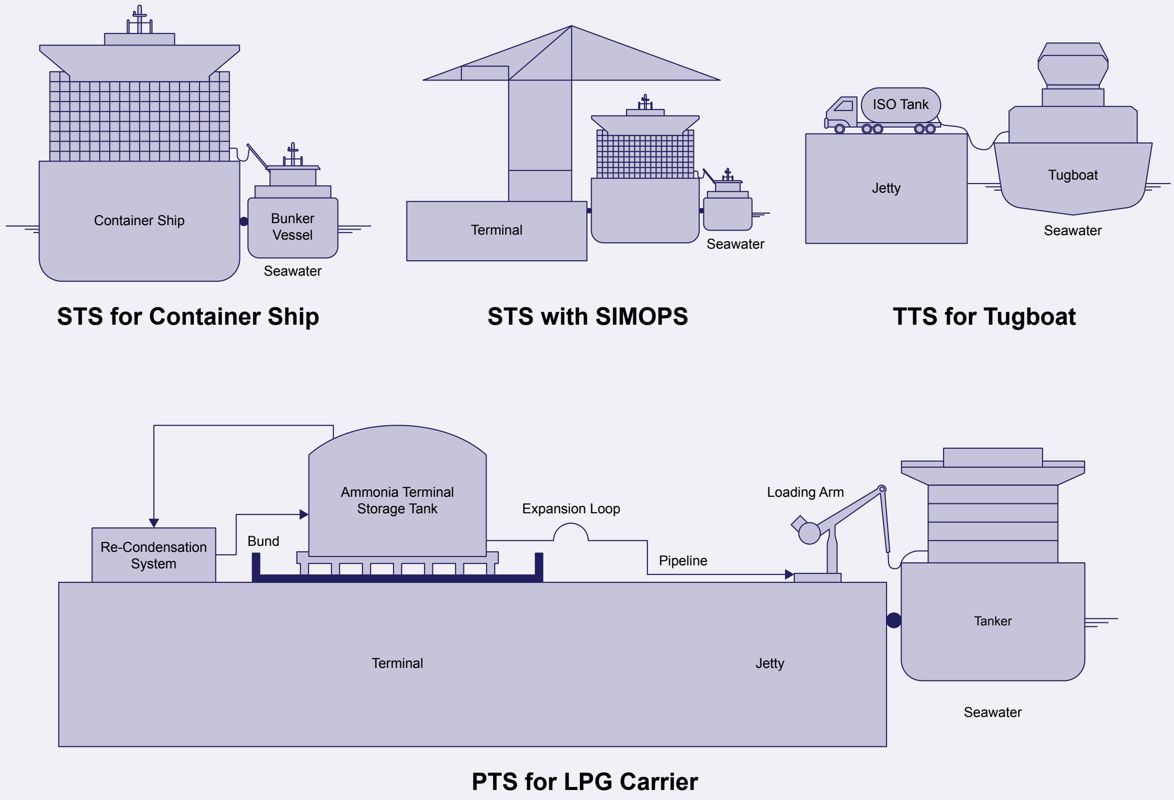


Figure 3.7 Different ammonia bunkering modes

Truck-to-ship (TTS) Bunkering

For truck-to-ship bunkering, the tank transported by truck is usually a pressurised tank with a small quantity of ammonia. Configurations 1, 2, 3, 4, 5 and 6 will not be possible. Additional cooling and electricity are needed when bunkering ammonia from the NR tank to FR/SR tank (configuration 7 or 8). Configuration 9 (NR to NR) is the most suitable for truck-to-ship bunkering. A bunker hose connects the ISO tank and the manifold of the ammonia receiving vessel. Multiple trucks equipped with standard ISO tanks can bunker ammonia simultaneously. Like LNG TTS bunkering, ammonia TTS bunkering is suitable for tugboats and inland vessels.

Ship-to-ship (STS) Bunkering

Ship-to-ship bunkering is the most popular bunkering mode, and SIMOPS is common in Singapore ports. NR tank capacity will not be able to match the ocean-going vessels' bunker volume. Configurations 16, 17 and 18 will be impractical. For the early adoption in Singapore, FR or SR tanks for ammonia bunker vessels will be feasible. In addition, when the bunker tank and receiving tank are under different temperatures or pressures, an additional BOG system, cooler or heater are needed, which makes the bunkering system more complicated. Therefore, configurations 10 (FR to FR) and 14 (SR to SR) are the most suitable for ammonia ship-to-ship bunkering. For ammonia bunker vessels, we take references from an ammonia carrier. Container ships, tankers and bulk carriers are three main types of potential ammonia bunker receiving ocean-going vessels.

Terminal Pipeline-to-ship (PTS) Bunkering

Most terminal tanks are FR tanks for pipeline-to-ship bunkering, so FR to FR bunkering will be possible for ammonia PTS bunkering. Configuration 19 (FR to FR) will be the most practical for terminal pipeline-to-ship bunkering considering the same storage condition of the bunker supply tank and receiving tank. Based on the safety considerations, a re-condensation system and bund are needed for a terminal tank. Liquid ammonia is transferred from the ammonia terminal storage tank to receiving vessel via pipeline, expansion loop and loading arm.

Cassette Bunkering

Ammonia can be supplied as a “cassette” type cell system. Cassette bunkering does not provide the flexibility to change the temperature and pressure of fuel. The container tank for cassette bunkering can be FR/SR/NR tank, which can be delivered by truck or bunker vessel. There are 6 configurations in ammonia cassette bunkering (configurations 28 to 33). It is similar to a road tanker inside a container-shaped steel frame, and a non-refrigerated tank is preferred. The whole container can be lifted or driven onboard and connected to the fuel system for vessel usage.

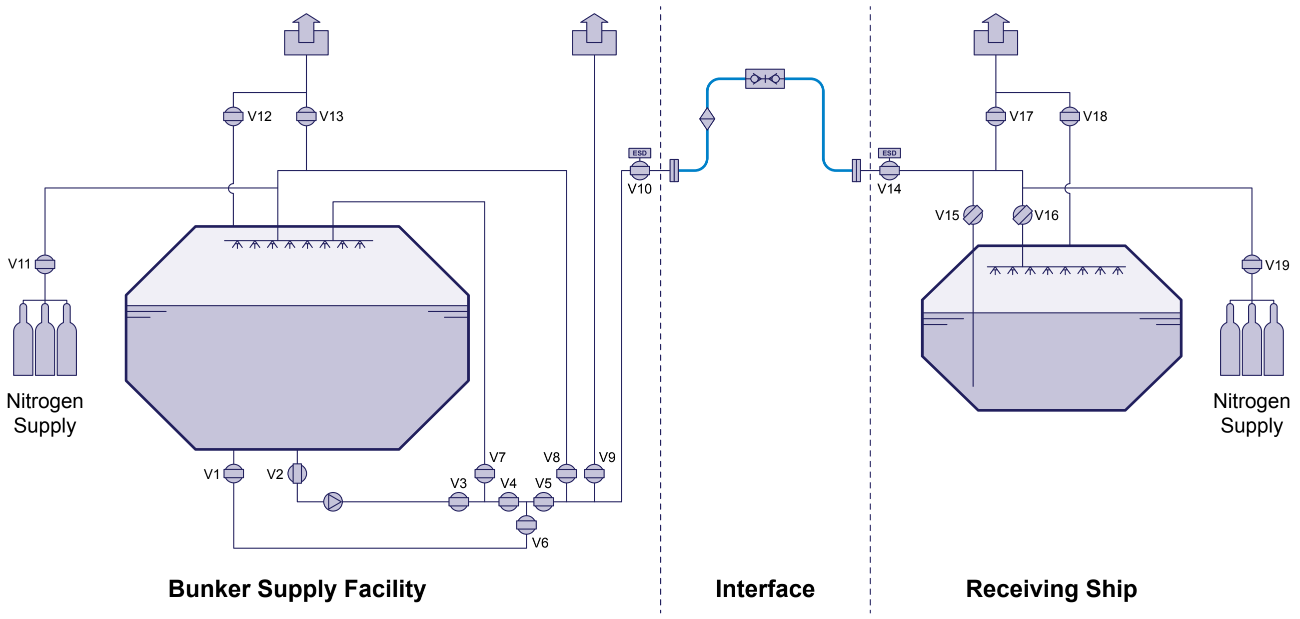
Other Bunkering Modes

Other possible bunkering modes may be applied in the ammonia bunkering operation, such as remote bunkering with automation and offshore bunkering by floating storage unit (FSU). Land space is required for ammonia terminal storage tanks. Singapore is a land-scarce country, so the Floating Hydrocarbon Storage and Bunker Facility (FHSBF) is an alternative way to store ammonia and bunker in Singapore in the future. FSU, as the bunker facility is similar to a bunker vessel, and its design will be similar to a ship-to-ship bunkering process.

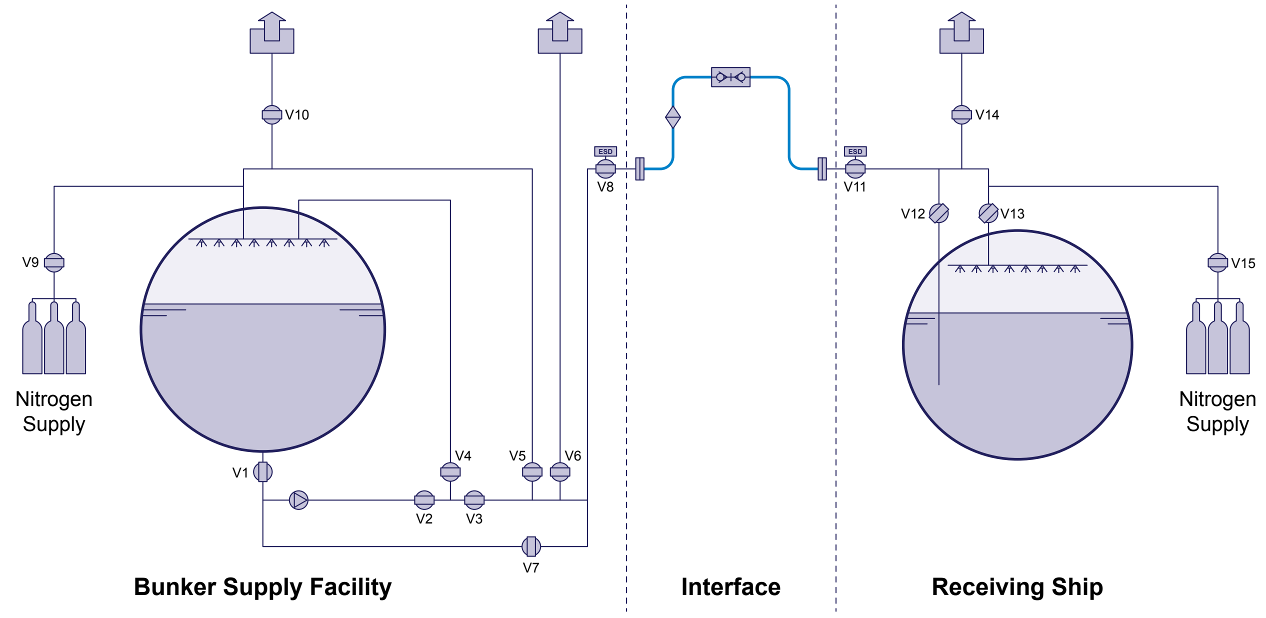
In summary, configurations 9, 10, 14 and 19 are selected for further discussion. The following sections will describe the bunkering concept and operation steps of FR to FR, SR to SR and NR to NR.

3.3.3 Bunkering Concept and Safety Designs

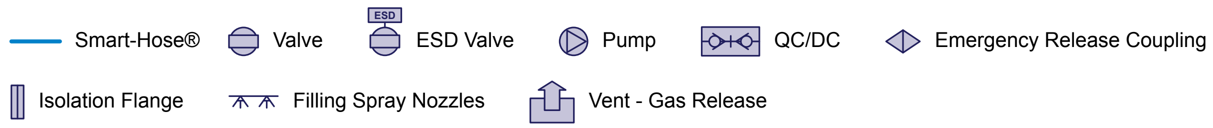
Figure 3.8 shows the ammonia bunkering concept for FR, SR and NR applications, which shares similar operating principles to LNG bunkering [7]. The transfer can be attained by pumping or utilising pressure differential between the bunker supply tank and receiving tank. The entire bunkering system consists of liquid, purging, and venting lines. A vapour return line is not used to make the process simple.



“FR to FR” or “SR to SR” application



“NR to NR” application



Symbol description

Figure 3.8 Ammonia bunkering concept

Liquid Line

Ammonia can be directly transferred by differential pressure. Pumps are used when the pressure differential is insufficient to transfer liquid ammonia. The larger the pressure difference, the more efficient ammonia bunker transfer. For bunker vessels, pumps would be installed in the cargo tank. A booster pump works against the pressurised tank of receiving vessel. In addition, hose pressure loss should be considered for designing a bunkering system. The pressure loss is correlated to flow rate and hose diameter based on the Darcy-Weisbach equation [22]. Hoses should be handled with care, not dragged over a surface or rolled. Lifting bridles and saddles should be provided during ammonia bunkering operations. The hose needs to be supported and secured at several locations so that the hose cannot be bent to a radius less than recommended by the manufacturer. Excessive weight on the ship's manifold should be avoided. If there is an excessive overhang, the manifold should be given additional support.

The hose can be designed with integrated valves at each end of the hose. If there is a catastrophic hose failure, the hose safety system will instantaneously shut off the flow in both directions. No human intervention is needed if the hose is designed as a passive safety device. Using multiple small hoses instead of one large hose can minimise any accidental loss of containment and increase the transfer rate.

Hoses shall be lifted by a marine loading arm using an Emergency Release System (ERS). Fresh air respiratory protection equipment (RPE) is required for all connections/disconnection of arms/hoses from the vessel and sampling. A powered emergency release coupling (PERC) is a hydraulically operated device to quickly disconnect the loading arm in an emergency [23]. If there is an ammonia release, the lower part of the coupling and its attendant valve remain attached to the receiving ship's manifold, while the upper part and its attendant valve remain attached to the loading arm, which is then free to rise clear of the ship. A double pipe (pipe-in-pipe) design with nitrogen in between should be used for transferring ammonia via pipeline. A sudden drop in temperature indicates ammonia leakage from the inner pipe.

Purging Line

Purging operations using non-condensable gas, such as inert gas N_2 for hoses and pipes, should be carried out to eliminate moisture and oxygen to prevent stress corrosion cracking (SCC). If the fuel tank is empty, air purging should be conducted first, followed by N_2 purging. It is recommended to install a nitrogen generator onboard. Due to the purging operation, there could be more N_2 in the ammonia supply tank and receiving tank. The oxygen content can be verified with a calibrated portable oxygen meter until it drops below <1%. It would be preferable if the purging operation is provided by a bunker supply vessel.

Venting Line

For ammonia loading operation, the vapour return line transfers ammonia vapour from the receiving tank back to the bunker supply tank. N_2 and saturated NH_3 vapour occupy the headspace of the tank. The vapour return line is to prevent a pressure build-up in the receiving tank due to liquid transfer and associated boil-off. To simplify the bunkering system concept design, the project team does not suggest a vapour return line for ammonia bunkering operation.

There are several options to handle ammonia vapour. One option is to vent directly into the atmosphere. A pressure release valve is required to release NH_3 and N_2 under emergency. The

1-way pressure relief valve can prevent outside air from entering the tank. Venting from fuel tanks and piping systems can be done with as low risk as possible [24]. The safety distance from vent mast outlets and the ventilation opening design must follow regulations like IGC Code and IBC Code. The minimum safety distance should consider the dispersion of the worst-case scenario of fully venting from the relief valve.

Breakaway Coupling and Emergency Shut Down (ESD) System

Breakaway couplings can be installed at the connection to the ship's manifold to minimise spillage during excessive movement. Dry breakaway coupling can eliminate the need for inerting and purging before and after disconnection. The bunkering system should use a safety and emergency shut-off valve to control ammonia release. Activation of the Emergency Shutdown System automatically closes bunker manifold valves and gas supply to the engine room. Typical conditions that can trigger the activation of ESD include fire detection, gas detection, high bunker tank level or pressure detection. Hydraulic couplers with auto-shutoff vs a bolted flange are typically used.

Electrical Grounding

For terminal-to-ship bunkering, the loading arm is made of metal, and metal is a good electrical conductor with a very low resistance to electricity flow. Due to possible differences in electrical potential between the ship and the terminal, there is a risk of electric arcing at the manifold during the connection and disconnection of the shore hose and loading arm [23]. Similarly, flexible hose strings containing metallic connections may induce arcs between the flanges of each hose. Each manifold is earthed to prevent the electrical arc, and the hose strings and metal arms need to be fitted with an insulating flange near the coupling, which is installed at the lower end of the loading arm or supply side of the hose [25].

Another solution is to use a single length of non-conducting hose without internal bonding. The insulating flange or a single length of the non-conducting hose must not be short-circuited by contacting external metal. Suppose the bonding cable is required based on some national and local regulations. In that case, it should first be checked whether it is mechanically and electrically sound, and the connection point should be clear of the manifold area [23]. Meanwhile, the cable should be attached before the hose connection and removed after the disconnection.

Personal Protective Equipment

Due to ammonia's toxic nature, personnel must wear proper personal protective equipment (PPE) during ammonia bunkering operations to minimise injuries in case accidents happen. There are three levels of PPE ensembles available for use with ammonia.

Level A - Fully covered and sealed, pressurised chemical suit capable of temperatures down to -40°C, and complete with large flexible front window, integral booties and gloves. Under gloves and booties shall be donned along with Self-Contained Breathing Apparatus (SCBA), followed by the level A suit donned over the outside. Usually, it takes 15 to 20 minutes with help to don the level A ensemble. A dense gas ammonia cloud can be as cold as -65°C which could cause the standard level A suit to crack if the wearer was caught in a very dense cloud or was sprayed with liquid. Low-temperature level A suits are also available, suitable for temperatures down to -70°C. However, they are very expensive.

Level B - Chemical splash suit with a hood that seals around the SCBA face mask, with boots and gloves taped or an O-ring sealed to the suit. The SCBA is donned over the top of the level B suit. The level B ensemble can be donned without help in 5 to 10 minutes.

Level C - Fully equipped Hi-Vis vest placed over long trousers and long-sleeved workwear with industrial footwear. The level C ensemble is also known as the ASTI vest and includes the following items carried in the vest:

- Lapel-mounted personal ammonia detector
- Full face compact Air Purifying Respirator complete with K2 filter
- Nomex hood
- LED right angle vest mounted flashlight
- Safety goggles with anti-fog spray for Air Purification Respirator (APR)
- Elbow-length chemical safety gloves
- Chemical break open eyewash

The fully equipped ASTI vest is comfortable and is designed to be worn full-time whilst the individual is working in or around ammonia equipment or facilities. Where level A or B ensembles are available, they are usually located in areas where trained personnel can easily retrieve them in a minimum amount of time and not in areas which could be considered at high risk in the event of an ammonia leak or spill. All personnel should be issued with their own personal, fully equipped level C ensemble, which they will each be responsible for, and to ensure they wear it at all times when on duty. All personnel must be trained in all levels of the available ensembles.

Figure 3.9 Examples of PPE

Figure 3.9 shows a combination of level B and level C PPE. An Air Purification Respirator (APR) with an approved K2 filter forms part of the level C ensemble and must be fit-tested to ensure a proper seal as it is a negative pressure device. Facial hair will prevent a proper seal from being achieved. Therefore, the wearer must be clean-shaven or have no facial hair. A one-piece chemical splash suit with integral booties and having the gloves O-ring sealed to the suit sleeves forms part of the level B ensemble. The level B ensemble usually includes an SCBA positive pressure device rather than an APR. It is common practice for the level B ensemble to be required for personnel carrying out ammonia transferring operations whilst connecting and disconnecting loading arms. The ship crew shall be properly trained to handle ammonia and to deal with emergencies in the event of accidental loss of containment.

3.3.4 Bunkering Operation Steps

Figure 3.10 outlines the general ammonia bunkering process, from planning, pre-delivery, during delivery to post-delivery process. In the planning process, a risk assessment should be completed. The ammonia system and transfer equipment shall be checked. The operators shall determine the safety and monitoring zones for the intended operation and prepare an ammonia bunkering plan, followed by notifying the relevant authority/terminal to commence ammonia bunkering operations. The last steps of the planning process include completing the compatibility assessment and preparing equipment and mooring arrangement for intended operations.

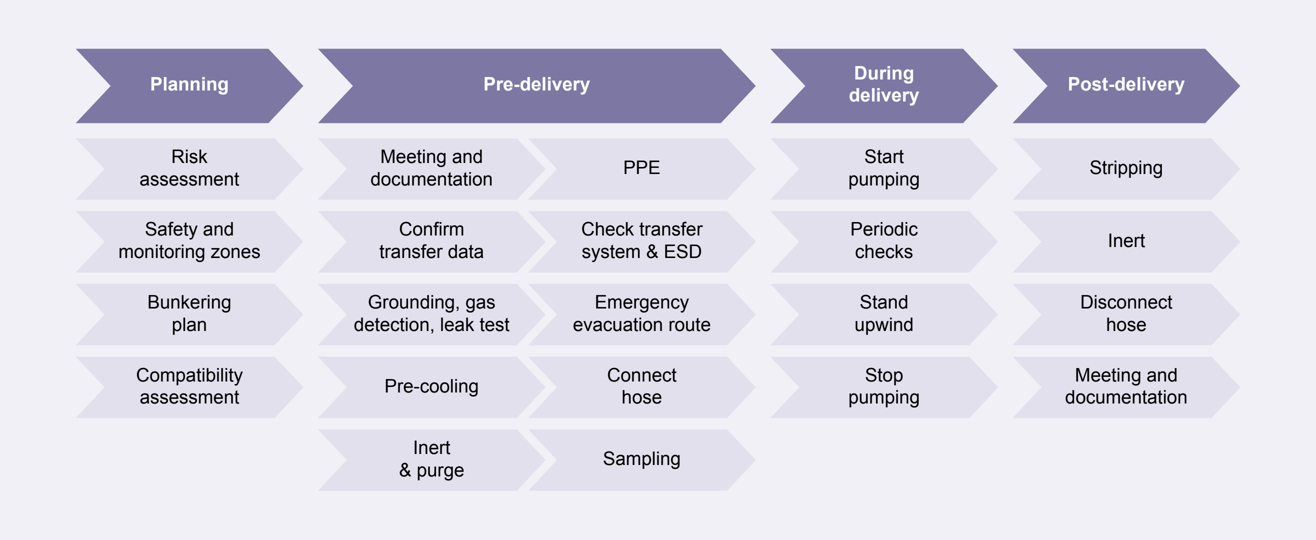


Figure 3.10 Ammonia bunkering operation steps

In the pre-delivery process, bunker suppliers and ship operators shall conduct a pre-delivery meeting to confirm documentation and all necessary administrative procedures. The supplier and operator shall also ensure that PPE requirements are followed, and that truck and vessel are safely secured and moored. Ammonia transfer data, such as pressure, temperature, flow rate and quantity, shall be confirmed. The supplier and operator must check and ensure the transfer system, the gas detectors and other safety devices are in good operating condition. Mitigation control measures shall be in place and ready for deployment in an emergency. Wind direction shall be checked to identify the emergency evacuation route. Finally, the supplier can connect the hose and carry out inerting for oxygen removal and nitrogen purge, followed by a leak test, ESD test and sampling process.

During the bunker delivery, the supplier shall start the pump at an idle speed and check the flow (via flow indicator / tank percentage gauge or rotary gauge). The supplier and operator must also check the surroundings and transfer parameters, such as vapour management. Once done, the pump can be increased to operating speed, and operators shall stand upwind within 8 metres of an emergency shut-off to monitor the product transfer. Finally, the pump can be stopped when the transfer is complete. In the post-delivery step, the supplier shall conduct stripping and inerting operations. All valves should be closed before the supplier disconnects the bunker hose. A post-transfer meeting with the ship operator shall be held for the issuance of BDN and completion of all other documentation.

FR to FR or SR to SR Bunkering Application

Figure 3.11 shows a single-line FR/SR tank to FR/SR tank bunkering operation with 8 main steps: initial precooling, bunker hose connection, inerting, purging, pumping, stripping, final inerting and disconnecting. The operational principle of FR and SR transfer is the same, and the SR storage tank shall be designed to withstand higher pressure. The bunkering supply facility can be a truck, bunker vessel/barge, or terminal tank. The bunker supply facility with an SR tank needs some flexibility to change the temperature and pressure of liquid ammonia. Initially, all valves are closed. It should be noted that there may be some differences between the conceptual design in this study and the actual ammonia bunkering implemented in the future. It is possible that some of the procedures generically represented in this section may not be followed if under different specific project arrangements and risk assessments.

- Step 1: Precooling. The first step occurs during bunker vessel mooring up against the receiving ship. For FR and SR tanks, bunkering lines are pre-cooled in advance. As shown in the blue line, valves V1, V5, V6 and V8 are opened. Cold ammonia exits the supply tank from the bottom and slowly pushes the warm ammonia in the pipe into the top of the supply tank. The transfer pump for bunkering also requires precooling. Additionally, valves V4 and V7 are opened.

- Step 2: Bunker hose connection. Valves in step 1 will be closed. Smart-Hose® will be handled by a crane or loading arm and connected to the manifold of receiving vessel. The manifold will be earthed, and an insulating flange near the coupling is required to prevent electrostatic.

- Step 3: Inerting. Inert gas is required to remove moisture and oxygen in the piping and hose to prevent SCC. As shown in the green line, all valves in the previous steps are closed, and valves V9, V10, V14 and V19 are opened. The bunker supply facility and receiving ship are both equipped with nitrogen supply, so the inerting process can be conducted by either the bunker supply facility or receiving ship.

