Environmental and human health impact assessment of ammonia, methanol and very low sulphur fuel oil used as vessel fuels

Specific spill scenarios defined for Port of Rotterdam, the English Channel, and the Strait of Malacca

DHI Project No. 11829078

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Acknowledgements:

This report presents the findings of a study, carried out by DHI A/S, encompassing the quantification of environmental and human health impacts associated with spills of ammonia, methanol, and Very Low Sulphur Fuel Oil (VLSFO) from vessels in the context of specific spill scenarios defined for Port of Rotterdam, the English Channel, and the Strait of Malacca. This study was commissioned as part of a broader project aimed at assessing the potential environmental impacts of using ammonia as a shipping fuel. The results include other relevant shipping fuels to provide a neutral and science-based comparison. The partners of the project include A.P. Moller Maersk A/S, Environmental Defense Fund Europe, Nippon Yusen Kabushiki Kaisha, CMA CGM, DFDS A/S, American Bureau of Shipping, MAN Energy Solutions, Svitzer A/S, Havenbedrijf Rotterdam N.V., and Mærsk Mc-Kinney Møller Center for Zero Carbon Shipping. The partners have provided valuable input by validating technical assumptions and quantified results. It is important to note that while the partners have contributed to validating the technical aspects, they have not participated in the interpretation of the results. The project has been catalyzed, led, and funded by A.P. Moller Maersk A/S.

Approved by

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Non-exhaustive list of key assumptions that are further described and supplemented by methods and models presented in the report.	
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Release and mixing of fuel spill in the ambient water	Port of Rotterdam ▪ Instantaneous release of the fuels after the accident is assumed ▪ Ammonia and methanol are assumed completely mixed with the upper water layer immediately after the spill (conservative assumption for environmental exposure assessment) or present as a 1-cm layer on the water surface (conservative assumption for human exposure assessment). English Channel and Strait of Malacca: ▪ Movement of the vessel after the collision and during the spill event is neglected. ▪ Heat exchange between the fuel and the water is neglected which means that ammonia is assumed released as a liquid before mixing with the water. ▪ Ammonia and methanol are assumed to move towards the water surface due to buoyancy, and dissolution or mixing in the water column will occur. A water partitioning ratio of 0.5 was assumed for ammonia and methanol. VLSFO is assumed to form an oil-slick on the water surface directly after the spill. Described in Section 5.3.2.
Description of VLSFO	The following properties of VLSFO were assumed: Density: 900-1000 kg/m^3 Pour point 0-30°C Flash point: > 60°C

	The above properties were met by a VLSFO from Shell. Described in Section 2.3.1.
Environment	
Ammonia – evaporation from sea surface	The heat transfer to the ammonia pool is assessed to be the rate determining process for the evaporation. The evaporation rate was therefore calculated from the heat balance. Liquid ammonia will be heated by the ambient air and water and by solar radiation. Described in Section 2.1.2.
Ammonia – evaporation from water column	Ammonia will evaporate from the upper layers of the water column. To calculate the evaporation from an aqueous solution, the two-layer film model was applied, where the substance in aqueous solution passes two stationary films consisting of water and air. In these two layers, the substance seeks equilibrium between the water phase and the air phase. This equilibrium is described by Henry's constant, H (Pa m^3/mol), where the air concentration at equilibrium is equal to the water concentration multiplied by Henry's constant. Described in Section 2.1.2.
Ammonia – nitrification and nitrate reduction	Ammonia (NH_4^+) is transformed to nitrate (NO_3^-) in the process known as nitrification: $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$. The removal of ammonia by nitrification was included in the exposure modelling. Nitrate may be transformed to nitrous oxide (N_2O) and nitrogen (N_2) in the process called denitrification: $NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2$. The effects connected to the release of nitrous oxide to the atmosphere or to the utilization of nitrate as nutrient by algae and plants (eutrophication) were not evaluated. Described in Section 2.1.2.
Methanol – evaporation	Methanol may evaporate from the upper water layer. The equations used for the simulation of the evaporation of ammonia (Section 2.1.2) were also used for methanol.
Methanol - biodegradation	Methanol is readily biodegradable in accordance with the OECD criteria in tests for ultimate, aerobic biodegradability. The half-life (T½) of methanol in seawater was estimated to 5 days at 20°C. The biodegradation rate was simulated by first order kinetics with correction for temperature. Described in Section 2.2.2.
VLSFO – environmental fate	The following fate processes were included in the exposure modelling: **Spreading** expressed as the increase of the area of surface oil slick driven by density, viscosity, surface tension **Evaporation** driven by vapour pressure **Dissolution** driven by water solubility

	Dispersion driven by wave action where oil droplets are dispersed into the sea due to wave action on the oil slick **Emulsification –** the formation of water-in-oil emulsions is driven by wind and wave action, while the stability of the water-in-oil emulsions is driven by the contents of wax and asphaltenes. The changes in density, viscosity and pour point of the oil slick resulting from the above-mentioned processes were considered in the exposure modelling. Described in Section 2.3.2.
VLSFO – photooxidation and biodegradation	Photooxidation and biodegradation were not included in the exposure modelling as these processes are of minor importance in the relevant time window for the simulations. Described in Section 2.3.2.
Hydrodynamic conditions and weather	For the Port of Rotterdam and the English Channel, a non-extreme year represented by meteorological and hydrodynamic conditions in 2013 was selected and evaluated during the four seasons: winter (December-February), spring (March-May), summer (June-August), and autumn (September-November). For the Strait of Malacca, a non-extreme year represented by meteorological and hydrodynamic conditions in 2019 was selected and evaluated during the four seasons: Northeast monsoon (November-March), Inter monsoon (April-May), Southwest monsoon (June-August), and Inter monsoon (September-October). Described in Section 4.3.1 The fate of airborne chemicals is highly dependent on the ambient wind direction and speed, the ambient temperature, and the degree of cloudiness. The assumptions on wind direction, wind speed, and the air and water temperatures in Rotterdam are described in Section 5.3.2.
Environmental effects assessment	
Ammonia – Predicted no-effect concentration (PNEC)	The PNEC used for un-ionized ammonia in the present study was obtained from the REACH registration dossier for ammonia: PNEC (marine water), un-ionized ammonia, NH_3: 0.001 mg/L. This PNEC value for un-ionized ammonia (NH_3) was used to derive PNECs for total ammonia (NH_3 + NH_4^+) by accounting for the pKa dependency on salinity and temperature and the pH in the ambient water in the Port of Rotterdam, the English Channel, and the Strait of Malacca. Described in Section 4.2.2.

Methanol - PNEC	The PNEC for methanol was derived following the assessment factor method as described in Section 4.2.3: PNEC (marine water), methanol: 1.7 mg/L.
VLSFO - PNEC	The hydrocarbons found in a laboratory prepared water accommodated fraction of VLSFO were paired with PNECs published in a background document from the OSPAR Commission and used to derive PNECs for the VLSFO fractions semi-volatiles and volatiles. The PNECs used in the impact assessment of VLSFO were: PNEC (marine water), VLSFO semi-volatiles: 1.15 µg/L PNEC (marine water), VLSFO volatiles: 8.5 µg/L Described in Section 4.2.4.
Human health effects assessment	
Ammonia – Derived no-effect level (DNEL)	The DNEL for the general population was obtained from the REACH registration dossier for ammonia. The DNEL for workers is equivalent to the EU short-term occupational exposure limit (OEL): DNEL, general population: 10.3 ppm DNEL, workers: 50 ppm. Described in Section 5.2.2.
Methanol - DNEL	The DNEL for the general population was obtained from the REACH registration dossier for methanol. The DNEL for workers was obtained from Finland as no EU short-term DNEL exists: DNEL, general population: 20 ppm DNEL, workers: 250 ppm. Described in Section 5.2.3.
VLSFO - DNEL	Only the volatile substances in VLSFO are transported via air, and representative DNELs for volatile hydrocarbons, i.e., C9-C10 aromatics, were used in the present study. The DNELs were taken from the REACH registration dossier for Hydrocarbons, C9-C10, aromatics, >1% naphthalene (EC number 946-365-8) assuming a molar mass of 120 g/mole in the conversion from mg/m^3 to ppm: DNEL, general population: 6.5 ppm DNEL, workers: 31 ppm. Described in Section 5.2.4.
Acute exposure guideline levels (AEGLs)	The United States AEGLs describe the human health effects of once-in-a-lifetime, or rare, exposure to airborne chemicals. The AEGLs are set by the National Academies through a collaborative effort of public and private sectors.

	AEGLs are designed to protect the general population, including the elderly and children. Described in Section 5.2.
Emergency response planning guidelines (ERPGs)	The Emergency Response Planning Committee of the American Industrial Hygiene Association has developed ERPGs that estimate the concentrations at which most people will begin to experience health effects if they are exposed to a hazardous airborne chemical for 1 hour. The ERPGs do not include sensitive members of the public. Described in Section 5.2.

Summary

Ammonia and methanol are emerging maritime fuels with the potential to generate large reductions of greenhouse gas emissions from shipping. The aim of this study was to perform a comparative environmental and human health impact assessment of ammonia, methanol, and traditional very low sulphur fuel oil (VLSFO) based on exposure scenarios describing assumed accidental spills of the three fuels in the sea. The exposure scenarios in the present study include:

- Hole in the bunkering hose in the Port of Rotterdam
- Complete rupture of the bunkering pipe in the Port of Rotterdam
- Collision in the English Channel
- Collision in the Strait of Malacca.

The environmental and human impact assessments were conducted by using the principles described in the *ECHA Guidance on information requirements and chemical safety assessment* which is used in support of the European chemicals' regulation REACH (Regulation (EC) No. 1907/2006 of the European Parliament and of the Council). The impact assessments compare the predicted exposure of the marine environment or a human population with the appropriate estimated 'no-effect level', i.e., the predicted no-effect concentration (PNEC) for the marine environment and the derived no-effect level (DNEL) for humans. The predicted exposures of the human population to ammonia were compared to two additional toxicity thresholds, i.e., the acute exposure guideline levels (AEGLs) and the emergency response planning guidelines (ERPGs), to provide perspective to the results.

The study contributes to the assessment of the impact, or severity, of accidental spills of the vessel fuels by the evaluation of specific defined spill events. It is important to note that this study is not a complete risk assessment, as neither the likelihood of the spill events nor the efficacy of any risk-mitigating measures were evaluated. The long-term indirect impacts of ammonia spills were also not assessed.

The physical-chemical properties of ammonia, methanol, and VLSFO are different and determine the behaviour of the fuels if released into the sea. Ammonia and methanol are readily soluble in water and will be dispersed by currents and tidal water exchange. VLSFO contains volatile and semi-volatile fractions (low molecular weight hydrocarbons) that are soluble or miscible in seawater and a poorly water-soluble 'heavy fraction' (high molecular-weight hydrocarbons).

Environmental impact assessment

If released to the sea, ammonia, methanol, and VLSFO may affect marine organisms. The environmental impact of ammonia, methanol, and the water-soluble fractions of VLSFO was assessed by comparing the predicted environmental concentration (PEC) and the PNEC. The PEC is the predicted concentration of the chemical in the marine environment determined by modelling the chemical's dispersion and environmental fate. The PNEC is the concentration in the environment below which adverse effects are not expected to occur due to exposure to a chemical.

Predicted no-effect concentration (PNEC)

The European regulation of chemicals, REACH, requires that a PNEC shall be established for substances that are manufactured, imported, or used in quantities of 10 tonnes or more per year.

The PNEC is the concentration of the substance below which adverse effects in the environmental sphere of concern are not expected to occur. The exposure to the substance is estimated for defined exposure scenarios, and the result is expressed by the predicted environmental concentration (PEC). The PEC is compared with the PNEC. The toxic effects of the substance on the environment can be considered negligible if the PEC does not exceed the PNEC.

Source: European Chemicals Agency (ECHA). Guidance on information requirements and chemical safety assessment, Chapter R.10: Characterisation of dose [concentration]-response for environment.

In the present study, the environmental impact was described by the risk characterization ratio (RCR) which is the ratio of the PEC to the PNEC:

$$\mathrm{RCR} = \frac{\mathrm{PEC}}{\mathrm{PNEC}}$$

An RCR < 1 (i.e., PEC < PNEC) means that immediate adverse effects in the environment due to exposure to the chemical will likely not occur. In the present study, the results of the exposure modelling were expressed by mapping sea areas in which the PEC exceeds the PNEC and, thus, RCR > 1 leading to the interpretation that adverse effects in the marine ecosystem may occur.

There are many uncertainties in assessing the environmental effects of exposure to a chemical from results obtained in laboratory studies with test species – for example, the effects assessment uses aquatic toxicity data for a limited set of test species to predict adverse effects in marine ecosystems with a vast number of highly diverse species, and laboratory studies do not include all effects of concern or all life stages that are important for the survival of the species in the environment.

The PNEC is commonly derived by dividing the selected lowest effect concentration, e.g., the median lethal concentration (LC50) or the no observed effect concentration (NOEC), by an assessment factor to account for the fact that ecotoxicological studies can never fully represent the diversity of species in the aquatic environment.

A very simplistic interpretation of the environmental impact was applied and considered reasonable as the predicted durations of the exposure to fuel concentrations exceeding the PNEC are between 1 and 5 days:

Negligible impact on the marine environment:

- PECs below PNEC mean that adverse effects caused by the exposure to the released fuel are negligible.

Moderate impact on the marine environment:

- PECs equivalent to or moderately above PNEC, defined as 1-10 x PNEC in the present study, imply that the exposure to the released fuel may cause adverse effects (including death) to sensitive species and individual organisms.

High impact on the marine environment:

- PECs markedly above PNEC, defined as more than 10 x PNEC in the present study, imply that the exposure to the released fuel may cause adverse effects (including death) to a broad range of species representing different taxonomic groups such as bivalves, corals, crustaceans, echinoderms, and fish, including their early life stages.

For ammonia, methanol, and dissolved VLSFO, the highest PECs are found near the location of the assumed accidental spill with a dispersion driven by tidal water exchange (Port of Rotterdam) or the dominating currents (English Channel and Strait of Malacca). The PECs of especially ammonia and dissolved VLSFO exceed the PNECs in large sea areas during the first two days after the assumed accidental spills. Within two days the PECs of ammonia, methanol, and dissolved VLSFO decrease to levels below PNEC primarily due to evaporation, spreading and mixing in the English Channel and the Strait of Malacca. Because of the lower water exchange in the Port of Rotterdam, it takes up to five days for all the examined fuels to reach PECs below the PNECs. Based on the above interpretation of ‘negligible’, ‘moderate’, and ‘high’ impact, a cautious assessment was made for the assumed spills in the Port of Rotterdam, the English Channel, and the Strait of Malacca.

Port of Rotterdam

Due to the relatively low volumes released to the sea, the assumed spills in the exposure scenario ‘Hole in the bunkering hose’ do not lead to PECs that exceed the PNECs. For the most serious of the two exposure scenarios in Port of Rotterdam, i.e., ‘Complete rupture of the bunkering pipe’, the PECs are below the PNECs two days (methanol) or five days (ammonia and dissolved VLSFO) after the spill:

- **Ammonia** may cause adverse effects (including death) to sensitive species or individual organisms in a sea area of up to 6 km^2 during the first five days after the spill.
- **Methanol** may cause adverse effects (including death) to sensitive species or individual organisms in a sea area of up to 1 km^2 during the first day after the spill.
- **Dissolved VLSFO** may cause adverse effects (including death) to a broad range of species representing different taxonomic groups in a sea area of 3 km^2 during the first two days after the spill. Adverse effects (including death) to sensitive species or individual organisms may occur in a sea area of 12 km^2 during the first two days after the spill.

English Channel

The PECs are below the PNECs two days after the spill:

- **Ammonia** may cause adverse effects (including death) to a broad range of species representing different taxonomic groups in a sea area of 125 km^2 during the first day after the spill. Adverse effects (including death) to sensitive species or individual organisms may occur in a sea area of up to approx. 4000 km^2 during the first two days after the spill.
- **Methanol** is not expected to cause adverse effects as the PECs are below the PNEC.

- **Dissolved VLSFO** may cause adverse effects (including death) to a broad range of species representing different taxonomic groups in a sea area of 11 km^2 during the first day after the spill. Adverse effects (including death) to sensitive species or individual organisms may occur in a sea area of up to approx. 500 km^2 during the first two days after the spill.

Strait of Malacca

The PECs are below the PNECs two days after the spill:

- **Ammonia** may cause adverse effects (including death) to sensitive species or individual organisms in a sea area of 327 km^2 during the first day after the spill.
- **Methanol** may cause adverse effects (including death) to sensitive species or individual organisms in a sea area of 40 km^2 during the first day after the spill.
- **Dissolved VLSFO** may cause adverse effects (including death) to sensitive species or individual organisms in a sea area of 61 km^2 during the first day after the spill.

The exposure to **non-dissolved VLSFO** may cause long-lasting adverse effects. The model predictions of the exposures to non-dissolved VLSFO indicate a probability higher than 25% that coastal sea areas in the English Channel and the Strait of Malacca may be impacted by oil in amounts that will cause adverse effects to marine life. The potential impact of the stranding of non-dissolved VLSFO includes:

- Inhibition of growth or death of macroalgae, seed plants, benthic invertebrates (e.g., bivalves, corals, echinoderms, and worms), and fish
- Serious negative impact (e.g., reduced insulation capacity) or death of sea birds and seals
- Serious negative impact on ecosystems functions caused by, e.g., deterioration of habitats and loss of prey.

Human health impact assessment

Accidental spills of the fuels during bunkering may lead to chemical concentrations in air that affect humans by inhalation. The human health impact of ammonia, methanol, and VLSFO was assessed by comparing the predicted exposure level (PEL) of a human population with the DNEL. The relevant PEL for the present study is the airborne concentration of the chemical which was determined by modelling the dispersion of the chemicals in air. The DNEL is the level of exposure to a chemical substance above which humans should not be exposed.

Derived no-effect level (DNEL)

The European regulation of chemicals, REACH, requires that a DNEL shall, when possible and taking data availability into account, be established for substances manufactured, imported, or used in quantities of 10 tonnes or more per year.

The DNEL is the level of exposure above which humans should not be exposed. The exposure of a human population to the substance is estimated for defined exposure scenarios, and the result is expressed by the predicted exposure level (PEL). The PEL is compared with the DNEL for the appropriate exposure route. The risk to humans can be controlled if the PEL do not exceed the DNEL.

Source: European Chemicals Agency (ECHA). Guidance on information requirements and chemical safety assessment, Chapter R.8: Characterisation of dose [concentration]-response for human health.

The present human health impact assessment covered only possible effects caused by inhalation, and the impact was expressed by the risk characterization ratio (RCR) which is the ratio of the PEL to the DNEL:

$$\mathrm{RCR} = \frac{\mathrm{PEL}}{\mathrm{DNEL}}$$

An RCR < 1 (i.e., PEL < DNEL) means that unacceptable effects to humans due to exposure to the chemical substance will likely not occur. In other words, the impact on humans can generally be considered acceptable if the PEL < DNEL.

The human health impact assessment was carried out for the two exposure scenarios assumed for the Port of Rotterdam.

The human health impact assessment of ammonia, methanol, and VLSFO showed that the potential impact on human health of a spill of ammonia is higher than the impacts of similar spills of methanol and VLSFO. The dispersion of the fuels in the air is highly influenced by wind direction and speed, and the impacted areas will have the form of a plume oriented in the wind direction.

The predicted air concentrations of the fuel chemicals at different weather conditions (‘typical, winter’, ‘typical, summer’, ‘worst-case, winter’, and ‘worst-case, summer’) were related to the DNELs for the general population, and e.g.:

- For ‘worst-case, winter’, the PELs in the ‘Hole in the bunkering hose’ scenario would be 10 times higher than the DNEL (general population) at distances of up to 263 m for ammonia, 23 m for methanol, and 78 m for VLSFO.
- For ‘worst-case, winter’, the PELs in the ‘Complete rupture of the bunkering pipe’ scenario would be 10 times higher than the DNEL (general population) at distances of up to 3800 m for ammonia, 229 m for methanol, and 182 m for VLSFO.

Adverse effects to humans may occur after exposure to air concentrations exceeding the DNEL. Due to the variation in susceptibility of human individuals, there is no precise way to describe the possible effects to human health resulting from exposure to a chemical substance. However, human exposure limits such as the AEGLs and the ERPGs used in the United States in relation to accidents may illustrate the nature of effects at air concentrations exceeding certain trigger levels.

When the most serious scenario ‘Complete rupture of the bunkering pipe’ is considered, the predicted exposure levels of ammonia exceed AEGL-3 and ERPG-3 values associated with serious health effects at distances of 271 m and 389 m, respectively. This indicates that the predicted concentrations of ammonia may reach a level that requires effective mitigating measures aiming to reduce the potential impacts and the risk of serious health effects. The potential impact on human health should be evaluated considering that the duration of the exposure to ammonia predicted by the exposure modelling is less than 15 minutes.

Although real-life applications will include safeguards and mitigation measures, this study focuses on the fate of spilled fuels and their potential immediate impacts in conservative scenarios, and no mitigation strategies were included. Nevertheless, appropriate mitigation strategies may greatly minimize the volume of fuels released, thereby substantially reducing the potential impacts in real cases of spills. Furthermore, the present impact assessment is based on assumed spill scenarios and does not include an assessment of the likelihood that the spill event will happen. A large spill of ammonia in a port implies a risk of serious health effects to workers and the general population, which should be evaluated by a probabilistic risk assessment combining the likelihood and the severity of events leading to exposure of humans to airborne ammonia. As a follow-up project, a probabilistic risk assessment should be conducted. This assessment, which was outside the scope of the current study, should include an evaluation of both the likelihood of such spills to happen and the most effective risk management measures and technologies available to mitigate potential impacts.

1 Introduction

The present environmental and human health impact assessment of ammonia, methanol, and very low sulphur fuel oil (VLSFO) used as vessel fuels was conducted by DHI. DHI is an independent, international consulting and research organisation established in Denmark and today represented in all regions of the world.

Ammonia and methanol are emerging maritime fuels with the potential to generate large reductions of greenhouse gas emissions from shipping. The aim of this study was to perform a comparative environmental and human health impact assessment of ammonia, methanol, and traditional VLSFO based on exposure scenarios describing assumed accidental spills of the fuels in the sea /17/. The study addresses the aquatic toxicity and human health impacts if the assumed spills occurred. The study does not consider the likelihood of the exposure scenarios and the effects of mitigation strategies to reduce the potential risks.

The exposure scenarios are described in Chapter 3 and include:

- Hole in the bunkering hose in the Port of Rotterdam
- Complete rupture of the bunkering pipe in the Port of Rotterdam
- Collision in the English Channel
- Collision in the Strait of Malacca.

