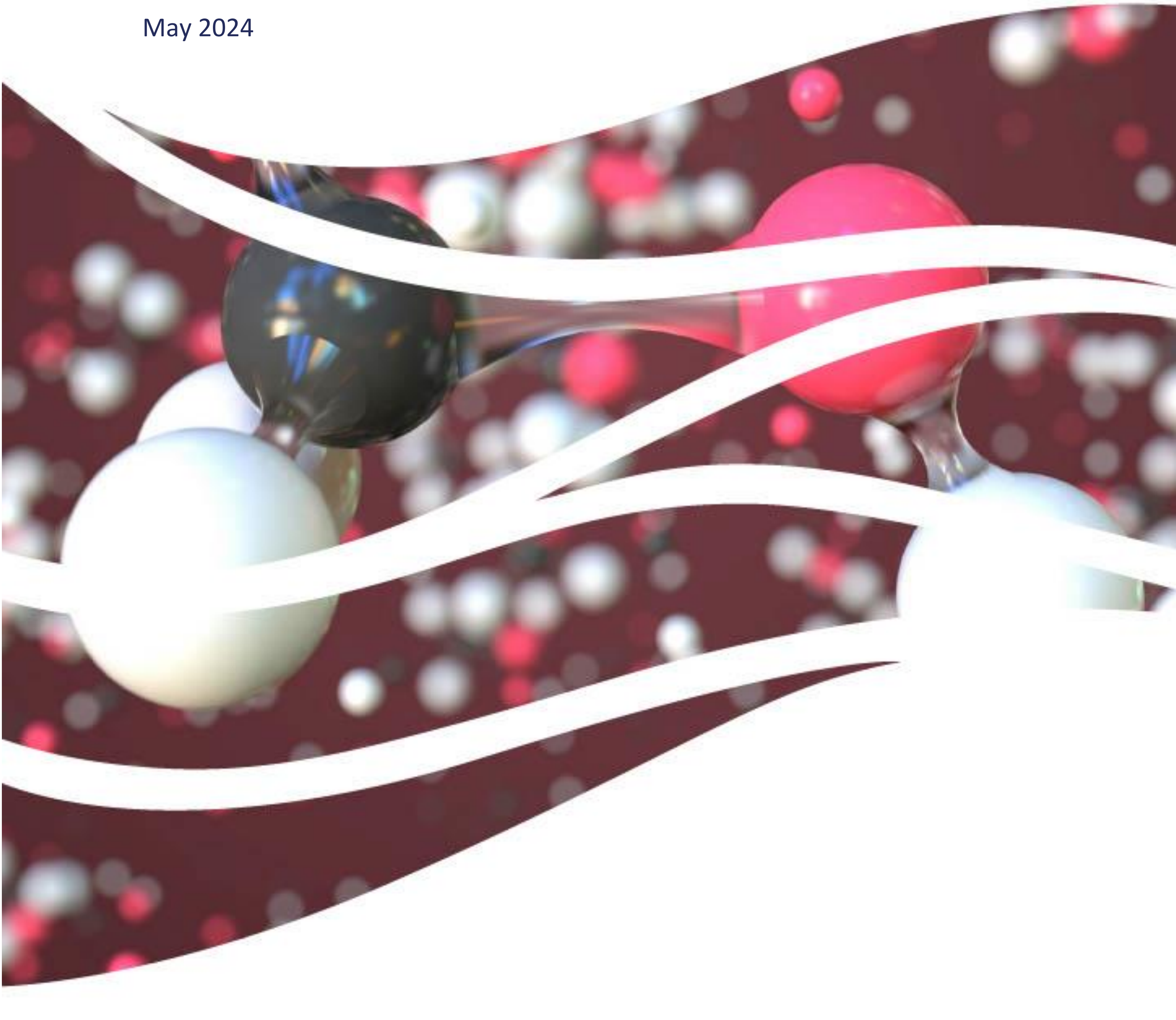
ITOPF

PROMOTING EFFECTIVE SPILL RESPONSE

FATE, BEHAVIOUR AND POTENTIAL DAMAGE & LIABILITIES ARISING FROM A SPILL OF METHANOL 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 **methanol** as a non-traditional marine fuel.

