ITOPF

PROMOTING EFFECTIVE
SPILL RESPONSE

FATE, BEHAVIOUR AND POTENTIAL DAMAGE & LIABILITIES ARISING FROM A SPILL OF AMMONIA INTO THE MARINE ENVIRONMENT

Report for the International Group of P&I Clubs Alternative Fuels Working Group

May 2024

I. Introduction

ITOPF, as part of the International Group of P&I Clubs Alternative Fuels Working Group, has been requested to provide a series of brief summary documents to describe the expected fate and behaviours of the following alternative fuels and to outline the possible damage and liabilities that may arise from incidents involving vessels carrying these fuels as bunkers.

The alternative fuels covered are:

- Biofuels
- Liquefied Natural Gas (LNG)
- Liquefied Petroleum Gas (LPG)
- Hydrogen
- Ammonia
- Methanol

ITOPF has also been requested to provide a summary document for lithium-ion batteries as a new technology for vessel propulsion.

A review of Nuclear as a means of vessel propulsion will be described separately, with the summary report provided by ENCO.

This report shall focus on **ammonia** as a non-traditional marine fuel.

Ammonia is one of the most widely produced chemical compounds in the world with global production estimated to be 235 million tonnes (Mt) per year.[1] The primary uses of ammonia are within the petrochemical and fertiliser industries and as a refrigerant. Currently, ammonia is traded as aqueous ammonia (generally 28% ammonia in water) or as anhydrous ammonia (100% ammonia). For the purpose of this report, 'ammonia' refers to anhydrous ammonia (NH_3).

Ammonia is considered to be a promising low- or zero-carbon fuel for the shipping industry, as it is easier to store than LNG or hydrogen and does not have any tank-to-wake emissions, meaning that it does not have any direct CO_2 emissions when combusted on-board. However, well-to-tank emissions, upstream CO_2 emissions from the production, transportation, transformation and distribution of the fuel to the vessel, vary depending on the source of hydrogen used to synthesise the ammonia. Currently, ammonia is primarily produced from natural gas, which has a high carbon intensity. Ammonia from fossil sources such as natural gas or coal is referred to as **brown ammonia**. Ammonia from fossil sources with carbon capture and storage (CCS) is labelled as **blue ammonia** and CO_2 emission-free ammonia from renewable electricity is labelled **green ammonia**.[2]

There are currently no ammonia-fuelled vessels in operation, with 13 ammonia-fuelled ships on the official order books (12 newbuild and one retrofit).[3] Eight of these are to be bulk carriers, three will be gas carriers and two will be tug vessels.[3]

Due to its widespread global use, there is extensive experience in land-based production, storage and transport of ammonia as well as in the carriage of ammonia in liquefied-gas carriers.[1] As between 18 Mt and 20 Mt of ammonia is transported annually by ship, there are specific requirements already in place for, *inter alia*, storage, distribution, and personal protective equipment (PPE) under the International Code of the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code).[4] This code, adopted by the International Maritime Organisation (IMO), has been mandatory under the International Convention for the Safety of Life at Sea (SOLAS) Chapter VII since 1986 and can assist in providing some of the statutory requirements to guide its application on ammonia-fuelled vessels.[1] In addition, there is the International Code of Safety for Ship Using Gases or Other Low-flashpoint Fuels (IGF Code), which provides an international standard for ships operating with gaseous or low-flashpoint liquids as fuel. This code provides mandatory criteria to minimise the risk to the ship, its crew and the environment. Currently, the IMO Sub-Committee on Carriage of Cargoes and Containers

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[1] European Maritime Safety Agency. 2022. "*Potential of ammonia as fuel in shipping*", EMSA, Lisbon

[2] DNV-GL. 2020. *"White Paper 2020: Ammonia as a marine fuel"*. DNV-GL. Høvik, Norway

[3] DNV-GL. 2024. "Alternative Fuel Insights Platform". https://afi.dnv.com/ (last accessed: 15/02/24), DNV-GL, Høvik, Norway

[4] DNV-GL. 2023. *"Energy Transition Outlook 2023: Maritime Forecast to 2050"*, DNV-GL. Høvik, Norway

(CCC) as well as class societies and other organisations such as Lloyd's Register are developing guidelines, rules and regulations on the safety of ammonia as a shipping fuel.

