

Ammonia as a marine fuel

Risks and perspectives

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Authors

Dr. Martin Cames

Nora Wissner

Jürgen Sutter

Contact

info@oeko.de

www.oeko.de

Head Office Freiburg

P. O. Box 17 71

79017 Freiburg

Street address

Merzhauser Straße 173

79100 Freiburg

Phone +49 761 45295-0

Office Berlin

Borkumstraße 2

13189 Berlin

Phone +49 30 405085-0

Office Darmstadt

Rheinstraße 95

64295 Darmstadt

Phone +49 6151 8191-0

Table of Contents

List of Figures	5
List of Tables	5
List of Abbreviations	6
Summary	7
1 Introduction	9
1.1 Characteristics and production of ammonia	9
1.1.1 Current production and use	10
1.1.2 Certification of green ammonia	11
1.2 Recent industry projects and ambitions	12
2 Risks and environmental impacts	15
2.1 Toxicity	15
2.1.1 Toxicity of ammonia	15
2.1.2 Toxicity of heavy fuel oil	19
2.1.3 Toxicity of methanol	20
2.1.4 Hazard statements of ammonia compared with other fuels	22
2.1.5 Conclusions on toxicity	24
2.2 Risks and leakages	24
2.3 Impact of emissions	26
3 Technology on board	28
3.1 Internal combustion engine	28
3.1.1 Ammonia combustion	28
3.1.2 Combustion emissions	29
3.1.3 Bunkering and storage	31
3.1.4 Application in marine shipping and transition	33
3.1.5 Conclusion	34
3.2 Fuel cell	35
3.2.1 PEMFC and SOFC	35
3.2.2 Conclusion	36
4 Infrastructure	37
4.1 Production costs	37

4.2	Production capacities	37
5	Synergies with other sectors	40
6	Comparison with other marine fuels	42
7	Conclusions	45
8	References	47
9	Annex	54

List of Figures

Figure 1:	Green ammonia production process	11
Figure 2:	Ammonia emissions in the EU	40

List of Tables

Table 1:	Comparison of post-fossil fuels and fossil heavy fuel oil (HFO) based on key environmental criteria	8
Table 2:	Overview of ammonia projects in the maritime sector	13
Table 3:	Ammonia toxicity exposure levels	15
Table 4:	Comparative toxicity of ammonia to various marine fish	18
Table 5:	Short term toxicity of methanol	21
Table 6:	Long-term toxicity of methanol	22
Table 7:	Hazard statements of ammonia compared with other fuels	22
Table 8:	Oil spill characteristics and properties of different fuel types	25
Table 9:	Comparison of fuel properties	32
Table 10:	Comparison of post-fossil fuels and fossil HFO based on key environmental criteria	43
Table 11:	Percentage of un-ionized ammonia at different pH and temperatures	54
Table 12:	Freshwater NOEC values as total ammonia-N in µg/l at different pH levels	54
Table 13:	Species mean acute values (SMAVs) of ammonia for several aquatic species	55
Table 14:	Maximum acceptable toxicant concentration (MATC) of HFO at various stages of rainbow trout early ontogenesis	58
Table 15:	Summary of HFO sample ecotoxicity data for fish, daphnia and algae	59
Table 16:	Median lethal concentrations and median effective concentrations estimated using oil loading (% v/v or µg/g), concentrations of total petroleum hydrocarbons by fluorescence (µg/l), and estimated polycyclic aromatic hydrocarbon concentration (µg/l) in toxicity test solutions	59

List of Abbreviations

CI	Compression Ignition
DAC	Direct Air Capture
ECA	Emission Control Areas
EGR	Exhaust Gas Recirculation
FC	Fuel Cell
GHG	Greenhouse gas
H ₂	Hydrogen
HFO	Heavy Fuel Oil
ICE	Internal Combustion Engine
IMO	International Maritime Organization
MATC	Maximum Acceptable Toxicant Concentration
MGO	Marine Gas Oil
Mtoe	Million tonne oil equivalent
N ₂	Nitrogen
NH ₃	Ammonia
NH ₄ ⁺	Ammonium Ion
NO _x	Nitrogen oxides
NOEC	No effect concentration
N ₂ O	Nitrous oxide
PEMFC	Proton Exchange Membrane Fuel Cell
SCR	Selective Catalytic Reduction
SI	Spark Ignition
SMAV	Species Mean Acute Values
SMR	Steam Methane Reforming
SO _x	Sulphur oxide
SOFC	Solid Oxide Fuel Cell
TRL	Technology Readiness Level
VLFSO	Very Low Sulphur Fuel Oil
WAF	Water Accommodated Fraction

Summary

The decarbonization of the shipping sector ultimately requires the switch to alternative post-fossil fuels. Ammonia has recently received increasing attention as a potential marine fuel that could drive this decarbonization. In the context of a growing hydrogen economy, ammonia is also interesting as the cheapest form in which to transport hydrogen over long distances and in large volumes. It is a basic chemical which is globally traded and produced; it has mainly been used for fertilizer production to date. However, ammonia has hitherto not been used as a marine fuel. It is a carbon-free energy-carrier but also toxic. If ammonia were to be used in shipping, it needs to be safe for humans and the (marine) environment. While decarbonizing the sector, ammonia should not result in higher emissions or environmental risks.

This study assesses whether these potential risks and challenges of ammonia have been sufficiently considered and whether this impacts ammonia's suitability as a future marine fuel. The study summarises the state of the art and focuses on ammonia's impact on marine ecosystems as well as the environmental impact of combusting ammonia.

Considering its toxicity, various studies show that the acute ecotoxicity of ammonia to fish and aquatic invertebrates is very high and has a similar order of magnitude to the acute toxicity of Heavy Fuel Oil (HFO). Ammonia also has long-term toxic effects on fish and aquatic invertebrates. However, under real environmental conditions, ammonia concentrations are expected to decrease more rapidly after a spill than with HFO. At the same time, a huge influx of ammonia into a water body can lead to eutrophication because ammonia is a nitrogen source for algae and microorganisms. If ammonia is spilled into water, it floats on the water surface and rapidly dissolves within the water body into ammonium hydroxide while concurrently boiling into the atmosphere as gaseous ammonia. The ratio of ammonia dissolved in the water versus its release to the atmosphere as vapour depends on the dynamics of the release.

Ammonia can be used as a marine fuel in both internal combustion engines and fuel cells. The combustion of ammonia or ammonia mixtures can lead to emissions of nitrogen oxides (NO_x), nitrous oxide (N_2O) and to the direct slip of ammonia (NH_3). There have been no marine ammonia engines to date, either in the testbed or in pilot projects. Sufficient empirical data on the emissions from combusting ammonia does not exist yet. Further research is thus necessary to clarify the quantity of emissions and to develop technologies for reducing or avoiding them.

The application of exhaust gas aftertreatment systems seems to be a promising solution for NO_x emissions and ammonia slip. To ensure the climate benefit of green ammonia, issues with N_2O emissions must be solved as N_2O has a high global warming potential. The elimination of N_2O emissions (or their reduction to a negligible minimum) needs to be proven in typical marine engines. Stringent N_2O emissions regulations could ensure that ammonia engines are designed in a way which guarantees fulfilment of the long-term goal of climate-neutral maritime shipping. To incentivize the development of suitable marine machinery, N_2O could, for example, be covered by maritime carbon pricing policies or limited to tolerable levels through stringent emission standards based on carbon dioxide equivalents. Ammonia combustion will likely require a pilot fuel to facilitate combustion. Dual fuel engines will thus be a promising pathway for ammonia to enter the maritime sector. Ammonia engines are expected by 2024. First pilot projects might start shortly thereafter with a potential commercial scale-up starting in the late 2020s.

Fuel cells could circumvent the problem of emissions from combustion engines but their commercial use in deep sea shipping is even further away than ammonia internal combustion engines (ICEs).

The use of ammonia in fuel cells should thus be pursued alongside the development of ammonia engines.

Table 1 compares ammonia with other fuels when used in ICEs based on key environmental criteria. The comparison is done horizontally across fuels. The higher the given number, the better the performance of the fuel. Ammonia’s potential to reduce greenhouse gas (GHG) emissions compared to other fuels needs to be evaluated with uncertainties in terms of N₂O emissions. Since we apply a well-to-wake approach, methanol is considered climate-neutral even though it is a carbon-based post-fossil fuel.

Table 1: Comparison of post-fossil fuels and fossil heavy fuel oil (HFO) based on key environmental criteria

Criterion	Ammonia	Hydrogen	Methanol	HFO
GHG reduction potential	4*	5	5**	1
Air pollutants	3	5	4	1
Aquatic ecotoxicity	2	5	5	1
Human toxicity	2	5	3	3
Flammability	2	1	2	5
Explosion risks	4	2	5	5

Notes: Ranking: 1= high risk/ low performance to 5=low risk/ high performance, *uncertainty about N₂O emissions, **well-to-wake
 Source: Authors’ own compilation

Ammonia is a future fuel candidate as it is a carbon-free energy carrier and thus likely to be cheaper than other post-fossil fuels. Robust safety guidelines will be necessary for the safe handling of ammonia onboard ships. Due to its risk profile, its use may not be applicable in all segments of the maritime sector, for example in passenger ships. The maritime sector will likely rely on different post-fossil fuels in future depending on the market segment. In addition, stringent well-to-wake regulation including all GHG emissions will be required from the outset to prevent that decarbonization through ammonia is undermined by significant N₂O emissions.

1 Introduction

The transition towards a carbon neutral society requires that all sectors reduce their greenhouse gas (GHG) emissions to zero over the course of this century. Despite improving energy efficiency through technical and operational measures this requires a shift from fossil to renewable energies. For most sectors, the direct use of renewable energy or electricity is the most efficient approach to achieve this goal. However, for some sectors including the maritime transport sector, the direct use of electricity is limited to certain niches of the market (e.g. ferries, short-sea shipping) due to the limited energy density of batteries. For deep-sea shipping the use of synthetic fuels produced from renewable electricity is one of the most promising options for decarbonization. These post-fossil green fuels may or may not contain carbon (e.g. green methanol versus green ammonia). But even if post-fossil fuels like methanol emit carbon dioxide (CO₂), they are – from a well-to-wake perspective – carbon-neutral if the CO₂ required to produce them stems from non-fossil sources such as direct air capture (DAC). It is not yet clear which of the potential options (e.g. green hydrogen, green methanol or green ammonia) is the most appropriate post-fossil fuel. They all have advantages and disadvantages in terms of inputs, efficiency, cost, environmental risks, handling, etc. Even though ammonia has been a well-established product for almost a century, which is produced in and traded between many countries, it is mainly used for fertilizer production rather than as a fuel to date.

Recently, the use of ammonia as a marine fuel has received increasing attention. Ammonia is already being promoted by various stakeholders as one of the most promising future fuels. Studies have investigated its potential from a cost and production perspective (DNV GL 2020b; EDF 2019; LR; UMAS 2019b; T&E 2018). A recent mapping of worldwide pilot and demonstration projects showed that there is an increasing number of projects which focus on ammonia as a fuel, especially for large ships (GMF 2021a).

Against this background, this study assesses whether the potential risks and challenges of ammonia are being sufficiently taken into account and whether this impacts ammonia's suitability as a future marine fuel.

The switch to zero- or low-carbon fuels is only one (technical) measure to reduce GHG emissions from maritime transport. Energy efficiency improvements through operational or technical measures (e.g. speed reduction, propeller retrofit, hull coating) are often easier and less costly to implement. The use of zero- or low-carbon fuels should not hinder the uptake of energy efficiency measures. The use of alternative fuels and energy sources on-board a ship is though the biggest lever to reduce GHG emissions (DNV GL 2019). Different policies in a coherent policy mix are needed, therefore, to incentivize the different measures.

The first chapter will outline the characteristics and production of ammonia. Chapter two focuses on the risks and environmental impacts of using ammonia as marine fuel. Chapter three examines the propulsion technologies which can be used for ammonia and the respective changes to current practices, like bunkering, and machinery. Chapter four addresses infrastructure aspects, e.g. global production capacities. Potential synergies of using ammonia with other sectors are explored in chapter five. The final chapter situates ammonia in relation to other fuels. A comparison is drawn with a focus on environmental criteria.

1.1 Characteristics and production of ammonia

Ammonia (NH₃) is an important basic chemical which is widely used, especially in the fertilizer industry. It is a colourless gas at atmospheric conditions with a characteristic pungent smell. It is

lighter than air and caustic. The increased use and production of ammonia by humans has significantly altered the global nitrogen cycle, mainly through the application of ammonia-based fertilizers (The Royal Society 2020). While the industrial fixation of nitrogen (N_2), as ammonia-based fertilizers, is important to produce food (chapter 5), a lot of nitrogen is lost in the production-process-consumption chain. These losses spread into the environment, namely soil, air and water. They can hereby have negative effects on the environment, including humans. Ammonia and nitrogen can be a key driver for terrestrial or coastal eutrophication, air quality issues from particulate matter, GHG emissions and stratospheric ozone loss, and exacerbate fresh water pollution or biodiversity loss (Erisman et al. 2013). A further description of emission impacts can be found in section 2.3.

Ammonia is basically a hydrogen (H_2) carrier and has therefore gained attention in context of a future hydrogen economy. It is a zero-carbon synthetic energy carrier that is potentially relevant for the decarbonization of various sectors in need of alternative energy carriers, like hydrogen-based fuels (called “post-fossil fuels” here). Ammonia has a higher energy density than hydrogen but a lower energy density than carbon-based fuels like methanol (Table 9, p. 32).

1.1.1 Current production and use

Over 80% of global ammonia production is used for the production of fertilizers because ammonia is a key intermediate product for all nitrogen fertilizer products (Hansson et al. 2020a). The remainder is used in a variety of industrial applications. In 2018, global ammonia production was about 180 million tonnes (Mt); the major share being produced in China (Argus 2020; Yara 2018). In 2018, the capacity of ammonia production was around 220 Mt in 2018 indicating some ‘spare capacity’ (Argus 2020). The last two decades saw a growth in installed ammonia production capacity and production (Alfa Laval et al. 2020). Ammonia prices have fluctuated since 2000 and the price of one ton of ammonia was about 200 US\$ in 2020 (Argus 2020). Studies have already been undertaken on the future price of post-fossil fuels like green ammonia; these studies are often based on different assumptions (Brynolf et al. 2018; Hank et al. 2020; LR; UMAS 2019a). The future development of green ammonia production is still uncertain, making the comparison of predicted prices difficult. This study will not explore the cost developments of ammonia but rather the implications of its properties on safety and fuel systems.