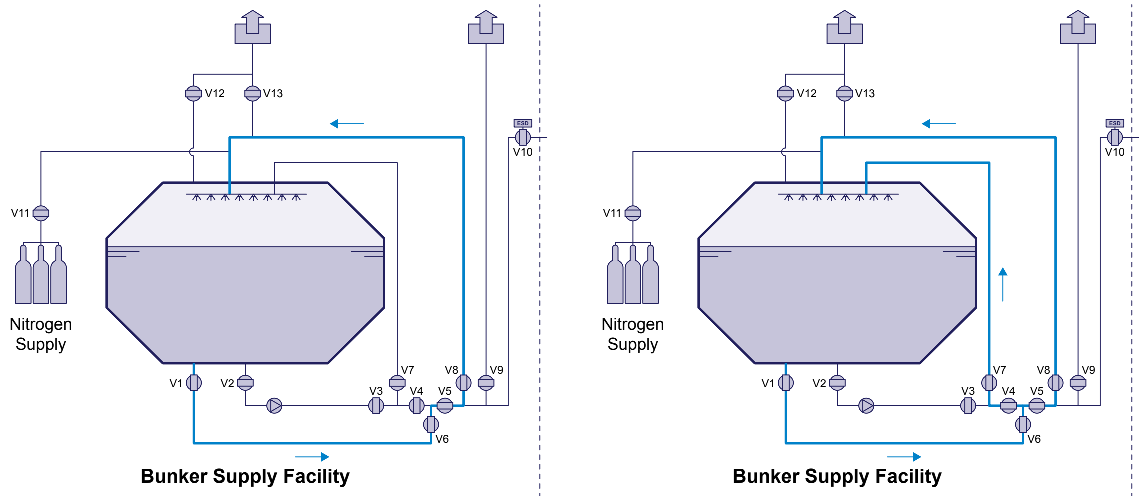
- Step 4: Purging. The remaining system is purged with ammonia vapour to remove the remaining nitrogen. As shown in the orange line, valve V19 will be closed, and valves V9, V10, V14 and V16 will be opened. Ammonia vapour can move out from the receiving tank. After the pipe and hose are cleaned, valve V10 should be closed quickly to prevent too much ammonia vapour escape through the vent.

- Step 5: Transferring. Top filling and bottom filling are two ways of the pumping process. The top filling can help reduce the pressure in the receiving tank, and the bottom filling can maintain a satisfying pressure. As shown in the blue line, valves V2, V3, V4, V5, V10, V14, and V16 are opened for top filling. Valves V2, V3, V4, V5, V10, V14, and V15 are opened for bottom filling. The sequence between the top filling and bottom filling helps to control the pressure in the receiving tank. The maximum level for filling an ammonia tank is 85% of the total volume according to the fertiliser industry requirements.

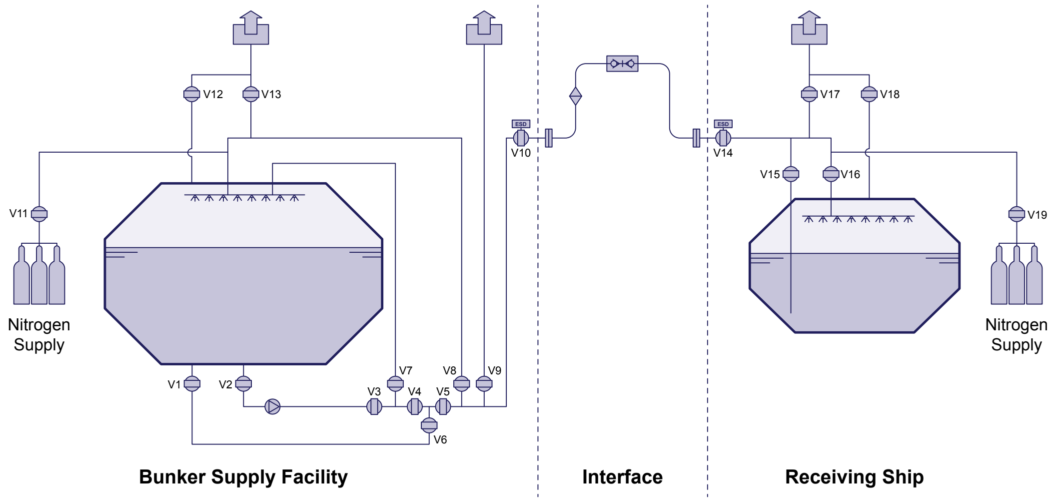
- Step 6: Stripping. After stopping the pump, a stripping process is required to drain the liquid remaining in the bunker hose. As shown in the diagram, the ammonia liquid in the blue line will be drained to the supply tank, and the ammonia liquid in the orange line will be transferred to the top of the receiving tank. There shall be a pressure build-up area by rising temperature in the interface to push the remaining ammonia liquid to both tanks. For the blue line, valves V4, V5, V7, and V10 are opened, while valves V14 and V16 are opened for the orange line.

- Step 7: Inerting. This step is similar to step 3.

- Step 8: Disconnecting.

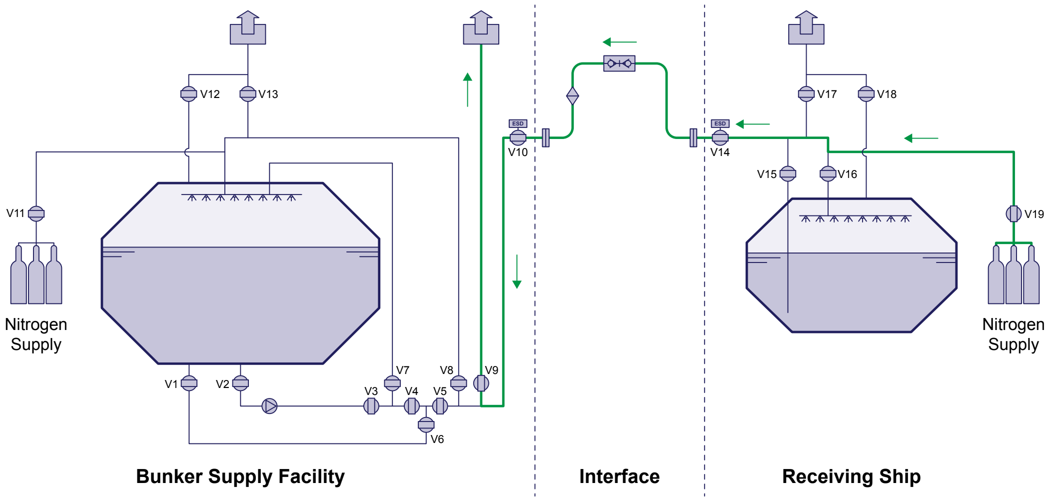


Step 1: Precooling

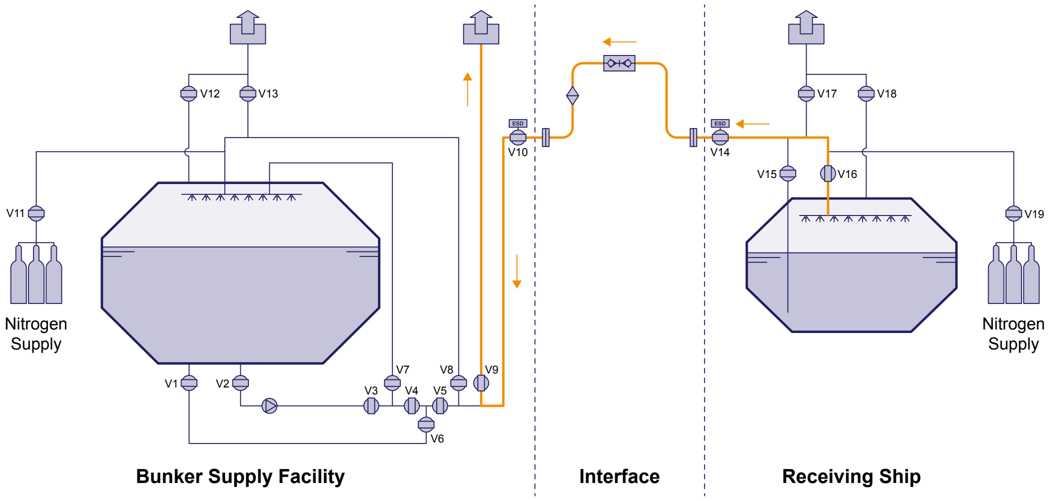


Step 2: Bunker hose connection

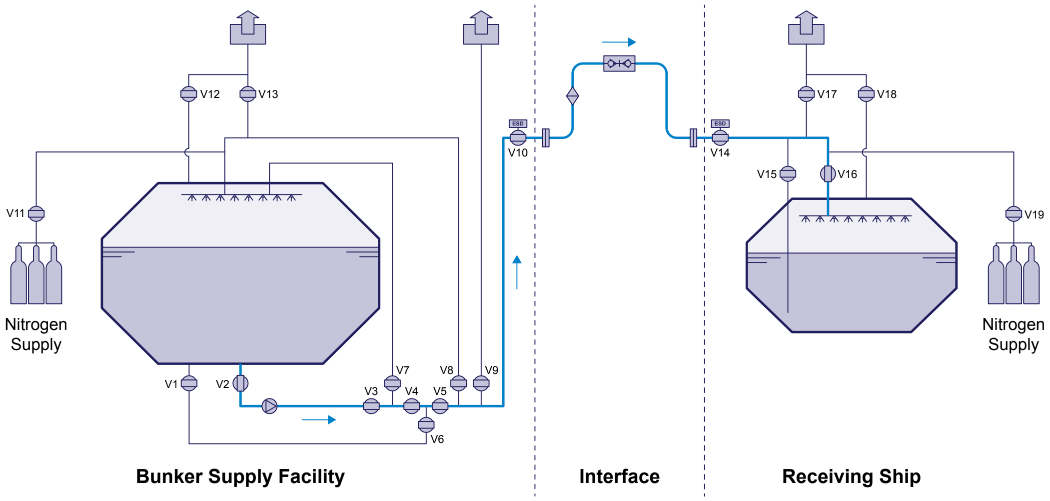
Figure 3.11 FR to FR or SR to SR ammonia bunkering operation steps



Step 3: Inerting

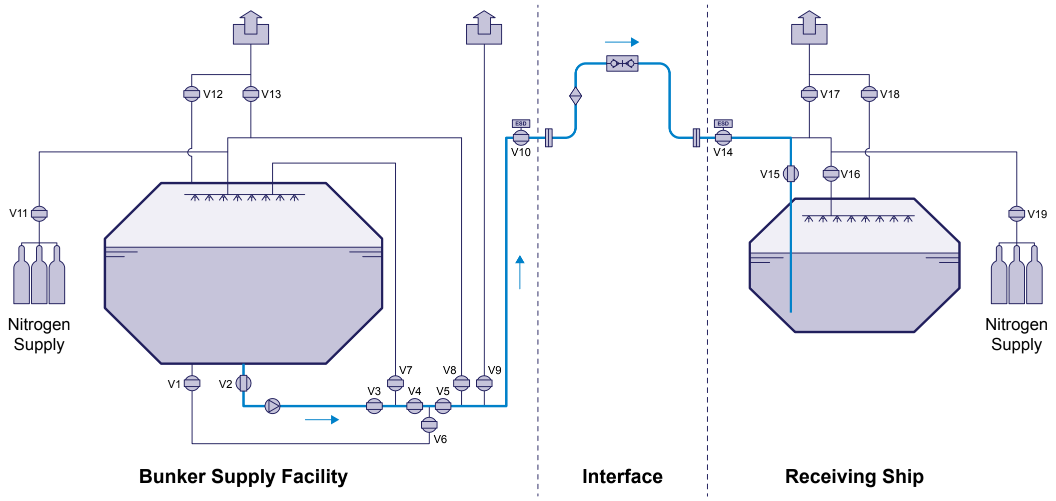


Step 4: Purging

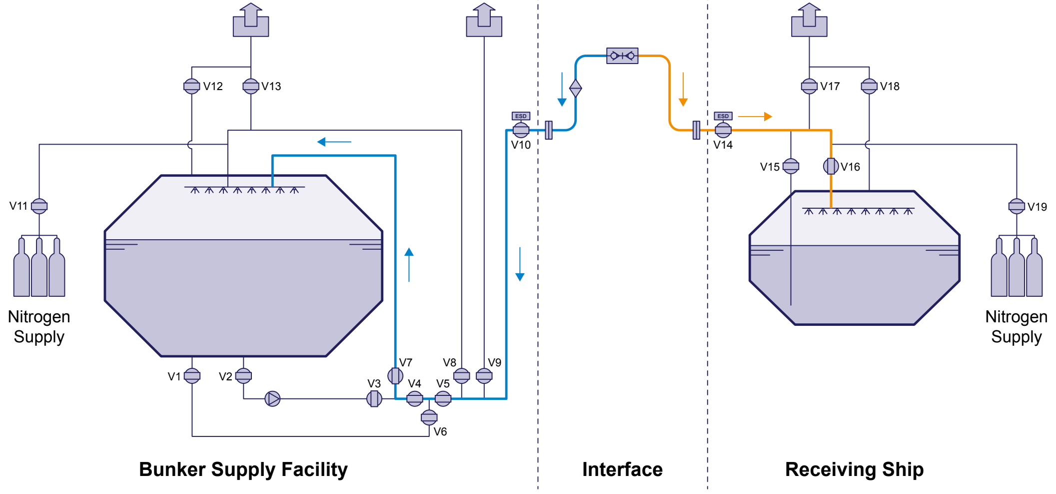


Step 5: Transferring - Top filling

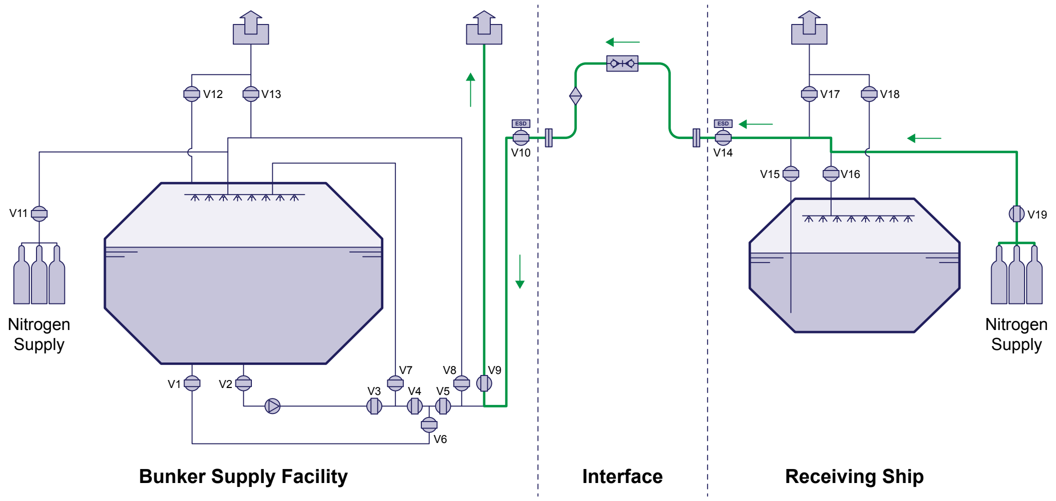
Figure 3.11 FR to FR or SR to SR ammonia bunkering operation steps (Cont'd)



Step 5: Transferring - Bottom filling



Step 6: Stripping



Step 7: Inerting

Figure 3.11 FR to FR or SR to SR ammonia bunkering operation steps (Cont'd)

NR to NR Bunkering Application

Figure 3.12 shows NR tank to NR tank bunkering operation with 7 main steps: bunker hose connection, inerting, purging, pumping, stripping, final inerting and disconnecting. The bunkering supply facility can be a truck, bunker vessel/barge, or terminal tank, while a truck with an ISO tank will be the common NR tank supply facility. These 7 main steps are similar to the FR tank bunkering process. To be noted, ammonia temperature in NR tank is ambient temperature. When bunkering ammonia from NR tank to NR tank, an initial precooling process is not required.

- Step 1: Bunker hose connection. In this step, all valves are closed initially. Smart-Hose® is recommended. The manifold will be earthed, and an insulating flange near the coupling is required to prevent electrostatic.

- Step 2: Inerting. As shown in the green line, valves V6, V8, V11 and V15 are opened. The bunker supply facility and receiving ship are both equipped with nitrogen supply, so the inerting process can be conducted by either the bunker supply facility or receiving ship.

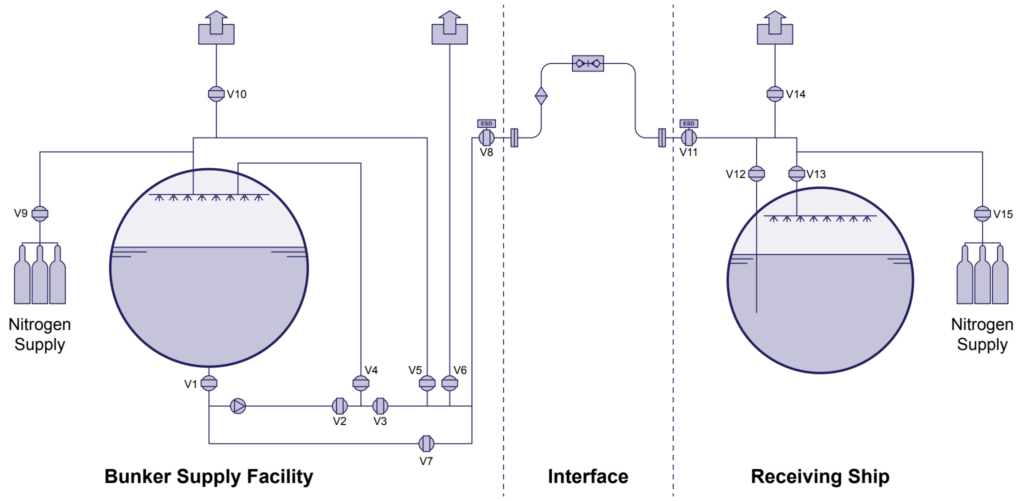
- Step 3: Purging. As shown in the orange line, valve V15 will be closed, and valves V6, V8, V11 and V13 will be opened. Ammonia vapour can move out from the receiving tank. After the pipe and hose are cleaned, valve V13 should be closed quickly to prevent too much ammonia vapour escape through the vent.

- Step 4: Transferring. As shown in the blue line, valves V1, V2, V3, V8, V11, and V12 are opened for top filling. Valves V1, V2, V3, V8, V11, and V13 are opened for bottom filling. The sequence between the top filling and bottom filling helps to control the pressure in the receiving tank.

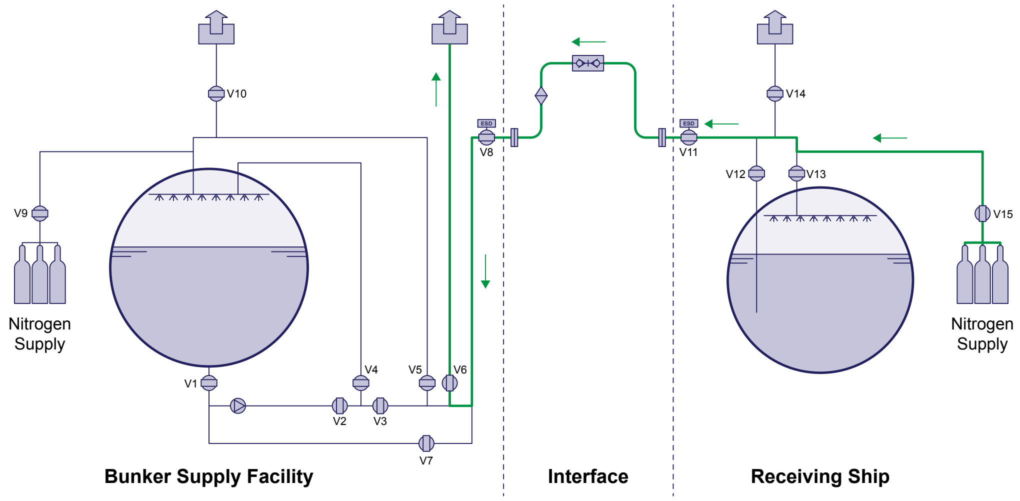
- Step 5: Stripping. As shown in the diagram, the ammonia liquid in the blue line will be drained to the supply tank, and the ammonia liquid in the orange line will be transferred to the top of the receiving tank. There shall be a pressure build-up area by rising temperature in the interface to push the remaining ammonia liquid to both tanks. For the orange line, valves V11 and V13 are opened. While for the blue line, the pressure difference may not be sufficient, so a pump is required for this step. At the same time, valves V2, V4, V7, and V8 are opened.

- Step 6: Inerting. This step is similar to step 2.

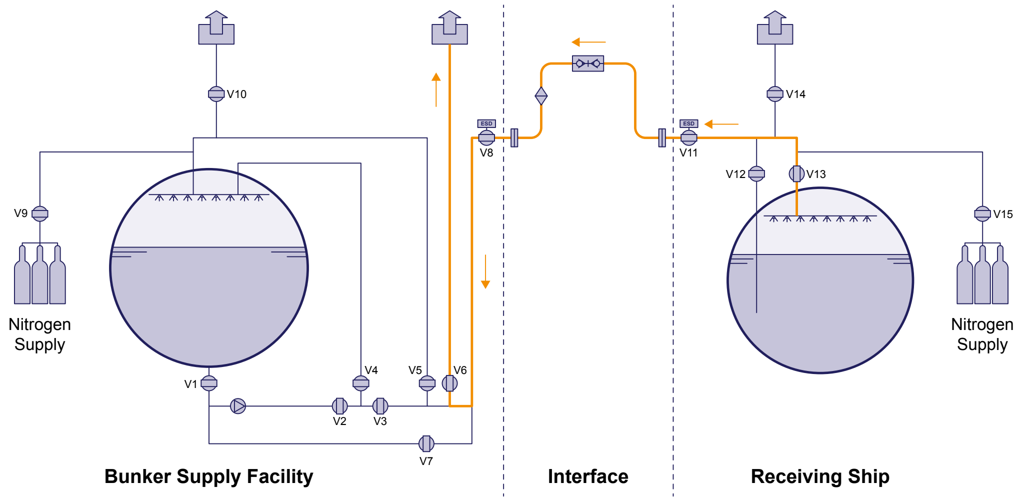
- Step 7: Disconnecting.



Step 1: Bunker hose connection

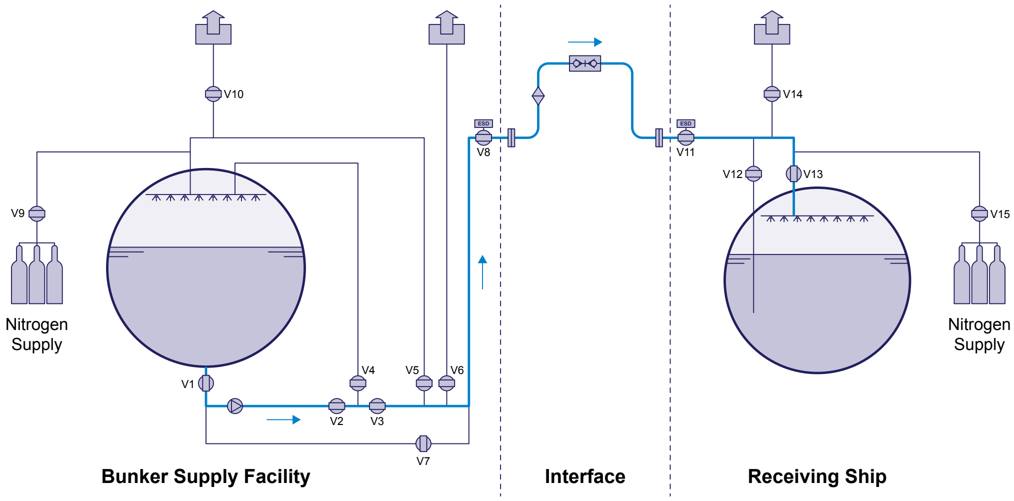


Step 2: Inerting

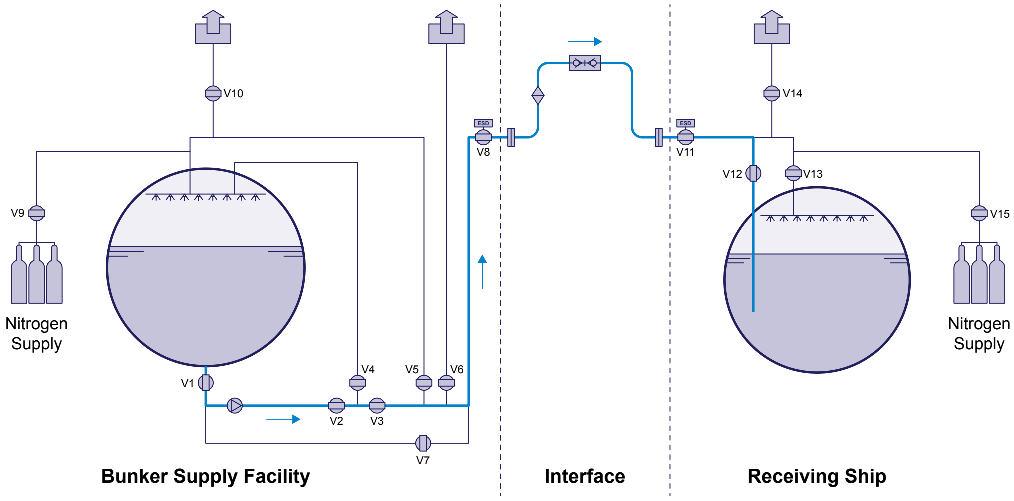


Step 3: Purging

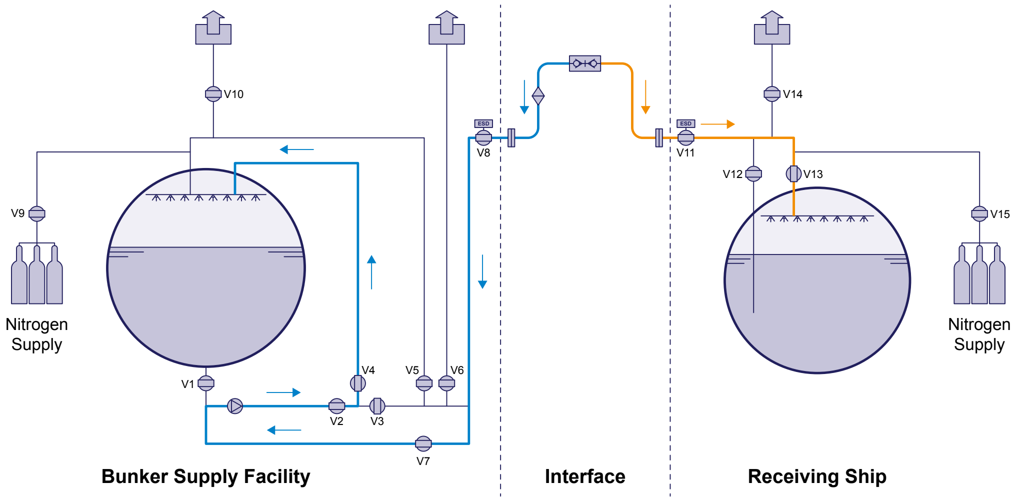
Figure 3.12 NR to NR ammonia bunkering operation steps



Step 4: Pumping - Top filling



Step 4: Pumping - Bottom filling



Step 5: Stripping

Figure 3.12 NR to NR ammonia bunkering operation steps (Cont'd)

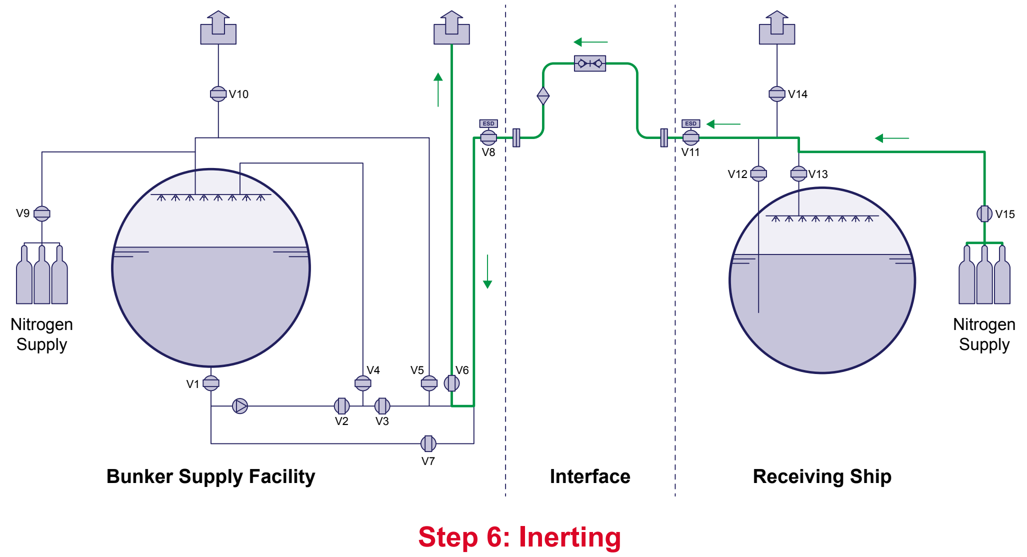


Figure 3.12 NR to NR ammonia bunkering operation steps (Cont'd)

3.3.5 Requirements for Ammonia Quality and Quantity

Ammonia dual-fuel engines will be the trend for ammonia-fuelled vessels because it is difficult for conventional engines to use pure ammonia due to its poor ignition property. For example, the compression ignition (CI) engine will likely use diesel or DME mixing with ammonia for large ships by modifying the two-stroke ammonia-diesel dual-fuel engine. For spark ignition (SI) engines, ammonia mixed with hydrogen or gasoline can be a solution for small ships since it is difficult to increase the capacity [26].