The use of dual-fuel engines is increasingly commonplace within the shipping industry and allows for flexibility between alternative fuels such as ammonia and more conventional fuel oils (e.g. heavy fuel oil, marine diesel oil or even biofuels). In the future, there may be potential for multiple alternative fuels to be used on the same vessel. This means that, in the event of an incident, there may be potential for multiple alternative fuels to be spilled simultaneously. This could result in a combination of the risks and hazards outlined in ITOPF's alternative fuel summary documents. An incident of this type would require a complex and highly specialised response to be mounted to counteract these risks.

The introduction of ammonia as a shipping fuel creates new challenges related to safe ammonia fuel bunkering, storage, supply and consumption for different ship types. Therefore, the fate and behaviour of the substance and associated damages and liabilities should be outlined. To date, ITOPF has not been involved in a case involving a spill/release of ammonia.

II. Storage and transportation

At ambient conditions, ammonia is a toxic, colourless gas with a characteristic irritating and pungent odour. Ammonia can be stored and transported via multiple combinations of refrigeration and pressurisation. It is primarily stored and transported as a refrigerated liquid just below its boiling point of -33 °C under its own vapour pressure[5] . It can also be stored and transported as a compressed liquid in pressurised tanks (Type C) as well as a semi-refrigerated, compressed liquid (typically at -10 °C).[2]

III. Fate and behaviour of ammonia when spilled in the marine environment

The Standard European Behaviour Classification (SEBC) categorises ammonia as a gas / dissolver (GD). During an incident, ammonia's hazards will be the drivers for the first actions and emergency response, followed by specific actions linked to its behaviour classification. Some of ammonia's key properties that play a role in its hazards, fate and behaviour when spilled are listed in Table 1.

Table 1: Summary of key ammonia properties dictating its hazards, fate and behaviour.[5,6]

	Properties	Behaviour
Boiling Point	-33.3 °C	At ambient conditions, ammonia is a gas.
Liquid Specific Gravity (@ -33 °C)	0.682	Ammonia is less dense than water; therefore, as a liquid, ammonia will float if spilled on water.
Vapour Specific Gravity (@ -33 °C) in presence of water vapour	>1.0	When ammonia initially vaporises in the presence of water vapour, it will form a whiteish cloud denser than air above the ground/sea surface.
Vapour Specific Gravity (@ 20 °C)	0.597	Vapours of ammonia at ambient conditions are lighter than air (buoyant) and will easily disperse in open or well-ventilated areas.
Solubility (@ 20 °C)	529 kg/m^3	Ammonia is highly soluble in water.
Flammability Range	15.5 – 27 (v/v) %	Outside of this range, the ammonia/air vapour mixture is not flammable.

[5] CEDRE. 2006. *"Ammonia – Chemical Response Guide"*, CEDRE, Brest, France

[6] NOAA. 1999. "Anhydrous ammonia – CAMEO chemicals profile". June 1999, NOAA, Washington DC, USA

When spilled into the marine environment above the waterline, part of the liquid ammonia rapidly boils, releasing ammonia vapours (Figure 1). The ammonia that comes in contact with water will dissolve (and part of it will also evaporate). Studies have indicated that for large surface spills, approximately 60% of the spilled volume would dissolve with the remaining ammonia evaporating.[7] This evaporation/dissolution ratio was generally seen to remain unchanged when spilled underwater at a shallow depth. However, if the spill source was deeper underwater (< 2 m), the quantity of vapours produced and lost to the atmosphere may reduce to between 5 to 15% of the spill volume.[7]

When spilled in large quantities, the ammonia vapours will rapidly absorb and condense moisture from the air, forming a whiteish cloud of ammonium hydroxide (NH_4OH), denser than air that can travel laterally several hundreds of metres just above the sea/ground surface, especially in high wind conditions.[5,8] When ammonia vapour temperatures increase to ambient conditions, they become less dense than air and will therefore rise and dissipate into the atmosphere.