The **Port of Rotterdam** is the largest port in Europe located in and near the city of Rotterdam in the Netherlands. Port of Rotterdam is one of the world’s largest ports in terms of annual cargo tonnage. Two accidental spills differing mainly in the amounts of fuel emitted during bunkering were assumed and formed the basis for environmental and human health impact assessments.

The **English Channel** between England and France is the waterway connecting the North Sea and the Atlantic Ocean. The width of the English Channel varies from 240 km at its widest point to only 34 km in the Strait of Dover. Approximately 500 ships pass through the English Channel each day making the channel one of the world’s busiest shipping lanes. An accidental spill connected to a collision was assumed and formed the basis for an environmental impact assessment.

The **Strait of Malacca** between the Malay Peninsula and Sumatra is the waterway connecting the Andaman Sea (Indian Ocean) and the South China Sea (Pacific Ocean). The width of the Strait of Malacca varies from 250 km in the north to 65 km in the south. Approximately 200 ships pass through the strait each day. An accidental spill connected to a collision was assumed and formed the basis for an environmental impact assessment.

The environmental impact assessment in this study focuses on the fuel concentrations after the spills and the aquatic toxicity of the substances in the fuels. It should be noted that the study did not include assessments of certain indirect and long-term environmental effects of the fuel spills:

- All the examined fuel spills are expected to cause lethal toxic effects to marine life (such as fish) in the vicinity of the spill location, either because of the acute toxicity of the fuel substances or due to the depletion of oxygen. The effects of oxygen depletion would be part of the ‘overall’ adverse effects and were not specifically evaluated.

- For ammonia, the effects on climate of nitrous oxide (N_2O) released to the atmosphere and the eutrophication resulting from the utilization of nitrate (NO_3^-) as nutrient by algae and plants were not evaluated. A spill of ammonia fuel would contribute to eutrophication together with nutrient loadings from other sources such as agriculture.
- For methanol, the effects of formaldehyde, an intermediate in the aerobic biodegradation of methanol, were not evaluated. Formaldehyde is incorporated into bacterial biomass and eventually mineralized to CO_2 /46/.
- For VLSFO, the long-term effects of bioaccumulation of substances in the oil were not evaluated.

The present impact assessment is based on assumed spill scenarios, and the likelihood of the spill events was not evaluated. In addition, the possible implementation of risk-mitigating design of vessels and fuel tanks, or other mitigation measures were not considered in the assessments. Nevertheless, appropriate mitigation strategies may greatly minimize the volume of fuels released, thereby substantially reducing the potential impacts in real cases of spills.

A probabilistic risk assessment should be conducted in the future, including an evaluation of both the likelihood of such spills and the most effective risk management measures and technologies available to mitigate and minimize potential impacts.

The study was initiated on 21st February 2023 and ended with the release of the final report on 25th November 2024. During this period, the assessment methods and interim results were presented and discussed at four workshops including maritime stakeholders selected by A.P. Moller-Maersk. The results of the study may aid the maritime industry by enhancing knowledge and encouraging further exploration into the implementation and use of alternative fuels, particularly regarding their potential impacts in the event of spill accidents.

2 Physical-chemical properties and environmental fate

2.1 Ammonia

Ammonia is an inorganic compound with the chemical formula NH_3. It is readily soluble in water, where it acts as a base forming the ammonium ion NH_4^+.

2.1.1 Physical-chemical properties

Table 2.1 shows the physical-chemical and thermodynamic properties of ammonia that are relevant for the environmental and human exposure modelling.

Table 2.1 Physical-chemical properties of ammonia.

Property	Value	Unit	Reference
Physical-chemical properties			
Molar mass (Mw)	17	g/mol	-
Density at -33ºC	681.9	kg/m^3	/7/
pK_a	10.0423-0.0315536·t(ºC)+0.14737·I[1] (I=ion strength)		/1/
Boiling point	-33.23	ºC	/7/
Henry's law constant, H	$1.82 \cdot \exp\left(-4100 \cdot \left(\frac{1}{T(K)} - \frac{1}{298.15\ K}\right)\right)$	$(m^3 \cdot Pa)/mol$	/20/
Vapour pressure, VP	VP = exp(0.00831-3.59E-4/T(K))	Pa	/32/ Data from /34/ fitted by DHI.
Water solubility at 25ºC	482	g/L	/7/
Viscosity of liquid ammonia at -33.5ºC	0.255	cP	/7/
Surface tension of liquid ammonia at 20ºC	21.97	Dynes/cm	/36/
Thermodynamic properties			
Heat capacity (liquid)	80.8	J/mol K	/33/
Heat capacity (gas)	37	J/mol/K	/33/
Heat of vaporisation at -33ºC, H_{vap}	23.4 1.38	kJ/mol MJ/kg	/38/

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[1] Ion strength is calculated from the salinity: I ≈ S(‰)/58.44 mol/L.

Property	Value	Unit	Reference
Heat of mixing $NH_3(g) \Rightarrow NH_3(dissolved)$ at 25ºC	35.3	kJ/mol	/39/

2.1.2 Environmental fate

Evaporation from the sea surface

The simulations of the evaporation of ammonia from the sea surface were carried out by the DHI oil spill model /3/. Minor modifications of the model were made to adapt the model to the properties of ammonia:

Emulsification: Ammonia will not form a water-in-oil emulsion, and, therefore, this process was not included in the simulations.

Evaporation: The heat transfer to the ammonia pool is assessed to be the rate determining process for the evaporation. The evaporation rate was therefore calculated from the heat balance. Liquid ammonia will be heated by the ambient air and water and by solar radiation.

The heat transfer from air to ammonia, Q_a, was calculated from:

$Q_a = h_a \cdot Area \cdot (Temp_{air} - Temp_{ammonia})$

The heat transfer from water to ammonia, Q_w, was calculated in a similar way:

$Q_w = h_w \cdot Area \cdot (Temp_{water} - Temp_{ammonia})$

The heat transfer coefficients, h_a and h_w, depend on wind speed, and current speed. The below equations were used in the calculation:

$$h_a = \frac{C_{p,air} \cdot U_{10}^{0.78} \cdot \rho_{air}}{Pr_{air}^{-0..67}} \frac{W}{K \cdot m^2}$$

$$h_w = \frac{C_{p,water} \cdot U_{current}^{0.78} \cdot \rho_{water}}{Pr_{water}^{-0..67}} \frac{W}{K \cdot m^2}$$

Where:

$C_{p,air}$ heat capacity of air: 1.0098 J/g/ºC

Pr_{air} is Prandlts number for air: 0.706

U_{10} is the wind speed (m/s)

ρ_{air} is the density of air

$C_{p,water}$ heat capacity of water: 4.19 J/g/ºC

Pr_{water} is Prandlts number for water: 9.46

$U_{current}$ is the current speed

ρ_{water} is the density of water.

Measured data for the radiation energy was included in the dataset of meteorological data Q_E (J/m^2/d).

Therefore, the evaporation from the sea surface was calculated by:

$$\text{Rate of evaporation} = \frac{\text{Area} \cdot (Q_E + h_a \cdot (\text{Temp}_{\text{air}} - \text{Temp}_{\text{ammonia}}) + h_w \cdot (\text{Temp}_{\text{water}} - \text{Temp}_{\text{ammonia}})}{H_{\text{vap}}}$$

Evaporation from the water column

Ammonia will evaporate from the upper layers of the water column. To calculate the evaporation from an aqueous solution, the frequently applied two-layer film model was used, where the substance in aqueous solution passes two stationary films consisting of water and air. In these two layers, the substance seeks equilibrium between the water phase and the air phase. This equilibrium is described by Henry's constant, H (Pa m^3/mol), where the air concentration at equilibrium is equal to the water concentration multiplied by Henry's constant.

The rate at which matter transfers from the aqueous solution to the aqueous film layer was described by the mass transfer coefficient k_w, and the rate from the air film layer to the air was described by the mass transfer coefficient k_a. The two mass transfer coefficients are dependent on the wind speed. In addition, k_w depends on the substance's diffusion coefficient in water, and k_a depends on the substance's diffusion coefficient in air. The overall rate constant, k_{evap}, is calculated by the equation /28/:

$$k_{\text{evap}} = \frac{1}{\frac{1}{k_w} + \frac{1}{k_a \cdot k_H}}$$

Where:

k_w (m/s) = $(4 \cdot 10^{-6} + 4 \cdot 10^{-7} \cdot U_{10} \cdot U_{10}) \cdot \exp(0.285 \ln(32/Mw))$

k_a (m/s) = $(0.02 \cdot U_{10} + 0.003) \cdot \exp(0.335 \ln(18/Mw))$

$$k_H = \frac{H}{8.314 \cdot T}$$

Where:

T is the absolute temperature (K)

R is the gas constant = 8.314 Pa m^3/mole K

M_w is the molar mass of ammonia

H is Henry’s constant for ammonia

U_{10} is the wind speed in 10 m height (m/s)

The evaporation rate is then expressed by the below equation:

$$\text{Evaporation rate } \left(\frac{\text{mass}}{\text{time}}\right) = -\text{Area} \cdot k_{\text{evap}} \cdot C_i$$

C_i is the concentration of ammonia (=1).

Nitrification

Ammonia released by an accidental spill from a vessel will serve as a source of nitrogen for bacteria in the same way as ammonia produced during the decomposition of organic nitrogen compounds. Ammonia mainly exists as ammonium ion (NH_4^+) at pH 8 which is normally found in the marine surface water (see Figure 4.1). In aerobic environments (with the presence of molecular oxygen, O_2), such as the sea surface, ammonia can be oxidized to nitrate (NO_3^-) in the process known as nitrification:

- *Nitrification* is the transformation of ammonia to nitrate: $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$.

The oxidation of NH_4^+ to NO_2^- (nitrite) is catalyzed by nitrite-forming bacteria, while the final oxidation of NO_2^- to NO_3^- is catalyzed by nitrate-forming bacteria. Two types of bacteria are thus required for the complete oxidation of ammonia to nitrate. The requirement for two bacteria could point to the assumption that nitrite might accumulate during nitrification, but this is generally not the case as nitrite-forming and nitrate-forming bacteria are usually present together in the environment.

DHI's nutrient model was used for the calculations of the rate of nitrification, and the rate of nitrification was described by:

$$\text{Nitrification rate}\left(\frac{\text{g N}}{\text{m}^3\ \text{day}}\right) = \text{k}_{\text{nitrification}} \cdot \text{C}_{\frac{\text{NH}_4^+}{\text{NH}_3}}\left(\frac{\text{mg N}}{\text{L}}\right) \cdot \theta^{\text{temperature (°C)}-20} \cdot \frac{\text{DO}}{\text{DO} + \text{DO}_{50\%}^{\text{sat}}}$$

Where:

$C_{\frac{NH_4^+}{NH_3}}$	is the total concentration of NH_3+NH_4^+ (mg N/L).
DO	is the concentration of dissolved oxygen (mg/L). A concentration of DO of 8 mg/L was assumed in the calculations.
$DO_{50\%}^{sat}$	is the half-saturation concentration for nitrification (set to default 2 mg/L).
$K_{nitrification}$	is the first order rate constant set at the default value 1.54 d^{-1}. This value was selected as a reasonable prediction considering the actual measurements in the publicly available 'Database of nitrification and nitrifiers in the global ocean' /31/ reporting measured nitrification rates as a function of light, temperature, salinity, pH, and O_2.

Nitrate reduction

Nitrate can be transformed to reduced forms of nitrogen under anoxic conditions (without the presence of molecular oxygen, O_2) or at least microaerobic conditions with very low levels of O_2. The reduction of nitrate is briefly described for completeness, although the surface water in the sea is normally aerobic due to the mixing of the surface layer. However, the presence of organic matter and spilled fuel may increase bacterial oxygen consumption and lead to anoxic or microaerobic hot spots. Nitrate can be transformed by either assimilatory nitrate reduction or denitrification:

- *Assimilatory nitrate reduction* is the transformation of nitrate to ammonia and organic nitrogen: $NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+ \rightarrow$ Organic N.

- *Denitrification* is the transformation of nitrate to nitrous oxide (N_2O) and nitrogen (N_2): $NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2$.

The prediction of the gaseous products of denitrification is complicated, other than nitrogen (N_2) is the main product under anoxic conditions, while nitrous oxide (N_2O) dominates under microaerobic conditions.

The effects connected to the release of nitrous oxide into the atmosphere or to the utilization of nitrate as a nutrient by algae (and plants) were not evaluated in the present study.

2.2 Methanol

2.2.1 Physical-chemical properties

Table 2.2 shows the physical-chemical and thermodynamic properties of methanol that are relevant for the environmental and human exposure modelling.

Table 2.2 Physical-chemical properties of methanol.

Property	Value	Unit	Reference
Physical-chemical properties			
Molar mass (Mw)	32	g/mol	-
Density at 20ºC	791.8	kg/m^3	/8/
pK_a	-		
Boiling point	64.7	ºC	/8/
Henry's law constant, H	$0.476 \cdot \exp\left(-5200 \cdot \left(\frac{1}{T(K)} - \frac{1}{298.15\ K}\right)\right)^{\square}$	$(m^3 \cdot Pa)/mol$	/22/ /27/
Vapour pressure, VP	$VP = \exp(0.04098 - 2.347 \cdot T(K))$	Pa	Data from /9/. Fitted by DHI.
Water solubility at 25ºC	Miscible	-	/8/
Viscosity of liquid methanol at -25ºC	0.544 - 0.59	mPa s	/8/
Surface tension of methanol at 20ºC	22.70	mN/(mK)	/2/
Flash point	11	ºC	/13/, /14/
Thermodynamic properties			
Heat capacity (liquid)	81.2	J/mol K	/13/, /14/
Heat capacity (gas)	116	J/mol/K	/13/, /14/
Heat of vaporisation	37.34	kJ/mol	/13/, /14/

2.2.2 Environmental fate

Mixing in water

Methanol is readily miscible in water, and it is assumed to readily be mixed into water upon release.

Evaporation

Methanol may evaporate from the upper water layer. The equations used for the simulation of the evaporation of ammonia (Section 2.1.2) were also used for methanol.

Biodegradation

Methanol is readily degradable in accordance with the OECD criteria in tests for ultimate, aerobic biodegradability. Biodegradation is expected to be the dominant mechanism of methanol loss once the concentrations resulting from a fuel spill have been diluted below toxic levels /46/. Based on experimental biodegradation data in artificial seawater /25/, the half-life (T½) of methanol in seawater was conservatively estimated to 5 days at 20°C assuming first order kinetics. The estimated T½ is within the range of half-lives of methanol of 1 to 7 days reported for unacclimated aqueous aerobic biodegradation /46/. The biodegradation rate was simulated by first order kinetics with correction for temperature using the rule of thumb that the T½ increases by a factor of 2-3 when the temperature decreases by 10°C /29/. Methanol is a simple substance with only one carbon in the molecular structure, and, therefore, the T½ of methanol was assumed to increase by a factor of 2 for every 10°C decrease (and, conversely, the T½ was assumed to decrease by a factor of 2 for every 10°C increase).

The temperature dependence of the degradation rate constant was expressed by an Arrhenius type equation:

$k_t = k_{lab} \cdot \exp[-A\,(t - t_{lab})]$, where:

> k_t is the degradation rate constant at the temperature t (ºC)
>
> k_{lab} is the degradation rate constant at the temperature t_{lab} (ºC) derived from experimental studies
>
> *A* is a constant representing the assumption that the half-life decreases with a factor of 2 for every 10ºC increase of the temperature.
>
> The constant *A* can be calculated by assuming that the temperature t is 10ºC higher than t_{lab} ($t = t_{lab} + 10$), which means:
>
> $k_t = k_{lab} \cdot \exp[-A\,(t - t_{lab})] \leftrightarrow k_t = k_{lab} \cdot \exp[-A \cdot 10]$
>
> If the degradation rate constant k_t is doubled when the temperature increases by 10ºC, then:
>
> $k_t = k_{lab} \cdot \exp[-A \cdot 10] = 2 \cdot k_{lab} \leftrightarrow -A \cdot 10 = \ln 2 \leftrightarrow A = \frac{-\ln 2}{10}$

Using the estimated half-life (T½) for methanol of 5 days at 20°C, then:

$$\mathrm{k_t}\ (\mathrm{d}^{-1}) = \frac{ln2}{T½} \rightarrow \mathrm{k_t}\ (\mathrm{d}^{-1}) = \frac{ln2}{5}$$

The temperature dependence of the degradation rate constant (k_t) can now be calculated by the equation:

$k_t = k_{lab} \cdot \exp[-A\,(t - t_{lab})] \rightarrow \mathrm{k_t}\ (\mathrm{d}^{-1}) = \frac{ln2}{5} \cdot \exp[0.069 \cdot (\,t(°C) - 20°C)]$

2.3 Very low sulphur fuel oil

VLSFO is a complex mixture of several different hydrocarbons, and its properties will change due the various fate processes.

2.3.1 Physical-chemical properties

Several VLSFOs exist on the market. The following properties of the VLSFO were assumed in the present study /21/:

Density: 900-1000 kg/m^3

Pour point: 0-30°C

Flash point: > 60°C

The above properties were met by a VLSFO from Shell which is characterized in a report by SINTEF /30/. The properties of the Shell VLSFO (hereafter simply referred to as VLSFO), shown in Table 2.3, were used in the exposure modelling.

Data on the true boiling point, density, viscosity at 2°C and 13°C, content of asphaltenes and wax were retrieved from the SINTEF report /30/. The true boiling point curve is shown in Figure 2.1.

Table 2.3 Physical-chemical properties of VLSFO.

Parameter	Unit	Value	Comments
Density (at 288K)	kg/m^3	990	Reference /30/
Kinematic viscosity (at 293K)	m^2/s	0.0167	Reference /30/
Boiling point		See Figure 2.1	Reference /30/
Pour point	ºC	3	Reference /30/
Flash point	ºC	100	Reference /30/
Max water content in water-in-emulsion	%	57	Reference /30/
Asphaltene content	%	4.8	Reference /30/
Wax content	%	4.9	Reference /30/
Surface tension without surfactant	N/m	0.015	Reference /30/
Interfacial tension (water-oil)	N/m	0.0104	Reference /30/

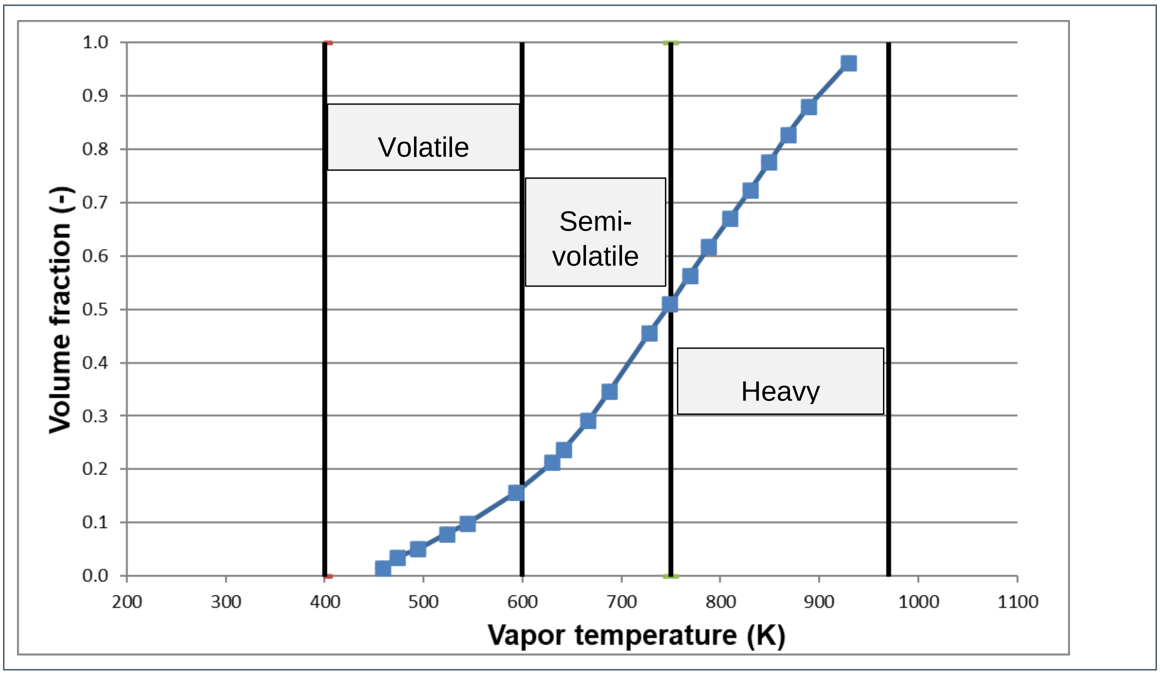


Figure 2.1 Boiling point curve for the selected VLSFO.

The composition of the VLSFO was described by the percentage of each of the three oil fractions: volatile, semi-volatile, and heavy (Table 2.4). Each of these fractions was assigned a minimum and maximum boiling point and vapour pressure which changes during evaporation. In addition, assumptions for the content of wax and asphaltenes in the VLSFO are needed for the modelling. Wax and asphaltenes were assumed to be non-volatile.

Table 2.4 **Assumed composition and oil fractions in VLSFO.**

Parameter	Oil fraction					Comments
	Volatile	Semi-volatile	Heavy	Wax	Asphal-tenes	
Concentration (wt%)	21.3	31.1	37.8	4.9	4.8	See Figure 2.1
Boiling point (K)						See Figure 2.1
Water solubility (mg/L)	6.14	0.16	0.0061			
Molar mass (g/mole)	191	361	693			
Pour point (°C)	15.9	48.0	96.2			
Density (kg/m^3)	872	1008	1034	940	1150	Derived from the fluid composition data

Minor amounts of the hydrocarbons may dissolve in the water column either by dissolution from the surface or from the dispersed oil droplets in the water column. Once dissolved in the water column, the dissolved oil fraction enters the Eulerian part of the oil spill model /3/.

2.3.2 Environmental fate

The environmental fate of the VLSFO was simulated by the DHI oil spill model /3/ supplemented with an advanced module enabling the prediction of the concentration of the dissolved oil compounds in the water column.

The following fate processes were included in the exposure modelling:

- **Spreading** expressed as the increase of the area of surface oil slick driven by density, viscosity, and surface tension
- **Evaporation** driven by vapour pressure
- **Dissolution** driven by water solubility
- **Dispersion** driven by wave action where oil droplets are dispersed into the sea due to wave action on the oil slick
- **Emulsification** – the formation of water-in-oil emulsions is driven by wind and wave action, while the stability of the water-in-oil emulsions is driven by the contents of wax and asphaltenes.

The changes in density, viscosity, and pour point of the oil slick resulting from the above-mentioned processes were considered in the exposure modelling.

By using the assumed composition of the VLSFO described in Table 2.4, the influence of photooxidation and biodegradation was considered.