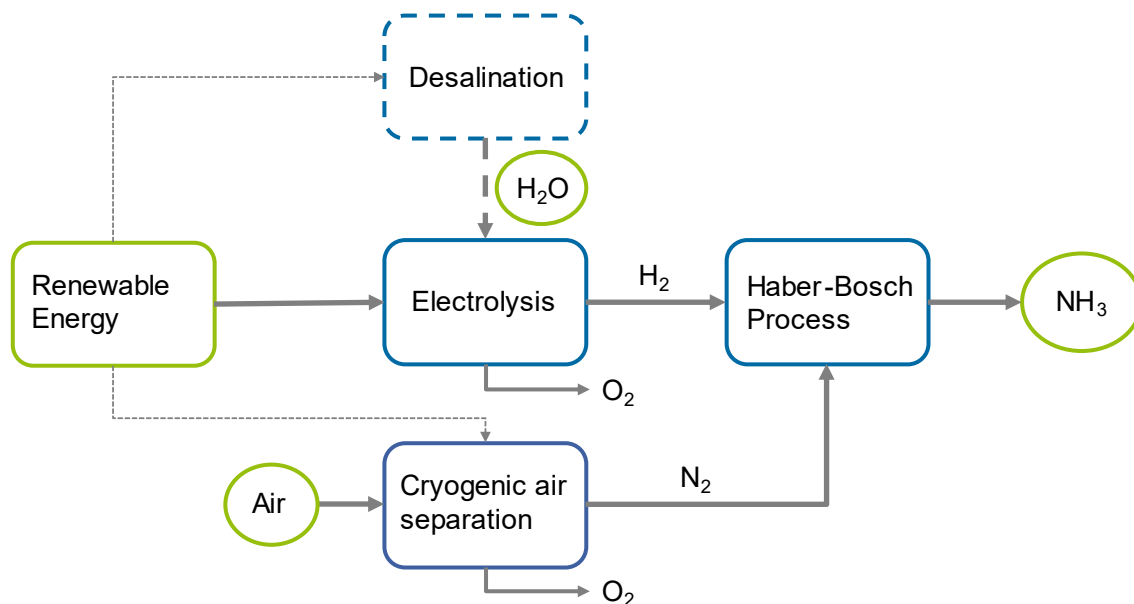
The established process to produce ammonia, called Haber-Bosch, revolutionized the use of fertilizers over a century ago. The process is very energy-intensive though. Current ammonia production is still based on fossil fuels and contributes 1.8% to global CO_2 emissions GHG emissions (The Royal Society 2020). The production relies mainly on natural gas whereby most of the energy is consumed by the production of hydrogen via steam methane reforming (SMR) (The Royal Society 2020). It should be noted that exact data on emissions from ammonia production is scarce because it is often aggregated with overall emissions from fertilizer production. The combustion of fossil fuels during production leads to CO_2 and methane emissions. Most of the ammonia produced globally is further upgraded into fertilizers like urea or nitrates (Yara 2018). To produce nitrate fertilizers, nitric acid is produced through the oxidation of ammonia which leads amongst others to nitrous oxide (N_2O) emissions (Wood and Cowie 2004). This nitric acid production is a very large source of industrial N_2O emissions. The use of ammonia as an energy carrier in shipping will thus likely have no N_2O upstream emissions as these further processing steps are not necessary.

Today, ammonia is produced by feeding natural gas into a steam methane reformer to produce hydrogen. The hydrogen serves as an input to the Haber-Bosch process which converts it together with nitrogen (N_2) from air into ammonia using a catalyst under high temperature and pressure. There

are different air separation technologies to retrieve nitrogen. Cryogenic distillation is the most common technology and used for over 90% of nitrogen production today (EDF 2019; Hank et al. 2020). Air is separated into nitrogen and oxygen by so-called cryogenic air separation units (ASUs) by exploiting their boiling point temperatures (EDF 2019). The Haber-Bosch process and the SMR have high technology readiness levels (TRL) and energy efficiencies of 73% to 82% and 70% respectively (LR; UMAS 2019a; The Royal Society 2018).

To produce 'green' ammonia based on renewable energy, the hydrogen for the Haber-Bosch process is produced via water electrolysis with renewable electricity and nitrogen is supplied by cryogenic air separation (Oeko-Institut 2019a). Low-temperature electrolysis technologies, alkali and proton exchange membrane, have TRLs of 9 and 8 and an efficiency of about 65% (Brynolf et al. 2018). The TRL of solid oxide electrolyzers is a bit lower but the efficiency is higher with about 80% (Agora Verkehrswende; Agora Energiewende; Frontier Economics 2018). A simplified overview of the production process is shown in Figure 1. The efficiency for the whole process chain (low-temperature water electrolysis and Haber-Bosch) stands at 52%, but efficiency improvements in electrolyzers are expected, potentially leading to a 60% efficiency in the long term (Oeko-Institut 2019a). There are less energy-intensive alternative production methods under development (e.g. solid-state ammonia synthesis), but they are likely not commercial and applicable on a large-scale in the short term (KR 2020; Cerulogy 2018). The overall efficiency depends ultimately on the electrolysis and the production location (e.g. if further shipment of intermediate or end-product is needed).

Figure 1: Green ammonia production process



Source: Own compilation based on EDF (2019) and Hank et al. (2020)

1.1.2 Certification of green ammonia

Conventional (and fossil) marine fuels have a wide range of properties. Very low sulphur fuel oil (VLSFO) has been increasingly used since 2020 to comply with stricter global sulphur emission

limits. VLSFO encompasses fuels with different characteristics; ship operators, therefore, need to deal with varying combustion qualities, etc. The advantage of ammonia is that the physical properties of ammonia are the same, irrespective of a fossil or renewable origin (Alfa Laval et al. 2020). If ammonia is bunkered, ship operators do not need to account for varying fuel and thus combustion properties, which facilitates global use of ammonia as a fuel. However, this advantage comes with a downside. As fossil and green ammonia cannot be distinguished, there are opportunities for fraud. Fossil and green ammonia might be mixed, or fossil ammonia might simply be labelled as produced with renewable energy. Green ammonia will (at least in the short term) be much more expensive than fossil ammonia. Buyers of green ammonia, like ship operators, might need proof of what they are paying for to comply with policies. There is hence a need for a certification of green ammonia. If an ammonia production plant includes an electrolyser to produce hydrogen and uses renewable energy for the whole ammonia production process, the produced ammonia could be certified or the certificate for using renewable electricity would need to be passed on to the end-consumer. The main component influencing the upstream GHG emissions is the production of hydrogen. With a growing interest in hydrogen to decarbonize many sectors, the certification of green hydrogen and derived fuels is a key requisite to ensure environmental integrity. The production of green ammonia can benefit from this development if green hydrogen is purchased or the ammonia plant including the green hydrogen production gets certified. Such a certificate could be used by ship operators to prove emission reductions achieved through using green ammonia.

Robust systems of guarantees of origin are required (Oeko-Institut 2020). Examples for certification are the current European Energy Certification System (ECCS) for renewable energy¹ or the pilot certification system for green hydrogen in context of the CertifHY project,² whose criteria may not ensure sustainability. Different factors need to be taken into account in the certification (of green hydrogen) (Oeko-Institut 2019b):

- electricity supply (e.g. additionality, CO₂ footprint),
- water supply (e.g. desalination),
- human rights (e.g. land rights),
- land use (e.g. competition).

The development of a certification system should be initiated soon as developing and establishing one in the maritime sector may be time-intensive.

1.2 Recent industry projects and ambitions

The number of initiatives, research and demonstration projects exploring the use and production of (green) ammonia has increased in recent years. For example, the Getting to Zero Coalition³ is an alliance of over 140 companies and other (maritime) stakeholders established in 2019 and engaged in realizing ocean-going “zero emission vessels” (ZEV) by 2030. The coalition also explores ammonia as one of the potential post-fossil fuels.

¹ Association of Issuing Bodies (AIB) – Certification: <https://www.aib-net.org/certification>.

² CertifHY guarantees of origin (GOs) for green hydrogen: <https://www.tuvsud.com/de-de/presse-und-medien/2019/januar/hin-zu-einem-neuen-wasserstoffmarkt-certifhy-herkunftsnachweise-fuer-gruenen-wasserstoff>.

³ GtZ Coalition: <https://www.globalmaritimeforum.org/getting-to-zero-coalition>.

Engine manufacturers have announced the development ammonia internal combustion engines (ICE). Various projects have been announced recently, partially involving a big number of partners. An overview of ammonia-related projects in the maritime sector is provided in Table 2. Ammonia is also on the agenda of states: Japan launched a “Roadmap of Zero Emissions for Shipping” which includes ammonia-fuelled ships (MLIT Japan 2020). A consortium has been formed in this context, too (Table 2). The German Federal Ministry of Education and Research is funding the Campfire project and the EU supports a project on ammonia fuel cell (Table 2).

Table 2: Overview of ammonia projects in the maritime sector

Name of project/ initiative/ vessel	Project partners	Propulsion	Other details
NoGAPS ⁴ (Nordic Green Ammonia Powered Ship)	Global Maritime Forum, engine manufacturers (MAN ES, Wärtsilä), classification societies, finance stakeholders	ICE	Ammonia-fuelled deep-sea vessel by 2025
MAN ammonia engine ⁵	MAN ES	ICE 2-stroke	Engine development by 2024
CASTOR ⁶	MAN ES, Yara, MISC, Samsung Heavy Industries, Lloyds Register	ICE	system perspective / infrastructure around port
Wärtsilä ammonia engine ⁷	Wärtsilä	ICE 4-stroke	Engine development
ZEEDs ⁸	Wärtsilä, Grieg Maritime Group	ICE	Ammonia-fuelled tanker by 2024
Colour Fantasy ⁹	16-party consortium incl. Color Line, ABB, Wärtsilä, DNV GL	unknown	Passenger vessel / Ro-Ro cruise liner, retrofit
Japanese consortium	MLIT Japan, MAN ES, Imabari, ClassNK and others	ICE	Ammonia-fuelled ship incl. Supply infrastructure
Dutch consortium ¹⁰	C-Job Naval Architects, Proton Ventures, Enviu	ICE / FC	Ammonia tanker fuelled by its own cargo
Campfire ¹¹	Big consortium incl. Yara, Carnival, Sunfire	ICE / FC	Whole value chain of ammonia supply to a ship

⁴ NoGAPS and other initiatives: <https://www.ammoniaenergy.org/articles/maritime-ammonia-ready-for-demonstration/>.

⁵ MAN ES –2-stroke: <https://man-es.com/discover/two-stroke-ammonia-engine>.

⁶ Announcement CASTOR initiative: <https://www.lr.org/en/latest-news/unveiling-the-castor-initiative/>.

⁷ Wärtsilä 4-stroke: <https://www.wartsila.com/media/news/30-06-2020-world-s-first-full-scale-ammonia-engine-test--an-important-step-towards-carbon-free-shipping-2737809>.

⁸ <https://www.ammoniaenergy.org/articles/grieg-maritime-and-wartsila-to-build-ammonia-fueled-ammonia-tanker/>.

⁹ <https://www.ammoniaenergy.org/articles/maritime-ammonia-ready-for-demonstration/>.

¹⁰ <https://www.ammoniaenergy.org/articles/pilot-project-an-ammonia-tanker-fueled-by-its-own-cargo/>.

¹¹ Campfire: <https://wir-campfire.de/>.

Name of project/ initiative/ vessel	Project partners	Propulsion	Other details
Maersk Mc-Kinney Moller Center for Zero Carbon Shipping ¹²	Maersk Mc-Kinney Moller Center for Zero Carbon Shipping, Maersk, Yara and others	-	Supply-chain in port of Singapore
ShipFC ¹³	14-party consortium incl. Yara, Wärtsilä, Equinor	SOFC	EU funded retrofit of vessel Viking Energy by 2024

Source: Authors' own compilation

¹² https://www.maersk.com/news/articles/2021/03/10/maritime-industry-leaders-to-explore-ammonia-as-marine-fuel-in-singapore#utm_source=organic%20post&utm_medium=twitter&utm_campaign=Maersk%20Ammonia%20Partnership%20Singapore&utm_term=M_5D70B49A812E7_60486DDF6093D.

¹³ ShipFC: <https://www.ammoniaenergy.org/articles/viking-energy-to-be-retrofit-for-ammonia-fuel-in-2024/>.

2 Risks and environmental impacts

2.1 Toxicity

Ammonia has many advantages compared to other post-fossil fuels (chapter 6). It has been pointed out, however, that ammonia is also toxic to aquatic and terrestrial species (Alfa Laval et al. 2020; Vries 2019). A more detailed investigation of ammonia's toxicity to marine ecosystems has hitherto been lacking. The following describes ammonia's effects on various freshwater and marine organisms and compares it with conventional heavy fuel oil (HFO) and another promising fuel for the future, namely methanol.

2.1.1 Toxicity of ammonia

Human toxicity

Ammonia is a toxic, corrosive, hardly inflammable gas. It has a strong odour and is very irritating to the eyes, throat and respiratory tract - even in small concentrations in the air. Table 3 shows the toxicity threshold depending on the time of exposure indicating that robust guidelines for the safe handling of ammonia are necessary. Section 2.2 describes potential risks and safety measures in this context.

Table 3: Ammonia toxicity exposure levels

Concentration / time	Effect
10000 ppm	Promptly lethal
5000 – 10000 ppm	Rapidly fatal
700 – 1700 ppm	Incapacitation from tearing of the eyes and coughing
500 ppm for 30 minutes	Upper respiratory tract irritation, tearing of the eyes
134 ppm for 5 minutes	Tearing of the eyes, eye irritation, nasal irritation, throat irritation, chest irritation
140 ppm for 2 hours	Severe irritation, need to leave the exposure area
100 ppm for 2 hours	Nuisance eye and throat irritation
50 – 80 ppm for 2 hours	Perceptible eye and throat
20 – 50 ppm	Mild discomfort, depending on whether an individual is accustomed to smelling ammonia

Source: The Fertilizer institute: Health effects of ammonia, cited in Alfa Laval et al. (2020)

Ecotoxicity

Ecotoxicological data is described based on the registration dossier for ammonia from the European Chemicals Agency (ECHA)¹⁴ and supplemented by further studies.

Ammonia is a non-persistent and non-cumulative toxicant to aquatic life. Overall, ammonia has been shown to be very toxic to many different freshwater and marine animal species, both acutely and chronically. The toxicity of ammonia to aquatic organisms is highly dependent on physicochemical

¹⁴ <https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15557/6/1>.

factors, most notably pH. In aqueous solution, ammonia exists in two forms, un-ionized ammonia (NH_3) and ammonium ion (NH_4^+). With increasing pH, the fraction of the un-ionized ammonia also increases. Table 11 (Annex, p. 54) provides percentages of un-ionized ammonia at different pH and temperatures. The un-ionized form is the primary cause of toxicity in aquatic systems. This is relevant to the marine environment as the pH of seawater is relatively high, with typical pH values of approx. 8.

ANZECC; ARMCANZ (2000) have calculated chronic NOEC¹⁵ values at a common pH value of 8 by converting data reported at different pH values to total ammonia. For freshwater, a NOEC value of 900 $\mu\text{g/l}$ total ammonia-N¹⁶ was reported. This corresponds to 35 $\mu\text{g/l}$ un-ionized ammonia-N at 20° C. For marine conditions, a NOEC value of 910 $\mu\text{g/l}$ total ammonia-N was calculated. The differences in the degree to which the marine and freshwater NOEC values change with pH are due to the different data types and the different equations applicable to each system. Table 12 (Annex, p. 54) provides calculated NOEC values for different pH values.

Short-term toxicity to fish¹⁷

Several studies have been conducted on toxicological effects on fish of ammonia and read-across substances¹⁸. Since ammonia is present in aqueous solution primarily as an ammonium ion (NH_4^+), comparisons with the toxic effects of the corresponding ammonium salts, like ammonium chloride, are also permissible.

Thurston and Russo (1983) analyze the toxicity of ammonia to fathead minnow (*Pimephales promelas*), using ammonium chloride. The 96-h median lethal dose (LC_{50})¹⁹ ranged from 0.75-3.4 mg/l un-ionized ammonia (34-109 mg/l total ammonia-N). The toxicity decreased with increasing temperature from 12 °C to 22 °C. In the same study, Thurston and Russo (1983) also examines the acute toxicity of ammonia to hatchery reared rainbow trout (*Oncorhynchus mykiss* = *Salmo gairdneri*). The investigated fish ranged from young fry (<0.1 g, 1-day old) to adults (2.6 kg) which were 4 years old. The 96-h LC_{50} was 0.6-1.1 mg/l un-ionized ammonia (11-48 mg/l total ammonia-N).

In an earlier study, Thurston et al. (1981) exposes rainbow trouts (*O. mykiss*) and cutthroat trouts (*Oncorhynchus clarkii* = *Salmo clarkii*) to ammonium chloride for 96 hours. Under fixed conditions, the 96-h LC_{50} in rainbow trout was 0.163 -0.500 mg un-ionized NH_3/l (21.6 to 31.6 mg/l total ammonia-N) and 0.296 -0.327 mg un-ionized NH_3/l (26.3 to 29.1 mg/l total ammonia-N) in cutthroat trout. Under fluctuating conditions, LC_{50} values for un-ionized ammonia of 0.099 -0.292 g/l (10.5 - 22.3 mg/l total ammonia-N) were measured in rainbow trout and 0.194 -0.217 mg/l (17.3 -19.3 mg/l total ammonia-N) were measured in cutthroat trout.