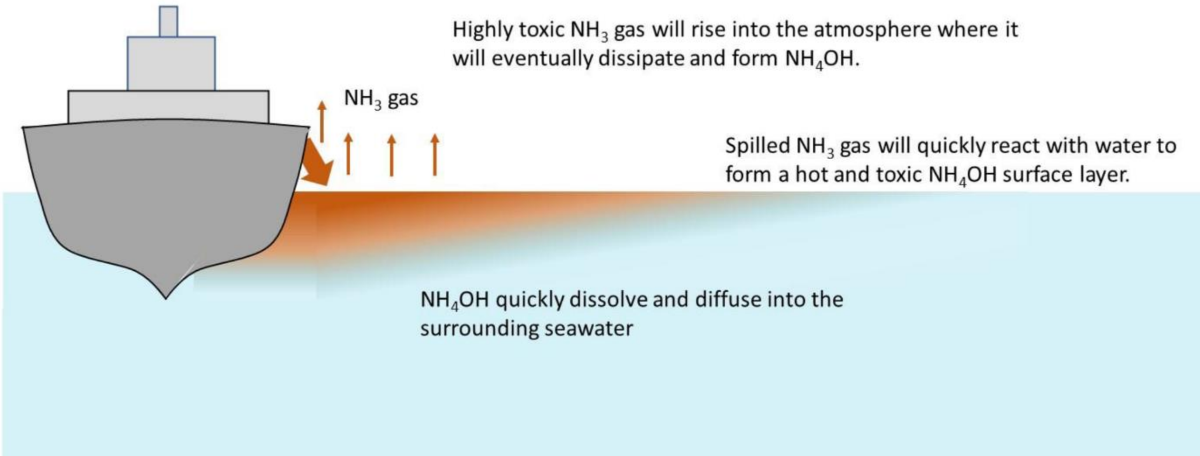

Figure 1: Diagram of expected fate and behaviour of an ammonia spill from a ship[8]

The ammonia that dissolves in seawater will rapidly form a corrosive, caustic solution of NH_4OH, which is less dense than seawater and will therefore form a layer on the water surface. The violent reaction between ammonia and water is exothermic and therefore a localised temperature increase will be observed on the water surface at the incident location. The resultant NH_4OH concentrations and elevated temperatures will decrease with distance from the incident location. The rate at which the NH_4OH plume disperses depends on the intensity of mixing in the aquatic environment, influenced by tidal currents combined with wind-induced wave action. Therefore, a release in high-energy open water will disperse more rapidly in comparison to a release in a low-energy environment such as a sheltered port or inland waterway.

IV. Hazards of ammonia spilled in the environment

Ammonia's hazards can lead to direct impacts to health and safety, mainly through its toxicity and reactivity. The ecotoxicity of ammonia, on the other hand, could lead to damage over a more extended period in comparison to the health and safety impacts.

Toxicity

Ammonia is a toxic and corrosive substance that is also hygroscopic, meaning it has a high affinity for water. When spilled into the atmosphere, it will seek water from its nearest source, which can include the human body and will react to form a caustic, corrosive solution, NH_4OH, with a pH greater than 11.[5] This places the eyes, lungs and skin at greatest risk due to their high moisture content. Caustic burns can also result from ammonia

[7] Raj, P.K., Kalelkar, A.S. 1974. *"Prediction of Hazards of Spills of Anhydrous Ammonia on Water"*. Report no. CG-D-74, USCG