Methanol is considered to be a promising low-carbon fuel for the shipping industry, as it is easier to store than ammonia, LNG or hydrogen with low tank-to-wake emissions. 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 methanol. Currently, methanol is primarily produced from natural gas, which has a high carbon intensity.[1] Methanol from fossil sources such as natural gas and coal are referred to as **grey methanol** and **brown methanol** respectively. Methanol from fossil sources with carbon capture and storage (CCS) is labelled as **blue methanol** and CO_2 emission-free methanol from biomass sources or renewable electricity is labelled **green methanol.**

Methanol has been shipped globally, handled and used in a variety of applications for more than 100 years, and therefore the industry has experience in handling and transporting, both in tank trucks and in bulk vessels. Methanol has also been used as an automotive fuel blend with gasoline for spark-ignited engines. As a consequence, a more established understanding and knowledge of material compatibility and the safety requirements necessary to reduce risks of spills/leaks exists in comparison to other more technically immature fuel types.

Methanol's popularity as a low-carbon fuel is clear, with the orderbooks for ships capable of using methanol as fuel being 20 times larger than the gross tonnage of methanol-fuelled ships currently in operation.[2] Methanol has typically been used for tankers carrying methanol as cargo with 23 ships in operation and 14 on the orderbooks, however in 2023, the containership segment was the dominant ship type with 142 ships on order able to use methanol as bunkers.[2] This is demonstrated by the maiden voyage of the LAURA MAERSK, the first methanol-fuelled containership that travelled from Ulsan, South Korea to Copenhagen, Denmark in July 2023.[3]

Global methanol supply reached 109.6 million tonnes (Mt) in 2023 and, as the majority of this was shipped globally as well as methanol being available at more than 100 major ports, there are specific requirements already in place for, *inter alia*, storage, distribution, and personal protective equipment (PPE).[2,4] For methanol carried as cargo this falls under the International Code of the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code). This code, adopted by the International Maritime Organisation (IMO), has

[1] FCBI Energy. 2015. *"Methanol as a Marine Fuel Report"*, FCBI Energy. London, UK

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

[3] Maritime Executive. 2023. "First green methanol-fuelled boxship starts maiden voyage for Maersk" https://maritime-executive.com/article/first-green-methanol-fueled-boxship-starts-maiden-voyage-for-maersk. 17th July 2023. Florida, USA

[4] Methanol Market Services Asia (MMSA), 2024. *"Global Methanol Supply and Demand Balance."* MMSA. Singapore

been mandatory under the International Convention for the Safety of Life at Sea (SOLAS) Chapter VII since 1986. In addition, the International Code of Safety for Ships using Gases or Other Low-flashpoint Fuels (IGF Code), adopted in November 2020 following six years of review, provides guidelines and mandatory criteria to minimise risks for crew members onboard methanol-fuelled ships.[5]

The use of dual-fuel engines is increasingly commonplace within the shipping industry and allows for flexibility between alternative fuels such as methanol and more conventional fuel oils (e.g. heavy fuel oil or marine diesel oil). 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.

In the experience of ITOPF, the potential exists for incidents to occur during handling, transportation and loading/unloading operations. ITOPF has attended two incidents where methanol has been involved and one where ethanol was involved as cargo, and these are detailed in Table 1. The case involving ethanol cargo is included in this paper as it is chemically similar to methanol and behaves in the same way once released into the marine environment.

Table 1: ITOPF attendances involving methanol/ethanol

Vessel Name	Date	Location	Incident Type	Cargo
BOW MARINER	28th Feb 2004	70 km off Norfolk, USA	Failure to inert tanks leading to explosion, sinking and oil spill	Ethanol
VICUÑA	15th Nov 2004	Dom Pedro II Port, Paranaguá, Brazil	Explosion during cargo unloading and oil spill	Methanol
BUNGA ALPINIA	26th Jul 2012	Labuan Port, Malaysia	Fire during cargo loading, explosion and oil spill	Methanol

All three incidents involved significant explosions caused by highly flammable vapours from the cargo. ITOPF did not provide technical advice on cargo impacts during these incidents and, instead, were mobilised due to the subsequent spills of bunker fuel oil that were caused by the explosions.