Photooxidation mediated by sunlight transforms oil hydrocarbons to polar, water-soluble substances and thus enhances the dissolution process in marine water. The mechanisms of oil photooxidation are not fully understood, but apparently aromatic hydrocarbons are more susceptible to photooxidation /42/, /43/. A study designed to examine the potential for photooxidation of crude oils under optimal conditions showed that saturated compounds like alkanes were resistant, while aromatic compounds, especially alkyl substituted ones, were sensitive to photooxidation /43/. Photooxidation is dependent on the light intensity, and the importance of photooxidation for the removal of an oil spill decreases in seasons with dense cloud cover and sparse sunlight. Furthermore, evaporation is the major removal process for many (aromatic) hydrocarbons and reduces the amounts available for photooxidation.

Biodegradation by microorganisms is a significant process for the total removal of oil from the marine environment. The biodegradation of hydrocarbons in the water column depends on the dissolved oxygen concentration, the water temperature, and the physical state of the oil. The breakup of oil and the transport of small particles to the water column are very important for the biodegradation, as, e.g., oil droplets degrade much faster than undispersed oil and surface slicks /44/, /45/.

Photooxidation and biodegradation were not included in the exposure modelling as these processes are of minor importance and usually overshadowed by evaporation /45/ in the relevant time window for the simulations. The oil density will increase with the evaporation of the lighter hydrocarbons and possibly also by particles adhering to the oil. Objects with a higher density than that of water will sink if immersed in water. Therefore, if the calculated density of the oil slick exceeded the density of the ambient water, the settling of the oil was included in the modelling.

3 Exposure scenarios

The exposure scenarios defined for the environmental and human impact assessments are described in Tables 3.1-3.4 below. The parameters were chosen based on the literature /41/ and on discussions with maritime experts and project partners participating in various workshops hosted by A.P. Moller Maersk A/S. Throughout the workshops, a conservative approach was followed for selecting the parameters. For example, the amount of fuel released in the maritime environment in case of collision (7600 m^3) represents a 95% full tank completely spilled. For the two collision scenarios, it was agreed to model the same amounts of fuel spilled across fuel types to even the comparison. Methanol fuel tanks were taken for comparison, noting that for VLSFO this is a very conservative approach since multiple independent fuel tanks are commonly used. Additionally, for the two collision scenarios, the center of the hole is assumed to be 8 m below the water surface, with a diameter reflecting the size of a bulbous bow, based on data from ship drawings. We acknowledge that this is a conservative assumption and that a hole of this size is highly unlikely (almost an impossible outcome for a collision). Nevertheless, it is important to note that this parameter has little relevance to the results since our assumption involves the full content of the fuel tank leaking into the marine environment regardless of the hole's actual size.

Table 3.1 Accidental spill exposure scenario in Port of Rotterdam. Spill event: Hole in the bunkering hose.

Port of Rotterdam – Hole in the bunkering hose			
Geographical coordinates for the position of bunkering	51°57'11.1"N 4°00'03.4"E 51.953071, 4.000951		
Dimension of leak	Hole size (diameter): 12 mm		
Location of spill	18 m above water surface		
Duration of spill	60 seconds		
	Ammonia	**Methanol**	**VLSFO**
Fuel pressure	1.5-2 bar	1.5-2.5 bar	4 bar
Fuel temperature	-33 °C	atmospheric	atmospheric
Fuel tank volume	8000 m^3	8000 m^3	8000 m^3
Volume of fuel in tank	7600 m^3	7600 m^3	7600 m^3
Fuel density	681.9 kg/m^3	791.8 kg/m^3	860-991 kg/m^3
Spill rate	0.8 kg/s	1 kg/s	1.5 kg/s
Amount of fuel spilled	48 kg ~0.07 m^3	60 kg ~0.08 m^3	90 kg ~0.09 m^3

Table 3.2 Accidental spill exposure scenario in Port of Rotterdam. Spill event: Complete rupture of the bunkering pipe.

Port of Rotterdam – Complete rupture of the bunkering pipe			
Geographical coordinates for the position of bunkering	51°57'11.1"N 4°00'03.4"E 51.953071, 4.000951		
Dimension of leak	Rupture of two hoses, each with hole size (diameter) of 20 cm		
Location of spill	18 m above water surface		
Duration of spill	30 seconds		
	Ammonia	**Methanol**	**VLSFO**
Fuel pressure	1.5-2 bar	1.5-2.5 bar	4 bar
Fuel temperature	-33 °C	atmospheric	atmospheric
Fuel tank volume	8000 m^3	8000 m^3	8000 m^3
Volume of fuel in tank	7600 m^3	7600 m^3	7600 m^3
Fuel density	681.9 kg/m^3	791.8 kg/m^3	860-991 kg/m^3
Spill rate	152 kg/s	176 kg/s	~220 kg/s
Amount of fuel spilled	9092 kg ~ 13.3 m^3	10557 kg ~13,3 m^3	12300 kg ~12.4 m^3

Table 3.3 Accidental spill exposure scenario in the English Channel. Spill event: Collision.

English Channel - Collision			
Geographical coordinates for the position of collision	51°02'14.4"N 1°28'5.9"E (West bound) → coming from Rotterdam		
Dimension of leak	Hole size (diameter): 8 m		
Location of spill	Center of hole 8 m below water surface		
Duration of spill	12 hours		
	Ammonia	**Methanol**	**VLSFO**
Fuel pressure	atmospheric	atmospheric	atmospheric
Fuel temperature	-33 °C	ambient	ambient
Fuel tank volume	8000 m^3	8000 m^3	8000 m^3
Volume of fuel in tank	7600 m^3	7600 m^3	7600 m^3
Fuel density	681.9 kg/m^3	791.8 kg/m^3	860-991 kg/m^3
Spill rate	432 kg/s	501 kg/s	628 kg/s
Amount of fuel spilled (*)Corrected by author 2025-01-06	5182 t (*) 7600 m^3	6018 t (*) 7600 m^3	7532 t (*) 7600 m^3

Table 3.4 Accidental spill exposure scenario in the Strait of Malacca.

Strait of Malacca - Collision			
Geographical coordinates for the position of collision	1°06'25.2864"N 103°36'36.8748"E		
Dimension of leak	Hole size (diameter): 8 m		
Location of spill	Center of hole 8 m below water surface		
Duration of spill	12 hours		
	Ammonia	**Methanol**	**VLSFO**
Fuel pressure	atmospheric	atmospheric	atmospheric
Fuel temperature	-33 °C	ambient	ambient
Fuel tank volume	8000 m^3	8000 m^3	8000 m^3
Volume of fuel in tank	7600 m^3	7600 m^3	7600 m^3
Fuel density	681.9 kg/m^3	791.8 kg/m^3	860-991 kg/m^3
Spill rate	432 kg/s	501 kg/s	628 kg/s
Amount of fuel spilled (*)Corrected by author 2025-01-06	5182 t (*) 7600 m^3	6018 t (*) 7600 m^3	7532 t (*) 7600 m^3

4 Environmental impact assessment

4.1 Environmental impact evaluation

The environmental impact assessment was conducted by using the principles described in the *ECHA Guidance on information requirements and chemical safety assessment* which is used in support of the European chemicals' regulation REACH (Regulation (EC) No. 1907/2006 of the European Parliament and of the Council). The impact assessment compares the result of the exposure estimation, expressed as the predicted environmental concentration (PEC), with the predicted no-effect concentration (PNEC). In this study, the PEC is the concentration of the chemical in the marine environment predicted by the exposure modelling described in Section 4.3. The PNEC is the concentration in the environment below which adverse effects are not expected to occur due to exposure to the chemical.

The risk characterization ratio (RCR) is the ratio of the PEC to the PNEC:

$$\mathrm{RCR} = \frac{\mathrm{PEC}}{\mathrm{PNEC}}$$

An RCR < 1 means that adverse ecotoxic effects in the marine ecosystem due to exposure to the chemical will likely not occur. In the present impact assessment, the results of the exposure modelling were expressed by mapping the sea areas in which the PEC exceeds the PNEC and, thus, RCR > 1 leading to the interpretation that adverse effects in the marine ecosystem may occur.

4.2 Predicted no-effect concentration

4.2.1 Derivation of PNEC

The PNEC is based on the available information from ecotoxicological studies. The relevant environmental compartment in the present impact assessment is marine water, and the PNEC should be derived from data obtained via ecotoxicological studies of ecologically relevant saltwater species. As studies with saltwater species are not always available, the PNEC may be derived by using available data on both freshwater and saltwater organisms /11/, /12/. Ecotoxicological studies may lead to various types of effect concentrations including:

- EC50: median effect concentration causing adverse effects on 50% of the exposed test organisms. Different endpoints (effects) might be investigated, e.g., the growth rate (algae) or immobilization (crustaceans),
- LC50: median lethal concentration causing a lethal effect to 50% of the test organisms (e.g., fish), or
- NOEC: no observed effect concentration, i.e., the highest concentration at which no adverse effects are observed.

The PNEC may be calculated by dividing the lowest effect concentration by an assessment factor to account for the fact that ecotoxicological studies can never represent the diversity of species in the aquatic environment. Marine ecosystems can be rich in their variety of organisms with different functional roles and may include unique groups of organisms (e.g., corals and echinoderms) that are not found in fresh waters. A high assessment factor of

1000 is normally used when the ecotoxicological data consist of an EC50 or LC50 from short-term acute studies. A lower assessment factor of usually 10 can be applied when NOEC values from long-term chronic studies representing organisms belonging to different trophic levels are available /11/.

4.2.2 Ammonia

Un-ionized ammonia (NH_3) dissolved in water partly dissociates and forms the ammonium ion, NH_4^+. The ratio between NH_3 and NH_4^+ is highly influenced by pH and to a lesser extent temperature (see Figure 4.1). The toxicity of total ammonia is mainly caused by un-ionized ammonia (NH_3), while the ammonium ion (NH_4^+) is less toxic. This means that the toxicity of total ammonia (NH_3 + NH_4^+) increases with pH because of the increasing fraction of NH_3 at higher pH.

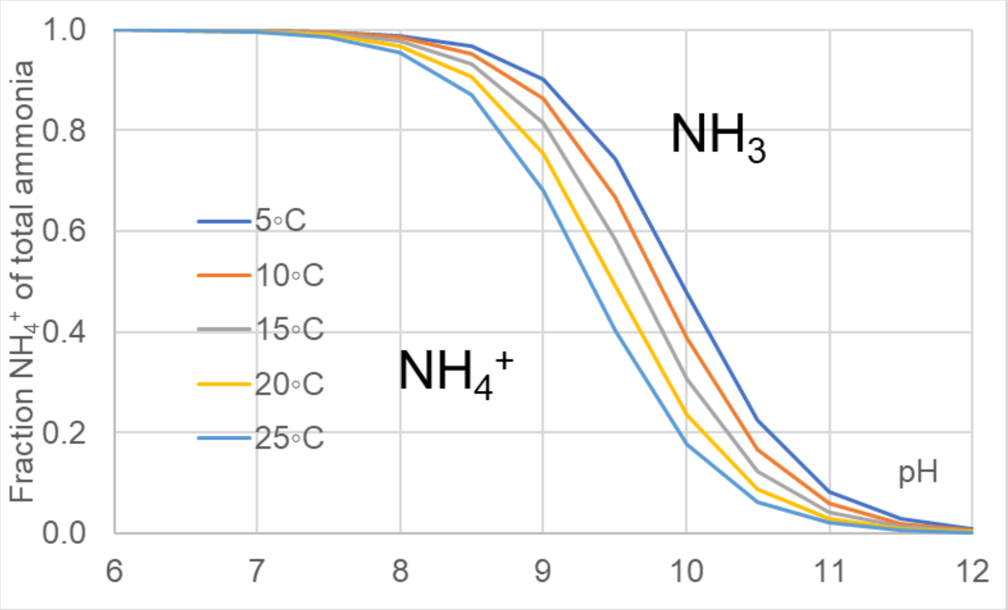


Figure 4.1 **Speciation of ammonia as a function of pH and temperature. Salinity set to 30 g/kg.**

The PNEC used for total ammonia in the present study was calculated from the PNEC in the REACH registration dossier for un-ionized ammonia (NH_3):

PNEC (marine water), un-ionized ammonia, NH_3: 0.001 mg/L.

The PNEC of 0.001 mg/L stated in the REACH registration dossier is close to an updated marine environmental quality standard of 0.00066 mg/L for un-ionized ammonia suggested by the Environment Agency (England and Wales) /40/.

The PNEC for un-ionized ammonia (NH_3) was used to derive PNECs for total ammonia (NH_3 + NH_4^+) by accounting for the pKa dependency on salinity and temperature and the pH in the ambient water in the Port of Rotterdam, the English Channel, and the Strait of Malacca. The following equation was used for the calculations:

$$\mathrm{PNEC\ (total\ ammonia)} = \frac{\mathrm{PNEC}_{\mathrm{un-ionized\ ammonia}}}{1 - \mathrm{f}_{\mathrm{un-ionized\ ammonia}}}.$$

Where, the fraction of un-ionised ammonia, $\mathrm{f}_{\text{un-ionized ammonia}}$ is calculated by:

$$f_{\text{un-ionized ammonia}} = \frac{[H^+]}{K_a + [H^+]}$$

$[H+]$ concentration of H^+-ions = 10^{-pH}

pK_a calculated as a function of temperature and salinity from the equation stated for pK_a in Table 2.1.

The temperature in the Port of Rotterdam and the English Channel depends on the time of the year, and, therefore, monthly average values of temperature and salinity were obtained. An average value of pH 8.1 (standard deviation of 0.04) for the year 2020 representing waters in and near to the English Channel was obtained from the ICES database /16/. The monthly average temperatures and salinities together with the derived PNECs for total ammonia (NH_3 + NH_4^+) are presented in Table 4.1 and Table 4.2. During the year, the PNEC values vary from 0.025 mg/L to 0.076 mg/L in the Port of Rotterdam and the English Channel.

Table 4.1 Temperature and salinity in Port of Rotterdam and derived PNEC values for total ammonia.

Month	1	2	3	4	5	6	7	8	9	10	11	12
T(ºC)	5.4	4.7	3.7	6.2	10.5	14.2	18.0	19.4	18.0	15.4	10.5	8.4
Salinity (‰)	21.1	20.5	19.5	20.4	17.2	14.1	18.5	22.1	21.5	25.2	18.1	25.3
PNEC (mg/L)	0.068	0.071	0.076	0.064	0.046	0.035	0.027	0.025	0.028	0.034	0.046	0.056

Table 4.2 Temperature and salinity in the English Channel and derived PNEC values for total ammonia.

Month	1	2	3	4	5	6	7	8	9	10	11	12
T(ºC)	10.5	9.3	8.1	7.9	10.2	12.7	15.7	17.1	17.9	16.7	14.2	11.5
Salinity (‰)	35.0	35.0	35.0	34.9	35.1	35.0	35.0	35.1	35.1	35.1	35.0	35.0
PNEC (mg/L)	0.051	0.056	0.061	0.061	0.052	0.044	0.035	0.032	0.030	0.033	0.039	0.047

The temperature in the Strait of Malacca varies little throughout the year, and, thus, an average temperature of 30.4ºC, an average salinity of 32.6‰ and a pH of 7.84 ± 0.14 /15/ were used. These values resulted in a PNEC for total ammonia (NH_3 + NH_4^+) of 0.022 mg/L.

Water quality criteria are sometimes used in the same way as PNEC. The U.S. Environmental Protection Agency formulated a water quality criterion for ammonia in saltwater. For a salinity of 30‰, a temperature of 10ºC and pH 8, the water quality criterion is set at 2.2 mg total ammonia/L. For the same conditions, Australia and New Zeeland formulated a water quality criterion at 0.91 mg total ammonia/L. These water quality criteria are approximately 20 to 40 times higher than the calculated PNEC for almost similar environmental conditions in the English Channel in January (Table 4.2). Compared to the water quality criteria established in USA, Australia, and New Zealand, the

PNECs used in the present study are conservative, reflecting a more cautious approach to protecting the marine environment.

4.2.3 Methanol

Methanol is recognized as a chemical with low acute toxicity to aquatic organisms /18/. The acute aquatic toxicity of methanol, measured as EC50 or LC50, is generally in the g/L range as seen from the acute toxicity data for freshwater and marine organisms obtained from the REACH registration dossier for methanol (*), the US EPA ECOTOX database /35/ (**), and a study of static renewal bioassays /18/ (***):

Fish (fresh water)

LC50 (*Pimephales promelas*, 96 h): 28100 mg/L (*)

LC50 (Rainbow trout, *Oncorhynchus mykiss*, 96 h): 20100 mg/L (*)

LC50 (*Lepomis macrochirus*, 96 h): 15400 mg/L (*)

LC50 (*Oreochromis mossambicus*, 96 h): 15320 mg/L (***)

Fish (marine)

LC50 (*Agonus cataphractus*, 96 h): 28000 mg/L (**)

Crustaceans (fresh water)

EC50 (*Daphnia magna*, 48 h): 18000 mg/L (*)

LC50 (*Moina micrura*): 4820 mg/L (***)

Crustaceans (marine)

LC50 (*Artemia salina*, 48 h): 46782 mg/L (**)

LC50 (Brown shrimp, *Crangon crangon*, 96 h): 1700 mg/L (**)

LC50 (*Nitocra spinipes*, 96 h): 12000 mg/L (**)

Molluscs (marine)

LC50 (*Cerastoderma edule*, 96 h): 5,745 mg/L (**)

LC50 (Blue mussel, *Mytilus edulis*, 96 h): 15200-16700 mg/L (**)

Micro-algae (fresh water)

EC50 (*Selenastrum capricornutum*, 96 h): Approx. 22000 mg/L (*)

Oligochaete worm (fresh water)

LC50 (*Branchiura sowerbyi*): 54890 mg/L (***)

Based on the above ecotoxicological data, the LC50 for the marine crustacean brown shrimp (*Crangon crangon*) of 1700 mg/L was selected as the most sensitive organism and used for the derivation of the PNEC for marine water. An assessment factor of 1000 applies to the above dataset which includes two taxonomic groups (molluscs and oligochaetes) in addition to algae, crustaceans, and fish. The PNEC was thus calculated by using the LC50 for brown shrimp and an assessment factor of 1000 /11/: $\mathrm{PNEC} = \frac{1700}{1000}$ mg/L = 1.7 mg/L.

PNEC (marine water), methanol: 1.7 mg/L.

4.2.4 VLSFO

VLSFO is a complex mixture of several different hydrocarbons. The aquatic toxicity of VLSFO depends mainly on the substances that are dissolved or at least miscible in water. It is assumed that a water accommodated fraction (WAF) prepared in the laboratory contains specific hydrocarbons in concentrations which is a reasonable approximation of the dissolution of hydrocarbons in the water after a spill of VLSFO.

In a study of marine fuel oils, VLSFO was mixed with water (VLSFO:water = 1:40) to prepare a WAF, and the concentrations of hydrocarbons in the WAF were analyzed /30/. The hydrocarbons found in the WAF /30/ were paired with PNECs published in a background document from the OSPAR Commission /24/ and used to derive PNECs for the VLSFO fractions semi-volatiles and volatiles (Table 4.3). OSPAR is the Convention for the Protection of the Marine Environment of the North-East Atlantic.

Table 4.3 shows PNECs assigned to sub-fractions of the oil, i.e., groups of hydrocarbons, by using the data from the OSPAR Commission /24/ and the results of concentration-based weight of evidence calculations leading to PNECs for *semi-volatiles* and *volatiles*. The aggregated concentrations for groups of hydrocarbons were based on chemical analyses of the individual substances /30/.

Table 4.3 Predicted no-effect concentrations (PNECs) for groups of hydrocarbons contained in water accommodated fraction (WAF).

Fraction	Sub-fraction	PNEC (µg/L)	Concentration in WAF (µg/L) /30/
Total		-	1595
Heavy fraction		No PNEC assigned [1]	744
Semi-volatiles		1.15 [2]	578
	Decalins	70.5	0.08
	Naphtalenes	2	475
	PAH/2-3 ring	0.29 [3]	26.4
	PAH/4-5 ring	0.008 [4]	0.88
	C0-C5 phenols	1.2 [5]	76
Volatiles		8.5 [2]	273
	BTEX [8]	8 [6]	189
	C3-benzenes	10 [7]	73
	Other	10 [7]	11

Notes (Table 4.3):

[1] The substances in this fraction are considered to have low aquatic toxicity and hence no PNEC was assigned.

[2] PNEC derived as a weighted average of the PNECs of the individual substances in the WAF (C_i) and their PNECs: $\mathrm{PNEC} = \frac{\sum C_i}{\sum \frac{C_i}{\mathrm{PNEC}_i}}$

[3] Weighted average of PNECs based on WAF concentrations of the polyaromatic hydrocarbons (PAH): acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, C1-phenanthrenes/anthracenes, C2-phenanthrenes/anthracenes, C3-phenanthrenes/anthracenes, C4-phenanthrenes/anthracenes, dibenzothiophene, C1-dibenzothiophenes, C2-dibenzothiophenes, C3-dibenzothiophenes, C4-dibenzothiophenes, and ethyl dibenzothiophene.

[4] Weighted average of PNECs based on WAF concentrations of the polyaromatic hydrocarbons (PAH): fluoranthene, pyrene, benz(a)anthracene, chrysene, C1-chrysenes, C2-chrysenes, C3-chrysenes, C4-chrysenes.

[5] Weighted average of PNECs based on WAF concentrations of phenol, C1-phenols (o- and p-cresol), C2-phenols, C3-phenols, C4-phenols, and C5-phenols.

[6] Weighted average of PNECs based on WAF concentrations of benzene, toluene, and ethylbenzene.

[7] PNEC for ethylbenzene.

[8] BTEX: mixtures of benzene, toluene, and the three xylene isomers, all of which are aromatic hydrocarbons.

The PNECs used in the impact assessment of VLSFO were:

PNEC (marine water), VLSFO semi-volatiles: 1.15 µg/L

PNEC (marine water), VLSFO volatiles: 8.5 µg/L

4.3 Environmental exposure modelling

4.3.1 Modelling tools

The basis for the modelling of dispersion of dissolved substances (ammonia, methanol, and VLSFO) and non-dissolved oil (VLSFO) is DHI's high-resolution MIKE FM 3-dimensional hydrodynamic models. The models describe the 3D hydrodynamic regime of water level, current, salinity, and temperature and have been extensively calibrated and validated against measurements /5/, /6/.

For the Port of Rotterdam and the English Channel, a non-extreme year represented by meteorological and hydrodynamic conditions in 2013 was selected and evaluated during the four seasons: winter (December-February), spring (March-May), summer (June-August), and autumn (September-November).

For the Strait of Malacca, a non-extreme year represented by meteorological and hydrodynamic conditions in 2019 was selected and evaluated during the four seasons: Northeast monsoon (November-March), Inter monsoon (April-May), Southwest monsoon (June-August), and Inter monsoon (September-October).