Additives may be added to ammonia bunker fuel. Anti-corrosion agents such as water may be added to ammonia to prevent SCC. Combustion-supporting agents such as H_2 may also be present. Therefore, sampling operation is critical to meet the ammonia bunker quality. A sampling cylinder (or bomb) would be used to collect the bunker. With LNG bunkering operation as the reference, this study recommends taking at least 3 samples from the bunker supply vessel [4]. For the ammonia storage terminal, sampling operation is carried out using the Dopak sampling system [17].

In terms of ammonia bunker quantity, there are different quantity measurements. A weighbridge can directly indicate the weight difference before and after the bunkering operation for truck-to-ship bunkering. Level gauge could be installed in both bunker supply tank and receiving tank for quantity measurement. The mass flow meter (MFM) is also used for ammonia metering. Although no "cappuccino effect" is expected for the liquid ammonia transfer, the MFM system should be used to avoid any measurement errors due to the ship's motion effect.

Chapter
3

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Chapter
4

Safety Analysis of Ammonia Bunkering

4.1 Identification of Hazards

4.1.1 Modes of Failure of Ammonia Containment

Material Compatibility and Corrosion

External corrosion and weld-related issues are the main causes of the loss of integrity in carbon steel vessels and pipework systems handling ammonia. The less common causes are Stress Corrosion Cracking (SCC) [1] and embrittlement coupled with hydraulic shock (liquid hammering effect). Cast iron, cast steel, carbon steel, aluminium and stainless steel are compatible with ammonia. Past internal inspections of ammonia containment systems made from these materials revealed minimal corrosion. The likely areas where corrosion may occur on carbon steel systems are on the external surfaces, particularly those under insulation, where they are at temperatures below the dew point which means they are continuously, or worse still, intermittently wet. Copper, zinc or their alloys cannot be used with ammonia as they are the most susceptible to ammonia-induced stress corrosion cracking.

Stress corrosion cracking (SCC) is a phenomenon of cracks formed in carbon steel in contact with high-purity ammonia. Residual welding stress levels combined with applied stress may be sufficient to initiate SCC [2]. In SCC, the surface usually remains un-attacked, or only small fine cracks are observed. These fine cracks, on rare occasions, can penetrate deep into the material, worst-case penetrating through the entire thickness of the steel and threatening the integrity of the ammonia-containing equipment, resulting in catastrophic failure or rupture [3]. SCC can occur in atmospheric pressure (-33°C) storage tanks and unrefrigerated pressurised vessels. The likelihood of SCC in carbon steel can be reduced by ensuring a minimum water content of 0.2% in ammonia. Modern material inspection techniques, particularly for uninsulated and unrefrigerated vessels, can detect early signs of cracking to eliminate potential failures. Using stainless steel will also dramatically reduce the risk of SCC to virtually zero.

Embrittlement failure may occur when carbon steel with a coarse grain structure is exposed to temperature below -28°C, particularly when subjected to shock or impact. The grain structure of carbon steel is a function of the heat treatment during the manufacturing process. Carbon steel with a coarse grain structure is more susceptible to embrittlement failure. Hence, carbon steel for low-temperature applications, as in the case of ammonia containment systems, must be specially treated to ensure a fine grain structure resistant to embrittlement failure. Coupons from each batch are to be impact-tested at low temperature in a “Charpy” impact test machine to ensure the material has a minimum of 19 Joules of impact test energy resistance. ASTM A333 states the requirement for certifying low-temperature carbon steel material for piping. Using certified carbon steel or stainless steel will dramatically reduce the risk of loss of containment due to embrittlement failure.

Material failures, as described above, are not the most common failure modes as the chemical industry is well-equipped with knowledge, standards and guidelines for material compatibility for ammonia systems. Equipment failure due to maintenance or mechanical integrity issues and human error related to lack of training and/or deviation from operating procedures pose a higher risk.

Physical Damage from External Impacts

Physical damage to system components from equipment collisions may also occur during ammonia transfers. Loading arms or hoses may be disconnected or ruptured by external impacts from cargo falling or a collision between ships, trucks, and equipment. However, modern loading arms are designed to minimise any release if the final flange connection is separated. Smart-Hoses® are also commonly used in the industry for any hose transfers as they are designed to retain the hose contents should an accidental disconnection occur. The use of modern, well-designed, fit-for-purpose equipment will greatly mitigate the risk of an uncontrolled, accidental release during ammonia transfers.

Improper Connection and Equipment Failure

Leakages from valves, flanges and couplings could potentially occur if training, operating, and maintenance procedures are not adequately implemented. Equipment and devices are available to reduce the likelihood of such failure. For example, all ammonia globe isolating valves have a back seat function which enables the spindle seals to be safely replaced whilst keeping the line live.

Over/Under Pressure Conditions

Over/under pressure conditions may lead to rupture or collapse of piping systems and storage containments. All ammonia pressure vessels are designed to comply with internationally recognised codes such as ASME VIII or ISO 16528, and their pressure relief devices (PRDs) are designed to comply with codes such as ISO 5149. These codes ensure that the pressure vessels can sustain sufficient pressure and can be evacuated to a complete vacuum with no risk of collapsing. During the pumping of saturated liquid ammonia through pipes and hoses, hydrostatic overpressure may occur. The liquid gets locked between two closed valves (one may be a non-return valve), and the surrounding heat enters to cause the liquid to expand rapidly and drives the pressure to a catastrophic level. Strategic placement of PRDs along the piping systems will be required to eliminate the risk.

Extreme Temperature

Atmospheric pressure (0 to 70 kPa g) ammonia storage tanks are required to be fitted with PRDs and vacuum breaker devices. This is to allow for excessive flows due to external heat sources, such as fire, to prevent damage or rupture of storage tanks. Excessive pressure may build up in the pressurised ammonia storage tanks when they are exposed to excess heat. This will cause a release of ammonia through the PRD or from equipment failure. A BLEVE can occur when the pressurised vessel fails, and liquid ammonia is suddenly exposed to atmospheric pressure, causing explosive vaporisation of a large fraction of the tank contents that can spread over a large area [4]. When pressurised ammonia vapour is subjected to extremely low temperatures, condensation-induced shock (or hydraulic shock) may occur. Rapid condensation can create a vacuum in a closed system and produce a rapid inrush of ammonia from other parts of the system. When this high-velocity fluid reaches an obstruction, the rapid deceleration will exert a strong force on the obstruction to cause component failure [5]. This phenomenon has occasionally been experienced in old ammonia refrigeration plants using poorly controlled hot gas defrost systems. The introduction of “soft defrost” technology has greatly reduced the risk of this occurring in recent decades. Where there is a risk of exposure to climates of extreme temperature, the vessels should be designed for pressures up to and in excess of 2,500 kPa g, equivalent to the saturated ammonia temperature of 60°C. Such vessels shall be painted white or a light cream colour to minimise the solar load. These measures have been proven effective in preventing discharge from PRDs in extreme climates.

4.1.2 Conditions of the Loss of Containment Scenario

The loss of containment of ammonia scenarios can be classified according to the state of ammonia (gaseous, liquid, sub-cooled or saturated) stored in the containment as follows:

A. *Ammonia gas* through the vent or pressure relief devices. Any escaping gas will be lighter than air and make its way up into the atmosphere. The release of ammonia gas is likely to pose a relatively low hazard and risk.

B. *Ammonia liquid at atmospheric pressure and -33°C* leaking from a terminal atmospheric storage tank (into a bunded area). Wispy traces will be visible just above the liquid ammonia surface, and above that will be clear gas rising into the atmosphere. This ammonia vapour poses a relatively low hazard and risk to the surrounding areas.

C. *Sub-cooled ammonia liquid* such as that being pumped from an atmospheric pressure bunker vessel or terminal storage tank (-33°C) through a loading arm or bunkering hose. When this leaks to atmospheric pressure, there will be very little or no flash gas to propel it through the breach, and it will present a medium risk and hazard level. However, once liquid ammonia enters the sea or other water bodies, it has a high potential to form a hazardous ammonia cloud which is denser than air and raises the hazard and risk level.

D. *Saturated ammonia liquid at pressure*, such as that stored in the unrefrigerated road, rail, barge or nurse tanks and ISO containers. When this leaks into the atmosphere, it will invariably create an aerosol, violently propelled by the flash gas generated in the breach. It forms a dense gas cloud heavier than air and presents a high hazard and risk level to the surrounding areas, particularly those downwind.

Other considerations in the loss of containment scenarios include the circumstances in which the spill occurs, e.g. during storage, during connection, pre-bunkering procedures, disconnection or post-bunkering procedures, and the environment in which the spill occurs, on land, in the bund, in the sea. The size and location of the breach, whether at the top or bottom of the tank, at the beginning or tail end of a long pipe, will also affect the discharge pattern. All these will determine the rate, quantity and duration of the release, which will ultimately affect the dispersion and consequence. The types of release can be classified as follows [6]:

A. *Instantaneous release* where the spill occurs in a very short duration of time. E.g., the catastrophic rupture of equipment such as tanks, pipes, hose etc. Such releases are modelled as a puff-release model.

B. *Semi-continuous release* in which a given volume is spilt at a finite rate over a finite duration of time. E.g., leaks from a small tank, pipes/hoses or flanges, which can be isolated and stopped within minutes. Such releases are modelled as the continuous release of material within a fixed duration of time.

C. *Continuous spill* in which the spill continues at a finite rate for a long duration of time. E.g., leaks from a large tank or through passing valves which cannot be isolated and stopped. Such releases are modelled as the continuous release of material over an hour or until the tank empties.

Based on literature review, consultation with industry partners as well as taking references from the UK Health and Safety Executive Failure Rate and Event Data (UK HSE FRED) document [7] and the Dutch Publication Series on Dangerous Substances (PGS 3) Guidelines for quantitative risk assessment (TNO Purple Book) [8], the following loss of containment scenarios are likely to be encountered during ammonia bunkering:

1. Leak and/or rupture of iso-tank
2. Leak and/or rupture of shore storage tanks
3. Leak and/or rupture of ammonia fuelled ship fuel tanks
4. Leak and/or rupture of ammonia storage tanks on ocean-going vessels
5. Leak and/or rupture from storage tank piping (pipeline)
6. Leak and/or rupture from ship tank piping
7. Leak and/or rupture of connecting hose (due to manufacturer defect, mishandling, mis-operation) or pull-away incidents
8. Leak and/or rupture from loading arm swivel joints
9. Leak from valves, flanges, coupling, gasket failure, pumps, etc.
10. Overfill of bunker tankers

Leak and rupture of connecting hoses or pull-away incidents are assessed as one of the most common likely cases of the loss of containment for ammonia bunkering. Hoses are used commonly in the conventional bunkering process as they provide flexible connections to transfer products from one container to another. These hoses are routinely handled by people in a dynamic work environment. Hence, they are subjected to a high degree of stress and wear-and-tear, especially at the shore or out in the sea. The entire hose assembly systems are the weakest link in transferring and bunkering operations. Hose assemblies may get damaged from use, coupling ejections or pull-away incidents can happen. Smart-Hoses® have been widely used for land-based ammonia liquid transfer operations in the chemical industry for years. They can minimise the ammonia spill should a coupling separation, pull-away or hose rupture occur.

4.2 Mechanism of Ammonia Dispersion Upon Released into Environment

Dispersion Phases

The ammonia release process can be divided into three phases. The first phase is the initial flash at the *initial expansion zone*, where the released ammonia is expanded from the storage pressure at the opening to the atmospheric pressure. With this sudden depressurisation, a portion of the liquid will flash off or vaporise as vapour. The vapour phase is at a higher velocity than the liquid phase, and this induces the entrainment of the liquid phase, aerosolising it into fine droplets [9]. The initial flash depends on the release's mode and condition, as discussed in Section 4.1.2.

The second phase is at the *entrainment zone*, where the released ammonia will induce the entrainment of the surrounding air and gain heat from the air to further vaporise the liquid droplets. The cooling effect of this vaporisation process may cause condensation of water vapour in the air and affect the ammonia cloud density. Characteristics of the initial flash, such as the exit velocity, liquid fraction, droplet size and exit temperature, will subsequently affect the internal buoyancy or density (buoyant, neutral or dense) of the ammonia cloud. The higher the liquid fraction of ammonia released, the denser the cloud mixture [10]. The degree of initial dilution of the released ammonia with air and the humidity of the air also affect the density of the ammonia cloud. The higher the humidity of the surrounding air, the greater the degree of dissolution of ammonia in the water vapour in the air. More heat is generated from this exothermic process to vaporise the liquid fraction of the ammonia in the mixture, resulting in a less dense cloud. On the other hand, when there is more water vapour in the air, more water vapour will condense as water droplets if the temperature in the ammonia cloud is below the dew point, adding to the density of the ammonia vapour cloud [10]. All these factors exert a varying degree of influence on the ammonia cloud density and its behaviour (buoyant, neutral, or dense) [10].

The final phase is at the *passive dispersion zone*, where the ammonia cloud continues to be diluted by mixing with the surrounding air. Its velocity gradually reduces until it reaches the ambient wind velocity [6]. A dense ammonia cloud behaves considerably differently from buoyant gas clouds. The momentum from the exit velocity will raise the ammonia cloud vertically, and then the dense ammonia cloud will slump toward the ground and move downwind. The density of the ammonia cloud suppresses the vertical mixing and allows the ammonia cloud to travel at ground level before it warms up [2]. As the dense ammonia cloud move downwind, they are diluted with air until they eventually become neutrally buoyant. Atmospheric conditions and stability will determine the passive dispersion pattern.

Rainout and Pool Formation

The portion remaining after the initial flash will *rain out to form a pool* on the surface. When the spill happens on land, the pool will spread due to gravitational effects and lose mass through evaporation or seepage into porous ground and deposition on vegetation and soil. When the spill happens on water surfaces such as the sea, lake and river, the pool will lose mass through the vaporisation of liquid ammonia on the water surface and dissolution of ammonia in the water.

Behaviour of Ammonia Cloud Released from Refrigerated Storage Tanks

When liquid ammonia is released slowly from a refrigerated storage tank on land into the bund, only about 0.2% of the liquid will flash into vapour at the initial release point. The liquid ammonia collected in the bund will slowly vaporise while absorbing heat from the surrounding. The vaporisation rate will depend on the heat transfer rate between the surrounding air and the surface in contact with the liquid pool [10].

Behaviour of Ammonia Cloud Released from Non-Refrigerated Storage Tanks

When saturated liquid ammonia is released into the atmosphere from a pressurised vessel (at 25°C), approximately 20% of the liquid ammonia will immediately flash to vapour. For every 1 L/s of a liquid leak, about 150 L/s of flash vapour will form. The expansion ratio of 150 will violently drive the release of the remaining 80% of the leak mass flow, which remains as liquid, and atomises it into small droplets as an aerosol. The aerosol will be at a very low temperature, well below the dew point, and water vapour in the air will condense out and form part of the heavy, dense ammonia cloud along with the remaining ammonia liquid droplets [11] [12]. The dense ammonia cloud can stay close to the ground for some distance depending on the weather and ground conditions, increasing the potential for exposure of workers and the public. The dense ammonia cloud will be visible and have a high concentration of ammonia in the 20,000-ppm range, which makes it very dangerous and shall be avoided at all costs.

4.2.1 Fate of Ammonia Released in Air

Ammonia is a highly reactive and soluble alkaline gas, and it is the only primary alkaline gas in the atmosphere. Hence, it plays an important role in determining the overall acidity of precipitation, cloud water and airborne particulate matter [13]. Ammonia clouds in the air can be removed from the troposphere by atmospheric moisture (clouds, rain, fog) or by reacting with the acidic components of the atmosphere (e.g., sulphuric, nitric and hydrochloric acids). Ammonia is also able to catalyse the atmospheric oxidation of sulphur dioxide to sulphur trioxide. The ammonium salts (ammonium sulphates, ammonium nitrate, ammonium chloride, etc.) formed from such reactions will form part of the aerosols in the atmosphere and affect the opacity of the atmosphere [14]. Ammonium ions and aerosols have a longer atmospheric lifetime than ammonia and may stay airborne for several weeks before being washed out in precipitation. In contrast, the lifespan of ammonia itself is relatively short, ranging from hours to days, as it gets transported by winds and converted to ammonium or deposited near sources by dry deposition to land or water surfaces [15].

Ammonia released in the environment will ultimately either convert to ammonium salts or be subject to dry or wet deposition onto the earth's surface, causing adverse effects such as eutrophication and acidification [16]. A nonreactive surface, such as a smooth and dry concrete surface, may limit absorption or adsorption, while natural surfaces such as vegetation generally promote dry deposition [16]. Wet deposition is defined as the natural processes by which a material is scavenged by atmospheric hydrometeors (cloud, fog drops, dew, rain, snow), commonly termed precipitation, and is consequently delivered back onto the earth's surface [17].

Higher ammonia levels are found near emission sources confined to the lower tropospheric layer. Previous studies indicated a 50% reduction in concentration at a 600 m distance from the source while a 70% reduction at a 4 km distance from the source [13]. From a safety point of view, the hazards posed by the released ammonia gas are short-lived as the ammonia release will be diluted, dispersed, and absorbed by the environment.

4.2.2 Fate of Ammonia Released in Water

Ammonia is very soluble in water, and it dissolves in water in an exothermic reaction where it is partially hydrolysed into ammonium hydroxide with an equilibrium constant $K_b = 1.774 \times 10^{-5}$ at 25°C. Henry's law can only be used to compute the amount of ammonia that will dissolve in pure water or dilute an aqueous solution. However, for aqueous solutions containing significant concentrations of salts, such as seawater, ammonia's solubility should be computed using the Pitzer model that considers the interaction of ammonia with dissolved ions and neutral molecules [14].

Ammonia's density is 0.684 g/cm^3 at the normal boiling point. It is buoyant in water and fully miscible with water. Any liquid spill will spread rapidly across the water's surface while boiling and mixing with the water simultaneously [11]. The heat released from the dissolution of ammonia in seawater will rapidly increase the pool vaporisation rate of ammonia.

The amount of ammonia that will be dissolved and absorbed into the sea water is also affected by the chemical and biological activities and physical processes that will take place. Ammonia may be taken up readily by phytoplankton in the water and may interact with sediment through adsorption and desorption [18].

In general, approximately 30% to 40% of ammonia spilt onto the water surface will become airborne, forming an ammonia cloud that disperses downwind, while the remaining 60% to 70% will dissolve into the water [2] [11].

4.2.3 Rain Effects on Ammonia Dispersion

Ammonia released into the atmosphere may be removed by rain during a rainstorm or by the clouds if the ammonia vapour cloud extends beyond the cloud base height. The process where clouds remove ammonia is termed washout (in-cloud scavenging), and the process where ammonia is removed by rain is termed rainout (below-cloud scavenging) [17].

As rain is very common in Singapore, the impact of rain on the dispersion of the released ammonia cloud needs to be evaluated. Below-cloud scavenging process is complicated as it involves multiple phases (air, aerosol particles and rain droplets) and several mass transfers and chemical reactions. The size distribution of rain droplets during the entire duration of the rainfall provides additional complications to the process.

For the rain to remove ammonia from the atmosphere, first, there must be an interception of ammonia by the rain droplets. Interception occurs when ammonia gas is brought into contact with the rain droplet and adhered directly to the falling rain droplet [19]. Mass transfer will then take place at the surface of the rain droplet for ammonia to transfer from the gaseous phase to the liquid phase (gas-phase diffusion) and subsequent dissociation and liquid diffusion into the rain droplet. During the scavenging process, the amount of ammonia dissolved and absorbed into the rain droplet will be determined by the solubility of ammonia and the chemical reactions that will take place between ammonia and the other dissolved gases in the rain droplets [17] [20]. It was found that the observed ammonium ion concentrations were only between 0.03% to 3% of the calculated values. The amount of ammonia removed by rain droplets is found to be less than 10% of the total ammonium found in the atmosphere [21].

The height of rain clouds in Singapore ranges from 300 m to below 2,000 m [22]. A large raindrop will take 30 seconds to 2 minutes to reach the ground, while a smaller raindrop will take 1 to 5 minutes [23] [34]. As a result, the ammonia removal rate by rain droplets is expected to be much lower than the removal rate by cloud droplets or water droplets in the form of fog or mist in the air [25]. In Singapore, rainfalls are usually intense with large droplets, so the contact time and exposed surface area are much reduced.

The complexity of the below-cloud scavenging process led to many attempts to quantify and simplify the relationship between airborne species concentrations, meteorological conditions and wet deposition rate. The scavenging coefficient is the parametrisation of the rate of loss of gases from the atmosphere by precipitation [26]. Several studies have developed the scavenging coefficient theoretically and empirically to simplify the formula to determine the rate at which ammonia can be removed by rain. Scavenging coefficients are a function of location, time, rainstorm characteristics, and aerosol size distribution of ammonia.

Except for rainfall during the northeast monsoon in December, much of the rain in Singapore is from heavy thunderstorms with a maximum intensity of 80 to 110 mm/h [27]. Thunderstorms have a short lifespan of approximately 30 minutes or less. They are often accompanied by a high wind speed of 20 to 80 km/h, which may reduce the scavenging efficiency as the ammonia vapour cloud may be diluted and disperse away from the rain column, further reducing the contact time. Assuming a contact time of 10 mins and a scavenging coefficient of 2×10^{-4}, the percentage of ammonia that the rain can remove is approximately 10%. Hence, the impact of rain on the dispersion of ammonia is not expected to be significant during heavy thunderstorms.

4.3 Simulation Method

Simulation software is used in this study to model and simulate the progress of released ammonia from the initial release point to far-field dispersion while accounting for the toxic effects of the release. The software also simulates the rainout from the release and the spreading and vaporisation of the rainout pool.

Liquid ammonia release is a two-phase release, and the density of the ammonia cloud changes as it interacts with the surroundings. Process Hazard Analysis Software Tool (PHAST), a Unified Dispersion Model (UDM) that can predict the full range of dispersion stages (Figure 4.1), is used in this study. The full dispersion stages include the (i) initial turbulent expanding jet; (ii) dense spreading and turbulent mixing with the atmosphere; (iii) slumping dense phase due to gravity; (iv) buoyant elevated phase (dominance of internal buoyancy), and (v) passive dispersion phase (dominance of ambient turbulence).

Based on the input parameters, the software carries out the discharge calculations to determine the release characteristics of ammonia (temperature, mass flow rate, velocity, liquid fraction) to describe how the materials are released and the subsequent expansion (final droplet size) to atmospheric conditions. The software generates results to predict the area affected and the vapour concentration at any distance of interest.