II. Storage and transportation

At ambient conditions, methanol is a toxic, colourless, and flammable liquid. Since it is a liquid at ambient temperature and pressure, it does not require storage and handling under pressure, like LPG, or at the refrigerated or cryogenic temperatures associated with ammonia, LNG and hydrogen. However, due to methanol's corrosivity to some materials, such as some aluminium and titanium alloys, the materials used in the storage and transportation need to be carefully considered. Alternative options for fuel tanks and pipes include non-metallic materials such as nylon, neoprene, or non-butyl rubber.[5]

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

The Standard European Behaviour Classification (SEBC) categorises methanol as a dissolver that evaporates (DE). During an incident, methanol's hazards will be the drivers for the first actions and emergency response, followed

[5] Methanol Institute. 2023. *"Marine Methanol: Future-Proof Shipping Fuel."* Brussels, Belgium

by specific actions linked to its behaviour classification. Some of methanol's properties that play a key role in its hazards, fate and behaviour when spilled are listed in Table 2.

Table 2: Summary of key methanol properties dictating its fate and behaviour [6]

	Properties	Behaviour
Boiling Point	64.5 °C	At ambient conditions, methanol is a liquid.
Liquid Specific Gravity (@ 20 °C)	0.792	Methanol is less dense than water; therefore, as a liquid, methanol will float if spilled on water.
Vapour Specific Gravity (@ 20 °C)	1.1	Vapours of methanol at ambient conditions are denser than air and will spread above the ground/water surface when spilled.
Solubility	Fully miscible	Methanol has no limit to its solubility in water.
Flammability Range	6.0 – 36.5 (v/v) %	Outside of this range, the methanol/air vapour mixture is not flammable.
Flash Point	12 °C	Above this temperature, highly flammable methanol vapours are produced.

When spilled into the marine environment, methanol would float, rapidly spreading on the sea surface and dissolving into the water column while simultaneously undergoing evaporation (Figure 1).

Vapours emanating from the sea surface will not immediately rise due to their density and will spread over the ground or water surface when spilled. The vapour cloud has a larger flammability footprint than lighter and more volatile LNG and hydrogen that readily rise and disperse. The extent of the vapour cloud spreading will mainly depend on the rate of the spill and the metocean conditions. Even in moderate wind speeds, an ignition of the vapour cloud and subsequent fire may still be able to propagate back to the leak source until all methanol is consumed below the LFL or is extinguished.