¹⁵ No effect concentration (NOEC) is a risk assessment parameter that represents the concentration of a pollutant that will not harm the species involved.

¹⁶ Ammonia-N ($\text{NH}_3\text{-N}$) is the nitrogen present in the form of ammonia.

¹⁷ <https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15557/6/2/2>.

¹⁸ A read-across substance is a chemical which is used to predict properties for another chemical due to structural similarity, see https://echa.europa.eu/documents/10162/13628/raaf_en.pdf/614e5d61-891d-4154-8a47-87efebd1851a

¹⁹ The median lethal concentration, LC_{50} , is the concentration required to kill 50 % of a tested population after a specified test duration. LC_{50} values are frequently used as a general indicator of a substance's acute toxicity.

Another study by Calamari et al. (1981) investigates the toxicity of ammonium chloride in different developmental stages of rainbow trout (*O. mykiss*) under flow-through conditions. The 96-h LC₅₀ was higher during the hatching stage compared to later development stages: from egg to hatch > 0.486, in fry stages 0.160 - 0.370, and in fingerling stages 0.440 mg un-ionized NH₃/l.

Rice and Bailey (1980) reports an acute LC₅₀ value of 0.068 mg/l for un-ionized ammonia in a study where pink salmon (*Oncorhynchus gorbuscha*) were exposed to ammonium sulphate in clean freshwater for 96 hours.

The effects of calcium and sodium on the acute toxicity of ammonium chloride is investigated in lake trout (*Salvelinus namaycush*) and Atlantic salmon (*Salmo salar*) by Soderberg and Meade (1993). They find no effect of calcium to Atlantic salmon fry or smelts, while sodium reduced toxicity to salmon smelts with no effect to fry. Both sodium and calcium reduced the toxicity of ammonia to lake trout fingerlings but had again no effect on fry.

The influence of pH and temperature on the toxicity of ammonia is analyzed by Dabrowska H. and Skiora H. (1986). Acute toxicity studies of ammonium chloride were conducted with common carp (*Cyprinus carpio*) resulting in 48-h LC₅₀ mean range of 1.60-1.96 mg un-ionized NH₃/l (103-109 mg/l total ammonia). With a higher pH, they found an increasing toxicity of ammonia; and with a higher temperature, a decrease in toxicity effects.

McCormick et al. (1984) analyzes the toxicity of ammonia to green sunfish (*Lepomis cyanellus*). The 96-h LC₅₀ concentrations ranged from 0.5-1.73 mg/l NH₃ (corresponding to 9- 272 mg/l ammonia-N) depending on pH value.

Additional data for acute toxicity of ammonia on several aquatic species taken from EPA (2013) are provided in Table 13 (Annex, p. 55) based on species mean acute values.

Long-term toxicity to fish²⁰

The toxicity of ammonia to early life stages of rainbow trout (*O. mykiss*) in freshwater is investigated by L.G. Solbé and Shurben (1989). If exposure started after 24 hours and lasted for 73 days, a concentration of 0.027 mg unionized NH₃/l resulted in a mortality of more than 70 %, especially in the eggs. If exposure started after 24 days (eye-egg stage), mortality at 0.27 mg unionized NH₃/l was only 40%. (Rice and Bailey 1980) reported a NOEC value of 1.2 mg/l un-ionized ammonia for alevins of pink salmon (*O. gorbuscha*).

In a study by Colt and Tchobanoglous (1978) juvenile channel catfish (*Ictalurus punctatus*) were exposed to 12 ammonia concentrations ranging from 48-2048 mg un-ionized ammonia-N/l for 31 days. The growth of the fish was reduced by 50% at 517 µg/l un-ionized ammonia-N and no growth occurred at 967 µg/l un-ionized ammonia-N and higher. Above 500 µg/l un-ionized ammonia-N, there was increasing damage to the dorsal and pectoral fins. The overall NOEC for the growth and weight was < 48 µg un-ionized ammonia-N/l.

Table 4 shows additional values for LC₅₀ and EC₅₀²¹ of ammonia to various marine fish.

²⁰ <https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15557/6/2/3>.

²¹ The half maximal effective concentration (EC₅₀) is defined as the concentration substance required to obtain a 50% effect.

Table 4: Comparative toxicity of ammonia to various marine fish

	Species	TA-N (mgL-1)	UIA-N (mgL-1)
4-Day LC ₅₀	Sea bass (<i>Dicentrarchus labrax</i>)	40	1.7
4-Day LC ₅₀	Sea bream (<i>Sparus aurata</i>)	57	2.5
4-Day LC ₅₀	Turbot (<i>Scophthalmus maximus</i>)	59	2.6
4-Day LC ₅₀	Catfish (<i>Ictalurus punctatus</i>)	45	1.6
4-Day LC ₅₀	Rainbow trout (<i>Oncorhynchus mykiss</i>)	22	0.3-0.6
8-Day LC ₅₀	Sea bass (<i>Dicentrarchus labrax</i>)	>22.3	>0.9
20-Day LC ₅₀	Sea bream (<i>Sparus aurata</i>)	15.7	0.89
28-Day LC ₅₀	Turbot (<i>Scophthalmus maximus</i>)	38	1
20-Day EC ₅₀	Sea bream (<i>Sparus aurata</i>)	15.7	0.89
28-Day EC ₅₀	Turbot (<i>Scophthalmus maximus</i>)	17-19	0.50-0.65
55-Day EC ₅₀	Turbot (<i>Scophthalmus maximus</i>)	17-21	0.60-0.75
55-Day EC ₅₀	Sea bass (<i>Dicentrarchus labrax</i>)	22	0.9

Notes: LC₅₀ = Lethal concentration for 50% of the population, EC₅₀ = Concentration reducing growth by 50%, TA-N = Total ammonia nitrogen, UIA-N = Unionized Ammonia

Source: Lemarié et al. (2004), Wajsbrodt et al. (1993), Ruyet et al. (1995), Person-Le Ruyet and BOEUF (1998), Colt and Tchobanoglous (1978), Haywood (1983)

Overall, the various studies show that the long-term toxicity of ammonia to fish is also very high.

Short-term toxicity to aquatic invertebrates²²

The acute toxicity of ammonia (48-h LC₅₀ value) was found to be 101 mg/l for *C. tentans* (Gersich and Hopkins 1986). In another toxicity study, *Chironomus tentans* and *Lumbriculus variegatus* were exposed to various concentrations of ammonium chloride (Schubaur-Berigan et al. 1995). For non-ionized ammonia, the LC₅₀ to *L. variegatus* was 0.455 mg/l at a pH of 6.3 and 0.72 mg/l at a pH of 6.52 to *C. tentans*. For total ammonia, the LC₅₀ was 6.6 mg/l at a pH of 8.59 for *L. variegatus* and 82.4 mg/l at a pH of 8.53 for *C. tentans*. With an increasing pH, total ammonia was more toxic to both species.

Kohn et al. (1994) exposed four species of marine amphipoda (*Rhepoxynius abronius*, *Eohaustorius estuarius*, *Ampelisca abdita* and *Grandidierella japonica*) to ammonia in seawater. *A. abdita* was found to be the most sensitive to ammonia, with a median lethal concentration (LC₅₀ 96-h) of 49.8 mg/l total ammonia (0.83 mg/l as un-ionized ammonia). *R. abronius* was also relatively sensitive with a LC₅₀ of 78.7 mg/l total ammonia (1.59 mg/l un-ionized ammonia). *E. estuarius* and *G. japonica* were less sensitive, with estimated LC₅₀ values of 125.5 mg/l and 148.3 mg/l total ammonia, respectively (2.49 mg/l and 3.35 mg/l un-ionized ammonia).

Long-term toxicity to aquatic invertebrates²³

²² <https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15557/6/2/4>.

²³ <https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15557/6/2/5>.

Reinbold and Pescitelli (1982) examine long-term effects of ammonium chloride exposure to *Daphnia magna* and identified a NOEC of 0.79 mg/l. Daphnid growth (determined by length) was significantly reduced at the higher test concentration of 1.3 mg/l NH₃ and the reproduction was also affected.

Toxicity to aquatic algae and cyanobacteria²⁴

The effect of ammonia concentration on growth and physiology of the unicellular green alga *Chlorella vulgaris* was studied by Tam and Wong (1996). With algal growth, there was a decrease in nitrogen content in the medium due to uptake and assimilation of nitrogen. The 18-day EC₅₀ was found to be 2700 mg/l. As ammonia is an important nitrogen source, ammonia is hardly toxic for algae.

Toxicity to aquatic plants other than algae²⁵ and to microorganisms²⁶

Ammonia is used by aquatic plants and by microorganisms as a source of nitrogen and is also produced by bacteria from other nitrogenous compounds. Therefore, it is not toxic to aquatic plants and microorganisms.

2.1.2 Toxicity of heavy fuel oil

Mason D. King et al. (2020) reviewed studies published between 1993 and 2020 on the impact of oil spills on birds. Petroleum pollution shows a range of negative effects on birds, mainly through plumage contamination, systemic toxicity and embryotoxicity.

The ecotoxicological data for heavy fuel oil (HFO) is described based on the registration dossier for *fuel oil, heavy, high-sulfur* (EC Number: 295-396-7, CAS Number: 92045-14-2)²⁷ from the European Chemicals Agency (ECHA) and supplemented by further studies.

Short-term toxicity to fish

The acute toxicity for HFO was studied for rainbow trout (*Oncorhynchus mykiss*). In a test, (OECD 203; KS=1) reported by ECHA²⁸ the fish were exposed to water accommodated fractions (WAFs)²⁹ of Intermediate fuel oils 30-380 (CAS 68476-33-5). The LC₅₀ was determined with 79 mg/l. Other studies with other HFO samples ranged from >94 to >1000 mg/l for 96-h LC₅₀.

Long-term toxicity to fish³⁰

Long-term toxicity of HFO to fish was estimated using the PETROTOX computer model, which is based on the aqueous-phase concentrations of hydrocarbons and coefficients that describe the partitioning of the hydrocarbons between the water and organism. Redman et al. (2012) calculated a NOEC freshwater value for fish based on mortality of 0.1 mg/l.

²⁴ <https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15557/6/2/6>.

²⁵ <https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15557/6/2/7>.

²⁶ <https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15557/6/2/8>.

²⁷ <https://echa.europa.eu/registration-dossier/-/registered-dossier/13342/6/2/1>.

²⁸ <https://echa.europa.eu/registration-dossier/-/registered-dossier/13342/6/2/1>.

²⁹ Water accommodated fractions (WAF) = water in contact with floating oil.

³⁰ <https://echa.europa.eu/registration-dossier/-/registered-dossier/13342/6/2/1>.

Stasiūnaitė (2003) studied toxic effects of HFO on different development stages of rainbow trout (*Oncorhynchus mykiss*). Results show that alevins are more sensitive to HFO than eggs. At a concentration of 0.75 g/l HFO, a significant mortality rate of alevins occurred. Effects on growth and yolk sac resorption were already measured at a concentration of 0.02 g/l HFO. Table 14 (Annex, p. 55) shows maximum acceptable toxicant concentration (MATC) of HFO at various stages of early ontogenesis of rainbow trout from this study.

Martin et al. (2014) investigate the long-term toxicity of various HFOs (HFO 6303, weathered HFO 6303, HFO 7102, and MESA) to rainbow trout (*Oncorhynchus mykiss*) embryos. HFO WAF was non-toxic and contained no detectable concentrations of hydrocarbons due to high density and viscosity that prevented droplet formation. Toxic alkyl polycyclic aromatic hydrocarbons (PAHs) were detected in the samples with chemically dispersed HFO and stranded HFO for the fish embryos. HFO was more toxic to fish than crude oil. Since HFO sinks and can strand in spawning shoals, there is a long-term risk to fish embryos from the long-term release of PAHs. For median lethal concentrations and median effective concentrations for the samples, see Table 16 (Annex, p. 55).

Short-term toxicity to aquatic invertebrates

In an acute toxicity test reported by ECHA,³¹ *Daphnia magna* was exposed to the WAF of heavy cracked fuel oil (MRD-10-579). The 48-h EC₅₀ was found to be 0.22 mg/l based on mobility (EMBSI 2012a). Other studies using WAF methodology examined the impact on *Daphnia magna* of other HFO samples and showed a wide range of EC₅₀ values from 2 to >1000 mg/l.

Long-term toxicity to aquatic invertebrates³²

Long-term toxicity to aquatic invertebrates in ECHA database was also estimated using the PETROTOX computer model (Redman et al. 2012). The estimated freshwater invertebrate NOEC value is 0.27 mg/l for *Daphnia magna*.

Toxicity to aquatic algae³³

In a 72-hour growth inhibition test *Pseudokirchneriella subcapitata* was exposed to the WAF of heavy cracked fuel oils (MRD-10-579). The 72-h EC₅₀ was measured as 0.32 mg/l and NOEC was determined as 0.05 mg/l based on growth rate. In other studies, the EC₅₀ values ranged from 0.75 to >107 mg/l based on growth rate.

Concawe (2011) investigate toxicity tests for several HFO samples on rainbow trout (*Oncorhynchus mykiss*), the crustacean zooplankter (*Daphnia magna*) and green algae (*Pseudokirchneriella subcapitata*). Table 15 (Annex, p. 58) shows the results for these HFO sample ecotoxicity tests.

2.1.3 Toxicity of methanol

Methanol is the first and simplest aliphatic alcohol. The leading effect of methanol in humans is central nervous system toxicity and neurotoxicity including optical nerve toxicity.

³¹ <https://echa.europa.eu/registration-dossier/-/registered-dossier/13342/6/2/1>.

³² <https://echa.europa.eu/registration-dossier/-/registered-dossier/13342/6/2/1>.

³³ <https://echa.europa.eu/registration-dossier/-/registered-dossier/13342/6/2/1>.

The description of the ecotoxicological data for methanol is based on the registration dossier for *methanol* (EC Number: 200-659-6, CAS Number: 67-56-1) from the European Chemicals Agency (ECHA).³⁴ Data on the toxicity of methanol are given in Table 5. The results show that methanol is hardly toxic for aquatic organisms (fish, invertebrates and algae).

Table 5: Short term toxicity of methanol

Organisms	Parameter	Value [mg/l]	Species
Fish	LC ₅₀ (96h)	28100	<i>Pimephales promelas</i>
	LC ₅₀ (96h)	20100	<i>Oncorhynchus mykiss</i>
	LC ₅₀ (96h)	15400	<i>Lepomis macrochirus</i>
Daphnids	EC ₅₀ (48h)	18000	<i>Daphnia magna</i>
	EC ₅₀ (48h)	> 10000	<i>Daphnia magna</i>
Green algae	EC ₅₀ (96h)	ca. 22000	<i>Selenastrum capricornutum</i>
Microorganisms	EC ₅₀	19800	activated sludge
	IC ₅₀ ³⁵	>1000	activated sludge
	IC ₅₀	880	<i>Nitrosomonas</i>
	toxic limit concentration	530 - 6600	<i>Pseudomonas, Microcystis aeruginosa</i>

Source: ECHA³⁶

Long-term toxicity

According to ECHA, there are no guideline studies on long-term toxicity of methanol to aquatic species available. Methanol belongs to a category of chemicals acting with a non-specific mode of action (simple narcosis). Therefore, the chronic toxicity to aquatic organisms can be reasonably predicted from data on acute toxicity by using an appropriate acute-to-chronic ratio (ACR). An ACR of 10 has been proposed in the literature for this kind of chemical. With Structure-Activity Relationship models (QSARs), data for long-term toxicity of methanol have been predicted (Table 6).

³⁴ <https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15569/6/2/1>.

³⁵ The half maximal inhibitory concentration (IC₅₀) is defined as the concentration of a substance required to obtain a 50% effect in inhibiting a specific biological or biochemical function.

³⁶ <https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15569/6/2/1>.