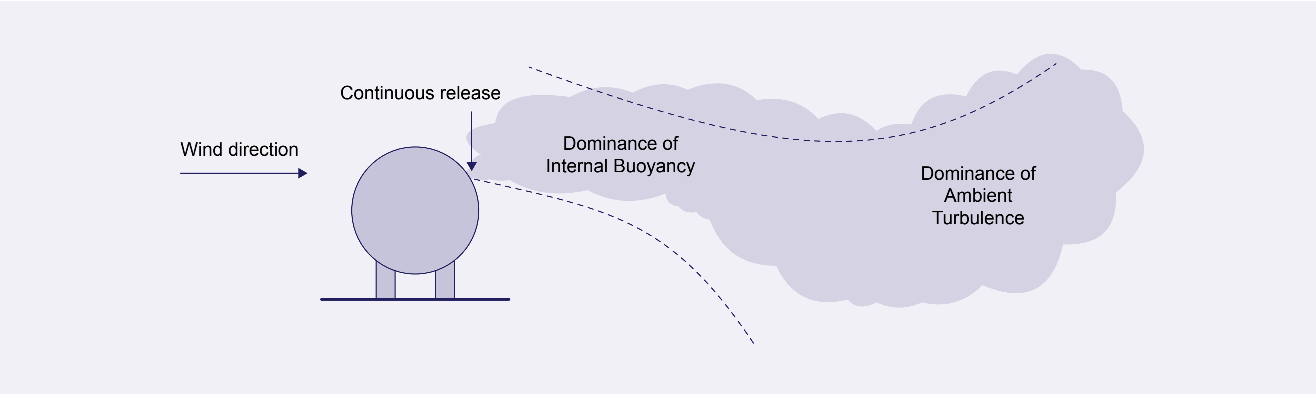


Figure 4.1 Ammonia dispersion in the atmosphere

Upon release, a portion of ammonia release will vaporise and aerosolise into the atmosphere as the ammonia cloud. The other portion will rain out and form a pool on the surface. If the surface where the spill happens is on land and relatively impervious, ammonia in the pool will continue to gain heat from the surroundings and vaporise into the atmosphere. If the surface is porous, the portion of the ammonia will seep into the ground. If release takes place over the water surface, the portion of the ammonia on the water surface will continue to gain heat from the surroundings and vaporise into the atmosphere, and the other portion will dissolve into the water, depending on the solubility constant of ammonia at the temperature of the pool (Figure 4.2).

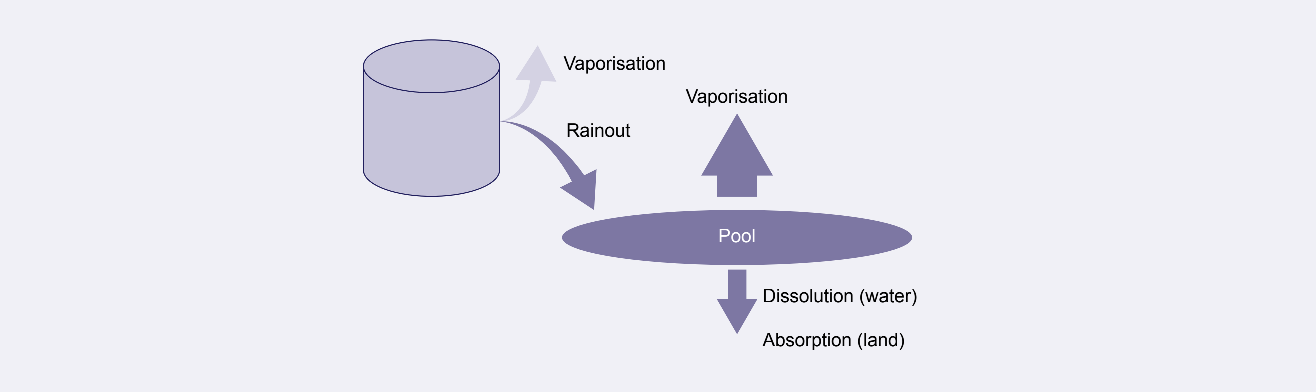


Figure 4.2 Ammonia dispersion upon discharge

The passive dispersion phase in the software model is based on the Pasquill-Gifford models derived from the diffusion equation. The dispersion is assumed to follow a Gaussian distribution whose standard deviations depend on the atmospheric turbulence and the distance from the source or the release duration.

The Pasquill-Gifford plume model describes the steady-state concentration of ammonia released from a continuous source and is defined by the following equation for release height H above ground level, wind moving in *x* direction at constant velocity *u* [4]. This model applies to continuous release from a crack in the tank or pipes or leak from flanges or couplings (Figure 4.3).

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

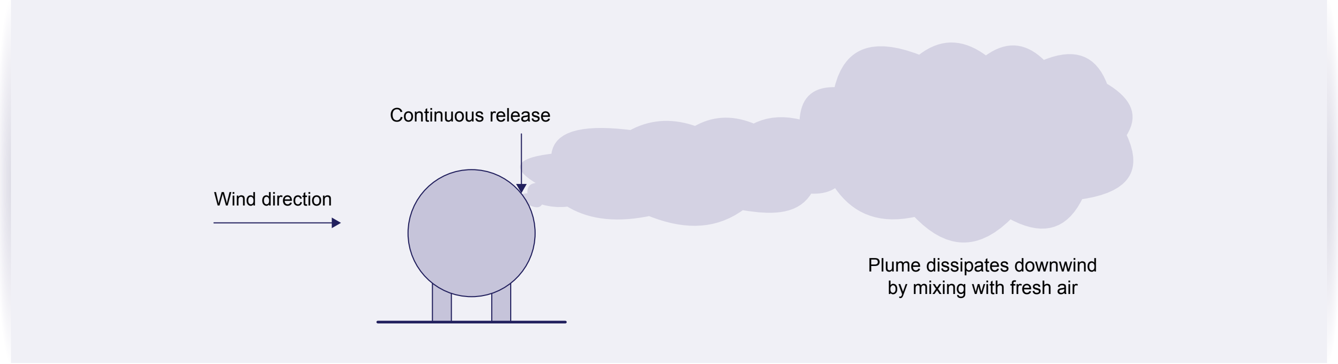


Figure 4.3 Gaussian continuous release model

The puff model describes the temporal concentration of ammonia from a single release of a fixed amount. The model for an instantaneous point source at ground level, wind moving in *x* direction at constant velocity *u*, is described by the following equation [4]. This model applies to catastrophic rupture of tanks or pipes [4], with no continuous pool vaporisation. The vapour cloud will move away from the rupture point (Figure 4.4).

$$C(x,y,z,t) = \frac{Q_m^*}{\sqrt{2}\pi^{3/2}\sigma_x\sigma_y\sigma_z}\exp\{-\frac{1}{2}\left[\left(\frac{x-ut}{\sigma_x}\right)+\frac{y^2}{\sigma_y}+\frac{z^2}{\sigma_z}\right]\}$$

σ_y, σ_z : dependent on atmospheric stability class and downwind distance *x*
Q : mass release rate (steady-state)
H : release height

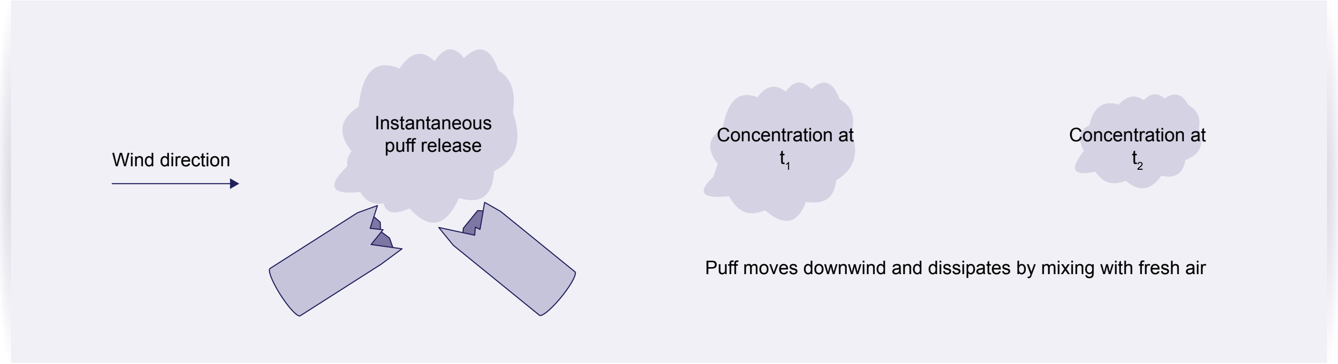


Figure 4.4 Gaussian instantaneous puff model

Finally, the toxic effect of ammonia will be evaluated based on the toxic calculations carried out, and the probability of death is determined using toxic probit functions. PHAST will also generate the consequence results in terms of (i) concentration at a distance, (ii) distance to the hazardous concentration of interest, and (iii) footprint of the cloud at a given time.

4.4 Consequence Analysis

4.4.1 Overview

Ammonia Release Scenarios

Simulations are carried out for selected hypothetical locations where ammonia bunkering may likely take place in Singapore. These locations will determine the likely modes of bunkering, which will, in turn, determine the supply and receive tank types and size, state of ammonia transfer (saturated or pressurised), and the connectors, hose and loading arms to be used for the transfer during bunkering. Six ammonia release scenarios are selected for the safety analysis, as shown in Table 4.1. Weather parameters for the consequence analysis of these release scenarios are selected based on the historical weather data of Singapore obtained from the Meteorological Service Singapore [28] to [43] and are presented in Table 4.2.

Scenario	Bunkering Mode	Supplying	Receiving	Release Point
A	Shore-to-ship	Shore Tank FR	Chemical Tanker FR	Hose rupture at the highest point of a loading arm
B	Truck-to-ship	ISO Tank NR	Tugboat NR	Hose rupture at inlet manifold of a tugboat
C	Ship-to-ship	Bunker tanker FR	Container ship FR	Hose rupture at inlet manifold of a container ship
D	SIMOPS	Bunker tanker FR	Container ship FR	Hose rupture at inlet manifold of a container ship
E1	Truck-to-ship	ISO Tank NR	Tugboat NR	Venting
E2	Ship-to-ship	Bunker tanker FR	Container ship FR	Venting

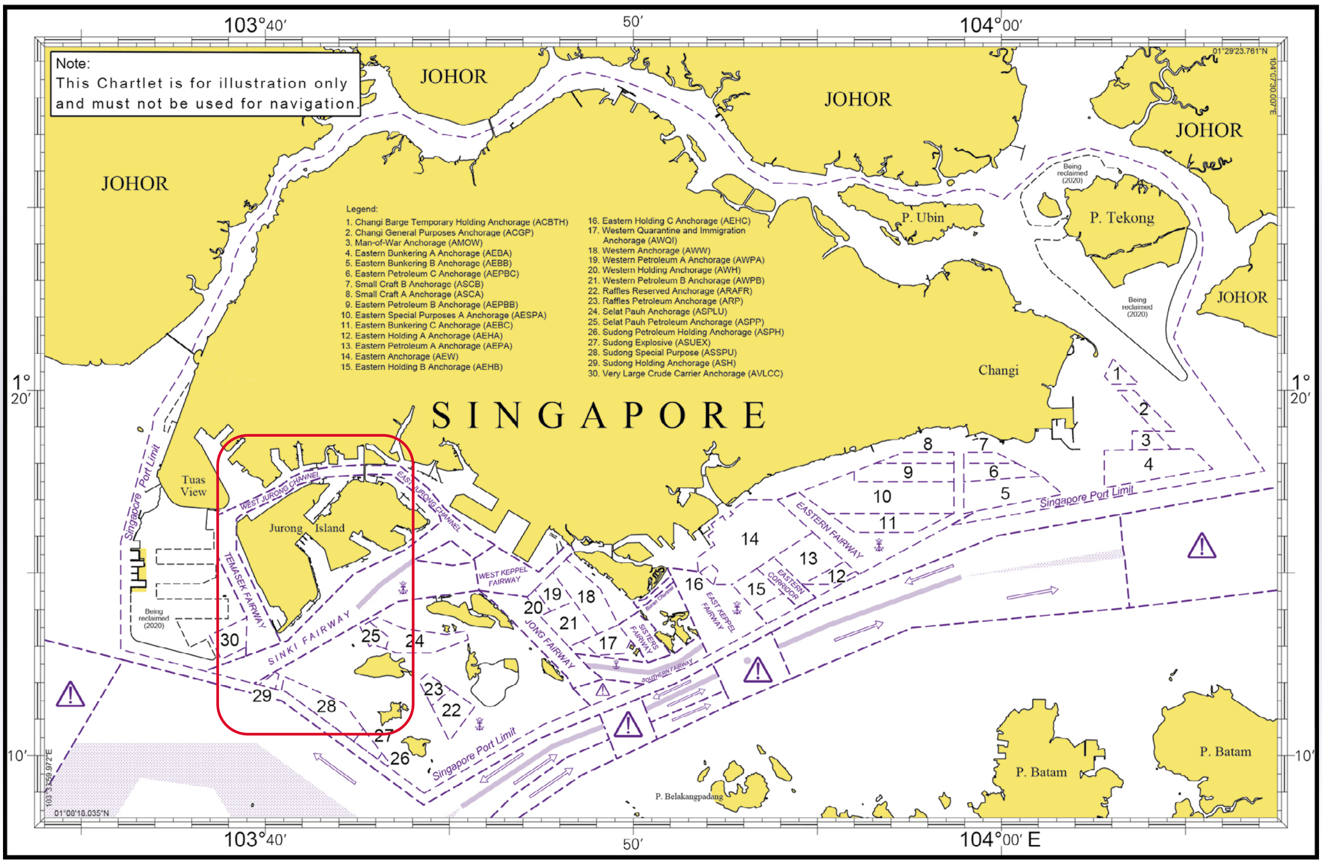
Table 4.1 Overview of ammonia release scenarios

Parameters	Atmospheric Stability	Wind Speed	Humidity	Ambient Temperature	Surface Temperature	Solar Radiation
Day	Class C	3 m/s	70%	33°C	38°C	1 kW/m^2
Night	Class E	2 m/s	90%	24°C	26.5°C	0

Table 4.2 Inputs of weather parameters for consequence analysis

Hypothetical Bunkering Locations and Assumptions

Like conventional marine fuel bunkering, the potential ammonia bunkering location could be onshore or offshore at the terminal, jetty, and anchorage areas. Figure 4.5 shows anchorage and fairways in the Port of Singapore (updated on 19 Nov 2020). The locations in the circle were used as hypothetical ammonia bunkering locations for release simulation in this section. Jurong Port jetty, near the LNG TTS bunkering, could be one of the potential locations for truck-to-ship ammonia bunkering. There are many LNG and other chemical tanks located on Jurong Island. For terminal pipeline-to-ship bunkering, the southern point of Jurong Island could be the potential bunkering location. Singapore's potential location for ship-to-ship ammonia bunkering could be the Sudong Special Purpose Anchorage (ASSPU), where LNG vessels, LPG vessels, and chemical tanks are anchored. ASSPU is the furthest location of the Singapore Port limit from the mainland of Singapore. The nearby Tuas mega port is under construction. Some places in Tuas mega port could be the potential location for ship-to-ship ammonia bunkering with cargo handling simultaneous operations.



Source: Maritime and Port Authority of Singapore

Figure 4.5 Port of Singapore – anchorage and fairways (19 Nov 2020) [44]

Several assumptions are made when conducting ammonia dispersion simulation in this study. The overall process shall be as simple as possible, so there is no vapour return line in the bunkering process flow. When the ammonia bunker receiving vessel is harbour craft, we keep the size of the existing fuel tank, and the endurance will be reduced due to the lower energy density of ammonia. However, the endurance shall be maintained for ocean-going vessels, so the fuel tank's capacity is increased. The capacity of the ammonia fuel tank is calculated based on the same energy content as HFO or LNG considering the differences in the energy density values. Before the bunkering operation, the fuel tank is not empty due to the safety consideration. It contains at least a sufficient amount for harbour craft to ensure a round trip from the furthest operating location to the bunkering point within the Singapore port limit.

Toxic Effects and Consequence Analysis

Acute Exposure Guideline Levels (AEGLs) are used in this safety study. AEGLs values are conservative as they represent threshold exposure limits (exposure levels below which adverse health effects are not likely) for the general public, including susceptible individuals such as infants, children, elderly persons with asthma, and those with other illnesses. AEGLs consider both *ammonia concentration* and *exposure time*. AEGL-1, AEGL-2, and AEGL-3 are developed for each of the five exposure periods and are distinguished by varying degrees of severity of toxic effects, as presented in Table 4.3.

Guidelines	10 min	30 min	1 h	4 h	8 h
AEGL-1	30 ppm	30 ppm	30 ppm	30 ppm	30 ppm
AEGL-2	220 ppm	220 ppm	160 ppm	110 ppm	110 ppm
AEGL-3	2,700 ppm	1,600 ppm	1,100 ppm	550 ppm	390 ppm
AEGL-1	Notable discomfort, irritation, or certain asymptomatic non-sensory effects. Effects are not disabling and are transient and reversible upon cessation of exposure.				
AEGL-2	Irreversible or other serious, long-lasting adverse health effects of an impaired ability to escape				
AEGL-3	Life-threatening health effects or death				

Table 4.3 Acute Exposure Guideline Levels (AEGLs)

Lethality Footprints

Impacts of toxic hazards are based on a combination of two parameters: concentration and exposure duration. Exposure duration to a certain concentration must be sufficiently long for death to occur. Similarly, a sufficiently high concentration must be reached over a certain exposure duration before death can occur. The probit calculation method used in PHAST calculates the probability of lethality from a given toxic exposure. It depends on the probit parameters specified in the software's toxic properties' settings for ammonia. The method calculates the probit value for a given toxic dose, and uses the probability of lethality for this probit and gives a range of lethality values between 0 (0%) and 1 (100%). For the toxic dispersion calculations for ammonia release, PHAST will generate distance versus probability results (footprint, downwind etc.). Lethality footprints for 3%, 10% and 50% lethality are presented, and this is with reference to the requirements in the Singapore Quantitative Risk Assessment (QRA) guidelines [45].

Cloud Footprints and Maximum Cloud Footprints

The ammonia vapour cloud and ammonia pool footprints are presented in the consequence analysis to show the toxic effects of the released ammonia. The footprints are taken at a height of 1.5 m for dispersion over land and 0 m for dispersion over the sea. The cloud footprints generated show the contours for the concentration of the 10-min AEGL-2 (220 ppm) and AEGL-3 (2,700 ppm), assuming the personnel in the vicinity will proceed to evacuate the area upon activation of alarm or detection of ammonia smell (odour detection threshold of 5 ppm); hence the exposure limit will not be longer than 10 minutes. The cloud footprints at different timing are captured and presented. The maximum cloud footprints at the end of 1 hour are also presented using the 1-h AEGL-2 (160 ppm) and AEGL-3 (1,100 ppm).

The footprints obtained are useful for establishing emergency response plans for parties involved in the ammonia bunkering process. The 2020 Emergency Response Guidebook published by the US Department of Transport recommended using AEGL-2 values to determine the downwind distance *"to which people may become incapacitated and unable to take protective action and incur serious health effects after a single, or rare, exposure"*. The Initial Isolation Zone and Protection Action Zone are recommended in the guidebook (shown in Figure 4.6) [46].

Initial Isolation Zone	Defines an area surrounding the incident in which people may be exposed to dangerous and life-threatening concentrations of material
Protection Action Zone	Defines an area downwind from the incident in which people may become incapacitated and unable to take protective action and/or incur serious or irreversible health effects

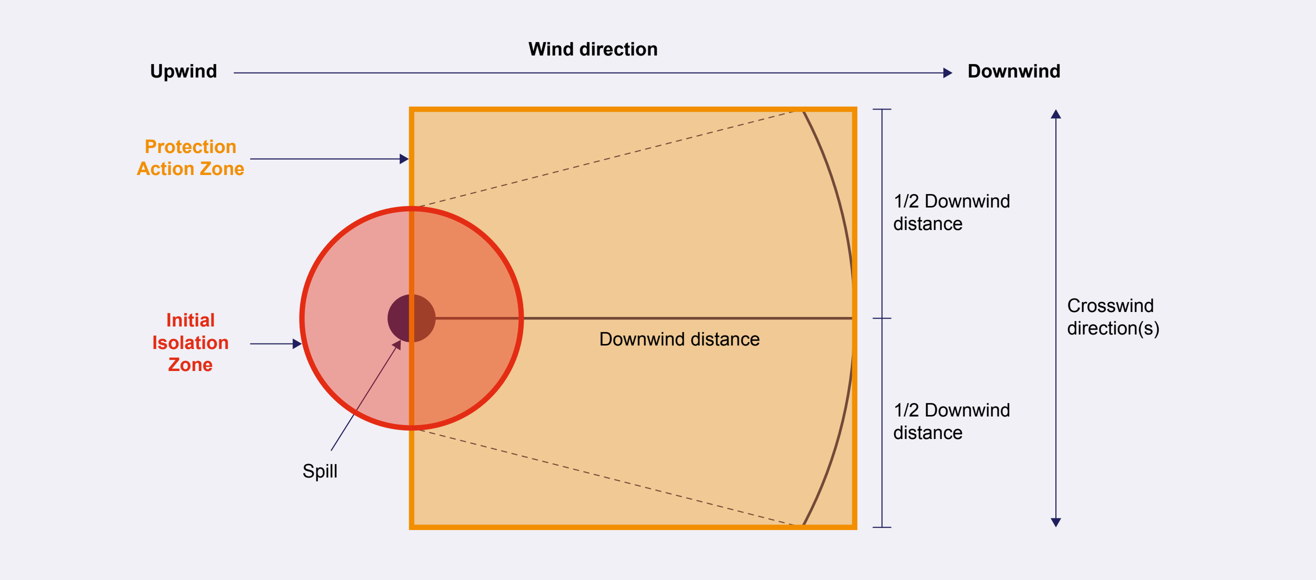


Figure 4.6 Schematic of initial isolation zone and protection action zone

Averaging Time

As indicated in the TNO Purple Book [8], the averaging time for toxics should be comparable to the exposure time. The averaging time for toxics is set at 10 minutes, and this is an arbitrarily selected value to be between a short release with an exposure time between 30 to 60 s and a long release with an exposure time of 30 minutes.

4.4.2 Shore-to-ship Bunkering - Scenario A

Ammonia is usually stored in an insulated double-containment atmospheric tank on land. Table 4.4 shows the inputs for ammonia release scenario A. In this scenario, we assumed an atmospheric storage tank size of 10,000 m^3, constructed of carbon steel and elevated approximately 2 m above ground to prevent ice formation under the tank. The outer tank will withstand a temperature of up to 260°C. It will be capable of containing refrigerated liquid and gas resulting from potential leaks from the inner tank. The tank is seated in a 2.3 m high impervious bund with a dimension of 42.1 m by 38.4 m. The bund will provide further containment for potential release from the inbound jetty pipeline. The pumps are submerged in the tank.

The wind direction is set from the southeast direction towards Jurong Island to demonstrate the impact on the neighbouring establishments. Based on the historical meteorological data from Singapore National Environment Agency (NEA), the wind comes from the southeast more than 10% of the time.

Parameters	Value
Location	Jurong Port Universal Terminal at Jurong Island
Shore Tank Capacity	10,000 m^3 (max 85% filled)
Bunker Vessel Capacity	17,500 m^3 (max 85% filled) Ammonia Carrier
Temp & Pressure	-33.4°C, 1 atmospheric pressure
Connection	8” pipeline, 1,000 m long and 8” hose 40 m long
Flowrate	1,500 m^3/h
Bund	42.1 m x 38.4 m x 2.3 m
Hose Diameter	8-inch
Orifice Size	8-inch
Release Direction	Horizontal
Release Elevation*	10 m
Release Duration	60 s
Wind Direction	From sea to land
Scenario in the Simulation	User-defined model using parameters from short pipe (Ø8”) rupture

*Note: Elevation is made with reference to ground level on land as dispersion is assumed over land. The wind direction is set towards inland to assess the impact zone on the surrounding neighbours on Jurong Island.

Table 4.4 Inputs for shore-to-ship bunkering scenario A

Based on the Dutch TNO Purple Book [8], the failure rates or frequencies of loss of containment due to leak or rupture from a double-containment atmospheric storage tank is in the order of 10^{-5} to 10^{-8} per year, and that for permanent pipeline leak and rupture range from 10^{-5} for a minor leak to 10^{-7} per year for full bore rupture. The failure rates and frequencies of loss of containment due to leak from the loading arm is in the order of 10^{-4}. Hence, the loss of containment in this bunkering scenario will be simulated on the hose rupture at the highest point of the loading arm. It is assumed that ESD is in place, and isolation time is set at 1 minute.

Figure 4.7, Figure 4.8 and Figure 4.9 show the cloud footprints, maximum cloud footprints and lethality footprints of scenario A. The ammonia vapour cloud during the day is transported further downwind during the day during the first 300 s of release. However, the vapour cloud is dispersed and diluted rapidly within 10 minutes, and the footprints are much smaller than the footprints for release at night. By 20 mins, the footprints for the release during the day are confined to less than 400 m downwind.