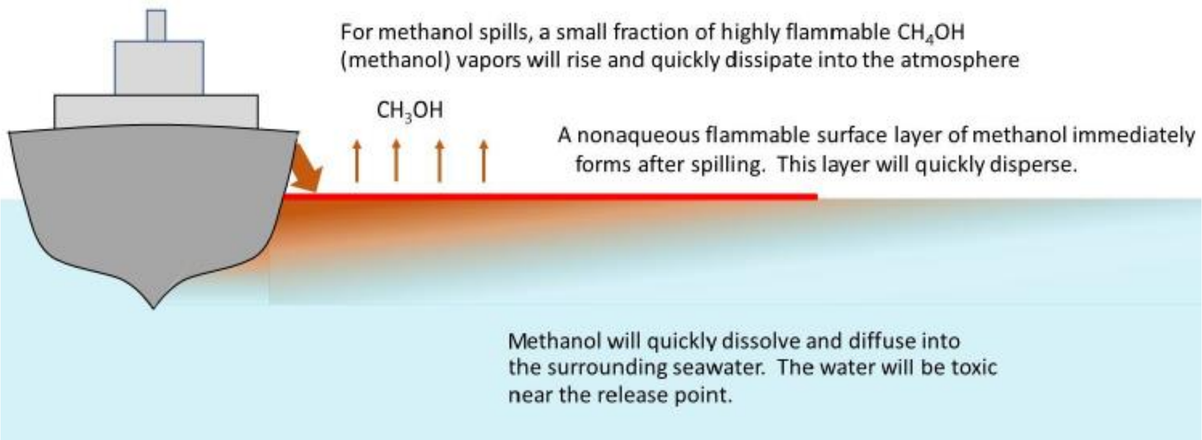


Figure 1: Diagram of expected fate and behaviour of a methanol spill from a ship[7]

[6] NOAA. 1999. *"Methyl Alcohol – CAMEO chemicals profile"*. June 1999, NOAA. Washington DC, USA

[7] Kass, M.D., Sluder, C.S., Kaul, B. 2021. *"Spill behaviour, detection, and mitigation for emerging nontraditional marine fuels."* Oak Ridge National Laboratory. Report no. ORNL/SPR-2021/1837. US Department of Energy.

The rate at which methanol dissipates depends on the amount of mixing in the aquatic environment, influenced by tidal currents combined with wind-induced wave action.[8] Although many environmental factors will influence the fate of methanol, a methanol release in open water is likely to disperse to non-toxic levels (<1%) at a much faster rate than petroleum hydrocarbons with some studies giving methanol a half-life between one and seven days.[8] Studies have stated that this short half-life is predominantly due to biodegradation. As methanol is naturally occurring in the environment, microorganisms exist that can oxidise methanol into formaldehyde, and then subsequently formic acid until carbon dioxide and water remain.[8]

Volatilisation is also stated to play a major role in the decomposition of methanol in the marine environment.[10]

IV. Hazards of methanol when spilled in the marine environment

Methanol's hazards can lead to direct impacts to health and safety, mainly through its flammability, explosivity and toxicity.

Flammability

Methanol and its vapours are highly flammable with a flammability range of 6 – 36.5 (v/v) %, which can be detected with specialised equipment.[6] Outside of this range, the methanol/air mixture is not flammable. This is greater than conventional fuels such as diesel, which has a much smaller flammability range of 0.6 - 5.5 (v/v) %. In addition, the flash point of methanol is 12 °C, meaning that 12 °C is the lowest temperature at which vapours emanate from methanol in sufficient quantities to form an ignitable vapour/air mixture.[5] Noted that methanol flames are almost invisible to the eye during daylight.

In an unconfined space, a release of methanol from a tank or pipeline will flow from the puncture hole and spread over a large area, forming a thin layer that will undergo evaporation and possible dissolution if in contact with water. Only a small area near the immediate leak would likely reach the concentration above the 6% lower flammability limit (LFL) that would allow methanol to ignite.

In a confined space, where flammable vapours cannot spread and dissipate, a small leak could lead to a flammable vapour/air mixture. Note that inside a fuel storage tank, the percentage of methanol is almost pure and, as such, the conditions are not in its flammability range. However, following a leak/rupture, a dense vapour cloud will form and once it has mixed with air, when its concentration reaches between the LFL and the upper flammability limit (UFL), the mixture can sustain a flame if ignited. If ignition occurs immediately, a flash fire is likely to result and continue until all the fuel is consumed.

Explosivity

As methanol has a wide explosive range (6 – 36.5 (v/v) %), even small leaks have the potential to burn or explode. If leaked methanol concentrates in a confined space, there is a significant risk of combustion and explosion, meaning that a spark or hot surface may cause ignition. Ignition of a flammable vapour/air mixture may result in a possible deflagration to detonation transition (DDT) and a subsequent large explosion. These events are unpredictable and not well understood at this time.

Methanol released in sufficient quantities can create a harmful overpressure which may result in direct and indirect hazards from building damage or flying debris. Overpressures can occur as a result of the ignition of a cloud of released flammable gas.