Table 6: Long-term toxicity of methanol

Organisms	Parameter	Value [mg/l]	Species
Fish	NOEC (predicted chronic value)	447	<i>Pimephales promelas</i>
	NOEC (200-h)	7900 - 15800	<i>Oryzias latipes</i>
Daphnids	NOEC (21-d)	208 (predicted)	<i>Daphnia magna</i>
	NOEC (21-d)	122	<i>Daphnia magna</i>

Source: ECHA³⁷

2.1.4 Hazard statements of ammonia compared with other fuels

Table 7 shows the hazard statements of ammonia compared with other fuels according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Table 7: Hazard statements of ammonia compared with other fuels

Hazard statements	Hazard category	Ammonia ³⁸	CNG ³⁹	LNG ⁴⁰	LSHFO ⁴¹	VLSFO ⁴²	HSHFO ⁴³	MGO ⁴⁴	MeOH ⁴⁵	H ₂ ⁴⁶
H220 Extremely flammable gas	1A		X	X						X
H221 Flammable gas	2	X								
H225 Highly Flammable liquid									X	
H226 Flammable liquid and vapour	3							X		
H227 Combustible liquid	4				X					

³⁷ <https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15569/6/2/1>.

³⁸ Sigma-Aldrich, Safety Data Sheet Ammonia.

³⁹ https://www.boconline.co.uk/en/images/10021935_tcm410-55840.pdf.

⁴⁰ <https://www.pgworks.com/uploads/pdfs/LNGSafetyData.pdf>.

⁴¹ https://sasoldcproducts.blob.core.windows.net/documents/Safety%20Datasheets/2b5bc04e-d0a6_ZA_Low%20Sulphur%20Heavy%20Fuel%20Oil_EN-ZA.pdf.

⁴² <https://monjasa.com/wp-content/uploads/VLSFO-SDS-Final.pdf>.

⁴³ https://deutschemax.com/sites/default/files/files/MSDS_deutsch.pdf

⁴⁴ https://www.bomin.com/fileadmin/content/global_content/downloads/bomin-matrix/SDS_Bomin_DMA.pdf.

⁴⁵ https://ch-msds.shell.com/MSDS/000000000808_DE_EN.pdf.

⁴⁶ https://produkte.linde-gas.at/sdb_konform/H2_10021694EN.pdf.

Hazard statements	Hazard category	Ammonia ³⁸	CNG ³⁹	LNG ⁴⁰	LSHFO ⁴¹	VLSFO ⁴²	HSHFO ⁴³	MGO ⁴⁴	MeOH ⁴⁵	H ₂ ⁴⁶
H280 Contains gas under pressure; may explode if heated	Compressed gas		X							X
	Liquefied gas (b)	X*								
H281 Contains refrigerated gas; may cause cryogenic burn or injury	Refrigerated liquefied gas	X								
H304 Toxic if swallowed					X	X	X		X	
H304 May be fatal if swallowed and enters airways	1							X		
H311 Toxic in contact with skin									X	
H314 Causes severe skin burns and eye damage	1B	X								
H315 Causes skin irritation	2				X					
H331 Toxic if inhaled	3	X							X	
H332 Harmful if inhaled	4				X	X	X			
H350 May cause cancer	1B				X	X	X			
H351 Suspected of causing cancer	2							X		
H361 Suspected of damaging fertility or the unborn child	2				X	X	X			
H370 Causes damage to organs, optic nerve, central nervous system										
H373 May cause damage to organs through prolonged or repeated exposure	2				X	X	X			
H410 Very toxic to aquatic life with long lasting effects	1	X			X	X	X			
H411 Toxic to aquatic life with long lasting effects	2							X		

Notes: CNG: Compressed Natural Gas, LNG: Liquefied Natural Gas, VLSFO: Very low sulphur fuel oil, LSHFO: Low sulphur Heavy Fuel Oil, MGO: Marine Gas Oil

H: Hazard statement, 2: Physical hazard, 3: Health hazard, 4: Environmental hazard

Source: Authors' own compilation

2.1.5 Conclusions on toxicity

For the safe handling of ammonia onboard, robust safety guidelines are necessary. Even in small concentrations in the air, ammonia can be extremely irritating to the eyes, throat and respiratory tract.

Ammonia is a non-persistent and non-cumulative toxicant to aquatic life. Ammonia has been shown to be very toxic to many different freshwater and marine animal species, both acutely and chronically. The un-ionized ammonia is the primary cause of toxicity in aquatic systems. As the share of un-ionized ammonia in aqueous solution depends on pH, the toxicity of ammonia to aquatic organisms is very strongly dependent on the pH value, with higher toxicity corresponding to a higher pH. This is relevant to the marine environment, as the pH of seawater is relatively high, with typical pH values around 8. Other factors such as temperature, carbon dioxide, dissolved oxygen and salinity have a much smaller effect on the toxicity of ammonia.

Overall, the various studies show that the acute ecotoxicity of ammonia to fish and aquatic invertebrates is very high and in a similar order of magnitude as the acute toxicity of HFO. Studies show that ammonia also has long-term toxic effects on fish and aquatic invertebrates, but under real environmental conditions, ammonia concentrations are expected to decrease more rapidly after a spill than with HFO, because ammonia is a nitrogen source that is assimilated and therefore degraded by algae and microorganisms. However, this degradation through uptake as a source of nitrogen leads to significant eutrophication, which can result in an algal bloom with known effects such as a depletion of oxygen levels in the water or the release of toxins by the algae (section 2.3).

Unlike ammonia and HFO, methanol is not very toxic to fish and aquatic invertebrates.

2.2 Risks and leakages

In comparison to other fuel sources, ammonia presents several constraints as an energy carrier. Due to its vapour pressure, ammonia is highly volatile at atmospheric conditions, resulting in undesirable health and safety effects. If compressed ammonia is released, condensation and droplet formation result in the formation of 'ammonia clouds' at the ground level. These clustered concentrations of ammonia in the air are a critical problem, especially for distributors and users. (Brenchley et al. 1981)

If ammonia is spilled into water, it floats on the water surface, rapidly dissolving within the water body into ammonium hydroxide (NH_4OH), while at the same time boiling into the atmosphere as gaseous ammonia. The fraction of ammonia dissolved in water is highest for an underwater release with up to 95%. In this case, very little ammonia is released as vapour. For large releases at the surface, the ratio of ammonia in solution vs. ammonia in the vapour phase depends on the dynamics of the release and varies between 50% and 60% for rapid releases at the surface. For slow, continuous release at the surface, the ratio is approx. 66% (Raj et al. 1974).

Various studies have developed models for the spilling of ammonia during a ship accident and its dispersal in the water, e.g. Dharmavaram et al. (1994), Galeev et al. (2013) and Raghunathan (2004):

When liquid ammonia spills on water, rapid boiling ensues, resulting in the liberation of dense, white mist of ammonia vapour containing a large proportion of aerosols. The cloud is lighter than air and

rapidly rises into the atmosphere, while at the same time drifting horizontally on the prevailing wind. Vapour liberation can be continuous, as in a continuous spill, or more or less in a puff, in the case of an instantaneous spill. The rate of ascent depends on the wind speed. When the wind is light, the cloud forms a characteristic mushroom cloud before dissipating. The toxic hazard at the surface is lower in light winds than in strong winds because of the faster ascent.

For comparison, Table 8 shows some key considerations on behaviour and impacts of various oil-based fuels when spilled (NRPG; NE 2018).

Table 8: Oil spill characteristics and properties of different fuel types

Fuel type		Characteristics and properties		
Marine Fuel	Composition	Behavior when spilled	Spill Cleanup	Ecological Impacts
Bunker C/ Fuel oil No. 6	Residual oil	May sink or become neutrally buoyant. Forms tar balls and patties. Emulsifies (incorporates water).	Limited technologies for on-water recovery. Most of the cleanup will likely involve remediating shorelines and oiled substrate.	Coats feathers and fur. Persistent and sticky, can have long-term impacts to shoreline, intertidal, and benthic communities.
Intermediate Fuel Oil (IFO) 380	Residual oil (~98%) blended with distillate	May sink or become neutrally buoyant. Emulsifies (incorporates water) and may increase 2-3 times original spill volume.	Fresh product may be recoverable within hours of initial spill, but it becomes more difficult to recover with skimmers as oil emulsifies it. Weathered oil will coat surfaces and may be difficult to remove from coarse sediments and substrate.	
Intermediate Fuel Oil (IFO) 180	Residual oil (~88%) blended with distillate			
Low sulphur marine fuel oils	Residual oil blended with distillate (higher ratio of distillate to residual)	Initial laboratory and mesoscale testing suggest that it will behave similar to other residual oils, emulsifying and generally acting as a persistent fuel.	Poorly studied. Information from recent pipeline spill in Hawaii and the Wakashio VLSFO spill in Mauritius suggests that residual blends will pose similar response challenges to other residual fuels.	Poorly studied, likely to be similar to IFO. May have higher initial toxicity than residual fuels because of higher percentage of distillate, which will initially disperse or evaporate.
Marine diesel oil (MDO)/ Fuel oil No. 2	Distillate fuel that may have traces of residual oil	High percentage will evaporate or disperse into water column within first few hours of release. Will remain floating but slick will spread in open water.	Can be skimmed from surface if contained to sufficient thickness. As oil spreads and weathers, more difficult to recover.	High initial toxicity to wildlife, particularly in water column, but oil is less persistent in environment. Will still harm fur and feathers when it comes into contact.
Marine gas oil (MGO)	100% distillate			

Source: NRPG; NE (2018)

Leakages of ammonia are easily detectable due to its unique smell. Vries (2019) describes potential risks such as leakages, fires or ship collisions and mitigations strategies to avoid or limit impacts. To

avoid leakages of liquid and gaseous ammonia to cargo hold, engine room, compressor room, and areas in between, several strategies could be implemented:

- Flow and ammonia detection to alert crew and enable them to close valves stopping/limiting the impact;
- Locating piping in separate trunk to reduce the likelihood and impact of leakage;
- Ventilation to reduce the impact of the limited amount of spilled ammonia;
- Redundancy in supply line to assure operation can continue reducing the impact.

Locating piping in separate trunks and redundancy in supply lines also reduce the likelihood of a fire hazard. Furthermore, a pressure transmitter can alert the crew and valves can be automatically closed to isolate pressure and temperature in the system. Pressure build-up before valves can be reduced by a pressure relieve system of the storage tank.

Ammonia is highly corrosive towards copper, zinc, nickel and their alloys, and plastic. These materials must not be used in ammonia service. Iron and steel are usually the only metals used in ammonia storage tanks, piping and fittings. As the pH of ammonia lies between 9.0 and 9.4 it is not corrosive to ferrous materials. While anhydrous liquid ammonia can cause stress corrosion cracking (SCC) of vessels made of carbon steel and high-strength low-alloy steel at -33°C, stainless steels have shown no cracking tendencies in ammonia under any conditions (Technion 2017). Copper alloys also are susceptible to SCC in aqueous ammonia solutions at ambient temperature. For seals, nitrile rubber is usually used instead of conventional rubber because it is decomposed by ammonia. As for the requirements to the nickel alloy, the nickel concentration must be kept below 6% (MAN 2019).

2.3 Impact of emissions

Ammonia is linked to the global nitrogen cycle (section 1.1) and excess ammonia entering air, water and soil can contribute to air pollution, acidification and eutrophication of ecosystems or climate change (van Damme et al. 2018). The upstream emissions for using ammonia as a marine fuel mainly depend on the use of fossil or renewable energy (section 1.1.1), whereas the downstream emissions of ammonia or other associated emissions vary on the technology used onboard the ship (chapter 3). To understand the relevance of these emissions for the technical aspects of using ammonia as a fuel, the following describes the effects of ammonia emissions (and related emissions) in more detail.

As described in section 2.2, ammonia can get in contact with the marine environment due to spills where it is typically rapidly dissolved within the water body. Ammonia can also boil into the atmosphere as a gas. Ammonia emissions to air have an indirect cooling effect. Ammonia is an aerosol precursor and emissions of ammonia into the air thus contribute to the formation of particulate matter which has a negative radiative forcing (RF) (Myhre et al. 2013).

Emissions of nitrogen compounds (ammonia, ammonium or nitrogen oxides) can contribute to environmental effects which are caused by (over-)enrichment of a water body or soil with nutrients (like nitrogen and phosphorus) – a process called eutrophication (World Ocean Review 2017). An oversupply of nutrients causes an increase in algal growth which can cumulate in large (or even harmful) algal blooms. These algae die off in masses and are decomposed by oxygen-consuming microorganisms. This increases the oxygen consumption in the water body and can result in oxygen-deficient or -depleted zones. These conditions can be deadly for fish, crustaceans and other marine

life forms. Oxygen-depleted zones have been observed in many places like Chesapeake Bay or coasts in the Baltic Sea. These sometimes called 'dead zones' typically occur when there is a lot of nutrient run-off from agriculture and little mixing of the water column. Generally, eutrophication leads to changes in the structure and functioning of the entire marine ecosystem and instability. The reduction in ecosystem health leads to a decreased quality of ecosystem services such as fisheries, aquaculture and recreation (European Environment Agency 2019).

The combustion of ammonia might lead to emissions of nitrogen oxides (NO_x), including NO and NO_2 . NO_x emissions have an impact on climate. On the one hand, NO_x emissions have a warming effect (positive RF) through ozone production. On the other hand, there is also a cooling effect through the reduction of the lifetime of methane and thus methane's concentration in the atmosphere, and through the contribution to nitrate aerosol formation (Myhre et al. 2013). Overall, it is estimated that anthropogenic NO_x emissions have a negative RF (cooling effect) but the calculation of the net climate effect of NO_x is challenging due to different time scales of chemical interactions and high reactivity. NO_x is an air pollutant, especially in coastal regions (ICCT 2014).

Nitrous oxide (N_2O) emissions are of concern when it comes to the combustion of ammonia (section 3.1.2) as N_2O is a strong GHG with a global warming potential (GWP) of 298 over a 100-year time frame and including climate-carbon feedbacks (Myhre et al. 2013). Ammonia is part of the global nitrogen cycle and can therefore indirectly contribute to N_2O emissions which may also be part of the cycle (World Ocean Review 2017). The process responsible for converting nitrogen compounds into N_2O is called denitrification which takes place under anoxic or hypoxic conditions (e.g. in parts of the water column or soils). The IPCC (2019) lists a default value of 1% for the share of ammonia, or rather ammonia related nitrogen (ammonia-N), from atmospheric deposition which is converted into N_2O . This default value is very sensitive to environmental conditions. It is therefore currently difficult to estimate values for these indirect N_2O emissions which could potentially be initiated on the medium-term through an influx of ammonia in the marine environment if used as a marine fuel.

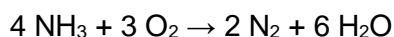
3 Technology on board

There have been demonstrations of co-combusting ammonia in coal power plants and gas turbines on land (DNV GL 2020a). Gas turbines are still used in naval vessels, but internal combustion engines (ICE) are the most common form of power generation in shipping (Vries 2019). Nowadays, two- or four-stroke diesel engines are mostly used in maritime transport, but fuel cells are gaining interest of the industry. On a marine vessel, ammonia could thus be used as a fuel in an ICE or in a fuel cell (FC). The following sections describe these technology options, associated emissions and transition strategies.

3.1 Internal combustion engine

3.1.1 Ammonia combustion

Evidence of ammonia being used in combustion engines goes back to the Second World War. Ammonia was mixed with coal gas to fuel buses and vehicles in Belgium during this war and the US military experimented with ammonia as a fuel for vehicles in the 1960s (CUT 2014; DNV GL 2020a). Afterwards, research on ammonia as a fuel was paused. Since the 2000s and 2010s, it has become an area of research again. However, there is only a limited number of published tests on running an ICE on ammonia. Both compression ignition (CI) engines, like the diesel engine, and spark ignition (SI) engines, e.g. engines following the Otto principle, are investigated (as reviewed in Dimitriou and Javaid (2020), Hansson et al. (2020b) and Vries (2019)). Most research focused on smaller, automobile-sized engines, not suitable for use in large ships (DNV GL 2020a). The overall reaction of ammonia combustion is (Kobayashi et al. 2019; Li et al. 2014):



Ammonia is generally a flammable gas, but it is relatively hard to ignite. The following properties are challenging for combustion: high auto-ignition temperature (651°C), low flame speed, narrow flammability limits and high heat of vaporization (CUT 2014). These can result in unstable combustion conditions at very low or very high engine speeds (EDF 2019; Kim et al. 2020). Although some researchers have successfully operated an engine on ammonia only, the engine performance is limited compared to ammonia-mixtures with for example hydrogen (Dimitriou and Javaid 2020; Vries 2019).