[8] Kass, M. D., Sluder, C. S. Kaul, B. C. (2021). *Spill Behaviour, Detection, and Mitigation for Emerging Nontraditional Marine Fuels* (No. DTMA91X20A65). United States. Department of Transportation. Maritime Administration.

dissolving into body tissue. Exposure to high concentrations of ammonia can result in permanent personal injury and death. The odour threshold for ammonia is around 20 ppm, in comparison to the most severe acute exposure guideline level (AEGL-3), whereby life-threatening health effects or death is likely to take place if exposed to 3,800 ppm of ammonia for five minutes.[5] This low odour threshold allows early warning for personnel that a release has occurred.

Ecotoxicity

Although many environmental factors influence the fate of ammonia, it is considered non-persistent and does not accumulate in the tissues of organisms and as a consequence will be lost to the environment at a much faster rate than a spill of petroleum hydrocarbons.

However, ammonia can be acutely toxic to aquatic organisms due to its effect on the central nervous system, which can lead to convulsions and death. Sublethal concentrations of ammonia can cause a reduction in hatching success, reduction in growth rate and morphological development and pathologic changes in organ tissues.[9]

In addition, the NH_4OH plume present following the reaction of ammonia with water, results in a caustic solution, with pH levels above 11. This can directly result in damage to tissues, mucous membranes, exoskeletons and shells of aquatic organisms through caustic burns. Indirect impacts may include disruption to nutrient cycles and food chains.

When dissolved in water, ammonia exists in two forms: the unionised ammonia (NH_3^0) and the ammonium cation (NH_4^+). NH_3^0 is toxic in the environment, whereas NH_4^+ is less so, as the former can cross membranes of aquatic organisms more readily than the latter. The major factor that determines the proportion of NH_3^0 or NH_4^+ in water is the pH, although temperature also influences the equilibrium. Increases in pH and water temperature lead to a shift in equilibrium favouring the more toxic NH_3^0 and therefore aquatic organisms in warmer, more alkaline waters are likely to be more vulnerable to ammonia toxicity.[10]

The final breakdown compound of ammonia, nitrates are a key nutrient source for algae and other aquatic plants. Following breakdown of an ammonia spill, elevated nitrates may lead to an algal bloom, potentially leading to hypoxic or anoxic conditions that could impact marine organisms at all trophic levels.[10]

Reactivity

Ammonia is highly reactive with many substances including various industrial materials. In the presence of moisture, it reacts with and corrodes copper, brass, zinc, and other alloys, forming a greenish/blue colour. This reactivity could lead to hazards when incompatible materials or other chemical cargoes are carried on-board an ammonia-fuelled vessel, possibly leading to violent or explosive reactions.

Flammability

Unlike other possible alternative fuels such as methanol and hydrogen, ammonia has a relatively narrow flammability range, between 15.5 and 27 (v/v) % and therefore outside of this range, the vapour mixture is not flammable.[6] In addition, due to a relatively high ignition energy, without a catalyst or the presence of combustible material, it is difficult to ignite ammonia. These properties reduce the fire risk, especially in open air.

In particular conditions, if liquid ammonia were to be spilled and ignition were to occur, a pool fire may result and continue until all the fuel is consumed. The height of the flames and the extent of the pool spreading will mainly depend on the rate of the spill and the metocean conditions. If flammable vapours come into contact with an ignition source, a flash fire can result, which is typically short in duration.

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[9] Levit, S.M. 2010. *"A literature review of effects of ammonia on fish".* November 2010, Center for Science in Public Participation, Montana, USA

[10] Environmental Defense Fund (EDF), Lloyd's Register and Ricardo Plc. 2022. *"Ammonia at sea: studying the potential impact of ammonia as a shipping fuel on marine ecosystems."* November 2022, EDF, New York, USA

Note that in the event that a fire was to start on-board, ammonia breaks down from temperatures of 450 °C to form hydrogen, which is highly flammable.[5]

Explosivity

In particular conditions, ammonia could potentially undergo a boiling liquid expanding vapour explosion (BLEVE), which is an explosion caused by the rupture of a tank containing a pressurised liquid that has reached a temperature above its boiling point, in the case of ammonia -33 °C. This would be the case if the temperature of the tank were to raise and gas release systems were to fail.