In particular conditions, typically a fire, methanol could potentially undergo a boiling liquid expanding vapour explosion (BLEVE), which is an explosion caused by the rupture of a tank containing a liquid that has reached a temperature above its boiling point, in the case of methanol, 64.5 °C. This could occur if the temperature of the tank were to raise and gas release systems were to fail.

[8] Malcolm Pirnie, Inc. 1999. *"Evaluation of the fate and transport of methanol in the environment"*. Washington DC.

Asphyxiant

Like with any gas in a confined environment, high concentration of methanol vapours displace oxygen in the air, decreasing oxygen availability and therefore leading to asphyxiation to those present in these confined environments. Methanol vapours will not dissipate in enclosed unventilated areas as vapours are denser than air.

Toxicity

The likely routes of acute methanol exposure are via inhalation or dermal contact. In the event of mild exposure to methanol and its vapours, the symptoms are similar to ethanol intoxication, with headaches, dizziness, nausea and blurry vision being commonplace. If the exposure is significant, there may be a latent period for 10 – 48 hours, until more serious symptoms such as violent abdominal pain, temporary or permanent blindness, coma and possibly death due to respiratory failure occurs. The latent period is due to methanol being metabolised into formaldehyde and formic acid, which are the main toxic agents responsible for the above effects. It should be noted that for toxic effects to take place via inhalation and dermal contact, prolonged periods of high methanol concentrations, (approximately 3,000 ppm for 8 hours or 20,000 ppm for 1 hour), would be required.[9]

Ecotoxicity

As methanol concentrations rapidly decrease in the water column due to spreading, biodegradation and volatilisation and has a low aquatic toxicity and bioaccumulation potential, direct environmental damage is expected to be negligible.[10, 11] Significant biodegradation due to microbial activity may lead to hypoxic or anoxic conditions in sheltered waters, however this is expected to be short-lived due to methanol's non-persistence in the marine environment.

V. Damage and liabilities arising from incidents involving methanol

Methanol 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. Methanol, 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 methanol 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 methanol would likely be for different measures, primarily source control.

Methanol'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 methanol 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.

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[9] Machiele, P.A. 1989. *"A perspective on the flammability, toxicity, and environmental safety distinctions between methanol and conventional fuels."*. US Environmental Protection Agency.

[10] Katsumata, P.T., and Kastenberg, W.E. 1996. *"Fate and transport of methanol fuel from spills and leaks."* Hazardous Waste and Hazardous Materials 13 (4), pp. 485 – 498

Due to the flammability of methanol and its vapours and possible resulting explosions, the main focus of this claim heading would be i) detection and monitoring, ii) prevention and control of fire or explosion 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 potential presence of a flammable vapour/air mixture, which may pose a risk to local environmental and economic sensitivities. This can lead to the delimitation of exclusion zones. In addition, due to spillage in the water column, ROVs installed with methanol sensors may be deployed to assess the extent of localised methanol concentrations.

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 the risk to sensitivities. In addition, water curtains, water spray, water cannons or fog are techniques that can be used to fight fire or reduce the risk of fire. These are typically deployed from specialised firefighting vessels. In comparison to oil spills, responders will need to be highly trained for HNS incidents.

iii) The removal of methanol bunker fuel from a casualty could fall 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 could come from the impacts from: fire or explosion hazard and toxic concentrations of methanol in the water body in the immediate vicinity of an incident. Both mechanisms could result in mortality for wildlife in the immediate proximity to the incident or other sublethal effects including burns, physical explosion damage, impaired reproduction or developmental defects.

Rehabilitation for burns and fire damage may be possible by wildlife responders, in addition to 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 methanol cargoes and has particular relevance to spills involving methanol bunkers.

Due to the flammability and explosivity hazard of methanol, a clear and acute risk exists to people near a release/spill. Vapours, from large unignited methanol spills near developed (residential or industrial) areas would quickly encounter an ignition source, ignite and the vapour cloud fire could potentially burn back to the source, and depending on confinement, result in an explosion. Populations, present outdoors, within the flammable and explosive boundaries of the vapour cloud would be at risk of loss of life or injuries due to high thermal radiation (heat from the fire), the contact with the flame (burn), force exerted from an explosion and inhalation of hot combustion products. People inside buildings are less likely to be directly impacted by direct thermal impact injuries from a fire but could be at risk of structural collapse in the event of an explosion.