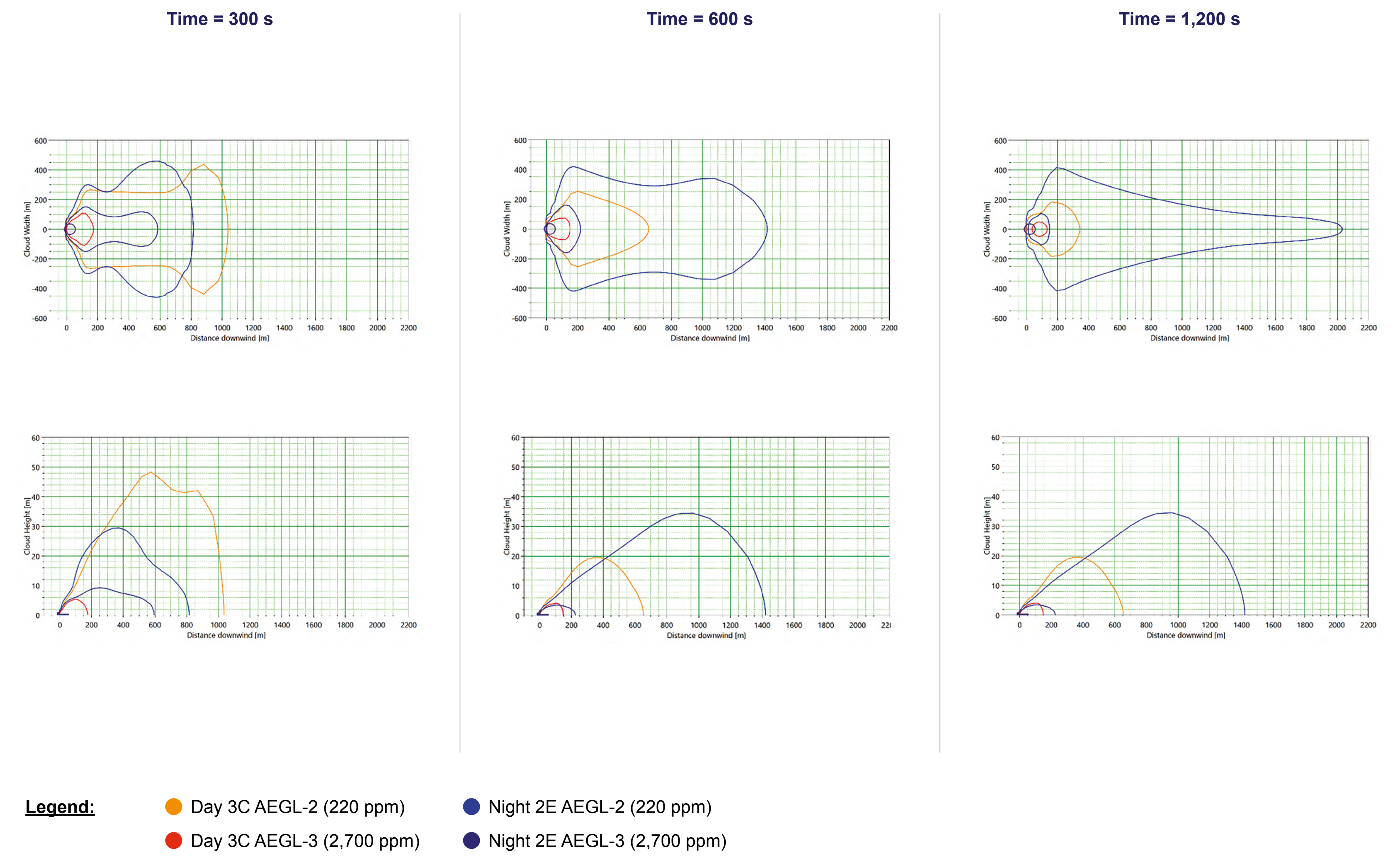
A total of 17,040 kg of ammonia is released in 1 minute. The rainout rate is 84% during the day and 87% at night (shown in Table 4.5). The remaining 16% during the day and 13% at night are flashed directly into the atmosphere as gaseous ammonia or aerosolised ammonia droplets. The vaporisation of ammonia into the atmosphere continues from the rainout pool collected on the ground. The vaporisation rate during the day is higher than at night, reaching a maximum of 36 kg/s during the day and 30 kg/s at night. Approximately 4% of the total ammonia released remained in the pool at the end of 1 hour for the release during the day, while approximately 10% of ammonia remained at night due to the lower vaporisation rate.

	Day 3C	% of Mass Released	Night 2E	% of Mass Released
Total Mass Released	17,040	-	17,040	-
Mass Released as Vapour Cloud	2,801	16%	2,279	13%
Mass Rainout as Pool	14,239	84%	14,761	87%
Mass Vapourised from the Pool	13,706	80%	13,066	77%
Mass Remaining in Pool at 1 h	533	4%	1,695	10%

Table 4.5 Mass balance for shore-to-ship bunkering scenario A

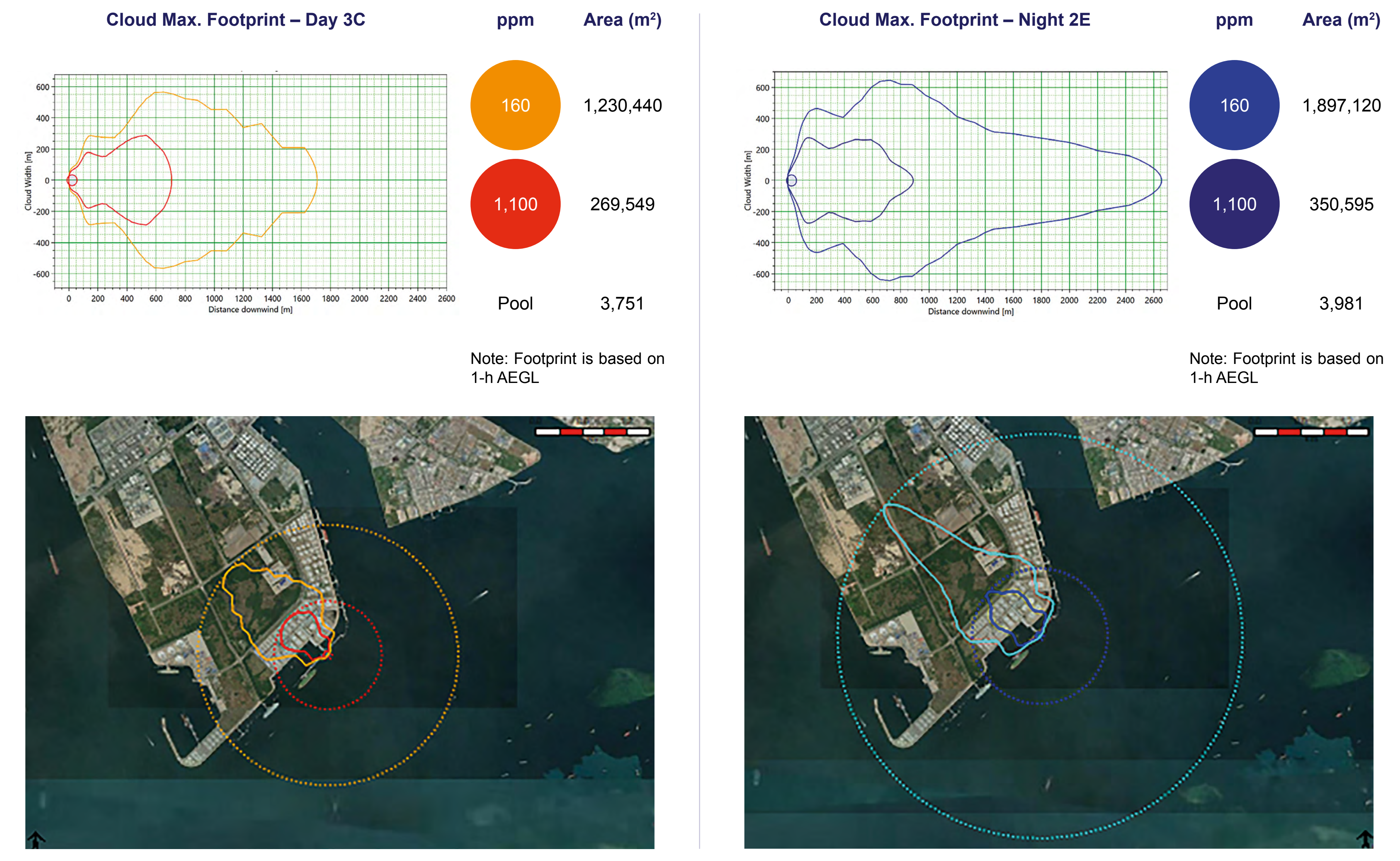
Although the 1-h AEGL-2 maximum cloud footprint reached a downwind distance of approximately 1.7 km and 2.7 km during the day and night, respectively, the 3% lethality footprints only reached a maximum downwind distance of approximately 400 m. This indicated that the vapour cloud further downstream does not remain at one location sufficiently long enough to cause fatality. The 3% lethality footprint at night is approximately 1.5 times that for the day, as the more stable atmosphere at night is able to sustain the vapour cloud concentration. A lower wind speed also results in lower dispersion and dilution.

Nevertheless, the vapour cloud went beyond the premise boundary, reaching neighbouring establishments and public roads for both releases during the day and at night. A 10-minute exposure to a concentration of 220 ppm has the potential to cause irreversible or other serious, long-lasting injury to people within the AEGL-2 footprints. Hence, additional safety measures shall be taken to limit the spread of the ammonia vapour cloud. For example, reducing the isolation time in the case of hose rupture from 60 s to 30 s can limit the released quantities and reduce the lethality footprint by more than 70% for releases day and night. Installing permanent or mobile fluid curtains can potentially provide effective mitigation of ammonia. Studies in the USA and Europe have demonstrated that such fluid curtains can produce significant mitigation effects when well-designed systems are applied for soluble gases like ammonia [47].



Note: No more AEGL-2 and AEGL-3 footprints at 3,600 s after the release. Only liquid pool remains for both day and night conditions.

Figure 4.7 Cloud footprints for shore-to-ship bunkering scenario A



Cloud Max. Footprint – Day 3C

ppm	Area (m^2)
160	1,230,440
1,100	269,549
Pool	3,751

Note: Footprint is based on 1-h AEGL

Cloud Max. Footprint – Night 2E

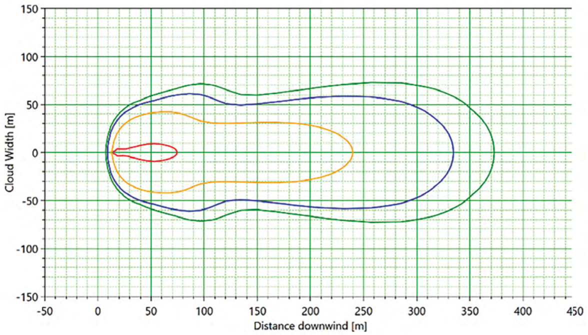
ppm	Area (m^2)
160	1,897,120
1,100	350,595
Pool	3,981

Note: Footprint is based on 1-h AEGL

Note: The AEGL-2 and AEGL-3 footprints only apply for dispersion over land.

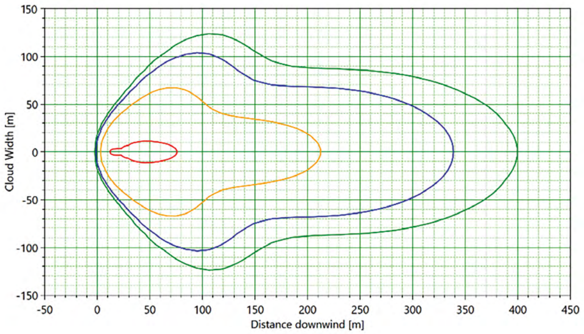
Figure 4.8 Maximum cloud footprints for shore-to-ship bunkering scenario A

Lethality Footprint – Day 3C



%	Area (m²)
0.03	44,984
0.1	33,317
0.5	14,000
0.99	746

Lethality Footprint – Night 2E



%	Area (m²)
0.03	66,439
0.1	46,061
0.5	17,396
0.99	989

Note: The lethality footprints only apply for dispersion over land.

Figure 4.9 Lethality footprints for shore-to-ship bunkering scenario A

4.4.3 Truck-to-ship Bunkering - Scenario B

A standard 24 m^3 ISO tank containing ammonia is used in this simulation. Based on the UK HSE FRED document [7] and the PGS 3 Guidelines for QRA [8], the failure rates or frequencies of loss of containment due to rupture of a pressurised LPG vessel or road tankers and tank wagons is in the order of 10^{-6} to 10^{-7} per year. Hence, the loss of containment for these loss scenarios is not simulated in our study. Based on the literature review, hose rupture at the hose connection to the bunker vessel is one of the most likely points of loss of containment. It is assumed that ESD is in place for the connection between the truck and the receiving vessel, and the isolation time is set at 1 minute. The inputs for ammonia release during truck-to-ship bunkering are shown in Table 4.6.

Parameters	Value
Location	Jurong Port
ISO Tank Capacity	20 m^3 (max 85% filled)
Temperature & Pressure	30°C, 12 bar
Connection	2” hose, 15 m long
Flowrate	20 m^3/h
Wind Direction	From sea to land
Orifice Size	2-inch
Release Direction	Horizontal
Release Elevation*	0.4 m
Release Duration	60 s
Scenario in the Simulation	User-defined model using parameters from short pipe (Ø2”) rupture

*Note: Elevation is made with reference to ground level on land as dispersion is assumed over land. Terrain: 10 cm low crops, occasional large obstacles.

Table 4.6 Inputs for truck-to-ship bunkering scenario B

Figure 4.10, Figure 4.11 and Figure 4.12 show the cloud footprints, maximum cloud footprints and lethality footprints. The quantity of ammonia released is relatively small in this release scenario, where only 198 kg of ammonia is released. There is no rainout, and the vapour cloud forms a puff right after the end of the release at 63.8 s. The ammonia AEGL-3 and AEGL-2 cloud footprint are fully dispersed by 116 s and 243 s during the day, while the AEGL-3 and AEGL-2 cloud footprint is fully dispersed by 162 s and 417 s at night.

Although the maximum cloud footprint has reached beyond the premise of Jurong Port, the ammonia AEGL-2 and AEGL-3 cloud footprints are completely dispersed within 8 minutes. Hence the injury from the ammonia release in this scenario is likely low. In addition, the ammonia cloud is moving downwind as a puff with a small footprint at any instant.

As the released quantity is very small and the ammonia cloud gets diluted and dispersed rapidly, the 3% lethality footprint is very small and extends only approximately 80 m downwind. However, it does extend onto the surrounding berths. Although the maximum cloud footprint has reached a distance of 800 m, the 3% lethality footprint is limited to less than 100 m from the release source for both day and night weather conditions. Despite the small footprint, any accidental release may affect the people working at the other berths. Additional safety measures should be taken to minimise the release quantity by installing safety devices such as ESD or Smart-Hose®. The movement of the vapour cloud can also be limited or blocked with emergency response installation, such as a water curtain or physical barriers.

This study simulated lethality footprints at different heights, as shown in Figure 4.12 (1.5 m height) and Figure 4.13 (0.5 m height). It is assumed that 1.5 meters is the height of ammonia inhalation when people are standing, and 0.5 meters is the height when crawling down. For 3%, 10%, 50% and 99% lethality footprints, the footprint areas at 1.5 m height are smaller than those at 0.5 m height, regardless of day and night conditions. Therefore, when people are escaping from ammonia, changing from standing to crawling down does not reduce the fatality rate.

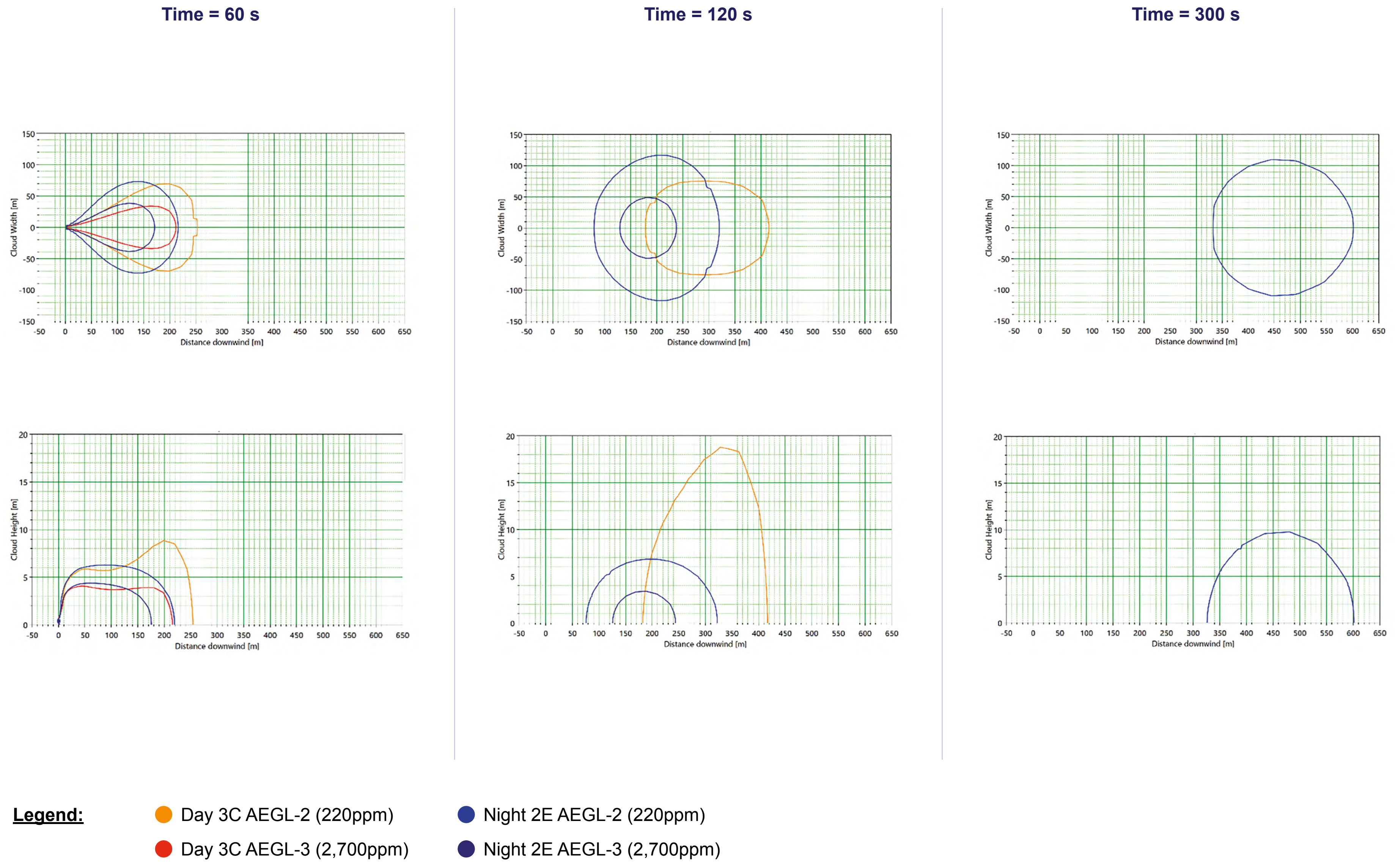
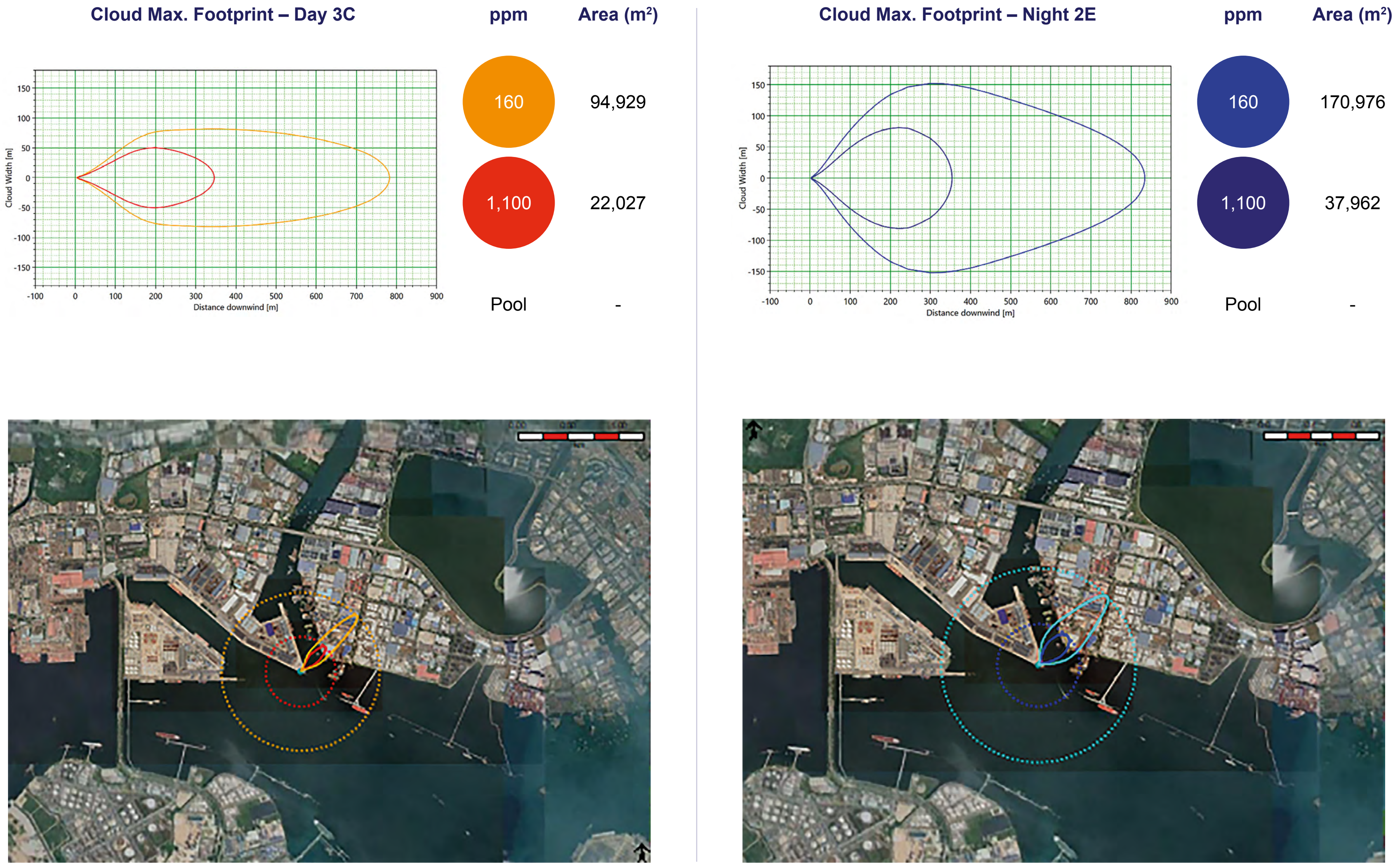


Figure 4.10 Cloud footprints for truck-to-ship bunkering scenario B



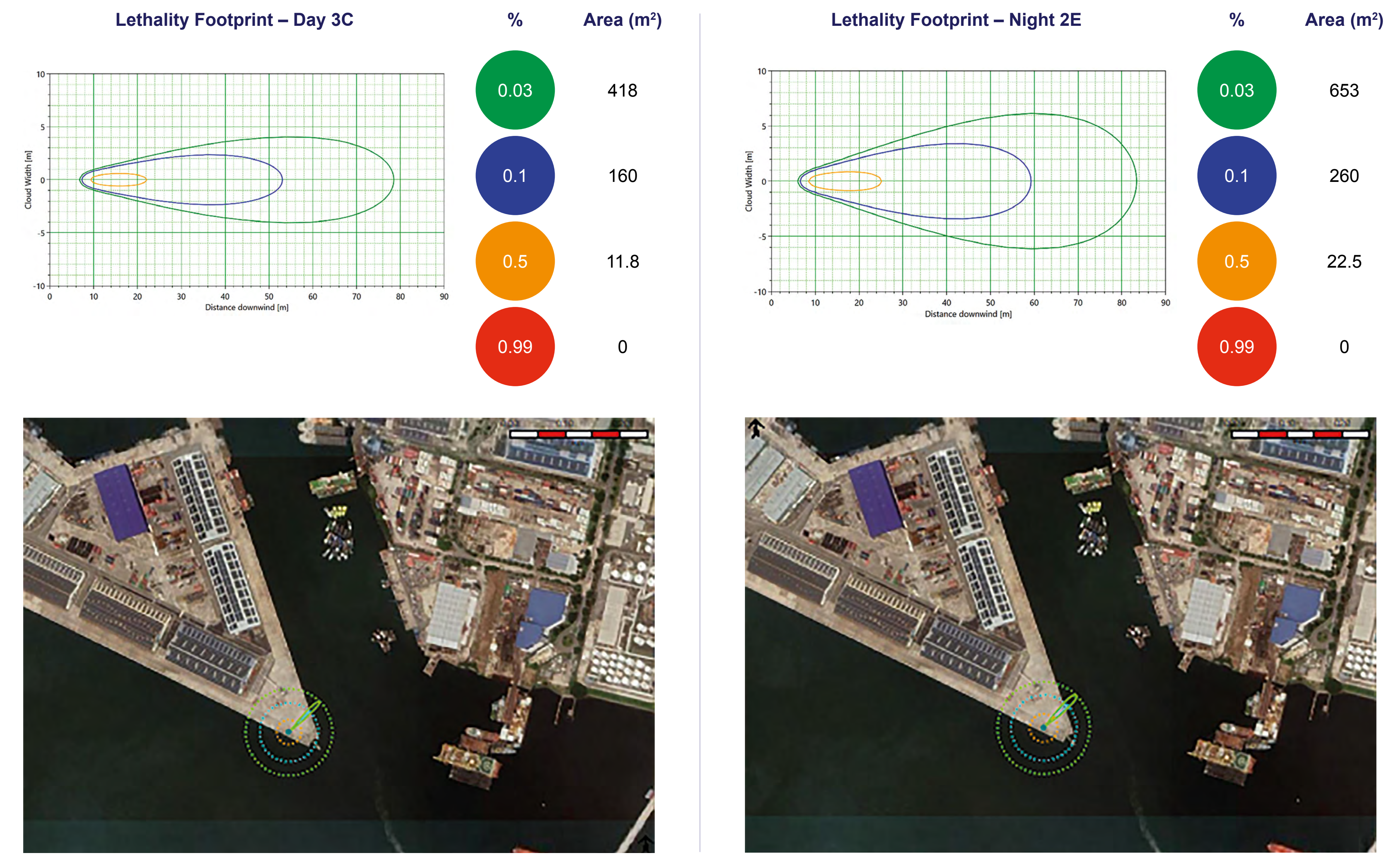
Cloud Max. Footprint – Day 3C

ppm	Area (m^2)
160	94,929
1,100	22,027
Pool	-

Cloud Max. Footprint – Night 2E

ppm	Area (m^2)
160	170,976
1,100	37,962
Pool	-

Figure 4.11 Maximum cloud footprints for truck-to-ship bunkering scenario B



Lethality Footprint – Day 3C

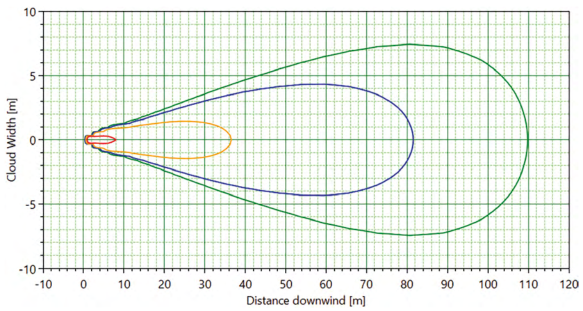
%	Area (m²)
0.03	418
0.1	160
0.5	11.8
0.99	0

Lethality Footprint – Night 2E

%	Area (m²)
0.03	653
0.1	260
0.5	22.5
0.99	0

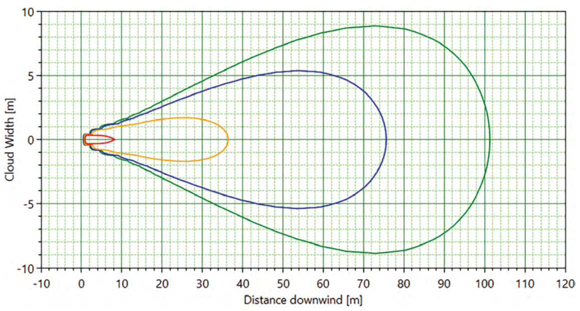
Figure 4.12 Lethality footprints at 1.5 m for truck-to-ship bunkering scenario B

Lethality Footprint – Day 3C



%	Area (m^2)
0.03	1,062
0.1	479
0.5	77
0.99	3.4

Lethality Footprint – Night 2E



%	Area (m^2)
0.03	1,162
0.1	535
0.5	88
0.99	3.9

Figure 4.13 Lethality footprints at 0.5 m for truck-to-ship bunkering scenario B

4.4.4 Ship-to-ship Bunkering - Scenario C

Table 4.7 shows the ammonia release scenario C inputs during the ship-to-ship bunkering operation.