Temperature

The low temperature that liquid ammonia can be stored will result in freezing of any tissue (plant or animal) upon contact and can cause materials to become brittle and lose their strength or functionality.

V. Damage and liabilities arising from incidents involving ammonia

Ammonia carried as bunkers is not covered specifically by an International Convention at present, with liabilities relating to a release, or risk of a release, a result of national legislation. Ammonia, carried as cargo in bulk, is covered by the International Convention on Liability and Compensation for Damage in Connection with the Carriage of Hazardous and Noxious Substances by Sea, 2010 (2010 HNS Convention). While not in force at the time of writing, this Convention sets out the potential liabilities arising from damage caused by HNS substances. Furthermore, while this Convention does not apply to HNS carried as bunker fuel the same damage can be expected equally from an incident involving ammonia carried on-board to power the ships' engines and are set out below.

Clean-up and Preventive Measures

In comparison to the costs associated with clean-up and preventive measures from a traditional spill of persistent hydrocarbon bunker fuel oil, the costs for this claim heading for a spill of ammonia would likely be for different measures.

Ammonia's non-persistence in the marine environment, means established oil pollution clean-up measures are inappropriate (e.g. collection and recovery using booms and skimmers). Spilled ammonia is not recoverable and therefore allowing natural attenuation to occur is the only appropriate option. For this reason, no protracted clean-up operations extending over a large geographic area, as is often seen with traditional persistent hydrocarbon oil spills, are required. Similarly, waste management is expected to be negligible in comparison to persistent hydrocarbon oil spills.

Due to the toxicity of ammonia to humans, the main focus of this claim heading would be i) detection and monitoring, ii) safe prevention and control of release and iii) possible bunker fuel removal.

i) Monitoring would include the use of expert atmospheric plume modelling, use of multi-gas monitors, sensors, mounted possibly on drones (UAVs) to evaluate the concentration and trajectory of an ammonia vapour cloud, which may pose a risk to local populations and other sensitivities. This can lead to the delimitation of exclusion zones and inform whether there is a requirement for evacuation of a nearby area. In addition, due to the dissolution of ammonia in the water column, ROVs installed with pH and temperature sensors may be deployed to assess the extent of caustic NH_4OH plumes.

ii) Costs associated with controlling the leak (e.g. stopping/controlled release/concentration reduction) without posing a risk to the lives of responders could be a technically reasonable and effective way of mitigating against fire, preventing further releases and reducing risks to sensitivities. In addition, the use of water curtains and water spray may be an appropriate measure to reduce the movement of a toxic vapour cloud by knocking it down to the ground. Any active response to an ammonia spill must be carried out by highly skilled and trained responders that are equipped with specialised equipment and chemically compatible Personal Protective Equipment (PPE).

iii) The removal of ammonia bunker fuel from a casualty could come under the 2007 Nairobi Convention if so decided, although note this convention refers only to bunker fuel oil.

The above clean-up and preventive measures rely on availability of specialist equipment (e.g. HAZMAT PPE, UAVs and ROVs for monitoring, etc.), modelling capabilities and specialist trained personnel. These resources may not be commonly available across the world and therefore these actions may only be possible in highly prepared areas, where immediate deployment of this equipment would be possible. Due to possible lack of available mitigation measures, the below damages related to these incidents may be increased in these circumstances.