Many of the central parameters in the environmental exposure modelling are conservative (see, e.g., Chapter 3), and meteorological and hydrodynamic conditions for non-extreme years were used in the modelling to avoid overly cautious assessments.

The modelling of the dispersion of dissolved substances (ammonia, methanol and dissolved VLSFO) was carried out using the MIKE ECO Lab model /4/. MIKE ECO Lab is a numerical model for ecological simulations, customized to describe physical, chemical, and biological processes and properties related to environmental problems. The concentration of the substances will change over time because of advection or dispersion, dissolution, evaporation, and biodegradation.

The modelling of the dispersion of non-dissolved VLSFO was carried out using the DHI oil spill model /3/ which is based on a particle tracking concept simulating the movement of discrete particles in a flow field. The spilled oil is represented by a collection of particles, each representing an oil mass with associated physical and physical-chemical properties. The mass and the properties of each particle will change over time because of weathering. It is assumed that once the oil has reached a coast, it stays and does not return to the sea.

4.3.2 Highest median approach

The outcome of the environmental exposure modelling is numerous predicted concentrations that were affected by the horizontal and vertical distribution in the water and the time elapsed after the spill. To determine representative PECs in the higher end of all predicted concentrations, a conservative highest median approach was used:

- One accidental spill was simulated every week throughout a full calendar year, i.e., 52 individual simulations were made.
- The transport and fate of the chemicals in each spill were simulated from the day of the spill and until 30 days after the spill. During this 30-day period, the concentrations of the target chemicals (ammonia, methanol, dissolved VLSFO) were calculated many times each day.
- The predicted concentrations of the target chemicals were evaluated for each spill, and the medians of the highest predicted concentrations within a defined time-window (e.g., 0-1 day after the spill) were selected. By this evaluation, each of the 52 individual simulations was connected to a set of highest medians representing periods of 0-1 day, 1-2 days, 2-5 days, 5-10 days, and 10-30 days after the spill.
- The highest medians obtained for the 52 individual simulations were evaluated to enable impact assessments representing a defined period such as a season (e.g., winter, summer) or the full calendar year.

With the above-described approach, the concentration in a relevant water volume resulting from an equivalent spill would likely not exceed the PEC used in the impact assessment. For this reason, the implemented highest median approach can be considered conservative and appropriate for the nature of this study.

4.4 Environmental impact assessment for marine water

The results of the impact assessment are presented by mapping the sea areas in which the predicted environmental concentration (PEC) exceeds the predicted no-effect concentration (PNEC). The PECs for the full calendar year used in this study were obtained by using the highest median approach described in Section 4.3.2.

The sea areas defined by coloured lines in Figures 4.2-4.10 show the PECs of the individual fuels after the spill as a function of multiples of PNEC, i.e., 0.1 x PNEC, 1 x PNEC, 5 x PNEC, 10 x PNEC, and 100 x PNEC. Furthermore, Figures 4.2-4.10 illustrate the change of the size of these sea areas as affected by the time elapsed after the modelled spill event.

The applied colour legends used in Figures 4.2-4.10 are:

0.1	0.1 x PNEC
1	PNEC
5	5 x PNEC
10	10 x PNEC
100	100 x PNEC

Each of the coloured lines in Figures 4.2-4.10 represents a specific simulated fuel concentration. The highest fuel concentrations are found close to the spill location immediately after the spill. With time, the fuels spread from the spill location and are affected by environmental fate processes (see Chapter 2). For example, in Figure 4.5 (Collision in the English Channel; day 0-1), the sea water concentration of ammonia is *10 x PNEC at the orange line*, whereas a lower concentration of *5 x PNEC is found at the yellow line*. It follows from this example that the fuel concentrations decrease further away from the spill location, and, thus in Figure 4.5, the simulated concentrations of ammonia are 5-10 x PNEC in the sea area between the yellow and orange lines. An impact is indicated, and adverse effects in the marine ecosystem may occur when PEC > PNEC.

4.4.1 Port of Rotterdam

This section presents the results of the impact assessment of the exposure scenarios for bunkering of fuel in Port of Rotterdam. The assumed spills in the exposure scenario ‘Complete rupture of the bunkering pipe’ lead to PECs exceeding the PNECs inside the port (Figures 4.2-4.4 and Table 4.4).

The volumes of the assumed spills in the exposure scenario ‘Hole in the bunkering hose’ are 189 times lower than the spilled volumes in the scenario ‘Complete rupture of the bunkering pipe’. The spills in the ‘Hole in the bunkering hose’ scenario do not lead to PECs that exceed the PNEC for the three analyzed fuels. Therefore, the results from this exposure scenario are not graphically presented here.

Ammonia

The highest PECs of ammonia, and thus the highest exceedance of PNEC, are found near the spill location with a dispersion towards the entrance to the harbour driven by tidal water exchange. The PECs are below the PNEC five to ten days after the spill for the ‘Complete rupture of the bunkering pipe’ scenario (Figure 4.2).

The change of the PECs with time and the affected sea areas are shown in Table 4.4, and are summarized as follows:

- The PECs of ammonia exceed the PNEC by 1-5 times in a sea area of 2 km^2 and by 5-10 times in a sea area of 1 km^2 in the period from 0-1 day after the spill.
- One to two days after the spill, the PECs exceed the PNEC by 1-5 times in a sea area of 6 km^2.
- Two to five days after the spill, the PECs exceed the PNEC by 1-5 times in a sea area of 4 km^2.

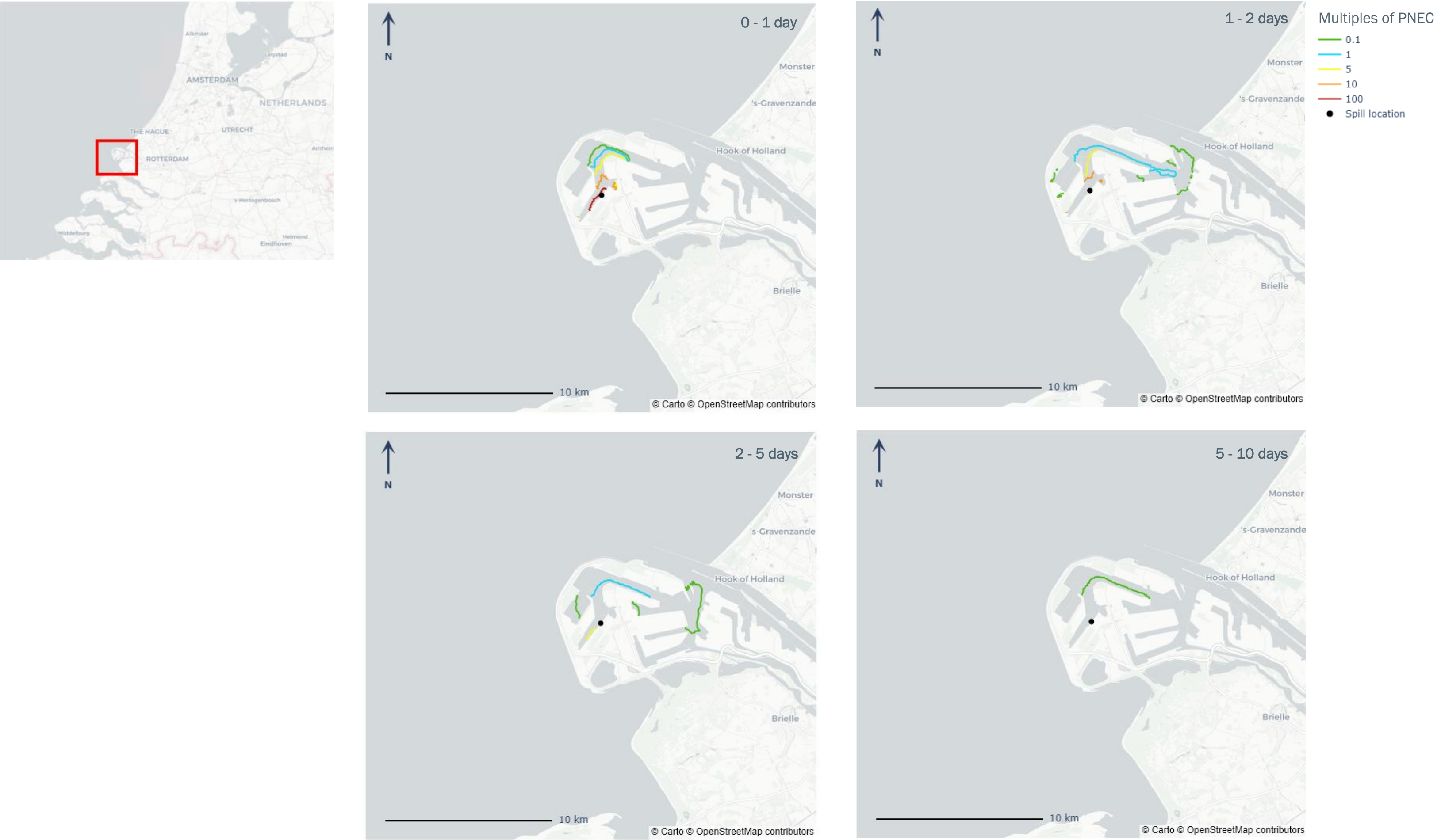


Figure 4.2 Development of the predicted environmental concentrations (PECs) of ammonia in the days after the assumed spill in the exposure scenario: Complete rupture of bunkering pipe in Port of Rotterdam. The black dot indicates the spill location. The PECs are shown as a function of multiples of the predicted no-effect concentration (PNEC). The PECs are higher than the PNEC on the inside of the blue line and lower than the PNEC outside the blue line. An impact is indicated when PEC > PNEC.

Methanol

The highest PECs of methanol, and thus the highest exceedance of PNEC, are found near the spill location with a dispersion towards the entrance to the harbour driven by tidal water exchange. The PECs are below the PNEC two to five days after the spill for the ‘Complete rupture of the bunkering pipe’ scenario (Figure 4.3).

The change of the PECs with time and the affected sea areas are shown in Table 4.4, and are summarized as follows:

- The PECs of methanol exceed the PNEC by 5-10 times in a sea area of 1 km^2 in the period from 0-1 day after the spill.

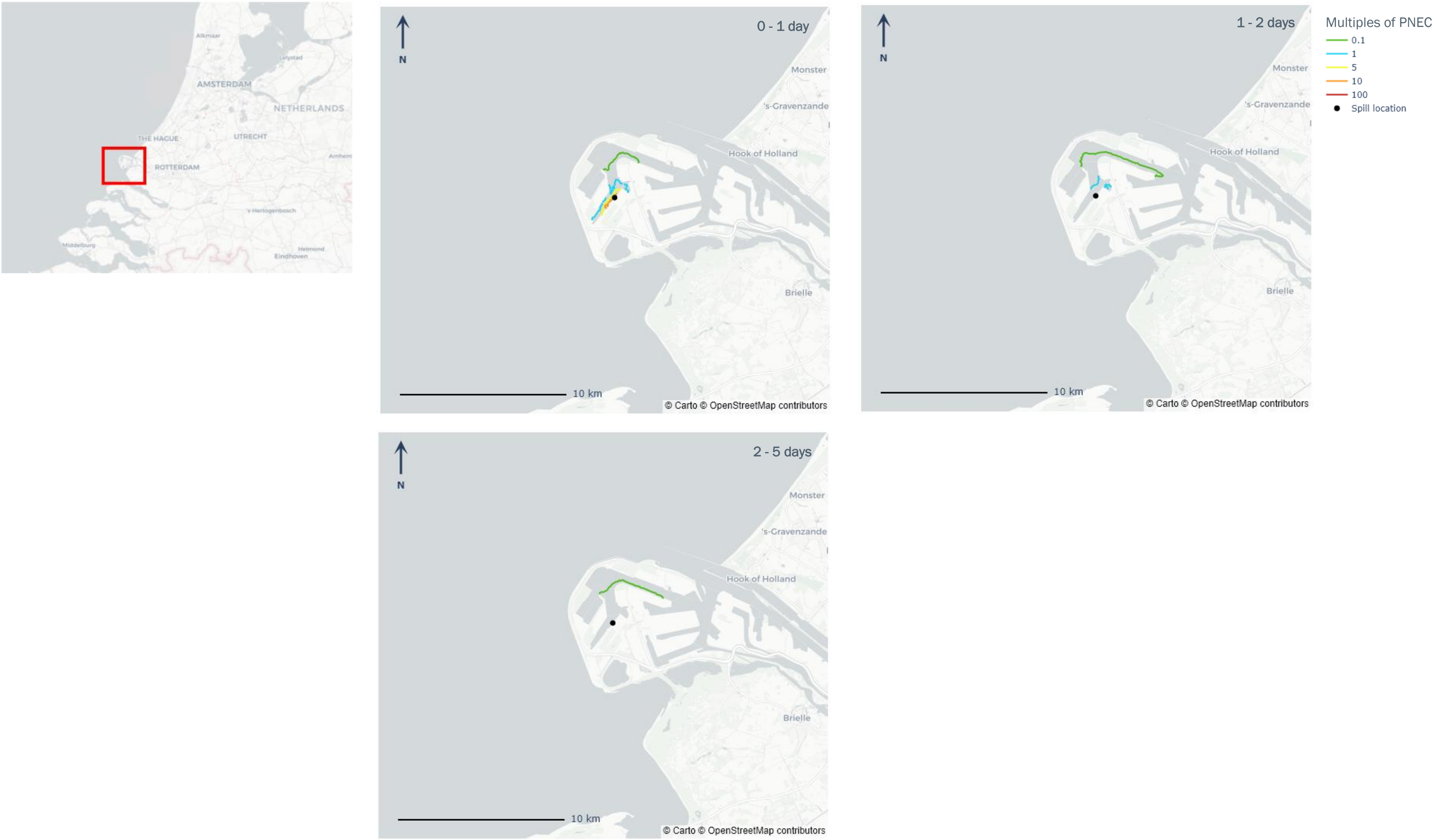


Figure 4.3 Development of the predicted environmental concentrations (PECs) of methanol in the days after the assumed spill in the exposure scenario: Complete rupture of bunkering pipe in Port of Rotterdam. The black dot indicates the spill location. The PECs are shown as a function of multiples of the predicted no-effect concentration (PNEC). The PECs are higher than the PNEC on the inside of the blue line and lower than the PNEC outside the blue line. An impact is indicated when PEC > PNEC.

VLSFO

The highest PECs of dissolved substances in VLSFO, and thus the highest exceedance of PNEC, are found near the spill location with a dispersion towards the entrance to the harbour driven by tidal water exchange. For the ‘Complete rupture of the bunkering pipe’ scenario, ten to thirty days after the spill, the PECs are largely below the PNEC except for small areas in the inner part of the port, where the PECs exceed the PNEC by 1-5 times (Figure 4.4).

The change of the PECs with time and the affected sea areas are shown in Table 4.4, and are summarized as follows:

- One to two days after the spill, the PECs of dissolved VLSFO exceed the PNEC by 1-5 times in an area of 6 km^2, by 5-10 times in a sea area of 3 km^2, and by 10-100 times in a sea area of 3 km^2.
- Five to ten days after the spill, the PECs of dissolved VLSFO exceed PNEC by 1-5 times in a sea area of 1 km^2.

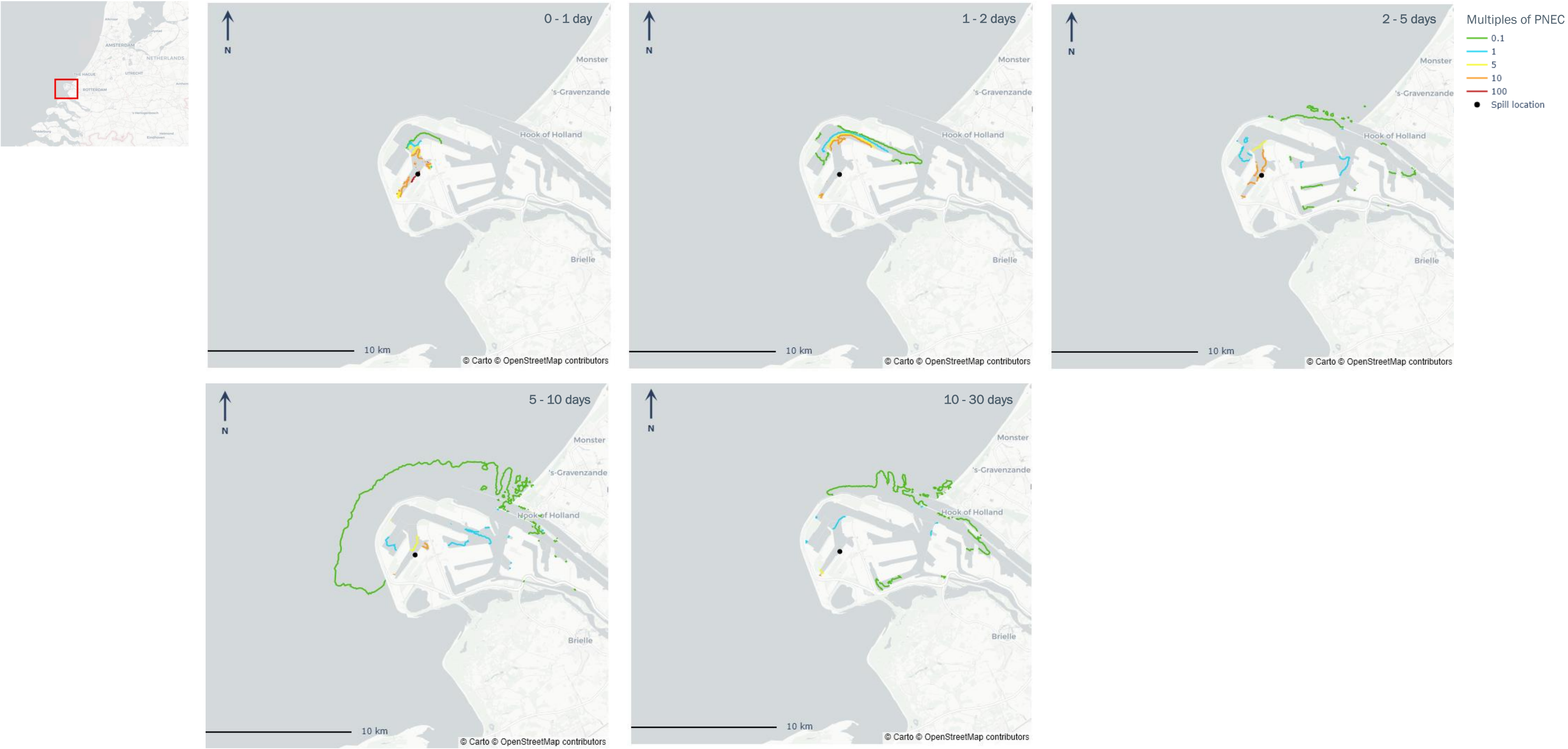


Figure 4.4 Development of the predicted environmental concentrations (PECs) of dissolved VLSFO in the days after the assumed spill in the exposure scenario: Complete rupture of bunkering pipe in Port of Rotterdam. The black dot indicates the spill location. The PECs are shown as a function of multiples of the predicted no-effect concentration (PNEC). The PECs are higher than the PNEC on the inside of the blue line and lower than the PNEC outside the blue line. An impact is indicated when PEC > PNEC.

4.4.2 English Channel

This section presents the results of the impact assessment of the exposure scenario ‘Collision’ in a coastal sea area in the English Channel.

Ammonia

The highest PECs of ammonia, and thus the highest exceedance of PNEC, are found near the spill location with a dominating northbound dispersion because of the residual northern current direction. During the first day after the spill, the PECs near the spill location markedly exceed the PNEC. The PECs are below the PNEC two to five days after the spill (Figure 4.5).

The change of the PECs with time and the affected sea areas are shown in Table 4.4, and are summarized as follows:

- The PECs of ammonia exceed the PNEC by 1-5 times in a sea area of 1580 km^2, by 5-10 times in a sea area of 624 km^2, and by 10-100 times in a sea area of 125 km^2 in the period from 0-1 day after the spill.
- One to two days after the spill, the PECs exceed PNEC by 1-5 times in a sea area of 4052 km^2.

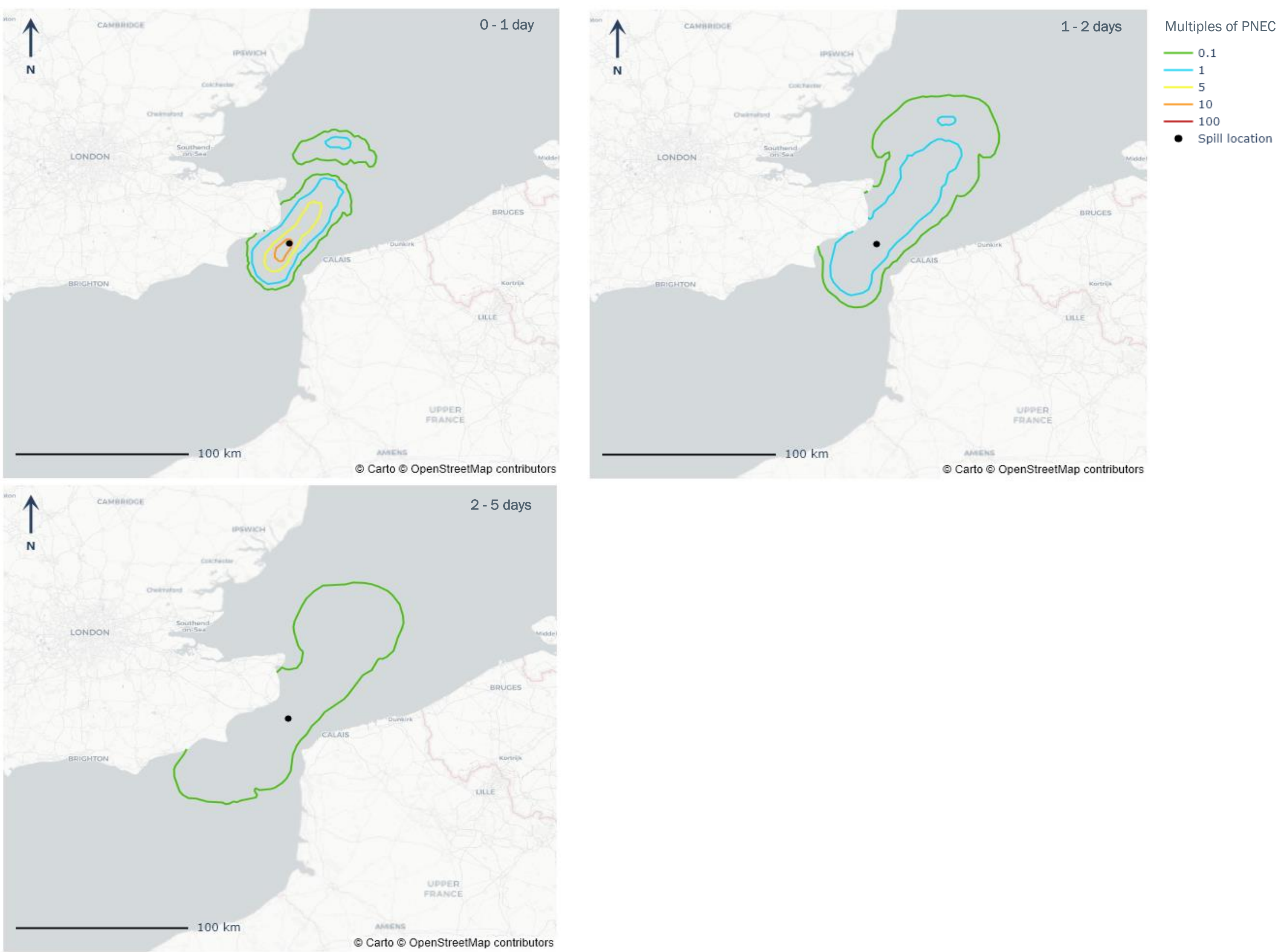


Figure 4.5 Development of the predicted environmental concentrations (PECs) of ammonia in the days after the assumed spill in the exposure scenario: Collision in the English Channel. The black dot indicates the spill location. The PECs are shown as a function of multiples of the predicted no-effect concentration (PNEC). The PECs are higher than the PNEC on the inside of the blue line and lower than the PNEC outside the blue line. An impact is indicated when PEC > PNEC.