Parameters	Value
Location	Anchorage 28 ASSPU
Bunker Vessel Type	17,500 m^3 NH_3 carrier
Container Ship Type	14,800 TEU LNG dual fuel container ship
Temperature	-33.4°C, 1 atm
Connection	8” (203 mm) hose, 40 m long
Flowrate	1,500 m^3/h
Hose Diameter	8 inch
Orifice Size	8 inch
Release Direction	Horizontal
Release Elevation*	18.35 m
Release Duration	60 s
Scenario in the Simulation	User-defined model using parameters from short pipe (Ø8”) rupture

*Note: Elevation is made with reference to sea level, and dispersion is assumed to be over the sea.

Table 4.7 Inputs for ship-to-ship bunkering scenario C

Figure 4.14, Figure 4.15 and Figure 4.16 show cloud footprints, maximum cloud footprints and lethality footprints.

The ammonia cloud (based on AEGL-2) forms a puff about 2.5 minutes after the initial release during the day and moves rapidly downwind. The vaporisation rate from the pool (maximum radius 31 m) reached a peak of 131 kg/s at 60 s. The unstable atmosphere and higher wind speed during the day move the entire puff ammonia cloud randomly and rapidly downwind. The ammonia cloud concentration fell below AEGL-2 (220 ppm) approximately 27 minutes after the release.

At night, the puff ammonia cloud (based on AEGL-2) was formed only after about 4.5 minutes, with a peak pool vaporisation rate of 97.4 kg/s at 70 s. The initial footprint of the release at night follows a plume release model as ammonia continues to vaporise slowly from the pool. After the puff is formed, its movement is restricted by the more stable atmosphere and the lower wind speed at night. Hence, the distance travelled by the puff is limited. The ammonia cloud concentration fell below AEGL-2 (220 ppm) after approximately 17 minutes.

The higher wind speed during the day and the relatively more unstable atmosphere has brought the puff further downwind during the day compared to the night condition where the atmosphere is more stable, and wind speed is slightly lower at 2 m/s. The cloud footprint is smaller during the day at most points in time but moves over a larger distance as compared to the cloud at night. As a result, both the maximum cloud footprints (AEGL-2 and AEGL-3) are much larger for the release during the day compared to the night due to the higher movement of the ammonia vapour cloud that is moving in a puff model after pool vaporisation was completed.

The temperature difference between the sea surface and the ambient air is 3°C during the day and 4°C at night. The ambient air is warmer than the sea surface during the day and cooler at night. As a result, there is less vertical movement and dispersion of the ammonia cloud during the day than at night. Hence, it takes longer for the ammonia cloud concentration to fall below the AEGL-2 level during the day.

A total of 17,040 kg of ammonia is released in this scenario. The rainout rate during the day is 80% and 82.6% at night (shown in Table 4.8). The higher ambient temperature during the day resulted in more ammonia being released as a vapour cloud and dispersed by the wind and the atmosphere.

Based on the solubility constant applied in the simulation model, approximately 49% of the ammonia released will dissolve in seawater, with a peak dissolution rate of 192 kg/s during the day and 136 kg/s at night. The pool is fully vapourised or dissolved for approximately 3 minutes during the day and 5 minutes at night.

As a result, both the maximum cloud footprint and the lethality footprints are much larger for release during the day than at night. Both vaporisation rate and solution rate are higher during the day compared to the night, and hence a smaller pool remains on the water surface during the day compared to the night. The maximum cloud footprints for 1-hour AEGL-2 (160 ppm) reached a distance of approximately 6.6 km during the day and 3.2 km at night. Ammonia cloud concentration fell below 1-hour AEGL-2 (160 ppm) after 30 minutes of the release during the day and 19 minutes at night. The 3% lethality footprints reached an approximate distance of 1.3 km during the day and 700 m at night. Similarly, additional safety measures such as mandatory installation of ESD and use of Smart-Hose® will reduce the quantity released and the footprints. The movement of the vapour cloud can also be limited or blocked with emergency response installation, such as a water curtain or physical barriers on board vessels.

	Day 3C	% of Mass Released	Night 2E	% of Mass Released
Total Mass Released	17,040	-	17,040	-
Mass Released as Vapour Cloud	3,384	20%	2,964	18%
Mass Rainout as Pool	13,656	80%	14,076	82%
Mass Vapourised from the Pool	5,260	31%	5,680	33%
Mass Dissolved in Sea	8,396	49%	8,396	49%

Table 4.8 Mass balance for ship-to-ship bunkering scenario C

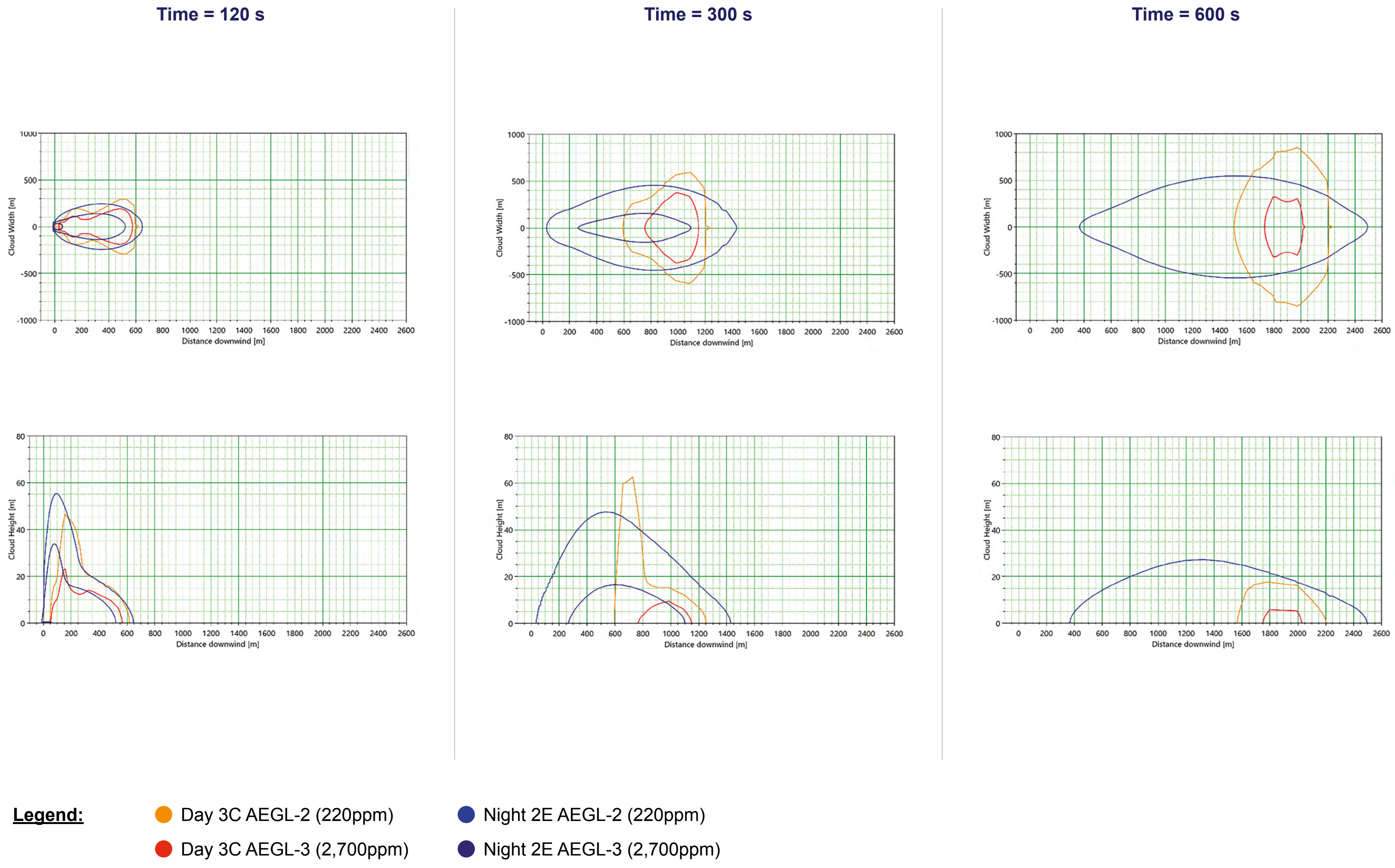
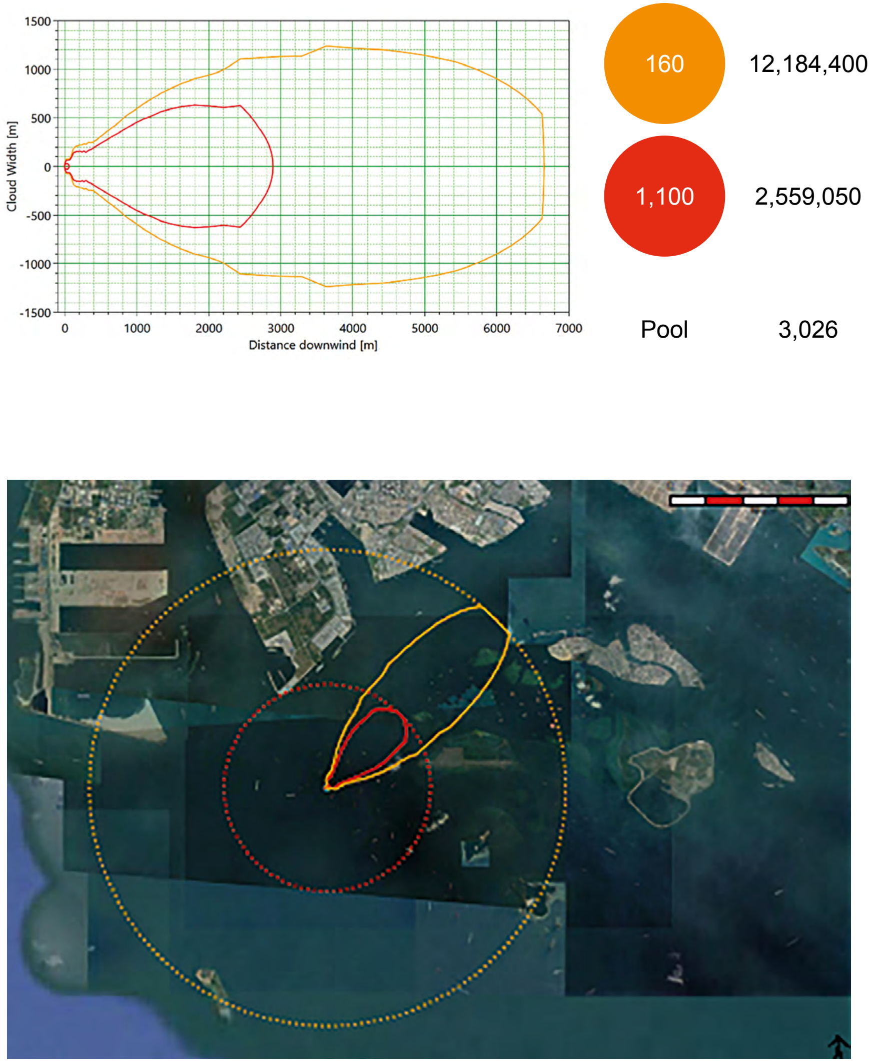
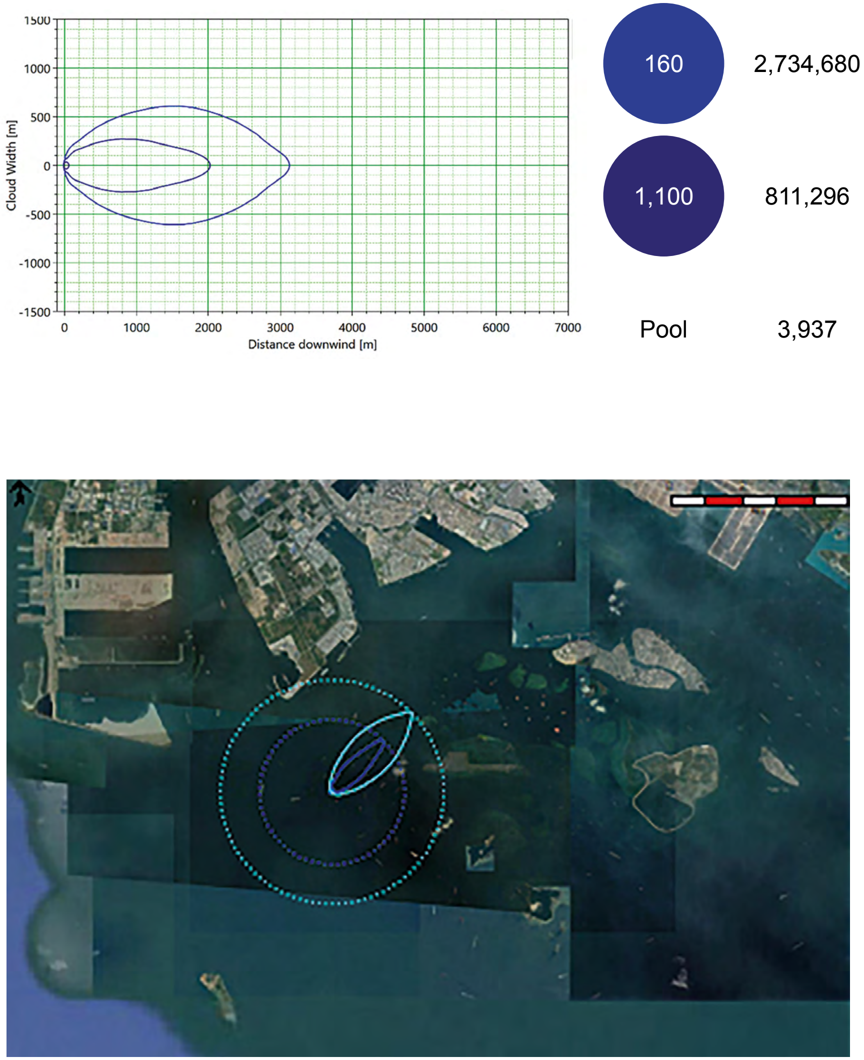


Figure 4.14 Cloud footprints for ship-to-ship bunkering scenario C



Cloud Max. Footprint – Day 3C

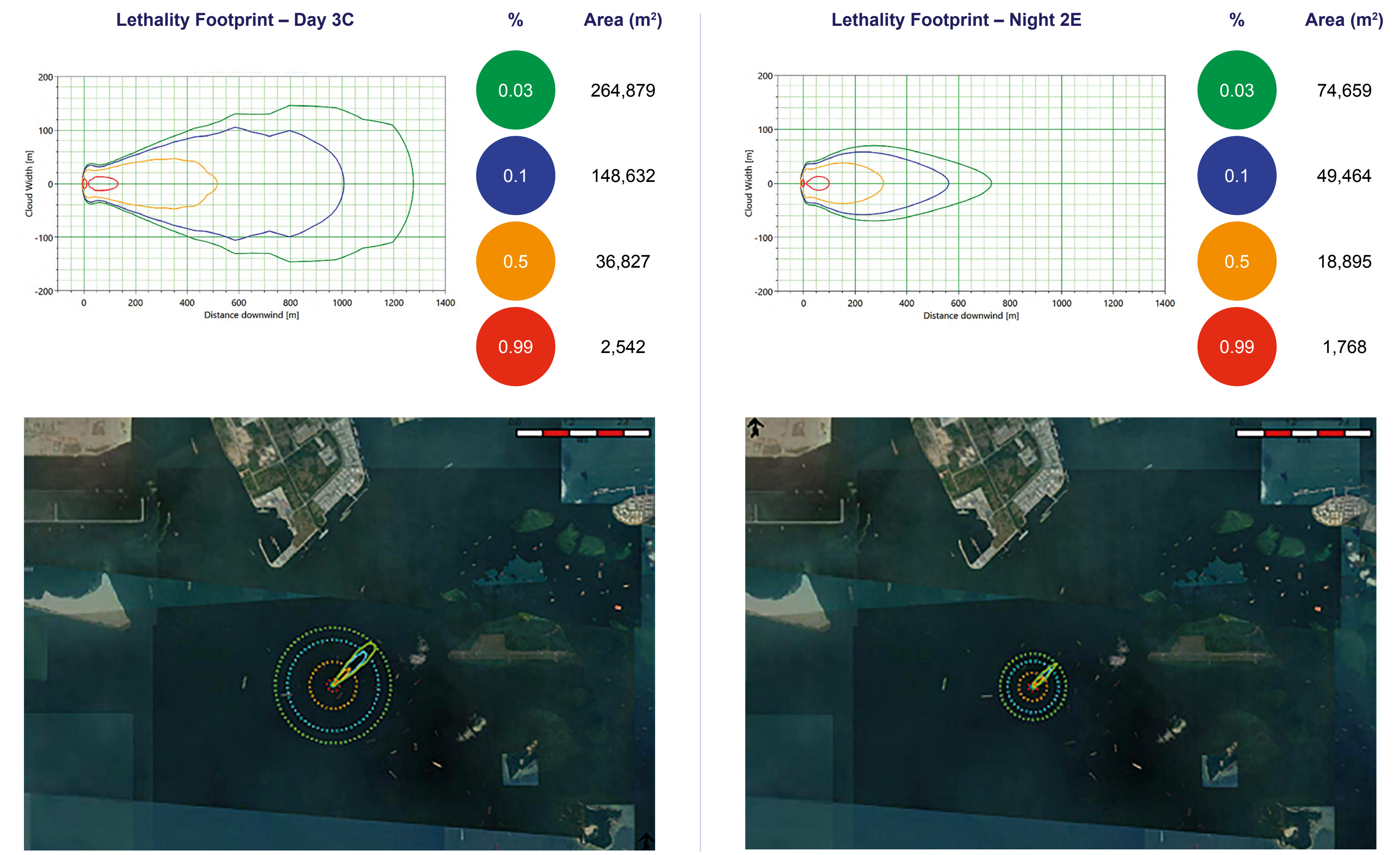
ppm	Area (m^2)
160	12,184,400
1,100	2,559,050
Pool	3,026



Cloud Max. Footprint – Night 2E

ppm	Area (m^2)
160	2,734,680
1,100	811,296
Pool	3,937

Figure 4.15 Maximum cloud footprints for ship-to-ship bunkering scenario C



Lethality Footprint – Day 3C

%	Area (m²)
0.03	264,879
0.1	148,632
0.5	36,827
0.99	2,542

Lethality Footprint – Night 2E

%	Area (m²)
0.03	74,659
0.1	49,464
0.5	18,895
0.99	1,768

Figure 4.16 Lethality footprints for ship-to-ship bunkering scenario C

4.4.5 SIMOPS - Scenario D

Table 4.9 shows the inputs for ammonia release scenario D during SIMOPS operation.

Parameters	Value
Location	PSA Pasir Panjang Terminal
Bunker Vessel Type	17,500 m^3 NH_3 carrier
Container Ship Type	14,800 TEU LNG dual fuel container ship
Temperature & Pressure	-33.4°C, 1 atm
Connection	8” (203 mm) hose, 40 m long
Flowrate	1,500 m^3/h
Hose Diameter	8 inch
Orifice Size	8 inch
Release Direction	Horizontal
Release Elevation*	13.35 m
Release Duration	60 s
Scenario in the Simulation	User-defined model using parameters from short pipe (Ø8”) rupture

*Note: Elevation is made with reference to ground level at the terminal for dispersion over land. Refer to Scenario C for dispersion over the sea.

Table 4.9 Inputs for SIMOPS scenario D

Figure 4.17, Figure 4.18 and Figure 4.20 show cloud footprints, maximum cloud footprints and lethality footprints of scenario D for the dispersion of ammonia cloud as a plume downwind over land. The AEGL-2 ammonia cloud remained as a plume model discharge for more than 20 minutes. The ammonia cloud concentration only falls below 10-minutes AEGL-2 (220 ppm) 48 minutes after the initial release during the day and 60 minutes after the initial release at night as ammonia continues to vaporise slowly from the pool on the land surface throughout the 1-hour period.

For the dispersion over land, the unstable atmosphere and higher wind speed during the day dispersed and diluted the ammonia cloud more than the stable and lower wind speed at night for the dispersion over land. The ambient air is cooler than the land surface on both day and night, and the temperature difference between the land surface and the ambient air is 5°C during the day and 2.5°C at night. The larger temperature difference results in greater vertical movement and dispersion of the ammonia cloud. Hence the cloud footprints during the day are smaller than the cloud footprints at night for dispersion over land. This is the opposite of what was observed in Scenario C for dispersion over water.

Although the 1-hour AEGL-2 maximum cloud footprint (160 ppm) reached a downwind distance of 1.5 km during the day and 2.5 km at night, the concentration is reduced rapidly by the dispersion and dilution effect of the atmosphere. Hence, the lethality footprints for the ammonia cloud dispersion over land are small, with the 3% lethality footprint reaching a maximum downwind distance of 310 m during the day and 340 m at night.

	Day 3C	% of Mass Released	Night 2E	% of Mass Released
Total Mass Released	17,040	-	17,040	-
Mass Released as Vapour Cloud	3,162	19%	2,505	15%
Mass Rainout as Pool	13,879	81%	14,535	85%
Mass Vapourised from the Pool	13,357	78%	5,680	75%
Mass Remaining in the Pool	522	3%	1,675	10%

Table 4.10 Mass balance for SIMOPS scenario D (dispersion over land)

Similar to the release over the sea, the rainout rate is approximately 80% to 85% of the total ammonia released, with the remaining dispersing in the atmosphere upon release (as shown in Table 4.10). The rainout pool on the land vapourised slowly, reaching a peak of approximately 30 kg/s at around 90 s after the release. 4% and 12% of the total ammonia released remained on the land surface at the 1-hour mark after the release during the day and night, respectively. Pool temperature on the land reached a minimum of -58°C to -60°C. The pool vaporisation rate is very low compared to the pool formed over the sea, where the pool vaporisation rate reached a maximum of 131 kg/s for the day and 97 kg/s for the night within 1 minute of release. This is due to a large amount of heat released by the exothermic dissolution of ammonia in seawater.

Figure 4.19 and Figure 4.22 show the dispersion of ammonia clouds over the sea at the SIMOPs location. The scenario for dispersion over the sea is identical to Scenario C. The ammonia cloud (10-min AEGL-2 and AEGL-3) formed a puff at approximately 2.1 to 2.4 minutes and 3.6 to 4.5 minutes after the release during the day and at night, respectively. The puff of ammonia cloud formed travelled rapidly and randomly downwind in the unstable and higher wind speed atmosphere during the day. The stable and lower wind speed at night had limited the motion of the entire ammonia puff. As a result, both the maximum cloud footprint and the lethality footprints are much larger for release during the day than at night.

The 3% lethality footprint for the dispersion of ammonia clouds over the sea during the day is 7 times larger than the footprint for the dispersion over land. The 3% lethality footprints for the dispersion of ammonia clouds over the sea at night is only 1.2 times larger than the footprint for the dispersion over land.

A safety distance of 300 m to 350 m on land is required based on this simulation for ammonia bunkering for similar container ships at terminals or jetties. A safety distance of 1.3 (day) and 700 (night) is required for ammonia bunkering for similar container ships at the anchorage.

Lethality footprints at different heights under release scenario D are also simulated and presented in Figure 4.20 (1.5 m height) and Figure 4.21 (0.5 m height). For 3%, 10%, 50% and 99% lethality footprints, the footprint areas at 1.5 m height are smaller than those at 0.5 m height for both day and night conditions. Therefore, when people are escaping from ammonia, changing from standing to crawling down does not reduce the fatality rate. 99% lethality footprint increased by 2.6 times during the day and 3.8 times at night when a person changed from standing to crawling or lying down. The lethality rate increases significantly when a person is closer to the ground in this scenario.