The cleaning and rehabilitation of wildlife is another potential cost associated with clean-up and preventive measures. These impacts would most likely be caused by ammonia's toxicity in the atmosphere and NH_4OH's corrosivity in the water column in the vicinity of the incident resulting in lethal or sublethal effects. Decontamination and rehabilitation may be possible for wildlife that have been exposed to elevated concentrations of ammonia and impacts may include caustic burns and respiratory damage. However, for those exposed to significant ammonia concentrations, irreversible damage may have been caused and euthanasia may be the most suitable option. In addition, the potential recovery of dead wildlife and any associated costs related to this would fall under clean-up and preventive measures.

Personal Injury and Loss of Life

This claim heading is included within the HNS Convention for ammonia cargoes and has particular relevance to spills involving ammonia bunkers.

Due to vapour toxicity, a clear and acute risk exists to people near an ammonia release as exposure can result in damage to the skin, eyes, throat, and lungs with permanent damage and death possible after exposure to high concentrations of ammonia vapours (> 4,000 ppm in air).[5] Populations, present outdoors, within the boundary of the vapour cloud would be at risk of loss of life or injuries due to inhalation and dermal contact of toxic and corrosive vapours, leading to eye and respiratory irritation, caustic burns and possibly respiratory damage, coma and death. People inside buildings that are sealed (windows shut) are less likely to be directly impacted by the presence of a vapour cloud.

Although ammonia is difficult to ignite and its flammability range is narrow, a flammability and explosive risk, although less likely, still exists. Populations in the immediate vicinity of the incident or within the boundary of the vapour cloud could be at risk of high thermal radiation (heat from fire), the contact with the flame (burn), force exerted from an explosion and inhalation of hot combustion products. People inside buildings could be at risk of structural collapse in the event of an explosion. The list of those at risk include the ship's crew, bunkering operators, stevedores, passengers and other relevant nearby parties (e.g. surveyors, port operators). In the event that the incident location is in close proximity to a populated area, members of the wider public may also be at risk. Injuries caused by dermal contact with low temperature liquid ammonia would be restricted to those on-board the vessel or first responders. If directly exposed to these low temperatures, frostbite may occur, however, it is considered that the corrosivity of the substance would cause more damage than low temperature exposure.

The costs associated with these effects may be extensive, dependent in part on applicable international conventions and local legislation and should therefore be considered when dealing with liability and compensation.

Environmental Damage

The environmental impact of ammonia in the marine environment is not as widely researched as the impact associated with spills of, more persistent, hydrocarbon oils. Studies have been undertaken on the ecological impact of ammonia to the aquatic environment, however these focus on long-term chronic levels of ammonia run-off caused by industry rather than instantaneous releases of large quantities of ammonia that may be observed during a shipping incident. In the initial stages of a large ammonia release, an acute negative impact in the nearby vicinity of the incident location would be observed in the form of pH and water temperature increase as a caustic plume of NH_4OH is formed. However, in moderate- to high-energy environments, the pH and temperature would return to pre-spill levels quickly, especially with increased distance from the vessel. However, subsequent ammonia breakdown and nitrate abundance in low-energy environmental with minimal turbulence (e.g. wetlands, saltmarshes, mangroves) could lead to eutrophication, possible anoxic water conditions and potential mortality/damage on all trophic levels.

The potential effect of a large-scale spill of ammonia on marine ecosystems is not well understood, and therefore post spill studies to establish the severity and extent of environmental damage may be technically reasonable. Depending on the longevity of the witnessed environmental impact, restoration projects may be appropriate but would likely be minimal and confined to a small area.

Property Damage

Costs arising for property damage will be spatially confined to properties in close proximity to the incident. For example, if a toxic and corrosive NH_4OH plume or vapour cloud were to result from an ammonia spill, property damage to vessels (commercial, leisure or fishing), aquaculture facilities and possibly port structures may occur if located near the casualty. Although less likely, flammability and explosivity risks exist following an ammonia spill, which could also cause physical damage to the previously mentioned property types.