Methanol

The PECs of methanol decrease to levels below the PNEC during the first day after the spill, after which exceedance of the PNEC is not expected (Figure 4.6).

Figure 4.6 **Predicted environmental concentrations (PECs) of methanol day 0-1 after the assumed spill in the exposure scenario: Collision in the English Channel. The black dot indicates the spill location. The PECs are shown as a function of multiples of the predicted no-effect concentration (PNEC). A blue line (not present) would indicate the distance from the spill location at which the PEC is equivalent to the PNEC. The PECs thus decrease to a level below the PNEC during the first day after the spill, and the green line indicates the distance at which the PEC is 10 times lower than the PNEC. An impact is indicated when PEC > PNEC.**

VLSFO

The highest PECs of dissolved substances in VLSFO, and thus the highest exceedance of PNEC, are found near the spill location with a dominating northbound dispersion because of the residual northern current direction. During the first day after the spill, the PECs near the spill location markedly exceed the PNEC. The PECs are below the PNEC two to five days after the spill (Figure 4.7). The change of the PECs with time and the affected sea areas are shown in Table 4.4, and are summarized as follows:

- The PECs exceed the PNEC by 1-5 times in a sea area of 531 km^2, by 5-10 times in a sea area of 26 km^2, and by 10-100 times in a sea area of 11 km^2 in the period from 0-1 day after the spill.
- One to two days after the spill, the PECs of dissolved VLSFO exceed PNEC by 1-5 times in a sea area of 436 km^2.

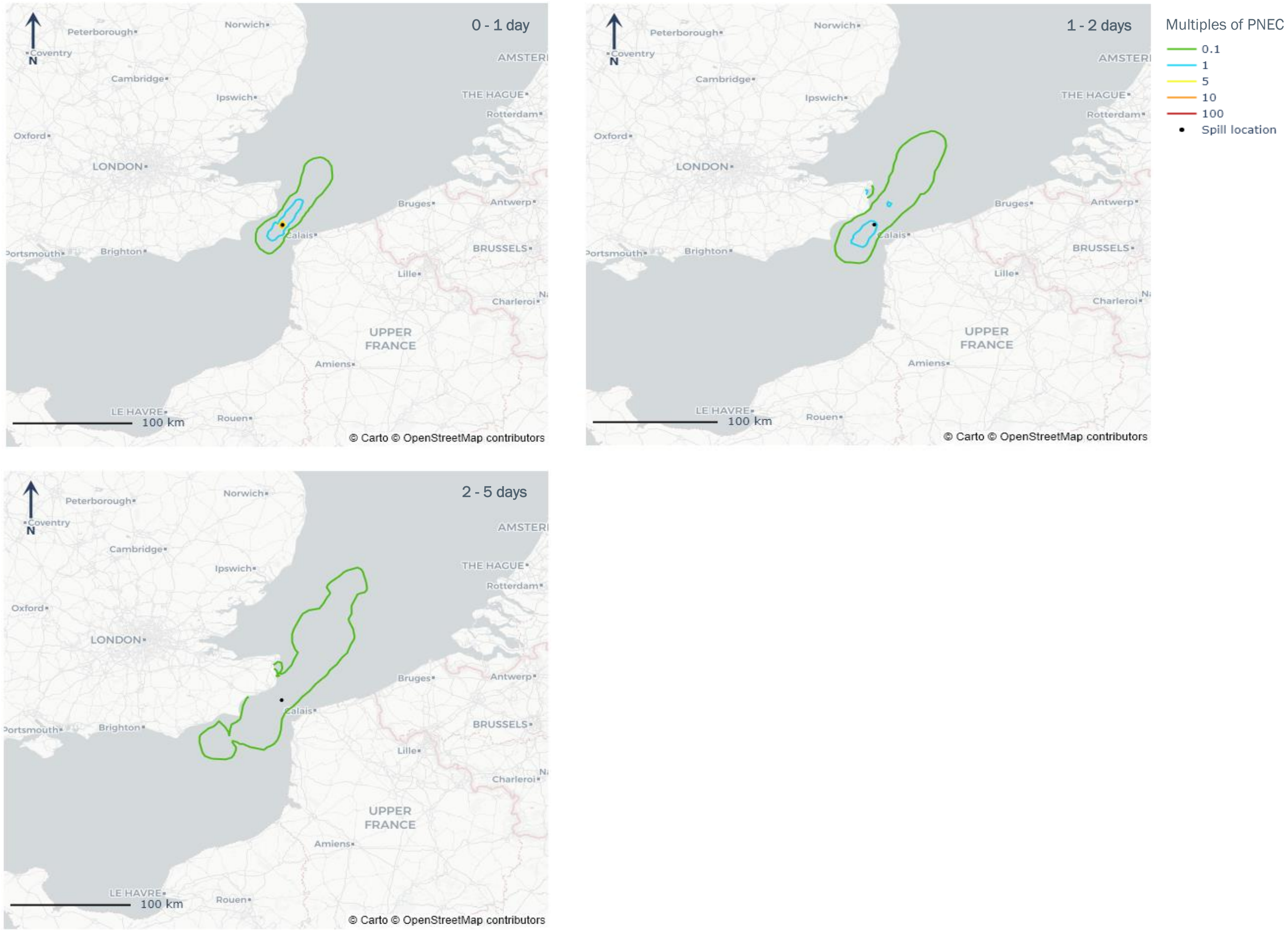


Figure 4.7 Development of the predicted environmental concentrations (PECs) of dissolved VLSFO in the days after the assumed spill in the exposure scenario: Collision in the English Channel. The black dot indicates the spill location. The PECs are shown as a function of multiples of the predicted no-effect concentration (PNEC). The PECs are higher than the PNEC on the inside of the blue line and lower than the PNEC outside the blue line. An impact is indicated when PEC > PNEC.

4.4.3 Strait of Malacca

This section presents the results of the impact assessment of the exposure scenario ‘Collision’ in a coastal sea area in the Strait of Malacca.

Ammonia

The highest PECs of ammonia, and thus the highest exceedance of PNEC, are found near the spill location with a dominating north-westbound dispersion because of the residual north-western current direction. The PECs are below the PNEC one to two days after the spill (Figure 4.8).

The change of the PECs with time and the affected sea areas are shown in Table 4.4, and are summarized as follows:

- The PECs of ammonia exceed the PNEC by 1-5 times in a sea area of 290 km^2 and by 5-10 times in a sea area of 37 km^2 in the period from 0-1 day.

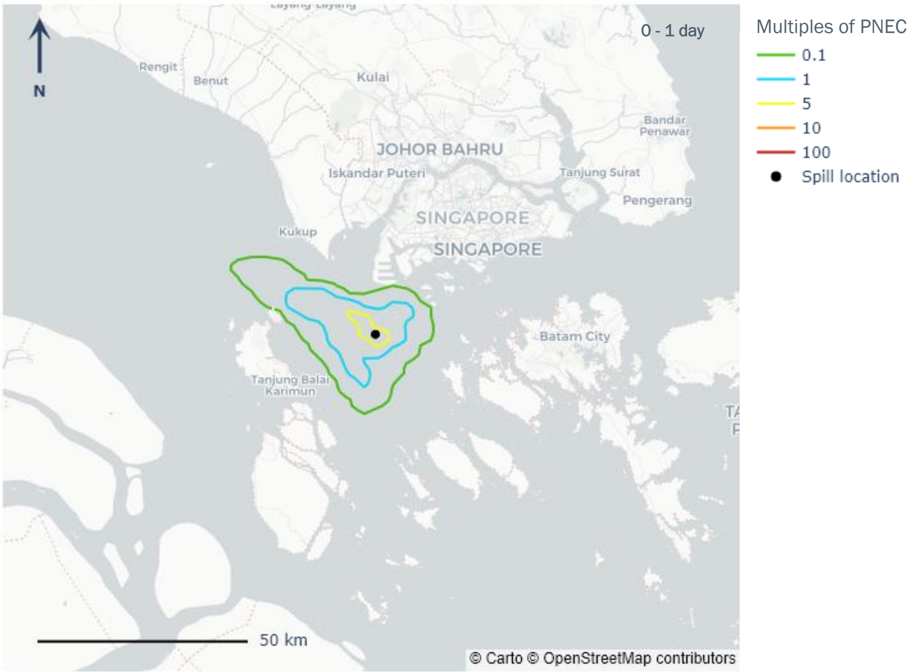


Figure 4.8 Predicted environmental concentrations (PECs) of ammonia day 0-1 after the assumed spill in the exposure scenario: Collision in the Strait of Malacca. The black dot indicates the spill location. The PECs are shown as a function of multiples of the predicted no-effect concentration (PNEC). The PECs are higher than the PNEC on the inside of the blue line and lower than the PNEC outside the blue line. An impact is indicated when PEC > PNEC.

Methanol

The highest PECs of methanol, and thus the highest exceedance of PNEC, are found near the spill location with a dominating north-westbound dispersion because of the residual north-western current direction. The PECs are below the PNEC one to two days after the spill (Figure 4.9).

The change of the PECs with time and the affected sea areas are shown in Table 4.4, and are summarized as follows:

- The PECs of methanol exceed the PNEC by 1-5 times in a sea area of 40 km^2 in the period from 0-1 day.

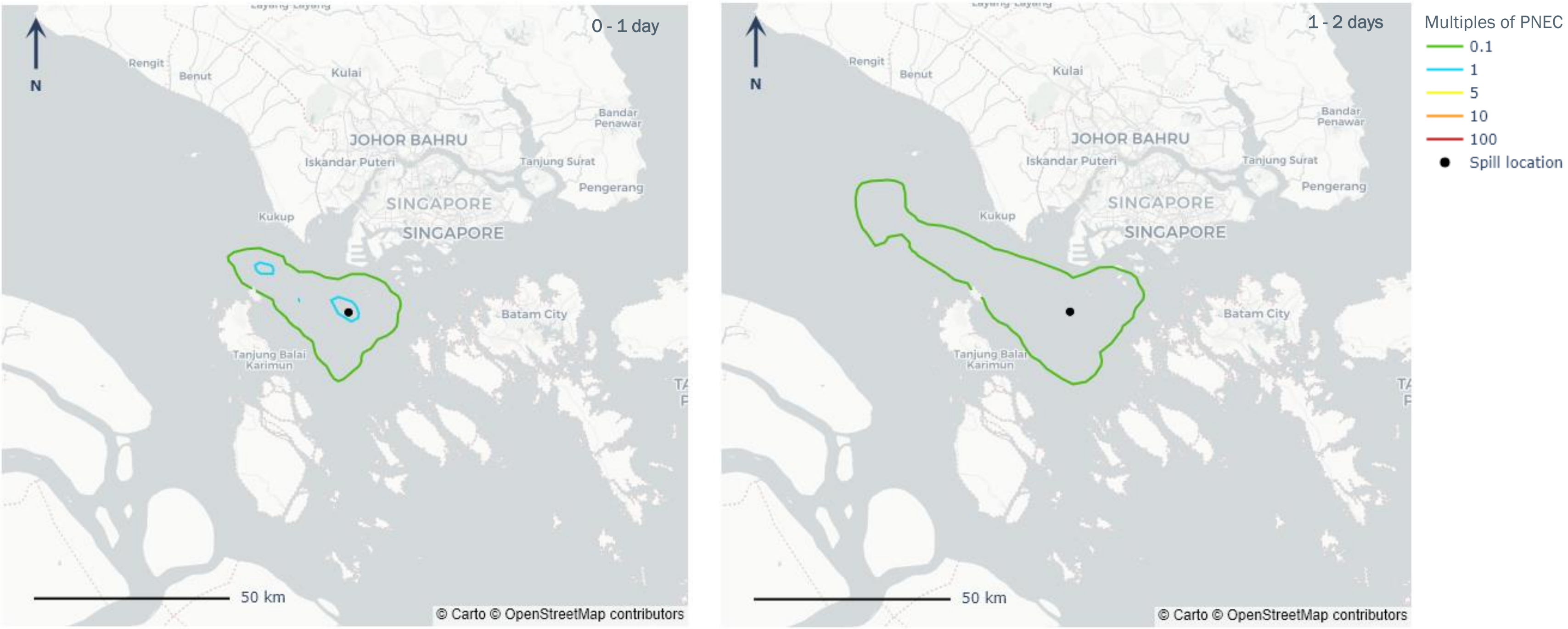


Figure 4.9 Development of the predicted environmental concentrations (PECs) of methanol in the days after the assumed spill in the exposure scenario: Collision in the Strait of Malacca. The black dot indicates the spill location. The PECs are shown as a function of multiples of the predicted no-effect concentration (PNEC). The PECs are higher than the PNEC on the inside of the blue line and lower than the PNEC outside the blue line. An impact is indicated when PEC > PNEC.

VLSFO

The highest PECs of dissolved substances in VLSFO, and thus the highest exceedance of the PNEC, are found near the spill location with a dominating north-westbound dispersion because of the residual north-western current direction. The PECs are below the PNEC two to five days after the spill (Figure 4.10).

The change of the PECs with time and the affected sea areas are shown in Table 4.4, and are summarized as follows:

- The PECs of dissolved substances in VLSFO exceed the PNEC by 1-5 times in a sea area of 61 km^2 in the period from 0-1 day after the spill.
- One to two days after the spill, the PECs of dissolved VLSFO exceed the PNEC by 1-5 times in a sea area of 11 km^2.

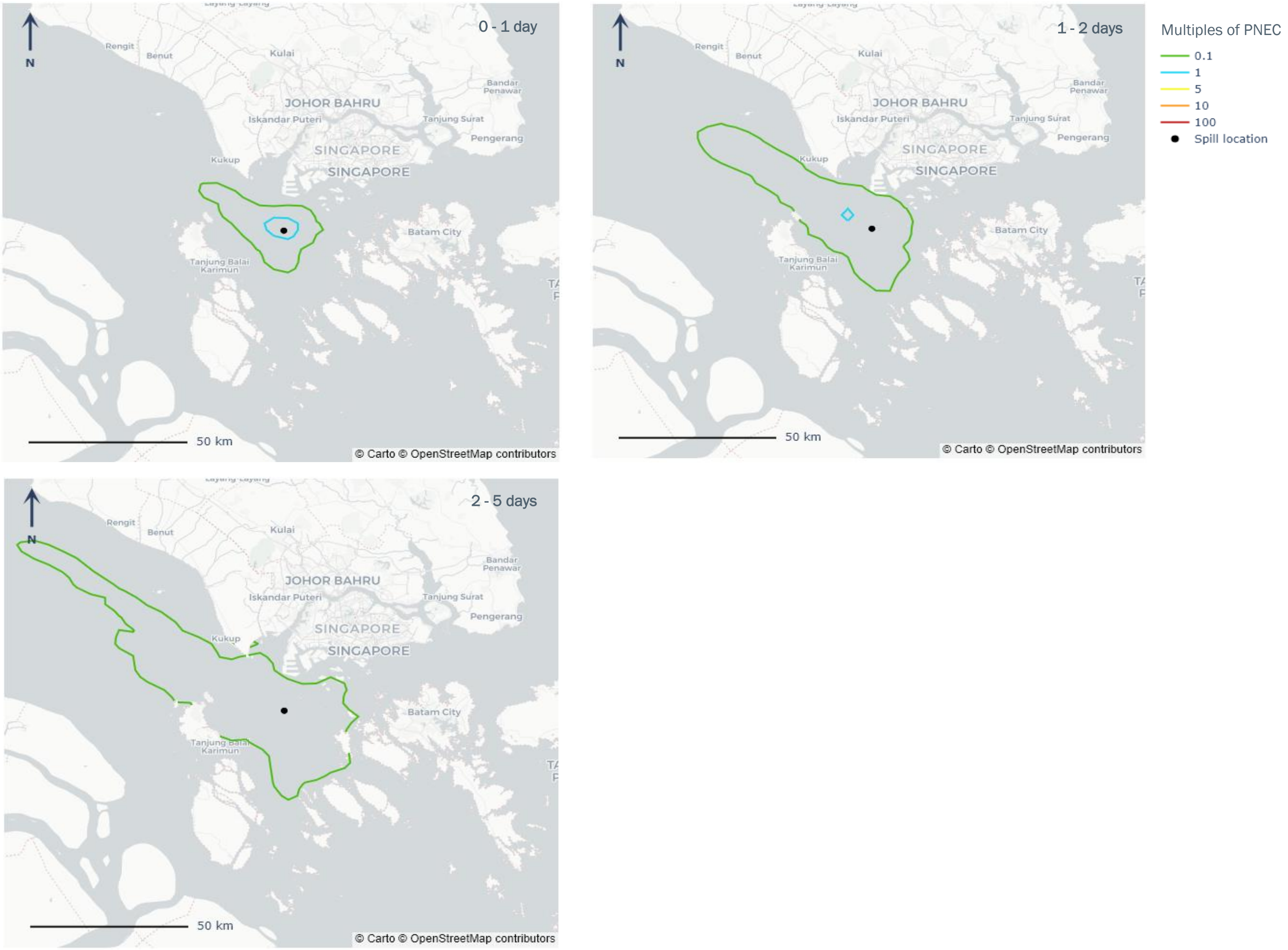


Figure 4.10 Development of the predicted environmental concentrations (PECs) of dissolved VLSFO in the days after the assumed spill in the exposure scenario: Collision in the Strait of Malacca. The black dot indicates the spill location. The PECs are shown as a function of multiples of the predicted no-effect concentration (PNEC). The PECs are higher than the PNEC on the inside of the blue line and lower than the PNEC outside the blue line. An impact is indicated when PEC > PNEC.

4.5 Environmental exposure to non-dissolved VLSFO

This section describes the potential environmental exposure to non-dissolved substances in VLSFO in the English Channel and the Strait of Malacca where the ship collisions leading to the fuel spills are assumed to occur. The results of the assessment are presented by sea areas with indications of:

- The probability that non-dissolved VLSFO will reach a certain sea area or coast (‘the probability of occurrence’).
- The shortest time for the transport of the non-dissolved VLSFO from the spill location to sea areas or coasts in the region (‘the shortest transport time’).
- The potential coast impact and the amount of non-dissolved VLSFO that may be transported to the coast.

Generally, the probability of occurrence, the transport time, and the potential coast impact are influenced by the prevailing direction of wind and currents. The exposure modelling included 52 spill simulations (one per week in a full calendar year) to cover the varying hydrodynamic conditions throughout the year.

4.5.1 English Channel

The highest probability of occurrence of non-dissolved VLSFO exceeding 50% is found from the spill location and up to 25 km to the northeast. The probability of occurrence decreases to 25%, 10%, and 5%, respectively, at distances of 100 km, 200 km, and 250 km to the northeast. To the south and southwest, the probability of occurrence is 10% at 50-100 km, while it is 5% or less more than 100 km from the spill location (Figure 4.11).

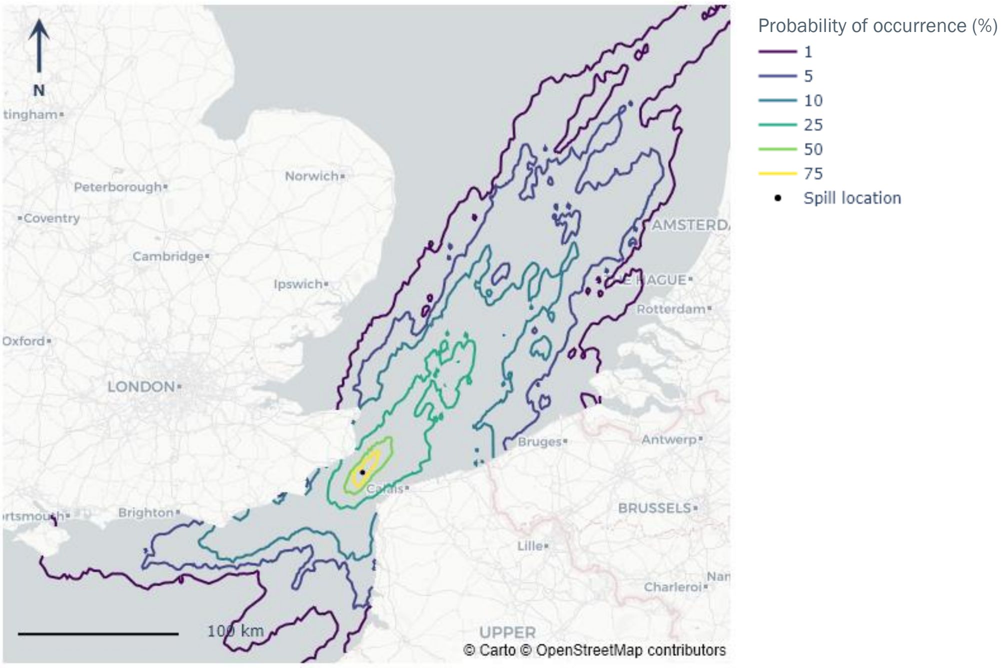


Figure 4.11 **The probability that non-dissolved VLSFO will reach a certain sea area or coast after the assumed spill in the exposure scenario: Collision in the English Channel.**

To the northeast the shortest transport time of the non-dissolved VLSFO is 1 day, 3 days, and 6 days, respectively, for travel distances of 100 km, 200 km, and 300 km, and near the location of the spill, the VLSFO will reach the coastline in the Strait of Dover within one day (seen in Figure 4.12 in which the Strait of Dover is surrounded by the yellow line). To the southwest, the transport times are longer (i.e., the VLSFO travels shorter distances per day).