In addition, the toxicity of methanol vapours is likely to pose a risk to nearby populations, especially due to methanol vapours being denser than air and possibly spread just above the ground surface. Populations, present outdoors in close proximity to the incident location would be at risk of loss of life or injuries due to inhalation and dermal contact of toxic vapours, leading to nausea, violent abdominal pain, temporary or permanent blindness and possibly even coma and death due to respiratory failure.[9]

The list of those at high risk include the ship's crew, bunkering operators, stevedores, passengers and other relevant nearby parties (e.g. surveyors, port operators). This is the most likely public safety impact of a methanol spill. Table 1 shows the methanol (and ethanol) incidents that ITOPF has attended. The death tolls for these incidents were reported to be 21 for the BOW MARINER incident, four for the VICUÑA explosion and five for the BUNGA ALPINIA case and all were reported to be crew members or port operators.

The asphyxiant risk due to displacement of oxygen by methanol vapours would be restricted to those on-board the vessel or first responders where vapours aggregate in confined spaces or in very close proximity of the source of the spill.

The costs associated with these 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 methanol in the marine environment is not as widely researched as the impact associated with spills of, more persistent, hydrocarbon oils. Limited studies have been undertaken on the ecological impact of large-scale methanol spills to the aquatic environment. As methanol is readily biodegradable and has a low aquatic toxicity and bioaccumulation potential, damage to the marine environment is expected to be minimal and short-lived.[11]

The potential effect of a large-scale spill of methanol 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. Due to the acute and localised nature of any environmental impact, restoration projects would likely be minimal and, if any, confined to a small area.

Property Damage

Costs arising for property damage would be spatially confined to properties in close proximity to the incident. For example, if a catastrophic fire or explosion were to result from a methanol spill, significant property damage to port structures, vessels (commercial, leisure or fishing), buildings and aquaculture facilities may occur if located near the casualty.

Types of property damage experienced during a persistent hydrocarbon oil spill are not relevant in a spill of methanol, in particular 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 in the aftermath of a fire or explosion and could be significant. Due to the likely short timeframes of a methanol spill, mitigation measures (e.g., placement of water curtains, lift out of vessels) would be more difficult to put in place. However, with sufficient notice of a methanol-fuelled vessel in distress, safety zones could be assigned, limiting entry to permitted vessels only. This would mitigate against damage to vessels. Following explosions on-board the BUNGA ALPINIA in Labuan Port, Malaysia, ITOPF was aware of a property damage claim from a homeowner one km away from the incident location, for structural damage to his stilted home.

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 have 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 a methanol incident, both consequential and pure economic loss could be experienced.

In the event of 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, 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

[11] GESAMP. 2023. "Hazard Evaluation of Substances Transported by Ships". PPR.1/Circ. 13. 30 June 2023. IMO. London, UK

fishing bans imposed by authorities. Despite the very short residence time of methanol in the environment and the low aquatic toxicity and bioaccumulation potential of the substance, there is a possibility that fishing bans may still be imposed, due to the lack of understanding of the impacts of methanol.

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 methanol in the environment, 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. There might be claims arising from organisations impacted in the immediate vicinity of the incident location, however these are to be short-lived and in the order of days rather than weeks to months, unless significant impact from a fire/explosion occurs.

VI. Conclusions

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

Claims from **clean-up and preventive measures** are expected to arise from different measures, such as source control, fire-fighting measures, 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 fire, explosions, toxic and asphyxiating vapours 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, in certain circumstances, to establish the severity and extent of damage. Restoration measures are likely to be minimal and, if any, confined to a small area. Rather than **property damage** claims involving cleaning and cosmetic repair of oiled property, methanol claims are likely to be a result of fire or explosion 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 fire or 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.