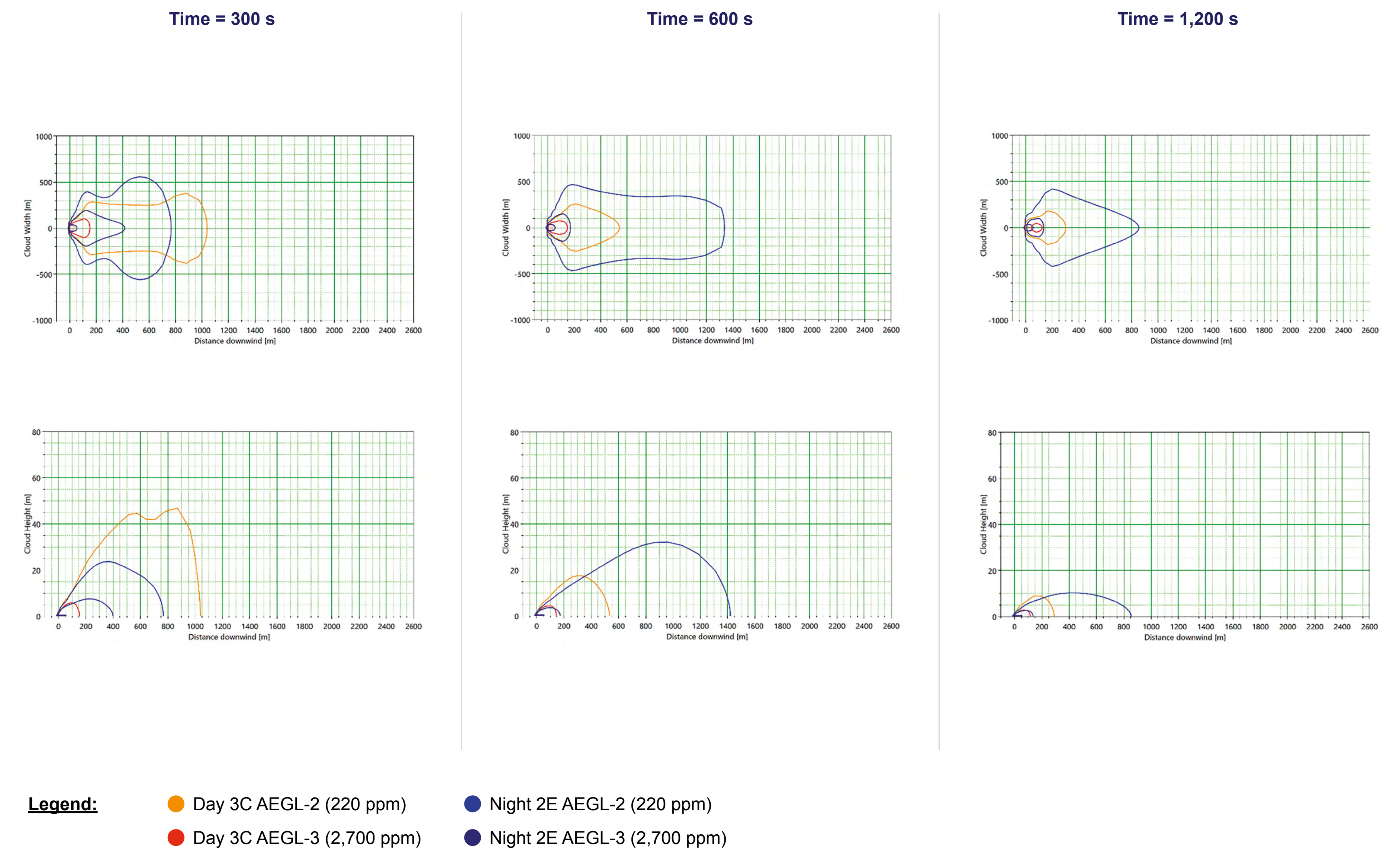
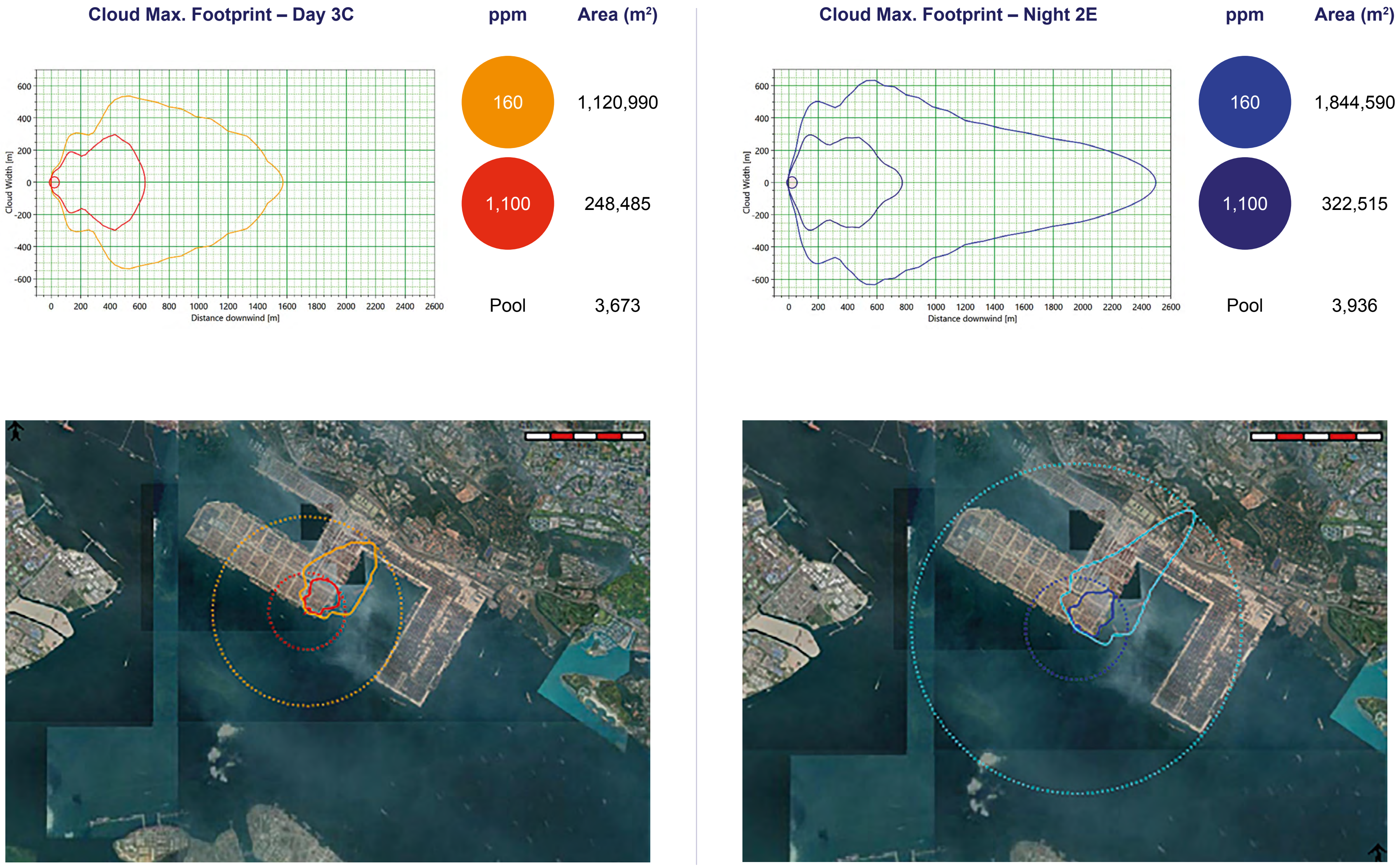


Figure 4.17 Cloud footprints for SIMOPS scenario D (dispersion over land)



Cloud Max. Footprint – Day 3C

ppm	Area (m^2)
160	1,120,990
1,100	248,485
Pool	3,673

Cloud Max. Footprint – Night 2E

ppm	Area (m^2)
160	1,844,590
1,100	322,515
Pool	3,936

Figure 4.18 Maximum cloud footprints for SIMOPS scenario D (dispersion over land)

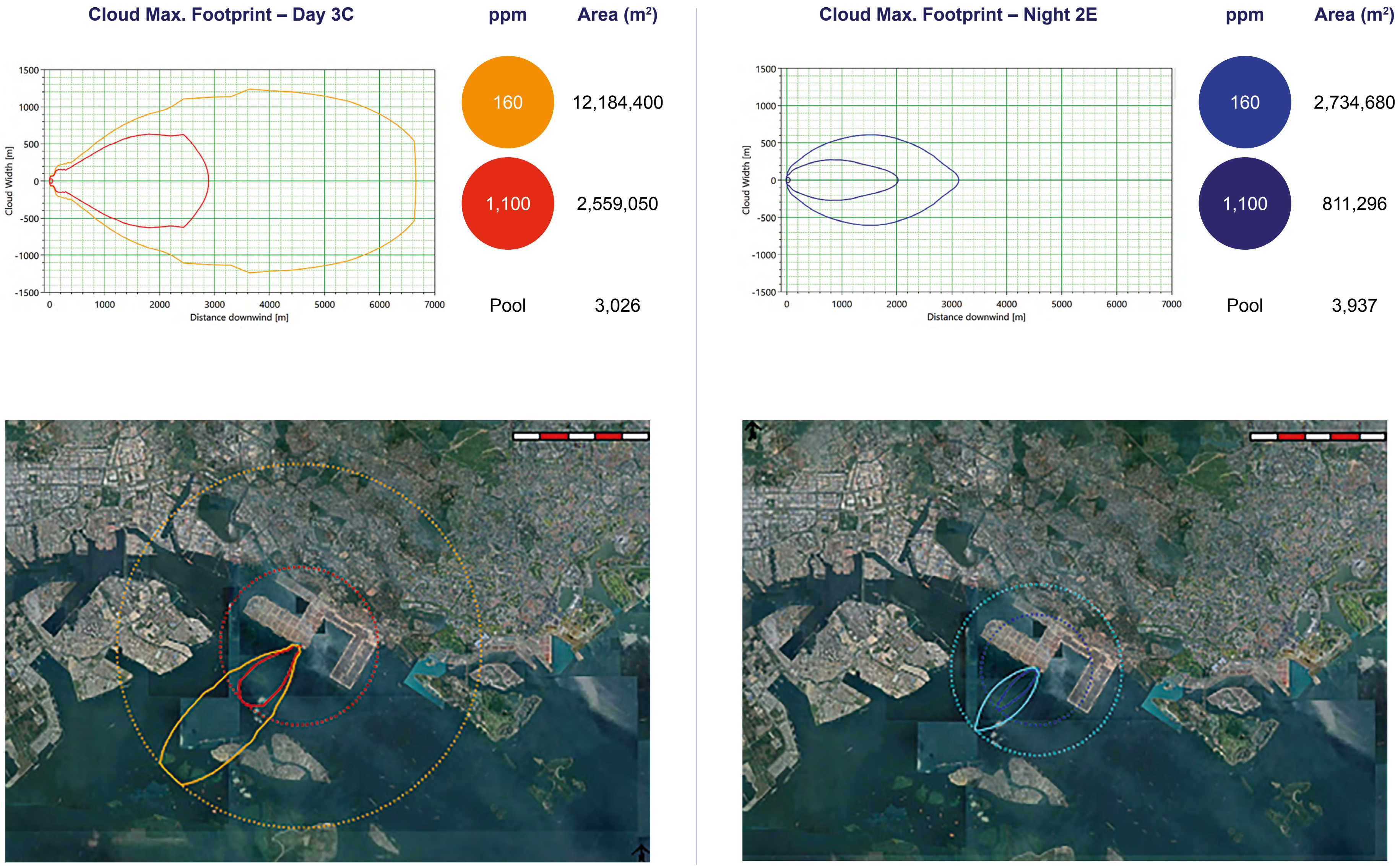
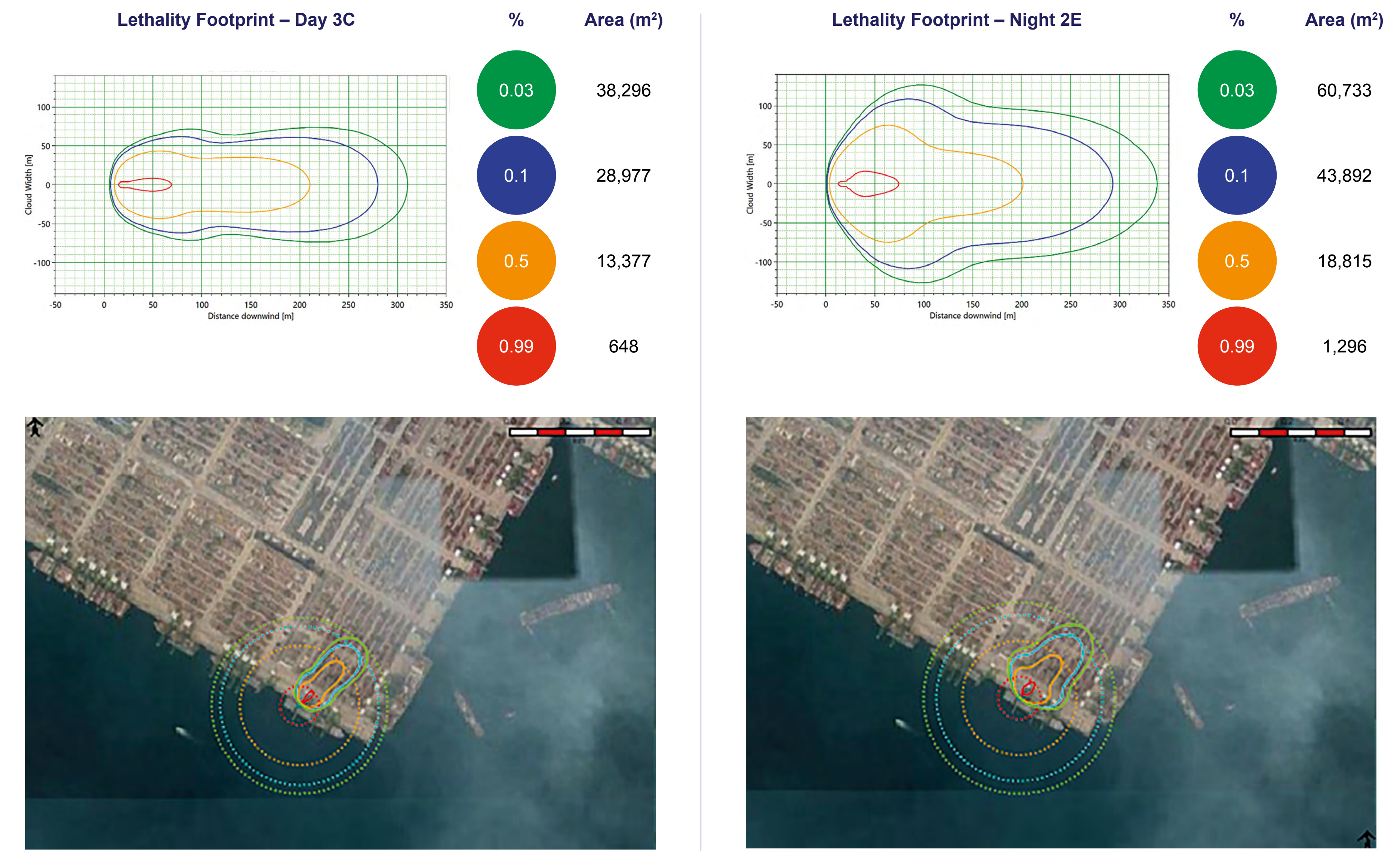


Figure 4.19 Maximum cloud footprints for SIMOPS scenario D (dispersion over the sea)



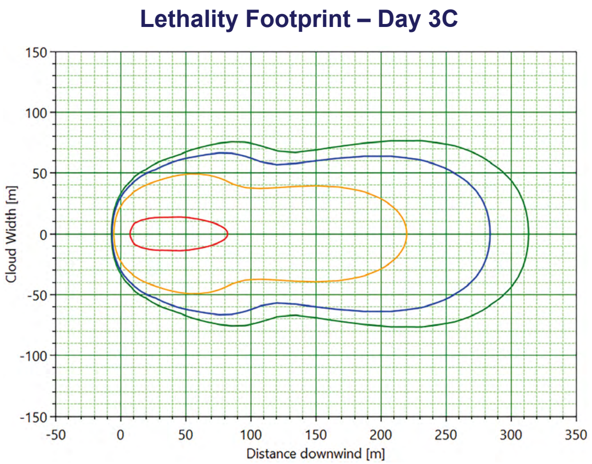
Lethality Footprint – Day 3C

%	Area (m^2)
0.03	38,296
0.1	28,977
0.5	13,377
0.99	648

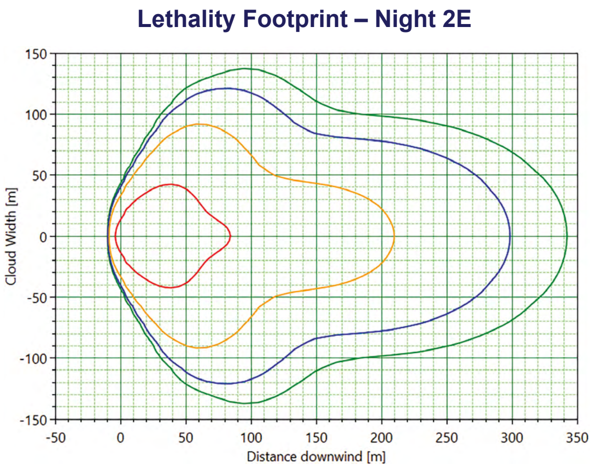
Lethality Footprint – Night 2E

%	Area (m^2)
0.03	60,733
0.1	43,892
0.5	18,815
0.99	1,296

Figure 4.20 Lethality footprints for SIMOPS scenario D (dispersion over land at 1.5 m)

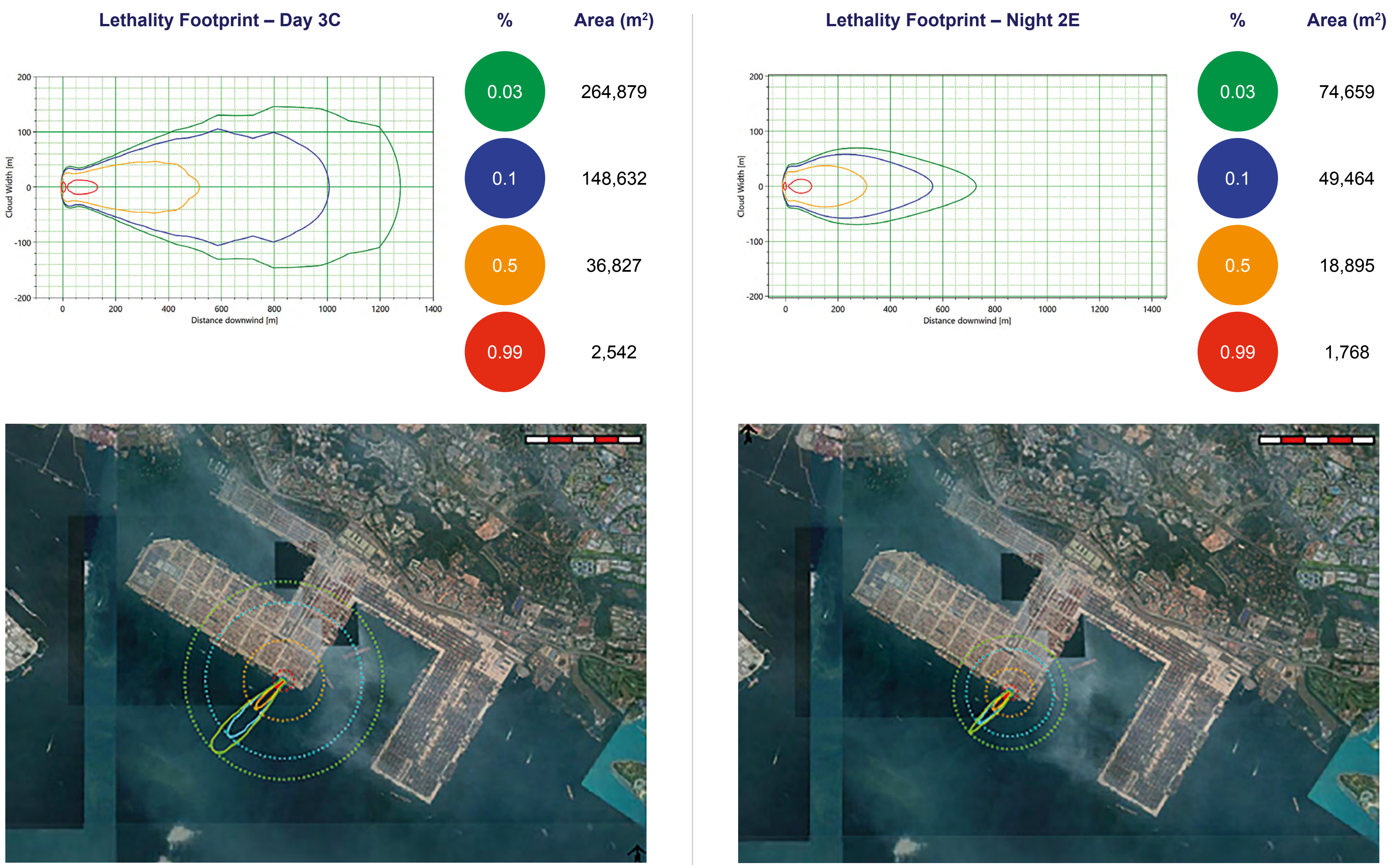


%	Area (m^2)
0.03	41,996
0.1	32,635
0.5	16,951
0.99	1,679



%	Area (m^2)
0.03	67,004
0.1	50,155
0.5	24,481
0.99	4,974

Figure 4.21 Lethality footprints for SIMOPS scenario D (dispersion over land at 0.5 m)



Lethality Footprint – Day 3C

%	Area (m²)
0.03	264,879
0.1	148,632
0.5	36,827
0.99	2,542

Lethality Footprint – Night 2E

%	Area (m²)
0.03	74,659
0.1	49,464
0.5	18,895
0.99	1,768

Figure 4.22 Lethality footprints for SIMOPS scenario D (dispersion over the sea)

4.4.6 Venting - Scenario E1 & E2

Ammonia bunkering operation steps are introduced in Chapter 3. After gas inerting in the pre-delivery process, the system is purged with ammonia vapour to remove the remaining nitrogen. In the post-delivery process, a stripping process is required to drain the liquid remaining in the bunker hose. If the ammonia vapour during the purging and stripping process is vented into the atmosphere, the toxic effects of the ammonia cloud need to be studied. In this section, venting during the truck-to-ship bunkering (Scenario E1) and venting during ship-to-ship bunkering (Scenario E2) are selected.

The inputs for the simulation of venting scenario E1 and scenario E2 are summarised in Table 4.11. The venting volume is assumed to be 5 times the volume of the bunker hose. Ammonia vapour is assumed to be the ideal gas. The total quantity of venting ammonia vapour can be calculated according to the Ideal Gas Law.

$$n = PV/RT$$

Where P, V and T are the pressure, volume and temperature; n is the molarity of the substance; R is the ideal gas constant.

	Scenario E1	Scenario E2
Bunkering Mode	Truck-to-ship	Ship-to-ship
Bunker Hose	2-inch, 15 m	8-inch, 40 m
Vent Mast / Pipe	0.5 inch	2-inch
Venting Point	Tugboat	Container ship
Ammonia Release Volume	0.15 m^3	6.48 m^3
Temperature of Ammonia Vapour	30°C	-30°C
Gauge Pressure	0.015 bar	0.015 bar
Orifice Size	0.5 inch	2-inch
Release Direction	Horizontal	Horizontal
Release Elevation	8 m above jetty	54 m above sea

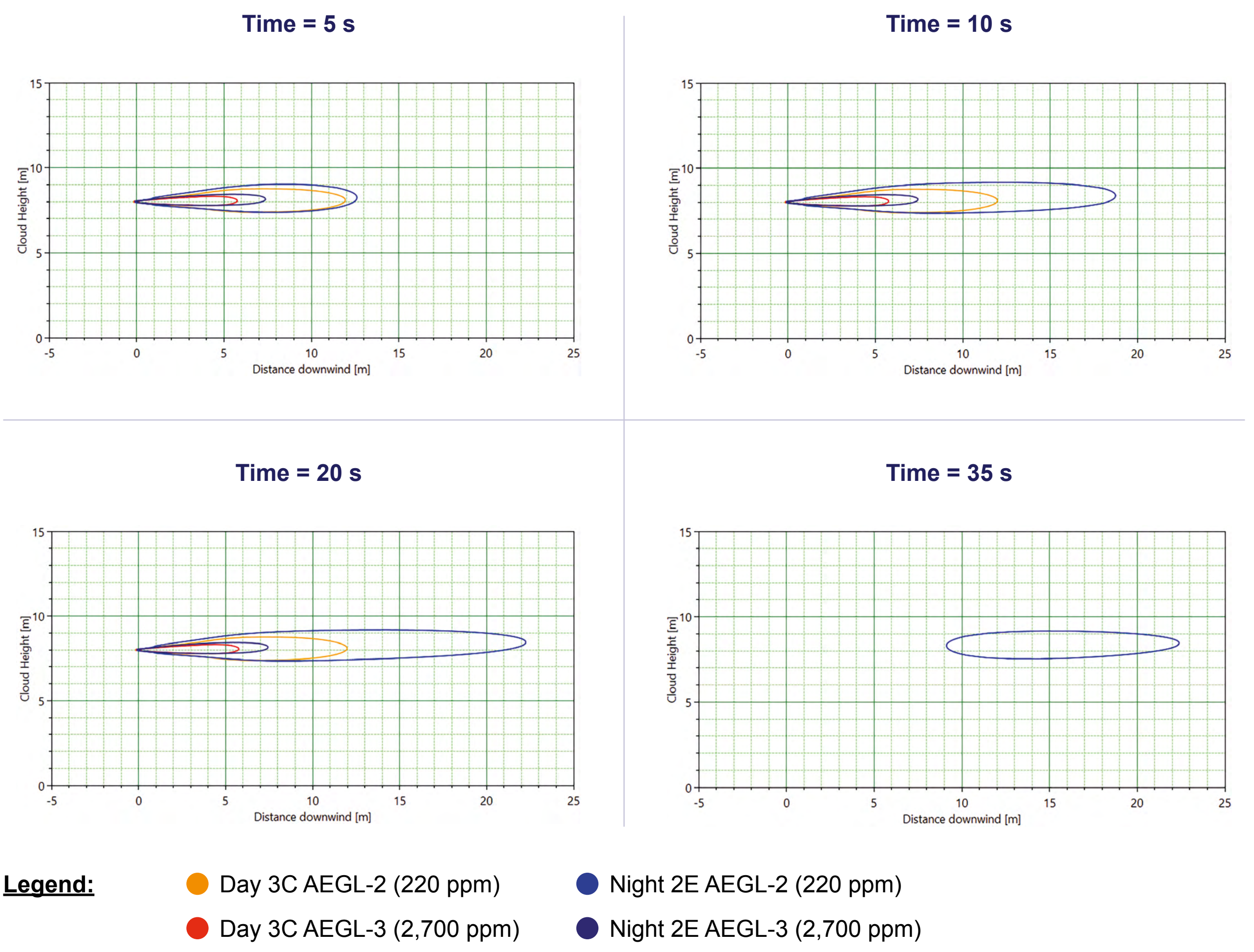
Table 4.11 Inputs for venting scenarios E1 & E2

Figure 4.23 shows the side view of venting scenario E1 during the truck-to-ship bunkering operation. The ammonia cloud is carried downwind at an elevated height in both day and night conditions without reaching the deck or sea level.