Challenges of pure ammonia combustion exist for both CI and SI engines. Due to its high-auto ignition temperature, ammonia requires a higher compression ratio (35:1 and higher) than used in typical CI engines (16-23:1) (KR 2020; Dimitriou and Javaid 2020). It is difficult to design such an engine and therefore studies on CI engines have mainly examined mixing ammonia in different fuel ratios under various conditions (Dimitriou and Javaid 2020). The addition of a second fuel, with lower auto-ignition temperature, can help to combust the mixture and allows for a more stable combustion. As the minimum ignition energy of ammonia is high, the design of SI engines, like the ignition plugs, would have to be adjusted for combustion (KR 2020; CUT 2014). A complete combustion of ammonia would still be difficult due to its low flame speed. Therefore, also research on SI engines has focussed on the combustion of ammonia in mixtures. SI engines running on ammonia would likely be used for smaller ships, whereas modified two-stroke (dual fuel) CI engines could be suitable for larger ships (KR 2020).

The literature provides examples of a variety of fuels which were used to help the combustion of ammonia, for example diesel, methanol, DME or hydrogen. While for SI engines, ammonia might

preferably be better mixed with gaseous fuels like methane, fuels with higher cetane numbers (like diesel) are better suited to enable combustion of ammonia in CI engines (CUT 2014). Significant amounts of pilot or ignition fuel were used for both of these engine types in most studies (Hansson et al. 2020a). However, there are studies confirming up to 95% ammonia share (by energy) in a CI engine in dual fuel mode with diesel (Dimitriou and Javaid 2020). Tests have also been on using hydrogen as a secondary fuel to ammonia in SI as well as CI engines (CUT 2014; Dimitriou and Javaid 2020; Hansson et al. 2020b).

Using hydrogen to combust ammonia is particularly interesting because hydrogen is zero-carbon and could potentially be retrieved by cracking ammonia directly onboard. An ammonia-hydrogen mixture can have similar properties as methane and is thus easier to ignite than pure ammonia (Vries 2019). While different mixing ratios have been tested, ammonia ratios of up to 95% (by weight) have been achieved, meaning 70% ammonia and 30% hydrogen by volume (Dimitriou and Javaid 2020; Kim et al. 2020). Vries (2019) analyzes different marine propulsion set-ups and concluded that an ammonia-hydrogen mixture in a CI engine is feasible. The ammonia engine (with an ammonia hydrogen mixture) is expected to have an efficiency of around 50% (KR 2020; Vries 2019).

Most of the studies mentioned have not conducted real-world tests with typical large diesel engines used in maritime transport. The variety of industry projects announced (section 1.2) might fill the knowledge gap on using ammonia in ICE. MAN announced, for example, that hydrogen and DME will be investigated as pilot fuels for their ammonia CI engine (MAN 2019). The option of burning ammonia with the aid of hydrogen as pilot fuel is a very promising option from a climate perspective.

3.1.2 Combustion emissions

For the decarbonization of the maritime sector, future marine fuels need to be climate neutral from a well-to-wake perspective and assessed on a CO₂e basis. Although ammonia does not contain carbon, GHG emissions could be released during its production (upstream) or during its use as a fuel on-board a ship (downstream). Upstream emissions can be reduced close to zero if ammonia is produced with renewable energy as explained in section 1.1.1. Downstream, or tank-to-propeller, emissions will depend on the propulsion technology used (ICE or FC) and respective combustion processes (mixing ammonia with other fuels).

Ammonia by itself will not emit CO₂ emissions upon combustion as it is a zero-carbon energy carrier. The reaction, detailed in section 3.1.1, shows that the combustion of ammonia generally results in nitrogen and water. The use of carbon-based pilot fuels could, however, generate CO₂ emissions. The level of these emissions is dependent on the amount of pilot fuel used to combust ammonia. Particulate air pollutants like SO_x are not of concern if ammonia is used as a fuel. However, tests indicate that the combustion of pure ammonia or ammonia mixture potentially leads to GHG or harmful emissions (Alfa Laval et al. 2020; Vries 2019; DNV GL 2020a):

- nitrogen oxide (NO_x),
- ammonia slip (unburnt ammonia),
- nitrous oxide (N₂O).

NO_x and NH₃ slip

NO_x emissions are mainly generated by the reaction of nitrogen (N) and oxygen (O) from the air under high temperatures in the combustion process. Several factors influence NO_x formation. Even

though ammonia contains more nitrogen than conventional marine fuels, NO_x formation during combustion is rather dependent on temperature and pressure than purely on the abundance of nitrogen (Concawe 2020). Tests with high-speed small-scale engines have shown that ammonia-hydrogen mixtures have a similar performance to diesel fuel (Vries 2019). For reference, emission factors for NO_x from the combustion of HFO and MGO are 76-79 and 52-58 kgNO_x/t of fuel (IMO 2020). Carbon-based post-fossil fuels like green diesel, but also gas-to-liquid fuels, already have improved combustion characteristics resulting in lower NO_x and particulate matter emissions than their fossil counterparts (Concawe 2020). More research is needed on the exact NO_x levels from different ammonia mixtures, preferably with hydrogen, in larger marine engines.

The relationship between NO_x and ammonia slip is unfortunate. Literature on CI engines shows that NO_x emissions tend to be produced at high combustion temperatures and unburnt ammonia at low temperatures, with no “ideal” temperature level eliminating both of these emission species (Dimitriou and Javaid 2020). Additionally, emissions of unburnt ammonia can occur during unstable combustion conditions. However, there is insufficient research on the exact ammonia slip levels in large marine engines (Vries 2019).

Solutions to both NO_x emissions and ammonia slip exist. There are ammonia slip catalysts which are already developed for land-based and road transport (EDF 2019). Unburnt ammonia and NO_x emissions can be reduced through engine calibration and more controlled combustion conditions, e.g. by applying exhaust gas recirculation (EGR, MAN 2019). These are currently the topic of research (EDF 2019). Exhaust gas aftertreatment systems to reduce NO_x emissions, like the selective catalytic reduction (SCR), are already widely used in the maritime sector (ICCT 2014). In the SCR system, ammonia is used as a reducing agent to reduce NO_x to nitrogen (N₂) and water vapour in presence of a catalyst (EDF 2019; MAN 2019). The advantage of ammonia-fuelled ships is that the reducing agent is already onboard and thus readily available (Alfa Laval et al. 2020).

To reduce the negative impacts of NO_x emissions globally (section 2.3), MARPOL Annex VI prescribes global NO_x emission limits which are set for diesel engines depending on the engine maximum operating speed and the construction date of the ship.⁴⁷ Ships built after 2011 have to comply with the NO_x limit “Tier II”. Tier II standards are expected to be met by combustion process optimization.⁴⁸ NO_x emissions of an ammonia-hydrogen mixture in a slow-speed two-stroke engine could be 14 g/kWh, if a similar performance to diesel combustion is assumed (as in Vries (2019)). This would be compliant with Tier II. Tier III applies in NO_x emission control areas (NECAs) to ships built after 2016 and could reduce NO_x emissions by 70% compared to Tier II.⁴⁹ NECAs have existed in the coastal waters of North America in the United States Caribbean Sea for ships built in 2016 or later. From 2021, Tier III also applies in the North and Baltic Sea around Europe but, again, only for newly built ships. To comply with Tier III, ships might use dedicated NO_x emission control technologies like EGR or SCR (EDF 2019). SCR can reduce NO_x emissions effectively even beyond the Tier III standard (over 90%, ICCT 2014).

N₂O

There is a risk of N₂O emissions when combusting ammonia (DNV GL 2020a; EDF 2019; KR 2020). From the literature review, it can be derived that the main origin of N₂O emissions is the combustion process. A few studies also revealed N₂O formation as a by-product in aftertreatment systems like

⁴⁷ IMO – Air pollution from ships: <https://www.imo.org/en/OurWork/Environment/Pages/Air-Pollution.aspx>.

⁴⁸ <https://dieselnet.com/standards/inter/imo.php>.

⁴⁹ EC – Air emissions from maritime transport: <https://ec.europa.eu/environment/air/sources/maritime.htm>.

SCR (Kamasamudram et al. 2012; EDF 2019). N₂O might result from a reaction of NO_x and ammonia over the SCR catalyst, but could be minimized by the calibration of the SCR system and by using catalysts which produce less N₂O (Kumar et al. 2015).

N₂O emissions can occur under certain conditions during the combustion as tests with ammonia-diesel mixtures have shown (Gill et al. 2012; Kobayashi et al. 2019; Zincir 2020). Studies from Niki et al. (2019a; 2019b) indicate that N₂O emissions can be reduced at high combustion temperatures and by applying multiple fuel injections into the cylinder. High combustion temperatures also reduce ammonia slip but lead unfortunately to higher NO_x emissions (see above). This indicates that future engines could minimize N₂O and ammonia slip by operating on high temperatures, whereas NO_x would be reduced by SCR for compliance with ECAs. Interestingly, catalysts for the combined removal of NO_x and N₂O are commercially available according to Alfa Laval et al. (2020). Optimizing the combustion process and eliminating any remaining emissions with exhaust gas aftertreatment systems might therefore be a way forward. Whether these methods would also work in ammonia-hydrogen mixtures has not, however, been established. Studies which listed N₂O as a potential emission species were conducted in different testing set-ups and with different methods. Fossil marine fuels like HFO and marine diesel oil emit around 0.18 kgN₂O/t of fuel (IMO 2020). A comparison with current fossil fuels is not possible given the lack of strong evidence and reliable data.

Ammonia needs to perform better than fossil fuels to be an alternative for the decarbonization of the sector. Therefore, the elimination of N₂O emissions (or the reduction to a negligible minimum) needs to be proven in typical marine engines. Engine optimization tests on how to deal with N₂O and tests of potential exhaust gas cleaning systems are being undertaken now – but today the technology is not proven yet.⁵⁰

Conclusion

Further research is necessary to clarify the quantity and type of emissions resulting from burning ammonia in varying ratios with other fuels. The application of exhaust gas aftertreatment systems seems to be a promising solution in the case of unavoidable NO_x emissions and ammonia slip. For any climate benefit of green ammonia, issues with N₂O emissions must be solved. Stringent N₂O emission regulations need to be established to ensure that ammonia engines are compatible with the long-term goal of climate-neutral maritime shipping. To incentivize the development of adequate marine machinery, N₂O could, for example, be covered by maritime carbon pricing policies or be limited to tolerable levels through stringent emission standards on the basis of carbon dioxide equivalents.

3.1.3 Bunkering and storage

Ammonia is usually transported and stored in its liquid form to reduce its volume and avoid undetectable leakage. The liquefaction can be carried out at low cost through pressurization or cooling (UBA forthcoming). Ammonia can be stored in refrigerated tanks at -33°C at 1 bar or in pressurized tanks at 25°C at 10 bars. Table 9 provides an overview of the fuel properties of ammonia in comparison to other fuels. Ammonia is, for example, easier to store and transport than hydrogen,

⁵⁰ DNV (2020) - The role of combustion engines in decarbonization – seeking fuel solutions: <https://www.dnv.com/expert-story/maritime-impact/The-role-of-combustion-engines-in-decarbonization-seeking-fuel-solutions.html>.

but less convenient compared to methanol (KR 2020). The storage conditions of ammonia (temperature and pressure) are very similar to liquefied petroleum gas (LPG) (Alfa Laval et al. 2020; MAN 2019). Despite existing vessels transporting ammonia, LPG carriers may also be used for transporting ammonia as a cargo (DNV GL 2020a). Ammonia has 3.5 times the volume of HFO or in other words, the tank size would be 4.1 times larger than an MGO tank and twice the size of an LPG tank due to the lower energy density (KR 2020; MAN 2019). Additionally, the space requirement of an ammonia tank is also dependant on the energy efficiency of the propulsion system (e.g. FC or ICE). The Ammonia engine is expected to have an efficiency comparable to existing marine engines of around 50%, as mentioned in section 3.1.1. A more detailed comparison with other fuels is offered in chapter 6.

Table 9: Comparison of fuel properties

Fuel type	LHV [MJ/kg]	Volumetric energy density [MJ/l]	Storage pressure [bar]	Storage temperature [°C]	Tank volume*
Liquefied Ammonia	19	12.7	1 or 10	-34 or 20	4.1
Liquefied Hydrogen	120	8.5	1	-253	7.6
Methanol	20	15.8	1	Ambient	2.3
Methane	50	23.4	1	-162	2.3
LPG	46	25.5	1	-42	2
MGO	43	36.6	1	Ambient	1
HFO	40	35	1	Ambient	1

Notes: LHV: lower heating value; *tank volume relative to conventional MGO tank
 Sources: KR (2020), Vries (2019), MAN (2019)

The properties of ammonia thus require ammonia-fuelled vessels to have larger fuel tanks onboard vessels to bunker an equivalent amount of HFO based on the energy content. Retrofitting larger ammonia tanks on vessels might thus lead to cargo space loss. Instead, a ship could refuel more often to avoid any loss of cargo space. A higher refuelling frequency might in turn lead to time losses and thus revenue losses. A study carried out on the application of hydrogen FCs on deep-sea container shipping routes in the Pacific Ocean indicates, however, that cargo space loss due to larger fuel tanks will likely be very limited and that refuelling stops can be mostly avoided in return for a very small percentage of cargo space loss, even on long-range Pacific routes (ICCT 2020). As the energy density of ammonia is higher than for hydrogen, the impact on operation and refuelling might be even lower. It is not necessarily a given, therefore, that using ammonia results in significant revenue losses due to refuelling or cargo space loss. The extent to which a higher refuelling frequency will be necessary is subject to more detailed research on different vessel types and routes. DNV GL (2019) expect that a typical bunker interval for liquefied ammonia will likely be similar to LNG-fuelled vessels with a length of weeks to months. And LNG ships are already increasingly used in deep-sea shipping despite this change in bunkering intervals compared to HFO.

Due the corrosiveness of ammonia some materials should be avoided (section 2.2). More specifically, copper alloys, alloys with a nickel concentration above 6% and plastics should be

avoided in the fuel system (MAN 2019). These requirements are deemed manageable as many common materials, like stainless steel or carbon, are compatible with ammonia, meaning that most standard pipes etc. can be used with ammonia (EDF 2019). The toxicity of ammonia (chapter 2) requires certain changes and safety measures compared to conventional fuel system set-ups. Some of the HFO-specific equipment will not be needed anymore (e.g. heaters or a settling tank) but new systems will be needed in the engine room like the liquid fuel supply system (LFSS) and the SCR. The design of the LFSS depends on the engine technology used. MAN (2019) also works on the corresponding LFSS to its ammonia engine. Many new vessels are already equipped with SCR systems to comply with Tier III NO_x standards in existing NECAs (section 3.1.2). These vessels will already have relevant storage and handling equipment onboard to deal with the ammonia or urea used for SCR. New systems onboard a ship are mainly of concern due to the investment costs, which are not the focus of this report. Studies have been conducted on the cost perspective of ammonia and other post-fossil fuels (DNV GL 2020b; LR; UMAS 2019a; Korberg et al. 2021).