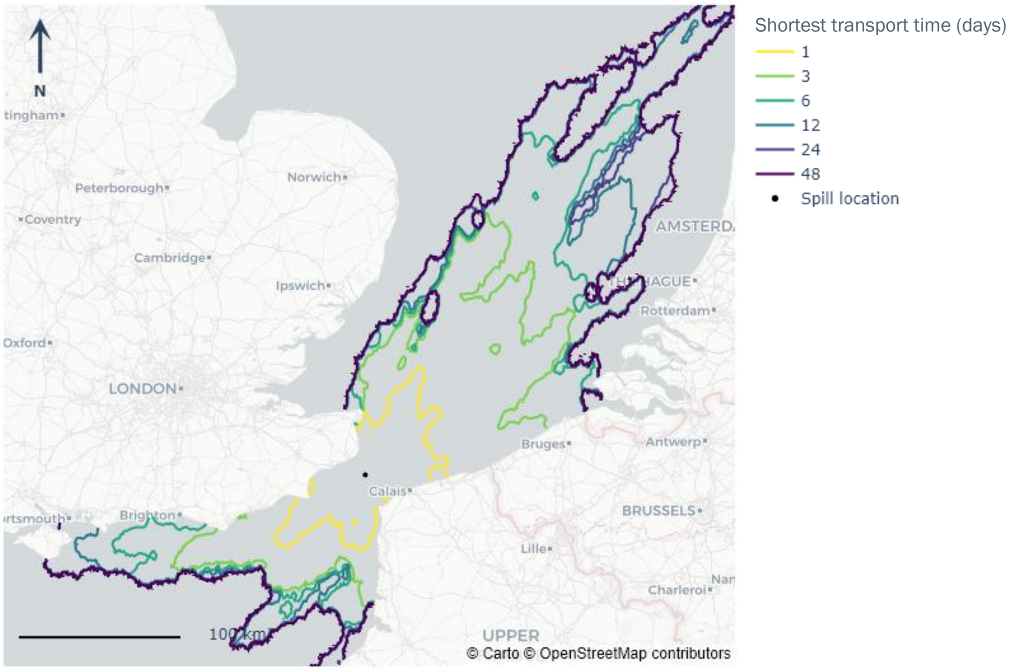


Figure 4.12 **The shortest time for transport of non-dissolved VLSFO from the spill location to sea areas or coasts in the region after the assumed spill in the exposure scenario: Collision in the English Channel.**

The model prediction of the non-dissolved VLSFO that may potentially be transported to the coast is the worst-case for each specific point on the coastline, and, thus, the indicated amounts of VLSFO stranding on the coast cannot occur in all points. If the assumed spill of fuel occurred, more than 100 tons VLSFO per km of coastline may reach the coasts in the Strait of Dover:

- On a 220-km coastline on the French coast, i.e., the 150 km coastline northeast from Calais and the 70 km coastline to the south of Calais
- On a 200-km coastline on the English coast (Figure 4.13).

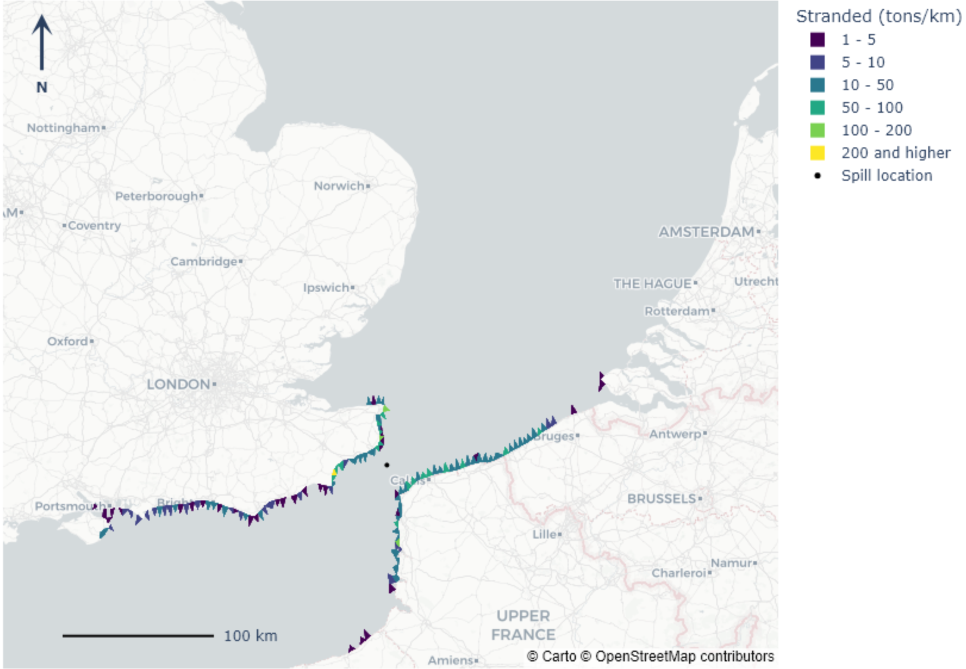


Figure 4.13 **The potential amounts of non-dissolved VLSFO that may possibly be transported to the coast after the assumed spill in the exposure scenario: Collision in the English Channel. The coloured marks indicate the worst-case for each specific point at the coastline, and the indicated amounts of VLSFO stranding on the coast cannot occur in all points.**

4.5.2 Strait of Malacca

The highest probability of occurrence of non-dissolved VLSFO exceeding 50% is found near the spill location and up to 15 km to the northwest. The probability of occurrence decreases to 25%, 10%, and 5%, respectively, at distances of 50 km, 100 km, and 200 km to the northwest. To the south, southwest, and southeast the probability of occurrence is reduced to 5% at 60 km from the spill along the coast of Singapore and Sumatra. A band of 1% probability of occurrence runs through the Strait of Singapore in the northeast direction (Figure 4.14).

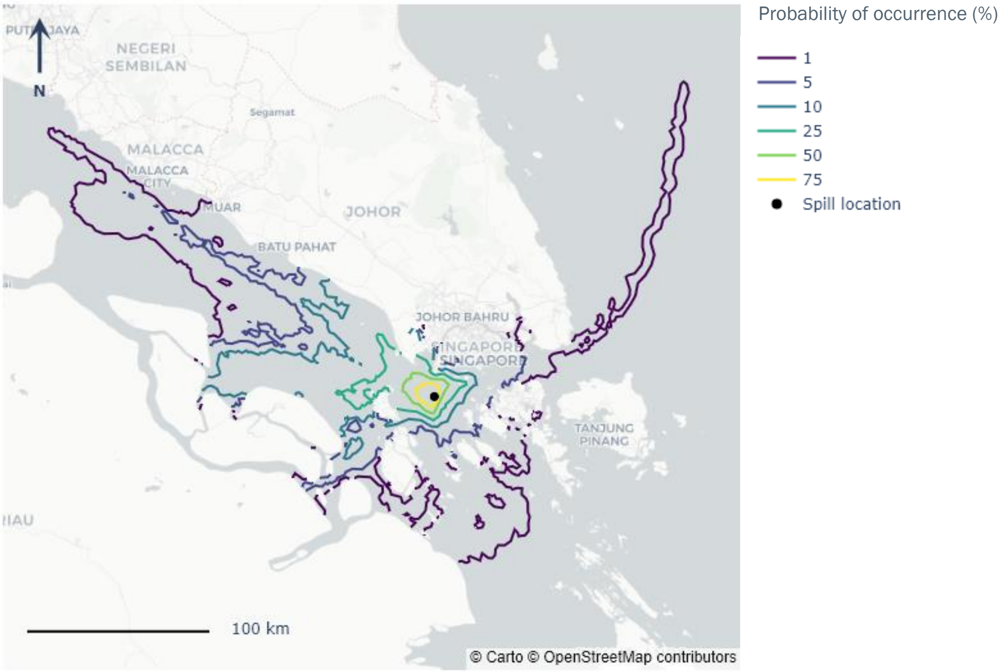


Figure 4.14 **The probability that non-dissolved VLSFO will reach a certain sea area or coast after the assumed spill in the exposure scenario: Collision in the Strait of Malacca.**

To the northwest into the Strait of Malacca, the shortest transport time is 1 day, 3 days, 6 days, respectively, for travel distances of 30 km, 100 km, and 150 km, and near the location of the spill, the VLSFO will reach the coastline around Singapore within one day. To the southeast the transport times are longer (i.e., the VLSFO travels shorter distances per day), but due to the archipelago islands, the potentially affected coastal sea area will be larger or similar to the potentially affected coastal sea area to the northwest (Figure 4.15).

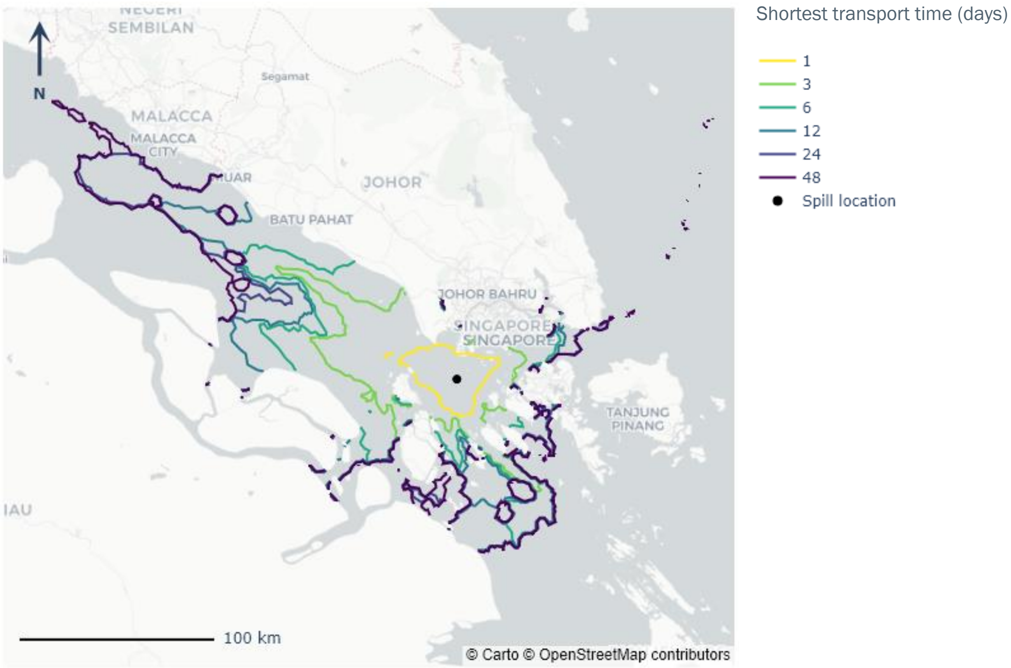


Figure 4.15 **The shortest time for transport of non-dissolved VLSFO from the spill location to sea areas or coasts in the region after the assumed spill in the exposure scenario: Collision in the Strait of Malacca.**

The model prediction of the non-dissolved oil that may potentially be transported to the coast is the worst-case for each specific point on the coastline, and, thus, the indicated amounts of oil stranding on the coast cannot occur in all points. The potential impact of the assumed spill of fuel is that 10 to more than 200 tons VLSFO per km coastline may reach the coasts in the Strait of Malacca at distances up to 100-150 km from the spill location (Figure 4.16).

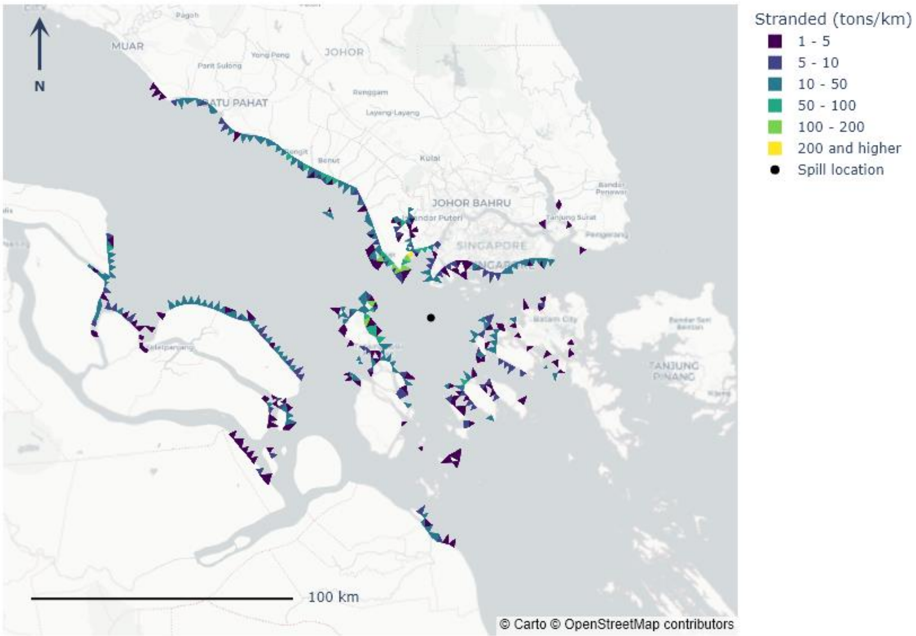


Figure 4.16 The potential amounts of non-dissolved VLSFO that may possibly be transported to the coast after the assumed spill in the exposure scenario: Collision in the Strait of Malacca. The coloured marks indicate the worst-case for each specific point at the coastline, and the indicated amounts of VLSFO stranding on the coast cannot occur in all points.

4.6 Possible impact on the marine environment

The potential ecotoxicity impact on the marine environment of an assumed spill of fuel can be considered by evaluating the factor by which the predicted environmental concentration (PEC) exceeds the predicted no-effect concentration (PNEC) and the size of the impacted sea area.

In the present study, the environmental impacts of ammonia, methanol, and dissolved VLSFO are illustrated by sea areas where the PECs exceed multiples of fuel specific PNECs (Figures 4.2-4.10). The size of these sea areas is summarized in Table 4.4.

The sea areas may be differentiated into three categories:

- PECs below PNEC
    - Labelled **0.1-1** in Table 4.4 – sea area limited by the green line (0.1 x PNEC) with increasing PECs up to the blue line (PNEC)

- PECs equivalent to PNEC or moderately above PNEC (1-10 x PNEC in the present study)
    - Labelled **1-5** in Table 4.4 – sea area limited by the blue line (PNEC) with increasing PECs up to the yellow line (5 x PNEC)
    - Labelled **5-10** in Table 4.4 - sea area limited by the yellow line (5 x PNEC) with increasing PECs up to the orange line (10 x PNEC)

- PECs markedly above PNEC (more than 10 x PNEC in the present study)
    - Labelled **10-100** in Table 4.4 - sea area limited by the orange line (10 x PNEC) with increasing PECs up to the red line (100 x PNEC – only seen as small sea areas near the spill location).

It is important to note that the PNEC is the concentration in the environment below which exposure to a substance is not expected to cause adverse effects on marine flora and fauna. However, the PNEC does not indicate a substance concentration above which adverse effects can be expected.

There are many uncertainties in assessing the environmental effects of exposure to a chemical from results obtained in laboratory studies with test species – for example, the effects assessment uses ecotoxicity data on a limited set of test species to predict adverse effects in marine ecosystems with an enormous number of highly diverse species, and laboratory studies do not include all effects of concern or all life stages that are important for the survival of the species in the environment.

The PNEC is commonly derived by dividing the selected lowest effect concentration, e.g., the median lethal concentration (LC50) or the no observed effect concentration (NOEC), by an assessment factor to account for the fact that ecotoxicological studies can never represent the diversity of species in the aquatic environment (Section 4.2.1).

To illustrate the possible impact of the fuels on the marine environment, it was assumed that the concentration causing adverse effects to 50% of the test organisms is generally 1000 times higher than the PNEC. This assumption led to the following simplistic interpretation of the environmental impact, which is considered reasonable as the predicted durations of the exposure to fuel concentrations exceeding the PNEC are two days in the scenarios in the English Channel and the Strait of Malacca and up to five days in the Port of Rotterdam scenario:

Negligible impact on the marine environment:

- PECs below PNEC mean that adverse effects caused by the exposure to the released fuel are negligible.

Moderate impact on the marine environment:

- PECs equivalent to or moderately above PNEC, defined as 1-10 x PNEC in the present study, imply that the exposure to the released fuel may cause adverse effects (including death) to sensitive species and individual organisms.

High impact on the marine environment:

- PECs markedly above PNEC, defined as more than 10 x PNEC in the present study, imply that the exposure to the released fuel may cause adverse effects (including death) to a broad range of species representing different taxonomic groups such as bivalves, corals, crustaceans, echinoderms, and fish, including their early life stages.

For the two collision scenarios, the PECs of ammonia and dissolved VLSFO exceed the PNECs in large sea areas during the first two days after the assumed accidental spills. After two days the PECs decrease to levels below PNEC due to environmental fate processes, spreading and mixing in the English Channel and the Strait of Malacca. Because of the lower water exchange in parts of the Port of Rotterdam, it takes more than two days to reach PECs below the PNECs for all the examined fuels. Based on the above interpretation of ‘negligible’, ‘moderate’, and ‘high’ impact, a cautious assessment was made for the assumed spills in the Port of Rotterdam, the English Channel, and the Strait of Malacca.

Port of Rotterdam

For the most serious of the two exposure scenarios in Port of Rotterdam, i.e., ‘Complete rupture of the bunkering pipe’ with a spill duration of 30 seconds (Table 3.2), the PECs are below the PNECs two days (methanol) or five days (ammonia and dissolved VLSFO) after the spill:

- **Ammonia** may cause adverse effects (including death) to sensitive species or individual organisms in a sea area of up to 6 km^2 during the first five days after the spill.
- **Methanol** may cause adverse effects (including death) to sensitive species or individual organisms in a sea area of up to 1 km^2 during the first day after the spill.
- **Dissolved VLSFO** may cause adverse effects (including death) to a broad range of species representing different taxonomic groups in a sea area of 3 km^2 during the first two days after the spill. Adverse effects (including death) to sensitive species or individual organisms

may occur in a sea area of 12 km^2 during the first two days after the spill.

English Channel

In this exposure scenario, a collision with the full release of the fuel in the tank is assumed. The PECs are below the PNECs two days after the spill (ammonia and dissolved VLSFO):

- **Ammonia** may cause adverse effects (including death) to a broad range of species representing different taxonomic groups in a sea area of 125 km^2 during the first day after the spill. Adverse effects (including death) to sensitive species or individual organisms may occur in a sea area of up to approx. 4000 km^2 during the first two days after the spill.
- **Methanol** is not expected to cause adverse effects as the PECs are below the PNEC.
- **Dissolved VLSFO** may cause adverse effects (including death) to a broad range of species representing different taxonomic groups in a sea area of 11 km^2 during the first day after the spill. Adverse effects (including death) to sensitive species or individual organisms may occur in a sea area of up to approx. 500 km^2 during the first two days after the spill.

Strait of Malacca

In this exposure scenario, a collision with the full release of the fuel in the tank is assumed. The PECs are below the PNECs two days after the spill of the three fuels:

- **Ammonia** may cause adverse effects (including death) to sensitive species or individual organisms in a sea area of 327 km^2 during the first day after the spill.
- **Methanol** may cause adverse effects (including death) to sensitive species or individual organisms in a sea area of 40 km^2 during the first day after the spill.
- **Dissolved VLSFO** may cause adverse effects (including death) to sensitive species or individual organisms in a sea area of 61 km^2 during the first day after the spill.

Table 4.4 Sea areas in which PECs of ammonia, methanol, and dissolved VLSFO exceed multiples of PNEC as affected by the time elapsed after the spill: 0.1-1 x PNEC; 1-5 x PNEC; 5-10 x PNEC; 10-100 x PNEC; >100 x PNEC. Exposure scenarios: Port of Rotterdam – Complete rupture of bunkering pipe; English Channel – Collision; and Strait of Malacca – Collision.

Time after spill	Ammonia					Methanol					VLFSO				
	Sea areas (km^2) with PECs exceeding multiples of PNEC														
	0.1-1	1-5	5-10	10-100	>100	0.1-1	1-5	5-10	10-100	>100	0.1-1	1-5	5-10	10-100	>100
Port of Rotterdam 0-1 day	3	2	1	0	0	2	0	1	0	0	2	0	0	0	0
1-2 days	1	6	0	0	0	6	0	0	0	0	2	6	3	3	0
2-5 days	4	4	0	0	0	3	0	0	0	0	3	1	0	0	0
5-10 days	5	0	0	0	0	1	0	0	0	0	99	1	0	0	0
10-30 days	0	0	0	0	0	0	0	0	0	0	12	0	0	0	0
English Channel 0-1 day	2097	1580	624	125	0	1617	0	0	0	0	2481	531	26	11	0
1-2 days	5588	4052	0	0	0	2886	0	0	0	0	5575	436	0	0	0
2-5 days	10664	0	0	0	0	244	0	0	0	0	10047	0	0	0	0
5-10 days	2276	0	0	0	0	0	0	0	0	0	16088	0	0	0	0
10-30 days	0	0	0	0	0	0	0	0	0	0	14732	0	0	0	0
Strait of Malacca 0-1 day	510	290	37	0	0	655	40	0	0	0	476	61	0	0	0
1-2 days	0	0	0	0	0	1251	0	0	0	0	1385	11	0	0	0
2-5 days	0	0	0	0	0	19	0	0	0	0	2341	0	0	0	0
5-10 days	0	0	0	0	0	0	0	0	0	0	1572	0	0	0	0
10-30 days	0	0	0	0	0	0	0	0	0	0	6	0	0	0	0

Non-dissolved VLSFO

The exposure to **non-dissolved VLSFO** may cause long-lasting adverse effects. The model predictions of the exposures to non-dissolved VLSFO (Figures 4.11-4.16) indicate a probability higher than 25% that coastal sea areas in the English Channel and the Strait of Malacca may be impacted by oil in amounts that will cause effects to marine life. The potential impact of the stranding of non-dissolved VLSFO includes:

- Inhibition of growth or death of macroalgae, seed plants, benthic invertebrates (e.g., bivalves, corals, echinoderms, and worms), and fish
- Serious negative impact (e.g., reduced insulation capacity) or death of sea birds and seals
- Serious negative impact on ecosystems functions caused by, e.g., deterioration of habitats and loss of prey.

5 Human health impact assessment

5.1 Human health impact evaluation

The human health impact assessment was carried out by using the principles described in the *ECHA Guidance on information requirements and chemical safety assessment* which is used in support of the European chemicals' regulation REACH (Regulation (EC) No. 1907/2006 of the European Parliament and of the Council). The impact assessment compares the result of the exposure estimation, expressed as the predicted exposure level (PEL) of a human population, with the derived no-effect level (DNEL). The DNEL is the level of exposure to the chemical substance above which humans should not be exposed. DNELs aim to ensure the human population is adequately protected. DNELs are required for the REACH registration of chemical substances manufactured, imported, or used in quantities of 10 tonnes or more per year.

The present impact assessment covers only possible effects caused by inhalation, and, therefore, the relevant PEL is the concentration of the chemical in air.