The side views of the clouds increase over time, reaching the maximum at around 23 s. The maximum distance of ammonia AEGL-2 and AEGL-3 clouds is about 12 m and 5.7 m during the day and 22.3 m and 7.4 m at night. The dispersion during the day is smaller than those at night. The AEGL-2 and AEGL-3 clouds are fully diminished within 34 s and 32 s during the day and within 38 s and 33 s at night.

Similar to venting scenario E1, the footprints of scenario E2 during the day are smaller than the footprints at night, as shown in Figure 4.24. The ammonia cloud remains elevated near the release height and does not reach the deck or sea level. The side views of the cloud increase over time, reaching a maximum of around 70 s. The maximum travelling distance of ammonia AEGL-2 and AEGL 3 clouds is 58 m and 27.5 m during the day and 112.6 m and 50.5 m at night. The AEGL-2 and AEGL-3 clouds are fully dispersed away within 106 s and 98 s during the day and within 109 s and 100 s at night.

Compared to the previous ammonia release scenarios described in Section 4.4.1 to Section 4.4.4, the toxic impact of venting scenario E1 and scenario E2 is much smaller. Ammonia vapour is lighter than air, and the venting point is high enough to ensure that the ammonia cloud will not touch down and cause casualties on the ground, deck, or sea level. Hence, in this case, there are no lethality footprints at the height of 1.5 m above the jetty for the truck-to-ship bunkering or at the height of 1.5 m above the deck for the ship-to-ship bunkering.


Time = 5 s

Time = 10 s

Time = 20 s

Time = 35 s

Figure 4.23 Side view of the cloud for venting scenario E1

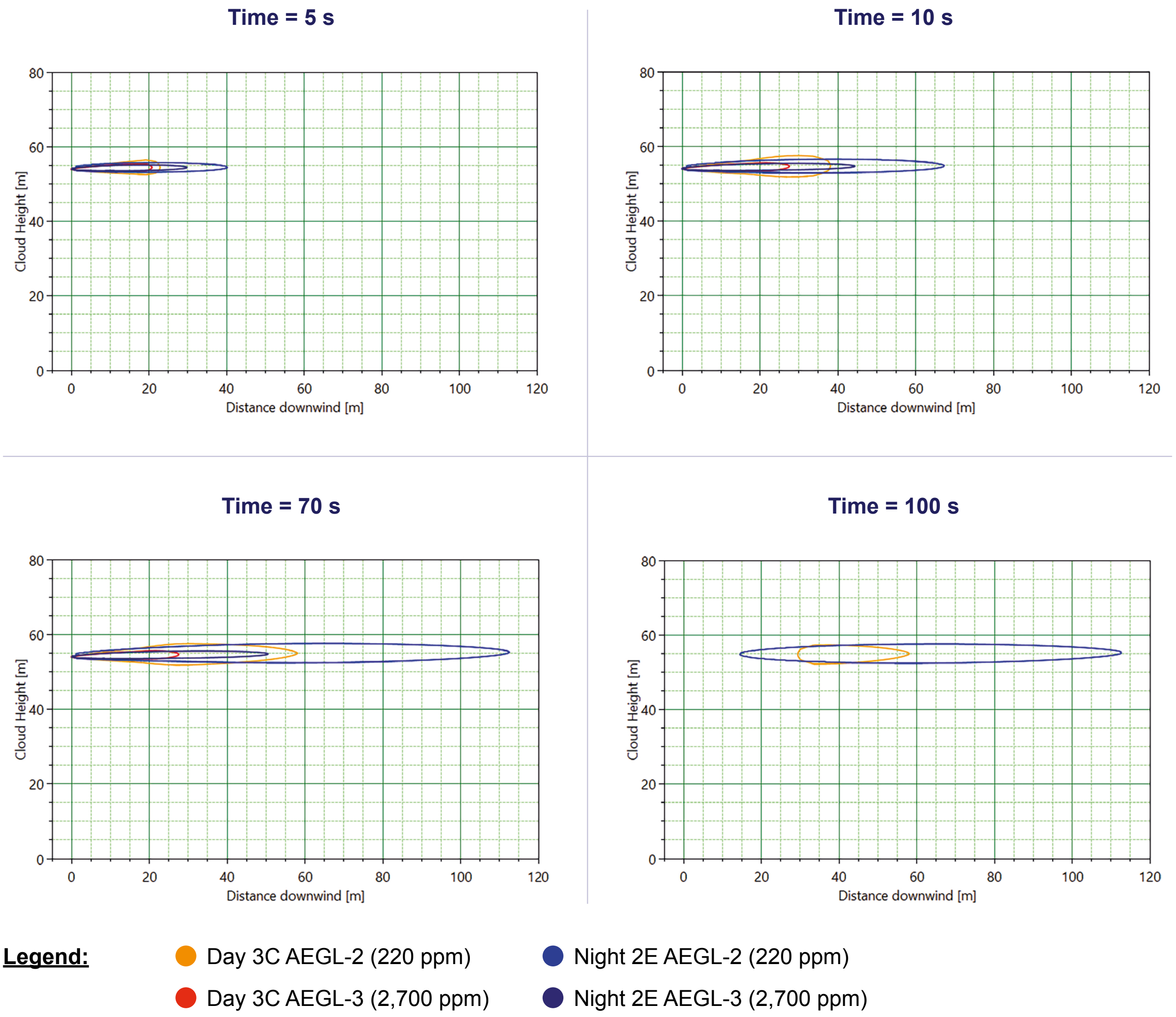


Figure 4.24 Side view of the cloud for venting scenario E2

Chapter
4

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Chapter
5

Mitigation Measures

The simulation results of ammonia dispersion in Chapter 4 are based on the condition that no mitigation measure exists. It is also based on the requirement of Singapore QRA that the isolation time of a fully automated blocking system is 1 minute. However, safety equipment must be present in the actual implementation of ammonia bunkering. For example, a Smart-Hose® can shorten the ammonia release time to a few seconds if the hose connection is the release point. ESD systems can reduce the likelihood of overfilling fuel tanks through automatic shutdown at a high level and reduce the amount of released ammonia by closing valves and stopping transfer pumps under hazardous conditions. These precautions can reduce ammonia release volume significantly, reducing the impacts on human beings and the surroundings.

In the chemical industry, the common methods of preventing or mitigating the dispersion of gases include using bunds, foam, solid barriers and fluid barriers in the form of water spray barriers, steam barriers or air curtains [1]. For liquid release, dilution, neutralisation and foam or solid covers are useful to reduce the toxicity of the chemical and the vaporisation rate. This study discusses mitigation measures during ammonia bunkering, including absorption, separation, and physical barriers.

5.1 Absorption and Separation

Water Curtain

A water curtain is one of the most effective and economical systems for ammonia post-release mitigation [2]. This makes use of the fact that ammonia is highly soluble in water; ammonia vapour can be dissolved and removed or reduced to a concentration below a harmful level. The mitigation effects include:

1. Mechanical effects of acting as a barrier;
2. Mechanical effects of dispersion and dilution by air entrainment;
3. Mechanical effects of imparting upward momentum;
4. Thermal effects by heating ammonia gas;
5. Physicochemical effects of gas absorption, with or without chemical reaction [3].

Ammonia vapour in the air can also be reduced effectively using adequate volumes of water applied through spray or fog nozzles. Downwind movement of the ammonia cloud can be controlled by directing the water fog nozzles towards the point of ammonia release from a downwind position. It should be noted that water should not be used directly on liquid ammonia spills as it will accelerate vaporisation due to the exothermic dissolution of ammonia in water. Water should only be directed in the form of fog or spray at the ammonia cloud rising from the liquid pool. In the event of a large vapour release from a tank, the tank should not be sprayed with water to avoid heating the ammonia liquid in the tank [4].

Several studies have proved that the peacock tail-type water curtain can decrease the ammonia concentrations in air and thus prevent the ammonia vapour cloud from travelling further distances [2] [5] [6]. Computational Fluid Dynamics (CFD) simulation is a popular tool to show how effectively a water curtain could mitigate ammonia dispersion. In CFD modelling, these numerical simulations were based on Navier-Stokes equations. They used the discrete phase model (DPM) Eulerian-Lagrangian framework to solve the relations between gas and water droplets, including the continuous phase (toxic gas) and discrete phase (water droplet) [2] [5]. Physical ammonia dispersion experiments and Goldfish tests were conducted to verify the simulation accuracy [2]. The simulation of the effectiveness of a water curtain agrees well with the experimental results that ammonia concentration decreases rapidly behind the curtain envelope.

The water curtain works by producing an obstacle-like stagnation and a swirling backflow behind it. Effective mitigation happens in an obstacle-like stagnation region [5], where the effectiveness is proportional to the total number and the average volume of a single droplet [11]. However, the discharge rate determines the maximum efficiency of the water curtain [2]. The distance between the water curtain and the release source can also affect efficiency, but it is not as significant as the discharge rate [2]. A multi-stage installation can be used to enhance performance [2].

In addition to the CFD simulation, mathematical models can be applied to investigate the effectiveness of ammonia absorption, taking into account the two-phase feature of the ammonia vapour cloud and the thermodynamic properties of the cloud-water curtain system [7] [8]. Mastellone et al. (2003) proved that the water curtain could intercept and absorb the ammonia cloud from accidents occurring in open areas [7]. It was found that the ammonia concentration in water droplets increases exponentially with water droplets' size dropping below 1 mm [8]. Hence, it is recommended to create droplets less than 1 mm to achieve high mitigation efficiency. A fog curtain with smaller water droplets can be used as a step forward. It is also possible to integrate different types of droplets producing mechanisms. A possible configuration may combine fine sprays and coarser sprays in one unit, creating a large absorption surface area and enhanced vertical dispersion in the path of the ammonia dispersing cloud [6].

Experience shows that using fogging nozzles, spray nozzles, or water curtains against an ammonia cloud or aerosol on land can result in the formation of a nasty aqua-ammonia run-off solution which can be difficult to cope with and dispose of in the hours after an accidental release. This solution may find its way into the drainage, stormwater or nearby waterways and create problems by the re-evaporation of ammonia gas or pH changes to waterways, potentially damaging marine life. The Incident Commander will need to evaluate the ammonia cloud and weather conditions to assess whether water dispersion will be the best way to mitigate the potential problem. There have been many examples where water dispersion techniques were used to mitigate an ammonia cloud. However, this exacerbated the situation on the ground, as described above. It would have been more desirable to tarp and cover the aerosol and knock the ammonia down to a cold liquid pool in the bund where it can evaporate as a clear gas and rise up into the atmosphere. This will limit the impact on the surroundings.

Absorption

In addition to the water curtain, solid-state adsorbent provides an alternative way to capture ammonia. Several inorganic salts are known to react with ammonia and fix it into the solid framework of the complexes according to the following chemical reaction [9].

$$M_aX_b(NH_3)_n + (m-n)NH_3 \Leftrightarrow M_aX_b(NH_3)_m$$

Where M is an alkaline earth metal; X denotes the fluoride (F), chloride (Cl), bromide (Br), iodide (I), sulphate (SO_4), or nitrate (NO_3) groups; (m-n) is the indication of ammonia adsorption capacity.

Several ammonia adsorbents are considered, such as anhydrous $MgCl_2$, $CaCl_2$, and $BaCl_2$. A study was performed on these absorbents at temperatures ranging from 25°C to 300°C [9]. It was found that $MgCl_2$ has the maximal sorption capacity. However, the dynamic sorption capacity decreases with temperature [9]. At 25°C, 1 mole of anhydrous $MgCl_2$ can absorb 3.2 moles of ammonia [9]. However, these absorbents have not found large-scale, widespread practical use in mitigating ammonia releases.

Neutralisation

The ammonia liquid collected in the bund (on land), containment (onboard vessel) or within the boom (water bodies surfaces) can be absorbed or neutralised by absorption or neutralisation agent to prevent further vaporisation of ammonia vapour into the atmosphere [12]. However, a neutralisation agent shall be applied on a mole-to-mole basis. 3,000 tonnes of ammonia leakage, of which approximately 2,000 tonnes will dissolve in water, and 4,300 tonnes of hydrochloric acid will be required to neutralise the ammonia in water. Neutralisation chemicals are normally unavailable in large quantities, and it will also be hazardous to handle and transport such large quantities of acids. In addition, the neutralisation reactions are exothermic, and the large quantities of heat generated may result in further vaporisation of ammonia into the atmosphere. The use of solids to absorb the ammonia vapour may not be operationally and economically feasible. A mechanical blower can project large quantities of pulverised or dust-like sorbent through the ammonia vapour cloud. However, the availability and transportation of such large quantities of sorbent and the subsequent clean-up of the sorbent from the water will limit the applicability of this method.

5.2 Physical Barriers

Solid Physical Barriers to Limit the Dispersion

Solid physical barriers such as a fence or wall (permeable or impermeable) can be erected to contain or limit the spread of ammonia clouds [1]. A physical barrier, such as a “tarp and cover”, placed in front of an ammonia aerosol release, contains the released liquid and knocks it down to be collected within a confined bund or containment on board. This can minimise the immediate effects of the aerosol and dense gas cloud. A study was conducted to test the effectiveness of various readily available objects carried by all fire trucks to increase the number of mitigation tools available to first responders and pre-deployment groups arriving at the accident scene. It was found that 84% of the released mass can be recovered, and downwind ammonia gas concentrations can be reduced by 85% by the use of “tarp and cover” methods at the release point. Increasing the distance between the physical barrier and the release point will reduce mass recovery to about 50% or more. This method can be deployed as an initial measure in an emergency as it is simple and requires less preparation. The risk of ammonia deflagration outdoors in the open air is incredibly low because the concentration is unlikely to rise to Lower Flammability Limit (LFL), and the very high ignition energy required will not usually be available. An accidental ammonia release indoors in a confined space is a different story, where the concentration can easily rise to LFL, and with the right ignition energy source, a deflagration can occur [14].

On the other hand, releases with impingement such as “tarp and cover”, which knock the ammonia down into a cold liquid pool in the bund, will greatly limit the negative effects the aerosol or dense gas cloud has otherwise had on the surrounds. However, the liquid pool’s evaporation that delivers clear light gas into the atmosphere may extend for a longer duration until all the liquid is gone. In some cases, the liquid could be pumped back into a tank and returned to the original containment system to speed up the process.

Ammonia cloud footprints can be reduced by limiting the evaporation rate of the liquid pool after the spill. The evaporation rate of ammonia, particularly refrigerated ammonia, can be greatly reduced if the spill is contained within a bund or containment structure. A bund with a smaller floor area but higher walls have a smaller surface area available to heat the liquid ammonia into gas. The high wall also acts as a physical barrier to the flow of the vapour horizontally. The material used in the bund construction or containment will also affect the heat transfer rate to the liquid ammonia pool in the bund. Heat transfer rate can be reduced by more than 95% by using an insulating material such as polyurethane and Cellofoam compared to uninsulated concrete [1].

For spillage into the sea, placing a boom around the spill can help limit the ammonia pool's spread on the water, reducing the ammonia's evaporation into the atmosphere. The boom shall be rapidly deployable and is constructed of material inert to ammonia. Existing floating booms for oil spills or specialise customise booms for ammonia booms may be used [12]. Based on PHAST simulation output and literature data, the depth of the liquid ammonia pool is only a few inches, reaching a maximum of 20 to 30 cm in the initial few seconds of release. Hence surface booms are sufficient to limit the spread of the ammonia liquid pool.

Foams can be used to reduce the rate of evaporation by insulating the surface of the ammonia liquid pool. The foam can absorb and scrub the vapour and aerosol from the ammonia cloud. The application of foams to reduce vaporisation from liquid ammonia spill was proven effective and economical [12] [13]. However, the foam must be suitable and compatible with ammonia. Vapour mitigation and neutralising agent foams to suppress ammonia vapour and maintain a neutral pH level are available commercially for liquid ammonia spills [4]. Similar methods of containment are used for LNG, where high expansion foam is recommended by NFPA 11 and NFPG 471 for LNG spill hazards mitigation [13].

Isolation Room

Cargo officers, chief engineers and other crews shall be trained in safe work practices and understand all normal and non-routine operations tasks. They shall be aware of ammonia hazards and are trained for emergency operations. When there is an ammonia release, the ammonia vapour cloud travels downwind, clinging to the surface, and moving upward only after a great distance when it gains buoyance by ambient heat and dilution. This gives a clear indication of the evacuation route, and people shall escape immediately, laterally and upwind to a safe refuge area [10].

Escaping to an isolation room can be an alternative measure if there is no upwind route. The isolation room, equipped with an airlock, should be designed to stop the infiltration of ammonia. At the same time, the isolation room should be equipped with an ammonia scrubber, allowing the intake of clean, fresh air to support the breathing of refugees. Any shower room in the amenities sections can be used as a very effective Shelter-in-Place area in an ammonia emergency. They need to turn off ventilation, seal around doors, turn on the shower with towels, and use wet cloths over the mouth and nose. The running water shower will absorb ammonia from the air in the room and take it down the drain, which will keep the concentrations in the room at manageable levels. A good practice is that each deck shall be equipped with at least one isolation room to ensure that people can seek shelter quickly and stay long enough until the ammonia level drops below a harmful level by natural dispersion and dilution. Based on the ammonia handling experience, decontamination showers and eyewashes shall be maintained in operational conditions and prominently marked so that the locations can easily be identified.

Blower to Change Release Direction

Release direction significantly impacts the ammonia cloud coverage in a three-dimensional space. Our study has shown that the vertical upwards release results in the largest lethality footprints for both day and night conditions. Based on the 3% lethality footprints, if the vertical release can be prevented, the lethality footprints will be reduced by 70% to 80% if the release is during the day and more than 90% if the release takes place at night. From the designing perspective, the overall system shall be designed so that any possible vertical upward release is limited to minimum probability. As an additional measure, blower fans can be used to change the ammonia dispersion direction, which creates a local space where ammonia is directed away from the escape route. Moreover, suction fans installed near the potential release points can also help prevent ammonia from accumulating near the release point. A more detailed investigation and validation will be considered in our future work.

Chapter 5

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Chapter
6

Conclusion

Ammonia is a carbon-free fuel that finds potential in reducing global GHG emissions. It is feasible to produce ammonia from renewable or low carbon feedstocks, giving significantly reduced life cycle GHG emissions of ammonia to be used as a fuel. Ammonia can easily be condensed into liquid at relatively low pressures and ambient temperatures (e.g. -33°C at 1.01 bara/1 atmospheric pressure or +25°C at 10 bara), making its distribution easier and cheaper than other types of cryogenic liquid fuels such as LNG and liquid hydrogen. The existing worldwide infrastructure to transport ammonia as fertiliser has been operating for many decades. For marine fuel application, anhydrous ammonia has several unique characteristics that make its storage, transportation, handling, bunkering and energy conversion different from conventional marine fuels, which deserves a comprehensive investigation.

Most of the world's current ammonia production is used for fertiliser and other industries. Therefore, a massive increase in production is needed to provide fuel for the maritime industry. The use of ammonia in the maritime sector may compete with the ammonia demand from other sectors, such as fertilisers and biofuel production, if additional production is not brought online. Both green and blue ammonia are seen as the potential marine fuel to achieve maritime decarbonisation aspirations. However, their production is currently on a small scale and limited to a few countries. Green ammonia production relies on hydrogen produced from wind, solar, biomass or even nuclear energy, which is expected to achieve large-scale production. Blue ammonia is produced when carbon dioxide from grey ammonia production is captured and sequestered. Future increased use of ammonia will require appropriate NO_X mitigation.

The liquid and gaseous phase physical states of ammonia follow the principles prescribed by the pressure-enthalpy diagram. The diagram can help illustrate boil-off gas and flash gas management, and rollover prevention. There are numerous possible ammonia bunkering combinations determined by the modes of operation, the physical state of ammonia and the types of supply and receiving vessels/tanks. The safest and most popular way of storing and shipping (by sea) anhydrous ammonia liquid globally at present is to use atmospheric pressure and insulated tanks, holding the liquid at -33°C. The most preferred option for ammonia bunkering in Singapore is ship-to-ship bunkering. Liquid ammonia at -33°C will be pumped from one onboard atmospheric pressure tank to the other onboard atmospheric pressure tank via an interconnecting hose. The possible ammonia bunkering locations could be in the western anchorages designated for chemical and LPG tankers.

This study has attempted to develop an ammonia bunkering process with a simple configuration. There are 8 main steps involved: initial precooling, bunker hose connecting, 1st inerting, purging, transferring, stripping, 2nd inerting and bunker hose disconnecting. However, the actual operation of ammonia bunkering has not been established due to the lack of practical experience and concerns about its toxicity. When the toxic impact of an ammonia release is concerned, the best choice is to run experiments to find out the dispersion pathway and the cloud coverage. The next alternative is to run scenario-based simulations by established gas dispersion models. And in this study, there are six scenarios chosen and simulated extensively by PHAST software.

Ammonia release induces several phenomena, as follows. Suppose anhydrous ammonia is released only as a gas; it is lighter than air and will rise into the atmosphere and then drifts horizontally in the prevailing wind direction, posing a relatively lower hazard and risk to the people around. When liquid ammonia is released from refrigerated atmospheric storage tanks on land, the released liquid, in the absence of water, will slowly vaporise, posing a relatively low hazard and risk. When sub-cooled ammonia liquid is released from a hose or loading arm, there will be little flash gas to propel the escaping liquid into aerosols, posing a medium hazard and risk level. However, if pressurised saturated ammonia liquid at ambient temperature is released, it will create an aerosol cloud that is violently propelled by the flash gas. The ammonia cloud will pose a high hazard and risk level to the surrounding area.

Based on the review of the literature, safety reports and consultation with industry partners, it can be concluded that leakages from the rupture of connecting hoses or pull-away incidents are one of the most common causes of the loss of containment for ammonia bunkering. The hoses are routinely handled by people in a dynamic work environment and are subjected to a high degree of stress and wear-and-tear. The entire hose assembly system is the weakest link in transferring and bunkering operations.

Simulations were carried out for various bunkering modes: shore-to-ship, truck-to-ship, ship-to-ship and SIMOPS, which include four loss-of-containment scenarios. The 3% lethality footprint is used as an indicator for ease of understanding of the impact.

- *Scenario A Shore-to-Ship bunkering:* A total of 17,040 kg of ammonia is released in 1 min from the refrigerated storage with a rainout rate of more than 80%. The 3% lethality footprints reach a maximum downwind distance of 370 m during the day and 400 m at night.

- *Scenario B Truck-to-Ship bunkering:* 198 kg of ammonia is released in 1 min from the pressurised storage condition, with no rainout, and the vapour cloud forms a puff right after the end of the release. The ammonia cloud concentration falls below the AEGL-2 level by about 4 min during the day and 7 min at night. Although the maximum cloud footprint has reached a distance of approximately 800 m, the 3% lethality footprint is less than 100 m from the release source for both day and night conditions.

- *Scenario C Ship-to-Ship bunkering:* A total of 17,040 kg of ammonia is released in 1 min with a rainout rate of approximately 80%, of which approximately 60% of this rainout will eventually be dissolved in seawater. The 3% lethality footprints reached a maximum distance of 1.3 km during the day and 700 m at night. The maximum cloud and lethality footprints are significantly larger during the day than at night.

- *Scenario D SIMOPS:* 17,040 kg of ammonia is released in 1 min. The dispersion pattern of ammonia over the sea is the same as that in scenario C. For the ammonia dispersion over land, the 3% lethality footprints reached a maximum distance of 310 m during the day and 340 m at night.

For bunkering operations at the jetty using a pressurised ISO tank, a safety distance of approximately 84 m is required in the worst-case scenario, assuming the hose rupture from the ISO tank is stopped within 1 min. This safety distance can be greatly reduced if safety devices are available to stop the leak within a shorter duration, and mitigation measures can be immediately activated and deployed.

For bunkering operations at the port using refrigerated ammonia carriers, a safety distance of approximately 310 to 340 m is required, assuming no additional safety devices or procedures are available to limit the release. However, it is not feasible to maintain such a large safety distance at a port. Hence, additional operational measures, such as reducing the response time to shut the valve and reducing the transfer flow rate, will be needed to ensure ammonia bunkering can be safely carried out at the port. The ability for immediate activation and deployment of emergency response equipment or procedures will also reduce the safety distance.

For bunkering operations at anchorage using refrigerated ammonia carriers, a much larger safety distance of 1.3 km for the day and 700 m for the night is required based on the worst-case scenario. Similarly, this safety distance can be reduced with additional operational precautions and installing safety and emergency equipment.

Based on the comparison of ammonia dispersion patterns over the sea and land, it can be concluded that the cloud footprints and the lethality footprints can be reduced significantly if the released ammonia rainout pool can be contained within the decks of the supplying and receiving vessels. The extent and impact of the release are much greater once ammonia enters the water bodies. However, it should be noted that this is only applicable to the release scenarios simulated in this study.

In addition to understanding ammonia dispersion, mitigation measures shall be considered to reduce the hazardous impacts of an ammonia release. Existing measures include water curtain, absorbent, and physical barriers that remove ammonia from the ambient or direct it to a no man's area. Among them, the water curtain is the most adopted, which still deserves further improvement for ammonia bunkering operations.

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