Types of property damage experienced during a persistent hydrocarbon oil spill are not relevant in a spill of ammonia, in particular, damage caused by coating by oil of vessel hulls, shoreline infrastructure, surface fishing and aquaculture gear. Instead, replacement of, or structural repair to damaged property may be necessary if the corrosivity of ammonia has caused weakening of physical structures, especially of those made from copper, brass, zinc and other chemically incompatible alloys.

Due to the possible short timeframes of an ammonia spill, mitigation measures (e.g., placement of water curtains, lift out of vessels) may be more difficult to put in place. However, if well prepared or with sufficient notice of an ammonia-fuelled vessel in distress, safety zones could be assigned, limiting entry to permitted vessels only. This would mitigate against damage to vessels.

Economic Loss

Economic loss can be split into "consequential loss", whereby compensation is payable for loss of earnings suffered by the owners of property which has been impacted and "pure economic loss", whereby compensation is payable for loss of earnings suffered by persons whose property has not been impacted. In the event of an ammonia incident, both consequential and pure economic loss could be experienced.

In the event of a corrosive NH_4OH plume, vapour cloud or a fire/explosion, loss of earnings/income claims from damaged commercial, leisure or fishing vessels, factories, and other commercial etc. property, could be liable for compensation. If the incident was in the immediate vicinity of aquaculture facilities, toxic concentrations of ammonia in the water column, localised increase in pH and seawater temperatures or a fire/explosion could lead to mortality of stock and associated loss of earnings. Pure economic loss could be experienced from loss of earnings from those impacted by any fishing bans imposed by authorities. Despite ammonia being non-persistent with no bioaccumulation potential, fishing bans may still be imposed, due to the lack of research and understanding of the long-term ecological impacts of ammonia.

In addition, if vessels are delayed due to port closures or impacts to their journey to abide by safety zones, demurrage costs may apply, which could be significant. Losses due to the closure of ports and other areas identified as being at potential risk as a result of safety zones demarcated during an emergency may potentially be claimed also. An interruption of flow to water intakes may also cause pure economic loss claims, however due to the short residence of ammonia in the water column, these are likely to be short-lived.

Finally, impact to the local tourism industry is expected to be less in comparison to areas impacted by an oil spill. Claims may arise from organisations impacted in the immediate vicinity at the time of the incident; however, these impacts are likely to be short-lived and in the order of days rather than weeks to months. An exception to this would be in the possible event that a eutrophication event in a low-energy pristine environment caused a reduction in amenity value, reducing tourism numbers visiting the area and impacting the nearby tourist industry.

VI. Conclusions

In conclusion, ammonia's short residence time in the marine environment and high toxicity and reactivity means that claims arising from incidents involving this alternative fuel would greatly contrast those associated with conventional persistent hydrocarbon oil spills.

Claims arising from **clean-up measures and preventive measures** are expected to arise from different measures, such as source control, monitoring via expert modelling or sensors mounted on UAVs/ROVs and possible bunker fuel removal. Traditional clean-up measures will not be possible and therefore, claims from a protracted spill clean-up operation will not arise. However, **personal injury and loss of life** claims may be significant. Risks from toxic exposure to ammonia can cause significant respiratory damage and could lead to death or life-altering injuries to crew, passengers, nearby operators and members of the public.

Claims arising from **environmental damage** are likely to be geographically confined in comparison to damage from oil spills. Post spill studies may be undertaken to better understand the severity and extent of damage from ammonia spills. Restoration measures may be appropriate but are likely to be minimal and confined to a small area. Rather than **property damage** claims involving cleaning and cosmetic repair of oiled property, claims are likely to be a result of corrosive damage or possible fire/explosion damage and therefore, structural repair or replacement may be required, which would likely be more costly and potentially time-consuming. **Economic loss** claims resulting from a toxic and corrosive vapour cloud/NH_4OH plume or from a fire/explosion could include port closure/disruption and associated demurrage costs, losses from damaged/destroyed property, local aquaculture losses from mortality of stock, and local losses resulting from fishing bans. Impacts to commercial water intakes and tourism may also occur.