The risk characterization ratio (RCR) is the ratio of the PEL to the DNEL:

$$\mathrm{RCR} = \frac{\mathrm{PEL}}{\mathrm{DNEL}}$$

An RCR < 1 means that unacceptable effects to humans due to exposure to the chemical substance will likely not occur. In other words, the impact on humans can generally be considered acceptable if the PEL < DNEL.

5.2 Derived no-effect levels

5.2.1 Derivation of DNELs

The derivation of DNEL is described in the *ECHA Guidance on information requirements and chemical safety assessment, Chapter R.8: Characterisation of dose [concentration]-response for human health* /10/. The derivation of DNELs is based on toxicological studies establishing dose-response relationships.

Only exposure via inhalation is relevant for the present human health impact assessment. Other exposure routes, such as oral and dermal exposure, are considered negligible in a situation such as the assumed accidental spills of vessel fuels.

There are two main types of DNELs, a $\mathrm{DNEL}_{\text{long-term}}$ for long-term exposure and a $\mathrm{DNEL}_{\text{acute}}$ for short-term exposure. The $\mathrm{DNEL}_{\text{acute}}$ will always be equal to or higher than the $\mathrm{DNEL}_{\text{long-term}}$ /10/. In the actual case of an accidental release of fuels, $\mathrm{DNEL}_{\text{acute}}$ values for short-term inhalational exposure were applied. A $\mathrm{DNEL}_{\text{acute}}$ is established for effects occurring after a single exposure contrary to repeated exposures where $\mathrm{DNEL}_{\text{long-term}}$ is used. $\mathrm{DNEL}_{\text{acute}}$ is generally defined as a DNEL for effects that occur after exposure for a short period of time from minutes to a few hours. A $\mathrm{DNEL}_{\text{acute}}$ for inhalation should be derived for a limited duration of exposure of usually 15 minutes /10/. The accidental release of fuel in the scenarios in the present impact assessment implies that a single exposure can reasonably be assumed for ammonia, methanol, and VLSFO.

$DNEL_{acute}$ was therefore considered the relevant exposure limit representing the spill events. The exposure modelling predicts the duration of the exposure to ammonia to be less than 15 minutes, whereas the exposures to methanol and VLSFO exceed 1 hour. It could be argued that long-term DNELs should be used for the impact assessment of methanol and VLSFO because the duration of the exposures exceeds the 15-minutes reference time for $DNEL_{acute}$. This would however not influence the actual impact assessment – for methanol, the $DNEL_{acute}$ was extrapolated from $DNEL_{long\text{-}term}$, and, thus, the two values are identical /8/, and, for VLSFO, a $DNEL_{long\text{-}term}$ was used as proxy in the absence of a $DNEL_{acute}$ /49/. The DNELs for ammonia, methanol, and VLSFO used in the assessment are shown in Tables 5.1-5.3.

DNELs are usually derived for workers and the general population. The duration of the occupational exposure of workers is assumed to be longer compared to the duration of the exposure of the general population. The DNEL for workers is sometimes based on accepted occupational exposure levels (OELs) that existed before REACH. The OEL is generally country-specific, but the EU has defined an OEL for several substances which is equivalent to the DNEL for inhalational exposure.

5.2.2 Ammonia

The below DNELs for ammonia were applied in the present study (Table 5.1).

Table 5.1 Derived no-effect levels (DNELs) for ammonia.

Limit value	General population (ppm)	Workers (ppm)
$DNEL_{acute}$ (short-term)	10.3 (1)	50 (2)

(1) Short-term $DNEL_{acute}$ from the REACH registration dossier for ammonia /7/
(2) EU short-term occupational exposure limit (OEL) /17/

5.2.3 Methanol

The DNELs for methanol applied in the present study are stated in Table 5.2.

Table 5.2 Derived no-effect levels (DNELs) for methanol.

Limit value	General population (ppm)	Workers (ppm)
$DNEL_{acute}$ (short-term)	20 (1)	250 (2)

(1) Short-term $DNEL_{acute}$ from the REACH registration dossier for methanol /8/ ($DNEL_{acute}$ extrapolated from long-term DNEL)
(2) Short-term $DNEL_{acute}$, Finland (no EU short-term DNEL exists) /17/

5.2.4 VLSFO

Only the volatile substances in VLSFO are transported via air, and representative DNELs for volatile hydrocarbons, i.e., C9-C10 aromatics, were used in the impact assessment (Table 5.3).

Table 5.3 Derived no-effect levels (DNELs) for volatile substances (C9-10 aromatics) in VLSFO.

Limit value	General population (ppm)	Workers (ppm)
$\text{DNEL}_{\text{long-term}}$ (1)	6.5	31

(1) DNELs taken from the REACH registration dossier for Hydrocarbons, C9-C10, aromatics, >1% naphthalene (EC number 946-365-8) /49/ assuming a molar mass of 120 g/mole in the conversion from mg/m^3 to ppm (only long-term DNELs are available)

Box 5.1. Exposure limits.

The present human health impact assessment was carried out in accordance with the EU chemicals' regulation, REACH. The derived no-effect levels (DNELs) used for chemical safety assessments under REACH and in the present study imply that no effects on humans are accepted.

Other existing limit values for human exposure to chemicals are used in relation to accidents. For example, in the United States, acute exposure guideline levels (AEGLs) describe the human health effects of once-in-a-lifetime, or rare, exposure to airborne chemicals. The AEGLs are set by the National Academies through a collaborative effort of public and private sectors. The limit values are based primarily on acute toxicity data and not sub-chronic or chronic data, and thus they do not reflect the effects from frequent exposure. The AEGLs are used for emergency planning, prevention, and response activities related to the accidental release of chemicals and hazardous materials. They are designed to protect the general population including the elderly and children, i.e., groups that are generally not considered in the development of workplace exposure levels. The AEGLs are defined as follows:

- AEGL-3: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.
- AEGL-2: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.
- AEGL-1: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

The Emergency Response Planning Committee of the American Industrial Hygiene Association has developed emergency response planning guidelines (ERPGs) that estimate the concentrations at which most people will begin to experience health effects if they are exposed to a hazardous airborne chemical for 1 hour. The ERPGs do not include sensitive members of the public such as old, sick, or very young people that may experience adverse effects at lower concentrations. The ERPGs are defined as follows:

- ERPG-3: The maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects.
- ERPG-2: The maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.
- ERPG-1: The maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing more than mild, transient adverse health effects or without perceiving a clearly defined objectionable odour.

The below table compares the DNELs for ammonia and methanol with the above mentioned AEGL- and ERPG-limit values.

	Ammonia	Methanol
$DNEL_{acute}$	10.3 ppm (15 min)	20 ppm (15 min)
AEGL-1	30 ppm (30 min)	530 ppm (60 min)
AEGL-2	220 ppm (30 min)	2100 ppm (60 min)
AEGL-3	2700 ppm (10 min) 1600 ppm (30 min)	7200 ppm (60 min)
ERPG-1	25 ppm (60 min)	200 ppm (60 min)
ERPG-2	150 ppm (60 min)	1000 ppm (60 min)
ERPG-3	1500 ppm (60 min)	5000 ppm (60 min)

5.3 Human exposure modelling

5.3.1 Modelling tool: ALOHA

The human health impact assessment was carried out for the two exposure scenarios assumed for the Port of Rotterdam (Chapter 3). The US EPA/NOAA software ALOHA (Areal Locations of Hazardous Atmospheres) /34/ was applied for the calculations of human exposure. The software is used to plan and make responses to chemical emergencies. ALOHA is a well-documented tool /23/ that can predict how a toxic cloud disperses after a chemical release dependent of the weather situation (primarily wind and temperature).

The output from ALOHA includes locations where the maximum air concentration exceeds specified limits. In addition, the air concentrations as a function of time can be displayed at any point of interest.

5.3.2 Values for scenario specific parameters in ALOHA

Partitioning of fuels into water

Ammonia. The partitioning into water of a spill of ammonia on the water surface was investigated in a detailed study /26/. The interactions between ammonia and water are complex, and scientific studies of the partitioning of ammonia into water are limited. The exposure modelling was therefore based on simplified assumptions derived from the experiments described below.

A laboratory experiment with spilled amounts up to 12 gallons showed that the fraction of dissolved ammonia varied between 0.65 and 0.82 with an average of 0.73 /26/. Another experiment carried out in a pool with spilled amounts of 1 and 5 gallons resulted in a partitioning into water of a fraction of 0.56 for both 1 and 5 gallons. The partitioning increased to 0.66 for a continuous spill /26/. Finally, an experiment carried out in a lake with a spilled amount of 50 gallons showed a partitioning into water of a fraction between 0.53 and 0.63 /26/.

Based on the above-mentioned results, the calculations were carried out by use of a conservative assumption of a partitioning into water of 0.5, which means that 50% of the spilled ammonia will dissolve in water, and the other 50% will stay on the water surface.

The same study /26/ predicted a maximum radius of an ammonia spill:

$$\mathrm{R_{max}(feet)} = 2.5 \cdot (\mathrm{Gallons\ spilled})^{0.375}$$

Corresponding to:

$$\mathrm{R_{max}(meter)} = 6.168 \cdot (\mathrm{m^3\ spilled})^{0.375}$$

This equation was used to estimate the initial area and thickness of the ammonia spill if it resulted in a slick thickness above 0.01 m, otherwise an initial slick thickness of 0.01 m was assumed.

Methanol. When a large volume of methanol is suddenly released in the sea, it will immediately collect on the water surface because the density of methanol (791.8 kg/m^3) is between the densities of water and air. Methanol has a low viscosity and spreads rapidly on the water surface. Methanol is volatile with a vapour pressure of 17 kPa at 25^{o}C, it is very water soluble and partitions readily into the water phase. Once dissolved in water, methanol will evaporate slowly as it has a low Henry's constant of 0.46 Pa m^3/mole.

It has not been possible to find data on how a surface slick of methanol is formed and how a spill develops. Therefore, a water partitioning ratio of 0.5 was used for methanol (as for ammonia), which is a conservative approach as methanol partitions more readily into water compared to ammonia. The initial area and thickness of the methanol slick were calculated by the Fays equation /37/ in a similar way as for VLSFO (see below).

VLSFO. VLSFO is poorly soluble in water and assumed initially to form an oil slick on the water surface. The initial area and thickness of the oil slick were calculated by the Fays equation /37/:

$$\frac{\Delta\rho \cdot g \cdot V}{d^3} + d \cdot \left(\frac{\sigma}{V} - \frac{\rho}{t^2}\right) - \frac{\rho \cdot \vartheta^{\frac{1}{2}} \cdot d^3}{V \cdot t^{\frac{3}{2}}} = 0$$

Where:

ρ	is the oil density (kg/m^3)
$\Delta\rho$	difference between water and oil density (kg/m^3)
ϑ	kinematic viscosity of water ($1 \cdot 10^{-6}$ m^2/s)
σ	net surface tension, set to 0.015 N/m
t	time after release (s) (set to the duration of release: 60 s or 30 s)
d	diameter of slick (m) at time t

g	gravity (9.81 m/s^2)
V	volume of spill (m^3)

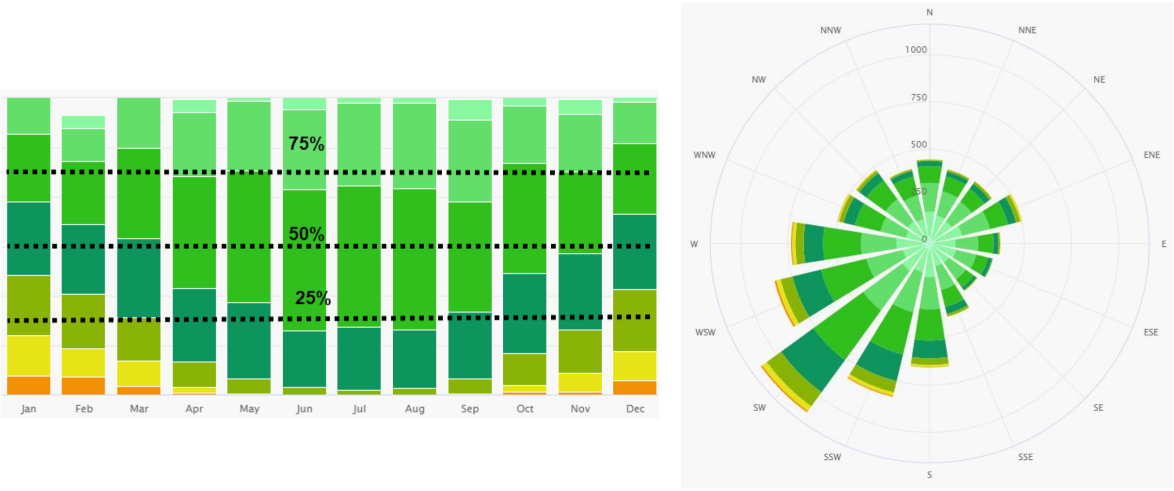
Weather conditions

The fate of airborne chemicals is highly dependent on the ambient wind direction and speed, the ambient temperature, and the degree of cloudiness. A study investigating the operational risk during bunkering of ammonia focusing on the Port of Singapore identified key parameters influencing the fate of ammonia for small, medium, and large release scales /41/. The wind speed was found to be the most important factor for the spreading of airborne ammonia in a small to medium release scenario (comparable to the ‘Hole in the bunkering hose’ scenario), while hose diameter was the most important factor in a large release scenario (comparable to the ‘Complete rupture of the bunkering pipe’ scenario) /41/.

The wind direction, wind speed, and air and water temperatures in the Port of Rotterdam vary throughout the year. Figure 5.1 shows the wind speed and the windrose for Rotterdam throughout the year (based on weather data covering 30 years).

Wind direction and speed. The most typical wind directions in Rotterdam are southwest (SW: >12% of the time), west-southwest (WSW: 10% of the time), south-southwest (SSW: 10% of the time) and west (W: 8.5% of the time) – see below Figure 5.1.

During winter (December, January, February), the windspeed in Rotterdam exceeds 8 m/s more than 50% of the time whereas during summer (June, July, August), the windspeed exceeds 8 m/s less than 50% of the time.



(a): Wind speed. The figure shows the percentile of time, where the windspped is above a certain wind speed, e.g., the windspeed is above 8 m/s approximately 50% of the time in March (reference /47/).

(b):The wind rose for Rotterdam shows how many hours per year the wind blows from the indicated direction (reference /47/).

Figure 5.1 **Wind speed and wind rose for Rotterdam.**

Air and water temperatures. Table 5.4 shows the average air and water temperatures in Rotterdam.

Table 5.4 Average temperatures (°C) in Rotterdam (air temperatures from reference /48/, https://www.holiday-weather.com/rotterdam/averages/water temperatures from reference /5/).

Month	Air temperature (ºC)	Water temperature (ºC)
January	3	5.4
February	4	4.7
March	6	3.7
April	9	6.2
May	13	10.5
June	15	14.2
July	17	18.0
August	17	19.4
September	15	18.0
October	10	15.4
November	7	10.5
December	4	8.4

Based on the information on wind and temperature described above, the assumptions on the weather conditions described in Table 5.5 were used in the exposure modelling. For the typical weather conditions, average values were used for wind direction, wind speed, water and air temperatures, and cloudiness, differentiating between winter and summer conditions due to the large difference between these two seasons. Wind speed is the most important parameter determining the exposure of humans, and a low wind speed (calm weather) increases the time in which humans are exposed to chemicals in air. Worst-case weather conditions (during winter and summer) were defined in the exposure modelling by assuming very low wind speeds. The lowest windspeed accepted by ALOHA is 0.59 m/s which was applied for the worst-case, summer calculations. A slightly higher windspeed of 1 m/s was applied for the worst-case, winter calculations as wind speeds are usually higher during winter. Temperature influences the exposure of humans to airborne chemicals as higher temperatures increase the evaporation rate and, thus, increase the concentrations of chemicals in the air. Therefore, temperatures were assumed to be in the higher end in the exposure modelling, but extreme temperatures were disregarded.

Table 5.5 **Assumptions on typical and possible worst-case weather conditions in Rotterdam applied in exposure modelling by ALOHA.**

Parameter	Typical	Worst-case, winter	Worst-case, summer
Wind direction	SW	WSW	WSW
Wind speed [m/s]	Winter: 8.6 Summer: 5.9	1.0	0.59
Water temperature [°C]	Winter: 6.5 Summer: 17.3	5.0	17.3
Air temperature [°C]	Winter: 3 Summer: 17	7.4	17
Cloudiness	Winter: Overcast Summer: Partly cloudy	Partly cloudy	Sunny

5.4 Accidental spills and dispersion in air

5.4.1 Dispersion of airborne substances

The estimated time for complete evaporation of the spilled ammonia from the water surface is 5 to 8 min for the scenario ‘Hole in the bunkering hose’ and 8 to 14 min for the scenario ‘Complete rupture of the bunkering pipe’. Considering the typical and possible worst-case weather conditions in Rotterdam (Table 5.5), the evaporation time increases in the order: ‘typical, summer’ < ‘typical, winter’ < ‘worst-case, summer’ < ‘worst-case, winter’.

The evaporation time for methanol exceeds 1 hour under all examined weather conditions in both exposure scenarios. Any residues of methanol on the water surface will most likely be dissolved in the water within this time frame.

The evaporation time for C9-C10 aromatics used in the impact assessment of VLSFO generally exceeds 1 hour except for the ‘typical, summer’ conditions for which ALOHA predicts an evaporation time of 53 min.

The 15-minutes time-weighted average concentration predicted by ALOHA was compared to the DNEL in the impact assessment. The definition of DNEL is the level of exposure to a chemical substance above which humans should not be exposed. Using the DNEL for impact assessments implies a high level of safety for human populations. The acute exposure guideline levels (AEGLs) described in Box 5.1 have been used as the limit values in other studies of accidental release of ammonia during bunkering /41/. The lowest AEGL category, AEGL-1, implies harmful effects like notable discomfort, irritation, or certain asymptomatic non-sensory effects that are transient and reversible upon cessation of exposure (see Box 5.1). For ammonia, $DNEL_{acute}$ is 10.3 ppm whereas AEGL-1 is 30 ppm. The $DNEL_{acute}$ applied in the present study thus represents a more cautious safety threshold for human exposure at air concentrations three times lower than AEGL-1. Nevertheless, all the exposure limits presented in Box. 5.1 (i.e., AEGL- and ERPG-limit values) were implemented in the comparison to put the obtained results into perspective.

The results of the impact assessment are presented as “critical distances” representing the distance at which the predicted air concentrations equal 10 x DNEL, 5 x DNEL, and 1 x DNEL, respectively. Critical distances are highly influenced by wind direction and wind speed, and the impacted areas will have the form of a plume oriented in the wind direction. The derived critical distances for the two considered bunkering scenarios in Port of Rotterdam (‘Hole in the bunkering hose’ and ‘Complete rupture of the bunkering pipe’) for the three analyzed fuels are presented below (Table 5.6-5.11).

Table 5.6 Critical distances (m) for ammonia. Port of Rotterdam: Hole in the bunkering hose.

Emission case	Target	Distance (m) for reaching a concentration		
		1 × DNEL	5 × DNEL	10 × DNEL
Typical, winter	General population	≤ 318	≤ 138	≤ 97
Typical, summer		≤ 379	≤ 163	≤ 114
Worst-case, winter		≤ 888	≤ 379	≤ 263
Worst -case, summer		≤ 925	≤ 473	≤ 341
Typical, winter	Workers	≤ 140	≤ 61	≤ 42
Typical, summer		≤ 166	≤ 72	≤ 51
Worst-case, winter		≤ 385	≤ 166	≤ 117
Worst-case, summer		≤ 479	≤ 218	≤ 153

Table 5.7 Critical distances (m) for ammonia. Port of Rotterdam: Complete rupture of the bunkering pipe. *The ALOHA model is limited to calculating air concentrations up to 10,000 m from the source.

Emission case	Target	Distance (m) for reaching a concentration		
		1 × DNEL	5 × DNEL	10 × DNEL
Typical, winter	General population	≤ 8000	≤ 2500	≤ 1600
Typical, summer		≤ 8600	≤ 2900	≤ 1900
Worst-case, winter		10000 *	≤ 5200	≤ 3800
Worst-case, summer		10000 *	≤ 4700	≤ 3400
Typical, winter	Workers	≤ 2500	≤ 990	≤ 680
Typical, summer		≤ 3000	≤ 1100	≤ 750
Worst-case, winter		≤ 5300	≤ 2500	≤ 1800
Worst-case, summer		≤ 4700	≤ 2300	≤ 1800

Table 5.8 **Critical distances (m) for methanol. Port of Rotterdam: Hole in the bunkering hose.**

Emission case	Target	Distance (m) for reaching a concentration		
		1 × DNEL	5 × DNEL	10 × DNEL
Typical, winter	General population	≤ 64	≤ 27	≤ 18
Typical, summer		≤ 93	≤ 41	≤ 28
Worst-case, winter		≤ 80	≤ 34	≤ 23
Worst-case, summer		≤ 118	≤ 52	≤ 36
Typical, winter	Workers	≤ 16	< 10	< 10
Typical, summer		≤ 25	< 10	< 10
Worst-case, winter		≤ 20	< 10	< 10
Worst-case, summer		≤ 32	≤ 11	< 10

Table 5.9 **Critical distances (m) for methanol. Port of Rotterdam: Complete rupture of the bunkering pipe.**

Emission case	Target	Distance (m) for reaching a concentration		
		1 × DNEL	5 × DNEL	10 × DNEL
Typical, winter	General population	≤ 326	≤ 135	≤ 88
Typical, summer		≤ 482	≤ 202	≤ 138
Worst-case, winter		≤ 817	≤ 345	≤ 229
Worst-case, summer		≤ 918	≤ 388	≤ 266
Typical, winter	Workers	≤ 119	≤ 50	≤ 34
Typical, summer		≤ 121	≤ 36	≤ 19
Worst-case, winter		≤ 200	≤ 73	≤ 48
Worst-case, summer		≤ 237	≤ 86	≤ 54

Table 5.10 Critical distances (m) for VLSFO. Port of Rotterdam: Hole in the bunkering hose.

Emission case	Target	Distance (m) for reaching a concentration		
		1 × DNEL	5 × DNEL	10 × DNEL
Typical, winter	General population	≤ 114	≤ 50	≤ 34
Typical, summer		≤ 155	≤ 67	≤ 47
Worst-case, winter		≤ 283	≤ 115	≤ 78
Worst-case, summer		≤ 298	≤ 119	≤ 79
Typical, winter	Workers	≤ 51	≤ 20	≤ 11
Typical, summer		≤ 69	≤ 29	≤ 19
Worst-case, winter		≤ 119	≤ 50	≤ 34
Worst-case, summer		≤ 123	≤ 51	≤ 35

Table 5.11 Critical distances (m) for VLSFO. Port of Rotterdam: Complete rupture of the bunkering pipe.