Bunkering of ammonia can take place via terminals or trucks onshore and via a bunkering ship. Safe loading and unloading of ammonia from/to terminals is possible, but DNV GL (2020a) point out that safety might be improved if bunkering takes place via a bunkering ship as an intermediate between the terminal and the ammonia-fuelled vessel. Especially in case of large amounts of ammonia, like for deep-sea vessels, the use of a bunkering ship should be preferred as well as in densely populated areas (DNV GL 2020a). For a fast and cost-efficient expansion of ammonia bunkering, small gas tankers could be converted to ammonia bunker barges (Alfa Laval et al. 2020). The use of bunkering ships was also applied for LNG in order to reduce bunker infrastructure investment costs and provide flexibility. The differences can lead to challenges, for example, in terms of safety. Tank type A (fully refrigerated) and C (semi- or fully pressurized), according to the IGF code, are used for transporting ammonia as a cargo and could also be used as fuel tanks (DNV GL 2021). Temperature and pressure conditions of the ammonia tank onboard the ammonia-fuelled vessel might not always be the same as the storage conditions of the bunkering vessel or terminal. DNV GL (2020a) recommend the use of pressurized tanks because it would allow the bunkering from ships (with pressurized or semi-refrigerated tanks) without major modifications. Alfa Laval et al. (2020) point out that a Type C pressurized tank also allows for a flexible installation on the deck or in an integrated design of a ship.

3.1.4 Application in marine shipping and transition

Dual fuel engines can run both on liquid and gaseous fuels and are available as two- and four-stroke marine engines. These engines are basically hybrids and have many features in common with CI and SI engines. Typically, the operation of dual fuel engines involves a mixing of the primary fuel with air in the cylinder, like in SI engines, with subsequent compressions-ignition of a diesel pilot fuel, like in CI engines. Dual fuel engines have been increasingly used in the global shipping fleet, often complementing HFO or MGO with LNG, methanol or LPG, and are available for all ship sizes (EDF 2019). Typically, these engines run on either one of these fuels (but allowing an easy switch between the fuels). They might also be mixed in varying degrees. Often one fuel acts as a pilot fuel for the combustion of the second one. Considering the need for mixing ammonia with another fuel to facilitate combustion (section 3.1.1), dual fuel engines are an optimal starting point for the use of ammonia in marine vessels.

MAN (2019) expect that ammonia as a fuel could enter the maritime sector either as a dual fuel retrofit solution for existing electronically controlled engines, as an “ammonia-ready” engine or as a new built ammonia engine. There is no distinct definition for “ammonia-ready”; the term can describe engines which run on other fuels than ammonia (e.g. LPG) but are in theory able to run on ammonia

in the future. Two major engine manufacturers are already working on developing an ammonia engine for two-stroke and four-stroke marine engines (section 1.2).

MAN (2018) indicate that 3000 of MAN engines can be retrofitted to run on ammonia and many new engines installed are dual fuel capable. Based on section 3.1.1, it seems possible, therefore, to use existing (dual fuel) engines to run on ammonia. However, the combustion properties of ammonia would require modifications to the fuel supply system, an appropriate ammonia tank and relevant adjustments to the engine to allow for a stable combustion. The profitability of a retrofit might depend on the cost of those modifications. The retrofitting of ships which already have dual fuel engines is practical as a pilot fuel like diesel is readily available. The ship operator can easily switch between fuels, for example to comply with limits in emission control areas (ECAs). Mixing ammonia with fossil fuels can already lead to substantial emission reductions. A mix of MGO and ammonia in a ratio of 1:9 could offer a GHG emission reduction of up to 80% (KR 2020). Depending on the materials used, the corrosiveness of ammonia might hamper retrofits to old vessels.

The new MAN ammonia engine is based on the existing ME-LGI engine concept from their dual fuel series (MAN 2019). This engine concept is already used for LPG dual fuel engines (ME-LGIP) which are thought to be easily converted to run on ammonia (retrofit) or to be designed as “ammonia-ready” from the beginning, while still allowing for LPG combustion (MAN 2019). The MAN ME-LGIP engines can run with varying portions of gaseous and liquid fuels (Alfa Laval et al. 2020). The additional similarities between ammonia and LPG in storage conditions (see above) make LPG fuelled vessels, LPG carriers and ammonia carriers promising candidates to be the first vessels to run on ammonia (DNV GL 2019; MAN 2019). Already today ammonia is transported by around 70 LPG carriers (Alfa Laval et al. 2020).

Overall, dual fuel engines seem to be a good starting point for ammonia retrofits in the short term while also allowing flexibility during the transition of the sector and the limited availability of green ammonia in the near future (section 4.2). Dual fuel ammonia engine and fuel systems are among the most promising “future-proof” options for the industry, also regarding costs (DNV GL 2020b). EDF (2019) outlines a timeline for ammonia propulsion technologies, starting with further development and first demonstrations of ammonia in CI and SI engines until 2025 and subsequent commercialization for scale-up from 2025 and the late 2020s respectively. The deployment of ammonia in maritime shipping is subject to a timely revision of the necessary regulatory framework. Today the IGC code prohibits the use of ammonia as a toxic cargo also as a fuel. This hinders potential first deployments of ammonia on ammonia carriers and would need to be addressed in a timely manner.

3.1.5 Conclusion

The performance of pure ammonia combustion is limited but mixing ammonia with other fuels (e.g. hydrogen) can help to overcome these disadvantageous properties and improve the performance (CUT 2014; EDF 2019; Vries 2019). More research on engines and respective fuelling systems specifically for marine applications is needed, especially on the potential emissions from ammonia combustion. Dual fuel engines will be the most promising pathway for ammonia to enter the maritime sector with possible first use cases in LPG carriers.

3.2 Fuel cell

The use of ammonia in fuel cells (FC) has the potential for higher efficiency, less noise, reduced air pollutants and reduced space compared to ICE (EDF 2019). However, ammonia fuel cell systems for marine applications are currently more costly than the use of ICE, which is considered a main bottleneck for their uptake in shipping (Vries 2019; DNV GL 2019). In principle, there are two options: either ammonia is used indirectly as a hydrogen carrier or directly in a fuel cell. The most promising fuel cell types for the maritime sector are proton exchange membrane fuel cells (PEMFC) and solid oxide fuel cell (SOFC).

3.2.1 PEMFC and SOFC

The PEMFC is already used in road transport and are also commercial and tested in marine applications (Hansson et al. 2020b; KR 2020). The PEMFC requires highly purified hydrogen as a fuel and therefore ammonia would need to be cracked into hydrogen and nitrogen on-board a vessel (Hansson et al. 2020b). After cracking, the hydrogen would need to be purified to reach the required purification levels of hydrogen for the PEMFC. Using ammonia as a hydrogen carrier has the advantage that ammonia is easier to store and requires less space than hydrogen itself (Table 9). Emissions of NO_x and fuel slip are not expected for PEMFC (Vries 2019). The PEMFC has a higher tolerance for engine load variations than the SOFC allowing for a more flexible operation (DNV GL 2019). The load response requirements differ depending on the ship type. While this advantage of the PEMFC is not as relevant for a bulk carrier, it is relevant for a tug boat, for example, which has to cope with high fluctuations of load response (Vries 2019). However, the hydrogen cracking reduces the efficiency of the system and increases cost and size of the propulsion system (ICCT 2018). Additionally, the PEMFC is very sensitive to ammonia impurities (DNV GL 2020a).

For the second option, ammonia can be directly used in SOFCs (Hansson et al. 2020b). The SOFC operates at higher temperatures (~1000°C) than the PEMFC and no cracking or purification step is needed (KR 2020). The technology readiness level (TRL) of SOFC is lower than that of PEMFC because there have been no tests with ammonia SOFC in marine applications and SOFCs have been mostly studied for land-based power generation (Hansson et al. 2020b; KR 2020). An EU-funded project will explore the application of an ammonia SOFC on a vessel (section 1.2). SOFC is a promising candidate as a fuel for the future due to its direct use of ammonia but it is uncertain which emissions are associated with an SOFC considering the lack of tests (Hansson et al. 2020b). As noted before, the emissions will likely be significantly lower than what can be expected from ICE (EDF 2019). The higher operation temperature of the SOFC compared to a PEMFC make NO_x emissions more likely, but there are options to prevent them (Vries 2019). More evidence from demonstration projects is needed, however. KR (2020) notes that it could be envisioned to deploy the SOFC in combination with PEMFC or batteries to achieve a sufficient power output for the main and auxiliary engine.

When ammonia is used in a FC system (including the FC and an electric engine), the same conditions regarding materials and tanks apply as in an ICE system onboard a ship. While FC typically achieve higher efficiencies requiring less fuel and hence tank space, the power output per FC module is still rather low (UBA forthcoming). FC can be stacked to increase the power output, but this in turn requires more space. Application of FC for large ships as the main propulsion system is, therefore, still limited. Retrofitting ships to run on FC is possible but constrained. In addition to the capital costs, FC are not an easy retrofit solution for the short term because they might require additional space and an electric propulsion engine (DNV GL 2019; UBA forthcoming). Equipment

like scrubbers for fossil fuels are not needed anymore. A study by ICCT (2020) on deep-sea container shipping indicates that cargo space loss due to FC might actually be small, or even zero. The different impacts on space onboard a ship need to be weighed for each propulsion system in the end. It should also be noted that currently no FC has a lifetime comparable to the lifetime of a ship (UBA forthcoming).

It is thus uncertain to what extent ammonia FC will be deployed in shipping. While there is an increasing number of FC projects in shipping (UBA forthcoming), there is only one project on the use of ammonia in a FC (section 1.2). PEMFC would likely take off sooner because PEMFC are further developed than SOFC. At the moment, FC seem to be rather suitable for short-sea shipping (DNV GL 2019).

3.2.2 Conclusion

While ammonia FCs have advantages, their development and deployment on a large-scale will take more time than the use of ammonia in ICE (EDF 2019). The combustion of ammonia in ICE offers the potential for short-term GHG reduction and is less expensive. However, the application and development of SOFC for marine applications should be further pursued given their better performance in terms of energy efficiency and emissions. The necessary power output of FC to power deep-sea vessels might be enhanced by further research, by stacking of FC or by adding batteries.

4 Infrastructure

The future supply of ammonia to the maritime sector could build on substantial experience in trading and producing ammonia globally. Many aspects of infrastructure, storage and transport have a high level of maturity (The Royal Society 2020). Ammonia can be transported as a gas or liquid. For transport of large quantities of cargo, refrigerated tanks on ships will be the likely form of ammonia transport as these become economical at large storage volumes whereas land-transport will likely happen with pressurized tanks (EDF 2019). Ammonia is also the cheapest form to transport hydrogen on long distances and in large volumes (BNEF 2020). If hydrogen production is scaled up globally, ammonia infrastructure can benefit from this by being a transport medium for hydrogen. Around 11% of global ammonia production is exported and mainly transported by ship (Yara 2018). 170 ships are capable of transporting ammonia as a cargo today (Alfa Laval et al. 2020). Any transport of ammonia involving fossil fuels impacts of course the well-to-wake performance of GHG emissions. (Green) ammonia carriers using their own cargo as fuel would be a practical approach in this regard (section 3.1.4). Alfa Laval et al. (2020) provide an overview of the importing and exporting ports in different regions, creating a comprehensive network of ports that handle ammonia. In around 120 ports, there is infrastructure for ammonia exports or imports. Many terminals are part of ammonia or fertilizer plants located close to the sea. Therefore, expanding existing supply infrastructure seems less of an issue compared to the upscaling of the production of green ammonia.

4.1 Production costs

In the current fossil-based production, a major part of the costs to produce ammonia is determined by the natural gas prices (Hansson et al. 2020b). The competitiveness of green ammonia will depend on future prices of renewable energy, any carbon pricing influencing natural gas prices and capital expenditure for ammonia plants. It will be important that investment costs for green ammonia production decrease because these are much higher at the moment for a green ammonia plant than for the conventional production route (DNV GL 2020a). Electrolysers make up the biggest share of capital expenditure today, but these costs are expected to decrease if the technology gets upscaled. The production cost of green ammonia is estimated to range between 100-150 €/MWh in the near future, mainly depending on the electricity prices, compared to a fossil-based ammonia of around 55 €/MWh (Hank et al. 2020; Korberg et al. 2021; IRENA 2019). Hochman et al. (2020) projects production costs to be below 100 US\$/MWh in 2040, whereas IRENA (2019) estimate green ammonia prices to be around 80 US\$/MWh in 2040. Future prices are, however, highly dependent on electricity prices and assumptions on the investment costs. Decisive for ammonia's uptake in shipping are not only the production costs, but also costs for transport, storage and equipment onboard a ship. Korberg et al. (2021) offers a comparison of the costs of post-fossil fuels including operational and capital expenditures on the ship. They conclude that the total cost of ownership (TCO) of ammonia is slightly higher than for methanol but the lowest cost solution for eliminating the carbon content of future fuels. However, LR; UMAS (2020) project lower TCO for ammonia than for methanol arguing that it does not require expensive direct air capture (DAC) for CO₂. The differences can partially be explained by the uncertainty about future for DAC which is also very energy intensive.

4.2 Production capacities

In 2018, about 180 Mt of ammonia were produced globally. The capacity of ammonia production is about 20% higher (220 Mt in 2018) indicating some 'spare capacity' (Argus 2020). The production of

ammonia has hitherto steadily increased and future growth in demand and supply is expected (Alfa Laval et al. 2020; IEA 2020).

In recent years, several green ammonia demonstration and pilot plants have started or been announced, e.g. in the UK, Japan, Morocco and Australia.⁵¹ In Germany, the company Aquamarine already has plans for a large-scale green ammonia plant but will start with a smaller plant in the first stage: a 100 MW solid oxide electrolyser will produce hydrogen that will be processed to 300 t NH₃/day by 2024.⁵² In Denmark, a facility with 1 GW of electrolysis aims to be Europe's largest green ammonia production facility supplying agriculture and shipping. A larger project has started in Saudi Arabia to build a four GW green ammonia plant by 2025.⁵³

Global marine fuel consumption was approx. 238 Mtoe in 2018 (IMO 2020). To meet these needs, an equivalent amount of about 500 Mt of ammonia would be necessary because the energy density of ammonia is roughly 50% lower than of HFO/MGO (Table 9). If only 30% of the global fleet were powered by ammonia, an additional 150 Mt of ammonia would be needed, which is almost as much as current global production. However, this amount could already fuel the entire fleet of container vessels, which is the sector with the highest fuel consumption (IMO 2020).

As the shipping sector is expected to grow in the future, the energy demand (and the respective demand for post-fossil fuels like green ammonia) will also grow. For example, EDF (2019) calculates that between 255 and 493 Mt of ammonia per year would be needed to power the complete international fleet of container and dry bulk vessels in 2050.

It is worth considering the amount of ammonia needed in 2030 to obtain an idea of the scale of investment and production needed in the short term. GMF (2021b) calculates that decarbonizing shipping by 2050 would require a 93%-share of ammonia in the global fleet by 2046 and a 5% uptake of ammonia in 2030, if ammonia emerges as the dominant fuel of the future. The corresponding fuel consumption is 15.8 Mtoe or about 33 Mt of ammonia. This amount would have to be increased though substantially to cover 93% of the energy demand of more than 15 GJ projected for 2046 in their scenario.

In other words, the current ammonia production is not able to supply the entire shipping fleet, irrespective of the demand from other sectors like the agricultural sector. To even supply a smaller portion of the shipping fleet with ammonia, additional production capacities are needed. Besides the need for an increase in renewable energy, the bottleneck for scaling-up green ammonia production is the production capacity for electrolysers (Alfa Laval et al. 2020). It should be noted that there might be additional (even though comparably small) volumes of ammonia needed for its use in SCR systems if ammonia is applied on a large scale. The future demand for green ammonia can be met by installing new production facilities. In addition, production capacities can be partially increased by revamping existing plants and by using the "spare" capacity from today (Alfa Laval et al. 2020). In existing plants, green hydrogen can be partially introduced to replace hydrogen from SMR. For their decarbonization scenario by 2050, UMAS (2020) estimates that 1.4-1.9 trillion US\$ of investments would be necessary to decarbonize shipping with ammonia as the primary fuel. It is uncertain today if and to what extent ammonia will be part of the future fuel mix in shipping. Green ammonia

⁵¹ Brown (2018) – Green Ammonia plants, commercially available today:

<https://www.ammoniaenergy.org/articles/green-ammonia-plants-commercially-available-today/>.

⁵² <https://blog.topsoe.com/haldor-topsoe-and-aquamarine-enters-into-a-memorandum-of-understanding-with-the-purpose-of-building-a-green-ammonia-facility-based-on-soec-electrolysis>.

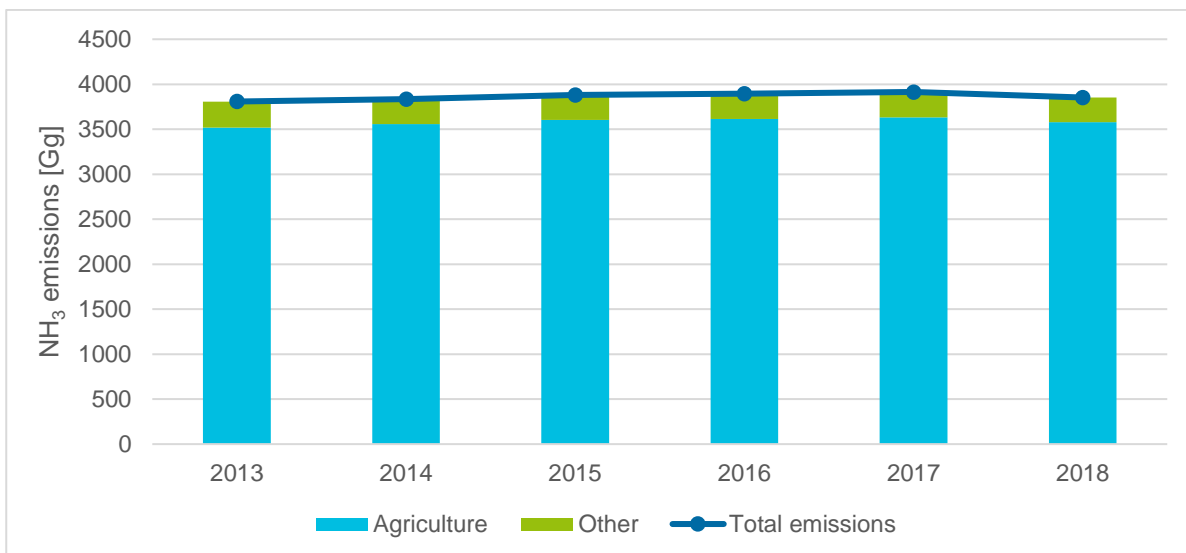
⁵³ <https://www.ammoniaenergy.org/articles/saudi-arabia-to-export-renewable-energy-using-green-ammonia/>.

production facilities will not be stranded assets, however, independently of the demand from maritime transport and whether ammonia will be used in ICE or FC. Green ammonia is also needed for the decarbonization of other sectors (see next chapter). Policies supporting the scale-up of green ammonia can thus be considered a no-regret policy (UBA forthcoming).

5 Synergies with other sectors

The total volume of global ammonia emissions and their attribution to specific sources or regions remain uncertain. Top-down estimates from satellite observations and bottom-up activity data differ (van Damme et al. 2018). The majority of ammonia emissions stem from anthropogenic sources, namely agricultural, industrial and domestic activities (van Damme et al. 2018). Point sources of ammonia emissions to air are typically intensive animal farming or fertilizer production sites. Larger diffusive areas of emissions can likely be attributed to crop fields and the burning of biomass (van Damme et al. 2018). Ammonia emissions in the EU have increased slightly in the period from 2013 to 2017 (Figure 2). In 2018, total ammonia emissions decreased slightly to approx. 3 850 Gg. For a number of years, over 90% of ammonia emissions have come from the agriculture sector (with more than 2/3 from livestock) in the EU (Figure 2). In Germany, 12% of ammonia emissions (68 Gg) in the agricultural sector can be attributed to synthetic fertilizer (Thünen-Institut 2021).

Figure 2: Ammonia emissions in the EU



Source: EEA (2020)

Plants (or crops) require nutrients to grow. Nitrogen (N) is one of the primary nutrients for plants and is essential for the growth and development of a plant (Yara 2018). To increase agricultural production and counterbalance nutrient depletion in soils, fertilizers have been deployed globally to provide these nutrients to the plants. Besides organic fertilizers like manure, global food production heavily relies on synthetic fertilizer today. Ammonia is an important intermediate for all nitrogen fertilizer products (Yara 2018). Although there are considerable losses of ammonia (or rather nitrogen fertilizers) in agriculture, this is not intended. Considering the benefit of fertilizer application, the agricultural sector needs to attempt to close the loop to minimize the ammonia losses. These losses are mostly very diffuse. Therefore, it is not practical to collect these losses in order to reuse them in agriculture or as a fuel in the maritime sector. It is rather a matter of reducing the applied amounts of fertilizer or applying them in a more precise way. In future, overfertilization needs to be reduced and improved farming methods need to be applied. Anyhow, the agricultural sector needs to deal with the GHG emissions and respective climate impacts caused by the application of fertilizers and associated ammonia losses.

The reliance of the agricultural sector on (synthetic) ammonia can provide synergies but also competition for the use of ammonia as a marine fuel. Upstream emissions of ammonia production are accounted for in the industry sector and thus any GHG emission savings will be attributed to that sector. The upstream emissions of ammonia production are also relevant for agriculture and shipping, e.g. as the GHG performance of future marine fuels will be judged on a well-to-wake perspective (section 3.1.2). Increasing demand from both agriculture and maritime transport could increase pressure on the fertilizer industry to decarbonize their production. This can create a synergy for agriculture and shipping because the upscaling of green ammonia production might be achieved faster (economies of scale) and thereby reduce the cost for both sectors. There might also be competition between the sectors due to the limited availability of green ammonia in the short term. If the world population continues to grow and the agricultural system remains as it is, the reliance on synthetic fertilizer might increase even more in the future. This would put additional pressure on the (green) ammonia market.

Green ammonia production could benefit from the increasing interest in hydrogen. If demand for green hydrogen increases, more electrolyser capacity will be built. This will decrease the cost of electrolysis which is also needed for a green ammonia plant. Additionally, if more (green) hydrogen is available on the market, ammonia plants can feed this hydrogen into their existing process substituting hydrogen generated by SMR (section 1.1.1). Considering the already huge demand and thus competition for hydrogen, it remains questionable whether any of this hydrogen will be available for use in existing (revamped) ammonia plants.

6 Comparison with other marine fuels

It is not yet clear which sustainable alternative fuel will be most suitable for shipping. This chapter compares green ammonia with a range of other post-fossil fuels and a typical fossil marine fuel. The selected fuels, as shown in Table 10, are hydrogen, ammonia, methanol and (fossil) HFO. While the focus of this report is on environmental criteria, other aspects are important too.

The availability and technological readiness of the onboard technology varies among the fuel considered. The shipping industry has gained first experiences with methanol-fuelled ships and methanol-specific ICE are available (UBA forthcoming). Methanol can be used in SI engines or modified CI or dual fuel engines. Regulations for using methanol as a marine fuel are only partially developed. The development status of ammonia engines is described in chapter 3 and far lower than the established fossil fuels like HFO. Tests on ammonia combustion are still ongoing. It seems that modification or new engine designs will be necessary to use ammonia because a pilot fuel will be needed. Hydrogen is generally a less promising marine fuel than ammonia. This is mainly due to it having unfortunate fuel properties for application in shipping (Table 9). There is no hydrogen-fuelled ICE commercially available and the application of hydrogen might be limited to niche applications using FC (UBA forthcoming). Marine regulations on the use of ammonia or hydrogen are still lacking.

All renewable fuels are dependent in the upscaling of renewable energy and the subsequent production of green hydrogen. Their availability is, therefore, constrained today (DNV GL 2020b). There is no global hydrogen bunkering network yet, even though there is a huge interest in a global hydrogen economy. The dependency of the green ammonia production on green hydrogen as well as the existing global network of ammonia bunker location is described in chapters 3.2.2 and 5. Compared to globally available HFO, methanol still lacks the necessary infrastructure. In contrast to hydrogen and ammonia, green methanol production has the additional drawback of requiring non-fossil CO₂. Ideally, the CO₂ would be retrieved from direct air capture, which is still very expensive and which does not have a high technological readiness. Comparing the production efficiencies, hydrogen has the potential to reach the highest efficiencies (64-70%) in the long term (Oeko-Institut 2019a). The efficiency of green ammonia production is expected to be approx. 60% in the long term, whereas methanol production might have an efficiency of 56% (Oeko-Institut 2019a).

Cost estimations for post-fossil fuels vary a lot as these are dependent on projections of future prices of renewable electricity and DAC (to provide CO₂ for methanol). Green ammonia, methanol and hydrogen are expected to be much more expensive than fossil fuels (DNV GL 2020b). In the long term, the price gap might decrease because of economies of scale and more stringent carbon pricing policies. In 2030, fuel costs might range between 140 and 210€/MWh (Brynolf et al. 2018; Agora Verkehrswende; Agora Energiewende; Frontier Economics 2018). Hydrogen and ammonia are expected to have lower production costs since expensive direct air capture is not required. However, the energy density of those fuels can lead to higher operational costs compared to methanol because ships might bunker more often or lose cargo space due to larger fuel tanks. Investment costs might also be higher as changes to fuel systems and engines might be more expensive compared to methanol. Again, cost projections addressing all these aspects are to be treated with caution. There is a lack of real-world data as hydrogen and ammonia engines are not yet in use. A study by LR; UMAS (2020) on the total cost of ownership (TCO) shows that green ammonia and hydrogen are less expensive than vessels powered by green methanol. (Korberg et al. 2021) calculates that the TCO of methanol is lower than for ammonia and that hydrogen is even more expensive.

Environmental criteria

Table 10 below shows the comparison of ammonia with three other fuels if used in an ICE based on key environmental criteria. The comparison is done horizontally across fuels. The higher the given number, the better the performance of each fuel in the category. The comparison is based on literature and expert judgement.

Table 10: Comparison of post-fossil fuels and fossil HFO based on key environmental criteria

Criterion	Ammonia	Hydrogen	Methanol	HFO
GHG reduction potential	4*	5	5**	1
Air pollutants	3	5	4	1
Aquatic ecotoxicity	2	5	5	1
Human toxicity	2	5	3	3
Flammability	2	1	2	5
Explosion risks	4	2	5	5

Notes: Ranking: 1= high risk/ low performance to 5=low risk/ high performance, *uncertainty about N₂O emissions, **well-to-wake
Source: Authors' own compilation

The **GHG reduction potential** of ammonia used in ICE is discussed in section 3.1.2. Even though ammonia does not emit any CO₂, there is uncertainty around N₂O emissions. Until the issue is clarified or solved, ammonia's GHG reduction potential should be evaluated with caution. Methanol, if based on renewable energy and CO₂ from air, can be considered climate-neutral from a well-to-wake perspective as the CO₂ emitted should equal the CO₂ captured from air (LR; UMAS 2020). A comparison based on tank-to-wake would naturally result in a different ranking but would not reflect the complete climate impact. Compared to current fossil fuels, green hydrogen will likely achieve a 100% reduction (LR; UMAS 2020).

Air pollutants are not the focus of this study. They are relevant, however, when comparing the overall environmental impacts of fossil fuels to post-fossil fuels. The comparison provided in Table 10 is based on the emission of air pollutants directly from the engine, without the installations of exhaust gas aftertreatment systems. Hydrogen is again expected to perform very well. Green methanol still emits small amounts of NO_x. NO_x levels from ammonia combustion are not yet quantifiable. HFO performs the worst as in addition to NO_x emissions other pollutants like SO_x and black carbon are also emitted when HFO is combusted.

Aquatic ecotoxicity is discussed in section 2.1. Acute ecotoxicity of ammonia to aquatic organisms is very high and is in a similar order of magnitude as the acute toxicity of HFO. Ammonia also has long-term toxic effects to aquatic organisms, but under real environmental conditions, ammonia concentrations will decrease rapidly after a spill and will be assimilated by algae and microorganisms. However, this degradation through uptake as a source of N leads to significant eutrophication. Unlike ammonia, HFO also has a short- and long-term toxicity to birds. Methanol is not very toxic to aquatic organisms. Hydrogen is not considered toxic.

Human toxicity was not a focus of this study. However, ammonia can be extremely irritating to the eyes, throat and respiratory tract, even in small concentrations in the air, and has therefore be handled very carefully. The dominant effect of methanol in humans is central nervous system toxicity

and neurotoxicity including optical nerve toxicity. Heavy fuel oils are considered to be toxic if swallowed and can cause skin irritation. Hydrogen is not considered toxic.

Flammability is the ability of a chemical to burn or ignite, causing fire or combustion. Ammonia is rated as flammable gas and methanol as flammable liquid. While HFO is considered non-flammable, hydrogen is an extremely flammable gas with a wide flammability range of between 4% and 75% in air.

Ammonia has a low **explosion risk** when heated, while HFO and methanol are not considered explosive. Hydrogen forms an explosive mixture with oxygen. The potential for an explosion of a flammable hydrogen-air mixture is very high, e.g. an explosion can occur because of electrostatic charging of dust particles at high temperatures.

7 Conclusions

The aim of this study is to assess ammonia's potential as a marine fuel with a focus on environmental impacts. The acute ecotoxicity to aquatic organisms of ammonia is comparable to HFO. In the long term, spills of ammonia seem to be of lesser concern than for HFO because ammonia concentrations would decrease fast.

To address the risks of ammonia, amendments to the IGF and IGC code are required to

- enable its use as a fuel in shipping (and not only as a cargo),
- account for a safe handling of ammonia on-board,
- introduce standards and protocols in the case of accidents or leakages to the environment.

Marine ammonia engines do not yet exist, but various research and industry projects are under way. Ammonia will likely be combusted in mixtures with other fuels to overcome ammonia's difficult combustion properties. Ammonia-hydrogen-mixtures are particularly interesting for the complete decarbonization of the sector.

Dual fuel engines will be the most promising pathway for ammonia to enter the maritime sector with possible first use cases in LPG carriers. Pilot fuels like diesel (or LPG in LPG carriers) might be used. Ammonia engines are expected by 2024. First demonstration projects might start shortly thereafter with a potential commercial scale-up starting in the late 2020s.

Ammonia is a carbon-free energy carrier, but combustion emissions could be harmful to the environment if they remain unaddressed. NO_x emissions can be eliminated via common exhaust gas aftertreatments like SCR. Future engine tests will need to minimize ammonia slip through engine optimization. Any remaining ammonia slip might also be addressed via exhaust gas aftertreatments. N₂O emissions from ammonia combustion are a major concern due to the high GWP of N₂O. Stringent N₂O emission regulations need to be established to ensure that ammonia engines are compatible with the long-term goal of decarbonizing maritime shipping. N₂O could be integrated, therefore, in carbon pricing policies or limited through emissions standards. Further research is necessary to clarify the quantity and type of emissions resulting from burning ammonia in varying ratios with other fuels and to develop appropriate abatement technologies.

Fuel cells could circumvent the problem of emissions from combustion engines but their commercial use in deep sea shipping is even further away than its use in ICEs. The use of ammonia in fuel cells should thus be pursued alongside the development of ammonia engines.

Ammonia is produced and transported globally because it is a key intermediate for agricultural fertilizer. The demand from shipping for ammonia could build on an existing global network of ammonia infrastructure. In the short term, supply of green ammonia will be limited. Green ammonia production would need to increase considerably in order to supply even a small amount of the maritime sector. This is, however, true for all post-fossil fuels. There are potential synergies with the decarbonization of other sectors which will also need green ammonia, like agriculture. Robust certification systems for green ammonia will have to be developed as soon as possible.

In conclusion, ammonia is a candidate for a future marine fuel as it is a carbon-free post-fossil fuel and thus likely to be cheaper than other post-fossil fuels. Due to its risk profile, its use may not be applicable in all segments of the maritime sector, e.g. passenger ships. The maritime sector will likely rely on different post-fossil fuels in future depending on the market segment. If ammonia is to contribute to short-term emissions reductions in shipping, the pace of engine development and

subsequent deployment needs to increase. In line with the precautionary principle and to provide incentives for the new technologies to avoid all GHG emissions, the environmental integrity needs to be ensured by means of stringent regulation which cover all greenhouse gases and particularly include N₂O.