Emission case	Target	Distance (m) for reaching a concentration		
		1 × DNEL	5 × DNEL	10 × DNEL
Typical, winter	General population	≤ 280	≤ 119	≤ 81
Typical, summer		≤ 380	≤ 162	≤ 111
Worst-case, winter		≤ 672	≤ 267	≤ 182
Worst-case, summer		≤ 689	≤ 275	≤ 187
Typical, winter	Workers	≤ 122	≤ 47	≤ 27
Typical, summer		≤ 166	≤ 69	≤ 44
Worst-case, winter		≤ 275	≤ 114	≤ 79
Worst-case, summer		≤ 283	≤ 117	≤ 81

Figure 5.2 and Figure 5.3 graphically present the critical distances at which the airborne concentrations of ammonia, methanol, and VLSFO equal the DNEL values for the different emission cases. Higher concentrations in the air occur closer to the point of the spill. Note that due to data availability, in this assessment short-term $DNEL_{acute}$ values are used for ammonia and methanol, while $DNEL_{long\text{-}term}$ values are used for VLSFO.

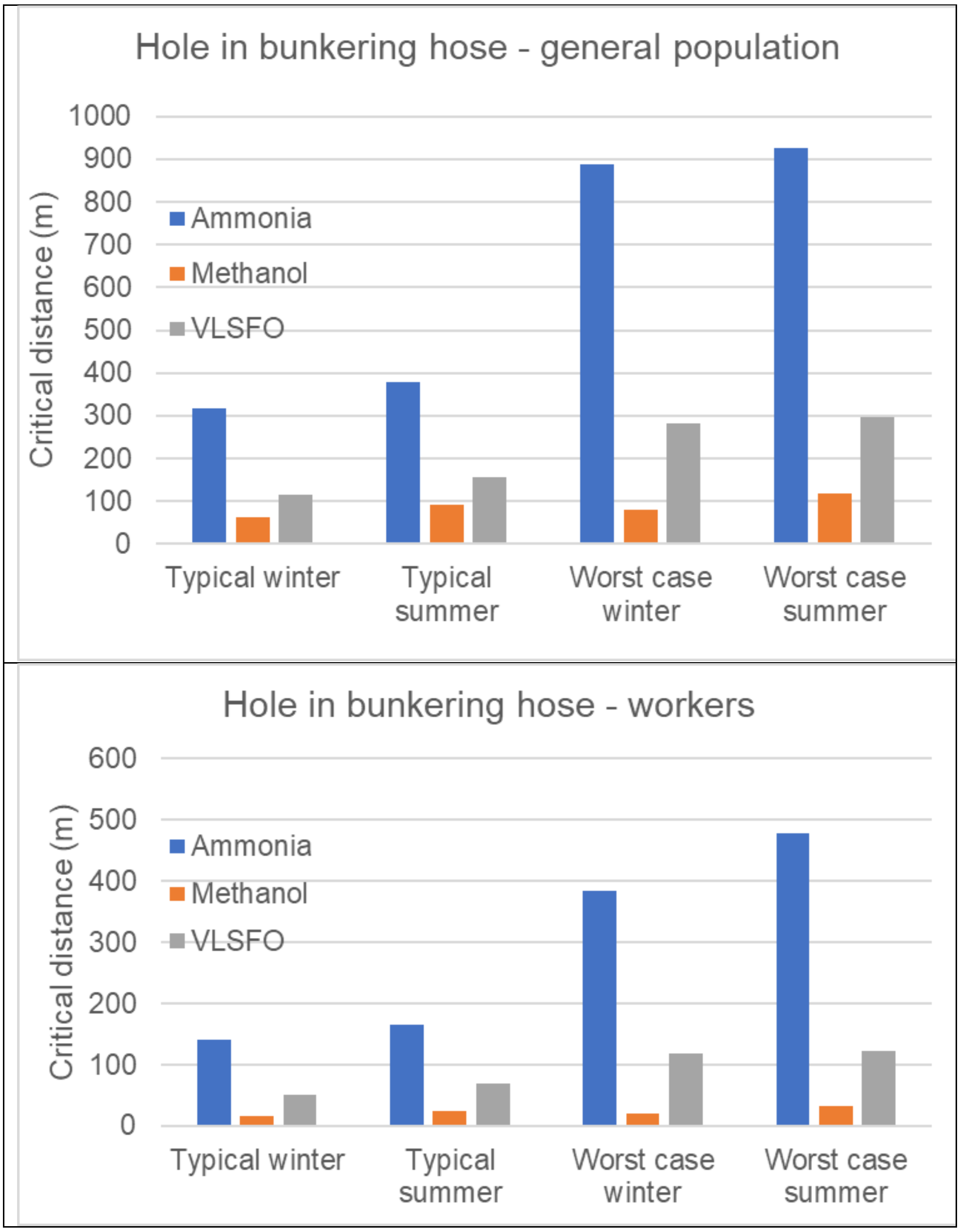


Figure 5.2 **Port of Rotterdam: Hole in the bunkering hose. Calculated distances at which the predicted concentration in air equals the derived no-effect level (DNEL).**

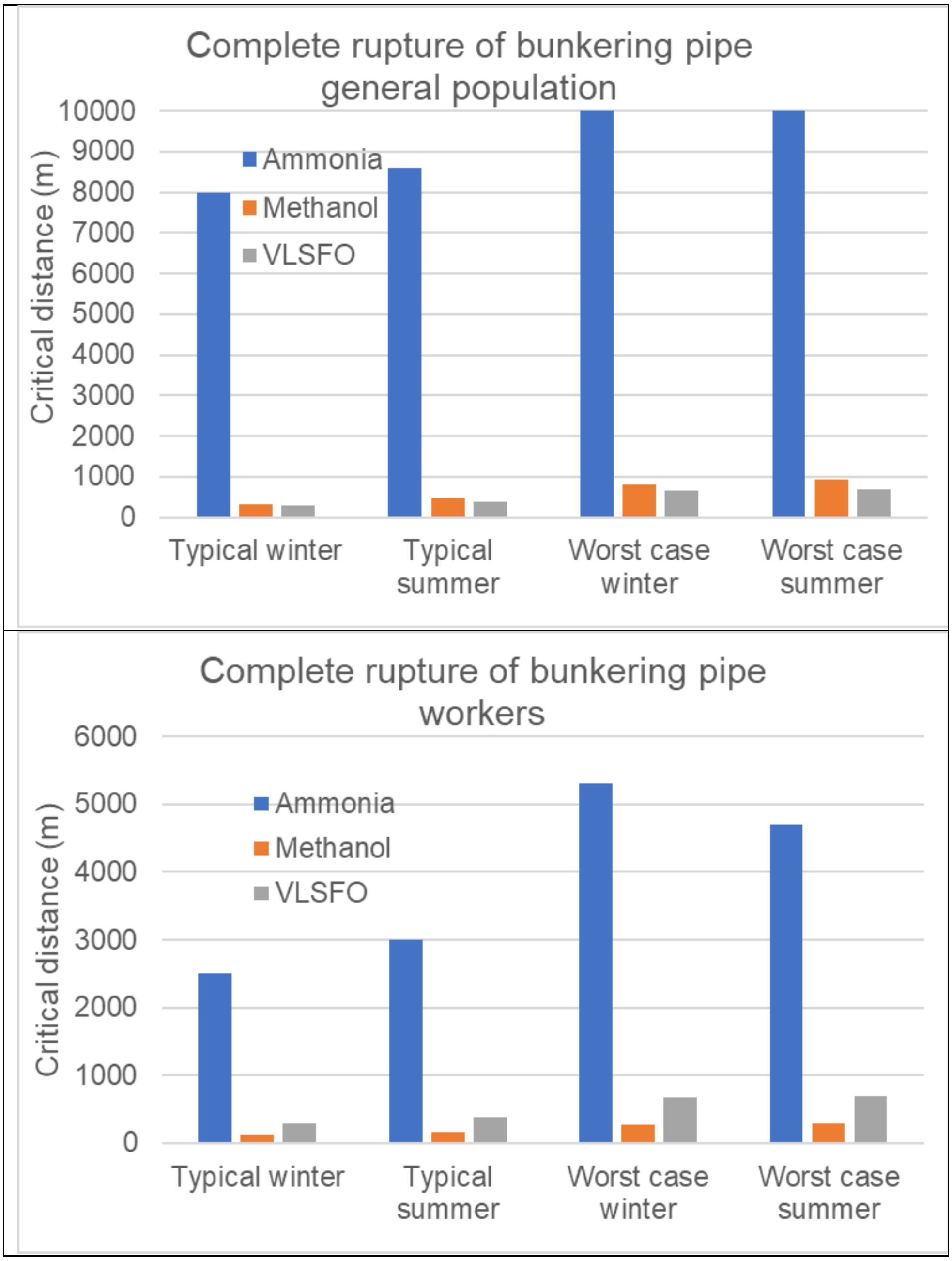
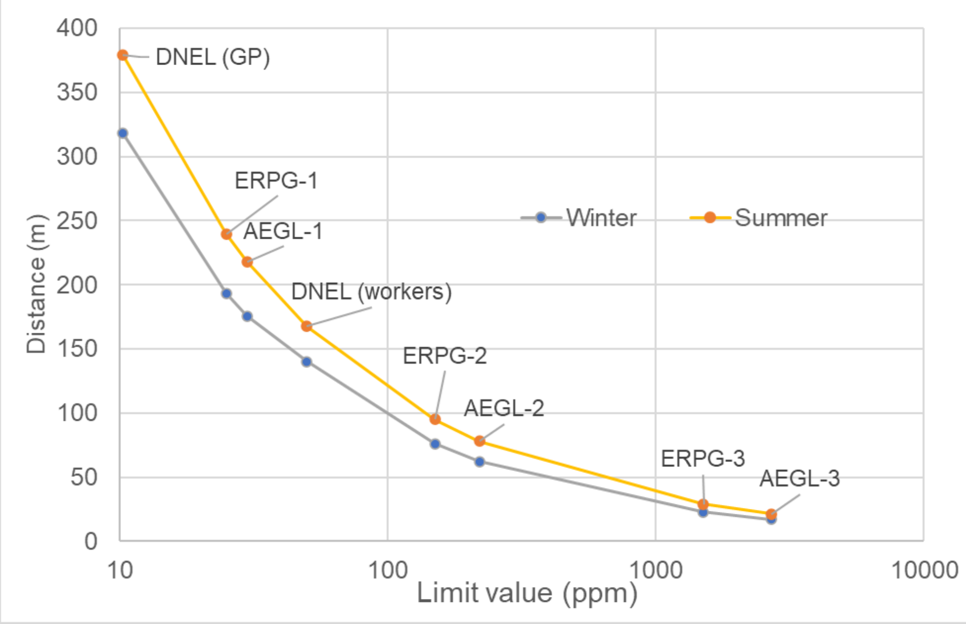
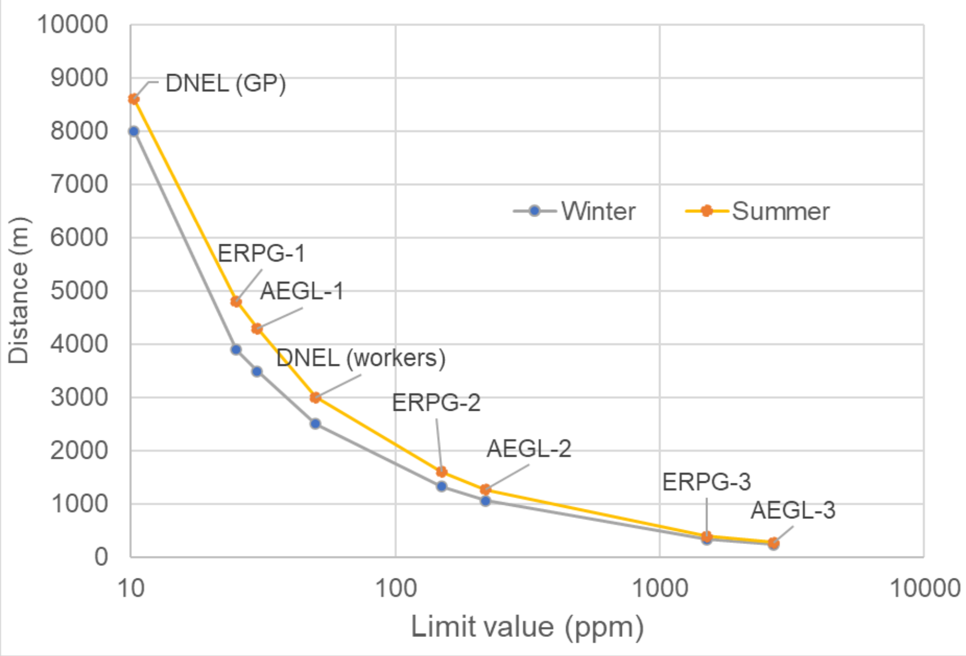


Figure 5.3 **Port of Rotterdam: Complete rupture of the bunkering pipe. Calculated distances at which the predicted concentration in air equals the derived no-effect level (DNEL).**

Recalling the exposure limits presented in Box 5.1, the distances at which the ammonia concentration in the air equals DNEL, AEGL, and ERPG values for ammonia were calculated. This analysis is carried out only for ammonia due to its toxicity. The results are shown in Figure 5.4 for the two exposure scenarios under typical winter and summer conditions.



Port of Rotterdam: Hole in the bunkering hose



Port of Rotterdam: Complete rupture of the bunkering pipe

Figure 5.4 Calculated distances at which the air concentration of ammonia under typical winter and summer conditions equals the limit value (logarithmic scale in x-axis). DNEL, derived no-effect level (GP, general population); AEGL, acute exposure guideline levels; ERPG, emergency response planning guidelines.

5.5 Possible impact on humans

The human health impact assessment of ammonia, methanol, and VLSFO showed that the potential impact of a spill of ammonia would be higher than the impacts of similar spills of methanol and VLSFO because the predicted air concentrations exceeding DNEL reach longer distances. Table 5.12 presents the maximum distances from the spill at which the predicted concentrations in air exceed the DNELs for the general population in emission cases leading to the lowest exposure (‘typical, winter’) and a high exposure (worst-case, ‘winter’). Closer to the spill, the predicted air concentrations (i.e., the PELs) are several times higher than the DNELs (Tables 5.6-5.11).

Table 5.12 Distances (m) from the spill at which the predicted air concentrations of the fuels exceed the derived no-effect levels (DNELs) for the general population.

Fuel	Hole in bunkering hose		Complete rupture of bunkering pipe	
	Lowest exposure: Typical, winter	Worst-case, winter	Lowest exposure: Typical, winter	Worst-case, winter
Ammonia	≤ 318	≤ 888	≤ 8000	10000 *
Methanol	≤ 64	≤ 80	≤ 326	≤ 817
VLSFO	≤ 114	≤ 283	≤ 280	≤ 672

**The ALOHA model is limited to calculating air concentrations at distances up to 10,000 m.*

The duration of the possible human exposure to airborne methanol and VLSFO exceeds 1 hour, whereas it is less than 15 min for ammonia. Adverse effects to human health may occur after exposure to air concentrations exceeding the DNEL. Due to the variation in susceptibility of human individuals, there is no precise way to describe the possible effects to human health resulting from exposure to a chemical. However, the AEGL and ERPG values presented in Box 5.1 can be used to illustrate the nature of effects at air concentrations exceeding the level triggering a specific exposure limit. The predicted time for complete evaporation of the spilled ammonia, and thus the predicted exposure duration, is 5 to 8 min for the scenario ‘Hole in the bunkering hose’ and 8 to 14 min for the scenario ‘Complete rupture of the bunkering pipe’. This information was used for calculating 15-minutes time-weighted average air concentrations that were compared to the AEGLs and ERPGs. Calculations were made for ammonia only, as the results obtained suggest that the potential impact on human health in case of a spill of ammonia is higher than the impacts of similar spills of methanol and VLSFO. The distances at which the air concentration of ammonia exceeds defined exposure limits under typical summer weather conditions and the associated description of impact are shown in Table 5.13.

The potential health effects after exposure to ammonia should be evaluated considering that no mitigation measures were assumed in the exposure modelling.

The present impact assessment is based on assumed spill scenarios and does not include an assessment of the likelihood that the spill event will happen. A large spill of ammonia in a port implies a risk of serious health effects to workers and the general population, which should be evaluated by a probabilistic risk assessment combining the likelihood and the seriousness of events leading to exposure of human to airborne ammonia. A probabilistic risk assessment, which is outside the scope of this study, should include the best available risk management measures in the specific port.

Table 5.13 Distances (m) from the spill at which the predicted 15-min-time weighted air concentrations of ammonia exceed specific exposure limits under typical summer weather conditions in Rotterdam. Exposure limits: Derived no-effect level for the general population (DNEL, general population), acute exposure guideline levels (AEGLs), and emergency response planning guidelines (ERPGs).

Exposure limits	Hole in bunkering hose	Complete rupture of bunkering pipe
DNEL (general population): Level of exposure above which humans should not be exposed	≤ 379	≤ 8600
ERPG-1: Nearly all individuals could be exposed for up to 1 hour without experiencing more than mild, transient adverse health effects or without perceiving a clearly defined objectionable odour	≤ 240	≤ 4800
AEGL-1: The general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic non-sensory effects - the effects are not disabling and are transient and reversible upon cessation of exposure	≤ 218	≤ 4300
ERPG-2: Nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action	95	1600
AEGL-2: The general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.	78	1300
ERPG-3: Maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects	29	389
AEGL-3: Airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death	21	271

6 Concluding remarks

The present study compared the potential environmental and human health impacts of accidental spills of ammonia, methanol, and very low sulphur fuel oil (VLSFO) used as vessel fuels. The impact assessments were based on exposure scenarios defining assumptions for accidental spills during bunkering in the Port of Rotterdam and collisions in the English Channel and the Strait of Malacca. Only the acute aquatic toxicity and the immediate human health impacts of the spills were assessed, whereas the long-term impacts and the likelihood of the spill events were not evaluated.

The environmental impact of the water-soluble fuel substances was assessed by comparing the predicted environmental concentration (PEC) and the predicted no-effect concentration (PNEC). The PNEC is the concentration in the environment below which adverse effects are not expected to occur due to exposure to a chemical. The environmental impact and the size of the impacted sea area resulting from the assumed spills depend on the hydrodynamic conditions and the temperature.

In the bunkering accidental scenario in the Port of Rotterdam, ‘Complete rupture of the bunkering pipe’, the water-soluble substances in VLSFO may cause adverse effects, including death, to a broad range of species in a sea area of 3 km^2, while adverse effects, including death, to sensitive species or individual organisms may occur in a sea area of 12 km^2. Adverse effects, including death, to sensitive species or individual organisms may occur in sea areas of 6 km^2 and 1 km^2 after a spill of ammonia and methanol, respectively. The assumed spills in the Port of Rotterdam scenario ‘Hole in the bunkering hose’ do not lead to PECs that exceed the PNECs due to the relatively low volumes released to the sea.

In the scenario ‘Collision’ in the English Channel, the assumed spills of ammonia may cause adverse effects, including death, to a broad range of marine species in a large sea area of 125 km^2. This also applies to the water-soluble substances in spilled VLSFO, although in a smaller sea area of 11 km^2. Methanol is not expected to cause adverse effects in the scenario ‘Collision’ in the English Channel as the PECs are below the PNEC.

In the scenario ‘Collision’ in the Strait of Malacca, a spill of ammonia may cause adverse effects, including death, to sensitive species or individual organisms in a sea area of 327 km^2. This also applies to the water-soluble substances in VLSFO in a sea area of 61 km^2 and to methanol in a sea area of 40 km^2.

For the analysed scenarios, the PECs decrease to levels below the PNECs within 2 to 5 days in the Port of Rotterdam and within two days after the assumed spills in the English Channel and the Strait of Malacca.

The non-dissolved fraction of VLSFO may cause long-lasting adverse effects in the marine environment. The predicted exposure to non-dissolved VLSFO indicates a high risk that coastal sea areas in the English Channel and the Strait of Malacca may be impacted by oil in amounts that will likely cause serious effects to marine life, including plants, invertebrates, sea birds and seals.

The human health impact resulting from the assumed spills of ammonia, methanol, and VLSFO was evaluated for different weather conditions and in two bunkering scenarios in Port of Rotterdam, i.e., ‘Hole in the bunkering hose’ and ‘Complete rupture of the bunkering pipe’. The human health impacts are highly influenced by the wind direction and the wind speed, the temperature, and the degree of cloudiness.

In the impact assessment, the predicted exposure levels (PEL) in air resulting from the assumed spills of fuel were compared with the derived no-effect level (DNEL), i.e., the level of exposure to a chemical substance above which humans should not be exposed. The results show that the potential impacts of a spill of ammonia are higher than the impacts of similar spills of methanol and VLSFO. More specifically, across the two bunkering scenarios, the critical distances where fuel concentrations, or PEL, were equal to or higher than the DNEL for the general population ranged for ammonia from 318 to at least 10000 meters, for methanol from 64 to 918 meters, and for VLSFO from 114 to 689 meters.

The nature of the possible effects of airborne ammonia may be illustrated by comparison with exposure limits intended for emergency planning, prevention, and response activities such as the acute exposure guideline levels (AEGLs) and the emergency response planning guidelines (ERPGs). For example, when the most serious scenario is considered, i.e., ‘Complete rupture of the bunkering pipe’, the predicted exposure levels of ammonia exceed AEGL-3 and ERPG-3 values (see Box 5.1) at distances of 271 meters and 389 meters, respectively.

To properly interpret these results, it is important to keep in mind that the potential health and environmental impacts after exposure to ammonia, methanol, and VLSFO were evaluated assuming no mitigation measures in the exposure modelling. Mitigation strategies are of utmost importance to address the potential impacts of the fuels in case of an accidental release during bunkering. A study of the operational risk during bunkering of ammonia using the Port of Singapore as example /41/ suggested that emergency response plans and containment measures should be implemented and possibly include:

- Active mitigation systems such as automated shut-off valves, pressure relief devices, or containment strategies to limit the release of fuel
- Passive mitigation measures such as barriers or structures that can limit the spread of hazardous substances and reduce the affected area.

Finally, the present impact assessment is based on assumed spill scenarios and does not include an assessment of the likelihood that the spill events will happen. A large fuel spill, especially of ammonia, in a port implies a risk of serious health effects to workers and the general population which should be evaluated by a probabilistic risk assessment combining the likelihood and the seriousness of events leading to exposure of humans. A probabilistic risk assessment should include the best available risk management measures in the specific port to properly support the industry in decision-making. While a probabilistic risk assessment is outside the scope of this study, the study aimed to aid the maritime industry by enhancing knowledge regarding the potential direct impacts of ammonia, methanol, and VLSFO in the event of spill accidents and encouraging further exploration into the implementation and use of alternative fuels.

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