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9 Annex

Table 11: Percentage of un-ionized ammonia at different pH and temperatures

pH	Temp [°C]								
	10,0	12,5	15,0	17,5	20,0	22,5	25,0	27,5	30,0
6,5	0,06	0,07	0,09	0,10	0,13	0,15	0,18	0,21	0,26
6,6	0,07	0,09	0,11	0,13	0,16	0,20	0,23	0,27	0,32
6,7	0,09	0,11	0,14	0,17	0,20	0,24	0,29	0,34	0,40
6,8	0,12	0,14	0,17	0,21	0,25	0,30	0,36	0,43	0,51
6,9	0,15	0,18	0,22	0,26	0,32	0,38	0,45	0,54	0,64
7,0	0,19	0,23	0,27	0,33	0,40	0,47	0,57	0,67	0,80
7,1	0,23	0,28	0,34	0,41	0,50	0,60	0,71	0,85	1,01
7,2	0,29	0,36	0,43	0,52	0,63	0,75	0,90	1,06	1,26
7,3	0,37	0,45	0,54	0,66	0,79	0,94	1,12	1,34	1,58
7,4	0,47	0,56	0,68	0,82	0,99	1,18	1,41	1,68	1,99
7,5	0,59	0,71	0,86	1,03	1,24	1,48	1,77	2,10	2,49
7,6	0,74	0,89	1,08	1,30	1,56	1,86	2,22	2,63	3,11
7,7	0,92	1,12	1,35	1,63	1,95	2,33	2,78	3,29	3,89
7,8	1,16	1,41	1,70	2,04	2,45	2,92	3,47	4,11	4,85
7,9	1,46	1,76	2,13	2,56	3,06	3,65	4,33	5,12	6,02
8,0	1,83	2,21	2,66	3,20	3,82	4,55	5,39	6,36	7,47
8,1	2,29	2,77	3,33	3,99	4,76	5,66	6,69	7,87	9,22
8,2	2,86	3,46	4,16	4,97	5,92	7,02	8,28	9,72	11,30
8,3	3,58	4,31	5,18	6,18	7,34	8,68	10,20	11,90	13,90
8,4	4,46	5,37	6,43	7,66	9,07	10,70	12,50	14,60	16,90
8,5	5,56	6,67	7,96	9,45	11,20	13,10	15,30	17,70	20,30

Source: ANZECC; ARMCANZ (2000)

Table 12: Freshwater NOEC values as total ammonia-N in µg/l at different pH levels

pH	Freshwater NOEC value (µg/l as total ammonia-N)	Marine NOEC value (µg/l as total ammonia-N)
6.0	2570	5960
6.1	2555	5870
6.2	2540	5760
6.3	2520	5630
6.4	2490	5470
6.5	2460	5290
6.6	2430	5070
6.7	2380	4830

pH	Freshwater NOEC value (µg/l as total ammonia-N)	Marine NOEC value (µg/l as total ammonia-N)
6.8	2330	4550
6.9	2260	4240
7.0	2180	3910
7.1	2090	3560
7.2	1990	3200
7.3	1880	2840
7.4	1750	2490
7.5	1610	2150
7.6	1470	1850
7.7	1320	1560
7.8	1180	1320
7.9	1030	1100
8.0	900	910
8.1	780	750
8.2	660	620
8.3	560	510
8.4	480	420
8.5	400	350
8.6	340	290
8.7	290	240
8.8	240	200
8.9	210	170
9.0	180	140

Source: ANZECC; ARMCANZ (2000)

Table 13: Species mean acute values (SMAVs) of ammonia for several aquatic species

Species	Scientific name	SMAV [mg TAN/l]
Insect	<i>Erythromma najas</i>	2515
Caddisfly	<i>Philactis quaeris</i>	994.5
Beetle	<i>Stenelmis sexlineata</i>	735.9
Crayfish	<i>Orconectes immunis</i>	1550
Crayfish	<i>Orconectes nais</i>	303.8
Midge	<i>Chironomus riparius</i>	1029
Midge	<i>Chironomus tentans</i>	451.8
Mayfly	<i>Drunella grandis</i>	442.4

Species	Scientific name	SMAV [mg TAN/l]
Aquatic sowbug	<i>Caecidotea racovitzai</i>	387.0
Isopod	<i>Asellus aquaticus</i>	378.2
Threespine stickleback	<i>Gasterosteus aculeatus</i>	281.5
Mayfly	<i>Callibaetis skokianus</i>	364.6
Mayfly	<i>Callibaetis sp.</i>	166.7
Dragonfly	<i>Pachydiplax longipennis</i>	233.0
Mottled sculpin	<i>Cottus bairdii</i>	222.2
Western mosquitofish	<i>Gambusia affinis</i>	219.3
Oligochaete worm	<i>Lumbriculus variegatus</i>	218.7
Tubificid worm	<i>Tubifex tubifex</i>	216.5
Marsh ramshorn snail	<i>Planorbella trivolvis</i>	211.6
Scud	<i>Hyalella azteca</i>	192.6
Stonefly	<i>Skwala americana</i>	192.4
Mozambique tilapia	<i>Oreochromis mossambicus</i>	185.2
Amphipod	<i>Crangonyx pseudogracilis</i>	270.5
Amphipod	<i>Crangonyx sp.</i>	122.2
Tubificid worm	<i>Limnodrilus hoffmeisteri</i>	170.2
Pouch snail	<i>Physa gyrina</i>	164.5
Damselfly	<i>Enallagma sp.</i>	164.0
Water flea	<i>Chydorus sphaericus</i>	162.6
Fathead minnow	<i>Pimephales promelas</i>	159.2
Brook trout	<i>Salvelinus fontinalis</i>	156.3
Lake trout	<i>Salvelinus namaycush</i>	159.3
Shortnose sturgeon	<i>Acipenser brevirostrum (LS)</i>	156.7
White sucker	<i>Catostomus commersonii</i>	157.5
Mountain sucker	<i>Catostomus platyrhynchus</i>	136.2
Water flea	<i>Ceriodaphnia acanthine</i>	154.3
Water flea	<i>Ceriodaphnia dubia</i>	134.2
Water flea	<i>Simocephalus vetulus</i>	142.9
Channel catfish	<i>Ictalurus punctatus</i>	142.4
Red swamp crayfish	<i>Procambarus clarkii</i>	138.0
Atlantic salmon	<i>Salmo salar (LS)</i>	183.3
Brown trout	<i>Salmo trutta</i>	102.0
White perch	<i>Morone americana</i>	132.7
White bass	<i>Morone chrysops</i>	144.0
Striped bass	<i>Morone saxatilis</i>	246.2
Sunshine bass	<i>Morone saxatilis x chrysops</i>	70.22

Species	Scientific name	SMAV [mg TAN/l]
Water flea	<i>Daphnia magna</i>	157.7
Water flea	<i>Daphnia pulex</i>	99.03
Clawed toad	<i>Xenopus laevis</i>	122.5
Flatworm	<i>Dendrocoelum lacteum</i>	119.5
Walleye	<i>Sander vitreus</i>	117.1
Central stoneroller	<i>Campostoma anomalum</i>	115.9
Rainbow dace	<i>Cyprinella lutrensis</i>	196.1
Spotfin shiner	<i>Cyprinella spiloptera</i>	83.80
Steelcolor shiner	<i>Cyprinella whipplei</i>	80.94
Dwarf wedgemussel	<i>Alasmidonta heterodon (LS)</i>	109.0
Pink papershell	<i>Potamilus ohioensis</i>	109.0
Green sunfish	<i>Lepomis cyanellus</i>	150.8
Pumpkinseed	<i>Lepomis gibbosus</i>	77.53
Bluegill	<i>Lepomis macrochirus</i>	104.5
Common carp	<i>Cyprinus carpio</i>	106.3
Golden trout	<i>Oncorhynchus aguabonita</i>	112.1
Cutthroat trout	<i>Oncorhynchus clarkii</i>	78.92
Pink salmon	<i>Oncorhynchus gorbuscha</i>	180.7
Coho salmon	<i>Oncorhynchus kisutch (LS)</i>	87.05
Rainbow trout	<i>Oncorhynchus mykiss (LS)</i>	82.88
Chinook salmon	<i>Oncorhynchus tshawytscha (LS)</i>	82.39
Topeka shiner	<i>Notropis topeka (LS)</i>	96.72
Leopard frog	<i>Rana pipiens</i>	96.38
Long fingernailclam	<i>Musculium transversum</i>	89.36
Smallmouth bass	<i>Micropterus dolomieu</i>	150.6
Largemouth bass	<i>Micropterus salmoides</i>	86.02
Guadalupe bass	<i>Micropterus treculii</i>	54.52
Great pond snail	<i>Lymnaea stagnalis</i>	88.62
Guppy	<i>Poecilia reticulata</i>	74.66
Johnny darter	<i>Etheostoma nigrum</i>	71.45
Orangethroat darter	<i>Etheostoma spectabile</i>	77.17
Rio Grande silvery minnow	<i>Hybognathus amarus</i>	72.55
Spring peeper	<i>Pseudacris crucifer</i>	61.18
Pacific tree frog	<i>Pseudacris regilla</i>	83.71
Mucket	<i>Actinonaias ligamentina</i>	63.89
Pheasantshell	<i>Actinonaias pectorosa</i>	79.46
Giant floater mussel	<i>Pyganodon grandis</i>	70.73

Species	Scientific name	SMAV [mg TAN/l]
Shortnose sucker	<i>Chasmistes brevirostris</i>	69.36
Pagoda hornsnail	<i>Pleurocera uncialis</i>	68.54
Golden shiner	<i>Notemigonus crysoleucas</i>	63.02
Pebblesnail	<i>Fluminicola sp.</i>	62.15
Lost River sucker	<i>Deltistes luxatus</i> (LS)	56.62
Mountain whitefish	<i>Prosopium williamsoni</i>	51.93
Atlantic pigtoe	<i>Fusconaia masoni</i>	47.40
Pondshell mussel	<i>Utterbackia imbecillis</i>	46.93
Pink mucket	<i>Lampsilis abrupta</i> (LS)	26.03
Plain pocketbook	<i>Lampsilis cardium</i>	50.51
Wavy-rayed lampmussel	<i>Lampsilis fasciola</i>	48.11
Higgin's eye	<i>Lampsilis higginsii</i> (LS)	41.90
Neosho mucket	<i>Lampsilis rafinesqueana</i> (LS)	69.97
Fatmucket	<i>Lampsilis siliquoidea</i>	55.42
Rainbow mussel	<i>Villosa iris</i>	34.23
Oyster mussel	<i>Epioblasma capsaeformis</i> (LS)	31.14
Green floater	<i>Lasmigona subviridis</i>	23.41
Ellipse	<i>Venustaconcha ellipsiformis</i>	23.12

Notes: SMAV= species mean acute values. SMAVs are calculated from the geometric mean for different measures of effect based on the results of toxicity tests within a given species (e.g., all EC₅₀ values from acute tests for *Daphnia magna*); LS = Federally listed as threatened or endangered species
 Source: EPA (2013)

Table 14: Maximum acceptable toxicant concentration (MATC) of HFO at various stages of rainbow trout early ontogenesis

Parameter	*MATC, g/l HFO
Mortality	
embryo	0.53
hatching	0.13
alevin (from hatching to 20 days after hatching)	0.06
Heart rate	
embryo	0.13
newly hatched alevin	0.06
20-day-old alevin	0.03
Respiratory frequency	
newly hatched alevin	0.06
20-day-old alevin	0.03

Parameter	*MATC, g/l HFO
Growth	
newly hatched alevin	0.03
20-day-old alevin	0.01

Notes: *MATC – subchronic value (geometric mean of lowest-observed-effect concentration and no-observed-effect concentration)
Source: Stasiūnaitė (2003)

Table 15: Summary of HFO sample ecotoxicity data for fish, daphnia and algae

Name	Fish LD ₅₀ (mg/l)	Daphnia ED ₅₀ (mg/l)	Algae IrL50 (mg/l)
Light fuel oil (CAS No 68476-33-5)	>1000	>1000	100-300 **
Heavy fuel oil (CAS No 68476-33-5)	100-1000 **	220-460 **	30-100 **
Heavy fuel oil (CAS No 68476-33-5)	>96	2.0	1.5-6.3 **
Slurry (CAS No 64741-62-4)	>94	3.2	1.0-4.0 **
Intermediate fuel oils 30-380 (CAS No 68476-33-5)	79	10	7.3-22 **
Heavy fuel oil (CAS No 64741-62-4)	>95	>99	0.75 ⁺ (0.6-1.3) **
Flashed combined tar CAS No 64741-80-6	>98	>95	>107

Notes: ** Assignment of the LD₅₀, ED₅₀ or IrL50 values is based on the two loading rates which straddle the 50% effect. ⁺ A statistical evaluation of the data by probit analysis produced a definitive result of 0.75 mg/l

Source: Concawe (2011)

Table 16: Median lethal concentrations and median effective concentrations estimated using oil loading (% v/v or µg/g), concentrations of total petroleum hydrocarbons by fluorescence (µg/l), and estimated polycyclic aromatic hydrocarbon concentration (µg/l) in toxicity test solutions

	25-d LC ₅₀ (95% confidence limits)	25-d EC ₅₀ (95% confidence limits)	
		BSD severity index	Normal embryos
Nominal loading of oil added to water (% v/v)			
H6303 WAF	>0.01 ^a	>0.01	>0.01
H6303 CEWAF	0.037 (VL)	0.037 (0.016-0.058)	0.013 (0.006-0.020)
Nominal loading of oil stranded on gravel (µg/g)			
H6303	505 (459-551)	448 (360-536)	198 (VL) ^b
H6303W	591 (435-747)	587(50-1124)	<198
H7102	1031 (VL)	921 CVL)	< 198
MESA	4607 (2663-6551)	3731 (2271-5191)	774 (633-915)
Concentration of TPH-F (µg/l)^c			

	25-d LC ₅₀ (95% confidence limits)	25-d EC ₅₀ (95% confidence limits)	
		BSD severity index	Normal embryos
Oil added to water			
H6303 WAF	>45	>45	>45
H6303 CEWAF	473 (236-710)	338 (239-437)	140 (93-187)
Oil stranded on gravel			
H6303	52 (VL)	49 (18-81)	49 (VL)
H6303W	74(36-112)	66(50-81)	<279
H7102	121 (VL)	120 (VL)	<229
MESA	1109(965-1251)	1076(1002-1150)	359 (328-390)
Estimated concentration of TPAHs (µg/l)^c			
Oil added to water			
H6303 WAF	>5	>5	>5
H6303 CEWAF	28 (17-39)	22 (17-27)	11 (8-14)
Oil stranded on gravel			
H6303	5(VL)	5 (2-7)	5(VL)
H6303W	7(4-9)	6 (5-7)	<19
H7102	10 (VL)	10 (VL)	<16
MESA	53 (22-79)	53 (50-56)	23 (22-25)

Notes: ^a LC50s and EC50s marked with > indicate (hat the highest response was less than 50% of the maximum; LC50s and EC50s marked with < indicate the lowest response was more than 50% of the maximum.

^b Confidence limits are very large because of the shape of the exposure-response relationship.

^c Estimated concentrations of summed polycyclic aromatic hydrocarbons (TPAHs) were calculated using the equation from the correlation of measured concentrations of total petroleum hydrocarbons and PAH from Figure ID.

LC₅₀ = median lethal concentration; EC₅₀ = median effective concentration; BSD = blue sac disease; VL = very large confidence limits; H6303 WAF == water accommodated fraction of heavy fuel oil (HFO) 6303; H6303 CEWAF = chemically enhanced WAF of HFO 6303; H6303 = stranded HFO 6303; H6303W = stranded artificially weathered HFO 6303; H7102 = stranded HFO 7102; MESA = stranded medium South American crude; TPH-F = total petroleum hydrocarbons by fluorescence.

Source: Martin et al. (2014)